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TOMO II: INCIDENCIA DE LA CONTAMINACION ATMOSFERICA SOBRE LAS AGUAS SUBTERRANEAS.

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ESTUDIO DE LA INCIDENCIA DE LA CONTAMINACION ATMOSFERICA EN LA CALIDAD DE LAS AGUAS SUBTERRANEAS: INVENTARIO, EVALUACION Y METODOLOGIA.

INDICE

1.- INTRODUCCIÓN

En el ámbito del presente proyecto se contempla la recopilación, estudio y síntesis de información bibliográfica acerca del tema que constituye su objetivo central: la incidencia de la contaminación atmosférica sobre la calidad de las aguas subterráneas.

Esta labor se ha llevado a cabo mediante los procedimientos habituales de consulta a bibliotecas, bancos de datos internacionales y otros centros de documentación. Los aspectos a investigar son múltiples, dado que se trata de una problemática compleja, en la que convergen y se imbrican elementos diversos y a veces incluso dispares, que es preciso integrar en el marco del objetivo propuesto.

Con esta perspectiva, la recopilación y síntesis bibliográfica se planteó en base a tres grandes aspectos:

1. ***Problemática de la contaminación atmosférica.*** Comprende la información relativa al origen, emisión, difusión y deposición de los contaminantes atmosféricos. Su objetivo es evaluar la naturaleza y el volumen de los mismos, así como los procesos en virtud de los cuales se produce su salida de la atmósfera hacia la superficie terrestre.

2. ***Incidencia de la deposición de contaminantes atmosféricos.*** Los metales pesados y los componentes ácidos de la deposición, son los principales responsables de la amenaza que la contaminación atmosférica ejerce sobre la calidad del agua subterránea. En tal sentido, la investigación bibliográfica realizada ha puesto de manifiesto que, si bien existe abundante información sobre la incidencia de estos productos sobre la vegetación, suelos, aguas superficiales, flora y fauna acuáticas, etc., son escasísimos los datos acerca de sus posibles efectos sobre las aguas subterráneas. Evidentemente esta circunstancia está relacionada con el hecho de que el suelo y la zona no saturada, constituyen en principio una protección eficaz frente a dichas sustancias, lo que

justificaría esta focalización de la atención hacia medios más vulnerables, donde sus efectos se manifiestan tan grave como espectacularmente (alteraciones de la vegetación debido a la lluvia ácida, p. ej.).

No obstante este comportamiento como barrera frente a la contaminación está fuertemente condicionado por factores locales, tanto intrínsecos al propio medio como ajenos a éste. De aquí que, por ejemplo, determinados tipos de suelos resulten mucho más vulnerables a la acidificación que otros, debido a la ausencia en aquéllos de materiales con capacidad de neutralización; o bien que, en caso de que persistan fenómenos de deposición ácida sobre un área concreta, puedan llegar a alterarse las propiedades del suelo favoreciendo la lixiviación de determinados metales pesados.

3. ***Legislación sobre emisiones.*** Este tercer aspecto completa el estudio bibliográfico. Su objetivo es el análisis del tratamiento legal de esta problemática en España y en el ámbito de la Comunidad Económica Europea, así como su enfoque en la legislación de los Estados Unidos. Su interés radica en el hecho de que estas normativas son responsables de regular las aportaciones a la atmósfera de aquéllas sustancias que, posteriormente y por efecto de la deposición, van a incorporarse al suelo y eventualmente a las aguas subterráneas.

2.- PROBLEMATICA DE LA CONTAMINACIÓN ATMOSFÉRICA

2.1.- CONCEPTOS GENERALES

El término "*contaminación atmosférica*" ha sido definido por el *Engineers Joint Council* norteamericano, como la "*presencia en la atmósfera de uno o más contaminantes, tales como polvos, humos metálicos, gases, nieblas, olores, humos, o vapores, en cantidades y de características y duración tales como para ser perjudiciales para la vida humana -vegetal o animal- o para las propiedades, o que interfieren excesivamente con el disfrute confortable de la vida y de los bienes*".

La Comunidad Económica Europea en su Directiva de 28/6/84 indica que "*se entenderá por contaminación atmosférica la introducción en la atmósfera, por el hombre, directa o indirectamente, de sustancias o de energía que tengan una acción nociva de tal naturaleza que ponga en peligro la salud del hombre, que cause daños a los recursos biológicos y a los ecosistemas, que deteriore los bienes materiales y que dañe o perjudique las actividades recreativas y otras utilizaciones legítimas del medio ambiente*".

Finalmente, en el Anexo I de la Orden del Ministerio de Industria de 18 de Octubre de 1976, publicada en el B.O.E. nº 290 de 3 de Diciembre del mismo año, se define "*contaminante de la atmósfera*" como "*partículas sólidas o líquidas, vapores y gases, contenidos en la atmósfera, que no forman parte de la composición normal del aire, o que están presentes en cantidades anómalas*".

De estas definiciones se deduce que la contaminación de la atmosféra es una alteración de su composición, transitoria o perenne, con efectos no deseables sobre las diferentes formas de vida de nuestro planeta, o sobre los bienes y propiedades del ser humano.

Las principales fuentes de contaminación se centran en tres apartados fundamentales: transporte, combustión fija (generación de energía eléctrica) e industria. A modo de ejemplo, las tablas 1 y 2 reflejan respectivamente y en valores porcentuales, la aportación de las diversas fuentes y la distribución en función del tipo de contaminante atmosférico correspondientes a los Estados Unidos.

A nivel general se admite que los cinco principales contaminantes son: monóxido de carbono, óxidos de azufre, hidrocarburos, materia particulada y óxidos de nitrógeno.

2.2.- CLASIFICACIÓN DE LOS CONTAMINANTES

Los contaminantes atmosféricos pueden clasificarse en base a criterios diversos: origen, estado físico, tipología, volumen de emisión, efectos sobre el medio ambiente, etc. En el presente capítulo se hará referencia fundamentalmente al estado físico o forma de presentación de estas sustancias. Según este criterio se distinguen:

a. Contaminantes particulados.

b. Contaminantes gaseosos.

Ambos se describen en los siguientes apartados. Asimismo, un epígrafe adicional se ocupa del origen de los contaminantes atmosféricos y su clasificación en función de este factor. Dicha clasificación es de uso generalizado, por lo que se ha considerado oportuno incluirla en el presente capítulo.

2.2.1.- ESTADO FÍSICO: CONTAMINANTES PARTICULADOS Y GASEOSOS

A. *CONTAMINANTES PARTICULADOS*

En función de sus dimensiones, la materia particulada se divide en:

Fuente	Contaminante	% Relativo	% Total
Transporte	CO	77,2	51,4
	Hidrocarburos	13,6	
	NO_x	7,7	
	Aerosoles	0,8	
	SO_x	0,7	
		100,0	
Combustión fija	SO_x	55,0	15,7
	NO_x	22,6	
	Aerosoles	16,3	
	CO	4,1	
	Hidrocarburos	2,0	
		100,0	
Industria	Aerosoles	36,4	14,1
	CO	30,3	
	SO_x	18,9	
	Hidrocarburos	13,9	
	NO_x	0,5	
		100,0	
Residuos sólidos	CO	66,3	4,2
	Hidrocarburos	16,8	
	Aerosoles	11,8	
	NO_x	3,4	
	SO_x	1,7	
		100,0	
Varios	CO	44,4	14,6
	Aerosoles	27,8	
	Hidrocarburos	22,4	
	NO_x	4,9	
	SO_x	0,5	
		100,0	
Total			100,0

TABLA 1.- CONTRIBUCION DE LAS DIVERSAS FUENTES DE EMISION A LA CONTAMINACION ATMOSFERICA EN ESTADOS UNIDOS[1] (% en peso)

Contaminante	Fuente	% Relativo	% Total
CO	Transporte	73,7	53,8
	Varios	12,0	
	Industria	7,9	
	Residuos sólidos	5,2	
	Combustión fija	1,2	
		100,0	
Hidrocarburos	Transporte	53,0	13,3
	Varios	24,6	
	Industria	14,7	
	Residuos sólidos	5,3	
	Combustión fija	2,4	
		100,0	
Aerosoles	Industria	40,8	12,5
	Varios	32,4	
	Combustión fija	20,5	
	Residuos sólidos	4,0	
	Transporte	2,3	
		100,0	
SO_x	Combustión fija	73,0	11,9
	Industria	22,5	
	Transporte	3,3	
	Varios	0,6	
	Residuos sólidos	0,6	
		100,0	
NO_x	Transporte	47,1	8,5
	Combustión fija	42,0	
	Varios	8,4	
	Residuos sólidos	1,7	
	Industria	0,8	
		100,0	
Total			100,0

TABLA 2.- DISTRIBUCION DE CONTAMINANTES EN FUNCION DE LAS FUENTES DE EMISION EN ESTADOS UNIDOS[1] (% en peso)

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[1] Fuente: Journal of A.P.C.A., 22,5 (1972)

I. Iones

II. Materia suspendida
  - Núcleos de Aitken
  - Materia particulada suspendida

III. Materia sedimentable

El rango de tamaños se extiende -excluyendo las dispersiones groseras, nubes, niebla y gotas de lluvia- desde $6x10^{-4}$ a $1\ x10^{2}\mu$ de radio.

I.- Iones

Partículas de tamaño inferior a $10^{-1}\mu$ portadoras de cargas eléctricas. Pueden estar constituídas por moléculas gaseosas o agrupaciones moleculares con un exceso o deficiencia de electrones (iones pequeños, tamaño inferior a $10^{-3}\mu$), o por materia particulada finamente dividida que ha perdido o ganado carga eléctrica (grandes iones, comprendidos entre 10^{-3} y $10^{-1}\mu$).

Los iones pequeños, encuadrados en la primera de estas categorías, se forman por la acción directa de las radiaciones (solar, cósmica,...), mientras que los grandes iones se producen bien por combinación de los anteriores con las partículas de los aerosoles, o con las gotas de agua en la atmósfera. Otros procesos generadores de iones son: combustión, transporte de polvo en aire seco, fusión de metales y pulverización de líquidos. Debido a esta diversidad de orígenes, la naturaleza química de los iones resulta notablemente variada.

La concentración atmosférica de los iones presenta variaciones entre las diferentes estaciones climatológicas: mayor cantidad en verano que en invierno en el caso de los iones pequeños, y relación inversa para los iones grandes. Asimismo a lo largo del día los valores máximos corresponden al principio de la mañana, y los mínimos al inicio de la tarde.

La conductividad eléctrica de la atmósfera depende de su contenido en iones pequeños, habiéndose observado que en zonas contaminadas su valor es inferior al de zonas rurales y sobre el mar, como consecuencia de la unión de los pequeños iones a la materia particulada y consecuente sedimentación.

II.- **Materia suspendida**

Se distinguen dos grupos:

a) Núcleos de Aitken (o núcleos de condensación activos).

Su tamaño está comprendido entre $0,5 \times 10^{-2}$ y $10^{-1} \mu$. Son responsables de la formación de las gotitas que dan lugar a una nube. Asimismo, la condensación del vapor atmosférico se ve favorecida por la presencia de estas partículas sólidas extrañas, cuya superficie es humedecida por el vapor.

Se forman en la naturaleza por evaporación del agua de mar pulverizada, tormentas de polvo, actividad volcánica, fuegos forestales y radiaciones alfa, beta, gamma o ultravioleta. Entre las actividades industriales, los procesos de combustión son los principales responsables de la formación de estas partículas. Su composición química es diversa, predominando fundamentalmente compuestos orgánicos y una serie de metales tales como cobre, manganeso y sodio.

La concentración atmosférica de los nucleos de Aitken sigue un ritmo diario, incrementándose durante las horas del día y disminuyendo tras la puesta de sol, hasta alcanzar un valor mínimo en las últimas horas de la noche. En atmósfera urbana, los valores máximos coinciden con las situaciones de aumento del tráfico rodado.

b) Materia particulada suspendida

Son dispersiones en un medio gaseoso o en la atmósfera de partículas sólidas o líquidas (radio comprendido entre 10^{-1} y $10^{1} \mu$), que por poseer una velocidd de sedimentación muy baja permanecen suspendidas durante mucho tiempo, siendo arrastradas lejos de su lugar de emisión por las corrientes de aire. Este grupo, por tanto, está integrado por los aerosoles.

Un aerosol se define como una dispersión de partículas sólidas o líquidas de tamaño inferior a 100µ en un medio gaseoso. Dentro del grupo de los aerosoles se distingue una serie de estados físicos, cuya terminología inglesa es más amplia que la española. Son: dust, fog, mist, smoke, fume y smog, y su traducción castellana no puede ampliarse más que a cuatro vocablos: polvo, niebla, neblina o bruma y humo. En base a sus respectivas definiciones técnicas, su equivalencia en castellano sería la siguiente:

Dust: Suspensión de partículas sólidas generadas por manipulación, machacamiento, molienda, impactación, agitación, pulido, detonación y decrepitación de materiales sólidos orgánicos o inorgánicos, tales como rocas, minerales, metales, carbón, madera y granos. Los polvos no floculan, excepto bajo fuerzas electrostáticas, no se difunden en el aire, pero sedimentan por la acción de la gravedad. El tamaño de las partículas de polvo suele ocupar la totalidad del rango de tamaños, siendo su forma irregular y con aristas.

Fog: Es un vocablo técnico indeterminado, aplicado a aerosoles líquidos visibles originados por condensación del estado gaseoso. Su margen de tamaños está comprendido entre 2 y 60µ.

Mist: Se aplica a dispersiones de gotitas líquidas, muchas de las cuales son suficientemente grandes para ser visibles sin ayuda óptica. Se origina bien por condensación de estado gaseoso, o por dispersión de un líquido, mediante salpicadura, atomización o espumación, borboteo o ebullición. Ejemplos de este tipo de aerosol lo constituyen las nieblas de aceite, originadas en operaciones de fresado y amolado, nieblas ácidas o alcalinas, producidas en procesos electroquímicos, nieblas de pinturas aplicadas por pulverización y condensación de vapor de agua para formar nubes. El margen de tamaños es muy amplio: 0,01µ a 50µ.

Smoke: Se define como suspensión de partículas sólidas -carbón y hollín-, resultantes de un proceso de combustión incompleta. En algunos casos, como sucede con el humo del tabaco, pueden existir partículas líquidas. Su tamaño suele ser inferior a 1μ.

Fume: Partículas sólidas generadas por condensación del estado gaseoso, originado por sublimación o volatización de metales y a menudo acompañada por una reacción química (normalmente una oxidación). Las partículas sólidas que forman un *fume* son extremadamente finas, usualmente esféricas e inferiores a 1μ. En la mayoría de los casos, el metal caliente reacciona con el aire frío para formar un óxido. Los *fumes* floculan y algunas veces coalescen. Ejemplos de este tipo de partículas son los humos que se desprenden de metales fundidos, en operaciones de soldadura y corte de metales, y en la combustión de ciertos metales como el magnesio.

Smog*[1]*: Es un término derivado de los vocablos smok y fog, que se aplica a grandes contaminaciones atmosféricas debidas a aerosoles, originadas por una combinación de causas naturales e industriales. El margen de tamaños de las partículas sólidas y líquidas que constituyen este tipo de aerosol, oscila entre 0,01 y 2μ.

Se observa pues, que los vocablos dust, fog, mist y smoke, equivalen respectivamente a polvo, niebla, neblina y humo, mientras que fume, debe ser asimilado al término de "humo metálico"; por el contrario para smog, no se encuentra un vocablo o apelación castellana apropiada.

III.- **Materia Sedimentable**

Está constituida por partículas sólidas de tamaño comprendido entre 10^1 y $5x10^2\mu$, aunque las técnicas usuales de medición admiten partículas hasta 1 mm; puede denominarse pues como "polvo grueso". Su

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[1] El "smog" es un termino sugerido en 1.911 por H.A. Des Voeuxs, para describir la mezcla de smoke y fog que se desplegaba sobre el cielo de Londres y de otras ciudades inglesas.

velocidad de sedimentación es apreciable, lo que supone un tiempo de permanencia en la atmósfera relativamente corto.

Los componentes más frecuentes de la materia sedimentable son de naturaleza inorgánica, fundamentalmente sílice, sulfatos, cloruros, nitratos, hierro, calcio, aluminio, magnesio, plomo, cinc, manganeso y cobre. Respecto a los constituyentes orgánicos, se trata de sustancias procedentes de la combustión incompleta del carbón o de los derivados petrolíferos, tales como alquitranes e hidrocarburos aromáticos policíclicos.

La presencia de metales pesados en ésta y en anteriores categorías de la materia particulada, constituye un elemento de gran interés, puesto que se trata de sustancias con gran capacidad de alterar la calidad de las aguas subterráneas.

Si bien el apartado 3.2. se ocupa monográficamente de este tema, cabe adelantar aquí algunos datos relativos al contenido de estos elementos en la atmósfera. En tal sentido, la tabla 3 recoge los rangos de concentración de una serie de elementos asociados a la materia particulada de la atmósfera, correspondientes a áreas urbanas, rurales y remotas, elaborada en base a datos extraídos de aproximadamente 200 referencias bibliográficas[1].

TABLA 3

RANGOS DE CONCENTRACIóN DE UNA SERIE DE ELEMENTOS
ASOCIADOS CON LA MATERIA PARTICULADA DE LA ATMOSFERA (mg/m^3)

Location	As	Cd	Ni	Pb	V	Zn	Co	Cr	Cu	Fe	Hg	Mn	Se	Sb
Remote	0.007-1.9	0.003-1.1	0.01-60	0.007-64	0.001-14	0.03-460	0.001-0.9	0.005-11.2	0.029-12	0.62-4160	0.005-1.3	0.01-16.7	0.0056-0.19	0.0008-1.19
Rural	1.0-28	0.4-1000	0.6-78	2-1700	2.7-97	11-403	0.08-10.1	1.1-44	3-280	65-14530	0.05-160	3.7-99	0.01-3.0	0.6-7
Urban														
Canada	7.7-626	2-103	4-371	353-3416	10-130	65-1390	1-7.9	4-26	17-500	700-5400	<5	20-270	n/a	13-125
U.S.A.	2-2320	0.2-7000	1-328	30-96270	0.4-1460	15.-8328	0.2-83	2.2-124	3.-3140	130-13800	0.58-458	4-488	0.2-30	0.5-171
Europe	5-330	0.4-260	0.3-1400	10-9000	11-73	160-8340	0.4-18.3	3.7-227	13-2760	294-13000	0.1-5	23-850	0.01-127	2-470
Other	20-85	0.6-177	2.3-158	1.3-11020	1.7-180	110-2700	0.3-10	tr-277	2.0-6810	21-32820	1.2-1.8	1.7-590	n/a	7-36

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[1] Schroeder, W.H. *"Toxic trace elements associated with airbone particulate matter: a review"* Journal of the Air Pollution Control Association. 37 (11) pp. 1267-85 (1987).

Estos resultados ponen de manifiesto un claro predominio del hierro y plomo; destacan también aunque en menor medida las concentraciones de cadmio, zinc, cobre, manganeso y níquel. Asimismo y aunque no figuran en esta tabla, destacan como especies abundantes el calcio y aluminio, seguidos del sodio, potasio y magnesio.

B. *CONTAMINANTES GASEOSOS*

La expresión de la concentración de los contaminantes gaseosos se realiza en ppm ó ppb en volumen, si bien es más frecuente el empleo del microgramo por metro cúbico de aire ($\mu g/m^3$). En condiciones normales de presión y temperatura, ambas unidades se relacionan mediante la siguiente expresión:

$$\mu g/m^3 = ppm \times 41,3 \times PM$$

La composición química de la atmósfera se recoge en la tabla adjunta:

	ppm v/v
Nitrógeno	780.880
Oxígeno	209.490
Agua	1.000-40.000
Argón	9.300
Dióxido de carbono	350
Neon	18
Helio	5,24
Metano	1,4
Kripton	1,14
Hidrógeno	0,5
Oxido nitroso	0,2-0,4 (áreas rurales)
Xenon	0,09
Monóxido de carbono	0,08-0,5 (áreas rurales)
Dióxido de azufre	0,007 (áreas rurales)
Mercurio	$0,2-0,8 \times 10^{-6}$
Ozono	0,01-0,045 pCi/l
Radón	0,01-0,04

A continuación se examinan los principales contaminantes gaseosos.

I.- Compuestos de carbono

CO y CO_2 son los más importantes. Ambos proceden respectivamente de los procesos de combustión incompleta y completa que tienen lugar en los motores de los vehículos automóviles, calefacciones domésticas y procesos industriales.

El monóxido de carbono es un parámetro especialmente importante en el control de la contaminación del aire en las grandes ciudades, por su incidencia directa sobre la salud humana. En lo que respecta al CO_2 la atención se centra sobre su incidencia a largo plazo en relación con el denominado "efecto invernadero".

Entre los hidrocarburos detectados en la atmósfera se encuentra una amplia gama de compuestos orgánicos volátiles: compuestos alifáticos (propano, hexano, etileno, etc.), aromáticos (benceno y tolueno), alcoholes, aldehídos, cetonas, hidrocarburos halogenados, ésteres, éteres, etc. Estas sustancias resultan de gran interés por su participación en la formación del smog fotoquímico.

II.- Compuestos de azufre

Los principales contaminantes de naturaleza sulfurada son los óxidos de azufre, sulfuro de hidrógeno (H_2S) y los mercaptanos (RSH).

a) Oxidos de azufre

De los dos óxidos de azufre -SO_2 y SO_3-, sólo el primero de ellos se encuentra en forma gaseosa, ya que el SO_3 reacciona con el vapor de agua para dar gotículas de ácido sulfúrico.

El anhídrido sulfuroso es el más común de los contaminantes gaseosos detectados en el ambiente urbano, originándose a partir de la oxidación de los compuestos de azufre presentes en los combustibles sólidos y líquidos. Asimismo se encuentra asociado a ciertos procesos industriales, entre los que destacan los relacionados con la generación de energía eléctrica a partir de combustibles fósiles. Resulta nocivo para la salud humana, y es corresponsable junto con otros compuestos de la deposición ácida (seca y húmeda).

b) Sulfuro de hidrógeno y mercaptanos

Ambos son contaminantes ocasionales y minoritarios de la atmósfera urbana, si bien pueden manifestarse en ciertas áreas industriales. Sus efectos son diversos, destacando su capacidad para oscurecer pinturas y objetos metálicos como consecuencia de la formación de sulfuros metálicos, así como su desagradable olor.

El origen de estos contaminantes se debe, en el caso del H_2S, a escapes accidentales de ciertos procesos industriales, degradación anaeróbica de la materia orgánica, etc. los mercaptanos aparecen en los gases residuales producidos durante la fabricación de pulpa de celulosa por el método Kraft.

III.- Compuestos de nitrógeno

Comprenden los óxidos de nitrógeno, el amoniaco y los peroxiacilnitratos (o nitratos de peroxiacilo).

a) Oxidos de nitrógeno

Los compuestos más importantes y comunes son el dióxido de nitrógeno (NO_2) y el óxido nítrico (NO). El **dióxido de nitrógeno** se forma durante los procesos de combustión, por oxidación de parte del nitrógeno del aire que alimenta el proceso, y en procesos industriales tales como la obtención de ácido nítrico, nitración de la celulosa y obtención de celuloide y películas de fotografía. La fuente fundamental de formación del **NO** es la oxidación parcial de nitrógeno atmosférico en el interior de los motores de combustión interna.

b) Amoniaco y peroxiacilnitratos (PAN)

El amoniaco es un contaminante que aparece en raras ocasiones, generalmente debido a fugas en instalaciones industriales. Las fábricas de abonos, ácido nítrico y productos orgánicos son las principales fuentes de producción.

Los nitratos de peracilo son compuestos de estructura compleja de tipo orgánico, en los que figura el grupo NO_2. Se forman por complicados procesos de tipo fotoquímico, en los que intervienen determinados hidrocarburos activados por medio de óxidos de nitrógeno.

Los nitratos de peracilo poseen un marcado carácter fitotóxico, aun en las concentraciones habituales que oscilan alrededor de las 30 ppb. Su participación en la formación del smog fotoquímico es importante.

IV.- Ozono y oxidantes

La presencia en atmósfera urbana de concentraciones anómalas de ozono, así como de ciertas sustancias orgánicas oxidantes (p. ej., peróxidos), es la señal característica de una contaminación tipo oxidante (ver apartado 2.2.2.B.).

Los efectos del ozono derivan de su fuerte capacidad oxidante, que puede generar daños en la vegetación, desintegración del caucho, corrosión de metales, irritación de la piel y de las mucosas oculares y respiratorias.

V.- Compuestos halogenados

El ácido fluorhídrico se encuentra presente en las emisiones de ciertas actividades industriales, siendo las principales la metalurgia del aluminio y la fabricación de fertilizantes fosfatados y de cemento y, en menor cuantía, la combustión de carbón mineral, donde los fluoruros aparecen como impurezas.

En lo que respecta al cloro y sus compuestos -especialmente el HCl-, su presencia también se relaciona con emisiones de origen industrial (fábricación de cloro, sosa y HCl).

2.2.2.- ORIGEN: CONTAMINANTES PRIMARIOS Y SECUNDARIOS

Contaminantes primarios son los emitidos directamente por fuentes o focos identificables, mientras que los secundarios se originan en la misma atmósfera, bien por reacción entre dos o más contaminantes primarios, o con alguno de los constituyentes normales del aire, con o sin la intervención de procesos de fotoactivación.

A. *CONTAMINANTES PRIMARIOS*

Suelen clasificarse teniendo en cuenta simultáneamente los conceptos definitorios de su constitución química, estado físico y cantidad emitida, de lo que resultan 8 categorías diferenciadas:

1. Partículas sólidas inferiores a 100μ.
2. Partículas sólidas superiores a 100μ.
3. Compuestos de azufre.
4. Compuestos orgánicos.
5. Compuestos de nitrógeno.
6. Oxidos de carbono.
7. Compuestos hologenados.
8. Sustancias radiactivas.

B. *CONTAMINANTES SECUNDARIOS*

Una masa de aire contaminado es química y físicamente inestable, y al igual que cualquier otro sistema tiende a aproximarse al estado de mínima energía libre. La velocidad y mecanismos de reacción, los estados de transición y los intermedios de reacción, están influenciados por factores tan diversos como la concentración relativa de los reaccionantes, grado de fotoactivación, fuerzas dispersivas meteorológicas, influencia de la topografía local y humedad relativa.

Como ejemplo de este tipo de reacciones cabe citar las que tienen lugar entre gotículas líquidas de nieblas ácidas con polvos de óxidos metálicos para originar aerosoles salinos, la formación de nieblas ácidas por disolución de anhídridos en estado gaseoso en gotas de agua, y las reacciones de oxidación catalítica sobre partículas o superficies metálicas, como es el caso de la formación de nieblas de ácido sulfúrico por oxidación de nieblas de ácido sulfuroso.

La reacción ambiental probablemente más estudiada es la de formación del "smog fotoquímico", que juega un papel destacado especialmente en la contaminación de algunas ciudades. Se inicia por una reacción en cadena en la que el NO_2 se disocia en NO y radicales O, los cuáles inician a su vez reacciones en cadena sobre otros compuestos orgánicos presentes en la atmósfera, que conducen a la formación de compuestos químicos tan reactivos y por tanto, de gran capacidad tóxica, como el ozono, formaldehído, acroleína, hipoperóxidos orgánicos, nitratos de peroxiacetilo (PAN), etc., que conducen a una serie de fenómenos atmosféricos y efectos fisiopatológicos muy perjudiciales.

A pesar de la diversidad de contaminantes químicos existentes en la atmósfera, del estado físico en que se encuentran en el ambiente, y de la variedad de características meteorológicas y topográficas existentes, se admite que existen dos tipos básicos de contaminación de la atmósfera, íntimamente relacionados con la formación de contaminantes secundarios. Se trata de la contaminación *reductora* ("tipo Londres") y contaminación *oxidante* ("tipo Los Angeles"), que suponen dos condiciones extremas de contaminación definidas sobre las características específicas de los episodios y situaciones típicas ocurridas repetidas veces en estas dos ciudades, y que se recogen en la Tabla 4.

TABLA 4

CONTAMINACIÓN OXIDANTE Y REDUCTORA

Características	Londres	Los Angeles
Compuestos más frecuentes	SO_x,materia partic. y CO.	O_3, NO_x, CO_2, hidrocarburos y mat. particulada.
Combustibles	Carbón mineral y petróleo.	Petróleo.
Fuentes industriales	Diversas.	Diversas.
Combustión de basura	Grande.	Pequeña.
Efectos	Reducción.	Oxidación.

Los rasgos predominantes de la contaminación "tipo Londres" son: presencia de óxidos de azufre, monóxido de carbono, polvo de origen industrial y hollín, procedentes en su mayoría de la combustión del carbón mineral. La contaminación "tipo Los Angeles" es originada por los procesos fotoquímicos atmosféricos. Los óxidos de nitrógeno -fundamentalmente el NO_2- y los hidrocarburos, constituyen los principales generadores de la contaminación fotoquímica, implicando el proceso la absorción de energía por el NO_2 para formar NO y oxígeno atómico. La reacción entre el oxígeno atómico y molecular da origen al ozono (O_3), que es el principal agente oxidante del smog fotoquímico. Reacciones posteriores entre el ozono y los hidrocarburos olefínicos reactivos, producen otros muchos productos de naturaleza diversa, no perfectamente conocida.

2.3.- <u>FUENTES DE EMISIÓN</u>

2.3.1.- CONCEPTOS DE EMISIÓN E INMISIÓN

El proceso de contaminación atmosférica se inicia con la emisión de los productos contaminantes a partir de sus respectivas fuentes, y prosigue con su difusión en el medio gaseoso, muy variable en el tiempo, según las propiedades de las sustancias emitidas y las condiciones ambientales.

La evaluación de la contaminación debe comenzar pues desde la misma iniciación del proceso, es decir, desde la **emisión** de los productos. Por **emisión** se entiende la ***totalidad de sustancias (sólidas, líquidas y gaseosas) que pasan a la atmósfera tras abandonar las fuentes de las que proceden.*** De acuerdo con esta definición, emisiones son los gases de escape de los automóviles, los humos de las chimeneas, los vapores de diversos procesos industriales, etc., en el momento en que abandonan su fuente de procedencia y pasan a formar parte del aire adyacente.

Una vez producida la emisión, los compuestos se distribuyen por la atmósfera según un proceso de difusión que depende principalmente de dos tipos de factores:

- específicos del contaminante, como pueden ser velocidad de salida, temperatura, forma, tamaño, peso, etc., y
- meteorológicos: velocidad del viento, gradiente de temperatura, humedad, etc.

La difusión de los contaminantes es un proceso cuya terminación es difícil de especificar, ya que representa una dilución continua de aquéllos en la atmósfera.

La evolucion de los contaminantes está relacionada con el concepto de ***inmisión.*** Como tal, se entiende ***la permanencia de los compuestos de forma continuada o temporal en la atmósfera presente a nivel del suelo.***

La inmisión determina pues la concentración de los contaminantes en el ambiente gaseoso, en puntos suficientemente alejados de las fuentes como para no poder discernir cuál de ellas es la causante de los niveles de contaminación alcanzados. **Hablar por tanto de valores de inmisión, es equivalente a referirse a concentraciones ambientales de los contaminantes en estudio.**

Los niveles de emisión e inmisión se hallan regulados en la mayoría de los países mediante la especificación de límites máximos. La denominada Concentración Máxima de Emisión (C.M.E.), representa la mayor cantidad de contaminante que una fuente es autorizada a emitir. Este valor no se expresa siempre en las unidades de concentración habituales -masa por unidad de volumen-, sino que con cierta frecuencia adopta otras formas distintas. Así por ejemplo, la C.M.E. de los vehículos suele expresarse en unidades de masa por unidad de longitud, es decir, gramos por kilómetro recorrido, o gramos por milla. A su vez, en el caso de las emisiones industriales se emplean las unidades de masa emitida por masa producida, o de masa emitida por unidad de tiempo, es decir, gramos por tonelada y gramos por hora, respectivamente.

En el caso de la inmisión, el correspondiente límite se denomina Concentración Máxima de Inmisión (C.M.I.), en terminología inglesa Maximum Ground Level Concentration. Este valor representa la limitación de tipo sanitario que regula la calidad del aire en cuestión. Suele estar acompañado en las normas legales por el máximo período de tiempo en que es autorizada su existencia.

2.3.2.- CLASIFICACIÓN DE FUENTES CONTAMINANTES

Los focos o fuentes productoras de la contaminación atmosférica se agrupan en dos tipos: móviles (vehículos) y fijos (calefacciones e industrias).

a) Móviles

Los vehículos con motor de explosión (gasolina) emiten monóxido de carbono, hidrocarburos, óxidos de nitrógeno y compuestos de plomo.

Los motores de combustión (diesel) emiten partículas sólidas y líquidas: CO, CO_2, SO_2, SO_3, y NO_x. Las partículas sólidas están constituídas por hollines -partículas de carbono sin quemar- y se forman debido a la combustión incompleta del combustible; son el origen de los "humos negros", muy visibles. Las partículas líquidas, que dan lugar a los "humos azules", están constituídas por pequeñas gotas del combustible, parcialmente quemado, y aparecen cuando el motor funciona de forma incorrecta. Los demás contaminantes gaseosos resultan menos significativos en estas emisiones. Dado que los motores diesel realizan la combustión con un exceso de aire, el contenido de CO es casi inapreciable. Los compuestos de azufre, SO_2 y SO_3, se deben al contenido de azufre del gasóleo.

b) Fijos

La contaminación atmosférica generada por las instalaciones de calefacción fijas, se origina a partir de la combustión del carbón, fuel-oil y gases empleados. El cuadro adjunto resume los principales contaminantes producidos por cada uno de estos combustibles.

Combustible	Contaminantes
Carbón:	CO, SO_2, cenizas volantes, hollines, óxidos metálicos, NO_x.
Líquidos: *(gasóleo, fuel-oil)*	CO, SO_2, SO_3, NO_x, hidrocarburos volátiles no quemados, partículas carbonosas.
Gases:	CO, NO_x.

En lo que respecta a la contaminación de origen industrial, el origen de las emisiones es enormemente amplio y variado. La directiva de la C.E.E. de 28/6/84 recoge en su Anexo 1 la relación de los sectores industriales cuyas emisiones es necesario controlar, la cuál constituye un excelente punto de referencia para clasificar los focos importantes. Dicha relación se refleja en la tabla 5.

La contaminación atmosférica de origen industrial es más difícil de definir y sobre todo de cuantificar que la procedente de otras fuentes, debido a la enorme incidencia que en la misma tienen los siguiente parámetros:

- Tipología de los procesos industriales.
- Tecnologías utilizadas.
- Situación y edad de los equipos e instalaciones industriales.

TABLA 5

INSTALACIONES INDUSTRIALES PRODUCTORAS DE EMISIONES GASESOSAS CONTAMINANTES (Anexo 1 de la Directiva C.E.E. de 28/6/84)

1. **Industria de la energía**

1.1. Coquerías

1.2. Refinerías de petróleo crudo (con exclusión de las empresas que fabrican únicamente lubricantes a partir del petróleo crudo)

1.3. Instalaciones de gasificación y licuefacción del carbón

1.4. Centrales térmicas (con exclusión de las centrales nucleares) y otras instalaciones de combustión de una potencia nominal calorífica de más de 50 MW

2. **Producción y transformación de metales**

2.1. Intalaciones de calcinación y sinterización de una capacidad de más de 1000 t por año de minerales metálicos

2.2. Instalaciones integradas de producción de fundición y de aceros brutos

2.3. Fundiciones de metales férricos que tengan instalaciones de fusión de una capacidad total superior a 5 t

2.4. Instalaciones de producción y de fusión de metales no férricos que tengan instalaciones de una capacidad total superior a 1 t para los metales pesados o 0,5 t para los metales ligeros ..

3. **Industrias de productos minerales no metálicos**

3.1. Instalaciones de fabricación de cemento y producción de cal por hornos rotatorios

3.2. Instalaciones de producción y de transformación de amianto y fabricación de productos a base de amianto

3.3. Instalaciones de fabricación de fibras de vidrio o fibra mineral

3.4. Instalaciones de fabricación de vidrio (ordinario y especial) de una capacidad anual superior a 5000 t

3.5. Instalaciones de fabricación de cerámica de construcción, en particular de ladrillos refractarios, tubería cerámica, ladrillos para muros y solado y tejas de cubierta

4. **Industria química**

4.1. Instalaciones químicas para la producción de olefinas, derivados de olefinas, monómeros y polímeros

4.2. Instalaciones químicas para la fabricación de otros productos orgánicos intermedios

4.3. Instalaciones para la fabricación de productos químicos inorgánicos de base

5. **Eliminación de residuos**

5.1. Instalaciones de incineración de residuos tóxicos y peligrosos

5.2 Instalaciones de tratamiento de otros residuos sólidos y líquidos por incineración

6. **Industrias diversas**

Instalaciones de fabricación de pasta de papel por método químico de una capacidad de producción de 25000 t o más al año

- Materias primas empleadas.
- Tipos de combustibles.
- Localización geográfica de la industria, que define las condiciones meteorológicas y topográficas de la dipersión de contaminantes.

A su vez, estos parámetros tienen en el campo industrial una significación mucho más amplia y compleja, debido sobre todo a la diversidad de contaminantes y a la falta de un conocimiento completo de estos problemas en el momento actual.

Las actividades industriales que pueden contaminar la atmósfera son muchas, pero es preciso tener en cuenta que todas ellas vienen condicionadas por dos factores:

- Volumen de emisión de contaminantes.
- Tipo y características de los mismos.

Atendiendo a estos criterios y singularmente al primero de ellos, existen diversas clasificaciones de las industrias en función del impacto ambiental de sus emisiones a la atmósfera. La tabla 6 refleja una relación de sectores industriales y de sus respectivos contaminantes atmosféricos característicos.

En términos generales cabe afirmar que el papel protagonista en la contaminación atmosférica de origen industrial corresponde a la industria básica. La incidencia de la industria transformadora es mucho menor, ya que generalmente sus emisiones se limitan a las derivadas de sus servicios de generación de calor (calefacción), o vapor.

2.3.3.- LA COMBUSTIóN COMO FUENTE DE CONTAMINACIóN

2.3.1.1.- Generalidades

La importancia de los procesos de combustión en el contexto de la

TABLA 6

CONTAMINANTES DERIVADOS DE DIVERSAS ACTIVIDADES INDUSTRIALES
("Medio Ambiente en España" (1978), p.151)

	Tipo de actividad	PS	SO_2	(3) NO (1)	(2) HC	(1) SO_3	F	Olores	Cl_2	Hg	ClH	Be	Co	Pb	Asb.	SH_2
I	Central Térmica	●	●	●												
	Generadora de calor	●	●	●												
II	Incineradores	●		●												
	Plantas de depuración															
III	Almacenamiento combustibles				●											
IV	Acido sulfúrico		●			●										
	Acido nítrico			●												
	Reducción de fósforo	●					●									
	Detergentes y jabones	●														
	Acido fosfórico	●														
	Pinturas y barnices	●						●								
	Cloro-sosa								●	●						
	Acido clorhídrico										●					
V	Curtido de pieles							●								
	Fertilizantes fosfatados	●					●									
	Preparación de alimentos	●					●									
	Secado de grano	●														
	Algodón (preparación)	●														
VI	Fabricación de berilio											●				
	Refinado de mercurio									●						
	Hierro y acero	●	●	●			●						●			
	Metalurgica no férrea	●	●	●												
	Aluminio	●					●									
	Fusión de plomo	●		●										●		
	Ferro-aleaciones	●		●												
	Fundición de hierro gris	●		●									●			
	Fundición de latón y bronce	●		●												
VII	Plantas de cemento	●	●	●												
	Plantas de asbestos														●	
	Plantas de asfalto	●		●	●			●								
	Plantas de cal	●														
	Lavado de carbón	●														
	Preparación de grafito				●											
VIII	Refinerías de petróleo	●	●	●	●			●					●			●
	Plantas petroquímicas															
IX	Fabricación de pasta de papel	●	●					●		●						●
		24	8	13	4	1	5	5	1	3	1	1	3	1	1	2

(1) Se refiere a mezcla $SO_3 + SO_4H_2$.

(2) Hidrocarburos inquemados referidos como CaH.

(3) Oxidos de nitrógeno expresados como NO_2

contaminación atmosférica, justifica el interés de destacar algunos aspectos concretos de dicha relación causa-efecto.

La incidencia en España (datos 1972) de la combustión respecto al volumen global de emisiones resulta notablemente significativa, como lo demuestran las siguientes cifras:

FUENTE	EMISIONES (%)
Combustión fija	
- Térmicas	14,8
- Otras instalaciones	23,6
Transporte	33,4
Industria	28,2

El desglose por tipo de contaminante de estas emisiones es el siguiente:

FUENTE	Emisiones (%)			
	SO_2	Partículas	NO_x	CO
Combustión fija				
. Térmica	30	18	34	--
. Otras instalaciones	28	50	--	--
Transporte	--	2	53	80
Industria	42	30	13	20

Estos resultados indican que las instalaciones de combustión fija existentes en nuestro país, aportaban a las cifras globales de emisión de contaminantes un 58% del SO_2, el 68% de las partículas y un 34% de las NO_x.

Asimismo, según los datos del Inventario Nacional de Focos de Contaminación Atmosférica Producida por la Industria (M.I.N.E.R.,1981), la distribución por sectores industriales de las emisiones de SO_2, NO_x y partículas, arroja el siguiente balance:

TABLA 7

DISTRIBUCIÓN SECTORIAL DE CONTAMINANTES EN ESPAÑA

	CONTAMINANTES					
	SO_2		NO_x		Partículas	
SECTORES	1	2	1	2	1	2
Alimentario	46.459	3,03	9.146	3,07	29.783	3,01
Paraquímico	64.870	4,23	36.444	12,23	19.738	1,99
Química Inorgánica	39.708	2,59	16.560	5,55	20.644	2,08
Química Orgánica	7.833	0,51	1.510	0,51	17.836	1,80
Siderurgia	98.406	6,42	7.809	2,62	239.730	24,29
Metalurgia No férrea	41.171	2,69	827	0,28	18.950	1,91
Construcción	19.728	1,28	2.637	0,88	38.496	3,89
Cemento	50.033	3,26	10.991	3,69	268.832	27,17
Papel	44.441	2,89	7.983	2,68	20.915	2,11
Energía	**1.119.946**	**73,07**	**204.121**	**68,49**	**314.179**	**31,76**
TOTAL	1.532.595	100,00	298.028	100,00	989.103	100,00

1 = Total Nacional (t/año)
2 = % Sectorial

Es importante destacar la aportación del sector energético al total de contaminantes emitidos, que según estos resultados sería de:

SO_2............. 73,07%
NO_x............. 68,49%
Partículas...... 31,76%

Las actividades humanas producen alrededor el 60% del total de emisiones de azufre a escala global, pero en el caso del noroeste de Europa y este de Norteamérica, esta cifra alcanza respectivamente el 90 y 99% de la emisión total de azufre. Aproximadamente un 90% del azufre liberado por dichas actividades se emite en forma de SO_2. A escala global, el empleo de combustible fósiles supone un 82% del SO_2 de origen antrópico; en el caso del carbón, la aportación alcanza un 56% del total del SO_2 procedente de actividades humanas. En Europa y Norteamérica, dicho porcentaje asciende al 60%.

Las principales fuentes de NO_x en la troposfera son los combustibles fósiles y la combustión de la biomasa asociada a la agricultura. Las contribuciones respectivas son del 40% y 25% de la emisión total de NO_x, lo que practicamente duplica la aportación de fuentes naturales, siendo incluso superior en áreas industrializadas.

Las emisiones de NO_x procedentes de combustibles fósiles en Norteamérica exceden en un factor entre 3 y 13 a las de fuentes naturales, si bien estas últimas no se encuentran bien definidas. Algo similar ocurre en Europa, donde dichos combustibles contribuyen en un 80% a la emisión total de NO_x de esta región. Los porcentajes de emisión de NO_x por tipo de combustible para Europa y Estados Unidos son los siguientes:

	CARBÓN	PETRÓLEO Y DERIVADOS	GAS NATURAL
EUROPA (1979)	32	60	-
ESTADOS UNIDOS (1985)	32	46	18

La emisión de HCl procedente de la combustión del carbón, incineración de residuos y fabricación de compuestos orgánicos, representa el 89% de las emisiones de este producto en los Estados Unidos (1985). También en este país y en los que respecta al HF, la combustión del carbón y la producción primaria de aluminio contribuyen respectivamente en un 78% y 15% a la emisión total. El flúor liberado en la combustión puede hallarse bajo alguna/s de estas formas: HF gas o SiF_4, y como flúor particulado. El SiF_4 puede hidrolizarse a ácido fluorsilícico (H_2SiF_6) tras la emisión, por reacción con el vapor de agua. En resumen y a escala global, la aportación de cloruros y fluoruros procedente de la combustión de carbón resulta relativamente poco importante.

2.3.3.2.- Definición

a) Combustión completa

La combustión es una reacción compleja entre el oxígeno del aire y los combustibles, consistente en un proceso de oxidación a través de mecanismos de reacciones rápidas en cadena.

Los productos de la misma, cuando es perfecta, no pueden considerarse nocivos, pues son asimilables a los que proceden de los organismos vivos. En efecto, cuando se quema un combustible cualquiera se obtiene, al término de la combustión, anhídrido carbónico y agua, que resultan de la oxidación completa del carbono y del hidrógeno del combustible por el oxígeno del aire. Como todos los combustibles contiene también, pero en menor cantidad, azufre. La combustión completa debe dar lugar igualmente a la formación de anhídrido sulfuroso (SO_2) y también a óxidos de nitrógeno (NO_x) por reacción, a altas temperaturas, del nitrógeno y oxígeno del aire.

b) Combustión incompleta

Se dice que una combustión es incompleta cuando, mezclados con los humos de la combustión, aparecen gases combustibles, así como partículas sólidas de carbono no quemadas.

Generalmente, las causas de una combustión incompleta pueden ser una insuficiente cantidad de aire, o bien una mezcla defectuosa del combustible con el comburente, aún en presencia de exceso de aire.

Así, por ejemplo, si la combustión es incompleta por defecto de oxígeno, durante el desarrollo de la misma baja la temperatura de la llama, lo que supone que ciertos átomos de carbono y de hidrógeno no dispondran de la energía necesaria para la formación de radicales libres que conducen finalmente al CO_2 y H_2O. Esto hace que en la reacción se presenten estados de equilibrio intermedios que tienen como consecuencia:

- Emisión o recombinación de átomos de carbono, que aparecen en los humos como materia particulada inquemada.

- Combinación de átomos de carbono y oxígeno en cantidades muy pequeñas, y formación de CO.

- Recombinación de átomos de carbono e hidrógeno, lo que conduce a la formación de hidrocarburos ligeros y pesados.
- Emisión de hidrocarburos parcialmente oxidados (aldehidos, ácidos, etc.).

2.3.3.3.- Productos emitidos

Los principales son:

- SO_2, SO_3
- NO_x
- Materia particulada
- CO (concentraciones usualmente muy bajas)
- CO_2 (no considerado tradicionalmente como contaminante)

Las concentraciones y cantidades emitidas son función de:

- Combustible (tipo, calidad y cantidad)
- Tipo de caldera
- Condiciones de operación
- Naturaleza y eficiencia de sistemas de depuración.

a) Oxidos de azufre

SO_2

Las **cantidades** emitidas son directamente proporcionales al contenido de azufre en el combustible. En el caso del fueloil el porcentaje emitido sobre el total de azufre introducido es prácticamente el 100%; para carbón esta cifra puede bajar hasta el 90-95%.

Las **concentraciones** emitidas son función del exceso de oxígeno en los humos. Por ejemplo, para fueloil pesado nº 2 con 3,5% de azufre y 3% de exceso de aire, la concentración es de 2100 ppm (aprox. 6000 mg/Nm^3).

Para carbón con 0,9% de azufre (22% de cenizas) e idéntico exceso de aire, alcanzaría un valor de 900 ppm (aprox. 2550 mg/Nm^3).

Las **emisiones específicas** son función del consumo, también específico, de la instalación, inversamente proporcional a la potencia de la misma. Por ejemplo, para una potencia de 600 MW y los tipos de fueloil y carbón antes mencionados, resultan respectivamente 13,5 y 7 g/Kwh.

SO_3

Procede de la oxidación del SO_2. Su presencia es función de las condiciones de combustión (exceso de oxígeno). Las concentraciones son más bajas para el carbón (<20 ppm para carbón de 2-3% de azufre) que para el fueloil (usualmente varias decenas de ppm), debido a la reducción del SO_3 o neutralización con cenizas alcalinas. Su presencia es muy importante debido a que eleva drásticamente el punto de rocío de los gases, dando lugar a las nieblas ácidas de H_2SO_4.

b) *Oxidos de nitrógeno (NO_x).*

El 90-95% corresponde a óxido nítrico (NO) y el resto al dióxido de nitrógeno (NO_2). El origen del NO_x es doble: térmico, procedente del nitrógeno molecular del aire, con gran dependencia de la temperatura de llama y del tiempo de residencia a alta temperatura; y NO_x del nitrógeno combinado presente en el combustible, función de la riqueza en oxígeno de la atmósfera de combustión en fases iniciales y del exceso de oxígeno global.

Las emisiones de NO_x procedentes de fueloil se encuentran influenciadas por el nitrógeno del combustible y el exceso de aire, situándose entre 0,6-1,3 g/Kw/h (200-700 ppm, 250-500 mg/Nm^3). En el caso del carbón vienen condicionadas principalmente por el tipo de instalación, con rangos de 2-2,6 g/Kwh (500-650 ppm, 650-850 mg/Nm^3).

c) Oxidos de carbono e hidrocarburos

Teoricamente, cuando se realiza una combustión completa de carbón en el aire, los gases resultantes deben contener una proporción en volumen del 21% de dióxido de carbono y 79% de nitrógeno. La mayoría de los actuales combustibles contienen hidrógeno, de ahí que el gas resultante sea una mezcla de dióxido de carbono, vapor de agua y nitrógeno.

El óxido de carbono es un producto de la combustión incompleta de los diversos combustibles, como consecuencia de un reglaje deficiente de las instalaciones de combustión. En condiciones normales de funcionamiento y cuando la combustión se está produciendo con un rendimiento adecuado, la emisión de CO debida a fuentes estacionarias es mínima. Por tanto, desde el punto de vista de la contaminación del aire, el CO emitido por equipos fijos de combustión, raramente es causa de problemas.

La emisiones de CO a la atmósfera, provienen principalmente de los motores de gasolina, que suelen trabajar con un bajo exceso de aire. Se estima que su contribución a la contaminación por CO oscila alrededor del 64%. Los motores Diesel, por el contrario, al trabajar con mayores coeficientes de exceso de aire, emiten menores cantidades de CO a la atmósfera.

En las combustiones incompletas, se emiten también hidrocarburos policíclicos, especialmente hidrocarburos aromáticos policondensados, tales como los benzopirenos, pireno, perileno y benzoperilenos.

d) Partículas

Las comprendidas entre 5-10μ sufren deposión rápida, mientras que las inferiores a 5μ (especialmente las submicrónicas) permanecen durante largo tiempo (varios días) en el aire en forma de aerosoles. Atendiendo a su origen se tiene:

Carbones.- Los contenidos de cenizas son importantes, usualmente 12-16% e incluso hasta 30%. A la materia particulada que producen se añaden inquemados, usualmente en proporción menor del 5%, función del exceso de oxígeno para un mismo carbón molido a idéntica finura. La ceniza volante producida tiene un 3% en peso menor de 5 micras, un 20% entre 5 y 10, 40% entre 10 y 20 y un 30% entre 20 y 50.

Para 500 MW, el consumo de 50 t/h de carbón (15% cenizas) a plena carga se traduce en aproximadamente 12 g/Nm^3 a la entrada del precipitador electrostático; con eficacia del 99,0 las emisiones son de 120 mg/Nm^3 equivalentes a 220 Kg/h. La casi totalidad (en peso) se deposita en un radio de una decena de kilómetros, a un promedio de 0,1 g/m^2.semana.

La fracción submicrónica no se ve afectada por el paso a través del precipitador y, en consecuencia, la composición en metales de la ceniza volante se enriquece en As y Sb entre otros.

Fueloils.- La materia particulada emitida es de dos tipos:

Cenizas, en muy pequeña cantidad y proporción procedentes de materiales inorgánicos no combustibles (0,5 g/Kg).

Inquemados, divididos a su vez de dos categorías: hollines y cenosferas. Los primeros formados por cracking y condensación en fase gaseosa de hidrocarburos insaturados, para dar partículas muy finas (<0,1 micras) que pueden aglomerarse. Las cenosferas son pequeñas esferas huecas procedentes de la combustión incompleta del residuo carbonoso sólido, en el que terminan las gotas de combustible atomizado.

La formación de inquemados depende de la naturaleza del combustible (asfaltenos-conradson), del grado de atomización, (temperatura y agente) y de las condiciones de combustión (exceso de aire, temperatura de llama). El 99% de inquemados en centrales térmicas de fueoil son cenosferas.

Existe una problemática reciente derivada de la modificación de la estructura de refino, con procesos de cracking térmico (visbreakings) y mayores concentraciones (no sujetas a especificación) de asfaltenos y conradson. Los niveles de emisión en consecuencia han subido apreciablemente.

2.4.- DISPERSIÓN DE CONTAMINANTES EN LA ATMÓSFERA

2.4.1.- INTRODUCCIÓN

La dispersión de contaminantes en la atmósfera se ha estudiado extensamente durante los últimos veinte años. Sin embargo, aún existen importantes lagunas de conocimiento, tanto a niveles teóricos como de bases de datos experimentales completas y suficientes. En general, la experiencia acumulada demuestra que los modelos y soluciones desarrollados para un determinado lugar, no son directamente extrapolables a otros, aunque sí pueden serlo las metodologías elaboradas y la experiencia acumulada.

El control de los residuos contaminantes debe apoyarse, entre otras cosas, en el conocimiento detallado de las emisiones, su destino y la dosis a que están sometidos los receptores potenciales. Para el caso de los contaminantes aéreos la situación se complica de modo importante, debido a que las emisiones se hacen en un fluído móvil, sin un confinamiento claramente definido, que se caracteriza por un comportamiento dinámico extraordinariamente aleatorio.

2.4.2.- PROCESOS DE DISPERSIÓN DE CONTAMINANTES

El proceso esquemático de la dispersión de contaminantes en la atmósfera se indica en la Fig. 1. La dispersión clásica, a partir de la emisión, se considera como el resultado de una difusion relativa debida a la turbulencia atmosférica, que desgaja la nube de humos mientras se efectúa su transporte por el viento.

Es importante destacar que en el momento de su emisión, los contaminantes quedan influenciados por las relaciones entre la geometria

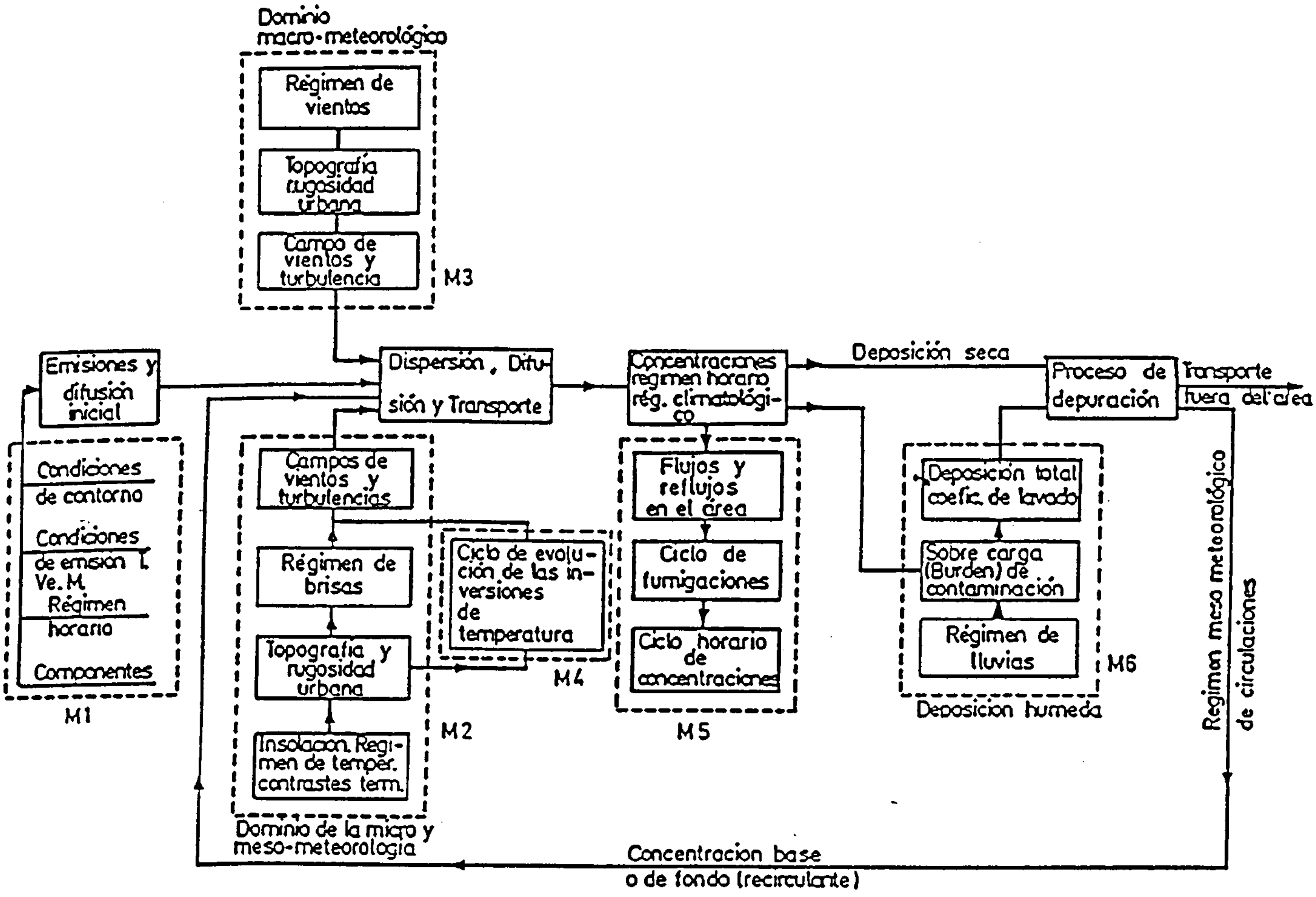


Figura 1.- Esquema de los procesos de dispersión (difusión más tranporte) y Transmisión (dispersión más deposición) de las emisiones a la atmósfera. El número asociado con cada módulo es indicativo de su dependencia de los anteriores y de su complejidad. Así, la evolución del campo de concentraciones en el ambiente (M5) depende de las emisiones (M1), de los efectos meteorológicos locales (M2), condicionados por la situación metereológica general (M3), y el ciclo de estabilidad atmosférica (M4).

del punto emisor respecto al resto de la fábrica o edificios colindantes (M1), por la estabilidad atmosférica (M4), y por los vientos inducidos (M2) o modificados por el entorno topográfico. En general, todos estos factores interaccionan de forma no lineal, y el cálculo de las concentraciones o de los niveles de inmisión a partir de las emisiones, estabilidades y vientos, no resulta un problema trivial.

Existen, en efecto, muchas situaciones para las cuales las formulaciones más simples del cálculo de altura de chimeneas y difusión de contaminantes no son ni adecuadas ni aplicables. Situaciones de este tipo, con circulaciones restringidas y poca ventilación, pueden darse como resultado de: estancamientos y atrapamientos en valles u hondonadas, recirculaciones causadas por efectos costeros y de ladera-valle, desprendimientos a sotavento de colinas, etc. A éstas deben añadirse las de escapes accidentales, paradas imprevistas, etc. El resultado es que pueden existir condiciones puramente meteorológicas, topográficas, de operación o una combinación de ellas, en las que los valores límite de inmisión pueden excederse sobre áreas extensas y durante períodos prolongados.

2.4.3.- COMPORTAMIENTO DE LOS PENACHOS

Partiendo del supuesto de un penacho ideal que contiene partículas y gases, se tiene que en el momento en que el humo se evacúa, las partículas de más peso empiezan a abandonar el penacho y a proyectarse sobre el suelo por efecto de la fuerza de la gravedad, mientras que las más finas continúan en aquél hasta perder su energía cinética y caer a su vez al suelo, y así sucesivamente hasta que tan sólo quedan aquellas partículas que se comportan como un gas, y se adaptan al proceso de dispersión de éste. En otras palabras, se registran dos procesos de deposición bien definidos, siempre claro está, en el supuesto de unas condiciones ideales.

Aunque con ligeras modificaciones, estas condiciones se presentan a menudo, aunque entre los procesos de contaminación existen casos muy característicos e importantes. El estudio del proceso ideal de dispersión tiene un gran interés para estudiar los valores medios diarios de contaminación, pero cuando el penacho deja de comportarse idealmente debido a la existencia de capas de inversión, vientos muy fuertes, torbellinos muy localizados, etc., puede descender hacia el suelo con toda su carga dando lugar a valores de contaminación elevados, muy localizados y de corta duración, valores que se apartan de manera notable del caso ideal. De ahí el interés que tiene definir estos tipos de penachos no ideales.

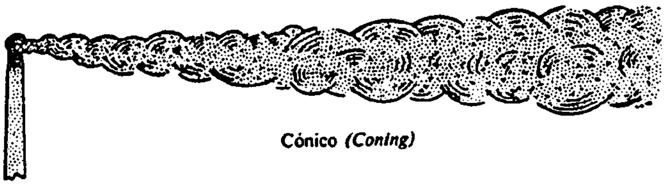
Estos distintos tipos *-coning, fanning, trapping, fumigating, looping, lofting-* que en castellano se denominan: cónico, tubular, aprisionado, fumigante, serpenteante y antifumigante, se presentan en la fig. 2.

El caso de difusión ***serpenteante*** se suele dar en atmósferas inestables con predominio de vientos ligeros: los penachos tocan el suelo, se elevan y vuelven a descender, y así sucesivamente, lo que se traduce en elevados valores de concentración. Este tipo de penacho es típico durante los días muy soleados del verano, que originan en la atmósfera condiciones térmicas muy inestables, y también cuando la turbulencia mecánica es de tipo muy acusado.

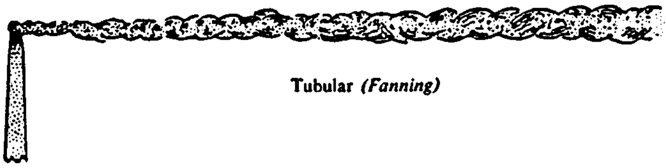
El tipo ***cónico*** se produce en condiciones idénticas pero más moderadas que las anteriores. Suele aparecer en días soleados pero nublados, es decir, en los días tormentosos del verano, si bien también lo hace en la primavera y otoño, debido a que las nubes reducen considerablemente los efectos térmicos. En este caso el viento ejerce una influencia fundamental.

El tipo ***tubular*** puede compararse a un gas que por una tubería inmaterial se propaga desde la boca de la chimenea, en condiciones de gran estabilidad atmosférica y ausencia de efectos mecánicos. Es típico de las horas de caída de la tarde, de la noche y del amanecer.

Por último, existen dos tipos de dispersión idénticos pero de

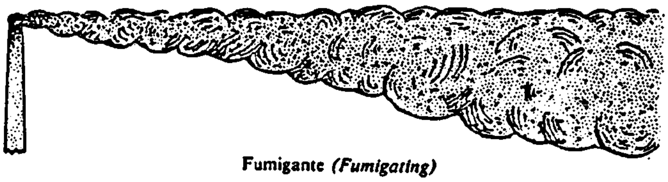


Cónico *(Coning)*

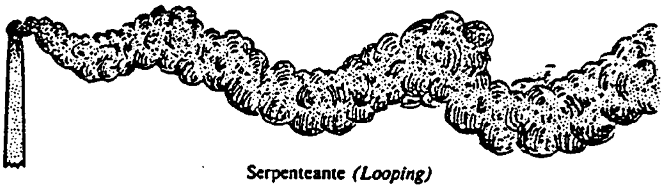


Tubular *(Fanning)*

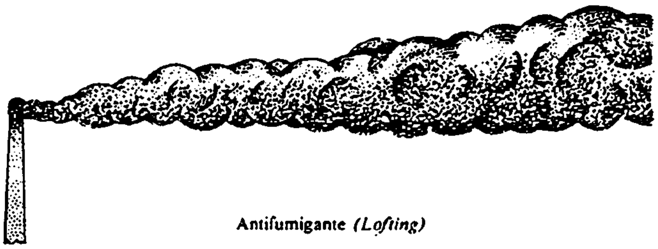
Aprisionado *(Trapping)*



Fumigante *(Fumigating)*



Serpenteante *(Looping)*



Antifumigante *(Lofting)*

FIG. 2.- Tipos de penacho

aspectos inversos. La ***fumigación*** se produce cuando un penacho de humos queda aprisionado en una capa de inversión, la cual se rompe por la parte inferior dejando escapar el penacho, que se proyecta hacia el suelo. Es este uno de los tipos de dispersión más peligrosos, por la elevada concentración de contaminantes que produce en un determinado momento. Es el más típico y corriente, ya que puede originarse a partir de un penacho tubular engendrado durante las horas nocturnas de gran estabilidad. A la salida del Sol, la Tierra se calienta y se forma una capa muy inestable a nivel del suelo que, a medida que avanza el día, va progresando hasta alcanzar la capa de inversión en su primer punto. En este momento, el penacho se dispersa produciendo la fumigación del suelo.

Con respecto a la ***antifumigación***, el caso es totalmente inverso, es decir, el penacho emitido por la chimenea tiene la suficiente energía como para atravesar la capa de inversión, y los gases que descienden quedan retenidos por la lámina de aire correspondiente al segundo punto de inversión, mientras que el resto sigue difundiéndose como si la inversión no existiera. Como se puede deducir éste es el mejor caso de elevación y dispersión de los penachos de humos y, de ahí el gran interés en contar con chimeneas elevadas de hasta 200 m de altura. Este es un fenómeno típico del atardecer, ya que la masa de aire estable se desarrolla de abajo a arriba, cuando el suelo pierde rápidamente el calor almacenado durante el día.

Otro tipo de penacho que se puede asociar a la fumigación es el tipo ***aprisionado***, que se forma cuando la emisión tiene lugar en una atmósfera inestable. El penacho se eleva hasta alcanzar una capa de inversión que no puede atravesar, y que lo rechaza hacia el suelo. Por tanto, al penacho de fumigación típico se le podría llamar de fumigación *por rotura* y a éste de fumigación *por choque*.

2.4.4.- MODELOS DE DISPERSIÓN

Para evaluar el impacto ambiental de las emisiones y predecir el rango de concentraciones en ambiente se han desarrollado, durante las

En resumen, en lo que respecta a la generación de productos ácidos se distinguen dos rutas básicas de formación. La primera engloba una secuencia de reacciones en fase gaseosa en la cuál los radicales libres, generados por vía fotoquímica (luz solar), juegan un papel fundamental. La segunda, propia de ambiente seco y soleado, tiene lugar por reacción de los óxidos de azufre y nitrógeno con los radicales hidroxilo.

$$OH + SO_2 \rightarrow HSO_3 + \text{sulfatos ácidos} \qquad [1]$$

$$OH + NO_2 \rightarrow HNO_3 \qquad [2]$$

Un ejemplo de las transformaciones por vía fotoquímica es la oxidación del NO a NO_2 en un penacho la cuál, tras uno pocos segundos de viaje, transcurriría por el siguiente mecanismo:

$$NO + O_3 \rightarrow O_2 + NO_2 \qquad [3]$$

El agente oxidante -ozono- proviene del aire en el que el penacho se diluye y en cuyo interior, al menos en las primeras decenas de kilómetros de viaje, el NO se encuentra en exceso respecto al O_3 ambiental. El resultado es que el contenido de ozono en el penacho disminuye debido a que la reacción [3] es rápida, de modo que el proceso avanzará hacia los límites de aquél, dónde se produce la mezcla con el aire del ambiente. Precisamente esta mezcla suele ser el proceso más lento y en consecuencia, el que determina la velocidad de formación del NO_2.

En términos generales y particularmente en condiciones de verano soleado, la conversión de al menos la mitad del NO en NO_2 tiene lugar aproximadamente a las dos horas de viaje del penacho.

En lo que respecta a la formación de productos ácidos por reacción con radicales OH, en el caso de la reacción [1] el proceso puede evolucionar hacia la formación de H_2SO_4, si bien una fracción del sulfato aerosol formado va a ser neutralizado por el amoniaco de origen natural para dar $(NH_4)_2SO_4$.

Evidentemente la velocidad de producción de especies ácidas por naturaleza de la superficie. Asimismo, el valor de Vg varía considerablemente en función del tipo de contaminante gaseoso, característica ésta estrechamente relacionada con la afinidad química de las superficies, y particularmente con la solubilidad en agua.

Durante el transporte a través de la capa de mezcla, los cálculos realizados acerca de la velocidad media de deposición, para el SO_2, por ejemplo, indican que éste es eliminado mediante deposición seca a un ritmo aproximado del 2-4%/hora. **Si bien el arrastre por las precipitaciones es probablemente un proceso más rápido, la deposición seca constituye el mecanismo de eliminación del SO_2 más importante, siendo también el más eficiente para el NO_2, NO, y los aerosoles de sulfatos y nitratos. Asimismo constituye el proceso dominante en las proximidades del punto de emisión, mientras que la deposición húmeda prevalece en áreas remotas.**

b) Deposición húmeda

El arrastre de gases y partículas por las precipitaciones puede desarrollarse a través de dos procesos: ***rainout*** en los que el material se incorpora a las gotas en el interior de la nube, y ***washout*** en los que lo hace por debajo de esta última. Asimismo, hay dos formas de abordar el problema: a través del coeficiente de sorción o arrastre (scavenging coefficient), o del coeficiente de lavado (washout ratio).

Coeficiente de sorción

El flujo de contaminantes hacia el suelo debido a la deposición húmeda puede expresarse como:

$$F_w = \int_0^H \Lambda\ (z,t) . \chi (z,t) . dz$$

siendo Λ un coeficiente de sorción o arrastre, χ la concentración de contaminante y H la capa atmosférica donde se produce tal sorción o arrastre por hidrometeoros. Por analogía con la deposición seca se puede definir una velocidad de deposición húmeda:

$$V_w = \frac{F_w}{\chi_{(0,t)}}$$

de forma que si se supone que los contaminantes estan distribuidos de forma uniforme en toda la capa, entonces:

$$V_w \approx \int_0^H \Lambda\ (z,t).dz = \bar{\Lambda}\ .H$$

En el caso de partículas, Λ depende del tamaño de éstas y de las gotas, y de un coeficiente de colisión entre ambas, considerándose irreversible el proceso de sorción. La eficiencia de la colisión depende también de la distribución de tamaño de las partículas contaminantes.

El problema es más complejo en el caso de los gases, puesto que si bien el proceso de captura de partículas es irreversible, ello no es aplicable a las moléculas de gas, salvo casos excepcionales de determinada composición química del hidrometeoro y del contaminante. El flujo de una especie gaseosa hacia un hidrometeoro, es proporcional al denominado coeficiente de transferencia másica entre el contaminante y los elementos químicos presentes en los hidrometeoros (K_c en cm/s), e inversamente proporcional a la velocidad de caída y tamaño de estos últimos. Así:

$$\chi_{(ac)} = \frac{6\ K_c}{\bar{D}_p . V_t}\ \chi_z$$

Cuanto menor es el tamaño del hidrometeoro, más efectiva es la sorción de los contaminantes gaseosos. Por ejemplo, para el caso del NO_3H: Λ(rainout) $\approx$ 0,2 s^{-1} y Λ (washout) $\approx$ 2,10^{-4} s^{-1}, a igualdad de contenido total de agua.

Coeficiente de lavado

Otro método de cálculo de la deposición húmeda es el que utiliza el llamado coeficiente de lavado (washout ratio), que se define:

$$V_r = \frac{K_o}{\chi_o}$$

siendo K_o y χ_o la concentración de contaminante contenido en la precipitación y en el aire junto al suelo, expresadas normalmente en unidades masa/volumen. De esta forma, el flujo de contaminante hacia el suelo debido a la precipitación será:

$$F_w = K_o . p_o = \chi_o . V_r . p_o$$

Y como por otra parte:

$$V_w = F_w / \chi_o = V_r . p_o \quad \text{y también} \quad V_w \simeq \Lambda . H$$

los coeficientes de sorción (V_w) y de lavado (V_r) pueden relacionarse:

$$\bar{\Lambda} \simeq \frac{V_r . p_o}{H}$$

Según se ha comprobado experimentalmente, el coeficiente de lavado disminuye con la cantidad de precipitación debido, probablemente, a las razones anteriormente señaladas con respecto a la relación entre el tamaño de las gotas y la eficiencia de la sorción, entre otras razones. La ventaja de este procedimiento radica en que es posible realizar medidas directas del coeficiente de lavado. La mayor parte de ellos tienen un valor incluído entre 10^{-3} y 10^{-5} para partículas y entre 10^{-4} y 10^{-6} para los gases.

El empleo del coeficiente de lavado resulta más apropiado para estimaciones a largo plazo, mientras que para predicciones a plazo más reducido, es aconsejable utilizar el método del coeficiente de sorción o arrastre, siempre que se conozcan o puedan estimarse la distribución vertical de los contaminantes, distribución de tamaño de partículas, características de la precipitación, etc.

Finalmente, para ilustrar de forma gráfica lo expuesto acerca de la problemática de la contaminación atmosférica, se recoge en la fig. 7 un esquema general, en el que se representan los procesos que tienen lugar desde la emisión de los contaminantes a la atmósfera, hasta su salida de ésta a través de los distintos mecanismos de deposición.

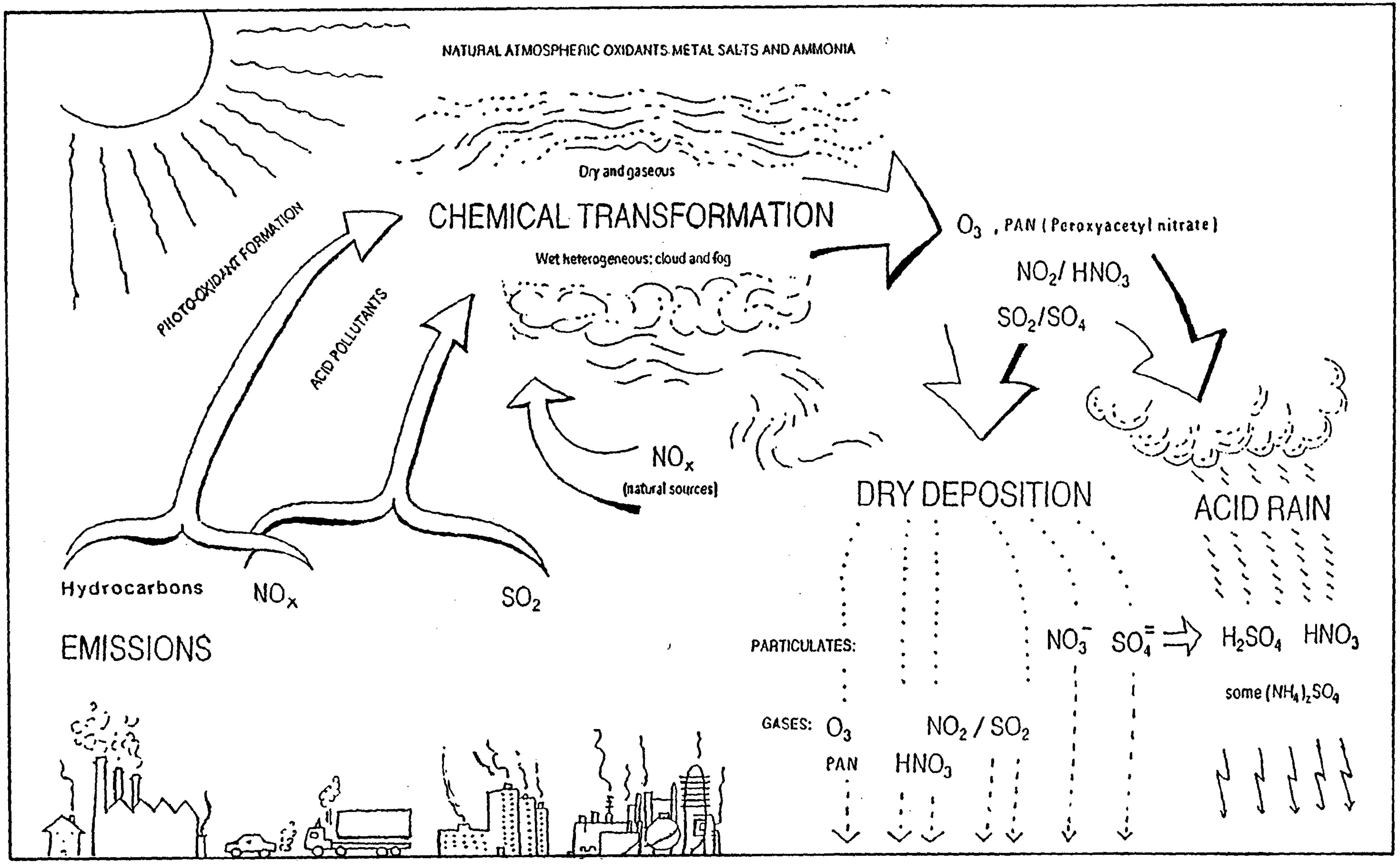


FIG. 7.- Procesos que afectan a los contaminantes en la atmósfera

3.- EFECTOS DE LA DEPOSICIÓN DE CONTAMINANTES ATMOSFÉRICOS

3.1.- CONSIDERACIONES GENERALES

Los procesos de deposición -seca y húmeda- transfieren a la superficie del terreno los contaminantes primarios y secundarios presentes en la atmósfera. Ello supone su incorporación a un nuevo ambiente geoquímico -suelo, roca, agua superficial, etc.-, en cuyo seno el término "contaminante" modifica notablemente su significado, puesto que se produce un cambio radical respecto a los procesos que gobernaban su presencia y comportamiento antes de la deposición, y es también otra la sensibilidad del medio receptor respecto a su presunta nocividad.

Evidentemente las primeras consecuencias de la deposición se manifiestan en la superficie inmediatamente en contacto con la atmósfera,y en tal sentido son los suelos, el agua superficial -especialmente lagos- y la vegetación, los que soportan el impacto directo de los agentes contaminantes. A efectos de considerar su presunta influencia sobre las aguas subterráneas, es preciso destacar fundamentalmente dos tipos de procesos: deposición de metales pesados (en adelante M.P.) y lluvia ácida. Si bien los efectos directos suelen ser los más espectaculares (p. ej., el deterioro de masas forestales por lluvias ácidas), existen otros que no siendo tan evidentes, también pueden ser fuente de graves perjuicios para el medio natural. En tal sentido es preciso hacer referencia a la problemática que plantea la **lixiviación de elementos traza -particularmente metales pesados- hacia la zona saturada**, referida tanto a la fracción que aporta la deposición atmosférica, como a la que preexiste en el terreno y es removilizada por su influencia. En efecto, puesto que la migración de los M.P. en solución requiere, entre otros factores, de un bajo valor de pH en la solución del suelo, es evidente que la lluvia ácida va a favorecer dicha removilización: es decir, que ambos factores ejercerán un efecto sinérgico sobre la calidad de las aguas subterráneas.

Además de favorecer la removilización de los M.P., los procesos de acidificación pueden llegar a incidir de forma directa en el pH del agua subterránea, en la medida que el suelo y la zona no saturada suprayacentes sean incapaces de neutralizar el aporte de H^+ del agua de lluvia. En tal sentido los materiales de menor contenido en carbonatos -granitos, gneises, pizarras, etc.-, y los suelos con bajo índice de saturación de bases (ver apdo. 3,3), serán los más favorables a la acidificación.

Si bien la exploración bibliográfica realizada en esta etapa del Proyecto, ha puesto de manifiesto abundantes referencias acerca de la incidencia de los metales pesados de origen atmosférico y la lluvia ácida sobre el suelo, las plantas y las aguas superficiales -particularmente lagos-, han sido por el contrario escasísimas las que abordan sus efectos sobre las aguas subterráneas, como ya se adelantó en la introducción de este estudio. Esta cicunstancia puede atribuirse, entre otros, a dos importantes factores.

I. La atención hasta el momento se ha centrado en el impacto evidente y directo sobre el suelo, la vegetación y las aguas superficiales, como fenómenos que se manifiestan de forma inmediata o a corto plazo, y que sin duda resultan gravemente perjudiciales para el medio afectado.

II. El suelo y la zona no saturada constituyen en principio una barrera frente a los contaminantes atmosféricos, debido a su capacidad de neutralización de componentes ácidos y de retención de los M.P. Además, las aportaciones de origen atmosférico no resultan tan importantes como las de otras fuentes de contaminación "tradicionales" (p. ej., residuos industriales).

Es evidente que, sin perjuicio de las acciones encaminadas a evaluar el impacto directo de la contaminación atmosférica sobre el suelo, plantas, etc., es preciso asumir que también las aguas subterráneas se hallan implicadas en esta problemática, puesto que el comportamiento como barrera frente a la contaminación del tramo insaturado suprayacente, ciertamente no resulta perfecto. Prueba de ello es el enorme interés actual por el estudio de los procesos físico-químicos que se desarrollan en esta porción del terreno, motivado por su influencia decisiva sobre la migración vertical de contaminantes, y al hecho clave de su consideración más como un **elemento de retardo** frente al avance de la contaminación, que como barrera impermeable a la misma (a este respecto existen ejemplos tan representativos como el de los pesticidas y los nitratos, de amplísima difusión en la literatura científica).

En base a estos antecedentes, se ha fijado como objetivo del presente capítulo la síntesis de la información bibliográfica recogida acerca de los dos temas básicos planteados: metales pesados y lluvia ácida, en la que se contemplarán aspectos fundamentales tales como por ejemplo, su influencia sobre el suelo, eslabón de capital importancia en el proceso de migración de los contaminantes hacia la zona saturada.

3.2.- METALES PESADOS

3.2.1.- ORIGEN Y CARACTERÍSTICAS DE LAS EMISIONES

Como se expuso en el apartado 2.2.1., los M.P. aparecen asociados a la materia particulada presente en la atmósfera.

Las fuentes naturales de los aerosoles que contienen M.P. comprenden: polvo terrestre, aerosol marino, emisiones volcánicas, incendios forestales y emisiones biogénicas. En lo que respecta a las fuentes de origen antrópico, destaca con especial relevancia la producción de energía eléctrica a partir de combustibles fósiles, así como también la industria de fundición de metales no férreos, otras operaciones metalúrgicas (hierro y acero, fundamentalmente, etc.), fabricación de cemento y vehículos de transporte, incineradores, etc.

Los principales elementos traza que se encuentran en las cenizas de los diversos tipos de carbón empleado en las centrales térmicas son, en orden decreciente de concentración: hierro, zinc, plomo, vanadio, manganeso, cromo, cobre, níquel, arsénico, cobalto, cadmio, antimonio y mercurio (ver tabla 3, apdo. 2.2.1.)

La C.E.E. realizó en 1983 un estudio[1] acerca de la movilización de M.P. procedentes de centrales que emplean combustibles fósiles, elaborado en base a una profunda revisión y síntesis de un amplísimo volumen de información. En el mismo se ofrece una excelente visión de los diversos factores que caracterizan estas emisiones en lo referente a los M.P., algunos de los cuales se consideran de interés para esta exposición y por tanto se recogen aquí.

Como punto de referencia inicial, en la tabla 8 se señala una serie de parámetros característicos de una central térmica tipo de 1000 MW, que emplea hulla como combustible. Destaca la importante reducción de la emisión de cenizas volantes que supone el empleo de precipitadores electrostáticos. La tabla 9 recoge un amplio barrido de la composición química y mineralógica de estas cenizas volantes. El constituyente dominante de las esferas que integran las cenizas es un vidrio de silicato de aluminio, formado en la combustión de los minerales de la arcilla presentes en el carbón. Aparecen también mullita ($3\ Al_2O_3 \cdot 2\ SiO_2$), corindón ($\alpha$-$Al_2O_3$), haluros y sulfatos de alcalinos, sulfato cálcico, silicatos y óxidos de hierro, estos últimos formados durante la combustión de los minerales piríticos presentes en el carbón, y residuos de carbón inquemado en forma de coque.

La composición de las cenizas de hulla difiere de las provenientes de la combustión del lignito y también del fuel-oil:

- Los lignitos presentan un bajo contenido en arcillas, por lo que las esferas de silicatos de aluminio son menos frecuentes. Abundan por el

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[1] Sabbioni, E.; Goetz, L.- *Mobilization of heavy metals from fossil-fuelled power plants, potential ecological and biochemical implications - IV. Assessment studies of the European situation.* EUR 6998 (1983).

Fuel:	hard coal	
	average net calorific value: (European mean 1978)	23,580 KJ/Kg
	average specific consumption: (European mean 1978)	9550 KJ/KWh generated
	ash 15% (815°C)	= 13.5% (1500°C)
	sulphur	1.5%
	moisture	5 %

coal pile extension (12-16 m high)	1 - 2.5 hectares
coal stored	100,000 - 200,000 metric tons

Flows	metric tons/h	metric tons/year at 50% full load
coal consumption	405	1.8×10^6
air consumption (25% excess)	3700	1.6×10^7
bottom ash (10%)	5.5	2.4×10^4
fly ash ESP (90%)	49.2	2.2×10^5
fly ash emitted by the stack (99.5% precipitator efficiency)	0.25	1.1×10^3
flue gas (stack)	4060	1.8×10^7
in which:		$(1.3 \cdot 10^{10}\ m^3)$
CO_2	840	3.7×10^6
CO	up to 4.3	up to 1.9×10^4
SO_2	11.6	5.1×10^4
NO_x	1.4	6.1×10^3
HCl	0.85	3.7×10^3

Tabla 8.- Consumo de carbón (hulla) y cantidad de productos generados en la combustión para una unidad de 1000 MW (50% de carga total anual)

80-90%	:	Al-silicate-glass-spheres (with Ca, Mg, K, Na, As, V, Fe, Pb, Ba etc.)
rest	:	hematite-magnetite-spheres (with Ti, Cr, Cu, Co, etc.) anhydrite ($CaSO_4$) quartz, cristobalite, SiO_2 - glass mullite ($Al_6 Si_2 O_{13}$) feldspars $M_2O \cdot Al_2O_3 \cdot 6SiO_2$ M = K, Na, Ca ½ mixed crystals of $Na_3 K(SO_4)_2$ - $K NaSO_4$ - $K_3Na(SO_4)_2$ $KAl (SO_4)_2$ sulphates: e.g. $(K, Na)_2 (Ca, Pb, Zn)_2 (SO_4)_3$, partially with Cl $ZnSO_4$ (zinkosite) fluorite (CaF_2) BaF_2 Ca-phosphates corundum ($\alpha - Al_2O_3$) hercynite ($FeAl_2O_4$) coke-particles

Tabla 9.- Composición de las cenizas volantes procedentes de la combustión de carbón

contrario los granos de cuarzo parcialmente fundidos, así como también, las partículas de anhidrita.

- La combustión de fuel-oil produce fundamentalmente inquemados sólidos, formados por coquización del combustible líquido. Los M.P. tales como V y Ni, se encuentran presentes en granos tan finos que su composición no resulta identificable por rayos X. El vanadio aparece preferentemente en forma de V_2O_5.

La tabla 10 recoge la clasificación de los M.P. de acuerdo con su distribución en varios residuos de combustión. Aunque existen algunas discrepancias entre las distintas fuentes de información, pueden considerarse válidas las siguientes conclusiones cualitativas:

- Hg, Br y Cl son totalmente emitidos en la fase gas, mientras que el Se lo es sólo de forma parcial.

- As, Cd, Sb, Pb, Se (parcialmente) y Zn evidencian un enriquecimiento en las cenizas volantes emitidas por la chimenea, respecto a su concentración de entrada en el precipitador electrostático, y a su vez de esta última respecto a las de la escoria. Ga y Mo suelen incluirse en este grupo (existe también alguna referencia similar respecto a Te y Tl).

- Cr, Ni, Co, In, V y U muestran un comportamiento poco definido que origina controversia entre los diversos trabajos. No obstante se admite que su factor de enriquecimiento[1] es pequeño.

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[1] El enriquecimiento de los elementos traza en las cenizas volantes del carbón puede expresarse por un *factor de enriquecimiento* (FE), definido mediante la siguiente ecuación:

$$FE = \frac{[x]_a/[Al]_a}{[x]_c/[Al]_c}$$

donde $[x]_a$ y $[x]_c$ son respectivamente las concentraciones del elemento x en las cenizas volantes y en el carbón, y $[Al]_a$ y $[Al]_c$ las del aluminio en estos mismos productos. Además del Al se emplean también otros elementos tales como el S_c y otras tierras raras, los cuáles muestran una distribución uniforme en los productos de combustión del carbón.

Tabla 10.- Clasificación de los M.P. en función de su distribución en diferentes residuos de combustión

Clase I, incorporada a la escoria, distribuída por igual entre escoria y cenizas volantes	Comportamiento intermedio entre las Clases I y II	Clase II, enriquecimiento en las cenizas volantes	Clase III, como vapor en el flujo de emisión
Al, Ba, Ca, Ce, Co, Eu, Fe, Hf, K, La, Mg, Mn, Rb, Sc, Si, Sm, Sr, Ta, Th, Ti	**Cr, Cs, Na, Ni, U, V**	**As, Cd, Cu, Ga, Mo, Pb, Sb, Se, Zn**	**Hg, Se, Br, Cl**
Al, Ca, Ce, Cs, Fe, Mg, Mn, K, Na, Th, Ti, Sc	**Ba, Be, Co, Cr, Cu, Ni, Sr, U, V**	**As, Cd, Ga, In, Mo Pb, Se, Sb, U, Zn**	**Hg, Br, Se**
Al, Fe, Nb, Rb, Sr, Zr, Y		**As, Cu, Mo, Pb Sb, Se, Zn**	
Ce, Fe, Na		**As, Br, Cr, Ga, Hg, Pb, Sb, Se, Zn**	**Hg, Se, Br, Cl**
		Br, As, Hg, Mo, Pb, Sb, Se, Te, Tl	

- Al, Ba, Ca, Co, Eu, Hf, Fe, K, La, Mg, Mn, Na, Nb, Rb, Sc, Si, Sm, Ta, Th y Ti tienden a incorporarse a la escoria, si bien también aparecen en las cenizas volantes.

La definición de este comportamiento diferencial, es particularmente importante a efectos de evaluar su incorporación al terreno por deposición.

La tabla 11 recoge los factores de enriquecimiento para una serie de elementos traza, contenidos en las partículas emitidas por las chimeneas de 7 centrales térmicas. La tabla 12 refleja el orden relativo de volatilidad para un conjunto de elementos y su compuestos, los cuáles volatilizan parcial o totalmente a la temperatura de combustión (≈ 1500 °C), así como algunas especies que hierven o subliman por encima y por debajo de dicha temperatura.

3.2.2.- PRODUCCIÓN DE METALES PESADOS EN LAS CENTRALES TÉRMICAS EUROPEAS (EUR-9)[1]

La evaluación de la cantidad de M.P. movilizados a través de los residuos de la combustión, constituye un elemento de particular importancia en la valoración del impacto que puede originar su deposición.

Desafortunadamente no se conocen datos (probablemente no estén elaborados) acerca del volumen de M.P. liberados por los procesos de combustión en España. Sin embargo, si existen estimaciones respecto a los demás países de la C.E.E. excepto Grecia y Portugal, concretamente en el estudio al que se hizo mención en el apartado precedente. Esta información constituye no obstante una excelente referencia sobre múltiples aspectos

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[1] EUR-9: B, Bélgica; D, Rep. Fed. de Alemania; DK, Dinamarca; F, Francia, I, Italia; IRL, Irlanda; Lx, Luxemburgo; N, Holanda; UK, Reino Unido.

Tabla 11.- Factores de enriquecimiento para una serie de elementos traza contenidos en las partículas emitidas por las chimeneas de 7 centrales térmicas

Trace element	Mass Balance Study - Power Plant						most reasonable veighed mean value
	Allen	Valmont	Chalk Point	Huntington	Four Corners 625 MW	Four Corners 520 MW	
As	6	-	6.3	6.6	7.9	5.7	6.5
Cd	-	-	-	-	6.0	-	6.0
Cr	3.0	-	1.1	2.5	2.6	1.75	2.2
Cu	1.3	1.7	-	-	-	-	1.5
Hg	-	-	-	-	-	-	a)
Mo	-	3.0	-	1.8	3.5	2.7	2.7
Ni	0.9	-	1.6	-	-	-	1.4
Pb	8.1	3.1	3.7	-	3.8	-	4.0
Sb	6.7	-	4.0	7.0	5.3	4.0	5.3
Se	5.5	1.7	5.7	3.0	5.3	4.5	4.8 a)
Th	0.76	-	-	0.95	0.90	0.90	0.9
Tl	-	-	-	-	-	-	6.5 b)
U	-	-	-	3.3	2.5	1.9	2.6
V	2.5	-	0.75	2.0	2.5	2.2	2.3
Zn	7.8	2.5	1.5	4.3	4.3	3.0	3.9
Sc	1.0	-	1.0	1.0	1.0	1.0	1.0
Fe	0.84	1.0	0.83	1.1	0.9	0.94	1.0

a) 89% of Hg and 12.15% of Se as originally contained in coal are emitted in the gaseous phase

b) no data available, assumed to be equal to the behaviour of As

Tabla 12.- Ebullición y sublimación de sustancias inorgánicas presentes durante la combustión del carbón

Species boiling or sublimating, <1550°C	Species boiling or sublimating, > 1550°C
As, As_2O_3, As_2S_3	Al, Al_2O_3
Ba	BaO
	BeO
Bi	Bi_2O_3
Ca	C
Cd, CdO, CdS	CaO
$Cr(CO)_6$, $CrCl_3$, CrS (155°C)	Co, CoO, CoS
K	Cr, Cr_2O_3
Hg	Cu, CuO
$Ni(CO)_4$	Fe, Fe_2O_3, Fe_3O_4, FeO
$PbCl_2$, PbO, PbS	MgO, MgS
Rb	Mn, MnO, MnO_2
S	Ni, NiO
	Pb (1620-1750°C)
Se, SeO_2, SeO_3	Si, SiO_2
Sb, Sb_2S_3, Sb_2O_3	Sn, SnO_2
	SrO
SnS	Ti, TiO_2, TiO
Sr	U, UO_2
Tl, Tl_2O, Tl_2O_3	
Zn, ZnS	ZnO

<u>Relative order of volatility</u>

Oxides, sulphates, carbonates, silicates and phosphates:
As, Hg > Cd > Ph, Bi, Tl > Ag, Zn > Cu, Ga > Sn > Li, Na, K, Rb, Cs

Elemental state:
Hg > As > Cd > Zn > Sb ≥ Bi > Tl > Mn > Ag, Sn, Cu > Ga, Ge

Sulphides:
As, Hg > Sn, Ge > Cd > Sb, Pb ≥ Bi > Zn, Tl > Cu > Fe, Co, Ni, Mn, Ag

de esta problemática, por lo que en este capítulo será empleada de forma reiterada.

La fig. 8 refleja de forma esquemática los diferentes aspectos cuyo conocimiento es necesario para predecir la movilización de M.P. procedentes de las centrales térmicas de carbón (siempre con referencia a los nueve países de la C.E.E. antes citados). En tal sentido es preciso conocer, en primer lugar:

I. Previsión del consumo de carbón para cada Estado Miembro. La tabla 13 recoge esta información, elaborada en base a datos de la DG XVII (D$^{\underline{on}}$ Gral. de la Energía comunitaria).

II. Valores medios del contenido de M.P. en los carbones empleados en la C.E.E.. Se listan en la tabla 14.

En base a los datos reflejados en las tablas 13 y 14, se realiza la estimación de la movilización de M.P. en las centrales térmicas de cada Estado Miembro. La tabla 15 ofrece las predicciones para los años 1980, 1985 y 1990, en comparación con la situación de 1978, que en la fig. 9 se expresa de forma gráfica. La movilización global prevista para 1990 puede resumirse como sigue:

	M.P. (Tm)
Hg, Cd, Te, U	50-500
Se, Sb, Th	500-1.000
Mo, As, Cu, Cr	1.000-10.000
Ni, Pb, V	10.000-20.000

3.2.3.- MOVILIZACIÓN DE LOS M.P. EN FUNCIÓN DEL TIPO DE RESIDUO

Si bien los resultados de la tabla 15 expresan la movilización total de las M.P., en ellos no se tiene en cuenta su distribución entre los diferentes residuos de combustión. Este dato resulta imprescindible para predecir, cualitativa y cuantitativamente, qué M.P. van a ejercer un

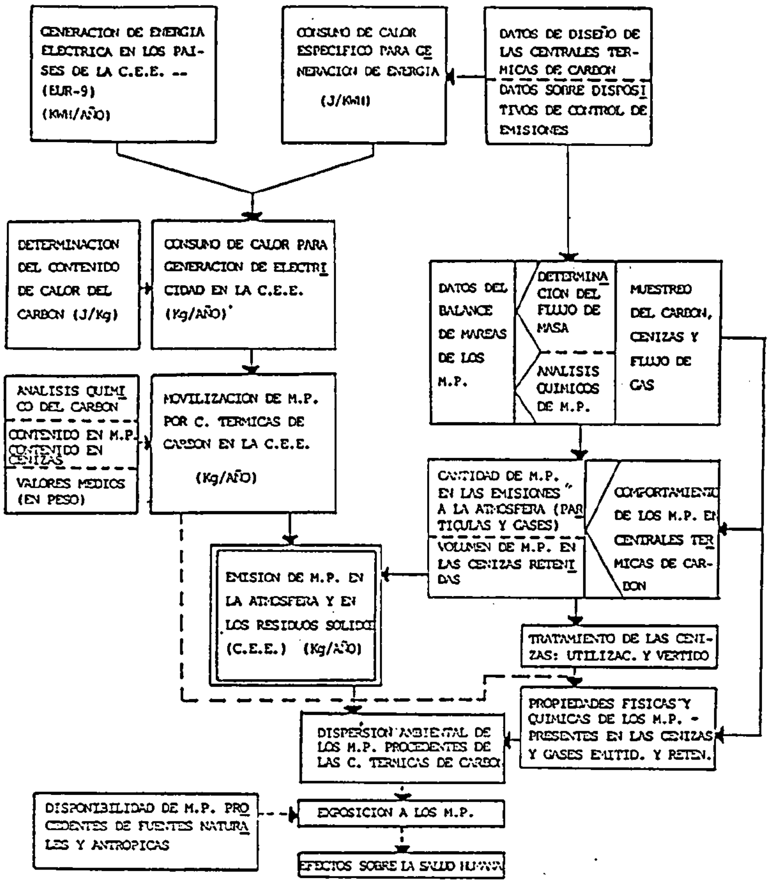

Fig. 8.- Información necesaria para predecir la movilización de metales pesados a partir de las centrales térmicas de carbón de los países de la CEE (EUR-9)

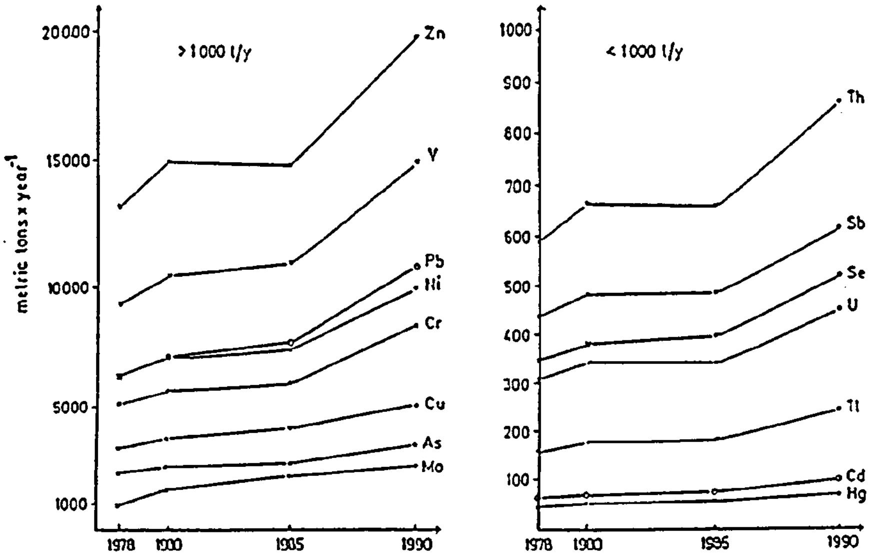

Fig. 9.- Movilización de los metales pesados a partir de las centrales térmicas de carbón de los países de la CEE (EUR-9)

Constituent	Member State									
	B	D	DK	F	I	IRL	LX	N	UK	EUR-9
As	30.6	558	49	222	21	0.3	0.01	17	1405	2303
Cd	2.4	19	2.5	11.5	1.1	0.02	0.5×10^{-3}	0.9	25	62.4
Cr	282	963	216	824	92	1.3	0.04	75	2675	5128
Cu	197	1270	108	192	46	0.7	0.02	37	1505	3356
Hg	1.8	15.4	1.4	4.6	0.6	0.008	0.3×10^{-3}	0.5	23.4	47.7
Mo	10	539	22.5	105	9.7	0.14	5×10^{-3}	7.8	251	945
Ni	259	1733	186	870	80	1.1	0.04	65	3177	6371
Pb	400	2618	260	1008	111	1.6	0.05	90	1839	6328
Sb	9	55	10.8	78	4.6	0.07	2×10^{-3}	3.7	276	437
Se	7.5	62	8.3	30	3.6	0.05	2×10^{-3}	2.9	234	348
Th	18.8	81	19.6	137	8.4	0.12	4×10^{-3}	6.8	318	590
Tl	4.7	39	4.9	23	2.1	0.03	1×10^{-3}	1.7	84	159
U	10	39	10.8	71	4.6	0.07	2×10^{-3}	3.7	167	306
V	338	2890	319	1490	137	2.0	0.07	111	4013	9300
Zn	776	2810	524	3940	225	3.2	0.1	182	4765	13225

1978

Constituent	Member State									
	B	D	DK	F	I	IRL	LX	N	UK	EUR-9
As	34	618	66	248	45	0.5	n.d.	26	1514	2552
Cd	2.6	21	3.3	12.8	2.3	0.025	n.d.	1.3	27	70.3
Cr	312	1065	290	922	198	2.2	n.d.	114	2883	5786
Cu	218	1406	145	215	99	1.1	n.d.	57	1622	3763
Hg	2.0	17	1.9	5.1	1.3	0.014	n.d.	0.73	25	53
Mo	11.4	596	30	118	21	0.23	n.d.	12	270	1059
Ni	286	1917	251	973	171	1.9	n.d.	99	3424	7123
Pb	442	2897	350	1126	239	2.7	n.d.	138	1982	7177
Sb	9.9	60	14.5	87	9.9	0.11	n.d.	5.7	297	484
Se	8.3	64	11.2	33	7.7	0.09	n.d.	4.4	252	381
Th	21	90	26	154	18	0.2	n.d.	11.5	342	663
Tl	5.2	43	6.6	26	4.5	0.05	n.d.	2.6	90	177
U	10.9	43	14.5	79	9.9	0.11	n.d.	5.7	180	343
V	374	3195	429	1664	293	3.3	n.d.	169	4325	10452
Zn	858	3110	706	4403	482	5.4	n.d.	278	5136	14978

1980 (previsto)

Constituent	Member State									
	B	D	DK	F	I	IRL	LX	N	UK	EUR-9
As	37	716	108	149	76	6	n.d.	35	1524	2651
Cd	2.9	25	5.4	7.7	3.8	0.3	n.d.	1.8	27	74
Cr	342	1235	475	554	334	26	n.d.	154	2902	6022
Cu	239	1630	238	129	167	13	n.d.	77	1633	4126
Hg	2.2	20	3.0	1.1	2.1	0.2	n.d.	1.0	25.4	57
Mo	12.5	692	49.7	71	35	2.8	n.d.	16	272	1151
Ni	314	2223	410	585	289	23	n.d.	133	3447	7424
Pb	485	3359	572	678	403	32	n.d.	186	1995	7713
Sb	10.8	69	24	52	17	1.3	n.d.	7.7	299	481
Se	9.1	74	18	20	13	1.0	n.d.	6.0	254	395
Th	25.1	104	43	92	30	2.4	n.d.	14	345	656
Tl	5.7	49.4	10.8	15.4	7.6	0.6	n.d.	3.5	90.7	184
U	12	49	24	48	17	1.3	n.d.	7.7	181	340
V	410	3705	702	1001	494.	39	n.d.	228	4354	10937
Zn	941	3605	1156	2649	813	64	n.d.	375	5170	14774

1985 (previsto)

Constituent	Member State									
	B	D	DK	F	I	IRL	LX	N	UK	EUR-9
As	44	912	140	78	350	51	n.d.	74	1798	3447
Cd	3.4	31.5	7	4	17.5	2.6	n.d.	3.7	32	102
Cr	402	1573	616	288	1540	224	n.d.	326	3424	8393
Cu	281	2076	308	67	770	112	n.d.	163	1926	5703
Hg	2.5	17.6	3.9	1.6	9.8	1.4	n.d.	2.1	30	69
Mo	14.7	881	64	37	161	23.5	n.d.	34	321	1536
Ni	369	2831	532	304	1330	194	n.d.	281	4066	9907
Pb	570	4277	742	352	1855	270	n.d.	392	2354	10812
Sb	12.7	88	31	27	77	11.2	n.d.	16.3	353	616
Se	10.7	94	23.8	10.4	60	8.7	n.d.	12.6	300	520
Th	29.5	132	56	48	140	20.4	n.d.	29.6	407	863
Tl	6.7	62.9	14.0	8.0	35	5.1	n.d.	7.4	107	246
U	14.1	63	31	25	77	11.2	n.d.	16.3	214	452
V	482	4718	910	520	2275	332	n.d.	481	5136	14854
Zn	1106	4592	1498	1376	3745	546	n.d.	792	6099	19754

1990 (previsto)

n.d. = no data available

Tabla 15.- Movilización de metales pesados (Tm) generados por las centrales térmicas de carbón (hulla) europeas (EUR-9) impacto preferente sobre determinados comportamientos del ecosistema (atmósfera, suelo, agua, etc...).

En orden a predecir, para cada país de la CEE, las cantidades de M.P. liberadas en el entorno de las centrales térmicas, resulta necesaria la siguiente información.

I. *Movilización total de M.P. y predicción del futuro consumo de carbón* (tablas 13 a 15).

II. *Cantidad total de cenizas producida y forma en que se distribuye, desde su entrada al precipitador electrostático, hasta su salida por la chimenea.* La tabla 16 ofrece una estimación de las cenizas totales, así como del volumen de cada uno de sus diferentes tipos, producido por la combustión de hullas y lignito en centrales térmicas de los 9 países de la CEE considerados[1].

III. *Conocimiento cuantitativo del reparto de los M.P. entre los residuos de la combustión, determinando para ello la* ***penetración relativa*** *del elemento (emisión/consumo).* La tabla 17 refleja la penetración en valores porcentuales, calculada en base al valor medio ponderado de los factores de enriquecimiento elemental expresados en la tabla 11. Cuanto menor es la eficiencia del precipitador, la penetración porcentual de los M.P. se incrementa.

Este incremento de la penetración es, sin embargo, algo inferior al decrecimiento de la eficiencia del precipitador, debido a que esta menor eficiencia afecta a la captura de las partículas más

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[1] Se ha supuesto:
- Contenido de cenizas del carbón: 15% (Tª cenizas = 800°C)
- Tipo de caldera: lecho seco (90% cenizas volantes y 10% cenizas del lecho)
- Eficiencia del precipitador electrostático: 99,5%
- Cenizas volantes a la salida del precipitador: 0,5%
- Cenizas volantes emitidas: 0,45% de las cenizas totales.

Member State	from hard coal and coke				from brown coal, lignite, peat			
	1978	1980	1985	1990	1978	1980	1985	1990
B	635	700	770	900	-	-	-	-
D	5200	5750	6700	8500	5750	6090	5860	5860
DK	660	890	1460	1900	-	-	-	-
F	3100	3450	2100.	1100	115	140	105	105
I	285	610	1030	4700	95	110	110	110
IRL.	4.1	6.8	81	690	150	175	205	210
LX	0.14	n.d.	n.d.	n.d.	-	-	-	-
N	230	350	470	1000	-	-	-	-
UK	11300	12150	12250	14450	-	-	-	-
EUR-9	21400	24000	24800	33200	6100	6500	6300	6300

CENIZAS TOTALES

n.d. = no data available
ash content hard coal (1600°C) assumed 13.5%
ash content brown coal assumed 5.5% [68]

Member State	from hard coal and coke				from brown coal, lignite, peat			
	1978	1980	1985	1990	1978	1980	1985	1990
B	570	630	690	810	-	-	-	-
D	4700	5200	6000	7600	5175	5480	5275	5275
DK	600	800	1300	1700	-	-	-	-
F	2800	3100	1900	970	104	126	95	95
I	260	550	920	4300	86	100	100	100
IRL	3.6	6.1	73	620	135	158	185	190
LX	0.12	n.d.	n.d.	n.d.	-	-	-	-
N	205	315	425	900	-	-	-	-
UK	10150	10950	11000	13000	-	-	-	-
EUR-9	19300	21550	22300	29900	5500	5850	5650	5660

CENIZAS VOLANTES (pptador)

n.d. = no data available
fly ash yield assumed 90% (dry bottom boiler)

Member State	from hard coal and coke				from brown coal, lignite, peat			
	1978	1980	1985	1990	1978	1980	1985	1990
B	2.9	3.2	3.5	4.1	-	-	-	-
D	23.4	25.9	30.2	38.3	25.9	27.4	26.4	26.4
DK	3.0	4.0	6.6	8.6	-	-	-	-
F	14.0	15.5	9.5	5.0	0.5	0.6	0.5	0.5
I	1.3	2.7	4.6	21.2	0.4	0.5	0.5	0.5
IRL	0.02	0.03	0.4	3.1	0.7	0.8	0.9	0.9
LX	$0.6x10^{-3}$	n.d.	n.d.	n.d.	-	-	-	-
N	1.0	1.6	2.1	4.5	-	-	-	-
UK	50.9	54.7	55.1	65.0	-	-	-	-
EUR-9	96.3	108.0	111.6	149.4	27.5	29.3	28.3	28.3

CENIZAS EMITIDAS (en chimenea)

n.d. = no data available
ESP efficiency assumed to be 99.5%

Tabla 16.- Producción de cenizas en las centrales térmicas de carbón europeas (EUR-9) de acuerdo con las previsiones de consumo de la DG XVII/D/2 (en miles de Tm)

Tabla 17.- Penetración (% de elementos para calderas de lecho seco con una producción de cenizas volantes del 90%, equipadas con un precipitador electrostático del 99,5% de eficiencia)

Element	Penetration %	Element	Penetration %
As	2.93	Sb	2.39
Cd	2.7	Se[a)]	14.3
Cr	0.99	Th	0.405
Cu	0.68	Tl	2.93
Hg[a)]	89	U	1.17
Mo	1.22	V	1.04
Ni	0.4	Zn	1.76
Pb	1.8	Sc	0.45

a) Incluyendo también los vapores

Penetración (%) = $Y_{fa} \times (100-eff_{ESP}) \times EF / 100$

Y_{fa} = rendimiento en cenizas volantes (%)

eff_{ESP} = eficiencia del precipitador electrostático (%)

EF = factor de enriquecimiento en las cenizas volantes emitidas

Tabla 18.- Penetración (%) de elementos para dos centrales térmicas cuyos precipitadores electrostáticos poseen diferente eficiencia

Element	ESP efficiency 99.8%	ESP efficiency 97%	Value used in the present work ESP efficiency 99.5%
As	1.06	11.5	2.93
Cd	n.d.	8.8	2.7
Cr	0.30	3.8	0.99
Cu	n.d.	n.d.	0.68
Hg	n.d.	n.d.	89 b)
Mo	0.19	5.1	1.22
Ni	n.d.	n.d.	0.4
Pb	n.d.	5.5	1.8
Sb	0.93	7.7	2.39
Se	0.51[a)]	7.7[a)]	2.16 a) 14.3 b)
Th	0.14	1.32	0.405
Tl	n.d.	n.d.	2.93
U	0.46	3.7	1.17
V	0.29	3.7	1.04
Zn	0.64	6.3	1.76
Sc	0.15	1.46	0.45
Al	0.13	1.1	0.45
Fe	0.16	1.32	0.45

n.d. = no data available

a) only particulate

b) particulate plus vapour

pequeñas, las cuáles contienen cantidades relativamente elevadas de M.P. respecto a su masa total. La tabla 18 muestra las penetraciones en función de la eficiencia del precipitador.

3.2.4.- PREVISIÓN DE LA EMISIÓN DE M.P. EN LOS PAISES DE LA CEE (EUR-9)

La tabla 19 ofrece la estimación del contenido de M.P. en las emisiones por chimenea correspondiente al período de 1980-1990, en comparación con la situación de 1978, calculada en base a la previsión de la movilización total (tablas 14 y 15), predicción de las diferentes cenizas producidas (tabla 16) y valores de penetración para cada elemento (tabla 17).

En orden a valorar el grado de influencia de la eficiencia del precipitador electrostático sobre la emisión de M.P. en chimenea, la tabla 20 ofrece una comparación de la descarga de M.P. en dos centrales de similares características, con excepción de la eficiencia del precipitador. Los resultados indican que se produce un notable incremento en los M.P. emitidos cuando la central trabaja con una eficiencia del 97%.

La tabla 21 refleja en términos porcentuales la fracción de la masa total de cenizas emitidas, correspondiente a cada una de las categorías de tamaño de partícula en que éstas se agrupan. La tabla 22 muestra para esta misma clasificación, la distribución porcentual de masas correspondiente a una serie de 15 elementos traza. Combinando estos datos con las previsiones de liberación de M.P., se obtiene, a modo de ejemplo, la previsión de la emisión de 1985 en función del tamaño de las partículas, tal como se recoge en la tabla 23.

3.2.5.- INCIDENCIA AMBIENTAL DE LA DEPOSICIÓN DE M.P.

El conocimiento acerca del comportamiento de los M.P. incorporados al suelo por la deposición, resulta fundamental para predecir su posible

Constituent	Member State									
	B	D	DK	F	I	IRL	LX	N	UK	EUR-9
As	0.9	16.3	1.4	6.5	0.6	0.009	0.3×10^{-3}	0.5	41.1	67.4
Cd	0.065	0.51	0.068	0.31	0.03	0.0005	0.014×10^{-3}	0.024	0.68	1.68
Cr	2.8	9.5	2.1	8.2	0.9	0.013	0.4×10^{-3}	0.74	26.5	50.8
Cu	1.3	8.6	0.7	1.3	0.3	0.005	0.1×10^{-3}	0.25	10.2	22.8
Hg	1.6	13.7	1.25	4.1	0.53	0.007	0.27×10^{-3}	0.45	20.8	42.5
Mo	0.12	6.5	0.27	1.28	0.12	0.002	0.06×10^{-3}	0.094	3.05	11.5
Ni	1.04	6.9	0.74	3.5	0.32	0.004	0.2×10^{-3}	0.26	12.7	25.5
Pb	7.2	47.1	4.7	18.1	2.0	0.03	1×10^{-3}	1.6	33.1	113.9
Sb	0.21	1.3	0.26	1.9	0.11	0.002	0.05×10^{-3}	0.09	6.6	10.4
Se	1.1	8.9	1.2	4.3	0.5	0.007	0.3×10^{-3}	0.4	33.5	49.8
Th	0.08	0.33	0.08	0.55	0.03	0.5×10^{-3}	0.02×10^{-3}	0.03	1.3	2.4
Tl	0.14	1.14	0.14	0.67	0.06	1×10^{-3}	0.03×10^{-3}	0.05	2.46	4.66
U	0.12	0.46	0.13	0.83	0.054	0.8×10^{-3}	0.02×10^{-3}	0.043	1.95	3.58
V	3.5	29.9	3.3	15.4	1.4	0.02	0.7×10^{-3}	1.1	41.5	96.3
Zn	13.6	49.3	9.2	69.1	3.9	0.06	2×10^{-3}	3.2	83.6	232.1

1978

Constituent	Member State									
	B	D	DK	F	I	IRL	LX	N	UK	EUR-9
As	1.0	18.1	1.9	7.3	1.3	0.015	n.d.	0.8	44.3	74.6
Cd	0.07	0.57	0.09	0.35	0.06	0.7×10^{-3}	n.d.	0.035	0.73	1.9
Cr	3.1	10.5	2.9	9.1	2.0	0.02	n.d.	1.1	28.5	57.3
Cu	1.5	9.6	1.0	1.5	0.7	0.008	n.d.	0.4	11.0	25.7
Hg	1.78	15.1	1.7	4.5	1.2	0.013	n.d.	0.64	22.3	47.2
Mo	0.14	7.2	0.36	1.43	0.26	0.003	n.d.	0.15	3.3	12.9
Ni	1.14	7.7	1.0	3.9	0.68	0.0076	n.d.	0.40	13.7	28.5
Pb	8.0	52.1	6.3	20.3	4.3	0.05	n.d.	2.5	35.7	129.2
Sb	0.24	1.4	0.35	2.1	0.24	0.0026	n.d.	0.14	7.1	11.5
Se	1.2	9.2	1.6	4.7	1.1	0.01	n.d.	0.63	36.0	54.5
Th	0.085	0.36	0.11	0.62	0.073	0.8×10^{-3}	n.d.	0.046	1.39	2.69
Tl	0.15	1.26	0.19	0.76	0.13	0.001	n.d.	0.076	2.63	5.19
U	0.13	0.50	0.17	0.92	0.12	0.0013	n.d.	0.067	2.11	4.0
V	3.9	33.1	4.4	17.2	3.0	0.034	n.d.	1.75	44.8	108.2
Zn	15.1	54.6	12.4	77.3	8.5	0.095	n.d.	4.9	90.1	262.9

1980 (previsto)

Constituent	Member State									
	B	D	DK	F	I	IRL	LX	N	UK	EUR-9
As	1.08	20.9	3.2	4.4	2.2	0.18	n.d.	1.0	44.6	77.5
Cd	0.08	0.68	0.15	0.21	0.10	0.008	n.d.	0.05	0.73	2.0
Cr	3.4	12.2	4.7	5.5	3.3	0.26	n.d.	1.5	28.7	59.6
Cu	1.6	11.1	1.6	0.88	1.14	0.09	n.d.	0.52	11.1	28.1
Hg	1.96	17.8	2.7	2.8	1.9	0.18	n.d.	0.89	22.6	50.8
Mo	0.15	8.4	0.6	0.86	0.43	0.034	n.d.	0.19	3.3	14.0
Ni	1.26	8.9	1.64	2.34	1.16	0.09	n.d.	0.53	13.8	29.7
Pb	8.7	60.5	10.3	12.2	7.3	0.58	n.d.	3.35	35.9	138.8
Sb	0.26	1.65	0.57	1.25	0.41	0.03	n.d.	0.18	7.1	11.5
Se	1.3	10.6	2.6	2.9	1.9	0.14	n.d.	0.86	36.3	56.6
Th	0.10	0.42	0.17	0.37	0.12	0.01	n.d.	0.057	1.40	2.65
Tl	0.17	1.44	0.32	0.45	0.22	0.018	n.d.	0.10	2.65	5.37
U	0.14	0.57	0.28	0.56	0.20	0.015	n.d.	0.090	2.12	3.98
V	4.24	38.3	7.3	10.4	5.1	0.40	n.d.	2.4	45.1	113.2
Zn	16.5	63.3	20.3	46.5	14.3	1.1	n.d.	6.6	90.7	259.3

1985 (previsto)

Constituent	Member State									
	B	D	DK	F	I	IRL	LX	N	UK	EUR-9
As	1.3	26.7	4.1	2.3	10.2	1.5	n.d.	2.2	52.6	100.8
Cd	0.09	0.85	0.19	0.11	0.47	0.07	n.d.	0.10	0.86	2.75
Cr	4.0	15.6	6.1	2.86	15.2	2.2	n.d.	3.2	33.9	83.1
Cu	1.9	14.1	2.1	0.46	5.2	0.76	n.d.	1.1	13.1	38.8
Hg	2.2	15.7	3.5	1.4	8.7	1.2	n.d.	1.9	26.7	61.4
Mo	0.18	10.7	0.78	0.45	1.96	0.29	n.d.	0.41	3.9	18.7
Ni	1.5	11.3	2.1	1.2	5.3	0.78	n.d.	1.1	16.3	39.6
Pb	10.3	77.0	13.4	6.3	33.4	4.9	n.d.	7.1	42.4	194.6
Sb	0.30	2.1	0.74	0.64	1.84	0.27	n.d.	0.39	8.42	14.69
Se	1.53	13.4	3.4	1.49	8.58	1.24	n.d.	1.80	42.9	74.3
Th	0.12	0.53	0.23	0.19	0.57	0.08	n.d.	0.12	1.65	3.50
Tl	0.20	1.84	0.41	0.23	1.02	0.15	n.d.	0.21	3.13	7.20
U	0.16	0.74	0.36	0.29	0.90	0.13	n.d.	0.19	2.50	5.28
V	5.0	48.8	9.4	5.4	23.5	3.4	n.d.	5.0	53.2	153.7
Zn	19.4	80.6	26.3	24.1	65.7	9.6	n.d.	13.9	107.0	346.6

n.d. = no data available

1990 (previsto)

Tabla 19.- Contenido de M.P. en las emisiones por chimenea de los paises de la CEE (EUR-9)

Tabla 20.- Contenido en M.P. en las emisiones a la atmosféra estimadas para los países de la CEE (EUR-9) en 1985, calculado para dos tipos de eficiencia del precipitador electrostático

	ESP efficiency	
	99.5%	97%
As	77.5	305
Cd	2.0	6.5
Cr	59.6	229
Cu	28.1	n.d.
Hg	50.8	50.8
Mo	14.0	59
Ni	29.7	n.d.
Pb	138.8	424
Sb	11.5	37
Se	56.6	78
Th	2.65	8.7
Tl	5.37	21.2[a)]
U	3.98	12.6
V	113.2	405
Zn	259.3	931

n.d. = no data available

[a)] penetration assumed to be equal to that of As

Tabla 21.- Relación entre la masa y el tamaño de partícula en las emisiones de sólidos por chimenea

Size fraction microns	mass fraction of total emitted ash %
0 - 1.5	10
1.5 - 3	26
3 - 7	35
7 - 15	16
15 - 40	10
> 40	3

Tabla 22.- Distribución porcentual de la masa frente al tamaño de particulas para los M.P. presentes en las emisiones de sólidos

Diámetro de partila (micras)	Contenido en M.P. de las partículas emitidas por chimenea (%)														
	As	Cd	Cr	Hg[a)]	Mo	Ni	Pb	Sb	Se[a)]	Th	Tl	U	V	Zn	Sc
0 - 1.5	35	35	43	93	74	32	49	40	39	20	35	48	64	35	19
1.5 - 3	29	26	20	1	8	21	19	29	14	42	29	17	17	26	41
3 - 7	32	33	30	2	17	13	17	27	35	34	32	34	18	33	36
7 - 15	3	5	5	2	1	8	7	4	8	3	3	1	1	5	3
15 - 40	1	1	2	2	0	26	8	0	4	1	1	0	0	1	1

a) sólo MP contenidos en partículas, no en fase vapor

As, Cr, Mo, Sb, Se, Th, U, V, Zn, Sc para una eficiencia del precipitador del 99,8%
Hg, Ni, Pb para una eficiencia del precipitador del 96%
Cd se supone un comportamiento similar para Cd-Zn, así como para Tl-As

Tabla 23.- Previsión de la emisión de M.P. en función del tamaño de particulas en el territorio de los países de la CEE (EUR-9) para 1985.

Element	Particle size in microns				
	0 - 1.5	1.5 - 3	3 - 7	7 - 15	15 - 40
As	27.1	22.5	24.8	2.3	0.8
Cd	0.7	0.52	0.66	0.1	0.02
Cr	25.6	11.9	17.9	3.0	0.6
Hg	49 a)	0.3	0.5	0.5	0.5
Mo	10.4	1.1	2.4	0.1	-
Ni	9.5	6.2	3.9	2.4	7.7
Pb	68.0	26.4	23.6	9.7	11.1
Sb	4.6	3.3	3.1	0.5	-
Se	52.0[a)]	1.1	2.6	0.6	0.3
Th	0.53	1.11	0.9	0.08	0.03
Tl	1.9	1.6	1.7	0.16	0.05
U	1.9	0.68	1.36	0.04	-
V	72.4	19.2	20.4	1.2	-
Zn	90.8	67.4	85.6	12.9	2.6

a) inclusive of vapours

migración desde este horizonte hacia las aguas subterráneas. La naturaleza e intensidad de la interacción metales/componentes del suelo, es la responsable de que, en determinadas circunstancias, llegue a producirse una removilización de los M.P. retenidos y su consecuente migración hacia horizontes inferiores.

Como punto de referencia inicial, la tabla 24 recoge para una serie de M.P. los valores de deposición total (Kg/Ha/año), seca y húmeda, para áreas urbanas, rurales y remotas.

Una vez introducidos en el suelo, los M.P. pueden interaccionar directamente con sus componentes a través de una compleja serie de procesos químicos, físicos y biológicos.

El suelo constituye una eficiente barrera para la migración de los M.P., a menos que el elemento se encuentre bajo forma disuelta. Las condiciones de pH y los componentes orgánicos e inorgánicos del suelo, influyen decisivamente en la movilidad de los M.P. en su seno. Las tablas 25, 26 y 27 ofrecen una orientación inicial al respecto. En ellas se recoge, respectivamente, la afinidad de los M.P. por los distintos componentes del suelo, su concentración a diferentes valores de pH y, finalmente, su comportamiento (movilidad) respecto a los diferentes procesos genéticos.

Los diferentes componentes del suelo se encuentran en equilibrio dinámico, tal como refleja la figura adjunta.

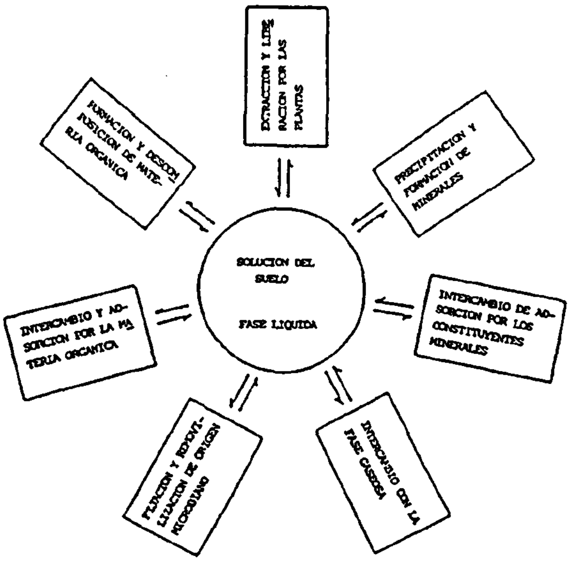


Tabla 24.- Deposición de M.P. en áreas urbanas, rurales y remotas

Deposition rate (kg/ha/yr)	As	Cd	Co	Cr	Cu	Hg	Fe	Mn	Ni	Pb	Sb	Se	V	Zn
Remote														
Bulk	0.00031	0.000002–0.00005		0.003	0.000012–0.0019	0.0002		0.0062		0.000012–0.0093	0.00016			0.000011–0.025
Dry						0.002								
Rural														
Bulk	0.01–<10	0.0012–<0.1		0.01–0.5	0.018–0.5	0.00073–0.01	0.85	0.021–0.5	0.01–0.5	0.01–<2.72	<0.01	<0.01	0.01–12.4	0.04–11
Dry	<0.0036	<0.047		<0.02		<0.02		<0.31	0.09	<0.72			<0.25	<2.02
Wet	<0.8	<0.094		<0.57	0.033	<0.0002	0.54	<0.25	<0.87	<2.1			<4.8	0.095–<7.92
Urban														
Bulk	0.0025–<1.1	0.007–0.26	<1	10.6	0.002–3.01	0.015	0.4–10.0	<1.0	0.1–5.95	0.05–12.36			0.043–8.3	0.07–15.8
Dry	0.002–<0.003	<0.094	0.00009	0.0026–0.4	0.119	0.00005	0.117	0.0027–<0.83	0.0044–<1.1	0.042–<2	0.006		0.003–<0.35	0.053–5.94
Wet	0.001–<1.23	0.001–<0.17	0.000036	0.00084–<0.7	0.164	0.0003	0.042	0.0023–<0.99	0.0044–<2.74	0.026–<26.5	0.004		0.044–<9.04	0.12–11.9
Washout ratio	110	125–5000		150	140–751		250–951	370–5000	125	76–169			110	179–1000
Dry deposition velocity (cm/s)	<0.1	0.4–8.0	0.3–1.9	0.5	0.5–1.1		0.3–1.9	0.4–0.9	0.45–2.0	0.16–0.3	0.06–<0.4	<0.1–0.6	0.2–0.7	0.4–4.5

Tabla 25

AFINIDAD DE LOS MP POR LOS COMPONENTES DEL SUELO

Material	Relative affinity	Reference
Al oxides (amorphous)	Cu > Pb > Zn > Cd	Kinniburgh et al. (1976)
Geothite	Cu > Pb > Zn > Cd	Forbes et al. (1974)
Fe oxides (amorphous)	Pb > Cu > Zn > Cd	Kinniburgh et al. (1976)
Mn oxides	Cu > Zn	Murray (1975)
Fulvic acid (pH 5.0)	Cu > Pb > Zn	Schnitzer and Skinner (1967); Schnitzer (1969)
Humic acid (pH 4-7)	Zn > Cu > Pb	Verloo and Cottenie (1972)
Humic acid (pH 4-6)	Cu > Pb > Cd > Zn	Stevenson (1977)

Tabla 26

ELEMENTOS TRAZA EN SOLUCIONES DE SUELOS NATURALES DE DIFERENTE pH OBTENIDOS POR CENTRIFUGACION

	Tipo de suelo y rango de pH				
Elementos	Arenoso ácido (2,5-1)	Arenoso (1-1,5)	Silty (5,5-6,5)	Loamy (7-7,5)	Calcáreo (7,5-7,8)
B	-	-	-	200	800
Cd	107	-	-	-	-
Co	-	-	-	- 0,5	5
Cu	783	76	20	50	50
Fe	2223	1000	500	200	100
Mn	5965	8000	5000	100	700
Mo	-	-	-	5	5
Pb	5599	-	-	-	-
Zn	7137	1000	5000	100	300

Nota: los valores representan la media aritmética ($\mu g/l$) de 4-5 muestras

Tabla 27

PRINCIPALES TIPOS DE PROCESOS DE FORMACION DE SUELOS Y TENDENCIAS EN EL COMPORTAMIENTO DE LOS ELEMENTOS TRAZA

			Comportamiento de los elementos traza en la superficie del suelo	
Proceso	Zona climática más favorable	Unidad de suelo típica[1]	Acumulación	Migración
Escasa alteración química	Hielos o desierto	R,Q e Y	-	-
Podzolización	Fríos nórdicos	O y P	Co,Cu,Mn,Ni,Ti,V,Zr (en horizonte iluvial)	B,Ba,Br,Cd,Cr, I,Li,Mn,Rb,Se, Sr,V, y Zr
Aluminización	Templada fresca y húmeda	B,L,M,W y A	Co,Mn,Mo y V	B,Ba,Br,Cu,I, Se y Sr
Sialitización	Templado caluroso y tropical seco	V y K	B,Ba,Cu,Mn,Se y Sr	-
Laterización	Trópico húmedo	A,F, y N	B,Ba,Cu,Co,Cr,Ni,Sr, Ti y V	-
Alcalinización	Cálido con estaciones secas	Z,S y (X)	B,Co,Cr,Cu,Mo,Ni,Se, Zn y V	-
Formaciones hidromórficas	Suelos intrazonales	-	B,Ba,Co,Cu,I,Mn,Mo, Se,Sr, y U (en horizonte orgánico)	B,Br,Co,Cu,Mn, Ni,U y V

[1] Según clasificación FAO/UNESCO

En el marco de este equilibrio, los metales pesados aparecen involucrados en una serie de procesos que pueden conducir a su inmovilización o, por el contrario, a su migración hacia horizontes inferiores. A continuación se realiza un breve examen de dichos procesos, responsables en último término de que los M.P. procedentes de la deposición atmosférica, lleguen o no a incorporarse al agua subterránea. En primer lugar se consideran los principales mecanismos de **captura** de los M.P., y en segundo los procesos que favorecen su **removilización**.

A. RETENCIÓN DE LOS M.P. EN EL SUELO Y ZONA NO SATURADA

La tabla 28 resume los principales mecanismos de retención de los M.P. en el suelo y zona no saturada, que a continuación se exponen brevemente:

A1. Precipitación de los M.P.

La concentración de un ión metálico en los estados iniciales de la precipitación, depende primordialmente de las especies aniónicas en disolución, más que del tipo y concentración del mismo, así como del pH. Con excepción del AgCl, HgCl y $PbCl_2$, los cloruros y sulfatos de los M.P. más comunes son solubles, mientras que los carbonatos, hidróxidos y sulfuros se disuelven con dificultad.

Los procesos de precipitación de *hidróxidos metálicos* tienen lugar bajo formas diversas, y su comportamiento frente a los procesos de coprecipitación o posterior redisolución será diferente. La forma "activa", probablemente equivalente en la mayor parte de los casos a un precipitado amorfo o formado por una agregación desordenada de finos cristales, es concretamente la que se deriva de soluciones fuertemente sobresaturadas. Estos precipitados pueden persistir en equilibrio metaestable con la solución, y convertirse lentamente -a escala de tiempo geológico- en formas inactivas o viejas ("aged forms"). Estas formas inactivas también pueden formarse por precipitación de

-Hidróxidos -Carbonatos -Sulfuros de metales pesados	Se produce la precipitación al excederse los productos de solubilidad
Hidróxidos y óxidos de Fe/Mn	Sorción física Sorción química (intercambio de H^+ en posiciones fijas) Coprecipitación al excederse el producto de solubilidad
Materia orgánica-humus	Sorción física Sorción química (intercambio de H^+ en grupos $COOH^-$, OH^-) Complejos
Carbonato cálcico	Sorción física Pseudomorfosis (en función del volumen y el tiempo) Coprecipitación al excederse el producto de solubilidad

Tabla 28.- Mecanismos de asociación de los metales pesados con los componentes del suelo

Tabla 29

LOGARITMO NEGATIVO DE LOS PRODUCTOS DE SOLUBILIDAD DE HIDROXIDOS DE LOS METALES PESADOS (CONSTANTES DE IONIZACION TOTAL), CARBONATOS Y SULFUROS (pH=7 a 25°C)

Hydroxides		$-\log K_T$	Sulfides		$-\log K_{sp}$	Carbonates	$-\log K_{sp}$
$Mn(OH)_2$	(aged)	10.9	MnS	(pink)	9.6	$MnCO_3$	10.2
$Mn(OH)_2$	(cryst.)	12.7	MnS	(green)	12.6		
$Cd(OH)_2$	(aged)	14.4	CdS		27.8	$CdCO_3$	11.3
$Fe(OH)_2$	(aged)	15.1	FeS		17.2	$FeCO_3$	10.5
$PbO + H_2O$	(red)	15.3	PbS	(galena)	27.5	$PbCO_3$	13.1
$Co(OH)_2$	(blue)	14.2	CoS	(alpha)	20.4	$CoCO_3$	12.8
$Co(OH)_2$	(pink, aged)	15.7	CoS	(beta)	24.7		
$Zn(OH)_2$	(amorphous)	15.5	ZnS	(wurtzite)	21.6	$ZnCO_3$	10.8
$ZnO + H_2O$	(aged)	16.8	ZnS	(sphalerite)	23.6		
$Ni(OH)_2$	(active)	14.7	NiS	(alpha)	18.5	$NiCO_3$	6.9
$Ni(OH)_2$	(aged)	17.2	NiS	(gamma)	25.7		
$CuO + H_2O$	(active)	19.7	CuS		36.1	$CuCO_3$	9.6
$CuO + H_2O$	(tenorite)	20.5	Cu_2S		48.0	$Cu_2(OH)_2CO_3$	33.8
$HgO + H_2O$	(red)	25.4	HgS		52.4		
$Cr(OH)_3$	(aged)	37.4					
$Fe(OH)_3$	(aged)	39.1					

soluciones poco sobresaturadas.

Se recoge a continuación un ejemplo de este tipo de reacciones, concretamente para el caso del hidróxido de cadmio:

$$Cd(OH)_2 \text{ ("aged")} \rightleftharpoons Cd^{2+} + 2OH^-;\ K_T = [Cd^{2+}] \times [OH^{-2}] = 10^{-14,4}$$

$$Cd(OH)_2 \text{ ("aged")} \rightleftharpoons CdOH^+ + OH^-;\ K_1 = [CdOH^+] \times [OH^-] = 10^{-9,5}$$

$$CdOH^+ \rightleftharpoons Cd^{2+} + OH^-;\ K_2 = \frac{[Cd^{2+}] \times [OH^-]}{[CdOH^+]} = 10^{-4,9}$$

La constante de equilibrio K_T expresa la ionización total.

Los *sulfuros* de los M.P. son prácticamente insolubles a pH neutro, mientras que la solubilidad de los *carbonatos* es altamente dependiente de la presión parcial de CO_2 (todos los carbonatos tienden a ser más solubles en presencia de CO_2), como se observa a continuación.

$$Me(II)\ CO_3 + H_2O + CO_2 \rightleftharpoons Me^{2+}(aq) + 2(HCO_3)^-(aq)$$

La tabla 29 ofrece algunos ejemplos acerca de la solubilidad en agua pura de una serie de hidróxidos, sulfuros y carbonatos metálicos, y la tabla 30 indica los rangos de pH en que se produce la precipitación. Resulta pues factible establecer una escala de movilidad de los cationes metálicos en la fase acuosa del suelo, en función de su capacidad para formar estos compuestos insolubles. En el caso de un suelo en régimen de oxidación, la movilidad en orden decreciente sería la siguiente:

$Mg^{2+}=Ca^{2+}>Ag^+>Hg^{2+}>Mn^{2+}>Cd^{2+}>Ni^{2+}=Co^{2+}=Pb^{2+}>Be^{2+}>Zn^{2+}=Cu^{2+}>Cr^{3+}>Bi^{3+}>$
$Sn^{4+}>Fe^{3+}>Zr^{4+}>Sb^{3+}$.

Estos datos son solamente una guía para reconocer su comportamiento, puesto que en los sistemas naturales la solubilidad real va a ser el resultado de la interacción de un gran número de factores. La fig. 10, por ejemplo, muestra las diferentes curvas de solubilidad del cadmio y zinc en función del contenido en CO_2 a diferentes pH. Asimismo, el tipo de producto que resulta de la precipitación viene definido por la relación pH-Eh, tal como refleja la fig. 11.

Tabla 30

ASOCIACIONES GEOQUIMICAS Y ALGUNAS PROPIEDADES DE ELEMENTOS MAYORITARIOS Y TRAZA

Elementos mayoritarios y traza	pH de precipitación del óxido hidratado	Radio Iónico (Å)	Electronegatividad (Kcal/g átomo)	Potencial iónico (carga/radio)	Diámetro del ión hidratado en solución acuosa (Å)
K^{+}	—	1.7—1.6	0.8	0.6	3.0
Na^{+}	—	1.2—1.1	0.9	0.9	4.5
Cs^{+}	—	2.0—1.9	0.7	0.5	2.5
Rb^{+}	—	1.8—1.7	0.8	0.6	2.5
Ca^{2+}	—	1.2—1.1	1.0	1.8	6.0
Mg^{2+}	10.5	0.8	1.2	2.5	8.0
Sr^{2+}	—	1.4—1.3	1.0	1.5	5.0
Ba^{2+}	—	1.7—1.5	0.9	1.3	5.0
Pb^{2+}	7.2—8.7	1.6—1.4	1.8	1.9	4.5
Sc^{3+}	—	0.8	1.3	3.7	9.0
Fe^{2+}	5.1—5.5	0.9—0.7	1.8	2.6	6.0
Cu^{2+}	5.4—6.9	0.8	2	2.5	6.0
Ge^{4+}	—	0.5	1.8	8.3	—
Mo^{4+}	—	0.7	—	5.5	—
Mn^{2+}	7.9—9.4	1—0.8	1.5	2.0	6.0
Zn^{2+}	5.2—8.3	0.9—0.7	1.8	2.6	6.0
Fe^{3+}	2.2—3.2	0.7—0.6	1.9	4.4	9.0
Co^{2+}	7.2—8.7	0.8—0.7	1.7	2.6	6.0
Cd^{2+}	8.0—9.5	1.03	—	—	—
Ni^{2+}	6.7—8.2	0.8	1.7	2.6	6.0
Cr^{3+}	4.6—5.6	0.7	1.6	4.3	9.0
Mn^{4+}	—	0.6	—	6.5	—
Li^{+}	—	0.8	1.0	1.2	6.0
Mo^{6+}	—	0.5	1.8	12.0	—
V^{5+}	—	0.5	—	11.0	—
Al^{3+}	3.8—4.8	0.6—0.5	1.5	5.6	9.0
Be^{2+}	—	0.3	1.5	5.7	8.0
Cr^{6+}	—	0.4	—	16.0	—
Ga^{3+}	3.5	0.7—0.6	1.6	4.9	—
La^{3+}	—	1.4—1.3	1.1	2.3	9.0
Sn^{2+}	2.3—3.2	1.3	1.8	1.5	—
Y^{3+}	—	0.9	1.2	3.1	—
Si^{4+}	—	0.4	1.8	12.0	—
Ti^{4+}	1.4—1.6	0.7	1.5	5.8	—
Zr^{4+}	2.0	—	1.4	4.3	11.0

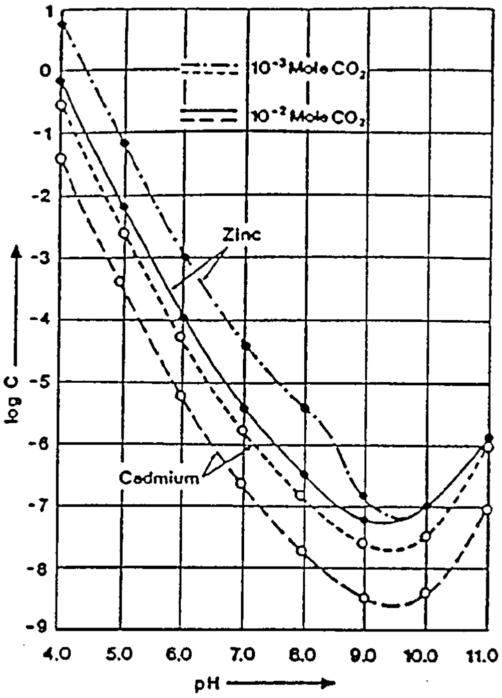


FIG. 10.- Solubilidades del Zn y Cd en agua en función del pH, para concentraciones de CO_2 disuelto de 10^{-3} y 10^{-2} mol/l. Fuerza iónica = 0,0; log C en moles de Zn o Cd.

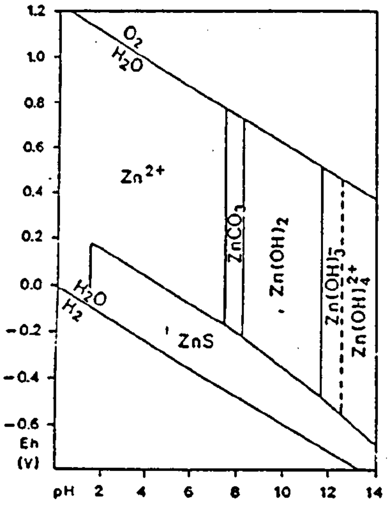


FIG. 11.- Campos de estabilidad de formas sólidas y de especies disueltas predominantes del Zn en el sistema Zn + CO_2 + S + H_2O a 25°C y 1 atm., en relación con el pH y Eh. Actividad del Zn disuelto = 10^{-5} mol/l; CO_2 disuelto y especies sulfuradas = 10^{-3} mol/l.

Tabla 31

Area superficial específica y capacidad de cambio de diversas sustancias sorbentes activas

Material	Specific surface area (m^2/g)	Exchange capacity (meq/100 g)
Calcite (< 2 μm)	12.5[a]	-
Clay minerals:		
Kaolinite	10 - 50[b]	3- 15[e]
Illite	30 - 80[b]	10- 40[e]
Chlorite	-	20- 50[e]
Montmorillonite	50 -150[b]	80-120[e]
Freshly precipitated Fe-hydroxide	300[c]	10- 25[e]
Amorphous silicic acid	-	11- 34[e]
Humic acids from soils	1900[d]	170-590[f]

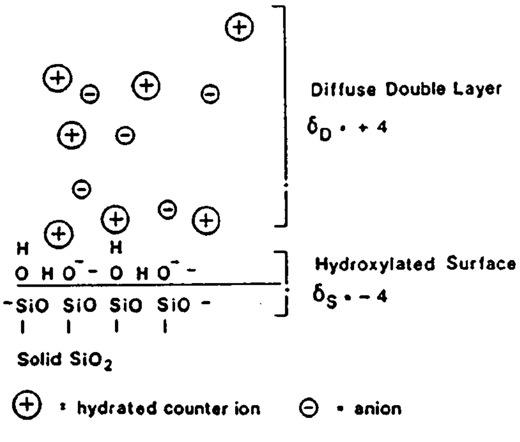
[a] Suess, 1973. [b] Heling, pers. comm. [c] Fripiat and Gastuche, 1952. [d] Gapon, 1947. [e] Scheffer and Schachtschabel, 1966. [f] Marshall, 1964.

A2. Intercambio catiónico y adsorción

Ciertos materiales -presentes en el suelo y la zona no saturada- caracterizados por disponer de una gran área superficial (minerales de la arcilla, precipitados de hidróxidos de hierro, sílice amorfa y sustancias orgánicas), son capaces de *sorber* cationes de la solución, y *liberar* cantidades equivalentes de otros cationes. El mecanismo de este intercambio catiónico se basa en la capacidad de atracción de iones positivos por una serie de posiciones cargadas negativamente: SiOH-, $AlOH_2$-, grupos AlOH- en las arcillas, grupos FeOH- en los hidróxidos de hierro y grupos OH- carboxílicos y fenólicos en sustancias orgánicas. Para el caso, por ejemplo, de una arcilla, las reacciones que tendrían lugar serían del tipo de las siguientes:

Ca-arcilla + Zn^{2+} = Zn-arcilla + Ca^{2+}
Ca-arcilla + $2Na^{+}$ = Na_2-arcilla + Ca^{2+}

El balance de cargas negativas en la red del material resulta de un proceso selectivo, el cuál tiene lugar mediante una sorción preferencial de cationes específicos, y la liberación de cargas equivalentes asociadas a otras especies. Mediante este proceso, los materiales formados por granos finos con un gran área superficial, son capaces de acumular iones de M.P. en la interfase sólido-líquido, como resultado de la acción de fuerzas intermoleculares. Este fenómeno se denomina ***adsorción***. La figura adjunta refleja esquemáticamente este proceso para el caso de la superficie de un silicato en contacto con un electrolito.



La suma de cationes cambiables (incluyendo H^+) se denomina ***"capacidad de cambio"***, que se expresa en miliquivalentes (meq)/100 g. material. La tabla 31 recoge algunos ejemplos.

A3. Adsorción sobre minerales de la arcilla

El pH constituye un factor dominante en los procesos de adsorción de los M.P. sobre los minerales de la arcilla, puesto que los iones H^+ compiten con aquéllos por las posiciones de intercambio. En condiciones extremadamente ácidas, los cationes de los M.P. pueden llegar a ser liberados totalmente.

Los minerales de la arcilla poseen una afinidad selectiva por ciertos metales, en la que intervienen factores tales como la valencia de los iones, electronegatividad, potencial de ionización, etc., y que permiten establecer secuencias como la siguiente:

$$Pb > Ni > Cu > Zn$$

En el caso del plomo, por ejemplo, su especial afinidad por los minerales de la arcilla estería justificada por su radio iónico, muy similar al del potasio, que es uno de los metales que se incorpora primariamente a aquéllas. No obstante hay que señalar que en el campo de la adsorción de M.P. en arcillas existen procesos y comportamientos aún no bien comprendidos. Por ejemplo, se ha observado que la adsorción de metales en los sistemas naturales resulta en muchos casos muy inferior a la esperada, incluso en ocasiones insignificante. La justificación a este comportamiento se hallaría en la competencia por parte de otros procesos (precipitación y floculación de sustancias orgánicas y minerales, adsorción en hidróxidos de hierro, etc.), que reducirían notablemente el contenido en M.P. disponible para su adsorción por las arcillas.

A4. Sorción y coprecipitación por hidróxidos de hierro y óxidos de manganeso

Los óxidos hidratados de aluminio, hierro y manganeso, -particularmente los óxidos e hidróxidos de Fe y Mn bajo condiciones de oxidación-, constituyen verdaderas *trampas* de acumulación de M.P. en los sistemas acuosos; incluso a bajas concentraciones, $Fe(OH)_3$ y MnO_2 pueden controlar su distribución, a través de procesos de sorción y coprecipitación. La siguiente reacción constituye un ejemplo de dichos procesos:

$$Mn\text{-}OH^{o} + Co^{2+}(aq) = Mn\text{-}O\text{-}CO^{+} + H^{+}(aq)$$

Ahora bien, en medio reductor los M.P. objeto de sorción se removilizan y pasan nuevamente a la solución, convirtiéndose en una fuente de los mismos. Este mecanismo es especialmente efectivo en presencia de materia orgánica disuelta.

Los óxidos e hidróxidos de Fe y Mn aparecen normalmente como una capa o recubrimiento de los minerales, así como de las partículas finas que se encuentran dispersas en los medios acuosos en forma amorfa, microcristalina o cristalina. Las formas activas presentan una elevada superficie específica: 300 m^2/g para el MnO_2 y 230-320 m^2/g para FeOOH. Su formación está condicionada por diversos factores:

a) En aguas con un rango de pH desde alcalino-neutro hasta ligeramente ácido, el hierro es oxidado por el oxígeno disuelto, mientras que para el manganeso se requieren pH mucho más elevados. Para ambos metales, la oxidación crece en un factor 100 por cada unidad de pH incrementada.

b) La oxidación química del manganeso está influenciada por la presencia de *iones inorgánicos* tales como HCO_3^- o $SO_4^=$, que inhiben o catalizan el proceso.

c) Las sustancias orgánicas, especialmente las que contienen grupos funcionales COOH- y OH-, son capaces de reducir el Fe(III) y MnO_2. Sin embargo, las mismas sustancias pueden también catalizar la oxigenación: el sistema Fe(II)/Fe(III) actúa en estos casos como un catalizador del proceso de oxidación de la materia orgánica.

d) Los oxidos e hidróxidos de Fe y Mn ejercen su influencia sobre los M.P., pero también éstos actúan sobre aquéllos de forma recíproca: el cobre, por ejemplo, cataliza la oxidación del sulfato ferroso por el oxígeno disuelto.

e) El $Fe(OH)_3$ coloidal, parcialmente peptizado por sustancias orgánicas, puede ser adsorbido por los minerales de la arcilla si se excede su producto de solubilidad.

A5. Asociación metales pesados-materia orgánica

La afinidad de las sustancias orgánicas y sus productos de descomposición por los M.P., influye de forma muy importante sobre su comportamiento en medio acuoso, debido fundamentalmente a su capacidad para (1) formar complejos con los metales e incrementar su solubilidad; (2) alterar la distribución entre las formas oxidada y reducida; (3) reducir su toxicidad así como la disponibilidad para la vida acuática; (4) ejercer cierta influencia en la extensión del proceso de adsorción sobre la materia en suspensión, y (5) afectar la estabilidad de los coloides que contienen M.P.

La materia orgánica presente en los sistemas acuosos puede estar formada por los residuos de productos de origen biológico, así como por sustancias orgánicas sintéticas. Los *ácidos húmicos* constituyen el principal producto de descomposición de las sustancias orgánicas de origen biológico, los cuáles disponen de una elevada capacidad de adsorción de cationes, estimada entre 200 y 600 meq metal/100 g. ac. húmicos. Un ejemplo de estos procesos sería:

$$\text{Ac. orgánicos} + M^{+} \rightarrow \text{Complejo organo-metálico (COM)}$$

$$\text{COM} + M^{+} \rightarrow \text{Humato (como precipitado)}$$

La eficiencia de los procesos de retención hasta aquí descritos, puede resumirse en los siguientes términos:

1. *Sorción.* La capacidad de sorción de los M.P. obedece a la siguiente secuencia:

   MnO_2 > ácidos húmicos > óxidos de hierro> minerales de la arcilla

   La capacidad de sorción de los óxidos de hierro es al menos 10 veces menor que la de los óxidos de manganeso.

2. ***Coprecipitación con óxidos e hidróxidos de Fe y Mn.*** En sistemas acuosos en condiciones de oxidación, los óxidos e hidróxidos de Fe y Mn muestran una elevada capacidad para reducir la concentración de M.P. en la fase líquida. Por ejemplo, ciertas experiencias realizadas con aguas naturales conteniendo hidróxidos de Fe/Mn, demostraron que mediante la coprecipitación se lograban unos porcentajes de reducción en las concentraciones de cobalto, zinc y cobre del 67%, 86% y 98% respectivamente.

3. ***Formación de complejos y floculación con la materia orgánica.*** En sistemas con presencia de materia orgánica, el papel de los óxidos de Fe y Mn está eclipsado por la competencia de los ácidos húmicos y de las arcillas de elevado contenido en materia orgánica. Asimismo, cuando los metales forman complejos con los ácidos húmicos, la solución se comporta como si no existiesen otros iones en el medio de reacción, los metales dejan de estar disponibles para los sulfuros, hidróxidos, carbonatos, etc. y en consecuencia, previenen la formación de sales insolubles. Por otra parte, la capacidad de adsorción de los M.P. por los materiales adsorbentes (partículas en suspensión, p. ej.), puede verse notablemente reducida por la presencia sobre éstos de películas orgánicas formadas por procesos de floculación.

B.- REMOVILIZACIÓN DE LOS METALES A PARTIR DE LOS SEDIMENTOS

Puede producirse como consecuencia de los siguientes procesos:

B1. Cambios en las condiciones redox, generalmente descensos en el potencial de óxido-reducción, que pueden dar lugar a la disolución parcial o completa de los hidróxidos de hierro y manganeso, y la consiguiente liberación de los M.P. incorporados o adsorbidos.

B2. Descenso del pH, que conduce a la disolución de carbonatos e hidróxidos, así como a incrementar la desorción de los cationes metálicos debido a la competencia con el ión H^+ (caso de la lluvia ácida, p. ej.).

B3. Incremento en el uso de agentes acomplejantes naturales y sintéticos, los cuáles forman complejos solubles con los metales pesados, que de otra manera se hallarían adsorbidos en las partículas sólidas.

B4. Transformaciones bioquímicas en virtud de las cuáles los metales pesados son transferidos desde el suelo a las plantas y organismos animales, o bien son descargados directamente o vía productos de descomposición.

B5. Incremento de la salinidad, en virtud de la cuál los cationes alcalinos y alcalinotérreos pueden competir con los iones metálicos adsorbidos en las partículas sólidas.

B1. Cambios redox y liberación de metales

Un cambio hacia condiciones reductoras puede provocar la puesta en solución de los metales que coprecipitaron o fueron adsorbidos por los hidróxidos de Fe y Mn. No obstante, en tales condiciones pueden también desencadenarse otro tipo de procesos, que en último término condicionarán su presencia en solución. Tal es el caso de la formación de sulfuros (su presencia a nivel de trazas puede disminuir significativamente la movilidad de los metales) y de quelatos con ciertas sustancias orgánicas.

Se exponen a continuación las principales reacciones redox que involucran a los óxidos e hidróxidos de Fe y Mn.

$$Fe^{3+} + e^- = Fe^{2+}$$
$$Fe(OH)_3(s) + HCO_3^- + 2H^+ + e^- = Fe(CO_3)(s) + 3H_2O$$
$$Fe(OH)_3(s) + 3H^+ + e^- = Fe^{2+} + 3H_2O$$
$$Fe(OH)_3(s) + H^+ + e^- = Fe(OH)_2(s) + H_2O$$
$$1/2\ FeS_2(s) + 2H^+ + e^- = 1/2\ Fe^{2+} + H_2S(g)$$
$$1/2\ Fe^{2+} + S(s) + e^- = 1/2\ FeS_2(s)$$
$$1/16\ Fe^{2+} + 1/8\ SO_4^{2-} + H^+ + e^- = 1/16\ FeS_2(s) + 1/2\ H_2O$$
$$1/14\ Fe(OH)_2(s) + 1/7\ SO_4^{2-} + 3/7\ H^+ + e^- = 1/14\ FeS_2(s) + 5/7\ H_2O$$
$$\begin{aligned}1/14\ Fe(CO_3)(s) + 1/7\ SO_4^{2-} + 17/14\ H^+ + e^- = 1/14\ FeS_2(s) + 1/7\ H_2O &+ \\ &+ 1/14 HCO_3^-\end{aligned}$$
$$1/2\ MnO_2(s) + 1/2\ HCO_3^- + 3/2\ H^+ + e^- = 1/2\ MnCO_3(s) + 3/8\ H_2O$$
$$Mn^{2+} + 2e^- = Mn(s)$$
$$1/2\ MnCO_3 + 1/2\ H^+ + e^- = 1/2\ Mn(s) + 1/2\ HCO_3^-$$
$$MnOOH(s) + HCO_3^- + 2H^+ + e^- = MnCO_3 + 2H_2O$$
$$MnO_2 + H^+ + e^- = MnOOH$$

B2. Influencia del pH

La liberación de M.P. por efecto de un descenso del pH, es un fenómeno que ha sido ampliamente estudiado en relación con las aguas ácidas procedentes del drenaje de minas de sulfuros metálicos, donde el incremento de la acidez tiene lugar como consecuencia de la oxidación del ión $S^{=}$ a $SO_4^{=}$, con liberación de iones H^+. Por ejemplo, en el caso de la pirita (FeS_2) se tendría:

Inicio del proceso

$$FeS_2\ (s) + O_2\ (aq) \rightarrow Fe^{2+}\ (aq) + SO_4^{2-}\ (aq) + H^+\ (aq)$$

Ciclo de propagación

$$Fe^{2+}\ (aq) + O_2\ (aq) \xrightarrow{\text{bacterias}} Fe^{3+}\ (aq)$$
$$Fe^{3+}\ (aq) + FeS_2\ (aq) \longrightarrow Fe^{2+}\ (aq) + SO_4^{2-}\ (aq) + H^+\ (aq)$$

La acidificación de los suelos tanto de origen natural como inducida por factores antrópicos (lluvia ácida, p. ej.), obviamente influye en la movilidad de los M.P. en este medio (ver tablas 26 y 30), favoreciendo el fenómeno de lixiviación hacia la zona saturada. A este respecto la naturaleza del suelo y especialmente su capacidad de neutralización resultan decisivos. El capítulo 3.3. se ocupa de estos aspectos.

B3. Removilización por agentes orgánicos

Existen diversas posibilidades de solubilización de los metales por sustancias orgánicas: (1) mediante la reducción a estados de valencia inferiores que resultan más solubles, como por ejemplo, la reducción del Fe y Mn por el ácido tánico, y del Mn y V por la turba, lignito y ácidos húmicos; (2) por formación de suspensiones coloidales o complejos solubles con los ácidos orgánicos. Los ácidos húmicos descomponen rápidamente los sulfuros -calcopirita, esfalerita, galena, pirita, etc.- y silicatos, tales como micas, cloritas y arcillas, y también los óxidos metálicos.

B4. Removilización por la actividad microbiana

Como se mencionó en el punto A.5., los M.P. pueden formar asociaciones con la materia orgánica disuelta o particulada. Después de su deposición por floculación, adsorción o precipitación, estas sustancias experimentan un proceso diagenético que supone un incremento del peso molecular, y la disminución de algunos grupos funcionales, dando lugar a una acumulación relativamente estable de metales pesados. No obstante, estos últimos pueden ser removilizados y reintegrados al medio acuoso por efecto de la actividad microbiana.

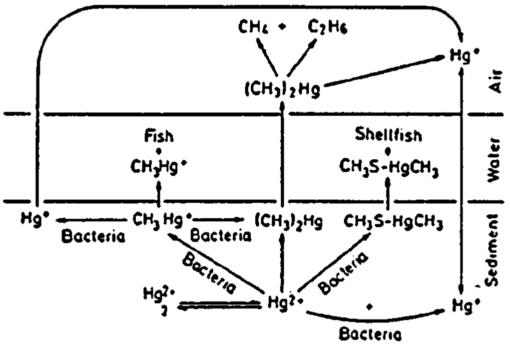
Los tres procesos más importantes que conducen a dicha removilización son:

a. *Degradación de la materia orgánica*, dando lugar a compuestos de menor peso molecular.

b. *Modificación de las condiciones redox y de pH* como consecuencia de la actividad metabólica de los microorganismos.

c. *Conversión de compuestos inorgánicos a complejos metálicos* por sustancias orgánicas, mediante procesos de oxidación y reducción catalizados por reacciones enzimáticas.

La acción microbiana sobre el ciclo del mercurio constituye un buen ejemplo de este tipo de procesos de removilización de metales. Cuando se produce un incremento de las sustancias tóxicas, frecuentemente los microorganismos son capaces de realizar una destoxificación, si bien generando productos que pueden ser más tóxicos para los organismos superiores. Tal es el caso de la producción bacteriana de metilmercurio, la cuál puede considerarse como un medio de resistencia frente a este metal, mediante su conversión a una forma orgánica y subsecuente secreción. La fig. adjunta refleja el ciclo biológico del mercurio en el medio natural.



Ciclo biológico del mercurio en el ambiente

La capacidad de transformar los compuestos de mercurio a $(CH_3)_2Hg$ se extiende a una amplia gama de microorganismos: bacterias aerobias, anaerobias y hongos.

B5. Incremento de la salinidad

El fenómeno de la desorción de los metales por efecto de la competencia de los cationes, favorece su puesta en disolución y por consiguiente, su posible migración hacia la zona saturada. Las causas que pueden dar lugar a un aumento de la concentración salina en el suelo son múltiples. Destacan, por ejemplo, el uso masivo de sal en ciertas zonas para combatir los efectos del hielo en vías públicas, el riego con aguas de salinidad natural o inducida muy elevada, etc.

Por último y a modo de resumen, la tabla 32 recoge un balance de entradas (atmósfera) y salidas (lixiviación y a través de las plantas) de elementos traza en una serie de diferentes tipos de suelos. Estos resultados indican que, para la mayoría de los elementos considerados, predomina la acumulación en el suelo. Solamente en áreas de bosque con suelos ácidos se detecta un fenómeno de lixiviación de Mn, Fe y Be que supera la aportación atmosférica.

3.3.- LLUVIA ÁCIDA

3.3.1.- CONSIDERACIONES GENERALES

Tal como se observa en la fig. 12, las precipitaciones de carácter ácido influyen de manera diversa sobre el medio receptor: deterioro de la vegetación, solubilización de sustancias tóxicas, corrosión de materiales, etc. Entre estos efectos figura el de la posible afección de las aguas subterráneas, como consecuencia fundamentalmente de dos tipos de procesos: acidificación del agua y aporte de sustancias de naturaleza y/o en concentraciones no deseables según criterios de calidad. Obviamente la influencia del horizonte edáfico y de la zona no saturada resulta decisiva, puesto que la composición inicial del agua de lluvia se altera sensiblemente a su paso por este tramo de terreno; el comportamiento de cada uno de sus componentes frente a los diversos procesos que se desarrollan en este medio, determinará en último término el potencial contaminante del lixiviado que percola hacia el acuífero.

En virtud de su capacidad de neutralización frente a componentes ácidos así como de retención de sustancias, particularmente metales pesados, el suelo y la zona no saturada constituyen una barrera protectora del acuífero frente a la lluvia ácida. Sin embargo su eficacia es limitada, puesto que existe la posibilidad real de que ciertos componentes nocivos -intrínsecos del agua de lluvia y/o liberados del terreno- superen dicha barrera y alcancen la zona saturada.

Tabla 32

BALANCE DE ENTRADAS/SALIDAS DE ELEMENTOS TRAZA PARA SUELOS DE VARIOS ECOSISTEMAS (g Ha^{-1} año^{-1})

Elemento	Entrada (atmósfera)	Salidas (flujo de agua o plantas)	Tipo de suelo	Ecosistema y localidad
		Van Hook et al		
Cd	21	7 (a)	Franco ligeramente ácido, derivado de dolomías	Bosque deciduo. Tennessee (U.S.)
Pb	286	6		
Zn	538	149		
		Hansen and Tjell		
Cd	3	0,3 (b)	Sin datos	Campo agrícola. (Dinamarca)
Pb	260	0,3		
Zn	250	120		
		Zöttl et al		
Be	0,3	5,6 (c)	Podzol marrón	Bosque de pinos. Schwarzwald. (Alemania Occ.)
Cd	4,5	1,4		
Co	5,6	4,3		
Cu	18	7		
Ni	34	17		
Mn	70	430		
Pb	110	6		
Zn	210	76		
Fe	300	2.000		
		Heindrichs and Mayer		
Bi	0,4	0,2 (c)	Marrón ácido, franco limoso	Bosque de abedules y abetos. Solling Mountains. (Alemania Occ.)
Hg	0,4	0,2		
Tl	1,2	0,3		
Sb	3	0,3		
Cd	13	9		
Ni	15	14		
Cr	22	2		
Mn	200	6.300		
Cu	224	108		
Zn	3.900	1.900		
Fe	1.600	1.900		
		Tyler		
Cd	2	5 (b)	Suelo forestal podzólico	Bosque de abetos (lisímetro). Hässleholm (Suecia)
Cr	8	10		
Ni	10	9		
V	12	28		
Cu	20	29		
Pb	150	81		
Zn	180	270		
Fe	2.000	13.000		
		Ruszkowska y datos no publicados		
Cd	5	- 3 (c)	Podzólico ligeramente - franco	Lisímetros. Putawy. (Polonia)
Cu	39	18 (b) 25		
B	71	29 40		
Mn	181	35 90		
Pb	207	- 40		
Zn	547	163 180		
		Bubliniec		
Cu	40	40 (d)	Suelo marrón	Bosque de robles. Zvolen (Checoslovaquia)
Mo	70	50		
Fe	840	1.040		
B	1.460	80		
Mn	2.480	1.930		

Nota: Métodos de cálculo basados en a) escorrentía superficial, b) agua de drenaje, c) agua de infiltración, d) absorción y evacuación por árboles.

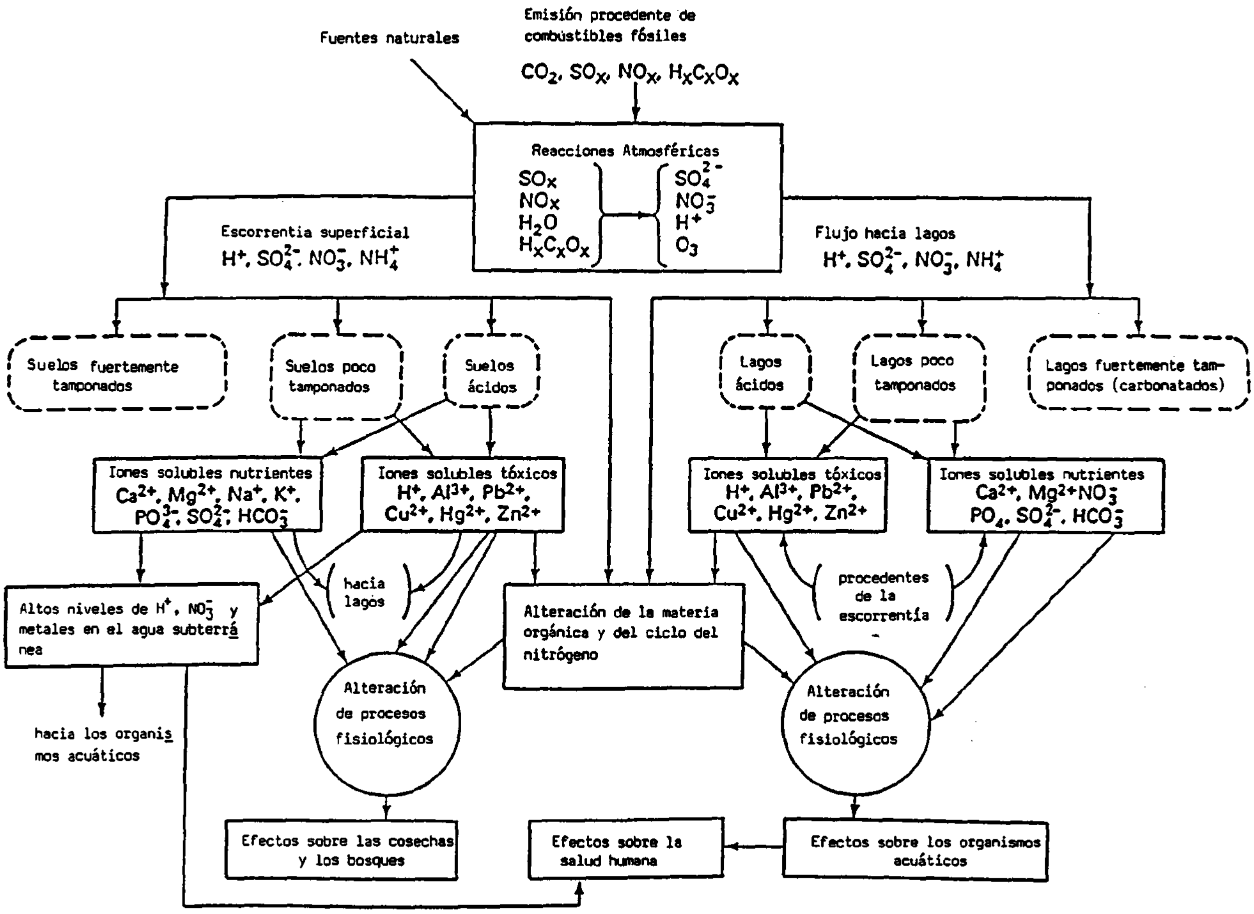


FIG. 12.- Formación, deposición y efectos de la lluvia ácida

Queda fuera de los objetivos de este estudio profundizar acerca de los complejos procesos que gobiernan el comportamiento de los contaminantes en este medio. Sin embargo si conviene examinar algunos de los aspectos más importantes relativos concretamente al fenómeno de acidificación de suelos, dada su enorme importancia en el contexto global de la problemática ambiental en cuestión. Tal es el objetivo de los siguientes apartados.

3.3.2.- NATURALEZA Y PROPIEDADES DEL SUELO

En términos generales, el suelo se compone de una compleja mezcla de materiales silíceos (arenas), minerales de la arcilla de dimensiones coloidales (caracterizados por la presencia de cargas negativas procedentes de la sustitución isomórfica de cationes por otros de carga menor), óxidos de hierro y aluminio, y diversos materiales orgánicos, a menudo también con carga eléctrica.

Entre sus propiedades más importantes figuran:

1. El suelo constituye una matriz física de la que las raíces de las plantas extraen nutrientes inorgánicos, agua y oxígeno. El agua se mueve a través de sus espacios intersticiales merced a fuerzas capilares y por gravitación, produciéndose asimismo un intercambio de gases -CO_2, N_2, O_2, etc.- con la atmósfera.

2. Los cationes son adsorbidos en el suelo por los minerales de la arcilla y la materia orgánica, y liberados cuando la solución del suelo se vuelve más diluída o modifica su naturaleza y condiciones. Los aniones monovalentes son adsorbidos en mucha menor extensión. En consecuencia, el comportamiento de los iones amonio y nitrato resulta diferente en el suelo: el NH_4^+ es retenido fuertemente mientras que el NO_3^- es repelido por la carga negativa de los coloides del suelo, lo que favorece su lixiviación.

3. El suelo contiene una amplia variedad de materiales cuyas propiedades

le confieren una importante capacidad tampón del pH frente a la adición de ácidos o bases. Destacan entre ellos: fosfatos orgánicos e inorgánicos, ácidos húmicos y fúlvicos, compuestos fenólicos, carbonatos y bicarbonatos, silicatos, etc.

4. La actividad biológica en suelos fértiles y húmedos es intensa. Los organismos involucrados son principalmente bacterias, actinomicetos, hongos y algas, así como también una amplia población de pequeños animales. Si bien todos ellos participan en algún grado en los ciclos del nitrógeno y del azufre, solamente algunas pocas especies de bacterias llegan a afectar al pH del suelo.

3.3.3.- **HIERRO Y ALUMINIO EN EL SUELO**

El pH influye de forma decisiva sobre el comportamiento en el suelo del hierro y del aluminio. Ambos participan en las reacciones de hidrólisis bajo la forma de catión trivalente. Los iones Al^{3+} pueden ser desplazados de los minerales de la arcilla, pasando de esta forma a la solución, y dando lugar a productos de hidrólisis que a su vez son reabsorbidos por las arcillas, favoreciendo de esta forma el proceso:

$$M^{2+} + \text{Arcilla-}Al^{2+} \rightleftharpoons \text{Arcilla-}M^{+} + Al^{3+} \qquad [1]$$

$$Al^{3+} + H_2O \rightleftharpoons AlOH^{2+} + H^{+} \qquad [2]$$

$$AlOH^{2+} + 2OH^{-} \rightleftharpoons Al(OH)_3 \quad pK = 5,1 \qquad [3]$$

Los minerales de la arcilla presentes en suelos de apreciable contenido de protones disociables (pH 4-5) se muestran inestables, descomponiéndose y liberando iones aluminio en cantidad suficiente como para neutralizar parte de la carga negativa neta de los coloides del suelo. En lo que respecta al hierro, su presencia bajo forma soluble en concentraciones apreciables es muy poco frecuente, limitándose fundamentalmente a suelos ácidos de naturaleza sulfatada.

El comportamiento de los suelos ácidos -con excepción de los ricos en turba (pobres en minerales arcillosos)-, se encuentra pues más influenciado por su alto contenido en aluminio soluble, que por la propia concentración de iones H^+. La presencia de formas de aluminio soluble en la solución del suelo, modifica el grado de acidez de los materiales orgánicos. La mayor parte de los grupos ácidos carboxílicos presentan constantes de disociación en el rango 10^{-4}-10^{-5}, mientras que las curvas de valoración a menudo indican un rango del orden de 10^{-6}. Esta anomalía es el resultado de la incorporación de los iones hierro y aluminio a las posiciones de intercambio de la materia orgánica, que neutraliza la acidez de los grupos carboxílicos.

3.3.4.- EL SUELO COMO TAMPÓN DEL pH

El suelo posee la capacidad de amortiguar -dentro de ciertos límites dependientes de su propia naturaleza- las variaciones de pH inducidas por la adición de ácidos o bases. Tal como describen las reacciones [1], [2] y [3], las partículas de arcilla se comportan como un ácido débil, debido fundamentalmente al equilibrio que se mantiene entre el aluminio adsorbido y el que se encuentra en solución. Si los protones formados en la reacción [2] son neutralizados por la adición de una base, el aluminio en solución precipitará en forma de hidróxido (reacción [3]). En consecuencia el pH se mantiene debido al movimiento del aluminio adsorbido hacia la solución. Este efecto tampón funciona igualmente en sentido inverso, es decir, cuando se añaden ácidos al suelo. Para el caso del Fe^{3+} se observa un mecanismo similar.

Las reacciones que involucran a los fosfatos y la materia orgánica del suelo poseen también un efecto amortiguador. Si el pH es neutro o alcalino, los ácidos orgánicos disuelven el hidróxido de aluminio (y de hierro a inferior pH), actuando los grupos carboxilato disociados como tampones frente a posteriores adiciones de ácidos; cualquier reacción de oxidación de estos grupos consume acidez.

Por último, también los minerales silicatados poseen un efecto tampón, puesto que al no encontrarse en equilibrio con los iones H^+ del suelo, consumen (lentamente) una fracción de éstos, liberando a su vez aluminio entre otros cationes.

3.3.5.- ACIDIFICACIÓN DEL SUELO

La presencia en la lluvia de especies tales como los ácidos sulfúrico y nítrico procedentes de los combustibles fósiles, puede provocar la acidificación del suelo. La fig. 13 indica la integración de estas sustancias en los respectivos ciclos del azufre y del nitrógeno.

Sin embargo, la acidificación del suelo existe también como proceso natural, especialmente en los climas templados y húmedos. Dicho proceso está controlado por el ácido carbónico y los ácidos húmicos producidos por la actividad biológica, siendo concretamente estos últimos los responsables, por ejemplo, de la acidez natural de los suelos podzólicos característicos de amplias regiones de Europa y Norteamérica. La tabla 33 resume los principales procesos de acidificación de suelos, incluído la lluvia ácida.

Los procesos de acidificación natural, con excepción de la nitrificación, no producen aniones de ácidos fuertes, mientras que en las zonas afectadas por lluvia ácida predominan estos últimos, particularmente nitratos y sulfatos. Los procesos de acidificación afectan esencialmente a los fenómenos de reemplazamiento de los cationes cambiables, tales como calcio y magnesio, por protones e iones aluminio. La liberación de bases y la movilización del aluminio resultan pues los procesos clave, tales como ilustra la fig. 14.

En orden a predecir la capacidad de un suelo para contrarrestar los efectos de la deposición ácida, es preciso disponer de información acerca de, entre otros, los siguientes factores: índices de saturación de bases, capacidad tampón y contenido de sustancias alcalinas (carbonatos, p. ej.). Tomando como referencia la clasificación de suelos establecida por los organismos FAO y UNESCO, así como la empleada en los Estados Unidos (ver equivalencia en tabla 34), se ofrece a continuación un análisis de la sensibilidad de cada una de estas tipologías a la deposición ácida, elaborado en base a los tres criterios antes mencionados.

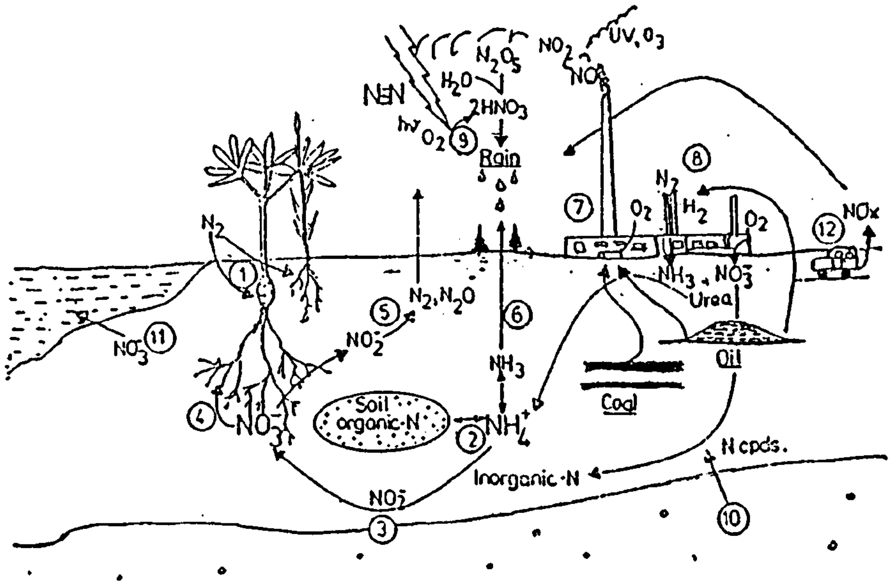


FIG. 13A.- PROCESOS MAS IMPORTANTES EN EL CICLO DEL NITROGENO

La mayor parte del nitrógeno de los ecosistemas se encuentran bajo formas bioorgánicas o en la materia orgánica del suelo. Sólo una pequeña proporción se halla en forma inorgánica, disponible para su uso por bacterias y plantas. El nitrógeno inorgánico procedente de la combustión también forma parte del ciclo del nitrógeno, con una importante aportación al fenómeno de la lluvia ácida. Las principales fases del ciclo del nitrógeno son:

1. Fijación biológica del N
2. Amonificación del N orgánico
3. Nitrificación autotrófa del amonio a nitrato
4. Absorción del N por plantas y microorganismos
5. Desnitrificación heterótrofa del NO_3^- a N_2
6. Volatilización del amonio hacia la atmósfera
7. Oxidos de N de origen industrial
8. Fijación industrial del N
9. Oxidos de N formados durante las tormentas
10. N procedente de los materiales de la litosfera
11. Lixiviación a partir de ríos, lagos y oceános
12. N procedente de los automóviles

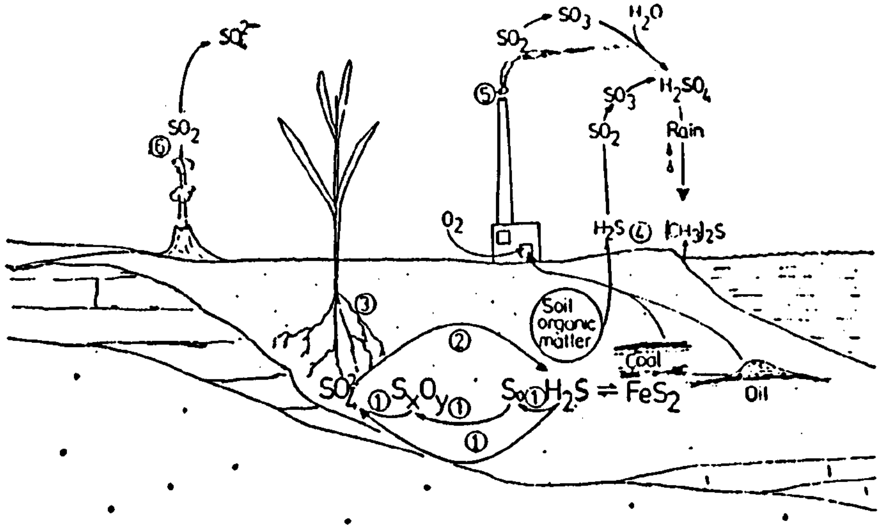


FIG. 13B.- PROCESOS MAS IMPORTANTES EN EL CICLO DEL AZUFRE

Aunque menos abundante que el nitrógeno en la materia bio-orgánica, resulta sin embargo de gran importancia. El ciclo oxidación-reducción de sus formas inorgánicas es muy similar al del ciclo del nitrógeno. La oxidación del azufre procedente de combustibles fósiles durante el proceso de combustión, contribuye también a la generación de lluvia ácida. Las fases más importantes del ciclo del azufre son:

1. Oxidación autótrofa a sulfato
2. Reducción heterótrofa a sulfuro
3. Absorción por plantas y microorganismos
4. Volatilización del H_2S procedente de la materia orgánica
5. Oxidos de azufre procedente de procesos de combustión
6. Azufre de origen volcánico

FIG. 13.- Ciclos del nitrógeno y el azufre y su relación con las emisiones de origen industrial y la lluvia ácida

TABLA 33

PROCESOS DE ACIDIFICACIÓN DE SUELOS

PROCESOS	OBSERVACIONES
1. Mineralización, liberación de iones aluminio seguida de hidrólisis	
2. Mineralización, liberación de iones hierro seguida de hidrólisis	
3. Formación de ácidos orgánicos y materia orgánica	$CO_2 + RCH_2OH \rightarrow RCOO^- + H_2O + H^+$
4. Asimilación biológica de los iones amonio procedentes del suelo	$NH_4^+ + RCOCOOH + 2[H] \rightarrow RCHNH_3^+COO^- + H^+ + H_2O$
5. Nitrificación de iones amonio en el suelo	$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O$
6. Lixiviación de aniones con cationes (nitrato o carboxilato)	
7. Aplicación de superfosfatos	$Ca(H_2PO_4)_2 + H_2O \rightarrow CaHPO_4 + H^+ + H_2PO_4^-$ (el efecto es temporal, puesto que todo el fosfato es eventualmente utilizado como monovalente)
8. Oxidación de la pirita de los residuos mineros	$2FeS_2 + 7H_2O + 7/2O_2 \rightarrow 4SO_4^{=} + 8H^+ + 2Fe(OH)_3$
9. Lluvia ácida	Si bien los suelos pueden hallarse tamponados, la persistencia de las precipitaciones ácidas durante muchos años puede superar dicha capacidad.
10. Fermentación anaerobia de compuestos orgánicos	P. ej.: $6(CH_2O) \rightarrow 2H_2 + 2CO_2 + CH_3CH_2CH_2COOH$

TABLA 34

CLASIFICACIÓN DE SUELOS U.S.A. Y FAO/UNESCO

U.S.A.	FAO/UNESCO
Entisoles	Fluvisoles, Regosoles, Lithosoles
Inceptisoles	Cambisoles
Aridisoles	Xerosoles, Yermosoles, Solonchaks, Solonetz
Mollisoles	Chernozems, Phaeozems, Kastanozems
Alfisoles	Luvisoles
Ultisoles	Acrisoles
Spodosoles	Podzoles
Oxisoles	Ferralsoles
Vertisoles	Vertisoles
Histosoles	Histosoles
	Arenosoles

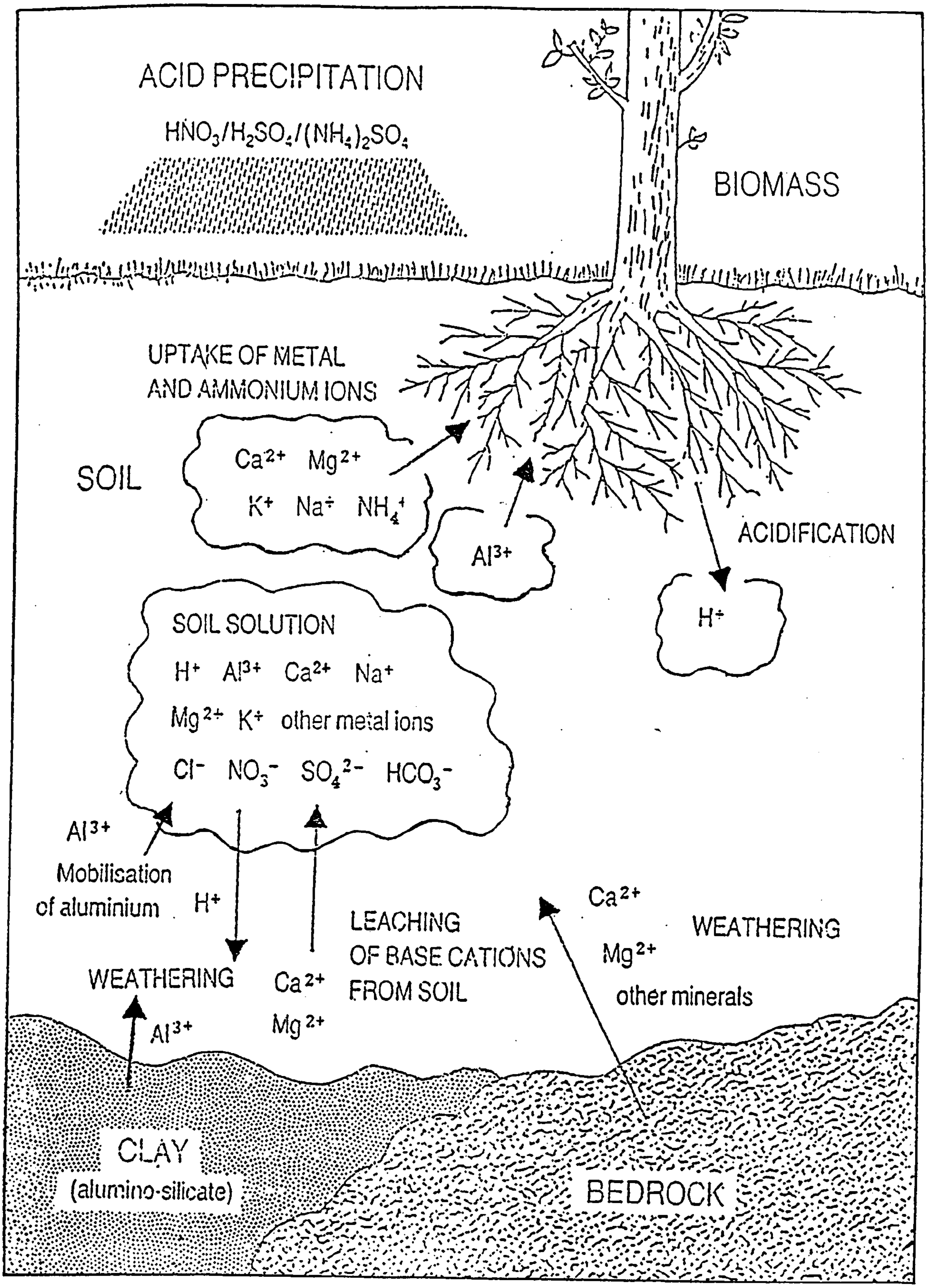


FIG. 14.- Incidencia de la lluvia ácida sobre los procesos del suelo

ENTISOLES.- Suelos poco desarrollados con un perfil escasamente diferenciado. Incluyen los formados a partir de depósitos aluviales recientes *(Fluviosoles)*, suelos ligeramente desarrollados sobre materiales sueltos *(Regosoles)*, sobre roca sólida *(Litosoles)*, etc. Debido a esta gran variedad, su sensibilidad a la acidificación no puede definirse de forma específica.

INCEPTISOLES.-Tampoco se encuentran muy desarrollados, si bien poseen un perfil más diferenciado que en el caso de los entisoles, debido principalmente a procesos de alteración *(Cambisoles)*. Al igual que aquéllos, tampoco puede asignárseles una sensibilidad específica: los inceptisoles arcillosos, por ejemplo, son poco sensibles a la deposición ácida, mientras que en los de tipo arenoso resulta más acentuada.

ARIDISOLES.- Son los suelos de los desiertos y de otras regiones secas. Algunos son salinos *(Solonchaks)* y otros alcalinos *(Solonetz)*. Debido a que su pH en condiciones naturales suele ser superior al recomendable para el crecimiento de las plantas, un aporte ácido sería beneficioso. No obstante, se trata de zonas con escasa precipitación, por lo que es previsible que dicho aporte sea muy reducido.

MOLLISOLES.- Son suelos con un oscuro y potente horizonte superficial, que posee un importante contenido de humus. Comprenden según la clasificación FAO/UNESCO los *Chernozems, Phaeozems, Kastanozems*, etc. Muestran un grado de lixiviación relativamente pequeño y cierto contenido de carbonato cálcico. Su capacidad tampón y el porcentaje de saturación generalmente son elevados, por lo que su sensibilidad a la acidificación se considera baja.

ALFISOLES Y ULTISOLES.- Ambos presentan un alto contenido de arcilla, y en el caso de los Alfisoles también un elevado porcentaje de saturación en bases, que resulta inferior en los Ultisoles. En consecuencia la sensibilidad a la acidificación resulta inferior en el primer caso respecto del segundo.

OXISOLES.- Corresponden a los suelos rojos típicos de climas tropicales húmedos. Suelen poseer un elevado contenido en arcilla, si ben se trata fundamentalmente de óxidos de hierro y aluminio y caolinita, cuya capacidad de cambio es baja. El contenido en humus es reducido, siendo importantes los procesos de alteración y lixiviación. En consecuencia, su capacidad tampón y pH son bajos, por lo que es previsible que las precipitaciones ácidas tengan un efecto significativo sobre este tipo de suelos.

VERTISOLES.- Son los suelos arcillosos negros situados en regiones tropicales y en otras zonas cálidas. A menudo contienen carbonato cálcico o, al menos, un elevado grado de saturación en bases. La arcilla es casi exclusivamente esmectita, cuya capacidad de cambio es alta. En consecuencia, estos suelos disponen de una capacidad tampón y un porcentaje de saturación de bases muy elevado, que le confieren una escasa sensibilidad a la acidificación.

HISTOSOLES.- Están compuestos total o predominantemente de materia orgánica (turba), cuyo grado de humificación afectará a la capacidad de intercambio catiónico (elevada en comparación con la de suelos minerales) y, en consecuencia, a su capacidad tampón. El índice de saturación de bases es muy variable. Algunos suelos orgánicos son poco sensibles a la acidificación debido a la presencia de carbonato cálcico. Otros, sin embargo, resultan extraordinariamente ácidos ($pH \approx 3$), por lo que un aporte de acidez a través de la lluvia apenas resultaría perceptible. En términos generales los Histosoles se consideran suelos poco sensibles a la acidificación, debido a su elevada capacidad tampón.

ARENOSOLES.- La característica más común de estos suelos es su textura arenosa. Este grupo incluye suelos de carácter ácido en grado variable y de baja capacidad de neutralización, por lo que se consideran sensibles a la acidificación.

4.- LEGISLACIÓN SOBRE EMISIONES

4.1.- PRINCIPIOS E INSTRUMENTOS

4.1.1.- INTRODUCCIÓN

En la actualidad, en la normativa legal de la mayoría de los países industrializados se establece algún tipo de control sobre las emisiones de contaminantes a la atmósfera de las centrales térmicas de generación de energía. Ello es consecuencia de la fuerte contribución de este sector a las emisiones totales en aquellos países. En muchos casos este control se extiende a otros tipos de instalaciones industriales, fuentes móviles e incluso a instalaciones para calefacción.

Las diversas disposiciones nacionales se inspiran, en gran medida, en los mismos principios. Es corriente encontrar, especialmente en preámbulos y leyes marco, condicionamientos de tipo general tales como:

- limitar todos los impactos ambientales adversos.
- adoptar tecnologías de control que correspondan al estado de la técnica (en general con alguna consideración adicional relativa a la viabilidad económica).
- obligación de no producir ningún tipo de molestias o daños al público, etc..

Este tipo de requerimientos resulta útil como indicador del espíritu o intención del legislador, pero su alcance práctico es extraordinariamente limitado, por la dificultad de probar incumplimientos sin recurrir a formulaciones cuantitativas, cuando como ocurre en la mayoría de los procedimientos judiciales, hay que demostrar intencionalidad.

Es precisamente en el desarrollo de los principios generales, donde los criterios utilizados y las diferencias en los métodos de efectuar el control son considerables. Estas diferencias son reflejo de las circunstancias sociopolíticas, el nivel de industrialización y la situación ambiental de cada país, e incluso de la época en que se desarrollaron las normas actualmente en vigor.

Es corriente ver no sólo diferentes niveles de emisión permitida, sino también distintos tipos de límites y sistemas de regulación e incluso, en algunos casos cada vez menos frecuentes, la ausencia total de límites de emisión.

Además, una característica peculiar de los límites de emisión, por comparación son los niveles de calidad de aire admisibles, es su carácter subordinado. En ningún caso pueden considerarse como un fin en sí mismos, son solamente un medio para asegurar un estatus ambiental que se considera aceptable en función de otros objetivos más generales como pueden ser:

- mantener la calidad del aire.
- mejorar la calidad en zonas problemáticas.
- garantizar la ausencia de riesgos para la salud pública.
- reducir las emisiones al mínimo compatible con el mejor control técnicamente alcanzable, etc.

Por las razones anteriores los límites de emisión de diferentes países no son susceptibles de comparación sencilla. Además de diferencias en la forma de expresión, reflejo en muchos casos de la preferencia del legislador o de la tradición histórica de cada país, existen otras más importantes como pueden ser:

a) Diferencias de tipo conceptual, asociadas a los objetivos con que se han establecido las diferentes normas y los medios de implementarlas:
    - Solucionar problemas de contaminación preexistentes.
    - Forzar el desarrollo de tecnologías de control más eficaces.

- Especificar los medios por los que debe alcanzarse el control establecido.

- Dejar en manos de la industria los procedimientos para alcanzar el cumplimiento de los límites por los medios que considere más económicos.

b) Diferencias de definición asociadas a:

- La fijación de valores límites no sobrepasables en ningún caso, o de valores de referencia ligados a lo que se considera tecnología de control adecuada. En muchos casos este tipo de diferencias está detrás de los procedimientos con los que cada país establece los límites.

- Los procedimientos establecidos para la verificación, incluyendo aspectos tales como: métodos de medida, periodicidad de los controles establecidos, etc.

- La definición de las condiciones de aplicabilidad de los límites, de lo que se considera cumplimiento de los mismos y las consecuencias del incumplimiento.

c) diferencias de aplicaciones e interpretación, asociadas a:

- La asignación de la responsabilidad para la realización de los controles.

- La capacidad técnica y de recursos de los organismos encargados de la vigilancia del cumplimiento de los límites, para desarrollar una eficaz labor de policía.

- La casuística en la interpretación de las divergencias administración-empresas por el poder judicial, recogida en la jurisprudencia del país.

A continuación se presenta una breve síntesis de los métodos de control más utilizados, su alcance y los problemas asociados con cada uno de ellos.

La primera gran subdivisión se establece entre métodos de control indirecto y métodos de control directo de las emisiones.

4.1.2.- MÉTODOS DE CONTROL INDIRECTO

Estos métodos son genuinamente formas de prevención, de las más simples, para evitar efectos adversos de emisiones de contaminación en exceso, sin recurrir al empleo de límites de emisión.

Requieren un importante grado de cooperación entre las industrias implicadas, y los diferentes niveles de la administración con competencias asignadas por la ley.

Entre los más empleados se encuentran los siguientes:

I.- Control de los emplazamientos

Muy útil para evitar efectos de alcance local, sea por exceso de emisiones, por tratarse de zonas especialmente sensibles, por motivos de mesometeorología y topografía local u otros. También permite incorporar consideraciones socioeconómicas asociadas con los problemas de desarrollo regional.

Sin embargo, su efectividad es prácticamente nula para prevenir problemas asociados al transporte a larga distancia, intercambios transfronteras, lluvias ácidas, etc.

II.- Especificaciones relativas a los combustibles

Constituyen también un método muy efectivo y flexible de control de emisiones. Han sido, junto con la especificación de una altura mínima de chimenea, el procedimiento tradicional de emisiones de óxidos de azufre.

Existen en muchos países, especialmente para zonas muy industrializadas o de alta densidad de población, en forma de límites al contenido de azufre, cenizas u otros precursores de contaminantes en los combustibles, asociados a condiciones de utilización, de tipo geográfico o para actividades y sectores industriales específicos.

Estas especificaciones permiten el empleo de técnicas de control de las emisiones totales en cada fuente por métodos de mezcla de combustibles. También posibilitan reorientar los consumos sectoriales de los combustibles de peor calidad ambiental. Por ejemplo, en algunos países se limita el empleo de combustibles de baja calidad a instalaciones de tamaño suficiente como para que resulte económico el empleo de tecnologías avanzadas de control. Este es un método empleado tradicionalmente para carbones de alto contenido en cenizas, dado el desarrollo de la tecnología de control de emisiones de partículas.

III.- Especificaciones técnicas sobre equipos y/o condiciones de operación

Especificaciones de este tipo suponen intentos de concretar orientaciones de tipo general sobre el empleo de la "mejor tecnología disponible" y similares. Son muy variadas, pudiendo citarse entre las más empleadas para centrales térmicas:

- límites a las pérdidas por humos, u otra forma de especificar un rendimiento energético mínimo.
- especificación de un rendimiento mínimo a los equipos de depuración de contaminantes.
- prescripciones relativas a modos de operación y mantenimiento (soplados de hollín, limpiezas periódicas, etc.).
- características técnicas y/o modificaciones en los equipos de combustión.
- limitaciones de altura de chimenea.

- especificaciones de pretratamiento de combustible.

Este tipo de medidas adecuadamente aplicadas ha permitido reducciones sustanciales en las emisiones de contaminantes, especialmente hollines e inquemados gaseosos procedentes de pequeñas instalaciones.

IV.- Medidas de apoyo a tecnologías más limpias

Entre las más comunes se encuentran:

- subvenciones, para la instalación o mejora de rendimiento de equipos de depuración, cambios en el proceso, ahorro de energía, etc.
- tratamiento fiscal y créditicio especial a instalaciones de demostración que empleen tecnologías de combustión más limpia.

4.1.3.- MÉTODOS DE CONTROL DIRECTO

Los métodos de control directo de las emisiones emplean normas de tipo cuantitativo para establecer el nivel máximo de emisión permitido. Entre los diversos esquemas comúnmente utilizados conviene apuntar diversas características diferenciales importantes:

I.- Valores límites o valores indicativos

Una primera diferencia se encuentra en la definición como valores recomendados -indicativos- o valores límites, cuya transgresión es punible. Los efectos reales de esta diferencia son difíciles de establecer, sin efectuar un análisis exhaustivo de la práctica administrativa y judicial. En el fondo de la diferencia subyace la idea de que la relación entre los niveles de emisión y la calidad del aire, que es el objetivo final a proteger, no es simple y puede parecer excesivo perseguir los "excesos de emisiones" en general, sin considerar la existencia o no de efectos adversos.

II.- Límites generales o límites específicos

Como alternativas en la reglamentación de límites se encuentran:

- límites de tipo general, presentes como parte de la legislación básica.
- límites de tipo general, especificados en reglamentos o normas técnicas separadas y más fáciles de actualizar.
- límites específicos, establecidos por tipos de industria, considerando en ocasiones diferencias zonales.
- límites específicos establecidos para cada instalación concreta.

Los límites específicos por instalación son la herramienta más flexible, ya que permite tener en cuenta todos los condicionantes locales, y actualizar los niveles de exigencia a los desarrollos tecnológicos caso por caso.

En favor de esquemas más rígidos de los límites de aplicación general por sector, con actualizaciones periódicas, está el hecho de que los límites específicos puedan introducir distorsiones de competencia, especialmente conflictivas cuando las empresas afectadas corresponden al sector privado.

III.- Formas de expresión

Asociados a razones históricas, y/o a los procedimientos y normas empleados en los estudios previos al establecimiento de los límites o en la verificación de su cumplimiento. Las formas de expresión más utilizadas son:

- Concentración: masa de contaminante por unidad de volumen de gases emitidos (en general en miligramos por m^3 de gases en condiciones normales: mg/Nm^3) en unos casos y en otros proporción (partes por millón) en volumen.

- Intensidad de Emisión: masa de contaminante máxima que puede emitirse por unidad de tiempo. Este tipo de expresión no es muy común en límites para centrales térmicas, pero se encuentra en la legislación de algunos países.

- Factor de emisión: masa de contaminante emitida normalizada por un factor indicador del nivel de producción. Para centrales térmicas son comunes unidades de ng de contaminante/Julio de energía de entrada (o de salida): ng/J. En algún caso incluso peso de contaminante generado por unidad de combustible empleado.

La dificultad asociada a los límites primitivos expresados en concentración, radica en que podía conseguirse el cumplimiento de una normativa determinada, diluyendo los gases procedentes de la combustión con aire exterior, sin disminuir por ello la cantidad total de contaminante emitido.

IV.- Procedimientos de verificación

Para un mismo nivel de control resultante, los valores numéricos concretos de los límites están estrechamente ligados a los procedimientos y métodos de medida a emplear para verificarlos.

Es normal en muchas reglamentaciones de límites establecer las normas de medida que deben emplearse para su verificación, incluyendo aspectos como duración de la toma de muestra, volumen mínimo de muestreo y número mínimo de muestras necesario para admitir la validez de los resultados.

Desde el punto de vista de garantizar que los niveles establecidos se cumplen realmente en operación normal de la planta, el procedimiento más viable es el autocontrol basado en sistemas de medida continua. Un somero análisis estadístico revela que, en cuanto se reduce la frecuencia de muestras tomadas, la probabilidad de detectar valores extremos disminuye de modo importante.

V.- Condiciones de cumplimiento

Se refieren a diferencias de aspectos tales como:

- Definición de las condiciones de aplicabilidad de los límites (lo que normalmente se entiende por "condiciones de operación normal").
- Frecuencia con la que pueden excederse los límites y duración de las condiciones de excepción.
- Margen de excedencia permisible y/o tolerancia de medición.

4.2.- LEGISLACIÓN ESPAÑOLA SOBRE EMISIONES

4.2.1.- DISPOSICIONES LEGALES MÁS IMPORTANTES

* Ley 38/1972 de protección del ambiente atmosférico

Es una ley básica, que deja lo fundamental de los desarrollos para otras disposiciones posteriores más específicas, la primera de las cuales tardó 3 años en publicarse.

En su art. 3 se define el nivel de emisión como la cuantía de cada contaminante vertida sistemáticamente a la atmósfera en un período determinado, medida en las unidades que sean de aplicación a cada uno de ellos.

En el mismo artículo se faculta al gobierno para establecer límites de emisión de carácter general o particulares, más estrictos, cuando se estime que existe perjuicio grave para las personas o bienes localizados en el entorno del foco emisor. Asimismo en estos casos puede exigirse la adopción de medidas correctoras según el estado de la técnica, para la reducción del vertido de contaminantes a la atmósfera.

actividad, la aplicación de los mejores medios prácticos disponibles para la reducción de emisiones o mejorar la dispersión.

Para las centrales térmicas autorizadas a quemar carbones u otros combustibles de baja calidad, se admite que los límites recogidos en el anexo IV sean rebasados, si persisten las causas originales y por razones de interés social local, siempre que no se superen los límites de inmisión fijados (art. 52).

Para el control, inspección y vigilancia de las instalaciones potencialmente contaminadoras de la atmósfera, el art. 69 establece que dichas inspecciones deberán realizarse al menos una vez al año, y siempre que exista denuncia justificada de que se esté produciendo una emisión excesiva.

En dicha inspección se comprobará si se respetan los valores límite de emisión y de calidad de aire (art. 70). En caso contrario se establece un régimen de vigilancia intensiva sobre la industria en cuestión.

Estos aspectos se desarrollan posteriormente con mayor detalle en la O.M. de 18 de Octubre de 1976.

El art. 72 señala que si la Administración competente considera económica y técnicamente oportuno y viable, podrá exigirse la instalación de equipos de medida con registro incorporado para controlar la emisión continua y periódicamente.

Las industrias del grupo A del catálogo de actividades potencialmente contaminadoras, deberán efectuar al menos una medida de los contaminantes vertidos a la atmósfera cada 15 días, así como un balance estequiométrico semanal de azufre y halógenos. Las industrias del grupo B deberán efectuar controles periódicos de sus emisiones (no se indica la periodicidad).

La Ley contempla la elaboración de un catálogo de actividades potencialmente contaminadoras, así como las condiciones para instalar, ampliar o modificar dichas actividades, y prevé también la regulación posterior de las características y calidades de los combustibles de aplicación doméstica e industrial.

* Decreto 833/1975

Este Decreto, verdadero Reglamento de la Ley, desarrolla sus aspectos más importantes.

Así, en el título V, art. 44 se define el límite de emisión como la concentración máxima admisible de cada tipo de contaminante en los vertidos a la atmósfera...

En el anexo IV se establecen los límites de carácter general, a que deberán sujetarse las emisiones de contaminantes procedentes de actividades potencialmente contaminadoras, cualquiera que sea su localización. Sin embargo, en el art. 45 se establece la posibilidad de adoptar límites más estrictos para determinadas actividades, atendiendo a aspectos como tipo y volumen de contaminantes emitidos, localización, etc.

Los niveles de emisión que no deben superarse, lo son (art. 46) sin dilución previa con aire, salvo casos justificados y debidamente autorizados.

Para los contaminantes o actividades no especificados en el Decreto, se establece que las emisiones serán tales que las inmisiones cumplan lo establecido sobre normas técnicas de inmisión, y/o en su defecto, no sobrepasar 1/30 de las concentraciones máximas permitidas en ambiente interior por el decreto de 30/IX/1961.

En el art. 49 se establece que cuando exista perjuicio directo y grave para las personas o bienes localizados en el área de influencia del foco emisor, el Ministerio competente deberá exigir a los titulares de la

Según el art. 74 los aparatos de medida de emisiones deberán corresponder a tipos previamente homologados y contrastados por el Ministerio de Industria, pudiendo dicho organismo concertar con laboratorios oficiales autorizados la labor de contrastación.

Las empresas deberán comunicar a la autoridad competente por razón de la actividad y a los ayuntamientos implicados, con la mayor urgencia posible, cualquier anomalía en los sistemas de depuración de los efluentes gaseosos que pueda repercutir en la calidad del aire de la zona (Art. 79).

En el art. 83 se definen como faltas graves:

La emisión superior a tres veces el límite fijado en la autorización de funcionamiento durante un período superior a media hora por día.

La emisión superior a tres veces los límites admisibles durante un período máximo de media hora por día, para industrias del grupo A, en zonas de atmósfera contaminada.

Para las centrales térmicas los límites de emisión establecidos en en anexo IV son:

PARTÍCULAS SÓLIDAS

Emisión en (mg/Nm^3)

COMBUSTIBLE	POTENCIA (Mw)	INSTALACIONES ANT. a 23/4/75	INSTALACIONES POST. a 23/4/75
Carbón	<50	750	500/400 (1)
	50-200	500	350-300
	>200	350	200-300
Fuelóleo	<50	250	200
	50-200	200	175
	>200	175	150

OPACIDAD

Carbón: Ringelman 1 (para contenido en cenizas <20%), admitiéndose hasta Ringelman 2 un máximo de dos minutos cada hora, y Ringelman menor de 3 en el período de encendido, máximo de tres horas.

Fuelóleo: Ringelman 1 admitiéndose hasta Ringelman 2 un máximo de dos minutos cada hora.

DIOXIDO DE AZUFRE (2)

Emisión en (mg/Nm^3)

COMBUSTIBLE	POTENCIA (Mw)	INSTALACIONES ANT. a 23/4/75
Hulla o antracita	todas	2.400
Lignito		9.000
Fuelóleo	todas	5.500

Notas:

(1) Los límites inferiores se aplican en zonas de atmósfera contaminada.

(2) Si el porcentaje de azufre del combustible >1,5% o si el porcentaje en cenizas >20%, se aplicarán límites específicos.

* Decreto 2204/1975 sobre calidades y condiciones de empleo de combustibles y carburantes

Para los carbones, el art. 2 especifica que la composición dada en los anexos, corresponde al estado de suministro al consumidor.

El art. 4 define como combustibles limpios, en lo que se refiere a contenido de azufre, la energía eléctrica, el gas natural, los gases licuados del petróleo, los gases manufacturados, y otros combustibles con contenido de azufre igual o inferior al 0,7% en peso. Asimismo se definen como combustibles de menor poder contaminante, además de los anteriores, los combustibles líquidos con un contenido de azufre <1,2% y los sólidos de calidad número 1 del anexo IX de ese decreto.

El art. 10 señala que en instalaciones industriales que se encuentren a menos de 2 Km de un núcleo urbano de más de 10000 habitantes, no podrán consumirse combustibles que contengan más del 3% de azufre.

En zonas declaradas de atmosfera contaminada, solo podrá quemarse carbón de calidad nº 1 en actividades domésticas y de servicios, y de calidades 1 y 2 en actividades industriales.

Las centrales térmicas e instalaciones industriales de potencia calorífica global superior a 2000 termias/hora, situadas en zonas de atmósfera contaminada o con frecuentes emergencias, deberán disponer de una reserva de combustibles especiales para asegurar su funcionamiento durante seis días por lo menos (art. 13).

* Orden de 18 de octubre de 1976

En su art. 8.1, se especifica que cualquier instalación, ampliación o traslado de industrias potencialmente contaminadoras de la atmósfera, deberá presentar ante la administración competente un proyecto independiente del de la planta, que en el caso de las centrales térmicas de carbón de potencia mayor o igual a 8000 termias/hora, deberá incluir un análisis completo del carbón, inmediato y elemental, así como el análisis complementario (azufre pirítico, sulfato, orgánico y fijo, carbonatos, halógenos, fósforo y arsénico, y análisis de las cenizas).

Según el art. 10 de la orden, en el citado proyecto se deberá incluir una memoria del cálculo de la altura de las chimeneas.

En el art. 11 se establece que las chimeneas de las nuevas instalaciones industriales irán provistas de orificios de toma de muestras, de forma que se eviten turbulencias y anomalías que puedan afectar a la representatividad de las muestras.

Los niveles de emisión se medirán en chimenea (Art. 16), salvo cuando los efluentes no estén canalizados, en cuyo caso se medirán en ambiente exterior.

El cumplimiento de los niveles de emisión debe observarse durante el tiempo en que esté en funcionamiento la instalación en las condiciones normales de funcionamiento. Salvo que en la autorización de puesta en marcha se especifique otra cosa, dichos niveles de emisión serán medidos durantes un mes, si se superan las siguientes cantidades:

- 15 Kg/h de polvos.
- 100 Kg/h de SO_2 -20 Kg/h de óxidos de nitrógeno (expresados como NO) (salvo en caso de combustión).
- 5 Kg/h de CO
- 1 Kg/h de cloro
- 1 Kg/h de compuestos inorgánicos de cloro
- 1 Kg/h de " " de flúor
- 1 Kg/h de compuestos orgánicos (expresados como C)

y durante una semana si son menores.

El artículo 28 impone a las empresas industriales potencialmente contaminadoras de la atmósfera, el ejercicio de un autocontrol de las emisiones de contaminantes aéreos, pudiendose exigir a las empresas la instalación de equipos de medida continuos, regulados y comprobados por la administración.

Las empresas del grupo A deberán realizar al menos una medida cada quince días a los contaminantes emitidos a la atmósfera. En el caso de que no se disponga de los equipos adecuados realizarán balances de azufre, halógenos, etc.

* Desarrollos recientes

La O.M. del Ministerio de Industria y Energía de 25 de junio de 1984, es aplicable a todas las centrales termoeléctricas de potencia superior a 50 Mw que quemen carbón, y las de fuel-oil o gas natural de potencia superior a 200 Mw. La citada orden obliga a dichas centrales a instalar, preferentemente en chimenea, aparatos de control con transmisión de datos al cuadro de mandos de la central. Dichos aparatos deberán permitir la medida en forma continua de las emisiones de SO_2, partículas y óxidos de nitrógeno de cada hogar o grupos de ellos concectados a la misma chimenea de la central (art. 1).

El art. 4 establece la obligación de disponer en el entorno de las centrales térmicas una red automática para la medida de inmisiones de SO_2, partículas y NO_2, tal que sea posible el tratamiento informatizado de los datos que generen.

Las centrales de carbón deberán disponer de un equipo de análisis del contenido de azufre en el carbón utilizado, con capacidad suficiente para la determinación del mismo en todas las partidas adquiridas. Equipos y emplazamientos deberán cumplir las exigencias más severas en estos aspectos de los países de la C.E.E.

4.3.- LEGISLACIÓN EN OTROS PAISES

4.3.1.- COMUNIDAD ECONÓMICA EUROPEA

La política comunitaria de lucha contra la contaminación atmosférica, contempla la promulgación de normas de calidad del aire con el establecimiento de normas de emisión más o menos estrictas, combinando aspectos técnicos y económicos, y el mantenimiento de unos valores de calidad del aire fijados con criterios sanitarios o de protección del medio. Ya se han establecido valores límite y valores guía de concentración en ambiente para dióxido de azufre y partículas en suspensión (80/779/CEE), plomo (82/94/CEE), y dióxido de nitrógeno (85/203/CEE).

El Consejo Europeo de Jefes de Estado y de Gobierno celebrado en Stuttgart en junio de 1983, estableció los dos grandes ejes en torno a los que girará la acción comunitaria relativa a la contaminación atmosférica a lo largo de la presente década: la lucha contra la lluvia ácida y la supresión del contenido de plomo de las gasolinas.

A continuación se resumen las disposiciones adoptadas en relación con la contaminación atmosférica procedente de fuentes fijas.

* Directiva 84/360/CEE, de 28/VI/84, relativa a la lucha contra la contaminación atmosférica procedente de instalaciones industriales

Se acostumbra a denominarla "Directiva-Marco 84/360".

Esta directiva establece una serie de principios que deberán aplicarse en los estados miembros a partir de Julio de 1987, en lo que concierne a determinados tipos de instalaciones industriales que emiten contaminantes a la atmósfera.

Además de la prevención y reducción de la contaminación atmosférica, la Directiva busca la armonización de las dispares legislaciones nacionales en la materia. Estas disparidades, que tenderían a acentuarse en los próximos años, pueden originar distorsiones de competencia en el Mercado Común, al someter a las empresas a diferentes cargas financieras según el Estado en que se encuentren.

La Directiva prevé, esencialmente, la instauración de un sistema que somete la construcción, explotación y modificación sustancial de determinadas instalaciones industriales fijas a la exigencia de autorización previa. La autoridad competente no podría conceder esta autorización más que si se cumplen las siguientes condiciones (art. 4):

- que se hayan tomado todas las medidas apropiadas para la prevención de la contmainación atmosférica, incluída la utilización de la mejor tecnología disponible, a condición de que la aplicación de tales medidas no suponga costos excesivos.

- que la explotación de la instalación no suponga contaminación atmosférica de un nivel significativo, en particular por la emisión de compuestos de azufre, compuestos de nitrógeno, monóxido de carbono, compuestos orgánicos (especialmente hidrocarburos, excluído el metano), metales pesados y sus compuestos, polvos, amianto, fibra de vidrio y de roca, cloro y compuestos de cloro, flúor y compuestos de flúor (Anexo 2).

- que no se sobrepase ningún límite de emisión aplicable.
- que se hayan tenido en cuenta todos los valores límites de calidad del aire aplicables.

Los sectores industriales sometidos al régimen de autorización previa se recogen en el Anexo 1 de la Directiva, e incluyen a las centrales térmicas no nucleares de potencia calorífica nominal superior a 50 Mw.

En la misma línea se establece que el Consejo podrá, en caso necesario, fijar límites comunitarios de emisiones de contaminantes prioritarios, desarrollando directivas de aplicación sectoriales. Es de destacar que se trata de límites de emisión y no valores indicativos como los contemplados, por ejemplo, en el sistema británico tradicional.

* Proposición de directiva relativa a la limitación de emisiones de contaminantes a la atmósfera procedentes de grandes instalaciones de combustión (83/704)

Presentada el 15/XII/83 por la Comisión al Consejo de Ministros de la CEE, esta directiva proponía la fijación de un objetivo global de reducción de las emisiones anuales totales para grandes instalaciones de combustión (potencia térmica nominal mayor o igual a 50 Mw) antes de finales de 1995, del orden del 60% para los óxidos de azufre, 40% para los óxidos de nitrógeno y 40% para las partículas, respecto de los correspondientes a 1980, tomado como perído de referencia.

Esta directiva se inspira ampliamente en el Reglamento alemán en vigor desde el 1/VII/83. Como resumen de sus aspectos más importantes señalaremos:

a) Campo de aplicación: grandes instalaciones de combustión de potencia termica nominal igual o mayor que 50 Mw y cualquier tipo de combustible (sólido, líquido o gaseoso). Se excluyen las instalaciones de combustión destinadas a secado o tratamiento de materiales por contacto con los gases de combustión (excepto las sometidas a la directiva anterior), y los dispositivos de postcombustión.

b) Se aplica tanto a las instalaciones nuevas como a las antiguas. Para las instalaciones antiguas (autorizadas antes del 1/I/85), la Directiva propone establecer programas anuales de reducción progresiva de emisiones procedentes de estas fuentes, no más tarde del 31/XII/86, para alcanzar en 1995 los objetivos generales de reducción de emisiones globales establecidos. Queda un amplio margen de flexibilidad en las medidas a tomar.

Para las instalaciones nuevas (autorizadas después del 1/I/85), la Comisión propone que todas las autorizaciones previas se subordinen al cumplimiento de unos valores límite comunitarios. Sin embargo, para instalaciones de potencia termica nominal inferior a 100 Mw, la fecha anterior se retrasa 5 años. Este retraso tiene, entre otros motivos, el de facilitar el desarrollo de calderas de CLF de potencia superior a 50 MW.

Para instalaciones de más de 50 Mw los límites de emisión que se aplican son las siguientes (expresados en mg/Nm^3):

PARTICULAS SOLIDAS:

- Combustible sólido: ≤ 50
- Combustible líquido: ≤ 50
- Combustible gaseoso: ≤ 5 en general
  ≤ 10 para gas de alto horno
  ≤ 100 para gases de siderurgia

OXIDOS DE AZUFRE (expresados como SO_2)

- Combustible sólido:	≤ 400	en general desde 1/1/85
	≤ 250	en general desde 31/12/95
	≤ 2000	hogar de parrilla o carbón pulverizado y potencia < 300 Mw
- Combustible líquido:	≤ 400	en general desde 1/1/85
	≤ 250	en general desde 31/12/85
	≤ 1700	instalaciones de potencia < 300 Mw
- Combustible gaseoso:	≤ 35	en general
	≤ 100	para gas de coquería
	≤ 5	para gas licuado

OXIDOS DE NITRÓGENO (como NO_2)

- Combustible sólido:	≤ 800	en general desde 1/1/85
	≤ 1300	hogar de carbón y extracción de cenizas fundidas, desde 1/1/85
	≤ 400	en general desde 31/12/95
	≤ 800	hogar de carbón y extracción de cenizas fundidas, desde 31/12/95
- Combustible líquido:	≤ 450	desde 1/1/85
	≤ 220	desde 31/12/95
- Combustible gaseoso:	≤ 350	desde 1/1/85
	≤ 180	desde 31/12/95

Puede verse que la imposición de límites de emisión se plantea en dos etapas. Según estimaciones de la comisión, el valor límite 85 para SO_2 puede cumplirse con una desulfuración de un 90% de rendimiento aproximadamente, mientras que el limite 95 requeriría un rendimiento en torno al 95%.

c) Derogaciones temporales: se preve la posibilidad de que los estados miembros soliciten exenciones temporales en los siguientes casos:

- Pocas emisiones globales en relación con el total de la Comunidad.
- Planes energéticos basados en combustibles autóctonos de baja calidad.

- Regímenes transitorios para casos de avería en los equipos de depuración o problemas de aprovisionamiento de combustibles.

d) Restricciones al uso de chimeneas altas: se establece un límite de 200 m., con ciertas excepciones.

e) Puesta en práctica de las medidas:

- Condiciones de referencia: los límites de emisión se expresan en condiciones normales (0°C, 1 atm. y gas seco) y un exceso de aire de referencia, que se especifica como un 6% de O_2 presente en los gases residuales.

- Condiciones de medida y registro: medidas continuas de SO_2, NO_x, partículas sólidas y O_2 para instalaciones nuevas y antiguas con más de 10.000 horas de vida útil. Se admiten determinaciones alternativas y control limitado a medidas aisladas. No será necesaria la medida de NO_2 en caso de que represente menos del 5% de las emisiones de NO_x totales, pero deberá tener en cuenta por cálculo.

- Condiciones de cumplimiento: Se considera que los límites se respetan si a lo largo de un año civil las emisiones son tales que:

  Para medidas continuas:

  - Ningún valor medio diario sobrepasa los valores descritos en la tabla.
  - El 97% de los valores medios de 30 min. no sobrepasan el 120% de los valores límites de emisión.
  - Ningún valor medio de 30 min. sobrepasa el 200% del límite.

  Para medidas aisladas:

  - Todos los resultados están por debajo del límite.

En su formulación original esta propuesta fue sometida a críticas importantes por parte del Centro Europeo de la Empresa Pública (CEEP), con excepción de los representantes alemanes. Hay que tener en cuenta que una parte importante de las instalaciones afectadas por la directiva pertenecen al sector público. En síntesis, los puntos de crítica pueden resumirse como sigue:

- La Directiva está elaborada sobre bases insuficientes. El estado actual de los conocimientos hace prematuro cualquier intento de hacer balance objetivo de las ventajas a esperar de los controles de emisión propuestos, y los gastos que pueden ocasionar.

- Las medidas son dispendiosas desde el punto de vista económico. Según el CEEP el análisis de costos en que se apoya la directiva es incorrecto, su evaluación de costos para la reducción del 60% de las emisiones de óxidos de azufre respecto de los niveles de 1980 es del orden de 4,1 a 6,1 miles de millones de dólares anuales, sin considerar los costos de reducción del 40% de las emisiones de NO_x y partículas.

- Las medidas son poco realistas desde el punto de vista técnico (en particular la reducción del 40% de los óxidos de nitrógeno). Además, según la CEEP los límites previstos para 1996 son imposibles de alcanzar actualmente, por lo que la Dirección adelanta desarrollos tecnológicos futuros.

- Las medidas están en contradicción con algunas de las políticas internas de la CEE. Penalizando, por ejemplo, el uso del carbón en calderas convencionales.

Por otra parte, un informe del Comité de representantes permanentes de los Estados miembros de la CEE, de mediados de junio de 1984, señalaba importantes diferencias entre ellos:

Alemania y Holanda consideraban la propuesta de la Comisión como un mínimo aceptable. Francia, Bélgica y Dinamarca serían partidarios en general de la propuesta de directiva, considerando que las reducciones propuestas son un poco elevadas. Bélgica mostraba su preocupación por el calendario y los costos.

Italia y el Reino Unido mostraban serias reservas acerca de la eficacia real de las medidas propuestas desde el punto de vista de la protección del medio ambiente, los costos de puesta en práctica e incidencia de la situación económica de las empresas, la oportunidad de fijar límites comunitarios y los problemas técnicos planteados por el control de las emisiones de óxidos de nitrógeno. Estos mismos países señalaban que las excepciones propuestas por la Comisión, tendrían como consecuencia un reparto desigual del esfuerzo pedido a los estados miembros.

Los griegos, irlandeses y luxemburgueses también mostraban su desacuerdo general. Según ellos, la proposición no tendría en cuenta adecuadamente las situaciones industriales y energéticas de sus respectivos países. La puesta en práctica de las medidas propuestas tendría como consecuencia una agudización de la situación de competencia, y un retraso en el desarrollo de la industria energética de sus países, cuya contribución a la contaminación transfronteras sería mínima.

En la actualidad la discusión se centra en la consideración del año base de cálculo de emisiones, los porcentajes y los plazos para alcanzar las reducciones de emisiones.

4.3.2.- REPUBLICA FEDERAL DE ALEMANIA

La regulación más importante relativa a calidad del aire es la Ley para la Protección de los Efectos Peligrosos de la Contaminación del Aire, Ruido, Vibraciones y Procesos Similares (BImSchG) de 15/III/74.

Existe un sistema de "instalaciones sometidas a exigencia de autorización" (98 categorías). Estas instalaciones no deben generar efectos perjudiciales para el medio ambiente, y las medidas de control deben tomarse según el estado de la tecnología, entendiendo como tal los métodos avanzados de control de emisiones que hayan sido probados en operación suficientemente.

Las normas de calidad del aire y los límites de emisión están recogidos en su caso en las Instrucciones Técnicas para la Purificación del Aire (TA Luft), y los gobiernos regionales son los responsables de su aplicación. Los límites de emisión se han establecido tradicionalmente de modo que no supongan costos desproporcionados, y normalmente se basan en campañas previas de medidas en instalaciones modernas.

Además, los gobiernos locales pueden imponer medidas adicionales, en zonas contaminadas o condiciones meteorológicas desfavorables, tales como restricciones de ubicación, o el uso de determinados combustibles (<0,3% en peso de S en el gas oil, tipo A en la CEE). En Berlin el porcentaje máximo permitido de azufre en el lignito es el 1%.

Con fecha 1/7/1983 entra en vigor la 13th BImSChG Regulation, con el objetivo de reducir drásticamente las emisiones de dióxido de azufre, óxidos de nitrógeno, monóxido de carbono, compuestos halogenados, polvo, compuestos tóxicos y metales pesados. La regulación se aplica a grandes instalaciones de combustión de potencia superior a:

- 50 Mw (para combustibles sólidos o líquidos)
- 100 Mw (para combustibles gaseosos)

Se excluyen las instalaciones de combustión de residuos, las baterías de coke, turbinas de gas e instalaciones de postcombustión.

Las plantas existentes con tiempo de vida proyectado de más de 30.000 horas pueden ser equiparadas, en cuanto a necesidades de equipos de control para SO_2, a las nuevas plantas, y deberán cumplir los nuevos límites dentro de los cinco años siguientes a la promulgación de la ordenanza. Las antiguas han continuado con los límites anteriores hasta el 1-7-85 si la potencia de la instalación es superior a 300 Mw, y continuarán hasta el 1-7-88 en los demás casos. A partir de 1993 todas las plantas deberán cumplir los nuevos límites, sea cual fuere el tiempo de vida proyectado.

Se considera que los límites se respetan si a lo largo de un año civil las emisiones son tales que:

- Ningún valor medio diario sobrepasa los valores descritos en la tabla.

- El 97% de los valores medios de 30 min. no sobrepasan el 120% de los valores límites de emisión.

- Ningún valor medio de 30 min. sobrepasa el 200% del límite.

Los límites de emisión se expresan en condiciones normales (0°C, 1 atm y gas seco) y un exceso de aire de referencia que se especifica como % de O_2 presente en los gases residuales.

El operador de la instalación está obligado, como parte de las responsabilidades exigidas en la autorización, a medir sus emisiones y los niveles de inmisión para evitar efectos ambientales peligrosos.

Aunque no tiene estatus legal, la TA Luft requiere, en diversas instalaciones, que las emisiones de partículas, SO_2, CO y NO_x se midan en continuo. Esto se aplica a centrales térmicas, excepto para emisiones procedentes de unidades que quemen combustibles gaseosos con capacidad menor de 400 Mwth (megavatios térmicos). En plantas pequeñas se realizan medidas cada 3-5 años.

Con esta reglamentación se pretende disminuir las emisiones de SO_2 en la R.F.A., para las aproximadamente 1500 instalaciones afectadas por el decreto, desde 2 Mt/año a unas 0,7 Mt/año.

En 1978 se adoptaron diversas medidas legales para dotar a la Administración de un instrumento que le permitiera requerir datos de emisiones y de proceso hasta de dos años anteriores.

Los límites de emisión que se aplican son los siguientes:

PARTÍCULAS SÓLIDAS

Combust.	Capacidad de la planta	Especificación	Límite de emisión (mg/Nm^3)
Todos	> 50 Mw th	plantas nuevas	50 (2,5,6)

Combust.	Capacidad de la planta	Especificación	Límite de emisión (mg/Nm^3)
Todos menos carbón y madera	≥ 50 Mw th	plantas nuevas	suma de As, Pb, Cd, Cr, Ni, Co ≤0,5 (3,5,6)
Lignito	"	plantas existentes (a modificar)	80 (2,5,6)
Otros	"	" "	125 (2,5,6)
Todos menos carbón y madera	"	" "	suma de As, Pb, Cd, Cr, Ni, Co ≤1,5 (3,5,6)
Líquidos	≥ 50 Mw th	plantas nuevas	50 (2,5,6)
Líquidos	"	plantas existentes (a modificar)	50 a 100 (2,5,6)
Gas	< 100 Mw th		< Ringelman 2
Gas de siderurgia	≥ 50 y < 100 Mw th		50 (4,5,15,16)
Gas de horno alto	≥ 100 Mw th	plantas nuevas	10 (3,5,6)
Gas de siderurgia	"	" "	100 (3,5,6)
Otros gases	"	" "	5 (3,5,6)

ÓXIDOS DE AZUFRE

Combust.	Capacidad(1) de la planta	Especificación	Límite de emisión (mg/Nm^3)
Todos	≥ 50 < 100	Todas las nuevas Menos CLF	2000 (8) (2,5,6)
Todos	≥ 50 < 300	Plantas nuevas de CLF	400 ó 25% de emisión residual (2,5,6)
Todos	≥ 50 < 300	Existentes (9) (tiempo limitado)	2500 (10) (2,5,6)
Todos	≥ 100 ≤ 300	Todas las nuevas Menos CLF	2000 y 40% de emisión residual (11,2,5,6)

Combust.	Capacidad(1) de la planta	Especificación	Límite de emisión (mg/Nm^3)
Todos	≥ 300	Nuevas y modificadas (12)	400 y 15% de emisión residual (13,14,2,5,6)
Líquidos	≥ 50 < 100	Plantas nuevas	1700 (11,2,5,6)
Líquidos	≥ 50 ≤ 300	Existentes (tiempo limitado) (9)	2500 (10,2,5,6)
Gas Oil ≤ 3% S	> 100 < 300	Plantas nuevas	1700 y 40% de emisión residual (2,5,6)
Gas Oil ≤ 3% S	> 300	Nuevas y existentes (a modificar)	400 y 15% de emisión residual (13,14,2,5,6)
LPG	≥ 100 MW th	Plantas nuevas	5 (3,5,6)
Gas de coquería	"	" "	100 (3,5,6)
Gas industrial	"	" "	200 a 800 (3,5,6)
Otros	"	" "	35 (2,5,6)

ÓXIDOS DE NITRÓGENO (como NO_2)

Combust.	Capacidad de la planta	Especificación	Límite de emisión (mg/Nm^3)
Todos	> 1 < 50	-	Lo más bajo posible (7,15)
Todos	≥ 50	Nuevas, extrac. escoria seca	Mejor tecnología disponible (7) máximo 800 (2,5,6)
Todos	≥ 50	Nuevas, extrac. escoria fundida	Mejor tecnología disponible (7) máximo 1800 (2,5,6)
Carbón	≥ 50	Pulverizado, escoria seca, existentes	Mejor tecnología disponible (7) máximo 1300 (2,5,6)

Combust.	Capacidad de la planta	Especificación	Límite de emisión (mg/Nm^3)
Carbón	≥ 50	Pulverizado, escoria fundida existentes	Mejor tecnología disponible (7) máximo 2000 (2,5,6)
Todos	≥ 50	Otras existentes	Mejor tecnología disponible (7) máximo 1000 (2,5,6)
Líquidos	≥ 50	Plantas nuevas	Mejor tecnología disponible (2,5,6) máximo 450 (7)
Líquidos	≥ 50	Existentes	Mejor tecnología disponible (2,5,6) máximo 700 (7)
Gas	≥ 100	Plantas nuevas	Mejor tecnología disponible (2,5,6) máximo 350 (7) (2) cuando ≥ 400Mwth (1); (3) cuando ≤400 Mwth (1)
Gas	≥ 100	Existentes	Mejor tecnología disponible (2,5,6) máximo 500 (7) (2) cuando ≥ 400Mwth (1); (3) cuando ≤400 Mwth (1)

MONÓXIDO DE CARBONO

- C. sólido: 250 mg/Nm^3
- C. líquido: 175 mg/Nm^3 (4,5,15,6) si < 50 Mwth
  (2,5,6) si ≥ 50 Mwth
- C. Gaseoso: 100 mg/Nm^3 (2,5,6)

CLORUROS INORGANICOS GASEOSOS (como HCL)

Combust.	Capacidad de la planta	Especificación	Límite de emisión (mg/Nm^3)
Todos	≥ 50, ≤ 300	Nuevas, excepto CLF	200 (3,5,6)

Combust.	Capacidad de la planta	Especificación	Límite de emisión (mg/Nm^3)
Todos	> 300	Nuevas, excepto CLF	100 (3,5,6)
Líquido	⩽ 50	Plantas nuevas	30 (3,5,6)

FLUORUROS INORGANICOS GASEOSOS (como HF)

Combust.	Capacidad de la planta	Especificación	Límite de emisión (mg/Nm^3)
Todos	⩽ 50, ⩽ 300	Nuevas, excepto CLF	30 (3,5,6)
Todos	> 300	Nuevas, excepto CLF	15 (3,5,6)
Líquido	⩾ 50	Plantas nuevas	5 (3,5,6)

NOTAS:

(1) Capacidad por planta, no por unidad.

(2) Medida continua: medidas diarias por debajo de límite, el 97% de las medias semihorarias por debajo del 120% del límite y todos los promedios semihorarios por debajo del 200% del límite.

(3) Vigilancia por medida una vez cada tres años: al menos tres medidas, todas las medidas dentro de límites.

(4) Medida continua o por intervalos dependiendo del tamaño y emplazamiento, combustible y condiciones de autorización.

(5) 0°C, 1013 mbar, seco.

(6) 7% O_2 para combustión en parrilla y lecho fluidizado. 5% O_2 para combustión pulverizada con escoria líquida, 6% O_2 para otros quemadores de combustible sólido.

(7) A establecer en la autorización, cifras previstas para plantas de ⩾ 300 Mwth: 200 mg/Nm^3.

(8) Aplicable 2500 mg/Nm^3 durante un año si no se dispone de carbón bajo en azufre.

(9) Plantas con un período de vida a 10.000 h, válido hasta 1993, luego igual que las nuevas.

(10) Aplicable 3200 mg/Nm^3 durante un año si no se dispone de carbón bajo en azufre.

(11) Emisión media resultante 1000 mg/Nm^3.

(12) A modificar en menos de 5 años.

(13) 650 mg/Nm^3 y máxima eficacia de retención cuando se empleen combustibles de contenido de azufre muy alto o muy variable.

(14) Plantas existentes con vida de más de 30.000 h: 2500 mg/Nm^3 (10), hasta 1993.

(15) En revisión.

El Gobierno Federal Alemán estaba trabajando en el desarrollo de diveras enmiendas a la Ta Luft para la primavera de 1985, entre ellas las destinadas a regular las instalaciones de combustión de menos de 50 Mw de potencia.

4.3.3.- ESTADOS UNIDOS

La Clean Air Act de Diciembre de 1970 y posteriores enmiendas, permiten la legislación de programas imponiendo el uso de tecnologías de control de emisiones de alto rendimiento para fuentes nuevas, e imponen regulaciones de protección especial para determinadas regiones.

Las normas para fuentes preexistentes (en 1970) están ligadas a los National Ambient Air Quality Standards, establecidos por la EPA e impuestos a través de las normativas de control de la contaminación atmosférica de los diferentes estados.

La Clean Air Act insta a cada estado a desarrollar planes de control, con el fin de mantener y mejorar los estándares de calidad de aire. Estos planes están sancionados por la E.P.A. y, en general, están diseñados para minimizar los efectos de las emisiones en las zonas próximas, teniendo en cuenta las características dispersivas en las mismas. Pero por otra parte, en la sección 123 de la Clean Act se hace especial hincapié en la limitación de las emisiones a la hora de obtener unos determinados estándares de calidad de aire, regulando más desde el punto de vista del control de emisiones que desde el de la dispersión.

Las fuentes nuevas o modificaciones importantes posteriores a 1970 están sometidas a regulaciones más exigentes. Las centrales térmicas están sometidas a límites establecidos, con carácter general, para calderas de vapor desde esa fecha. Para centrales térmicas construidas después del 18/8/78 (y algunas centrales de lignito posteriores al 22/12/76) existen límites específicos. Los diversos límites en vigor se recogen anualmente en el CFR (Code of Federal Regulations), parte 50, título 40. Los que se refieren a centrales térmicas están recogidos en el subapartado Da.

Pasadas las pruebas de funcionamiento inicial en las condiciones que se especifican, los límites para partículas sólidas y óxidos de nitrógeno se aplican en todo momento, excepto en períodos de arranque, parada o averías. Los límites para óxidos de azufre se aplican también en todo momento, excepto durante períodos de arranque, parada o averías y si, durante condiciones de emergencia, se siguen los procedimientos especificados. La determinación del cumplimiento de los límites para óxidos de azufre y de nitrógeno se basa en la emisión media para 30 días sucesivos de operación de la caldera. Al final de cada día de operación se calcula una nueva emisión media de SO_2 y NO_x para determinar el cumplimiento de las normas.

El propietario u operador de las plantas afectadas debe instalar, calibrar, mantener y operar sistemas de medida continuada, y registrar sus resultados para medir capacidad (salvo si se queman sólo combustibles gaseosos), óxidos de azufre (salvo si se quema sólo gas natural) a la salida y a la entrada del sistema de control y óxido de nitrógeno.

El cumplimiento de los limites impuestos para partículas sólidas se comprueba mediante la medida contínua de algún parámetro relacionado con la masa total de partículas emitidas, tal como la opacidad o bien se recurre a los métodos manuales discontinuos normalizados por la EPA. Cada fuente está sujeta a controles periódicos, a discreción de las agencias de control.

A continuación se presenta un resumen de los límites actualmente aplicables a plantas cuyo input energético supere los 73 Mw.

Contaminante	Combustible	Especif. de la planta	Emisión (ng/J)
Partículas	Carbón (incluyendo mezclas carbón/madera)	Generadores de vapor posteriores a 17/8/71	43
	Carbón y combustibles derivados del mismo	Centrales térmicas posteriores a 18/9/78	13 (1,2)
SO_2	Líquido	Generadores de vapor posteriores a 17/8/71	340
	Sólido	Generadores de vapor posteriores a 17/8/71	520
	Combinación líquido/sólido		340*Y+520*Z/ Y+Z (3)
	Sólido	Centrales térmicas posteriores a 18/9/78	520 & 260 (4)
	Líquido/gas	Centrales térmicas posteriores a 18/9/78	340 (5) ó 86 (6)
NO_x	Carbón	Generadores de vapor posteriores a 17/8/1971	300 (7)
	Lignito	" "	260 (8,9)
	"	" "	130 (7)
	"	" "	86 (8)
	Combustibles derivados del carbón	Centrales térmicas posteriores a 18/9/78	210 (10)
	Carbón subbituminoso, bituminoso y antracita	" "	260
	Residuos de carbón	" "	exento

Contaminante	Combustible	Especif. de la planta		Emisión (ng/J)
	Combustibles líquidos	"	"	210 (10)
	Comb. gaseosos derivados del carbón	"	"	210
	Otros combust.	"	"	86

NOTAS:

(1) 1% de la concentración potencial de combustión (CPC).

(2) Menos del 20% de opacidad, excepto un período de 6 minutos cada hora que puede ser menos de 27%.

(3) X = porcentaje de gas, Y = porcentaje de líquido, Z = porcentaje de carbón.

(4) 10% de la concentración potencial de combustión (90% de reducción) ó 30% de CPC (70% de reducción) cuando las emisiones sean menores de 260 ng/J.

(5) 10% de la CPC (90% de la reducción).

(6) La reducción no se aplica si las emisiones son menores de 86 ng/J.

(7) Excepto lignitos o combustibles fósiles sólidos que contengan 25% o más de residuos de carbón.

(8) A los lignitos de Dakota del Norte, Dakota del Sur y Montana, cuando se queman en quemadores ciclónicos, se les aplica el valor 340 ng/J.

(9) Se aplica el limite de 340 ng/J a cualquier combustible que contenga el 25% en peso de lignito, si dicho lignito ha sido previamente tratado. A los demás lignitos se les aplica el límite de 260 ng/J.

(10) Combustibles líquidos derivados del carbón y pizarras bituminosas 210 ng/J, resto de combustibles líquidos 130 ng/J.

4.4.- TENDENCIAS ACTUALES Y PERSPECTIVAS

I) Control de los emplazamientos

La tendencia actual en la mayor parte de los países industrializados es la de exigir evaluaciones de impacto ambiental multimedio, para proyectos industriales importantes, incluidas las centrales térmicas. Los problemas asociados a estas evaluaciones se entrelazan, en muchos casos, con el nivel actual del conocimiento científico-técnico a nivel general, y con la experiencia y el know-how existente en la comunidad científica y los niveles técnicos de la administración y de las empresas implicadas, en cada país.

II) Especificaciones relativas a los combustibles

Como ya se ha señalado, el método de especificar una calidad de combustible asociada a cada utilización se ha aplicado tradicionalmente a carbones de alto contenido en cenizas, dado el desarrollo de la tecnología de control de emisiones de partículas, y a los combustibles líquidos para consumo doméstico o en zonas problemáticas. Es común encontrar limitado el uso de combustibles de baja calidad a grandes plantas, y especificaciones más estrictas de calidad de combustibles para usos domésticos o en plantas de baja capacidad.

En la actualidad ésta parece ser también la tendencia en algunos de los países industrializados para el control de los óxidos de azufre, basada en la consideración de que las tecnologías de control necesarias pueden soportarse para escalas de planta del orden de los 300 Mw en instalaciones en fase de proyecto.

III) Especificaciones técnicas sobre equipos y/o condiciones de operación

Para instalaciones grandes, las tendencias recientes pueden resumirse como sigue:

- *Altura de chimenea.* La tendencia tradicional ha sido la construcción de chimeneas progresivamente más altas, como medio prácticamente exclusivo de reducir los efectos de las emisiones de contaminantes gaseosos.

  Si bien el empleo de chimeneas altas continuará en el futuro (siempre como medio de prevención de condiciones de emergencia), las consideraciones de costo económico y el desarrollo de los convenios internacionales sobre transporte de contaminantes a larga distancia, tenderán a limitar, salvo excepciones, la altura máxima de chimenea a emplear.

- *Características y modificaciones de los equipos de combustión.* Este ha sido el método tradicional en los países en que se ha intentado el control de emisiones de óxidos de nitrógeno, y seguirá siendo importante en el futuro, especialmente en instalaciones que no requieran de la utilización de tecnología de control de óxidos de azufre por el tipo de combustible.

IV) Medidas de apoyo

El tratamiento especial a instalaciones de demostración de tenologías de combustión más limpias, es el procedimiento empleado actualmente como medio de impulsar el desarrollo de alternativas tales como la combustión en lecho fluidizado.

Es también general la tendencia a apoyar las medidas encaminadas a la reducción de consumo de combustibles y ahorro de energía, o modificaciones de proceso que permitan reducir las emisiones. Sin embargo, las subvenciones a la instalación o mejora de rendimiento de sistemas de control, tienden a ser más selectivas con criterios de innovación tecnológica.

V) Límites de aplicación general

Existe una tendencia común en los países avanzados a fijar límites de aplicación general, con una casuística cada vez más desarrollada en el sentido de incorporar diferencias respecto a la tecnología, los combustibles empleados y la antigüedad de las plantas, estableciéndose pocas excepciones y reconociéndose a la administración la capacidad para imponer límites más rígidos en situaciones especiales.

VI) Formas de expresión

La tendencia actual en los países que mantienen normas con límites de concentración, es definir con detalle las condiciones de referencia del volumen al que se refiere la masa de contaminante: temperatura, presión, gases secos o húmedos, y condiciones de exceso de aire que se consideran normales, en función del tipo de combustible y equipo empleado. En general se adopta un determinado % O_2 o de CO_2 de referencia, al que se corrigen las concentraciones medidas.

El otro criterio de uso común actualmente (ng/J de calor de entrada), requiere la determinación de mayor número de parámetros, asociados, por un lado, con el caudal de gases emitidos, y por otro, con las características y cantidad de combustible consumido.

En general, la determinación de estos parámetros auxiliares implica procedimientos de medida y verificación elaborados (éste no es el caso en Estados Unidos por ejemplo, donde la conversión de los resultados de medida de concentración a ng/J de entrada se apoya en la aplicación de una sencilla fórmula, establecida en función del tipo de combustible, medida de diluyente y concentración. Este procedimiento simplificado se apoya en un conocimiento exhaustivo de la estadística de consumo y análisis de los combustibles que se están empleando, y del margen de variabilidad -error- que se comete con la simplificación).

VII) Procedimientos de verificación

Si se parte de la idea de que las condiciones de excedencia de los límites corresponden a estadística de valores extremos, se justifican claramente algunas tendencias comunes en las normativas más recientes:

- establecer la obligación de informar de las emisiones en exceso, aún cuando correspondan a condiciones de operación anormales.
- definir los límites como valores que no deben sobrepasarse nunca en programas de verificación por muestreo con métodos de medida discontinua.
- especificar la realización de los programas de verificación a carga máxima.
- el recurso creciente a técnicas de medida continua.

Además, las disposiciones de verificación apoyadas en métodos de medida continua incorporan, por razones ligadas al estado de desarrollo de la tecnología de medición, especificaciones muy variadas, según el desarrollo tecnológico de cada país, acerca de:

- comprobación de la representatividad de las medidas con motivo de la instalación inicial.
- calibración periódica de los instrumentos.
- procedimientos alternativos de medida para los períodos de avería de los equipos de medida, etc.

VIII) Condiciones de cumplimiento

En la definición de las condiciones de cumplimiento de límites verificados por procedimientos de medida continua, las tendencias existentes están relacionadas con el tiempo de promediado y con la forma de incorporar la tolerancia de medición en la propia definición de los límites.

La idea subyacente es la de combinar tiempos de promediado adecuados para eliminar el efecto de los errores aleatorios, pero no tan largos como para permitir puntas de emisión que puedan resultar peligrosas.

Hay que tener en cuenta que una de las razones más importantes de la vigilancia contínua es la de proporcionar datos de las emisiones al operador de la planta, que le permitan tomar decisiones en plazos de tiempo relativamente cortos.

4.5.- NORMATIVA ESPAÑOLA Y COMUNITARIA

4.5.1.- NORMATIVA ESPAÑOLA

* Decreto 2414/1961, de 30 de Noviembre, por el que se aprueba el Reglamento de actividades molestas, insalubres, nocivas y peligrosas (B.O.E. 7/XII/61 y corrección de errores B.O.E. 7/III/62).

* Decreto 1775/1967, de 22 de Julio, sobre el régimen de instalación, ampliación y traslado de industrias (B.O.E. 25/VII/67).

* Decreto 1776/1967, de 22 de Julio, por el que se clasifican determinadas industrias a efectos de su instalación, ampliación y traslado (B.O.E. 25/VII/67).

* Ley 38/1972, de 22 de Diciembre, de protección del ambiente atmosférico (B.O.E. 26/XII/72, pp 23032-23034).

* Decreto 3025/1974, de 9 de Agosto, sobre limitación de la contaminación atmosférica producida por los vehículos automóviles (B.O.E. 7/XI/74).

* Decreto 833/1975, de 6 de Febrero, por el que se desarrolla la Ley 38/72, de 22 de Diciembre, de protección del ambiente atmosférico

(B.O.E. 22/I/75, pp 8391-8416 + modificaciones).

* Decreto 795/1975, de 20 de Marzo, por el que se desarrolla el art. 11 de la ley de protección del ambiente atmosférico (B.O.E. 18/IV/75).

* Decreto 2204/1975, de 23 de Agosto, por el que se tipifican las características, calidades y condiciones de empleo de los combustibles y carburantes (B.O.E. 19/IX/75, pp 19861-19867).

* Real Decreto 1280/1976, de 9 de Abril, por el que se incluyen en el grupo 2º del art. 2º del Decreto 1775/1967, de 22 de Julio, las industrias dedicadas a la fabricación de hormigón preparado, y se regula el régimen de sanciones aplicables por incumplimiento de las obligaciones establecidas (B.O.E. 4/VI/76).

* Orden de 10 de Agosto de 1976, del M. de la Gobernación, por la que se establecen las normas técnicas para el análisis y valoración de los contaminantes de naturaleza química presentes en la atmósfera (B.O.E. 5/XI/76, pp 21822-21832 y correcciones B.O.E. 10/I/77, pp. 455).

* Orden de 18 de Octubre de 1976, del Ministerio de Industria, sobre prevención y corrección de la contaminación industrial de la atmósfera (B.O.E. 3/XII/76, pp. 24097-24117 y correcciones en B.O.E. 23/II/77, pp 4397).

* Orden de 1 de Febrero de 1977, del Ministerio de la Gobernación, sobre la Red Nacional de Vigilancia y Prevención de la Contaminación Atmosférica (B.O.E. 18/II/77, pp 3936).

* Real Decreto 378/1977, de 25 de Febrero, sobre medidas liberalizadoras en materia de instalación, ampliación y traslado de industrias (B.O.E. 14(18)/III/77).

* Orden de 13 de Junio de 1977, del Ministerio de Industria, por la que se dictan normas complementarias del Decreto 378/1977 de 25 de Febrero, sobre medidas liberalizadoras en materia de instalación, ampliación y

traslado de industrias (B.O.E. 18/VI/77).

- Real Decreto 2512/1978 de 14 de Octubre, para aplicación del art. 11 de la Ley 38/1972 de 22 de Diciembre (B.O.E. 25/X/78 pp 24854-24856).

- Real Decreto 547/1979 de 20 de Febrero, sobre modificación del Anexo IV del Decreto 833/1975, de 6 de Febrero, por el que se desarrolla la Ley 38/72, de 22 de Diciembre, de protección del ambiente atmosférico (B.O.E. 22/III/79).

- Real Decreto 735/1979 de 20 de Febrero, donde se fijan las normas generales que deben cumplir las Entidades Colaboradoras (B.O.E. 9/IV/79 pp 8385).

- Real Decreto 2624/1979, de 5 de Octubre, por el que se modifica el 735/1979 de 20 de Febrero, en el que se fijan las normas generales que deben cumplir las Entidas Colaboradoras (B.O.E. 16/XI/79 pp 26485-26486)

- Decreto 2826/1979, de 17 de Diciembre, por el que se complementa y modifica el Real Decreto 2512/1978, de 14 de Octubre, para aplicación del art. 11 de la Ley 38/1972 de 22 de Diciembre (B.O.E. de 20/XII/79).

- Orden de 25 de Febrero de 1980, del Ministerio de Industria, por la que se regulan las Entidades Colaboradoras en materia de medio ambiente industrial (B.O.E. 24/III/80 pp. 6525-6527).

- Real Decreto 2135/1980, de 26 de Septiembre sobre liberalización industrial (B.O.E. 14/X/80).

- Orden de 19 de diciembre de 1980, del Ministerio de Industria, sobre normas de procedimiento y desarrollo del Decreto 2135/1980, de 26 de Septiembre sobre liberalización industrial (B.O.E. 24/XII/80, correcciones B.O.E. 17/1/81).

- Orden de 22 de Octubre de 1981, del Ministerio de Industria, por la que se modifica la de 25 de Febrero de 1980 regulando las Entidades Colaboradoras en materia de Medio Ambiente industrial (B.O.E. 18/XI/81, pp. 27066).

- Real Decreto 2403/1982, de 12 de Agosto, por el que se fijan nuevas especificaciones para los diversos tipos de fuel-oil (B.O.E. 17/IX/82, pp 26320-26321).

- Orden de 25 de junio de 1984, del Ministerio de Industria y Energía, sobre instalación en centrales térmicas de equipos de medida y registro de emisión de contaminantes a la atmósfera (B.O.E. 4/7/84, p. 19535).

- Resolución de 2/7/85, de la Dirección General de la Energía, por la que se prorroga el plazo de instalación de equipos de medida y registro de la emisión de contaminantes a la atmosfera establecido por la orden de 25/6/84 (B.O.E. 9/7/85, pp 21588).

- Real Decreto 1613/1985, de 1 de Agosto, por el que se modifica parcialmente el Decreto 833/1975 de 6 de Febrero, y se establecen nuevas normas de calidad de aire en lo referente a contaminación por dióxido de azufre y partículas (B.O.E. 12/IX/85, pp. 28797-28799).

- Resolución de 17/IV/86, de la Dirección General de la Energía, por la que se establece un período de pruebas para el ajuste y calibrado de los equipos de medida, control, registro y transmisión de datos relativos a la emisión de contaminantes a la atmósfera a que se refieren la Orden de 25/6/84, y la Resolución de 2/7/85 de la Dirección General de la Energía (B.O.E. 25/4/86, pp. 14766-14768).

- Real Decreto legislativo 1302/1986, de 28 de Junio, de evaluación de impacto ambiental (B.O.E. 30/6/86, pp. 23733-23735).

4.5.2.- DIRECTIVAS C.E.E.

* Directiva 70/220/CEE, de 20/III/70, referente a la armonización de las legislaciones de los estados miembros relativa a las medidas a tomar contra la contaminación del aire por los gases provenientes de motores de encendido controlado que equipan vehículos a motor (B.O. L 76 6/IV/70 + adaptaciones).

* Directiva 72/306/CEE, de 2/VIII/72, referente a la armonización de las legislaciones de los estados miembros relativa a las medidas a tomar contra la contaminación del aire por los gases provenientes de motores diesel destinados a la propulsión de vehículos (B.O. L 190/1 20/VIII/72).

* Directiva 74/290/CEE, de 28/V/74, incorporando la adaptación al progreso técnico de la Directiva 70/220/CEE, referente a la armonización de las legislaciones de los estados miembros relativa a las medidas a tomar contra la contaminación del aire por los gases provenientes de motores de encendido controlado que equipan vehículos a motor (B.O. L 159 15/VI/74).

* Directiva 75/716/CEE, de 20/XI/75, relativa a la armonización de la legislación de los estados miembros referente al contenido en azufre de ciertos combustibles líquidos (B.O. L 307 27/XI/75).

* Directiva 77/102/CEE, de 30/XI/76, incorporando la adaptación al progreso técnico de la Directiva 70/220/CEE, referente a la armonización de las legislaciones de los estados miembros relativa a las medidas a tomar contra la contaminación del aire por los gases provenientes de motores de encendido controlado que equipan vehículos a motor (B.O. L 32 3/II/77).

* Directiva 77/537/CEE, de 28/VI/77, referente a la armonización de las legislaciones de los estados miembros relativa a las medidas a tomar contra las emisiones de contaminantes procedentes de motores diesel destinados a la propulsión de tractores agrícolas o forestales de

ruedas (B.O. L 220/38 29/VIII/77).

- Directiva 79/611/CEE, de 29/VI/78, referente a la armonización de las legislaciones de los estados miembros relativas al contenido de plomo en la gasolina (B.O. L 197 22/VII/78).

- Directiva 78/665/CEE, de 14/VII/78, incorporando la adaptación al progreso técnico de la Directiva 70/220/CEE, referente a la armonización de las legislaciones de los estados miembros relativa a las medidas a tomar contra la contaminación del aire por los gases provenientes de motores de encendido controlado que equipan vehículos a motor (B.O. L 223 14/VIII/78).

- Directiva 80/779/CEE, de 15/VII/80, relativa a los valores límite y valores guía de calidad atmosférica para el anhídrido sulfuroso y las partículas en suspensión (B.O. L 229 30/VIII/80 y modificación 81/857/CEE, de 19/X/81).

- Directiva 82/844/CEE, de 3/XII/82, relativa a un valor límite para el plomo contenido en la atmósfera (B.O. L 378 31/XII/82).

- Directiva 83/351/CEE, de 16/VI/83, incorporando adaptación al progreso técnico de la Directiva 70/220/CEE, referente a la armonización de las legislaciones de los estados miembros relativa a las medidas a tomar contra la contaminación del aire por los gases provenientes de motores de encendido controlado que equipan vehículos a motor (B.O. L 197 20/VII/83).

- Proposición de directiva 83/704, relativa a la limitación de emisión de contaminantes en la atmósfera procedentes de grandes instalaciones de combustión (C 49 21/II/84).

- Directiva 84/360/CEE, de 28/VI/84 relativa a la lucha contra la contaminación atmosférica procedente de instalaciones industriales (B.O. L 188 16/VII/84).

- Directiva 85/203/CEE, de 7/III/85, relativa a las normas de calidad del aire para dióxido de nitrógeno (B.O. L 87 27/III/85).

- Directiva 85/210/CEE, de 20/III/85, referente a la armonización de las legislaciones de los estados miembros relativas al contenido en plomo de la gasolina (B.O. L 96 3/VI/85).

- Directiva 85/580/CEE, de 20/XII/85, sobre la adaptación, en razón de la adhesión de España y Portugal, de la Directiva 85/203/CEE referente a las normas de calidad del aire para el dióxido de nitrógeno.

- Directiva 85/581/CEE, de 20/XII/85, sobre la adaptación, en razón de la adhesión de España y Portugal, de la Directiva 85/210/CEE referente a la aproximación de legislaciones de los Estados miembros relativas al contenido de plomo en la gasolina.

- Decisión del Consejo 86/277/CEE, de 12/VI/86, relativa a la celebración del Protocolo del Convenio de 1979 sobre la contaminación atmosférica transfronteriza a gran distancia, relativo a la financiación a largo plazo del Programa de cooperación para la vigilancia continua y la evaluación del transporte a gran distancia de contaminantes atmosféricos en Europa (EMEP).

- Directiva del Consejo 87/219/CEE, de 30/III/87, por la que se modifica la Directiva 75/716/CEE relativa a la aproximación de las legislaciones de los Estados miembros en materia de contenido de azufre de determinados combustibles líquidos.

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ESTUDIO DE LA INCIDENCIA DE LA CONTAMINACION ATMOSFERICA SOBRE LA CALIDAD DE LAS AGUAS SUBTERRANEAS: INVENTARIO, EVALUACION Y METODOLOGIA

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NIVELES DE METALES PESADOS EN SUELOS PROXIMOS A UNA CENTRAL TERMICA

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Facultad de Ciencias
Universidad Autónoma de Madrid

I.INTRODUCCION

La investigación relativa a los efectos contaminantes en suelos, por metales pesados emitidos por centrales térmicas, está escasamente desarrollada.

Diversos investigadores (Föstner et al.,1981; Page et al., 1979;Kleing et al.,1975;Natusch et al.,1974)han comprobado la existencia de elementos tóxicos emitidos por centrales térmicas durante la combustión del carbón.Entre los elementos más significativos se encuentran:Co,Cr,Cu,Ni, V,Hg,Cd,Se,As,Zn y Pb.

Otros investigadores (Kleing et al.,1975 y Wangen et al.,1980),han encontrado, en suelos y plantas próximos a centrales térmicas,concentraciones apreciables de Co,Cd,Zn, Pb,Cu,Cr y Ni,con preferencia según la dirección dominante del viento.

El presente trabajo aborda esta problematica estudiando la dispersión y los niveles de Cd,Cu,Ni y Zn en suelos situados en la zona de influencia próxima (un radio de 15 Km.)a una central térmica del NO de España.Se pretende de este modo,contribuir a evaluar el impacto ambiental producido por la contaminación de metales pesados en suelos.

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II.AREA DE ESTUDIO

La central térmica objeto de estudio está situada en un valle relativamente abierto conformado por la cuenca del rio Sil.Dentro de un radio de 50 Km.,la zona se presenta confinada por una serie de elevaciones que alcanzan cotas de 1500 m.

El viento, considerado como uno de los factores que gobiernan la distribución de la deposición seca,presenta una dirección dominante según los sectores oestesuroeste-estenoreste.

Los suelos representativos de la zona son clasificados dentro de los órdenes entisol, inceptisol y alfisol de la Soil Taxonomy(USDA,1975).

En terminos generales ,se trata de suelos caracterizados por un escaso desarrollo de los horizontes edafogenéticos ,pH ácidos,texturas dominantes del tipo franco -arcillo -limosas;bajas capacidades de cambio; desaturación elevada ;moderados contenidos en materia orgánica y pobres contenidos en elementos nutritivos.

Podemos considerar globalmente, que la suceptibilidad de los suelos de la zona de estudio a la contaminación por metales pesados es moderadamente elevada.

III.MATERIAL Y METODOS

El muestreo se realizó según una malla circular en torno a la central con un radio de 15Km.,tomando muestras en sectores radiales.La densidad de muestreo se intesificó en los sectores a favor de la dirección dominante del viento,tratando de combinar este factor con la diversidad tipológica de los suelos de la zona.

Las muestras se tomaron mezclando el suelo en los 10 primeros centímetros de profundidad,por considerar la superficie del suelo como la zona más afectada por la deposición seca.

Los métodos de análisis de suelos empleados en este trabajo son los propuestos por U.S.Department of Agriculture(1972).Los metales pesados fueron determinados por absorción atómica y espectrometria de emisión(IPC).

IV.RESULTADOS

Los resultados obtenidos se ofrecen en las tablas y gráficos adjuntos.

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TABLA 1.ANALISIS QUIMICOS E INDICES FITOTOXICOS

(elementos totales el ppm).

muestra	x	y	pH	CO%	Cd	Cu	Ni	Zn	equiv.Zn	Zn:Cd
1	20	13	5.2	3.1	6	17	16	231	393	39
2	20	19	5.5	1.6	5	19	24	331	561	66
3	15	17	5.3	.2	0	77	3	190	368	
4	23	12	4.3	.5	0	23	32	250	552	
5	17	13	4.7	4.3	7	136	25	240	712	34
6	22	24	5.8	.1	3	3	16	100	234	33
7	15	13	6.3	.9	0	8	13	100	220	
8	17	23	5.4	2.8	0	2	14	135	251	
9	14	13	5.2	3.6	0	12	25	100	324	
10	14	16	5.9	1.6	0	13	24	140	358	
11	15	24	5	2.3	3	13	24	24	458	80
12	17	25	6.1	.1	0	16	44	190	574	
13	21	16	5.1	.1	8	35	33	270	604	34
14	23	19	5.3	.6	0	12	14	200	336	
15	20	29	5.1	2.2	0	15	15	65	215	
16	20	24	6	4.3	0	41	36	80	450	
17	27	23	6	2.4	6	31	36	80	430	13
18	31	25	5.4	5.5	.1	21	23	240	466	2400
19	31	21	4.5	3.8	0	7	18	200	358	
20	35	21	5	.5	6	19	16	290	456	48
21	27	15	4.2	.2	0	18	15	232	388	
22	26	15	5.4	1.5	0	29	28	200	482	
23	24	10	6.4	1.6	0	28	26	310	574	
24	14	22	6.2	.4	0	46	33	250	606	
25	12	22	5.6	2	.1	98	31	50	494	500

podemos observar que el valor medio obtenido para los elementos estudiados supera su rango habitual en suelos.

El valor adoptado ,como limite máximo admisible para estos elementos en el suelo, por la CEE, esta ampliamente rebasado para el cadmio y de zinc en algunas muestras,pudiendo considerar estos casos como suelos contaminados.

El valor minimo del rango establecido por la CEE,es superado por los cuatro elementos considerados,si bien en el caso del cromo tan sólo en una muestra.

Los sectores más afectados por la contaminación parecen ser aquellos que se encuentran a favor de la dirección del viento, sin observarse una variación apreciable con la distancia dentro de los 15 Km considerados.

El factor equivalente de Zn,considerado como un indice de fitotoxicidad potencial por diversos autores,supera en la mayoria de las muestras el valor limite de 250 ,aceptado como umbral de fitotoxicidad.

Otro criterio ampliamente utilizado es la relación Zn/Cd,fundamentado en el efecto antagónico de estos elementos en relación à las plantas.Parece recomendable que este indice se aproxime a 1000,hecho que no sucede en nuestro caso.

V.DISCUSION

Comparando los resultados obtenidos de Cu,Cd,Ni y Zn (TABLAS 1 y 2) con los rangos medios de referencia establecidos para estos elementos en el suelo (TABLA 3),

TABLA 2.RESUMEN ESTADISTICO.

DETERMINACION	pH	CO%	Cu(ppm)	Cd(ppm)	Ni(ppm)	Zn(ppm
NUMERO DE MUESTRAS	25	25	25	25	25	25
MEDIA	5.4	1.8	29.6	1.8	23.4	188.6
MEDIANA	5.4	1.6	19	0	24	200
MODA	5.4	1.6	12	0	24	100
VALOR MINIMO	4.2	0.1	2	0	3	50
VALOR MAXIMO	6.4	5.5	136	8	44	331

TABLA 3.CONCENTRACIONES DE REFERENCIA (PPM).

ELEMENTO	Cu	Cd	Ni	Zn
NIVEL MEDIO	25	<0.5	20	50
RANGO CONTAMINANTE CEE	50-140	1-3	30-75	150-300

VI.CONCLUSIONES

Del estudio cabe deducir que los suelos situados dentro de la zona de influencia de la central térmica presentan niveles anormalmente elevados de cadmio y zinc, pudiendo deducirse que algunos suelos se encuentran contaminados en estos elementos.

Los indices de fitotoxicidad estudiados revelan la existencia, en la mayoria de los suelos, de una fitotoxicidad potencial elevada.En este sentido los pH ácidos y la alta desaturación de los suelos no contribuye a favorecer la situación.

Parece dificil demostrar, en base al estudio realizado, que la central térmica sea la causante de la contaminación citada, ya que no se han evaluado otras posibles fuentes de contaminación como pueden ser la actividad agricola o industrial de la zona.

HEAVY METALS in the ENVIRONMENT
International Conference Athens, 10—13 September 1985

ENVIRONMENTAL IMPACT OF TRACE METALS FROM DISPOSED ASH OF COAL-BURNING POWER PLANTS

G. BIGNOLI, L. GOETZ and E. SABBIONI

ABSTRACT

In the context of the programme of action of the European Communities on the environment directed to prevent and reduce pollution, a study on the potential impact of trace metals (TM) on groundwater, food chains and man as a result of coal combustion in electric power plants has been undertaken at the JRC-Ispra. It has been estimated that about 30 million tons of fly ash will be produced in the countries of the EC in the year 1990 as a result of the use of hard coal in electrical power stations. Using data obtained by our laboratory studies a fly ash leaching in dynamic environmental models, we have simulated Cr migration and its possible chemical speciation from fly ash repository through the different environmental compartments to man. Information on Cr impact on groundwater, soil, vegetation and intake by man comprise the most important results of this long-term approach.

1. INTRODUCTION

As concerns future energy demands in the European Community it is envisaged that there will be an increased use of coal for electrical energy production which will result also in an increased mobilization of TM to the environment /1/. The magnitude of this release is substantially comparable to that originating from major sedimentary cycles such as from rivers and natural sediments /2/. However, because of the complexity of the possible interactions of TM with the biosphere and with man, the nature of the risks that metals released from coal-fired power plants represent is uncertain. It has also been estimated that 530,000 m^3 per year of fly ash containing TM and in particular 200 ppm of chromium /3/ should be retained by the filters of a typical 2500 MW CFPP. This amount today poses significant environmental and ecological problems because most of this waste must be disposed of in some way such as in land fills and could be leached by water /4/.
The long-term assessment of the environmental and toxicological impact of Cr released from stored coal ash is related to the study and use of particular dynamic models /5/ and to the results of laboratory studies on water leaching using nuclear and radiochemical techniques /4/.

2. MODEL AND RESULTS

Fig. 1 shows the results of Cr and As as obtained by laboratory studies and matematically implemented by a computer as the input for TM to the environmental models developed :

- a geochemical model which treats Cr migration from an ash repository 10 m thick, to the groundwater system ;

- Cr migration by irrigation from groundwater to surface soil and by food chains to man.

The system analysis method has been applied to predict Cr (VI) movement through the soil system /6/ considering its particular mobility and biochemical interactions with soil components /7/ which can reduce Cr (VI) to Cr (III) which is considered not to be bioavailable for vegetables and grass /8/. The same figure shows the long-term Cr exposure of man (average lifetime 70 years) as a result of the applied exposure model in comparison with present intake /9/ and as a function of the distance from the fly ash repository which he lives.
It is important to note that even if half life of 50 years for a typical CFPP is considered the remaining Cr for commitment to the population is due to its continuous leaching from the repository.

3. CONCLUSIONS AND NEEDS FOR FURTHER RESEARCH

The results clearly demonstrate the need to consider the possible speciation and chemical forms of TM an element which may be responsible for the mobility and bioavailability in the environment and organisms. The more mobile chemical form of chromium (Cr (VI)), determines the effective intake of this element by man and, therefore, the more realistic evaluation of the nature of the biological risks. The results obtained for chromium using the critical path analysis approach allow us to make specific recommendations for further research :

(i) chemical and environmental parameter studies such as soil distribution coefficient between TM and soil components ;

(ii) studies of the uptake by plants as related with the particular chemical state because even the present results demonstrate that vegetable diet is the most important Cr pathway to man ;

(iii) biochemical and toxicological studies to determine more realistic dose response relationships for TM which at present are scarce.

Since such criteria are largely developed from toxicological studies on laboratory animals, studies on animals should also take into account the chemical form and the biochemical mechanisms under long-term, low-level exposure conditions. These studies impose special requirements on the analytical techniques to be used as neutron activation analysis and radiochemical tracer techniques.

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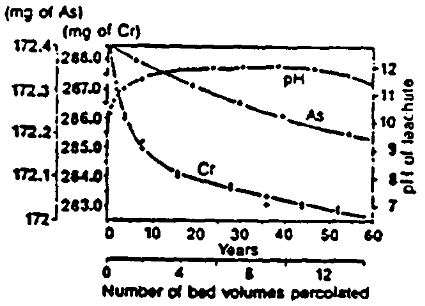
FIGURE CAPTIONS :

Figure 1. General view of trace metals pathway modelling released from coal fly ash deposit.

LABORATORY LEACHING STUDIES



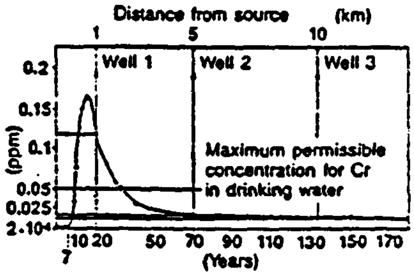
Remain Cr and As content of a fly ash column of 1 cm^2 of cross section and 10 m of length submitted to a continuous rainfall rate of 1 my^{-1}

$I(t) = a[\exp - bt] + c[\exp - dt]$

$dI/dt = L(t)$ is the
input to geochemical model

Input to geochemical model

LONG-TERM PREDICTION GROUND WATER



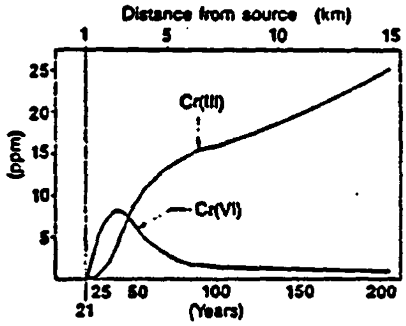
Increase of Cr(VI) concentration in groundwater and in pumping wells. (Background level = 2·10⁻⁴ ppm of Cr)

System analysis method

$Q_i = \sum_{j=1}^{n} K_{ij}Q_i - (\sum_{j=1}^{n})K_{ij}Q_i - \lambda_i Q_i + I_i$

Input to dynamic environmental model

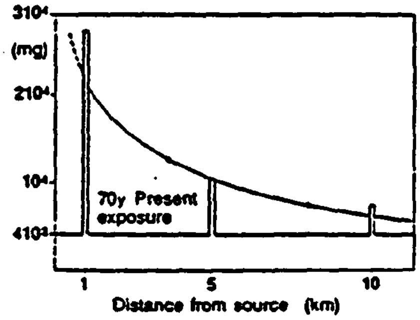
BEHAVIOUR IN SOIL



Behaviour and chemical transformation of Cr in soil

Uptake by plants

CONTRIBUTION TO MAN EXPOSURE



Long-term Cr exposure at the different distances from the fly ash repository. (Daily intake ≅ 150 μg)

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TRANSPORT OF AIRBORNE MERCURY EMITTED BY COAL BURNING INTO AQUATIC SYSTEMS

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ABSTRACT

Concentrations of watersoluble and insoluble mercury compounds in air, precipitation and smoke from coal combustion have been measured.

It has been found that in western Sweden 10-20 % of airborne mercury is in an oxidised watersoluble form. The corresponding figure from one boiler is ∿70 %.

INTRODUCTION

Faced with the possibility of increased use of coal for energy production the Swedish government decided some years ago to sponsor a comprehensive investigation of all kinds of emissions connected with the combustion of coal and their eventual impact on the environment. One of the problems to be elucidated emphasized the consequences of the emission of mercury.

At the time when this project was started our understanding of the behavior and transport of Hg in the environment was rather incomplete. Therefore, this study had to be undertaken in two steps.

The first one comprised the establishing of the present concentration levels of different important mercury species in air, precipitation and natural water. Data obtained should be evaluated in terms of transportation mechanisms.

The objective of the second step was to characterise the concentration and properties of mercury in smoke produced by coal combustion.

A short survey of the results hitherto obtained is given in this presentation.

Total mercury in the air

During the initial stage of this study total airborne mercury (Hg_T) was monitored at 14 different sites in Sweden using the well-known gold trap technique(1) These measurements showed that there was a very even geographical distribution of Hg_T indicating a slight decrease ot the concentration with latitude and possibly somewhat higher concentration at the Baltic Sea region as compared with the Swedish westcoast. Further, at all places there is a clear seasonal variation with a maximum in January-March and a minimum in May-July. A secondary maximum may exist in September to October.

These features are shown in Fig. 1 where the monthly averages of Hg_T are given for the period October -79 to September -80 from places representing the Baltic Sea region (Hoburg at the south end of the island Gotland) and the Swedish westcoast (Rörvik, located 40 km south of Gothenburg).

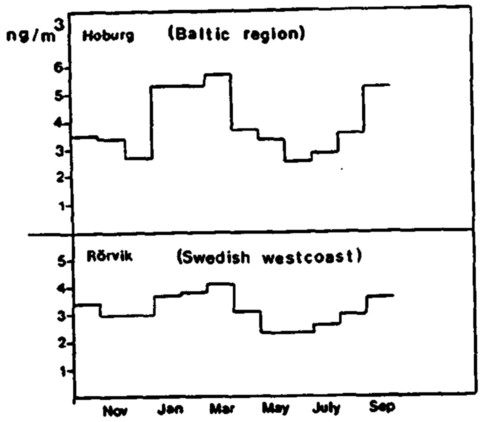

Fig. 1.

Next, it was important to elucidate if Hg_T was varying with high-level wind directions which would indicate the eventual existence of long-range transport.

For that reason the same data material used in Fig. 1 was divided into 4 groups corresponding to high-level winds from N-E, E-S, S-W, and W-N. This was done using 18 h trajectories supplied by the Norwegian Meteorological Institute.

The result is shown in Fig. 2 (the solid line).

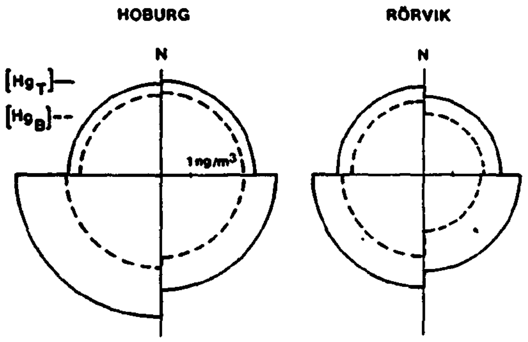

Fig. 2. Wind-rose diagrams for $[Hg_T]$ and $[Hg_B]$, Hoburg (Baltic region), and Rörvik (Swedish westcoast).

As the shape of these wind-roses for Hg_T was resembling the shape of the corresponding wind-roses for black particles (soot) there seemed to be a possible correlation between the concentrations of these two pollutants.

For that reason, linear regression equations of the type $[Hg_T] = [Hg_B] + m[C]$ were calculated. Here $[Hg_T]$ is the concentration (ng/m^3) of total airborne mercury, $[C]$ is the concentration (µg/m^3) of soot (carbon), $[Hg_B]$ (background mercury) is the intercept, i.e. the value of $[Hg_T]$ for $[C] = 0$, and finally, m is the slope ng Hg/µg C.

The result is given in Table 1.

TABLE 1. Hoburg and Rörvik Oct. -79 to Sept.-80. $[Hg_T]$ denotes the concentration of total mercury in ng/m^3, $[C]$ the concentration of soot (µg/m^3) and $[Hg_B]$ the concentration of soot-independent mercury (background mercury) in ng/m^3, W is the high-level wind sector, n the number of $[Hg_T]$ - $[C]$ pairs, r the correlation coefficient and m the slope ng Hg/µg C.

	W	n	r	m	$[Hg_T]$	$[Hg_B]$	$[C]$
Hoburg	N-E	23	0.48	0.15	3.17	2.80	2.39
	E-S	20	0.67	0.18	3.92	2.84	6.05
	S-W	20	0.65	0.13	4.88	3.20	12.67
	W-N	26	0.39	0.26	3.14	2.67	1.79
Rörvik	N-E	17	0.46	0.10	2.62	2.08	5.35
	E-S	20	0.77	0.13	3.32	1.97	11.00
	S-W	23	0.72	0.072	3.81	2.80	14.10
	W-N	29	0.35	0.073	2.97	2.53	6.08

The values of $[Hg_B]$ are also seen in Fig. 2 (dashed lines)

This result indicates that the total airborne gaseous mercury consists of two parts. The big part (∿80 %) is not correlated to soot particles and consequently may not be produced by combustion. This part is considered here as a kind of a background (Hg_B).

The smaller part (∿20 %), however, is directly proportional to the soot particle concentration, which may mean that this part of the airborne gaseous mercury has been released by the same sources as the soot particles. (See also ref. 2).

The watersoluble mercury

It is well known that in air and natural water mercury is present in different molecular forms.

The following are considered to be the most important:

Hg^0 (metallic vapor)

$HgCl_2$ (mercury chloride)

CH_3HgCl (methyl mercury chloride)

Hg^0 is only slightly soluble in water. On the contrary, $HgCl_2$ and CH_3 HgCl are easily soluble.

The high concentrations of mercury in precipitation found by many authors may, consequently, indicate the presence of the last two or similar compounds in important concentration in the atmosphere.

In such case, at equilibrium conditions, these mercury compounds would be distributed among air and precipitation according to Henry's law.

Thus, for the further study of the behavior of mercury in the atmosphere numerical values of the respective Henry law constants were necessary.

When this investigation was at its start, the distribution between gas and water was known only for Hg^0 (3).

On my suggestion in 1980, A. Iverfeldt and O. Lindqvist determined the constants needed (4). At the moment, the figures given in Table 2 are at hand.

TABLE 2. Distribution of different mercury species between air and water.

Species	Temp. C^0	Assumed concent. in air ng/m^3	Equilibrium concentration in water ng/l	Comments
CH_3 HgCl	10	1	110	True equilibrium
	25	1	67	" "
$HgCl_2$	10	1	33	Stoichiometric equilibrium $\|Cl^-\| = 0.2\cdot10^{-3}M$
	25	1	32	
Hg^0	10	1	0.0099	True equilibrium
	25	1	0.0036	" "

The concentration ratios in Table 2 indicate that it should be much easier to find $HgCl_2$ and CH_3 HgCl in precipitation than in the gas phase (air).

For that reason, a number of precipitation samples on the Swedish westcoast were analysed.

The procedure used was based on reduction to Hg^0 and capturing the last on gold for subsequent thermal desorption and spectrophotometrical analysis. Reduction was performed using $NaBH_4$ and $SnCl_2$, respectively. In the first case, all dissolved mercury was obtained (Hg^1aq), in the second case only $HgCl_2$-types mercury ($Hg^1{}_{inorg}aq$) (5, 6).

The result is summarized in Table 3.

TABLE 3. Precipitation data
Swedish westcoast 1981 - 82

Precipitation	Hg-type	Concentration range ng l^{-1}
Rain	Hg^1 aq	20 - 50
Snow	Hg^1 aq	50 - 100
Snow	Hg^1_{inorg} aq	∿ 10

In first place, Table 3 indicates that 80 - 90 % of the watersoluble mercury in precipitation is of the type that is not reduced by $SnCl_2$.

If it is assumed that this part consists of an organic mercury compound (Hg^1_{org}) probably CH_3 HgCl, and true Hg^1_{inorg} is $HgCl_2$, the figures in Table 2 and Table 3 give for the possible concentration of watersoluble mercury in air the figures given in Table 4.

TABLE 4. Calculated concentrations of watersoluble mercury in air
Swedish westcoast Nov. -81 to Jan. -82

Species	Concentration ng/m^3
Hg^1_{inorg} (g)	0.3
Hg^1_{org} (g)	0.3
Hg^1 (g)	0.6

Direct measurements of Hg^1(g) at ground level using a new method based on filtration of air through a polymer that retains all oxidised forms of mercury but is inert to Hg^0 have given the data collected in Table 5.

TABLE 5. Watersoluble mercury in air
Swedish westcoast

Year	Month	No. of samples	Average concentration in ng/m^3			q = Hg^1/Hg_T %
			Hg_T	Hg^0	Hg^1	
-81	Aug.	7	2.2	2.0	0.2	9
	Sept.	3	2.9	2.5	0.5	17
	Oct.	8	3.0	2.7	0.3	10
	Nov.	5	3.0	2.5	0.6	20
-82	Febr.	13	4.94	4.52	0.43	8.7
	March	22	3.58	3.21	0.37	10.3

From Table 5 two conclusions now may be drawn.

1. The concentration of watersoluble mercury in air as compared with the concentration in precipitation indicates a possible state near equilibrium.

2. The watersoluble fraction which represents that part of the total mercury which is in oxidised state is in Fig. 5 denoted as q. As is seen from this table q amounts to 10 - 20 %.

About the same q-values have also been found in air samples taken up to 1500 m above ground (to be reported later on).
On the other side, in the same connection it has been shown that Hg_T (and, consequently, also Hg^o) clearly decreases with height. At 1500 m above ground its concentration is ∿60 % of the value at ground level.

The possible conclusion is that mercury is emitted at ground level by natural and/or anthropogenic processes. This is certainly true for Hg^o. Concerning Hg^1 it may be partly emitted in the same way and/or formed through oxidation of Hg^o in the atmosphere. There are strong indications of the existence of such oxidation processes.

Hg^1, especially Hg^1_{org}, is an undesired form of mercury as it enters ecosystems and is enriched in eco-chains. For that reason it seemed very important to elucidate in which form that part of atmospheric mercury is emitted which is correlated to soot particles.

This will be discussed in the next section.

Watersoluble mercury in smoke from coal combustion

The above mentioned implies that the content of different mercury forms had to be determined in smoke from combustion of coal.

Obviously, there are many parameters to be considered in such investigations necessitating many measurements.

At the moment, only a few have been performed. However, as the results are rather interesting such measurements from one boiler will be reported.

The measurements were undertaken as follows.
A stream of smoke was drawn through a quartz fiber filter and then through two quartz bubblers in series containing water with known (very low) mercury blank. Part of the gas leaving the bubblers was drawn through gold traps.

The water was analysed using the same reduction technique as described earlier in connection with the analysis of precipitation, giving Hg^1 and Hg^1_{inorg}, and the gold traps were analysed for Hg^o.

The result obtained is presented in Table 6.

TABLE 6. Concentration and ratios of mercury species in smoke from a coal fired boiler.

$\mu g/m^3$				%	
Hg^0	Hg^1_{inorg}	Hg^1_{org}	Hg_T	Hg^1/Hg_T	Hg^1_{org}/Hg_T
0.62	0.07	0.73	1.43	56	51
0.52	0.53	1.07	2.13	75	50
0.83	0.83	1.17	2.83	71	41

As is seen from this table the combination of the boiler construction, the firing conditions and the kind of coal used in this case have resulted in gaseous emission of total mercury amounting to 1 - 3 $\mu g/m^3$.

Most important is the observation that in average ∿70 % of this total mercury was watersoluble. About 50 % of it was not reducible with $SnCl_2$ indicating the possibility of being organic mercury compounds.

When this is written the identification of this mercury species is going on.

SUMMARY

It has been established that there is a concentration of total airborne mercury at remote places in southwestern Sweden amounting to 2 - 4 ng/m^3. About 20 % of it is probably anthropogenic.

As the concentration in this fraction is proportional to the concentration of soot particles it is probably emitted in connection with coal burning.

The total airborne mercury includes a watersoluble fraction of 10 - 20 %. A big part of this last fraction (∿80 %) has stability properties indicating organic mercury compounds, possibly methyl mercury salts.

The smoke from coal burning seems to have a similar composition. However, its watersoluble concentration fraction may be near 70 %. This fraction can be easily wet and dry deposited into aquatic systems.

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CONTAMINACION ATMOSFERICA DE LAS CENTRALES TERMICAS: SITUACION ACTUAL Y PERSPECTIVAS LEGISLATIVAS

Emilio CASTIELLA VILLACAMPA y Olga ASUAR ALONSO

TRAS el ingreso de España en las Comunidades Europeas, las instalaciones de combustión de nuestro país deberán adaptarse a una nueva legislación relativa a la contaminación atmosférica qye será común a todos los países que las integran, con algunas particularidades que se describirán más adelante.

En concreto, las centrales térmicas con potencia térmica nominal igual o superior a 50 MW, se regirán por la "Directiva del Consejo de 24 de noviembre de 1988 sobre limitación de emisiones a la atmósfera de determinados agentes contaminantes de grandes instalaciones de combustión" (88/609/CEE).

Esta nueva directiva considera la importancia de la prevención y la reducción de la contaminación atmosférica modificando el tratamiento que recibía hasta ahora el tema de la contaminación ambiental: ya no hace hincapié en el tema "quien contamina, paga", sino que lo hace en el criterio de la reducción de la contaminación atmosférica en su propio origen. Este cambio de actitud es muy significativo, porque no es suficiente pagar por cualquier deterioro ecológico que pueda producirse, sino que deben evitarse, en la medida de lo posible, dichos defectos, asumiendo que el hombre es un mero usufructuario de la Tierra y tiene la obligación de legarla a las generaciones venideras en iguales o mejores condiciones que él la heredó.

Para adaptarse a estos criterios paulatinamente, las centrales térmicas europeas, y con ellas las españolas, han ido adoptando medidas tendentes, primero, a cuantificar la magnitud de sus emisiones y, posteriormente, a limitarlas, a medida que se comprobaba el carácter nocivo a corto o medio plazo, y posiblemente también a largo plazo, de ciertas sustancias en el ambiente. La selección de estas sustancias se llevó a cabo por el grupo Intergubernamental sobre Vigilancia del Medio, de las Naciones Unidas, definiendo los contaminantes prioritarios, indicadores de la calidad del aire, de acuerdo con los siguientes criterios:

a) La gravedad de los efectos sobre la salud y el bienestar del hombre, sobre el clima, y sobre los ecosistemas terrestres o acuáticos, teniendo en cuenta la estabilidad de los ecosistemas en cuestión.

b) La persistencia y resistencia a la degradación en el medio ambiente, así como la acumulación en el hombre y en las cadenas alimentarias.

c) La posibilidad de que la transformación química en los sistemas físicos y biológicos origine sustancias secundarias más tóxicas o más perjudiciales que el compuesto original.

d) Omnipresencia o movilidad.

e) Frecuencia y magnitud de la exposición.

f) El posible valor de la información obtenida para evaluar el estado del medio.

g) La posibilidad de utilizarlo, por su distribución generalizada, para realizar mediciones uniformes dentro de un programa mundial, regional o local.

A partir de los cuales se eligieron, para la Red Mundial de Vigilancia, los siguientes contaminantes del aire:

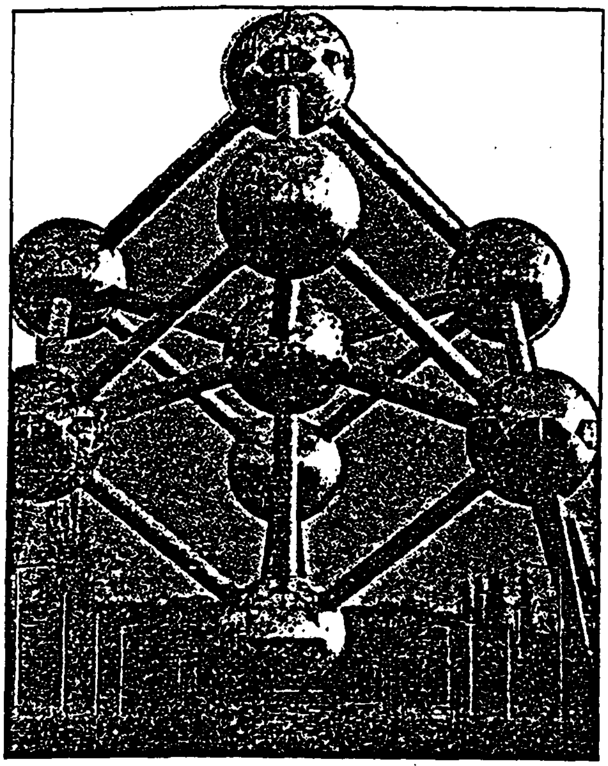
- Anhídrido sulfuroso, SO_2.
- Partículas en suspensión.
- Oxidos de nitrógeno, NOx.
- Ozono, O_3.
- Plomo, Pb.
- Monóxido de carbono, CO.
- Anhídrido carbónico, CO_2.
- Asbestos.
- Hidrocarburos reactivos.

A pesar de lo cual, generalmente se opera con menos parámetros, siendo los más utilizados: SO_2, NOx, CO, CO_2 y partículas sólidas.

A continuación, aunque de una manera sucinta, no podemos dejar de describir los efectos negativos de tales compuestos sobre el medio ambiente, con objeto de poner de manifiesto la necesidad de la limitación de su emisión (debe señalarse que, actualmente, tienen limitada su emisión: SO_2, NOx y partículas, aunque no se descarta que en un futuro no muy lejano pueda limitarse también la emisión de óxidos de carbono).

— **Partículas sólidas:** pueden ser partículas de metales, carbón, alquitrán, cenizas, óxidos, etc. Su presencia en exceso en el aire puede incidir localmente reduciendo la temperatura, ya que reducen la radiación solar sobre la Tierra, incrementando la reflexión de la misma. Adicionalmente, pueden producir procesos de catálisis sobre la superficie y dar lugar a reacciones tóxicas. En general son más dañinas las partículas más pequeñas, por su mayor poder de reacción y penetración dentro de los organismos.

— **Anhídrido sulfuroso SO_2:** en combinación con la humedad ambiente, contribuye a la formación de las tristemente



famosas lluvias ácidas, entendiéndose por "lluvia ácida" un conjunto de procesos que tienen en común producir un mismo resultado: la acidificación del agua de lluvia y, con ella, la acidificación de los lagos y bosques. Este efecto, a medio o largo plazo, degrada y anula la vida vegetal y piscícola continental, con el consiguiente riesgo para el resto de la vida sobre el planeta. La emisión de SO_2 por las centrales térmicas que queman combustible sólido es inversamente proporcional a la calidad del combustible.

— **Oxidos de nitrógeno, NOx:** sus efectos fundamentales se deducen de su participación en los fenómenos atmosféricos de formación del denominado "smog fotoquímico". Reaccionan con la humedad ambiental, con el ozono como catalizador, produciendo ácido nítrico, el cual, junto con el ácido sulfúrico mencionado anteriormente, contribuye a la formación de lluvias ácidas con efectos negativos a medio plazo. A más largo plazo, parece que pueden tener un carácter mutante sobre las bacterias nitrogenadas, prolongándose su efecto a toda la cadena alimentaria.

— **Monóxido de carbono, CO:** su exceso en la atmósfera puede producir efectos mortales sobre el hombre, ya que el monóxido forma con la hemoglobina un complejo muy estable (carboxihemoglobina) que impide el transporte de oxígeno de ésta a las células.

— **Anhidrido carbónico, CO_2:** absorbe parte de la radiación infrarroja que refleja la superficie de la tierra hacia el exterior, calentando la atmósfera, mares y tierras. Este aumento de temperatura del agua hace que el CO_2 disuelto pase parcialmente a la atmósfera y que aumente la cantidad de vapor de agua en la misma, que también absorbe radiación infrarroja, aumentando el efecto de calentamiento o "invernadero". Esto puede originar una disminución de los hielos polares y, consecuentemente, un aumento del nivel de los océanos.

LIMITES DE SO_2

Bajo estas premisas, se ha editado la Directiva del Consejo sobre limitación de emisiones a la atmósfera que, en concreto para las instalaciones existentes en España antes del 1 de julio de 1987, establece los siguientes porcentajes de reducción sobre emisiones de 1980 en tres fases para SO_2:

— 1993: 0 %.
— 1998: − 24 %.
— 2003: − 37 %.

mientras que para las nuevas instalaciones, se establecen unos valores límite de emisión de la siguiente forma:

Combustibles sólidos:

$50 \leq W < 100$ MW: La Comisión lo decidirá en 1990.
$100 \leq W < 500$ MW: $[SO_2] \leq 2400\text{-}4W$ mg SO_2/Nm^3.
$W \geq 500$ MW: $[SO_2] \leq 400$ mg SO_2/Nm^3.

Combustibles líquidos:

$50 \leq W < 300$ MW: $[SO_2] \leq 1700$ mg SO_2/Nm^3.
$300 \leq W < 500$ MW: $[SO_2] \leq 3650\text{-}6{,}5$ W mg SO_2/Nm^3.

donde W es la potencia térmica generada en MW.

Asimismo, se establece que las nuevas instalaciones que quemen combustibles sólidos nacionales podrán superar los valores límite de emisión fijados anteriormente cuando no puedan respetarse las emisiones de dióxido de azufre sin recurrir a una tecnología excesivamente costosa, debido a las características especiales del combustible. Esto sólo será admisible cuando se alcance los índices de desulfuración establecidos, y que son los siguientes:

$100 \leq W < 170$ MW th: índice de desulfuración ≥ 40 %.
$170 \leq W < 500$ MW th: índice de desulfuración $\geq 0{,}15$ W + 15 %.
$W \geq 500$ MW th: índice de desulfuración ≥ 90 %.

No obstante, todo lo anterior se particulariza el caso de España, permitiéndosele la autorización, hasta el 31 de diciembre de 1999, de nuevas centrales eléctricas de una potencia térmica nominal igual o superior a 500 MW que utilicen combustibles sólidos nacionales o de importación y que entrando en operación antes de final del año 2005, cumplan los siguientes requisitos:

— Combustible sólido de importación:
$[SO_2] \leq 800$ mg/Nm³.
— Combustible sólido nacional:
Indice de desulfuración ≥ 60 %.

siempre y cuando la capacidad total autorizada no supere los 2.000 MW para instalaciones que utilicen combustibles sólidos nacionales ni los 7.500 MW para instalaciones que utilicen combustibles sólidos de importación.

LIMITES DE NOx

Análogamente al caso del SO_2, para las emisiones de NOx procedentes de centrales españolas existentes el 1 de julio de 1987, se establecen dos plazos:

— 1993: + 1 %.
— 1998: − 24 %.

mientras que los valores límite de emisión de NOx para las nuevas instalaciones son:

— Combustible sólido en general: $[NOx] \leq 650$ mg/Nm³.
— Combustible sólido con menos del 10 % volátil: $[NOx] \leq 1300$ mg/Nm³.
— Combustible líquido: $[NOx] \leq 450$ mg/Nm³.
— Combustible gaseoso: $[NOx] \leq 350$ mg/Nm³.

LIMITES EN CENIZAS

Los valores límite de emisión de cenizas para nuevas instalaciones son:

- Combustible sólido: W $\geq$ 500 MW th: [ceniza] $\leq$ 50 mg/Nm^3 W $<$ 500 MW th: [ceniza] $\leq$ 100 mg/Nm^3.
- Combustible líquido: [ceniza] $\leq$ 50 mg/Nm^3.
- Combustible gaseoso: [ceniza] $\leq$ 5 mg/Nm^3.

MEDIDA DE CONTAMINANTES

Adicionalmente a la normativa europea descrita anteriormente, de obligado cumplimiento para España, existe en nuestro país una reglamentación relativa a la medida de contaminantes emitidos por las centrales térmicas (decreto del 25 de junio de 1984) y a la frecuencia y modo de presentación a la Administración de los informes que recogen las emisiones de las centrales térmicas (resolución del 17 de abril de 1986 de la Dirección General de la Energía).

Esta última resolución exige que, durante los diez primeros días del mes siguiente al período que se informa, se remita a la Dirección General de la Energía la siguiente información mensual:

- Tabla 1: Concentraciones medias diarias de emisión por chimenea de SO_2, NOx y partículas (en mg/m^{3}N) normalizadas a un contenido en oxígeno predeterminado, en base seca.
- Tabla 2: Valores de concentraciones mediohorarias de cada mes, normalizadas al contenido en oxígeno predeterminado, agrupados por frecuencias absolutas en intervalos de tamaño t (el tamaño se determina el primer mes de funcionamiento).
- Tabla 3: Energía en barras de salida de central, cantidades totales de SO_2, NOx y partículas emitidas diariamente y por KWh producido, calculados en función de las emisiones medidas.
- Listado: Listado ordenado de los valores de concentraciones promedio mediohorarios, de los cuales deberán envairse los n valores mediohorarios más altos, siendo n igual al 10 % del número de períodos informados (Fig. 1).

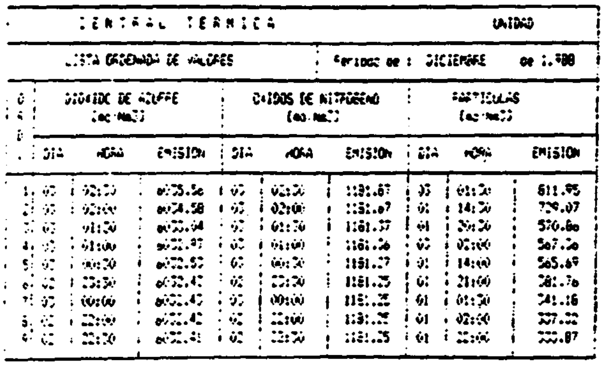


Fig. 1.—Listado ordenado de los N valores mediohorarios más altos.

En principio, la normativa comentada anteriormente, se refiere a emisiones reales, por lo que las centrales deberían disponer, preferentemente en las chimeneas, de equipos de medida de las emisiones de SO_2, NOx y partículas; pero dado que esto no es siempre posible en las unidades actuales en operación, pueden obtenerse unos valores bastante aproximados a partir de un balance estequiométrico que considere la composición real del combustible y otros parámetros, medidos en tiempo real, tales como potencia generada, opacidad o extinción, exceso de oxígeno en economizador, cantidad de combustible consumido, temperatura de humos en chimenea, etc.

Resulta evidente que no puede manejarse tal cantidad de información sin disponer de una unidad de procesamiento de datos, es decir, un ordenador dedicado a esta tarea. Para ello, la solución más sencilla y completa consiste en instalar una aplicación de adquisición de datos, tratamiento de los mismos y emisión de partes mensuales en un ordenador personal. Dicha aplicación puede ser tan versátil y completa como se desee, aunque una instalación tipo constaría de los siguientes elementos:

- Un ordenador personal con disco duro de 20 Mb.
- Un monitor monócromo o en color.
- Una impresora de 80 columnas.
- Una o varias tarjetas de adquisición de datos en tiempo real.
- Una tarjeta gráfica.
- Toda la instrumentación necesaria, convenientemente cableada al ordenador.

Se han desarrollado diferentes tipos de programas de control de emisiones por chimenea, pasando seguidamente a describir el programa EMISION-DT de EPTISA-GHESA-TRSA, EMPRESARIOS AGRUPADOS, S. A. y sus aplicaciones en centrales térmicas de fuel-oil.

Este programa en concreto está concebido de modo que sea fácilmente utilizable por el usuario, aun cuando éste no esté muy familiarizado con el uso de ordenadores siendo el propio programa el que lleva el control de la aplicación y guía al usuario hasta el fin deseado a través de diversos menús suficientemente autoexplicativos. Todos los datos introducidos manualmente desde teclado, así como los generados por el propio programa, se almacenan en ficheros secuenciales, de modo que siempre se puede acceder a ellos, ya sea a través de los menús o a través de los informes y gráficos generados debiéndose inicialmente introducir la configuración de la Central, para lo que se utilizan los cuadros de configuración que se describen a continuación:

I. Configuración del Proyecto. En principio, todos los datos que componen este cuadro serán constantes durante toda la vida de la Central, a excepción del número de unidades en funcionamiento en el caso de Centrales con más de un Grupo. Estos datos son: Nombre de la Central, diámetro de la chimenea y del punto de medida de extinción/opacidad, oxígeno de referencia para normalización, potencia nominal, potencia mínima, etc.

II. Configuración de las tarjetas de adquisición de datos, que recogerán las variables recibidas en tiempo real y los valores máximo y mínimo de tales variables. Se incluye un campo adicional de opción gráfica.

III. Configuración de los valores calculados por el programa. En este cuadro se incluyen todos los parámetros de interés calculados por la aplicación, debiéndose completar con los fondos de escala esperados para representación gráfica.

IV. Configuración del trigger temporal. Tiene como objeto determinar a partir de qué momento se desea que comience automáticamente la adquisición de datos en tiempo real.

V. Configuración del combustible. Se introducirá el análisis elemental del combustible utilizado.

VI. Configuración de las regresiones matemáticas. Dado que muchos parámetros sólo pueden determinarse a partir de otros parámetros por regresión matemática, se incluirán en este cuadro los valores constantes de tales regresiones.

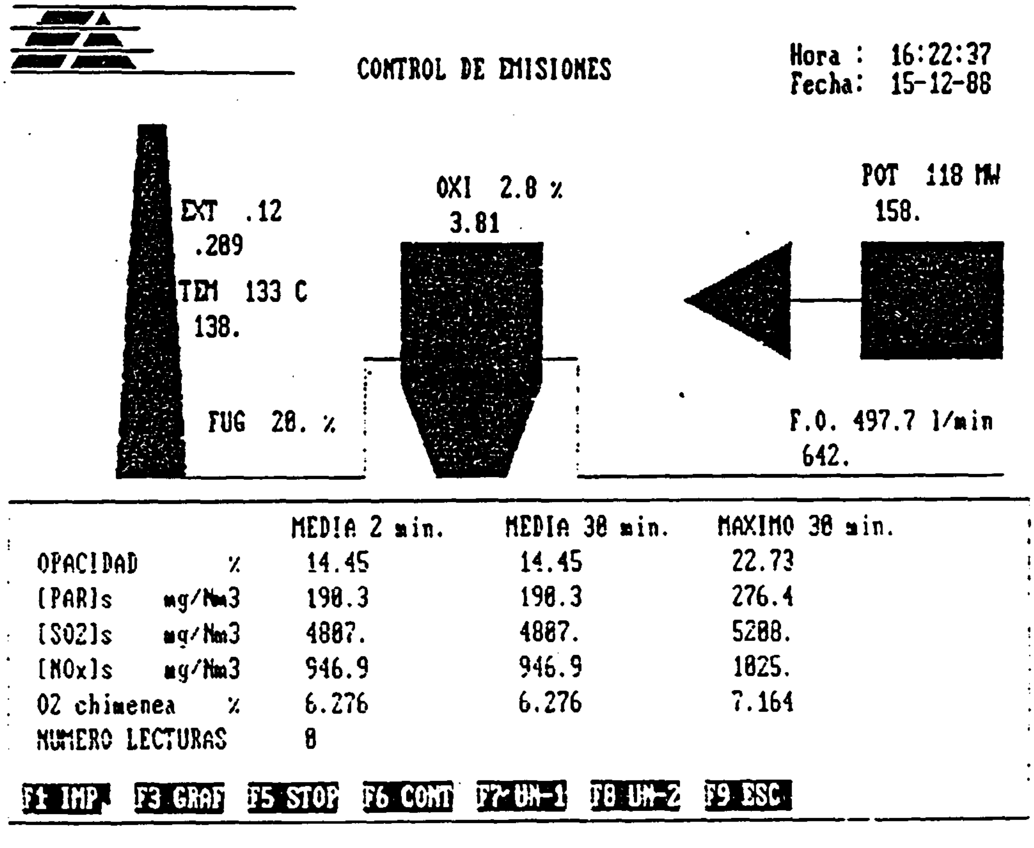
Una vez completada la configuración de la Central, se pasará a la función de ejecución, la cual realiza simultáneamente las siguientes tareas:

- Adquisición de datos en tiempo real de las señales.
- Seguimiento en tiempo real de las señales anteriores indicando los estados de "calibración" o "avería" cuando éstos se produzcan.
- Representación gráfica en tiempo real de los parámetros previamente seleccionados en el cuadro de configuración de las tarjetas.
- Seguimiento puntual (cada dos minutos) de todas las variables calculadas.

Cada media hora, el programa realiza las medias de todos los valores puntuales medidos y calculados y las graba en un fichero diario de tipo secuecial. Estos ficheros son la base para la obtención de todos los informes mensuales requeridos por la Administración y que se han descrito previamente. Adicionalmente el programa posee otras utilidades que los convierten en una herramienta muy versátil para el control de las emisiones, como pueden ser las siguientes:

- Sinóptico en diferido de la instalación. Utiliza como base los ficheros diarios con medias semihorarias grabados durante la fase de ejecución. Con esta opción, puede "recrearse" la evolución de las emisiones (Fig. 2).
- Representación gráfica en diferido, en todo similar al gráfico en tiemporeal, pero con valores medios semihorarios.
- Representación gráfica de un parámetro frente a otro parámetro en diferido. De gran utilidad para relacionar dos variables y establecer fórmulas de regresión (Fig. 3).
- Emisión de todos los partes mensuales requeridos por la Administración y grabación de los ficheros de listados ordenados decrecientes. Adicionalmente, generación de informes diarios y anuales.
- Conversión de los ficheros generados por la aplicación en ficheros utilizables por otras aplicaciones, tales como hojas de cálculo electrónicas.
- En caso de disponer de estaciones de vigilancia ambiental, el programa puede generar el mapa geográfico del emplazamiento con los niveles de inmisión de diversos contaminantes (Fig. 4).

En resumen, podríamos decir que es de vital importancia el control de las emisiones procedentes de centrales térmicas a la atmósfera y, por tanto, la Directiva de Consejo de 24 de noviembre de 1988, recientemente publicada, es un paso más hacia la protección del medio ambiente, y consecuentemente las centrales térmicas deben realizar un importante esfuerzo de adaptación. Hemos visto también que éstas últimas tienen a su alcance la capacidad de cuantificar sus emisiones y disponen de plazas aparentemente suficientes para reducirlas.



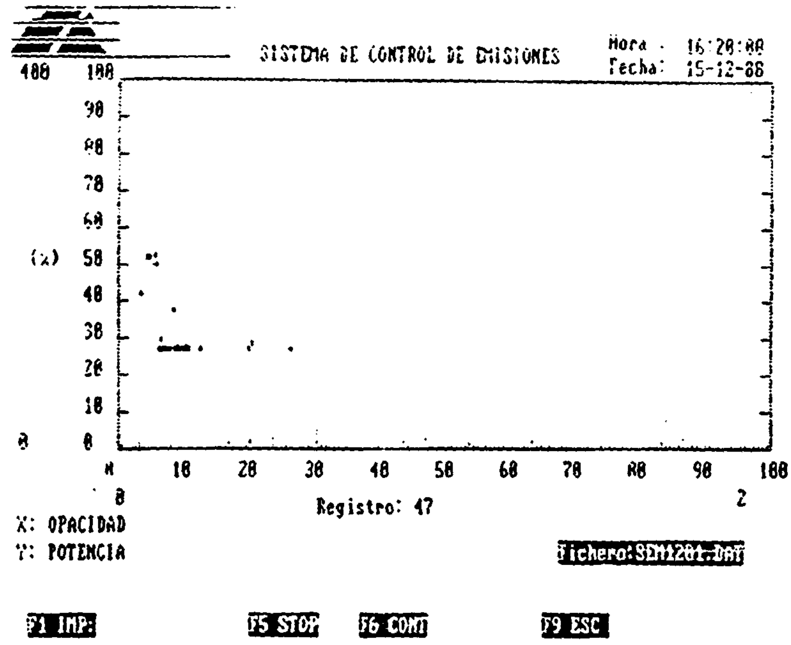
```
                    CONTROL DE EMISIONES          Hora :  16:22:37
                                                  Fecha:  15-12-88

     EXT  .12              OXI  2.0 %              POT  118 MW
      .209                  3.01                    150.
     TEM  133 C
      138.

      FUG  20. %                                   F.O. 497.7 l/min
                                                    642.

                     MEDIA 2 min.   MEDIA 30 min.   MAXIMO 30 min.
 OPACIDAD         %   14.45          14.45           22.73
 [PAR]s      mg/Nm3   190.3          190.3           276.4
 [SO2]s      mg/Nm3   4807.          4807.           5208.
 [NOx]s      mg/Nm3   946.9          946.9           1025.
 O2 chimenea      %   6.276          6.276           7.164
 NUMERO LECTURAS      0
```

Fig. 2.—Sinóptico en diferido.


SISTEMA DE CONTROL DE EMISIONES

Hora : 16:28:00
Fecha: 15-12-88

Registro: 47

X: OPACIDAD
Y: POTENCIA

Fichero:SDM1201.DAT

Fig. 3.—Representación gráfica de un parámetro frente a otro (en diferido).

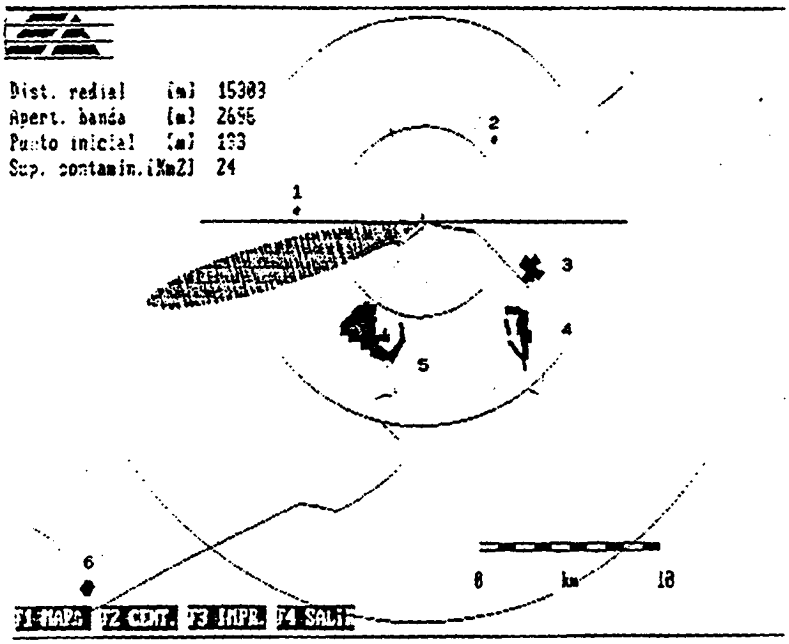

Dist. radial [m] 15303
Apert. banda [m] 2655
Punto inicial [m] 193
Sup. contamin.[Km2] 24

Fig. 4.—Representación geográfica de la inmisión de un

OGRAFIA

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ste y calibrado de los equipos de medida, control, registro y
smisión de datos relativos a la emisión de contaminantes a la
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Instituto de Estudios de la Energía

Curso sobre :

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Tema : 31 y 32

"Deposición seca y húmeda. Transformaciones químicas en la atmósfera"

Manuel de Castro.

LA GENERACION DE ENERGIA ELECTRICA Y EL MEDIO AMBIENTE

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"Deposición seca y húmeda. Transformaciones químicas en la atmósfera"

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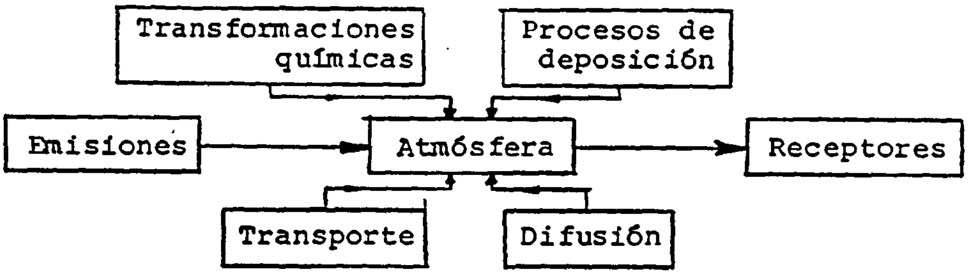
DEPOSICION SECA Y HUMEDA. TRANSFORMACIONES QUIMICAS



I.- Transformaciones químicas en la atmósfera

Las reacciones químicas en la atmósfera son responsables de la generación de contaminantes secundarios (ozono, sulfatos, etc.), que a veces son más perjudiciales para el medio ambiente que los emitidos directamente desde las fuentes (smog fotoquímico, lluvias ácidas). Las reacciones químicas pueden clasificarse en dos grandes grupos:

a) Termoquímicas, por las que las especies de caracter reductor se oxidan, dando lugar a productos termodinámicamente más estables.

b) Fotoquímicas, por las que se generan ciertas sustancias óxidas, termodinámicamente menos estables que sus precursoras, por medio de un aporte adiccional de energía procedente del Sol.

En los procesos de combustión los contaminantes gaseosos generados en mayor cantidad son los SO_x y los NO_x (exceptuando el CO_2).

I.1.- Química atmosférica de los SO_x.

A pesar de los grandes esfuerzos dedicados, el conocimiento de la química de los SO_x en la atmósfera es aún incompleto. No obstante, existen claras evidencias de que la mayoría del SO_2 en la atmósfera se oxida, formando ácido sulfúrico y sulfatos ácidos, los cuales dan lugar al aumento en la acidez de la precipitación. La concentración de sulfatos a sotavento de las fuentes de SO_2 depende del ritmo al que éste se oxida, produciendo SO_4H_2. La velocidad de oxidación es muy variable, dependiendo de las condiciones atmosféricas, ya que ésta puede producirse por varios procesos, incluyendo reacciones homogéneas con otros gases atmosféricos, reacciones heterogéneas sobre hidrometeoros o sobre otras partículas.

I.1.1.- Oxidación homogénea

El mecanismo que más contribuye a la oxidación homogénea del SO_2 es:

$$\begin{aligned}
HONO + h\nu\ (\lambda < 400\ nm) &\longrightarrow OH\cdot + NO \\
O_3 + h\nu\ (\lambda < 319\ nm) &\longrightarrow O_2 + O\cdot \\
O\cdot + H_2O &\longrightarrow 2\ OH\cdot \\
OH\cdot + SO_2 &\longrightarrow HOSO_2\cdot \\
HOSO_2\cdot + O_2 &\longrightarrow HO_2\cdot + SO_3 \\
HO_2\cdot + NO &\longrightarrow NO_2 + OH\cdot \\
SO_3 + H_2O &\longrightarrow SO_4H_2
\end{aligned}$$

Suponiendo una atmósfera urbana $[OH\cdot] \simeq 10^7 mol\cdot cm^{-3}$, el ritmo de oxidación del SO_2 será aproximadamente 4%/hr, o bien 96%/24hr. En una atmósfera rural $[OH\cdot] \simeq 1.5\cdot 10^6 mol\cdot cm^{-3}$, el ritmo de oxidación sería alrededor de 0.6%/hr, o bien 14.4%/24hr. Durante el verano la concentración de $[OH\cdot]$ es mayor que durante el invierno.

I.1.2.- Oxidación heterogénea sobre hidrometeoros

Cuando el SO_2 se encuentra en un medio acuoso, se produce de forma muy rápida (<1 seg.) el siguiente mecanismo:

$$\begin{aligned}
SO_2(gas) + H_2O(liquido) &\longrightarrow SO_2\cdot H_2O\ \text{(disuelto en agua)} \\
SO_2\cdot H_2O &\longrightarrow SO_3H^- + H^+ \\
SO_3H^- &\longrightarrow SO_3^=
\end{aligned}$$

Una vez producido el ion sulfito S(IV) hay dos mecanismos de oxidación a ion sulfato S(VI):

a) Por el oxígeno disuelto en el hidrometeoro con la presencia de catalizadores (Mn, Fe, etc)

b) Por otros oxidantes atmosféricos (H_2O_2, O_3, etc)

La importancia de uno u otro mecanismo depende, además de la concentración de los reactivos o catalizadores, del pH de la solución acuosa (ver figura 1), de la temperatura y, por supuesto, de la cantidad de agua presente en la nube. A una temperatura de 298 K y un contenido de agua de 1 gr/m^3, la velocidad de oxidación de S(IV) a S(VI) varía desde el 100%/hr en presencia de H_2O_2 a menos del 1%/hr en presencia de Mn ó Fe con $pH<4.5$.

I.1.3.- Oxidación heterogénea sobre partículas

La importancia relativa de la oxidación del SO_2 sobre la superficie de determinadas partículas, como cenizas de carbón, óxidos metálicos o sales metálicas, no está aún hoy día bien determinada. En estos casos la humedad del aire es muy importante. No obstante, parece que en condiciones de humedad relativa menor del 70% este mecanismo no es muy influyente

I.2.- Química atmosférica de los NO_x

En los procesos de combustión de carburantes fósiles se generan NO_x, la mayor parte de los cuales en forma de NO (90%) y el resto en forma de NO_2. La transformación química de estos dos compuestos en la atmósfera puede producirse por vía fotoquímica o termoquímica (ver figura 2).

I.2.1.- Fotoquímica de los NO_x

El mecanismo básico es:

$$NO_2 + h\nu\,(\lambda < 390\ \mathrm{nm}) \longrightarrow NO + O$$
$$O + O_2 \longrightarrow O_3$$
$$NO + O_3 \longrightarrow NO_2 + O_2$$

En presencia de hidrocarburos reactivos se generan radicales libres orgánicos e inorgánicos, los cuales producen una oxidación adiccional de NO a NO_2, dando lugar a una acumulación de ozono y a la producción de nitratos de peroxiacetilo (PAN), que son dos contaminantes característicos del "smog fotoquímico". En este proceso se producen asimismo NO_3H y nitratos. Mediante este mecanismo, la velocidad de conversión química de los NO_x puede llegar a ser del orden del 50%/hr o superior. No obstante, para que esto se produzca han de cumplirse dos requisitos: radiación solar suficiente y una proporción inicial NO_x/HC idónea, la cual no suele registrarse en penachos procedentes de combustiones industriales, a no ser que éstos pasen por atmósferas ricas en HC's como son las urbanas.

I.2.2.- Reacciones en medio acuoso

Al igual que ocurre con el SO_2, los NO_x en medio acuoso dan lugar a ion nitrito N(III), el cual se oxida a ion nitrato N(V). Sin embargo, el mecanismo químico es diferente, dependiendo de la concentración de NO_x, del pH y de la cantidad de agua presentes (ver figuras 3, 4 y 5). No obstante, estas reacciones productoras de N(III y N(V) no tienen demasiada importancia en el mecanismo de transformación química de los NO_x. Por contra, el NO_3H generado fotoquímicament es una sustancia que se incorpora con gran rapidez y eficiencia a los hidrometeoros, provocando una disminución en el pH de la precipitació

II.- Procesos de deposición

Los contaminantes atmosféricos son finalmente eliminados de la atmósfera por uno de los dos mecanismos siguientes (o por ambos al tiempo):

- Deposición seca: captura por el suelo, el agua o la vegetación de la superficie terrestre
- Deposición húmeda: absorción por hidrometeoros y posterior precipitación. Para referirse a este tipo de deposición se suelen utilizar otros términos: rainout (captación dentro de la nube) o washout (captación por bajo de la nube).

Estos procesos limitan el tiempo de residencia en el aire de los contaminantes, contrlan la distancia a la que son transportados y en definitiva determinan las concentraciones que éstos alcanzan. Es difícil determinar de forma global la importancia relativa de ambos procesos, aunque parece que la deposición seca contribuye algo más que la húmeda (60/40) en la eliminación de contaminantes, aunque es claro que la mayor o menor frecuencia de precipitación en una zona determinada es un factor decisivo.

II.1.- Deposición seca.

Exceptuándo las partículas mayores de 5-10 μm, el resto de ellas y, por supuesto, los gases se depositan en el suelo por efecto de la difusión turbulenta especialmente. El posterior impacto, la absorción química y otros procesos varios hacen que las sustancias sean retenidas.

A pesar del gran número de experiencias realizadas, los valor de deposición seca de gases y partículas pequeñas no son de validez general, pues incluso en superficies del mismo tipo los resultados discrepan considerablemente.

El flujo vertical descendente de una especie se representa por el producto de un parámetro empírico llamado velocidad de deposición V_d y la concentración que ésta alcanza en el aire a una altura z ($\chi(z)$)

$$F_d = V_d \cdot \chi(z)$$

El proceso de deposición seca puede ser contemplado conceptualmente como una analogía con el flujo de calor o electricidad a través de una serie de resistencias (ley de Omh), de forma que para los gases

$$V_d = (r_a + r_s + r_t)^{-1}$$

siendo r_a la resistencia aerodinámica que tiene en cuenta la difusión turbulenta del material hacia la proximidad inmediata al suelo (subcapa laminar), luego depende de los parametros meteorológicos habituales

r_s la resistencia dentro de la subcapa laminar que representa el transporte a través de dicha subcapa

r_t la resistencia de transformación que depende de la interacción fisico-química entre el material y la superficie

Para las partículas, $r_t=0$ pues se considera que si chocan con la superficie allí permanecen. También en este caso es preciso tener en cuenta la velocidad de caída (V_s) en caso de que ésta sea apreciable, de forma que:

$$V_d = (r_a + r_s + r_a \cdot r_s \cdot V_s)^{-1} + V_s$$

Para estimar la velocidad de deposición seca se utilizan tres métodos: modelos de caja, análisis de perfiles y medidas de correlación turbulenta. Los resultados con respecto a diferentes sustancias gaseosas pueden observarse en la figura 6. Para el caso de partículas, en la figura 7 se comprueba que las partículas mayores de 10µm se depositan por efectos gravitatorios, mientras que las menores de 0.1µm se comportan como gases prácticamente. Las de deposición menor son las comprendidas entre 0.1 y 1µm.

Cpmo puede suponerse, son muchos los factores que influyen en los procesos de deposición seca de gases, como efectos estacionales, diarios (luz solar, estabilidad atmosférica) y meteorológicos (temperatura, humedad, viento, etc). Además hay varios mecanismos de transferencia hacia el interior de las hojas: a través de su epidermis (resistencia cuticular), a través de los poros (resistencia de estomas), etc. La tabla I sugiere algunos valores de velocidades de deposición promedio para utilizar en modelos de transporte y difusión.

II.2.- Deposición húmeda.

El tratamiento teórico se suele dividir en "rain-out" (sorción dentro de la nube) y "wash-out" (sorción por bajo de la nube), aunque en aplicaciones prácticas los dos procesos se agrupan, ya que se pueden evaluar de forma similar. Asimismo, hay dos formas de abordar el problema: coeficiente de sorción (scavenging coefficient) y coeficiente de lavado (wash-out ratio).

II.2.1.- Coeficiente de sorción

El flujo de contaminantes hacia el suelo debido a la deposición húmeda puede expresarse como:

$$F_W = \int_0^H \Lambda(z,t) \cdot \chi(z,t) \cdot dz$$

siendo Λ un coeficiente de sorción o arrastre, χ la concentración de contaminante y H la capa atmosférica donde se produce tal sorción o arrastre por hidrometeoros. Por analogía con la deposición seca se puede definir una velocidad de deposición húmeda:

$$V_W = \frac{F_W}{\chi(0,t)}$$

de forma que si se supone que los contaminantes estan distribuidos de forma uniforme en toda la capa, entonces:

$$V_W \simeq \int_0^H \Lambda(z,t) \cdot dz = \bar{\Lambda} \cdot H$$

El problema surge en la evaluación de Λ. En el caso de partículas, pareca lógico que Λ dependa del tamaño de éstas, del de los hidrometeoros y de un coeficiente de colisión entre ambos:

$$\Lambda(D_p) = \int_0^\infty \frac{\pi}{4} \cdot (D_p + \tilde{D}_p)^2 \cdot (V_t(\tilde{D}_p) - v_t(D_p)) \cdot E(D_p, \tilde{D}_p) \cdot N(\tilde{D}_p) \cdot d\tilde{D}_p$$

siendo D_p y $\tilde{D}_p$ los tamaños de las partículas e hidrometeoros, respectivamente; v_t y V_t las velocidades de caída de las partículas y de los hidrometeoros respectivamente; $N(\tilde{D}_p)$ la distribución de tamaños de los hidrometeoros; y $E(D_p,\tilde{D}_p)$ la eficiencia de colisión.

Suponiendo que $V_t(\tilde{D}_p) \gg v_t(D_p)$ y que $(D_p+\tilde{D}_p)^2 \simeq \tilde{D}_p^2$, resulta:

$$\Lambda(D_p)=\int_0^\infty \frac{\pi}{4}\tilde{D}_p^2\cdot V_t(\tilde{D}_p)\cdot E(D_p,\tilde{D}_p)\cdot N(\tilde{D}_p)\cdot d\tilde{D}_p \quad ,$$

y teniendo en cuenta que:

$$p_o(\mathrm{mm/hr})=\int_0^\infty \frac{\pi}{6}\tilde{D}_p^3\cdot V_t(\tilde{D}_p)\cdot N(\tilde{D}_p)\cdot d\tilde{D}_p$$

puede suponerse que:

$$\frac{\Lambda_3}{p_o}\equiv E$$

Ahora bien, el problema se complica porque la eficiencia de colisión $E(D_p,\tilde{D}p)$ depende tambien de la distribución de tamaño de las partículas contaminantes. En las figuras 8 y 8bis se puede observar el valor de Λ_3(coeficiente de sorción volumétrico) normalizado con p_o, en función de $\bar{D}_g$ para varias desviaciones geométricas típicas, correspondientes a dos tamaños de hidrometeoros.

En el caso de gases, el problema es aún más complicado, pues al contrario del de las partículas aquí no puede suponerse que la captura de una molécula gaseosa es un proceso irreversible, salvo en casos muy particulares de composición química tanto del hidrometeoro como del contaminante. El flujo de una especie gaseosa hacia un hidrometeoro es proporcional al llamado coeficiente de transferencia másica entre el contaminante y los elementos químicos presentes en los hidrometeoros (K_c en cm/s), e inversamente proporcional a la velocidad de caída y tamaño de estos últimos. Así:

$$\chi(ac)=\frac{6\ K_c}{\tilde{D}_p V_t}\chi z$$

Observando la figura 9 se comprueba que cuanto menor es el tamaño del hidrometeoro, más efectiva es la sorción de los contaminantes gaseosos. Por ejemplo, para el caso del NO_3H: Λ(rainout)$\simeq 0.2\ s^{-1}$ y Λ(washout)$\simeq 2\cdot 10^{-4} s^{-1}$, en igualdad de contenido total de agua.

II.2.2.- Coeficiente de lavado

Otro método de cálculo de la deposición húmeda es utilizando el llamado coeficiente de lavado (washout ratio), que se define:

$$W_r = \frac{K_o}{\chi_o}$$

siendo K_o y χ_o la concentración de contaminante contenido en la precipitación y en el aire junto al suelo, expresadas normalmente en unidades masa/volumen. DE esta forma, el flujo de contaminante hacia el suelo debido a la precipitación será:

$$F_w = K_o \cdot p_0 = \chi_o \cdot W_r \cdot p_o$$

Y como por otra parte:

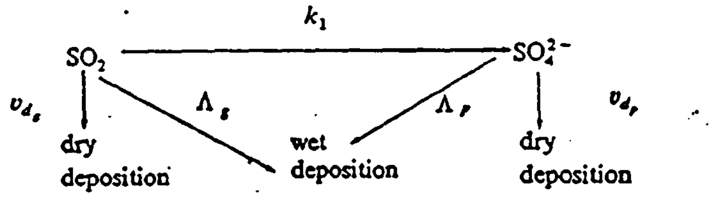
$$V_W = F_W/\chi_o = W_r \cdot p_o \quad \text{y tambien} \quad V_w \simeq \bar{\Lambda} \cdot H$$

los coeficientes de sorción (Λ) y de lavado (Wr) pueden relacionarse:

$$\bar{\Lambda} \simeq \frac{W_r \cdot p_o}{H}$$

segun se ha comprobado experimentalmente, el coeficiente de lavado disminuye con la cantidad de precipitación (ver figura 10), lo que puede deberse a las razones anteriormente señaladas con respecto a la relación entre el tamaño de las gotas y la eficiencia de sorción, entre otras razones. La ventaja de este procedimiento radica en que es posible realizar medidas directas del coeficiente de lavado. La mayor parte de ellos tienen un valor incluido entre 10^{-3} y 10^{-5} para partículas y entre 10^{-4} y 10^{-6} para los gases. Esta gran variabilidad en el valor de W_r se da no solo a igualdad de especie contaminante, sino tambien a igualdad de intensidad de precipitación. Esto es lógico pensarlo pues el proceso de sorción y arrastre de contaminantes por los hidrometeoros es muy complejo, y sería ingenuo esperar que todas las variables meteorológicas que intervienen en él puedan parametrizarse por medio de una sola variable. No obstante, prescisamente porque W_r representa el promedio de muchas variables (por ejemplo, distribuciones de tamaño de partículas e hidrometeoros, distribuciones verticales, tipos de precipitación, etc.), este método parece más apropiado para estimaciones a largo plazo, de forma que la gran variabilidad de valores del coeficiente de lavado se compensen entre los diferentes casos a lo largo de ese intervalo de tiempo. Para predicciones a más corto plazo, parece más apropiado utilizar el método del coeficiente de sorción o arrastre (scavenging coefficient), siempre que se conozcan o se puedan estimar la distribución vertical de los contaminantes, distribución de tamaño de partículas, características de la precipitación, tipo de precipitación, etc., que ignorar estos datos y utilizar directamente el coeficiente de lavado.

III.- Aplicación al caso de modelos de penacho gaussiano para SO_2



III.1.- Reacciones químicas

Entre las simplificaciones que un modelo gaussiano incluye está la suposición de que:

$$\int_{-\infty}^{\infty}\!\!\int\!\!\int\!\!\int_{0}^{\infty} \chi(x,y,z,t)\ dx\ dy\ dz\ dt = \int_0^\infty M\cdot dt = Q$$

sin embargo los procesos químicos que se han expuesto anteriormente hacen que esta condición deba modificarse, de forma que:

$$\int_0^\infty M\cdot dt = Q - R$$

Así, si $R(\chi) \simeq K_R\cdot\chi$ entonces:

$$\chi(t) = \chi(0)\cdot e^{-(K_1\cdot t)}$$

En el caso de reacción $SO_2 \longrightarrow SO_4^{=}$ homogénea:

$$K_1 : 3\cdot 10^{-6} - 8\cdot 10^{-6}\ s^{-1} \ \text{(aire rural)}$$
$$K_1 : 2\cdot 10^{-5} - 3\cdot 10^{-5}\ s^{-1} \ \text{(aire urbano)}$$

En el caso de reacción heterogénea en medio acuoso:

$$K_1 : 8\cdot 10^{-5} - 2\cdot 10^{-4}\ s^{-1}$$

III.2.- Deposición seca

Hay varios procedimientos para incorporar el efecto de la deposición seca de gases y partículas menores de 5-10 micras a la expresión del modelo de penacho gaussiano:

a) "Source depletion":

$$\partial Q/\partial x = -\int_{-\infty}^{\infty} V_d \cdot \chi(x,y,0) \cdot dy = -\left(\frac{2}{\pi}\right)^{1/2} \cdot \frac{V_d \cdot Q}{\bar{u} \cdot \sigma_z} \exp\left(-\frac{h^2}{2\sigma_z^2}\right)$$

b) "Partial reflection":

$$\chi(x,y,z) = \frac{Q}{2\pi \sigma_y \sigma_z \bar{u}} \cdot \exp\left(-\frac{y^2}{2\sigma_y^2}\right)\left[\exp\left(-\frac{(z-h)^2}{2\sigma_z^2}\right) - \alpha(x) \exp\left(-\frac{(z+h)^2}{2\sigma_z^2}\right)\right]$$

donde $\alpha(x) = f(V_d, x)$

c) "Mass deposition":

$$\chi(t) = \chi(0) \cdot \exp(-V_d \cdot t / H_z) \quad \text{para } x > x_g$$

siendo H_z=extensión vertical del penacho gaussiano.

En el caso de gas (SO_2) : $V_{dg} \simeq 0.44$ cm/s

en el caso de partícula ($SO_4^=$) : $V_{dp} \simeq 0.26$ cm/s

Ver tabla II.

III.3.- Deposición húmeda (washout)

Se utiliza tambien el procedimiento "mass deposition":

$$\chi(t) = \chi(0) \exp(-\Lambda \cdot t)$$

en el caso de gas (SO_2) : $\Lambda_g \simeq 10^{-5} - 3 \cdot 10^{-5}\ s^{-1}$

en el caso de partícula ($SO_4^=$) : $\Lambda_p \simeq 10^{-4} - 3 \cdot 10^{-4}\ s^{-1}$

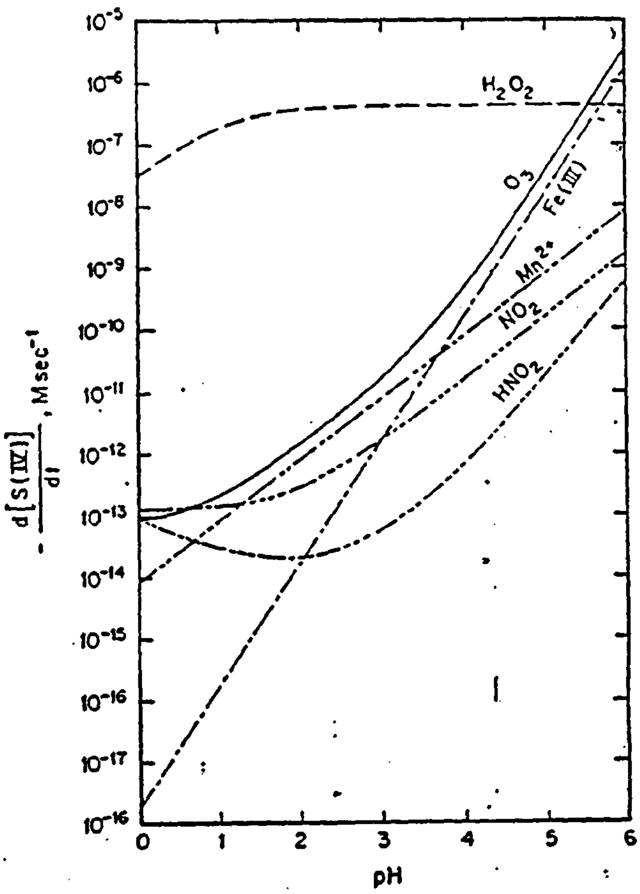


FIGURA 1

Comparison of aqueous-phase SO_2 oxidation paths. The rate of conversion of S(IV) to S(VI) as a function of pH. Conditions assumed are: $[SO_2(g)] = 5$ ppb; $[HNO_2(g)] = 2$ ppb; $[H_2O_2(g)] = 1$ ppb; $[NO_2(g)] = 1$ ppb; $[O_3(g)] = 50$ ppb; $[Fe^{3+}(aq)] = 3 \times 10^{-7}$ M; $[Mn^{2+}(aq)] = 3 \times 10^{-8}$ M.

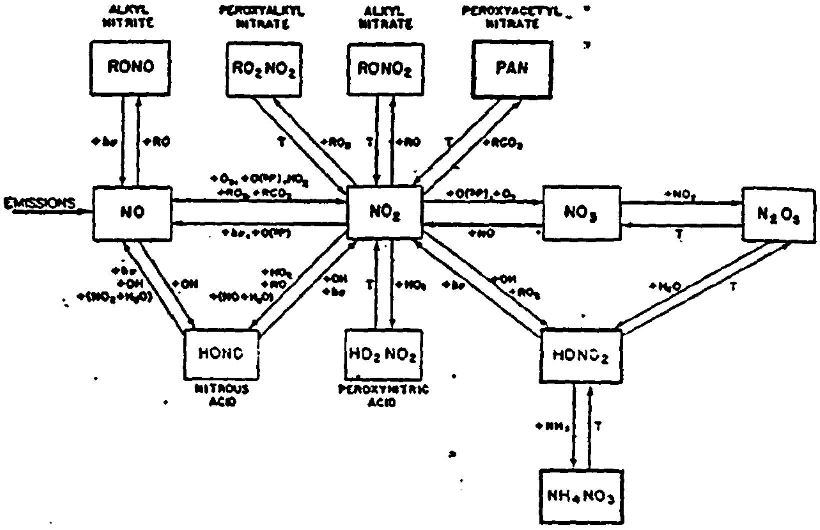


FIGURA 2

Atmospheric nitrogen chemistry (McRae and Russell, 1984).

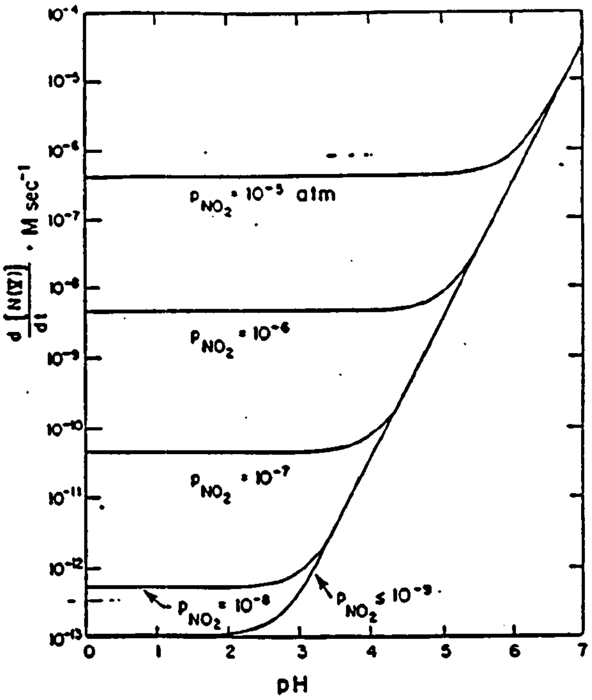


FIGURA 3

Rate of formation of N(V) as a function of pH and p_{NO_2}. For $p_{NO_2} >$ × 10^{-9} atm, along the horizontal portion of the curve the reaction $NO_2 + NO_2 \rightarrow$ N(III) + N(V) is the dominant mode of N(V) production. For $p_{NO_2} < 5 \times 10^{-9}$ a and low pH, H_2O_2 reaction is the dominant mode. The curved part of the line indica the transition between the NO_2–NO_2 reaction and the NO_2–O_3 reaction as th dominant N(V)-producing mechanism. The line at the high pH end represents the rat of formation of N(V) by the $NO_2^- + O_3$ reaction.

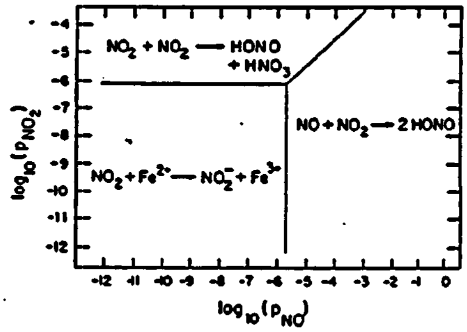


FIGURA 4

Regions of aqueous nitrogen reactions as a function of p_{NO_2} and p

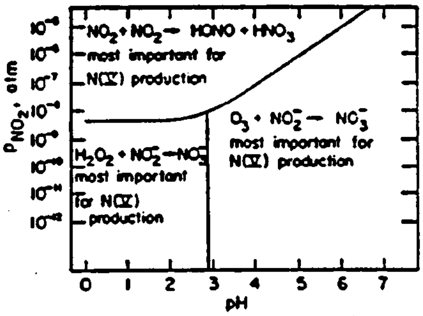


FIGURA 5

Reactions that contribut to N(V) production.

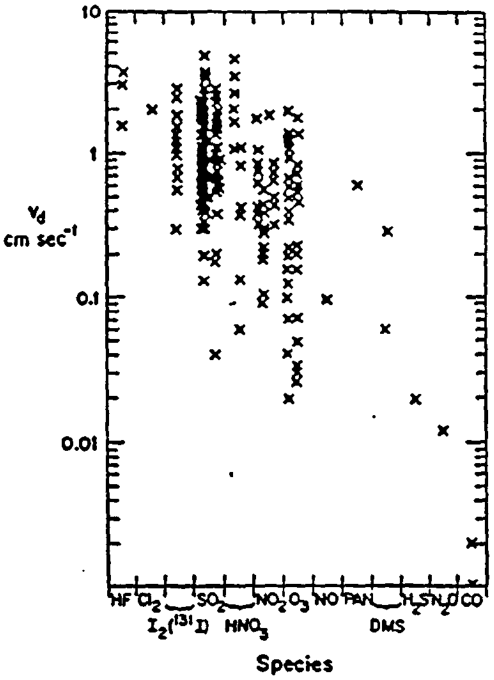


FIGURA 6

Experimental data on gas dry deposition velocities ranked approximately in order of reactivity (National Center for Atmospheric Research, 1982). DMS = dimethyl sulfide.

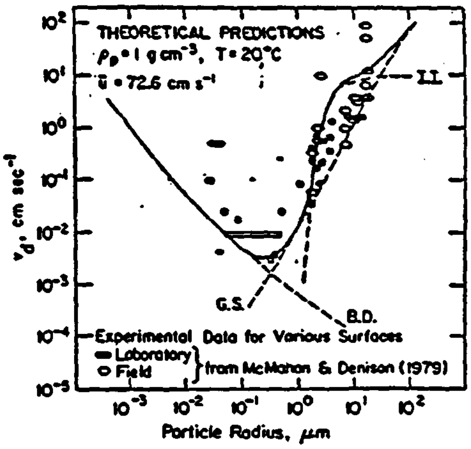


FIGURA 7

Experimental data on particle dry deposition velocities shown together with the solid curve representing the net deposition velocity as predicted by considering the mechanisms of Brownian diffusion (B.D.), gravitational settling (G.S.), and inertial impaction (I.I.) (National Center for Atmospheric Research, 1982).

TABLA I

SO_2 and Sulfate Average Deposition Velocities Used in Atmospheric Transport and Removal Calculations

Source	Material		v_d, cm sec^{-1}	
Henmi (1980)	SO_4^{2-}		0.4	
	SO_2		2.0	
Eliassen (1978)	SO_4^{2-}		0.2	
	SO_2		0.8	
Shannon (1981)	SO_4^{-2}, SO_2	summer	0.1	night
			0.9	noon
		winter	0.1	night
			0.6	noon

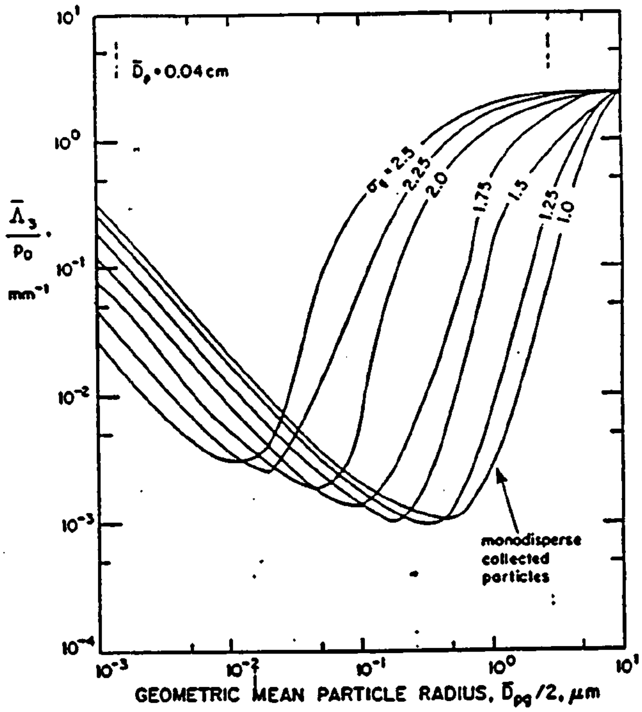


FIGURA 8

Mean scavenging coefficient for particle mass normalized by the rai rate as a function of the geometric mean particle radius, $\bar{D}_{pg}/2$, of the collect particles for various values of the geometric standard deviation σ_g of the collect particles. Collector particle diameter is $\bar{D}_p = 0.04$ cm.

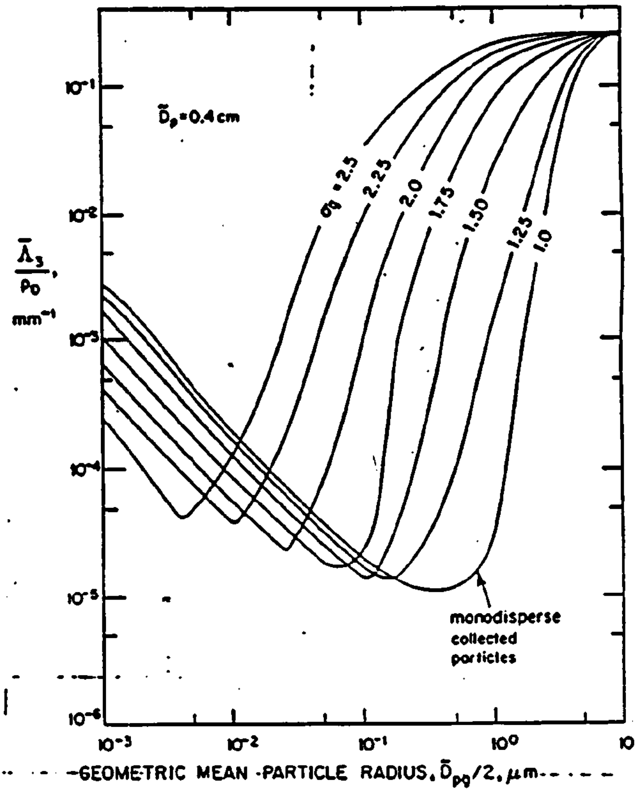


FIGURA 8 bis

Mean scavenging coefficient for particle mass normalized by the rainfal rate as a function of the geometric mean particle radius, $\bar{D}_{pg}/2$, of the colle particles for various values of the geometric standard deviation σ_g of the colle particles. Collector particle diameter is $\bar{D}_p = 0.4$ cm.

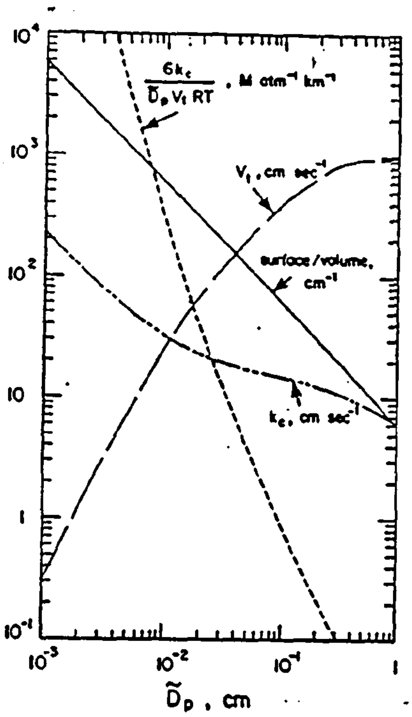


FIGURA 9

Mass transfer coefficient k_c, terminal fall velocity V_t, surface to volume ratio, and group $6k_c/\bar{D}_p V_t RT$ as a function of droplet diameter $\bar{D}_p$ (Levine and Schwartz, 1982).

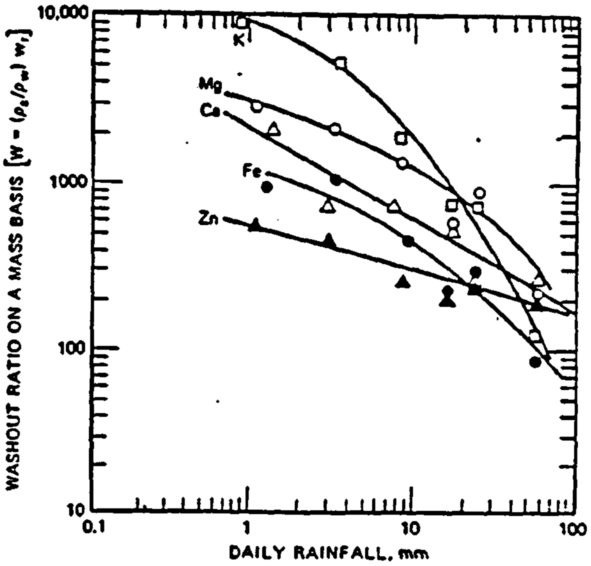


FIGURA 10

Variations of washout ratios with amount of daily precipitation. The washout ratio on a mass basis is about 3 orders of magnitude smaller than that on a volume basis (ρ_a = 1.23 × 10^{-3} g/cm³; ρ_w = 1.0 g/cm³). (Based on D. F. Gatz, Wet Deposition Estimates Using Scavenging Ratios, in *First Specialty Symposium on Atmospheric Contributions to the Chemistry of Lake Water,* ~~Sept. 28–Oct.~~ 1, 1975, pp. 2-29, International Association for Great Lakes Research, 1975.)

TABLA II

SO₂ Deposition Rates*

Surface	v_d, cm/sec	Comment
Short grass	0.5	0.1 m in height
Medium crop	0.7	1.0 m in height
Calcareous soil	0.8	Wet or dry
Acid soil	0.4	Dry
Acid soil	0.6	Wet
Dry snow	0.1	If wet, behaves like water
Water	0.7	
Countryside	0.8	
Cities	0.7	Based on London data only

*From T. A. McMahon and P. J. Denison, Empirical Atmospheric Deposition Parameters—A Survey, *Atmos. Environ.*, 13: 575 (1979); by permission of Pergamon Press, Ltd.

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Acid precipitation in historical perspective

Awareness of the acid rain problem has developed in many countries over more than a century

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Some years ago the terms "acid precipitation" and "acid rain" were bits of esoteric jargon used almost exclusively by scientists in certain specialized fields of ecology and atmospheric chemistry. Recently, these terms have become worrisome household words in many countries around the world. While they have inspired sensational and sometimes exaggerated headlines about "death from the sky," they also have prompted a more deliberate and careful examination of the role of humans in the biogeochemistry and chemical climatology of the earth. How did this transition come about? Who was responsible? Why did it take so long for acid precipitation to be recognized as an important environmental problem? What factors of scientific awareness and public perception have influenced the course of research on acid precipitation?

This brief article is an attempt to illuminate some of these questions. Our approach will be to review various steps in the transformation of the concepts of acid precipitation from the domain of scientific curiosity to the domain of public concern and debate.

Since the beginning of life on earth, plants have obtained an essential part of their nutrients from the atmosphere. From time to time, plants and animals have been injured by toxic substances dispersed in the atmosphere. When the industrial revolution started, people began to exert more and more influence on the biogeochemical circulation of the earth. We added progressively larger amounts of many kinds of substances to those that circulate naturally among the air, the water, the soil, and all living things. Some of these man-made materials were beneficial nutrients; some were inert; others were toxic or injurious depending upon their concentration or the nature of the organism receiving the deposition.

Because man now influences the chemical climate of the earth in so many important ways, it is essential that we understand the sources, transport, transformations, and chemistry of atmospheric deposition. We also must know the various effects that the deposited substances have on forests, fish, crops, soils, surface waters, and buildings and other structures (Figure 1).

Table 1 contains a historical resumé of the progress that has been made toward understanding these phenomena and their biological consequences. Contributions are presented in the chronological order of their occurrence, whether or not the work was recognized or accepted at the time. The names of major scientists, the country in which the research was conducted, and the principal contribution to science or public affairs are presented with appropriate references

FIGURE 1
About two-thirds of the total land area of North America receives acid precipitation[a]

[a] This map prepared in Jan. 1982 shows average annual pH from Sept. 1979 to Oct. 1980. It is based on the data developed by the National Atmospheric Deposition Program (NADP/NC-141) in the U.S. and the Canadian Network for Sampling of Precipitation (CANSAP) in Canada. These two networks prepared the first continent-scale map of atmospheric deposition for North America in 1980.

when that is possible.

Selecting particular accomplishments for inclusion in such a chronology is a hazardous undertaking because of the likelihood that some important contributions will not be given the credit or priority they deserve. I hope the table will serve a useful purpose, and look forward to receiving comments from anyone who may be interested in helping to describe the record more adequately.

Early awareness

Many features of the acid rain phenomenon were first discovered by an English chemist named Robert Angus Smith in the middle of the 19th century. In 1852, Smith published a detailed report on the chemistry of rain in and around the city of Manchester, England. In this remarkably early account, Smith called attention to the changes in precipitation chemistry as one moves from the middle of a polluted city to its surrounding countryside: "We may therefore find three kinds of air—that with carbonate of ammonia in the fields at a distance, that with sulphate of ammonia in the suburbs, and that with sulphuric acid, or acid sulphate, in town." Smith also pointed out that the sulfuric acid in city air caused the colors of textiles to fade and metals to corrode.

Twenty years later, in an extraordinary book entitled "Air and Rain: The Beginnings of a Chemical Climatology," Smith (1872) first used the term "acid rain" and enunciated many of the principal ideas that are part of our present understanding. On the basis of detailed studies in England, Scotland, and Germany, Smith demonstrated that precipitation chemistry is influenced by such factors as coal combustion, decomposition of organic matter, wind trajectories, proximity to the sea, and the amount and frequency of rain or snow. Smith proposed detailed procedures for the proper collection and chemical analysis of precipitation. He also noted damage by acid rain to plants and materials and commented on the atmospheric deposition of arsenic, copper, and other metals in industrial regions.

Unfortunately, however, Smith's pioneering and prophetic book apparently has been overlooked by essentially every subsequent investigator. Eville Gorham (1981) developed the first detailed analysis of Smith's early work for a report by the National Academy of Sciences.

Modern awareness

Contemporary concepts about acid precipitation and its environmental

TABLE 1

A historical resumé of progress toward understanding acid precipitation

Year(s)	Investigator and country	Principal contribution
1661–1662	Evelyn, Graunt, England	Noted the influence of industrial emissions on the health of plants and people, the transboundary exchange of pollutants between England and France; and suggested remedial measures including placement of industry outside of towns and use of taller chimneys to spread the "smoke" into "distant parts" (Evelyn, 1661; Graunt, 1662; see also Gorham, 1981)
1687	Hooke, England	On the basis of experiments by Brotherton, Hooke concluded that plants have "two-fold kind of roots, one that branches and spreads into the earth, and another that spreads and shoots into the air; both kinds of roots serve to receive and carry their proper nourishment to the body of the plant" (Hooke, 1687; see also Gorham, 1965; and Wittwer and Bukovac, 1969)
1727	Hales, England	Noted that dew and rain "contain salt, sulphur, etc. For the air is full of acid and sulphureous particles . . ." (Hales, 1727; see also Gorham, 1981)
1734	Linné, Sweden	Described a 500-year-old smelter at Falun, Sweden: ". . . we felt a strong smell of sulphur, . . . rising to the west of the city . . . a poisonous, pungent sulphur smoke, poisoning the air wide around . . . corrode(ing) the earth so that no herbs can grow around it" (Linné, 1734)
1852	Smith, England	Analyzed the chemistry of rain near Manchester, England and noted concentric zones with "three kinds of air—that with carbonate of ammonia in the fields at a distance, that with sulphate of ammonia in the suburbs, and that with sulphuric acid, or acid sulphate in the town." Smith also noted that sulfuric acid in town air caused fading in the color of textiles and corrosion of metals (Smith, 1852; see also Gorham, 1981, Austria)
1854–1856	Austria and Germany	Established "General Citizens Laws" prohibiting disposal of wastes by individuals on a neighbor's property. In the interest of encouraging industrialization, however, these same laws specifically excluded industries from legal liability when waste disposal caused pollution of water and air
1855–1856	Way, England	Completed a very detailed series of analyses of nutrient substances in precipitation at the Rothamsted Experiment Station and showed the value of these substances in crop production (Way, 1855)
1872	Smith, England	In a remarkable publication entitled "Air and Rain: The Beginnings of a Chemical Climatology," Smith first used the term "acid rain" and enunciated many of the ideas that we now consider part of the acid precipitation problem. These ideas included regional variation in precipitation chemistry as it is influenced by such factors as combustion of coal, decomposition of organic matter, wind direction, proximity to the sea, amount of rain, etc. After extensive field experiments, Smith proposed detailed procedures for the proper collection and chemical analysis of precipitation. He also noted acid rain damage to plants and materials and atmospheric deposition of arsenic, copper, and other metals in industrial regions (Smith, 1872; see Gorham, 1981)
1881	Brögger, Norway	Observed "smudsig snefeld" (dirty snowfall) in Norway and attributed it to either a large town or an industrial district in Great Britain (Brögger, 1881)
1909	Sørensen, Denmark	Developed the pH scale to describe the acidity of aqueous solutions (Sørensen, 1909)
1911	Crowther and Ruston, England	Demonstrated gradients in acidity of precipitation decreasing from the center of Leeds, England; associated the acidity with combustion of coal; and showed that both natural rain and dilute sulfuric acid inhibited plant growth and seed germination, as well as ammonification, nitrification, and nitrogen fixation in soil

Year(s)	Investigator and country	Principal contribution
		(Crowther and Ruston, 1911; see also Cohen and Ruston, 1912; and Gorham, 1981)
1919	Rusnov, Austria	Demonstrated that deposition of substances from the atmosphere accelerated the acidification of both poorly-buffered and well-buffered forest soils (Rusnov, 1919)
1921	Dahl, Norway	Recognized the relationship between acidity of surface water and trout production (Dahl, 1921, 1927)
1922	Atkins, England	Measured the alkalinity of surface waters and noted a relationship between alkalinity and biological productivity (Atkins, 1922)
1923	MacIntyre and Young, U.S.	Made the first detailed study of precipitation chemistry in the U.S. (MacIntyre and Young, 1923)
1925	Shutt and Hedley, Canada	Made very early measurements of the nitrogen compounds present in rain and snow and commented on the value of these compounds for crop growth (Shutt and Hedley, 1925)
1926	Sunde, Norway	Demonstrated the value of adding limestone to water in a fish hatchery (Sunde, 1926)
1939	Erichsen-Jones, Sweden	Demonstrated the relationship between acidity and the toxicity of aluminum to fish (Erichsen-Jones, 1939)
1939	Katz et al., Canada	Reported acidification and decreases in base saturation of soils caused by sulfur dioxide emissions from the lead–zinc smelter near Trail, British Columbia (Katz et al., 1939)
1939	Bottini, Italy	Detected hydrochloric acid in precipitation near the volcano on Mount Vesuvius, thus demonstrating that there are natural sources of strong acids in precipitation (Bottini, 1939)
1942	Conway, Ireland	Completed the first modern review of precipitation chemistry (Conway, 1942)
1948	Egnér, Sweden	Initiated the first large-scale precipitation chemistry network in Europe (Egnér et al., 1955; Rossby and Egnér, 1955)
1950–1955	Eriksson, Sweden	Enunciated a general theory of biogeochemical circulation of matter through the atmosphere (Eriksson, 1952, 1954, 1959, 1960)
		Expanded the regional network established by Egnér into the continent-wide European Air Chemistry Network, which has provided a continuing record of precipitation chemistry for three decades (Emanuelsson et al., 1954)
1953	Viro, Finland	Developed a regional chemical budget by comparing analytical data for precipitation and river waters in Finland (Viro, 1953)
1953–1958	Tamm, Sweden	Demonstrated the great dependence of mosses on atmospheric sources of nutrients, especially nitrogen (Tamm, 1953) and expanded this concept to include most forest plants (Tamm, 1958)
1953–1955	Various investigators in several countries	Simultaneously investigated precipitation chemistry data for evidence of atmospheric acidity (Barrett and Brodin, 1955, Sweden; Parker, 1955, and Gorham, 1955, England; Houghton, 1955, U.S.)
1954–1961	Gorham, England	Demonstrated that acidity in precipitation markedly influenced geological weathering processes and the chemistry of lake waters, bog waters, and soils (Gorham, 1955, 1958b, 1958c, 1961)
		Demonstrated that hydrochloric acid from combustion of coal rich in chlorine predominated in urban precipitation whereas sulfuric acid predominated in rural precipitation (Gorham, 1958a, 1958b)
		Established that acidity in precipitation affects the alkalinity and buffering capacity of lake and bog waters (Gorham, 1957, 1958b)
		Established that the incidence of bronchitis in humans can be correlated with the acidity of precipitation (Gorham, 1959)

effects originated in three seemingly unrelated fields of science: limnology (the study of lakes), agriculture, and atmospheric chemistry.

Progress in limnology. The relationship between rain or snow and the water in streams and lakes was obvious even to prehistoric man. But the connection between changes in the chemistry of rain and snow and alterations in the chemistry of lake waters remained obscure until the middle of the 20th century.

In a long series of papers beginning in 1955, Gorham (1955, 1957, 1958a-d, 1961, 1965), now professor of ecology at the University of Minnesota, built the major foundations for our present understanding of the causes of acid precipitation and its impact on aquatic ecosystems. On the basis of research both in England and in Canada, Gorham and his colleagues demonstrated the following principles:

- Much of the acidity in precipitation near industrial regions can be attributed to atmospheric emissions produced by the combustion of fossil fuels;
- Progressive losses of alkalinity in surface waters and increases in the acidity of bog waters can be traced to the atmospheric deposition of acidic substances by precipitation;
- The free acidity in soils receiving acid precipitation is due primarily to sulfuric acid;
- The incidence of bronchitis in humans can be correlated with the acidity of precipitation;
- Exposure to sulfur dioxide and the resultant acid rain contribute to the deterioration of vegetation, soils, and lake water quality around metal smelters.

Thus, by the mid 1950s and early 1960s, Gorham was the second scientist to establish a major part of our present understanding of the sources and environmental consequences of acid precipitation. But his pioneering research, like that of Smith a century before, was met by thundering silence from both the scientific community and the public at large. One plausible explanation is that Gorham's work, being highly interdisciplinary, was published in a diverse array of scientific journals. In any event, because Gorham's work was not recognized, there resulted a further lag in both the scientific and public awareness of acid precipitation.

Progress in the agricultural sciences. The importance of the atmosphere as a source of nutrients for the growth and development of plants was first recognized by Robert Hooke in 1687 (see also Gorham, 1965). From 1855 to 1916, scientists at the Rothamsted Experiment Station in England also demonstrated the relationship between nutrients in air and the growth of various crop plants (Way, 1855; Miller, 1905).

In the mid 1940s an imaginative Swedish soil scientist, Hans Egnér, developed a systematic way to look at the fertilization of crops by nutrients from the atmosphere. Working from his laboratory at the Agricultural College near Uppsala, Egnér created the first 20th-century network for the collection and chemical analysis of precipitation. A large number of sampling buckets were set out at experimental farms all over Sweden, and the major chemical constituents in what we now call bulk deposition (rain, snow, and dust fall) were measured on a regular monthly basis. The acidity of precipitation was one of several chemical parameters that were tested. Other agricultural scientists gradually expanded this network—first to Norway, Denmark, and Finland and later to most of western and central Europe. It came to be called the European Air Chemistry Network and it provided the first large-scale and long-term data on the changing chemistry of precipitation and its importance for agriculture and forestry (Emanuelsson et al. 1954; Egnér et al., 1955). In 1956, the International Meteorological Institute in Stockholm assumed responsibility for further coordination of the network. In 1957, as part of the International Geophysical Year, it spread eastward to include Poland and much of the Soviet Union. In marked contrast to monitoring efforts elsewhere in the world, the original European network with more than 100 collection stations has remained in continuous operation for nearly three decades.

Progress in the atmospheric sciences. Under the imaginative leadership of Carl Gustav Rossby and Erik Eriksson, the science of atmospheric chemistry began in Sweden and later spread across Europe and finally to North America (N.A.S., 1975). Rossby and Eriksson were convinced that atmospheric processes were efficient mechanisms for the long-distance as well as short-distance dispersal of many different substances. The data from Egnér's precipitation chemistry network provided the means to test various hypotheses about the trajectories of air masses, turbulent dispersal processes, and atmospheric scavenging and deposition processes (Rossby and Egnér, 1955). These observations led Eriksson to enunciate a general theory to describe the biogeochemical circu-

Year(s)	Investigator and country	Principal contribution
1957	Europe, U.S.S.R., and U.S.	During the International Geophysical Year, a one-year study of precipitation chemistry was made in Europe, the U.S.S.R., and the U.S.
1958–1959	Junge and Werby, Jordan et al., U.S.	Made the first regional studies of precipitation chemistry in the U.S. and noted the importance of atmospheric sulfur as a source of nutrients for crops (Junge and Werby, 1958; Jordan et al., 1959)
1959	Dannevig, Norway	Recognized the relationship between acid precipitation, acidity in surface waters, and disappearance of fish (Dannevig, 1959)
1960–1963	Gordon and Gorham, Canada	Established that exposure to sulfur dioxide and resultant acid rain contributed to the deterioration of lake quality, vegetation, and soils near metal smelters (Gorham and Gordon, 1960; Gordon and Gorham, 1963)
1960–1966	McCormick, U.S.	Operated the first continent-wide precipitation chemistry network in North America for six years (1960–66). Showed that precipitation is generally acidic east but alkaline west of the Mississippi River (Lodge et al., 1968)
1962	Carson, U.S.	Stimulated a global revolution in environmental awareness by publishing "Silent Spring" in which the term "poison rain" was used to describe concern about atmospheric transport and deposition of pollutants (Carson, 1962)
1967–1968	Odén, Sweden	Outlined the changing acidity of precipitation as a regional and temporal phenomenon in Europe (Odén, 1968, 1976)
		Used trajectory analysis of air masses to demonstrate that acidity in precipitation in Scandinavia was attributable largely to emissions of sulfur in England and central Europe (Odén, 1968)
		Demonstrated temporal trends in acidity and in the concentrations of major cations and anions in precipitation over various parts of Europe (Odén, 1968)
		Demonstrated the increasing acidity of Scandinavian rivers (Odén, 1968)
		Described biological uptake and ion-exchange processes by which natural acidification of soils would be accelerated by atmospheric deposition of ammonia and other cations (Odén, 1968)
		Postulated that acid precipitation would lead to displacement of nutrient cations, reduction in nitrogen fixation, and release of heavy metals (especially Hg) which would damage surface waters and groundwaters (Odén, 1968, 1976)
		Postulated acidity in precipitation as a probable cause of decline in fish populations, impoverishment of forest soils, decreased forest growth, increased disease in plants, and accelerated corrosion and other damage to materials (Odén, 1967, 1968)
1970	Odén and Ahl, Sweden	Discovered that soluble pollutants in snow accumulate in the snow pack and are released almost totally with the first meltwater in spring (Odén and Ahl, 1970)
1970	Hultberg, Sweden	Demonstrated the effect of acidity on fish populations in two Swedish lakes (Hultberg and Stenson, 1970)
1971–1972	Rodhe et al., Sweden	Developed the first quantitative analysis of long-distance transport of sulfur in Europe. Showed that distances of transport frequently exceed 1000 km, the residence time of sulfur in the air is 2–4 days, and fields of deposition are roughly symmetrical and slightly displaced to the northeast from sources of emission (Munn and Rodhe, 1971; Rodhe, 1972)
1972	Bolin et al., Sweden	Drafted Sweden's Case Study for the United Nations Conference on the Human Environment "Air Pollution Across National Boundaries: The Impact on the Environment of Sulfur in Air and Precipitation." Noted damage to materials as well as ecosystems by acid precipitation (Bolin et al., 1972)

Year(s)	Investigator and country	Principal contribution
1972	Hvatum, Norway	Demonstrated increasing content of lead near the surface of Norwegian peat bogs and postulated long-distance transport as the probable cause (Hvatum, 1972)
1972	Tyler, Sweden	Reported heavy metal accumulation in forest soils and speculated about their probable effects on forest productivity (Tyler, 1972)
1972	Granat, Sweden	Described the temporal and spatial deposition of sulfate and acid over northern Europe (Granat, 1972, 1976)
1972	Jonsson and Sundberg, Sweden	Established an experimental basis for the suspicion that acid precipitation had decreased the growth of forests in Sweden (Jonsson and Sundberg, 1972)
1972	Various agencies, Norway	Initiated the SNSF Project "Acid Precipitation: Effects on Forests and Fish (See *Ambio*, 1976, and Braekke, 1976)
1972–1980	Overrein, Norway	Demonstrated accelerated loss of calcium and other cations from soils receiving acid precipitation (Overrein, 1972) Provided leadership for the SNSF Project from its founding in 1972 until its completion in 1980 (*Ambio*, 1976; Overrein et al., 1980; Tollan, 1981)
1972	Likens et al., U.S.	Discussed the regional distribution of acid precipitation and its significance for aquatic and terrestrial ecosystems in North America (Likens et al., 1972) Indicated that nitric acid resulting from atmospheric transformation of NO_x adds to the acidity of precipitation in the eastern U.S. (Likens et al., 1972)
1972	Jensen and Snekvik, Norway	Showed that acidity in lakes and streams caused major decreases in salmon and trout populations in Norway (Jensen and Snekvik, 1972)
1972	Beamish and Harvey, Canada	Reported decline in fish populations due to acidification of lake waters in Canada (Beamish and Harvey, 1972)
1972–1980	Various investigators	Showed that mushrooms, mosses, and other vegetation in forests accumulate heavy metals, especially lead and cadmium. Found that wildlife feeding on these plants also accumulate the metals, sometimes making both the plants and the wildlife hazardous for human consumption (Munshower, 1972; Huckabee and Blaylock, 1974; Tyler, 1980)
1973	Malmer, Sweden	Summarized research on the ecological effects of increasing sulfur deposition, especially with reference to Swedish conditions (Malmer, 1973)
1973	Dickson et al., Sweden	Reported on the pH status of 314 lakes in western Sweden (Dickson et al., 1973)
1973	Wiklander, Sweden	Proposed a general theory to account for the effects of acid precipitation on soil chemical properties (Wiklander, 1973)
1973–1977	Ottar, Norway	Led the Organization for Economic Cooperation and Development in Europe in its continent-wide study of the long-range transport of air pollutants (Ottar, 1976; OECD, 1977)
1974	Almer et al., Sweden	Summarized the effects of changing lake water acidity on fish populations in Sweden (Almer et al., 1974)
1974	Grahn et al., Sweden	Discovered that *Sphagnum* (peat moss) invades acidified lakes and streams inducing a self-accelerating oligotrophication of the water body (Grahn et al., 1974)
1974	Cogbill and Likens, U.S.	Published maps showing changes in acidity of precipitation in the eastern U.S. between 1955–56 and 1972–73 (Cogbill and Likens, 1974)
1974	Hutchinson and Whitby, Canada	Established that strongly acid rain near Sudbury, Ontario is accompanied by deposition and/or mobilization of heavy metals (especially nickel, copper, cobalt, iron, aluminum, and manganese). Found toxicity of these metals sufficient to inhibit germination and establishment of many native and agricultural species of plants (Hutchinson and Whitby, 1974; Whitby and Hutchinson, 1974)

lation of matter on the earth (Eriksson, 1952, 1959, 1960).

The transport and deposition of water by atmospheric processes has been well known since the earliest observations of evaporation, cloud movement, and rain. But the notion that atmospheric transport and deposition were a major means for the dispersal and chemical transformation of many other substances was still only a working hypothesis in the early 1950s. Rossby and Eriksson championed these then-novel ideas and initiated various experimental tests of their hypotheses, using as a very powerful tool data from the European Air Chemistry Network. Rossby and Eriksson also sponsored a series of European conferences on atmospheric chemistry and dispersal processes, which attracted the interest of scientists in many other fields of inquiry including biology, forestry, agriculture, meteorology, and medicine (Eriksson, 1954). Both Gorham and Svante Odén were among the students at these conferences, but they never met personally until 1975.

Integration of knowledge

The first major unification of knowledge about acid precipitation in the fields of limnology, agriculture, and atmospheric chemistry was achieved by Odén, a soil scientist at the Agricultural College near Uppsala in Sweden. In 1961, as a young colleague of Egnér, Rossby, and Eriksson, Odén started a Scandinavian network to measure surface water chemistry. When data from this network were combined with those from the European Air Chemistry Network, a series of general trends and relationships began to emerge and were published by Odén in two different media—Stockholm's prestigious newspaper *Dagens Nyheter* (Odén, 1967) and in an Ecology Committee Bulletin (Odén, 1968). The newspaper report outlining Odén's audacious ideas about an insidious "chemical war" among the nations of Europe captured the attention of the press, who began the process of public education about acid precipitation in Europe. In much the same way, the Ecology Committee Bulletin stimulated scientific interest in acid precipitation and its ecological effects. Odén's analyses of air mass trajectories and temporal and geographical changes in precipitation chemistry clearly showed that:

- acid precipitation was a large-scale regional phenomenon in much of Europe with well-defined source and sink regions
- both precipitation and surface

waters were becoming more acidic

- long-distance (100-2000 km) transport of sulfur- and nitrogen-containing air pollutants was taking place among the various nations of Europe
- there were marked seasonal trends in deposition of major ions and acidity
- long-term trends in acidity could be detected in many countries of Europe.

Odén also hypothesized that the probable ecological consequences of acid precipitation would be changes in surface water chemistry, decline of fish populations, leaching of toxic metals from soils into surface waters, decreased forest growth, increased plant diseases, and accelerated damage to materials.

These conclusions and hypotheses led to a veritable storm of scientific and public concern about acid precipitation. Suddenly, limnological, agricultural, and atmospheric scientists began to argue and debate with each other about Odén's unconventional ideas and his general theory of atmospheric influences. Multidisciplinary discussions and international conferences ensued all over Europe and around the world as scientist after scientist was inspired (or provoked) into designing experimental tests to prove or to disprove Odén's ideas.

The Swedish government responded to the growing public and scientific controversies by initiating an inquiry that culminated in Sweden's Case Study for the U.N. Conference on the Human Environment: "Air Pollution Across National Boundaries: The Impact of Sulfur in Air and Precipitation" (Bolin et al., 1972).

The important ideas in both the Ecology Committee Bulletin and the Swedish Case Study were debated intensely all over Europe. Two major scientific initiatives followed in short order. The first took place in 1972 when three organizations in Norway joined together to establish the so-called SNSF Project: the Norwegian Interdisciplinary Research Programme "Acid Precipitation—Effects on Forest and Fish." These three organizations included the Norwegian Council for Scientific and Industrial Research, the Agricultural Research Council of Norway, and the Norwegian Ministry of Environment. The annual budget for the SNSF Project was about 10 million Norwegian kroner ($2 million) per year for 1972-1980. This huge project had two comprehensive goals:

- to establish as precisely as possible the effects of acid precipitation on forests and freshwater fish

Year(s)	Investigator and country	Principal contribution
1974	Shriner, U.S.	Demonstrated that simulated rain acidified with sulfuric acid can accelerate erosion of protective waxes on leaves, inhibit nodulation of leguminous plants, and alter host-pathogen interactions of plants (Shriner, 1974, 1976, 1978)
1975	Brosset et al., Sweden	Described the chemical transformations and trajectories that lead to "white episodes" and "black episodes" of acid deposition in western Sweden. Showed that gaseous nitric acid increases acid deposition. Established a state-of-the-art titration method for the determination of acidity in precipitation (Brosset et al., 1975)
1975–1982	Cowling, U.S.	Testified in congressional hearings concerning the inadequacy of research in the U.S. on the ecological effects of acid precipitation (Cowling, 1976)
		Together with many other scientists in the U.S. and Canada, began the development of a permanent network to monitor chemical changes in wet and dry deposition and to study their biological effects in various regions of the U.S. (Galloway and Cowling, 1978)
1975	Cragin, Greenland	Determined the chemistry of precipitation in Greenland from 1300 to 1975 A.D. Found a continuing trend of increasing sulfate and lead concentration beginning about 1800 and rising even more rapidly after 1945. (Cragin et al., 1975)
1976	Schofield, U.S.	Reported the results of lake surveys showing a decline in fish populations associated with acidification of lakes in the Adirondack Mountains of New York State (Schofield, 1976)
1976	Kucera, Sweden	Summarized evidence that acid precipitation accelerates the corrosion of metals (Kucera, 1976)
1976	Summers and Whelpdale, Canada	Summarized earlier studies of precipitation chemistry in Canada and identified northwest Alberta, southern Ontario and Quebec, and the Atlantic Provinces as areas of present or potential impact by acid rain and snow (Summers and Whelpdale, 1976)
1976	Leivistad and Muniz, Norway	Documented a massive fish kill on the Tovedahl River associated with snow melting in the spring of 1975 and established that dead and dying fish had lost control of their blood salt balance. (Leivistad and Muniz, 1976; Leivistad et al., 1976)
1976	Tyler, Sweden	Demonstrated that heavy metals in the litter layer of forests inhibit microbial processes, especially decomposition of organic matter (Tyler, 1976)
1976	Galloway, U.S.; Berry, Canada; Granat, Sweden	Developed standardized protocols for precipitation collectors and collection techniques (Galloway and Likens, 1976; Berry et al., 1976; Granat, 1976)
1976	Hultberg and Grahn, Sweden	Discovered a correlation between acidification of lakes and the mercury content of fish (Hultberg and Grant, 1976)
1976	Pough, U.S.	Showed that reproduction of salamanders is inhibited by acidity of surface waters (Pough, 1976)
1977	Hagström, Sweden	Showed that reproduction of frogs is inhibited by acidity of surface waters (Hagström, 1977)
1977	Rosenqvist Norway	Enunciated a general theory that acidification of soils and surface waters is due mainly to natural processes in soils and to changes in patterns of land use (Rosenqvist, 1977)
1978	Greszta, Austria	Demonstrated accumulation of heavy metals in forest soils leading to injury to young pine and spruce seedlings (Greszta, 1978)
1978–1980	Several investigators, U.S.	Showed that acid precipitation occurs in both urban and certain rural areas in the western U.S. (Liljestrand and Morgan, 1978; McColl and Bush, 1978; Lewis and Grant, 1980)

Year(s)	Investigator and country	Principal contribution
1979	Altshuller, U.S.; McBean, Canada	Documented the transboundary exchange of sulfur and nitrogen oxides between the U.S. and Canada (Altshuller and McBean, 1979)
1979	Odén, Sweden	Showed by studies of surface waters in Sweden that acidification due to sulfur deposition had begun during the early 1900s (Odén, 1979)
1979	Liljestrand and Morgan, U.S.	Completed a rigorous statistical analysis of trends in precipitation chemistry in the eastern and western U.S. (Liljestrand and Morgan, 1979)
1979	Cronan and Schofield, U.S.	Discovered that aluminum ions are leached by acid precipitation from soils into streams and lakes in concentrations toxic to fish (Cronan and Schofield, 1979)
1979	Galloway, U.S.; Whelpdale, Canada	Developed a new sulfur budget for eastern North America and showed that atmospheric sulfur in this region is predominantly of anthropogenic origin (about 95%) and that a substantial fraction (about 30%) of sulfur emissions in this region are deposited outside this region (Galloway and Whelpdale 1979)
1979	Carter, U.S.	Established a presidential initiative on acid rain calling for a 10-year-long, $10 million-per-year interagency program of research on acid precipitation and its environmental consequences in the U.S. (Carter, 1979)
1979	Henriksen, Norway	Developed a simple descriptive model for determining the extent to which acidification decreases the alkalinity of lake waters and applied this method to predict the vulnerability of lakes to acid deposition (Henriksen, 1979
1980	Hultberg and Wenblad, Sweden	Discovered acidification of groundwater in western Sweden, postulated acid precipitation as the probable cause, established by surveys of 1300 wells the frequency of heavy metal accumulation and plumbing problems associated with these wells (Hultberg and Wenblad, 1980)
1980	Abrahamsen, Norway	Summarized many years of research on the effects of acid precipitation on forests and concluded that fertilization effects, particularly by atmospheric deposition of nitrogen, tend to offset nutrient leaching and other detrimental effects. Also emphasized that negative effects of atmospheric deposition on growth are most likely when nutrient deficiencies or imbalances are increased by acid deposition (Abrahamsen, 1980)
1980	Wetstone, U.S.	Summarized the biological and materials damage of acid precipitation in relation to the pollution control laws in North America (Wetstone, 1980)
1980	Schindler et al., Canada	Established an experimental system for controlled acidification of whole lakes (Schindler et al., 1980). Demonstrated that acidification eliminated organisms of several trophic levels at pH values as high as 5.8–6.0 (Schindler, 1980). Also demonstrated that microbial reduction of sulfate could partially protect lakes against acidification (Schindler et al., 1980)
1980	Ulrich et al., Germany	Demonstrated a significnt correlation between amount of soluble aluminum in forest soils, death of feeder roots in spruce, fir, and birch forests, and widespread decline in the growth of these forests (Ulrich et al., 1980; Schuck et al., 1979)
1980	Various investigators, U.S.	Established an Integrated Lake Water Acidification Study (ILWAS), to determine detailed chemical budgets for H^+, SO_4^{--}, NH^{4+}, NO_3^-, Cl^-, and other ions in three lake watersheds with differing degrees of acidification (see Drabløs and Tollan, 1980, pp. 252–267; and EPRI, 1981)
1981	Norton et al., U.S.	Demonstrated by analysis of lake sediments that increased depletion of soil nutrients and increased atmospheric deposition of lead and zinc in northern New England started prior to 1880 (Hanson et al., 1981; Johnston et al., 1981)

- to investigate the effects of air pollutants on soils, vegetation, and water to the extent required to support the primary objective.

Lars Overrein of the Norwegian Forest Research Institute was appointed research director for this project from 1972–1980. The project produced a steady stream of technical and scientific reports on various aspects of acid precipitation and its effects. The SNSF project also sponsored two major international scientific conferences—one at Telemark, Norway, in June 1976 and the second at Sandefjord, Norway, in March 1980. Braekke (1976) and *Ambio* (1976) published major reports in connection with the conference at Telemark. The Sandefjord conference was designed to provide a forum for evaluation not only of recent research within the SNSF Project, but also the large amount of research currently being done elsewhere in the world (Drabløs and Tollan, 1980). A final report and bibliography from the SNSF Project was published at the end of 1980 (Overrein, Seip, and Tollan, 1980; Tollan, 1981).

The second major scientific initiative was conducted by the Organization for Economic Cooperation and Development (OECD) from 1973–1975. This was a study of the long-range transport and deposition of atmospheric sulfur in eastern and western Europe. The OECD findings, published in 1977, showed that the area of acid precipitation included almost all of northwestern Europe. The findings confirmed the idea that pollutants are transported long distances and showed that the air quality in each European country is measurably affected by emissions from all other European Countries (OECD, 1977).

In October of 1977, the Economic Commission for Europe originated the Cooperative Programme for Monitoring and Evaluating the Long-Range Transmission of Air Pollutants in Europe, which is now in operation. The Economic Commission has nearly completed formulating a multinational convention governing nations' responsibilities for combating the long-range transboundary transport of air pollutants. Arne Tollan and Brunjulf Ottar of the SNSF project were commissioned to develop working papers concerning both the atmospheric and biological influences of sulfur in the air and in precipitation.

North American awareness

Concern about acid precipitation and its ecological effects in North America developed first in Canada and then later in the U.S. Initial interests were focused on the effects of sulfur dioxide exposure and associated acid precipitation and heavy metal deposition in the vicinity of metal smelting and sintering operations (Katz, 1939; Gordon and Gorham, 1963), especially those near Sudbury, Ontario—the largest point source of sulfur in the world (Gorham and Gordon, 1960; Hutchinson and Whitby, 1974). During the early 1970s, interest spread to other parts of Canada as declining fish populations were discovered in more and more lakes of southern Ontario and Nova Scotia, remote from local sources of atmospheric sulfur (Beamish and Harvey, 1972). Very early measurements of nitrogen compounds in rain and snow were made by Shutt and Hedley (1925); the first measurements of the pH of precipitation in Canada were reported by Herman and Gorham (1957). A summary of acid precipitation studies in Canada was published in 1976 by Summers and Whelpdale (1976).

The first detailed research on precipitation chemistry in the U.S. was completed by MacIntyre and Young (1923). Emphasis was given to the importance of airborne nutrients for the growth of crops. This work was followed by the work of Junge and other atmospheric scientists during the 1950s (Junge and Werby, 1958). The earliest regional monitoring network for precipitation chemistry was maintained by a group of State Agricultural Experiment Station scientists from 1953-55 (Jordan et al., 1959) and the first national monitoring program was established under the auspices of the Air Pollution Program within the Public Health Service Laboratory at Cincinnati, Ohio. The data for 1960-66 were summarized by Lodge (1968). As has been the case for all such studies in North America, however, these early programs were redirected or terminated so that no continuing records are available of long-term trends in precipitation chemistry.

Scientific and public interest in acid precipitation and its ecological consequences were stimulated in North America by Svante Odén with a series of 14 lectures at various institutions in the U.S. during the fall of 1971, and also by Torsten Ahl and Odén at the 19th International Limnological Congress in Winnipeg, Manitoba, in 1974. A series of publications by Gene Likens, Charles Cogbill, James Galloway, Carl Schofield, and others provided further stimulus (Likens et al., 1972; Likens, 1976; Cogbill and Likens, 1974; Schofield, 1976; Gallo-

Year(s)	Investigator and country	Principal contribution
1981	Rodhe, Sweden; Crutzen, Vanderpol, Sweden	Developed a photochemical model for the formation of sulfuric and nitric acid during long-distance transport. The model shows that the transformation of both of these acids are coupled processes and that their transformation rates and distances of transport are influenced by hydrocarbons and various oxidants in the atmosphere (Rodhe et al., 1981)
1981	Rahn, U.S.	Demonstrated that the Mn/V ratio of aerosols can be used as a tracer to determine the source of acid aerosols in the arctic and suggested its use in determining source–receptor relationships for acid deposition in North America (Rahn, 1981)

Major international conferences documenting further progress

1950s	Eriksson, Sweden	The International Meteorological Institute sponsored a series of conferences on various aspects of atmospheric chemistry (Eriksson, 1954)
1975-1976	Dochinger and Seliga, U.S.	U.S. Forest Service sponsored the First International Symposium on Acid Precipitation and the Forest Ecosystem at Ohio State University, Columbus, Ohio (Dochinger and Seliga, 1976a, 1976b)
1976	Overrein et al., Norway	SNSF Project and the Norwegian Ministry of the Environment sponsored the International Conference on Effects of Acid Precipitation, Telemark, Norway (*Ambio*, 1976; Braekke, 1976)
1977	Husar and Lodge, U.S.; Moore, England	The U.N. Environmental Program and several other organizations sponsored an International Symposium on Sulfur in the Atmosphere, Dubrovnik, Yugoslavia (Husar et al., 1978)
1978	Hutchinson, Canada	NATO sponsored an Advanced Research Institute on Ecological Effects of Acid Precipitation in Toronto, Canada (Hutchinson and Havas, 1980)
1978	Howells, England	The Electric Power Research Institute (U.S.) and the Central Electricity Generating Board (Great Britain) sponsored an International Symposium on Ecological Effects of Acid Precipitation (Howells, 1979)
1978	Hendrey, U.S.	U.S. EPA and Brookhaven National Laboratory sponsored an International Workshop on Limnological Aspects of Acid Precipitation, Sagamore Lake, N.Y. (Hendrey, 1978)
1979	Shriner, U.S.	The Oak Ridge National Laboratory sponsored a symposium on the Potential Environmental and Health Effects of Sulfur Deposition, Gatlinburg, Tenn. (Shriner et al., 1980)
1979	Agle, U.S.; Turnbull, Canada	A group of Canadian and U.S. environmental protection organizations sponsored the Action Seminar on Acid Precipitation, Toronto, Canada (Reid, 1980)
1980	Overrein et al., Norway	The SNSF project sponsored an International Conference on Ecological Impacts of Acid Precipitation, Sandefjord, Norway (Overrein et al., 1980; Tollan, 1981)
1980	Miller et al., U.S.	The U.S. Forest Service and other U.S. and international air pollution organizations sponsored an International Symposium on Effects of Air Pollutants on Mediterranean and Temperate Forest Ecosystems, Riverside, Calif. (Miller, 1980)
1981	Schindler et al., Canada and U.S.	The National Academy of Sciences organized an international committee of scientists to prepare an authoritative overview entitled: "Atmosphere–Biosphere Interactions: Toward a Better Understanding of the Environmental Consequences of Fossil Fuels Combustion." (NAS, 1981)

way and Likens, 1976; Galloway et al., 1978; Likens et al., 1979). Experimental studies of various biological effects of acid precipitation were initiated at Cornell, North Carolina State, and other universities. David Shriner's (1978) dissertation demonstrated both direct injury to vegetation and various indirect effects through pathogens and parasites. Schofield's (1976) research on the extinction of fish populations in the Adirondack Mountains was especially alarming.

Growing awareness of the important impacts of acid precipitation on fish populations and potential effects on forests led the U.S. Forest Service to sponsor the First International Symposium on Acid Precipitation and the Forest Ecosystem in May 1975. The proceedings of this symposium and the associated workshop reports were published by Dochinger and Seliga (1976a, 1976b). At congressional hearings in July 1975, Cowling (1976) testified about the inadequacy of research on acid precipitation in the U.S. Specifically, he said that the lack of coordinated research programs on ecological effects and the absence of a stable monitoring network were the primary causes of the profound ignorance in North America about acid precipitation.

Both Canada and the U.S. have recently started long-term programs for the chemical analysis of precipitation. The Canadian Network for Sampling Precipitation began in 1976; the National Atmospheric Deposition Program was started in the U.S. in 1978 (Galloway and Cowling, 1978). By late 1981, some 50 sampling stations were operating in Canada and 93 in the U.S.

The data from these programs (Figure 1) show that the area receiving acid precipitation now embraces about two-thirds of the total land area of North America. Although sulfuric acid has been found to be the dominant source of acidity both here and in Europe, nitric acid accounts for almost one third, and the fraction is rising.

In 1978, the governments of Canada and the U.S. established a Bilateral Research Consultation Group on the Long-Range Transport of Air Pollutants to coordinate the exchange of scientific information on acid precipitation. This group documented the transboundary flow of air pollutants in eastern North America, and showed that about 11 times more oxides of nitrogen and two to four times more sulfur oxides are transported from the U.S. to Canada than the reverse (Altshuller and McBean, 1979, 1980).

In the late fall of 1978, Congress passed a resolution calling for bilateral discussions with Canada to preserve and protect mutual air resources. A joint statement on the issues was prepared in July 1979, and on Aug. 5, 1980, the governments of Canada and the U.S. signed a Memorandum of Intent to develop a bilateral agreement on transboundary air pollution including "the already serious problem of acid rain." To provide a suitable technical and scientific foundation for the formulation of such an agreement, five bilateral workgroups were established to prepare scientific reports on the following specific aspects of the problem: impact assessment; atmospheric modeling; strategies development and implementation; emissions, costs, and engineering assessments; legal, institutional arrangements; and drafting. Preliminary drafts of the first four of these reports were completed in early 1981 and are presently being refined in preparation for their submission to the Canadian Department of External Affairs and the U.S. Department of State in early 1982.

Coordinated research programs

During the past five years, significant efforts have been made in North America to develop well-coordinated programs of research on both the atmospheric and biological aspects of the acid precipitation problem. In the spring of 1976, a cadre of more than 100 scientists from various state agricultural experiment stations and other federal, state, private university, and industrial research agencies in the U.S. began the process of creating the organization now known as the National Atmospheric Deposition Program (NADP) to meet the need for a coordinated and long-term precipitation chemistry monitoring and effects research program. In mid-1976 the Department of Energy initiated the Multistate Atmospheric Power Production Pollution Study (MAP3S) to improve understanding of the transport, transformation, and fate of pollutants released by energy-related activities.

In the fall of 1977, the President's Council on Environmental Quality contracted with the NADP to draft "A National Program for Assessing the Problem of Atmospheric Deposition (Acid Rain)" (Galloway et al., 1978). This document provided the basis for a presidential initiative on acid precipitation, which former President Carter announced on Aug. 2, 1979, in his Second Environmental Message (Carter, 1979). The presidential initiative called for a 10-year program of research on the causes and consequences of acid precipitation. The Energy Security Act (PL 96-264) passed by Congress in June 1980 provided a legislative mandate for a national effort. Title VII of this act (the Acid Precipitation Act of 1980) also called for development of a National Acid Precipitation Assessment Plan. The purpose was to develop a firmer scientific basis for environmental and energy policy decisions regarding acid precipitation. After extensive interagency discussions, a formal proposal was issued in draft form by the Interagency Task Force on Acid Precipitation (ITFAP, 1981) in January 1981. Title VII also authorized additional financial support from Congress for a comprehensive national program of acid rain research. Leadership for this interagency program was vested with administrators of the National Oceanic and Atmospheric Administration (NOAA), the Department of Agriculture (DOA), and the EPA.

In 1981 the three designated cochairmen were Ferris Webster, an assistant administrator in NOAA; Anson Bertrand, director of the Science and Education Administration at DOA; and Andrew Jovanovich, an acting assistant administrator in EPA. The other agencies comprising the Interagency Task Force included the following: the Council on Environmental Quality (CEQ); the Departments of Commerce (DOC), Energy (DOE), Interior (DOI), State (DOS), and Health and Human Services (DHHS); the National Aeronautics and Space Administration (NASA); the National Science Foundation (NSF); and the Tennessee Valley Authority (TVA).

The National Acid Precipitation Assessment Program is now operational. It is designed as a 10-year-long, multiagency program of policy-oriented research. In the 1982 fiscal year, its cost will be about $18 million. This program is governed by the Federal Interagency Task Force on Acid Precipitation, which sets policy for the national program and oversees its implementation. The task force also has administrative responsibility for federally sponsored efforts and their coordination with ongoing research and monitoring conducted by the states, universities, industry, environmental organizations, and other groups in the U.S., Canada, Mexico, and Europe. The task force will annually report to the president and Congress on the status of knowledge, additional research needs, and alternative strategies for management of acid precipitation and its effects.

TABLE 2

Research tasks in the National Acid Precipitation Assessment Program

Areas and specific tasks	Priority	Leading agency	Participating agencies						Contributing agencies									Duration	
			NOAA	DOA	EPA	DOI	DOE	TVA	NOAA	DOA	EPA	DOI	DOE	NSF	TVA	NASA	Other	Start	(years)
Natural Sources		NOAA																	
Assessment of natural sources	High	NOAA	X								X	X	X	X		X		1981	2
Neutralizing materials in the atmosphere	High	NOAA	X							X	X		X	X	X	X		1982	3
Man-made sources		DOE																	
Modeling and economic analysis of emissions	High	DOE			X		X								X			1982	8
Synthesis of emissions data	Medium	DOE			X		X								X			1982	3
Atmospheric processes		NOAA																	
Long-distance transport and dispersion	High	NOAA	X			X					X			X	X	X		1982	5
Global circulation of acid substances	High	NOAA	X				X				X			X		X		1980	6
Aqueous-phase conversion processes	High	NOAA	X	X			X	X			X			X		X		1980	10
Scavenging of gases and aerosols	High	NOAA	X				X				X			X		X		1980	10
Atmospheric modeling	Low	NOAA					X		X		X				X			1981	4
Deposition monitoring		DOI																	
Global and national trends networks	High	DOI	X	X	X	X		X					X					1980	10+
Improving of research networks	High	DOI	X			X	X				X				X			1980	5
Dry deposition measurement methods	High	DOI	X		X		X			X		X						1982	3
Aquatic impacts		EPA																	
State and regional water surveys	High	EPA			X	X									X			1980	4
Modeling lake and stream responses	High	EPA			X	X							X	X	X			1981	5
Tolerance and susceptibilty of lakes	High	EPA		X	X	X								X	X			1980	5
Effects on watershed productivity	High	EPA		X	X	X		X					X	X				1980	10
Identification of vulnerable life stages	Medium	EPA				X					X		X	X				1980	5
Mitigation strategies for lakes	Low	EPA		X		X					X				X			1984	5
Acidification of drinking water	High	EPA			X	X											HHS	1980	4
Monitoring drinking water quality	Medium			X	X												HHS	1983	3
Treatment of drinking water	Medium	EPA			X							X						1983	3
Mobilization of toxic metals	Medium	EPA		X	X	X							X					1982	5
Metal contamination of fish	Medium	EPA				X					X	X						1981	2

TABLE 2 (continued)

Research tasks in the National Acid Precipitation Assessment Program

Areas and specific tasks	Priority	Leading agency	Participating agencies						Contributing agencies										Duration
			NOAA	DOA	EPA	DOI	DOE	TVA	NOAA	DOA	EPA	DOI	DOE	NSF	TVA	NASA	Other	Start	(years)
Terrestrial Impacts		DOA																	
Effects on growth and productivity of forests	High	DOA		X	X	X		X					X	X				1980	10
Identification of vulnerable life stages	Medium	DOA		X							X		X					1980	10
Effects on plant metabolism	Medium	DOA		X									X	X				1982	5
Effects on forest diseases and insects	High	DOA		X							X							1982	5
Effects on growth and productivity of crops	High	DOA		X	X	X		X					X	X				1980	5
Dose–response relationships of crops	Medium	DOA		X	X								X					1982	5
Effects on crop diseases and insects	Low	DOA		X									X				HHS	1982	5
Metal contamination of crops	Medium	DOA		X									X				HHS	1982	2
Predicting soil vulnerability	High	DOA		X	X	X												1982	3
Effects on soil nutrient status	High	DOA		X	X		X							X	X			1980	5
Effects on soil buffering capacity	High	DOA		X	X							X	X	X	X			1981	5
Mechanisms and amelioration of soil impacts	Low	DOA		X														1982	5
Effects on materials		DOI																	
Effects on construction materials	High	DOI			X	X												1980	5
Costs of materials effects	Medium	DOI			X		X											1984	3
Use of protective coatings	Low	DOI			X	X												1983	3
Control technologies		EPA																	
Development of limestone injection burner	High	EPA			X		X								X			1981	4
Assessments and policy analysis		EPA																	
Computer simulation models	High	EPA			X		X		X									1980	5
Models to guide policy decisions	High	EPA			X		X		X									1980	5
Analysis of emissions dispatching	Medium	EPA			X								X		X			1982	3
Special scientific and policy assessments	High	EPA	X	X	X	X	X							X	X	X	HHS, DOS	1981	10

Table 2 outlines the research efforts in the National Acid Precipitation Assessment Program. Note that a total of 43 specific research tasks are being undertaken. For purposes of coordination and planning, these 43 tasks have been grouped into nine general categories. Research on each specific task and area of scientific work is coordinated by an Interagency Task Group consisting of scientists and program leaders from the relevant member agencies. Each task group functions under the leadership of a representative from one of the eight agencies. The task group leaders for each area of research and their institutional affiliations are listed in Table 3. Chris Bernabo of NOAA has the interagency role of executive director of the task force. He is located at the Council on Environmental Quality and his responsibilities include coordinating the efforts of the nine task groups, overseeing interagency planning, and providing liaison with the task force.

Similarly comprehensive, well-coordinated, and well-funded programs of acid rain research have been initiated by the Province of Ontario and the federal Department of Environment in Canada and by the Electric Power Research Institute in the U.S. Especially noteworthy among these efforts are the Experimental Lakes Studies initiated in northern Ontario by David Schindler et al. (1980) and the Integrated Lake-Watershed Acidification Study sponsored by the Electric Power Research Institute (EPRI, 1981; see also Drabløs and Tollan, 1980, pp. 252-267).

Future research

We have come a long way since the earliest attempts of Smith, Gorham, and Odén to alert the scientific community and the public at large to the causes and consequences of acid rain. Much has been learned both in Europe and in North America. But much more remains to be learned about the many aspects and effects of the phenomenon. The pathway that has led to our present understanding has been illuminated by the remarkable insights of a few imaginative scientists as well as those of many others who have filled lesser voids in our knowledge.

Today, public interest in acid rain research is at an all-time high in many parts of the world. The challenge for us as scientists is to satisfy that curiosity by providing a more extensive understanding of the atmospheric processes, soil transformations, vegetational changes, alterations in water chemistry, effects on materials, and physiological influences of acid precipitation (ITFAP, 1981; NAS, 1981).

Research is the key to improved understanding. Improved understanding is the key to wiser public and private decisions that relate to the use of energy and to the quality of life in our society. Let us get on with the job of learning so that the challenge of managing acid precipitation and its effects can begin as soon as possible.

TABLE 3

Task group leaders in the Federal Interagency Task Force on Acid Precipitation

Area	Task group leader
Natural sources	Dr. Daniel Albritton Environmental Research Laboratory National Oceanic and Atmospheric Administration Boulder, Colo.
Man-made sources	Dr. David J. Beecy Office of Fossil Energy U.S. Department of Energy Washington, D.C.
Atmospheric processes	Dr. John Miller Air Resources Laboratory National Oceanic and Atmospheric Administration Silver Spring, Md.
Deposition monitoring	Dr. R. J. Pickering Water Quality Branch U.S. Geological Survey Reston, Va.
Aquatic impacts	Dr. Ray Wilhour Air Pollution Effects Branch Environmental Protection Agency Corvallis, Ore.
Terrestrial imacts	Dr. Leon Dochinger Forestry Sciences Laboratory U.S. Forest Service Delaware, Ohio
Effects on materials	Dr. Ray Herrman Field Support Laboratory National Park Service Fort Collins, Colo.
Control technology	Dr. Kurt Riegel Environmental Engineering and Technology Environmental Protection Agency Washington, D.C.
Assessments and policy	Dr. Lowell Smith Program Integration and Policy Staff Environmental Protection Agency Washington, D.C.

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Chairman of the National Atmospheric Deposition Program, **Ellis B. Cowling** *is Associate Dean for Research in the School of Forest Resources at North Carolina State University (Raleigh). A significant part of his educational, research, and administrative efforts have been aimed at the development of a more adequate understanding of acid precipitation and its effects on plants, animals, surface waters, and materials in the U.S. He holds a Ph.D. degree in plant pathology and biochemistry from the University of Wisconsin and the Filosofie Doktor degree in physiological botany from the University of Uppsala in Sweden.*

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3)

Mercury Residues in Soil around a Large Coal-Fired Power Plant

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Seventy soil samples were collected on a radial grid around the Four Corners power plant. The soil samples were analyzed for total mercury using a Zeeman atomic absorption spectrophotometer. Even though the plant emits 1-2% of all the mercury released by U.S. coal-fired utilities, the soil residue levels near the plant were low and did not differ statistically from background. Relatively high concentrations were found in the samples taken west of the plant near the fly ash ponds and just east of the plant. While the fate of mercury emitted by the plant is not yet known, it is not accumulating in the soil surrounding the plant's environs.

The toxicity and hazards of mercury are well established and its distribution throughout the environment has been documented (*1*). Due to the known hazards, a number of reports have focused on the sources of mercury resulting from man's activities. The combustion of coal is often cited as a significant mercury source and various emission estimates have been calculated (*2-4*).

The amount of mercury released to the atmosphere by coal-fired electric utilities can be estimated from the amount of coal consumed using the average mercury content of the coal and a release factor. Coal combustion by the electric utilities in the United States was about 365×10^9 kg in 1975, and is projected to increase to 854×10^9 kg by the year 2000 (*5*). The mercury level in U.S. coal has been estimated from different data bases to average 1000 ng/g (*3*), 300 ng/g (*4*), 200 ng/g (*2*), and 150 ng/g (*6*). The latter figure, representing the most recent data, was compiled from the largest data base and is probably the best estimate. Not all mercury in coal is released during combustion and a reasonable atmosphere release factor appears to be 0.9 (*7-9*). Therefore, the 1975 estimated mercury release from U.S. coal-fired electric utilities totalled about 49 000 kg.

The fate of this released mercury has not been extensively studied. Klein and Russell (*10*) studied heavy metal fallout around a 650-MW coal-fired power plant equipped with a 120-m stack. They state that the soils around the plant are enriched in mercury, but present no statistical proof. Bolton et al. (*9*) conducted a major study of trace elements at the 870-MW coal-fired Allen Steam Plant and found no significant evidence of elemental accumulation. Cannon and Anderson (*11*) reported on elements around the Four Corners Power Plant in New Mexico, but showed no significant elevation of mercury levels in plants or soil. The lack of statistical treatment, the small number of samples involved, and the terrain and background levels of mercury limit the usefulness of these studies. For these reasons, and as a part of a project to select a biological monitor, an investigation was conducted to determine whether a mercury gradient exists around coal-fired power plants.

The selection of a power plant was based upon the estimated potential for contamination. This report focuses on the soil sampling portion of this study. All samples were collected in December 1974.

The Four Corners Power Plant was selected because of its size (>2150 MW), its coal consumption (6.3×10^9 kg/yr), its length of operation (since 1963), and its relatively short stacks (two are 76 m and two are 91 m). In addition, the surrounding arid terrain (15 to 20 cm/yr precipitation) is undisturbed by cultivation and the soils are low in most elements including mercury (*11*).

Estimates of the mercury concentration of the coal burned by the plant vary considerably. Based upon a very limited sampling, Billings et al. (*7*) estimated the mercury concentration to be 300 ng/g. Green and Robinson (*12*) sampled five coal blending piles as well as the mine and found the average mercury concentration to be 375 ng/g. However, the U.S. Geological Survey analyzed 21 coal samples from the mine and reported an average value of 60 ± 20 ng/g (*13*). The latter analyses were made using accepted modern methods, although it was recognized that the analyses might be slightly low owing to mercury loss during drying and grinding. Thirteen samples of Four Corners coal were also analyzed by the Lawrence Radiation Laboratory for mercury. The concentrations varied from 67 to 390 ng/g with a mean of 179 ng/g (*14*). Data presented by the Arizona Public Service show 80 ng/g of mercury in the coal. If the true mean of these data is assumed to be between 100 and 200 ng/g, it can be calculated that the Four Corners Power Plant emitted roughly 1-2% of all mercury released by coal-fired power plants in the United States for 1974.

Sampling and Analysis

The sampling design selected was a radial grid employing 16 evenly spaced radii and five approximately logarithmically spaced circles, concentric around the power plant (Figure 1). The radii of the circles (A-E) were 1.0, 2.9, 6.8, 14.6, and 30 km. From the 80 sites on the grid, only 70 composite soil samples were collected since some sites fell on stripped land or in the cooling pond. Each sample was a composite of 10 subsamples collected 15 m apart. The upper 1 to 2 cm of soil was collected by trowel and stored in pint glass jars.

The samples were dried at 60 °C and sieved to 10 mesh (2 mm), and 5 replicates of 150 to 200 mg were analyzed directly using an Isotope Zeeman atomic absorption spectrometer (*16*). The Zeeman uses a 900 °C furnace for mercury analyses and no digestion procedures are required. The geometric mean of the replicate standard deviations (a measure of analytical precision) was 1.9 ng/g with a range of 0.2 to 21 ng/g. The standard deviation of the replicates could probably have been reduced if the samples had been pulverized to homogenize the sample. Eleven percent of the samples were randomly selected and reanalyzed for quality control purposes. Of the eight reruns, seven were within ±1 ng/g (0.9% deviation) of the original value while the eighth was off by 7 ng/g (23% deviation).

The instrumental calibration curve was calculated by regressing nanograms of mercury in six liquid standards with the instrumental readout in millivolts. The regression was verified using a U.S. Environmental Protection Agency liquid standard and two National Bureau of Standards standard reference materials, orchard leaves (no. 1571) and coal (no. 1632). The lower limit of detection was less than 1 ng.

Results

The overall arithmetic mean for the 70 samples was 16 ng/g with a range of 6 to 45 ng/g and an overall standard deviation of 6.7 ng/g (see Table I). In testing the data for normality, significant skewness and kurtosis were detected. These deviations from normality were eliminated from all statistical

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Table I. Mean Mercury Concentration in Soil by Site (ng/g)

radius no.	radius direction	concentric circle[a] A	B	C	D	E	mean	SD
1	NNE	–[b]	6	12	10		9.3	3.1
2	NE	45	9	12	13 (14)	19	20	15
3	ENE	30 (37)[c]	13	13	11 (10)	9	15	8.4
4	E	22	11 (11)	10	11	9	13	5.3
5	ESE	21	13	10	10	12	13	4.5
6	SE	16	14	10	14	11	13	2.4
7	SSE	23	-	9	6	14	13	7.4
8	S	12 (12)	20	-	14	11	14	4.0
9	SSW	14	20	12	-	12	14	3.8
10	SW	15	26	14	21	14	18	5.3
11	WSW	27	22	23	14 (14)	21	21	4.7
12	W	20	24	15 (16)	13	12	17	5.1
13	WNW	24	23	18	22	17	21	3.1
14	NW	16	15	16	26	11	17	5.5
15	NNW	-	14 (15)	13	-	-	14	0.7
16	N	-	7	23	30	-	20	12
mean		22	16	14	15	13	16	
SD		8.7	6.3	4.4	6.8	3.7		6.7

[a] Radii of circles A–E are 1.0, 2.9, 6.8, 15, and 30 km, respectively. [b] –, no sample. [c] Numbers in parentheses represent a reanalysis of the sample.

nalyses by a logarithmic transformation of the data.

Initially the data were subjected to a two-way analysis of ariance test using the five replicate analyses of each sample. 'he residual error was therefore a measure of laboratory recision only. Since the computer program could not ac-ommodate missing samples, six of the radii were dropped ·om the data analysis. The analysis of variance on the ten ;maining radii showed the following:

(a) A highly significant difference between circles (i.e., soil ıercury levels are related to distance from the power lant).

(b) A highly significant difference between radii (i.e., soil ıercury levels are related to compass direction from the power lant).

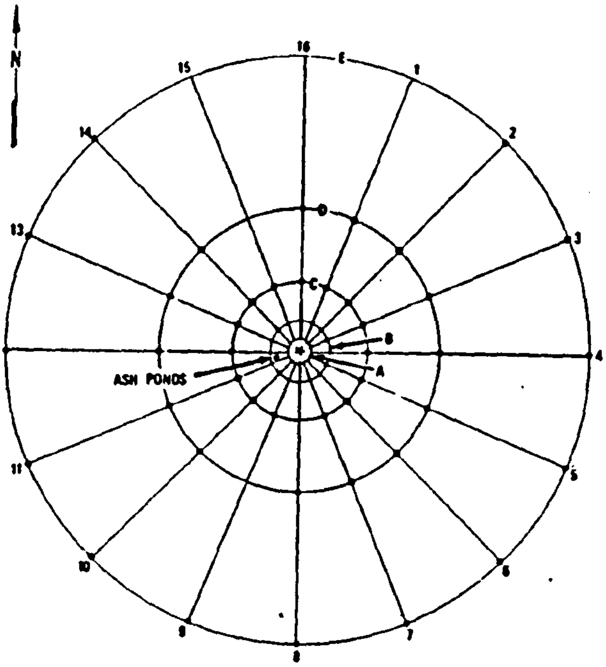
(c) A highly significant interaction effect (i.e., the type of 'fect due to radii varies significantly from circle to circle, or ıe type of effect due to circles varies significantly from radii ı radii).

Attempts at subdividing the data to eliminate the interac-ɔn effects were not successful.

Since it was possible that the analytical error was insignif-ant relative to field sampling error, a second approach was tempted. A nested two-way analysis of variance was em-oyed in which radii were grouped in twos or fours, which ovided a residual error term composed of both analytical d field sampling errors. The grouping of radii was conducted ıce it was felt that small changes in compass direction would ve an insignificant effect on residue levels. The results of ese analyses of variance were similar to those encountered eviously. Highly significant effects due to circles, radii, and .eraction were again discovered. Since the interaction effect .ıld not be eliminated, it must be concluded that the dis-bution of mercury residues around the plant is very com-·x. Therefore, no statement based on statistical analysis can made concerning the relationship of mercury residue levels ative to direction or distance from the plant.

These results are in agreement with a study by Horton et (17). They detected a significant negative correlation when nparing mercury levels in soil vs. distance from the power nt. Their analysis, however, did not encounter problems h interaction.

n an attempt to discern a distribution pattern of mercury, a plot was made of mean mercury residues by site. Isopleths of mercury residue levels were then plotted as shown in Figure 2. Aside from a couple of small scattered sites exceeding 20 ng/g, there are three areas with levels exceeding 20 ng/g. The area due west of the plant may be related to the fly ash ponds located in this section. The 25 ng/g high to the north-north-west cannot be accounted for by the wind direction, but another power plant (350 MW, 13 k north-northeast) is located in that area. The samples with the highest mercury levels detected were collected from an undisturbed island located in the cooling pond, sites 2A and 3A.



RADII OF CIRCLES- 1.0, 2.9, 6.8, 14.6 & 30.0 km.

* POWER PLANT
• SITES SAMPLED

Figure 1. Soil sampling sites around the Four Corners Power Plant

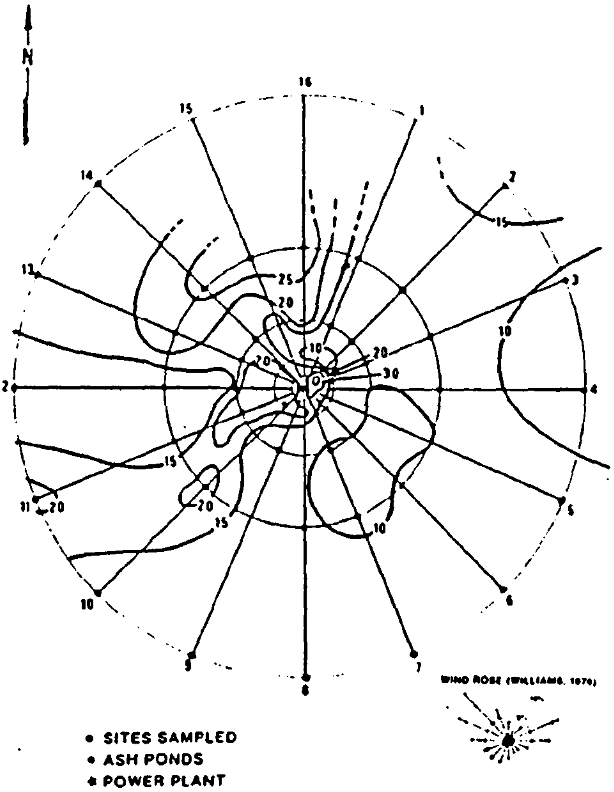


Figure 2. Distribution of mercury residues in soil around Four Corners Power Plant (ng/g)

Discussion

The 70 soil samples collected on a radial grid around the Four Corners Power Plant probably represent the most intensive sampling effort to date at that site. No statistically significant elevation of mercury residue levels was detected although some distribution patterns are evident. The levels of mercury detected are quite low, but in good agreement with soil data compiled by Cannon and Anderson (*11*). They reported an average value of 20 ng/g compared to 16 ng/g in this study. Shacklette et al. (*19*) reported the average mercury concentration in soil in the Western United States to be 83 ng/g, which is nearly twice as high as the maximum and 5 times higher than the mean value reported here.

The question then arises as to the fate of mercury emissions from the plant. The estimated annual release of mercury through stack emissions is 850 kg based upon a release factor of 0.9, a coal consumption of 6.3×10^9 kg/yr, and a mercury concentration of 150 ng/g. This value is just within Arizona Public Services' (*15*) emission estimate of 76 g/h plus or minus a factor of 2 for the plant operating at full load. Converting and using an operating factor of 70%, their estimate becomes 466 kg of mercury/yr. The total amount of mercury emitted by the plant since it began operating is about 6000 kg.

If all this mercury were evenly deposited within 5 or 10 km of the plant and remained in the top 2.54 cm of soil, the average soil concentration would have increased by 200 or 50 ng/g, respectively. However, the average mercury levels in soils around the power plant are considerably below these figures. These data agree with Lockeretz's deposition model (*20*), which indicates that the rate of mercury deposition from power plants is low compared to background rates. Apparently, the emitted mercury is being deposited over a much larger area or is being rapidly revolatilized in aerobic terrestrial environments (*21*).

The results of this study appear to conflict with data from a recent study by Anderson and Smith (*22*). Their report on coal-fired power plants states that the mercury residue levels in soils downwind from the plant are significantly higher than those upwind. This difference might, however, be due to the reported change in soil type. No evidence is presented to indicate that residue levels decrease with distance from the plant even though samples were collected from as far away as 18 km.

Conclusions

Detailed soil sampling and analyses for mercury residues indicate no significant differences in mercury residue levels in soils within 30 km of a large coal-fired power plant. These data are in general agreement with other studies which have reported little if any accumulation of mercury in soil or other media (*9, 11, 20*). This study fails to confirm the existence of the often cited potential problem of mercury accumulation around coal-fired power plants.

The emissions of mercury from power plants should also be compared with other sources of mercury release. Van Horn (*2*) indicates that U.S. coal-fired utilities emit 9% of all industrial releases to the atmosphere in the United States. Using the data of others, he also estimated that 1×10^6 kg/yr of mercury is volatilized from natural sources in the United States. From these data it was calculated that, in 1974, the emissions from coal-fired power plants amounted to about 4% of the natural degassing mercury loss.

Acknowledgment

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TECHNICAL REPORTS

Competitive Adsorption of Heavy Metals by Soils[1]

H. A. ELLIOTT, M. R. LIBERATI, AND C. P. HUANG[2]

ABSTRACT

The competitive adsorption of Cd, Cu, Pb, and Zn from 0.025 *M* $NaClO_4$ solutions onto four soils with differing chemical properties was investigated with batch adsorption experiments. For two mineral soils, adsorption under acidic conditions (pH 5.0) followed the sequence Pb > Cu > Zn > Cd, which corresponds to the order of increasing pK for the first hydrolysis product (e.g., $PbOH^+$) of the metal ions. In contrast, the order of selectivity for two soils containing 20 to 40 g kg^{-1} organic C was Pb > Cu > Cd > Zn, suggesting that organic matter (OM) increased Cd retention preferentially over that of Zn. When accompanied by a sizable reduction in cation exchange capacity (CEC), extraction of soil OM markedly reduced adsorption of all four metals. However, only Cd and Cu adsorption were appreciably smaller for a soil that maintained a sizable CEC following OM removal. Lead, and possibly Zn, adsorption by soils with substantial inorganic exchange sites may be unresponsive to organic waste amendments. For Cd and Cu, increased soil OM should restrict mobility and bioavailability, at least under acidic conditions where soluble metal complex formation is limited.

Additional Index Words: **Cd, Cu, Pb, Zn, selectivity sequence, organic C.**

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Understanding the processes governing the migration and plant availability of trace metals in soils is essential for predicting the environmental impact of spreading metal-containing wastes on agricultural land. The adverse effects of heavy metals are inseparably related to the soil's ability to adsorb and retain such elements. Rational management of land disposal practices is hindered by an incomplete understanding of the processes regulating the partitioning of trace elements between the solution and solid phases.

Although bivalent transition metal cations exhibit a similar pH-dependent adsorption behavior, the extent of adsorption at a given pH varies widely among metals. For equal initial solution metal levels, adsorption by acidic subsoils from the Atlantic Coastal Plain was found to follow the sequence Pb > Cu > Zn > Cd (Elliott et al., 1986). The same sequence was documented for other soils (Biddappa et al., 1981) or inferred from leaching experiments (Tyler and McBride, 1982; Scokart et al., 1983). This led some to conclude that Cd would be relatively more bioavailable than would other trace metals in soil systems (Baker, 1985). The validity of this selectivity series for the majority of soils is questionable, however, due to the range of types and amounts of clays, oxides, and organic matter found in soils. Each soil constituent has its own metal-sorbing properties, resulting in dissimilar adsorption sequences (Table 1).

Because of these differences, guidelines dictating maximum permissible metal loadings to soils would be more meaningful if a wider range of metal- and soil-specific factors were included in their development. A routinely measured soil property has been sought as a simple, reliable predictor of a soil's ability to restrict heavy metal movement and availability. Current guidelines and regulations for disposal of municipal sludges specify maximum allowable metal loadings based on soil textural class (Baker et al., 1985) or cation exchange capacity (USEPA, 1979). However, these parameters are unlikely to be reliable guides for predicting heavy metal mobility in soils (Korte et al., 1976; Harter, 1979). Other important retention factors such as surface area, Fe oxides, and organic matter (OM) have not been incorporated to any significant degree into criteria for land disposal of metal-containing wastes.

Soil organic matter has been of particular interest in studies of heavy metal retention by soils, because of its significant impact on cation exchange capacity (CEC) and more important, the tendency of transition metal cations to form stable complexes with organic ligands. In a study with 24 British soils, McLaren and Crawford (1973) concluded that the majority of the "available" Cu exists in an organically bound form. Udo et al. (1970) noted a strong correlation between total soil Zn and OM content, and concluded it was an important soil component

Table 1. Heavy metal affinity series for soil components.

Material	Relative affinity	Reference
Al oxides (amorphous)	Cu > Pb > Zn > Cd	Kinniburgh et al. (1976)
Geothite	Cu > Pb > Zn > Cd	Forbes et al. (1974)
Fe oxides (amorphous)	Pb > Cu > Zn > Cd	Kinniburgh et al. (1976)
Mn oxides	Cu > Zn	Murray (1975)
Fulvic acid (pH 5.0)	Cu > Pb > Zn	Schnitzer and Skinner (1967); Schnitzer (1969)
Humic acid (pH 4–7)	Zn > Cu > Pb	Verloo and Cottenie (1972)
Humic acid (pH 4–6)	Cu > Pb > Cd > Zn	Stevenson (1977)

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responsible for Zn retention in calcareous soils. Although a lack of correlation between total organic matter and the retention of Pb, Cu, Zn, and Ni may be found, OM content can be useful in explaining differences in retention between surface and subsurface samples of the same soil (Harter, 1983; Elliott and Liberati, 1981).

In contrast to a simple exchange phenomenon where retention is determined by valence and ionic radius, selectivity by organic matter depends on the specific electrochemical and structural properties of the ligand and metal ion. Several investigators have expressed the binding strength of metal-soil OM interactions in terms of stability constants between metal ions and extracted OM fraction (Schnitzer, 1969; Stevenson, 1976; Brady and Pagenkopf, 1978; Takamatsu and Yoshida, 1978). Although such techniques have been criticized due to adverse changes that occur during extraction (Zunino et al., 1975), they provide a rough estimate of relative metal binding strength. Given the range of selectivity sequences documented (Table 1), the relative binding strength depends on the nature of the organic matter and the system pH.

In the present study, the pH-dependent adsorption selectivity sequence of Cd, Cu, Pb, and Zn was documented for two mineral soils as well as two soils containing appreciable OM. The OM was then removed from the latter soils and the heavy metal adsorption properties of the treated samples were compared with those of the whole soils. The principal objective was to ascertain the metal retention sequence for each soil and explore its relationship to organic matter content. The findings were used to speculate on the role of organic matter and its influence upon mobility and bioavailability of heavy metals in land applied sludge.

MATERIALS AND METHODS

Selected properties of the four soils used in this study are given in Table 2. The Christiana (Typic Paleudulfs), Groveton (Typic Haplorthods), and Pocomoke (Typic Umbraquults) soils were collected as part of the NE-96 regional research project; characterization methods and additional soil properties can be found in Johnson and Chu (1983) and Harter (1979). Details on the chemical and physical properties for the Dothan soil (Plinthic Paleudults) have been described by Sparks et al. (1980). The specific surface area of the soils were evaluated as part of this research by N_2 gas adsorption and using the Brunauer, Emmett, Teller (BET) equation.

Batch adsorption experiments were performed by adding appropriate amounts of metal perchlorate stock solutions and distilled-deionized water to obtain 100 mL of solution containing 10^{-5} *M* of each metal (Cd, Cu, Pb, Zn) in 0.025 *M* $NaClO_4$ background electrolyte. One gram of soil was added just before pH adjustment using 0.1 and 1.0 *M* $HClO_4$ or NaOH. During pH adjustment, the sample bottles were purged with N_2 gas to minimize pH fluctuations due to CO_2 equilibrium and to suppress formation of metal carbonates in solution. The samples were then agitated in a temperature-controlled water bath at 25 °C for 24 h, a time previously found to be sufficient for equilibration (Elliott and Liberati, 1981). Final equilibrium pH values then were determined and a portion of the sample was centrifuged for 15 min at 1500 rpm. The concentration of the metals in the supernatant was determined by flame atomic absorption spectroscopy. The amount of metal absorbed by the soil was calculated as the difference between the amount of metal added and that removed after 24 h of equilibration.

Table 2. Properties of the soils.

	Christiana B2	Dothan B25tpl	Pocomoke Ap	Groveton Ap
Textural class	silty clay loam	sandy clay	loamy sand	silt loam
Sand, g kg^{-1}	195	498	794	204
Silt, g kg^{-1}	521	92	156	730
Clay, g kg^{-1}	284	410	50	66
Organic C, g kg^{-1}	0.5	1.6	20.5	42.5
DCB† iron, g kg^{-1}	47	36	trace	24
CEC, cmol(+) kg^{-1}	6.4	9.1	10.7	21.2
pH, 1:1 H_2O	4.6	4.7	4.2	6.2
Surface area, m^2 kg^{-1} × 10^{-3}	12.7	34.2	3.9	5.1

† Dithionite–citrate–bicarbonate extraction procedure.

The organic matter was removed from the soils by treatment with H_2O_2 following the method of Jackson (1956). The soils were then washed three times by shaking for 30 min in distilled-deionized water and centrifuged. The samples were air-dried prior to weighing for use in the batch experiments.

RESULTS AND DISCUSSION

The pH-dependent adsorption behavior of Cd, Cu, Pb, and Zn on the four soils is shown in Fig. 1, 2, 3A, and 4A. Although the extent of adsorption varied among all metals, a common pH-dependent trend, frequently observed for sorption of metals from dilute aqueous solutions (Shuman, 1975; Kuo and Baker, 1980; Harter, 1983), was observed. For all metals, the magnitude of adsorption varied directly with suspension pH. There is no general agreement on a single mechanism responsible for this behavior, but strong adsorption of metal hydroxo

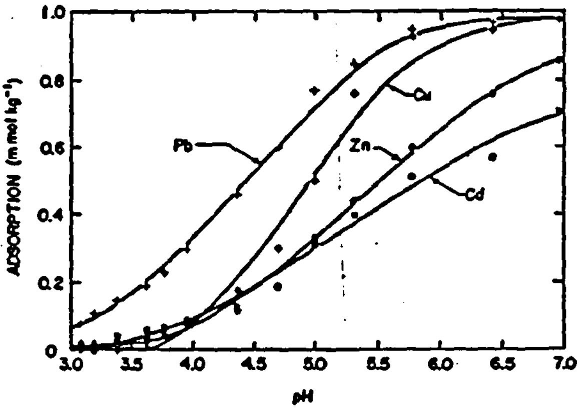

Fig. 1. The pH-dependent adsorption of heavy metals on the Christiana soil.

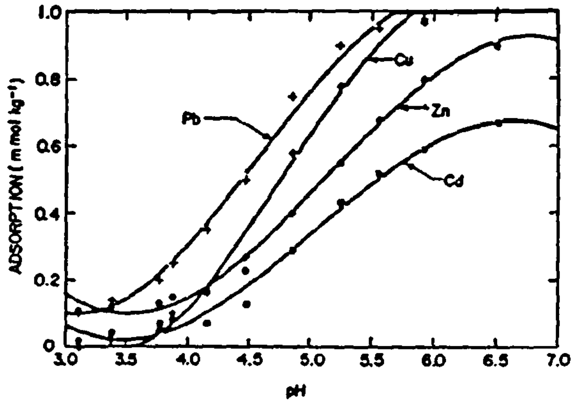

Fig. 2. The pH-dependent adsorption of heavy metals on the Dothan soil.

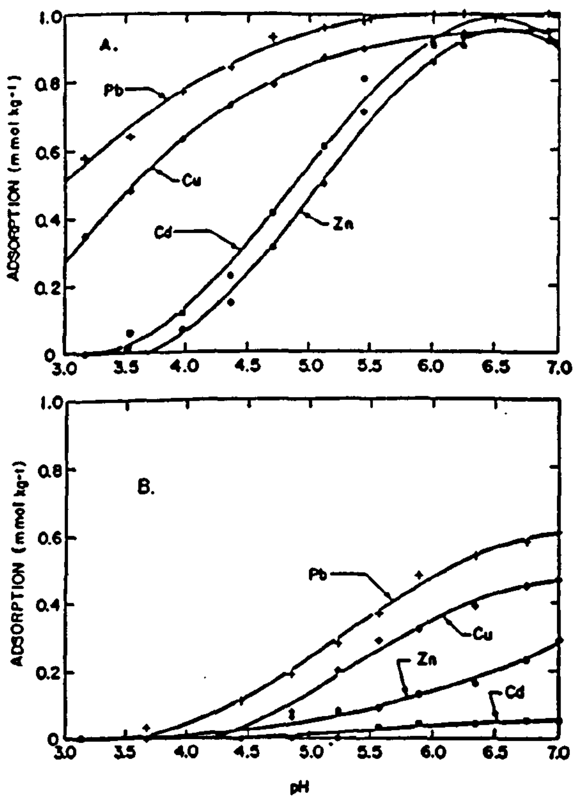

Fig. 3. The pH-dependent adsorption of heavy metals on Pocomoke: (A) whole soil and (B) following removal of organic matter.

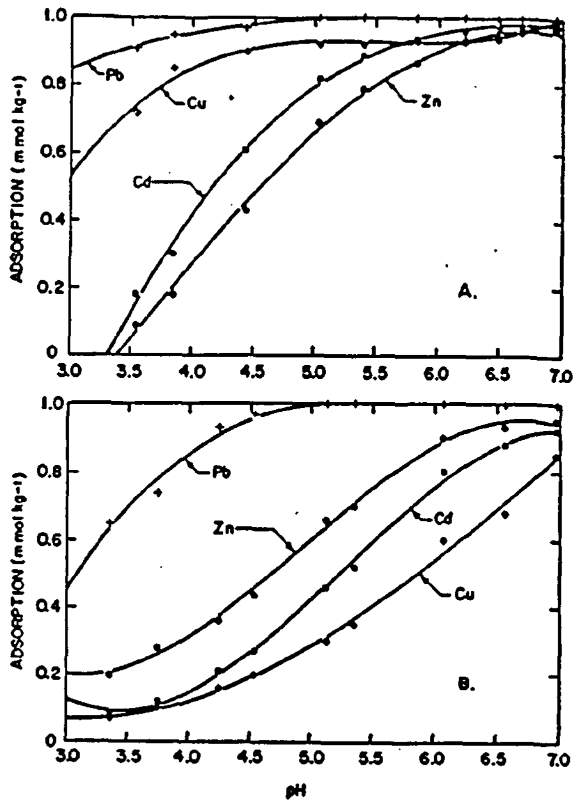

Fig. 4. The pH-dependent adsorption of heavy metals on Groveton: (A) whole soil and (B) following removal of organic matter.

complexes (Forbes et al., 1974), hydrolysis of Al on exchange sites (Cavallaro and McBride, 1980), competition by protons for sites (Newton et al., 1976), and acid-catalyzed dissolution of reactive oxide sites (Elliott and Huang, 1979) may be involved.

The relative affinity of cations for adsorbate surfaces has been measured by comparing the pH at which 50% of the original solution metal is adsorbed (Kinniburgh et al., 1976). Without extrapolation (e.g., Fig. 3B and 4A), this criterion would be unsuitable for the data obtained in this study. Alternately, we could select a pH level at which heavy metal adsorption could be compared. Low pH values (<4.0) are unsuitable because of weak metal retention for the Christiana and Dothan soils (Fig. 1 and 2). As the pH is increased, aqueous metal cations hydrolyze, resulting in a suite of soluble metal complexes according to the generalized expression for divalent metals:

$$M^{2+}(aq) + nH_2O \rightarrow M(OH)_n^{2-n} + nH^+ . \quad [1]$$

This hydrolysis may be accompanied by precipitation of metal hydroxides, which is experimentally indistinguishable from removal of metals from solution by adsorption. This masking effect of precipitation precludes comparison of the relative sorption affinities at near-neutral conditions. Thus, for the purposes of this study, a pH of 5.0 was selected for assessing a soil's metal selectivity preference.

Heavy metal selectivity for the Christiana and Dothan soils (Fig. 1 and 2) followed the sequence Pb > Cu > Zn > Cd while the order for the Pocomoke and Groveton (Fig. 3A and 4A) was Pb > Cu > Cd > Zn. A common feature for all soils is the relatively strong preference for both Pb and Cu. On the other hand, Zn and Cd are more weakly adsorbed and the Christiana and Dothan preferred Zn over Cd while the Pocomoke and Groveton exhibited greater retention of Cd relative to Zn.

It is interesting to note that both the selectivity sequence and the relative extent of adsorption were similar for Christiana and Dothan. This occurred despite a positive surface charge on the Dothan soil and a negative surface charge on the Christiana soil at pH 5.0. The zero points of charge (ZPCs) are roughly 6.0 and 2.0 for the Dothan and Christiana soil, respectively (Elliott, 1983). Clearly, for the Dothan soil adsorption is taking place at the structural cation exchange sites, even despite an unfavorable surface charge. Kuo and Baker (1980) also reported sorption of Cu, Zn, and Cd at pH levels well below the ZPC of acid soils.

The strong retention of Pb and Cu relative to Cd and Zn appears to be a common characteristic of soil components (Table 1), whole soils (Biddappa et al., 1981; Scokart et al., 1983), and sediments (Giblin et al., 1980). Biddappa et al. (1981) found most of the Pb and Cu in alluvial soils of Japan were present in an unextractable form, while Zn and Cd existed predominantly in the water soluble or readily exchangeable fractions. Lead and Cu deposited near a smelting facility remained fixed in the surface layers while Cd and Zn were more mobile, particularly for pH <6.0 (Scokart et al., 1983). In a study investigating the fate of metals applied with sludge to a salt marsh, Giblin et al. (1980) found nearly 100% of the Pb and Cu but only half of the Zn and 35% of the Cd were retained in the sediments. Because of the strong retention of Pb by soils, phytotoxic effects from Pb uptake are rare (Chaney, 1980).

As all of the metals were bivalent and had the same original solution levels, a correlation between ionic size and adsorption selectivity might be expected. For ion exchange materials, the strength with which cations of equal change are held is generally inversely proportional to the unhydrated radii. Thus, the predicted order of selectivity based on unhydrated radii is Pb^{2+} (0.120 nm) > Cd^{2+} (0.097 nm) > Zn^{2+} (0.074 nm) > Cu^{2+} (0.072 nm). The selectivity sequences observed for these soils support previous findings (James and Healy, 1972; Kinniburgh et al., 1976) that the unhydrated radius is limited as a predictive index for adsorption.

If the Christiana and Dothan soils are considered analogous to simple oxides, the observed adsorption sequence (Pb > Cu > Zn > Cd) is explicable in terms of the specific adsorption of metal hydrolysis products. For adsorption of hydrolyzable metals onto various oxides, the pH at which onset of adsorption occurs may be related to the pK of the first hydrolysis product of the particular metal (Forbes et al., 1974) where K is the equilibrium constant for the reaction in Eq. [1] and where $n = 1$. Ranking the metals in order of increasing pK values (Baes and Messmer, 1976):

$$\mathrm{Pb}\ (6.2) > \mathrm{Cu}\ (8.0) > \mathrm{Zn}\ (9.0) > \mathrm{Cd}\ (10.1)$$

also corresponds to the relative adsorption affinities observed for these soils. This suggests that the metal hydroxo complexes (e.g., MOH$^+$) are appreciably more adsorbable than free metal cations (M^{2+}). It is not known with certainty why hydroxo complexes are more strongly adsorbed than their unbound counterparts. James and Healy (1972) suggest addition of an $-$OH group reduces the free energy requirement for adsorption since removal or rearrangement of the absorbate hydration sheath is through to precede adsorption. This adsorption behavior, documented widely for oxide surfaces, also appears to satisfactorily explain the observed adsorption sequence for the two mineral soils Christiana and Dothan.

For the Groveton (Fig. 3A) and Pocomoke (Fig. 4A) soils, a reversal in the selectivity for Cd and Zn was observed, with Cd adsorbed to a greater extent. Based on their soil properties (Table 2), soil organic matter may be suspected in this phenomenon. Whereas the Christiana and Dothan soils are essentially devoid of OM, the Groveton and Pocomoke soils have 42.5 and 20.5 g organic C kg^{-1} (Table 2), respectively. Tyler and McBride (1982), however, found the order of metal mobility (Cd > Zn ≫ Cu) in column leaching studies to be the same for a peat soil (510 g C kg^{-1}) as for three mineral soils.

The observations in this study would be readily explained if the sorption sites on the organic matter preferentially bound Cd over Zn. Stability constants are available for ligands containing carboxylate and amino functional groups that are largely responsible for the metal-binding properties of organic material found in soils (Stevenson, 1977) and sewage sludge (Tan et al., 1971). Unfortunately, the literature provides no consistent trend for the relative stabilities of such complexes. Schnitzer and Skinner (1966) state that according to the scheme developed by Irving and Williams (1948), Zn should form more stable complexes than Cd, irrespective of the nature of the ligand. Yet, one can select certain ligands (e.g., acetate, EDTA) to which Cd binds more strongly than Zn, and others (e.g., citrate, ethylenediamine), which form more stable complexes in dilute aqueous solutions with Zn than with Cd (Tyler and McBride, 1982).

Table 3. Effect of OM removal on selected soil properties.

	Pocomoke Ap	Pocomoke Ap-OM	Groveton Ap	Groveton Ap-OM
Organic C†, g kg^{-1}	26	0.1	41	2
CEC, cmol(+) kg^{-1}	10.7	1.1	21.2	8.4
Surface area, m^2 kg^{-1} × 10^{-4}	3.90	0.58	6.05	13.59

† Organic C values provided for NE-96 regional research project soils (Table 2) differ slightly from those determined as part of this study.

The hypothesis that soil OM favors Cd retention over that of Zn would be strengthened considerably if Cd formed stronger complexes with fulvic or humic acid extracts from soils. Numerous investigations have focused on the kinetics and thermodynamics of organo-metallic interactions in soils (Schnitzer and Skinner, 1966; 1967; Schnitzer, 1969; Rashid, 1974; Stevenson, 1976; Bunzl et al., 1976; Brady and Pagenkopf, 1978; Takamatsu and Yoshida, 1978). While most studies have investigated either Cd or Zn alone, three studies considered both Cd and Zn. Bergseth and Stuanes (1976), investigating the selectivity of humic material for metals, concluded that Cd and Zn were bound about equally. Similarly, Bunzl et al. (1976) found nearly equal distribution coefficients for Cd and Zn adsorption by peat in the pH range 3.5 to 4.5. Stevenson (1977) used a potentiometric titration method to study transition metal complexes of humic acids and reported that the order of stability was Cu > Pb ≫ Cd > Zn. This stronger binding of Cd over Zn held for three humic acids from different sources.

In this study, OM was removed from the Groveton and Pocomoke soils by H_2O_2 oxidation. Table 3 shows this treatment was 95 and 99% efficient in removing organic C from the Groveton and Pocomoke soils, respectively. Heavy metal adsorption on the treated soils is shown in Fig. 3B (Pocomoke) and 4B (Groveton). Removal of OM modified the selectivity sequences from both soils, the relative affinity on the treated Groveton soil following the order Pb > Zn > Cd > Cu, while the order for the Pocomoke, Pb > Cu > Zn > Cd, was similar to the Christiana and Dothan whole soils. In both cases, OM removal reversed the relative adsorbability of Cd and Zn, with Zn being more preferred. This added credibility to the hypothesis that soil OM favors retention of Cd over Zn.

When the magnitude of response to OM removal was compared, the two soils behaved quite differently. For the Pocomoke soil, OM extraction markedly reduced adsorption of all four metals (Fig. 3A and 3B). In fact, below pH 4.5, nearly all metal adsorption capacity was lost after OM was extracted. This substantial suppression in metal binding capacity was also noted for the Groveton soil (Fig. 4B), but was limited to Cu and Cd. A minor effect was noted for Pb and Zn retention.

This dissimilar behavior of these two soils can be interpreted in terms of the impact of OM extraction on important adsorption-related properties. Extraction of OM reduced the CEC of the Pocomoke soil by 90%, while the treated Groveton soil lost only 40% of its original CEC (Table 3). For the Pocomoke, a loamy sand soil, OM represents the bulk of the metal-adsorption sites. The dramatic decrease in the surface area of the Pocomoke soil (Table 3), supports this claim. With the OM removed, the Pocomoke is primarily sand. Himes and Barber (1957) similarly reported the Zn retention capacity of a sandy loam soil was destroyed by OM oxidation but not altered by removal of hydrous silicates. The adsorption properties of this Pocomoke soil arises largely from its organic content, confirming the earlier conclusion of Tyler and McBride (1982) that OM can retard heavy metal movement in soils even under very acidic conditions.

In contrast to Pocomoke, several components of the Groveton soil are substantial contributors to the overall CEC, as indicated by roughly 40% of the CEC remaining after OM removal (Table 3). The Groveton soil has a finer texture and a substantial Fe-oxide content, and both tend to hinder movement of trace elements through soils (Korte et al., 1976). The OM removal more than doubled the surface area of the Groveton. Because OM often aggregates and cements soil particles, its elimination increases surface area. Since separation of mineral and organic fractions unblocks the exchange sites on mineral surfaces (Bohn et al., 1979), the percentage of the CEC change due to unavailable OM sites is difficult to assess. This CEC remaining after OM removal, however, seemed to be able to accommodate as much Pb and Zn as the nearly threefold CEC of the whole soil (Fig. 4A and 4B).

While Pb and Zn adsorption remained relatively constant following OM removal from the Groveton soil, Cu and Cd adsorption decreases roughly 65 and 38%, respectively, at pH 5.0. The competitive disadvantage caused by OM extraction suggests that the organic adsorption sites preferentially bind Cu and Cd. This fact is widely accepted for Cu because the well-established Irving-Williams rule predicts that Cu forms the most stable organic complexes among the bivalent transition metal cations. Hodgson et al. (1966) found that 98 to 99% of the Cu in soil solutions displaced from calcareous soils was bound as organic complexes and that Zn was complexed to a much lesser degree. The ability of certain soils to adsorb Cu and Cd was found to correlate with high soil OM (Petruzzelli et al., 1978). Even under acid conditions, OM can greatly retard Cd movement in soils (Tyler and McBride, 1982).

The Groveton response to OM removal was puzzling because Cu retention was less than that of Zn and Cd (Fig. 4B). The OM extraction was expected to yield the same sequence (Pb > Cu > Zn > Cd) as the Christiana (Fig. 1), Dothan (Fig. 2), and extracted Pocomoke (Fig. 3B) soils. In view of the documented sequence for pure Fe oxides (Table 1), it seems unlikely that the substantial Fe content of the Groveton (Table 2) differentially favored retention of Cd and Zn above that of Cu. The extraction procedure did not totally remove OM from the Groveton soil (Table 3), leaving perhaps partially oxidized fragments of OM capable of forming soluble complexes with Cu. Since complexation tends to reduce heavy metal adsorption by soils (Elliott and Denneny, 1982), this could help explain the relatively low Cu retention compared to Zn and Cd.

CONCLUSIONS

These findings have significance for land disposal of metal-containing sludges. A major portion of the OM present in stabilized sewage sludge resists decomposition in soils (Terry et al., 1979) and resembles humified OM (Gerritse et al., 1982). Codisposal of organic wastes and heavy metals appears to differentially affect the partitioning of the metals between the solid and soil solution phases. The heterogeneity of surface adsorption sites of the unamended soil is very important. Gerritse et al. (1982) concluded that for typical sludge rates, the impact of added organic matter on the adsorption capacity of many elements will be minimal. However, the lowest OM content of the soils described in their work was 25 g kg^{-1}. For siliceous soils essentially devoid of OM, additions of OM should enhance retention of most heavy metals under acidic conditions (Fig. 3A and 3B). Thus, when mineral soils are amended with heavy metals in a sewage sludge matrix, metal movement is greatly restricted, compared to the observed leaching for metal salt additions (Tyler and McBride, 1982). This work suggests that the added OM will enhance Cd retention to a greater degree than Zn. Soon (1981) did, in fact, find that sludge OM elevated the Cd sorption capacity of soil. This study supports the suggestion of Baker and Chesnin (1975) that biological activity leads to a progressive enrichment of Cd relative to Zn during soil development.

When metal retention properties arise from multiple components within the soil, a more complex behavior is observed. For soils with both structural and Fe-oxide adsorption sites, Pb retention may be relatively unaffected by OM additions (Fig. 4A and 4B). The work of Sposito et al. (1982) tends to support this, because they found that sludge application did not change the percentage of Pb present in the NaOH-extractable ("organic") soil fraction. Other researchers have documented a lack of correlation between Pb adsorption (Harter, 1979) or mobility (Scokart et al., 1983) and the amount of OM in a soil. A similar behavior may exist for Zn (Fig. 4A and 4B), but evidence based on the redistribution of Zn following sludge additions (Sposito et al., 1982) and the effect of OM on Zn binding (Himes and Barber, 1957; Scokart et al., 1983) is mixed.

Finally, it should be realized that these data apply for acid conditions where adsorption is more important than precipitation of solid phases (oxides, hydroxides, carbonates, etc.) in removing metal ions from solution. For near neutral and alkaline soils, solubility and complexation reactions (Elliott and Denneny, 1982) may be superimposed on adsorption processes, thereby complicating prediction of the relative retention of heavy metals.

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DUST EMISSION, ITS QUANTITY AND COMPOSITION, DEPENDING ON DUST COLLECTOR, COAL QUALITY AND OTHER FACTORS

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ABSTRACT

Dust emission measurements have been carried through at Danish coal-fired power stations. Investigations show that modern electrostatic precipitators can meet Danish emission standards even for high resistivity ash.

Modern electrostatic precipitators can reduce particulate emissions with a factor 10-20 compared to older precipitators.

Trace metals that are very strongly attached to the finest particulates (As, Cd, Mo, Pb etc.) show less reduction in emission.

INTRODUCTION

In these years focus is to a high degree drawn to the emission from the still growing number of coal-fired plants, and especially the emission of particulates and trace metals has had great importance in the debate.

Due to the high ash content in coal, effective dust collectors are necessary by coal-fired boilers. Washing of the coals in order to reduce the ash content will quite obviously increase the coal price, but on the other hand it will also mean reduction of demands for dust collectors, causing deductions in installation costs for dust collectors.

For many years wellknown technologies have been used concerning removal of particulates from the flue gas with high effiency. The three mostly known systems are multi-cyclones, electrostatic precipitators, and bag houses. Primarily the two last mentioned technologies are of interest at coal-fired power stations.

In the following is given an evaluation of the size of the emission and of the possibilities of limitation of it.

Ash in coal

The ash residue in coal is defined as that part of the coal being left after heating to 815°C to constant weight (ISO-standard 1171).

By coal mining it cannot be avoided that some of the mountain material around the coal seam goes with the coal, and it is also a fact that the coal seam contains uninflammable material.

The coal Denmark imports for the time being has an ash content in the area 5 - 25% with an average value around 10 - 15% (coal file of Danish Boiler Owners' Association, 1976-1980).

In table 1*is shown an analysis of imported coals from 6 countries, out of which 2 countries (Poland and South Africa) have so far delivered almost 80% of the total amount of imported coal to Denmark (ELSAM, 1978).

The trace element content of the coal is very similar to the average content of the earth's crust (Mason, 1958), but by combustion an essential concentration in the combustion residue takes place, and that is the reason for the wish of a cleaning of the coals before combustion. However, these possibilities are not to be discussed in this paper.

Conditions at plants

Different firing plants combust the coals so differently that the formation of fly ash varies considerably. Furthermore the handling of the plant has an essential influence on the amount of ash transported with the flue gas out of the boiler. - Investigations at a number of plants have shown the following distribution of the ash from the coals (Danish Boiler Owners' Association, 1975-1981), table 2:

Type of plant	Slag %	Fly ash %
Stokers and the like	80-90	10-20
Gate feed stokers	75-85	15-25
Spreader stokers	30-50	50-70
Drop tube	40-60	40-60
P-F	10-20	80-90
Fluidized bed	10-20	80-90

By pulverized-Firing (P-F) the coals are ground to fine particulates (e.g. 96% smaller than 200 µm and 80% smaller than 90 µm) and by this procedure the ash-formating minerals are evenly spread on very small coal particulates, and by combustion they are released. Melting together, sintering together and agglomeration may cause the ash particulates to obtain a size so big that they may be separated from the flame and fall to the bottom of the fire box. From this box the ash is removed as slag.

By far the greatest part of the ash (typically 80-90%) is, however, transported with the flue gas out of the boiler.

Generally is to be noticed that the particulate amount in the flue gas after the combustion chamber varies according to:

- Type of plant, firing method
- Loading of plant
- Operation of plant (air distribution, excess of air)
- Fuel (grain size, kind of ash, ash content)

* next page

		POLAND	SOUTH-AFRICA	AUSTRALIA	WEST-GERMANY	COLUMBIA	CHINA
Aluminium	Al	5200	6400	8800	9700	4200	4600
Silicon	Si	26000	33000	74000	53000	34000	39000
Sulphur	S	5500	8200	6800	14000	9300	8000
Chlorine	Cl	840	410	63	1300	200	100
Potassium	K	2000	1200	1400	3800	1300	1000
Calcium	Ca	5200	4000	460	1200	1600	1700
Titanium	Ti	730	1100	840	830	410	450
Vanadium	V	45	64	0-28	45	15	0
Chromium	Cr	-	21	<5-10	15	8	<5-10
Manganese	Mn	160	47	130	70	36	190
Iron	Fe	8500	8400	3800	11000	4300	12000
Cobalt	Co	-	-	<80	<200	<85	<240
Nickel	Ni	16	20	22	30	7	24
Copper	Cu	66	47	∿9	∿30	∿25	∿9
Zinc	Zn	140	20	45	220	74	37
Gallium	Ga	9	10	6	5	2	2
Arsenic	As	7	10	3	20	6	6
Selenium	Se	1	1	2	<1-3	4	<1-3
Bromine	Br	8	2	1	8	1	1
Rubidium	Rb	18	10	11	31	9	9
Strontium	Sr	120	250	140	70	59	230
Yttrium	Y	11	21	24	8	0	5
Zirconium	Zr	27	98	150	45	19	45
Niobium	Nb	-	2	0-2	5	1	2
Molybdenum	Mo	8	29	<2-10	<2-10	2	<2-10
Silver	Ag	2	3	3	2	3	3
Cadmium	Cd	-	2-9	<2-5	<2-5	<2-5	0-2
Tin	Sn	5	6-15	0-4	4	10	0-4
Antimony	Sb	-	-	<2-5	5	<2-5	<2-5
Barium	Ba	280	260	240	197	105	420
Lead	Pb	37	15	15	75	44	7
Thorium	Th	5	5	8	13	9	4

Table 1: Trace metal (ppm) in coal from 6 countries (Jacobsen, 1980)

Flue gas cleaning

As the flue gas from the combustion chamber contains considerable amounts of fly ash (1-50 g/m^3,n,t), a flue gas cleaning is absolutely necessary.

By choice of cleaning method the following conditions are of importance:

1) Emission standards
2) Particle size distribution in flue gas
3) Fly ash concentration
4) Flue gas temperature
5) Characteristics of flue gas cleaning methods
6) Installation costs, buying and operational costs (not to be discussed)

Re 1, Standards

Standards for particulate emissions from Danish power stations (> 100 MW thermal) have been established by the Danish Environmental Protection Agency. Those of particular relevance to recent and future coal-fired plants include:

- For all new coal-fired plants discharges to air must not contain more than 150 mg/m^3n,t, 12% CO_2 (calculated at reference condition, dry flue gas at 0°C, 1013 mbar of 12% CO_2 content).

Re2 Particle size distribution

The particle size distribution for fly ash from the different types of plants varies essentially.

A number of investigations have given the below mentioned particle size characteristics, according to type of plant, table 3:

Type of plant	Mass meridian µm	Smaller than 10 µm %
Stokers *	10 - 20	30 - 50
Gate-feed stokers	45 - 120	3 - 10
Spreader stokers	100 - 500	2 - 10
Drop tube *	10 - 60	20 - 50
P-F	12 - 25	15 - 45
Fluidized bed	100 - 300	20 - 30

*Until now only few references for these plants

Table 3: Fly ash characteristics according to type of plant. (After: Knud Hansen - 1953, Danish Boiler Owners' Ass., 1975-1981, FEA, 1977, EPA, 1974).

From this it is clearly to be seen that the dust from the different types of plants varies very much as to particle size distribution. Especially there is a significant change in the average particle size from the small firing plants to the big ones, among other things due to the air supply to the combustion.

Re 3, Fly ash

As mentioned earlier an essential part of the ash from the coal is transported with the flue gas out of the boiler, varying according to firing principle and operational conditions.

As level-statements the following values may be used, table 4:

Type of plant:	Fly ash concentration: Normally g/m^3,n,t	 Extremely g/m^3,n,t
Stoker	0.5-2	0.1-4
Chain grate	1-2	0.2-4
Gate-feed stoker	1-3	0.2-6
Spreader stoker	2-5	1-8
Drop tube	(2-5)	-
Coal dust firing	8-20	2-25
Fluidized bed	15-40	10-50

Table 4: Fly ash concentration according to type of plant. (After: Knud Hansen - 1953, Danish Boiler Owners' Ass., 1975-1981, CEC, 1980, Mann, 1978, FEA, 1977, Ray, 1977, Ensor, 1981)

Re 4, Flue gas temperature

The flue gas temperature should not directly influence the choice of precipitator, but e.g. bag houses are very sensitive to high flue gas temperatures, and a safety device by high temperature material may be very expensive. As an example the filter material is 4 times as expensive if the highest operational temperature is 200°C compared with 125°C. (Bahco-Ventilation, 1982).

Re 5, Flue gas cleaning methods

As a matter of fact only 4 methods of flue gas cleaning have a real possibility of meeting the emission standards. Out of these one, the ventiry scrubber, is not used in coal-fired plants in this country. To get an evaluation of the efficiency of the collectors, table 5 shows the efficiency of the dust collectors towards different particle sizes:

Type of dust collector:	Fractional rate of efficiency (%) 1 µm	 5 µm	 10 µm	 50 µm	 100 µm
Multi cyclone	60	90	95	98,5	99
Electrostatic precipitat.	98,5	99,5	99,8	99,9	99,95
Bag houses	99	99,5	99,9	99,95	99,95

Table 5: Fractional rate of efficiency for flue gas cleaning device. (After: UN-ECE-1979, Ensor, 1981, Knud Hansen, 1953, EPA, 1974, Ondov, 1979, Ray 1977, FEA, 1977, and Danish Boiler Owners' Association, 1976)

Generally it must be evaluated that only electrostatic precipitators and bag houses will be able to clean the flue gas for particulates to a satisfactory degree for secure observance of the emission standards for power plants.

As electrostatic precipitators are the mostly used collectors of dust in Denmark we shall look closer into these.

Generally it has been mentioned that the emission falls with increasing ASI-No. (Alkali-Sulphate-Index) for the coal ash. An analysis of a number of coal samples from different countries gives these average values:

Type of coal:	ASI-No.:
Polish coal	4
South African coal	4
West Canadian coal	3
Australian coal	2
German coal (Ruhr)	5
Russian coal (Petchora)	4
American coal	-
Columbian coal	4
British coal	6
Chinese coal	3

Other conditions that may influence the efficiency of the electrostatic precipitators are the softening temperature of the coal ash, the sulphur content of the coal, and the carbon-in-ash loss. A high softening point gives small-particulate ash by the combustion, while a low sulphur content gives poorer electrical qualities for the fly ash.

Analyses of coals from the following countries have given these results:

Country:	Softening temperature (hemisperical)	Sulphur in coal %
Poland	1240	0,67
South Africa	1360	0,98
West Canada	>1500	0,35
East Canada	1320	1,5
Australia	>1500	0,52
West Gernany	1370	0,96
USSR	1280	0,63
USA	-	-
Colombia	1260	0,66
England	1300	1,3
China	1200	0,67

Of the types of coal, coming to be used in an essential amount at Danish power stations, problems can be expected to arise with Australian and West Canadian coals.

Measurements at modern power stations show that electrostatical precipitators are able to clean the flue gas effectively for particulates, even when using difficult types of coal (i.e. high reisitivity ash).

At modern plants dust emissions can be expected to the following extent:

Polish coal:	$\sim$ 20 mg/m^3,n,t
South African coal	$\sim$ 15 mg/m^3,n,t
Canadian coal	$\sim$ 100 mg/m^3,n,t
Australian coal	$\sim$ 120 mg/m^3,n,t

The total particulate emission from Danish power stations is not likely to rise despite the heavy increase in installed power. The emission from the new plants will be so much smaller than the emission from the plants closed down that the emitted amount of fly ash will totally be unchanged or maybe vaguely decreasing.

The calculated average emission from modern and old power stations is shown in tables 6 and 7.

TABLE 6 : CALCULATED AVERAGE EMISSION
Modern plants with electrostatic precipitators
g/MWh (electrical power)

Coal exporter		POLAND	SOUTH AFRICA	WEST-GERMANY	COLOMBIA	CHINA
g/MWh:						
Particulates		30	23	20	25	50
SO_2		5100	7600	7400	5000	6700
NO_x		3000	3700	-	3400	2600
mg/MWh:						
Arsenic	As	7,5	10	22	6	6
Cadmium	Cd	1	2	<3	<3	1
Chromium	Cr	5	11	7	3	4
Copper	Cu	30	21	13	10	4
Molybdenum	Mo	-	7	<8		<8
Nickel	Ni	6	8	11	2	8
Lead	Pb	25	10	47	26	4
Selenium	Se	0,4	0,4	<0,5	1,3	<0,5
Thallium	Tl	-	-	-	-	-

TABLE 7 : CALCULATED AVERAGE EMISSION
Older plants with electrostatic precipitators
g/MWh (electrical power)

Coal exporter		POLAND	SOUTH AFRICA	WEST-GERMANY	COLOMBIA	CHINA
g/MWh:						
Particulates		600	450	400	500	1000
SO_2		5100	7600	7400	5000	6700
NO_x		3000	3700	-	3400	2600
mg/MWh:						
Arsenic	As	64	58	184	51	51
Cadmium	Cd	10	6	<25	<25	8
Chromium	Cr	315	295	108	54	<60
Copper	Cu	93	40	48	37	13
Molybdenum	Mo	51	255	<77	17	<77
Nickel	Ni	296	227	649	136	470
Lead	Pb	201	68	454	252	39
Selenium	Se	6	20	<9	22	<9
Thallium	Tl	-	-	-	-	-

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APORTACION AL TERRENO DE CONTAMINANTES ATMOSFERICOS MEDIANTE PROCESOS DE DEPOSICION HUMEDA.

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Resumen. En este trabajo se estudia el aporte al terreno de componentes inorgánicos procedentes de la atmósfera y eliminados de la misma mediante procesos de deposición húmeda. Para ello, se han establecido cinco estaciones, repartidas por la Península, cuatro con carácter rural y una con características urbanas, habiéndose recogido las muestras de precipitación en todas ellas mediante captadores "sólo húmedos" que diferencian la precipitación de la deposición seca. Los componentes de la precipitación, tanto aniónicos (cloruros, nitratos y sulfatos) como catiónicos (sodio, potasio, magnesio y calcio), se analizaron por cromatografía iónica.

Los estudios de estos componentes junto con el pH de las muestras, muestran el carácter alcalino de las mismas y la baja concentración de iones en la estación con el mayor carácter de fondo, frente a las demás estaciones.

La deposición en el suelo de estos contaminantes está grandemente influenciada por las características de emisión y es prácticamente independiente en la mayoría de los contaminantes de la cantidad de precipitación.

Abstract. The aim of this study is the determination of the input of atmospheric pollutants in several locations in Spain. The precipitation are collected by "only-wet" collectors and theirs anionic and cationic components are analyzed by ion chromatography.

The composition of the rain, and the pH show the "alkaline" character of the samples, and the low concentration of the different ions in these stations with less levels of pollutants (background stations).

The depositions in the soil of these atmospheric pollutants are influenced by the emission sources, and they are practically independent of the amount of the precipitation.

1.- INTRODUCCION.

La acidificación del suelo tiene aspectos cuantitativos (capacidad) y cualitativos (intensidad). La capacidad puede ser definida como la suma de los equivalentes de ácidos que pueden ser neutralizados por la adición de una base fuerte, a pH 7 u 8. La intensidad es expresada como la actividad termodinámica de los protones y es medida como valor de pH, siendo determinada por la fuerza de los ácidos que controlan la actividad del protón en la solución del suelo (Ulrich, B, 1983).

La acidificación del suelo significa una pérdida de la basicidad o un incremento de la acidez, ambas consideradas en términos de capacidad, y solo en rangos especiales, una pérdida de basicidad o un incremento de acidez se conecta con cambios en el pH, lo cual es especialmente verdadero cuando los cationes intercambiables (principalmente calcio, a veces extendido a magnesio) son reemplazados por iones aluminio. Hay que tener en cuenta que a veces los suelos se acidifican sin haber cambio en el pH.

Una de las causas de la acidificación del suelo es la contaminación atmosférica, aunque no hay que olvidar procesos biológicos internos en el suelo que lo acidifican en grado variable.

Esta acidificación, desde el punto de vista de la contaminación atmosférica como originante, se puede producir por procesos de deposición seca, pricipalmente de gases de carácter ácido y en una cuantía muy pequeña, o por procesos de deposición húmeda que son mucho más interesantes, pues van a introducir en el terreno muchos más contaminantes ácidos, que estan en la atmósfera en estado de partículas y proceden de la oxidación del dióxido de azufre y dióxido de nitrógeno, tanto en fase homogénea como heterogénea. Esta deposición húmeda o eliminación de los contaminantes atmosféricos por el agua, comprende a su vez dos procesos: los procesos de "rainout", por los cuales un contaminante se incorpora a una nube y posteriormente se eliminará, actuando el suelo entre otros de receptor, y los procesos de "washout", por los que el contaminante es eliminado mediante choque de las gotas de lluvia.

El objeto de este trabajo, es la evaluación de los niveles de contaminantes ácidos aportados al terreno por la precipitación, los cuales comprenden la suma de los contaminantes eliminados por procesos de "rainout" y "washout", es decir todo lo eliminado por deposición húmeda.

Para ello, nos hemos basado en las estaciones de la Red de Vigilancia de la Contaminación Atmosférica Transfronteriza (red EMEP), que en España (Instrumento de Ratificación núm.7293) dispone de cuatro estaciones de carácter rural, donde se miden los niveles de fondo. A ello, hemos incorporado una estación de carácter urbano para comparar y establecer las diferencias entre los diferentes grados de contaminación y el nivel de aporte de contaminantes al terreno.

2.- PARTE EXPERIMENTAL.

2.1.- Puntos de muestreo.

Como se ha indicado en el apartado anterior, para la realización de este estudio se han analizado muestras procedentes de cinco puntos diferentes, localizados todos ellos en España (Figura 1).

Punto 1- Localizado en la antigua sede de la Escuela Nacional de Sanidad (Ciudad Universitaria de Madrid), que está situada en la zona noroeste de la ciudad. Este punto está encuadrado dentro de la Red Mundial de Vigilancia de la OMS (WHO, 1976; WHO, 1978; WHO, 1980; WHO, 1984), y calificado como zona residencial.

Punto 2- Situado en un área rural, en San Pablo de los Montes (Toledo), y correspondiendo a una estación de la red EMEP.

Punto 3- Corresponde también a una estación de medida de niveles de fondo (red EMEP), y está localizada en el

Observatorio de la Cartuja (Granada).

Punto 4- Ubicado en Tortosa (Tarragona) y, al igual que los dos anteriores, forma parte de la Red de Vigilancia de la Contaminación Transfronteriza (red EMEP).

Punto 5- Localizado en Logroño (La Rioja), y también formando parte de la red EMEP.

Fig.1- Situación geográfica de las estaciones de muestreo.

2.2.-Sistemas captadores.

Para la toma de muestras de lluvia, se utilizó un captador ERNI ARS-721, provisto de un sensor, que en contacto con las primeras gotas de lluvia, activa un sistema que abre una tapadera, la cual permenece abierta hasta que la lluvia cesa. Este captador, recomendado por la Organización Meteorólogica Mundial, tiene como principal ventaja el diferenciar la deposición húmeda de la seca.

Una vez recogidas las muestras, son filtradas, tranferidas a frascos de polietileno y almacenadas en nevera a una temperatura aproximada de 5°C, hasta su posterior análisis.

2.3.-Métodos de análisis.

Se han analizado en las muestras recibidas en el laboratorio tanto los componentes aniónicos como los catiónicos, ambos por cromatografía iónica.

Las concentraciones de cloruros, nitratos y sulfatos en las muestras de lluvia, se determinaron por cromatografía iónica (Dionex mod. 2010i), con precolumna AG4A, columna separadora de aniones AS4A y columna supresora AFS.

Las condiciones en cuanto a eluyentes y regenerantes fueron: solución eluyente compuesta por 0,75 mM de bicarbonato sódico y

2,2 mM de carbonato sódico, y como regenerante se utilizó una solución 0,025 N de ácido sulfúrico.

Para la determinación de cationes (sodio, potasio, magnesio y calcio) se utilizó un cromatógrafo iónico Dionex 4010i con precolumna CG3, columna separadora de cationes CS3 y columna supresora de micromembrana CMMS.

En cuanto a los eluyentes utilizados, para la separación de los cationes divalentes se preparó un eluyente concentrado constituido por una solución 48 mM de HCl y 10,6 mM de DAP·HCl (ácido diaminopropiónico monohidrocloruro), mientras que para los cationes monovalentes se empleó un eluyente diluido formado por una solución 25 mM de HCl y 0,25 mM de DAP·HCl. En ambos casos el regenerante utilizado fue una solución 60 mM de KOH.

Los límites de detección para los parámetros estudiados fueron los siguientes:

Cl^- --------------- 0,05 mg/l
NO_3^-- N ----------- 0,04 mg/l
SO_4^{2-}- S ---------- 0,05 mg/l
Na^+ --------------- 0,01 mg/l
K^+ ---------------- 0,01 mg/l
Mg^{2+} -------------- 0,01 mg/l
Ca^{2+} -------------- 0,02 mg/l

El análisis de las muestras de precipitación se realizó previa filtración a través de filtros de 0,22 µm de poro.

Cuando las concentraciones de alguno de los iones encontrados en los análisis dieron valores por debajo del límite de detección, se tomó para el posterior estudio estadístico un valor arbitrario correspondiente a la mitad del límite de detección para dicho ión.

2.4.- Características del muestreo.

La toma de muestras de precipitación se realizó en periodos de 24 horas, recogiéndose éstas a las 9h. de la mañana del día siguiente al que comenzó la precipitación.

La duración total del muestreo ha sido de un año (1988), habiéndose recogido un total de 340 muestras en las cinco estaciones.

3.- RESULTADOS Y DISCUSION.

3.1.- pH de la precipitación.

El pH de la precipitación es considerado, en una primera aproximación, un índice de la calidad de la lluvia, en especial en lo referente a los compuestos de carácter ácido, sulfatos y nitratos, siendo considerada una lluvia como "ácida" cuando su pH es inferior a 5,6, debido a que este pH es el que corresponde a la disolución en el agua del dióxido de carbono atmosférico, a la presión y temperatura ambiente.

La figura 2 muestra la evolución de las medias mensuales de pH junto con la evolución de los volúmenes de lluvia caidos en cada mes, en las estaciones objeto de este trabajo. Como se puede observar en ella, el pH medio mensual de las precipitaciones en todas las estaciones a excepción de San Pablo de los Montes, es superior a 5,6, si bien es cierto que hubo algunos eventos de lluvia con pH inferior a 5,6.

El alto predominio de lluvias con pH superior a 5,6 demuestra una alta incidencia de "lluvias rojas". presumiblemente lluvias con polvo sahariano y que en 1988 se observaron durante los meses de verano.

Estas lluvias ~~junto con~~ Además de un incremento alto de pH, van acompañadas de elevadas cantidades de sulfato y calcio, puesto que el polvo del Sahara contiene entre el 5 y el 30% de calcita y algo de yeso (Lõye-Pilot y col., 1986).

Es de destacar los pH altos obtenidos en la estación de la Cartuja (Granada), la más próxima al continente africano.

Los pH medios mensuales más bajos se han encontrado en las estación que tiene un carácter más rural (San Pablo de los Montes), siguiendo una evolución coincidente con estudios anteriores (Fernández Patier y col., 1989) y con estaciones de carácter rural (Willison y col.,1985).

3.2.- Composición de la precipitación.

La composición media ponderada de la precipitación, expresada en mg/l durante 1988 en las cinco estaciones estudiadas, se muestra en la tabla 1.

Un exámen rápido de dicha tabla nos lleva a establecer diferencias entre las estaciones. El nivel de cloruros en la precipitación es bastante similar en cuatro de ellas, oscilando entre 0,57 y 0,76 mg/l, mientras que la otra (Tortosa) presenta una concentración unas cuatro veces superior (2,77 mg/l). Estas diferencias también se aprecian en los niveles de sodio, superiores unas tres veces en la estación de Tortosa (1,90 mg/l). La explicación a este fenómeno parece estar en la proximidad al mar, que es el foco emisor en este caso de iones cloruro y sodio, que si bien desde el punto de vista de la acidificación del suelo e incluso sanitario no tiene interés, sí juegan un papel importante en la alteración de materiales diversos.

En cuanto a los verdaderos componentes ácidos de la precipitación, esto es, nitratos y sulfatos, la concentración media máxima del primero se encuentra en Granada (0,63 mg/l), mientras que en otras tres estaciones (Madrid, Tortosa y Logroño), las concentraciones son prácticamente la mitad y en San Pablo de los Montes, aún más baja (0,12 mg/l).

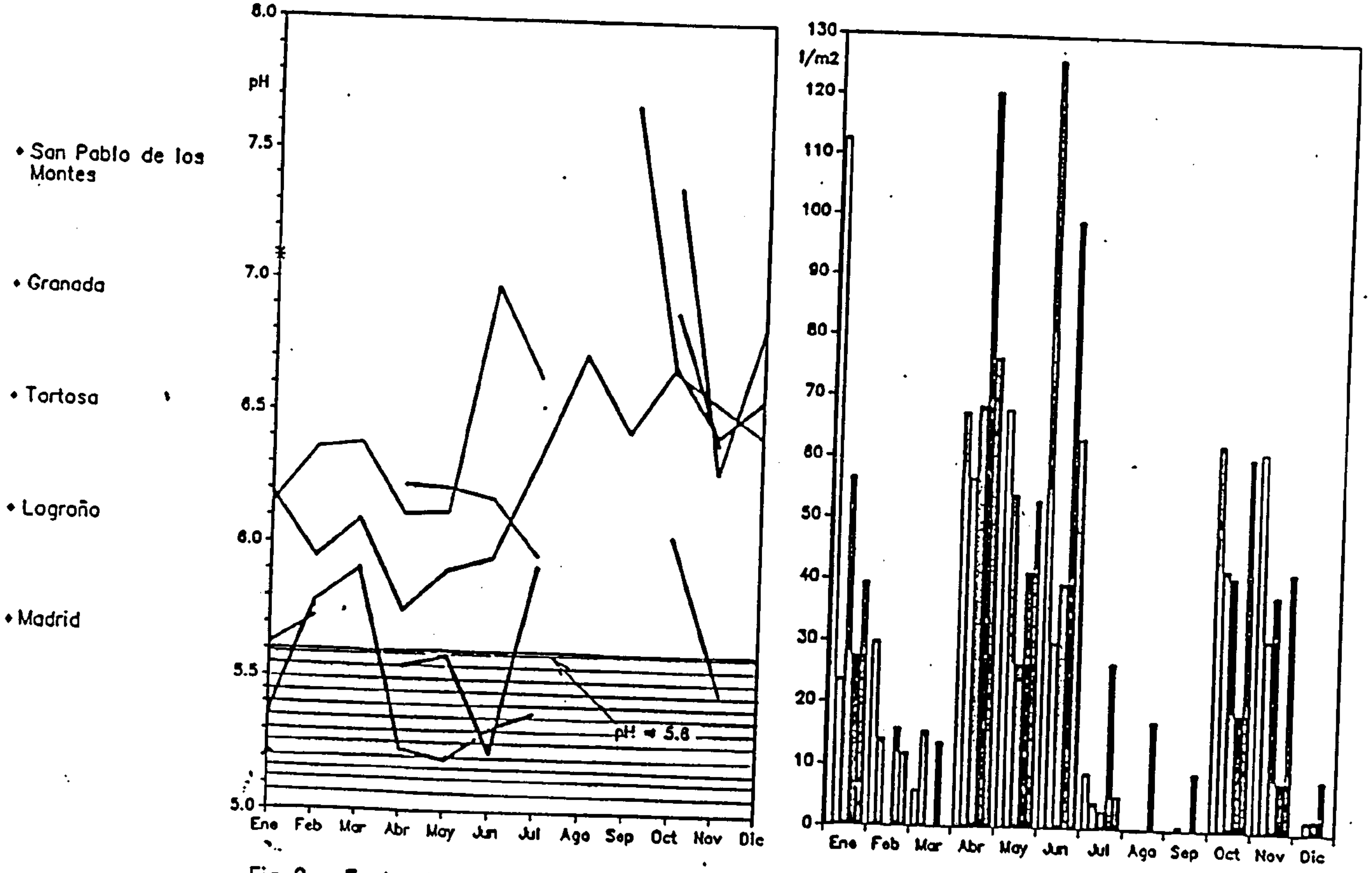

Fig 2.– Evolución mensual del pH y volúmenes de precipitación. 1988.

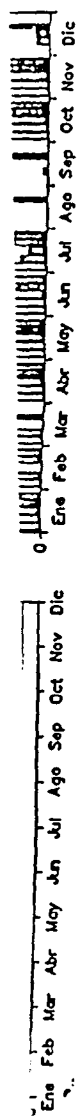

Fig 2.- Evolución mensual del pH y volúmenes de precipitación. 1988.

TABLA 1. Composición media de la precipitación (mg/l). 1988.

Estación	Periodo	n	Cl^-	NO_3^-- N	SO_4^{2-}- S	Na^+	K^+	Mg^{2+}	Ca^{2+}
Madrid	Invierno	7	0,49	0,13	2,01	1,04	0,08	0,26	3,89
	Primavera	31	0,53	0,45	1,30	0,59	0,11	0,15	2,63
	Verano	9	0,58	0,58	2,35	0,62	0,11	0,32	5,48
	Otoño	13	0,66	0,16	1,49	0,61	0,17	0,35	3,55
	Total	60	0,57	0,33	1,56	0,62	0,13	0,25	3,35
San Pablo	Invierno	24	0,57	0,09	0,39	0,56	0,04	0,12	0,81
	Primavera	39	0,68	0,17	0,56	0,65	0,05	0,06	0,41
	Verano	10	0,79	0,14	1,07	0,80	0,06	0,07	0,87
	Otoño	18	0,55	0,05	0,33	0,51	0,10	0,13	1,29
	Total	91	0,70	0,12	0,53	0,63	0,06	0,09	0,77
Granada	Invierno	20	0,84	0,19	1,24	1,03	0,15	0,20	1,45
	Primavera	19	0,62	0,30	0,91	0,45	0,12	0,18	1,68
	Verano	3	1,75	0,20	5,45	1,00	0,36	0,67	14,48
	Otoño	19	0,61	1,58	0,93	0,68	0,42	0,33	2,89
	Total	61	0,72	0,63	1,26	0,60	0,23	0,26	2,99
Tortosa	Invierno	6	0,92	0,12	0,62	S.M.	S.M.	S.M.	S.M.
	Primavera	19	1,22	0,34	0,98	1,00	0,11	0,28	2,45
	Verano	7	1,48	0,81	4,22	1,08	0,36	0,55	12,86
	Otoño	13	6,67	0,17	1,83	3,23	0,33	0,74	9,39
	Total	45	2,77	0,26	1,31	1,90	0,21	0,48	5,87
Logroño	Invierno	20	1,41	0,23	1,11	1,93	0,17	0,27	1,13
	Primavera	36	0,43	0,27	0,82	0,35	0,13	0,07	0.70
	Verano	15	1,18	0,68	2,28	0,62	0,22	0,23	3,67
	Otoño	12	1,07	0,30	2,31	0,86	0,23	0,34	2,95
	Total	83	0,76	0,36	1,30	0,52	0,16	0,14	1,63

(S.M.- Sin muestra).

La concentración media de sulfatos tiene, al igual que nitratos, un mínimo en San Pablo (0,53 mg S/l), siendo las demás concentraciones entre 2 y 3 veces superiores. Igual comentario puede ser realizado respecto a los cationes potasio y magnesio, con concentraciones mínimas en la estación toledana.

Los niveles medios de calcio tienen su valor máximo en Tortosa (5,87 mg/l) y su mínimo en San Pablo (0,77 mg/l) teniendo las otras tres estaciones valores intermedios.

Pero quizá sea interesante estudiar la evolución de la concentración de la lluvia en los diferentes periodos estacionales, la cual también se muestra en la tabla 1, siendo lo más representativo las variaciones estacionales de nitratos, sulfatos y calcio.

La concentración media de los nitratos y sulfatos, en la lluvia presenta los valores máximos en la primavera y verano , al igual que sucede en la concentración de los mismos en el aerosol atmosférico (Fernández Patier y col., 1987) lo cual puede interpretarse como una mayor formación fotoquímica de los mismos a partir de dióxido de nitrógeno y dióxido de azufre en la atmósfera, y al transporte del polvo de Sahara en el caso de los sulfatos.

En cuanto a los valores máximos de calcio en la época estival, concuerda plenamente con los altos pH de lluvias encontrados durante estos meses, sobre todo en Granada en el verano y Tortosa en el otoño, y coincidente además con valores altos de sulfatos, procedentes estos iones probablemente del desierto de Sahara.

3.3.- Deposición húmeda.

Mediante los procesos de deposición húmeda anteriormente citados, hay un aporte considerable de contaminantes al suelo procedentes de la atmósfera. El término de deposición húmeda es empleado usualmente en dos sentidos, uno agrupa a los procesos de eliminación de contaminantes atmosféricos por vía húmeda, y otro se refiere a la cantidad de contaminante que es eliminado de la atmósfera por estos procesos. Este último sentido, el de la evaluación cuantitativa, es el aquí tratado, que es considerado como el producto de la cantidad de precipitación por la concentración del componente existente en la precipitación.

La tabla 2 muestra la deposición húmeda durante 1988 de los compuestos considerados en este trabajo.

TABLA 2. Deposición húmeda anual (mg/m^2). 1988.

Estación	$l \cdot m^{-2}$	Cl^-	$NO_3^- - N$	$SO_4^{2-}-S$	Na^+	K^+	Mg^{2+}	Ca^{2+}
Madrid	335,64	200,95	117,12	552,80	177,86	37,24	70,65	964,06
San Pablo	545,64	346,72	63,22	286,87	255,95	25,80	34,65	309,93
Granada	276,46	200,23	174,98	349,57	147,69	57,15	64,22	731,39
Tortosa	277,28	766,05	72,75	360,81	386,27	43,68	97,74	1194,10
Logroño	411,34	312,77	148,02	534,89	192,55	59,78	51,76	599,02

La deposición húmeda de cloruros depende de la trayectoria seguida anteriormente por las masas de aire y su paso por zonas marítimas, así como de la existencia en ese punto de masas de aire procedentes de la costa.

Así, encontramos la deposición máxima en Tortosa (766 mg/m^2), que coincide también con la concentración media más alta de cloruros en la precipitación. Esto no siempre es coincidente, pues depende, según la definición de deposición húmeda, del volúmen de lluvia caido, y en este caso este volúmen es uno de los más bajos. Estudios realizados en Alemania muestran valores de 2544 mg/m^2 en zonas industrializadas, y 1686 mg/m^2 en zonas rurales (Kuttler, 1986).

La deposición de nitratos, expresada en nitrógeno, oscila entre 63 mg/m^2 (San Pablo) y 175 mg/m^2 (Granada), inferiores a los encontrados en Alemania, que oscilaban entre 0,4 y 0,8 g N/m^2 y los de Suecia 0,35 y 0,07 g/m^2 en el sur y norte respectivamente (Georgii y col., 1986). Otros estudios (Kuttler, 1986) realizados en zonas industrializadas y rurales, muestran deposiciones anuales mucho más elevadas (689 mg/m^2).

Menores diferencias se aprecian en la deposición húmeda de sulfatos, entre 287 mg/m^2 (San Pablo) y 552 mg/m^2 (Madrid), mostrándose claramente la influencia en este caso de los focos emisores próximos. Al igual que en nitratos, la deposición de sulfatos es muy baja en San Pablo a pesar de ser el sitio con una pluviosidad mayor de todos los estudiados. Comparándolo con las deposiciones en estaciones centroeuropeas y nórdicas, los niveles en las estaciones españolas son bastante menores, pues según Georgii y col. (1986) y Kuttler (1986), la deposición húmeda de sulfatos en Alemania está comprendida entre 1 y 2 g S/m^2, siendo la del suroeste de Suecia 1,2 g S/m^2 y sólo 0,3 g S/m^2 la del norte de Suecia. Valores similares de 1 g S/m^2 han sido encontrados por Raynor y Hayes (1982) en E.E.U.U.

En cuanto a la deposición húmeda de los cationes considerados, es importante hacer notar los valores superiores de sodio encontrados en Tortosa (386 mg/m^2 anuales), correspondiendo a la concentración media máxima en la precipitación de los puntos muestreados, y con la misma explicación que los cloruros. La bibliografía existente para la deposición húmeda de cationes es muy escasa, entre ellas destacaremos los trabajos de Brechtel y col. (1986) que encuentran en Alemania concentraciones cercanas a los 600 mg/m^2 anuales, si bién este trabajo no es comparable con el nuestro al utilizar captadores de la precipitación abiertos y colectar tanto precipitación como partículas atmosféricas sedimentables y en suspensión.

Los mismos comentarios pueden hecerse en cuanto a la deposición de potasio y magnesio, con valores mínimos en San Pablo de los Montes.

La deposición de calcio merece un comentario aparte, siendo destacable el bajo valor obtenido en San Pablo (310 mg/m^2) y el elevado valor de 1194 mg/m^2 hallado en Tortosa, que supera en dos veces el referido por Brechtel y col. (1986) en captadores abiertos y que tiene su explicación en las partículas procedentes del Sahara, cargadas de calcio y que son eliminadas por la lluvia como se ha expuesto anteriormente.

3.4.- Evolución mensual de la deposición húmeda.

En la figura 3 están representadas las deposiciones húmedas mensuales de los componentes inorgánicos estudiados en la precipitación.

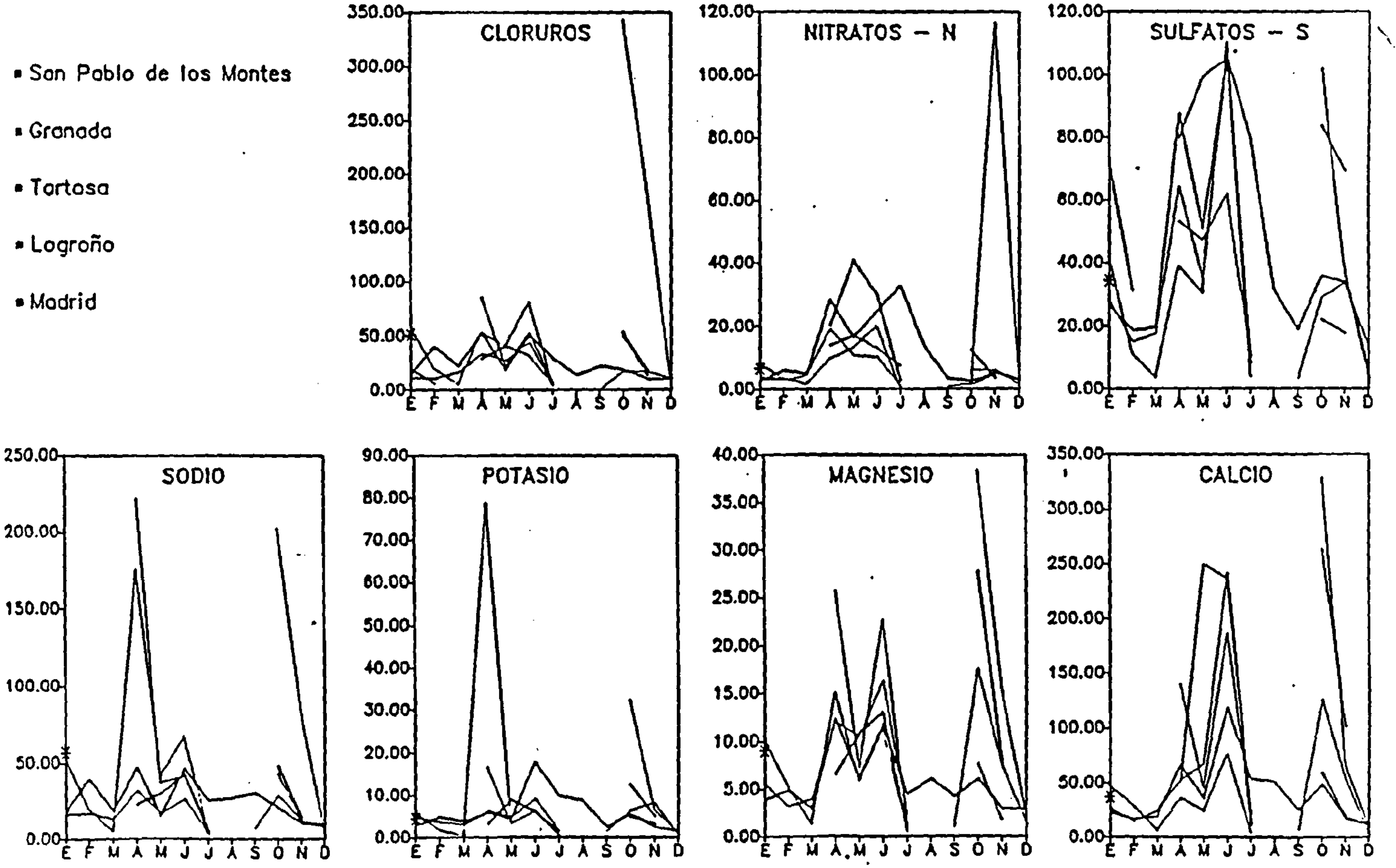

Fig 3.– Evolución de la deposición húmeda mensual (mg/m2). 1988.

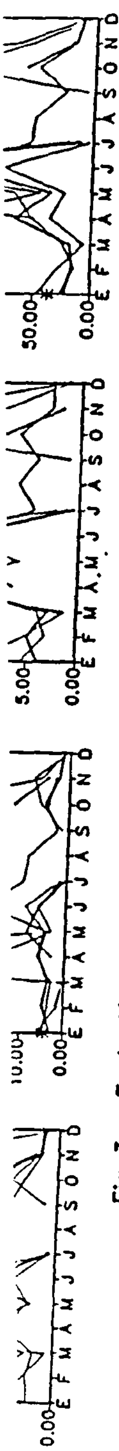

Fig 3.- Evolución de la deposición húmeda mensual (mg/m2). 1988.

Como se observa, la deposición de cloruros tiene un máximo en la estación de Tortosa durante los meses de Octubre y Noviembre, correspondiendo a lluvias con alto contenido en este ión, pues los volúmenes de lluvia caidos no son más elevados de los normales, superando los valores de deposición en 6-7 veces los valores de los otros meses. Igual comentario se puede hacer del catión que en la lluvia va unido a este anión, el sodio, con un valor alto en el otoño, al proceder ambos, como se ha dicho en apartados anteriores, del aerosol marino.

La deposición de sulfatos mensual es 2-3 veces mayor que la de nitratos y muestra bastante concordancia con la evolución de los volúmenes de precipitación (figura 2), obteniéndose en este caso deposiciones máximas cuando la cantidad de lluvia caida es mayor, relación que no es tan manifiesta en el caso de los otros iones, a excepción quizá del calcio, y por el orígen térreo común en algunas lluvias, principalmente las de otoño.

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INFLUENCIA DE LA DEPOSICION ATMOSFERICA EN LAS AGUAS SUBTERRANEAS

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Resumen:

Se presenta el estudio de los valores de deposición atmosférica de metales pesados en el terreno, a partir de los datos de precipitación obtenidos en una estación de fondo perteneciente a la red E.M.E.P. (Programa Europeo de Evaluación y Vigilancia de la Contaminación Atmosférica a Larga Distancia).

La cuantificación de los metales pesados depositados, así como los análisis de las aguas subterráneas que discurren por dicha estación de muestreo nos conducen a evaluar el conjunto de reacciones que tienen lugar en la zona no saturada y en el suelo de dicha area de estudio.

Cd, Cu, Ni, Pb, se analizan en las lluvias recogidas en un colector ERNI y en las aguas de un acuífero, muestreando en el pozo de abastecimiento a la estación; Estas aguas no están sometidas a ningun tipo de tratamiento.

Se pone de manifiesto la importancia que el estudio de los metales pesados tiene en la fuente principal de recarga a acuíferos: La deposición húmeda.

Abstract

From the rain data obtained in a background station included in the network E.M.E.P. (European Monitoring and Evaluation Progamme), heavy metal atmospheric deposition values in soil are studied.

The interactions rain, soil and grounwater which flow under this sampling station are also stadied.

Cd, Cu, Ni, Pb, in rain collected in ENRI collector and in not chorinated water from the aquifer are analyzed.

The importance of the study of heavy metals in wet deposition to undestanding the physico-chemical behavior of ground water supply be pointed out.

INTRODUCCION

Recientemente se ha empezado a comprobar el progresivo aumento de la acidificación del suelo y por tanto de las aguas subterráneas que circulan bajo él, a causa de procesos originados por la deposición atmosférica. Así, los resultados de gran número de análisis realizados a comienzos de 1.980 en aguas subterráneas suecas mostraron un claro aumento de la dureza y contenido en sulfatos, junto con un marcado descenso de la alcalinidad (Grimuall, 1.986), encontrándose asimismo contenidos en metales pesados más altos que los que habían sido habituales hasta entonces, este hecho se atribuyó a la movilización de los mismos debido al aumento de la acidez (Moskowitz, 1.986).

En las zonas rurales de atmósfera considerada como "limpia" la deposición atmosférica seca contribuye con una escasísima cantidad de metales pesados a causa de la pequeña velocidad de sedimentación de estos elementos (Gordon, 1.986), influyendo tambien su escasa concentración en el aerosol atmosférico y la gran proporción de partículas que poseen en el rango de tamaño más fino. Por lo contrario, los episodios de lluvia arrastran la mayoría de las partículas atmosféricas, consiguiendo un impacto superior al producido de forma constante por la deposición seca, pues en cortos periodos de tiempo se pueden depositar cantidades más elevadas de elementos traza que, por otra parte, al estar en medio acuoso se hallan en gran proporción en formas solubles, facilmente asimilables por el suelo y las plantas.

Los metales pesados se acumulan en la capa orgánica superior del suelo, en la que tiene lugar la descomposición de las hojas y de parte de la capa de las raices. Asimismo se ha observado que la capa mineral del suelo acumula solamente plomo, mientras el niquel, cobre y cadmio son eliminados por lixiviados de las aguas, incorporándose de esta manera al ciclo hidrológico (Mayer, 1.983).

La situación es que los metales pesados se acumulan en la parte biótica de los ecosistemas, mientras son eliminados de la parte mineral. Este hecho es lo que ha llevado a caracterizarlos como venenos de la biosfera.

MATERIAL Y METODOS

Este trabajo se ha desarrollado en San Pablo de los Montes, pequeña localidad enclavada al Suroeste de Toledo, a unos 50 kilómetros de distancia. Fué el lugar designado para situar la primera estación de la Red EMEP (Programa Europeo de Evaluación y Vigilancia de la Contaminación Atmosférica a Gran Distancia) en España. Sus coordenadas geográficas son: 4º 20'W, 39º 32'N y 917 m de altitud.

Desde el punto de vista geológico, San Pablo de los Montes se ubica en un amplio batolito granítico que ha metamorfizado los materiales paleozoicos. En el área meridional de dicha

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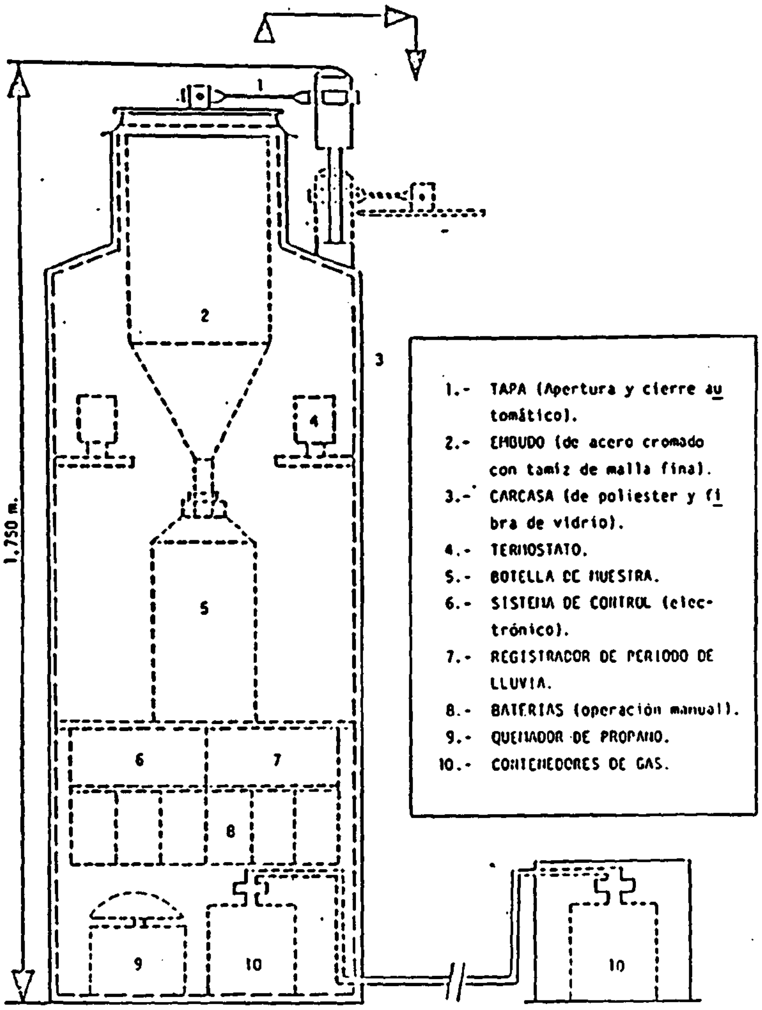

1.- TAPA (Apertura y cierre automático).
2.- EMBUDO (de acero cromado con tamiz de malla fina).
3.- CARCASA (de poliester y fibra de vidrio).
4.- TERMOSTATO.
5.- BOTELLA DE MUESTRA.
6.- SISTEMA DE CONTROL (electrónico).
7.- REGISTRADOR DE PERIODO DE LLUVIA.
8.- BATERIAS (operación manual).
9.- QUEMADOR DE PROPANO.
10.- CONTENEDORES DE GAS.

Figura 1: COLECTOR AUTOMATICO DE LLUVIA

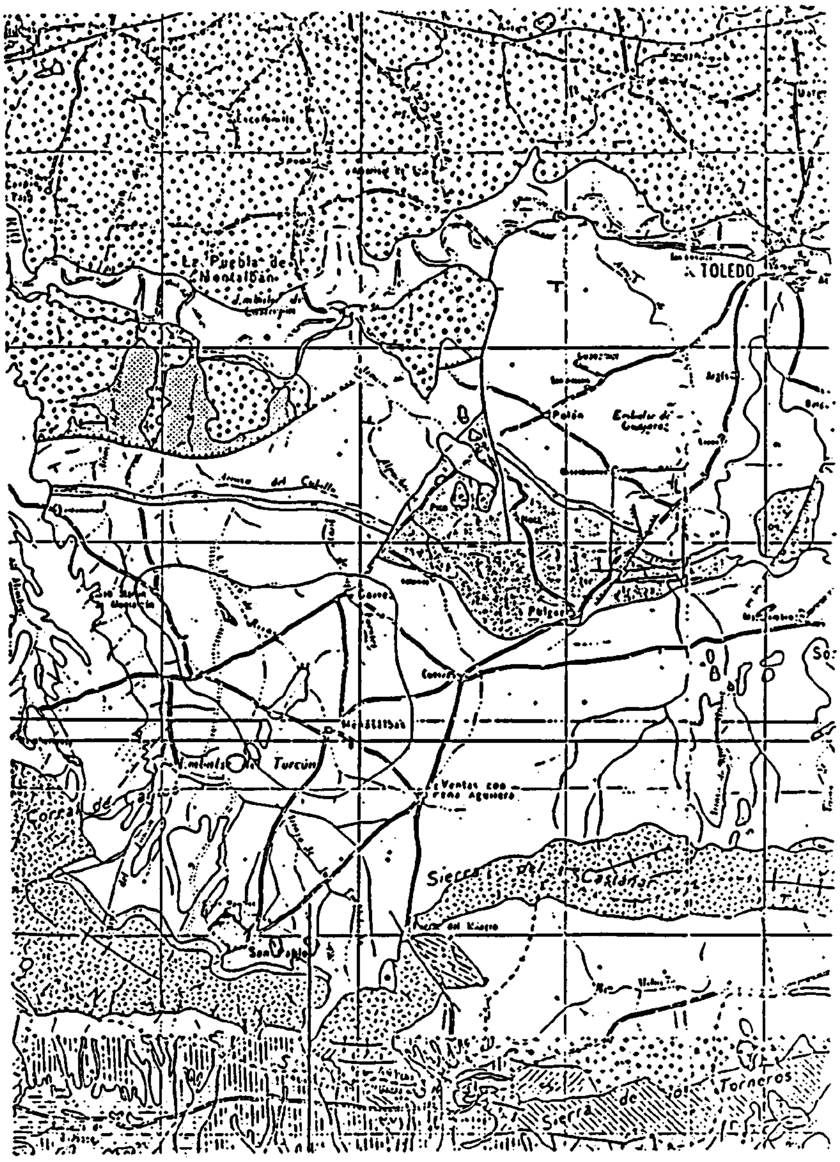

Figura 2: SITUACION DE LA ZONA DE ESTUDIO

zona aparece una serie del Cámbrico y Ordovícico constituida por cuarcitas, pizarras silíceas, areniscas ortocuarcíticas y unos pequeños afloramientos de calizas marmóreas, que son los materiales más antiguos descritos en la zona (Acadiense). Contribuye a dar caracter a la morfología de la región la existencia de importantes pedimentos de edad Villafranquiense, localmente denominados, "rañas" y de formaciones más tardías de ladera bien desarrolladas. Concretamente la zona de estudio se sitúa sobre un cuaternario muy poco potente formado por rocas resultantes de la alteración de granitos y cuarcitas que forman el substrato de la zona (I.G.M.E. Mapa 200.000 hoja de Toleto). Es muy característico en estas zonas que dichos materiales formados por pié de monte, formen acuíferos aislados.

En el aspecto meteorológico la estación de muestreo funciona practicamente como una completa, este aspecto es necesario para la determinación de temperatura, humedad, velocidad y dirección del viento, presión, radiación solar, precipitación y turbiedad atmosférica.

Durante los años 1.985, 1.986 y los tres primeros meses de 1.987 se recogieron en la zona de estudio 87 muestras de lluvia. Se captaron con un colector automático del tipo ARS-721 (Figura 1), dicho aparato se encuentra conectado a un sensor dotado de un electrodo rotativo de 110 mm. de diámetro, que detecta la cantidad de gotas por minuto en forma de pulsaciones que son transmimtidas a la unidad de evaluación para actuar sobre el mecanismo de apertura de la tapa. Los periodos de muestreo fueron de veinticuatro horas.

Asímismo, se tomaron muestras de agua de un pozo excavado junto a la plataforma de captación de muestras atmosféricas. Se trata de un pozo somero de aproximadamente 10 m., situado en los materiales silíceos característicos de la zona, que por su estructura pueden llegar a ser muy permeables.

En las muestras recogidas se determinaron: plomo, cadmio, cobre, hierro, manganeso y níquel, utilizando la técninca de Espectrometría de Absorción Atómica, en un aparato Perkin-Elmer 403 equipado con Horno de Grafito HGA-500.

Posteriormente durante 1.987 y 1.988 se continuó la captación de muestras de agua del pozo, con el objeto de iniciar un estudio a largo plazo de la evolución de las características fisico-quimicas del acuífero.

RESULTADOS Y DISCUSIÓN

El plomo se determinó sobre cada muestra de lluvia recogida en 1.985, 1.986 y primer trimestre de 1.987. A partir de las concentraciones individuales se calculó la media arítmetica correspondiente (Tabla 1).

La distribución de las concentraciones de plomo en lluvias es de tipo logarítmico normal con frecuencias elevadas en los intervalos con valor más bajo, (como puede observarse en la figura 3, en la que se presenta el histograma correspondiente.

Tanto los valores individuales como los medios, denotan concentraciones del orden de las registradas en la bibliografia para zonas rurales (Galloway, 1982). Se ha observado que los niveles medios de plomo se mantienen practicamente constantes a lo largo de los diversos perìodos estacionales estudiados, lo que era de esperar al carecer la zona estudiada de focos puntuales pròximos y acusar la contaminaciòn de las capas profundas de la atmosfera.

TABLA 1.- Media Aritmètica Anual de las Concentraciones de Plomo en lluvia.

	AÑO	
	1985	1986
Media aritmética (ug Pb/l)	3,30	2,41
Desviaciòn standard	2,60	3,64
Rango	(<1 - 13,4)	(<1 - 23,2)
Nº de datos	33	42

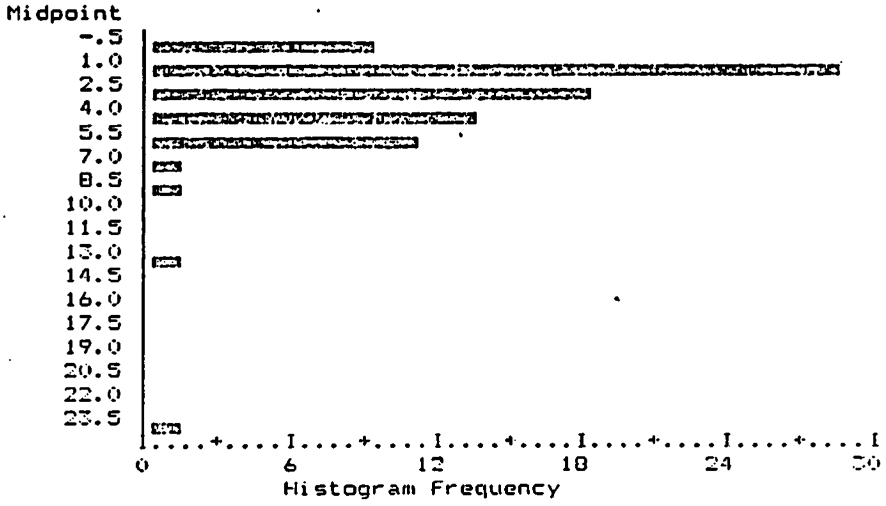

Figura 3.- Histograma de frecuencias de las concentraciones de plomo en lluvias

A la vista de la existencia de plomo en cantidades apreciàbles se estudiò la presencia de los metales Cd, Cu, Ni, Fe y Mn al objeto de establecer los niveles propios de la zona. Para ello se determinaron dichos elementos en las muestras recogidas en 1986 y 1987, cuyos resultados analíticon se recogen en la tabla 2. Las concentraciones obtenidas se encuentran, al igual que en el caso del plomo dentro de las reseñadas en la bibliografía (Galloway, 1982)

TALA 2.- Concentraciones medias de Metales Pesados en lluvias de San Pablo de los Montes

METAL	Media* Aritmética	Desviación Estandar
CADMIO	0,15	0,15
COBRE	0,57	0,60
HIERRO	1,52	1,07
MANGANESO	4,72	4,21
NIQUEL	2,42	1,59

*ug por litro

La influencia de la acidez sobre las concentraciones de los metales estudiados, se estableció mediante la determinación de los coeficientes de correlación entre la concentración de cada elemento y la correspondiente de hidrogeniones en cada muestra analizada, obteniendose los resultados que se incluyen en la tabla 3.

TABLA 3.- Coeficientes de correlación entre Metales Pesados e Hidrogeniones en muestras de lluvia

	r	p
Cd/H$^+$	0,6007	p 0,001
Cu/H$^+$	-0,2361	p 0,1
Fe/H$^+$	0,2765	p 0,05
Mn/H$^+$	0,1686	no sign.
Pb/H$^+$	0,5072	p 0,001
Ni/H$^+$	-0,2213	no sign

Las diferencias que se observan en la tabla 3 pueden ser atribuidas a las diferentes propiedades fisico-quimicas de los seis metales estudiados y a su comportamiento en el aerosol atmosférico. En el caso del cadmio, ya se había observado previamente, que en el aerosol atmosférico se hallaba siempre estrechamente unido a los compuestos causantes de la acidez (Santamaria, 1988) por lo que era de esperar que en la lluvia tambien existiera esa estrecha relación entre ambas, lo que se ha demostrado con el elevado coeficiente de correlación Cd/H obtenido -------

(r: 0,6007). Este hecho es característico de las zonas de baja contaminación, en las que la acidez está determinada especialmente por el transporte desde las zonas muy contaminadas, de los precursores de la misma, junto a los cuales se tranporta el cadmio, estando todos ellos asociados a las partículas de menor diámetro.

Asimismo. la estrecha relación existente entre plomo e hidrogeniones se resalta en el coeficiente de correlación obtenido entre ambos, con elevado nivel de significación. Ambos parámetros han mostrado oscilaciones simultáneas en los sucesivos periodos estacionales estudiados (Fernández, 1987).

Tomando como base las concentraciones metàlicas medias encontradas en la zona de estudio, se calculò la cantidad de cadmio, cobre, hierro, manganeso, niquel y plomo que se depositaron durante el año 1986 en San Pablo de los Montes, en orden a poder evaluar en un futuro el impacto de estos metales sobre el ecosistema. La deposición metálica calculada en Kilogramos por hectárea y año arrojò los siguientes resultados:

Cadmio:	$0,9 \times 10^{-3}$	Kg/ha/año
Cobre	1×10^{-3}	" " "
Hierro	$8,1 \times 10^{-3}$	" " "
Manganeso	$2,3 \times 10^{-2}$	" " "
Niquel	$1,5 \times 10^{-2}$	" " "
Plomo	$1,3 \times 10^{-2}$	" " "

Estas cifras son del orden de las revisadas en la bibliografía, resultando incluso bastante inferiores en algunos casos, lo que puede deberse a no ser una zona excesivamente lluviosa.

Una vez cuantificada la deposiciòn atmosférica de los metales estudiados, habria que evaluar el tipo de reacciones y tansformaciones que se dan en la zona no saturada del acuífero para de esta forma poder estimar qué evolución fisico-química va a tener el agua subterránea de la zona estudiada a largo plazo (Owen, 1981) Para ello se han tomado diversas muestras del acuífero que discurre bajo la estación de toma de muestras atmosféricas a fin de determinar la presencia de los metales más tóxicos dentro de los considerados. Se han determinado plomo, niquel cobre y cadmio. Los tres primeros acusaron concentraciones inferiores al límite de detección correspondiente (Pb 1 ug/l; N 2 ug/l; Cu 0,2 ug/l) en todas las muestras analizadas. Sin embargo, el cadmio mostró valores inferiores al L.D. (0,2 ug/l) en los muestreos realizados en 1985 y 1986, pero en las muestras posteriores, se acusaron valores más elevados (0,3-0,5 ug/l).

Teniendo en cuenta que en esta fase del estudio las precipitaciones fueron muy abundantes y que las características del terreno juegan un papel muy importante en la química final de las aguas subterraneas, la filtraciòn de la lluvia a traves del terreno puede ser la causa de la movilización del cadmio a partir de sus fuentes minerales. En este sentido Nilsson(285) afirmò que el cadmio contenido en aguas subterraneas refleja la quimica de los horizontes del suelo, producida por la percolación de aguas ácidas, así en el rango de pH comprendido entre 4,0-4,5 la solubilidad del cadmio en la capa mineral del suelo aumenta dramàticamente, ya que con el descenso de tan solo 0,2 unidades de pH, el cadmio en solución aumenta el doble.

Dado que estos terrenos son de tipo granítico, sus productos de alteración jugaran un papel muy importante en las interaciones que tendran lugar en el suelo antes de que el agua de lluvia alcance el acuífero. Los silicatos y otros componentes de los minerales de la arcilla pueden ceder al suelo algunos de los metales que albergan en su estructura e intercambiarse por iones existentes en aquel, de radio ionico parecido, de esta forma, el aporte de metales al suelo procedente del propio terreno se uniría al aporte descrito con que la lluvia contribuye.

La lluvia analizada durante el periodo de muestreo tiene un pH de 5,68, pero el valor del pH medio no es un dato representativo a la hora de evaluar las interaciones agua/suelo que van a ser en definitiva las que definan la evolución de las aguas subyacentes. Es por esto que, actualmente se estudian los porcentajes de muestras analizadas que estan comprendidas en un intervalo de pH definido. Así, de las 80 muestras de lluvia recogidas en 1987, un 60% de ellas estan comprendidas entre un pH de 5 a 6, valor este que aún siendo moderadamente ácido, es importante en los cambios de bases que se producirán en el suelo. Un 2% de las muestras tienen un pH inferior a 5. De la misma forma en 1988 se analizaron 91 muestras de las que un 49% tienen un pH comprendido en el intervalo de 5 a 6 y un 22% son inferiores a 5. Este último dato es de gran importancia, dado que la movilización de los metales estudiados se rige por un pH inferior a 5, como se puede observar en la tabla 3 donde el coeficiente de correlaciòn es muy significativo en el caso del cadmio y plomo.

Los hidrogeniones que aporta el agua de lluvia se retienen en los coloides orgánicos e inorganicos que tiene el suelo, así contribuyen a su adificación. Estos hidrogeniones pueden quedar retenidos en diversas estructuras de las minerales del suelo e intercambiarse con otros iones que posteriormente se liberarían pasando a otros ecosistemas. Por otra parte, los metales aportados por la lluvia pueden sustituir a un oxigeno de los cuatro que forman el tetraedro de silicio y oxigeno, asì dejan el suelo más susceptible a la acidez.

El intercambio de bases e intercambio catiònico en este tipo de suelos es moderado (Cwen [illegible])lo que ha de suponer, a efectos de la influencia de la deposición ácida en la aguas subterraneas, que el suelo no será capaz de neutralizar por completo los componentes acidos que procedan de la lluvia. La escasa cobertura vegetal en la zona, unido al espesor reducido del suelo, favorecen la acidificación de las aguas subterraneas que discurren bajo estos terrenos. Así las interaciones lluvia/suelo produciràn unos lixiviados ricos en calcio, magnesio, metales. etc. Esta acidificaciòn de las aguas subterraneas no se traduce necesariamente en un descenso del pH en ellas, sino que habitualmente la acidificación se manifiesta por la reducciòn de la relaciòn alcalinidad/dureza en las mismas (Grimvall 1986)

Con el periodo de muestreo establecido para este trabajo, no se puede concluir sobre la evolución del acuífero, pero sí adelantar que los aniones asociados a contaminantes atmosméricos (cloruros, sulfatos y nitratos) dan valores muy inferiores al límite tolerable por la Reglamentación Técnico Sanitaria (B.O.E. 1.982). Por otra parte el pH de las aguas del acuífero esté comprendido entre 7 - 8 y la conductividad da unos valores comprendidos entre 170 - 200 uS. Estos datos ponen de manifiesto que los hidrogeniones aportados por la lluvia se retienen en el suelo, siendo los propios componentes del mismo los que pasan a las aguas elevando la conductividad a un orden de magnitud superior (Santamaría, 1.988).

Por último hacer hincapié, en que tanto el área de recarga del acuífero (granitos y cuarcitos) como los materiales en los que se ubica, no son capaces de neutralizar la acidez de la lluvia, por lo que estas aguas subterráneas, a pesar de la capa que las protege serán vulnerables a la "acidificación".

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DOCUMENTATION OF AREAS POTENTIALLY INCLINED TO WATER ACIDIFICATION IN THE F.R.G.

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Abstract—Maps about areas in the F.R.G., which are potentially endangered by acidification, are prepared based on the soil and rock conditions and land use. These are compared with the actual low pH- (<pH 6.0) values in surface waters of the F.R.G.

Key words—acidification, buffer, hydrogen ion concentrations, surface waters

INTRODUCTION

The situation of water acidification is strongly differentiated in the F.R.G., as geology, soil properties, land utilization and pollutants charged into the air are extremely varied. With respect to geology, areas sensitive to acidification are primarily found in secondary mountain chains with carbonate-free or low-carbonate rocks (granite–gneiss areas, sandstone, slate). Moorland and sand areas, as those primarily common in the lowlands of Northern Germany are also sensitive to water acidification. In order to gain a more exact survey of the areas of the F.R.G. sensitive to acidification, various characteristics of rock and soil which are exposed to acid deposition are examined.

MAP-CONCEPTION

The course of soil acidification is dependent upon whether the acids are directly or indirectly deposited and upon the type and capacity of the soil buffer system. Water acidification is often closely linked to soil acidification; therefore in order to identify the areas which are sensitive to water acidification, various characteristics of rock and soil which are exposed to acid deposition are examined. The supply of bases in the soil, and the carbonate content of rock, with regard to agricultural land uses were examined and combined in the Synthesis Map.

In Base Map 1 (Fig. 1), the various buffering capacities of soils in GER is divided into the following four groups according to the supply of bases in the soil:

(1) Areas with low base supply in the soil;
(2) Areas with low–average base supply;
(3) Areas with average–sufficient base supply;
(4) Areas which have sufficient base supply so that acidification of waters is not expected.

The parameter "supply of bases in soil" was chosen in order to determine the sensitivity and buffering capacity of an individual soil type with respect to a specific amount of acid deposition. "The supply of bases" is also a comparable indicator which is available for all soil types. Of the four soil groups, the appearance of acidic waters is primarily expected in the areas indicated as having soils containing low–average base supplies [groups (1) and (2)].

In Base Map 2 (Fig. 2), exposed rock is categorized into three groups according to its carbonate content:

(1) Low-carbonate or carbonate-free areas;
(2) Areas with average carbonate content;
(3) Areas with rock rich in carbonate, where acidification of waters is also not expected.

This categorization was chosen because the carbonate content has been determined to be the most important factor in the buffering of the various acidic levels in exposed rocks. In areas containing small volumes of many different types of rock, the carbonate content fluctuates drastically, and thus the mean values were used to categorize such rock into one of the three groups described previously.

Base Maps 1 and 2 were combined and a *Synthesis Map* (Fig. 3), which also takes agricultural land use factors into account, was developed. In this map, areas with different levels of susceptibility to water acidification were identified. The following three degree of susceptibility were revealed:

Soil (supply of bases)	Rock (carbonate content)	Potential for water acidification
Low (1)	Carbonate free–low carbonate (1)	Very high (waters very endangered)
Low (1)	Carbonate content (2)	High (waters endangered)
Low–average (2)	Carbonate free–low carbonate (1)	High (waters endangered)
Low (1)	Carbonate-rich (3)	Low
Low–average (2)	Carbonate content (2) average	Waters slightly endangered

In mapping an area's potential for water acidification, the soil parameter carried more weight, as soils come into direct contact with sub-surface runoff and heavily influence the acidity level of the waters. The three categories for areas which are potentially endangered by water acidification are indicated by the pale tones. Forest and other areas, where no secondary buffering by agricultural land uses exists are represented by the darker tones. For the lowlands of Northern Germany, the moorland areas were additionally taken into account; in particular, the moor areas were mapped and are also represented by the darker tones. Although the areas sensitive to water acidification are distinctly delineated on the map by pale and dark tones, these delineations are in reality not so well defined; they merge with one another, depending on the given meteorological and hydrological conditions. During periods of increased water flow for example during snow melt, acidified water is carried far into the countryside.

As can be seen on the Synthesis Map, the waters in the mountain region and lowlands of Northern Germany are the most susceptible to acidification. In mapping these areas, it was not possible to distinguish between those areas inclined to water acidification due to acid deposition and those areas which are inclined to water acidification due to naturally occurring acidic conditions. Therefore the map only shows the potential for water acidification independent of its cause.

COMPARISON OF pH-VALUES WITH AREAS POTENTIALLY ENDANGERED BY ACIDIFICATION

In comparing the Synthesis Map with the actual pH-values of surface waters ($pH < 6.0$) (Fig. 4), an obvious regional distribution of pH-values can be seen. Such pH-values have been measured primarily in endangered areas where the buffer capacity has been somewhat exhausted by the acidic surface waters. In this figure three pH-ranges are distinguished.

Only the lowest measured pH-values for the time period between 1977 and 1985 could be mapped. The selected increments used in the mapping of the pH-values and the maximum value of pH 6 are hydrochemically and hydrobiologically justified. The upper limit of pH 6 was selected because, at lower pH-values, the first effects on water organisms and changes in the species makeup are first noticeable.

The cut-off value of pH 5.0 was chosen because under pH 5.0 the carbonic acid buffer system no longer functions. Furthermore, pH-values in this range are associated with the release of aluminium form the soil to the water. Waters in this pH range can be lethally toxic for many water organisms, e.g. river trout in the Mittelgebirge's brooks.

The cut-off value of pH 4.3 was used because it represents the titration endpoint of the measure of acidic capacity, K_s. At this and lower pH-values, only more acid-tolerant organisms are to be found in the waters.

SUMMARY AND EVALUATION

(1) A concept has been developed for the mapping of areas susceptible to the acidification of water, based on two main maps:

- —The buffer capacity of soils due to their base supply.
- —The buffer capacity of exposed rocks due to their carbonate content.

(2) These two basic maps have been united in one Synthesis Map which shows the areas of the F.R.G. susceptible to the acidification of water. Priority was given to the base supply of the soil. The land use was additionally taken into account. Within the potentially geogenic endangered areas—those areas which have been located—with the help of a forest scanner and the additional consideration of moorlands and heath soils which show no secondary buffering influences of agricultural land use and of settlements.

(3) The comparison of the geogenic potentially endangered areas in the Synthesis Map with the low current pH-values in surface waters show good correlations. In their regional distribution these areas are largely congruent. It has become obvious that waters with the lowest pH-values (<4.3) are to be found above all in large-scale forests on carbonate-

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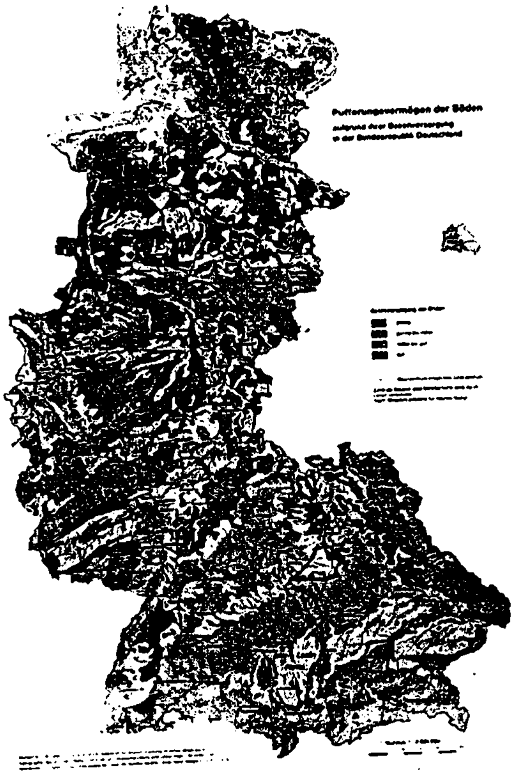
Fig. 1 (*facing page, top left*). Buffering capacity of soil according to its base supply. Red: low; yellow: low–average; green: average–sufficient; blue: areas which have sufficient base supply so that water acidification is not expected.

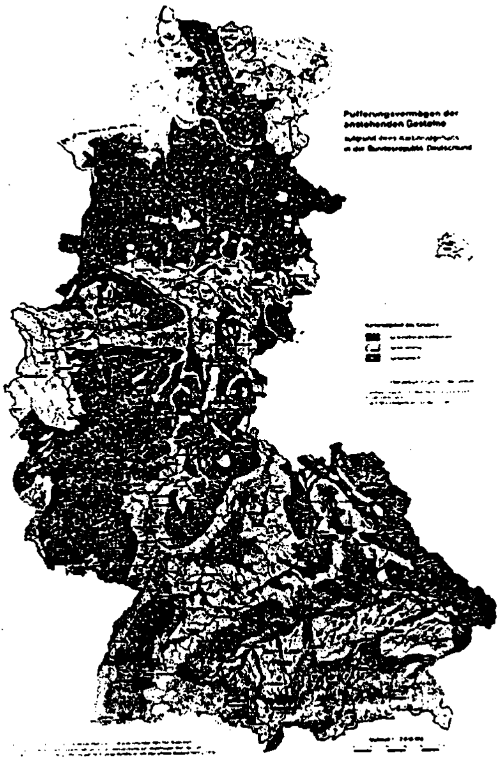
Fig. 2 (*facing page, top right*). Buffering capacity of exposed rock according to its carbonate content. Red: low-carbonate or carbonate-free areas; yellow: areas with average carbonate content; blue: areas rich in carbonates, where acidification of water is not expected.

Fig. 3 (*facing page, bottom left*). Map of areas potentially inclined to water acidification in GER-synthesis of Base Maps 1 and 2 with regard to agricultural land uses. Red: very endangered; orange: endangered; yellow: slightly endangered; pale tones: principally endangered due to type of rock, but buffering influences by land uses exist; darker tones: forests and other areas, actually endangered.

Fig. 4 (*facing page, bottom right*). Map of the actual pH-values ($<$pH 6.0) of surface waters in GER. Minimal measures pH-values between 1980 and 1985. Red: $<$pH 4.3; yellow: pH 4.3–5.0; green: pH 5.0–6.0.



Pufferungsvermögen der Böden
aufgrund ihrer Basenversorgung
in der Bundesrepublik Deutschland



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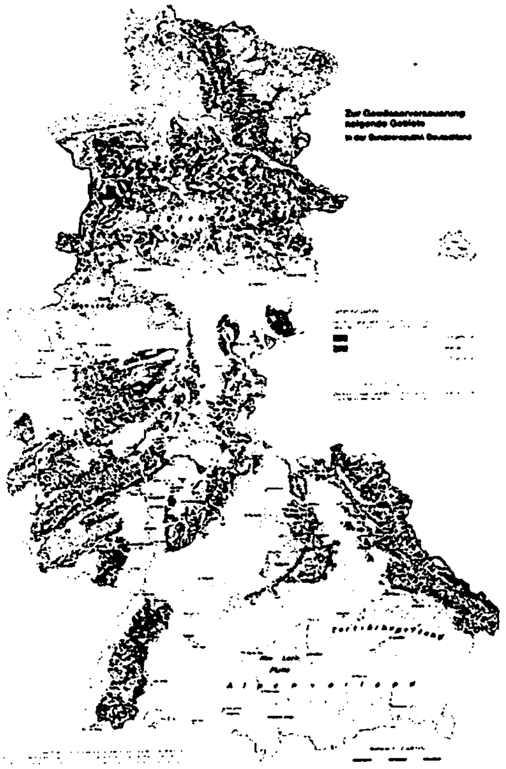
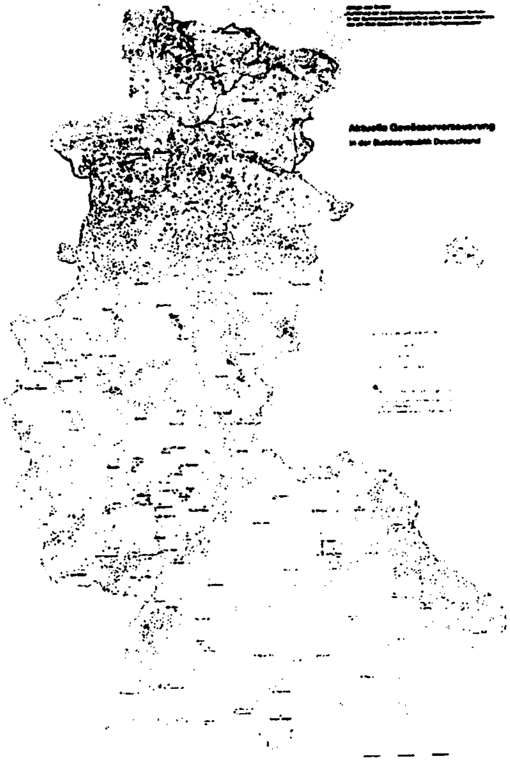


Zur Gewässerversauerung neigende Gebiete
in der Bundesrepublik Deutschland



Aktuelle Gewässerversauerung
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free–carbonate low rock and on soils with low base supply. On the other hand it is evident that the pH-values of surface waters are more favourable in areas where the soils show a certain base supply, even if they are on top of carbonate-free–low carbonate rock.

(4) The mapping does not differentiate between naturally acid and anthropogenic acid water. It is not possible to set up a map of the pH-values of surface waters from the existing data of acid deposition as no direct dependencies exist. Indications on the influence of acid rain on the quality of ground and surface waters are only possible with the additional study of soil and rock situations and the existing land use.

(5) The collected data only permitted a pH value description of the lowest values. A further division into time periods with minimum water flow or snowmelt, which would give interesting clues to the effects of fauna and flora, was not possible for the whole of Germany due to insufficient data material.

(6) The present maps also allow the interpretation of the degree and extent of an existing and possibly increasing acidification of water. The map of pH-values shows heavy acidification only in the upper course of rivers and above all in forest catchment areas.

The result of the acidification is ecological damage as waters, which had been thought of as free from anthropogenic influences of any kind and which represent the last refuge for some rare species of animals and plants, are afflicted.

Concerning the groundwater, only isolated data on the development of the pH-situation have been collected up to now. Therefore, these values were not included in the map of pH-values. However, the increasing acidification of terrestrial ecosystems, above all in areas susceptible to acidification, will presumably also lead to a decrease of the groundwater quality. In these areas the drinking-water quality is endangered by acid rain in the future.

K.- 30.785

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Acidic deposition – ecological effects on surface waters

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2 The chemistry of surface waters

This chapter is concerned with the change in chemical composition of surface waters which has been ascribed to acidic deposition from human activities. Lakes and streams are not isolated units but are intimately linked to the terrestrial components of the ecosystem. The nature of the catchment area often determines the way in which deposited chemicals influence the aquatic part of the ecosystem. The effect of changes in water chemistry on the organisms which live in and around the water, and which is the reason for concern about water chemistry, is covered in Chapter 3. Chapter 4 deals with the effects of acidification on water users other than aquatic species, that is the wildlife which depends on surface water systems.

In this chapter, the evidence that acidification of surface waters has taken place is first considered. This is followed by an examination of the possible causes of change, including deposition of acidic pollutants, other causes related to human activities and natural factors. There are more data available on changes in surface water chemistry than on any other component of the ecosystem considered here. However predictions of surface water quality are still dependent on many other variables, such as the effects of soils, and these should be included in models of the process. Details of the models of surface water acidification are beyond the scope of this review, but some of the best known and most widely referenced models are briefly described and an overview of their results is presented, especially those relating to prediction of acidification for other areas and reversibility of presently acidified waters.

Acidic deposition, whether in a dry or wet state, can reach aquatic systems either by direct deposition into a stream or lake or by passing through other components of the catchment area. Freshwater aquatic ecosystems usually take up only a small proportion of their catchment's land surface. Nilsson (1985) calculated that direct deposition of compounds containing hydrogen or sulphur atoms on the surface of Lake Gårdsjön in Sweden accounted for 37% to 44% of the hydrogen ion input to the lake. This lake takes up a larger percentage of the catchment area (30%) than many other lakes. In many catchments, most of the deposited material passes through vegetation (either living in the form of forest, crop or grass canopy or dead as in the forest litter layer), wetland, soil or over bedrock before reaching the water body. These systems are linked together so that the effects of acidic deposition on one component can cause secondary effects on another. Precipitation can be intercepted by a tree canopy and then travel through the soil and wetland areas before reaching a stream or lake. The effects of acidic deposition on the aquatic system depend not only on the original composition and quantity of the deposited material but also on the effect of deposited material on every system it passes through prior to discharge into the system of interest. The nature of the catchment area becomes less important only where the aquatic system receives runoff or snowmelt that has had little contact with the catchment area or where the lake or stream system forms a large proportion of the catchment area (Galloway and others, 1984). The effect of soils on the water passing through them is considered in *Acidic deposition - ecological effects of soils and forests* (Harter, 1989).

Acidification of an aquatic system, however caused, implies an increase in the hydrogen ion concentration or a decrease in pH but is more usefully defined as the loss of acid-neutralising capacity (ANC) or alkalinity. Acid neutralising capacity represents the ability of the water to neutralise added acids by the reaction of hydrogen ions with inorganic or organic bases such as bicarbonate. Alkalinity is often used interchangeably with ANC but strictly refers only to the bicarbonate, carbonate and hydroxide components of ANC (Malanchuk and Turner, 1987). In the extremely dilute surface waters considered in studies of acidification there is often little inorganic carbon present so the ANC due to the carbonate system is also low. In these circumstances such species as naturally formed weak organic acids (when dissociated) and aluminium-hydroxy compounds at pH levels <5.5) mobilised from soils or sediments can contribute to ANC (Galloway and others, 1984). Surface waters with an ANC of 0 µmol/L or less are acidic by definition. The pH at which ANC is 0 µmol/L is theoretically 5.65 in a bicarbonate solution. In field data collected from 1612 lakes in the northeastern region of the USA during the Eastern Lake Survey, the pH at which ANC = 0 µmol/L varied from about 4.9 to 6 (Linthurst and others, 1986a).

The acid buffering ranges described for soils in *Acidic deposition - ecological effects on soils and forests* (Harter, 1989) also apply to aquatic systems. In naturally acidic brownwater lakes, organic acids can dominate both the pH and buffering of the aquatic system, but this is not the case in clear oligotrophic (nutrient-poor) waters which have undergone changes in water chemistry. Loss of alkalinity can be due to either chronic long-term acidification or acute short-term acidification. Short-term acidification refers to the development of strong acidity during episodes of high acidity, such as spring snowmelt, lasting for only days or weeks. Because of the relatively short exposure periods, biological effects occur only at low alkalinity levels. Long-term acidification refers to the gradual loss of alkalinity over years or decades. As a result of chronic exposure, biological effects can occur at alkalinity<50 µmol/L and waters with alkalinity<200 µmol/L (prior to the onset of acidification) are generally considered sensitive to acidification (Galloway and others, 1984). Effects on living organisms are dealt with in Chapters 3 and 4 but in order to appreciate the following information on changes in water chemistry it is helpful to bear in mind the levels at which biological effects occur. Deleterious effects of acidification on aquatic organisms start to occur at about pH 6 for some species, which corresponds to about 40 µmol/L of alkalinity (range 10 to 90 µmol/L) in the northeastern USA. Many aquatic species are adversely affected in the pH range 5 to 5.5, as is shown in Chapter 3 (Schindler and others, 1985).

2.1 Trends in surface water chemistry

The evidence of change in the chemical characteristics of some aquatic systems over the past century depends on both comparisons of historical water chemistry data with present day figures and paleolimnological analyses of sediment profiles. Paleolimnology is the study of physical phenomena of lakes and other fresh waters in past times. The three analytical measures of importance in evaluating acidification of aquatic systems are pH, conductivity and alkalinity. There has been considerable controversy over the representativeness and accuracy of early measurements of water quality, especially of pH measurements. For example, sampling methods, instruments and techniques have changed over the years and there can be a lack of clear documentation of measurement methods and sample collection procedures used for the historic data. Changes in sampling container material could have affected results. Soft glass containers, once in widespread use, contribute 20 to 100 µmol/L of alkalinity when samples are stored for less than twelve days. Degassing of the sample can raise the pH by more than 0.5 units over the field value experienced by biota, through loss of carbon dioxide. The time during the day or year when the sample was taken, can influence the observed pH and alkalinity values through variation in biological factors in poorly buffered lakes. However many authors recognise these problems and make corrections to allow for them (Havas and others, 1984; Norton and Henriksen, 1983; Kramer and Tessier, 1982).

Galloway and others (1984) present a detailed review of trends in surface water quality in North America based on historic measurements. They concluded that waters not influenced by local urban or industrial discharges from areas exposed to acidic deposition and with soil and bedrock with a low potential to reduce acidity showed a decrease in pH of up to one unit, usually over a few decades, often combined with a decrease in alkalinity and an increase in sulphate. Similar data, indicating consistent decreases in pH or alkalinity, are not found for areas of similar lithology and land use practices, but which are not receiving significant acidic deposition. A similar pattern of pH decrease is also found in Europe in areas of similar geology. The typical shift in areas of southern and southeastern Norway is about 0.5 to 1 pH unit, over a few decades, but a decrease of more than 1.25 units has been seen in some lakes. Lake Gårdsjön and other lakes in the River Anråseå catchment on the Swedish west coast have shown a decrease of 1 to 1.8 pH units from the 1940s to the early 1970s (Hultberg, 1985b; Havas and others, 1984; US/Canada Memorandum of Intent Work Group 1, 1983; Overrein and others, 1981).

The recent development of methods for correcting older chemical survey data and reproducing obsolete analytical methods has led to the reappraisal of some historical surveys of lake water quality in three areas of the USA. These data show that the surveyed lakes in the Adirondack Mountains of New York have undergone substantial losses of alkalinity and reductions in pH, although the degree of loss depended on the assumptions made in correcting the historical data. The lakes surveyed in New Hampshire showed no consistent change in alkalinity while those in Wisconsin showed a significant increase in alkalinity (38 µmol/L) and pH (+0.5 units) even under conservative assumptions. In general, there was a strong tendency for declines in alkalinity to correspond to increases in sulphate concentration (Kramer and others, 1986). Increases in alkalinity in the Wisconsin lakes may be due to land use changes in their catchments from the construction and use of summer residences and feeder roads, which have been shown to exert a profound influence on the chemistry of the Wisconsin Lake population (Loucks and others, 1986). Rogalla and others (1986) found that a high variability in catchment/lake processes between lakes obscured regional patterns of change in alkalinity in the upper Midwest; an area of relatively low atmospheric deposition of acidity.

Direct measurement of the acidification rate of a lake in Ontario, Canada, by continuous monitoring has been reported by Dillon and others (1987). Water chemistry has been monitored in Plastic Lake since 1979, with no changes in either the sampling techniques or the analytical methodology over the period of the study. Between 1979 and 1985, Plastic Lake lost alkalinity at the rate of about 2 µmol/L y; pH decreased by 0.2 units. Acidification was accompanied by a decrease in base cation content in the lake but not an increase in sulphate concentration, probably indicating depletion of available cations in the lake catchment. The dissolved organic content of the lake and the organic anion concentration decreased simultaneously. This acidification process occurred despite a reduction in the deposition rate of strong acids over the period of study, as a result of continuing desorption of sulphate from the catchment. The biota of Plastic Lake have experienced major detrimental effects in the eight years of the study, as will be discussed in Section 3.1.

Both the acidification and deacidification processes have been monitored since 1968 by direct measurement, using the same sampling and analysis protocols over the whole period, for two lakes in southwest Sweden. During 1967 to 1977, sulphate concentrations increased almost linearly and identically in the two lakes from 50 to 150 µmol/L. In 1983-84, after a linear decrease, the corresponding concentration was 100 µmol/L. The alkalinity reserve was lost in one lake in 1971 when the sulphate concentration first reached 100 µmol/L - the same level at which alkalinity was lost in the other lakes in the region. In one lake, a reduction in pH from 6.8 to 4.5 was seen as the sulphate concentration increased, while a decrease in sulphate concentration was accompanied by a decrease in acidity from about 30 to 20 µmol/L of protons, corresponding to an increase in pH of 0.2 units. During the acidification and deacidification processes, sulphate concentrations increased and decreased by 10 and 6 µmol/L y respectively; the hydrogen ion concentration in one lake changed by 3.9 and 2 µmol/L y respectively while the concentration of base cations changed by 1 to 3 µmol/L y. There was a strong coupling between sulphate and hydrogen ion concentrations during the acidification but not during the deacidification phases. The hydrogen ion concentration was reduced in both lakes during deacidification at half the rate at which it increased during acidification. The increased sulphate concentration was balanced by decreased bicarbonate concentration and increased cation concentrations during the acidification phase. The decrease in sulphate concentrations during the deacidification phase was accompanied by a decrease in base cation concentrations in one lake and an increase in the other. This difference can be explained by the difference in soil cover and susceptibility to weathering of the two catchments. The large change in sulphate concentration with only a small change in pH may be due to changes in the concentration of aluminium, but this constituent was not monitored. The hysteresis effect in these two lakes, whereby the changes in sulphate concentration were tracked by changes in the hydrogen ion concentration during acidification but not during deacidification, was also seen in other lakes in the region. This indicates that sulphate loses part of its role in steering the ionic composition of these lakes during deacidification. This may be due to the influence of acidity produced by increased emissions of NO_x in the intervening years (Forsberg and Morling, 1987).

Most of the research on acidification of freshwater aquatic systems has been done on lakes but there are few acidic lakes for which even the fragmentary evidence of past water quality used in the historic comparisons are available. For this reason scientists have turned to the record of a lake's history contained in the lake sediments. The sediment contains physical, chemical and biological evidence which starts in deep sediments deposited thousands of years ago and proceeds upward toward the sediment surface to the present day. A sediment core can be subjected to paleolimnological analyses and dated in a variety of ways to reconstruct chronological sequences of input of pollutants to the lake and the response of the lake biota. One of the most successful and widely used methods of reconstructing the history of lake water quality is the identification and enumeration of the siliceous shells of diatoms preserved in the sediments. Diatoms are sensitive indicators of pH since the hydrogen ion concentration of water has the greatest influence on diatom flora. The various species are each more or less restricted to a particular pH range. By studying these pH relationships for present-day diatom assemblages, it is possible to calibrate the sedimentary diatom record so that the past pH of lake waters can be inferred with a standard error of between about 0.25 and 0.5 pH units. The chronology of sediment accumulation is established by a variety of dating methods. The main method used is often the detection of radioactivity from the lead-210 isotope, a natural component of lake sediments. The ratio-isotopes caesium-137 and americium-241, derived from nuclear weapons testing, can also provide useful information for dating at some sites. Compensation must be made for the mobility of radio-isotopes in the sediments in acidic waters, due to leaching by the acidic water column. This may be done by use of other markers, such as pollen and charcoal, to assist in dating (Battarbee, 1984a; Galloway and others, 1984).

Paleoecological methods should be calibrated in ecosystems with known pollution histories. Studies in the artificially acidified Lake 223 showed that application of standard techniques without calibration predicted a pre-acidification pH of 0.5 units lower than was the case. Errors of this type, if widespread, would cause the degree of recent acidification to be underestimated (Schindler, 1987).

The advantages of paleolimnological methods of assessing acidification are that they are potentially useful at all sites, short-term fluctuations are eliminated, the record is usually continuous and it can be extended backwards in time, if necessary, up to the age of the lake basin. The timing and rate of change can be assessed if a good dating control is available. However the reconstructions are usually unsuitable for resolving short-term (<3 years) variations in pH. Estimates of decrease in pH using this method are minima, since only decreases of >0.2 to 0.3 pH units can be detected and such decreases only occur after substantial losses of alkalinity have taken place. Data sets are available for regions in a range of countries including Norway, Sweden, Finland, the UK, the FRG, Canada and the USA (Davis and Smol, 1986; Battarbee and others, 1986).

The results of paleolimnological analyses show that long-term acidification of lakes situated in upland areas or regions of bedrock poor in bases is a natural process. The acidification process started soon after the glaciers retreated but the timing and rate of the process vary with location. In most cases the main period of change was the early post-glacial although further changes may have taken place later, usually associated with changes in soil and vegetation in the catchment. There is no evidence to suggest that these decreases have been progressive and continuous up to the present day. The large, rapid declines in pH seen recently in many areas are inconsistent with the small, gradual decreases characteristic of long-term natural acidification processes (Battarbee, 1984).

Evidence for an acceleration of the acidification process over more recent years (up to 150 years before the present (BP)) can be seen in studies of the diatom remains in lake sediments. Table 1 shows the results gained by diatom analysis techniques on data from lakes in a number of countries. The first diatom studies of acidification came from Norway in the early 1970s and a considerable data set of Scandinavian lakes has been built up. It is clear that accelerated acidification in Norway began for different lakes at different times between 1890 and 1930. For example pH decreases of between 0.5 and 0.8 units were inferred for the Norwegian lakes Nedre Målmesvatn, Hovvatn and Holmvatn beginning in about 1890, 1918 and 1927 respectively. In Sweden and Finland the recent acidification began after 1945. Lake Gårdsjön in Sweden showed a steady decline in pH from about 7 to 6 over approximately 12,500 years. A sudden decrease from about 6 to 4.5 started in the 1950s. Lake Hauklampi in southern Finland has shown a decrease of about 1 unit since 1960 (Battarbee and Charles, 1986; Battarbee, 1984; Renberg and Hellberg, 1982).

Evidence of recent lake acidification has also been found in the UK, the FRG and the Netherlands. In the UK, data from Galloway in southwest Scotland show that acidification started as early as 1850 in some lakes. Decreases ranging from 0.5 to 1.2 pH units were found for the lakes studied; which included one with the catchment partially situated on metamorphic rocks while the others were entirely granite (Battarbee, 1984; Flower and Battarbee, 1983). Acidification of a Welsh lake occurred over the past 120 years, with a distinct acceleration beginning in the early 1940s, similar to the process seen in Galloway (Fritz and others, 1986). Acidified lakes also occur in Cumbria and the Grampian region of Scotland (Battarbee and Charles, 1986). The results of a major paleolimnological survey of upland lake sites in the UK were reported by Battarbee and others (1988b). All the geologically sensitive sites in areas of high acidic deposition had been acidified, with pH declines varying between 0.5 and 1.5 units. Little change had taken place at non-sensitive sites in areas of high acidic deposition, or at sensitive sites in areas of low acidic deposition. Trace metal analysis showed that all sites had been contaminated by industrially-derived air pollutants since about 1900, with marked contamination by spherial carbonaceous particles, characteristic of oil-derived material. Contamination by magnetic particles, identifiable as power station fly ash from coal combustion, was found at some sites. The evidence at all sites pointed to acidic deposition as the primary cause of surface water acidification. The overall pattern of observations, including land use histories constructed from documentary evidence and pollen analyses as well as data from the lake sediments, could not be explained by alternate hypotheses. The afforestation effect observed at some sites was usually related to enhanced interception of pollutants rather than to a direct effect of the forest.

Evidence from lakes in various regions of the FRG suggests that recent sharp decreases in pH have taken place within the past 30 to 40 years, although the precise timing is not clear (Arzet and others, 1986). Steinberg and others (1987) reconstructed the long-term pH history of a lake in the northern Black Forest of the FRG using diatom records. The pH of the lake decreased by about 1 unit to pH 5.2 from the end of the last ice age until about 1800, by long-term natural acidification processes. About 200 years BP, the recent rapid acidification started, causing the pH to drop from 5.2 down to 4 to 4.3. A consideration of alternative causes of this acidification led the authors to conclude that natural acidification contributed only a small proportion and that industrially-derived acidic deposition was the primary cause. A method of dating using diatoms in surface waters where sedimentary records are absent shows that streams, rivers and pools in the Netherlands, Belgium, Denmark and parts of the FRG have become more acidic over the last 50 years. This is substantiated by studies of sedimentary diatom assemblages in shallow moorland pools in the Netherlands (Battarbee and Charles, 1986; Arzet and others, 1986).

Diatom studies of recent lake acidification have also been carried out in the USA and Canada. A decline of 0.4 to 0.8 pH units was seen in some unbuffered lakes of New Brunswick and Nova Scotia, Canada, during the past 70 years (Elner and Ray, 1987). The data show that weakly buffered lakes in some regions of the USA receiving appreciable atmospheric deposition of pollutants have become more acidic in recent years (Charles and others, 1987; Charles and Norton, 1986; Charles, 1984). Big Moose Lake in the Adirondack Park, NY, USA, had a pH of about 5.8 from before 1800 until about 1950. A large, rapid decline in pH began around 1950 leaving the lake with a diatom-inferred pH of about 4.6. Alkalinity reconstructions indicate a decrease of about 30 µmol/L over the same period. Measured pH has been about this value for the last ten years. Of eleven lakes studied in this region, six of the seven lakes with a current pH at or below 5 show evidence of recent acidification, while the other is a naturally acidic bog lake. None of the four lakes with a current pH above 5 shows any obvious evidence of a substantial decline in pH. The most rapid pH changes (a decrease of 0.5 to 1 pH units) occurred between 1930 and 1970. The best data for timing suggest that the onset of the rapid decline began in the 1930s to 1950s. The recent decrease in pH of Big Moose Lake could not be accounted for by natural acidification or processes associated with disturbances in the catchment. The magnitude, rate and timing of the recent acidification, and its relationship to indicators of coal and oil combustion, indicated that acidic deposition was the primary cause (Charles and others, 1987).

Thirteen lakes in northern New England have been studied (Charles and others, 1986; Battarbee and Charles, 1986). Decreases in pH of about 0.2 to 0.3 units (which is within the range of experimental error) were seen at four sites and three

Table 1 Acidification data for lakes in Europe and North America (Battarbee, 1984; Arzet & others, 1986; Charles and Norton, 1986; Elner & Ray, 1987)

Lake	Location	Year	Modem pH, observed	Approximate onset of acidifcation	Pre-acidification pH, predicted	Modem pH, predicted	pH, decline
Norway							
Langtjern	Buskerud	1975	4.68-5.16	-	4.3-6.2	<5.5	-
Övre Målmesvatn	Vest-Agder	1977	4.53	1927-37	4.4-6.5	<5.2	0.5
Övre Botnatjönn	Hordaland	1977	4.74	-	<5.0	<5.1	-
Rödlivatn	Hordaland	1977	6.23	-	5.1-6.8	5.2-6.9	-
Högleivvatn	Aust-Agder	1977	4.47	-	4.7-6.6	<6.3	-
Risvatn	Aust-Agder	1977	5.66	-	5.7-7.2	5.4-7.1	-
Hovvatn	S Norway	1978	4.4	1918	4.8-5.4	3.9-4.4	0.75
Blåvatnnr	Bergen	1978	5.1	1930	5.2	5.1	0.1
Norre Målmesvatn	Vest-Agder	1979	4.6	1890	4.9-5.3	4.4-4.5	0.6
Holmvatn	-	1978	4.7	1927	4.8-5.2	4.5	0.5
Dorsvatn	-	1978	5.0	-	5.0	5.0	0.0
Brårvatn	-	1979	5.2	1850	5.3-6.1	5.2-5.3	0.3
Botnavatn	-	1978	5.7	1920	5.9	5.7	0.2
Oppljosvatn	-	1979	5.8	-	5.8	5.8	0.0
Gronlivatn	-	1978	6.5	-	6.5	6.5	0.0
Sweden							
Stora Skarsjön	W Coast	1972	4.5	-	6.0	4.5	1.5
Gårdsjön	Bohuslän	1979	4.6	1950	6.0	4.5	1.5
Härsvatten	Bohuslän	1979	4.4	-	5.9	4.2	1.7
Lysvåtten	Bohuslän	1979	5.9	-	6.1	5.2	0.9
Finland							
Hauklampi	N Espoo	1982	4.75-4.9	1961-4	6.0-6.4	5.1-5.4	1.05
Orajärvi	N Espoo	1982	4.7-4.8	-	6.3	4.9	1.4
Häkläjärvi	N Espoo	1982	4.88-5.1	-	6.3	5.6	0.7
UK							
Loch Enoch	SW Scotland	1980	4.4-4.7	1850	5.2	4.3	0.9
Round Loch of Glenhead	SW Scotland	1980	4.5-5.0	1850	5.7	4.7	1.0
Loch Grannoch	SW Scotland	1980	4.4-4.9	1920-30	5.6	4.4	1.2
Loch Dee	SW Scotland	1980	4.9-5.9	1890	6.1	5.6	0.5
FRG							
Grosser Arbersee	Bavaria	-	4.2-5.2	1963	5.4-5.6	4.7	0.9
Kleiner Arbersee	Bavaria	-	4.1-5.1	1950	5.5-5.6	4.6-4.7	0.9
Herrenwiesersee	Black Forest	-	3.6-4.2	1954	4.6-4.7	3.8	0.9
Pinnsee	Lauenburg	-	4.1-5.1	1940	6.3	4.6-4.8	1.5
USA							
Honnedaga	Adirondacks	1976	4.7	1966	6.2	5.6	0.6
Woodhull	Adirondacks	1976	5.2	-	6.0	6.0	0.0
Seventh	Adirondacks	1976	6.5	-	6.5	6.5	0.0
Big Moose	Adirondacks	1982	4.7	1950	5.7	4.7	1.0
Upper Wallface	Adirondacks	-	4.9-5.0	1930-40s	5.1	4.7	0.4
Deep	Adirondacks	-	4.7	1940-50s	5.0	4.3	0.7
Woods	Adirondacks	-	4.7	-	5.2	4.8	0.5
Solitude Pond	New Hampshire	1979	4.8	1920	5.1	4.8	0.3
Speck Pond	Maine	1978	4.7	1920	4.9-5.2	4.7-5.0	0.2
Ledge Pond	Maine	1979	4.5	1905	4.9	4.5	0.4
Tumbledown Pond	Maine	1978	4.8	1970	5.05	4.8	0.25
E Chairback Pond	Maine	1979	5.0	1960	5.2	5.0	0.2
Klondike Pond	Maine	1978	5.9	1945	6.1	5.9	0.2
Branch Pond	Vermont	-	4.7	1930	4.8	4.5	0.3
Canada							
B	Ontario	1981	5.2	1962	6.2	4.7	1.5
C	Ontario	1981	5.2	1954	7.1-7.3	6.4	0.8
Big Indian	Nova Scotia	1981	-	Post 1939	6.1	5.3	0.8
Kinsac	Nova Scotia	1981	-	Post 1917	6.3	6.1	0.2
Round	Nova Scotia	1981	-	-	6.2	6.2	0.0
Emigrant	New Brunswick	1981	-	Pre-1948	6.5	6.1	0.4
Tomoowa	New Brunswick	1981	-	-	6.4	6.4	0.0
St Patrick's	New Brunswick	1981	-	-	6.8	6.8	0.0
Lily	New Brunswick	1981	-	-	6.2	5.7	0.5

other lakes showed decreases of 0.5 to 0.7 units. The decreases all started between 1920 and 1950. Four low alkalinity lakes in Michigan showed no recent pH shifts. Low alkalinity Rocky Mountain lakes also showed no evidence for recent declines in pH. A recent pH decrease of 0.4 to 0.5 units was seen in a Florida lake core.

Paleolimnological investigations show that several lakes in southern Norway which now have a pH of 4.4 to 4.7 and have lost their fish populations in recent decades were naturally quite acidic (pH 4.9 to 5.2) two hundred or more years ago. Recent acidification involved only a small decrease in pH (0.8 units) and yet the change in water chemistry was sufficient to lead to loss of the fish populations, suggesting that other water chemistry parameters played an important role. The effects of acidification on fish populations will be considered in Section 3.1. Davis and others (1985) used paleolimnological techniques to determine total organic carbon (TOC) concentrations. They concluded that concentrations of organic matter in the water decreased with the pH as acidification progressed, possibly by precipitation with acid-mobilised metals, increasing the clarity of the water as humic matter precipitated out. They suggested that ANC in these lakes before the start of acidification was due to the presence of humic organic matter rather than bicarbonate alkalinity. At this time, aluminium and trace metals were complexed with organic matter and so not toxic to fish. Decreases in inferred TOC concentrations at Lake Holmvatn began about ten years before the decreases in pH, possibly because the water was buffered by organics and aluminium. In this period, increasing input of mineral acids to the lake would have increased the tendency of organic molecules to aggregate and precipitate; both by adding protons to the molecules and by mobilising aluminium, iron and other metals in their inorganic form, which can react with organic matter to cause precipitation. At Lakes Holmvatn and Hovvatn the fish finally succumbed 20 to 30 years after rapid decreases in TOC began.

There is also evidence that is consistent with the occurrence of these changes in water chemistry in the Adirondacks, NY, USA. Lake liming experiments in Sweden and Norway have shown that when the pH of lakes is raised the reverse of some of these hypothesised processes occur - those involving diatoms, water clarity, dissolved organic matter and uncomplexed aluminium (Charles and Norton, 1986; Davis and others, 1985).

In addition to biological remains, lake sediments and peat cores can contain a variety of substances which are directly related to atmospheric deposition and which can help to provide information on the lake's history. Concentrations of polycyclic aromatic hydrocarbons (PAH), soot particles, lead, sulphur, and vanadium; as well as sulphur isotope ratios and magnetic particles can be interpreted to indicate trends in atmospheric deposition of substances derived from combustion of fossil fuels. Acidification of aquatic systems can be inferred from changes in concentrations of common elements and trace metals such as calcium, magnesium, sodium, potassium, zinc, lead, aluminium, manganese and iron. Disturbances in the catchment can be indicated by changes in the common elements and trace metals, pollen, charcoal and changes in the sedimentation rate based on lead-210 dating. Information from trace metal concentrations is the most widely available type of sediment chemistry data. Unfortunately, additional processes related to pre- or post-depositional mobilisation or to sediment compaction of sulphur make it impossible unambiguously to infer deposition rates from sediment accumulation rates. Catchment characteristics influence the speed with which compounds of a mainly industrial origin begin to have an effect on the life forms in lakes. Data from Finland show that there was a delay of up to one hundred years between a distinct increase in the deposition of certain compounds (lead and many PAH) and the start of detectable biological changes. Evidence for the acidity of deposition cannot be directly related to the chemistry of sediments but decreases in the pH of aquatic systems can be inferred from evidence of declines (relative to immobile elements) in the deposition rates of elements (such as zinc, manganese, and calcium) mobilised by increasing lake water acidity (Tolonen and others, 1986; Charles and Norton, 1986).

In the northeastern USA, lake sediments record an increase in the accumulation rate of lead, independent of most other elements, which started in the period 1850 to 1900 and fell into the period 1860 to 1880 in most lakes. Peak values were typically reached in the 1970s. Zinc sedimentation took a generally parallel course to that of lead, but in acidic lakes (pH <5.5) zinc accumulation rates declined relative to lead in recent sediment. This pattern was also seen in lake sediments in eastern Canada although the dating was different. This may be related to acidification or to processes involved in the transformation of sediment to rock. Copper, cadmium, chromium, arsenic and antimony deposition also increased in this period, although by less than the deposition of lead. The concentration and deposition rates of vanadium increased from 1920-40 to nearly the present, generally in parallel with oil consumption. Acidification of lake waters is shown by the loss of calcium, magnesium and zinc from sediments relative to titanium dioxide over the past century. These chemical trends pre-date biological evidence for water column acidification. Water column acidification could cause leaching of these elements from sediment which had already been deposited or reduce adsorption on sedimenting particles. Thus the chemical effects of acidification could affect sediments which pre-date the acidification of the water column. The effect could be real, however, since the effects of acidification on diatoms were seen to lag behind the chemical effects of metal pollution and acidification in time equivalent sediment for some lakes (Charles and Norton, 1986; Norton, 1986; Ouellet and Jones, 1983).

Elevated levels of lead and zinc in recent lake sediments have been seen in Norway, with the increase in concentrations starting prior to 1930 (Norton and Hess, 1980); in the UK, with increases starting from 1800 (Battarbee and others, 1985); and in the FRG in parallel with the acidification of the lakes studied (Arzet and others, 1986). Acidification of lake waters is seen in the decrease in zinc concentrations in the uppermost sediments of lakes with a pH of about 5 or less. Lead and zinc concentrations generally increased before any significant lake acidification indicated by biological data. Lead usually started increasing before zinc; concentrations of these metals increased by as much as 300 and 700% of background values respectively. In unacidified lakes with heavy metal build-up, the biological responses seen in acidified lakes were not found. The mobility, and possibly also the biological availability, of these metals in lake waters varies with element speciation, which is pH dependent to a large extent. Metal toxicity may therefore be a function of acidification (Norton, 1986; Norton and Hess, 1980; Davis and others, 1980).

2.2 Possible causes of change

A number of hypotheses have been proposed to explain observed changes in pH, alkalinity or sulphate concentrations in surface waters. While each is a plausible explanation, supported by experimental evidence, for acidification at some sites, none applies universally to all surface waters. Four main hypotheses have been suggested as the main cause of the observed recent acidification of surface waters. These are:

- Acidification of the soil of a catchment by natural causes (with the anions of organic acids or carbonic acid acting as the mobile anions), assuming that acidic deposition contributes only an insignificant fraction of the acidity. This is considered in *Acidic deposition - ecological effects on soils and forests* (Harter, 1989).
- Atmospheric deposition of acidic substances to both the body of water and its surroundings. This is considered in Section 2.3 of this report.
- Land use factors such as conifer afforestation, forestry practices and other disturbances, and changes in agricultural practices and animal husbandry; involving organic or bicarbonate anions acting as mobile anions (Krug and Frink, 1983; Rosenqvist, 1981, 1978).
- The buffering and solubility effects of naturally-occurring organic matter in sensitive waters cause strong acid deposition to alter the balance between organic acid anions and sulphate in runoff waters, but not the pH (Krug and others, 1985; Krug and Frink, 1983).

This section will deal with the latter two alternative explanations of water acidification.

It is possible to find instances where human activities of these types have affected lake chemistry. Lake Blåmissusjön in northern Sweden is a case in point where agricultural activities exposed sulphide-rich minerals. These formed free sulphates and sulphuric acid in the soil, leading to acidic runoff and lake acidification down to about pH 3 since about the 1940s. Cone Pond, NH, USA, has also suffered acidification in response to human activities, in this case deforestation by fire and subsequent pasturing of sheep. The lake has had a pH of 4.6 to 4.8 for at least 200 years. However, neither of these lakes are typical of the type of lake which has undergone acidification over the past few decades (Renberg, 1986; Ford, 1986).

Fuller and others (1987) found that whole tree harvesting changed stream chemistry in the White Mountains, NH, USA, largely by increasing the concentrations of nutrients. Increased nitrification, from the organic nitrogen pool, and mineralisation occurred, leading to acidification of the soil solution, increased adsorption of sulphates in the soil and loss of nitrogen to stream water. Substantial increases in streamwater concentrations of hydrogen and inorganic aluminium ions also occurred after removal of biomass. Higher losses of protons and strong acid anions were found than occur when fast forest growth is taking place. This is the reverse of what was suggested by proponents of the land use hypothesis. However, commercial clearcutting practices were not used in these experiments but the felled trees were left in place and herbicides applied to prevent vegetation regrowth; also the site may be unusual in its runoff characteristics.

Martin and others (1984) found that the effect of clearcutting on the nutrient loading of a number of streams in New England was usually small when comparisons were made of stream chemistry in clearcut and nearby uncut catchments with a wide variety of soil and forest types. The only area where consistent and substantial increases in stream nitrogen concentrations occurred was the White Mountains, NH; the investigators were unable to locate any other site where stream chemistry was altered as markedly.

Relatively few studies have been done on the effects of land use on surface water acidification but the Norwegian project on the effects of acid precipitation on forests and fish (Drablos and Sevaldrud, 1980; Timberlid, 1980; Drablos and others, 1980) did consider the issue. Three areas in southern Norway were examined. Several poorly buffered lakes with fish losses in the typical inland area of Femund, for which there were good historical data on land use, were considered. These lakes showed a slight acidification trend and damage to the fish population from 1950. In four of the five areas most of the affected lakes were situated above the timberline. The local dairy farms, haymaking from peatlands and most of the cattle pasturing were generally located several kilometres downstream from the acidified lakes. Acidified lakes were found in areas where reindeer pasturing had increased, where it was moderate and stable and where it had not occurred at all. In the Tovdal, Fyresdal and Nissedal areas, 78% of lakes in catchments which had never been farmed had no fish population left. In catchments containing abandoned farms, 60% of lakes were fishless, while even in catchments where farming was still carried out, 30% of the lakes had lost their fish stocks over the last decades. This is a considerable difference from what would be expected if agricultural activity had a strong influence on acidification.

In Telemark, Agder and Rogaland counties, pasturing of animals took place in the near outfield (200 to 300 m above sea level) and the remote outfield (300 to 600 m above sea level). Pasturing of the outfields took place over a larger area and was more intensive in the middle and to the end of the 19th century than it is today. This is not uniform, however, since pasturing pressure on the near outfield has decreased recently while in the remote outfields the pasturing pressure has increased in some areas. During the same period of time, the fish population has decreased or vanished at both elevations. The decline in fish stocks has been smaller in the near outfield area at lower elevations than in the remote area, where it should have been most serious if e decline of pasturing with a subsequent shift in the egetation cover had caused the acidification. None of these studies showed a systematic relationship between changes in use of the outfields and the trend toward regional lake acidification together with the decline in fish population (Timberlid, 1987, 1980; Drablos and Sevaldrud, 1980; Drablos and others, 1980).

Evidence from diatom remains can also be used to throw some light on the possible causes of acidification of aquatic systems. Many researchers have chosen to study lakes with a history of minimal disturbance from human activities in their catchment to avoid the influence of land use on the sedimentary record of the lake. This resulted in the lakes studied being mainly located in remote alpine and sub-alpine ocations. The recent acidification found in these studies cannot be related to land use since the catchments are virtually undisturbed. Among the lakes to which this applies re Hovvatn, Norway (Davis and Berge, 1980); Munajärvi, Vitsjön II, Matalajärvi and Valkjärvi, Finland (Tolonen and others, 1986); Kinsac, Nova Scotia, Canada (Elner and Ray, 987).

A decline in pH of about 0.5 to 1.2 units from the previously table conditions occurred at four lakes in Galloway, cotland, starting at dates ranging from 1840 to 1925. As wo of the lakes studied had non-forested catchments and at he other two the decline in pH predated the beginning of fforestation this acidification cannot be ascribed to fforestation processes (Battarbee, 1984; Flower and attarbee, 1983). The decline in agriculture, especially razing, at upland sites leading to regeneration of acid eathland communities was also investigated as a possible ause of lake acidification in Galloway. Pollen analysis, iatom analysis and trace metal analysis of a dated lake ediment core from a non-afforested catchment (Loch Enoch) ere compared. Recent lake acidification started in 1840 but ere was little change in the proportions of pollen from the rious species over the past 200 to 300 years. If the duction in grazing were the cause of lake acidification an crease in the most important heathland species, *Calluna lgaris* (a heather), should have taken place. Instead there as a gradual decrease in heather species and an expansion grass species, the result of a burning/grazing cycle mmon in the area, indicating that a change in land use has t caused soil acidification. Analysis of the trace metal ntent of the sediment showed an increased concentration of d, zinc and copper in the lake sediment since about 1800 ich could only be accounted for by atmospheric position. The atmospheric contamination of the lake diment by trace metals was correlated with sedimentary dence of acidification suggesting that, as these trace tals from industrial emission were transported to the lake, acidic pollutants could also have been deposited from the osphere (Battarbee and others, 1985).

analysis of the change in water quality found in a chment undergoing acidification by the change of etation to an acidic peatland environment was studied by es and others (1986). They used a sediment core to study nd Loch of Glenhead in Galloway right back to the t-glacial era. This was initially a non-afforested catchment which has sh[illegible] a sharp acidification since 1850. Woodland was replaced by acid peatland between 6000 and 4000 years BP and no further major changes took place in the region until the recent afforestation started about 30 years ago. Acid organic soils were gradually replacing mineral soils from 9000 years BP onwards. However, neither the early development of acid soils nor the later expansion of blanket peat caused acidification of the lake. Indeed a small but significant increase in mean water pH occurred at the time of blanket peat expansion. Round Loch had a pH between about 5.5 and 6 throughout the post-glacial period until the recent post-1850 acidification, when pH fell to the present value of about 4.7. From the results of previous studies, the authors concluded that nowhere in the UK did soil acidification and blanket peat formation during the post-glacial period result in the lowering of lake water pH below about 5 to 5.5.

No appreciable land use change has occurred in the acidified Llyn Hir catchment in west Wales, UK, since the introduction of sheep by the Cistercian monks in the 12th century so the recent acidification of the lake cannot be accounted for by land use changes. Acidification of Llyn Hir has occurred over the last 120 years, with a distinct acceleration beginning in the early 1940s. The lake pH was in the range from 6.1 to 6.5 from the 17th to the early 19th centuries but had dropped to the range of 4.5 to 5.1 in the early 1980s. The timing of the changes and trends of the atmospheric pollution indicators (trace metals, magnetics, cenospheres), paralleling the acidification process seen in the diatom record, are consistent with the acidification of the lake being caused by acidic deposition (Fritz and others, 1986)

Arzet and others (1986) found no evidence that changes in vegetation were responsible for the recent acidification of four lakes in the FRG (*see* Table 1). The two Bavarian lakes are situated in forest where the species composition has remained unchanged over centuries. Afforestation in the Black Forest (Baden-Württemberg) occurred from 1800, while the recent acidification trend in the lake studied started about 30 years ago. Acidification in the Lauenberg lake began in about 1940, prior to the start of afforestation after the Second World War. Moreover, if forest growth were responsible for acidification then organic ions should be the predominant anions in runoff from the clearwater acidified areas of concern, whereas sulphate is usually the major anion in these areas (Schindler, 1988).

In North America, the rapid decline in pH of Big Moose Lake in the Adirondacks, NY, USA, started in about 1950. Disturbances of the catchment were not likely to be responsible, as the only disturbance which occurred at the onset of the pH decline was the destruction of some trees by wind, affecting only 25% of the catchment. Moreover, previous disturbances such as logging in the late 1800s and early 1900s caused no apparent sizable shift in lake pH (Charles, 1984).

Similar conclusions were drawn from investigations of Big Moose and two other lakes in the Adirondacks, NY, as part of the Paleoecological Investigation of Recent Lake

Acidification (PIRLA) project (Charles and others, 1986). There was no record of fire or logging in the Upper Wallface Pond catchment. These disturbances occurred in the Deep Lake catchment but the acidification trend was not logically related to the disturbance. Charles and others (1986) concluded that 'the most reasonable explanation for the recent decrease in lakewater pH in the lakes is increased atmospheric deposition of strong acids, though watershed (catchment) disturbance and natural acidification can also play minor roles.'

Battarbee (1984) concluded that 'despite some ambiguous situations associated with land use changes, the weight of evidence favours acid precipitation as the main cause of recent acidification in the lakes so far studied. Its effect has yet to be disproved at any site and the temporal and spatial patterns of acidification within northwestern Europe, limited though the data are, are consistent with such an hypothesis. In all cases the onset of acidification postdates about 1800, after the development of coal as a major power source during the industrial revolution, and the later acidification of Swedish and Finnish lakes may be associated with a postwar increase in emissions from oil combustion as well as a change in the pattern of emissions.'

Krug and others (1985; Krug and Frink, 1983) suggested that the buffering and solubility effects of organic matter determined the alkalinity of sensitive waters. They acknowledged the present importance of strong acid deposition in the acidification of some surface waters, but argued that additions of sulphuric acid in rain would increase the flux of sulphate and decrease the flux of organic anions with little or no measurable change in pH. This implies that a reduction in strong acid deposition would induce the release of soil humic acids in nearly equivalent amounts. This buffering mechanism is advanced as an explanation for the suggested 'remarkably' low rate of cation export from catchments receiving substantial amounts of acidic deposition. LaZerte and Dillon (1984) used data from several catchments in Ontario, Canada, to evaluate the hypothesis. Their results showed that organic acids did not contribute significantly to the acidity of the studied catchment, on an annual basis, but that sulphuric acid was the primary source. The suggestion that a decrease in sulphate concentration would lead to an increase in the organic acid concentration rather than an increase in pH of the water was evaluated on lakes in the Sudbury area, where a decrease in local SO_2 emissions has reduced lake sulphate concentrations. No change in organic acid concentration was observed here, while the pH of the lakes studied increased substantially. Studies of three regions in Ontario with different rates of acidic deposition and soils of low pH showed that the flux of cations was greatest in the catchment where the acidic deposition rate was highest. The cation flux in the area with the lowest deposition rate of strong acid was greater than the input rate of strong acid, indicating that natural processes controlled the cation flux here. The remaining catchment had a strong acid deposition rate of an order of magnitude greater while the cation flux was 2 to 3.5 times greater. The authors concluded that, in acidic soils, cation flux is increased as a result of atmospheric deposition of strong acids.

Field studies in Canadian waters showed that the ability of organic matter to accept protons and thus buffer acidity varied seasonally. While organic anions buffered acidity added as sulphuric acid during the summer months, during the rest of the year the hydrogen ion concentration varied with the sulphate ion concentration. Waters containing a high concentration of organic anions are usually associated with the drainage of wetlands and appear to have a brown colour, while waters with a low concentration seem clear in normal conditions. In coloured streams, sulphate and organic anion concentrations showed opposing seasonal cyclic patterns while negative alkalinity (or acidity) was nearly the mirror image of sulphate concentration. Organic anions, which could constitute up to 65% of the anions in summer, were important contributors to stream acidity seasonally. The presence of organic matter could result in a pH value one unit lower than that in equivalent clear waters. During the summer months when sulphate concentrations were at their lowest, organic anions could maintain elevated hydrogen ion concentrations (pH 4.2 to 4.5). However, the highest hydrogen ion concentration (about pH 4.1) occurred when sulphate concentrations were highest and the organic anions relatively low or declining (Kerekes and others, 1986a; Gorham and others, 1986). Kerekes and others (1986a) concluded that the atmospheric deposition of sulphuric acid increased the acidity of dilute, organic waters in Nova Scotia, Canada, particularly during the periods of high water discharge from late autumn to spring.

This has also been seen in Scandinavia. Brakke and others (1987) assessed the relative contributions of acidity associated with weak acids (organic anions) and strong acids (mainly from sulphates) to the acidity status of 94 moderately humic (coloured) lakes in two areas of Norway. The two areas received precipitation with differing acidity and amounts of sulphates, but the pairs of lakes in these areas located on granitic bedrock, were of similar size and had similar ranges of concentration of base cations and total organic carbon (TOC). The difference in sulphate concentrations determined the difference in pH of lakes having equivalent concentrations of base cations and TOC. TOC contributed some strong acids in each area. Organic anions contributed significantly to lakewater acidity at about 4 to 5 mol/kg of TOC. While organic anions contributed to acidity, however, the high TOC lakes maintained a pH well above the levels toxic to the indigenous brown trout. Although the coloured lakes in the area receiving precipitation with higher sulphate concentrations and lower pH had sources of TOC in their catchment, the anion content was dominated by sulphates as was the case with clearwater acidic lakes in southern Norway. The organic acids made humic lakes more sensitive to acidic inputs from atmospheric deposition than clearwater lakes, for lakes with similar concentrations of base cations. The higher values of strong acidity in southern Norway correlated with higher excess sulphate, because strong mineral acids were superimposed on organic contributions to acidity.

This does not mean that all lakes with a low pH have reached that state by means of acidic deposition. However, acidification has been shown to occur in areas without concomitant land use changes and organic anions are not a major cause. In these cases, acidic deposition must be considered as a likely cause of observed surface water acidification. None of these data provide a firm conclusion as to the rate of chemical change in surface waters. Galloway and others (1984) drew two conclusions from an extensive review of work on alternate explanations of surface water acidification. Firstly, that acidification of clear surface waters, poor in nutrients, to pH values below 5 occurs only in regions receiving acidic deposition, and regional acidification only occurs where acidic deposition is present. Secondly, regional surface water acidification occurs without land use changes in areas receiving acidic deposition. In addition, there is no body of data available which indicates consistent decreases, of such magnitudes and at such rates, in alkalinity or pH of surface waters at otherwise undisturbed sites not receiving acidic deposition. The logical conclusion is that acidic deposition (either remote or local in origin) has caused acidification of some surface waters. Furthermore, it is reasonable to conclude that other surface waters of similar sensitivity that receive similar levels of acidic deposition have become or are now being acidified.

2.3 Relationships between chemical change and atmospheric deposition

Evidence of changes in the chemical characteristics of some aquatic systems over the past century was presented in Section 2.1. Only a small proportion of those data can indicate whether acidic deposition could be the cause of these changes since not enough information is available for analysis. This section will consider whether changes in aquatic chemistry could be caused by the deposition of atmospherically transported material. The levels of major ions found in sensitive catchments and the importance of various ions for acidification are considered. The relationship of sulphates in surface water to atmospheric deposition of sulphate is discussed, including evidence that sulphate is the dominant anion in acidified clearwater lakes. The effects of reductions in the deposition of sulphates and of nitrate deposition on water chemistry are also considered.

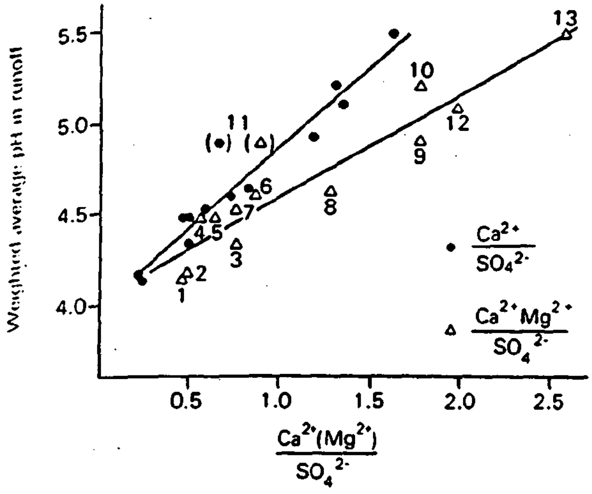
To assess the impact of acidic deposition it is necessary to measure the total input, that is both wet and dry deposition. Measurements of wet deposition only, which are taken to investigate the composition of precipitation, are inadequate for assessing impacts because total deposition is underestimated not only near emissions' sources but also in remote areas. Bulk deposition measurements collect wet deposition and an undefined portion of the dry deposition and so, although not perfect, they are more useful for chemical budget calculations than measurements of wet deposition alone. Calibrated lakes or catchments are those for which the input and output rates of substances are measured and can be used to infer dry or total deposition of acidic substances. Both anions and cations in atmospheric deposition should be measured to enable calculations of the net loss of base cations from the catchment. In addition, the effects of the acidifying ions are partially dependent on the rates of deposition of accompanying neutralising cations (Federal/Provincial Research and Monitoring Coordinating Committee, Canada, 1986; Galloway and others, 1984).

The most important ions in deposition which are associated with acidification are hydrogen (or negative alkalinity), sulphate, nitrate and ammonium. The measurement of only free acid (hydrogen ions, often given in pH units) is inadequate for assessing the impact of acidic deposition since this ignores the contribution to base neutralising capacity (BNC) from substances such as the ammonium ion which can provide 25-50% of the input of acid relative to hydrogen ion deposition. The reactions of sulphur and nitrogen compounds in the soil are discussed in *Acidic deposition - ecological effects on soils and forests* (Harter, 1989) but generally nitrogen compounds are retained in the ecosystem, although possibly with significant internal production of

Table 2 **Average pH and concentrations (mg/L) of major constitutents in runoff from calibrated catchments in Norway, Sweden and North America** (Hultberg, 1985a)

Element	Storgama Norway	Birkenes Norway	L Gårdsjön SW Sweden	Hälsingland Central Sweden	Hubbard Brook NH, USA	ELA Rawson Lake Canada	Muskoka-Haliburton Canada	Sudbury Canada
pH	4.5	4.5	4.2	4.7	4.9	5.5	5.1	4.7
Ca^{2+}	0.8	1.3	1.5	2.3	1.7	2.2	6.6	5.7
Mg^{2+}	0.2	0.5	1.4	0.6	0.4	0.8	1.7	1.3
K^+	0.3	0.3	0.6	0.35	0.2	0.4	0.6	0.5
Na^+	0.8	2.8	6.5	1.8	0.9	1.3	1.2	2.1
Al_{tot}	0.16	0.63	0.71	0.32	0.23	-	0.17	0.32
Fe	-	-	0.40	-	-	0.37	0.60	0.60
Mn	-	-	0.051	-	-	-	0.068	0.14
NH_4^+-N	<0.07	<0.07	0.03	0.03	0.03	-	0.05	0.06
Cl^-	1.0	4.4	11.0	1.3	0.5	0.3	1.1	5.7
SO_4^{2-}-S	1.3	2.4	3.8	1.9	2.1	1.1	3.9	5.7
NO_3^--N	0.19	0.098	0.046	0.05	0.44	-	0.14	0.038
DOC	-	-	10.0	15.0	0.3-2.0	-	-	-
Alk*	<0.0	<0.0	<0.0	<0.0	0.96	3.7	8.0	<0.0

* Alkalinity as mg/L HCO_3^-



Sites 1 to 3 - Lake Gårdsjön, SW Sweden
4 - Birkenes, Norway
5 - Storgamma, Norway
6 and 7 - Langtjern, Norway
8 to 10 - Hälsingland, central Sweden
11 - Hubbard Brook, NH, USA
12 - Muskoka-Haliburton, Canada
13 - ELA (Rawson Lake tributary), Canada

Figure 1 Linear regressions between runoff pH versus ratios of excess base cations (calcium and magnesium) and excess sulphate from calibrated catchments in countries of the northern hemisphere (Hultberg, 1985a)

acidity. Sulphates tend to pass through to the aquatic system, although sulphate adsorption takes place in some soils, mainly those which have not undergone glaciation. Thus in many systems a sulphate balance is achieved; within the limits of error in the measurement of dry deposition, the amount of sulphate entering in deposition is approximately equal to the amount leaving the catchment (Federal/Provincial Research and Monitoring Coordinating Committee, Canada, 1986; Galloway and others, 1984).

Sulphur in undisturbed surface waters can come only from the weathering of sulphur bearing minerals or atmospheric deposition. Where sulphur compounds are not available in bedrock, atmospheric deposition is the primary source. This is especially true in areas of granite bedrock with thin soils which have no reactive sulphur sources but which receive acidic deposition. In these areas, sulphate can still become the dominant ion in low alkalinity waters (Galloway and others, 1984).

The mean concentrations of the major constituents in runoff from several calibrated catchments lying on granite terrain, and therefore sensitive, in Europe and North America are shown in Table 2. The range in concentration of each element is less than tenfold between the studies and the ammonium range is only twofold. However, differences stand out for pH, calcium, magnesium, total aluminium, sulphate and nitrate ions. Hultberg (1985a) used these data to calculate the ratio of excess, or non-marine, calcium to excess sulphate and the sum of excess calcium and magnesium to excess sulphate. Linear regressions of these data with weighted-average runoff pH, shown in Figure 1, give high correlations between pH in the runoff water and the ratios of base cations to sulphate. This indicates that an increased concentration of sulphate can acidify the runoff water where base cation release or sulphur retention cannot absorb the increased input. As pH decreases in runoff water the aluminium concentration increases, but this has little effect on runoff pH although it can adversely affect the biota.

The relationship between atmospheric deposition of sulphates and surface water sulphate concentration is shown by plotting the mean and range of excess sulphate exported from catchments across eastern North America on an approximately west to east axis that transects the region of considerable atmospheric deposition of sulphate. Figure 2 illustrates this, together with the wet deposition of excess sulphate at each location and estimated total (wet plus dry) deposition of sulphate at four monitoring stations. There is a

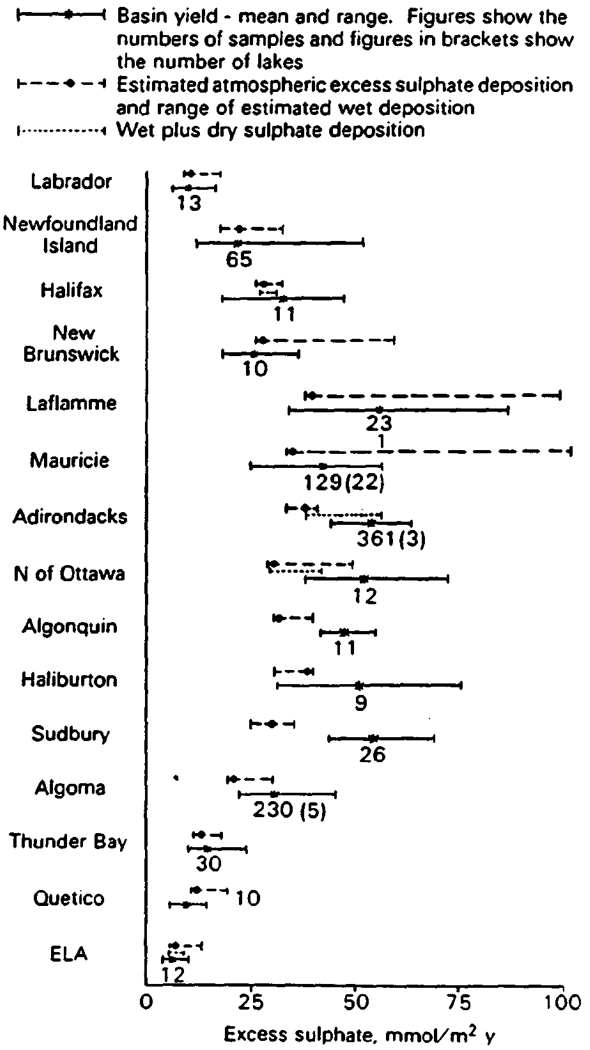


Figure 2 Mean and range of basin specific yield of excess sulphate compared with estimated excess sulphate deposition in precipitation for 1980 and the range of estimated wet deposition for 1977 to 1980 from the CANSAP precipitation network. The wet plus dry deposition of sulphate data are calculated from 1980 measurements of sulphur oxides in air at four APN stations. Data are shown on an approximately west to east axis (US/Canada Memorandum of Intent, Work Group 1, 1983)

clear positive relationship between excess sulphate deposition and sulphate in the runoff water. In the areas of highest deposition, however, sulphate export exceeds deposition, probably due to dry deposition of sulphur compounds, which tends to be underestimated in many deposition measurements. The agreement between catchment sulphate yields and measured wet and dry deposition is extremely good, showing that dry deposition is greatest near the centre of the continental pollution plume downwind of industrial sources and is less important in remote areas. This good agreement also indicates that most of the sulphate in these lakes comes from atmospheric deposition and that there is little retention of sulphate in their catchments (Thompson and Hutton, 1985; US/Canada Memorandum of Intent Work Group 1, 1983).

The dependence of surface water sulphate concentrations in North America on atmospheric deposition of sulphate is also shown by the statistically significant correlation between sulphate in surface water and sulphate concentrations in precipitation over a wide range of concentrations, as illustrated in Figure 3. Southeastern Canada and the northeastern USA receive precipitation with a high concentration of sulphates and they have surface waters with high concentrations of sulphates. Similarly those areas receiving precipitation with low concentrations of sulphates, such as the Rocky Mountains, Colorado, Labrador and northern Quebec, have surface waters with low concentrations of sulphates. If data from these latter areas are used as a baseline for North America, the estimated background sulphate concentration in North American lakes is 10 to 20 µmol/L. Lakes in eastern North America receiving acidic deposition, by contrast, have sulphate concentrations of 50 to 84 µmol/L. This suggests that about 40 to 60 µmol/L of sulphate (average of 50 µmol/L) is derived from atmospheric deposition due to human activities. This applies to a large region of eastern North America, including some areas distant from sources of sulphur emissions. Aquatic systems in areas closer to sources of sulphur emissions will have larger increases in sulphate concentrations (Galloway and others, 1984).

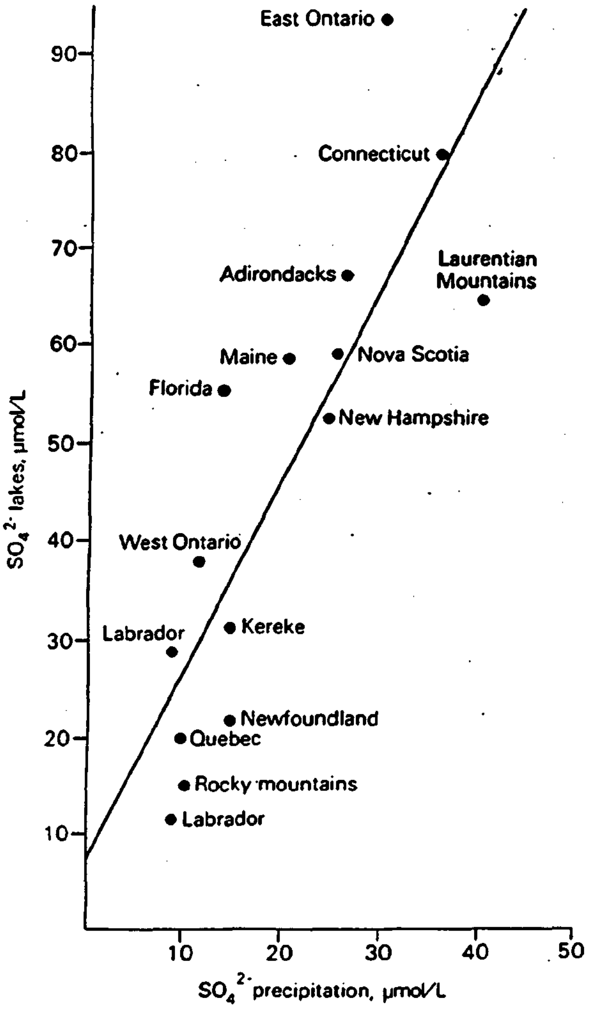


Figure 3 Mean concentration of excess sulphate for 15 lake groups in North America and mean excess sulphate concentration in wet deposition at nearby deposition monitoring stations (Galloway and others, 1984)

Dupont and Grimard (1986) also found a statistically significant relationship between both lake and precipitation sulphate concentrations and atmospheric sulphates and precipitation acidity in a survey of 1091 lakes in Quebec. The spatial distribution of lakes in four sulphate concentration classes was mapped with the weighted mean sulphate concentration in precipitation for two years. The general pattern showed a strong decreasing gradient from the southwest to the northeast, similar to the one observed for sulphate in precipitation. Lake sulphate concentrations were highly correlated with precipitation sulphate concentrations when lakes with <200 µmol/L of alkalinity were considered.

There is a declining gradient of wet sulphate deposition from south to north in Nova Scotia with the highest values being in the south, except for a localised increase around metropolitan Halifax due to local emissions (Kerekes and others, 1986b). Atmospheric deposition of excess sulphate and nitrate-nitrogen for 1977 to 1980 in the southwest of the province averaged 0.24 and 0.21 kmol/ha y respectively compared with 0.19 and 0.13 kmol/ha y respectively for the northeastern third of Nova Scotia. Precipitation pH increased from 4.5 to 4.8 from southwest to northeast along the same axis. Sulphate deposition in Halifax for 1982 was 0.44 kmol/ha y, while nitrate-nitrogen deposition was 0.15 kmol/ha y. That was equivalent to loadings of 42 kg/ha y of sulphate and 2.1 kg/ha y of nitrate-nitrogen (Underwood and others, 1987). Sulphate in Nova Scotia was predominantly deposited as sulphuric acid rather than the ammonium sulphate characteristic of general continental precipitation (Ogden, 1982). A study of over 80 wetlands and lakes in the province showed that excess sulphate concentrations ranged from 22.5 µmol/L in the south, about 15 µmol/L further north in the Kejimkujik area and <8.5 µmol/L in the northern areas with values >42.5 µmol/L in the Halifax area, reflecting the atmospheric deposition pattern of sulphate (Kerekes and others, 1986b). Although precipitation and lake water chemistry in Nova Scotia is dominated by chloride from sea salt, correction for marine influence shows that the dominant anion in both precipitation and lake water is sulphate (Underwood and others, 1987; Ogden, 1982).

Neary and Dillon (1988) compared the chemical attributes of 1168 soft water lakes in Ontario in zones of different levels of sulphate deposition. The results showed that the pattern of increasing sulphate deposition from north to south in Ontario results in a corresponding pattern of increasing lake sulphate concentration and decreasing lake alkalinity concentration and pH. The presence of organic acids did not explain these patterns. The levels of pH and alkalinity were highest where organic anion concentrations were highest.

Large scale surveys have recently been carried out in North America with the objective of assessing the water quality of a representative sample of lakes (>4 ha and ≤2000 ha in surface area) and determining which relationships in water chemistry are regional in nature (Jeffries and others, 1986; Linthurst and others, 1986a, b). Frequency distribution statistics were obtained for pH, ANC, sulphate and organic anion (A^-) concentrations. The Canadian regions surveyed were Ontario, divided into northwestern (NW ONT), northeastern (NE ONT) and south-central (SC ONT) sub-regions; Quebec (QUE) and Labrador (LAB); and the Maritime region, comprising Newfoundland (NF), Nova Scotia (NS) and New Brunswick (NB). The US Eastern Lake Survey covered the northeastern states, the upper midwest and the southeast of the USA. Only the results from the northeastern states will be considered here since this is the area where acidic deposition is most significant. The northeast was divided into the following sub-regions: Adirondacks (1A), Poconos/Catskills (1B), central New England (1C), southern New England (1D) and Maine (1E).

Figure 4 shows the distribution of lakes with ANC <200 µmol/L across five classes of sulphate (A, B) and organic anion (C,D) for three regions of eastern Canada (A,C) and the northeastern USA (B,D). Within each sulphate or organic anion class, the proportion of lakes characterised by each of the four ANC concentration classes are given. Sub-regions are arranged, within region for Canada, in order of decreasing median concentration of sulphate or organic anion. The geographic differences in median sulphate concentration in lakes in eastern Canada follow the general gradient of increasing sulphate deposition. The shift in distribution of sulphate concentration towards higher quintals in areas of higher deposition is apparent in Figure 4A. The highest percentages of acidic lakes in the northeastern USA were also associated with areas receiving the highest sulphate deposition. Figures 4A and 4B do not show a simple relationship between the distribution of ANC concentrations and lake sulphate concentrations, and therefore sulphate deposition. Patterns of atmospheric deposition alone are not enough to explain fully the distribution of acidic waters, it is necessary also to consider biogeochemical factors related to the lake catchments themselves to determine if there is a stronger relationship between ANC and sulphate concentrations (Jeffries and others, 1986; Linthurst and others, 1986a, b).

The role of natural organic anions in acidification can be examined in Figures 4C and 4D. The majority of lakes with negative ANC (acidic lakes) were found in the lowest organic anion class. Low ANC waters were found across all classes of organic anion concentration. In general, no

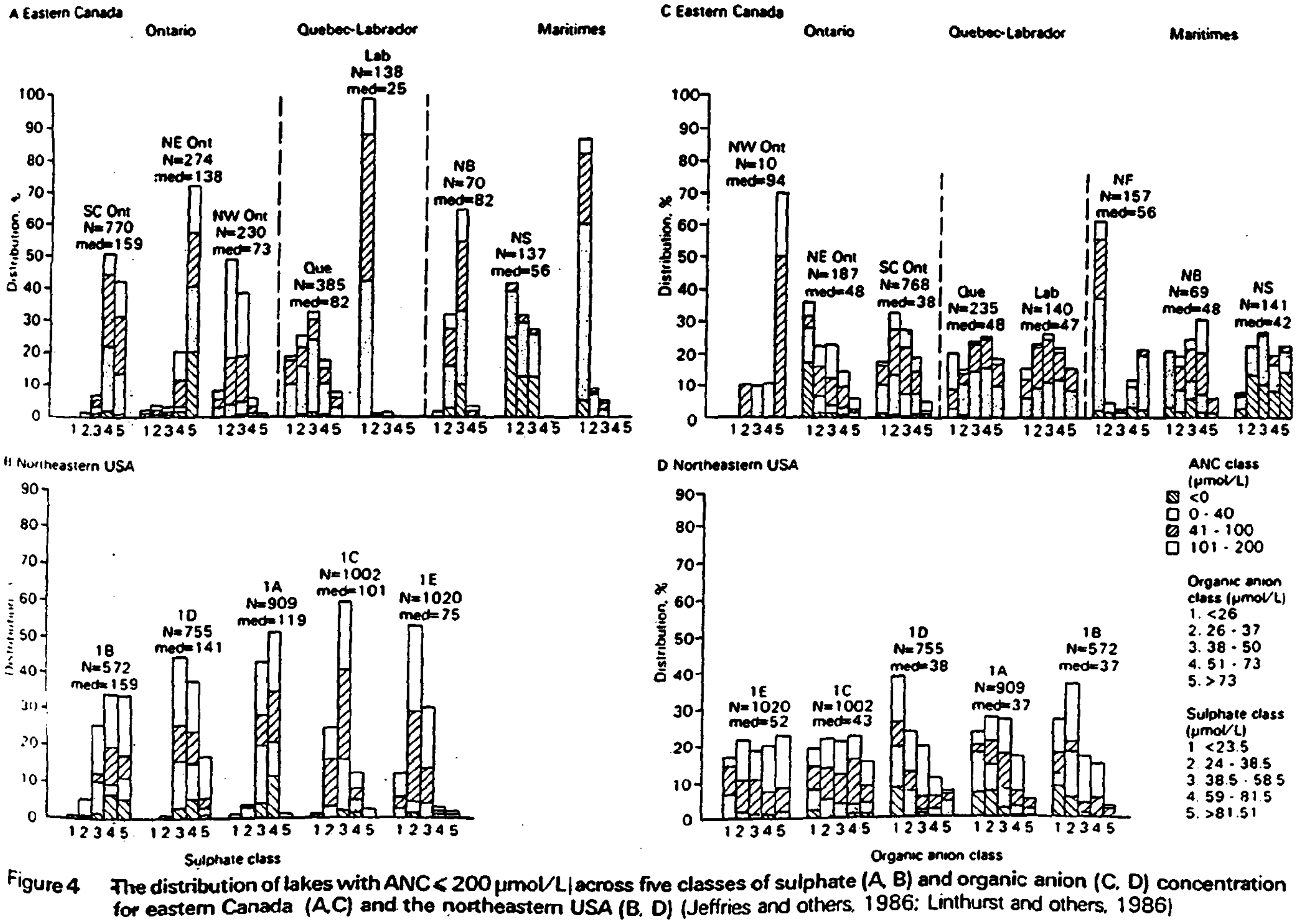


Figure 4 The distribution of lakes with ANC ≤ 200 µmol/L across five classes of sulphate (A, B) and organic anion (C, D) concentration for eastern Canada (A,C) and the northeastern USA (B, D) (Jeffries and others, 1986; Linthurst and others, 1986)

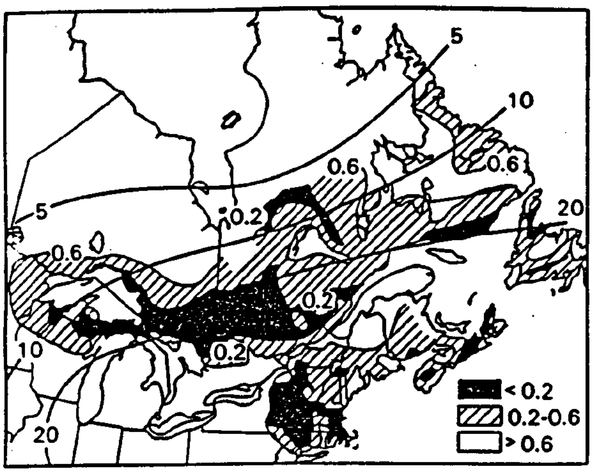


Figure 5 The average ratio of alkalinity to calcium and magnesium ion concentration in sensitive lakes of northeastern North America, with isolines showing the rate of sulphate deposition (kg/ha y). Values were corrected for sea salt where appropriate (Schindler, 1988)

relationship between increasing organic anion concentration and decreasing ANC concentration was found in either Canada or the USA. In fact, with increasing organic anion concentration, ANC tended to increase - the opposite of what would be found if organic anions were primarily responsible for lake acidification. This is in line with the findings of Kerekes and others (1986a) and Gorham and others (1986), discussed in Section 2.2, that while the presence of organic acids in streamwaters in Nova Scotia could result in a pH value 1 unit lower than that in comparable clear waters, the observed pH declines below this level were due to the presence of sulphates from atmospheric deposition. If the sensitivity of Canadian and eastern US lakes is compared, the percentage of low pH and low ANC lakes in the eastern USA is far lower than in Canada. Excluding northeastern Ontario and northwestern Ontario, 83% to 99% of the Canadian lakes had ANC <200 µmol/L, median ANCs ranged from 0 to 63 µmol/L. Lakes in the north eastern USA were less sensitive; 39% to 71% of lakes had ANC <200 µmol/L and median ANCs ranged from 112 to 297 µmol/L. This is because much of eastern Canada is underlain by the Precambrian Shield - non-calcareous bedrock which provides little ANC - while the eastern USA has deeper soils, deeper glacial tills and a smaller aerial extent of igneous bedrock (Jeffries and others, 1986; Linthurst and others, 1986a, b).

These lake survey data for the USA were analysed by Sullivan and others (1988). They found that median lake sulphate concentrations in the western, upper midwestern and northeastern USA and Florida correlated highly with estimated wet deposition. A statistically significant negative relationship was found between lake sulphate concentration and ANC in lakes with low base cation concentrations, suggesting that acidic deposition has depleted ANC in this type of lake. The data suggest that acidic lakes >4 ha in surface area are generally not found in areas receiving low levels of sulphate deposition. The authors conclude that most acidic lakes in the northeastern USA are currently acidic because of high sulphate relative to base cation concentrations rather than from organic acids and that temperate North American lakes of this size are not acidic in the absence of sulphate from human activities.

The replacement of lake alkalinity by sulphate causes decreased ratios of alkalinity to the sum of calcium plus magnesium ion concentration and increased ratios of sulphate to calcium plus magnesium ion concentration. Brakke and others (1988), using the US Eastern Lake Survey data, found that the ratio of alkalinity to calcium plus magnesium ion concentration changed with longitude across the northeastern USA. From the Adirondacks to Maine, the ratio increased as the deposition of hydrogen ion decreased. This indicates that bicarbonate ions have been replaced by sulphate in lakes in areas receiving high deposition of acids, and lakes with low concentrations of base cations have become acidic. Figure 5 shows the average ratio of alkalinity to calcium plus magnesium ion concentration in sensitive lakes of northeastern North America, with the rate of sulphate deposition superimposed. The data are taken from about 8000 Canadian lakes and the US Eastern Lake Survey. The average ratio in lakes of pristine areas usually ranges from 0.6 to 1.1. Average values for sensitive lakes in areas with highly acidic deposition are less than 0.2, while in individual lakes, zero or even negative values can occur. This figure shows that a clear relationship between the rate of sulphate deposition and the ratio of alkalinity to the sum of calcium plus magnesium ion concentration exists for this area of North America (Schindler, 1988).

Increases in the nitrate concentration of surface waters have been seen in Scandinavia. In the River Mörrusån in southern Sweden, with 90% of the catchment area forested, the nitrate-nitrogen concentration increased from <100 µg/L in 1965 to 300 µg/L in 1985. A similar increase was seen in lakes in southern Sweden not affected by agricultural or forestry fertilisers. During the last 10 to 20 years the nitrate concentration in water systems increased by 50-100% (Dickson, 1986). Figure 6 shows that in forest areas that experienced low deposition of nitrogen and sulphur, the nitrate concentration in runoff water was low, <0.05 kmol/ha y. High concentrations in runoff occurred when the wet deposition rate exceeded 1.5 kmol/ha y. High nitrogen runoff rates were associated with high sulphate leaching rates (Andersen, 1986).

2.3.1 Effects of decreased emissions

Another link between aquatic systems and atmospheric deposition has been seen in Europe. Sulphur emissions have decreased by about 20% in Europe since 1970, while local emissions in Sweden have reduced by about 60%. As a consequence, the concentration of sulphate in precipitation has reduced by about 20% in southern Scandinavia since the early 1970s. Since the average amount of precipitation did not change significantly over the period, then the wet deposition of sulphate also decreased by about 20%. Over the same period the concentration of nitrate in precipitation increased by about 34%. Sulphate concentrations of lake waters in western Sweden reached a maximum during the middle 1970s of 135 to 145 µmol/L, accompanied by pH values of 4.4 to 4.5. In 1977 this trend reversed and a

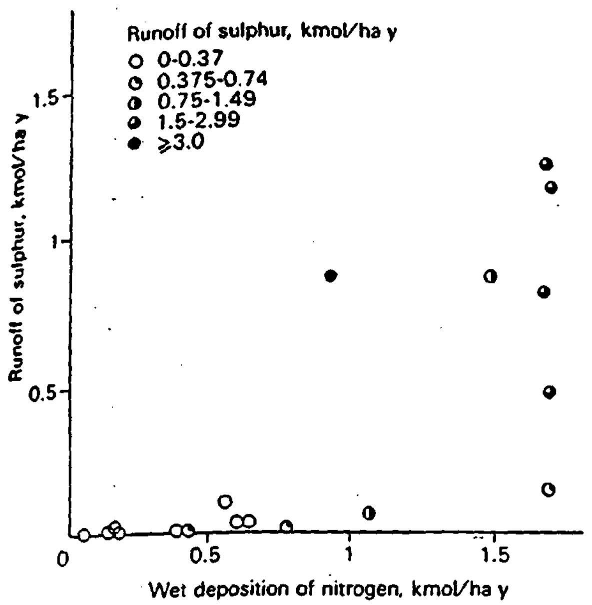


Figure 6 Impact of wet deposition of inorganic nitrogen compounds and total deposition of sulphate on the leaching losses of nitrogen from catchments in coniferous forests in north and central Europe (Andersen, 1986)

reduction in sulphate concentration of 20 to 50 µmol/L was found in some surface waters, amounting generally to a 20% decrease although reductions of up to 50% were seen in some systems. There was a reduction in the acidity of two lakes by about 47%, which corresponded to an increase in pH of 0.3 to 0.4 units from 4.4 to 4.7 and 4.6 to 5 respectively. There was a statistically significant relationship between sulphate and hydrogen ion concentration during both the acidification and deacidification phases. However, a hysteresis effect occurred between the phases so that when the sulphate concentrations decreased to previous levels, hydrogen ion concentrations were higher than during the preceding acidification phase. This effect has been seen in several lakes of western Sweden. This hysteresis may be due to acidity produced by increased emissions of nitrogen oxides in the intervening years. During the deacidification phase the sulphate concentration seemed to be losing part of the central role in steering the ionic composition of these lakes that it exhibited during the acidification phase, suggesting that reductions in sulphate emissions alone may not be sufficient to restore lakes to their former state (Forsberg and Morling, 1987; Forsberg and others, 1985; Rodhe and Granat, 1984). The rapid response to reduced sulphate concentrations seen in these lakes may be explained by the mechanism, based on soil-mediated processes, proposed by Reuss and Johnson (1986, 1985) and described in *Acidic deposition - ecological effects on soils and forests* (Harter, 1989).

Project RAIN (Reversing Acidification In Norway) comprises two parallel large-scale manipulations in which the chemistry of precipitation is experimentally changed over headwater catchments to investigate consequent changes in runoff chemistry. At Sogndal in western Norway, two pristine catchments were artificially acidified by addition of sulphuric acid at one site and sulphuric plus nitric acid at the other. At Risdalsheia in southern Norway, ambient acidic precipitation was excluded from an acidified catchment by a roof and clean precipitation was applied beneath the roof. Treatment began in winter 1984 at Sogndal and summer 1984 at Risdalsheia.

After 4 years of treatment, acid addition at Sogndal has caused major changes in runoff chemistry, including aluminium-rich runoff and recovery between episodes. Sulphate concentrations have increased from ~10 to 12.5 µmol/L to 25 to 28.5 µmol/L at the sulphuric acid only site and 17.5 to 22.5 µmol/L at the sulphuric plus nitric acid site. Addition of nitric acid caused only minor increases of nitrate in runoff. The increased sulphate concentrations were about 50% compensated by increased concentrations of base cations (mainly calcium and magnesium) and about 50% by decreased alkalinity. Chronic acidification of runoff was seen in the third and fourth years of treatment, to levels toxic to fish, caused entirely by addition of acids at levels typical of atmospheric deposition in southern Norway (Wright and others, 1988).

The exclusion of acidic deposition at Risdalsheia in southern Norway has resulted in lower concentrations of nitrate (from 35 to 7 µmol/L) and sulphate (from 55 to 26.5 µmol/L) in runoff. The decline in strong acid anions was compensated for partly by an increase in alkalinity (45%) and partly by a decrease in base cation concentrations (55%). The input-output budgets show that acid exclusion has reversed soil acidification and runoff has begun to recover to the pre-acidification chemical composition (Wright and others, 1988).

In the UK there has been a roughly 40% decline in national SO_2 emissions since the maximum in 1970 and reductions in both the concentration of excess sulphate in precipitation and the wet deposition of sulphate have been recorded in Scotland since the mid-1970s. Diatom analysis of sediment cores taken from two acidified lakes in Galloway, southwestern Scotland, between 1981 and 1986 show a trend towards progressively decreasing acidity at both sites. Water chemistry records show that there have been statistically significant decreases in both proton and sulphate concentrations since 1978. In Loch Enoch, decreases in mean proton concentration of 16 µmol/L (0.22 pH units) and in mean sulphate concentration of 12.5 µmol/L were seen, while decreases of 5 µmol/L in mean proton concentration and 13.5 µmol/L in mean sulphate concentration occurred in Round Loch of Glenhead. The diatom data from the lakes show that acidification stopped in the mid-1970s at both sites and that a small improvement in water quality has taken place since 1980. This trend towards decreasing acidification has also been observed at a nearby loch and at several sites with moorland catchments in other parts of Scotland. This suggests that a delay of only about ten years occurred in the response of Galloway lakes to a decrease in acidic deposition. The diatom data do not show a hysteresis effect such as was seen in the above Swedish studies (Battarbee and others, 1988b). Modelling results simulating long-term changes in the acidity of Scottish lakes and streams also indicate a recovery in some catchments in the 1980s, which corresponds with this trend in the diatom data (Neal and others, 1988) as will be seen in Section 2.4.

Table 3 **Excess sulphate yields and median pHs of rivers in Nova Scotia and Newfoundland (Thompson, 1987)**

	Watershed export of sulphates (kg/ha y)		Change in sulphate export	Median pHs of rivers	
	1971-1973	1982-1984	%	1971-1973	1982-1984
Nova Scotia					
Meteghan	49.9	19.4	-61	5.5	5.8
Kelley	39.0	18.3	-53	5.65	6.0
Wallace	41.4	21.9	-47	6.5	6.7
Tusket	35.7	20.9	-41	4.6	4.7
Roseway	35.8	15.7	-56	4.4	4.5
Mersey GL	30.2	15.3	-49	4.8	5.0
Mersey MF	29.0	15.5	-46	4.85	4.9
Medway	30.9	16.7	-46	5.0	5.6
La Have	37.9	21.2	-44	5.8	6.0
Liscomb	37.5	22.8	-39	4.8	5.05
St Mary's	36.7	19.8	-46	5.9	6.1
Clam Harbour	45.3	34.1	-25	6.3	6.4
Average change for area			-46		
Newfoundland					
Harrys	40.8	26.5	-35	7.7	7.8
Exploits	17.3	19.4	+11	6.3	6.4
Torrent	46.5	24.3	-48	6.9	7.0
Pipers Hole	17.4	7.6	-56	6.2	6.3
Indian Brook	18.6	5.7	-69	6.6	6.7
Isle aux Morts	48.5	26.7	-45	5.5	6.1
Garnish	30.1	13.9	-54	6.1	6.3
Rocky	30.9	9.2	-70	6.1	6.4
Average change for area			-46		

A similar state of affairs is seen in Canada where surface water quality has improved after reductions in emissions of SO_2. Table 3 shows changes in the sulphate yields from catchments in Nova Scotia and Newfoundland. From the early 1970s to the early 1980s the sulphate export from the catchments declined by nearly 50%. Atmospheric models have calculated an expected reduction in sulphur deposition of 20% to 25%. The agreement is satisfactory considering the expected error in model calculations and in the measurements. The areal pattern of excess sulphate yield of rivers on the Island of Newfoundland was in accordance with the known pattern of precipitation across the island. Median pH values in the early 1980s were generally higher than in the early 1970s, except for those rivers dominated by organic acids. The largest decreases in acidity were seen for the rivers with pH values in the range 5 to 5.5 in the early 1970s (Thompson, 1987; Martin and Brydges, 1986).

Surface waters in the Sudbury area of Canada are atypical of the aquatic systems suffering acidification, because of the extremely high loadings of acidic deposition and large atmospheric inputs of heavy metals from local smelter operations. It has been suggested that therefore the responses observed in Sudbury lakes cannot be directly extrapolated for predictions of responses of lakes in other regions where lower concentrations of acidic deposition were received from distant sources. However, surface waters near Sudbury do seem to be showing similar patterns of response to those seen in Europe in more typical ecosystems. It seems likely then that the improvement in water quality near Sudbury, tied to reductions of local emissions of SO_2, does have some validity for the more lightly-impacted ecosystems, although the time-frame may be different.

Water quality has improved in the Sudbury area following SO_2 emission reductions by the two largest smelters, of 70% and 75%, during the 1970s. Nearby Clearwater Lake has been monitored continuously since 1973. During the period 1973 to 1977, the sulphate concentration averaged 272.5 µmol/L. As can be seen in Figure 7, the sulphate concentration in the lake declined and by 1984 had reached 185 µmol/L, a drop of 32%. Between 1973 and 1977 the average pH of Clearwater Lake was 4.23. In 1984 the mean pH was 4.61 giving a relative change in hydrogen ion activity of 59% over about 7 years. The estimated contribution of organic acids was too small (2 to 3 µmol/L) to affect pH appreciably. The total aluminium concentration of the lake, which averaged 430 µg/L in 1973 to 1977, dropped to 190 µg/L by 1982 to 1984. The four other lakes studied also showed a rapid decrease in sulphate concentration after SO_2 emissions reduced and the pH of the lakes which had not been limed increased as sulphate decreased (Dillon and others, 1986).

The water chemistry of several lakes near Sudbury has been studied over 16 years from 1968 to 1984. In 1972 the Coniston smelter was closed and a 381 m chimney was brought into operation at the Copper Cliff smelter about 12 km away. This drastically reduced the local sulphate deposition around Coniston by about 75%, from a mean summer value of 1220 mg/m^2 per 30 days in 1970 to 310 mg/m^2 per 30 days (38 kg/ha y) by 1977. The pH of bulk deposition during the summer months increased from 2.74 to 3.4 in 1970 to 3.3 to 3.75 in 1977 and by 1984 the average pH of rainfall was 4.28, similar to that in the general Sudbury region (pH 4.27). In one extremely acidic lake close to the smelter, the pH increased from 4.05 in 1972 to 5.8 in 1984. Sulphate concentrations during the same period of 12 years dropped by 50%, despite continuing erosion and leaching of soluble sulphate from the catchment. In another initially less acidic lake nearby, sulphate concentrations decreased by 65% since 1970 and there is a trend towards increasing pH - although less dramatic than in the more acidic lake. Lake recovery was rapid and substantial in both lakes once SO_2 emissions decreased and the rate of recovery was more rapid than had previously been anticipated. The recovery in pH took place solely due to declines in SO_2 emissions. Reductions in nitrogen oxide emissions were not a factor (Hutchinson and Havas, 1986).

A larger scale survey was carried out in the summers of 1981 to 1983 to re-sample 209 lakes within about a 250 km radius of Sudbury, first sampled in 1974 to 1976. The original study identified a large zone of low pH (<5.5) lakes, with damaged fish populations, extending northeast-southwest of Sudbury, occupying an area of about 530,000 ha and containing a lake surface area of about 65,000 ha. Increases in pH from the 1970s occurred in the more acidic lakes, which tended to be located relatively close (within about 100 km) to Sudbury. No consistent pattern of change was evident for the near-neutral lakes, a large proportion of which were far removed from Sudbury. On average, the decrease in hydrogen ion concentration in lakes with pH <5.5 in the 1970s survey was about 50%. Elevated concentrations of sulphates (>100 µmol/L) were found up to >100 km from Sudbury in the 1970s and substantial reductions in sulphates had occurred up to the date of the 1983 survey. A statistically significant relationship was found between decreases in lakewater sulphate concentrations and distance from the Sudbury smelters. Data are also available for four streams in the Killarney area, located about 50 km southwest of Sudbury, where lake acidification is widespread. Monitoring data showed that these streams were subject to annual depressions in pH coinciding with snowmelt and high spring runoff, as is the common pattern. However, the severity of springtime pH decreases appeared generally reduced in 1981 and 1982 in comparison with 1979 and 1980, most likely reflecting changes in atmospheric deposition (Keller and Pitblado, 1986; Keller and others, 1986).

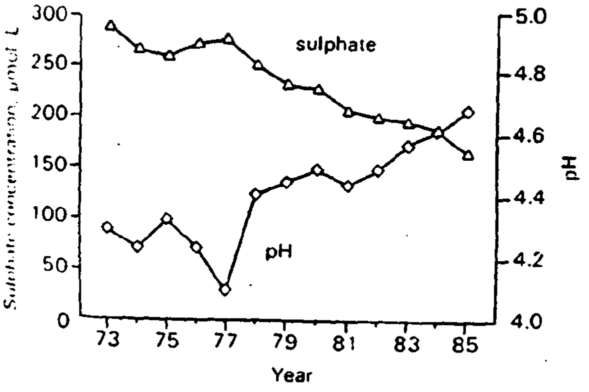


Figure 7 Sulphate concentration (µmol/L) and pH in Clearwater Lake 1973 to 1985, as whole-lake annual averages (Dillon and others, 1986)

A workshop on the reversibility of acidification of surface waters set up under the auspices of the Commission of the European Communities reviewed a range of experimental approaches and field studies. They concluded, based on available observations and supported by modelling work, that aquatic ecosystems will recover from acidification once acidifying deposition is removed. A return to pre-industrial precipitation composition would have benefits in improved water quality within a decade (Tollan and others, 1987).

Trace Elements
in
Soils and Plants

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Chapter 4

SOIL CONSTITUENTS

I. INTRODUCTION

Quantitatively, trace elements are negligible chemical constituents of soils, but are essential as micronutrients for plants. The first publications on trace elements were devoted to plant nutrition problems. Further, it was recognized that the behavior of trace elements in the soil differs widely for both the element and the soil and that these differences should be understood better for the prediction and effective management of the trace element status of soils. Although trace elements are mainly inherited from the parent rocks, their distribution within the soil profiles and their partitioning between the soil components reflect various pedogenic processes as well as the impact of external factors (e.g., agricultural practices, pollution).

Trace element associations with the particular soil phase and soil component appear to be fundamental in defining their behavior. The trace element composition of soils is relatively well established (Figure 7), although there are still diversities in analytical results, especially in the measurements of very small quantities. Currently, there is also a great deal of work on the distribution of these elements among soil components. One must realize, however, that present-day techniques for soil fractionation are quite drastic and cannot provide very comparative and representative results. Knowledge of the behavior and reactions of separate soil components with trace elements, although fundamental, should not be related directly to overall soil properties, and great caution is needed in using several theoretical models for predicting the behavior of trace elements in soils.

II. MINERALS

The mineral constituents of soils inherited from the parent rocks have been exposed for various periods of time to weathering and pedogenic processes. The soil mineral system, which is not necessarily in equilibrium with the soil solution, is complicated by the processes of degradation and neoformation of minerals, as well as by mineral reactions with organic compounds.

The common primary minerals in soils inherited from the parent material can be arranged in two parallel series, according to their susceptibility to weathering processes: (1) series of felsic minerals; plagioclases (Na – Ca) > K-feldspar > muscovite > quartz, and (2) series of mafic minerals; olivine > pyroxenes > amphiboles > biotite. These series are based on broad generalizations, and many exceptions may occur in particular soil environments. The primary minerals occurring in some soils are mostly of a larger dimension and are not involved in sorption processes. They are, however, considered to be the source of certain micronutrient elements.

The approximate composition of mineral constituents of surface soils presented in Figure 5 shows that quartz is the most common mineral in the soils, constituting 50 to more than 90% of the solid soil phase. Even in geochemical conditions favorable for the leaching of silicates, quartz remains as a basic soil mineral. Feldspars are of low relative resistance to weathering in soil environments and their alteration usually provides materials for clay mineral formation. Carbonates (calcite, dolomite) and metal oxides are usually accessory minerals in soils of humid climatic zones, while in soils of arid climatic zones they may be significant soil constituents.

The size and shape of mineral particles determine their ratio of surface to volume and mass, and this ratio determines their physical and chemical properties. Therefore, the grain-size composition (physical composition) of soils is considered to be one of the most important factors in soil characteristics and is included in the systems of soil evaluation and classification.

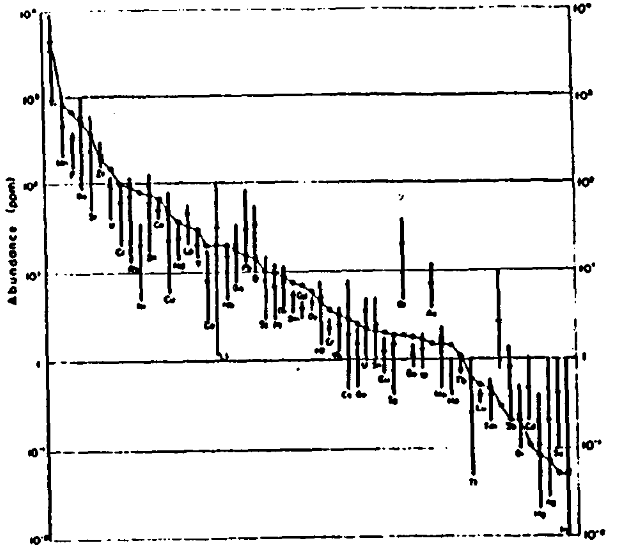

FIGURE 7. Trace elements in soils compared to their abundance in the lithosphere. Open circles, mean content in the lithosphere; black circles, mean content in topsoils; vertical lines, values commonly found in topsoils.

Sorption properties of the mineral part of soil material are associated principally with the clay and silt-size fractions. These fractions are a mixture of several aluminosilicate clay minerals with lesser amounts of quartz, feldspars, and various oxides and hydroxides. In certain soils carbonate and phosphate minerals are present, and in others, some minerals as sulfides and sulfates may occur.

A. Clay Minerals and Other Aluminosilicates

The boundaries of the mineral group described as "clay minerals" are not well defined, and they tend to enlarge with increasing knowledge. Thus, the division of minerals in this chapter does not relate to any classification system. The common clay minerals in soils can be subdivided into five groups:

1. Kaolinite
2. Montmorillonite, often referred to as smectites
3. Illite
4. Chlorite
5. Vermiculite

Each group includes many compositional and structural varieties; however, they are all 1:1 or 2:1 layer-type aluminosilicates. The structure and chemistry of soil clay minerals have been extensively described in many monographs.[49,201] The surface properties of minerals (area and presence of an electrical charge) seem to be fundamental for the buffer and sink properties of soils.

Table 15
SURFACE AREA OF VARIOUS SOILS

Kind of soil	Surface area ($m^2 g^{-1}$) a	Surface area ($m^2 g^{-1}$) b
Clays and loams	150—250	22—269
Silty loams	120—200	24—117
Sandy loams and loamy sands	10—40	4—67
Rendzinas	—	17—167

Note: Sources are as follows: a,5; b,182.

Clay minerals may contain negligible amounts of trace elements as structural components, but their sorption capacities to trace elements play the most important role. The affinity of trace ions for the clay surface has been examined by many investigators, and while many aspects have been clarified, still much remains to be learned about the adsorption processes.

Although clay mineral samples vary in chemical composition and in their nature, some general surface properties can be given for each mineral group (Table 14) that are responsible for values of the specific surface area of soil materials (Table 15). The capacity values (CEC) vary with the type of clay in the following sequence: montmorillonite, vermiculite > illite, chlorite > kaolinite > halloysite. The ability of the clays to bind the metal ions is correlated with their CEC, and usually the greater the CEC, the greater the amount of cation adsorbed.

The minerals of the montmorillonite group can expand and contract in response to charge and size of the absorbed cation between the clay platelets. Thus, their sorption capacity will differ when saturated with different cations. The microcations sorbed by montmorillonite are also easily released into the liquid phase and, therefore, can be an important pool of micronutrient supply to plants growing in particular soil conditions.

The bonding processes for absorbed microcations, although carefully studied, remain controversial.[2,227,356] It has been well demonstrated, however, that equilibrium and pH values are the most basic qualities in the reactions of sorption and release of microcations by clay minerals.

The chemical nature of transition metals adsorbed on clay minerals has recently been the subject of great interest. Clays containing exchangeable transition metal cations (mainly Cu, Fe, and Co) are known to act as electron or proton acceptors, thus they can be activators in transformations, decomposition, and polymerization of the adsorbed organic species.

Relatively little is known about the adsorption of metal ions on amorphous alumina and silica gels. The mechanisms of coprecipitation and mobilization of certain trace cations with alumina or silica gels may play a significant role in their behavior in the particular soil, especially in those of the tropical climate zone. There are suggestions that metal ions (mainly Cu^{2+}) can substitute for aluminum in the mineral structures, while soluble silicic acid promotes adsorption of Co, Ni, and Zn by clays.[317,793]

The strong adsorption of divalent trace cations (Cu, Pb, Zn, Ni, Co, Cd, and Sr) by freshly precipitated alumina gel is suggested by Kinniburgh et al.[392] to play a role in determining the availability to plants and the movement of some of these cations through the soil.

Some aluminosilicates are known to occur in soils as phyllosilicates (palygorskite, attapulgite, sepiolite) and as zeolites. They all have alternative 2:1-type open structures and are associated with the clay minerals. They can be inherited from parent materials, but also can be of pedogenic origin.[901] Most often these minerals were found in neutral or alkaline soil series, especially in the presence of salts (e.g., solonetz, solochaks, andosols, rendzinas). Some of them are more acid resistant than others in the soil environment. However, the detection of these minerals, especially zeolites, can be questioned due to possible destruction during chemical pretreatments of soil material.

Zeolites exhibit capacities to fix gases, vapors, and liquids, and they are known to be active in the sorption of Ba, Br, F, I, and also Mn and Sr. Barrer[44] has illustrated a high affinity of zeolites to sorb and to complex trace elements, particularly heavy metals and radionuclides.

Amorphous aluminosilicates occurring in soils are often described as allophane and imogolite. Allophanes are present in many soils, and the investigators pointed out their importance in the formation and transformation of noncrystalline clay materials and opaline silica.[851] Both allophane and imogolite make sequences of various types and are formed mainly in the soils developed under a warm humid climate. Allophanes are more stable in acid soils, and imologite is more stable in neutral and alkaline soils. Very often they occur as "gel films" that coat soil particles. The effect of these inorganic coatings may be diverse, both increasing and decreasing trace element sorption, also they may reduce the biological availability of occluded trace elements.[356]

All of these mineral constituents have relatively high CEC values and a great affinity to react with soil organic compounds. Under normal soil conditions, they are important trace element sinks.

B. Oxides and Hydroxides

Several oxide minerals, such as silicon oxides, titanium oxides, aluminum oxides, and hydroxides occur in soils. However, in relation to trace element behavior, the most important are Fe and Mn oxides. Al hydroxides can adsorb a variety of trace elements and in some soils the role of these oxides can be more important than that of Fe oxides in retaining certain trace elements. As Norrish[570] has stated, however, there is little direct evidence to support this view.

Oxides and hydroxides of Fe and Mn are relatively common constituents in soils and, having a high pigment power (mainly Fe oxides), determine the color of many soils. Fe and Mn oxides are present in soils in various mineral forms as well as in crystalline, microcrystalline, and amorphous oxides or hydroxides. Their structure and chemical properties are well described by Hem,[313] Jenne,[356] McKenzie,[524,526] and Schwertmann and Taylor.[699]

Although several minerals of the Fe oxides have been detected in soils, goethite is claimed to be the most frequently occurring form. Norrish[570] reported that simple oxides and hydroxides of manganese do not occur in soils and that the most common mineral forms are lithiophorite and birnessite. Chukhrov et al.[140] on the other hand, have identified vernadite — a simple hydrous oxide of Mn — as the most frequent form in the majority of soils.

These oxides are exposed to reduction and chelation solubility and oxidation-precipitation reactions, in which microbiological processes play an important role. Different nodules of Fe and Mn are known to originate from both chemical and microbial processes; also the formation of some crystalline minerals is known to be effected by microorganisms. The most common Fe-oxidizing bacteria *(Thiobacillium)* and Mn-oxidizing bacteria *(Metallogenium)* are able to tolerate high concentrations of several heavy metals (Zn, Ni, Cu, Co, and Mn). Thus, they are also involved in trace metal cycling in soils.

Fe and Mn oxides occur in soils as coatings on soil particles, as fillings in cracks and veins, and as concretions or nodules. Norrish,[570] using the electron probe analyzer, indicated that many trace elements in soils are concentrated along the deposited oxides in soil material. Fe and Mn oxides have a high sorption capacity, particularly for trace elements, of which large amounts can be accumulated in nodules and at Fe- and Mn-rich points (Table 16). The mechanisms of sorption involve the isomorphic substitution of divalent or trivalent cations for Fe and Mn ions, the cation exchange reactions, and the oxidation effects at the

Table 16
TRACE ELEMENTS IN IRON AND MANGANESE OXIDES (%)

Element	Iron minerals and concretions		Manganese minerals and concretions				
				Manganese nodules		Manganese minerals	
	Fe-rich points of surface soils (a)	Goethites (a,f)	Mn-rich points of surface soils (a)	(b)	(c)	From soils[a] (d)	From deposits[b] (e)
Fe	7.97—29.65	51.7—61.9	3.92—17.69	—	0.016	0.65—4.60	0.1—4.5
Mn	0.07—1.52	0.26—0.50	5.50—13.59	0.36—7.20	16.0	47.4—59.9	28—61
Ba	0.089—0.179	—	0.573—2.864	0.014—0.23	0.2	3.2—5.4	11.0—12.8
Cd	—	—	—	—	0.0008	—	—
Ce	—	—	—	—	0.072	—	—
Co	0.04—0.07	0.008[c]	0.54—2.44	0.0082—0.038	0.3	0.45—1.20	0.014—1.200
Cr	—	0.1[c]	—	0.003—0.012	0.0014	—	—
Cu	0.004—0.072	0.08	0.039—0.096	—	0.26	—	0.013—1.260
I	—	—	—	—	0.012—0.090	—	—
La	—	—	—	—	—	0.03—0.07	0.0002—0.534
Mo	—	0.85	—	—	0.041	—	—
Ni	0.026—0.063	0.017[c]	0.086—0.487	0.0039—0.0067	0.49	0.10—0.34	0.012—1.090
Pb	0.046—0.139	—	0.26—2.04	0.0034—0.010	0.087	—	—
Sb	—	—	—	—	0.0004—0.0025	—	—
Sr	—	—	—	—	0.0025	—	—
V	—	1.7	—	0.0008—0.011	0.044	—	—
Zn	0.072—0.257	1.73—2.35	0.032—0.554	0.0030—0.0033	0.071	—	0.005—0.380
Zr	—	—	—	—	0.065	—	—

Note: Sources are as follows: a, 570; b, 524; c, 94; d, 525; e, 837; and f, 881.

[a] Identified minerals: lithiophorite, birnessite, and hollandite.
[b] Identified minerals: psilomelane, cryptomelane, lithiophorite, and pyrolusite.
[c] In magnetite separated from soils (ignited weight).

surface of the oxide precipitates. Variable charges at the surface (mainly of Fe oxides) also promote the adsorption of anions. A high sorption capacity of Fe oxides for phosphates, molybdates, and selenites is most widely observed and is highly pH dependent, being lower at high pH values.[634] The amount of a particular ion that is adsorbed depends mainly on the pH of the equilibrium solution. The maximum adsorption values for various ions on Fe oxides range between pH 4 and 5.[699]

Some investigators give the order of preferential sorption of metals by goethite as Cu > Zn > Co > Pb > Mn,[697] while others have presented metal ion affinities for the oxide surface in the following orders: Cu > Pb > Zn > Co > Cd,[240] and Pb > Zn > Cd > Tl.[232] However, the extrapolation of these results to all soils is difficult. Apparently, hydrous oxides of Fe and Mn are the most important compounds in the sorption of trace metallic pollutants, and they exhibit diverse affinities to cations having approximately the same physical dimensions as Mn^{2+}, Mn^{3+}, Fe^{2+}, and Fe^{3+}; they are Co^{2+}, Co^{3+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{4+}, and Ag^{+}.

C. Carbonates

Carbonates present in soils are often in metastable and polymorphic varieties and thus sensitive to drainage conditions. Carbonates are common constituents in the soils where evapo-transpiration potential exceeds the rainfall. On the other hand, in soils with a high rate of percolating water, carbonates are easily dissolved and leached out. Nevertheless, Ca is usually the predominating cation in solutions of almost all soils.

Calcite is the most widespread and relatively mobile form of Ca carbonates present in soils; it is usually greatly dispersed and has a major influence on the pH of soils and therefore on trace element behavior.

Trace elements may coprecipitate with carbonates, being incorporated in their structure, or may be sorbed by oxides (mainly Fe and Mn) that were precipitated onto the carbonates or other soil particles. Metallic ions may also influence processes of carbonate precipitations.[356] The greatest affinity for reaction with carbonates has been observed for Co, Cd, Cu, Fe, Mn, Ni, Pb, Sr, U, and Zn. However, a wide variety of the elements under various geochemical environments may substitute for Ca in different proportions in nodular calcites. As Vochten and Geyes[828] observed, the secondary calcite crystals show a remarkably high content of Sr and Co — up to 1000 ppm concentrations. Carbonates can be the dominant trace element sink in a particular soil, but the most important mechanisms for regulating the trace element behavior by carbonates are related to variation of the soil pH.

D. Phosphates

Crystalline forms of phosphate minerals rarely occur in soils; however, many varieties of metastable and metamorphous phosphates are of importance in pedogenic processes. There are few data on the occurrence of Ca phosphates (apatite and hydroapatite) or other phosphates in soils. Rather, it has been suggested that an intimate mixture of Ca, Fe, and Al phosphates predominates in soils.[356]

Several of the rock phosphates contain a large amount of trace elements, of which F, and at times Cd, are highly concentrated (Table 17). Some substitutions for Ca by trace elements are known to occur in natural apatites; they are, however, of little importance in soils. Also many trace elements (Ba, Bi, Cu, Li, Mn, Pb, Re, Sr, Th, U, and Zn) can be incorporated, together with Fe^{3+} and Al^{3+}, in hydrated phosphates.[809] Norrish[570] reported extremely high concentrations of lead (1 to 35% PbO) in the phosphate concentrates occurring in ferralsols (lateritic podzolic soils).

E. Sulfides, Sulfates, and Chlorides

Sulfides, sulfates, and chlorides are negligible compounds in soils that developed in a humid climate, but in soils of arid climatic zones they can be the dominant controls of the behavior of trace elements. The metallic ions (mainly Fe^{2+}, Mn^{2+}, Hg^{2+}, and Cu^{1+}) may form relatively stable sulfides of acidic or neutral reducing potential in flooded soils. Several other heavy metals (Cd, Co, Ni, Sn, Ti, and Zn) can also be easily coprecipitated with iron sulfides.[356,928]

Table 17
TRACE ELEMENTS IN PHOSPHORITES AND PHOSPHATE FERTILIZERS (PPM)

Element	Phosphorites a	Phosphorites b	Phosphate fertilizers c
As	30	0.4—188	2—1,200
B	<50	3—33	5—115
Ba	100	1—1,000	<200
Be	<0.5	1—10	—
Cd	0.01—35 (75)(d)	1—10	7—170 (188)(e)
Ce	100	9—85	20
Co	<3—5	0.6—12	1—10
Cr	2—1,000	7—1,600	66—245
Cu	100	0.6—394	1—300
F	31,000	—	8,500—15,500
Hg	0.2	10—1,000	0.01—0.12
I	0.8—280	0.2—280	—
La	—	7—130	—
Li	—	1—10	—
Mn	30	1—10,000	40—2,000
Mo	0.03	1—138	0.1—60
Ni	<2—1,000	2—30	7—32
Pb	2—14	<1—100	7—225
Sb	0.2—7	1—10	—
Se	—	1—10	<0.5
Sn	0.2	10—15	3—4
Sr	1,000	1,800—2,000	25—500
Ti	600	100—3,000	—
U	90	8—1,300	—
V	300	20—500	2—180
Zn	300	4—345	50—1,450
Zr	30	10—800	50

Note: Sources are as follows: a, 94; b, 809; c, 381; d, 399; and e, 554.

The precipitation of metallic ions as sulfides is an important mechanism for regulating the solution concentration of both S^{2-} and metallic cations. Sulfides of heavy metals may be transformed into more soluble oxidized sulfates when flooded soil becomes drained and aerated.

Pyrite is the most common mineral of Fe sulfides in soils and other geochemical environments. Some other heavy metals which readily form sulfides may also be, as is Fe, remarkably related to microbial S cycling in soils, as was recently described by Trudinger and Swaine.[809]

Sulfides of heavy metals are not common in soils, especially in soils with good drainage. Sulfates of metals, mainly of Fe (jarosite), but also of Al (alunites) and Ca (gypsum, anhydrite), are likely to occur under oxidizing soil conditions. They are readily soluble and therefore are greatly involved in soil equilibrium processes. Sulfates of heavy metals are also readily available to plants, and their occurrence in soils has practical importance in agriculture.[671] Chlorides as the most soluble salts occur only in soils of arid or semiarid climatic zones.

III. ORGANISMS IN SOILS

Living organisms, often referred to as the soil biota composed of fauna and flora of various dimensions (macro-, mezo-, and microbiota), occur abundantly in soils. At the microbiota level the boundary between plant and animal cells becomes blurred. The importance of living organisms as reflected in biological activity of soils has been discussed in many textbooks.[187,651,856,898]

The abundance of microorganisms in topsoils varies with soil and climatic conditions and may reach as much as 20% of the total biota of a soil system. There is no easy way of knowing with certainty the biomass of microorganisms because this quantity can be determined only indirectly. The maximum weight of soil biota given by Richards[651] for a hypothetical grassland soil corresponds to 7 t ha^{-1} of microbiota (bacteria and fungi) and to 1.3 t ha^{-1} of mezobiota. Kovalskiy et al.[422] calculated that the biomass of bacteria and fungi present in the plow zone of soil (20 cm depth) range from 0.4 to 1.1 t ha^{-1}. The biomass of bacteria varies significantly during the growing season, and may increase about three times from spring to fall.[421]

Microorganisms are very important ecologically because they are the producing, consuming, and transporting members of the soil ecosystem and therefore are involved in the flow of energy and in the cycling of chemical elements. Thus, the microbiota is responsible for many different processes, from mobilization to accumulation of chemical elements, in soils. Although microorganisms are sensitive to both deficiencies and excesses of trace elements, they can adapt to high concentrations of these elements in their environment.

The role of microorganisms in geochemical cycling of the major elements is relatively well understood on the global level. The biogeochemical cycling of trace elements has received much less attention. With the recognition that microbial transformations of compounds of these elements can result in some problems of soil fertility as well as in the formation of some environmental pollution or detoxication processes, the importance of microbiota in cycling of trace elements, especially heavy metals, has been more extensively studied.

The basic microbial phenomena in cycling processes in the soil environment are

1. Transport of an element into or out of a cell
2. Charge alteration of an element
3. Interaction of an element with organic compounds to become a functional part of the system
4. Complexing an element by organic acids and other compounds produced by microorganisms
5. Microbial accumulation or mobilization of an element
6. Microbial detoxication of poisoned soil at a site

The most important microbial function in soil, however, is the degradation of plant and animal residues. It has become apparent that the quantity of trace elements needed or harmful for growth of microorganisms influences also the biological activity of soils.

All available evidence indicates that a low concentration of trace elements stimulates bacterial growth in soil, but a higher content is harmful, being usually most toxic to the bacteria that fix free N and to nitrifying bacteria.[305,812] Of the 19 trace elements studied by Liang and Tabatabai,[471] all inhibited mineral N production in soils. At the concentrations of 5 μ*M* g^{-1} of soil, the most toxic elements were Ag^{+} and Hg^{+}, while the least toxic were Co^{2+}, As^{3+}, Se^{4+}, and W^{6+}. Heavy metals especially are known for their toxicity to microbiota, with fungi and actinomycetes having the most resistance. Reduction of microbial growth and enzymatic activity is often reported for soils contaminated by heavy metals.[80,333,814] Mathur et al.[515] showed that the effect of a naturally high Cu content of histosols is most suppressive on levels of accumulated enzyme activities involved in the degradation of the major components of organic debris in soils. A low rate of decomposition of vegetation having a high concentration of Pb and Zn is apparently due to the same processes in nature.[837]

Suppression and/or stimulation of biosynthesis of microorganisms by heavy metals depends upon the nature of the organisms, the kind of metal, and the pH of soils. Even with one species the range of required or inhibitory concentrations of a given metal varies significantly.[421]

Based on data presented in the monograph by Weinberg,[854] it may be generalized that the highest concentration of Fe, Mn, and Zn required by various microorganisms (fungi, bacteria, bacilla, and actinomycetes) was around X00 μ*M* ℓ$^{-1}$. The inhibitory concentrations of these elements on vegetative growth and secondary metabolism of microorganisms have also been established at the above range.

Heavy metals are known to be the most toxic elements, especially to fungi. Somers[746] reported that the fungicidal action of trace cations is due primarily to the formation of an un-ionized complex with surface groups, e.g., phosphate, carboxyl, and sulfhydryl. This author showed that there is a relationship between the toxic concentration of the metal ion and its electronegativity value. The order of toxicity of aqueous solutions of nitrates and sulfates against conidia of *Alternaria tenuis* was given by Somers[746] as follows:

$$\begin{gathered}Os > Hg > Ag > Ru > Pb \approx Cr > P > Ce > Cu > Ni \\ = Be = Y > Mn = Tl > Zn > Li > Sr\end{gathered}$$

In soil systems, Hg, Cd, and As seemed to be the most harmful to ammonification processes, while Cu greatly reduced phosphate mineralization rate.[762,813]

Microorganisms can adapt to high concentrations of trace elements. This has been well illustrated by Aristovskaya[15] and Letunova[464] for several elements such as Fe, Mn, Mo, Se, and B (Figure 8). This adaptation is also well shown in various microbiogeochemical processes described in detail by Babich and Stotzky,[41] Gadd and Griffiths,[251] Kowalskiy,[419] and Zajic.[898] The sensitivity of microorganisms (mainly fungi) to different concentrations of trace elements has often been used in the determination of the availability of micronutrients such as Fe, Cu, Zn, and Mo.[531,572]

The physicochemical relationship between bacteria and mineral surfaces leads to diverse effects of dissolution and secondary precipitation of trace metal ions, including changes in their valence and/or conversion into organometallic compounds. A biological oxidation and reduction of Fe and Mn, for example, is one of the most important factor governing the solubility, and thus, the bioavailability, of these metals in soils. Many bacterial species are implicated in the transformation of trace element compounds, including even neoformation of certain Fe and Mn minerals.[148] This effect, however may also at times be an indirect effect. Bacteria also play the most important role in gley formation which affects the mobility of metals in soils.[81]

Microorganisms take up trace elements, several of which play important metabolic functions.[344,614,867] It has been shown by Kokke,[407] however, that cells of microorganisms may show quite variable affinities for radionuclides that are necessarily related to their biological function (Table 18).

A complex balance of trace elements required for microbial activity is of importance in soil productivity. The quantities of specific trace elements available to soil microorganisms can be the critical determinant in the establishment of a disease condition of certain plants. The trace element competition betwee[illegible]nts and microorganisms is apparent in various

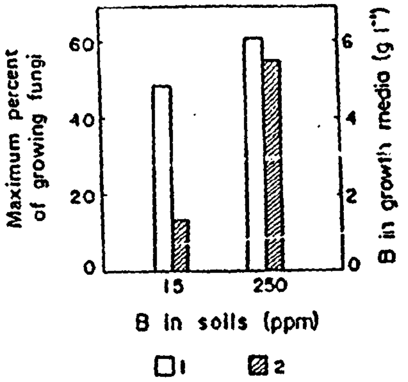

FIGURE 8. Tolerance of *Actinomycetes* from soils with various B contents to B concentrations in the growth media. (1) Growing fungi, in percent of total number; (2) maximum tolerable concentration of B in solution.[484]

Table 18
RADIONUCLIDE UPTAKE BY THE YEAST *CANDIDA HUMICOLA* AS A FUNCTION OF TIME[407]

Radionuclide	Initial concentration in growth media (μM l⁻¹)	Time of growth (days) 1	2	4	8	16
		% of initial concentration				
^{144}Ce	40	93	95	98	99	99
^{59}Fe	40	68	83	95	95	95
^{65}Zn	64	60	60	60	75	99
^{85}Sr	40	18	18	18	37	99
^{131}I	20	16	18	25	—	25
^{106}Ru	40	15	30	45	60	75
^{60}Co	40	3	5	5	18	77
^{147}Nd	40	3	3	3	5	12
^{137}Cs	40	1	2	2	3	5

reports, and it may react in different ways. Microbially induced decreases in the availability of trace elements result from a considerably high accumulation of certain elements by microbiota and also from the biological oxidation of compounds of these elements. Microbiological increases of availability, on the other hand, are caused by microorganisms capable of reducing certain compounds (principally, Mn and Fe) and also by their variable bioaccumulation of trace elements (Table 19).

Soil fumigation or steaming and many fungicides kill the fungi and therefore may interfere with the ability of plants to absorb micronutrients. The mechanisms of these phenomena are not yet fully understood; however, they may be related to an imbalance of soil microorganisms and their participation in the transport of ions into or within biological systems. As Martin[511a] reported, variable effects in plants of B, Cu, Li, Mn, and Zn toxicities or deficiencies of Cu, Mn, and Zn were found following soil fumigation.

Gadd and Griffiths[251] concluded that two main types of metal uptake by microorganisms can occur: the first involves nonspecific binding of the cation to cell surfaces, slime layers, extracellular matrices, etc., while the second involves metabolic-dependent intracellular uptake. The polygalacturonic acid, a common constituent of the outer slime layer of bacterial cells, can complex several trace metals.

Table 19
BIOACCUMULATION OF Cu, Mo, and V BY MICROBIOMASS IN TOPSOILS AT VARIOUS SEASONS[411]

Data on soil	Cu Soil (ppm)	Cu Biomass (kg ha⁻¹)	Mo Soil (ppm)	Mo Biomass (kg ha⁻¹)	V Soil (ppm)	V Biomass (kg ha⁻¹)
Low content of elements	48	0.004 (Sp) 0.006 (Sm) 0.028 (Fl)	6	0.0013 (Sp) 0.002 (Sm) 0.009 (Fl)	66	0.002 (Sp) 0.003 (Sm) 0.013 (Fl)
High content of elements	270	0.60 (Sp) 0.25 (Sm) 0.22 (Fl)	72	0.075 (Sp) 0.031 (Sm) 0.029 (Fl)	840	0.124 (Sp) 0.052 (Sm) 0.049 (Fl)
Control soil (chernozem)	73	0.019 (Sp) 0.069 (Sm) 0.059 (Fl)	10	0.005 (Sp) 0.017 (Sm) 0.013 (Fl)	148	0.005 (Sp) 0.019 (Sm) 0.015 (Fl)

Note: Sp, spring; Sm, summer; Fl, fall.

The adsorption of trace elements by microorganisms differs widely, as is shown on Tables 18 and 19. Although the mass of microbiota in soils has been calculated to be in the range of 0.X − X t ha⁻¹, the greatest amounts of metals fixed by microorganisms are the following (g ha⁻¹): Ni, 350; Cu, 310; Zn, 250; Co, 150; Mo, 148; and Pb, 8.4, which corresponds to 0.002 to 0.216% of their total abundance in the 20-cm topsoil level of 1 ha.[422,465]

Calculations made by Kovalskiy et al.,[422] and Letunova and Gribovskaya[465] indicated that at the annual rate, the total biocycling of about 11 generations of microbiota may, on the average, involve the following amounts of trace metals (kg ha⁻¹): Ni, 147; Zn, 104; Cu, 78; and Co, 28. Trace elements fixed by microbiomass may be much higher than these values for soils that increase their levels, as has been shown by Krasinskaya and Letunova.[426]

Microbioaccumulation of trace elements may be of great importance both in the cycling of trace elements in soil and in their availability to plants. Fungi and actinomycetes are the most resistant microorganisms to high concentrations of heavy metals, while nitrifying and rhizosphere microorganisms are the most sensitive.

Various waste waters, as well as slurries used for soil irrigation and amendment, can be sources of microbial and other pathogenic organisms of a serious health hazard to humans and animals. This problem has been recently reviewed by Kristensen and Bonde.[429] Bacterial leaching of heavy metals from sewage sludges is, however, a practical application of the biotransformation of the forms of chemical elements.[644]

More than 80% of microorganisms are believed to be adsorbed to soil organic matter and clay minerals.[884] Therefore, comparisons of results obtained for pure cultures of microorganisms may differ from those naturally occurring in soils.

The rhizosphere flora plays a special role in the bioactivity of soils and the availability of nutrients. Although effects of mycorrhizas have been almost always ascribed to an increased phosphate uptake, some observations indicate that they may also influence micronutrient supply. As Lambert et al.[436] and Woldendorp[884] reported, Zn, Cu, and Sr are the chief elements supplied to plants by a given type of mycorrhiza. Some negative effects occurring in rhizospheres may be observed when anaerobiosis around the root surface exists due to a high oxygen demand of microflora leads to the formation of ferrous iron compounds

Table 20
METALS IN SURFACE SOILS AND EARTHWORMS (PPM)

Metal	Soil	Earthworms	Ratio, worms/soil	Ref.
Cd	2	15	7.5	339
	4	4	1	339
	1.6	11.1	6.9	264
	0.9	14.4	16	264
	1.1	18	16	160
	0.6	12	20	160
	0.1	2.7	27	160
	4.1	10.3[a]	27.6	179
Cu	20	13	0.65	339
	232	11	0.04	339
	335	11	0.03	339
	52	28	0.53	160
	26	18	0.69	160
	9	5	0.55	160
Hg	3.8	1.29[b]	0.33	111
	0.1	0.04[b]	0.40	111
Mn	1330	82	0.06	339
	226	28	0.12	339
	164	27	0.16	339
Ni	26	31	1.19	264
	18	29	1.61	264
	12	32	2.66	264
Pb	1314	3592	2.73	339
	629	9	0.01	339
	700	331	0.47	264
	94	101	1.04	264
	170	62	0.36	160
	20	9	0.45	160
	830	100[a]	0.12	160
Zn	138	739	5.35	339
	992	676	0.68	339
	219	670	3.05	264
	49	400	8.16	264
	275	2000	7.27	160
	40	900	22.50	160
	81	662[a]	8.17	179

Note: Element concentrations expressed on dry weight basis. Organisms analyzed are *Lumbricus rubellus* or *L. terrestris*, except as indicated.

[a] Other Invertebrata.

[b] FW basis.

which are taken up by plants to concentrations that cause the physiological disorder known as Fe toxicity.[807]

Mezo- and macrobiota occurring in soils are also involved in biocycling of trace elements. Some species of soil fauna, especially earthworms (Annelida), ingest both decaying plant material and mineral soil components. These organisms are known to be able to accumulate certain trace elements in their tissues. Earthworms can selectively take up trace metals and, therefore, are sometimes used as indicators for soil contamination (Table 20). Although heavy metals in earthworms were often found to be significantly related to the corresponding metals in soils, many other factors may also influence this correlation. In soils highly contaminated by trace elements, mezo- and macrobiota are decreased, their metabolism is inhibited, and finally all organisms may vanish.

IV. ORGANIC MATTER

Organic matter of soils consists of a mixture of plant and animal products in various stages of decomposition and of substances that were synthesized chemically and biologically. This complex material, greatly simplified, can be divided into humic and nonhumic substances. Organic matter is widely distributed in soils, miscellaneous deposits, and natural waters. The amount of organic carbon in the earth as humus (50×10^{11} t) has been calculated to exceed that which occurs in living organisms (7×10^{11} t).[300]

The major portion of the organic matter in most soils results from biological decay of the biota residues. The end products of this degradation are humic substances, organic acids of low-molecular and high-molecular weights, carbohydrates, proteins, peptides, amino acids, lipids, waxes, polycyclic aromatic hydrocarbons, and lignin fragments. In addition, the excretion products of roots, composed of a wide variety of simple organic acids, are present in soils. It should be mentioned, however, that the composition and properties of organic matter are dependent upon climatic conditions, soil types, and agricultural practices.

The most stable compounds in soils are humic substances partitioned into the fractions of humic acid, fulvic acid, and humin, which are similar in structure, but differ in their reactions. Humic substances are of a coiled polymer chain structure and contain a relatively large number of functional groups (CO_2, OH, C=C, COOH, SH, CO_2H) having a great affinity for interacting with metal ions. Owing to a particular combination of different groups (mainly, OH and SH), humic substances are able to form complexes with certain cations. Some trace anions, such as B, I, and Se, are also well known to be organically bound in soils. Humic substances are also easily adsorbed by clay and oxide particles in soil and water environments, and these responses are highly dependent on trace cations.[779,780]

Interactions between humic substances and metals have been described as ion exchange, surface sorption, chelation, coagulation, and peptization. It should be emphasized that the existence of a particular site for each cation is not easy to prove because the metal may be bound to two or more ligands from different molecules. All reactions between organic matter and cations lead to the formation of water-soluble and/or water-insoluble complexes.

Sholkovitz and Copland[730] studied the complexing and chelation of trace elements with organic ligands in natural waters. Their studies led to the conclusion that solubilities of humic acid complexes with Fe, Cu, Ni, Cd, Cu, and Mn are the reverse of those predicted from inorganic solubility considerations. The complexing of these ions with humic substances led to the solubilization at high pH (range 3 to 9.5) and precipitation at low pH (range, 3 to 1).

Organic matter is of importance in the transportation (and subsequent leaching) and accumulation of metallic ions known to be present in soils and waters as chelates of various stability and in supplying these ions to plant roots. The ion exchange equilibrium has been extensively studied for determining the stability constant of metallo-organic matter complexes in soils. The values of stability constants determined by several authors described the ability of humic acids to form complexes with metals (Table 21). Metal-fulvic acid complexes with lower stability constants usually are more readily soluble and thus more available to plant roots.

The highest stability-constant values were reported by Takamatsu and Yoshida[771] for Cu^{2+}, Pb^{2+}, and Cd^{2+} complexed with humic acid at pH 5 and by Kitagishi and Yamane[409] for Cu^{2+}, Zn^{2+}, Ni^{2+}, and Cd^{2+} at pH 7. Andrzejewski and Rosikiewicz[28] observed that Mn^{2+}, Co^{2+}, and Ni^{2+} complexes with humic acids were partly soluble, while those of Cu^{2+}, Fe^{2+}, and Cr^{3+} were insoluble. Augustyn and Urbaniak[40] also stated that the higher retention

Table 21
STABILITY CONSTANTS EXPRESSED AS LOG K OF METAL FULVIC AND HUMIC ACID COMPLEXES AT VARIOUS pH LEVELS OF THE MEDIA

	pH 3		pH 3.5	pH 5				pH 7
Cation	FA (a)	HA (d)	FA (b)	FA (a)	FA (b)	HA (c)	HA (d)	HA (d)
Cu^{2+}	3.3	6.8	5.8	4.0	8.7	8.7	12.6	12.3
Ni^{2+}	3.2	5.4	3.5	4.2	4.1	—	7.6	9.6
Co^{2+}	2.8	—	2.2	4.1	3.7	—	—	—
Pb^{2+}	2.7	—	3.1	4.0	6.2	8.3	—	—
Zn^{2+}	2.3	3.1	1.7	3.6	2.3	—	7.2	10.3
Mn^{2+}	2.1	0	1.5	3.7	3.8	—	0	5.6
Cd^{2+}	—	5.3	—	—	—	6.3	5.5	8.9
Fe^{2+}	—	5.4	5.1	—	5.8	—	6.4	4.8
Ca^{2+}	2.7	0	2.0	3.4	2.9	—	0	6.5
Mg^{2+}	1.9	0	1.2	2.2	2.1	—	0	5.5
Fe^{3+}	6.1[a]	11.4	—	—	—	—	8.5	6.6
Al^{3+}	3.7[b]	—	—	—	—	—	—	—

Note: Sources are as follows: a, 692; b, 571; c, 771; and d, 395.

[a] Determined at pH 1.7.
[b] Determined at pH 2.4.

Table 22
TRACE ELEMENTS IN SOIL ORGANIC MATTER AND IN CLAY FRACTION (PPM DW)[756]

		Content of clay fraction (<1 μm)			
Surface soil	Element	Total	Organic matter	Humic acid	Fulvic acid
Chernozem	Cu	90	33.0	3.6	29.4
	Zn	116	41.5	3.4	38.1
	Mn	1110	262	Trace	254
	Mo	5	1.7	0.8	0.9
Podzol	Cu	44	17.9	1.2	16.7
	Zn	80	44.7	15.6	29.1
	Mn	1830	307	44	267
	Mo	3	0.7	0.2	0.5

by humic acid was of Fe^{3+}, Cu^{2+}, and Zn^{2+} as compared to other metallic ions. Fe^{3+} and Al^{3+}, however, form the most stable complexes with fulvic acid which greatly interfere with the crystallization of aluminum hydroxide polymorphs.[418]

The stability of metal complexes with fulvic and humic acids increases, in many cases, with increasing pH from 3 to 7 (Table 21). This is best illustrated for Pb, as studied extensively by Hildebrand and Blume.[319] The binding of Fe^{2+} and Fe^{3+} by fulvic acid in solution below pH 5.0 is very strong and, apparently, cannot be exchanged easily by other metals. A relatively high value of the stability constants of Ca^{2+} suggests that this metal can compete with Zn^{2+} and Mn^{2+} in ion exchange processes. Most likely, however, several heavy metals such as Cu^{2+}, Ni^{2+}, Co^{2+}, and Pb^{2+} will readily form stable organic complexes with fulvic acid and, most probably, also with other organic compounds.

Analyses of fractionated organic acids from soils by Stepanova[756] confirm the greater

affinity of fulvic acids for heavy metals (Table 22). Mickiewich et al.[533] also reported a much higher concentration mainly of Cu, Pb, and Ti in fulvic acid than was found in humic acid. Heavy metals in soils tend to accumulate in the organic substances, and the lower the metal content, the higher the energy linkage of the metallo-organic groups.[806]

The commonly used value of the stability constant of a complex can be defined as an equilibrium constant of a reaction that forms a soluble complex or chelate. In order to include information about the behavior of insoluble complexes, the value of the stability index has been proposed by Cottenie et al.[148] This index describes the ratio of a given metal fixed with organic substances to its amount in inorganic fractions. The stability index for pure humic and fulvic acids shows that heavy metals (Cu, Zn, Pb, Mn) form complexes several times more readily with humic acid rather than with fulvic acid, and that the highest proportion of Cu is fixed with humic acid over the range of pH 4 to 5, while with fulvic acid the range of pH is limited to 6 to 7. Both acids often show a higher affinity for Cu and Pb rather than for Fe and Mn. These findings agree with those reported by Van Dijk,[830] Stevenson and Ardakani,[737] Förstner and Müller,[242] Pauli,[601] Vlasov and Mikhaylova,[825] and Schnitzer and Khan[692] and indicate that the order of the stability constants of metallo-organic complexes, although quite variable depending on pH and other properties of the medium, can be presented in the following sequence: U > Hg > Sn > Pb > Cu > Ni > Co > Fe > Cd > Zn > Mn > Sr.

Schnitzer and Kerndorff[690] recently established the order of the affinity of metal ions to form water-insoluble complexes with fulvic acid. Although this order depends on the pH of the medium, it may be presented as follows:

$$Fe = Cr = Al > Pb = Cu > Hg > Zn = Ni = Co = Cd = Mn$$

The solubility of fulvic acid-metal complexes is strongly controlled by the ratios FA/metal, therefore, when this ratio is lower than 2, the formation of water-insoluble complexes is favored. There is diversity, however, in the interpretation of metal ion binding by peat, because as Bloom and McBride[80] reported, peat and humic acids are likely to bind, at an acid pH, most divalent cations (Mn, Fe, Co, Ni, and Zn) as hydrated ions. The exception is the Cu^{2+} ion coordinating with functional oxygens of the peat which results in strongly immobilized Cu^{2+} binding.

The index of organic affinities of trace elements in various coal samples was calculated by Gluskoter et al.[269] These authors distinguished three groups of elements:

1. With the highest organic affinity — Ge, Be, B, Br, and Sb
2. With medium organic affinity — Co, Ni, Cu, Cr, Se
3. With the lowest affinity, but occurring in all organic fractions — Cd, Mn, Mo, Fe, Zn, and As

The affinity of humic substances to accumulate trace cations has great importance in their geochemistry. The so-called "geochemical enrichment" factors of humic acid that was extracted from peat can reach a value of 10,000 from very low concentrations of cations in natural waters.[290,605] Trace elements migrating as anions (V and Mo) are reduced by humic acids and fixed in the cationic forms (VO^{2+}, MoO_4^{2+}). Metals complexed by fulvic acid presumably are more available to plant roots and soil biota than are those accumulated by humic acid which can form both water-soluble and water-insoluble complexes with metal ions and hydrous oxides.

Cottenie et al.[148] calculated that the humic acid of a soil containing 4% humus may bind 4500 kg Pb, 17,929 kg Fe, 1517 kg Cu, 1015 kg Zn, and 913 kg Mn per hectare. The ability of humic acid to complex with metals was calculated also by Ovcharenko et al.[587]

and expressed in grams per kilogram of humic acid, as follows: Cu, 3.3; Zn, 3.3; Co, 3.2; Fe, 3.0, and Mn, 2.6. Sapek[681] showed that the ability of humic acids to fix cations differs widely, and that those isolated from the A_0 horizon of podzolic soil have about two times lower sorption capacity to metals than those extracted from the B_h horizon of the same soil. In his experiment, the heavy metal content of air-dry humic acid reached more than 29%. All of these values were determined under laboratory conditions; in a natural soil system these proportions would be appreciably smaller. In general, however, it can be expected that up to 50% of total trace-element content is fixed by organic matter in mineral soils. These figures, however, can vary significantly.[756]

Owing to the relatively insoluble complexes of humic acids with heavy metals, especially in an acid medium, these complexes can be considered to be organic storage for heavy metals in soils. The organic matter may act as an important regulator of the mobility of trace elements in soils; however, in the majority of mineral soils, organic matter does not exceed 2% of total soil weight; therefore, it cannot be of the greatest importance in overall controls of trace element behavior in soils.

A high organic matter content of soil has a complex influence on the behavior of trace elements. The deficiency symptoms of plants grown on drained peatland or moorland (histosols) may be the result of a strong retention of Cu, Zn, Mo, and Mn by the insoluble humic acid.[135] A strong fixation of Cu in soils rich in humus is the most common and may result in a high Mo to Cu ratio in forage that is toxic to cattle. Applying organic matter to soil, however, raises the number of microorganisms that can reduce several cations, mainly Fe and Mn, and, in consequence, increase their availability. Increased organic matter content in Pb-amended plots is due to an enhanced preservation of stable humus, perhaps because of newly formed Pb-organic complexes with humic and fulvic acids which are protected from microbial attack.[881] However, there is also evidence that Pb complexes with low molecular weight humic substances were mobilized in the soil solution. On the other hand, some organic compounds present in root exudates and in humus can oxidize and therefore immobilize cupric compounds in soil.[81,189]

Simple organic compounds, such as certain amino acids, hydroxy acids, and also phosphoric acids naturally occurring in soils, are effective as chelating agents for trace elements. Cation chelation is an important factor in soil formation processes, as well as in nutrient supply to plant roots. The solubility of metal complexes depends on both the binding strength and the mobility of the complex thus formed, which is determined mainly by the size of the organic group involved. Strong binding of metal to a low molecular organic substance will appreciably increase its mobility in soil (Figure 9). Organic acids of leaf litter are known to be active in the mobilization of heavy metals in soils. An extract of pine needles dissolved more metals than an extract of oak leaves; in both cases, however, Cu and Zn were more readily complexed than were Co, Ni, and Cd.[87,974] In spite of a high mobilization of heavy metals, forest soil litter is also well known as an important sink of heavy metal and radionuclide pollutants, as reported by Pavlotskaya,[612,613] Van Hook et al.,[823] and Schnitzer and Khan.[692] The ability of simple organic acids to solubilize heavy metals may be of importance in their cycling. Rashid[612] calculated that each gram of amino acids occurring in the sediments may mobilize 4 to 440 mg of various metals, showing the highest affinity to Ni and Co and the lowest to Mn.

Several chelating agents are at present used in diagnostic extraction for available micronutrients in soils (see Norvell,[571] Mengel and Kirkby,[530] and Lindsay).[477] Of those commonly used are ethylenediaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA) which have been used for many years for determining plant-available trace elements in soils (Figure 10). Although the results differ when compared with other soil extractants and with uptake by plants, they are applied in many testing methods, and the ranges for critical levels are given for some micronutrients such as Cu, Zn, Mn, and Fe.

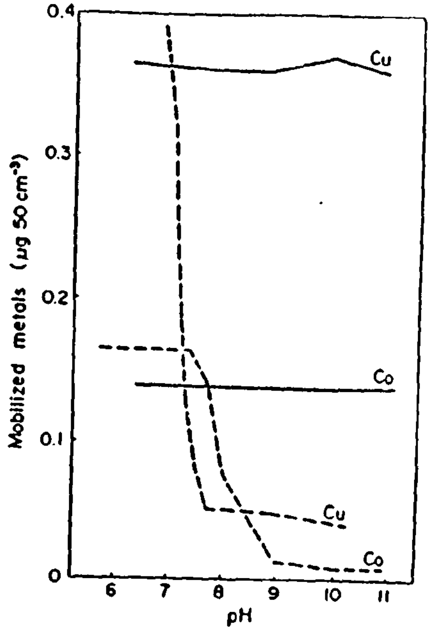

FIGURE 9. The effect of pH on the solubility of Co and Cu mobilized by aerobically decomposing alfalfa. Solid lines, complexed metals; broken lines, control solution of $CuCl_2$ or $CoCl_2$ alone.[81]

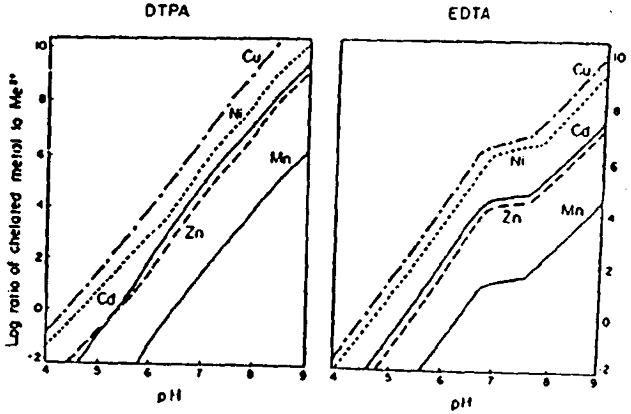

FIGURE 10. The effect of pH on metal chelating abilities of DTPA and EDTA.[illegible]

The DTPA soil test has also been developed to assess pollution by heavy metals of soils.[143] Soluble chelates of some trace metals, mainly Mn and Zn (i.e., Mn-EDTA; Na_2Zn-EDTA), are also effective as fertilizers.

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CHEMICAL PATHWAYS FROM STACK EMISSIONS TO SURFACE WATER

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INTRODUCTION

Although the possibility of the transport of pollutants over long distances has been recognised for many years (1) concern over the emission of pollutants into the atmosphere has, until relatively recently, centred on possible adverse health effects and on visible damage to agriculture and materials at high pollutant concentrations near to major sources. In 1972, however, the U.N. Conference on the Human Environment in Stockholm established a new dimension to the problem; the possibility that pollutants, particularly SO_2 from combustion sources, could be transformed to sulphuric acid during transport in the atmospheric boundary layer and ultimately be deposited as acidic rain or snow at remote sites several hundred kilometres from the source. Of particular concern in this context is the possible acidification of surface waters and the consequent destruction of fisheries in affected areas.

A complex chain of processes links the production of an anthropogenic atmospheric emission with its action in the aqueous environment. The gaseous products of combustion are normally carried away downstream by the wind together with those particulate products small enough to behave like a gas. In the atmosphere, turbulence generated by wind variations and thermal forces acts to disperse and dilute them in both lateral and vertical directions. A vertical limit to this process is frequently taken to be the height of the turbulent boundary layer ('mixing layer') over the earth which in turn depends on meteorological factors and topography. Its height can typically range from 200 m at night to 2000 m during the day. As a plume disperses in the mixing layer, ground level concentrations of gaseous pollutants fall off with increasing distance because of vertical and lateral dilution, absorption at the earth's surface, by chemical transformation in the gas phase or uptake in clouds and rain. All these processes combine to determine the chemical composition of precipitation occurring along the trajectory and their variation combined with diurnal, seasonal and meteorological changes determines the variability of precipitation composition.

This paper reviews what is known about the various processes in the pathways leading from stack emissions to precipitation composition and highlights some of the uncertainties.

CHEMICAL TRANSFORMATIONS IN THE ATMOSPHERE

Within the mixing layer primary pollutants can be removed by dry deposition, onto land or sea surfaces, or by precipitation scavenging. They can also undergo chemical transformation into secondary products which can then be removed by the same processes. In considering near-field effects it is the behaviour of the primary pollutant, and particularly the dispersion, that is of major interest. In contrast the time-scale involved in the long range transport of emissions is such that chemical reactions of emitted materials are important in determining the environmental impact at a receptor site.

In the case of SO_2 the main chemical transformation of interest is oxidation to sulphuric acid or sulphate aerosol. Nitric oxide is oxidised in the atmosphere to NO_2 and thence to nitric acid and possibly to nitrate aerosol, ending up ultimately in precipitation as nitrate ion. The mechanisms of these processes are complex and interdependent as well as being influenced by the degree of availability of other pollutants and natural atmospheric components.

Two basic routes to the formation of acidic products can be identified. The first involves a sequence of coupled gas phase reactions in which free radicals, generated photochemically by sunlight, play a major role. Many of the primary reactions occurring have been characterised in laboratory kinetic studies so that it is now possible to model the chemical evolution of a plume in some detail. A major problem, however, is that of combining the effects of dispersion with simultaneously occurring chemical reactions.

In some instances the rate determining step for chemical transformation may be dilution and mixing rather than the chemical processs itself. An example is the oxidation of nitric oxide in a plume which, after the first few seconds of travel is predominantly via

$$NO + O_3 \rightarrow O_2 + NO_2 \qquad \ldots (1)$$

In this instance the oxidant, ozone, is derived from the ambient air into which the plume is diluting and, for the first few tens of kilometres travel at least, NO in the plume exceeds ambient O_3. The result is that O_3 is depleted in the plume because reaction (1) is rapid, so that all the reaction proceeds subsequently at the plume edge where further ambient air is mixing with the plume. The slowest process can often be the mixing which thus determines the overall rate of formation of NO_2 (2).

Normally, and in particular in sunny summer conditions, the conversion of at least half of the NO to NO_2 occurs within about two hours of plume travel time. An extreme example of a much slower oxidation rate is shown by the data in Fig. 1. This shows a cross-wind profile of NO and NO_2 measurements made during an aircraft flight on 29 January 1981 over the North Sea about 105 km from the nearer of two major source areas. The results are plotted as the ratio NO_x/NO so that a value of 1.0 means that all of the nitrogen oxides are present as NO whilst a ratio of 2 means that 50% has been converted to NO_2. Also shown is the profile of a chemical tracer, SF_6 which identifies the position of the plume of interest. The measurements were unique in that the entire traverse of 260 km was flown in low stratus cloud which extended to within 100 m of sea level. Photochemical activity was therefore at a minimum and the O_3 level in the plume was only ~1-2 ppb increasing to ~20 ppb outside the plume. Even at this distance, corresponding to about 6 hour plume travel time, the major part of the NO remained unoxidised with only ~15% NO_2 at the centre of the "labelled" plume and 50% oxidised on the centre line of the more southerly plume. The increased extent of oxidation at the plume edges is clear evidence that oxidant availability was determining oxidation kinetics on that occasion.

The major route to the formation of acidic species under dry sunny conditions is via attack by the hydroxyl radical (3)

$$OH + SO_2 \rightarrow HSO_3 \rightarrow \text{acidic sulphate} \qquad \ldots (2)$$

$$OH + NO_2 \rightarrow HNO_3 \qquad \ldots (3)$$

The thermodynamics of the respective systems dictate that sulphate aerosol should

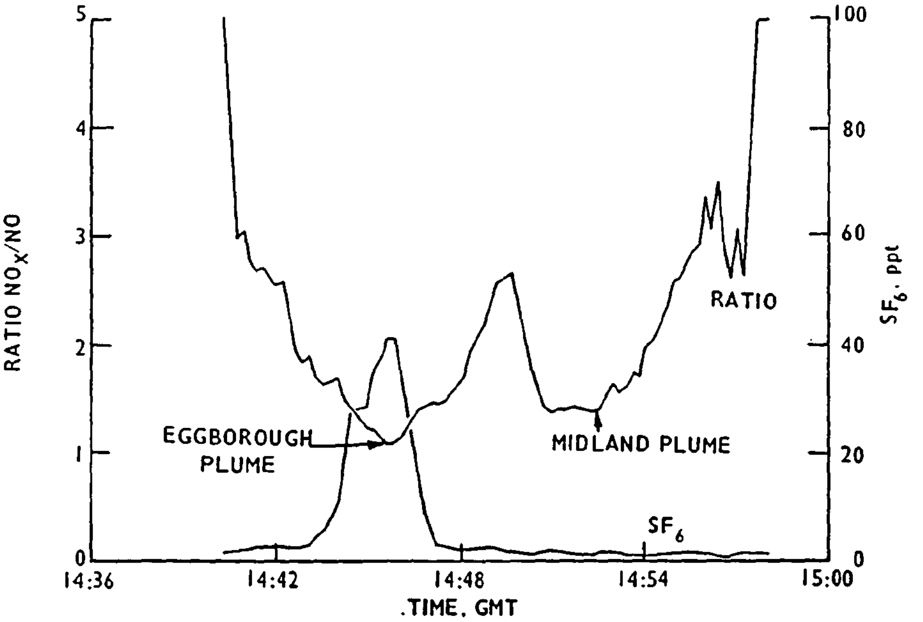

FIG. 1 28/1/81 RUN 4, 150 m

be the product in the case of SO_2 whereas nitric acid vapour is the predominantly stable form in the latter case. Experiments show that the sulphate aerosol is almost invariably partially neutralized by ammonia of natural origin.

The rate of acid production by this route thus clearly depends on both SO_2 or NO_2 concentrations and also on the OH concentration. OH concentrations are a complex function of plume dispersion rate, sunlight intensity and ambient air composition (4-6) as precursors to OH are supplied by the ambient atmosphere. Thus the rate of supply of reactive hydrocarbons, which are important precursors to OH, could become rate determining in the formation of acidic products under some conditions.

In the reactive plume model developed at CERL (7) the plume is assumed to expand at a pre-determined but variable angle vertically to fill the mixing layer and horizontally at a different angle. As it expands it is diluted by ambient air which itself can be of variable composition. The gases are assumed to be uniformly mixed within the plume. The ambient air chemistry is modelled using the appropriate emission inventories for hydrocarbons, SO_2, NO_x, O_3 etc. and is itself reactive. Other important input parameters are the latitude, time of year and time of day which combine to determine the incident sunlight. Because uniform mixing is assumed within the plume the model does not allow for diffusional limitation to reaction rates. It therefore represents the most favourable conditions for oxidation and acid production.

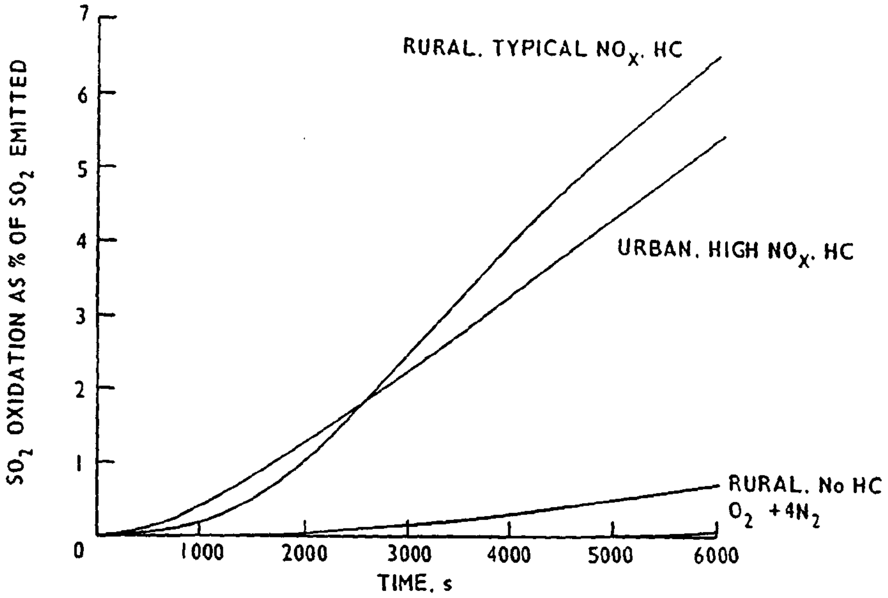

FIG. 2 THEORETICAL OXIDATION OF SO_2 IN A PLUME AS A FUNCTION OF TIME AFTER EMISSION. THE CURVES SHOW THE EFFECT OF MIXING AND DILUTION WITH AMBIENT ATMOSPHERES OF DIFFERENT HYDROCARBON AND OXIDANT CONTENTS. (COCKS AND FLETCHER, 1981)

In Fig. 2 the predicted oxidation rate of SO_2 for different ambient air compositions is shown for the early stages of transport ($t < 2h$). Dilution into pure air, that is simply 20% oxygen and 80% nitrogen, would effectively cause the oxidation of SO_2 to cease. It is only the presence in the ambient air of hydrocarbons and oxides of nitrogen which facilitate the production of high enough concentrations of OH and other oxidants for oxidation to proceed at rates approaching those actually observed.

The computational difficulty of combining the complex plume chemistry with the detailed physical dispersion has so far precluded the development of models that adequately account for both the chemistry and the plume structure for different dispersion conditions. Nevertheless the results from simple chemical models (7) do reproduce the main features often observed during measurements. For example, Fig. 3 shows the predicted conversion rate for SO_2 in a plume averaged over a period of about 6 hours from noon at latitude 50°30'N for an ambient air composition corresponding to average rural air. The expected conversion rate varies from a tenth of one per cent per hour or less at mid-winter to ~3% per hour at mid summer which is broadly in line with measurements (8,9,15). The recognition, through chemical modelling studies, that a number of parameters including sunlight intensity and oxidant level determine the overall rate of chemical conversion has helped to rationalize many of the differences in actual observations of SO_2 oxidation in plumes (9).

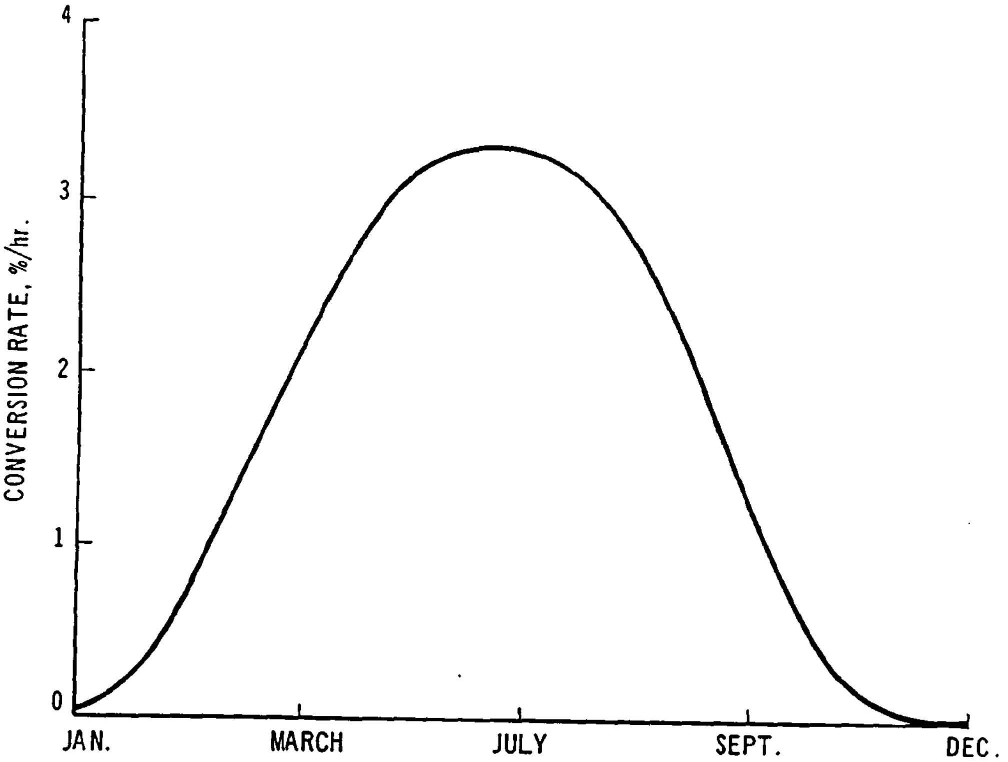

FIG. 3 PREDICTED AVERAGE CONVERSION RATE OF SO_2 IN A PLUME OVER A 6 HOUR PERIOD

Fig. 4 shows model predictions for the concentration of total acid for a typical plume from a 2000 MW coal-fired power station diluting into urban air (plume I). Details of the emissions and physical parameters are identical to those defined previously (7) with the addition of an emission of 200 ppm of HCl gas. The predictions are for a plume release time of noon on midsummer's day for a latitude of 53.5°N (Northern England). Also shown in Fig. 4 are the predicted behaviour of a plume containing 50% of the normal SO_2, NO_2 and HCl emissions (plume II) and a plume containing no SO_2 or HCl, corresponding to a fully scrubbed plume (plume III). The figure also shows Atlantic background of HCl which arises from the interaction of sodium chloride aerosol with acidic species produced during the transoceanic passage of air (10). In the model this is depleted by dry deposition and hence the land mass effectively removes about 30% of the HCl giving rise to the "rural HCl" shown in Fig. 4.

The high initial level of total acid in plumes I and II is due to the emitted HCl. This declines relatively rapidly through dilution while the concentrations nitric and sulphur acids increase through chemical transformation of SO_2 and NO. The predicted composition of the acid product at the end of 24 h of plume transport is given in Table 1.

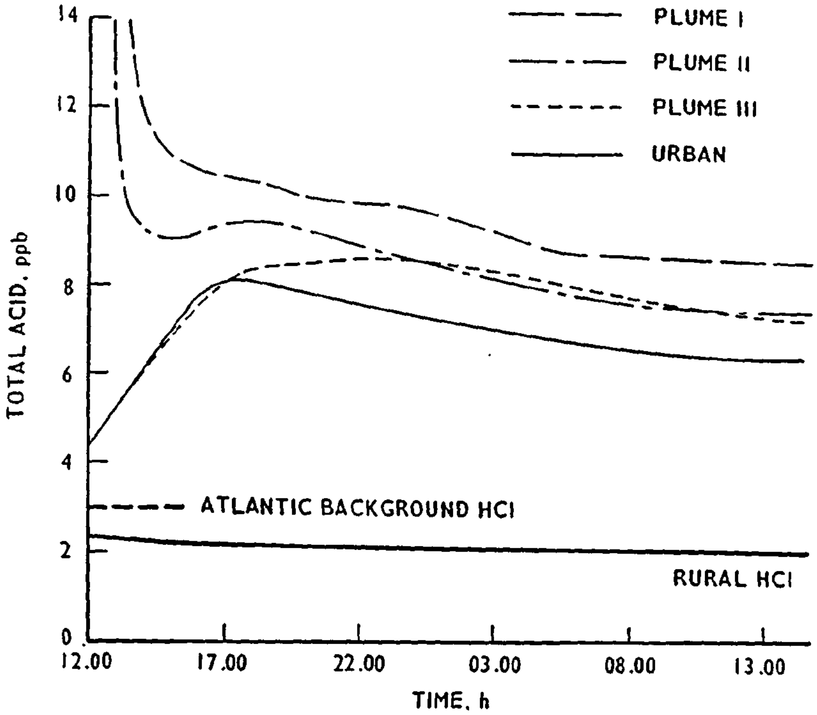

FIG. 4 PLUME EXPANSION INTO "URBAN" AMBIENT

The data in Fig. 4 and Table 1 illustrate the important point that typical urban air contributes significantly to the chemical impact at a long distance. Thus the model predicts that, in the absence of a point source plume, the urban ambient air contributes about 63% of the sulphur acid and 75% of the total acid concentration that would be produced in the presence of a plume.

Table 1: Concentrations after 24 Hours Plume Travel for Expansion into "Urban" Ambient

	ACIDIC SPECIES CONCENTRATION/ppb			
	Sulphur Acids	HNO_3	HCl	Total
Plume I	1.79	4.36	2.47	8.62
Plume II	1.47	3.83	2.24	7.54
Plume III	1.10	4.39	2.02	7.51
"Urban" Ambient	1.12	3.30	2.02	6.44

Similar calculations for plumes expanding into ambient air of different composition further illustrate the effect on acid production of the ambient air quality indicated by the results in Fig. 2. For example Table 2 shows the concentrations of acids predicted for 24 hours of plume travel and for expansion into a typical "rural" atmosphere (7). Comparison of Tables 1 and 2 then indicates that about 10% more sulphur acid products are produced from plume materials by expansion into "urban" air than into "rural" air.

Table 2: Concentrations after 24 Hour Plume Travel for Expansion into "Rural" Ambient

	ACIDIC SPECIES CONCENTRATION/ppb			
	Sulphur Acids	HNO_3	HCl	Total
Plume I	0.95	3.07	2.47	6.49
Plume II	0.66	2.56	2.24	5.46
Plume III	0.37	3.11	2.02	5.50
"Rural" Ambient	0.35	2.05	2.02	4.42

Acidic and other species produced in the gas phase cannot, however, be the sole contributors to precipitation composition. They are almost certainly totally absorbed by cloud droplets but gaseous SO_2 can also be absorbed and oxidized within clouds. This is the second of the major pathways for SO_2 oxidation in the atmosphere but evidence for its existence is limited and based almost solely on the results of laboratory measurements, apart from a few preliminary experiments in wave clouds (11).

As well as oxidation by dissolved oxygen, the possibility exists that the strong oxidants hydrogen peroxide and ozone can also oxidize SO_2 dissolved in cloud and rainwater (12). The atmospheric concentrations of these is much lower than that of oxygen but laboratory experiments have shown that the oxidation rates are so much faster that they can compete effectively. Calculations by Penkett et al. (12), based on experimentally measured rates, suggest that 50 ppb of ozone or 1 ppb of H_2O_2 would give oxidation rates two orders of magnitude greater than for atmospheric oxygen.

Oxidation in solution is further complicated by the fact that the acidity increases as the reaction proceeds and this decreases the extent of further dissolution of SO_2. For O_3 and O_2, the overall rate of sulphate production thus decreases as oxidation proceeds but with H_2O_2 the rate constant increases with acidity. Recent work (13) has shown that the rate of SO_2 oxidation by H_2O_2 is totally independent of pH so that this may be the only possible in-cloud oxidation mechanism for pH < 4.0.

In general, gas phase reactive plume models predict a more rapid production of nitric acid than of sulphur acids (7) and yet precipitation at most remote sites downwind of major sources in Europe contains more sulphate than nitrate and non-sea chloride is negligible although it has not often been specifically sought.

This is perhaps the best indication that in-cloud scavenging and precipitation washout contribute significantly to precipitation composition and, in particular, that it is by these pathways that sulphur acids come to exceed nitric acid in precipitation. Models to simulate in-cloud scavenging and chemical transformation are currently being developed at CERL and elsewhere.

Previous experimental and modelling studies of plume chemistry have not considered HCl either as a primary emission or as a component of the ambient air. Its importance is clearly related to the chlorine content of the fuel but two important effects can be predicted. The first is that it may directly affect or even dominate the acidity of precipitation and the second that it may influence the other chemical transformations in a plume. Measurements by Martin (14) show that, in some areas of the UK, precipitation acidity near to sources burning high chlorine coal is dominated by HCl but that this is not the case beyond a few kilometres from such sources. This suggests that, on average, HCl is fairly efficiently scavenged from the atmosphere.

Evidence for the possible effect of HCl on plume chemistry arises from the cloud water analysis shown in Table 3. These samples were collected from stratiform cloud within the mixing layer during a cross wind traverse about 105 km from a power plant plume over the North Sea on January 28 1981. An excess of chloride ion is evident and the low pH on that occasion was probably largely determined by the primary HCl emission. The consequence was probably that the solubility of SO_2 was reduced making it less available for oxidation in cloud droplets. This, along with the low concentration of oxidants meant that oxidation in the aqueous phase could not have been proceeding significantly at the time of the observations. Preliminary modelling studies (15) suggest that the measured sulphate arose predominantly from SO_2 oxidation in cloud in the ambient air into which the plume was mixing the acidity there being lower and oxidant level (O_3 ~ 20 ppb) higher.

Table 3: Cloud Water Samples 28 January 1981

1336-1545 GMT

concentrations in μeq/l

Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}	I.B. pH*	Cloud Water Content gm/m^3
1758	653	1481	952	1009	372	256	296	3.03	0.6
2901	779	1694	952	1339	137	229	229	2.63	0.6
3887	897	2250	843	1917	114	335	315	2.46	0.6
2407	815	2533	726	3700	76	500	315	3.24	0.5
2817	769	2563	543	2222	88	403	172	2.56	0.4

* pH calculated from ion balance.

DEPOSITION PROCESSES

Within the atmospheric mixing layer primary and secondary pollutants can be removed by dry deposition onto land or sea surfaces or by precipitation scavenging.

The range of mechanisms encompassed within dry deposition includes capture or absorption by, reaction with, or diffusion through any terrestrial surface, e.g. oceans, soil, plant tissues and man-made structures, or by solution in any aqueous films present on such surfaces. In each case it is normally assumed that the take-up is irreversible, but little is known about the extent of neutralisation of dry-deposited SO_2 by mineral dusts and ammonia. The result of such take-up is to deplete the atmosphere of gaseous pollutant in the immediate vicinity of the surface, thus producing a concentration gradient which maintains further transport of pollution to the absorbing surface. The overall resistance to this flux is usually expressed inversely as a deposition velocity, (V_g). Its value depends not only on thee meteorological conditions but on the nature of the surface. There is also a wide variation in V_g for different gaseous pollutants which is undoubtedly related to their different chemical affinity for surfaces including, particularly, their differing water solubility (16).

During transport within the mixing layer calculations using average deposition velocities show that SO_2, for example, is removed by dry deposition at rates equivalent to a first order rate constant of 2 to 4% per hour. Although precipitation scavenging, when it occurs is probably faster than this, dry deposition is nevertheless probably the major route through which SO_2 is removed from the atmosphere. For example, taking a deposition velocity of 1.0 cm/s the flux of sulphur from an atmospheric concentration of only 10 $\mu g/m^3$ of SO_2 approximates that from 1000 mm per year of rain containing 70 μ equ/litre of sulphate. Thus, apart from the most remote sites which also have high rainfall, dry deposition exceeds both wet deposition and chemical transformation as a loss mechanism for SO_2.

The processes by which precipitation scavenges gases and particles from the atmosphere can be conveniently divided into two classes. Those in which material is incorporated into cloud droplets are often designated as "rainout" whilst the scavenging by falling precipitation is termed "washout".

Various theoretical models have been developed to describe washout (17-19). The problem is essentially one of calculating the number of collisons between particles or gas molecules and the falling precipitation droplets and is complicated by the existence a size distribution of particles and droplets. For particulate washout the process is usually considered to be irreversible; that is that all particle-droplet collisions result in the irreversible capture of the aerosol particle by the precipitation droplet (17). This is not the case for sparingly soluble gases, including SO_2, for which scavenging may be limited by the solubility of the gas and the possibility exists of desorption of the dissolved gas by the droplet if it falls into a region where the gas phase concentration is lower (18).

The presence of ammonia gas in the atmosphere can significantly enhance the washout of SO_2 by its neutralizing effect which thus increases the solubility. Even so the calculations of Marsh (19) suggest that not more than half the sulphate in precipitation at remote sites comes from washout of SO_2 or of sulphate aerosol. Similar arguments apply to the other major anion found in precipitation, nitrate, although the high solubility of nitric acid vapour may result in a degree of removal by washout. Thus the evidence suggests that the major part of the dissolved material in precipitation is incorporated during the formation and growth of cloud droplets.

As with precipitation scavenging, material is incorporated into cloud water either by dissolution of gases or as aerosol particles. In principle aerosol could be incorporated either at the nucleation stage of cloud formation or subsequently by either Brownian attachment or by diffusophoresis. Brownian attachment is only important for Aitken nuclei ($r < 0.1$ μm) (20) whilst Goldsmith et al. (21) deduced that diffusophoresis in a water vapour flux typically accounts for less than 1 per cent of material scavenged during one cloud condensation cycle in the atmosphere. Thus uptake by gaseous diffusion and nucleation of cloud droplets on particles are probably the main processes involved in scavenging by clouds.

In clean maritime air, nucleation is probably predominantly on 'giant' sea-salt particles ($r < 1.0$ μm). Measurements indicating similar number densities for both nuclei and cloud droplets (~100 cm^{-3}) tend to confirm the hypothesis that virtually all sea salt particles at cloud level are involved in condensation (22). Over land, and particularly in industrialized regions, cloud droplet concentrations of 100-200 cm^{-3} are not uncommon and this difference between maritime and continental cloud suggests that a substantial proportion of continental aerosol can act as nuclei. For example a typical sulphate aerosol concentration of 10 μg m^{-3} and particles of unit density correspond to an aerosol number density of 2 cm^{-3} for a radius of $r = 1.0$ μm, or 250 cm^{-3} for $r = 0.1$ μm. Thus it is entirely feasible that virtually all pollutant sulphate aerosol can be taken up as cloud condensation nuclei.

On this basis the expected concentration of sulphate in cloud water derived from nucleation alone can be calculated. Thus a cloud liquid water content of 0.5 g m^{-3} and 10 μg m^{-3} of aerosol corresponds to a predicted concentration of sulphate in cloud water of 450 μ eq $litre^{-1}$. The expectation thus is that sulphate levels at least shall be substantially higher in cloud water than in precipitation in which typical concentrations at remote sites are ~70 μ eq $litre^{-1}$.

Table 4 shows the average composition of cloud water samples from non-precipitating stratiform cloud from measurements carried out during 1980-81 (15). The data are divided into samples upwind of the UK and downwind of the UK and, for comparison, the composition of precipitation at a typical remote inland site is included together with concentrations for an 'acid episode' in SW Norway on 2-4 March 1974. In each case the upwind samples were taken in comparatively clean air with SO_2 and NO_x levels below the measurable limit and correspondingly low aerosol loadings.

The expectation is that West Coast samples should reflect a long oceanic fetch by being relatively rich in sea salts whilst East Coast cloud samples would be relatively higher in anthropogenic species, SO_4^{2-} and NO_3^- and in natural land origin species Ca^{2+} and NH_4^+. These qualitative expectations are fulfilled by the mean values of analysis presented in the table and indeed by all the individual samples collected during the programme.

The data in Table 4 show that the ratios of the non-sea-salt ions in the East Coast cloud water are similar to those observed in precipitation, although of much higher concentration, typically a 5 to 10-fold difference. Such sulphate levels compare reasonably well with the values as high as 400 μ eq $litre^{-1}$ reported by Hegg and Hobbs (11) over Los Angeles and Washington but are higher than the average value found at the remote site at Whiteface Mountain (23) although the maximum value observed in that study was ~1200 μ eq $litre^{-1}$.

Table 4: Composition of Cloud and Precipitation

concentrations in μ eq/l

	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+	pH
Stratiform cloud, mean upwind UK	261	73	1154	905	112	53	237	126	4.3
Stratiform cloud, mean downwind UK	558	240	857	905	27	163	169	419	3.5
Precipitating cloud samples, (11.8.80)	90	55	83	47	20	-	-	20	5.4
Precipitation, mean OECD site(N10) (S. Norway)	68	29	25	21	3	14	5	30	4.35
Precipitation episode SW Norway (2-4.3.74)	230	150	-	-	-	65	27	180	3.92

These measurements indicate that substantial dilution through vapour deposition must occur during the growth of cloud droplets to precipitation elements. Consistent with this picture is the fact that samples from precipitating clouds had much lower concentrations that were only 1 to 2 times that of average precipitation (Table 4). During sampling of the stratiform clouds the mean cloud droplet radius was measured as ~6 μm. This would only need to grow to ~12 μm radius to achieve dilution to sulphate concentrations typical of precipitation. Clearly droplet accretion is also important in the growth of precipitation elements. The above results are in agreement with the conclusion (24-26) that the collision efficiency of droplets is less than 1% until the radius exceeds 15 μm. The observations are thus consistent with a model of cloud droplet growth predominantly by condensation up to ~12 μm followed by accretion until rain drop sizes are reached.

Another interesting feature of the results in Table 4 is that whereas the Na^+/Cl^- ratio for samples taken in clean maritime air is almost exactly that expected for sea salt, Cl^- exceeds Na^+ downwind of the UK. This suggests a major contribution to cloud composition of HCl from combustion sources and this is borne out by cloud measurements in specifically identified plumes (Table 3) (15).

CONCLUSIONS

This paper has sought to demonstrate the importance of chemical transformations and, in particular, of chemical kinetics in the atmosphere in determining the impact of atmospheric emissions on the aquatic environment through precipitation.

Direct measurements as well as modelling studies based on kinetic parameters determined in the laboratory have resulted in a reasonable understanding of the gas phase chemical transformation of major primary pollutants. The relative abundance of sulphate and nitrate in precipitation does not, however, reflect the measured or predicted rate of production of nitric acid and sulphate aerosol in typical plumes in which gas phase chemistry predominates and suggests that, on average at least, in-cloud chemical transformation along with direct precipitation scavenging accounts for a substantial part of the sulphate actually observed in precipitation at most sites.

The chemical interaction of pollutants from the same source and from different sources is brought out most clearly when considering the effect of ambient air composition on the gas phase chemistry in plumes. Equally however, oxidant availability during in-cloud oxidation of SO_2 may be of even greater importance and may sometimes be the rate determining factor for sulphate production. There is a need to investigate the importance of hydrocarbon precursors in this respect.

The chemistry of the ambient air is also important at long range, particularly when it is of urban origin, because this air itself contains many of the principal components that are also present in power plant plumes including SO_2, NO_x and their derivatives. Indeed, for NO_x at least after 24 h travel at a distance of ~1000 km from source, it may often be the case that most of NO_x in the now widely dispersed and diluted plume derives not from the plume source but from the much more widespread urban or rural sources which determine the quality of the ambient air.

Clearly the effect of changes in emissions either from point sources or from urban and rural area sources which determine ambient air composition cannot be predicted without considering the complex atmospheric chemical interactions exemplified in this paper. To be both soundly based and cost-effective any future control strategy must likewise rely on a thorough understanding of the chemical pathways linking source and effect and on the resolution by further research of the areas of uncertainty.

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Metals: Fallout Around a Power Plant

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Soils around a coal-burning plant are enriched in Ag, Co, Cr, Cu, Fe, Hg, Ni, Ti, and Zn. Plant materials [illegible] enriched in Cd, Fe, Ni, and Zn. Soil enrichments cor[illegible] with wind patterns and with the metal content of [illegible] except for Hg, which is only slightly enriched.

Airborne mercury resulting from fossil fuel consumption [illegible] frequently cited as a source of mercury in isolated lakes. Studies by Joensuu (1971) and Billings and Matson (1972) suggest that large quantities of mercury may enter the environment in this way. Bertine and Goldberg (1971) consider fossil fuel consumption to be a potentially significant source of atmospheric discharge of many metals in addition to mercury. The research reported in this paper was [illegible] up to gain an entry to this problem of atmospheric dis[illegible] specifically, to consider how much land area [illegible] be burdened by fallout from a major coal burner.

Study Area

The plant is located on the eastern shore of Lake Michigan. Except for a ridge of low dunes at the shoreline, the surrounding terrain is quite flat. Typically, the soil is sand with a thin cover of decomposed organic matter. The [illegible] potentially competing source of atmospheric discharge of metals is the city of Holland, lying six miles to [illegible] south, which has several metal industries. The plant [illegible] started up in 1962. Since then it has consumed about [illegible] tons of Ohio coal. It presently generates 650 MW, and discharges through a 400-ft stack equipped with precipita[illegible] which operate at about 90% efficiency.

Sampling and Analysis

The land sampling grid included 45 sites, with two sam[illegible] taken at each site. Usually, samples were soils from established wooded areas, one from under deciduous trees, [illegible] other from under coniferous trees. All samples were [illegible] from well-drained areas. The samples were 2 cm thick, and were screened to remove leaves, roots, pebbles. An additional 24 surface grabs were taken of sediments in Lake Michigan, up to 3 miles offshore.

The samples were analyzed as received, and the results corrected to a dry weight basis. Two-gram samples were weighed into screw-top centrifuge tubes, and initially oxidized at room temperature in an H_2SO_4-$KMnO_4$ medium. When the $KMnO_4$ oxidation appeared complete, 2 ml. of [illegible] $K_2S_2O_8$ was added and the tubes were sealed and placed [illegible] a 60°C oven for 30 min. The samples were then centri[illegible], and the supernatant was decanted and brought to volume. Mercury analysis was done by flameless atomic absorption, using the Mercometer (Anti-Pollution Technology Corp.). Conventional AA analyses for Fe, Ti, Zn, Co, Cr, Cu, Ni, Cd, and Ag were run on Perkin Elmer 303.

Results and Discussion

The analytical results, plotted as contour maps, are all quite similar to that of Cr (Figure 1). All patterns show marked enrichment northeast and southeast of the plant, with a pinched-in area of low concentration at about 80°. Enrichment patterns in the sediments do not coincide well with the land patterns, being complicated by the outward movement of fine particles resulting from wave action, by the general southward drift of near-shore sediments in this area, and by significant river discharge of metals. The Hg pattern differs from the others in that it lacks the region of very low concentration around and south of the plant.

To gain some insight into the possible entry of the discharged metals into the biota, samples of native grasses, maple leaves, and pine needles from four sites in the background region and four sites in the enriched region were collected and analyzed. The data (Table I) show highly significant increases in Cd, Fe, and Ni. Thus, cattle pastured in the enriched region are ingesting grasses with a considerably greater Cd content than cattle pastured in the background region.

The wind data presented in Figure 2 are the summary of 3-hr observations over four years at the U.S. Weather Bureau station at Muskegon, 18 miles north, and near the shoreline. The most frequent wind component is 13-18 mph. The pattern has been rotated 180° from the conventional wind rose, to better illustrate a resulting fallout pattern. The wind pattern is quite similar to the observed fallout patterns, with winds of maximum frequency directed northeast and southeast of the plant, relatively low frequency directed at about 80°, and a very low frequency of low-velocity winds. The main difference between the wind pattern and the fallout patterns is that the observed southern enriched zone is too large east to west. Possibly this is the result of the airborne debris of the city of Holland, reinforcing the pattern from the plant. The northeastern enriched region is centered about 6 miles from the plant; thus it appears that 13-18 mph winds are competent to transport the particulate emissions about 6 miles. The wind pattern shown has been empiricall[illegible] scaled accordingly; that is, a wind velocity vector of 15 mph corresponds to a map distance of 6 miles.

If the wind pattern, as scaled, adequately explains [illegible] observed fallout patterns, then it appears from the [illegible] pattern that about one fifth of the discharge fro[illegible]

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Table I. Trace Metals in Soils and Plant Materials around a Power Plant

Metal	Background soils, ppm	Enriched soils, ppm	Background plants, ppm	Enriched plants, ppm	Soil enrichment, tons	Total discharge, tons	Calcd discharge, tons
Fe	1500	2840	80	260	20,000	25,000	10,000
Ti	55.6	91.6	None detected		540	680	500
Zn	20.3	35.0	37	51	130	160	50
Co	2.3	4.6	None detected		34	42	5
Cr	4.65	6.5	None detected		28	35	10
Cu	2.8	4.6	10	8	26	32	15
Ni	2.4	4.0	0.5	2.1	24	30	15
Cd	0.55	1.46	0.12	0.35	14	18	
Ag	0.247	0.272	None detected		0.4	0.5	0.5
Hg	0.0079	0.0102	0.09	0.07	0.04	0.05	4

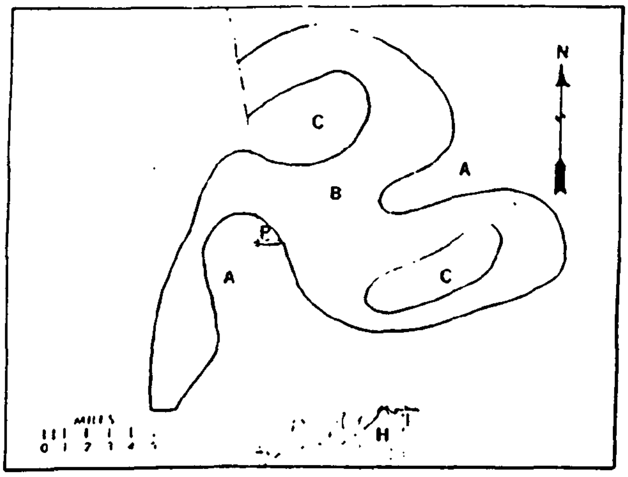

Figure 1. Chromium distribution around the power plant

P, plant; H, city of Holland; A, 0-5 ppm; B, 6-10 ppm; C, over 10 ppm

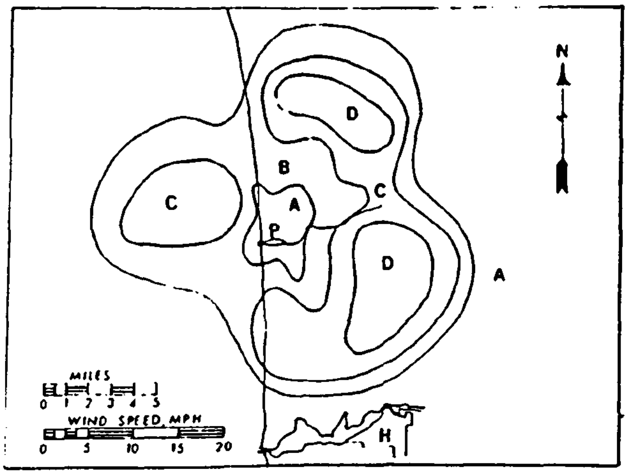

Figure 2. Wind distribution around the power plant

Total observations, 14,000. A, 0-125 observations, B, 126-250; C, 251-375; D, over 375.

plant enters Lake Michigan. As shown by Figure 1, however, this one fifth is not located where the wind pattern predicts, probably because of movement of sediments discussed previously.

By making the following assumptions, an approximate balance between coal consumption and the soil concentrations can be constructed:

- There is a single region enriched by coal burned at the plant. This region is shaped like the shaded land area of Figure 1. Outside this region the metals are at background concentration. The enriched area covers 115 mi² and encloses 23 of the 45 land sample sites.
- Enrichment is confined to the upper 2 cm of soil, which has a density of 2.7 gm/cm³.
- Except for Hg, metal concentrations in the coal are those presented by Bertine and Goldberg (1971). The concentration of Hg is taken as 0.3 ppm, an estimate possibly in error by a factor of 5.
- The precipitator works with 90% efficiency for all metals but Hg. All the mercury in the coal is discharged to the atmosphere (Billings and Matson, 1972).

Each assumption may be in error by a factor of 2 or 3, but less than an order of magnitude. The assumptions permit calculation of an observed total discharge, in metric tons, and a calculated discharge based on an assumed coal analysis. The numbers are shown in Table I. The range from Fe to Ag covers nearly five orders of magnitude, and only Hg shows a serious discrepancy, by about two orders of magnitude.

There are several possible explanations for the discrepancy:

- The assumed mercury concentration in coals may be too high. To remove the discrepancy would require that the mercury concentration must be about 0.003 ppm, which is unreasonably low. This explanation is probably incorrect.
- Mercury leaves the stack as the vapor, adsorbs on the particulates and deposits with the other metals. Once in the soil most of it is volatilized from the particulates by some unknown chemical or biological process and dispersed over a wider area.
- Mercury leaves the stack as the vapor, a small fraction is adsorbed on particulates and deposits, and the balance is dispersed over a wide area.

Although we cannot distinguish between the latter two explanations, it is clear that mercury discharged to the atmosphere by combustion of coal is much more widely dispersed to the environment than are other metals similarly discharged.

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BERYLLIUM POLLUTION FROM SLAG AND ASHES FROM THERMAL POWER STATIONS

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Abstract. Beryllium enters the environment principally from coal combustion. Be contents in the ashes from a Czechoslovak power plant were determined. The ashes used in the experiment were as follows: coarse (> 2.0 mm) and fine (2.0 to 0.2 mm) fraction from dump, and fine (< 0.2 mm) fraction from electrostatic precipitators. It was discovered that the acidic and the alkali aqueous extracts of these ashes contain various concentrations of Be (1 to 17% of total concentration). Wastewater has shown 3.15 and 3.4 μg Be L^{-1}. Thus, secondary long-term Be pollution emerges from the slag and ash dumps.

1. Introduction

Beryllium exhibits toxic and carcinogenic effects (Groth *et al.*, 1980; Reeves, 1979; Sunderman, 1984; IARC, 1980; SCTM, 1981). Its threshold limiting value is 2 μg Be m^{-3} and MAC occupational exposure value is 1 μg Be m^{-3}. Experimental evidence of carcinogenic effects of Be on mammals has been reviewed by Kuschner (1981); the phytotoxicity of this element is not yet fully understood (Lepp, 1981).

The amount of Be present in the evironment has increased dramatically over the past 50 yr. The world production of Be was about 20 × 10^3 tonne in 1979. The annual emissions of Be have been estimated to be 30 tonne. About 2 tonne of Be pollution results from special extraction plants and in the nuclear, electrotechnical, metal working, machinery, and ceramic industries.

The amount of atmospheric emissions of Be in Czechoslovakia is estimated to be 3.1 tonne yr^{-1}; in this respect this country assumes fifth place in Europe after USSR, Poland, GDR, and FRG (Pacyna, 1984). The main source of pollution is thermal power stations which burn coal containing Be, particularly brown coal mined at the North Bohemia Brown Coal Mining District which contains Be in amounts of 1.5 to 30 μg g^{-1} (annual extraction of coal about 1 × 10^8 tonne) (Bouška, 1981).

In 1976 to 1980 we monitored environmental pollution in the vicinity of a thermal power station burning coal from that mining district, and measured the concentration of Be and other potentially toxic elements along the chain: coal-slag-ashes-dust fallout-wastewater from the light ashes dumping ground-soil-plants within a distance of 15 km from the power station. We observed no significant changes in the accumulation of trace elements in crop plants, which are the first link of the food chain (Švácha *et al.*, 1979, 1980).

The aim of the present work was to estimate the Be content of the solid matter of the wastewaters, and to examine the liberation of this pollutant from the solid matter by acid and alkaline solutions at various pH.

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2. Materials and Methods

The Mělnik power station is a condensation type, with installed capacity of 1333 MW; its annual fuel consumption is about 5 × 10^6 tonne of brown coal with medium S content and about 30% ash. The dump, located to the west of the station, is a horizontal type and is divided into two parts by an hydraulic-fill earth dam. The situation is depicted in Figure 1.

The samples of were ground and homogenized in a ball grinder (Fritsch, FRG), their wet decomposition was performed in a home made Teflon-lined autoclave.

Beryllium was determined fluorometrically with morin on a Flaphokol III instrument equipped with a fluorometric adapter (Zeiss, Jena, GDR). The acidity of the solutions treated was measured on an OP-265/1 digital pH-meter (Radelkis, Hungary).

A reference stock solution of Be was prepared by dissolving 0.4506 g of Be in 50 mL of 1M–H_2SO_4 and diluting to 500 mL with water. A 0.064% solution of morin in ethanol was made up from the purified chemical (Koch–Light, U.K.). The other chemicals used of reagent grade purity were purchased from Lachema, Czechoslovakia.

Samples were collected in polyethylene bags, dried at 105 °C, and screened using 2.0 and 0.2 mm sieves to obtain a coarse fraction from the dump, a fine fraction (fly ashes) from the dump, and a fine fraction from an electrostatic precipitator in the power station.

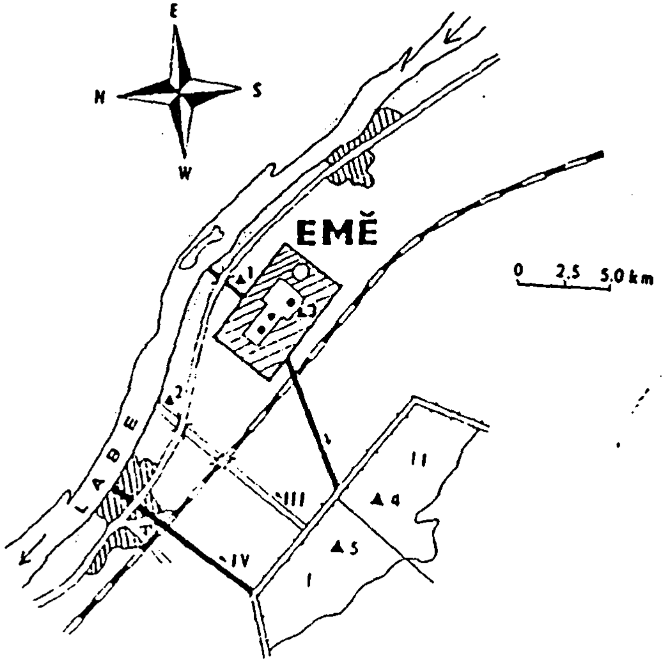

Fig. 1. Location of sampling sites in the surroundings of the Mělnik thermal power station.

For determining the total Be content, about 0.2 g samples were decomposed by pressure digestion with 8 mL of concentrated HCl and 2 mL of concentrated HNO_3 for 1 hr at 150 °C. The system was filtered through a Synpor filter, the filtrate was diluted and Be was determined (details concerning the optimized fluorometric determination of Be in environmental samples can be found in Kubizňáková, 1983).

Wastewater samples (1000 mL) were stored with 10 mL additions of concentrated HCl as a preservative. The polyethylene bottles were cleaned with 1M–HNO_3, and perfectly rinsed with redistilled water prior to use.

In order to see how easily Be can be released from actual samples by acidity in alkality, 50 mL volumes of 10^{-3}, 10^{-4}, and 10^{-5} M solutions of H_2SO_4 and sodium hydroxide were added to 5 g samples in polyethylene bottles, and the systems were allowed to stand for 40 days with occasional stirring. The suspensions then were filtered, pH of the filtrate was measured and the concentration of Be was determined.

3. Results and Discussion

The results are given in Table I. The long-term action of weakly acid or weakly basic solutions leads to a partial liberation of Be from the ashes. The total available Be concentrations in the coarse fraction from the ash dump (sample A), in the fly ash from the dump (sample B), and in the light ashes from the electrostatic precipitator (sample C) were 1.80, 1.87, and 1.58 μg g^{-1}, respectively. Acid medium releases Be best from the light ash from the precipitator (samples Nos. 16 to 18), whereas the coarse fraction from the dump is better attacked by alkaline solutions (samples Nos. 5 to 7). Virtually no Be was extracted from the ash on the dump (sample B), which is a fine fraction formed by abrasion. This fly ash contained Be in the highest amounts, and also has the highest pH (in the most basic medium).

During the hydraulic transport of the slag-ash slurry to the dump, the ash interacts with the water used, whereby the quality of the latter is markedly affected. Therefore, we also measured the average amounts of insoluble and soluble matter, pH, and Be concentrations in this water. The results are given in Table II. The pH was found to be higher by 0.3, and also the amount of insoluble and soluble matter was about 3 and 12%, respectively, higher in the wastewater than in the initial water source. (These values, naturally, refer to our specific case and cannot be generalized.)

Beryllium concentrations were determined both in the outflowing (recurrent) water from the dump and in the stagnant water directly on the dump. The values obtained were 3.15 and 3.4 μg L^{-1}, respectively. It should be noted that the dump comprises a variety of materials of different chemical composition, granularity, etc., and a number of local equilibria, influenced by diverse external factors, are involved.

The water draining from the dump affects the underground waters by increasing their level and gradients, and possibly also by contaminating them with a number of elements, including Be. It was, indeed, observed that if no wet feed is added, rapid draining and drying of the dump take place.

The concentrations of Be in the outflow waters were compared with the highest

TABLE I

Extraction of Be from ashes with acid and alkaline solutions

No.	Extractant	Be extracted		pH
		ng L^{-1}	%	
A. Coarse fraction from dump (sites 4, 5), grain size 2 mm, Be content 1.80 μg g^{-1}				
1	Water	67.5	3.8	6.79
2	$10^{-3}M$-H_2SO_4	45.0	2.5	6.33
3	$10^{-4}M$-H_2SO_4	45.0	2.5	6.33
4	$10^{-5}M$-H_2SO_4	78.8	4.3	6.75
5	$10^{-3}M$-NaOH	67.5	3.8	7.65
6	$10^{-4}M$-NaOH	146.3	8.1	6.55
7	$10^{-5}M$-NaOH	135.0	7.5	7.32
B. Fly ash from dump (sites 4, 5), grain size 2.0–0.2 mm, Be content 1.87 μg g^{-1}				
8	Water	22.5	1.2	7.49
9	$10^{-3}M$-H_2SO_4	45.0	2.4	8.11
10	$10^{-4}M$-H_2SO_4	< 0.5	-	7.08
11	$10^{-5}M$-H_2SO_4	< 0.5	-	7.11
12	$10^{-3}M$-NaOH	< 0.5	-	7.92
13	$10^{-4}M$-NaOH	< 0.5	-	7.35
14	$10^{-5}M$-NaOH	< 0.5	-	7.67
C. Light ash from electrostatic precipitator (site 3), grain size 0.2 mm, Be content 1.58 μg g^{-1}				
15	Water	22.5	1.5	7.39
16	$10^{-3}M$-H_2SO_4	22.5	1.4	7.39
17	$10^{-4}M$-H_2SO_4	270.0	17.1	7.38
18	$10^{-5}M$-H_2SO_4	135.0	8.5	7.38
19	$10^{-3}M$-NaOH	67.5	4.3	7.59
20	$10^{-4}M$-NaOH	67.5	4.3	7.48
21	$10^{-5}M$-NaOH	22.5	1.4	7.38

TABLE II

Characteristics of water of Mělnik power station

Parameter	Labe river (site 1)	Waste channel (site 2)	Difference (%)
Insoluble matter, mg L^{-1}	25.0	25.7	2.8
Soluble matter, mg L^{-1}	280.0	314.0	12.1
Total dry matter, mg L^{-1}	305.0	339.7	11.4
pH	7.1	7.4	-
Beryllium concentration, μg L^{-1}	0.5	3.15	530.0

admissible values as per EPA, which are 11 μg L^{-1} for surface waters and 1.1 μg L^{-1} for underground waters (EPA-Be 1978), and was found to be lower than the former. (No Czechoslovak standard giving the highest admissible concentrations of Be in waters exists. A USSR standard requires less than 0.2 μg Be L^{-1} in drinking water.)

Balance calculations showed that the power station contributes daily 100 g of Be to the wastewater pollution. Air pollution by volatile beryllium compounds (chloride, fluoride) also occurs. It is estimated that about 1% of the total Be contained in the coal is released to the air, the majority, however, remains in the slag. Liberation of Be from power station ashes was observed by Jiřele as early as 1967.

Our present knowledge of the environmental situation with respect to the pollution by this dangerous element is still incomplete, and additional data concerning the normal and elevated levels of Be both in the natural ecosystems and in ecosystems disturbed by the activity of man are necessary for a comprehensive and thorough evaluation.

4. Conclusions

Thermal power stations, which burn coal with high Be contents, are the most serious sources of environmental pollution by this element. In addition to the primary pollution by emissions, secondary pollution emerges from the slag and ash dumps. These dumps give rise to long-term pollution, from which both surface and underground waters become contaminated. The experiments presented in this paper give evidence that Be can be released from the solid matter rather readily. In view of the high toxicity of this metal, these observations should stimulate further interest in its behavior and transport in the environment.

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Depletion of soil aluminium by acid deposition and implications for acid neutralization

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In acid soils acid rain is often largely neutralized by dissolution of aluminium[1-3], which is potentially phyto-toxic[4]. Here we show that only a minor fraction of soil aluminium is readily dissolved. This most soluble fraction consists largely of non-silicate, organically bound aluminium, which has been formed in the course of soil development. The current rapid and irreversible depletion of this fraction constitutes a drastic change in soil genesis. Depletion may eventually result in reduced acid neutralization, as a consequence of decreased dissolution of aluminium, and should be accounted for in soil acidification models.

Dissolution of aluminium in acid soils is one of the most pronounced soil chemical effects of acidic deposition[1-3]. Aqueous aluminium is toxic to crop roots[4-6] and has also been associated with forest die-back[7]. Because of its toxicity the soil chemical behaviour of aluminium has been a major topic in agronomic[8,9] and ecological[10] studies. Most of these studies deal with short-term phenomena such as speciation, exchange characteristics and solubility control. Long-term effects on aqueous aluminium in soils, resulting, for example, from changes in the soil solid phase, are generally ignored. In many acid, sandy soils, however, an appreciable portion of the pools of various solid-phase aluminium fractions is currently leached from the soil. Table 1 indicates that leaching could lead to a significant depletion of certain soil aluminium fractions within several decades. The current depletion rates of extractable aluminium are significantly higher than the rates of aluminium transfer from silicate-bound to extractable soil aluminium. Maximum annual rates of formation of extractable aluminium amount to 0.030 mmol per kg of soil, as estimated from accumulation rates in the soil solid phase[11] (J.M. *et al.*, preprint) and from current rates of organic-aluminium precipitation[11]. Decreasing content of various fractions of solid-phase aluminium could affect the aqueous aluminium concentrations. Insight into these aspects is essential for evaluating long-term effects of acid deposition.

Data on the sources of dissolved aluminium were obtained from a laboratory leaching experiment. Air-dried, <2 mm fractions of soil samples from the Netherlands and New Hampshire, USA, were taken from the surface and sub-surface horizons of two podzols (Haplorthods) and of a recent driftsand (Udipsamment) (Table 1). Duplicate samples of each soil horizon (5.0 g) were leached 10, 25 and 50 times, respectively, with 100 ml aqueous hydrochloric acid at *p*H 3.0. After each acid addition the suspensions were kept in tightly capped centrifuge tubes at 20±2 °C for 24 hours. Suspensions were shaken manually three times in each 24 hours. The suspensions were centrifuged at 2,000 r.p.m. for 15 min, and 80 ml of the clear supernatants was decanted and replaced by 80 ml of fresh HCl solution. Sub-samples of each supernatant were pooled to give a single extract after 10, 25 and 50 HCl treatments. In each case, pooled leachates were analysed for all major solutes, dissolved aluminium concentrations were measured after 6, 24 and 72 hours in one additional leaching, and soil samples were freeze-dried and residual solid aluminium fractions were estimated by sequential selective dissolution (Table 1). Dissolved aluminium was assayed colorimetrically using pyrocatechol-violet.

We selected a leaching solution of *p*H 3.0, because this is close to the current *p*H of the water infiltrating many surface soils of forests and heathlands in north-western Europe[3] (J.M. *et al.*, submitted). We enhanced aluminium mobilization rates relative to those in the field by applying HCl at a rate of 20 mmol H^+ per kg of soil per 24 hours. This is considerably higher than the current acid load in the field (4 mmol H^+ kg^{-1} yr^{-1}).

Table 1 Pools of solid-phase aluminium in three acid, sandy soils from the Netherlands, and one from New Hampshire (USA), before laboratory leaching treatments, and annual aluminium mobilization rates from the respective soil layers in the field

Site	Soil	Depth horizon (cm)	Extractable aluminium* KCl	$Na_4P_2O_7$	$(NH_4)_2C_2O_4$ (mmol kg^{-1})	Total aluminium†	Annual removal of aluminium‡
Gerritsfles	driftsand	0-10 C	2.2	33.3	3.7	450	0.5
		10-40 C	0.7	35.7	6.3	427	0.3
Tongbersven	podzol	0-12 E	1.3	5.0	1.5	101	0.1
		12-35 B	13.7	196	3.3	446	0.4
Hasselsven§	podzol	0- 7 E	11.1	21.2	7.7	221	0.5
		7-22 B	16.3	55.8	13.5	273	0.1
Hubbard Brook	podzol	0- 5 E	1.2	7.8	3.0	1660	0.005
		15-30 B	5.8	322	51.1	2185	−0.004

* Solid-phase aluminium was extracted using selective dissolution. Soil samples (1 g) were sequentially extracted with 50 ml 1M KCl (0.5 hour), 50 ml 0.1M $Na_4P_2O_7$ (16 hours) and 50 ml 0.2M $(NH_4)_2C_2O_4$ adjusted to *p*H 3.0 (4 hours in the dark)[11]. Extracted amounts represent exchangeable aluminium (KCl), organic aluminium and minor amounts of non-crystalline hydrous oxides ($Na_4P_2O_7$) and most amorphous aluminium hydroxides ($(NH_4)_2C_2O_4$)[16,17]. Extracted aluminium was measured using colorimetry with pyrocatechol violet (KCl), inductive coupled plasma spectroscopy ($Na_4P_2O_7$), and atomic absorption spectroscopy with a nitrous oxide-acetylene flame ($(NH_4)_2C_2O_4$).

† Total aluminium, largely originating from aluminium silicates, was determined by X-ray fluorescence spectroscopy of a lithium tetraborate melt of the soil material.

‡ Calculated from bulk density (kg m^{-3}) (H. F. van Dobben and J. Mulder, manuscript in preparation), and estimated aluminium fluxes (kmol ha^{-1} yr^{-1}) (J.M. *et al.*, preprint). Monthly aluminium fluxes were estimated by multiplying the simulated soil water flux and the measured monthly dissolved-aluminium concentration in the soil solutions collected from suction plates in the field. Values for inorganic aluminium in the Hubbard Brook soils were taken from Driscoll *et al.*[11]. Negative numbers indicate immobilization.

§ Not included in the leaching study.

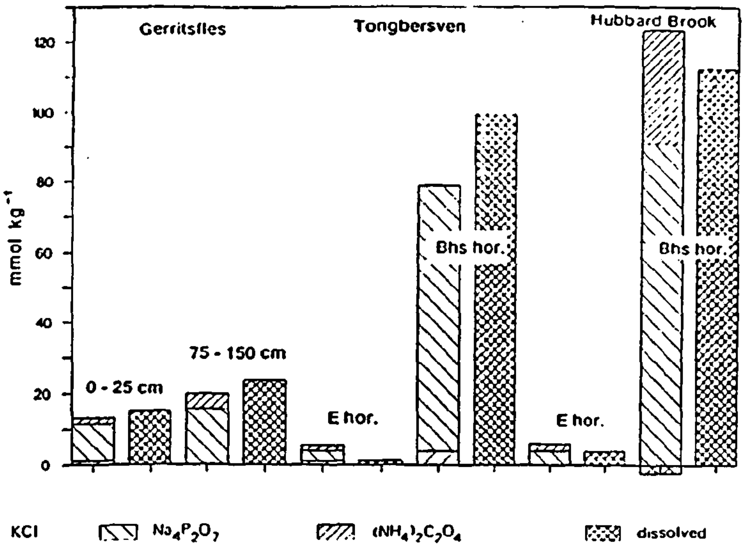

Fig. 1 The decrease in solid-phase aluminium, after 25 leachings with HCl (left bar, hatched) and the amount of aluminium removed in the leachates (right bar, cross-hatched) for six soil samples. Values are means of duplicates. Duplicates of dissolved aluminium were within 37% (E horizons) or 6% (all other horizons) of the mean; duplicates for the depletion of the $Na_4P_2O_7$-extractable fraction were within 38% (E horizons) or 22% (other horizons) of the mean. Note that in the Hubbard Brook Bhs horizon KCl-extractable aluminium increases slightly over the course of 25 leaching cycles. This increase is due to the strong increase in dissolved aluminium relative to that in field conditions[11].

The cumulative amount of aluminium dissolved by HCl is invariably close to the amount of extractable ('free') aluminium removed (Fig. 1). Our data indicate that the dissolution rate of 'free' aluminium is high relative to that of the more abundant aluminosilicates (Table 1). Organically complexed ($Na_4P_2O_4$-extractable) aluminium is the fraction that dissolves most, whereas the exchangeable fraction (KCl-extractable) contributes little to the total dissolved aluminium (Fig. 1). Thus, aluminium is transferred to solution mainly from the organically complexed solid phase, even when the pool of organic aluminium is small.

On addition of HCl, dissolved aluminium concentrations invariably rose to constant values within 24 hours, indicating attainment of chemical equilibrium. Charge balances of the leachates indicate that dissolved aluminium is present mainly as aquo-Al^{3+}. Only in the leachates of the podzol Bhs horizons is a significant fraction (20-30%) of dissolved aluminium organically complexed. (The podzol Bhs is a soil layer rich in organic-aluminium precipitates.) Dissolved aluminium concentrations are significantly correlated with the organic ($Na_4P_2O_7$-extractable) aluminium content of the soil sample (Fig. 2). This further indicates the importance of solid alumino-organics as a major source of dissolved aluminium. Because dissolved aluminium concentrations in our leachates increased rapidly to stable levels, but were highly undersaturated with respect to gibbsite ($p\mathrm{Al}-3p\mathrm{H}=-8.11$; ref. 13 and Fig. 3), exchange equilibrium between dissolved and adsorbed aluminium as described for forest-floor samples[12] may also hold for solid-phase alumino-organics in our mineral soils.

Following Cronan *et al.*[12], the exchange equilibrium $3H^+ + AlX = H_3X + Al^{3+}$ can be modelled as $[Al^{3+}]/[H^+]^3 = K_{ex}(AlX/H_3X)^n = K_{app}$, where n, K_{ex} (exchangeable) and K_{app} (apparent) are constants, square brackets denote activities of aqueous ions and AlX and H_3X are their mole fractions on the organic sorbent. Taking negative logarithms, this expression becomes

$$p\mathrm{Al}-3p\mathrm{H} = pK_{ex} - n\log(\mathrm{AlX}/\mathrm{H_3X}) = pK_{app}$$

The data in Fig. 3 indicate that pK_{app} increases with decreasing content of solid-phase alumino-organics. Only the first equilibrium extracts of the podzol Bhs horizons (represented by diamonds in Fig. 3) were close to equilibrium with gibbsite.

In general, the KCl-extractable aluminium fraction is assumed to represent readily mobilizable, exchangeable aluminium[14]. However, our data show that in a strongly acidic environment the $Na_4P_2O_7$-extractable aluminium fraction is a better estimate of readily mobilizable aluminium, exchanged against H^+.

In the field, 1-2% of organic aluminium is removed annually from the surface layers of the Dutch soils (Table 1). Note that the current rate of mobilization of aluminium from the uppermost soil layers is lowest where the content of soil organic aluminium is lowest. Based on the content of soil organic aluminium, the mobilization rates of aluminium are potentially high in the spodic B horizons. However, the availability of readily mobilizable aluminium is associated with a rapid acid consumption and consequently an increase in solution pH, which restricts further aluminium mobilization. Soil solutions in Bhs horizons are generally close to equilibrium with gibbsite. In the Dutch podzols the current depletion of alumino-organics is most pronounced in the upper few centimetres of the Bhs horizon, which was formed by precipitation of organic aluminium in the course of soil development. In such soils the

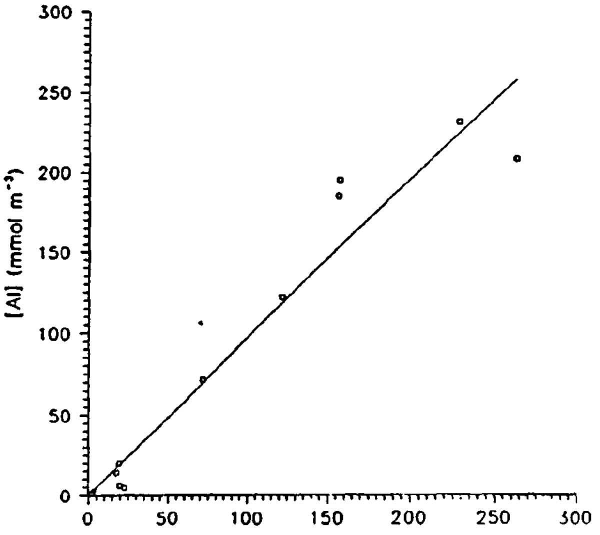

Fig. 2 Equilibrium aluminium concentrations in individual HCl leachates, after 10, 25 and 50 acid additions, as a function of $Na_4P_2O_7$-extractable aluminium. Data refer to all six soil horizons. Equilibrium concentrations of aluminium ([Al]) are significantly correlated ($R^2 = 0.9466$) with $Na_4P_2O_7$-extractable soil aluminium (Al_{pyro}): $[Al] = -0.60 + 0.98 \times Al_{pyro}$, where [Al] is in mmol m^{-3} and Al_{pyro} is in mmol kg^{-1}.

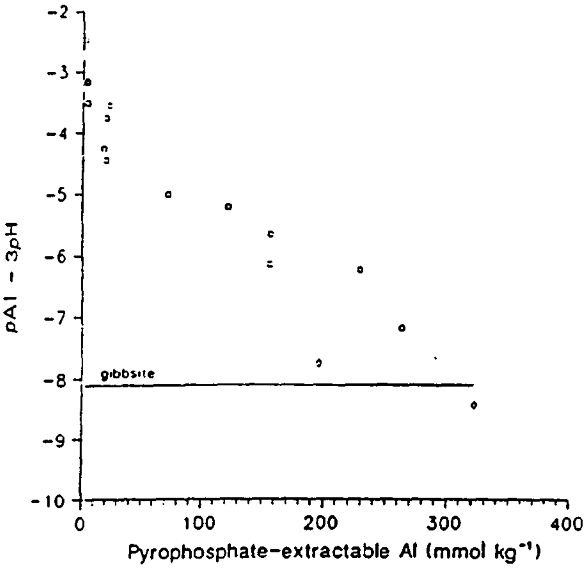

Fig. 3 Values for $pAl - 3pH$ in equilibrium leachates as a function of $Na_4P_2O_7$-extractable aluminium. Leachates are from all soil samples after 10, 25 and 50 HCl additions (squares). For the samples of the two podzol Bhs horizons values of the first leachate are also given (diamonds). Aluminium activities were calculated using the chemical equilibrium program ALCHEMI (ref. 18). For gibbsite we used $pK = -8.11$ (ref. 13).

introduction of acid rain produces a drastic change in the naturally occurring podzolization process.

The mobility of aluminium in the Hubbard Brook soils is significantly lower than in the Dutch soils (Table 1), because of higher soil-solution pH values, which is due, in turn, to a lower acid load and higher mobilization rates of base cations[15].

The current rapid depletion of organic aluminium in the rooting zone of many acid, sandy soils is irreversible on a timescale of decades or centuries. Because aqueous aluminium concentrations are in equilibrium with solid-phase alumino-organics, depletion upon continued acid deposition will inevitably lead to a reduction in dissolved aluminium concentrations. At the same time, soil-solution pH values, which are currently buffered in the pH range 3.5–4.2 by dissolution of aluminium[3] (J.M. *et al.*, preprint), may drop to values just below 3. Such dramatic changes in the soil solution chemistry of the rooting zone may have significant ecological consequences. Therefore, depletion of solid-phase organic aluminium and the associated changes in the chemical composition of soil solutions should be incorporated in current soil-acidification models.

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A new picture of the Moho under the western Alps

ECORS-CROP Deep Seismic Sounding Group*

The Moho—the boundary between crust and mantle first discovered by A. Mohorovicic[1]—is the main seismic marker in the continental lithosphere. The seismic nature of this interface, in terms of its position, topography, smoothness and continuity, may preserve imprints of the regional geodynamic evolution of the lithosphere. Here we report the results of a wide-angle seismic profiling experiment across the western Alps, which allows us to draw a cross-section of the Moho across this mountain belt. A tight sampling of this deep reflector shows abrupt changes in its depth and dip. The root zone of the chain (the zone of maximum crustal thickness) is well defined, with a 55-km-deep crust–mantle boundary. The Moho under the western Po plain is also clearly seen, and a shallow reflective structure is mapped under the Briançonnais zone in the 25–30 km depth range. This structure, if interpreted as lower-crustal or upper-mantle material, would support the hypothesis of a flaking of the lithosphere under the western Alps[2,3].

To prepare the layout of the vertical reflection line through the western Alps that formed the basis of the ECORS-CROP project[4,5] in 1986, a preliminary series of experiments[6] was conducted which aimed at mapping very deep interfaces along a cross-section extending from Grenoble (France) to the Po Plain (Italy). One-ton charges were detonated at five places (Fig. 1) and part of the recording array—low-frequency geophones and autonomous recorders—was deployed along fan profiles, a method which had already proved successful in other orogenic belts[7-9]. The fan radii were chosen so as to coincide with the theoretical maximum amplitude of reflections, corresponding to total reflection, at and beyond a critical distance. The Moho depth was assumed to be ~40 km, with an increase from west to east; the fan radii therefore ranged from 90 to 130 km. Because the velocity is assumed to be constant within the crust, and because each shot-station line is along the local strike of the Alps, no apparent dip of the reflector is expected. Each mirror point (triangles in Fig. 1) can therefore be plotted half-way between the shot-point and the station. With an average station spacing of 4 km along the fans, the reflectors are thus sampled every 2 km.

The fan data were processed to construct two composite cross-sections of the Alpine chain, showing the topography of deep reflectors (Figs 2 and 3). Figure 2*a*, corresponding to shots A, B and C, begins 30 km west of the Belledonne External Crystalline Massif (ECM) and extends through the Briançonnais and Piedmontese zones to the east of the Dora Maira Internal Crystalline Massif (ICM); Fig. 2*b* (shots D and LW) extends from the Gran Paradiso ICM to the Po Plain, intersecting the Sesia-Lanzo zone and the Canavese line, which marks the western limit of the chain. It should be understood that these

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HISTORICAL CHANGES IN ACID PRECIPITATION AND HEAVY METALS DEPOSITION ORIGINATING FROM FOSSIL FUEL COMBUSTION IN EASTERN NORTH AMERICA AS REVEALED BY LAKE SEDIMENT GEOCHEMISTRY

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ABSTRACT

The present study deals with the geochemical stratigraphic evolution of the most recent sediments in lakes of Eastern Canada (Quebec). In particular, the sediments from two representative soft water lakes (Tantare and Laflamme) in "undisturbed" watersheds on the southern edge of the Precambrian Shield were studied.

The increase in Al in the sediments of Lake Tantare since about 1950 is attributed to the processes of surface water acidification of this watershed induced by acid precipitation. The analogous upper strata of the sediments from Lake Laflamme, a non-acidified lake, show no such increase in Al content.

Pb, Zn and Hg levels in the sediments increased significantly from 1940 onwards. However, the subsequent reduction in the stratigraphic concentration of Zn since 1960 in both Lake Tantare and Lake Laflamme is, in all probability, the result of the important decrease of the total particulate emissions to the atmosphere from coal-fired plants. The same phenomenon may also explain Hg decrease during the same period. In contrast, Pb shows no such reduction in the more recent strata and the sustained increase of this element in the sediments is attributed to the progression in motor vehicle activity during the past twenty years.

Further data from other isolated lakes suggest that the major sources of heavy metal deposition and acid precipitation in the Province of Quebec are the emissions from fossil fuel combustion (coal and/or motor fuel) originating in the heavily industrialized American Midwest and Great-Lakes Regions.

INTRODUCTION

Paleolimnology is an integrative science which not only allows us to study several ecological variables as a function of spatial interrelations, but also as a function of changes in time. Lacustrine sediments may be regarded as integrators of allochthonous and autochthonous inputs and transformations resulting from the global metabolic activities of the lake-watershed system (Hutchinson et al., 1943; Zülling, 1956; Frey, 1969). It can be very difficult to differentiate concomitant changes in both autochthonous and allochthonous inputs (Hutchinson, 1970; Likens et al., 1970; Shapiro et al., 1971; Ouellet, 1974; Kemp and Thomas, 1976) from the evolution of sediments subjected to anthropogenic inputs from the lake catchment area. However, for lakes in remote or "undisturbed" watersheds allochthonous inputs will dominate any changes in total inputs and the sediments of these lakes will more accurately reflect any changes in atmospheric fallout from air masses originating from outside the watershed. As long-range atmospheric transport of pollutants derived from anthropogenic activities is now a well established fact (Husain and Samson, 1979; Canadian LRTAP Program, 1980), the fallout from air masses subject to such transport phenomena may indeed perturb otherwise "undisturbed" watersheds.

The present paper describes a study of Pb, Zn and Hg contents of sediments cores from two soft-water pristine lakes, Tantare and Laflamme, in the Laurentian Park region north of Quebec City. A brief discussion of the results for these metals in the most recent sediments from other isolated lakes in the province is also presented.

Lakes Tantare and Laflamme are exposed to similar meteorological conditions which suggest that the sediments of both lakes should show the same stratigraphic characteristics for atmospheric inputs. However, due to local geological conditions, Lake Tantare is only slightly buffered against the incoming acidic precipitation while Lake Laflamme is well buffered and suffers only short isolated periods of acid stress during spring melt (Jones and Bisson, 1980). The data of the sediment cores from these two lakes were thus analysed in a comparative fashion in order to see if any significant effects due to acidification (Al) and/or long-range transport of heavy metals (Pb, Zn and Hg) could be determined. The study on the other lakes was orientated primarily to the determination of the distribution of Pb in remote areas although the distribution of Zn and Hg was also investigated. A more complete description of the heavy metal contents (^{137}Cs, Co, Cu, Hg, Mn, Ni, Pb and Zn) of the above cores is the subject of a recent publication by Ouellet and Jones, (1982).

SITES DESCRIPTION

Some geographical and physical characteristics of 26 lakes studied (including Tantare and Laflamme) are shown in Table 1, while their geographic distribution is illustrated in Fig. 1. The distribution of the lakes may be further subdivided into three groups, lakes 10, 11 and 16-25 lying along the St. Lawrence River valley where the dominant winds are from the southwest, lakes 3-9, 12-14 and 26 in the interior plateau of Quebec between 50°N and 52°N where the dominant winds are more from the west and lakes 1 and 2 in the more northerly regions where dominant winds are west-south-west. The lakes vary in depth from 3 to 270m and in surface area from 0.1 to 2500 km^2. Lakes 1 to 11 are isolated and in contrast to lakes 12-26 do not have any human activities within their watershed; the data from lakes 1-11 are those particularly treated in the discussion below. The majority of the lakes are on the crystalline rocks of the Precambrian Shield, only lakes 18, 20, 23 and 24 being found on the paleozoic sedimentary rocks of the Saint-Lawrence Lowlands.

TABLE 1. General Description of Sites Studied

No.	Lake Name	Latitude ° '	Longitude ° '	Altitude m	Depth m	Area Watershed km²	Area Lake km²
1	Nedlouc	57 40	71 37	235	4	15	0.8
2	Desaulniers	53 33	77 36	145	10	62	11.4
3	Matamek (1)	50 21	65 56	120	65	460	12
4	Matamek (2)	50 21	65 54	120	100	460	12
5	MO-74-7	50 37	65 50	500	3	0.17	0.04
6	MO-74-8	50 27	65 49	364	5	0.21	0.04
7	Mistassini (1)	50 17	73 42	371	5	18130	2040
8	Waconichi	50 08	74 00	380	4	440	81.8
9	Clairy	51 18	72 42	385	6	28.7	5.7
10	Tantare	47 04	71 33	500	5.5	12.1	1.33
11	Laflamme	47 33	70 01	766	4.5	0.69	0.06
12	Manicouagan -4	51 48	69 08	366	155	23160	1960
13	Manicouagan -6	51 32	69 09	366	250	23160	1960
14	Manicouagan -13	51 20	69 08	366	270	23160	1960
15	Desroches	47 21	71 10	813	5.4	1.8	0.11
16	Saint-Jean (1)	48 31	71 56	99	23.0	73010	1000
17	Saint-Jean (2)	48 30	71 59	99	66.6	73010	1000
18	Atkins	44 45	75 51	116	3.3	9.1	0.92
19	Pink	45 28	75 48	157	21	21.3	0.93
20	Lemay	45 27	75 43	44	9	5.6	0.07
21	Beauport	46 57	71 17	262	12	6.7	0.77
22	Saint-Charles	46 56	71 23	149	7	160	3.2
23	Saint-Augustin	46 45	71 23	42	6	8.8	0.6
24	McKay	45 27	75 40	44	9	0.76	0.14
25	Waterloo	45 20	72 31	206	4.5	37.71	1.5
26	Mistassini (2)	50 14	73 49	371	3	18130	2340

The Tantare watershed (47°04' N, 71°31'W) lies 42 km north of Quebec City (Fig. 1, lake 10). The region is a part of the Laurentide highlands of the Precambrian Shield. The vegetation consists of a mixed forest cover of St. Lawrence lowlands type vegetation (maple, yellow birch) associated with boreal stands (fir, spruces, white birch), (Desloges and Lachance, 1977).

The total annual precipitation which averages 145 cm (30% snow) is among the highest for Eastern Canada. The watershed does not support any permanent human activity and is one of the rare lakes in Quebec known to have recently shown a decline in pH (Dickman et al., 1981). The present pH of this main water body varies from 4.9 to 5.2.

Lake Laflamme (Fig.1, lake 11), the watershed of which is also devoid of any permanent human activity, is located at a higher altitude (766 m) than Lake Tantare (500 m) and 50 km further to the northeast. The forest cover is dominated by balsam fir while white birch is a minor constituent. The total annual precipitation averages 155 cm (35% snow). It is a typical soft water humic lake of the Precambrian Shield with an average pH of 6.1.

The sampling of lacustrine deposits was carried out at, or near, the deepest point in the lake by means of piston and box core samplers.

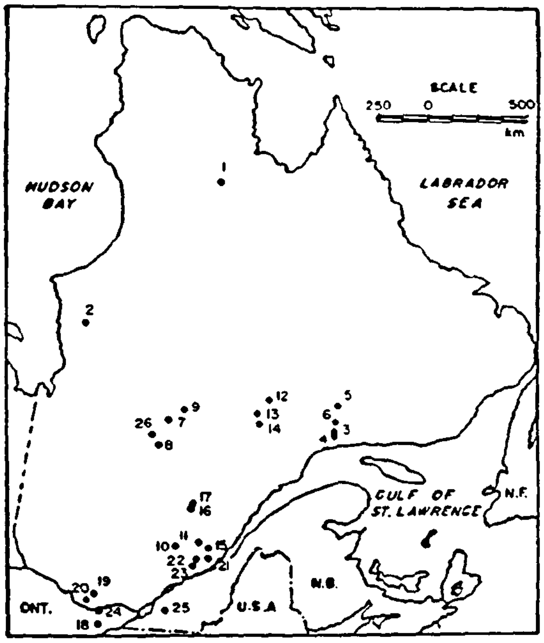

Fig. 1. Geographical localization of the lacustrine sediment deposits studied for their geochemical content in heavy metals

In the field, the cores were cut into 0.5 cm intervals. In the laboratory the samples were dried at 60°C for 48 hrs. All metals were determined by atomic absorption spectrophotometry as described by Guimont and Pichette (1979). The detection limits for each metal and for ^{137}Cs are: Al - 100 ppm; Hg - 0.005 ppm; Pb - 2 ppm; Zn - 2 ppm; and ^{137}Cs - 0.18 pCi/g. The standard deviations on 10 replicates for each metal at similar concentrations to those in the sediments were Al ± 2.0 ppm; Hg ± 0.005 ppm; Pb ± 0.2 ppm; Zn ± 0.08 ppm and ^{137}Cs ± 0.004 pCi/g.

To evaluate the rate of sedimentation, the two cores from Lakes Tantare and Laflamme were dated by quantifying the stratigraphic distribution of ^{137}Cs in the most recent sediments. ^{137}Cs content was estimated by using a Packard gamma counter, model Tri-Carb 3280, on 2 g of dry sediment. The photonic detection of the emissions was quantified at 662 kev, with a half-band width of 50 kev. Based on standard samples the efficiency of the counter was estimated at 9.85 percent. The number of disintegrations was counted for a period of 500 min.

The Sedimentary Anthropogenic Enrichment Factor (SAEF) for each element in the recent sediments is mathematically expressed by computing a ratio between the concentrations of the top stratigraphic levels and those of the natural backgrounds which are found deeper in the cores and correspond to the period around the turn of the century. Unlike the calculation of the Sedimentary Enrichment Factor (SEF) of Kemp et al., (1976), the paleolimnological data were not normalized as a function of the role associated with clay minerals in controlling the abundance of several elements. This is due to the fact that the lacustrine sediments of the present study are much more organic than those studied by Kemp.

As no historical data on the pH of precipitation in the Quebec City area from 1940-1979 are available, trends for the pH of precipitation for this period were estimated from the available historical data in the USA (Cogbill and Likens, 1974; Cogbill, 1976; Likens and Butler, 1981) and the current CANSAP data (1979). The present mean value for the pH of acidic precipitation in this area is 4.2.

RESULTS AND DISCUSSION

SAEF for Lakes Tantare and Laflamme

Figures 2 and 3 represent the stratigraphic distribution of ^{137}Cs, Hg, Pb, Zn and Al for the most recent sediments of Lakes Tantare and Laflamme respectively. The SAEF of each element appears at the base of each stratigraphic curve.

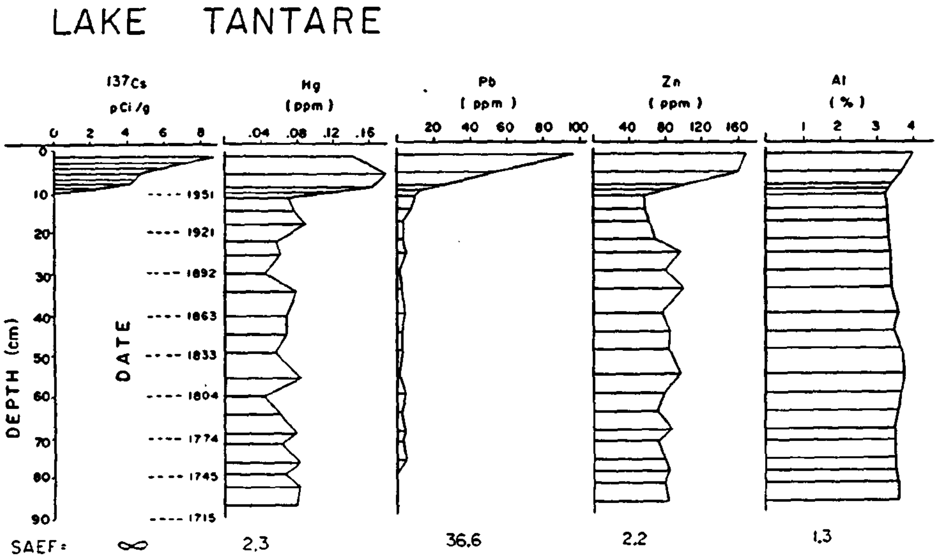

Fig. 2. Dated stratigraphical distribution of ^{137}Cs, Hg, Pb, Zn and Al for the most recent sediments of Lake Tantare.
SAEF: Sedimentation Anthropogenic Enrichment Factor

SAEF values range from 2.2 (Zn) to 36.6 (Pb) in the Lake Tantare core and from 1.5 (Hg) to 31 (Pb) in the core for Lake Laflamme. SAEF increases are not due to any change in organic carbon content in these sediments as the stratigraphic carbon curves do not reflect any major fluctuations in either lake (Ouellet and Jones, 1982). The geochemical evolution for the metals (^{137}Cs, Pb, Hg, Zn) may be divided into two groups. The first group, which consists of ^{137}Cs and

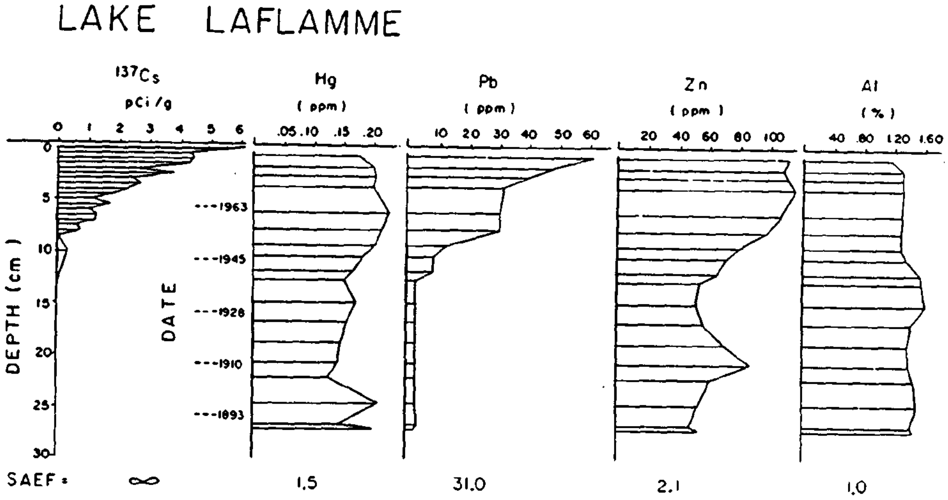

Fig. 3. Dated stratigraphical distribution of ^{137}Cs, Hg, Pb, Zn and Al for the most recent sediments of Lake Laflamme.
SAEF: Sedimentation Anthropogenic Enrichment Factor

Pb, reflects a rapid and sustained increase of the content of the elements in the recent sediments over the natural background level as shown by older sediments. The second group (Hg and Zn) shows an initial rise in the sediment concentration similar to the first group. This increase is followed, however, in the most recent strata, by a decrease or stabilisation of the heavy metal content.

In contrast, Al shows different behavior in the two lakes; the element tends to increase in the upper levels of the Tantare core and decrease in those of Lake Laflamme.

The two ^{137}Cs profiles for the sediment cores from Lakes Tantare and Laflamme are similar. The depths of 9.5 and 8.0 cm are approximately contemporary with the year 1952 corresponding to the first test of thermonuclear bombs. Unfortunately, the amount of ^{137}Cs found in the cores does not correlate well with the atmospheric production of this artificial element; Norton and Hess (1980) for Norwegian lakes, and Galloway and Likens (1977) for New England lakes, were also unable to establish a similarity between the known atmospheric production curve and the stratigraphic evolution of ^{137}Cs in the sediment cores. In spite of the poor correlation between the known atmospheric production of ^{137}Cs and the stratigraphic content of the cores, the annual sedimentation rate was estimated by this method to be of the order of 3.3 mm/year for Lake Tantare and of 2.8 mm/year for Lake Laflamme.

From the rate of sedimentation for Lake Tantare we can estimate the start of the increase in the Al content of the sediments at about 1950. As this element is not subject to long range atmospheric transport we believe that the Al increase in the recent sediments is the consequence of the mobilization of this metal within the watershed by acid rain which, by 1950, would have shown a mean pH value of 5.0 to

5.1 approximately in this particular area (Cronan and Schofield, 1979; Johnson, 1979; Driscoll et al., 1980). Jones et al., (1980a) have demonstrated that, at present, there is a significant loss of Al to the sediments of Lake Tantare as the waters from the catchment area pass through the lake basin. Average concentrations of Al in the incoming streams (pH 4.4) is 0.47 mg.l^{-1} while that of the lake epilimnetic waters (pH 5.1) is 0.20 mg.l^{-1}. For the non-acidified Lake Laflamme, the Al curve does not increase in the upper sediments for the same period. Total concentrations of Al in Lake Laflamme water (pH 6.1) have not been found to rise above 0.07 mg.l^{-1} and, under the mean flow conditions of the Lake Laflamme tributaries (pH 6.0), the average value for the total Al concentration in the incoming water is 0.05 mg.l^{-1} (Jones and Bisson, 1980). It would thus seem that the acidity of Lake Laflamme surface waters never reaches the level at which a sustained wash-in of Al from the catchment area, comparable to that observed at Lake Tantare, occurs.

Pb, Hg and Zn start to increase in concentration in the sediments about 1940. In contrast to the Pb trends in the upper strata, Hg and Zn concentrations decrease or stabilize simultaneously in both lakes in the early sixties. The greater mobility of these two elements in an acidified aquatic environment, which could have resulted in an increased concentration in the water and a decreased content in the sediment (Dickson, 1980; Norton and Hess, 1980), might be an acceptable hypothesis for Lake Tantare; as discussed above, this lake is well on its way to becoming strongly acidified. However, since Lake Laflamme does not yet show any apparent sign of acidifiation, another explanation for the stratigraphic behavior of Hg and Zn in these lacustrine sediments must be considered. Large scale inter-annual mixing of the sediment (physical or biological) can be ruled out, as indicated by the steep gradients observed for other sediment constituents (i.e. the group of ^{137}Cs and Pb) towards the top of the cores. One hypothesis for the simultaneous decreases of Hg and Zn during the last 20 years is a diminution in the emission loads of these pollutants into the atmosphere and consequently a decrease in the transport of the metals into the region of Lakes Tantare and Laflamme.

As historical data on the real emissions and transport of heavy metals into this region are not available, we have attempted to determine past trends in the emissions of Hg and Zn into the atmosphere by a study of the emission loadings of associated particulate materials. It is now well known that volatile elements (Se, As, Zn, Pb and Hg) are preferentially concentrated on fine particulate matter (fly ash $\leqslant$ 3 μm) from coal-fired power plants (Coles et al., 1979; Smith et al., 1979; Wangen, 1981). These particles are more susceptible to long-distance atmospheric transport than larger fly-ash particles.

Flagan and Friedlander (1978) who studied the mechanisms for sub-micrometer fly-ash particle formation in pulverized-coal combustion showed that Pb and Zn enrichment factors were high for these elements; Hg was not discussed. Natusch et al., (1974) showed that Pb and Zn concentrations are high on submicron particulates from coal-fired power plants. McElroy et al., (1982) have also pointed out the selective enrichment factors of several trace elements (As, Ba, Cd, Cr, Cu, Hg, Mn, Ni, Pb, V, Zn) and, in particular those for As, Zn and Hg, as a function of submicrometer size particles (1 → 0.1 μm); similarly Ondov et al., (1981) have reported high concentrations of Zn and other elements in submicron (0.1 µm) particles from a 430 MW pulverized-coal-utility boiler with electrostatic precipitators and flue-gas desulfurization system. Sievering et al., (1980) have associated Pb and Zn enriched submicron particulates over Lake Michigan with anthropogenic sources and have suggeted that these particulates are more prone to long range transport than other associated particulates.

The increase in the quantity and concentration of trace metals in atmospheric particulates due to anthropogenic activities is thus a well established fact. Galloway et al., (1980) have estimated from various data that in the U.S.A. the ratio of the mean concentration of certain trace metals in the atmosphere of the urban areas relative to the mean concentration of more remote regions is as follows: Zn (7000) = Pb (7000) ⩾ Cu (500) ⩾ Mn (375) ⩾ Co (200) ⩾ As (125) ⩾ Ag (100) ⩾ Ni (83) ⩾ Hg (40). Apart from wind-blown soil particles which have only a very limited geographical range, over 75% of the total TSP in the atmosphere of both urban (Washington DC) and rural areas originates from coal-fired furnaces and motor vehicle transport (Kowalczyk et al., 1982). These facts would indicate that the particulates generated by industrial processes in urban areas gradually fall out from the atmosphere as they are transported into the more remote non-populated regions. The association between the more volatile metals and the submicron particulates would favour the long range transport of these elements (Rahn, 1981; Davidson et al. 1981).

The important two fold reduction since 1960 in the TSP emissions (Fig.4a), with which several trace metals are associated, could thus be the major reason for the tendency of Hg and Zn concentrations to simultaneously decrease or level out in the recent sedimentary strata of Lakes Tantare and Laflamme. The evolution of Zn and Hg in the sediment of these lakes is thus composed of two distinct phases; the first reflects the increase in atmospheric inputs from 1940 to 1960 followed by a regression or stabilisation phase from 1960 to the present due to decreased atmospheric input into lake catchment areas. This phenomenon would then be independant of the acidification of the lake waters. Recently Goldberg et al., (1981) have discussed the same hypothesis in a study of the sediments of Lake Michigan. Heavy metal concentrations (Pb, Zn, Cu, Cd, Ni) in these sediments showed increasing concentrations in the strata representing the period 1930 to about 1968. After the latter date these elements showed slight decreases in concentration. By analysis of charcoal and fly-ash contents they concluded that the decrease was related to the installation of improved control devices to remove fly-ash from the stack gases.

It should be pointed out that, in the development of the technology that led to the reduction in total TSP emissions, collection efficiencies for large fly-ash particles (99.7%) are higher that those for submicron particles (McElroy et al., 1982). As submicron particles with their concentrated heavy-metal loadings contribute the most to the long range transport of these elements, decreases in atmospheric input to lake catchment areas are not expected to be as dramatic as those in the reduction of TSP.

In contrast to the regression of Zn and Hg, Pb profiles in both Lake Tantare and Lake Laflamme show a sustained increase in the SAEF. We believe that this phenomenon reflects mainly the continued increase in Pb submicron-particulate inputs into the atmosphere as a result of increased motor vehicle travel. Fig. 4a shows that even though TSP declined significantly from 1960 on, both SO_x and NO_x emission continued to increase. Approximately 50-60% of NO_x emissions and the majority of Pb emissions originate from motor vehicle travel (Gordon, 1980) and one would expect combined Pb emissions from both coal combustion and dispersed motor vehicle sources to continuously increase up to the present time, in contrast to the recent decline of Hg and Zn from the point source emissions of coal-fired power plants. The Pb SAEF curves for lakes Tantare and Laflamme seem to support this hypothesis; we should, however, point out that other workers have observed decreases in Pb in very recent sediments (Goldberg _et al_., 1981).

As both SO_x and NO_x contribute to the hydrogen ion concentration of the precipitation, we would also expect a continuous increase in the acidity of precipitation during this period. One should note the similarity between the estimated acidity curve for the Quebec City area with the evolution in the stratigraphic concentrations of Pb in the sediments of Lake Laflamme for the years 1940 to 1980 (Fig. 4b).

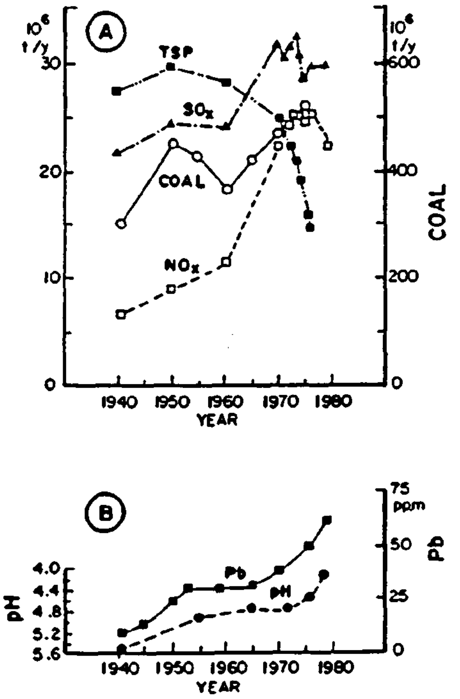

Fig. 4(a) Annual coal consumption and trends for atmospheric emissions of sulfur oxides (SO_x), nitrogen oxides (NO_x) and particulates (TSP) from EPA 1978.

4(b) Pb distribution in the dated strata of the sediment core of Lake Laflamme and the acidity trend of precipitation in the Quebec City area (1940-1980). The latter was estimated from Cogbill and Likens (1974), Cogbill (1976), Likens and Butler (1981) and CANSAP data.

Geographical Distribution of SAEF Values for "Undisturbed" Lakes

The isopleths of the Pb SAEF values for the most recent sediments of the remote "undisturbed" lakes (Fig. 5) have roughly a similar pattern to the pH isopleths of precipitation in the Province (Fig. 6). The figures show mainly an area of Pb SAEF values of 30-50 and pH values of 4.3-4.4 along the Saint-Lawrence River Valley to the north of which a gradual decrease in Pb SAEF values (3-20) and increase in pH (5-6) occurs. SAEF values for Zn and Hg in the most recent sediments of the remote lakes are lower than those of Pb, but do show definite enrichment for these metals (Table 2). The data would support the hypothesis of concomitant deposition of acidic pollutants and heavy-metal submicron particulates from air masses coming into the Saint-Lawrence River Valley from the Great Lakes region.

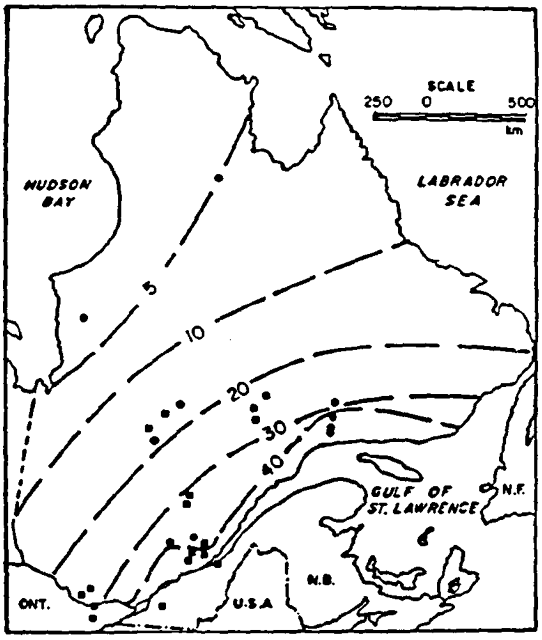

Fig. 5. Isopleths for Pb Sedimentary Anthropogenic Enrichment Factor interpolated from lake sediments having no anthropogenic activity within their watershed (•); (■ perturbated watersheds).

However, an alternate hypothesis to the transport of heavy metals into the remoter regions of Quebec by submicron particulates from fossil fuel combustion is the emission of particulates from smelting operations situated north of the Saint-Lawrence River Valley. In this study we can find no evidence to associate the origin of Pb and Zn in these remote lake sediments to the large smelting complexes located at Sudbury (Ontario) and Rouyn-Noranda (Quebec). Data in the literature suggest that metal pollutants emitted from Sudbury (Hutchinson and Whitby, 1974; Conroy et al., 1975; Scheider et al., 1981) and Rouyn-Noranda (Journault-Dupont 1979) smelters have from little to no influence over distances exceeding 100 km from the stacks.

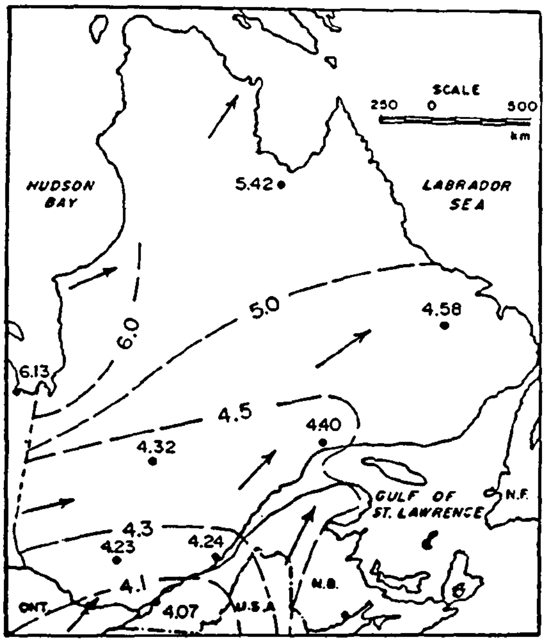

Fig. 6. Quebec Province, Canada: Precipitation pH (April-September 1977-79) and the annual mean wind direction (adapted from CANSAP 1979 and modified by Jones et al., 1980).

Crocket and Kabir (1981) found that even for volatile metals (As, Se, Pb), presumably associated with the smallest particulates emitted from the Sudbury smelter, that natural background levels were dominant 100 km from the stack. In similar research dealing with the atmospheric fallout in the vicinity of the base metal smelter located at Flin Flon, Manitoba, Franzin et al., (1979) give the following radii for zones affected by various metals: 264 km, Zn; 284 km, Cd; 87 km, Pb; 68 km, As and 60 km, Cu. As all these distances are much smaller than the distances between the two above complexes and any sampled sites of the present study, we conclude that the smelters contribute very little to atmospheric particulates containing Pb and Zn at a distance greater than 300 km from the stacks. Insufficient data on Hg emissions from smelters do not allow us to come to the same conclusion for this element as the one arrived at for Pb and Zn. As in the case of coal-fired power plants (Klein and Russel, 1973) the form in which mercury is emitted and its subsequent interaction with particulates and other aerosols in the atmosphere is largely unknown.

The high SAEF values for Pb, Zn and possibly Hg for remote sites on the Precambrian Shield are thus likely to originate from pollutants emitted by the combustion of fossil fuels in heavily industrialized regions to the south-west of the Saint-Lawrence River Valley. Acid precipitation originating from these areas would be expected to also contain heavy-metal particulates. Studies have recently demonstrated the association of acid rain with other atmospheric pollutants such

TABLE 2 Percentage Carbon (C%) and Sedimentary Anthropogenic Enrichment Factors (SAEF) for Sediments Cores from Several Lakes in Quebec and Ontario. The lakes are listed in increasing order (A) estimate of anthropogenic activities within the watershed.

			SEDIMENTARY ANTHROPOGENIC ENRICHMENT FACTOR		
A	No.	LAKE NAME	Hg	Pb	Zn
- - -	1	Nedlouc	1.2	5.0	1.4
- - -	2	Desaulniers	---	3.2	1.2
- - -	3	Matamek (1)	---	32.0	1.6
- - -	4	Matamek (2)	---	56.0	1.3
- - -	5	MO-74-7	---	28.0	0.9
- - -	6	MO-74-8	---	46.0	2.3
- - -	7	Mistassini (1)	4.3	46.0	2.1
- - -	8	Waconichi	2.3	5.2	1.1
- - -	9	Clairy	3.4	15.7	1.4
- - -	10	Tantare	2.3	36.6	2.2
- - -	11	Laflamme	1.5	31.0	2.1
—	12	Manicouagan-4	1.2	1.5	1.0
—	13	Manicouagan-6	2.1	2.8	1.4
—	14	Manicouagan-13	---	2.4	1.3
—	15	Desroches	1.6	3.2	1.6
▬	16	Saint-Jean (1)	8.6	10.0	1.7
▬	17	Saint-Jean (2)	---	28.0	1.7
▬	18	Atkins	---	10.0	---
▬	19	Pink	---	41.2	3.3
▬	20	Lemay	---	50.0	3.3
▬	21	Beauport	---	220.0	3.5
▬	22	Saint-Charles	---	29.0	2.0
▬	23	Saint-Augustin	2.5	16.8	2.1
▬	24	McKay	---	271.0	8.6
▬	25	Waterloo	3.0	23.8	2.3
▬	26	Mistassini (2)	10.0	5.0	1.2

- - -	No anthropogenic activity within the watershed
—	Few anthropogenic activities within the watershed
▬	Heavy anthropogenic activities within the watershed

as suspended particulates and heavy metals (Granat, 1972; Brezonik et al., 1980; Wangen, 1981). Husain and Samson (1979) have also shown that high episodic concentrations of sulfate, suspended particulates and their associated trace metals, appearing simultaneously over a broad geographical area encompassing the states of New York and New Jersey immediately to the south of Quebec originate in air masses coming out of the industrial Midwest. Although no similar data are available for the Province of Quebec, it appears reasonable to assume that the atmospheric pollutants originating from the American Midwest and Great-Lakes States are transported by the prevailing cyclonic disturbances along the Saint-Lawrence River Valley. Orographic lifting of the air masses leads to high precipitation on the southern slopes of the shield while drier conditions will prevail to the northern regions of the interior peneplain. Deposition results in increased heavy metal content in lakes and their catchment areas. The amount of metals deposited would decrease in lakes further to the north of the foothills area. In a similar manner, acid rain acidifies running waters, mobilizes aluminium from the catchment areas to the lake sediments and, over a period of time, further acidifies the lakes. This interpretation agrees, in part, with the works of Jones et al., (1980b), Grimard (1981) and Bobee et al., (1982) which all tend to demonstrate the stronger acidification of surface waters immediately to the north of the Saint-Lawrence River on the southern foothills of the shield compared to those areas further to the north of the province. The paleolimnological evidence also supports this hypothesis by demonstrating that the regression of Zn and possibly Hg in the sediments of the past two decades may be related to the reduction in the total TSP loadings for coal combustion during this period.

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ACID PRECIPITATION — AN INTERNATIONAL ENVIRONMENTAL PROBLEM

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ABSTRACT

The acidification is no longer confined to Scandinavia, it is a trans-World problem. The concept of acidification is bound up with the discharge into the atmosphere of sulphur dioxide, nitrogen oxides, and metals and other micropollutants - and the subsequent effects of these substances on the environment. The bulk of man-made emissions occurs over industrialized regions covering less than 5% of the earth's surface. In these regions, man-made emissions exceed the natural emissions by a factor of five to twenty. In the 1950's a sharp rise in oil combustion increased the SO_2 emissions in Europe to about 25 million tonnes of sulphur per year by 1970. European emissions of NO_x have increased from low values 100 years ago to the present value of about 6 million tonnes of nitrogen per year. Similar emission trends of SO_2 and NO_x have taken place in North America. Sulphur dioxide emissions in Europe are predicted to remain about the same as present-day emission through 1990. Further trends in emission will depend critically on the energy policies of each country and the entire region.

Strong acids have decreased the mean annual pH of precipitation in much of Northwestern Europe and large areas of North America to between 4 and 4.5. The sources and environmental consequences of acid deposition are often separated by hundreds, even thousands, of kilometres. Its impacts on aquatic systems in more susceptible areas of Europe and North America are clearly documented today. Tomorrow, the emission source areas exposed to the heaviest depositions will be facing serious direct and indirect effects on natural ecosystems, materials and possibly even human health. Further metal toxicity in soils, surface waters and groundwaters with consequences for terrestrial and aquatic life will most likely develop in both heavily polluted and sensitive areas.

INTRODUCTION

The time has come for greatly increased scientific and public awareness of atmospheric deposition in general, and acid precipitation in particular. Acid deposition is a modern phenomenon -- a product of man's interference with sulphur and nitrogen cycling both on a regional and global scale. Today acid deposition is recognized in many industrialized countries of the Northern Hemisphere, as one of the most urgent and important environmental problems of the 1980's.

Many lines of evidence show that most kinds of atmospheric pollution are caused, directly or indirectly, by the combustion of fossil fuels. Burning of coal and oil are the major sources of acid precipitation. The concept of acidification is bound up with the discharge into the atmosphere of sulphur dioxide, nitrogen oxides, and micro-pollutants, - and the subsequent effects of these substances on the environment.

The effects of acidification are becoming more and more manifest and widespread, producing environmental damage that is increasingly hard to comprehend and increasingly difficult or impossible to remedy. Atmospheric deposition of acidic and acidifying compounds and associated gaseous pollutants are having serious impacts on climate, human health, materials, water, aquatic organisms, vegetation, and soil.

In this presentation I shall seek to relate acid precipitation to the broad subject of atmospheric depostion and its consequences, - with particular reference to the natural environment.

EMISSION, TRANSPORTATION AND DEPOSITION

Acid deposition results in large parts from man-made emissions of sulphur and nitrogen oxides, Major sources include combustion of coal and oil, smelting of ores, exhausts from cars, and nitrogen fertilization. In this context, sulphur and nitrogen compounds giving rise to the acidifying properties of precipitation, are of prime interest. Their sources should be described with a view to finding their geographical distribution, emission rates, and seasonal variations. This is necessary for the purpose of modelling their transport and formulating abatement policies against their negative effects.

Calculations put the current world total of anthropogenic sulphur emissions into the atmosphere at about 75 - 100 million tonnes a year. Emission patterns in Europe show that a large proportion of the sulphur comes from urban areas of the European Continent and in the British Isles. Some 30 million tonnes of sulphur are emitted as SO_2 annually in Europe. Emissions of nitrogen oxides, calculated in terms of nitrogen, are estimated at about 6 million tonnes per year. In Northern Europe the man-made sulphur emissions count for about 90 per cent of total sulphur emissions in the area. Future sulphur emissions will be the combined result of changes in amounts of oil and coal burned and changes in use of control measures. SO_2 emissions in Europe are predicted to remain about the same as present-day emissions through 1990. Emissions of nitrogen oxides are predicted to increase in Europe. Future trends will depend critically on the energy policies of each country and the entire region.

Sulphur and nitrogen oxides are transformed in the atmosphere to sulphuric and nitric acids. High concentrations of ozone and photo-chemical oxidants, which are observed over large areas of Europe, and North America will increase the transformation rate. In part because of tall smokestacks, air pollutants often travel long distances. Hence, the source and environmental consequences of acid rain are often separated by hundreds, even thousands, of kilometres. A much used technique in analyzing source areas and transport directions of air pollutants is sector analysis, grouping together trajectories belonging to the same sector. Arctic haze and transarctic transport of air pollutants are partly caused by emission in the industrial regions of Europe and North America. Of particular interest for long-range pollutant transport is the build up of high concentrations of stagnant air near the ground. Observations show that such parcels of contaminated air sometimes move over long distances without much dilution.

In 1977 the OECD program on Long-Range Transport of Air Pollution (LRTAP) concluded: "....air quality in any one European country is measureably affected by emission from other European countries" -- an important scientific conclusion with important political implications. Air pollution was finally recognized as being a problem of the entire European Continent.

In large parts of Western Europe and North America there was a marked increase in the concentration of hydrogen and sulphate ions in the precipitation during the 1960-1970 decade. Strong acids have decreased the mean annual pH of precipitation in much of north-western Europe and parts of North America. In southern Scandinavia and eastern North America the present total sulphur load is 1.5 - 3 gSm^{-2} yr^{-1} and the pH in precipitation is 4.0 - 4.5. In Southern coastal areas of Norway, about 90 per cent of the acidity in precipitation comes from nondomestic sources. Long-term data at some stations in Northern Europe shows a drop in precipitation acidity of about 1 pH unit between 1955 and today.

Since the early 1970's there has been no obvious trend in the sulphate concentrations at Norwegian stations. Generally speaking, the sulphur content in precipitation in Europe has remained substantially constant for this same period. This apparent discrepancy may be explained in part by the greater proportion of dry deposition during recent years. The nitrate-ion content of the precipitation has shown a more steady increase over the last decades.

Model calculations of wet and dry deposition pattern over Europe show that in Scandinavia, particularly in Norway, the wet deposition outweighs the estimated dry deposition. If future sulphur emissions show an increase in regions that are already acidified, it need not mean that the precipitation there will become correspondingly more acidic. It may instead be that the increases in emissions will lead to a situation in which a greater proportion of the sulphur is dry deposited. Maximum total deposition occurs in the vicinity of source areas where dry deposition predominates. In more remote areas the wet deposition assumes greater importance.

Long-range transport appears to dominate the general deposition pattern of several heavy metals in Scandinavia. Studies of organic micropollutants in precipitation and in aerosols have identified a wide range of compounds in the same air masses that bring acid precipitation to Norway.

At present there are no reliable quantitative data about the geographical distribution of dry deposition of acidic or acidifying substances over North America. In the industrial regions of the eastern part of the continent it is generally assumed that dry deposition is about the same order of magnitude as wet deposition. In the more arid regions of the western states and provinces dry deposition is believed to be greater than wet deposition. Qualitative estimates will have to wait on the development of methods for the proper collection and analysis of dry deposition on a network basis.

Reliable precipitation chemistry networks have been established in both Canada and the United States during the past 5 years. Two-thirds of the total land area of North America receive precipitation with an average (precipitation weighted) annual value less than what would be expected for natural rainfall over the land surface (pH 5.6 - 6.5). The area receiving highly acid precipitation (> pH 4.6) in 1980 included large parts of eastern Ontario and southern Quebec, most of Newfoundland and Nova Scotia in Canada, and large parts or all of the following states in the United States: Wisconsin, Michigan, New York, New Hamshire, Vermont, Maine, Massachusetts, Connecticut, Rhode Island, Iowa, Missouri, Illinois, Indiana, Ohio, Pennsylvania, New Jersey, Delaware, Maryland, Kentucky, Virginia, Tennessee, North and South Carolina, Arkansas, Mississippi, Alabama, and Georgia.

IMPACT ON THE ENVIRONMENT

Air pollutants cause many environmental problems. Sulphur dioxide and nitrogen oxides exert both a direct and indirect influence on organisms and material. Foremost among the direct effects are health effects, plant damage, and corrosion due to high sulphur dioxide contents. The direct effects are determined by the concentration of pollutants in the air, and in general they decline rapidly with increasing distance from the source of emission. The estimated mean concentration of sulphur dioxide in Europe in the most heavily polluted areas is close to or even above levels at which it can do direct damage. Acidification effects, however, are the result of indirect influences depending mainly on two factors: the magnitude of wet and dry deposition, and the natural, inherent sensitivity of the soil and water to acidification.

Ecological Impacts - terrestrial ecosystems

Vegetation acts as an efficient filter of the chemical components in air and precipitation. Apart from well known damage to plants in heavily polluted atmospheres, direct effects of acid precipitation on forest trees have been shown by experiments with simulated acid rain. Acid deposition increases the leaching of some elements such as calcium and potassium from the foliage. The total effect is an increase in concentrations of most of the compounds in throughfall compared to incident precipitation.

On the basis of studies in Scandinavia, decreases in forest growth due to acid deposits have not been demonstrated. A temporary growth stimulation probably due to the nitrate-ions in the precipitation, has been recorded in some experiments. But the present data do not exclude the possibility that adverse influences may develop over time in susceptible forest ecosystems of Scandinavia.

West German scientists have concluded that large forest areas in Central Europe appear to be seriously threatened both by acid precipitation and by direct gas injury. The total damage ascribed to air pollution impacts includes deficiency of magnesium and/or calcium in combination with aluminium toxicity in the soil. The combination of high acidity and high concentrations of aluminium and heavy metals in soil is a very important feature of acid deposition.

At present there is no compelling evidence that the effects of ambient acid deposition on terrestrial ecosystems in North America are more detrimental than beneficial. Mainly on the basis of controlled exposures of crop plants and forest trees to simulated acid deposition, we have good reason to be suspicious, but no compelling evidence with which to conclude, that forest and agricultural ecosystems are presently being harmed by ambient acid deposition. However, in various source regions of Europe and North America economic damage to forests and agricultural crops is occuring as the result of dry deposition of toxic gases. Ambient concentrations of ozone, sulphur dioxide, and oxides of nitrogen, acting alone or in combination, are causing important damage and decreases in yield of both crops and forests.

The most serious consequence for terrestrial ecosystems of regional acidification at levels currently observed in many parts of Europe and North America may be the increasing rate of leaching of major elements and trace metals from forest soils and vegetation. As a result of atmospheric deposition, particularly of sulphur, increased quantities of aluminium and cadmium are leached out of the acidified soil and carried to ground water and surface water. The leaching of aluminium is greatest in the most acidified soils while the risk of cadmium leaching is greater in soils that are high in cadmium and undergo rapid acidification.

In the soil, dissolved aluminium interferes with the ability of plants to assimilate phosphorus, since the two elements react and form almost insoluble aluminium phosphate. Another negative effect of aluminium is that the fine root filaments of the trees are damaged.

Elevated aluminium contents in surface waters have been found to lead to large-scale mortality among fish. Aluminium in water causes precipitation of organic substances. The effect of this is that cadmium and other heavy metals become more toxic in soil, in ground water, and, in surface water.

The relative significance of strong acids and associated heavy metals found in heavily polluted areas has not been clearly established in terms of toxic effects on plants and soil organisms. It is important to keep in mind the possible long-term synergistic effects on ecosystems of the array of heavy metals and organic micropollutants commonly associated with acidifying air pollutants.

From an ecological point of view it is difficult to forecast the ultimate results of the atmospheric acidification and related air pollutants on terrestrial systems, and to judge the rate and even the direction of changes. In the more susceptible areas it seems to be a question of proportion and time required rather than whether any ecological effects appear or not.

Ecological Impacts - aquatic ecosystems

Acidification of inland waters is caused by strong acids, primarily sulphate and nitrate. Freshwater acidity is often a result of complex interactions between precipitation or meltwater and the terrestrial systems. Processes such as cation exchange, weathering and accumulation and release of various substances affect the composition of run-off waters. Thus the low pH-values often observed in connection with the first heavy rain in the fall, may largely be explained by a wash-out of sulphate accumulated during the summer or earlier. The first fractions of the meltwater contain considerably higher concentrations of ions than the bulk snow. The low pH levels often observed in lakes and streams during snowmelt are partly caused by this fractionation effect.

Freshwater bodies in many areas of northern Europe and North America that lie in and adjacent to areas where precipitation is most acid, are threatened by the continued deposition and further expansion of acid precipitation. The effect of acid precipitation on water acidity depends greatly on bedrock geology and the nature of the overburden. The most well-known susceptible areas are those with shallow soils and quartz-bearing bedrock, e.g. granite and gneisses. There is convincing evidence of a decrease in pH in freshwaters during recent decades in southern Scandinavia and other exposed regions in Europe and North America with similar geology. Both in Norway, and in other countries, recent regional acidification have been reported only in areas receiving acid precipitation (pH less than about 4.7). Extensive regional lake surveys have been carried out in Norway. Considering lakes with similar Ca-levels, there is a high correlation between concentrations of hydrogen and sulphate ions. The sulphate deposition explains in general the sulphate concentrations in the lake. The nitrate concentration in lakewater is always much lower than the sulphate concentration. Lakes with low pH often have elevated aluminium concentrations, and sometimes increased concentrations of other metals. Concentrations of mercury, manganese, cadmium and lead are higher in fish from acid, than from less acid, waters. Dissolved inorganic aluminium leached from soils and sediments is toxic to fish in surface waters at concentrations as low as 70 μgl^{-1}.

Empirical data from Sweden, Norway, Canada and the United States show that lakes in sensitive areas, with alkalinity <50 μEq/l have in general not been acidified when the catchments receive a sulphur load of 0.5 $gS/m^2 \cdot yr$ or less. Any reduction in acid deposition must be beneficial to aquatic ecosystems under acid stress. Further, large inputs of acid precipitation must lead to reduced neutralization capacity in susceptible soils, and to further fresh-water and groundwater acidification.

The recent acidification in Western Europe and North America has had profound impacts on aquatic life. All trophic levels are affected. In the four southernmost counties in Norway, more than half of the fish populations have been lost during the 1940-1980 period. Lakes in more than 13 000 km^2 of south Norway are practically devoid of fish, and in additional 20 000 km^2, the fish stocks are reduced.

In southern and central Sweden, fisheries damage is observed in 2 500 lakes and is assumed to have occurred in further 6 500 lakes with some observed symptoms of acidification. On the basis of lake chemistry, the fisheries of about 18 000 lakes with pH <5.5 are now affected.

In western Norway and south-central Sweden in large areas of unreactive geology, thin soils and waters of low alkalinity are expected to show signs of acidification over the next 50 years with present levels of total S deposition.

In Ontario, Canada, about 50 000 lakes on granitic terrain receive $\geq 0.7\ gSm^{-2}\ yr^{-1}$ and 2 500 lakes surveyed in the area indicate that 20% have alkalinity $\leq$ 40 $\mu eq\ l^{-1}$. In Quebec, the extent of sensitive areas is even greater. Based on Scandinavian experience, these lakes are expected to undergo acidification in the next several decades. Loss of salmon is reported for several rivers in Eastern Canada. In northern United States, loss of salmon fish species is reported in about 100 lakes.

High egg and fry mortality in acid water is regarded as the main reason for fish decline, but other population responses are also known. Massive kills of adult fish during acid-release episodes is well documented, and is caused by physiological stress from toxic combinations of water acidity and aqueous aluminium. The aluminium toxicity depends on water pH and seems to have a maximum around pH 5.

Acidified aquatic ecosystems show both reduced production and reduced decomposition. The fish in acid waters do not disappear for lack of food. Certain tolerant organisms come to dominate. This simplification of the plant and animal communities makes acidified ecosystems more vulnerable to changing conditions, and may mean an additional stress on the top predators, as food will not always be easily available.

It is not the symptoms but the causes of acidification that must be attacked. Desulphurization of fuels and stack gases apparently is the only viable solution to the problem.

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Trace Elements in Fly Ash and Their Release in Water and Treated Soils[1]

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ABSTRACT

Fly ash from a coal-fired power plant was separated into various-sized fractions which were then chemically characterized. The fly ash contained higher concentrations of B, Co, Cr, Cd, Mo, Ni, Pb, As, and Se than normally found in soils. Except for Cd, Co, and Pb, trace elements were more concentrated in the <53-μm than in the >250-μm fraction. Solubility of trace elements in water increased greatly as the equilibrium pH was lowered.

Three soils, an acid sand, a calcareous loamy sand, and a calcareous silt loam, were amended with five rates of fly ash up to 1.0% by weight and equilibrated at moisture contents of 1/3 bar or saturation for periods ranging up to 29 weeks. Solubility of trace elements in water and DTPA extracts were observed. Application of fly ash increased soil pH; the acid soil exhibited the greatest increase. Except for B, fly ash amendment up to 1.0% did not result in elevated concentration of either water-soluble or DTPA-extractable trace elements. Additions of fly ash to the acid soil decreased DTPA-extractable Fe, Mn, Ni, Co, and Pb. The data demonstrated that the alkalinity of fly ash plays a significant role in regulating the availability of trace elements in the amended soils.

Additional Index Words: **coal-fired power plants, heavy metals, environmental pollution, waste material.**

Increased efforts are being directed both toward developing alternate energy sources and making better use of existing reserves. Among traditional fossil fuel sources, coal exists in quantities capable of supplying a large portion of our nation's future energy needs. However, increased knowledge of the adverse health effects of particulate pollutants, together with a corresponding emphasis on the development of control devices, have led to the widespread collection of much of the fly ash which is produced by the burning of coal. In 1976, it was estimated that 34 million metric tons of fly ash would be produced in the United States (Brackett, 1973). Over the years, the commercial consumption of fly ash has been <10%. The nonutilized fly ash is dis-

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posed of primarily in lagoons (usually on site) and landfill areas. Since no consistent utilization trend is evident, it is expected that stockpiles of fly ash will continue to grow as reliance upon coal as a fuel source increases. Thus large quantities of this material are brought into contact with soil and water environments.

Depending on the coal source, fly ash varies widely in its pH (Plank and Martens, 1973; Furr et al., 1977) and trace element contents (Abernath et al., 1969; Furr et al., 1977; Swanson, 1972) which generally exceed those typically present in soils. Klein and Russell (1973) found that the soils around a coal-burning plant were enriched in Ag, Cd, Co, Cr, Cu, Fe, Hg, Ni, and Zn; plant materials were enriched in Cd, Fe, Ni, and Zn. Bradford et al. (1978), however, found no elevated concentrations of trace elements in the soil saturation extracts and native vegetation around the Mojave Generating station. Recently, Gutenmann et al. (1976) reported that white sweet clover voluntarily growing on beds of fly ash contained Se in excess of 200 ppm. They also found that water, plants, and insects from a fly-ash-contaminated pond contained elevated concentrations of Se.

There has been increased concern over the possible deterioration of the environment as a result of fly ash deposition on land. The objectives of this study were to determine the: (i) trace element concentration in different-size fractions of fly ash produced from western U.S. coal sources; (ii) release of trace elements from stockpiling of fly ash as related to equilibrium pH; and (iii) water solubility and DTPA extractability of trace elements from fly ash-treated soils.

MATERIALS AND METHODS

The fly ash used in this study was collected in January 1975 from the Mojave Generating Station near Bullhead City, Arizona. The pH of a saturated paste of the fly ash was 12.3 and the electrical conductivity (EC) of saturation extract was 7.5 mmhos/cm. The fly ash was composed primarily of Si, Al, Fe, and Ca (30–40%) and its alkalinity appeared to have derived mainly from oxides and hydroxides rather than carbonates (Phung et al., 1978). Particle size distribution analysis showed that 32.5% of the fly ash was in the sand-sized separate (2-0.05 mm), 63.2% in the silt-sized separate (0.05–0.002 mm), and 4.3% in the clay-sized separate (<0.002 mm).

Experiment 1

The fly ash and its component size fractions were analyzed to characterize their chemical composition. The fly ash was fractionated by mechanical sieving into the following particle sizes: >250 μm, 250 to 105 μm, 105 to 53 μm, and <53 μm. Samples (1 g) of each fraction were digested in a solution consisting of 7 ml of 3:1 concentrated HCl/HNO_3 (aqua regia), 1 ml of water, and 5 ml of an aqueous solution containing 48% HF for 2 hours at 110°C in 50-ml test tubes on a circular aluminum digestion rack. After cooling, boric acid (5.0 g) was added to neutralize the HF, and deionized water was added to bring the volume to 50 ml. The tubes were shaken for 1 hour, filtered, and the filtrates were analyzed for eight trace metals (Mn, Zn, Cu, Pb, Cr, Co, Ni, and Cd). Additional fly ash samples were digested in 4*N* HNO_3 (80°C, 12 hours) for B and F; HNO_3-H_2SO_4 for Se (Fine, 1965); H_2SO_4-$HClO_4$ for As (Small and McCants, 1961); and $HClO_4$ for Mo (Reisenauer, 1965).

To determine the release of trace elements in water from different fly ash particle sizes in relation to equilibrium pH, 0.2 to 5.0 g of fly ash were equilibrated by continuous shaking with 24 ml deionized water in 35-ml centrifuge tubes. Twice daily the pH was adjusted with HCl to 6.0 and 9.0. The suspensions attained equilibrium in 3 days after which the pH variation was ±0.2 unit. Deionized water was then added to bring the volume to 30 ml. The tubes were centrifuged, filtered, and the filtrates analyzed for B and the eight trace metals previously mentioned.

Table 1—General characteristics of the soils used in incubation study.

Series name	pH	O.M.	CEC	Soil moisture 1/3 bar	Saturation	Classification
		%	meq/ 100 g	—— %	——	
Baywood sand	5.2	2.2	6.5	3.75	25.0	Entic Haploxeroll
Calhi loamy sand	8.2	1.8	4.0	6.25	17.5	Typic Xeropsamment
Domino silt loam	7.8	4.3	14.0	32.50	47.5	Xerollic Calciorthid

Trace metals were determined by flame atomic absorption spectroscopy. Boron was determined by the curcumin method (APHA, 1971). Arsenic was measured by the arsine-molybdenum blue procedure (Small and McCants, 1961); Se by the amino-benzidine method (APHA, 1971); F by a specific-ion electrode method; and molybdenum by thiocyanate procedures (Reisenauer, 1965).

Experiment 2

An incubation experiment was conducted to evaluate the solubility and availability of trace elements in three soils amended with fly ash. Some properties of the soils used in this study are presented in Table 1. Air-dry soil (400 g) was mixed in 500-ml polystyrene containers with fly ash at rates of 0, 0.05, 0.1, 0.5, and 1.0% by weight. These rates are equivalent to the amounts of fly ash that are emitted from a generating station and deposited on 2.5 cm of soil in a 1,280-km^2 area over periods ranging from 3 to 50 years. Deionized water was added to the amended soils to bring the mixtures to their 1/3 bar and saturation water contents. The mixtures were thoroughly mixed and incubated at 25°C for varying periods up to 29 weeks. These moisture contents were maintained throughout the experiment by the weighing technique.

Duplicate samples of each treatment were removed weekly (later, biweekly and monthly) from the incubation room. Soil saturation extracts (SSE) were prepared (U.S. Salinity Lab. Staff, 1954). The DTPA extractability of trace metals was determined by shaking 10 g of air-dry-treated soil with 20 ml of 0.005*M* diethylenetriamine-pentaacetic acid (pH 7.3) extracting solution for 24 hours. The contents were then centrifuged and filtered.

The SSE extracts were measured for pH, EC, B, and other trace elements, including Cr, Mo, Ni, V, and Ag (Bradford et al., 1973), and Cu, Zn, Mn, Cd, and Pb (flameless atomic absorption spectroscopy). Due to low concentrations (<0.1 μg/g), a preconcentration treatment was used on the SSE for flameless determination which included mixing an aliquot (5 to 10 ml) of the extract with 5% ammonium pyrollidine dithiocarbamate (APDC) at pH 2.5 to 3.0 and extracting with 5 ml of methyl isobutyl ketone (MIBK). The DTPA extracts were analyzed for eight trace metals (Experiment 1).

RESULTS AND DISCUSSION

Trace Elements in Fly Ash

Except for Pb, Cd, and Co, the trace elements determined were more concentrated in the <53-μm than in the >250-μm fraction (Table 2). Boron, Zn, Cu, Se, and As showed an inverse relationship between concentration and particle size. Davison et al. (1974) reported that fly ash particles >74 μm exhibited no dependence of element concentration on particle size. They found, however, that airborne fly ash particulates (<10 μm)

Table 2—Concentrations of trace elements in various sized fractions of fly ash.

Particle size	B	F	Mn	Zn	Cu	Pb	Cr	Co	Ni	Cd	Se	As	Mo
μm	μg/g												
>250	148	72	100	56	45	55	38	40	41	4.1	8.5	6.5	20
250–105	169	66	117	64	52	55	49	45	49	5.3	10.4	7.2	28
105–53	337	68	120	70	62	63	46	45	49	2.7	11.6	8.4	36
<53	300	83	115	88	119	57	50	44	51	4.1	13.8	9.5	42
Avg.	239	72	113	70	69	58	45	44	48	4.1	11.1	8.2	38
Fly ash	293	70	120	74	64	56	44	43	49	4.1	12.9	8.9	40

showed increased concentrations of Pb, Te, Sb, Cd, Se, As, Zn, Ni, Cr, and S with decreasing particle size.

The B, Pb, Co, Cr, Ni, Cd, Mo, Se, and As contents (Table 2) were higher when compared to the concentrations of these elements in soils, as reported by Connor and Shacklette (1975). Thus, if large quantities of fly ash are incorporated into soil, the resulting mixture may be greatly enriched with these trace elements. Examples of elevated concentrations that may result in fly ash-amended soil are Mo (Doron and Martens, 1972), B (Phung et al., 1978; Plank and Martens, 1974), and Se (Gutenmann et al., 1976).

The release of trace elements in water was greatly influenced by the equilibrium pH of the fly ash suspension. To illustrate this point, average concentrations of the suspension density of 0.066 g/ml (2 g/30 ml) are presented (Fig. 1). Solubility of all trace elements analyzed was extremely low at the original pH of 12.3. However, as the equilibrium pH was lowered to 9.0, concentrations of B, Pb, Co, Cr, and Ni were greatly increased. Further releases of trace elements were observed when the equilibrium pH was lowered to 6.0. A similar pH effect on trace element solubility was reported by Theis and Wirth (1977). Copper and Cd were least affected by the equilibrium pH. With the exception of B, trace element solubility was not related to their total contents in fly ash irrespective of pH adjustment. The actual amounts of trace elements released from fly ash in natural waters (pH 7–8.5) from stockpiles of fly ash will depend largely on the pH, bonding between the element and the fly ash, its chemical form, and the chemical and physico-chemical properties of the water. Higher release rates of soluble trace elements from fly ash may occur in a ground water than in a surface water, due to the former's lower pH (higher CO_2 content). However, other processes (e.g., ion exchange, precipitation, and sorption/desorption) that affect the release of trace elements, prior to entering ground water, should also be considered.

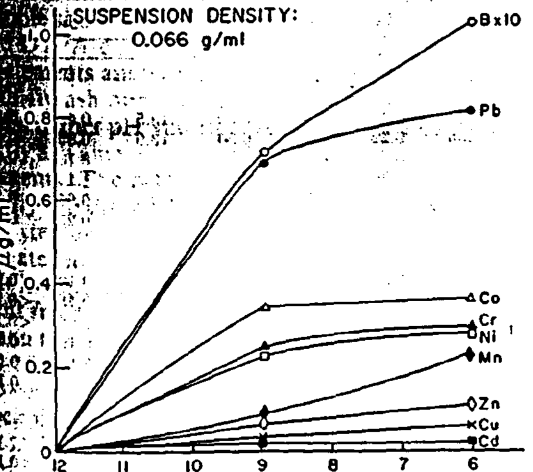


Fig. 1—Solubility of selected trace elements in fly ash as related to equilibrium pH.

Water-Soluble and DTPA-Extractable Trace Metals from Fly Ash-Amended Soils

Since soil pH is among the more important chemical properties governing the availability of trace elements to plants, the resulting pH's of the fly ash-amended soils were examined. Of the three soils studied, the acid Baywood soil showed the greatest increase in pH due to fly ash amendment (Fig. 2). The pH of this soil increased in relation to the amounts of fly ash added but gradually decreased with incubation time for all treatments except the 1% rate. The amended Domino soil did not show any significant increases in pH. This may be due partly to the buffering capacity and original pH of the soil. The moisture effect showed no discernible trend, although the resulting pH appeared to be higher at saturation than at 1/3-bar moisture content in the Baywood soil.

Fly ash additions also resulted in increased soluble salt concentration. Although the release of soluble salts from fly ash varied, the trend was similar to that of pH. The Baywood soil showed the greatest increase and the

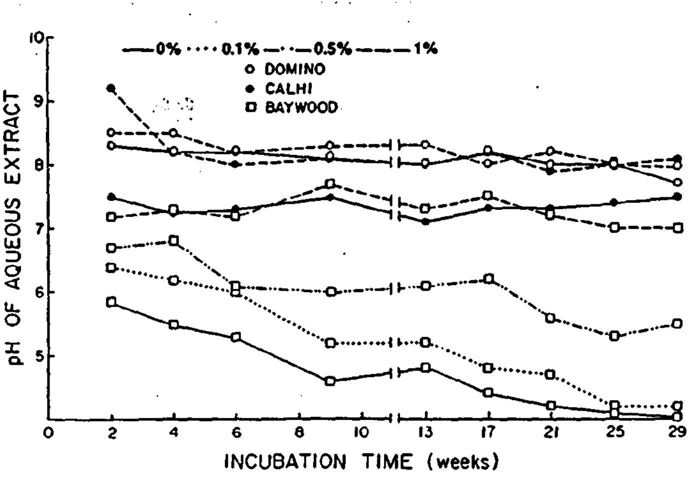


Fig. 2—Changes in pH of aqueous extracts with time and different rates of fly ash at 1/3-bar moisture content.

Table 3—Effects of fly ash application rate and incubation moisture on the concentrations of selected trace elements in soil saturation extracts.†

Fly ash rate	1/3 bar tension							Saturation						
	B	Mn	Cu	Zn	Mo	Ni	Pb	B	Mn	Cu	Zn	Mo	Ni	Pb
%	μg/ml													
	Baywood soil													
0	0.11	0.085	0.011	0.06	0.03	0.03	0.038	0.23	0.38	0.018	0.05	0.05	0.06	0.038
0.1	0.27	0.081	0.014	0.04	<0.02	0.04	0.082	0.46	0.87	0.012	0.08	0.03	0.05	0.070
1.0	1.14	0.008	0.014	0.03	0.03	0.03	0.034	1.47	0.019	0.018	0.04	0.07	0.06	0.031
	Calhi soil													
0	0.14	0.008	0.022	0.09	0.05	0.03	0.034	0.13	0.003	0.023	0.21	0.06	0.03	0.006
0.1	0.27	0.005	0.019	0.04	0.06	0.02	0.019	0.32	0.008	0.008	0.13	0.10	0.03	0.002
1.0	0.93	0.004	0.016	0.04	0.13	0.04	0.021	0.77	0.007	0.019	0.12	0.28	0.08	0.024
	Domino soil													
0	0.84	0.003	0.035	0.05	0.06	0.03	0.011	1.30	0.98	0.98	0.05	0.12	0.05	0.009
0.1	1.17	0.010	0.026	0.02	<0.02	<0.02	0.017	1.59	0.28	0.28	0.11	0.13	0.04	0.006
1.0	1.36	0.005	0.029	0.03	0.05	<0.02	0.021	1.79	0.42	0.42	0.08	0.12	0.04	0.002

† Values are averages of data for all sampling dates. Concentrations of Cr, Co, V, As, and Se were <0.02 μg/ml, and Ag and Cd <0.002 μg/ml.

Domino soil the least in EC. This is probably related to soil texture and CEC. The soluble salt concentrations are within the range for crops with low salt tolerance.

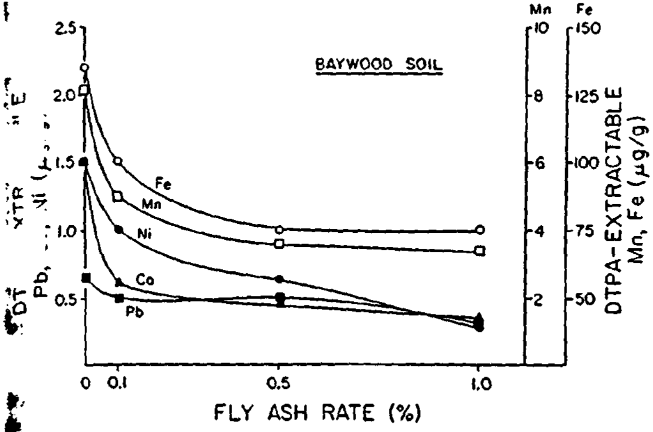
Except for B, fly ash amendment up to 1.0% did not result in elevated concentrations of water-soluble trace elements (Table 3). On the contrary, concentrations of some elements such as Mn in the Baywood soil, and Mn, Zn, Cu, and Pb in the Calhi soil, decreased at the 1.0% fly ash rate for the 1/3-bar water content. This may be attributed to the high alkalinity of the fly ash which reduced the solubility of these metals in the amended soils. In general, concentrations of the trace elements in the SSE of the fly ash-amended soils are comparable to those reported for 68 soils from California (Bradford et al., 1971).

Trace metals in coal are volatilized and possibly reduced to the elemental state during combustion before condensing and adsorbing onto the fly ash particles (Davison et al., 1974). Engle and Capp (1967) suggested that many of the elements in fly ash are released slowly into soil solution because they were trapped in silica spheres formed by burning of the pulverized coal. Results of our study indicate, however, that there was no definite relation between concentrations of the water-soluble trace elements in the amended soils and incubation time.

DTPA extracted significantly higher concentrations of trace metals than water extractions. The DTPA extractability, however, was relatively low, ranging from <1.0% for Zn, Mn, Co, Ni, and Cd to 1.0–3.0% for Cu, Pb, and Cr. Concentrations of these trace metals in the DTPA extracts varied greatly among soils and, in most instances, tended to decline with incubation time (Table 4). Since Cd was generally present in <0.1 μg/g in all three soils, its concentrations are not included in the table. Again, amendment of fly ash up to 1.0% did

Table 4—Changes in levels of DTPA-extractable trace metals in three fly ash-amended soils at two incubation soil moisture levels.

Incubation period	Fly ash rate	1/3 bar tension							Saturation						
		Cu	Zn	Ni	Pb	Mn	Co	Cr	Cu	Zn	Ni	Pb	Mn	Co	Cr
weeks	%	μg/g													
		Baywood soil													
4	0	0.20	0.44	1.4	1.1	4.1	0.30	0.40	0.25	0.40	1.5	0.60	13.5	0.55	0.40
	0.1	0.20	0.28	1.6	0.90	2.9	0.55	0.40	0.35	0.29	1.9	0.50	13.0	0.85	0.40
	1.0	0.25	0.30	0.80	0.65	2.2	0.15	0.20	0.37	0.32	0.80	0.50	10.6	0.10	0.40
29	0	0.25	0.26	1.5	0.65	4.1	1.5	0.30	0.30	0.30	1.1	0.65	12.2	1.1	0.40
	0.1	0.25	0.29	1.0	0.50	2.5	0.60	0.25	0.28	0.25	1.3	0.50	14.2	0.80	0.40
	1.0	0.20	0.24	0.30	0.30	1.7	0.35	0.20	0.22	0.27	0.80	0.45	8.3	0.25	0.40
		Calhi soil													
4	0	0.40	2.0	0.65	0.75	11.9	0.20	0.20	0.40	2.3	0.60	0.60	17.0	0.10	<0.10
	0.1	0.40	1.7	0.60	0.80	10.6	0.15	0.20	0.50	2.6	0.60	0.90	16.9	0.15	<0.10
	1.0	0.75	1.5	0.55	0.90	9.3	0.15	0.20	0.60	1.8	0.60	0.85	10.0	0.20	<0.10
29	0	0.30	2.3	0.20	0.60	12.8	0.10	0.10	0.30	1.6	0.20	0.80	16.2	0.10	0.10
	0.1	0.36	1.1	0.20	0.50	8.1	0.10	0.10	0.48	1.5	0.30	0.50	15.5	0.10	0.10
	1.0	0.36	1.2	0.30	0.55	5.9	0.10	0.10	0.47	1.0	0.25	0.50	10.2	<0.10	0.10
		Domino soil													
4	0	2.4	2.2	0.80	2.5	66	0.70	<0.10	1.4	1.4	1.0	3.1	186	1.3	<1.10
	0.1	2.7	2.1	0.80	2.9	108	1.2	<0.10	1.7	1.0	0.95	3.0	195	1.3	<0.10
	1.0	2.3	2.0	0.80	2.5	84	0.90	<0.10	1.9	1.4	0.95	2.8	178	1.2	<0.10
29	0	1.4	1.5	0.40	2.5	34	0.30	<0.10	1.9	1.0	0.60	1.9	168	1.3	<1.10
	0.1	1.3	1.4	0.40	2.0	37	0.30	<0.10	1.8	1.5	0.60	1.6	174	1.3	<0.10
	1.0	1.2	1.4	0.40	2.1	29	0.30	<0.10	1.9	1.4	0.60	1.8	172	1.3	<0.10



. 3—**Effect of fly ash application on the DTPA-extractable trace etals in a Baywood sand.**

t cause an increase in the extractability of all trace etals. Fly ash additions to the Baywood soil significantly decreased the amounts of DTPA-extractable Fe, n, Ni, Co, and Pb (Fig. 3), probably as a result of the vated pH. In the Calhi soil, while extractable Mn and n decreased with fly ash additions, Ni, Pb, Co, and Cr remained relatively constant (Table 4). The Domino soil s the least affected by additions of fly ash relative to DTPA extractability of trace metals. The results ggest the significance of original pH, texture, and probably CEC of the soil to be amended with fly ash.

CONCLUSIONS

Fly ash from western coals is strongly alkaline. on, Pb, Co, Cr, Ni, Cd, Mo, Se, and As exist in her concentrations in the fly ash than in most mineral ils. However, the water solubilities of trace elements in the fly ash are low and profoundly influenced by ticle size and equilibrium pH of the fly ash suspension.

Amendment of soils with fly ash increased pH and soluble salt content, which in turn reduced the solubility DTPA extractability of trace elements. Among the lements analyzed, only B was increased significantly h fly ash application. The Domino silt loam, which had a higher pH and finer texture, was the least affected ly ash amendment with respect to the release of trace ents. The results suggest that when selecting a site fly ash disposal, the alkalinity of the fly ash, soil pH and texture, as well as hydrogeologic conditions, ate, etc., should be carefully evaluated.

is concluded that the effect of trace element enrichment from fly ash deposition on water quality and vegetation (via root uptake) is insignificant in the vicinity of Mojave generating plant after 50 years' operation. vever, the release of trace elements from fly ash stockpiled in storage ponds or lagoons can be significant. Thus, the interface of energy production from , with the possible degradation of water resources ugh the disposal and use of fly ash, is an area that should be studied in more detail.

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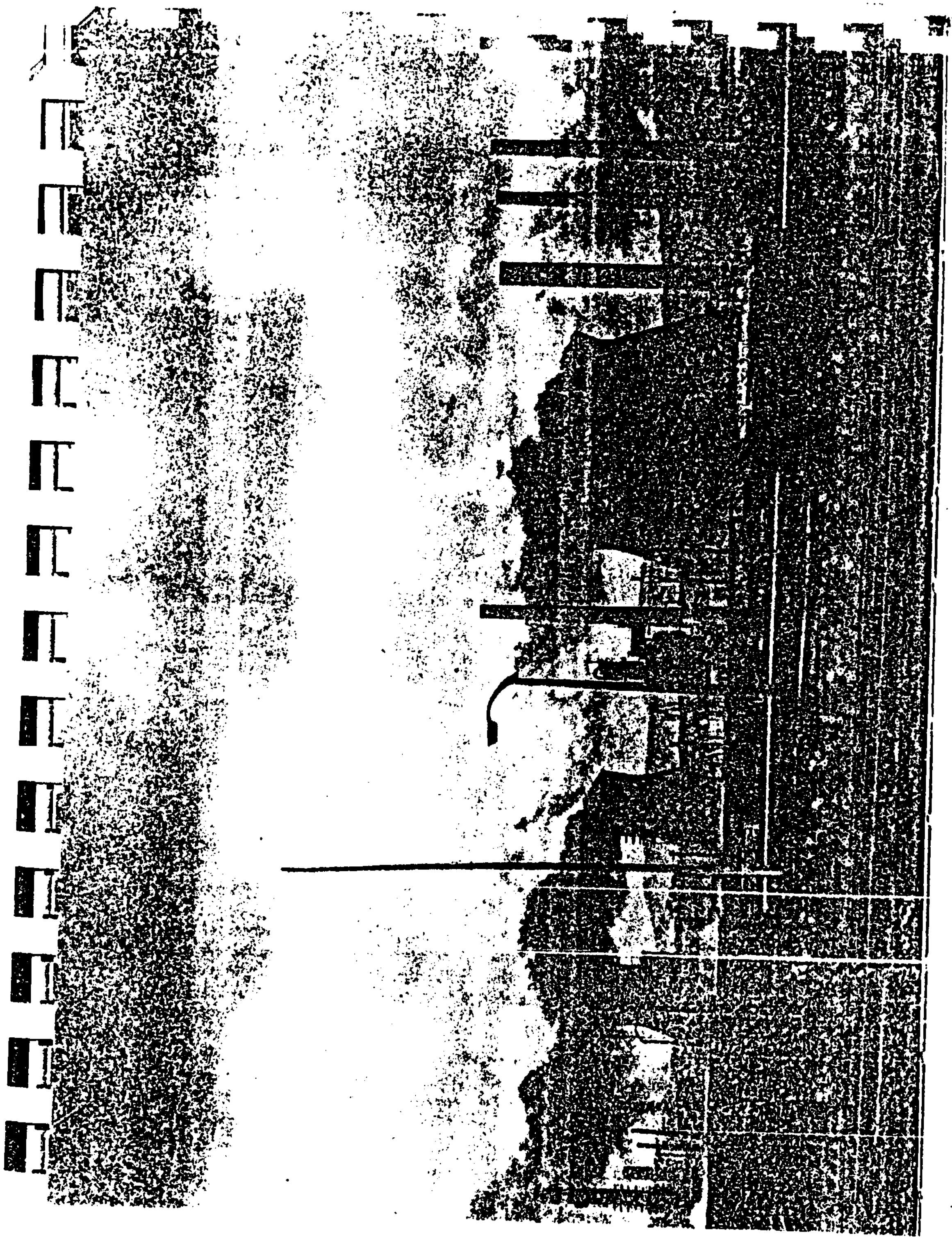

Fundamental Aspects of Pollution Control and Environmental Science 7

TRACE-ELEMENT CONTAMINATION OF THE ENVIRONMENT

(REVISED EDITION)

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Chapter 3

TRACE-ELEMENT CONTAMINATION OF THE ATMOSPHERE

3.1 GENERAL CONSIDERATIONS

Heavy metals are emitted into the air mainly as a consequence of high-temperature processes such as combustion, roasting and metallurgical operations. Some of the most toxic elements are among those involved (As, Bi, Cd, Hg, Se, Pb). In industrialized countries, deposition on pastures via polluted atmospheres is probably the most widespread and efficient route of heavy metal transfer into agricultural products (Ronneau *et al.*, 1983 [221]).

Valkovic [222] has classified atmospheric pollutants, on the basis of their physical and chemical composition, as inorganic gases, organic gases, inorganic particulates and organic particulates. On the basis of figures given by Ross, 1972 [223] for discharge of pollutants in these categories, the total weight of pollutants released into the atmosphere every year has been stated to be about 173 million tonnes, and the particulate fraction of this total amounts to 14.6 million tonnes. Such figures can be no more that rough estimates, for Vandegrift *et al*, 1971 [224] made a projected estimate for 1980 for particulate emission from electrical utilities in the United States alone of 4 million tonnes. The major sources of atmospheric pollution have been reviewed by Freedman and Hutchinson, 1981 [225], and these are generally recognized to be, transport, industry, power generation, space-heating and refuse burning. Hesketh, 1972 [226] has reported figures for the contributions for each class of pollutant from each source in the USA.

Most of the trace elements naturally present, or present as contaminants in the atmosphere are associated, largely as metal oxides, with the particulate fraction, and Schroeder [227] has stated that metals account for 0.01 to 3 per cent of particulates. On the basis of the figures quoted by Hesketh [226], half the total burden of particulate atmospheric pollution comes from industry and a quarter from power generation. The contributions from other kinds of human activity are on a much smaller scale.

In addition to being contaminated with particulate matter from industrial sources, the air is always substantially loaded with material derived from natural sources, and many of these particles are in the same size range (0.1-1.0 μm) as the smoke particles derived from human activities [222].

The trace elements present in the atmosphere which are dispersed in aerosols or associated with particulate matter are eventually removed by precipitation in rainfall or by gravitational fallout. There is, therefore, a continual transfer of trace-element contaminants from the atmosphere into the hydrosphere or into the soil, so that the air tends to be restored to an unpolluted state by natural processes. Air, therefore, provides a route for the contamination of the rest of the biosphere by trace elements discharged in smoke and fumes.

Mitchell, 1968 [228] calculated the average total planetary loading to be about 2 x 10^6 tonnes. It is clear that this loading must vary considerably from year to year. In the UK, there has been a considerable fall in the level of smoke in urban areas over the last twenty years, partly as a result of 'Clean Air' legislation and partly from a reduction in domestic consumption of coal, but as pollution from this source has declined, pollution from motor vehicle exhausts has increased [229].

Since the volume of water in the oceans is so enormous, any enhancement of trace element levels in ocean water brought about by fallout from the atmosphere will be insignificant in the long term. By contrast, contamination of soil from this source can often be significant, since many trace elements tend to remain near the soil surface after deposition. Trace-element contamination of soil resulting from atmospheric pollution from an industrial source can therefore lead to accumulation of contaminant elements in the surface horizon.

Although it has been stated by Sisler [230] that the chemical composition of the atmosphere is in equilibrium with the hydrosphere, it is clear that anything approaching an equilibrium situation could only be regarded as existing in a natural situation uninfluenced by human industrial activity. In the current situation, there is a net transfer of trace elements into the oceans from smoke, fumes and wind-blown dust from industrial sources. The quantities transferred in this way are then diluted virtually to extinction in ocean water. There is also a constant return of trace elements in ocean water to the land in wind-blown spray and in aerosols derived from the sea surface, although the composition of marine aerosols appears to be considerably different from that of bulk sea-water. This difference in composition is related to the physical mechanisms leading to aerosol formation, and it has been suggested that the most important process is the bursting of small gas bubbles at the ocean surface to produce aerosol particles in the range 1-20 μm [222, 231, 232]. It is probable that aerosol particles with diameters around 1 μm can be transported great distances before they are finally deposited.

Data published in the literature for the elementary composition of industrial smokes in British and North American cities have been summarised by Bowen, 1966 [180] and the levels given for trace elements which can give rise to pollution problems are given in Table 9. No figures are, unfortunately, available for mercury, although this is undoubtedly a widespread atmospheric contaminant. Hamilton, 1974 [233] has reported levels of mercury in dust collected from air samples in the London area in the range, 1-14 ppm, and substantial quantities of mercury are known to be discharged from coal-fired power plants (Freedman and Hutchinson, 1981 [225] p. 72).

On the basis of these figures, industrial smoke has to be regarded as a significant potential source of contamination of the atmosphere with arsenic, antimony, copper, fluorine, lead, manganese and nickel. The inhalation of all these elements at enhanced levels, with the possible exception of manganese, can be expected to produce adverse physiological effects. According to Schroeder [227], among 27 contaminant metals, cadmium, lead and nickel are a real or potential hazard to human health, while antimony and beryllium require careful control. Mercury, certainly, should also be included in this company.

TABLE 9

Trace element composition of smoke (μg/m^3 polluted air) Stocks, 1960 [234], Junge, 1963 [4])

Element	North American Cities	British Cities
As	0.01 - 0.02	0.01 - 0.2
Be	0.0001 - 0.0003	0.0001 - 0.001
Sb		0.004 - 0.25
Co		0.0007 - 0.004
Cr		0.002 - 0.02
Cu	0.05 - 0.9	0.02 - 0.25
F	0.01 - 0.4	
Pb	0.5 - 3	0.2 - 1.4
Mn	0.1 - 0.3	0.01 - 0.1
Mo		0.0005 - 0.006
Ni		0.002 - 0.2
Sn	0.01 - 0.03	

While levels of beryllium in smoke are generally low owing to the limited use of this element in industry, where there is a specific industrial source of dispersal, acute problems can arise. The processing phosphatic shale has been found by Severson and Gough, 1976 [235] to contaminate soil within a distance of 16 km from the source. Inhalation of beryllium compounds which are present in some industrial dusts is known to cause chronic pulmonary damage, and effects on the lungs have been reported by Conradi *et al.*[236].

The element selenium is also released into the atmosphere by industrial processes [221] and this supplements dimethyl selenide volatilised from soils by microbial action. It has been shown that a range of plant species, including grasses and crop plants can absorb, metabolise and translocate selenium from atmospheric dimethyl selenide (Zieve and Peterson, 1983 [237]).

Until quite recently, there was little published evidence of a substantial general effect on the trace-element composition of the soil resulting from air pollution, although this is the main long-term effect. The effects of air pollution on plants and soil have been reviewed by Webster, 1967 [189]. This work deals mainly with effects on plants, although references are made to enhancement of fluoride levels in soils and the possibility of enhancement of soil lead content, resulting specifically from exhaust fumes from motor vehicles. Other reviews of the literature on atmospheric pollution have also dealt primarily with direct effects on plants (Meetham *et al.*, 1964 [238]; Stern, 1968 [239]; Spedding, 1974 [5]).

There is no doubt that the contamination of the atmosphere with trace elements which commonly occurs in industrial areas can have pronounced effects on biological systems. The effects of inhalation of smoke containing particulate matter on the incidence of lung cancer in man, and on asthmatic and bronchitic subjects have been clearly demonstrated by medical statistics. Ruehling and Tyler [240] have discussed the depressant effect on the decomposition of spruce needle litter at a number of sites around two metal-processing industrial plants in central and south-eastern Sweden, emitting cadmium, copper, nickel and zinc, and cadmium, lead and nickel, respectively. Tyler has also reported inhibition of respiration rate and of phosphatase and urease activity in spruce mor, contaminated from a brass foundry in Sweden [241].

According to Tyler, 1972 [242], comparatively large quantities of deposited heavy metals may be stored in carpets of mosses and lichens and in humus layers in ecosystems. Perkins *et al.*, 1979 [243] have reported the accumulation of airborne fluoride by lichens in the vicinity of an aluminium reduction plant. Following the work of Lounama in Sweden [244], increasing attention is now being given to the accumulation of trace elements by mosses and lichens, for the dependence of these plants on the atmosphere for their mineral supply could make them suitable biological instruments for measuring metal contamination of the atmosphere. Andersen *et al.*, 1978 [245] have reported a significant linear correlation between bulk precipitation of heavy metals in the Copenhagen area and concentrations in lichens and bryophytes.

Goodman and Roberts [246] have used the content of the moss, *Hypnum cupressiforme* , with respect to cadmium, copper, lead, nickel and zinc, as a measure of atmospheric pollution with these metals downwind of the Swansea urban industrial complex in Wales. *Sphagnum* moss has been employed by Little and Martin [247], and Swaine *et al.*, 1983 [248] to monitor airborne pollution with respect to cadmium, lead and zinc around a lead and zinc smelting complex at Avonmouth in England.

The lead content of lichen has been used by Laaksovirta *et al.*, 1976 [249] as an indicator of lead emission adjacent to a highway in Southern Finlalnd. Jenkins and Davies [250] have reported a close correlation between the concentrations of contaminant trace elements in lichen ashes and values for the ash of material deposited from the atmosphere in North Wales, and have derived, from the average composition of the lithosphere, the following order of enrichment of trace elements to be expected in an organic soil due to contamination from the atmosphere: Bi, Pb, Cu > Sn, Zn, Ni > Mo, Be, Ge, Co, Cr > V, Mn. The relationship between the uptake of metals by mosses and lichens, and metal concentrations in contaminated air, however, appears sometimes to be complex and tenuous.

Both ice and snow are valuable and sensitive monitors of environmental pollution because of their normally very low metal content (Davies, 1980 [219]). The analysis of snow deposited at varying distances from a specific source of atmospheric pollution provides another means of measuring the level of contamination, and in this case, the levels measured are valid only for the time at which precipitation took place. This technique has been used by Kerin [251] to monitor lead pollution in the vicinity of a lead smelter in Yugoslavia.

It is a reasonable assumption that much of the trace-element contamination which occurs in urban areas derives from fallout from atmospheric pollution. As was pointed out in the previous chapter (2.7), there is not a great deal of difference between the levels of 'available' boron, copper, lead, nickel and zinc encountered in urban gardens and in urban parklands, where the main source of contamination is obviously atmospheric. There has been a pall of smoke over towns in the UK since the Industrial Revolution and huge quantities of domestic soot have been deposited locally, to the extent of darkening the color of the soil in many places. Hallsworth and Adams [252] have stated that over a relatively wide area of the Midlands of England, soils are receiving regular additions of chromium, copper, manganese, molybdenum, nickel and vanadium. In the author's view, cadmium, lead, mercury and zinc should certainly be added to this list.

The general level of contamination of the atmosphere with trace metals now characteristic of conurbations may be greatly enhanced when industrial activity supplements pollution from domestic sources. Two of the most serious point sources are coal or oil-fired power plants and metal smelters. Concern has been expressed for the environmental loading of trace metals currently emitted from such sources by Mastradone *et al.*, 1982 [253], and this aspect of the problem has received a great deal of attention in recent years. Zoller *et al.*, 1974 [254] and Gladney *et al.*, 1976 [255] have published data on the trace-metal composition of particulate matter in emissions from coal-fired power plants.

One of the major industrial areas in the USA is in north western Indiana along the south side of Lake Michigan. Industrial production records from this industrial urban complex indicate that approximately 650,000 tonnes of zinc, 80,000 tonnes of lead and 3,000 tonnes of cadmium were released into the atmosphere between 1900 and 1971. Reported activities did not include coal combustion (Pietz *et al.*, 1978 [256]).

Beavington [257] has reported enhancement of mean levels of acetic acid-extractable cadmium, lead and zinc and EDTA-extractable copper in soils from urban grassland, in the Wollongong city in Australia, up to ten times greater than in a rural control area. The highest levels found were in an industrial area, where the soil samples within 1 km of a metal-smelting complex were found to have mean 'available' levels of 2.8 ppm cadmium, 343 ppm copper, 21 ppm lead and 82 ppm zinc. These levels are quite alarming and very much higher than those normally associated with urban contamination.

Beavington also found correspondingly high levels of copper and zinc in herbage in the same city area [258] and reported a significant negative correlation between the herbage levels of these elements and distance from a copper smelter. Samples of urban herbage taken from within 1 km radius of the smelter, were found to contain mean levels of 170 ppm copper and 131 ppm zinc on a dry matter basis. Since the level of copper in uncontaminated rural herbage is seldom outside the range, 4-10 ppm dry matter, such a level of copper is quite unphysiological and would certainly be a serious hazard for grazing animals. The enhancement of herbage copper content in this area appears to be caused both by surface contamination of leaves and by increase in uptake by roots from contaminated soil, and reflects an exceptionally high level of atmospheric pollution with copper. Beavington, 1977 [259] has since reported total annual depositions per hectare of 30.7 kg copper, 8.4 kg zinc, 4.7 kg lead and 0.19 kg cadmium. This corresponds to an annual addition of copper equivalent to the total content of copper present in a typical uncontaminated soil. The annual cadmium addition to the soil is also a high proportion of the normal background level and dangerously high. It is of interest that vegetable gardens near this smelter contributed to the diet of local people and that they must have breathed daily an atmosphere heavily contaminated by potentially toxic metals.

High levels of cadmium, lead and zinc have been reported by Little and Martin [260] in elm leaves (up to 50 ppm Cd, 500 ppm Pb and 8,000 ppm Zn on a dry matter basis) and surface soils in the vicinity of the Avonmouth industrial complex, which includes the largest lead and zinc smelting plant in the world. Metal contamination of areas around smelting complexes has been described by a number of other workers [246, 251, 261-263]. This kind of contamination is a long-standing problem (Haywood, 1907 [264]) and it was recognized at the beginning of the century that livestock can be poisoned by the consumption of forage contaminated by lead and arsenic from smelter smoke. Methods were developed early in the century for removing solid particles from the smoke [265], but it is evident that smelters are a continuing major source of atmospheric pollution with metals. Schmitt *et al*,, [266] have reported the occurrence of lead poisoning in horses in British Columbia related to the presence of lead in surface soil, which had been accumulated from emissions from a nearby smelter.

From time to time, large quantities of a particular trace element are discharged into the environment at localized sites. On the 26th September 1976, an explosion occurred at a chemical plant in Manfredonia on the south-east coast of Italy, in which it was estimated that 10 to 30 tonnes of arsenic were dispersed in the atmosphere. Much of this arsenic was quickly deposited within a declared danger zone of six square miles and levels of 10,000 ppm arsenic were found in plants on the outskirts of the town shortly after the accident. Within a few days of this incident, 116 people had been admitted to hospital with suspected arsenic poisoning and it seems probable that arsenic levels in the soil in the area affected will be permanently enhanced.

The general situation seems to be that fallout of domestic soot and trace elements carried down by rain have produced a background level of trace element contamination in soils in urban areas which has been supplemented in the present century by fallout of lead originating in motor vehicle exhausts. Although effective measures have been taken to deal with this problem in the United States, this is still a major source of lead pollution of the atmosphere in many western countries. The general background of contamination produced by domestic chimneys and motor vehicle exhausts is differentially enhanced in certain areas by various kinds of atmospheric pollution from factory chimneys and from other sources which will be referred to in the following chapter (4.2).

A proportion of the atmospheric content of trace elements produced in urban areas must be deposited in areas downwind, so that there must also be a general background of contamination at a much lower level in soils in rural areas in industrialized and densely-populated countries. Some fallout can also be expected in nearby seas or even in other countries beyond, and Tyler [242] states that the high concentrations of cadmium and lead in the moss carpets of southern Norway and south-western Sweden, reflect an atmospheric deposition of these elements transported from remote sources, probably from continental Europe and the UK. Hanssen *et al*., 1981 [267] have published data based on analysis of moss samples indicating that arsenic, antimony, cadmium, lead, vanadium and zinc deposited in southern Norway are predominantly supplied by long distance aerial transport from other parts of Europe. Some of these elements exhibited a tenfold higher deposition than in the remoter more northerly regions of the country.

Fallout from atmospheric pollution into the ocean is unlikely to produce high local concentrations of any potentially toxic element. Dispersion of trace elements in the environment by this particular route is more efficient than by any other and no pollution problems have been reported as having arisen in this way. Problems can arise, however, from metal deposition in inland seas and lakes. Winchester and Nifong [268] have described a substantial degree of water pollution occurring in Lake Michigan due to the presence of potentially toxic metals in aerosol fallout.

Ruehling and Tyler 1970, [269] have stated that analyses of moss material preserved in old herbaria, show significant increases in metal levels from the mid-nineteenth century to the present, reflecting an increase in metal contamination of the atmosphere during this period. Also, Rassmussen, 1977 [270] has used epiphytic bryophytes as indicators of increases in the background of airborne metals in the period, 1951 to 1975. On the basis of comparisons with analyses of herbarium material, this worker has reported an increase in atmospheric metal levels in rural areas of Denmark by about one order of magnitude. National trends in trace-metal levels in ambient air in the United States have been reported by Foara and McMullen, 1977 [271].

There is a great deal of evidence that, while the greatest deposition of trace elements is concentrated locally near the source, transmission can be widespread as a result of long-range transport by wind [267, 272-275], so that natural ecosystems, even in areas remote from centers of population, are affected by the intrusion of contaminant elements into biological pathways. When non-essential elements, such as cadmium, lead and mercury are involved, the long-term consequences of this intrusion could be profound. Murozumi *et al* , [276] have reported the presence of contaminant lead in Greenland and Antarctic snow strata, and Weiss *et al*., [277] have presented evidence of enhanced levels of mercury in the Greenland ice sheet. There is now evidently widespread trace-element contamination in the polar regions, reflecting the continual circulation of air from the industrialized temperate zone towards the equator and thence to the poles via the upper atmosphere.

That fallout of trace elements from atmospheric pollution is widespread and far from confined to urban and industrial areas, is also borne out by data published by the UK Atomic Energy Authority, who determined, by neutron activation analysis, about 30 trace elements in airborne dust, rainwater and dry deposition, sampled at regular intervals in north-west England [278]. The highest concentrations measured in air were for chlorine, sodium, calcium, aluminium, iron, lead and zinc, and there were also measurable levels of antimony, arsenic and mercury, usually in the winter months, when there was a general increase in trace-element concentration. Further data were published on the atmospheric content and total deposition of a wide range of trace elements at seven non-urban sites (one in Shetland) in the UK in the years 1972 and 1973 [279]. The results of this survey have been summarized by Peirson and Cawse, 1979 [280]. Data have also been published for the North Sea and the Firth of

Clyde [281].

On the basis of these data, the equivalent additions to the top-soil in rural areas in the UK (Table 10) of elements known to be general urban contaminants, suggest that there is appreciable contamination of rural soils, from the atmosphere, with metals from industrial and urban sources. It is evident, for example, that over several years, the deposition of zinc at levels within the range in the table, could have a considerable effect on the content of zinc in the topsoil.

Rohbock *et al.*, 1981 [282] have monitored atmospheric metal deposition in the Federal Republic of Germany at 10 selected stations. This has involved analysis of dry deposited material and precipitation water for lead, cadmium, manganese and iron at regular intervals. Marked differences were found between metal deposition rates in unpolluted and polluted areas.

It may be that the enhanced levels of water-soluble boron generally found in the urban environment are largely due to fallout from soot from the burning of domestic coal [205]. The water-extractable boron content of uncontaminated rural soil is usually less than 1 ppm and five samples of soot from domestic chimneys have been found by the author to contain 640, 355, 650, 94 and 555 ppm water-extractable boron. Two samples of domestic coal ash were found to contain 375 and 75 ppm water-extractable boron, so wind-blown ash no doubt makes a contribution to boron contamination.

TABLE 10

Range of total deposition of trace elements per annum at rural sites

Element	ppm air-dry topsoil
Zn	0.14 - 0.85
Ni	0.02 - 0.36
Pb	0.07 - 0.28
Cu	0.04 - 0.21
Co	0.0006 - 0.093

The EDTA-extractable copper levels found in domestic soot were in the range, 20-50 ppm. A typical EDTA-extractable copper content in uncontaminated rural soil is 4 ppm, so fallout of soot is probably also a significant source of the background level of copper contamination. The mean copper content of rainwater in the Edinburgh area, was found to be 0.022 ppm in 1965, compared with a rural level in south-east Scotland of 0.012 (Mackenzie, 1965 [283]) and the mean addition to the soil from rain in the Edinburgh area was reported by the same author to average 0.65g copper per acre per day. This corresponds to an addition of 0.24 ppm of copper to the topsoil per annum, a level of increase which could theoretically account for the background level of soil contamination with copper commonly found in urban areas. If this level of contamination were sustained over 100 years, it would correspond to an addition of 24 ppm copper to the upper 20 cm of urban soil.

3.2 LEAD FROM PETROL

A major source of lead contamination of soil from atmospheric pollution is undoubtedly the exhausts of motor vehicles using petrol to which tetra-ethyl or tetra-methyl lead has been added, although smelting operations and smoke from fires and furnaces will also make a contribution. Contamination of herbage with lead from car exhausts is a well-established phenomenon. Warren and Delavault, 1960 [284] reported abnormally high concentrations of lead in vegetation (1,000 ppm in plant ash) in the vicinity of major highways in North America, and Cannon and Bowles [285] subsequently demonstrated that there was a concentration gradient of lead in herbage for a distance of 1,000 feet from major highways in the US.

A number of workers have since documented contamination of roadside environments with lead [249, 286-289] and Graham and Kalman [290] found levels of lead in forage grass from sites near woods in a suburban area, nearly 200 times the natural background level. There is undoubtedly substantial concomitant contamination of soil from this source and enhanced levels of lead have been reported in the bodies of small mammals living in roadside verges [61, 291]. Accumulation of lead derived from automotive exhausts in the organs of sheep has also been reported by Ward and Brooks, 1978 [65].

The general presence of a metal as toxic as lead in the urban environment has attracted considerable attention and the possible effects of direct inhalation of lead discharge in motor vehicle exhausts are of interest to clinicians and public health authorities. Indeed, the implications for health of the presence of lead in petrol have become a concern of environmentalists and a major public issue. This practice has continued for over 50 years and the quantity of lead directly dispersed as an atmospheric pollutant every year is enormous. The total world consumption of lead for use as lead alkyl additives to petrol was estimated at 350,000 tonnes in 1970, about 70 per cent of this amount being consumed in the USA [292]. Stoker and Seager [293] estimated in 1972 that about 180,000 tonnes of lead alkyls ended up in the atmosphere of the US, as emmission from motor vehicle exhausts, although steps have been taken to reduce the use of leaded gasoline progressively in the USA. An estimated figure of 700 tonnes of lead has been quoted by Ward *et al.*, [294] for the emission in New Zealand in 1970. Although consumption of lead alkyls in each country varies substantially from year to year, such figures convey an impression of the magnitude of this problem.

Although efforts are now being made in several industrialized countries to reduce this form of pollution, the total amount of lead which is continually being discharged from motor vehicle exhausts is still very great. Lead from this source probably makes the greatest single contribution to lead in the atmosphere and in some urban areas, this source may account for over 90 per cent of airborne lead [24]. It was estimated by the US National Academy of Science in 1972 that lead from automobile exhausts accounted for 98 per cent of the US atmospheric lead emission [295].

Combustion of leaded petrol in the automobile engine evidently produces complex halides which are discharged in association with the particulate fraction in the exhaust gases. These compounds are subsequently converted in the atmosphere to oxides and carbonates of lead [296]. About a quarter of the amount of lead in the gasoline consumed is retained in the engine and exhaust system.

After emission, a substantial proportion of the amount discharged in exhausts is quickly deposited in the larger lead-containing particles within 100 m of roadways. Lee and Goranson, 1972 [297] determined the particle-size distribution in the atmosphere in six urban areas in the USA and found that particles of diameter less than 1 μm constituted over 50 per cent of the weight of suspended matter in every area. Lee *et al.*, 1972 [298] also studied the relationship between the concentrations of copper, iron, lead, manganese, nickel, vanadium and zinc, and the size of the particles with which these metals are associated in the atmosphere in the same areas, and it was found that lead was concentrated in the smaller particles. With the exception of lead, vanadium and zinc, the concentrations of the metals present tended to decrease sharply with decrease in particle size, and for particles less than 0.5 μm in diameter, lead was actually the element present in highest concentration (2-4 per cent). Since particles less than 0.5 μm can be deposited in the lungs, lead associated with particulate matter appears to present a real inhalation hazard in urban areas where leaded gasoline is still being used.

Although there seems to be general agreement that most of the lead discharged from exhausts is in particulate form, an appreciable proportion remains as lead alkyl vapor. In the early seventies, Lawther *et al.*, [299] reported that in the air of Los Angeles, between 2 and 10 per cent of the lead present was in the form of lead alkyl vapor, and somewhat higher figures were reported for the air in Stockholm [300]. More recently, De Jonghe *et al.* 1981 [301] reported that around Antwerp the average alkyl lead concentration amounted to 5 to 13 per cent of the inorganic lead present in the air. This lead originated both from unchanged organic lead in exhaust fumes and from gasoline evaporation. In this form, lead can be absorbed directly into the bloodstream in the lungs and thereafter migrate into lipids present in nerve tissue.

In the United States the use of leaded gasoline has been largely phased out since 1970, although the initial impetus for the use of lead-free gasoline came not from any objection in principle to the dispersal of lead in the environment but from the need to cope with the problem of smog in the Los Angeles area. The catalytic converters required to control emissions by automobiles of the atmospheric pollutants responsible for the formation of smog are 'poisoned' by lead and require the use of lead-free gasoline. The use of these converters is compulsory in Japan and the USA.

Since the mid-seventies, lead-free gasoline has been generally available in the USA, and new automobiles have been designed to use only this kind of fuel. There has been a similar development in Canada, so that the dispersal of lead from motor vehicle exhausts has become a less serious problem in North America. However, at the time of writing (1983), it is estimated that 48 per cent of the gasoline used in the US still contains added lead.

Hoggan *et al.*, 1978 [302] reported a 50 per cent reduction in contamination of the urban atmosphere by lead particulates over the period 1971-76, as a result of increasing use of unleaded gasoline in the United States, although in some areas near interstate highways, the decrease in the proportion of traffic using lead fuel was evidently offset by the increase in traffic over the same period (Milberg *et al* , 1980 [303]). In the subsequent period, 1976-80, Pierrara *et al*, 1983 [304] have reported that a 37 per cent reduction in blood lead levels observed in the US Second National Health and Nutritional Examination Survey reflected the decrease in national usage of lead in gasoline production.

In the Soviet Union, leaded petrol has been prohibited since 1958, and elsewhere there is now pressure on Governments to reduce the lead content of petrol or to eliminate it altogether. Filters have therefore been designed for incorporation in exhaust systems which are capable of removing the bulk of the lead present. The Commission of the European Communities mounted a program in 1971 aimed at regular monitoring of lead levels in the air in major cities within the EEC, with a view to reducing the level of pollution, and an international symposium was jointly organized by the Commission and the US Environmental Protection Agency, on health aspects of lead in the environment. This was held in Amsterdam in 1972. The EEC Commission also reported in 1972 [305] that the average monthly airborne lead concentrations in the residential zone of metropolitan areas, frequently exceeded 1 μg/m^3, while at rural sites, all the monthly average levels were well below 0.5 μg/m^3. Daily averages of over 8 μg/m^3 were recorded in continental urban areas and similar levels (4.9-8.7 μg/m^3) were found in the air in central London in 1971 [299]. The EEC Commission subsequently directed that from 1981, the maximum concentration of lead permitted in gasoline would be 0.4 g/litre (Turner, 1979 [306]).

It now seems clear that inhaled lead originating in tetra-ethyl lead in high octane fuels can be absorbed into the body, because people living in cities have been found to have higher levels of lead in the blood than those in rural areas, and there is an association between high blood lead levels and occupations where there is constant exposure to exhaust fumes [307]. People employed in tunnels carrying motor vehicles, garage mechanics and traffic-control policemen in the USA have been reported as carrying blood levels of lead around 0.3 ppm, about twice the level found in the rural population. Caprio *et al*, [308] reported results of a study of a population of over 5,000 children between the ages of 1 and 5 years in New Jersey, which confirm the occurrence of excessive lead absorption in households in the vicinity of major urban highways. Blood lead levels are now commonly regarded as a useful index of several diagnostic biochemical effects and blood lead has now been correlated with air lead levels or with proximity to highways in a number of studies (Hammond, 1979 [309]).

As a result of the widespread concern felt about the elevation of blood lead levels in the urban environment, in February 1976, the European Parliament welcomed proposals by the EEC Commission to establish statutory biological standards and air quality standards for lead and to screen the population by monitoring blood levels in a sample of the population [310]. The European Parliament expressed the view that a maximum permissible blood level of 0.35 ppm could prove to be over-cautious, a statement which is difficult to reconcile with a pronouncement by Patterson [35], that the currently accepted 'safe' level in the USA (0.25 ppm) was at least ten times as high as would be necessary to provide a safe margin.

The various factors affecting blood lead concentrations in the UK have been discussed by Quinn, 1983 [311]. Patterson has suggested that the levels of lead now present in the blood and tissues of modern man are very much higher than those prevailing in pre-industrial times and that the natural level in blood corresponding to the conditions under which man evolved, is around 0.0025 ppm. On the basis of this view, what are now usually regarded as normal lead levels in Western Society could be indicative of lead toxicity at a sub-clinical level. If this is the case, we can expect children to be particularly affected, since they are known to be susceptible and there is a well-known association between lead toxicity and mental retardation or neurological illness in children [312].

There are evidently serious differences of opinion among scientific workers over what constitutes a normal blood level of lead, for Goldwater and Hoover [313], on the basis of analysis of blood from individuals in 16 countries, have suggested a 'normal' range for 'healthy' humans of 0.15 to 0.40 ppm. The lower limit of this 'normal' range is greater than the maximum level reported by Grimes *et al*, 1975 [314] for children in rural Ireland (0.13 ppm), while the upper limit is the same as the lower limit of the range found by McCallum in lead workers (0.4-0.8 ppm) [315], and is close to the threshold quoted by Patterson for acute lead poisoning (0.5-0.8 ppm). Waldron [316] suggested that adult blood lead levels should not be permitted to rise above 0.5 ppm and that for children, the upper limit should be 0.3 ppm. The possible implication of the former limit, that we should regard an adult blood level of say, 0.45 ppm, which is characteristic of industrial lead workers, as satisfactory in the population in general, is disturbing. There is a semantic difficulty here, for the words 'normal' and 'healthy' may not be adequate to describe a new ecological situation created by the general increase in blood and tissue levels over the natural level suggested by Patterson [35].

In contrast with other findings, Goldwater and Hoover [313] failed to relate blood lead levels to urbanization and industrialization. Lead is normally present as a contaminant in most analytical laboratories and, in view of the practical difficulties surrounding its determination at levels in biological material at levels less than 1 ppm, discrepancies between the findings of different investigators in this field are perhaps understandable.

Furthermore, the level of lead in blood does not appear to be a reliable measure of absorption of tetra-ethyl lead, which tends to dissolve and concentrate in lipids so that the brain and nervous system can be affected to an extent which is not reflected by the increase in blood level. Any attempt to monitor the effects on health of the discharge of lead from motor vehicle exhausts which is based solely on blood lead determinations is therefore likely to be inadequate.

The literature relating to the problem of lead pollution of the atmosphere in urban areas, arising from tetra-ethyl lead in gasoline is now extensive [36, 37, 317-326] and the environmental impact of lead from this source in the urban and industrial environment has now become a whole field of study in itself. Fortunately, this problem is now rapidly diminishing as more and more western countries introduce regulations to reduce the extent of lead dispersal. In 1983, the UK Government announced a decision to ban lead in British petrol from 1990 and the West German Government announced that catalytic converters would be fitted to all new cars in West Germany from 1986.

3.3 MERCURY

Mercury is a volatile metal and a significant proportion of the mercury dispersed in the environment takes the form of atmospheric pollution. It has been estimated by Van Horne, 1975 [327] that over 50 per cent of combined natural and industrial emissions of mercury enter the atmosphere. In addition to being present in smoke from some industrial sources, mercury vapor can be liberated from soils contaminated with mercury compounds as a result of reduction in the soil to elemental mercury. Waldron and Terry [328] have reported that both inorganic and organic mercurial fungicides are reduced in the soil, particularly in soils high in organic matter, and that in greenhouse conditions, the vapor produced can be damaging to plant leaves after brief exposures at a concentration of 2.15 mg/m^3. Earlier reports of toxic effects of mercury vapor extend over a century [329].

A major source of mercury contamination of the environment is now the chlor-alkali industry which uses a continuous flow mercury cathode cell to produce chlorine and caustic soda. D'Itri, 1972 [104] estimated that the loss of mercury into the environment in the USA from this single industrial process was in excess of 450 tonnes. Although the most serious effects of mercury pollution from this source affect the hydrosphere, some of this mercury is discharged into the atmosphere and there may be appreciable effects of fallout on the soil environment. Wallin, 1976 [330] has employed moss analysis to measure the deposition of airborne mercury from six Swedish chlor-alkali plants and has reported relatively high mercury levels in moss in close proximity to the plants, the mercury level decreasing exponentially with distance from the source.

Mercury pollution of soils caused by air transport has also been reported by Lindberg *et al.*, 1979 [331] in the vicinity of the Almaden mercury mine in Spain, the most important deposit of cinnabar in the world. These authors have reported accumulation of mercury by alfalfa in this area due both to root uptake and absorption of mercury vapor from the atmosphere.

3.4 FLUORINE

Fluorine is another potentially-toxic trace element which is dispersed by atmospheric pollution and it has long been recognized that damage to plants occurs and that there is a hazard to man and farm stock, in the vicinity of industrial plants processing fluoride-containing minerals. Such plants include factories for the production of aluminium, superphosphates and compound fertilizers based on the liberation of phosphoric acid from rock phosphate.

In October 1976, ten cows had to be destroyed on two farms in the vicinity of the British Aluminium Company's aluminium smelter at Invergordon in the north of Scotland, and problems of fluoride toxicity have been commonly associated elsewhere with the production of aluminium. Perkins *el al.*, 1979 [243] reported an accumulation of airborne fluoride by lichens in the vicinity of an aluminium reduction plant in North Wales, and Polamski *et al.*, 1982 [332] found a decreasing accumulation of airborne fluorides in soils over a distance of 9 km from an aluminium smelter in Switzerland. The consequences of contamination of soils with fluoride, however, appear to be much less serious than those of direct exposure to fluoride contaminated air.

Fluoride accumulation in both soil and vegetation has been reported by Thompson *et al.*, 1979 [333] in the vicinity of a phosphorus plant in Newfoundland and fluoride volatilization during the production of wet process phosphoric acid has been reported to be in the range, 46-99 kg F/tonne of P_2O_5 in the phosphoric acid produced [334]. However, scrubbers are now installed at points where fluorides are liberated, and they are absorbed in water to prevent atmospheric pollution.

To a limited extent, fluoride is recovered as fluosilicic acid (H_2SiF_6) during fertilizer manufacture, for use in fluoridation of water supplies or for use in the aluminium industry [334]. Although the volatilization of fluoride during the manafacture of fertilizers is now being minimized, the disposal of scrubber effluents and calcium fluoride (CaF_2) produced during the manufacture of superphosphates, provides a possible route for the dispersion of fluoride in the soil. Fluoride may also be volatilized during the manufacture of steel, glass, bricks and ceramics [219] and during the production of hydrofluoric acid (HF).

Such industries can produce high local concentrations of fluoride, but coal-burning may make a more general contribution to fluoride dispersal. Coal and shale have been reported as containing up to 120 and 500 ppm fluorine respectively [335], and Davison *et al.*, [336] have reported modal concentrations in northern England of 0.05 and about 0.3 μg F/m^3 at rural sites and in mining areas, respectively, the concentrations being particularly high near burning coal bings. The toxicity of gaseous fluorides, such as hydrogen fluoride (HF) and silicon tetrafluoride (SiF_4), to all biological systems is well-known [337], and fluoride is known to enter biological food chains. Wright and Davison, 1978 [338] have reported fluoride accumulation in the bodies of long-tailed field mice and field voles living in polluted environments. Damage to plants associated with characteristic hypochlorotic and necrotic lesions, commonly occurs in the vicinity of industrial sources of contamination. Scurfield, 1960 [339] has reported that as much as 150 km^2 of *Pinus ponderosa* forest has been affected by fluoride pollution of the atmosphere.

Gaseous fluorides are readily absorbed by leaves through the stomata and the metabolic effects of atmospheric fluorides on plants have been discussed by McCune *et al.* [340-342]. It has been stated by Pearson *et al.* [343] that fluoride absorbed by leaves is conducted towards the margins of broad leaves and to the tips of monocotyledonous leaves, so that little injury occurs at the sites of absorption, whereas the margins or tips of the leaves build up an injurious concentration. These authors state that apricot, plum, grape, gladiolus, tulip, iris and sweet corn are sensitive to fluoride injury, while resistant plants include celery, cucumber, cabbage, cauliflower, soybean and tobacco.

Fluorosis in farm animals resulting from high intake of fluoride is characterized by dental and skeletal defects. This disorder, although naturally endemic in some areas where the drinking water contains high levels of fluoride, is often associated with the presence of local concentrations of fluoride in fumes or wind-blown dusts from industrial sources, so that toxic levels are directly inhaled, or ingested as a result of the contamination of pasture herbage or fodder. Allcroft, 1959 [344] reported serious effects on animals in pastures adjoining brickworks, and air quality standards, based on the fluoride content of vegetation, proposed by Suttie in 1969 [345], have been adopted in some of the states in the USA. MacLean and Schneider [346] have stated that since the pattern of exposure of leaves to hydrogen fluoride affects the rate and amount of fluoride accumulated by timothy grass and red-cover, pollution abatement action to protect livestock from ingested fluoride should be based on the fluoride content of forage, rather than on the concentration of airborne fluorides. This view has been supported by Davison *et al.*, 1979 [347]. In view of the possibility of surface contamination, or direct inhalation of fluoride, perhaps it is necessary to take both the concentration in air and herbage into account.

Fluorosis is also sometimes associated with the use of mineral phosphates as dietary supplements for livestock, since these products may contain undesirably high levels of fluoride. The level present in mineral phosphate is a consequence of the geochemical conditions which obtained during deposition, and North African and North American mineral phosphate usually has about twice the content of fluoride (3-4 per cent) which is present in deposits in islands in the Pacific and Indian Oceans [167].

Most plant species appear to have a limited capacity to absorb fluorine, even from contaminated soils [348], and the fluorine content of uncontaminated plant material grown on such soils is normally low enough to make the development of fluorosis in livestock unlikely. A number of Australian grasses analyzed by Harvey [349, 350], some of which had been grown in areas irrigated by water substantially contaminated with fluoride, were found to contain fluorine levels restricted to the range 1 to 2 ppm. It appears, therefore, that serious long-term consequences of the dispersion of fluorine in the terrestial part of the biosphere are unlikely, once the source of contamination has been removed.

Although fluoride is very toxic at high concentrations, fluorine is a trace element naturally present in the diet which is essential for the formation of healthy bones and teeth, and resistance to dental caries is substantially reduced in children whose intake is inadequate at the stage of enamel formation. The average dietary intake of fluoride in the United Kingdom has been estimated by Walters *et al.*, 1983 [351] to be 1.8 mg/day, although the level ingested varies widely according to the amount of tea consumed. Tea leaves contain

relatively high levels of fluorine (100-200 ppm dry matter), and Walters *et al.* have stated that above-average consumption of tea could result in fluoride intakes as high as 8.9 mg/day. Much of the fluoride ingested by humans dependent on water from wells must originally have been obtained from the water supply. It has been established that the optimal level of fluoride in drinking water, for the prevention of dental caries, is about 1 ppm.

However, since the population no longer obtains most of its drinking water from wells, and most supplies are now obtained from reservoirs containing rain-water which has run off quickly from limited catchment areas, the levels of mineral nutrients present, such as calcium, magnesium and fluoride, may often be lower than those present in well water. The level of fluoride normally present in public water supplies is therefore often well below the desirable nutritional level of 1 ppm and sometimes it can be as low as 0.1 ppm. On the other hand, in some areas, particularly where water is obtained from deep wells, fluoride concentrations in drinking water are naturally as high as 4 to 8 ppm. In such areas, mottled enamel in teeth is common, though teeth have high resistance to dental caries.

Hundreds of communities in various parts of the world have now had the fluoride level of the water supplies adjusted to a level of 0.8 to 1.2 ppm and the value of this measure as a means of securing better dental health for a whole community has been clearly demonstrated [167] (pp. 356-8), although its effectiveness may be reduced for communities where tea drinking is habitual. Opponents of fluoridation usually describe it as 'mass medication', although this measure is not concerned with medical treatment, but is a preventive nutritional measure designed to minimize dental caries. Fluoridation can properly be described as a necessary adjustment of the supply of an essential nutrient which is deficient in the local water supply. In principle, it is difficult to distinguish fluoridation as a public health measure from the other measures which are now established as necessary to ensure that water is potable and possesses a desirable composition, for example, chlorination and adjustment of hardness.

In view of the numerous real environmental hazards to which the human population is now exposed, it is regrettable that so many of these should be ignored, while vigorous and largely unfounded attacks should be made on what is one of the most spectacularly successful public health measures ever devised.

TRACE METALS IN PRECIPITATION IN SWEDEN

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Abstract. Trace metals (Cd, Cu, Fe, Mn, Pb, and Zn) concentrations in atmospheric precipitation have been routinely monitored in Sweden since the autumn of 1983. Concentrations are highest in southern Sweden and decrease northward. It is postulated that the long range transport of anthropogenic pollutants from the rest of Europe is the major source of Cd, Pb, and Zn in precipitation. Evidence for this hypothesis is that enrichment factors indicate anthropogenic origin, and Swedish atmospheric emissions of Zn and Cd are 2 to 3 times smaller than deposition fluxes. Also, Cd, Pb, and Zn concentrations are correlated in both space and time and are also well correlated with $exSO_4^{=}$, a substance known to be of anthropogenic origin transported long distances.

1. Introduction

The advent of industrial processes, such as metal refining and fossil fuel combustion, has led to a substantial increase of trace metals in the atmosphere. The atmosphere, via wet and dry deposition, is now a significant source of many trace metals to ecosystems in and around industrial areas. Trace metals such as Cd, Hg, As, and Pb, which are highly toxic even at low levels (Gough *et al.*, 1979), are known to be accumulating in the biosphere (Hutton, 1984; Lindberg and Harriss, 1981; Salomons and Förstner, 1984; Tyler, 1984) and are to a great extent cycled through the environment by atmospheric transport (Lantzy and Mackenzie, 1979).

To assess any temporal or spatial changes in atmospheric trace metal deposition in Sweden, a survey of metal concentrations in mosses is performed every 5 yr (Rühling and Tyler, 1984). While moss studies are useful in assessing temporal and relative spatial differences in trace metal input, they do not provide information on the absolute magnitude of atmospheric deposition, or temporal variability on seasonal or shorter time-scales. Therefore, the routine monitoring of trace metals in atmospheric precipitation was begun in 1983 (SNV, 1985).

The determination of trace metals in precipitation is difficult because samples can be easily contaminated. Ross (1986) demonstrated that rainwater samples could be greatly contaminated by the storage bottles if the bottles were not washed in acid. This was due to the desorption of metals from the walls. Of the metals studied, contamination was greatest for Cd, Cu, and Zn. In some instances, Cu concentrations could be 50 times higher in samples collected and stored in water-washed bottles than in samples from acid-washed bottles.

The first results from this monitoring program indicated that trace metal wet deposition in Sweden is lower than several previously reported values for Scandinavia.

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Subsequently, this has led to decreased estimates of Cd, Cu, Pb, and Zn wet deposition fluxes to the Baltic Sea (Ross, 1986). A second consequence of reducing sample contamination is that correlations between metal concentrations could be observed. In this article, we study these correlations in greater detail and propose that they are a consequence of long range transport of anthropogenic pollutants from the rest of Europe.

2. Experimental

Precipitation is collected for trace metal analysis, on a monthly basis at 9 sites in Sweden (Figure 1, starting dates are given in the caption). At each site there are three bulk collectors. Collectors are placed in forest clearings, 1 m above the ground and at least 10 m from the nearest tree. The maximum distance between collectors does not exceed 40 m. Stations are at least 500 m from the nearest road and building. Trace metal concentrations are determined using graphite furnace atomic absorption spectroscopy (GFAAS). A description of the analytical methods and the procedures to avoid sample contamination are given in Ross (1984).

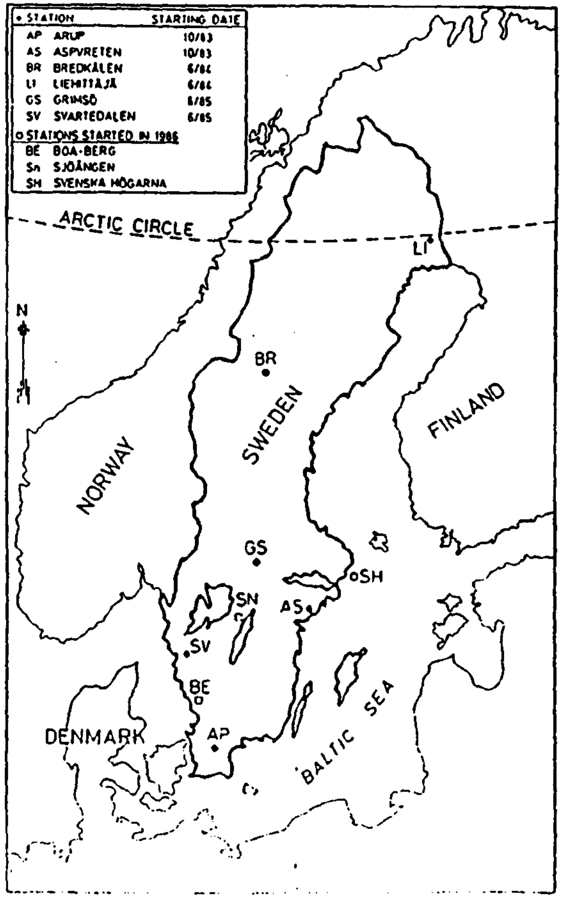

Fig. 1. Locations in Sweden where atmospheric precipitation is collected for heavy metal analysis.

3. Results

Trace metal concentrations are given in Table I. Highest concentrations are found in southern Sweden (stations AP and AS), and the lowest are at station BR. Concentrations at this station are a factor of 3 to 5 lower than at stations AP and AS. The

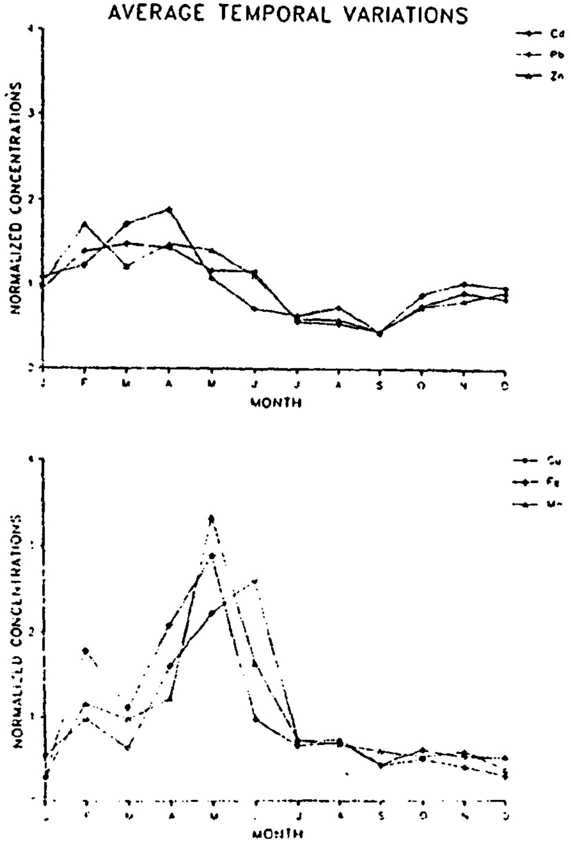

Fig. 2. Temporal variations in monthly trace metal concentrations. Concentrations have been normalized by dividing by the mean concentration.

TABLE I

Trace metal concentrations in precipitation and precipitation amount at 6 sites in Sweden. See Figure 1 for station locations and when measurements were started. Yearly precipitation amounts are given in parentheses.

	Cd	Cu	Fe	Mn	Pb	Zn	H_2O (mm)
	(units: μg L^{-1})						
Station AP ($n \approx 23$)							
Arithmetic mean	0.17	1.6	67	9.1	10	20	66
CV	67%	54%	110%	84%	60%	62%	56%
Minimum	0.036	0.53	12	2.6	4.2	4.4	5
Maximum	0.77	5.5	350	36	45	66	135
Median	0.13	1.5	45	6.2	8.1	18	60
Lower quartile	0.094	0.82	21	3.9	6.0	10	36
Upper quartile	0.24	1.9	72	12	13	27	92
1985 vol. wt. mean	0.13	1.3	40	8.8	7.5	17	(655)[a]
1984 vol. wt. mean	0.13	1.3	68	7.7	9.0	16	(614)[a]
Station AS ($n \approx 25$)							
Arithmetic mean	0.17	1.7	74	7.1	9.9	18	43
CV	69%	84%	120%	79%	62%	62%	64%
Minimum	0.022	0.47	7.7	1.5	2.6	5.2	5
Maximum	0.49	6.3	410	24	27	50	104
Median	0.15	1.1	46	5.5	8.5	15	39
Lower quartile	0.073	0.72	25	3.9	5.3	9.4	22
Upper quartile	0.22	2.4	74	6.9	12	24	66
1985 vol. wt. mean	0.17	1.9	55	6.0	10	19	(485)
1984 vol. wt. mean	0.13	1.0	53	5.6	7.8	14	(527)
Station BR ($n \approx 19$)							
Arithmetic mean	0.037	0.50	12	2.4	2.0	4.8	56
CV	59%	66%	80%	64%	55%	67%	54%
Minimum	<0.010	0.13	<0.2	0.08	0.03	0.9	10
Maximum	0.085	1.2	31	6.1	4.3	14	112
Median	0.034	0.40	8.4	2.7	1.8	3.7	53
Lower quartile	0.022	0.24	2.6	1.3	1.3	2.8	34
Upper quartile	0.042	0.72	19	3.5	3.0	7.0	76
1985 vol. wt. mean	0.033	0.53	10	2.6	1.8	4.4	(690)
Station LI ($n \approx 17$)							
Arithmetic mean	0.083	1.6	18	3.7	3.9	13	44
CV	80%	79%	70%	60%	64%	83%	75%
Minimum	0.016	0.39	2.7	1.2	1.0	2.5	5
Maximum	0.29	5.3	50	8.2	11	40	120
Median	0.066	1.2	17	2.7	3.3	8.1	43
Lower quartile	0.039	0.59	8.6	1.9	2.0	6.1	13
Upper quartile	0.11	2.2	21	5.1	4.7	17	66
1985 vol. wt. mean	0.088	1.5	18	4.9	4.1	13	(386)[b]
Station GS ($n \approx 5$)							
Arithmetic mean	0.084	1.1	26	2.9	5.9	9.8	74
CV	51%	59%	66%	44%	29%	42%	55%
Minimum	0.040	0.50	4.8	1.5	3.7	6.5	6
Maximum	0.15	2.0	46	5.0	7.9	16	121
Station SV ($n \approx 6$)							
Arithmetic mean	0.076	0.63	20	2.0	5.9	9.0	100
CV	30%	50%	66%	45%	26%	30%	38%
Minimum	0.049	0.35	6.5	0.98	3.3	5.5	39
Maximum	0.10	1.6	42	1.6	7.7	12	152

[a] 10 months only.

[b] 11 months only.

coefficient of variation (CV) is a measure of the variability of a data set and is defined as the standard deviation of the population divided by the arithmetic mean. For Cd, Cu, Mn, Pb, and Zn, CVs are typically 50 to 80%. Coefficients of variation for Fe are higher, ranging between 70 to 120% (Table I). Maximum and minimum concentrations at each station indicate that there can be large month to month variations. For all metals except Fe, typical ratios between maximum and minimum values are about a factor of 10 to 20. For Fe the differences are much greater, a factor of 30 to >150.

For stations AP and AS, 1984 and 1985 volume weighted mean (VWM) concentrations could be calculated. At station AP, Cd, Cu, Mn, Pb, and Zn concentrations are nearly the same for both years. Iron concentrations are about 30% higher in 1984. At stations AS in 1985, Cu concentrations are about 2 times higher. Cadmium, Pb, and Zn values are about 20% higher in 1985, while Fe and Mn concentrations are approximately the same.

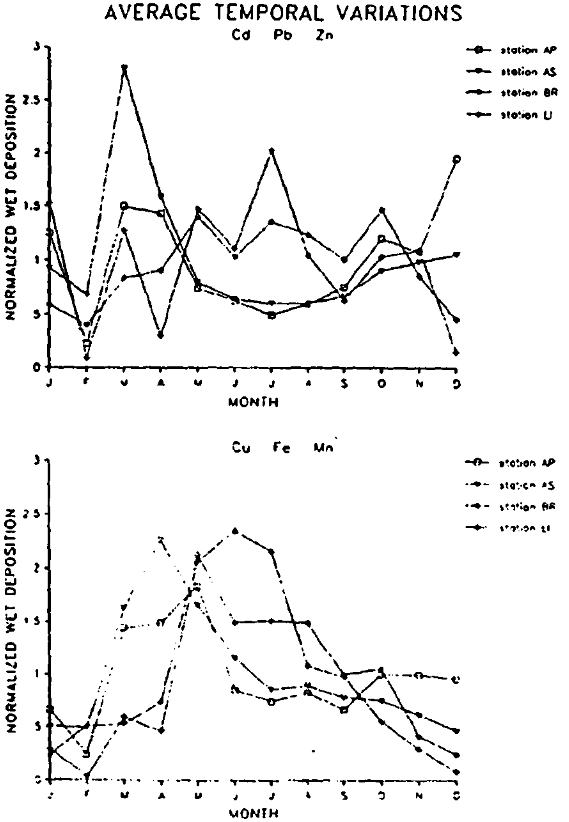

Fig. 3. Temporal variations in trace metal wet deposition at stations AP, AS, BR, and LI. Fluxes have been normalized by dividing by the average monthly wet deposition at each station.

In Figure 2 the temporal variation of trace metal concentrations are shown. Concentrations have been normalized by dividing by the average. Cadmium, Pb, and Zn concentrations have similar variations, concentrations are highest in February, March, and April. In contrast, concentrations of Cu, Fe, and Mn peak in the spring. In addition, variations in their concentrations are much larger than those of Cd, Pb, and Zn. We interpret the differences in temporal variations as an indication that the atmospheric processes which govern the deposition Cd, Pb, and Zn are different than those Cu, Fe, and Mn.

Figure 3 presents the average temporal variation of trace metal wet deposition at stations AP, AS, BR, and LI. At station AP and AS, highest trace metal wet deposition is in the spring. In contrast, stations BR and LI have maximum wet deposition in the summer half of the year. The differences in wet deposition for the southern stations and those in the north are most likely due to seasonal variations in precipitation.

TABLE II

A comparison of trace metal concentrations in precipitation falling in Sweden to values reported in the literature for other rural locations.

	Cd	Cu	Fe	Mn	Pb	Zn
	(units: µg L^{-1})					
Sweden[a]						
Station AP	0.13	1.2	48	7.6	8.2	16
Station AS	0.15	1.4	54	5.7	9.0	16
Station BR	0.033	0.46	12	2.4	2.0	4.2
Station LI	0.072	1.5	16	4.2	3.4	10
Rural sites[b]	0.5	5.4		5.7	12	36
FRG[c]	0.3	3.0–4.1	57		12–14	16–25
Ontario, Can.[d]						
South	0.12	1.6	52	4.7	7.0	4.9–10
Central	0.11	1.4	35	2.7	6.5	
North	0.12	1.6	40	3.1	3.0	
S.E. Appalachia, U.S.A.[e]		0.04–0.24		1.3–3.2	3.2–5.6	4.9–10
Delaware[f]	0.18	0.68	15	1.4	3.0	6.5
N. Dakota and Minnesota[g]						
	0.15–0.70	2.1–3.9	38–160	3–22	5.7–8.0	90–150
(snowpack)	0.05–0.73	0.55–3.8	50–810	3.2–78	4.9–17	2.7–33

[a] This study; volume weighted means

[b] Galloway *et al.*, 1982, medians

[c] Nürnberg *et al.*, 1983; Thomas, 1982, rural sites, daily samples, wet only collectors.

[d] Chan *et al.*, 1986, VMW monthly means, wet only collectors.

[e] Lindberg and Turner, 1983, 4 sites

Church *et al.*, 1984; monthly means, wet only collectors.

[g] Thornton and Eisenreich, 1982; wet only collectors, daily samples

3.1. CONCENTRATIONS COMPARED TO LITERATURE VALUES

In Table II (VWM) concentrations are compared to values reported in the literature for other rural sites. Concentrations are first compared to median values for rural locations estimated by Galloway *et al.* (1982) and then to other data sets where special care has been taken to avoid sample contamination.

Cadmium, Cu, and Zn concentrations in Sweden are significantly lower than the estimates made by Galloway *et al.* (1982). Ross (1986) and Barrie *et al.* (1987) have attributed this to sample contamination of a portion of the older samples. Cadmium, Cu, and Pb concentrations at rural sites in the Federal Republic of Germany (Nürnberg *et al.*, 1983; Thomas, 1982) are about two times higher than values in southern Sweden. In contrast, Fe and Zn concentrations are approximately the same. With the exception of Zn, concentrations in southern Sweden are similar to values found in southern Ontario (Chan *et al.*, 1986). However, there are differences in spatial trends; Cd, Cu, Pb, and Zn concentrations in Sweden decrease northward by a factor of 3 to 5 (compare concentrations at stations AP and AS to station BR). Only Pb has a similar gradient in Ontario, over approximately the same distance. Trace metal concentrations reported by Lindberg and Turner (1983) for precipitation in the southeastern Appalachian Mountains (U.S.A.) are similar to those at stations LI and BR. The concentrations at a mid-Atlantic site (Lewes, DE, U.S.A.) reported by Church *et al.* (1984), are also similar to the values found in Sweden.

Thornton and Eisenreich (1982) reported trace metal concentrations in precipitation collected in wet-only collectors and in snowpack along an east-west transect in north central U.S.A. Ranges of Cd, Pb, and Cu concentrations are similar to values found in Sweden. However, Zn concentrations are substantially higher, leading us to believe that their samples may have been contaminated. Zinc contamination by wet only collectors has been shown to be a severe problem by Slanina *et al.* (1979) and by Haraldson and Magnusson (1983).

In March 1984, the snowpack of northern Sweden was sampled for trace metals and major ions (Ross and Granat, 1986). Two of the sites were at stations BR and LI. In

TABLE III

Trace metal concentrations and precipitation amount at stations BR and LI for the winter of 1985 (December 1984–February 1985) and the 1984 snowpack

	Cd	Cu	Fe	Mn	Pb	Zn	H_2O
	(units, µg L^{-1})						(mm)
Station BR							
Wet deposition	0.041	0.73	3.5	1.0	1.0	5.1	117
Snowpack	0.018	0.20	4.3	0.98	1.25	1.4	257
Station LI							
Wet deposition	0.21	2.0	18	4.1	7.7	34	30
Snowpack	0.052	0.48	12	1.46	3.40	5.1	241

Table III the snowpack concentrations are compared to 1985 winter VWM concentrations at these stations. At station BR, Cd, Cu, and Zn concentrations are about 2 to 4 times higher in 1985 than in 1984, Mn values are approximately the same, while Fe and Pb concentrations are somewhat lower. With the exception of Fe, 1985 concentrations at station LI are 2 to 7 times higher than in 1984. We think these differences are partially due to the precipitation amount.

4. Discussion

4.1. ORIGIN OF TRACE METALS IN WET DEPOSITION

Enrichment of trace metals in wet deposition with respect to crustal material can be assessed by calculating an enrichment factor (EF). Assuming that all of the Fe in wet deposition is from crustal sources, then an EF for element X is defined as:

$$\mathrm{EF} = \frac{(X/\mathrm{Fe})_{\text{wet dep.}}}{(X/\mathrm{Fe})_{\text{crust}}} ,$$

where the mean composition of crustal material reported by Mason (1966) is used in the denominator. An EF approaching unity indicates that an element has few sources other than wind blown crustal material.

EFS are given in Table IV. All of the metals studied are enriched relative to crustal material. The order of enrichment is Cd > Pb > Zn ⩾ Cu > Mn. In the absence of other large natural sources, it is concluded that their major source is anthropogenic emissions. EFs at stations BR and LI are about two times larger than at stations AP and AS. Also, EFs for Cd, Cu, Pb, and Zn, are at least two times higher in winter and autumn than in spring and summer. This is partly attributed to snow cover, which reduces winter atmospheric Fe emissions.

TABLE IV

Enrichment factor (EF) relative to crustal material

	Enrichment factor				
	Cd	Cu	Mn	Pb	Zn
Station AP	1000	33	10	960	330
Station AS	970	30	7	880	300
Station BR	2500	140	17	1300	830
Station LI	2400	140	16	1600	1400
All stations:					
Spring	550	28	5	450	200
Autumn	1800	81	14	1600	600
Summer	500	41	10	520	200
Winter	2600	110	11	1600	920

TABLE V

Atmospheric anthropogenic Cd, Cu, Pb, and Zn emissions in Sweden for 1978 and 1984–1985 (Tom Hedlund, Swedish Environmental Protection Board, personal communication) and trace metal wet deposition to Sweden

Emission source	Cd	Cu	Fe[a]	Mn[a]	Pb	Zn
	(units: tonne yr^{-1})					
Mines	0.2	25			20	30
Ferrous metal production	0.6	7			52	280
Non-ferrous metal production	7	70			180	190
(Rönnskärsverket)	(2.1)	(26)			(88)	(83)
Gasoline combustion					700	
Other	0.4				9	12
1984–1985 Total	8	100			960	510
1978 Total	12	280			1600	1200
Wet deposition fluxes	(units: tonne yr^{-1})					
Southern Sweden[b]						
Mean concentration (μg L^{-1})	0.14	1.3	52	6.6	8.6	16
Flux (tonne yr^{-1})	13	120	4700	600	770	1400
Northern Sweden[c]						
Mean concentration (μg L^{-1})	0.053	0.97	14	3.4	2.7	7.1
Flux (tonne yr^{-1})	9.5	170	2500	610	490	1300
Wet deposition to Sweden	22	290	7200	1200	1300	2700

[a] No available information on Fe and Mn anthropogenic emissions.
[b] Area: 150000 km^2; wet deposition: 600 mm yr^{-1}.
[c] Area: 300000 km^2; wet deposition: 600 mm yr^{-1}.

Swedish Cd, Cu, Mn, Pb, and Zn anthropogenic emissions to the atmosphere are about 2% of the total for Europe (Pacyna, 1984). In Table V estimates of emissions from Swedish sources for 1978 and 1984, 1985 are given. These data indicate that in recent years a large scale decrease of trace metal emissions has occurred in Sweden. Metal production accounts for about 90% of the Cd and Zn anthropogenic emissions from Swedish sources. Lead emissions are mainly from gasoline combustion (70%) and metal production (25%). A significant portion of Cd, Cu, Pb, and Zn emissions occurs from a single point source, Rönnskärsverket, a large smelter on the Baltic coast of northern Sweden.

In Table V yearly wet deposition of trace metals to Sweden are also given. In calculating fluxes, the country was divided into two parts; southern Sweden (the bottom third of the country) and northern Sweden. Average trace metal concentrations in wet deposition in southern Sweden are the average of VWM concentrations at stations AP and AS. Concentrations for northern Sweden are the average of VWM concentrations at stations BR and LI. The yearly amount of wet deposition was taken to be 600 mm yr^{-1}, the climatological mean value for Sweden.

Yearly emissions of Pb in Sweden are only 26% lower than the wet deposition flux. In contrast, Cd, Cu, and Zn anthropogenic emissions are 3 to 5 times smaller than wet deposition fluxes. While estimates of anthropogenic emissions and wet deposition are uncertain, these calculations indicate that emissions in Sweden can not totally account for Cd, Cu, and Zn wet deposition.

4.2. LINEAR REGRESSION ANALYSIS

Linear regression analysis was used to study relationships in trace metal concentrations. Table VI presents the correlation coefficient (r) matrix. All correlations are significant to $p = 0.001$ level. Cd, Pb, and Zn concentrations have the highest correlation, with $r \approx 0.9$ (Figure 4). These results indicate that the processes governing Cd, Pb, and Zn deposition are on the average similar.

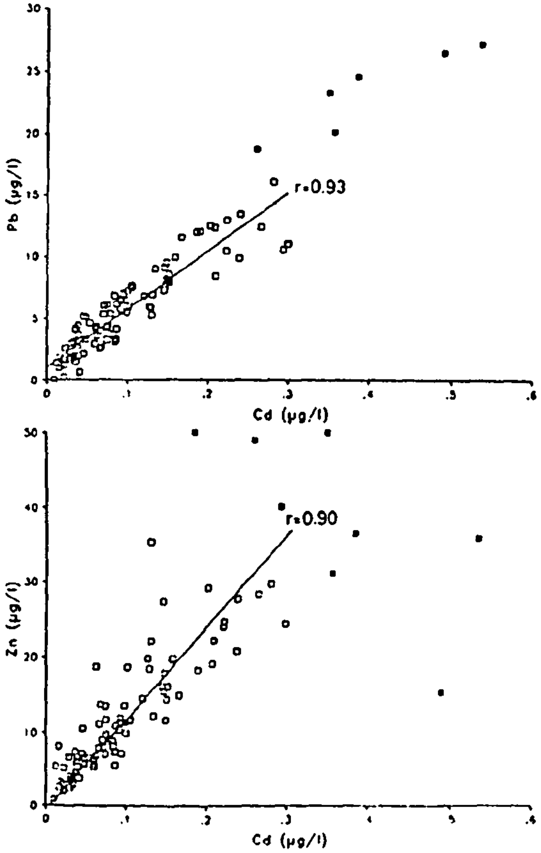

Fig. 4. Scatter plots of Cd to Pb and Zn. Regression lines and correlation coefficients are indicated. Points greater than the mean plus 2σ are darkened and were not used in the analyses.

TABLE VI

Correlation matrix (r) for trace metals in precipitation. In the linear regression analyses data greater than the mean plus 2σ were not used.

	Zn	Pb	Mn	Fe	Cu
Cd	0.90	0.92	0.51	0.46	0.61
Cu	0.68	0.54	0.63	0.48	
Fe	0.52	0.56	0.74		
Mn	0.58	0.54			
Pb	0.85				

TABLE VII

Regression (c = slope and b = intercept) and correlation (r) coefficients for the ratios Pb/Cd, Pb/Zn, and Cd/Zn. All correlations are significant to a 95% confidence level.

Pb/Cd	Pb/Zn	Cd/Zn
Correlation coefficient: r Regression coefficients: c (95% confidence interval) b (95% confidence interval)		
Station AP ($n \approx 19$)		
0.93	0.77	0.85
43 (34–51)	0.34 (0.20–0.48)	0.0080 (0.055–0.011)
2.1 (0.80–3.5)	2.9 (0.43–5.3)	0.014 (−0.030–0.058)
Station AS ($n \approx 21$)		
0.90	0.91	0.93
38 (30–47)	0.37 (0.28–0.45)	0.0089 (0.0073–0.011)
2.7 (1.4–4.1)	2.3 (0.91–3.7)	−0.0006 (−0.028–0.028)
Station BR ($n \approx 18$)		
0.71	0.58	0.78
35 (18–53)	0.20 (0.057–0.34)	0.0054 (0.0032–0.0076)
0.67 (−0.093–1.4)	1.0 (0.21–1.8)	0.011 (−0.002–0.024)
Station LI ($n \approx 14$)		
0.95	0.68	0.64
44 (36–53)	0.22 (0.079–0.37)	0.0045 (0.0012–0.0077)
0.36 (−0.31–1.0)	1.3 (−0.28–2.9)	0.027 (−0.009–0.062)
All stations ($n \approx 85$)		
0.93	0.85	0.90
47 (43–52)	0.40 (0.35–0.46)	0.0084 (0.0075–0.0092)
1.0 (0.54–1.5)	1.0 (0.27–1.7)	0.001 (−0.010–0.013)

It was also observed that Pb/Cd, Mn/Fe, Cd/Zn, and Pb/Zn ratios are fairly constant during the year. In contrast, Fe and Mn concentrations relative to Cd, Pb, and Zn are at least 2 times higher in summer than in winter. This indicates that atmospheric Fe and Mn during summer and winter elements have different sources, source strengths or atmospheric chemistry than Cd, Pb, and Zn.

In Table VII the regression (slope and Y-intercept) and correlation coefficients for Cd/Pb, Cd/Zn, and Pb/Zn ratios at stations AP, AS, BR, and LI are given. Cadmium, Pb, and Zn concentrations are well correlated at each station. The highest correlation is at station AS ($r \approx 0.90$) and the lowest is at station BR ($r = 0.58$–0.78). At all of the stations, Pb/Cd ratio has the highest correlation, and to a 95% confidence level, there is no significant difference in the slopes of the regression equations. Pb/Zn and Cd/Zn ratios at stations BR and LI are similar to one another, and are about 30 to 40% lower than the slopes at stations AP and AS.

Regression analyis of the 1984 snowpack survey also indicated that Cd, Pb, and Zn concentrations are highly correlated (Ross and Granat, 1986). A comparison of regression equations from the snowpack data and winter precipitation samples (December–February) indicate that for 14 of a possible 15 ratios there is no significant difference (95% confidence level) in the regression equations. Only the Zn : Cd coefficients were significantly different, and they varied by < 40%. The good agreement between the regression coefficients indicates that the processes determining trace metal deposition throughout Sweden during winter months are generally the same.

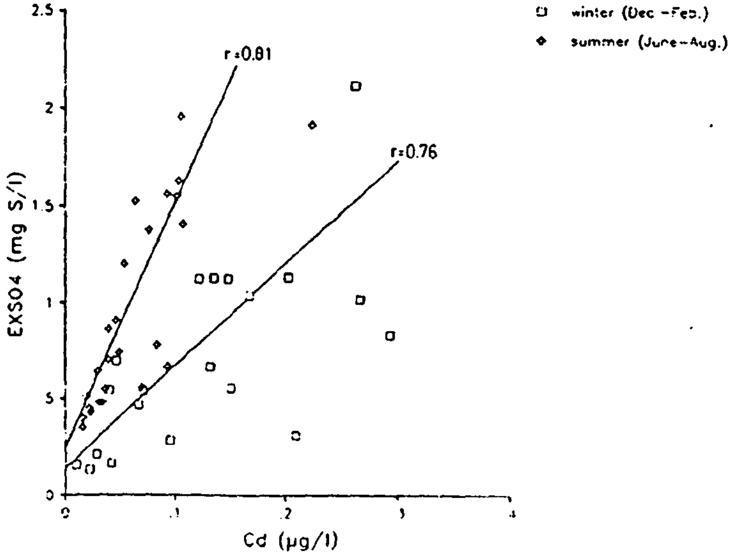

Fig. 5. Scatter plots of exSO$_4^=$ and Cd concentrations for winter and summer months. Regression lines and correlation coefficients are indicated. In both cases, correlations are significant to the 95% confidence level.

The very high EFs of Cd, Pb, and Zn indicate that their major source is anthropogenic emissions. However, Swedish emissions of Cd and Zn are smaller than wet deposition fluxes. Also Cd and Zn are not emitted to the atmosphere from gasoline combustion. Therefore, to explain and spatial correlation in Cd, Pb, and Zn concentration, it is concluded that their wet deposition is primarily governed by long-range transport of anthropogenic emissions from Europe.

At each station precipitation is also collected for major ion analysis (SNV, 1985). Trace metal and major ion collectors remain in the field for the same time, thus concentrations are directly comparable. To test the hypothesis that the major source of Cd, Pb, and Zn is long-range transport of anthropogenic pollutants, their concentrations were plotted against exSO$_4^=$ (i.e., that sulfate remaining after the sea salt component is subtracted) because it is widely accepted that exSO$_4^=$ wet deposition in Sweden is mainly governed by the transport of anthropogenic S from the rest of Europe (OECD, 1977). In Figure 5 exSO$_4^=$ concentrations are plotted against Cd for winter and summer months. Correlation coefficients are 0.81 and 0.72, respectively. While not presented, spring and fall correlation coefficients are 0.88 and 0.74. Similar correlations are found when Pb and Zn concentrations are plotted against exSO$_4^=$. We view these high correlations as support for our hypothesis that the major source of Cd, Pb, and Zn is long range transport.

Further evidence is given by the poor correlation of Cd, Pb, and Zn concentrations with Na (Figure 6). The regression coefficients to a 95% confidence level are not

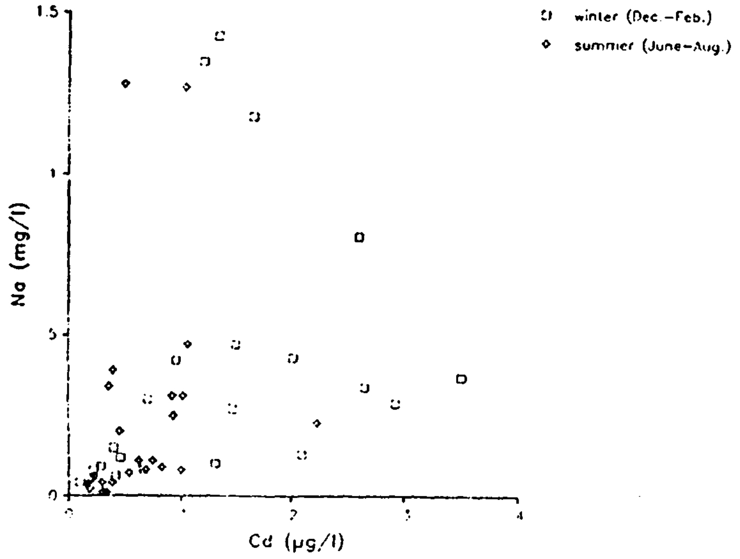

Fig. 6. Scatter plot of Na to Cd. In neither instance are correlations significant to the 95% confidence level.

significant. Since the primary source of atmospheric Na is sea salt, a poor correlation is expected if these metals arise from anthropogenic processes.

At all stations the Cd : Zn ratio has an intercept which is essentially zero. This indicates that in the absence of anthropogenic sources Cd and Zn background concentrations are small. At stations AP and AS, the ratios Pb/Cd and Pb/Zn have Pb-intercepts which are, to a 95% confidence level, significantly different than zero. Pb-intercepts are about 2.5 $\mu g\ L^{-1}$. In contrast, the Pb-intercepts at stations BR and LI are smaller or not different than zero. Since the existence of a large natural background of atmospheric Pb can be excluded (Settle and Patterson, 1982), the Pb-intercepts may reflect local anthropogenic sources. Pb is added to gasoline in the form of tetraalkyl lead (R_4Pb) as an anti-knock agent. Since southern Sweden is more densely populated than northern Sweden (about 90% of the population lives in the southern third of the country) and has more automobile traffic, one could expect some local influences on the atmospheric lead budget. If this explanation is correct one should see future decreases in the Pb-intercepts because Sweden is converting to lead-free gasoline.

5. Conclusions

The wet deposition of trace metals in Sweden is highest in southern Sweden and decreases northward. After comparing our results to values reported in the literature, it is concluded that the median values of Cd, Cu, Pb, and Zn concentrations in rural wet deposition, as summarized by Galloway *et al.* (1982), are an overestimate. We estimate typical concentrations are (in $\mu g\ L^{-1}$):

$$\text{Cd: } 0.03 \text{ to } 0.3\,; \qquad \text{Cu: } 0.3 \text{ to } 3\,; \qquad \text{Pb: } 1 \text{ to } 10\,; \quad \text{and} \quad \text{Zn: } 3\text{–}30\,.$$

Enrichment factors, relative to crustal material, indicate that Cd, Pb, and Zn are of predominantly anthropogenic origin. However, Swedish Cd and Zn anthropogenic emissions are smaller than wet deposition fluxes. Therefore, to explain the relatively high spatial and temporal correlation of Cd, Pb, and Zn concentrations, it is concluded that their primary source is anthropogenic emissions which have been transported long distances. Evidence for this hypothesis is that Cd, Pb, and Zn concentrations are well correlated to $\mathrm{exSO}_4^{=}$ and poorly correlated to Na.

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Commission of the European Communities

environment and
quality of life

Mobilization of heavy metals from fossil-fuelled power plants, potential ecological and biochemical implications

IV — Assessment studies of the European situation

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Joint Research Centre, Ispra Establishment - Italy

Directorate-General
Science, Research and Development
and
Joint Research Centre

1983

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Part IV

SECTION 3

ENVIRONMENTAL TRANSPORT

by

G. BIGNOLI, L. GOETZ and E. SABBIONI

4. DISPERSION OF HM EMITTED FROM THE STACK

4.1. General remarks

The production of electrical energy in coal-fired power plants always results in the release into the environment of measurable quantities of metal effluents which are potentially noxious for mankind. It is very important to be able to establish a sufficiently precise relationship between the pollutant quantities released into the environment (for instance, per unit of electrical power installed) and the dose to which a population is subjected, or could accidentally be subjected.

To reach this goal we must have available adequate models, permitting us to assess, a priori, the impact on the environment and population of a given release mode and extent of a given set of pollutants.

Finally, the ability to predict in quantitative terms the danger to a population associated with the exploitation of various types of power plants or other sources of pollution, should permit us to compare them on the basis of their impact on population health and safety, and to identify pollutant critical pathways and their governing parameters, so that adequate measures may be taken.

An important task in biological risk evaluation associated with a source of pollution and its consequences for a population, is to assess, the quantitative toxicological doses to man when the contaminant under study is released to the environment. With this thought in mind, biologists and ecologists have intensively examined heavy metal metabolism, phenomena migrations over a wide range of species under both laboratory, field conditions and global movements by particular modelling formulations.

A model is a formulation simulating a real phenomenon by means of which predictions can be made. The analysis of contaminant transfer from source to successive trophic levels of the food-chain has typically consisted of a series of mathematical equations identifying the fractional input and outflow rates from level to level.

The fundamental step in the method is to construct a compartmental model of the physical-biological system of interest. The compartments need not be spatial regions, but they must be distinguishable on some basis: such as different plants and their parts, chemical species, atmosphere as a compartment, human organs, etc.

Another fundamental aspect of the models is the form of the transfer functions between compartments. The linear assumption in the transfer functions is often a fairly good approximation of real systems, is easy to handle mathematically, and provides valuable insight into general techniques which should be useful when working with more complex nonlinear systems.

As a rule, in environmental models it is assumed that each compartment is homogeneous, and no concentration gradients exist inside. Although in general natural transfer processes show a time-dependent behaviour, it is often convenient to describe them by linear transfer functions with constant coefficients, of the type :

$$C_A = R\ C_B \qquad (1)$$

C_A and C_B being concentrations in compartment A and B respectively, and R the concentration ratio, which is assumed to be independent of time.
Otherwise, linear differential equations are required, thus taking into account the overall dynamics of the systems, of the type :

$$\frac{dQ_i}{dt} = I_i - K_i \cdot Q_i\ (t) \qquad (2)$$

where Q_i is the quantity of contaminant in the considered compartment; K_i is the rate constant between compartment and near environment and I_i is the input rate.

Upon integration, eq. (2) becomes

$$Q_i = \frac{I_i}{K_i}\left[1 - \exp\ (-K_i)\right] \qquad (3)$$

At equilibrium, we have

$$Q_i = \frac{I_i}{K_i} \qquad (4)$$

A system equation formed by a set of eq. (2) is able to represent a particular movement of a contaminant in environment and in living organisms.

When the models and their mathematical formulations are complex, the computer operation of the models makes it possible to predict probable outcomes, as the parameters in the model are changed, new parameters are added, or old ones removed. In other words, a mathematical formulation can often be evolved by computer operations to improve the fit of the real phenomenon, as reflected by in-situ data. Contrary to the feeling of many skeptics concenrning complex modelling, information on a relatively small number of variables often forms a sufficient basis for effective models because key factors or integrative factors often dominate or control a large percentage of the phenomenon. For this reason, it is not necessary to understand precisely how a component of a system is structured from simpler subcomponents in order to predict how it will behave.

In spite of this, many questions remain unsolved. In effect a simple source-pathway-receptor model, analogous to the ecological food chain, requires study and pathway identification, data on assimilation by each link in the pathway, and determination of the biological and physico-chemical turnover of elements. Frequently, information known for one biological system will not be applicable to other ecosystems. It is therefore difficult to draw specific conclusions concerning the environmental and biological concentrations of heavy metals in different trophic levels of ecosystems, especially for those metals which have complex chemical oxidation states [88], which are not necessary to organisms, and are not substitutes of the other chemical and biological elements.

There are also many advantages associated with the use of dynamic compartmental models. They are adaptable. The user can construct a model on the basis of the diversity of the region under consideration. Changes in regional characteristic can be represented by suitable compartmentalisation. When a model is mathematically represented, numerical methods exist to solve the associated differential equations and the asymptotic behaviour of such equations is known (eq. 3).

There are also disadvantages associated with the use of compartmental models. They treat the trace elements in each compartment as being distributed in a homogeneous manner.

It is thus difficult to represent continuously varying element distributions. There may be numerical problems with the system of differential equations used to represent transport; in particular, the system may be stiff. Finally, it is necessary to determine the compartments and define the rates of flow between them. The need to determine the compartments and the associated rate constants for a single element flowing between them is still a major problem. So far, it has been proposed that compartment models be used to represent the environmental transport of contaminants, but no general method for this determination has been presented.

Whether the coefficients are assumed to be constants or functions of time, the real problem is determining appropriate values for the particular situation being modelled. However, in any given situation, it is the modeller's responsibility to decide if these coefficients should be treated as constants or as a function of time [89]. Unfortunately, although it is easy to argue that the coefficients should be functions of time, it is much more difficult to obtain the environmental information needed to define them in this way.

Thus, in deciding how to define the coefficients, it is necessary to consider both the computational results desired and the environmental information available [90].

4.2 Terrestrial Models

The proposed establishment of coal-fired electric generating facilities has raised serious question of potential environmental damage. Concern has centered upon not only land and water quality aspects, but also upon the emissions resulting from plant operation. Pollutants which are normally associated with these emissions are residual ash and the oxides of sulphur and nitrogen. Potentially more dangerous pollutants are also released, including such toxic metals as mercury (Hg), lead (Pb), cadmium (Cd), chromium (Cr), zinc (Zn), vanadium (V) etc. The fate of these metals, once released to the environment via stack emissicn, is open to question. However, their documented toxicity coupled with their tendency to accumulate in biological systems means that an assessment of their interaction with the environment is of major importance.

In view of these considerations, a study was undertaken to predict the ultimate fate of heavy metal pollutants entering the environment from the stack emissions of a coal-fired electricity generating facility situated in the European Community.

This objective was accomplished by the development of a general model designed as TOXICO which estimates the mass flow transport of heavy metals in an environment continuum of soil, water (surface water, groundwater), atmosphere, biological transport, and their impact upon man and populations (Figure 15).

The environmental transport model, Figure 15, consists of three submodels that represent the most important receptors of the contaminations : the atmosphere, the soil, and ground and surface water. The purpose of this model is to represent the physico-chemical processes that result in the transport of metals throughout the earth's environment and their eventual accumulation. Metal release to, distribution through, and removal from the environment will generally be very slow. Cadmium for instance, does not appear to be very mobile in the environment, especially in soil, because it can rapidly form insoluble compounds. The second transfer process, represented in Figure 15 by a biological model takes place in a different time-scale and through different trophic levels to man. Here the time-scale is much shorter, and the movement must be represented by dynamical models which emphasize the contaminant features in the food chain leading to man and man's organs. Risk analysis and dose commitment calculations are the final goal of the global model developed.

The dynamic pathways of the global model are represented in Figure 16, and may be able to represent the different features which influence the movement of heavy metals in the biosphere. Such features include water-flow patterns, climatic conditions, chemical properties of soil, chemical properties of the heavy metal under consideration, agricultural practices, erosion rate, and the existence of sinks that tend to remove metals from the biosphere. In order to represent the dynamical movement, the system analysis based on system equations of the type eq. (2) was adopted.

4.3. Atmospheric Dispersion Model

The material released to the atmosphere is transported downwind and dispersed according to the normal atmospheric mixing processes. The estimation of dispersion in the atmosphere is commonly approached by solving the diffusion-transport equation. Several models have been developopped for this purpose using a variety of boundary conditions and simplifying assumption [94] . Most estimates of dispersion of material released to the atmosphere are based on the Gaussian plume diffusion model initially proposed by Sutton [95]. Pasquill [96] and Elliot [97] have shown that results predicted using Gaussian plume model vary little from predictions of other models and experimental measurements. Recently Gifford [98] took into account turbulent diffusion problems, the type of meteorological conditions defined by Pasquill, and expressed the basic equation for the Gaussian plume model in a more generalized form :

$$X(x,y,z) = \frac{Q}{2\pi \sigma_y \sigma_z \bar{u}} \exp\left[-\frac{1}{2}\left\{\frac{y^2}{2\sigma_y^2} - \frac{(z-h_2)^2}{2\sigma_z^2}\right\}\right] \qquad (5)$$

where $X(x,y,z)$ is the integrated airborn effluent concentration (g/m^3) at the point (x,y, z)

σ_y and σ_z are the horizontal and vertical deviations (m)

Q is the release rate from source (g/sec)

$\bar{u}$ is the mean windspeed (m/sec)

h_2 is the effective height of release (m)

x is the downwind distance (m)

z is the height above the ground of the sampling position (m).

This equation is derived for a gas, and the release aerosol is assumed to behave in a similar manner. The parameters that play an important role in depletion of air concentration, such as gravitational deposition, are not considered.

On the basis of a study by Chamberlain [99] for fall velocities of different sizes and densities of the particles, Van der Hoven [100] proposed a formulation for gravitational fallout to be used when sedimentation is important :

$$X\ (x,y,o) = \frac{Q}{2\pi\ \bar{u}\ \sigma_y\ \sigma_z} \exp\left\{-\frac{y^2}{2\,\sigma_y^2}\right\} \exp\left\{\frac{(h_e - x\ Vg/\bar{u})^2}{2\ \sigma_z^2}\right\} \quad (6)$$

This equation is practically derived from the integration of eq. (5) at groundlevel ($z=0$) but takes into consideration the gravitational velocity Vg.

In spite of this, the air concentrations derived from equations [6] applied to the dispersion, it considers only the wind effect and gravitational movement, but there exist a number of processes that may act to further reduce the concentrations of discharged quantity, in particular dry and wet deposition.

In our approach, we have taken into consideration the wet deposition, i.e. removal from the plume by the action of rain of the heavy metals released.

Removal of material from the plume is determined by the use of a washout coefficient, Λ, which is a function of precipitation rate, particle size spectrum, solubility in water, etc. By taking washout into account, the air concentration of the metal considered can be derived by substituting a modified source strength, QW, for Q in equation 6 where :

$$W = \exp - \left[\frac{\Lambda\ x}{\bar{u}}\right] \quad (7)$$

with Λ expressed in $\sec^{-1}$.

For this purpose, Engleman [101] presents a survey of experimental results for washout coefficients and the values of Λ vary between $0.3\ 10^{-4}\ \sec^{-1}$ at a rainfall rate of 10^{-4} m/hr to $10^{-3}\ \sec^{-1}$ at 10^{-2} m/hr of precipitation.

At this moment, in order to complete our mathematical formulation of the model, the meteorological conditions and their influence on plume depletion remain to be defined.

Pasquill [102] recommended a procedure for the calculation of the horizontal and vertical dispersion of a plume and he defined six weather categories, A – F, of atmosphere stability.

More recently Smith [103] and Pasquill [104] have enlarged on Pasquill's original scheme by obtaining numerical solutions to the diffusion equation for downwind distances up to 100 km.

The two authors introduced also into their calculation of the standard deviations the ground roughness length, whose values vary from less than 1 cm for water to excess of 1 m for urban areas.

In order to facilitate numerical analysis, Hosker [105] graphically transferred Smith's results into numerical equations. For a roughness length of 10 cm, the equation has been formed

$$\sigma_z = \frac{a\,x^b}{1 + c^d} \tag{8}$$

where values of the coefficients, a, b, c and d are given in Table 26, and the σ_z value obtained is applied in this study over all distances considered when eq. (6) is perpendicularly integrated.

4.3.1. Site Specific Calculation

A site specific is defined by many variables, such as polar coordinates, associated meteorological conditions etc. A range of meteorological conditions, stack-heights, windrose, can be used to evaluate the annual mean metal movements such as air concentrations, deposition rates on soil and vegetation.

In effect this procedure, based on average values, becomes interesting when evaluations are required for a large country and the release practice continues for a long period of time.

For this purpose, the annual average air concentration (g/m^3) of a metal, i, and in polar coordinates, at a distance, x, in a particular sector in the direction $\vec{\theta}$ was evaluated as :

$$QX\,(i,\, x,\, \vec{\theta}) = N\; Q(i) \sum_{K} \bar{X}_o\,(i,\, k,\, x)\; f\,(\vec{\theta},\, K) \qquad (9)$$

where Q (i) is the release rate of heavy metal i (g/sec)

$\bar{X}_o(i,K,x)$ is the air concentration per unit release rate of metal i in a dispersion condition, K, assuming a uniform windrose and derived from a wind perpendicular integration of equation 6 that gives

$$\bar{X}_o = \frac{Q}{2\pi\, \sigma_z\, \bar{u}}\; \exp \left\{ - \frac{(h_e - x\, V_g/\bar{u})^2}{2\, \sigma_z^2} \right\} \qquad (9')$$

expressed in g m^{-3}.

$f(\vec{\theta},K)$ is the fraction of time taken by a particular dispersion condition K, existing with the air movement in the sector of the direction $\vec{\Theta}$, and of width 360°/N, where N is the number of windrose sectors.

In order to test the principal equation 9, we have compared a unit atmospheric emission (1 g sec^{-1}) from a generic source with the other computed calculations [106] taking into account the following parameters :

- wind partitioning in all directions of the windrose
- stability category B (Table 1)
- stack height 100 m
- average particle sizes of 5 µm
- gravitational velocity of 0.05 m/sec.

The results are compared with other European regions in Figure 17.

Similarly, the average deposition rate, W, can be derived from $(x, \vec{\Theta})$ for the global release of metal i. It can be expressed as

$$\omega(i, x, \vec{\Theta}) = N\, Q_{(i)} \sum_{K} D(i, K, x)\, f\,(\vec{\Theta}, K) \qquad (10)$$

in $g/m^2\ sec^{-1}$.

Where D (i, K, x) is the deposition rate in $g/m^2\ sec^{-1}$ released.

The average annual quantity reaching soil and vegetation, (I_V, I_S) respectively, is easily calculated

$$\bar{I}_S = \omega\, S(\text{[illegible]}\, F_S) \qquad F_S[0-1] \qquad (11)$$

$$\bar{I}_V = \omega\, S(\text{[illegible]}\, F_V) \qquad F_V[0-1] \qquad (12)$$

where ω is the deposition rate in g/m^2 per year calculated by eq. (10)

S is the soil surface considered in m^2.

F_s, F_v are the fractions of deposition intercepted by soil and vegetation respectively considering both wet and dry deposition from atmosphere.

4.4. Soil-Groundwater Transport Model

The aim of this step is to gain an understanding of the behaviour of heavy metals in soil which is the basis for deriving the time required to translocate into groundwater. In particular, the description of the events to which heavy metals may be subjected after release into soil is a fundamental parameter for predicting mathematically the migration rate in the soil column. The nature and the strength of the interactions between metals and soil components are responsible at any given moment for the fraction of heavy metal available to move through the soil components, and thus determine the magnitude of the distribution coefficients of each element in the different soil components.

After their introduction into the soil, heavy metals can interact directly with soil components via a complex series of chemical, physical and biological processes [107].

Although a detailed description of the interaction of heavy metals with soil components is beyond of the scope of this work we report here some considerations on soil properties as well as in the mechanisms governing the movement of heavy metals in soils, which at least determine the extent of the fraction of trace elements suitable to the groundwater.

The surface soil constitutes an efficient barrier for heavy metal migration unless the component is dissolved into the soil solution. In particular the inorganic and organic components of the surface soil as well as soil pH play a fundamental role in the movement of heavy metals [108].
Inorganic colloids selectively absorb ions from multi-element solutions, the selectivity depending on the oxidation state as well as on the hydrate size of the ion.
It increases generally with decreasing hydrate ion size and follows the order $Me^{+} < Me^{2+} < Me^{3+}$ for ions of increasing oxidation state [109].

The organic matter is represented by different kinds of organic macromolecules forming the soil humus. Although its content rapidly decreases with soil depth it is important in the interaction with heavy metals. Two types of polymers constitute up to 90% of the total humus : humic acid (phenolic and other aromatic units which link amino acids, peptides and other possible substances) and polysaccharides. These components from a poly-dispersed system containing molecules with a molecular weight ranging from a few thousand to about 200,000 daltons [110].

Chemical, enzymatic and metabolic reactions form and degrade the organic matter dynamically so that the interactions with heavy metals are subjected to continuous changes to a greater extent than those accuring in the inorganic soil fraction [111].

After release to soil only a fraction of the heavy metal is available to migrate to the deeper layers and to enter the groundwater depending on many factors such as :

- the oxidation state of the element and the change of its complex. The negatively charged zincate, ZnO_2^{2-}, have a greater mobility with respect to the corresponding positively charged cation Zn^{2+}. Similar behaviour has been suggested for hexavalent with respect to the trivalent Cr [112].

- The physico-chemical properties of the soil such as particle size, geological nature, pH, phosphate, clay and organic matter content.
- The soil modification by plant species and the absorption through cell walls of the roots.
- The biological characteristics of the soil (chemical nature of the ligands and microfloral composition).
- The extent of modification by environmental factors such as temperature and rainfall.

At any given moment, the fraction of heavy metals which may percolate through the soil components and translocate to the groundwater is governed by many sequences. The length of time for which metal ions remain at the soil surface is regulated mainly by the interactions with the organic macromolecules forming the soil humus.

In order to percolate into groundwater heavy metals must be available in the soil solution. According to a very important and recent work [113] in a mature soil the mobility of a metal ion to the soil solution is governed by successive competitive interactions in the organic matter between simple complexes (type I, lichen acids and phenols), highly insoluble complexes (type III) acting both as a reservoir and as a source of metal ions in plant nutrition as well as complexes acting as a barrier against metal ion percolation through the soil column (type II). This dynamic equilibrium should ensure the availability of essential elements to plants, roots and microorganisms depending on the concentration of the complexants in the soil solution because oligoelements, except Mo, cannot form hydroxocomplexes at the pH values normally found in the soil [114]. The considerations are apparently very important when related to the possible intrusion of heavy metals as pollutants, since they could have negative effects on this dynamic equilibrium influencing the competitive interactions with the possibility of altering the normal behaviour of many trace elements by making them available in solution for percolation to subsoil compartments.

4.4.1. Modelling objective and formation of the block diagram

The objective of the modelling is to predict the time-dependent movement of heavy metals from sources to groundwater. As described under point 4.4. the migration to groundwater may be thought of as occurring through a number of separate compartments which are assembled into a rather complex network. To model this migration mathematically the soil column has been conceptually compartmentalized for simplicity into three subsystems such as surface soil, underlaying soil and groundwater strata to take into account the different pedological and physico-chemical characteristics (Figs. 18 and 19).

The soil surface is the first and most effective biological barrier for heavy metals in soil as demostrated by the high values of the distribution coefficients (K_d). It is characterized by high dynamic biological activity and is of particular importance for the uptake of heavy metals from plant roots.

The soil column can be sequentially considered as the second physico-chemical barrier for heavy metals. It is characterized by a low organic matter content and interactions with colloidal clay are predominant. The percolation rate is higher while the values of K_d are normally lower than those at the soil surface.

The groundwater stratum is difficult to define clearly because of the many possible situations in nature. The vertical flow of the contaminant is assumed to be distributed in water taking into account the specific ionic migration velocity. The turnover of the groundwater has been considered in a similar manner and the results of the movements were calculated.

The losses out of the system are due to :

- run-off from surface soil
- periodic harvesting of the vegetation produced
- groundwater pumping for irrigation purpose
- groundwater consumption by animals and man
- spontaneous migration of groundwater.

The model of the soil column takes into account only the downward vertical flow, and do as not consider any lateral losses or inputs. The column is one of the discrete elements of volume composing the large soil matrix considered. In other cases when the source of contamination is isolated in a point of soil matrix, such as waste deposit etc., the lateral dispersion of the flux becomes important, but the mathematical solution is complex [115, 116].

The applied method of dose prediction is based on the systems analysis which considers the dynamic behaviour of heavy metals through the soil as a function of time which can be expressed by a set of differential equations (see § 4.1. eq. 2).

If we apply the foregoing mathematical treatment to the model in Figure 19, we need, in order to describe it, as many equations as there are compartments into which the soil model is subdivided.

The solution of the system equations will describe the variation in time of the quantity q(mg) of the element considered at each level. For the compartments considered, we therefore have :

$$\frac{dq_S}{dt} = I_S(t) + q_V(t)\ k_{LS} + q_3(t)\ (k_{3S} + k_{3MS}) + q_1(t)\ k_{1S} - $$

$$- q_S\ (k_W + K_{S1})$$

$$\frac{dq_1}{dt} = q_S\ (t)\ k_{S1} - q_1(t)\ (k_{1S} + k_{12}) \qquad (13)$$

$$\frac{dq_V}{dt} = I_V(t) + q_1(t)\ k_{1V} - q_V(t)\ (k_{VC} + k_{VM})$$

$$\frac{dq_2}{dt} = q_1(t)\ k_{12} - q_2(t)\ k_{23}$$

$$\frac{dq_3}{dt} = I_3(t) + q_2(t)\ k_{23} - q_3(t)\ (k_{3MS} + k_{3S} + k_{3M} + k_{3C} + k_3)$$

The dynamic concentration of the heavy metal considered in the various compartments of the soil will be given by

$$C_i\ (t) = \frac{q_i\ (t)}{V} \qquad (14)$$

where V is the volume of the single compartment and when in it neither internal gradient nor physical discontinuities exist.

Furthermore, it is assumed that the amount of element i is distributed instantaneously throughout volume V of the compartment considered.

On the other hand, where the volume of a compartment is too large to assume an instantaneous distribution of the contaminant, we have considered the variation of the volume within which it will move :

$$C_i\ (t) = \frac{q_i\ (t)}{S \int_0^t V_i\ (t')\ dt'} \qquad (15)$$

where S is the soil column section, V_i is the velocity migration of element i in soil compartment and $V_i(t')dt'$ is the length of vertical migration in the time interval (t, t+dt).

The definition of the different compartments was decided on the basis of several considerations derived from pedological and physicochemical studies. The environmental characteristics are of importance to a definition of the different compartments of a model, but are not enough in themselves because the calculation of the associated rate constants is a major problem in modelling approach.

As indicated in the publications [89, 90] the dynamic compartmental models are very flexible. By a proper definition of the compartments and the flow rates between them, different environmental situations can be represented through appropriate definition of the corresponding intercompartmental rate constants. The way to calculate these rate constants is at present a point of controversy among modellers.

In this study, the most important rate constants have been calculated from the principal equation used to evaluate the vertical flow transport and contaminant distribution into the different soil levels considered :

$$V_i = \frac{W_w}{1 + \left[(1-p/p)\ \varrho Kd_i\right]} \qquad (16)$$

From this equation it is possible, with approximations, to evaluate the ionic migration velocity of element i into the soil of the specific compartment. In equation 15, V_i is the ionic element velocity considered in meters per years, W_w is the average pore water velocity (meters per year), ϱ is the soil bulk density (gr/cm^3), p is the soil porosity and Kd_i is the soil distribution coefficient of element i between solid and aqueous phase (cm^3/gr) :

$$Kd_i = \frac{\text{conc. of metal, i, adsorbed in solid phase}}{\text{conc. of metal, i, dissolved in water}} \qquad (17)$$

As can be seen from equation 16, the distribution coefficients are of great importance in governing the downward ion migration velocity of different elements through the soil column.

Unfortunately, the Kd values are rather difficult to measure with good precision, since they depend on a series of parameters and conditions, which can vary widely [117] .

The other important parameter to be taken into consideration in formula 16, is the water percolation velocity, W. Recently Beese and Wierenge [118] demonstrated the important role played by vegetation in water percolation and in the solute distribution patterns resulting in a more rapid decrease on the peak solute concentration in the upper part of the soil profile.

Many factors influence this parameter : soil componenets, porosity, hydraulic status etc.; in effect water velocity values between 2 and 50 cm per day for different surface soils and for different hydraulic conductivity conditions [119, 120] are normally indicated.

If D_1 is the thickness (meters) of soil represented by compartment 1 (Figure 19) and by knowing the vertical ionic velocity of the element considered in the soil matrix (equation 16), it is possible to calculate the time $T_{1,2}$ necessary to reach the underlying level : $T_{1,2} = D_1/V_{i,1}$ in years. Therefore, the rate constant K_{12} between compartments 1 and 2 of the soil column can easily be calculated : $K_{12} = 1/T_{1,2}$ in years^{-1}. The same approach has been used to calculate the other intercompartmental rate constants and losses from groundwater due to water movement.

It is worth noting that the times calculated at each level of the soil column modelled from equation 16, also represent the contaminant delay times through it.

As far as the heavy metal concentrations in groundwater are concerned, the capillary movements of water and associated metal become imperative.

In view of the difficulty in quantizing the capillary movement, we have assumed in a first approximation a rapid liquid-solid phase distribution of heavy metal in aquifer. The assumption that the material dissolved in the water is in equilibrium with the material absorbed by the soil matrix is expressed by the linear equation 17 with

$$Kd = \frac{f_S/M}{f_L/V} \tag{18}$$

where f_S is the concentration of metal i that is absorbed by solid phase

f_L is the concentration of the dissolved metal i in the water

M is the mass of solid phase in grams

V is the volume of liquid phase in litres.

By means of the linear equation 18, and when the Kd value is known, it is possible to determine the fraction of metal, f_S, that is absorbed on solid phase of the groundwater system under consideration :

$$f_S = Kd\ f_L \frac{M}{V} \tag{19}$$

or $f_S = 1 - f_L$ where f_L is the ionic fraction that remains in liquid phase. If $R = M/V$ by transformations equation 19 becomes :

$$f_S = \frac{Kd\ S}{Kd\ S + 1} \tag{20}$$

The effective quantity and concentration (mg/l) of the metal remaining in the liquid phase of groundwater after the absorption processes was calculated by eq. (14) and eq. (20) :

$$c_{i_3}\ (t) = \frac{q_{i,3}\ (t)\ (1 - f_S)}{V_3\ P_3\ 1000} \tag{21}$$

where $q_{i,3}(t)$ is the quantity (mg) of metal i present in the groundwater compartment as a function of time and taking into consideration the ionic movements and losses (system equation 13);

V_3 is the total volume of groundwater compartment (m^3);

P_3 is the porosity of the material composing groundwater system;

1000 is a constant to transform m^3 into litres.

When the groundwater is utilized to irrigate an agricultural soil surface or pumped for drinking water or domestic use (Figure 19), when the annual water consumption is known, it is possible to calculate losses and input rate of contaminant from this compartment and the surface soil respectively. The assigned parameter values together with their references, are given in Appendix A.

Ultimately, two rate constant calculations remain : the run-off and vegetal migration rate constants.

In our approach, when the rate of soil erosion, Ro is known, by means of formula 16 it becomes possible to calculate the depth of metal penetration into soil surface D_S (as a function of time, chemico-physical and pedological properties of soil) in order to calculate the soil surface volume, V_S, annually submitted to run-off leaching :

$$D_S(t) = \int_0^t V_i \, dt \tag{22}$$

$$V_S(t) = S \, D_S(t) \tag{23}$$

where S is the area of soil considered in the model. If the volume V_S of the upper soil compartment calculated by equation 23 is known, its soil density ϱ_S and the rate of soil erosion Ro (tons/ha/year), the runoff rate constant K_W (year^{-1}) is easily calculated

$$K_W = Ro/V_S \quad \varrho_S \tag{24}$$

It is interesting to note that the volume of this upper compartment S (Figure 19) is not a constant in the model, but it is automatically defined by the particular mobility of the metal considered. If the metal is characterized by a slow mobility into the soil matrix, the loss from the compartment caused by runoff becomes considerable. If the contrary is true, the vertical migration quantity as an input to near subsoil compartment will be very small.

Another loss mechanism for metals considered in the model is the physiological uptake of heavy metals by plants such as grass or vegetables, and their periodical harvesting.

Metal deposition quantities from the atmosphere are able to enter into vegetation by two mechanisms : foliar absorption through mesofillum and from soil through roots. For these purposes, the corresponding rate constant K_{1V} from soil to vegetation was calculated from the absorbed quantity of metal q_V (mg/y) during one year of agricultural practice :

$$q_V = \frac{q_1 \ CRV \ BIV}{V_1 \ \varrho_1 \ 10^6} \tag{25}$$

where q_1 is the quantity (mg) of element,i,in the soil surface compartment

CRV is the soil-vegetable concentration ratio

BIV is the biomass of vegetable in g/m^2 produced per year

V_1 is the volume of the soil surface compartment (m^3)

ϱ_1 is the soil density in g/cm^3

10^6 is the conversion constant (m^3 to cm^3).

The time (years) required for transport to the whole metal contaminant into vegetables would be :

$$T_{1V} = \frac{q_1}{q_V} = \frac{V_1 \ \varrho_1 \ 10^6}{CRV \ BIV} \tag{26}$$

the rate constant K_{1V} can easily be calculated : $K_{1V} = 1/T_{1V}$ (years^{-1}).

Similarly, is possible to adopt a concentration ratio, CRL, between the internal and external leaf zone [12] in order to calculate areal absorption and relative rate constant K_{LV}.

When metals are deposited on areal parts of vegetation they can be removed by weathering as in the mechanical action of wind and rain. This phenomenon has been measured under a variety of conditions [123] and the most commonly determined half-time value was $T_W \cong 30$ days.

The weathering rate constant (years^{-1}) between foliar surface and near soil we have taken into consideration in this study by the formulation :

$$K_{LS} = \frac{\ln (2)}{T_W} \, 365 \qquad (27)$$

4.5. Computer Implementation of the Models

The linear system of differential equation 16 which defines our model of heavy metal migrations from atmosphere to soil and groundwater was implemented in the IBM Continuous Systems Modelling Program III (CSMP III) simulation language (IBM 1975).

It allows the dynamic equations to be specified by Fortran-like statements and the use of FORTRAN subprograms for auxiliary calculations, such as the evaluation of input functions.

The relative case in making structural changes in the model and the output tabulation and graphical capabilities of CSMP III are significant advantages for the use of the simulation language in preference to direct FORTRAN programming interfaced with a software package for numerical integration of the differential equations.

By our mathematical formulation of the dynamic phenomena and using the CSMP III system program, we have obtained in a similar manner to that with which ecologists treat energy flux throughout the different trophic levels of the biosphere, a continuous and uninterrupted heavy metal migrations in the model and consequently the dynamic compartmental metal concentrations.

4.6. Results

4.6.1. Impact on air quality

On the basis of the atmospheric dispersion model described in paragraph 4.3. and using the data listed in Appendix A and the average emission (ton/y) of heavy metals from the stack of a coal-fired power plant unit of 500 MW_e at 50% full load, the average amount to atmosphere around the power plant situated at a distance of 10000 m and the increase over the total endogenous concentration [91, 92] were calculated. The results are presented in Table 27 and the calculations were performed taking into consideration B. Pasquill's Atmospheric Stability Category (Table 26) which defines a moderately unstable atmospheric condition.

Table 28 lists only the results for cadmium, taking into consideration the four Stability Categories and two distances from source.

4.6.2. Impact on soil

The assessment of heavy metal concentration increases on soil surface as a result of long term (40 years) deposition from the stack of a power plant unit of 500 MW_e, may be very useful for evaluating possible vegetation and groundwater contamination.

Table 29 shows the long-term effects that the amounts of metals can have on their background levels [93]. A small increase in the HM concentration is apparent from the Table. It is important to note that these results have been simply calculated from the average emission into the atmosphere under "static conditions" (no losses from soil compartment are considered). When the long-term fate of cadmium in soil is calculated by a dynamic model (Figures 18, 19), the increase is substantially reduced by about one order of magnitude.

4.6.3. Impact of Cd on atmosphere, soil and groundwater quality

By means of the parameter values listed in Appendix A and a specially-developed dynamic model, the flow of cadmium and its concentration in groundwater were calculated for a reference case of a power plant unit of 500 MWe. The results are presented in Figure 20 where : C_S, C_1, C_2, C_3 are the concentrations in the upper soil layer, soil trophic level, soil column and groundwater (mg/Kg) respectively. The calculations were performed for continuous stack emission over 100 years using computer implementation of the model.

The long-term effect (as a reference case) on groundwater quality in comparison with the present level in groundwater (0.0007 ppm) and with the maximum permissible level adopted in the EC is presented in Figure 21.

Both figures indicate that (using our modelling approach) the migration time of Cd through soil compartments to groundwater is 36 years.

The results reported here are clearly not site-specific. They are intended only to indicate the type of result one may reasonably expect to obtain from application of the model.

In spite of this, we have approached, as a first evaluation and only for cadmium, a global assessment for the Member States of the EC, taking into consideration the data inputs to the environmental model listed in Table 19, the surface territory and circular distribution of the individual areas comprising the EC, calculated in Table 30.

In order to estimate a more reasonable average cadmium impact on EC atmosphere, we have adopted an average distance from all sources of pollution that we have assumed to be centered within the area of the particular Member State considered (Table 30).

In effect this procedure, based on an average distance from total source of pollution, and which also represents the result includes in all stacks of the Member State; becomes interesting when the evaluation is required to calculate the environmental impact on a large country and when the release activity could continue for a long time.

The long-term dynamic effect of Cd on atmosphere, soil, groundwater and the relative increase over the background levels in the EC, are presented in Table 31 for all Member States of the European Communities, with the exception of Greece.

To conclude, the results obtained by modelling, demonstrate that possibilities exist for cadmium to migrate from stack to soil and groundwater and that it can influence water quality. For other heavy metals released from source, parameter values and environmental data are resuired in order to evaluate their potential impact on the biosphere.

4.6.4. Variability of parameter values and applied sensitivity analysis

The numerical data and environmental parameters that we have assumed to define the reference case, may be useful in a preliminary assessment.

In the present study, we have seen that, amongst the most relevant parameters governing the environmental concentration of heavy metals, the groundwater velocity and the distribution coefficient of the metal ion between aqueous and soil phase, are of very great importance.

The distribution coefficient directly determines the rate constant K_{23} between the soil column and the groundwater compartment (Figure 19); the water velocity, on the contrary, is responsible for influencing the cadmium loss from groundwater to environment, while the distribution coefficient Kd_3 is responsible for the quantity of HM that remains available in the groundwater liquid phase (eq. 18 and 21).

Both soil parameters are characterised by large variability values and are dependent on physico-chemical environmental conditions of the soil matrix and hydraulic status respectively. For these reasons, we have calculated the concentration in groundwater (ppm) versus time for three Kd_2, Kd_3 and W3 values; they are shown in Figures 22, 23 and 24, in which run 2 of the computer plot corresponds to the reference case for the parameter considered.

It is possible to see, in Figure 22, that the Kd_2 values applied to the soil column compartment also govern the soil column delay time for the cadmium to reach groundwater and its concentration in the water compartment. On the other hand, in Figure 24, when considering the groundwater velocity and distribution coefficient Kd_3 (Figure 23), the delay time in the soil column remains constant (typical of the reference case), while the cadmium concentration in groundwater is strongly influenced by these parameters.

One of the more interesting ways to analyse the dynamics of a system is to determine how sensitive its' various components are to each other. This can be done by a systems analysis technique known as "sensitivity analysis". Sensitivity analysis involves determining the amount and kind of change produced in a given system parameter by a change in another parameter. Because the compartments in a system are related to each other and since it is possible to alter any single parameter.or group of parameters and determine the effect of any other system parameter, it is readily seen that a great number of sensitivity analyses can be calculated for a system.

In the present study only the relative dynamic sensitivities of groundwater compartment cadmium contents are considered in relation to the two parameters already mentioned. We have calculated a sensitivity factor by utilizing the simple differentiation of values of plots represented in Figures 22, 23 and 24 and using the following equations :

$$S_{Kd_2}(\%) = \frac{[\Delta C]}{\Delta\, Kd_2} \cdot \frac{100 \cdot Kd_2}{[RC]}$$

$$S_{W_3}(\%) = \frac{[\Delta C]}{\Delta\, W_2} \cdot \frac{100 \cdot W_3}{RC}$$

where :

S_{Kd_2} and $S_{W_3}(\%)$ = are the sensitivity factors in percentage for the two parameters considered;

$[\Delta C]$ = (Concentration value minus Reference case concentration value) (Figures 22, 23 and 24);

ΔKd_2, ΔW_3 = (parameter value minus parameter value applied to reference case);

$[RC]$ = Reference case concentration value;

Kd_2, W_3 = Parameter values considered.

The sensitivity calculation values are presented in Table 32. It can be seen that the groundwater velocity and Kd_3 values influence the water concentration more than the Kd_2 parameter applied to the soil column. Nevertheless, the Kd_2 parameter substantially influences the retardation time of cadmium when it moves from the soil column compartment to groundwater (Figure 22). It is still possible to note that the zero value of the groundwater concentration and the high value of the sensitivity factor S, for $Kd_2 = 30$, calculated over 50 years, are due to the 64 years contaminant delay time in the soil column matrix. It is worth noting that the sensitivity factors are always negative. This is due to the fact that the cadmium concentration in the groundwater is a decreasing function of the parameters considered.

4.7. In-Field Studies (Selection from Literature)

Table 33 lists the environmental studies available today in the literature. For completeness not only atmospheric transport and deposition of HM emitted by the stack have been considered, but also the dispersion of HM in effluents from ash ponds and ash disposal areas, the availability of HM from power plant ash and uptake by plants and animals, as well as human health aspects related to the emission of HM by coal-burning.

Although Table 33 does not claim to be complete, the majority of the revelant papers are presented. Of 41 titles specified, 38 papers report results obtained on power plant areas in USA, and 3 were performed in Europe.

There is one paper [151] from Brown et al., the only one from an area situated within the EC, which provides data on HM release from ash ponds situated near water supply catchment areas in Great Britain.

Details on the reported in-field studies may be obtained from the original papers cited in the references.

the background concentration itself would contribute nearly 12000 µg d^{-1}. Inclusion of certain other food items such as vegetables, pulses such as dal, peas, etc. and meat, for which data are not available, would result in more than average intake for Cd also. It is interesting to note that the consumption figures are far short on the average for some of the essential metals like Fe and Cu.

4. Conclusions

Trace metals such as Cu, Mn, Zn and Cd were present in different species in river water. While Cu, Zn and Cd were present mainly as cationic entities, Mn was mainly in the anionic form. Most of those metals could be identified, in low abundance, in an unionized and non-dialyzable form, suggesting association with high molecular weight organic ligands.

Copper in the sediments was found mainly associated with the humic matter. Accumulation in the organic fraction in sediments, which is a time related process, can be used to determine the nature of the stream bed pollution and identification of fresh inputs which are technologically originated. The method could achieve good sensitivity for detecting stream pollution due to high concentration factors in the organic fraction.

Trace metal accumulation in the biological samples followed the trend observable in the general enhancement of levels attributable to industrial application. Apart from some of the transient higher concentrations observed in isolated instances the general trend did not indicate any preferential accumulation of trace metals in the species investigated.

The projected intake estimates of the local population, consuming the food items produced locally, indicate that the consumption of Zn and Cd, the industrial pollutants, equal or exceed the reference man intake, while the consumption of Cu and Fe, the essential metals, is far-short of the average.

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IMPACT OF THERMAL POWER PLANT EMISSIONS ON VEGETATION AND SOIL

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Abstract. Studies were made to assess the impact of a thermal power plant located at Obra on vegetation and soil in surrounding areas. Pollutant concentration in the area gradually decreased along a belt in the prevailing wind direction and a gradient of structural and functional changes in plants and soil was observed. Natural vegetation in the area varied significantly at different sites and on the basis of plant responses can be classified as insensitive, intermediate and sensitive.

The effect of the power plant emissions on soil and eco-physiological characteristics such as pH, organic matter and N, P, K and S concentrations in soil; leaf injury symptoms, number and distribution of plant species; chlorophyll content in leaves, percentages of photosynthetically active leaf area; accumulation of N, P, K, and S in leaves etc. seemed to be a function of the pollutant gradient existing in the area. There was a relationship between plant responses and changes in the chemical factors of soil and plants due to pollution. This study indicates possible elimination of plant species, first the trees then the shrubs and lastly the herbs and grasses from the environs of the thermal power plant. The increase in soil acidity in the area may cause cation-anion imbalance and microbe population reduction to affect soil fertility.

1. Introduction

Thermal power plants are point sources of pollution with a more or less definite pattern of pollution emission. The main pollutants present in thermal power plant emissions are SO_2, NO_2, CO, hydrocarbon, F and flyash. These pollutants may cause gradual degradation of the abiotic and biotic components of the ecosystem (Woodwell, 1970; Miller and McBride, 1975; Knabe, 1976). Such degradations are largely governed by environmental and other factors which determine the fall out pattern and the concentration of pollution.

An attempt was made to assess the effects of a thermal power plant on its surrounding areas, with special reference to vegetation. For this purpose the area around the Obra thermal power plant was selected.

1.1. STUDY AREA

Obra, where the thermal power plant is located, is situated at 24°22′ N latitude and 83° E longitude in the Mirzapur District of Uttar Pradesh. The general topography of the region is undulating, with hills, valleys and flats interspersed. The minimum and maximum elevations from sea level in the area are 255 and 445 m, respectively. The rocks in the region belong to the basal sub-group of the Semeri group of Vindhyans (Pre-cambrian), comprising quartzites, conglomerates, dolomites, limestones, shales, and porcelanites. At some places, there are exposed crystalline marbles. The rocks northeast of the thermal power plant are of the Bijawar group consisting of chlorite

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schists, phyllites, slates, limestones, shales, quartzites, haematites schists, silicious limestones, jaspar bands and instrusive dolomites (Auden, 1933).

The area has a typical monsoon climate, characterized by seasonal rhythm as prevailing in the rest of India (Basu, 1965). The whole year can be divided into three distinct seasons of summer (March through June), rainy (July through October) and winter (November through February).

The climax vegetation of the area is basically a mixed tropical deciduous forest, characterized by deciduous trees, shrubs and grasses. The shrubs are an undergrowth while grasses and herbaceous plants cover the open areas. The main crops cultivated in the area are sorghum, mustard, barley and pigeon-pea. In the urbanized area near the thermal power plant a variety of seasonal and perennial ornamental plants are grown.

1.2. THERMAL POWER PLANT

The daily coal consumption in the power plant is about 9120 tonne which helps to generate 550 MW of electricity. Based on the data provided by the power plant authorities, the coal contains 12.3% moisture, 35.83% ash, 24.13% volatile matter, 22.68% fixed C, 0.5 to 2% S and 3802 cal g^{-1} energy. The gaseous and particulate pollutants are emitted from two stacks of 104.5 and 120 m height. The average percentage density of the combustion plumes flowing from the stacks, when calculated with shades of gray of the Ringlemann chart, over a period of 2 h is about 90%. However, more often than not, the smoke density is found to be 100%.

The thermal power plant at Obra provides a single source of SO_2 pollution where pollutant concentration gradually decreases along a belt in the direction of the prevailing wind and therefore it may be possible to find a gradient of structural and functional changes in plants and soil along this belt. The changes in plant and soil may be quantified to assess the significance of air pollution in the area.

2. Materials and Methods

Eight sampling sites, northeast of the thermal power plant on a 9.5 km line-transect, were selected for census of plants and collection of plant and soil samples. Sites 1, 2, and 3 were located at 0.5, 1.5, and 3.0 km from the power plant respectively and were situated on the south ascending slope of a hill; sites 4 and 5, at 4.5 and 6 km respectively, were on a plateau; site 6 at 7.0 km was on a mild slope and sites 7 and 8, at 8.0 and 9.5 km respectively from the power plant, were on an ascending slope. The control site was selected at Chandraprabha sanctuary, at a distance of 20 km north of Obra.

At each site, the plants, especially tree species, were carefully examined for foliar damage; an inventory of trees, shrubs and grasses was prepared and leaves of *Diospyros melanoxylon*, *Lagerstroemia parviflora* and *Zizyphus nummularia* were collected for subsequent analyses. On the basis of their growth pattern, severity of foliar injury and level of tolerance, the plants were classified into sensitive, intermediate and insensitive groups.

Leaves of the above-mentioned plant species were collected separately from different sites. For each species, one batch of leaves, to be used for the quantitative determination of particulate matter, was stored carefully in paper bags and the other, to be used for pH measurements, chlorophyll, mineral and energy content analyses, was stored in an ice box.

Soil samples at each site were collected from 0,10, and 20 cm depths. These were composited, air-dried, powdered and stored in polythene bags for later determination of pH, organic matter, S, N, available P and exchangeable K.

The level and pattern of spatial dispersion of pollution were estimated by comparing the changes produced in plants and soils of the control and polluted sites.

2.1. PARTICULATE DEPOSITION

The particulate matter deposited on leaves on *D. melanoxylon*, *L. parviflora* and *Z. nummularia* was collected in water by repeatedly washing with distilled water. The pH of the leaf wash was determined with a pH-meter. The water was then evaporated to dryness, the weight of the residue was determined and the amount of deposition was calculated for a m^2 leaf area.

2.2. SOIL ANALYSIS

2.2.1. *pH*

A 20 g soil sample was mixed with 100 ml deionized water in a 500 ml conical flask. The mixture was shaken for 30 min on a horizontal shaker. The suspension was filtered through a Whatmann No. 44 filter paper and the pH was determined with a pH-meter, using a glass electrode.

2.2.2. *Organic Matter*

The percentage of organic matter in the soil sample was determined by using the rapid titration method of Walkley and Black described by Piper (1966).

2.2.3. *Minerals* (N, P, K, and S)

The amounts of total N, available P and exchangeable K in the soil samples were determined by following the methods given by Jackson (1958). For S determination, the method of Patterson (1958) was used.

2.3. LEAF ANALYSES

2.3.1. *Leaf-extract pH*

After carefully washing the leaves with distilled water, a 5 g leaf sample each of *D. melanoxylon*, *L. parviflora* and *Z. nummularia* was crushed separately in 50 ml deionized water and the pH of the leaf extracts was determined with a pH meter.

2.3.2. *Chlorophyll Determination*

For this purpose 0.5 g of the fresh leaf sample was finely ground in 80% acetone (acetone: water, 4 : 1 v/v). The homogenate was filtered through a piece of muslin cloth and the filtrate was centrifuged at 3000 × g for 15 min. The supernatant was decanted and its volume was made upto 25 ml by adding 80% acetone. The optical density of this chlorophyll extract was measured at 645 and 663 nm wavelengths with the help of a Spectronic-20 photoelectric-colorimeter. The chlorophyll content, expressed as mg g^{-1} dry wt. was calculated by using the formula of Maclachlan and Zalik (1963).

2.3.3. *Minerals* (N, P, K, and S)

For the determination of minerals in leaves, the microkjeldahl method was used for N (Piper, 1966), the wet digestion method was used for P (Jackson, 1958), the flame photometer was used for K (Jackson, 1958), and the turbidimetric method was used for S (Patterson, 1958).

TABLE I

Inventory of plant species (trees and shrubs) collected at different sites northeast of the thermal power plant at Obra

Plant Species	Site No.	1	2	3	4	5	6	7	8	Control
	Distance (km)	0.5	1.5	3.0	4.5	6.0	7.0	8.0	9.5	20
Trees										
Acacia catechu		+	+	+	+	+	+	+	+	+
Aegle marmelos		−	−	−	−	−	−	−	−	+
Anogeissus latifolia		−	−	−	+	+	+	+	+	+
Bauhinia [illegible]		−	−	−	−	−	−	−	−	+
Boswellia serrata		−	−	−	−	−	−	−	−	+
Buchanania lanzan		−	−	−	−	−	−	−	−	+
Butea monosperma		−	−	−	+	+	−	+	+	+
Cassia fistula		−	−	−	+	+	+	+	+	+
Diospyros melanoxylon		+	+	+	+	+	+	+	+	+
Flacourtia indica		−	−	−	−	+	+	+	+	+
Gardenia latifolia		−	−	−	−	−	−	−	−	+
Grewia tiliaefolia		−	−	−	−	−	−	−	−	+
Hardwickia binata		−	−	−	+	+	+	−	−	+
Lagerstroemia parviflora		+	+	+	+	+	+	+	+	+
Lannea grandis		−	−	−	−	−	−	−	−	+
Madhuca indica		−	−	−	−	−	−	−	−	+
Miliusa tomentosa		−	−	−	−	−	−	−	−	+
Phyllanthus emblica		−	−	−	−	−	+	+	+	+
Pterocarpus marsupium		−	+	+	+	+	−	−	+	+
	Total	3	4	4	8	9	8	8	9	19
Shrubs										
Holarrhena antidysenterica		−	−	+	+	+	+	+	+	+
Mimosa himalayana		−	+	+	+	+	+	−	+	+
Nyctanthes arbor-tristis		−	+	+	+	+	+	+	+	+
Zizyphus glaberrima		+	+	+	+	+	+	+	+	+
Zizyphus jujuba		+	+	+	+	+	+	+	+	+
Zizyphus nummularia		+	+	+	+	+	+	+	+	+
	Total	3	5	6	6	6	6	5	6	6

2.3.4. *Energy Content*

The caloric value of the plant material was determined using an Oxygen Bomb Calorimeter (Parr Instrument Co., U.S.A.) and expressed in Cal g^{-1} dry weight.

3. Results

The components of the natural vegetation in the Obra area were found to vary at different sites. The number of genera and species of trees, shrubs, herbs and grasses, generally increased at increasing distances from the power-plant (Tables I, II, and III). Trees of *Acacia catechu*, *Diospyros Melanoxylon* and *Lagerstroemia parviflora* were present

TABLE II

Inventory of plant species (herbs) collected at different sites northeast of the thermal power plant at Obra

Plant Species	Site No.	1	2	3	4	5	6	7	8	Control
	Distance (km)	0.5	1.5	3.0	4.5	6.0	7.0	8.0	9.5	20
Herbs										
Ageratum sp.		+	+	+	+	−	−	+	+	+
Amaranthus spinosus		+	+	+	+	+	+	+	+	+
Boerhaavia diffusa		−	−	+	+	+	+	+	+	+
Cassia tora		+	+	+	+	+	+	+	+	+
Crotolaria sp.		+	+	−	−	−	+	+	+	+
Cyperus rotundus		+	+	+	+	+	+	+	+	+
Desmodium triflorum		−	−	−	−	+	+	+	+	+
Eclipta alba		−	+	+	+	−	−	+	+	+
Euphorbia hirta		+	+	+	+	+	+	+	+	+
Evolvulus alsinoides		−	+	+	+	+	+	+	+	+
Herpestis monniera		−	+	+	−	+	+	+	+	+
Justicia simplex		+	+	+	+	+	−	+	+	+
Malvastrum tricaspidatum		−	−	−	+	+	+	+	+	+
Melilotus sp.		−	−	−	−	+	+	+	+	+
Phyllanthus simplex		−	−	−	+	+	−	+	+	+
Phaseolus sp.		−	−	−	−	+	+	+	+	+
Polygonum glabrum		+	+	+	+	+	+	+	+	+
Rungia repens		+	+	+	−	−	+	+	+	+
Scoparia dulcis		−	+	+	+	+	+	+	+	+
Sida acuta		−	+	+	+	+	+	+	+	+
Tridax procumbens		−	−	+	+	+	+	+	+	+
Tephrosia purpurea		+	+	+	+	+	+	+	+	+
Vernonia cinetea		−	−	+	+	+	+	+	+	+
Xanthium spinubesia		+	+	−	+	−	+	+	+	+
	Total	11	16	17	18	18	20	24	24	24

TABLE III

Inventory of plant species (grasses) collected at different sites northeast of the thermal power plant at Obra

Plant Species	Site No.	1	2	3	4	5	6	7	8	Control
	Distance (km)	0.5	1.5	3.0	4.5	6.0	7.0	8.0	9.5	20
Grasses										
Apluda mutica		–	–	–	–	–	–	–	–	+
Aristida adscencionis		–	–	–	–	–	–	–	–	+
Bothriochloa pertusa		–	–	–	–	–	+	+	+	+
Chrysopogon fulvus		–	+	+	+	+	+	+	+	+
Cynodon dactylon		+	+	+	+	+	+	+	+	+
Dactyloctenium aegyptiacum		–	–	–	+	+	+	+	+	+
Desmostachya bipinnatum		–	–	+	+	+	+	+	+	+
Dichanthium annulatum		+	+	+	+	+	+	+	+	+
Digitaria sanguinalis		+	+	+	+	+	+	+	+	+
Echinochloa colonum		–	–	–	–	–	+	+	+	+
Eragrostis tenella		+	+	+	+	+	+	+	+	+
Heteropogon contortus		+	+	+	+	+	+	+	+	+
Paspalidium flavidum		–	–	–	–	–	–	–	–	+
Saccharum munja		+	+	–	–	+	+	+	+	+
Setaria glauca		–	–	–	–	–	–	–	–	–
	Total	6	7	7	8	9	11	11	11	15

at all the sites. The number of tree species, which was 3 at site 1, increased to 8 at site 4 located at a distance of 4.5 km from the power-plant. Similarly, the minimum and maximum number of shrub species were at site 1 and 4, respectively, with *Zizyphus glaberima*, *Z. nummularia* and *Z. jujuba* species common to all sites. At the control site six species of shrubs were recorded. The situation with respect to herbs (Table II) and grasses (Table III), was slightly different from that of trees and shrubs, because the maximum species of the former were found at distances of 7 to 9.5 km and not at distances of 4.5 to 9.5 km as was the case for the species of the latter. The herbaceous plants common to all the sites were *Ageratum* sp., *Amaranthus spinosus*, *Cassia tora*, *Cypersus rotundus*, *Euphorbia hirta*, *Polygonum glabrum* and *Tephrosia purpurea*. Similarly, the common grasses were *Cynodon dactylon*, *Dichanthium annulatum*, *Digitaria sanguinalis*, *Eragrostis tenella* and *Heteropogon contortus*.

Leaf injury symptoms in the form of chlorosis and necrosis were commonly present in most of the plant species growing near the power plant. Mostly the trees showed necrosis but sometimes both chlorotic and necrotic areas were observed on their leaves. In case of grasses, irregular, bifacial necrotic streaks between larger veins were clearly visible. On the basis of their foliar injury symptoms and occurrence near, far and farthest from the power plant, the species were grouped into insensitive, intermediate and sensitive, respectively (Table IV).

The soil samples collected from different sites showed a decreasing trend for organic matter, S and exchangeable K and an increasing trend for pH, N and available P, as one moved away from the power plant (Figure 1).

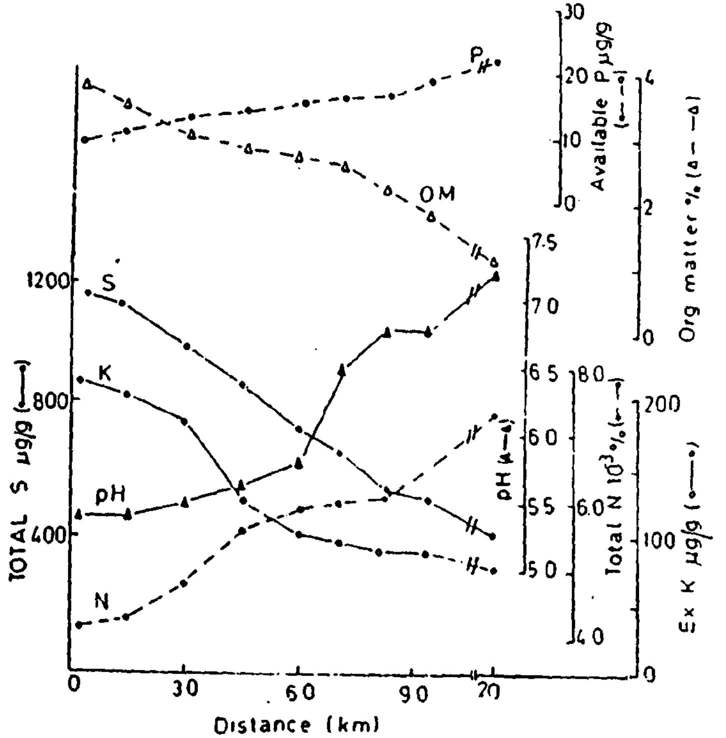

Fig. 1. Total N, available P, exchangeable K, pH, and organic matter in soil of different sites

The amounts of particulate matter deposited on the leaf surface of *D. melanoxylon*, *L. parviflora* and *Z. nummularia* at varying distances from the pollution sources are given in Table V. The dust deposits on leaves gradually decreased at increasing distance from the power-plant but beyond 4.0 km distance this change was less apparent. The maximum deposition of fly-ash was about 24.8 $g\ m^{-2}$ of *Z. nummularia* and 18.4 $g\ m^{-2}$ of *L. parviflora* collected at a distance of 0.5 km from the power plant. Similarly, the leaf weights increased at increasing distances from the power plant. The leaf-wash pH of leaves from different sites did not show any appreciable difference. For leaf-extract the pH values of *D. melanoxylon*, *L. parviflora* and *Z. nummularia* leaves were 5.5, 5.6, and 5.9, respectively, for plants growing at site 1. In these species, the leaf-extract pH increased to 6.6, 6.6, and 6.4 for the leaf-samples collected at site 8 (Table V).

TABLE IV

Relative sensitivity of plant species to thermal power-plant emissions

Sensitive	Intermediate	Insensitive
Aegle marmelos	*Anogeissus latifolia*	*Acacia catechu*
Apluda mutica	*Boerhaavia diffusa*	*Ageratum* sp.
Aristida adscensionis	*Bothriochloa pertusa*	*Amaranthus spinosus*
Bauhinia tomentosa	*Butea monosperma*	*Cassia tora*
Boswellia serrata	*Cassia fistula*	*Crotalaria* sp.
Buchanania lanzan	*Chrysopogon fulvus*	*Cyperus rotundus*
Echinochloa colonum	*Dactyloctenium aegyptiacum*	*Cynodon dactylon*
Flacourtia indica	*Desmodium triflorum*	*Dichanthium annulatum*
Gardenia turgida	*Desmostachya bipinnata*	*Digitaria sanguinalis*
Grewia tiliaefolia	*Eclipta alba*	*Diospyros melanoxylon*
Holarrhena antidysentrica	*Evolvulus alsinoides*	*Eragrostis tenella*
Lannea grandis	*Flacourtia indica*	*Euphorbia hirta*
Madhuca indica	*Hardwickia binata*	*Heteropogon contortus*
Miliusa tomentosa	*Herpestis monniera*	*Justicia simplex*
Nyctanthes arbor-tristis	*Malvastrum tricuspidatum*	*Lagerstroemia parviflora*
Paspalidium flavidum	*Melilotus* sp.	*Polygonum glabrum*
Phaseolus sp.	*Mimosa himalayana*	*Rungia repens*
Phyllanthus emblica	*Phyllanthus simplex*	*Saccharum munja*
Setaria glauca	*Pterocarpus marsupium*	*Tephrosia purpurea*
	Scoparia dulcis	*Xanthium spinulosia*
	Sida acuta	*Zizyphus jujuba*
	Vernonia cinerea	*Zizyphus nummularia*

As is apparent from Table VI, there were increases in the average and photosynthetic areas per leaf and decreases in the percentage of injured leaf area in the three species of trees, as one moved away from the power plant. The maximum leaf areas injured in *D. melanoxylon*, *L. parviflora* and *Z. nummularia* at site 1, were 43.56, 39.45, and 35.56%, respectively, but none of the plants at site 8 (9.5 km distance), showed any foliar injury. In the case of *L. parviflora* and *Z. nummularia* no injury was noticeable beyond site 5. At a distance of 0.5 km from the pollution source, the average area per leaf was lowest.

The chlorophyll contents in leaves also increased at increasing distances from the power plant and this applied to chlorophylls *a*, *b* and total (Table VI). The minimum amounts of total chlorophyll were recorded at site 1; the values being 2.22 mg g^{-1} dw for *D. melanoxylon*, 3.55 mg g^{-1} dw for *L. parviflora* and 2.20 mg g^{-1} dw for *Z. nummularia*. The respective values for the control site were 4.98, 6.25, and 4.84 mg g^{-1} dw.

The P and N contents in leaf samples of the three tree species consistently increased from site 1 through 8 (Figure 2). However, for S and K a reverse trend was noted. Incidentally, at any given site the S accumulation in *Z. nummularia* leaves was found to be the highest followed by *L. parviflora* and *D. melanoxylon*; at site 1, for example, these values were about 0.33, 0.29, and 0.28% respectively.

The caloric values of leaves, expressed as kcal g^{-1} leaf, are given in Table V. On

TABLE V

Particulate matter deposited on leaves, leaf weight, leaf wash and leaf extract pH and energy content of leaves of *D. melanoxylon*, *L. parviflora*, and *Z. nummularia* at different sites (A paired t-test between any two sites showed the values statistically significant)

Plant species	Parameters	Sites								
		1	2	3	4	5	6	7	8	Control
D. melanoxylon	Particulate matter (g m^{-2})	24.8 (0.45)	12.7 (0.30)	7.8 (0.50)	4.2 (0.20)	2.0 (0.10)	– –	– –	– –	– –
	Leaf weight (mg cm^{-2})	8.10 (0.01)	8.00 (0.01)	9.41 (0.04)	10.36 (0.07)	10.88 (0.06)	11.00 (0.06)	11.22 (0.05)	11.98 (0.05)	12.46 (0.08)
	Leaf wash pH	6.2	6.2	6.4	6.6	6.8	6.8	6.8	6.9	6.9
	Leaf extract pH	5.5	5.7	6.1	6.3	6.3	6.4	6.4	6.6	6.8
	Calorific Value (kcal g^{-1} dw)	39.64 (0.14)	40.16 (0.10)	41.33 (0.10)	42.38 (0.08)	43.26 (0.05)	43.74 (0.11)	44.06 (0.16)	45.98 (0.12)	46.65 (0.04)
L. parviflora	Particulate matter (g m^{-2})	18.4 (0.60)	9.2 (0.46)	4.6 (0.35)	22.8 (0.27)	– –	– –	– –	– –	– –
	Leaf weight (mg cm^{-2})	10.82 (0.02)	11.02 (0.02)	11.15 (0.15)	11.76 (0.16)	11.54 (0.14)	11.84 (0.14)	12.08 (0.08)	12.38 (0.18)	13.64 (0.20)
	Leaf wash pH	6.4	6.5	6.6	6.6	6.7	6.7	6.8	6.8	6.9
	Leaf extract pH	5.9	5.9	6.2	6.3	6.5	6.5	6.6	6.6	6.7
	Calorific Value (kcal g^{-1} dw)	38.64 (0.04)	39.68 (0.12)	40.46 (0.10)	41.39 (0.20)	43.65 (0.23)	44.28 (0.08)	44.46 (0.15)	44.84 (0.10)	45.44 (0.11)
Z. nummularia	Particulate matter (g m^{-2})	22.5 (0.55)	11.0 (0.42)	5.2 (0.35)	2.1 (0.10)	– –	– –	– –	– –	– –
	Leaf weight (mg cm^{-2})	9.42 (0.04)	9.62 (0.19)	9.54 (0.10)	9.84 (0.11)	10.20 (0.10)	10.38 (0.06)	10.47 (0.5)	10.88 (0.10)	11.36 (0.36)
	Leaf wash pH	6.5	6.4	6.4	6.7	6.7	6.8	6.8	6.8	6.9
	Leaf extract pH	5.9	6.0	6.0	6.2	6.2	6.3	6.4	6.4	6.7
	Calorific Value (kcal g^{-1} dw)	39.36 (0.19)	40.12 (0.20)	40.67 (0.11)	42.12 (0.26)	42.12 (0.26)	43.09 (0.16)	43.75 (0.17)	44.14 (0.09)	44.87 (0.14)

Values in parantheses are ± standard deviation.

TABLE I

Average leaf area, per cent damaged leaf area, chl. a and [illegible] and Z. nummularia at different sites (A paired t-test between the values of [illegible] significant

Plant species	Parameters	Sites 1	2	3	4	5	6	7	8	Control
D. melanoxylon	Av. Leaf area	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	42.72	44.58	48.24
	(cm²)	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	(0.65)	(0.85)	(1.60)
	Damage (%)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	5.54	–	–
	Chl. a (mg g⁻¹)	1.24	1.11	1.14	[illegible]	[illegible]	[illegible]	2.08	2.82	3.02
	Chl. b (mg g⁻¹)	[illegible]	1.12	[illegible]	[illegible]	[illegible]	[illegible]	1.60	1.72	1.96
	Total Chl	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	3.64	4.54	4.98
	(mg g⁻¹)	(0.01)	(0.02)	(0.02)	[illegible]	[illegible]	[illegible]	(0.04)	(0.06)	(0.12)
L. parviflora	Av. Leaf area	[illegible]	16.46	16.92	[illegible]	[illegible]	[illegible]	17.98	18.52	22.26
	(cm²)	(0.10)	(0.14)	(0.10)	[illegible]	[illegible]	[illegible]	(0.11)	(0.14)	(0.26)
	Damage (%)	39.45	26.36	[illegible]	[illegible]	[illegible]	–	–	–	–
	Chl. a (mg g⁻¹)	2.16	2.43	2.59	[illegible]	2.55	[illegible]	3.31	3.76	4.00
	Chl. b (mg g⁻¹)	1.39	1.42	1.68	[illegible]	1.91	1.94	2.16	2.12	2.25
	Total Chl	3.55	3.85	4.27	4.44	[illegible]	[illegible]	5.47	5.87	6.25
	(mg g⁻¹)	(0.03)	(0.03)	(0.05)	(0.04)	(0.10)	(0.11)	(0.10)	(0.08)	(0.15)
Z. nummularia	Av. Leaf area	9.56	8.89	9.96	10.54	11.22	11.81	11.93	12.85	15.54
	(cm²)	(0.04)	(0.05)	(0.05)	(0.13)	(0.10)	[illegible]	(0.06)	(0.12)	(0.15)
	Damage (%)	35.56	32.15	30.08	14.42	9.36	–	–	–	–
	Chl. a (mg g⁻¹)	1.36	1.48	1.80	[illegible]	[illegible]	[illegible]	2.54	2.94	3.46
	Chl. b (mg g⁻¹)	0.84	0.88	0.92	0.96	0.96	1.10	1.14	1.16	1.38
	Total Chl.	2.20	2.36	2.72	2.30	[illegible]	3.42	3.68	4.10	4.84
	(mg g⁻¹)	(0.01)	(0.01)	(0.30)	[illegible]	(0.16)	(0.10)	(0.16)	(0.14)	(0.72)

Values in parantheses are ± standard deviation.

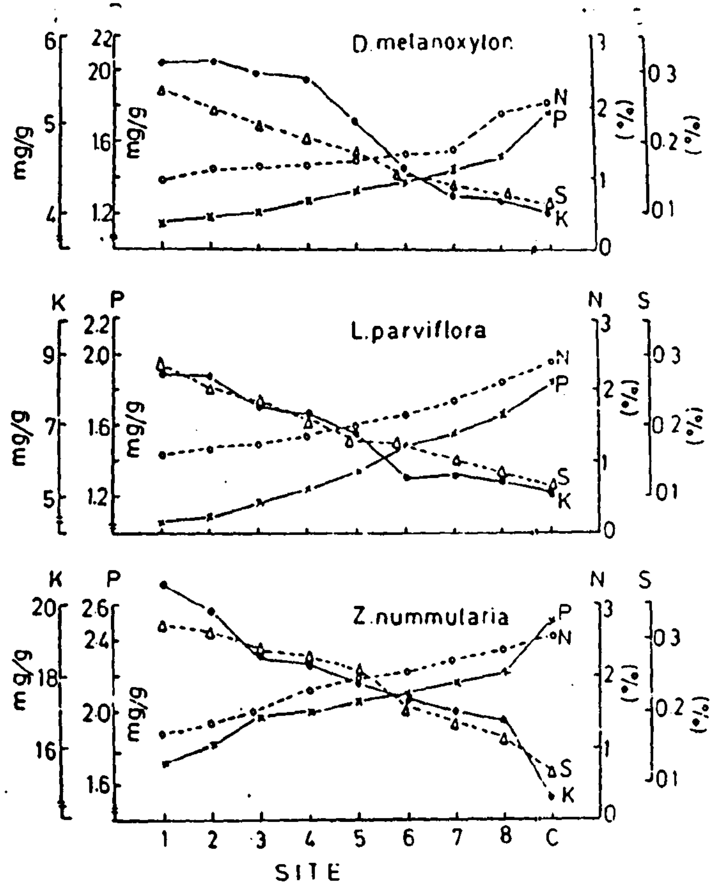

Fig. 2. N, P, S and K contents of *Diospyros melanoxylon*, *Lagerstroemia parviflora* and *Zizyphus nummularia* leaves at different sites.

moving away from the power plant, the energy contents in plant leaves gradually increased. At any given site the maximum energy was generally found in *D. melanoxylon* leaves followed by those in *L. parviflora* and *Z. nummularia*. The caloric values of leaves from polluted sites were always lower than those of the control site.

4. Discussion

Coal combustion produces SO_2 as the major pollutant which affects the vegetation and soil in the environs of the power-plant. The fall-out of pollutant in the area is governed by south west prevailing winds which disperse the stack plume mainly in the northeast direction where the pollutant concentration is higher than in any other direction. In spite of the undulating topography of the area, the pollutant fall-out follows a linear gradient, perhaps because of the stack height. The acidic nature of SO_2 causes a reduction in pH of rock surfaces, soil samples and leaf tissues. The fall-out gradient is amply demonstrated in terms of increasing pH and decreasing soil sulphate at distances away from the power plant, especially to the northeast. From these, it is evident that the pollutant concentration near the source remains higher than at distant locations.

Near the power plant, where there is a decrease in pH and an increase in S and K content of soil and leaf tissue, there is severe damage to vegetation but away from the power plant, with increasing pH and decreasing S and K contents in soil and plant materials, there is a gradual improvement in vegetation with less and less leaf injury. There is a significant relationship between plant response and changes in the chemical factors, such as pH and SO_4^{-2} of soil and plants due to pollution. This is in conformity with the findings of Rao and LeBlanc (1967), who correlated the fall-out pattern of SO_2 with the chemical indices of pH and SO_4^{-2} of water and soil in their studies with the epiphytic vegetation around an iron-sintering plant.

The variations in the number of trees, shrubs and herbs at different sites may be explained on the basis of a combination of factors of pollution concentration, micrometeorology and topography. The ambient and ground level concentrations of a pollutant at any site may vary horizontally as well as vertically due to changes in the adiabatic lapse rate and wind velocity during day and night time. Because of the rough terrain and better dispersal forces in the Obra area the ambient concentration of the pollutant usually remains higher than the ground-level concentration. Such a situation will cause greater damage to larger plants and vice-versa. It is not surprising, therefore, that the primary targets of pollution in the Obra area are the trees followed by shrubs and herbs. It is, therefore, clear that the responses of plants to SO_2 can be markedly influenced by the microenvironmental regimes under which they grow (Brennan and Leone, 1968; Dugger and Ting, 1970; Heck *et al.*, 1965; Heck, 1968).

The changes in the physico-chemical properties of soil and plants are mainly due to the acidity produced by SO_2. Sulfur dioxide fall-out and acid precipitation decrease vegetation growth directly affecting the plant system, mainly via the leaf and indirectly by causing acidity and mineral imbalances in the soil. Under acidic conditions, the soil microorganisms and decomposition process are affected (Tamm, 1976). In the present study the increased organic matter content in the soils of polluted sites may be attributed to soil acidity. Certain organic-matter-decomposing microorganisms, such as *Phoma* sp., *Cladosporium cladosporioides*, *Fusarium oxysporum*, *Cylindrocarpon* sp. and *Aspergillus nidulens* are reported to be extremely sensitive to acidic pH (Shukla 1976). Further, the decreases in available P and total N at the polluted sites may cause inhibition of microbial activity. Since these nutrients are not being released from the organic matter due to reduced decomposition rate this may lead to cation-anion imbalance in the long run.

Besides, the acidity of the plant growth medium will affect the relative uptake of cations and anions by the plants growing there (Reuss, 1976). The overall effect of acidity is not only on the increase of H^+ ions in the system but also on other ions present there. This assumption may account for the higher amounts of K in plants and soils collected from the highly polluted sites. It is possible that K being monovalent is released from the soil particles under acidic conditions, leading to a higher proportion of exchangeable K in soils of polluted sites. Such a situation may be a dangerous one, because the released K^+ will be easily leached under condition of heavy precipitation, thus causing a great loss of soil fertility.

The leaves of *D. melanoxylon*, *L. parviflora* and *Z. nummularia* in the vicinity of the power plant contained reduced amounts of chlorophyll. Under acidic conditions, the degradation of chlorophyll is possible. Rao and LeBlanc (1966) showed that exposure of the Lichen *Xanthoria fallax* to SO_2 caused conversion of chlorophyll to phaeophytin. Syratt and Wanstall (1969) noted the destruction of chlorophyll by SO_2, acting as sulphurous acid. In the present study the amounts of chlorophyll seem to be correlated with the levels of SO_2 concentration in the area.

The nutrient analyses of leaves of *D. melanoxylon*, *L. parviflora* and *Z. nummularia* give some evidence that absorbed SO_2 has been metabolized by the plants to some extent. Accumulation of sulphate in plants after SO_2 exposure has been noted by several workers (De Cormis, 1969; Gilbert, 1968; Guderian, 1977; Thomas, 1951). As under favorable growing conditions air pollutants tend to be taken up most readily by foliage, the uptake of metabolizable pollutants such as SO_2 and NO_x is related to plant metabolism rates (Bennett and Hill, 1973). Sulphur dioxide being highly soluble is effectively absorbed by the plant foliage. It lis known that SO_2 produces metabolizable substrates within mesophyll cells when exposure levels are low (Daines, 1968; Hill and Bennett, 1970; Thomas *et al.*, 1950). The excess of S in leaves accumulates as sulphate, which might be expected to provide a measure of the degree of leaf contamination and an index of the degree of SO_2 pollution.

The decrease of N in leaves from polluted areas signifies disturbance in the N metabolism of plants. It is known that SO_2 fumigation lowers protein content in plants (Pahlich, 1973). Also, the reduction of P in leaves from polluted areas indicates inhibition of metabolic activities.

It may be inferred that higher accumulation of S and K reduction in photosynthetic leaf area with interveinal necrosis, and reductions in chlorophyll, N and P contents are some of the changes in leaves produced by SO_2 pollution. Following these changes, the SO_2 sensitivity level of plants can be ascertained, for example, it may be said now that *Z. nummularia* is relatively less sensitive to SO_2 than are *L. parviflora* and *D. melanoxylon*.

The results of this study indicate possible elimination of plant species, first the trees then the shrubs and lastly the herbs, from the SO_2 polluted areas. The increase in soil acidity in such areas will cause cation-anion imbalance, and microbe population reduction which will eventually make the soil infertile and unfit for plant growth. Further, the changes produced in soil and vegetation due to thermal power plant emissions seem to be a function of the pollutant gradient existing in the area.

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CALL FOR PAPERS

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The Environmental Engineering Division of the American Society of Civil Engineers is to sponsor the 1983 National Conference on Environmental Engineering in Boulder, CO at the University of Colorado on July, 6-8, 1983. Individuals wishing to make technical presentations at this conference are requested to submit abstracts in all topics associated with Environmental Engineering aspects of air, noise, radiation, solid waste, water pollution and water supply management and public health engineering. In addition, abstracts are requested in a number of specific areas including:

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Toxic Trace Elements Associated with Airborne Particulate Matter: A Review

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This article provides a concise review of published literature pertaining to sampling and analytical methodologies, aerometric studies, source identification techniques and modeling activities for the elements arsenic, cadmium, nickel, lead, vanadium, zinc, cobalt, chromium, copper, iron, mercury, manganese, selenium and antimony, and their compounds, associated with airborne particulate matter. Sampling techniques discussed include filtration and inertial separation. Analytical methodologies such as atomic absorption and atomic emission spectrometry, neutron activation analysis, and X-ray fluorescence spectrometry are summarized. Data on atmospheric levels of 14 trace elements are presented in summary form from numerous studies in remote, rural and urban areas, and generally indicate that concentrations measured at rural locations are several orders of magnitude lower than those measured for urban areas. Source identification methodologies are discussed in terms of advantages and disadvantages, and various applications are cited for the following categories: size differentiation, enrichment factors, chemical mass balance, and multivariate models. Provided that reliable trace element data are available for both the source and the receptor, chemical mass balance and multivariate methods can account for up to 80 percent of all sources contributing to the observed ambient air concentration. Wet and dry deposition processes are reviewed and environmental measurement data are provided for each element for remote, rural and urban locations. Both wet and dry deposition fluxes need to be considered for trace elements when estimating the total annual amounts of various trace elements deposited at a particular locale. Global cycles and trace element budgets are introduced in the context of the types of models currently in use. Limitations include inadequate global scale surveys of heavy metal concentrations and the lack of knowledge of sources and/or sinks.

Airborne particulate matter is unique among air contaminants because of its potential complexity both in terms of chemical composition and physical properties. An adequate description of particles in the atmosphere requires specification of their density, concentration, size distribution, chemical composition, phase and morphology. In addition, a knowledge of how these parameters are influenced in the atmosphere by processes such as diffusion, dispersion, air mass type, atmospheric transport and transformation, vertical exchange phenomena, in-cloud scavenging, washout during precipitation, and dry deposition is desirable.

In recent years, investigations of atmospheric aerosols have progressed from relatively simple determination of total mass loading to particle size classification and determi-

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nation of chemical composition. It has been found that several toxic metals, including arsenic (As), cadmium (Cd), nickel (Ni), lead (Pb), vanadium (V), zinc (Zn), cobalt (Co), chromium (Cr), mercury (Hg), manganese (Mn), selenium (Se), antimony (Sb), and their compounds, are associated with the fine particulate matter size ranges in the ambient air. This is important not only from a health viewpoint since fine particles (aerodynamic diameter <2.5 μm) are respirable, but also because fine particles tend to persist in the atmosphere where they can undergo chemical reaction and be transported from their sources over long distances to pristine areas of the environment. This paper considers only the metals listed above, with special attention being given to the first six. Due to the vast amount of literature available on all the aspects of trace metals dealt with here, the most salient points have been extracted, and this information generalized to provide an overview of each topic. This literature review is derived from a comprehensive search and evaluation of worldwide scientific and technical information which had been published up to and including 1983. For those readers who may wish more recent information pertaining to this subject, selected additional references are provided in the bibliography section.

Natural sources of airborne particles include terrestrial dust, sea spray, biogenic emanations, volcanic emissions and emissions from fires. Chemical composition and size distribution of the particles are dependent on the actual source. Numerous anthropogenic activities can be significant sources of trace elements and their compounds. Some examples are power plants, smelters, incinerators, open hearth furnaces and transportation.

Major anthropogenic trace element emissions generally are considered to be from ducted exhausts associated with industrial or mobile sources. However, fugitive emissions from buildings or industrial sites, or from traffic resuspension, construction, agricultural practices, and by wind entrainment from storage piles or exposed surfaces may also arise. The resultant ambient air concentration is a function of the meteorology prevalent in an airshed, which is often characterized in terms of the ventilation factor (an indicator of the mixing layer depth and wind speeds in the lower atmosphere), as well as a function of the quality of the incoming air masses.

Description of dispersion and transportation processes must take all of these factors into account. Dispersion modeling attempts to explain mathematically the effects of the atmosphere on emitted pollutants, including advection, plume rise and wind shear. Receptor models develop a relationship between measured pollutant concentrations in the ambient air and the physical and chemical characteristics of different source emission types. In addition, several attempts have been made to account for the chemical transformations and physical processes that can occur in ambient air, and to describe how the pollutants are removed from the atmosphere. An understanding of the role and behaviour of toxic trace elements and their compounds associated with airborne particulate matter is important in formulating effective control strategies and avoiding or minimizing the risk of adverse human health effects.

Sampling and Analysis

Sampling

The amount of airborne particulate matter to be collected in a sampling protocol is determined by three primary requirements, i.e., the detection limits and configuration (i.e., single or multielement determination) of the subsequent analytical technique, the need to obtain an accurate sample weight, and the need to separate the sample into components of different size, density or composition. One of the

Table I. Advantages and disadvantages of some common filter substrates.

Filter substrate	Advantages	Disadvantages
Paper (cellulose)	Good mechanical strength and low flow resistance, thus can be used for high volume sampling. Low trace element impurities; cheap and simple to use.	Hygroscopic and may absorb water, thus cannot conveniently be used gravimetrically. Broad distribution of pore size and density, thus collection efficiency for <0.3 μm particles is poor. Cannot determine carbonaceous materials. Possible artifact formation, particularly for sulphate and nitrate.
Glass-fibre	Good mechanical strength and low flow resistance, thus can be used for high volume sampling. Inert to all extracting acids (except HF) and organic solvents. Cheap and simple to use.	Hygroscopic, thus requires equilibration to constant RH for gravimetric use. Broad distribution of pore size and density, thus collection efficiency for <0.3 μm particles may be poor. High trace element impurities, especially for Fe, Mn, Pb, and Zn. Cannot determine siliceous materials. Artifact formation, particularly for sulphate and nitrate.
Organic membrane	Soluble in most organic solvents for ease of removal of particles. Good for in-situ analysis using NAA or XRF (especially Teflon). Generally not hygroscopic. Low trace element impurities. Specific pore sizes available.	Low mechanical strength and generally high flow resistance, thus generally only suitable for low volume sampling. Cannot determine carbonaceous materials. Coarse particles may not stick to surface and may be lost during subsequent operations. High cost.
Graphite	Very low level of trace element impurities. Efficient particle collection characteristics. Can be used directly as electrodes in certain types of emission spectrometry. Can be dissolved in perchloric acid.	Low mechanical strength and high flow resistance, thus can only be used for low volume sampling. Cannot determine carbonaceous materials. High cost.
Metal membrane (most commonly silver)	Non-hygroscopic. Can be used directly as electrodes in spark-source mass spectroscopy. Useful in some types of compound speciation (e.g., Hg compounds).	High trace element impurities. High flow resistance. High cost.

Table II. Types of samplers commonly used to collect airborne particulate matter in ambient air.

Sampler type	Nominal flow rate m^3/min.	Number of size fractions	Comments
Standard hivol	1.1 to 1.7 (40–60 cfm)	1	Most frequently used with glass fibre or cellulose filters; particle collected range in diameter from 0.3 to 100 μm.
Hivol with size selective inlet 10 μm (PM-10) or 15 μm	1.1 to 1.7	1	Employed for estimation of inhalable particulate matter concentration in ambient air.
Hivol with cascade impactor head	Variable: ~0.5 to 1.7	Variable: typically 2 to 7 stages	Large impaction plates compared with other multiple-stage impactors.
Dichotomous sampler (virtual impactor)	Variable: e.g., 1.67×10^{-2}	2	Divides sample into two size fractions fine particles: <2.5 μm diameter; coarse particles: ≥2.5 μm diameter (upper limit depends upon sampler inlet used; cut-point depends upon sampler design/operation.
Multiple-stage impactor	Variable: $\sim 1 \times 10^{-3}$ to 2×10^{-1}	Variable: 1 to 7 or more stages	Particulate matter is classified as the air stream is accelerated through progressively smaller orifices.
Cyclone	Variable: $\sim 1 \times 10^{-3}$ to 1×10^{-2}	1	Inertial-type separation; actual flow rate depends upon cyclone dimensions.
Dustfall jar	Not applicable (passive device)	1	Size fraction not well defined; method lacks precision and accuracy; primarily of historical interest.

most important physical parameters in determining both the behaviour of trace elements and the sample collection efficiency is particle size. The particle collection characteristics of most common sampling devices are determined by equivalent aerodynamic diameter (defined as the diameter of a spherical particle of unit density whose aerodynamic behaviour in an airstream is the same as that of the particle under consideration).[1]

Commonly used sampling techniques for particles can be classified into two main categories: filtration and inertial separation. Particle collection is achieved by a combination of five distinct processes: direct interception, inertial deposition, diffusional deposition, electrical attraction and gravitational attraction. The combined effect of these five collection processes results in a complex dependence of collection efficiency on particle size in most common filter materials. Particle collection efficiency by filtration has been shown to be a complicated function of the face velocity of the airstream, the nature and composition of the filter, the size of the particles and their composition, with actual collection efficiencies varying considerably for different filter and particle types.[2]

Since significant mass functions of some trace elements (e.g., lead) are associated with particles whose sizes fall within the range of common filter "windows" (i.e., a filter size range through which particles are inefficiently collected), the best quantitation can be achieved by the use of high flow rates and filters with small pore sizes.[3] Factors which adversely affect filter collection efficiency are particle re-entrainment and vapourization. For example, species such as Hg, SeO_2, and As_4O_6 have sufficient vapour pressures at ambient temperatures that it is possible for substantial loss of these species to occur during filtration.[4-6]

Several types of filter materials have been used for collecting particulate matter. These include glass fibre, paper, organic membranes, metal membranes and graphite. Because of their versatility and relatively low cost, paper (cellulose) and glass fibre filters are most commonly used for high volume (hivol) and general purpose sampling. Specific disadvantages of cellulose filters are that they cannot be used for gravimetric mass determinations of the particulate matter due to significant accumulation of moisture and collection efficiency for fine particles is reported, by Liu *et al.* to be poor.[7] Organic membrane filters are used when sample size is not a prime consideration, or low impurity levels are required. Teflon filters, generally used on virtual impactor dichotomous samplers, and more recently with hivol samplers as well, have the advantages of inertness, very low impurity levels and convenience for direct analysis. However, carbonaceous materials in the total particulate loading cannot be reliably determined on these filters, preventing establishment of a complete mass balance of the aerosol from one measurement.

In comparison to other air filter materials, glass fibre filters appear to contain the highest impurity levels of the following trace metals: Cr (80 ng/cm^2), Fe (4000 ng/cm^2), Mn (400 ng/cm^2), Ni (<80 ng/cm^2), Pb (800 ng/cm^2), Sb (30 ng/cm^2), V (30 ng/cm^2) and Zn (160,000 ng/cm^2). Relatively high levels of Cr, Fe and Ni can be found on silver membrane filters (60, 300 and 100 ng/cm^2, respectively), while cellulose filters and polystyrene filters can contain similar amounts of Cu, Fe, Ni and Zn.[6]

The choice of filter material depends on the sampling situation and the analytical techniques used to determine the collected trace elements. The main considerations should be trace element impurity levels within the substrate material, collection efficiency and the ease of manipulation of the filter. Some advantages and disadvantages of a few common filter substrate are presented in Table I. An excellent discussion by M. Lippmann of the characteristics of different types of filter media and filter holders can be found in the ACGIH book on air sampling instruments.[8]

Various types of particulate matter samplers exist and are discussed briefly. Samplers commonly used to collect suspended particulate matter in ambient air and their major attributes are summarized in Table II. The hivol consists of a filter holder and an air pump drawing approximately 1.1 to 1.7 m^3/min of air through a fibrous matte filter. Particles are collected by impaction on the filter surface, which is weighed before and after exposure to determine the mass. Collection efficiency of the hivol is affected by wind speed and wind direction, and the inlet does not provide efficient collection of particles larger than about 50 μm.[9] Size selective inlets for hivol samplers have been designed to provide a single size fraction with an upper limit of 10 or 15 μm for measurement of "inhalable" particulate matter. This method provides a cost effective method of measuring size selective particles.

The dichotomous sampler collects two size fractions of particles: less than 2.5 μm, and 2.5 to 10 or 15 μm (depending on the sampler inlet used). The particles do not impinge upon a collection surface immediately after being accelerated through the inlet air jet, but pass through a void (virtual surface) and are collected by filtration downstream. The separation principle, involves acceleration of the particles and airstream through a nozzle, with 90 percent of the airstream being drawn off at right angles. The small particles follow the right angle air stream, while the larger particles, because of their inertia, continue towards the collection nozzle. The separated fractions are individually collected on fibrous matte or Teflon membrane filters.[10] This has become the preferred technique for size selective collection.

The cascade impactor provides a method of collecting an ambient particle sample which is divided into subfractions of specific particle size range. The method involves acceleration of the ambient air stream by drawing it through one or more converging nozzles or slots. The jet of air is directed towards a collection surface, which may be coated with an adhesive or grease to enhance collection. Large, high inertia particles are unable to follow the air stream and thus impact against the collection surface. Smaller particles follow the air stream and can either be directed to another impaction stage or collected on a filter. Several shortcomings of this method include bounce-off, re-entrainment, wall-losses, cross-sensitivity, lack of discreteness, and the fact that impactor use is highly labour-intensive.

A cyclone sampler is a type of inertial separator that traps particles larger than a specified diameter that cannot follow the streamlines on the abruptly changing circular direction of the air stream, and allows particles smaller than that diameter to pass through to the collection medium.[11]

Dustfall jars generally collect suspended particles larger than 50 μm aerodynamic diameter, and are subsequently analyzed using procedures such as those prescribed by ASTM Method D-1739-70.[12] The method is neither very precise nor accurate, as the collection pattern is complicated by the aerodynamic effects of the jar, the angle of approaching wind flow, the mounting brackets for the jar and the effects of adjacent structures.

Most metals are associated with particles in the atmosphere; however, there are notable exceptions to this rule. Metal species present in ambient air in the vapour phase include elemental mercury and organomercury compounds, tetraethyl and tetramethyl lead, arsenic and selenium oxides, elemental selenium, arsine and arsenic alkyls, and species such as nickel carbonyls. Collection of metals in the vapour phase from the atmosphere is normally by absorption into solution, adsorption onto a solid, or condensation to a liquid or solid in a cold trap.

Analysis

A major consideration in choosing an analytical method is its detection limit for the element(s) in question. The mass of most trace elements present in atmospheric samples are generally small (<1 to 500 μg), thus limiting the choice of analytical methodology.

Since its inception, atomic absorption spectrometry (AAS) has had extensive use and is currently the most widely employed technique for elemental analysis of airborne particles. A variety of techniques can be used to atomize and introduce an element into the analyzing region of the spectrometer. Typically, a flame or a heated graphite tube atomizer is used. Flame techniques generally have detection limits ranging from 0.1 to 10.0 ng/m^3 depending on the element being measured, whereas graphite tube techniques are two to three orders of magnitude more sensitive. Matrix effects can inherently decrease precision with either technique, but particularly for graphite tube atomizers. The major disadvantage of AAS is that each element must be determined sequentially, and thus for a large number of elements sample size can become critical.

Several forms of atomic emission spectrometry have been

Table III. Analytical detection limits of various techniques[a] for trace elements associated with airborne particulate matter.[6,10,13,14]

	Detection limits (ng/m^3)							
Element	Flame[b] AA	Graphite[c] Tube AA	ICP[d]	XRF[e]	INAA[f]	IPAA[g]	Graphite[h] Spark AES	DP-ASV[i]
As	20	0.5	40	0.75	4	0.2	10	—
Cd	0.2	0.02	2	13	—	—	2	0.005
Co	0.8	0.15	3	2	0.025	—	0.5	—
Cr	2	0.3	1	3	0.25	4.5	0.1	—
Cu	1	0.25	1	2	5	—	0.05	0.02
Fe	10	1.0	5	3	0.02	—	0.3	—
Hg	0.1[j]	—	200	7	0.1	—	1	—
Mn	1	0.1	1	2	0.6	—	0.03	—
Ni	4	1.5	6	1	20	0.05	0.1	—
Pb	2	0.2	8	5	—	12	—	0.025
Sb	—	—	200	17	1	0.3	1	—
Se	—	—	30	0.75	0.1	—	—	—
V	10	2.5	6	2.5	2	—	0.1	—
Zn	0.2	0.004	2	1	1	3	1	0.02

[a] AA = atomic absorption spectrometry; ICP = inductively coupled plasma emission spectrometry; XRF = X-ray fluorescence spectrometry; INAA = instrumental neutron activation analysis; IPAA = instrumental proton activation analysis; AES = atomic emission spectrometry; DP-ASV = differential polarography-anodic stripping voltammetry.

[b] 2000 m^3 of air sampled—low temperature ashed, followed by acidic extraction.

[c] Adapted from absolute (ng) detection limits by assuming 2000 m^3 sample volume and sample uptake to 10 mL of solution, with 20μL of solution applied to the graphite tube.

[d] Adapted from solution detection limits by assuming 10 m^3 sample volume and sample uptake to 10 mL. Optimum values, not necessarily representative of air particulate analyses.

[e] Adapted from absolute (ng) detection limits by assuming 72 m^3 of air sampled through 8.0 cm^2 area of Teflon filter.

[f] 80 m^3 of air passed through polystyrene filters; neutron flux of 10^{12} to 10^{13} n-sec^{-1}-cm^{-2}; 30 cm^3 Ge(Li) detector.

[g] 1000 m^3 of air passed through polystyrene filters; bombardment with 50 μA of 35 to 40 MeV electrons; 50 cm^3 Ge(Li) detector.

[h] Adapted from absolute (ng) detection limits by assuming a 10 m^3 sample volume. Optimum values, not necessarily representative of air particulate analyses.

[i] Adapted from absolute (ng) detection limits by assuming a 10 m^3 sample volume.

[j] Cold vapour flameless AA.

used for the analysis of trace elements in airborne particulate matter. These include arc-spark emission, plasma emission, atomic fluorescence spectrometry and flame photometry.

Activation analysis encompasses techniques such as instrumental thermal neutron activation analysis (INAA) which can provide simultaneous determination for up to 35 elements in suspended particulates with high precision, sensitivity and accuracy. Particles can be analyzed directly on a filter; however, several weeks are often required for analysis.

X-ray spectrometry includes a number of analytical techniques, some of which are increasingly used to analyze particles. Of these, energy dispersive x-ray fluorescence spectrometry (XRF) is most widely used. XRF is a multielement, nondestructive technique which can simultaneously determine up to 30 elements on the filter medium. It is often used to analyze dichotomous sampler filters. The technique involves the excitation of tightly bound electrons in the atoms by an x-ray generator and observations of the x-ray emissions accompanying de-excitation.[13] Other analysis techniques include spark source mass spectrometry,[14,15] and electrochemical methods such as anodic stripping voltammetry.[16]

A comparison of the analytical detection limits for selected trace elements by various instrumental techniques is presented in Table III. This table has been compiled from several sources[6,10,13,14] and presents, within the limitations of the available data, the detection limits expected during the analysis of real samples. Sample preparation is normally by wet ashing or a combination of low temperature dry ashing and acidic digestion. For glass fiber filter samples and samples containing siliceous material, an hydrofluoric acid digestion step may be required. Final sample volume has been assumed to be 10 mL. The analysis techniques of XRF, INAA, IPAA and graphite spark AES can normally determine elemental concentrations directly on the filter surface, provided that a suitable filter material is chosen (normally Teflon, polystyrene or cellulose; glass fibre is not suitable for surface analysis techniques). From Table III, the two forms of AAS provide good detection limits for most of the elements listed. However, only one element can be analyzed at a time. Multielement analysis techniques, such as XRF, ICP and INAA, require much larger investments in equipment and personnel.

Atmospheric Levels and Species

Determinations of trace elements in the atmosphere have, for the most part, been concerned with regions of high population density and with emissions from specific sources. However, a considerable amount of attention also has been recently focused on determining trace elements in rural and remote areas in order to estimate the regional and global effects of man's activities.

Sources

In order to interpret the significance of atmospheric levels of toxic trace elements, it is necessary to acquire some knowledge of their sources. Natural sources of aerosols containing trace elements include terrestrial dust, sea spray, volcanic emissions, forest fires and biogenic emissions. Anthropogenic sources of particles with relatively high loadings of toxic trace elements and their compounds are power plants (e.g., coal and oil fired electricity generating stations), primary and secondary non-ferrous metal smelters, incinerators, other metallurgical operations (e.g., iron and steel mills, ferroalloy and foundry furnaces), cement plants and transportation sources (e.g., vehicle exhaust, reintrained road dust). The chemical composition of emissions associated with most of these sources has been discussed in earlier reports and reviews.[17-25] A fine particle emission data base that contains information on chemical composition from various source tests also has been consolidated by the U.S. Environmental Protection Agency.[26]

Natural Sources

The toxic trace metals of concern in this review are present in various proportions in airborne dust, with chemical composition and size distribution reflecting the different types of sources. Generally, the major trace elements in crustal dust (in their order of abundance) are: iron, manganese, zinc, lead, vanadium, chromium, nickel, copper, cobalt, mercury and cadmium, varying in amount from approximately 0.2 μg/g for cadmium, for example, to 550 μg/g for manganese.[6] However, these abundances vary greatly throughout the world, reflecting different types of crustal materials. Oceanic aerosol contains trace amounts only of iron, manganese, lead, vanadium and zinc [amounts ranging from 0.009 (vanadium) to 5 μg/g (iron)].[6] The other relevant constituents are all present in ultratrace amounts. For example, the mean cadmium concentration in ocean water is reported to be 6 pg/g.[25] Other natural sources include forest fires, in which cadmium has been measued at levels of approximately 0.32 μg/g.[25] Some studies have been carried out on biological emanations of toxic trace elements, including the measurement of releases of zinc from leaves[27] and mercury from peas,[28] volatile exudates of vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, arsenic, lead, cadmium, and antimony from coniferous trees,[29] and the detection of gaseous alkyl arsenic compounds in greenhouse atmospheres and as emanations from soils treated with inorganic arsenic.[30] Some of the major elements emitted in the ash for volcanoes include iron, manganese, vanadium, zinc, cobalt, arsenic and antimony, in decreasing order of concentration.[31] Cadmium has been estimated to be 20 μg/g in volcanic emissions.[25]

Anthropogenic Sources

The principal trace elements often found in most types of coal-fired power plant ash are, in decreasing order of concentration, iron, zinc, lead, vanadium, manganese, chromium, copper, nickel, arsenic, cobalt, cadmium, antimony and mercury.[19,21,32] Many of these elements are reported to be enriched in the finest particles for which particulate control devices are least effective.[19] For example, analysis of both retained and emitted fly ash from a coal-fired generating station equipped with a cyclonic precipitation system indicated pronounced enrichment of the species: zinc, arsenic, lead, chromium, nickel, antimony and cadmium. Limited enrichment was found for iron, manganese and vanadium and essentially no enrichment for copper, tin and cobalt. It was hypothesized by these and other investigators that certain elements (i.e., with boiling points below the temperature of coal combustion) are volatilized and may either adsorb or condense onto entrained particles with greatest mass per unit weight for the smallest particles.[19,33] Oil-fired thermal generating station fly ash has been found to contain vanadium, iron, zinc, lead, copper, arsenic, cobalt, chromium, manganese and antimony.[32] Incineration of municipal waste is another potential source of the trace elements zinc, iron, mercury and lead with smaller amounts of tin, arsenic, cadmium, cobalt, copper, manganese, nickel and antimony, dependent on the feed type.[23,24] Open-hearth furnaces in steel mills contribute principally iron and some zinc, with lesser amounts of chromium, copper, manganese, nickel and lead. Emission data, measured in the plume of a major nickel smelter, indicate the predominantly emitted elements iron, copper and nickel were mainly associated with coarse particle sizes while lead, zinc and cadmium, found in lesser amounts, were primarily associated with the fine particle mass.[34] Emissions of vehicles burning regular gasoline con-

Table IV. Properties of some common oxides associated with ambient aerosols.[46,47]

Oxide	Melting point[a] °C	Boiling point[a] °C	Density g/cm³	Vapour pressure (mm Hg) 500 K	Vapour pressure (mm Hg) 1000 K
As_2O_3	313	457	3.74	1.9×10^{-9}	n/a
As_2O_5	(d.315)	—	4.32	6.3×10^{-7}	n/a
CdO	—	1559	8.15	3.3×10^{-37}	9.0×10^{-4}
CoO	1805	>2000	6.45	n/a	n/a
Cr_2O_3	2265	4000	5.21	n/a	n/a
Cu_2O	1230	1800	6.0	n/a	n/a
CuO	1326	—	6.4	n/a	1.53×10^{-4}
HgO	(d.500)	—	11.1	n/a	n/a
MnO	1780	2600	5.18	n/a	n/a
NiO	1984	>2000	7.45	1.3×10^{-72}	6.46×10^{-14}
PbO	886	1472	9.53	1.58×10^{-35}	4.5×10^{-3}
PbO_2	(d.290)	—	9.38	n/a	n/a
Sb_2O_3	655	1550	5.67	n/a	n/a
SeO	—	180	—	n/a	n/a
SeO_2	340	(d.322)	3.95	1.7×10^{-7}	n/a
SeO_3	118	(d.180)	—	6.35 (400 K)	n/a
V_2O_5	670	1750	3.56	n/a	n/a
ZnO	—	(d.1975)	5.6	n/a	n/a

[a] d. = decomposition.

tain lead with smaller amounts of zinc and iron.[35] As noted previously, smaller particles derived from high temperature combustion processes tend to be enriched with toxic trace elements such as arsenic, cadmium, chromium, lead, vanadium and zinc.[6] Accordingly, several investigators have noted implications with respect to health (i.e., greater pulmonary system penetration).

Chemical Forms

Little information is available, at present, about the chemical forms and physical/chemical transformations of toxic trace elements in the atmosphere. The analytical techniques normally used only provide information on total metal content rather than specific compounds or chemical species. In the absence of this type of information, it is generally assumed that many of the elements of anthropogenic origin (especially from combustion sources) are present in the atmosphere as oxides. Particulate matter in incinerator emissions may conceivably contain trace elements in the form of chlorides. Elements associated with windblown crustal dust or mechanical crushing activities (i.e., mainly large particles) presumably occur as sulphides, silicates, carbonates and other mineralized species. Nevertheless, of further importance, some metals have been found to be strongly correlated with sulphate in samples of airborne particulate matter.

Heterogeneous oxidation of sulphur dioxide in air can be catalyzed by species such as iron,[36–38] manganese[36] and cadmium,[39] while vanadium is suspected to catalyze the formation of sulphuric acid during oil combustion.[40] Furthermore, oxides of iron, manganese and lead are reported to adsorb SO_2.[41] Interactions of SO_2 and particulate matter have been discussed by Urone and Schroeder.[42]

It has been suggested that the elements arsenic, cadmium, manganese, nickel, lead, antimony, selenium, vanadium and zinc volatilize at high temperatures during fossil fuel combustion and condense uniformly on surfaces of entrained flyash particles as the temperature falls beyond the combustion zone.[43] Because of this, anthropogenic sources of trace element emissions can be more important, from a toxicity viewpoint, than natural sources where trace elements are usually bound within the matrix of natural aerosols. Significant coagulation and interaction can often occur between ambient particles (of both natural and anthropogenic origin) and emitted species, as evidenced by arsenic, copper and zinc being found coated on clay or mineral agglomerates.[44]

Certain trace metal compounds associated with road dust, which can accumulate from anthropogenic as well as crustal (soil) sources and can subsequently become re-entrained in the atmosphere, have been qualitatively examined by various extraction procedures.[45] In these samples, lead and zinc were found to be strongly associated with carbonate and iron-manganese oxide phases, with small amounts being associated with an organic phase. Approximately one-half of the cadmium was associated with carbonate and iron-manganese oxide phases, while copper was found to be mainly associated with the organic phase and, to a lesser extent, the carbonate phase. These associations influence the relative mobility and bio-availability of trace metals in the environment. In the road dust example cited, the degree of bio-availability was thus suggested to be cadmium > lead ≃ zinc > copper.

Oxidation of those species present as aerosol results from interaction with various atmospheric oxidants, such as molecular oxygen, ozone or hydrogen peroxide. Some common oxides associated with ambient aerosols are listed in Table IV along with some relevant physical properties for the pure state.[46,47] The presence of any one or several of these oxides has been measured in emissions of cement plants,[41] blast furnace and sintering operations,[38] secondary iron foundries,[44] non-ferrous smelting of arsenic-bearing ores,[49] zinc and lead smelters[50] and many other sources.[22]

Sulphation, and possibly nitration, of metallic oxides can be surmised to be an important transformation as particles age. A statistical assessment of multielemental measurements in a study in the rural and urban atmospheres of Arizona showed strong correlations of lead, copper, cadmium and zinc, with sulphates in the rural atmosphere, and moderate correlation of lead and copper, with sulphates and nitrates in the urban atmosphere.[51] This correlation may be due to similarities in particle size distribution (i.e., transport and residence time phenomena), identical sources or chemical associations between these metals and sulphate.

Atmospheric Concentrations

Measurements of trace elements associated with particulate matter in the atmosphere have been reported over the last 10 to 15 years for a large number of locations throughout the world. Table V summarizes data for the elements As, Cd, Ni, Pb, V, Zn, Co, Cr, Cu, Fe, Hg, Mn, Se, and Sb in terms of ranges of concentrations measured at remote, rural and urban locations.[52–197]

It is difficult to draw generalized conclusions from the data, especially when results are presented in the form of ranges, and not as mean values. Nevertheless, the following

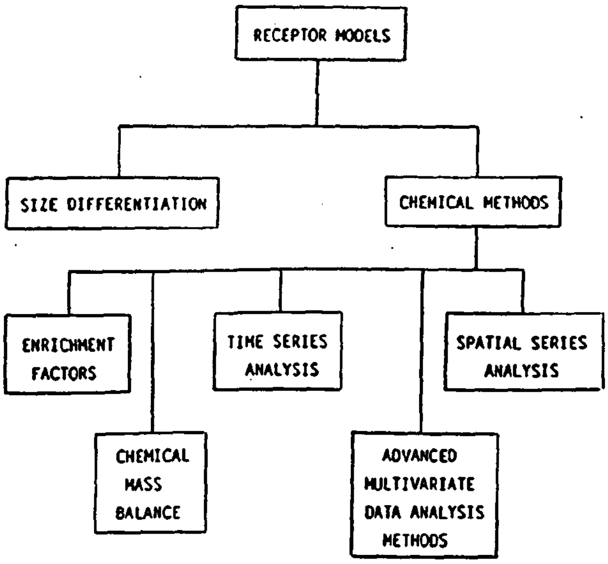

Figure 1. Receptor model types.[24]

trends are apparent. Individual trace element concentrations vary widely with location, ranging from less than one nanogram per cubic metre in remote areas to tens of micrograms per cubic metre in polluted urban areas. The remote areas recorded measurable concentrations of some of the elements associated with crustal origin, as well as some elements indicative of anthropogenic sources. The latter component supports the hypothesis of long range atmospheric transport into these remote areas. Data obtained for rural areas, although having considerable variation, generally show values that fall between those measured at urban and remote sites. The urban data are subdivided to reflect concentrations in different parts of the world. However, the ranges for each element in most cases do not vary greatly among the four general locations discussed (i.e. Canada, U.S.A., Europe and other).

Elements such as iron, lead and copper are measured in the greatest abundance on particulate matter, at all locations, whereas elements such as cobalt, mercury and antimony are found in the smallest quantities. Mercury, for example, is present in ambient air predominantly in the vapour phase and only about 5 percent has generally been found associated with particulate matter when collected with a hivol sampler. The quantities found in association with particles are a direct function of vapour pressure and source strengths of these elements, be they of anthropogenic or natural origin. Essentially, all the trace metals are enriched in urban aerosols, when compared to crustal dusts.

Atmospheric concentrations and related aspects of trace metals have been summarized and discussed in considerable detail in several recent publications (see Bibliography) and, consequently, will not be discussed further here.

Source Identification

Source oriented dispersion models have been traditionally used to estimate or predict the impact of a particular source at a receptor site. Alternatively, receptor oriented models have evolved more recently as a means to identify relative source contributions at a given site. Several approaches are summarized here. Particle mass contributions are apportioned to various source types using measured particle composition data, meteorological data and knowledge of source characteristics. Figure 1 provides a schematic illustration of the relation of various types of receptor models. Microscopic methods to distinguish source contributions, by examining ambient air samples, are not considered to be a practical tool for large scale quantitative assessments. Hence, emphasis generally has been directed toward chemical methods with the use of multielemental analytical techniques. Chemical methods have been described in detail in several major reviews[24,198,199] and have been summarized below. Table VI, summarizes the data input and output formats, advantages and disadvantages, and specific references to field studies.

Size Differentiation

The major parameter governing the atmospheric behaviour and ecological significance of natural and anthropogenic emissions of environmentally important metals is particle size. It is now generally accepted that elements associated with particles less than 1 μm tend to result from combustion and other high temperature sources, while large particles (greater than 10 μm) are likely to arise from wind action on soils, deposited dusts and fugitive emissions from dust-producing operations.[268] However, varying processes and emissions within each industrial sector and over time and space may confound the process of deriving a characteristic fingerprint of individual sources for each location. This method has been applied in many surveys, with variable success.[100,109,112,122,200,201,268–273] Generally, however, chemical methods are used in place of size differentiation methods in most surveys.

Enrichment Factors

The enrichment factor concept compares the elemental composition of the ambient aerosol of interest relative to an element characteristic of a background (natural) aerosol;

$$\mathrm{EF} = \frac{\mathrm{Ci/Cn\ (ambient)}}{\mathrm{Ci/Cn\ (background)}}$$

where Ci = element whose enrichment is to be determined,
and Cn = normalizing element assumed to be uniquely characteristic of the background.

Elements with an enrichment factor greater than 1.0 are assumed to be due to anthropogenic sources in the local or regional airshed of interest. Crustal elements are generally used as reference compounds for land based studies, i.e. silicon, iron, aluminum, scandium and titanium. For studies involving exchange across the ocean-air interface, sodium is the reference element of choice.

Most useful applications of this concept have been in interpreting small data sets by distinguishing major types of particles and potential sources. Enrichment factors derived in remote areas are often used to provide evidence concerning the nature and extent of long range transport of anthropogenic emissions.[51,63]

Chemical Mass Balance

The chemical mass balance (CMB) method uses typical emission characteristics of selected source categories, and elemental compositions of aerosols at a sampling site to statistically back-calculate the fractions of the overall aerosol contributed by all major source categories.[24,202,225] Atmospheric modifications such as condensation, volatilization, chemical reactions, deposition or meteorology are not accounted for in the simpler forms of this approach; it is assumed that the mass of each chemical component is conserved. Requirements of this method are a detailed knowledge of the elemental composition of both source and receptor samples and that source categories be reasonably distinct. This technique is not readily amenable to predictive modeling capability. Motor vehicle factors are included as a source in most studies; other studies have included components such as marine, steel, and cement.[24,111,224,226] This method is currently the most widely used of all the receptor models.

Table V. Concentration ranges of various elements associated with particulate matter in the atmosphere (ng/m^3).

Location	As	Cd	Ni	Pb	V	Zn	Co	Cr	Cu	Fe	Hg	Mn	Se	Sb
Remote	0.007–1.9	0.003–1.1	0.01–60	0.007–64	0.001–14	0.03–460	0.001–0.9	0.005–11.2	0.029–12	0.62–4160	0.005–1.3	0.01–16.7	0.0056–0.19	0.0008–1.19
Rural	1.0–28	0.4–1000	0.6–78	2–1700	2.7–97	11–403	0.08–10.1	1.1–44	3–280	55–14530	0.05–160	3.7–99	0.01–3.0	0.6–7
Urban														
Canada	7.7–626	2–103	4–371	353–3416	10–130	55–1390	1–7.9	4–26	17–500	700–5400	<5	20–270	n/a	13–125
U.S.A.	2–2320	0.2–7000	1–328	30–96270	0.4–1460	15.–8328	0.2–83	2.2–124	3.–5140	130–13800	0.58–458	4–488	0.2–30	0.5–171
Europe	5–330	0.4–260	0.3–1400	10–9000	11–73	160–8340	0.4–18.3	3.7–227	13–2760	294–13000	0.1–5	23–850	0.01–127	2–470
Other	20–85	0.6–177	2.3–158	1.3–11020	1.7–180	110–2700	0.3–10	tr–277	2.0–6810	21–32820	1.2–1.8	1.7–590	n/a	7–36
References	52–54,57–58 60–63,76,82,84–85,89,94,96–97,99,100 113–114,116,123,133–136,144,146–147,150,153,157,159,179–181,197.	10,25–51 57,62,70,75–76,78 80–81,83–85,88,90–93,97–98,101,106,109 110,115,117,119–121,123,128–131,133–135,137,139,144–145,147–148,150,155,157,159–161,163–169,171,171–176,177,178–182,185,189–190,196–197.	51–53,56–57,59–61,75,78,81–82,84,85,88,92,93–98,99,101,106,108,111,113,115,117,119–120,122–123,130–131,133–135,137–139,145–147 155,157,159,171,173,179,180,183,185,187,189,191.	10,51–57,59–62,64,67–75,77,78,80–88,90–95,97–101,103–106 108–112,115–124,130–134,136–148,150–152,154–155,157,159,160,164,170–172,175–176,178–180,183–194,196–197.	51–55,57–59,60,62–64,70,75–76,78–79,82–85,92–93,98–99,101,102,107,112,113,115,116,118–120,122–123,125,130–134,137,143–147,149–150,154–157,159,171,173–179,181,183,185,187,191.	10,51–65,57,59–62,65–68,70,75–76,78,81–86,89,90,93,96–97,99,101,102,104,107–114,116–117,119–123,125,127,130–131,133–134,136,138,139,142,144–150,152,155–157,159,160,164,171,174–175,179–181,183–184,187,189–191,196,197.	51,53–54,57,59,62,64,67,70,68,70,81–82,84–85,89–90,96,99,102,107,113,116,119–121,123,125,127–129,133–135,144–147,149–150,156–157,161,163,174,179–181.	10,51–57,59,61–65,67,75–76,79,81,82–84,85,89,92–93,99,107,111,113,115,117,119–120,125,127–131,133–135,137–139,143–147,150,152,155,157,161,163,171,173–174,179–180,187,189,196.	10–51,53–57,59–62,66,68,70,76,78,81,82,84,85,90,93,96,98–99,101,104,106,108,109,111,113,115,117,121,123,126,130–134,136,139,143–148,150,152,155–157,159,162,171,173,179–181,183,187,189–190,196–197.	10,51–57,59–68,70,72,75–76,78,81–85,89,92–93,96,99,101–102,104,107–109,111–114–116,117,119,120,122,125,131,133–136,139,143–147,149,150,152,154–157,159–161,163–164,171,174,179–181,183,185,187,189–191,196,197.	52,54,57–58,67,76,84–87,89,91,96,99,107,113,117,128,129,144,146,161,163,180,181.	10,51–57,59–62,64–65,70,75,76,78,81–85,89–90,92–93,99,101–102,104,106,109,111–114,117,119,120,122,123,125,127–129,130–131,133–134,136–137,139,143–150,152,155–157,159,161,153,171,173,174,179–181,183–185,189,191,197.	10,52–54,62,64,70,76,82,83–85,89,102,107,119–121,125,127,133–136,144,149–150,158,162,174,180.	52–54,57,62–65,67,70,76,82,84–85,88,89,96–97,99,102,107,113,114,119,121,125,127–129,133–135,139,144,147,149,150–156,157,161,163,174,179–181.

Table VI. A comparative summary of receptor models using chemical methods.

Method	Method description	Input	Output	Advantages	Disadvantages	References
Enrichment factor	Ratio of an element in ambient aerosol to the element in background aerosol is determined.	Concentrations of ambient and background levels of an element.	Ratio, which if >1.0, indicates anthropogenic origin.	Useful for interpreting small data sets, especially in remote regions (evidence of long range transport).	Not applicable to complex multiple source mixtures.	51,54,55,66,90,99, 127,136,150,163, 197,200–223
Chemical mass balance	Source emission data is "balanced" with concentrations at a sampling site.	Source emission chemistry and analysis of TSP measured at a receptor for trace elements and source categories.	Contributing factors to trace elements composition at receptor are identified, i.e., marine, auto, fuel, street, soil, incineration, etc.	Investigators claim CMB "accounts" for ≃80% of the observed concentrations.	It is necessary to have a knowledge of source emissions (elemental composition). Meteorological conditions, source emissions and ambient concentrations cannot be varied in time and space, although subsets of data representing specific conditions can be selected.	110,111,114,118,134, 202,214,224–232
Multivariate methods	Source contribution determined on the basis of the variability of elements measured on a number of filters.	Trace elements measured on a large number of filters and knowledge of source characteristics.	Contributing factors to trace element composition at receptors are identified.	Variability of ambient concentrations, source emissions and meteoroloy can be incorporated. The method usually accounts for ≃80% of the elements. Unexpected sources may be identified.	The models consider variation in the data set rather than absolute concentrations and are not effective on data sets where little variation exists. Prior knowledge of the number of sources and chemical features required.	51,77,92–103,125,130, 171,215,233–252
Time series correlation	Method based on the assumption that a comparison of the relationships between sites and periods of time accounts for the environmental conditions affecting them. Parametric time series analysis assumed to remove the variability of meteorology, etc. Residuals used to describe element source associations.	Chemical analysis of a continuous record of TSP, which is then analyzed into discrete time period averages.	Statistical residuals, after correlation matrices of the elements.	Qualitative. Used to confirm source identifies suggested by other models, and may assist in pinpointing new sources.	Method cannot determine specific source identities.	90,105,194,253–255
Spatial and meteorological patterns	Measured concentrations at different receptor sites are compared and presented as spatial isopleths, spatial correlation, pollution wind roses.	Chemical analyses of TSP data collected at various sites. As well, can include meteorological data for the time of sampling.	Statistical correlations, isopleth maps (visual).	Qualitative. Used to confirm source identities as part of hybrid models.	Method cannot determine specific source identities.	91,129,222,256–267

Multivariate Models

In general, multivariate statistical models can be divided into two methods, i.e. factor analysis and pattern recognition methods. Both approaches attempt to extract information statistically from a large number of samples about source contributions on the basis of the variability of such factors as element concentrations, source emissions and meteorology.

In one form of pattern recognition, the data set is characterized based on previously established patterns. Cluster analysis, another form of pattern recognition, requires no preconceived patterns. Discrete elements are grouped based on the degree of similarity between elements. The measure of similarity between species is based on the correlation coefficient; clustering is usually performed hierarchically and displayed as a dendrogram or as a non-linear map.[274] A drawback is that this technique does not allow quantification of the impact of a specific source of emissions. The technique has no predictive abilities and cannot be used to document changes in emissions over time.[233]

Factor analysis methods express each variable (concentration of the *i*th element on the *k*th filter) as a linear combination of factors. Hypothetical variables are selected so as to reproduce the measured variable correlations as closely as possible with the fewest possible factors. The coefficients of these factors are determined, starting with the correlation matrix of observed chemical components. Source identification is possible by comparing the elements having a high loading on a factor with the elements associated with known sources. Precise knowledge about the chemical characteristics of possible sources is required, and often proves to be a major drawback. As well, factor analysis cannot quantitatively determine the contribution of specific source types and cannot provide source information for each filter.

To overcome the limitations inherent in factor analysis, target transformation factor analyses (TTFA) was developed,[102] combining basic CMB principles with factor analysis. If one has accurate knowledge of the composition patterns of some components, TTFA allows one to "rotate" the raw solution matrices so that some of them line up with the known components. The errors of factor loadings and scores obtained by TTFA are calculated with the aid of an "error matrix" (difference between observed and TTFA reproduced data).[275] One major advantage of TTFA is the possibility of using other variables such as meteorological parameters in the overall analysis.

Multivariate models consider variations in the data set rather than absolute concentrations and are not effective on data sets in which little variation occurs. Components with very similar composition patterns cannot be resolved. On average, most elements can be accounted for within a factor of 2.

Removal Processes

Several literature reviews encompassing removal and deposition processes have recently been compiled.[46,276–279] Measured values of metal deposition appear to be characterized by large temporal and spatial variability, and are best known in the vicinity of strong point sources, although a few remote measurement data are available. Metals can be deposited either wet or dry from the atmosphere. Wet deposition rates can be parameterized by a scavenging or washout ratio, whereas dry deposition processes can be parameterized in terms of deposition velocity (see Bibliography, Item 5). An assessment of the relative importance of dry vs. wet deposition for the metals of concern in this study, is presented in Table VII and indicates the absence of any well defined trends among the elements considered. Dispersion models can account for deposition by incorporating the dry deposition velocity and/or washout ratio.

Deposition processes have been dealt with in considerable detail in a number of studies ranging from relatively simple to complex theoretical approaches. Particle size is one important parameter in determining the deposition or removal mechanism, i.e., gravitational settling, atmospheric eddy diffusion and molecular motion in the air near the surface. In the case of dry deposition, particles greater than 5 μm in diameter will be deposited primarily by gravitational settling. Inertial impaction-interception is the primary deposition process responsible for particles with diameters of 0.3 to 5 μm. Particles with diameters less than 0.3 μm are primarily deposited as a result of Brownian diffusion. These three general "regimes" are each governed by a resistance term, which defines the extent to which the combined effect of the parameters within that regime limit the deposition rate.

Table VII. Wet deposition vs. dry deposition of some common trace elements.[46]

Element	Percent dry deposition		
	Marine	Rural	Urban
As	[a]	[a]	20
Cd	40	40	60
Cu	50	[a]	[a]
Mn	50	50	50
Ni	60	50	50
Pb	60	30	20
V	40	[a]	[a]
Zn	70	40	50

[a] Not available.

Some variables influencing dry deposition processes in the atmospheric regime include atmospheric stability, aerodynamic roughness, pollutant concentration, relative humidity, solar radiation, air temperature, terrain, wind velocity and seasonal variation. The surface air layer regime is influenced by such factors as canopy growth, leaf vegetation, nonbiotic surfaces, pH effects, pollutant penetration and distribution, prior deposition loadings and the presence of water. The receptor regime is influenced by factors such as agglomeration, particle diameter, density, hygroscopicity, impaction, physical properties of pollutants, and resuspension.[279]

The simplest empirical expression for dry deposition assumes that the flux to a surface is directly proportional to the air concentration at a defined height above the surface, i.e.,

$$F = V_d X_z$$

where F = deposition flux of particles
V_d = dry deposition velocity
X_z = concentration of particles at height z

The relationship between deposition velocity and particle size is exponential. A minimum in the deposition velocity occurs at the size range of 0.3 to 0.5 μm, with Brownian diffusion increasing as particle size decreases below 0.3 μm, and deposition velocities increasing for particles below this size. Inertial interception-impaction increases as particle size increases above 0.5 μm, further increasing the deposition velocities. Order-of-magnitude particle deposition velocities to land and water surfaces are estimated to be 1 cm/s for particles between 1 μm and 10 μm in diameter, and 0.2 and 1.0 cm/s for particles between 0.1 μm and 1.0 μm in diameter, respectively. Generally V_d values are considered to be uncertain by a factor of 3.[46]

Wet removal of particles by precipitation involves an "attachment" process as well as actual "removal." The degree of attachment of the particles to the precipitation is itself a function of particle size and age, solubility and the prevailing condensation and evaporation conditions. Attachment can occur within a cloud (rainout) or below a cloud (washout).[46,277,280] The removal process is generally considered to

Table VIII. Deposition rates, velocities and washout ratios for selected metals in remote, rural and urban areas.[46,279]

Deposition rate (kg/ha/yr)	As	Cd	Co	Cr	Cu	Hg	Fe	Mn	Ni	Pb	Sb	Se	V	Zn
Remote														
Bulk	0.00031	0.000002–0.00005		0.003	0.000012–0.0019	0.0002		0.0062		0.000012–0.0093	0.00016			0.000011–0.025
Dry						0.002								
Rural														
Bulk	0.01–<10	0.0012–<0.1		0.01–0.5	0.018–0.5	0.00073–0.01	0.85	0.021–0.5	0.01–0.5	0.01–<2.72	<0.01	<0.01	0.01–12.4	0.04–11
Dry	<0.0036	<0.047		<0.02		<0.02		<0.31	0.09	<0.72			<0.25	<2.02
Wet	<0.8	<0.094		<0.57	0.033	<0.0002	0.54	<0.25	<0.87	<2.1			<4.8	0.095–<7.92
Urban														
Bulk	0.0025–<1.1	0.007–0.26	<1	10.6	0.002–3.01	0.015	0.4–10.0	<1.0	0.1–5.95	0.05–12.36			0.043–8.3	0.07–15.8
Dry	0.002–<0.003	<0.094	0.00009	0.0026–0.4	0.119	0.00005	0.117	0.0027–<0.83	0.0044–<1.1	0.042–<2	0.006		0.003–<0.35	0.053–5.94
Wet	0.001–<1.23	0.001–<0.17	0.000036	0.00084–<0.7	0.164	0.0003	0.042	0.0023–<0.99	0.0044–<2.74	0.026–<26.5	0.004		0.044–<9.04	0.12–11.9
Washout ratio	110	125–5000		150	140–751		250–951	370–5000	125	76–169			110	179–1000
Dry deposition velocity (cm/s)	<0.1	0.4–8.0	0.3–1.9	0.5	0.5–1.1		0.3–1.9	0.4–0.9	0.45–2.0	0.16–0.3	0.06–<0.4	<0.1–0.6	0.2–0.7	0.4–4.5
References	168,279, 282–284.	85,164, 168,279, 283,285–293.	168,279, 285.	164,168, 214,282, 283,285, 286.	164,168, 214,276, 279,282, 284,287, 289–291, 294–297.	168,214, 292,294, 298–300.	164,276, 279,285, 286,297 301,302.	164,168, 214,276, 279,282, 283,285, 291,293, 297.	164,168, 276,279, 283,285, 286,295, 296.	164,168, 214,276, 282–293, 295,297, 302–305.	168,279, 282,285.	168,279.	164,168, 279,283, 285,289, 297.	164,168, 214,276, 279,282–285,288, 291–293, 295–297, 302.

be a function of precipitation amount, growth processes, storm intensity, and seasonal variations (ice crystal growth vs water droplet growth).[46]

Simple empirical models involve the use of scavenging coefficients or scavenging ratios, and are based upon the concept that wet deposition processes can be treated as exponential decay processes. The scavenging coefficient is defined within the equation,

$$X_t = X_0 e^{-st}$$

where X_t, X_0 = airborne concentration of pollutant at times t and 0, respectively,
s = scavenging coefficient (time^{-1})

The deposition rate is then

$$L_{wet} = X_{av} sHt$$

where L_{wet} = deposition rate due to scavenging
X_{av} = average concentration through H
H = scavenging height

Scavenging (or washout) ratio is an alternative approach to the quantitative definition of wet deposition and has been defined as the ratio of the contaminant mass in precipitation falling through a column of air, compared with the mass in the column of air,[278] such that:

$$W = \frac{Kd}{X}$$

where W = scavenging ratio
K = concentration of contaminant in precipitation
X = concentration of contaminant in unscavenged air
d = density of air

Using this approach, the wet deposition rate is given by

$$L_{wet} = \frac{WXJ}{d}$$

where J = rainfall rate

Both wet scavenging coefficients and scavenging ratios have been found to increase with particle size and decrease with precipitation intensity.[278] Models attempting to account for in-cloud scavenging rarely attain an accuracy better than a factor of 3 on an event basis.[280,281]

Table VIII presents selected values of deposition rates and includes measured deposition velocities and washout ratios for each metal. The ranges of metal concentrations in precipitation vary widely within the categories of remote, rural and urban areas. Because of such variations, the sparsity of measured data, especially in remote areas, and differences in sampling techniques, it is difficult to assign a "representative" rate, velocity or ratio to each element in each location. For example, bulk deposition rates for all elements were in the range of 1 × 10^{-6} to 1 × 10^{-2} kg/ha/yr for remote areas, 1 × 10^{-4} to 10 kg/ha/yr for rural areas, and 1 × 10^{-3} to 10 kg/ha/yr for urban areas. Dry deposition rates ranged from approximately 1 × 10^{-3} to 1 kg/ha/yr in rural areas, and 10^{-5} to 10 kg/ha/yr in urban areas. Experimentally, the usual approach of determining washout ratios is to collect precipitation and then measure the trace metal concentration in the precipitation sample as well as in the ambient air. Mass washout ratios with units of (μg/kg rain)/(μg/kg air) have been used in this review. This results in a number smaller by a factor of approximately 815 than washout ratios calculated on a concentration basis in units of (μg/m^3 rain)/(μg/m^3 air). Washout ratios (shown in Table VIII) varied among the elements and between studies of the same element, and values ranged from as low as approximately 100 for As, Ni, Pb and V to as high as 5000 for Cd and Mn. Dry deposition velocities were generally in the same range for all the elements, i.e., 1 × 10^{-1} to 1 cm/s.

The relative importance of wet and dry deposition processes will be a function of distance from the source, particle size range, meteorological conditions, time of year (season) as well as other factors. Knowledge of both the wet and dry deposition processes and their relative importance is necessary in determining the total atmospheric residence time of toxic trace elements, the distances over which they can be transported, their ambient air concentrations and their impact on terrestrial and aquatic ecosystems. At the present time, wet deposition fluxes can be more easily and reliably determined than dry deposition fluxes. That is, methods for directly measuring dry deposition fluxes are still at the research stage and have not yet been implemented on a routine monitoring basis. Insofar as bulk measurements do not differentiate between wet and dry loadings, data derived by bulk measurement techniques are considered to be of more limited value.

Global Cycles

On a global scale the atmosphere constitutes a prime vehicle for the movement and redistribution of many heavy metals. Processes such as dispersion, coagulation, washout and sedimentation are averaged over a long time period, over a continental to global scale. Contributions attributed to these processes are accounted for in either the source or sink flux.

The simplest type of model treats selected portions of the oceans and the atmosphere as compartments or boxes in which the particulate matter or trace element is assumed to be uniformly distributed. Exchange rates are determined between adjacent boxes in the form of a set of mass balance equations.[306] Movement and pathways are often obtained from experimental studies using radionuclides and from fallout from nuclear explosions.[307]

Residence times of trace metals constitute an important parameter in determining exchange rates between oceanic and atmospheric compartments. The ocean generally act as a sink for toxic metals.[308] In the atmosphere, heavy metals are mostly associated with particulate matter whose residence time is usually much less than, but can be as long as, 40 days.[309] For these pollutants, the troposphere as a whole is not an appropriate reservoir for studying their budgets and cycles; often a consideration of local or regional budgets would be more appropriate.[310] A rough estimate of total particle production on a global scale is between 1 and 4 × 10^9 tonnes/year with 5 to 20 percent of that figure of anthropogenic origin.[311] Each metal would only comprise a proportion of that figure; however, the values are still significant.

According to several studies[312,313] the polar atmosphere is only loosely coupled with the circulation in mid and lower latitudes. Snow samples collected in the Antarctic from 1880 to 1977 and analyzed for Cd, Pb, Zn, Cu, Fe and Mn were found to exhibit relatively unchanged concentrations over the years.[313]

Semi-empirical models provide an alternative to the box models. Global distributions of metals are examined as a function of time, eddy diffusion coefficient field, and chemical life-time of substance. Such models are based on large-scale Fickian diffusion in a vertically and zonally well-mixed troposphere which is symmetric about the equator. However, verification of such models can pose a problem due to lack of measured data to support the theories.[306]

The most complex type of model currently in use is the large scale, general circulation model. Global-scale dispersion is predicted from instantaneous three-dimensional wind fields based on a grid whose horizontal dimension is typically a few hundred kilometres. The difficulty of model verification still exists, and it is likely that the lack of knowledge of sources and/or sinks, and inadequate data for global distribution of heavy metals will remain one of the major limitations of such a general circulation model.[306]

The construction of even a rudimentary global cycle for a particular element can often be useful as an overview, by considering and providing an initial assessment of the sources, mechanisms of transformation and transport, and sinks for pollutants in the environment. However, such models have limited application due to the numerous assumptions that must be made and the lack of ability to verify modelled results on local, regional or continental scales.

Conclusions

The atmospheric pathways of the trace elements As, Cd, Ni, Pb, V, Zn, Co, Cr, Cu, Fe, Hg, Mn, Se and Sb, and their compounds, have been discussed in this literature review, with attention being given to specific aspects of sampling, analysis, sources, chemical forms, concentrations, and receptor as well as source oriented models on various spatial scales. These trace elements are most commonly sampled by filtration, using glass fibre or paper filters and hivol air samplers, with special studies using more diverse and sophisticated sampling devices and filter media. The most widely used analytical method, for trace elemental analysis, is atomic absorption spectrometry; other applicable methods include atomic emission, INAA, XRF, and PIXE spectrometry.

Primary sources of trace metals include terrestrial dust, sea spray, volcanic emissions, forest fires, biogenic emissions, power plants, smelters, incinerators, industrial furnaces and vehicle emissions. Physical and chemical transformations of some trace metals are known; however, this field still requires considerable further research. Individual trace element concentrations vary widely with location; ranging from less than one nanogram per cubic metre in remote areas to tens of micrograms per cubic metre in polluted urban areas, indicating strong local anthropogenic influences in the latter case, and concentrations attributable to natural sources and/or long range transport in the former situation.

Receptor-oriented models are used extensively to apportion trace element concentrations to source types, using procedures such as size differentiation, enrichment factors, chemical mass balance, and multivariate methods. They have been shown capable of accounting for up to 80 percent of the ambient sample constituents.

Deposition measurements for toxic trace elements are scarce and are often not very reliable. Bulk, dry and wet deposition rates are summarized for various locations, as well as dry deposition velocities and washout ratios. Dry deposition velocities reported are generally in the range of 1×10^{-1} to 1.0 cm/s for trace elements at various locations, while washout ratios (expressed on a mass basis) varied from approximately 100 to 5000 among the various elements.

Trace metals are generally associated with airborne particulate matter whose atmospheric residence time is less than, but can be as long as, 40 days. Box models, semi-empirical models, and large scale general circulation models are used to simulate "global" transport of such metals, but are not considered to be very accurate in most cases due to the numerous assumptions required.

It is evident that the literature on toxic trace elements associated with airborne particulate matter is voluminous. However, although this subject has received much attention in recent years, the need for further work should be emphasized. Research and development of improved sampling and analysis techniques, and more definitive studies of atmospheric transport, transformations and deposition processes are some of the areas requiring additional efforts.

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EFFECT OF ASH DISPOSAL PONDS ON GROUNDWATER QUALITY AT A COAL-FIRED POWER PLANT

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(*Received August 1985*)

Abstract—The impact of fly and bottom ash disposal ponds on groundwater quality was investigated at the coal-fired Columbia Power Plant at Portage, Wis. Groundwater sampling was conducted utilizing a network of piezometers and multilevel wells located at various cross-sections of the ash disposal facility. Analyses were performed for 16 major and minor elements, pH and conductivity. Data for a 3-yr monitoring program established the existence of large B, Na and SO_4 plumes in the groundwater system surrounding the ash disposal area. Substantial amounts of B, Na and SO_4 were present in the plume and portions were discharged into an adjacent wetland as the plumes moved with groundwater flow. The secondary fly ash settling pond was the major source of B and SO_4, while the main source of Na was from previous releases to the aquifer from the use of Na_2CO_3 to condition fly ash to enhance removal of SO_2 from flue gas by electrostatic precipitation. Movement into the groundwater of heavy metals such as Cu and Zn was not observed and their concentrations are likely attenuated in the pond.

Key words—coal-fired power plants, fly ash, leachates, ponds, groundwater, wells, groundwater movement, groundwater pollution, groundwater quality, wetlands, plumes, boron, sodium, sulfate, heavy metals, attenuation

NOMENCLATURE

$\bar{v}$ = velocity
k = permeability
i = hydraulic gradient
n = porosity
Q = discharge rate
A = cross-sectional area
ES = enforcement standard
PAL = preventive action limit.

INTRODUCTION

The use of coal for power generation is expected to increase in the United States due to the gradual depletion of domestic petroleum reserves. Over 60% of the electrical power in the United States is generated from coal burning (Murarka, 1982). However, coal combustion by electric utilities presents potential environmental problems, notably from rain acidification and ash disposal.

Total ash production in the United States has increased steadily since 1966. By 1990, the waste generated by burning coal is predicted to increase to 150 million tonnes yr^{-1} (Murarka, 1982). Most of this waste is coal ash (fly ash and bottom ash). Since 1973 most coal-fired power plants have been equipped with electrostatic precipitators to reduce particulate emission to the atmosphere causing accumulation of fly ash which constitutes the bulk of the total ash generated by electric utilities. Because commercial utilization of fly ash is small (< 20% of the amount produced is used), accumulating ash is a major waste disposal problem. Ash is commonly disposed through on-site ponding and transport to nearby landfills.

The leachability of major and trace elements which are often enriched on the surface of the fly ash particles have been elucidated (Shannon and Fine, 1974; Natusch, 1976; Eggett and Thorpe, 1978; Elseewi *et al.*, 1980; Helmke *et al.*, 1981; Stanforth *et al.*, 1984). Ponding of fly ash provides constant contact of the fly ash with water resulting in the enhanced leaching of toxic elements and eventual contamination of groundwater. Field investigations of contaminant migration to groundwater from ash disposal ponds indicate movement of trace elements (Theis *et al.*, 1978; Hardy, 1981) and major ions (Hardy, 1981) away from the pond. However, mobilization of potentially toxic metals may be limited by attenuation processes, i.e. adsorption and/or precipitation reactions on solid phases present in the ash ponds and subsurface environment (Theis and Wirth, 1977; Talbot *et al.*, 1978; Theis and Richter, 1979). In the field investigation of Theis *et al.* (1978) they found rapid attenuation for most metals very close to the pond. Metals were found to accumulate in the soil due to precipitation and adsorption by hydrous Fe and Mn oxides. In a related study using field data aided by a chemical equilibrium computer model, Theis and Richter (1979) attempted to assess the factors influencing the attenuation of trace metals in the soil/groundwater environment. Results show that the major solubility control for Cd, Ni and Zn is adsorption by Fe and Mn oxides while Cr, Cu and Pb are controlled by precipitation of discrete phases. The

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partitioning of heavy metals between solution and particulate phases is most affected by pH, p(FeOOH), p(MnO_2) and p(SO_4^{2-}).

Fly ash contains high concentrations of major and trace elements. The potential exists for these elements to be released into the environment when the ash comes in contact with water. Concerns are being expressed regarding groundwater and surface water pollution resulting from the disposal of ash. This study was conducted to investigate the impact of a ponded ash disposal site on groundwater quality focusing primarily on the movement of contaminants in the groundwater system around the ash disposal facilities.

MATERIALS AND METHODS

Site

The study was conducted at the ash disposal facility of the 1050 MW coal-fired Columbia Generating Station operated by the Wisconsin Power and Light Company located on the

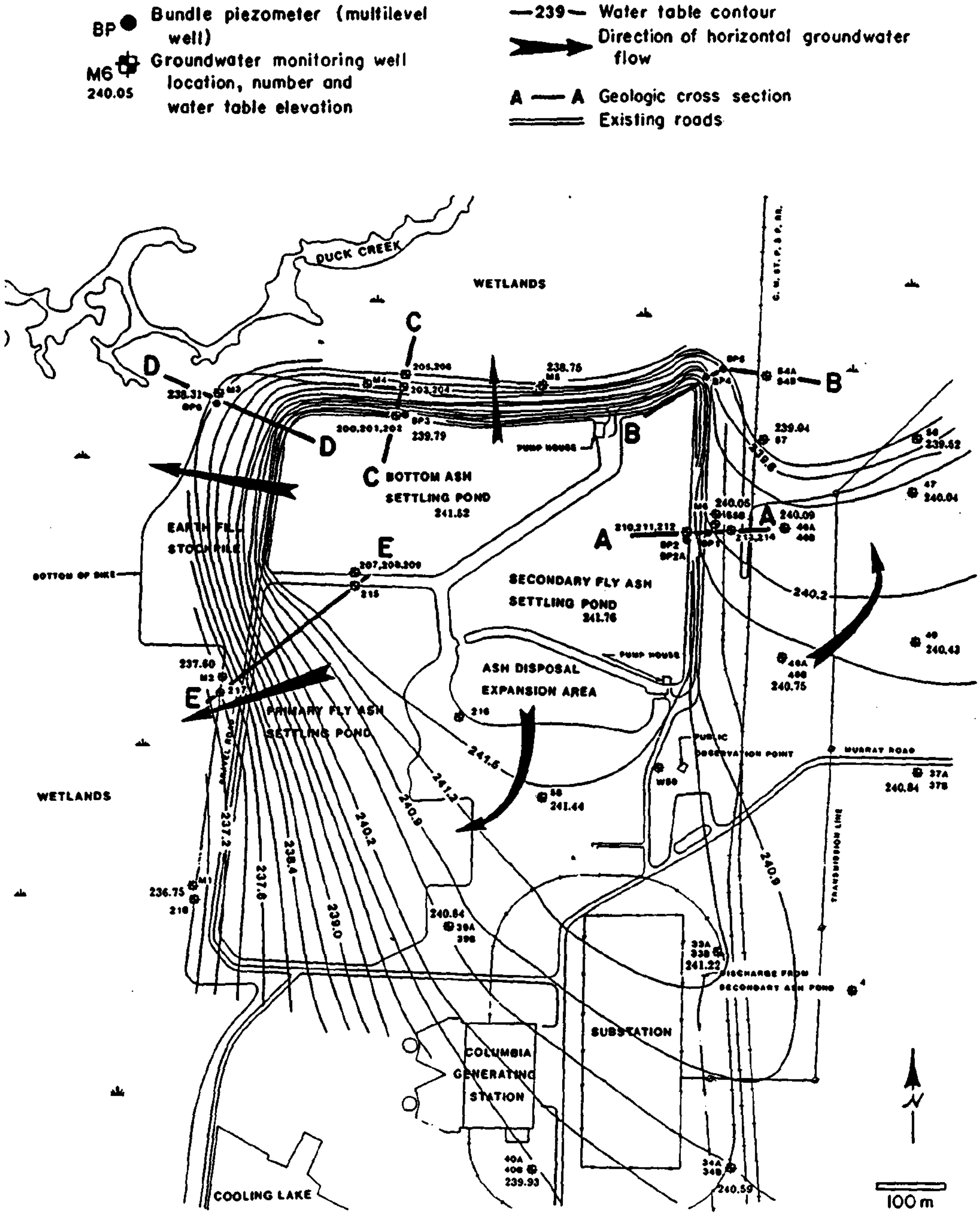

Fig. 1. The ash disposal facility, location of cross sections and monitoring wells and water table map for 8 June 1983.

eastern bank of the Wisconsin River 6.4 km southeast of Portage, Wis. The generating station consists of two units equipped with electrostatic precipitators. Each unit burns about 4500 tonnes day^{-1} of low sulfur content subbituminous coal from Montana (Unit I) and Wyoming (Unit II). Unit I began service in May 1975 and Unit II in April 1978. To increase the efficiency of the electrostatic precipitators, Na_2CO_3 was used as a fly ash conditioner from December 1977 to May 1979 and NH_4HSO_4 thereafter.

The ash disposal facility has an area of 29 ha with an average depth of 7.6 m divided into primary and secondary fly ash ponds and a bottom ash pond (Fig. 1). The original facility consisted of primary and secondary settling ponds but in the summer of 1977 approx. 50% of the secondary pond was converted to a separate bottom ash pond. Fly ash produced during Unit I operation is sluiced hydraulically to the primary fly ash pond to allow settling of the ash, then the sluice water is diverted to the secondary fly ash pond for further settling of particulates. Fly ash from Unit II is handled almost dry and is disposed of in the ash disposal expansion area. Bottom ash from both units is sluiced to the bottom ash pond. About 370 and 150 tonnes of fly and bottom ash are disposed of daily in the ponds. Range of elemental composition of the fly ash is shown in Table 1. The fly ash yields alkaline leachate with pH ~ 12.0 (Stanforth *et al.*, 1984).

The ash disposal site located on glacial deposits is underlain by fine to medium sands with occasional lenses of silt and clay overlying sandstone (Fig. 2). Subsoil pH ranged from 7.1 to 8.8, organic matter content was 0.2–0.8% and cation exchange capacity was 2.7–22 m-equiv $(100\,g)^{-1}$. Table 1 shows the elemental composition of the subsoils. Permeabilities of the subsoils ranged from 10^{-2} to $10^{-5}\,cm\,s^{-1}$. The sandstone—encountered 10–20 m below the ground surface—showed an average permeability of $10^{-3}\,cm\,s^{-1}$ (Warzyn, 1979). Local groundwater flows in all directions from the ash ponds and the secondary fly ash and bottom ash ponds serve as recharge areas; discharge was into the adjacent wetlands on the northern and western sides of the ponds (Fig. 1). Regional groundwater flow is in a westerly direction beneath the ash disposal site toward the Wisconsin River (Gibbs, 1973).

Monitoring network

Locations of cross sections and monitoring wells are shown in Fig. 1. In the initial 1980 study 17 piezometers each consisting of a 5.1 cm i.d. polyvinyl chloride (PVC) pipe and a 0.91 m well screen were used. These were arranged in three nests of three piezometers and four nests of two piezometers. Fifteen of the wells (Nos. 200–214) were drilled by Warzyn Engineering Inc., Madison, Wis in December 1979; two wells (55B, M6) were drilled in 1975. In addition, 30 × 5.1 cm PVC wells were installed between 1975 and 1979 and were utilized for either water table measurements or occasional groundwater quality sampling.

Seven multilevel sampling wells or bundle piezometers (BP) were installed by Warzyn in February 1982 and 1983. These multilevel sampling devices (modified from Pickens *et al.*, 1978) complemented the existing monitoring wells and allowed the collection of various water samples through the aquifer using a single borehole so that better delineation of vertical concentration profiles of contaminants could be obtained. Each bundle piezometer was constructed using a central core of 1.9 cm i.d. PVC pipe with varying lengths of 1.3 cm o.d. polypropylene tubing taped to the outside of the PVC core. Each sampling tube had a 7.6-cm screen at the bottom consisting of a drilled polypropylene tube with a double layer of nylon mesh wrapped around it. The PVC core also had a screen at its bottom so that it could be used as a sampling port. Figure 2 shows the depths of the wells in relation to the subsurface strata.

Sampling and analysis

The sampling scheme was designed to provide reproducible sample collection of chemically unaltered filtered groundwater from the monitoring wells. In 1980, samples were taken monthly from February to August. Four samplings were made in 1982 (May, June, July, September) and four in 1983–1984 (April, July, October, February). Groundwater samples were collected after withdrawal of twice the volume of standing water in the wells. An acrylic bailer was used to collect samples from the well during the 1980 sampling program. The sample was transferred through a 0.71 cm Teflon tube to a plexiglass filtration chamber and filtered under N_2 pressure through a series of 8.0 and 0.4 μm Nucleopore filters in a mobile laboratory. The collection scheme was changed during the 1982 and 1983 sampling program. An all plastic in-line filtration system (GeoFilter) attached to a peristaltic pump was used to collect a sample from the well. This arrangement was designed to avoid sample contact with air and was less tedious than the method described above. Pumped water was passed through 0.4 μm Nucleopore filters (142 mm dia). Surface water samples from the ponds and wetlands were collected in a manner similar to the procedure above.

Conductivity and pH were determined *in situ* immediately after filtration of the samples. Conductivity was determined using a YSI Model 33 meter in conjunction with a YSI 3300 probe; a Barnsted Digi-Sense pH meter equipped with a VL5992-20 combination electrode was utilized for pH mea-

Table 1. Elemental composition of Columbia fly ash and subsoils around the ash disposal site

Element	Fly ash*	Subsoil†	Element	Fly ash*	Subsoil†
	$(mg\,g^{-1})$			$(\mu g\,g^{-1})$	
Al	63–97	2.4–13	As	18–40	
Ba	5.0–6.5		B	800–930	4–19
Ca	100–210	2.8–98	Cd	1.3–10	
Fe	33–63	2.5–9.9	Cr	49–55	
K	2.1–4.5	0.18–2.3	Cu	83–150	10–38
Mg	24–38	2.7–50	Hg	<0.002	
Mn	0.9–1.0	0.16–0.47	Pb	6.0	
Na	2.1–2.9	0.074–0.39	Se	3.9–9.5	
Na‡	24–26		Zn	53–85	7–40
P	1.1	0.14–0.53			
Si	210–220				
SO_4	15–16	0.28–3.0			
SO_4‡	92				

*Values taken from various sources (Talbot *et al.*, 1978; Hanson, 1979; Helmke *et al.*, 1981; Stanforth *et al.*, 1984).

†Range of values in 10 samples.

‡Na and SO_4 contained in Na_2CO_3-conditioned fly ash.

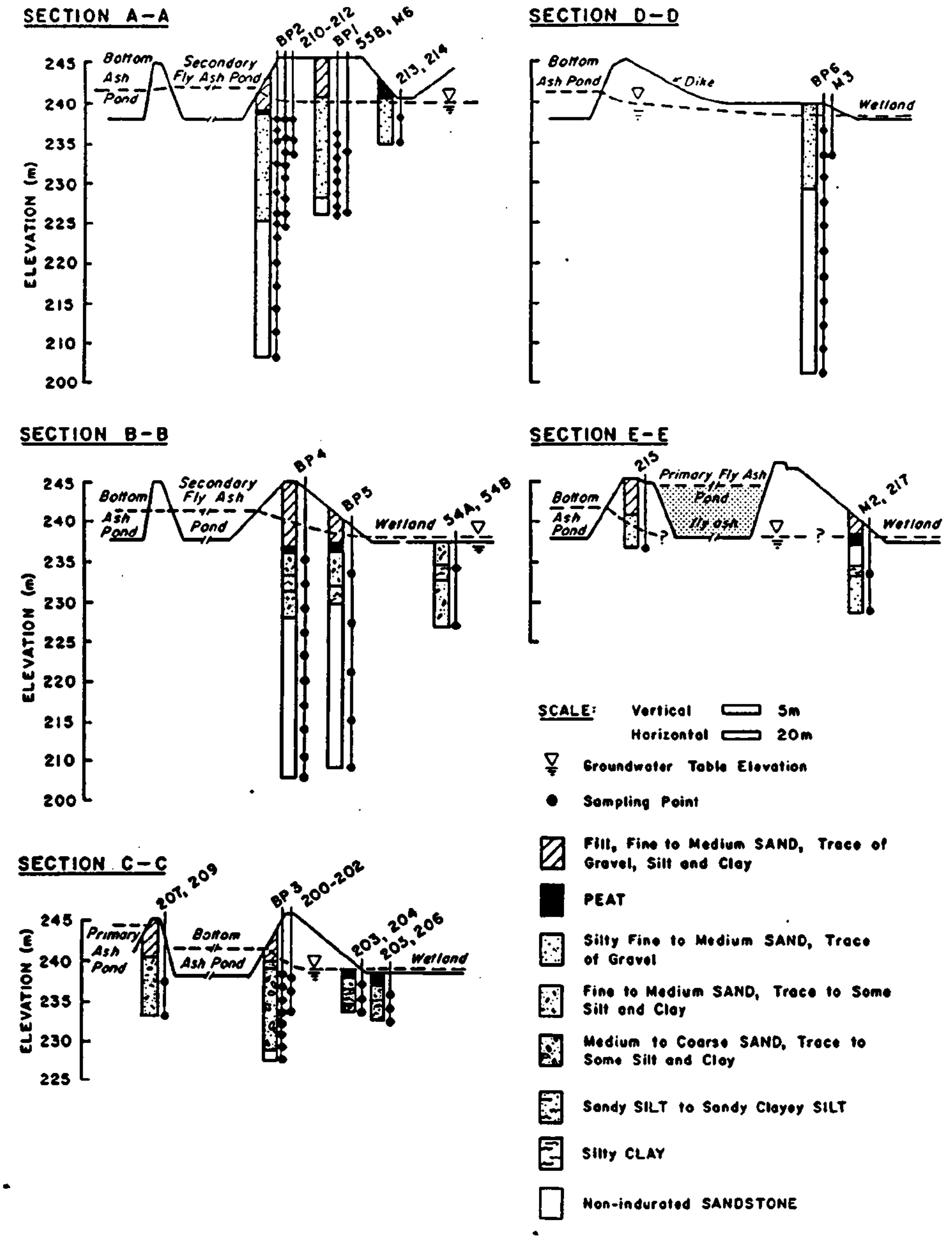

Fig. 2. Geologic cross sections and sampling points.

surements. Dissolved oxygen was measured directly in the well after withdrawal of standing water using a YSI Model 58 DO meter with a YSI 5739 probe.

In the laboratory, a 2 ml sample was diluted to 25 ml and analyzed for reactive silica (Strickland and Parsons, 1968). The remaining sample was acidified with ultrapure HNO_3 to a final concentration of 1%; subsampled into a 30 ml linear polyethylene bottle and stored at 4°C until used.

Acidified samples were analyzed for dissolved Al, B, Ca, Cu, Fe, K, Mg, Mn, Na, P, S and Zn using an Applied Research Laboratories Inductively Coupled Plasma Spectrometer Model 3400 System (ICP). Selected samples were analyzed occasionally for dissolved As, Ba and Cl using standard methods (U.S. EPA, 1979).

Subsoil samples obtained during well drilling were analyzed for elemental composition by the HCl-HNO_3 digestion procedure. Digests were filtered and filtrates were analyzed for Al, B, Ca, Cu, Fe, K, Mg, Mn, Na, P, S and Zn using the ICP. Organic matter content, pH, and cation exchange capacity were determined according to the soil testing procedures of Liegel *et al.* (1980).

RESULTS AND DISCUSSION

Leachate plumes and groundwater flow

Data strongly indicate that leachate from the secondary fly ash pond of the Columbia ash disposal facility releases significant amounts of Na, SO_4 and B to the surrounding groundwater system. Distinct plumes of Na, SO_4 and B were identified in the aquifer beneath the eastern (section A–A) and northeastern (section B–B) dikes downgradient from the secondary fly ash pond (Table 2). Plumes of these conservative elements behave similarly and exhibit thick deep plumes (26–>30 m) which essentially followed the direction of local groundwater flows. The thick plumes—extending into the sandstone—close to the pond suggest a rather steep downward groundwater flow probably resulting from rapid infiltration of leachate. The horizontal local groundwater flow (Fig. 1) affected the movement of the plumes. In section B–B, the plumes moved in a straight northeasterly fashion toward the wetland east-northeast of the ash disposal facility with the top of the plume staying close to the water table along the flow path. In contrast to section B–B, the flow pattern in section A–A is more complex because the tops of the plumes further away from the pond were detected at 15 m below water table (BWT). However, in this section,

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Table 2. Mean (SD) concentrations for Na, SO_4 and B in groundwater do
secondary fly ash pond

Location (Well No.)	DBWT* (m)	Na	SO_4 (mg l^{-1})
Section A–A for 1980			
Secondary fly ash pond		29 (5.7)	280 (72)
Dike (210–212)	2.7–4.0	10 (1.1)	51 (16)
	5.2–8.2	200 (22)	380 (86)
Dike (55B, M6)	4.0–7.0	3.7 (1.3)	4.5 (1.1)
	13–15	11 (7.4)	99 (76)
Dike (213, 214)	1.8–5.2	1.9 (0.76)	13 (3.6)
Section A–A for 1982			
Secondary fly ash pond		37 (19)	280 (12)
Dike (210–212, BP2)	2.7–4.0	35 (0.12)	110 (10)
	5.7–8.2	110 (22)	230 (22)
	9.8–16	95 (36)	270 (38)
Dike (55B, M6, BP1)	4.0–7.0	1.8 (0.72)	4.0 (2.0)
	8.5–10	2.8 (0.63)	84 (1.6)
	12	54 (8.8)	170 (24)
	13–15	110 (24)	290 (80)
Dike (213, 214)	1.8–5.2	3.0 (1.3)	42 (36)
Section A–A for 1983			
Secondary fly ash pond		24 (8.2)	270 (75)
Dike (BP2, BP2A)	2.7–4.0	50 (21)	140 (53)
	5.2–8.2	91 (18)	230 (22
	9.8–16	43 (16)	270 (46
	17–33	110 (36)	280 (50)
Dike (BP1)	8.5–10	9.7 (1.7)	57 (1.7
	12	53 (9.9)	130 (25
	13–15	110 (2.8)	320 (46)
Section B–B for 1983			
Secondary fly ash pond		24 (8.2)	270 (75)
Dike (BP4)	3.4	64 (2.1)	250 (16)
	6.4–25	160 (35)	280 (42)
	28	31 (14)	100 (59)
	31	3.6 (2.4)	20 (7.0)
Dike (BP5)	5.2–11	170 (19)	290 (5.2)
	17	250 (38)	460 (87)
	23–30	180 (29)	300 (18)
Wetland water (near BP5)		39 (11)	150 (21)
Wetland (54A, 54B)	4.0	3.2 (1.2)	240 (59)
	12	160 (17)	540 (53
Wetland water (near 54)		32 (14)	93 (46
Background levels		2.3 (1.0)	9.6 (9.
Wisconsin River		6.3 (1.6)	18 (0.
F-value		60†	62†
$LSD_{0.01}$		14	26

*Depth below water table.
†Significant at $\alpha = 0.01$.

wetland north of the ash disposal facility (section C–C, Table 3). A portion of each element appeared to be discharged in the wetland close to the toe of the dike. In section D–D (Table 3), plumes of Na, SO_4 and B were observed 120 m downgradient from the bottom ash pond. Concentrations of the elements at 26 m BWT far exceeded the levels found in the bottom ash pond. It is suspected that the secondary fly ash pond is the source of additional solutes in this part of the groundwater system. This may be caused by the influence of the westerly regional groundwater flow in the sandstone aquifer beneath the ash disposal site.

The primary fly ash pond does not impact the quality of the groundwater system even though it contains the poorest water quality among the three ponds. Concentrations of the elements found in the groundwater adjacent to the primary fly ash pond (section E–E, data not shown) were similar to those observed beneath the north dike downgradient from the bottom ash pond (section C–C, Table 3). This similarity in groundwater quality indicates that the main source of the constituents is the bottom ash pond. Groundwater flow beneath the primary fly ash pond originates largely from the bottom ash pond; groundwater contours show that the surface water in the primary fly ash pond is perched (Warzyn, 1980). Data lends support to the theory that fly ash particles have caused some sealing of the pond resulting in reduced seepage from the primary fly ash pond.

The major source of Na in the groundwater was release of Na to the aquifer from previous use of Na_2CO_3 as fly ash conditioner (December 1976–May 1979). Because of the low Na content in the pond (30 mg l^{-1}) after 1979, only a small amount was contributed by recent pond water. Most dissolved SO_4 in the pond infiltrates into the aquifer with the groundwater flow as indicated by similar or even higher levels of SO_4 in the plume than in the pond. Because of the progressive increase of SO_4 levels in the plume as it moves downgradient, SO_4 levels in the plume exceed those in the pond suggesting that another source of SO_4 is also present. Higher SO_4 release to the aquifer may have occurred during the time that Na_2CO_3-conditioned fly ash was placed in the pond. The high Na concentration in the fly ash tends to increase the solubility of SO_4 because Na_2CO_3 prevents the formation of ettringite—a stable mineral containing SO_4 (Hanson, 1979).

Movement of Na, SO_4 and B is generally unrestricted once the ions migrate to the aquifer. This is borne out by the more or less constant concentrations of elements in the plume in the horizontal direction (Table 2). Although some adsorbents (oxides and clay minerals) may be present in the ash pond and in the subsurface environments around the ash disposal facility they seem not to be a factor in attenuation of Na and SO_4. Thus, Na and SO_4 are mobile in the aquifer beneath the ash disposal site and may be transported to great distances depending on the groundwater flow regime. This may occur in other coal-fired power plant ash disposal ponds with subsurface environments similar to the Columbia ash disposal facility.

Decreases in B concentration in the plume of approx. 40% (2.8 to 1.7 mg l^{-1}) from that found in the pond strongly implicate attenuation of the element at some point between the pond and the aquifer.

Table 3. Mean (SD) concentrations for Na, SO_4 and B in groundwater downgradient from the bottom ash pond

Location (Well No.)	DBWT* (m)	Na	SO_4	B
		(mg l^{-1})		
Section C–C for 1980				
Bottom ash pond		24 (2.2)	200 (23)	0.79 (0.24)
Dike (200–202)	1.5–6.1	20 (4.6)	150 (52)	0.62 (0.26)
Dike (203, 204)	1.5–5.2	57 (14)	180 (18)	0.54 (0.042)
Wetland (205, 206)	1.5–6.1	3.3 (0.56)	14 (2.3)	0.058 (0.011)
Section C–C for 1982				
Bottom ash pond		20 (4.1)	160 (15)	0.52 (0.080)
Dike (200–202, BP3)	1.5–6.1	24 (1.8)	140 (20)	0.63 (0.20)
	7.6–11	76 (27)	87 (34)	0.71 (0.22)
Dike (203, 204)	1.5–5.2	55 (3.7)	180 (11)	0.67 (0.066)
Wetland water (near 203)		43 (14)	48 (9.3)	0.58 (0.12)
Section D–D for 1983				
Bottom ash pond		28 (9.1)	200 (69)	0.68 (0.28)
Dike (BP6)	1.5–7.6	45 (21)	210 (27)	1.2 (0.12)
	11–17	34 (15)	190 (20)	1.0 (0.14)
	26	110 (22)	260 (54)	1.5 (0.40)
	32	18 (8.3)	70 (12)	0.17 (0.027)
Wetland water (near BP6)		18 (15)	120 (150)	0.45 (0.48)
Background levels		2.3 (1.0)	9.6 (9.6)	0.076 (0.026)
Wisconsin River		6.3 (1.6)	18 (0.80)	0.035 (0.029)
F-value		32†	33†	34†
$LSD_{0.01}$		12	32	0.26

*Depth below water table.

†Significant at $\alpha = 0.01$.

Perhaps, attenuation of B occurs at the bottom of the pond—i.e. at the ash/soil water interface. Visual observation shows the presence of a loose fly ash layer blanketing the bottom of the secondary fly ash pond. This layer of fly ash, resulting from secondary settling, possibly acts as a partial barrier for B migration to the aquifer by readsorbing fractions of dissolved B as leachate passes through the ash layer. Pagenkopf and Connolly (1982) reported that the release of B from fly ash is controlled principally by adsorption on hydrous oxides of Al, Fe and Si and to some extent coprecipitation of borate species with hydrous oxides. However, these constituents if present in the subsurface environment of the Columbia ash disposal site do not appear to play a major role in reducing the concentrations of B in the plume as it moves downgradient through the porous media. Under the pH condition of the plume (7.1–8.8), the dominant aqueous species of B is $B(OH)_3$ as shown by a chemical equilibrium calculation using MINEQL (Westall *et al.*, 1980). This species has little affinity for oxides and clay minerals (Keren *et al.*, 1981).

In summary, based on the concentrations, distribution and possible attentuation of Na, SO_4 and B, plume movement can be depicted in relation to local and regional groundwater flows (Fig. 3 shows the east–west cross section of the plume profile). The major plume originating from the secondary fly ash pond moves largely in an easterly-northeasterly direction; some portion moves westerly under the influence of regional flow. A minor plume contributed by the bottom ash pond moves in westerly and northerly directions.

Relationship of major ions and ionic strength

The high concentration of Na and SO_4 in the plume drastically changed the groundwater chemistry (Table 4). The predominantly Ca/Mg $(HCO_3)_2$ water of the regional groundwater was transformed to Na_2SO_4 water when the aquifer water mixed with pond leachates. Consequently, the ionic strength of the plume was influenced largely by Na and SO_4 while the ionic strength of the regional groundwater was from Ca, Mg and HCO_3. Similar ionic strength and electrical conductivities were found for the secondary fly ash pond and plume suggesting that although leachate from the pond significantly altered the major ion composition of the plume it did not change the ionic strength or electrical conductivity.

pH

The pH of the plume ranged from 7.1 to 8.8, about 3–4 units below the pH of the secondary fly ash pond (Table 4). It appears that the pH of the affected groundwater is not increased abruptly by the strongly alkaline water seeping from the secondary fly ash pond.

Trace and other elements

Although levels of Al, As, Ba, Cu, P, Si and Zn are elevated in the Columbia fly ash particles (Table 1),

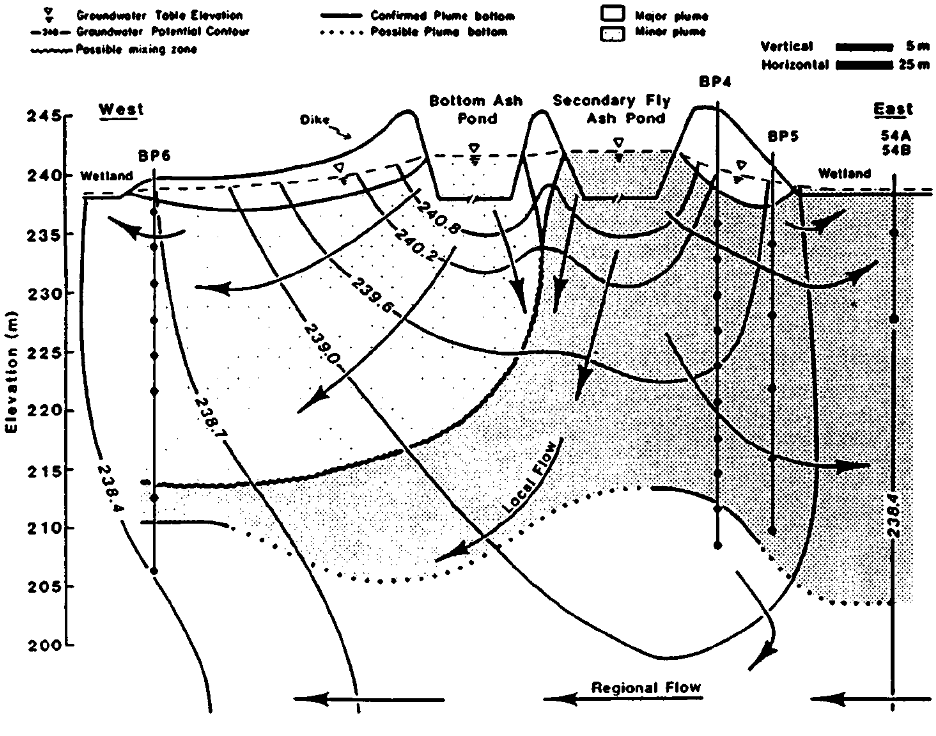

Fig. 3. Generalized plume profile.

Table 4. Major ionic species*, ionic strength (I)*, electrical conductivity (EC)* and pH

Source	Ionic species (mmol l⁻¹) Ca	Mg	Na	SO_4	HCO_3	I (mmol l⁻¹)	EC (μS cm⁻¹)	pH
Secondary fly ash pond	3.5 (0.11)	0.02 (0.02)	1.1 (0.36)	2.8 (0.78)	2.6 (1.1)†	14 (0.92)	890 (130)	10.1–11.1
Groundwater								
Non-plume, top	2.8 (0.66)	2.5 (0.08)	2.2 (0.92)	1.4 (0.56)	10 (2.1)	20 (1.7)	1000 (210)	6.9–7.6
Plume	0.94 (0.23)	0.65 (0.14)	6.6 (2.3)	3.2 (0.75)	3.1 (0.95)	15 (3.1)	910 (190)	7.1–8.8
Transition	1.2 (0.15)	0.92 (0.19)	1.4 (0.58)	1.1 (0.63)	3.2 (0.01)	8.9 (2.2)	550 (120)	7.7–7.8
Non-plume, bottom	0.97 (0.06)	0.83 (0.08)	0.16 (0.10)	0.21 (0.08)	3.1 (0.07)	5.8 (0.44)	380 (20)	7.7–7.9
Background	2.0 (0.25)	1.9 (0.09)	0.10 (0.03)	0.10 (0.08)	7.6 (0.45)	12 (1.4)	620 (70)	6.7–8.0
Wetland water	1.7 (0.19)	1.4 (0.03)	1.4 (0.61)	0.96 (0.49)	5.4 (0.07)	12 (1.8)	640 (60)	7.1–8.0
Wisconsin River	0.62 (0.05)	0.46 (0.01)	0.27 (0.07)	0.19 (0.01)	1.8 (0.11)	3.7 (0.16)	240 (2)	7.3–7.8
F-value	32‡	259‡	17‡	19‡	30‡	29‡	12‡	
$LSD_{0.01}$	0.50	0.15	1.8	0.85	1.8	2.8	220	

*Number in parentheses is SD.

†$CO_3 + OH$.

‡Significant at $\alpha = 0.01$.

the dissolved concentrations in the ash ponds and groundwater are low—mostly below detection limits. It is likely that they are retained mainly in the ash pond as particulates. Earlier investigation (Andren *et al.*, 1980) confirmed the existence of hydroxide and carbonate solid phases of Ca and Mg and hydroxide phases of Al and Fe in the Columbia ash pond. In the present study, a calculation using MINEQL (Westall *et al.*, 1980) predicts the presence of $Al(OH)_3$ and $Fe(OH)_3$ solid phases in the groundwater. The existence of these adsorbents in the aquifer may limit the movement of As, Ba, Cu and Zn to groundwater. Theis *et al.* (1978) and Theis and Richter (1979) have shown that although trace metals from a fly ash pond migrated to groundwater, their movement was retarded due to adsorption and precipitation by hydrous Fe and Mn oxides.

ENVIRONMENTAL IMPLICATIONS

Table 5 compares the water quality observed in the groundwater plume with Wisconsin groundwater quality standards (WDNR, 1985). The enforcement standard (ES) of the elements listed are the same as the U.S. EPA water quality criteria for domestic water supplies (U.S. EPA, 1976). Sulfate, Na and Mn appear to be the main constituents affecting the impairment of groundwater around the ash disposal area. Only 25% of the plume samples had B concentrations exceeding the preventive action limit (PAL), as defined by WDNR (1985). However, the high concentrations of B are likely to affect the quality of groundwater if used for irrigation because the criteria of 0.75 mg l⁻¹ (U.S. EPA, 1976) is exceeded by all samples. It is interesting to note that levels of As, Ba, Cu and Zn in the plume are below the ES.

The impact of the groundwater plume on the wetland can be assessed by estimating the time of travel of horizontal groundwater flow and the quantity of constituents in the plume.

Velocity of horizontal groundwater flow is estimated by Darcy's law for saturated flow:

$$\bar{v} = \frac{ki}{n}$$

were $\bar{v}$ is velocity, k is permeability, i is hydraulic gradient and n is porosity. Substituting measured and previously determined values, ($k = 1.2\ \text{m day}^{-1}$, $i = 0.01$ and $n = 0.30$ for fine–medium sand), $\bar{v}$ is equal to $0.040\ \text{m day}^{-1}$. Travel time—for the 61 m average distance between ponds and discharge areas—is 4–5 yr.

The volume of groundwater passing beneath the ash disposal site is:

$$Q = kiA$$

where Q is discharge rate and A is cross-sectional area. Given a groundwater flow cross sectional area of 15,000 m² (cross section length of secondary fly ash pond is 500 m and thickness of plume is 30 m),

Table 5. Comparison of groundwater quality of plume with standards

Parameter	ES*	PAL*†	Plume‡	% of samples exceeding ES	% of samples exceeding PAL
	[mg l^{-1} except EC (μS cm^{-1}) and pH]			ES	PAL
As	0.05	0.005	<0.010		
Ba	1.0	0.20	<0.40		
Cl	250	125	10–12		
Cu	1.0	0.50	<0.012–0.43		
Fe	0.30	0.15	<0.011–2.4	19	35
Mn	0.05	0.025	0.031–0.40	93	100
SO_4	250	125	160–580	68	100
Zn	5.0	2.5	<0.010–2.4		
B		2.1	1.1–3.0		24
Na		12.3	51–290		100
EC		1120	600–1400		6
pH		8.1	7.1–8.8		26

*The enforcement standard (ES) and preventive action limit (PAL) were promulgated under NR140 of the Wisconsin Administrative Code (WDNR, 1985).

†For B, Na and EC, the PAL is background level plus 3 SD or background level plus 2.0 and 10 mg l^{-1} for B and Na, respectively, and 200 μS cm^{-1} for EC, whichever is greater. Background (SD) levels are 0.076 (0.026) and 2.3 (1.0) mg l^{-1} for B and Na, respectively, and 620 (70) μS cm^{-1} for EC. For field pH, PAL is one pH unit plus background level which is 7.1.

‡Range of values in 140 plume samples.

approx. 180 m^3 of groundwater influenced by ash leachate is discharged daily. Using average concentrations of 1.7, 170 and 310 mg l^{-1}, respectively, for B, Na and SO_4 in the plume the annual loadings of these elements in the plume moving in an easterly–northeasterly direction are 0.12, 12 and 22 tonnes of B, Na and SO_4, respectively. Only 16% of the Na loading is suspected to have originated from the recent pond water; the remainder already existed in the aquifer.

An extensive portion of the aquifer—extending into the sandstone—surrounding the secondary fly ash pond has been influenced by the leachate plume. Because horizontal groundwater flow is slow and attenuation is negligible, total mass of B, Na and SO_4 have built up with time in the aquifer. As the plume—containing substantial quantities of B, Na and SO_4—continues to move and a portion of it is discharged, the release to the wetland will continue so long as the ponds are maintained in their present arrangment. Elevated levels of B, Na and SO_4 already exist in the wetland. However, whether these levels are harmful to aquatic life in the wetland is yet to be established.

Because groundwater from the disposal area continues to discharge to the wetland, further monitoring is needed. Periodic sampling of soil, water and aquatic biota will establish whether wetland contamination is increasing with time or has reached an equilibrium due to dilution by runoff and groundwater discharges from other recharge areas. Laboratory investigations may be needed to ascertain the toxicological implications of present levels of B, Na and SO_4 on aquatic biota.

The secondary fly ash pond will remain in periodic use for bottom ash sluice water when the present disposal system is switched to dry landfilling. Some form of sealing may be necessary to reduce groundwater contamination, if the constituent levels in the ponds suggest it is necessary.

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DIVISION S-4—SOIL FERTILITY AND PLANT NUTRITION

Atmospheric Sulfur as Related to Acid Precipitation and Soil Fertility[1]

E. L. SUAREZ AND U. S. JONES[2]

ABSTRACT

In experiments conducted to determine the major acidic components of precipitation in the southeastern United States, amounts of sulfur (S) deposited on the soil with rainfall were estimated and relationships between applied sulfur and crop yields in South Carolina were established.

Precipitation was collected at three locations from 10 Apr. 1979 to 3 Apr. 1980, at Clemson, S. C., Experiment, Ga., and Franklin, N. C., using a wet/dry collector. Conductivity, pH, and ionic components were determined in the rainfall and particulate matter. Sulfur in the air was collected at Clemson on a 30-d interval in a standard lead peroxide sampler. Soil samples were taken from 15 locations in South Carolina and analyzed for sulfur.

It was observed that the average loading concentration of anions in rainwater increased during the spring–summer months and decreased during the fall–winter months. Sulfuric and nitric acids were found to be the major components of acid rainfall. Rainfall and air deposition contributed approximately 10.7 and 1.8 kg/ha of sulfur per year, respectively, at Clemson. Atmospheric deposition from the particulate matter contributed an estimated 3.0 kg/ha of sulfur during the year.

Increases in corn grain and silage yields were obtained with the application of 18 kg/ha of sulfur at Darlington, S. C. A relationship between applied sulfur and crop response for the other crops considered could not be established. A need for reevaluating the findings and recommendations for sulfur fertilizers was apparent because of the contribution of atmospheric-deposited sulfur to the soil and plant sulfur supply.

Additional Index Words: **acid rain, atmospheric deposition, atmospheric sulfur, mass loading rates.**

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ACID PRECIPITATION has been defined as rain or snow with pH values of < 5.6, which is the minimum pH value expected for pure water in equilibrium with atmospheric carbon dioxide (CO_2) at 25°C. That atmospheric depositions of ions are constantly changing is clearly documented by Cogbill and Likens (1974) in the history and character of acid precipitation in eastern North America.

Various contaminants have always been present in the atmosphere. Several of them, such as sulfur (S) and nitrogen (N) compounds, are present mostly in a partially oxidized state. A high oxidation state is the distinguishing characteristic of acidic precipitation.

Experiments conducted to determine if S is one of the major contributors to acid rainfall have shown that significant quantities of S are being added to the soil by dry deposition and precipitation. Sulfur dioxide (SO_2) is also adsorbed on soil from the air. Deposited or adsorbed S, upon infiltration into soils, increases the hydrogen ion concentration by leaching calcium (Ca) and other essential plant nutrients from the soil profile. On the other hand, S in the atmosphere can supplement the soils' limited supplies of this nutrient element.

In humid regions, ground limestone used to neutralize acidity in cultivated soils may overshadow acid precipitation influences. In the same regions, however, large areas of poorly buffered, unlimed, forested soils are significantly influenced by acid precipitation percolating through the soil profile.

The objectives of this research were to determine the time and space variations in the deposition of atmospheric S and its contribution to plant-available supplies. The temporal and spatial variations considered were those that have taken place in the southeastern U.S. during 1979 to 1980.

MATERIALS AND METHODS

Short-term Experiments

Particulate matter and precipitation were collected from 10 Apr. 1979 to 8 Apr. 1980 at three sites. At Clemson, S.C., the sampling device was located on the campus of Clemson University. The sampling site at Franklin, N.C., was located 80 km northwest of Clemson. At Experiment, Ga., the sampler was located 51 km south of Atlanta and 300 km from Clemson. The latter two stations, because of the geographic proximity to the main station at Clemson, provided means to corroborate the data. Each site was equipped with one wet/dry collector manufactured by Aerochem Metrics at Miami, Fla. The wet/dry collector contained two high-density polyethylene buckets with a capacity of 13 L and an effective horizontal surface area of 638 cm^2. One of these, the "dry bucket," was normally covered. During periods of precipitation a sensor activated a motor which moved the cover from the wet collector to the dry collector. When the sensor dried, the motor moved the cover back to the wet bucket. The wet bucket was changed on Tuesday each week and the dry bucket on Tuesday every 2 months. The buckets were weighed, and a 20-ml aliquot was taken from the wet bucket for pH and conductivity measurements using a Markson Electromark Analyzer no. 4403.

The buckets were sent to the Central Analytical Laboratory, Illinois State Water Survey, Champaign, Ill., to determine the concentration of sodium (Na^+), magnesium (Mg^{2+}), potassium (K^+), and calcium (Ca^{2+}) using absorption spectroscopy, and ammonium (NH_4^+), sulfate (SO_4^-), nitrate (NO_3^-), chloride (Cl^-), and phosphate (PO_4^{3-}) using wet chemical techniques with a Technicon Autoanalyzer. Correlations between each of the acidic components and the hydrogen ion (H^+) concentration in rainfall were conducted to examine interrelationships.

Air samples were collected at Clemson from 1 Apr. 1970 to 31 Mar. 1980. Sulfur in the air was determined in a representative sample collected in a standard lead peroxide sampler obtained from Research Appliance Co., Gibsonia, Pa. The sampler consisted of a cylinder wrapped with a cotton fabric having a surface area of 100 cm^2 and coated with a lead peroxide paste. The cylinders were exposed freely to the air but were protected from rain by a cowl. After a 30-day exposure period, the fabric and coating were removed from the cylinder and the amount of S was determined by the turbidimetric barium sulfate method (Jordan et al., 1959).

Long-term Experiments

Precipitation and air samples were collected from 1 Jan. 1979 through 31 Dec. 1980 at 15 locations near Blackville, Cameron, Darlington, Clemson, Columbia, Wedgefield, Wateree, Fort Motte, Sumter, Saint Matthews, and Charleston, S.C. Sulfur in precipitation was determined in a representative sample collected in a standard 3-L plastic bucket, 20 cm in diameter and 180 cm above ground, with a metal ring to protect the rainwater collected from pollution by birds (Jones and Suarez, 1980). After a 30-d exposure period, the entire quantity of water was taken from the bucket, screened through a 20-mesh sieve, and evaporated to dryness in a S-free hood. The residue was taken up in a solution of 0.5*N* $NH_4C_2H_3O_2$ in 0.25*N* CH_3COOH, filtered, and washed. Sulfur was precipitated and determined colorimetrically with methylene blue (Lazrus et al., 1965). The air samples were collected, and S was determined in the same fashion as for the short-term experiment explained above.

Uniform field experiments were conducted from 1973 to 1980 with 'Keowee' barley (*Hordeum vulgare* L.) on Cecil sandy loam near Clemson; with 'Purple Top' turnip (*Brassica rapa* L.) and 'Miami' snapbean (*Phaseolus vulgaris* L.) on Lakeland sand near Columbia; with 'Walter' tomato (*Lycopersicon esculentum* Milli.) on a Wagram loamy sand near Columbia; with 'Davis' soybean (*Glycine max* L.), 'Silver Queen' sweet corn (*Zea mays* L.), and 'Ashley' cucumber (*Cucumis sativus* L.) on Marlboro loamy sand near Blackville; and with 'S.C. 236' field corn (*Zea mays* L.) on Norfolk loamy sand near Darlington. The basic fertilizer, 27-4-15 manufactured from urea-ammonium phosphate and muriate potash, contained S-free materials. Soil pH was maintained about 6.0 by the use of $Ca(OH)_2$.

Treatments consisted of 0, 9, 18, and 36 kg/ha of S broadcast as $CaSO_4 \cdot 2H_2O$, 18 kg/ha S and 14 kg/ha of Mg as $MgSO_4 \cdot 7H_2O$ and 14 kg/ha of Mg as $CaMg(CO_3)_2$ replicated five times in a randomized, complete block design. The treatments were repeated on the same plots during successive years. Plot size was 41 m^2 for soybean, sweet corn, and cucumber, 49 m^2 for field corn, 5.5 m^2 for turnip, tomato, and snapbean, and 18.6 m^2 for barley. Cecil sandy loam is a clayey, kaolinitic, thermic Typic Hapludult (ClC). Wagram loamy sand is a loamy, siliceous, thermic Arenic Paleudult (WgB). Marlboro loamy sand is a clayey, kaolinitic, thermic Paleudult (MbA). Lakeland sand is a thermic, coated Typic Quartzipsamment (LaB), and Norfolk loamy sand is a fine-loamy, siliceous, thermic Typic Paleudult (NoB).

Soil samples were taken for the 1973–1980 experiments with a hand post-hole digger at the 0 to 15, 15 to 30, and 30 to 45-cm depths. Five grams of soil were extracted with 20 ml of 0.5*N* $NH_4C_2H_3O_2$ in 0.25*N* CH_3COOH by shaking for 5 min. About 0.2 g of charcoal was added and the extract was filtered. Sulfur was precipitated as $BaSO_4$ by seeding with a $BaSO_4$ solution. After 5 min, the $BaSO_4$ concentration was estimated employing the standard turbidimetric method by reading on a spectrophotometer at 420 nm (Jordan et al., 1959).

RESULTS AND DISCUSSION

Short-term Experiments

Precipitation Deposit

The weekly average measurements of rainfall components for all three locations in South Carolina, North Carolina, and Georgia are summarized in Table 1. That no correlation was evident between the weekly pH measurements of precipitation among the three locations implies that the local pH was affected by different seasonal patterns.

The inorganic acid-causing components in precipitation for South Carolina are, for the most part, sulfuric and nitric acids, which account for 64.8% and 22.7% of the total equivalent concentration, respectively. When correlation among the weekly loading concentration of the major rainwater components was examined (Table 2), the highest correlation was obtained between the SO_4^{2-} and NO_3^- ion concentrations and H^+ ion concentration. This indicated that the H^+ ion was present in relatively constant proportion to S and N in the atmosphere, producing sulfuric and nitric acids.

The summation of the actual monthly loading concentrations over the 1-year period gave a total annual concentration of the acidic components in precipitation for South Carolina (Table 3). Based on the average weekly fallout in mg/m^2, South Carolina was considered to have 100% of the acid-forming components in rainwater. When compared on a mass basis to the other locations, South Carolina had approximately 16% more acid-forming components in precipitation than North Carolina and approximately 36% more than the amount at Georgia.

Table 1—Weekly averages of the chemical composition of precipitation at three locations from 10 Apr. 1979 to 8 Apr. 1980.

Component†	Location South Carolina	 North Carolina	 Georgia
		mg/L	
SO_4^{2-}	3.28 ± 0.54	2.97 ± 0.75	5.99 ± 2.49
NO_3^-	1.48 ± 0.20	1.43 ± 0.51	2.20 ± 0.57
Cl^-	0.45 ± 0.07	0.43 ± 0.12	1.41 ± 0.37
PO_4^{3-}	0.002 ± 0.001	0.004 ± 0.002	0.011 ± 0.007
Ca^{2+}	0.18 ± 0.04	0.33 ± 0.12	0.77 ± 0.25
Mg^{+}	0.06 ± 0.01	0.09 ± 0.03	0.15 ± 0.05
K^+	0.03 ± 0.01	0.18 ± 0.10	0.26 ± 0.09
Na^+	0.49 ± 0.09	0.55 ± 0.12	1.60 ± 0.38
NH_4^+	0.30 ± 0.07	0.37 ± 0.17	1.05 ± 0.51
H^+	0.04 ± 0.01	0.02 ± 0.01	0.03 ± 0.01
		μmho/cm	
Conductivity, field	23.88 ± 2.43	14.82 ± 1.33	21.28 ± 2.53
Conductivity, lab	27.38 ± 3.33	17.01 ± 1.55	20.94 ± 3.90
pH, field	4.48 ± 0.07	4.51 ± 0.07	4.44 ± 0.11
pH, lab	4.46 ± 0.05	4.65 ± 0.09	4.98 ± 0.09

† Simple average values and SE from 52 replicates.

Table 2—Correlation coefficients among the weekly hydrogen ion concentration and the weekly acid rainwater component concentrations for South Carolina from 10 Apr. 1979 to 8 Apr. 1980.

	SO_4^{2-}	NO_3^-	Cl^-	PO_4^{3-}
H^+	0.946 ($P < 0.01$)	0.944 ($P < 0.01$)	0.344 ($P < 0.02$)	0.576 ($P < 0.01$)
SO_4^{2-}	-	0.947 ($P < 0.01$)	0.464 ($P < 0.01$)	0.622 ($P < 0.01$)
NO_3^-	0.947 ($P < 0.01$)		0.326 ($P < 0.03$)	0.558 ($P < 0.01$)

An examination of the monthly wind statistics for South Carolina (Purvis, 1971) shows an annual cycle. Wind direction is predominantly from the northeast during the fall and winter and from the west-southwest during the spring and summer and has an average speed of 6 to 20 km/hr. The most probable components which affect rainfall composition in South Carolina emigrate during spring and summer from the highly populated and industrialized Atlanta area, which is southwest of the North Carolina and South Carolina locations. This could account for the higher concentration of acid-forming components observed during that period at the South Carolina location. Franklin, North Carolina located at a much higher elevation (722 m), would not be affected as much since it is further north and is influenced by a different pattern of prevailing winds and by different pollution trends. The elevation at Clemson, S.C., is 231 m and at Experiment, Ga., is 268 m. The lowest pH value measured in South Carolina during the period covered by this study was 3.64 during the summer season and the highest was 6.10 during the fall season.

Particulate Deposit

Table 4 shows that the deposition of anions in the particulate matter increased during the October–December period, when the loading rates of anions inprecipitation were at their lowest (Table 3). In the particulates, sulfate increased slightly during the October–December period, when the anthropogenic activity usually increases. More research on particulate matter is needed to make a better estimate of its acid-forming components. Data indicate that about

Table 3—Accumulated monthly and annual concentration of acidic components and hydrogen ions in rainfall for South Carolina from 10 Apr. 1979 to 8 Apr. 1980.

Date	SO_4^{2-}	NO_3^-	Cl^-	PO_4^{3-}	H^+
			mg/L		
April-May	3.67	1.57	1.27	0.005	0.04
May-June	12.94	6.55	2.73	0.004	0.12
June-July	30.09	12.55	2.14	0.006	0.32
July-August	10.44	4.77	1.63	0.006	0.16
August-September	21.24	6.16	0.43	0.005	0.26
September-October	18.64	6.32	1.54	0.010	0.29
October-November	8.55	3.54	1.32	0.015	0.10
November-December	7.39	3.30	3.64	0.012	0.10
December-January	5.98	3.18	1.31	0.010	0.09
January-February	8.02	5.46	0.73	0.012	0.17
February-March	11.69	6.32	1.09	0.012	0.24
March-April	12.08	8.24	3.05	0.015	0.27
Total	150.93	68.26	20.68	0.112	2.16

Table 4—Particulate matter chemical analysis for South Carolina from 3 Apr. 1979 to 4 Dec. 1979.

	Deposition									
Date	Ca^{2+}	Mg^{2+}	K^+	Na^+	NH_4^+	NO_3^{2-}	Cl^-	SO_4^{2-}	PO_4^{3-}	H^+
	mg/m²									
April-June	18.89	5.52	17.76	12.09	9.50	35.72	3.31	97.22	11.97	0.10
June-August	18.60	2.82	4.00	9.02	7.18	1.10	0.48	114.90	0.09	0.12
August-October	10.16	1.39	2.20	12.09	6.61	3.50	0.92	73.28	0.01	0.01
October-December	28.98	17.01	44.73	89.01	50.85	79.56	162.99	280.44	27.27	0.54
Accumulated total	76.63	26.74	68.69	122.21	74.34	119.88	167.70	565.84	39.34	0.77

2 kg/ha S was deposited during the 8-month period. Projected to 12 months, approximately 3 kg/ha S would be deposited per year.

Gaseous Sulfur Deposit

Accumulation of SO_2-S from air and SO_4^{2-}-S from precipitation at the South Carolina station are compared in Fig. 1. A trend toward less SO_2-S in the air during May through August than during the fall-winter months seems apparent. This is generally the reverse of rainwater SO_4^{2-}-S accumulation trends which peak in the summer. It was observed that the average monthly concentration of anions in precipitation increased during high temperature seasons and decreased during low temperature seasons (Table 3). During high temperature seasons, the solubility of SO_2 in water decreases, providing an effective limit to the oxidation of $H_2SO_3^-$. However, high concentration of cations, with catalytic effects, will rapidly increase the solubility of SO_2 in rainwater (Prince and Ross, 1972).

An annual deposited accumulation of 8.5 kg/ha of S in the air was observed compared to 10.7 kg/ha of S in rainwater at Clemson, S.C. (Fig. 1). Alway et al. (1937) reported that 22% of the air S adsorbed by the lead peroxide candle was adsorbed by the soil. Multiplying this factor by 8.5 kg/ha gives 1.8 kg ha^{-1} year^{-1} of S being deposited in the soil from the air.

Long-term Experiments

Precipitation Deposit

Jones and Suarez (1980) compared 1973–1975 with 1953–1955 collections of S in precipitation at Clemson, S.C. The data indicate an increase in S supplied through precipitation from an average of 8.9 kg ha^{-1} year^{-1} in the 1953–1955 period to 10.1 kg ha^{-1} year^{-1} 20 years later.

For the 1953 to 1978 period, Jones and Suarez (1980) and Jones et al. (1979) determined the temporal and spatial variations in atmospheric S loading rate for 15 locations in South Carolina using the Chesnin and Yien (1959) method. In this paper, the colorimetric analytical method by Lazrus et al. (1965) was used to determine the S loading rate for the 1979 to 1980 period at the same 15 locations in South Carolina. Although the absolute values are not identical, the upward trend of total S added to the soil from air and precipitation during the 1973 to 1978 period continued during the 1979 to 1980 period.

Table 5—Average annual deposited sulfur into the soil from air and precipitation at 15 locations in South Carolina from 1 Jan. 1979 to 31 Dec. 1980.

Year	Air S		Alway's factor	S adsorbed by soil		S in precipitation	Total S S added to soil†
	kg/ha		%	kg/ha			
1979	8.1	×	22	= 1.8	+	6.5	= 8.3 ± 0.54
1980	7.7	×	22	= 1.7	+	8.7	= 10.4 ± 0.54

† Simple average values and SE from 15 replicates.

Gaseous Sulfur Deposit

Air S deposits were adjusted using Alway's factor (22%) to estimate gaseous S adsorbed by the soil. The adjusted gaseous values were added to the appropriate precipitation S data to generate approximate values for total S added to the soil during the 1979 to 1980 period (Table 5) at 15 locations in South Carolina. When air S was combined with precipitations S, deposition rates increased significantly from 8.3 kg/ha in 1979 to 10.4 kg/ha in 1980 at rural locations of South Carolina. A significant difference was noted between the years 1979 and 1980 at the 99% level.

Field Experiments

Table 6 shows the effects of zero and 18 kg/ha rates of S addition for all crops and locations. Increased yields ($P < 0.10$) of corn grain in 1975, 1976, 1978, and 1980 and silage in 1977 were obtained with the S addition at Darlington. Data for the other crops at the other locations indicated no response to S rates

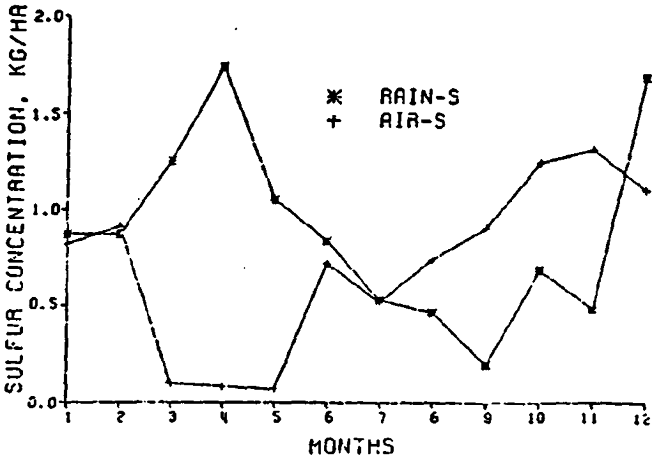

Fig. 1—Sulfur deposition in rain and air at Clemson, S.C., from 10 Apr. 1979 to 8 Apr. 1980.

Table 6--Crop response to 18 kg/ha of sulfur in South Carolina for the 1973-1980 period.

Location	Soil symbol	Crop	No. tests†	Yield	
				Without sulfur	With sulfur
				t/ha	
Clemson	CIC	Barley	5	4.20	3.91
Darlington	NoB	Corn grain	6	4.59	5.00‡
Darlington	NoB	Corn silage	1	8.05	8.86‡
Blackville	MbA	Cucumber	1	17.98	16.43
Blackville	MbA	Soybean	3	2.27	2.22
Blackville	MbA	Sweet corn	1	4.06	4.18
Columbia	LaB	Snapbean	3	2.70	2.51
Columbia	LaB	Turnip	3	23.40	26.30
Columbia	WgB	Tomato	3	13.21	13.44
Columbia	WgB	Tomato (Mulched)	3	16.37	17.99

† Defined as one experiment at one location for 1 year.

‡ Level of significant differences = $P < 0.10$.

or sources after 8 years of cropping. Complete data on the corn experiment at Darlington are included in another paper (Jones et al., 1979).

The acetate-extractable soil SO_4^{2-}-S level of the 0 to 30-cm depth was 9 ppm in the control treatment at Darlington. At the other locations the SO_4^{2-}-S level of the 0 to 30-cm soil depth was 32, 17, and 4 ppm at Clemson, Blackville, and Columbia, respectively. There were no significant crop responses to rates or sources of S fertilizer during 1975 to 1980 at these other locations. This may indicate that S is supplied to the crops from the subsoil or from the atmosphere or from both.

The crop response research reported for the 1973-1980 period supports, in general, the critical level of 14 ppm in the soil reported by Bardsley and Kilmer (1963). However, the general fertilizer recommendation of 9 kg/ha of S for South Carolina was made based on data by Jordan (1964) when the average amount of S being deposited with precipitation was approximately 6 kg/ha. It is evident from research that S in precipitation increased significantly from 1979 to 1980. For these reasons the findings and general recommendations for S fertilizer should be reevaluated from time to time with carefully designed long-term experiments.

SUMMARY

No correlation was noted between the weekly measurements of precipitation pH for the three locations: Clemson, S.C., Franklin, N.C., and Experiment, Ga. This indicates that the pH was affected by different seasonal patterns at all three locations.

Sulfuric and nitric acids are the inorganic components that contribute most to rainfall acidity. The average concentration of S and other measured ions in precipitation increased during the spring-summer months and decreased during the fall-winter months in South Carolina. Conversely, the S in the air as SO_2 increased during the winter-spring months and decreased during the summer-fall months.

The percentage contributions of SO_4^{2-}, NO_3^-, Cl^-, and PO_4^{3-} to South Carolina rainfall acidity were 64.8, 22.7, 12.3, and <0.1, respectively. South Carolina has 16% more of the acid-forming components than North Carolina and 36% more than Georgia.

Rainfall contributed 10.7 kg/ha of S per year, and air contributed 1.8 kg/ha of S per year to soils at Clemson, S.C. Deposited particulate matter contributed 2 kg/ha of S during an 8-month period and increased significantly during the winter months. Adding the total S deposition from rainwater, air, and the estimated 3 kg/ha of S in the particulate matter for a 12-month period, we obtained 15.5 kg/ha, sufficient to replace a large part of the sulfur removed by crops in South Carolina.

Increased yield of corn grain in 1975, 1976, 1978, and 1980 and silage in 1977 were obtained with 18 kg/ha of S at Darlington, where the acetate-extractable soil SO_4^{2-}-S level was 9 ppm. The other locations showed no response to rates or sources of fertilizer S during the study period; this indicates that crops are supplied with enough S from the subsoil or the atmosphere.

ACKNOWLEDGMENT

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Field investigation of trace metals in groundwater from fly ash disposal

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The expected increase in the use of coal as an energy source has resulted in several investigations into the environmental cycling of coal-related pollutants. Among these is the release of various toxic trace metals, which are associated with coal during the combustion process. A portion of some of these metals exhibit a volatile behavior (such as mercury, and to a lesser extent, arsenic) and are emitted as vapors in stack gases. The more refractory metals, however, condense as oxides onto the particulate residue known as fly ash. The mode of formation of fly ash and its physical and chemical properties have been reviewed extensively elsewhere.[1-4] Fly ash is composed chiefly of alumina, silica, lime, and iron oxides in an amorphous core. Figure 1 gives typical ranges of the metallic components of several fly ashes. The extent of enrichment of many trace metals on fly ash is sometimes large, occasionally reaching 100 times the concentration originally found in the coal.

Usually, precipitators or scrubbers collect the fly ash from the gas stream. Approximately 40 million tons are produced in the U. S. annually, and this quantity is likely to increase. Common disposal practice involves on-site ponding, followed at appropriate intervals by mining and subsequently depositing the material as fill. Large portions of the trace metals on fly ash have been shown to exist in a surface-sorbed form often associated with iron or manganese oxide reservoirs.[4] As such, they must be considered as potentially able to be released into aqueous solution. The purpose of this study was to investigate in detail a ponded fly ash disposal site, with particular emphasis placed on the extent, if any, of trace metal migration in groundwater from natural pond seepage.

SITE DESCRIPTION

Field studies were conducted at the coal-fired Michigan City Generating Station of the Northern Indiana Public Service Company. This station has a generating capacity of 735 MW. Of special interest is a newly constructed 520 MW unit which went into service in 1974.

Figure 2 gives a schematic site layout of the ash ponding facilities located on-site (numbers refer to the sample wells and borings which were made as part of this study). The system consists of two sets of ash ponds, each containing a primary and a secondary settling unit. The volume of each primary pond is approximately 62 000 m^3 (16.5 mil gal). Under normal operating conditions, each set of ponds is used in an alternate fashion; that is, while one primary pond is being filled, the other is allowed to dry for the removal operation. Pond water overflow is recycled during the ash sluicing process. Each pond cycle has a duration time of 6 to 9 months. These ash ponds were constructed and put into operation at the time of the latest plant expansion in early 1974.

The site is located in a dunal region adjacent to Lake Michigan. Pond elevations, when full, are 9.6 m (31.5 ft) above the lake datum. The area is underlain by a clean, porous sand of considerable uniformity. Sieve analyses made from several of the on-site borings are shown in Figure 3. The effective size varied between 0.16 and 0.18 mm, and the coefficient of uniformity was approximately 1.5.

During this study, the Michigan City Generating Station burned coal mined in southern Illinois. The amount of fly ash produced varied, but averaged 310 to 365 metric tons/day (340 to 400 tons/day).

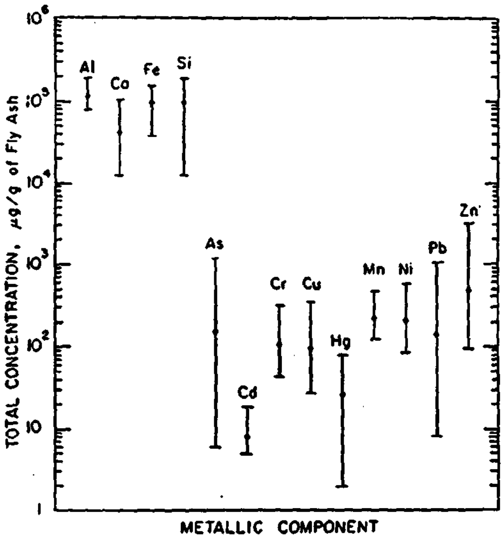

FIGURE 1. Total metal analysis among several fly ashes. Bracketted lines represent ranges, dots are average values (source: Theis and Wirth[4]).

EXPERIMENTAL PROCEDURES

Sampling wells. A series of twenty-one, 2-in. sampling wells were installed during the year in and around the power plant site. These are located in Figure 2. As a rule, wells were drilled to a depth of 1.5 to 2.5 m (5 to 8 ft) beneath the groundwater table. The well casings are polyvinyl chloride pipe, which are slotted for the portion beneath the water level. Wells were capped and sealed between sampling periods. In addition, soil samples were taken at each half-meter depth and saved for later analysis.

Water sampling and analysis. An effort was made to adhere to a monthly sampling schedule. However, the unusually severe winter weather conditions made the site inaccessible for long periods of time; therefore, this schedule was necessarily compromised. A typical sampling regime consisted of the following steps:

1. Measurement of groundwater surface elevation.
2. Initial pumping of the well to remove standing water.

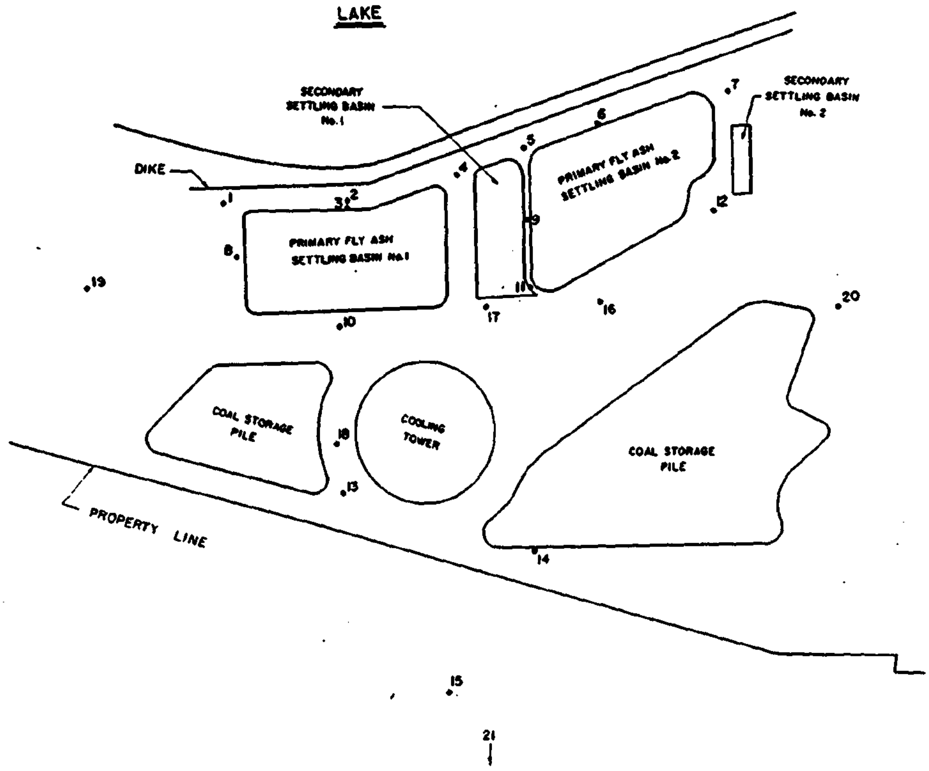

FIGURE 2. Fly ash disposal site layout (approximate scale 3000:1).

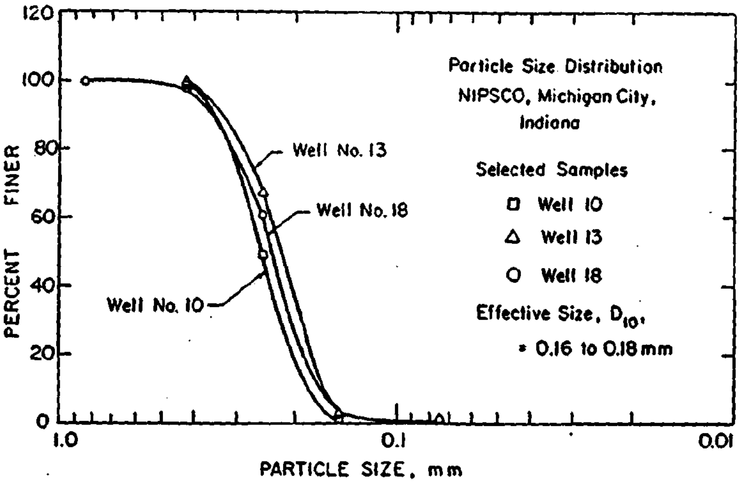

FIGURE 3. **Sieve analyses for representative soil samples from disposal site.**

3. Removal of approximately one l of new water from well and division into two equal aliquots.
4. Immediate acidification to pH 5 (using acetic acid) of one aliquot to prevent oxidation of ferrous iron.
5. Immediate measurement of temperature, pH, and oxidation reduction potential of the other aliquot.
6. Filtration of both aliquots (0.45 μm).
7. Further acidification of the first aliquot to pH-1 with perchloric acid.

Samples were transported back to the laboratory and stored under refrigeration prior to analysis. The unacidified sample was analyzed immediately for alkalinity, chloride, orthophosphate, calcium, and total hardness. Procedures as given in "Standard Methods"[5] were used.

Trace metals were determined on the acidified aliquot by the use of atomic adsorption spectrophotometry with a graphite furnace attachment. A summary of all analyses and methods is given in Table I. Analysis for mercury was discontinued shortly after the monitoring began because levels were consistently beneath the detection limit (0.2 μg/l). In general, ferrous iron determinations closely agreed with total iron due to the insolubility of iron (III) at the pH values encountered.

Soil analysis. Soil samples obtained during the drilling of wells were analyzed for total component concentrations according to the method of Bernas.[11] In this procedure, the sample is digested under heat and pressure in aqua regia/hydrogen fluoride and analyzed. Those trace metals given in Table I (except for mercury) were determined again by atomic absorption.

Soil grain size analyses were made in accordance with American Society for Testing and Materials D 422, Particle-Size Analysis of Soils.[12] Grain size distribution curves for some soil samples recovered from depths of

TABLE I. **Analytical methods for groundwater components.**

Specie	Method	Ref.
Na^+	atom. abs.	6
K^+	atom. abs.	6
Ca^{2+}	EDTA titrimetric	5
Total Hardness	EDTA titrimetric	5
Alkalinity	H_2SO_4 titrimetric	5
SO_4^{2-}	turbidimetric	5
Cl^-	agentometric	5
PO_4^{3-}	ascorbic acid	5
Al	atom. abs.	7
As	atom. abs.—Ni	8
Cd	atom. abs.	7
Cr	atom. abs.	7
Cu	atom. abs.	7
Hg	flameless atom. abs.	9
Mn	atom. abs.	7
Ni	atom. abs.	7
Pb	atom. abs.	7
Se	atom. abs.—Ni	8
Si	atom. abs.	7
Zn	atom. abs.	7
Fe^{2+}	bathophenanthroline	10
Fe_T	atom. abs.	7

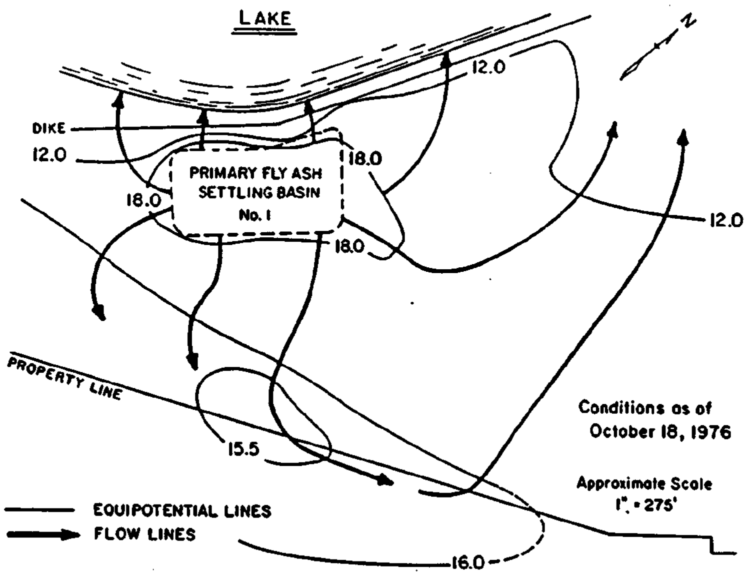

FIGURE 4. Flow lines around ash pond Number 1 for October 18, 1976 sampling day.

1.5 to 2 m below ground surface are shown in Figure 3.

Coefficient of permeability was estimated using published correlations of effective grain size, D_{10}, and coefficient of permeability, k (Leonard [13]). The D_{10} of these uniform sand soils is approximately 0.2 mm, and the coefficient of permeability 0.1 cm/s.

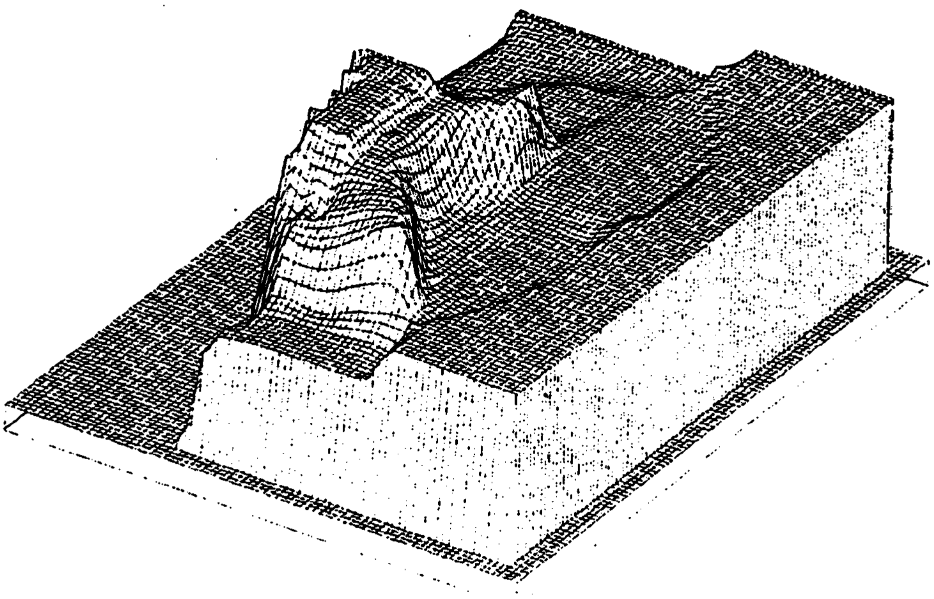

FIGURE 5. Three-dimensional view of prevailing groundwater surface for October 18, 1976. Lake is to the left.

RESULTS AND DISCUSSION

For the major portion of this study, only the first primary pond (Figure 2) was actually loaded with fly ash. Pond 2 was allowed to dry for the eventual removal of the ash to the final fill site. Most of the data to be presented, then, have been generated by the seepage characteristics of the first pond.

The hydrologic characteristics of the disposal site are of considerable importance in assessing the movement of dissolved constituents in the groundwater. Water seepage from the ponds significantly alters the flow of groundwater in the general vicinity. Figure 4 shows typical flow lines around Pond 1. The prevailing groundwater flow is, of course, toward the lake. The pond, however, brings about a counter-flow which extends outward a distance of 100 to 150 m, depending upon other hydrological factors. This effect is illustrated more clearly in Figure 5, which gives a three-dimensional view of the groundwater surface when the pond is full. It is possible to see a "saddle point" where the pond flow and the natural groundwater flow meet. Wells 18 and 13 (Figure 2) were located as close as possible to this point. This information is important for two reasons. First, the extent of the pond influence determines the approximate path length of the seepage water. This is important in determining the ultimate degree of attenuation of dissolved species. Second, the groundwater chemical characteristics change abruptly at this point. As will be seen, such a change can bring about significant alterations in trace metal forms.

TABLE II. Composition of fly ash at Michigan City.

Component	Concentration
Al_2O_3	30.2%
SiO_2	25.9%
Fe_2O_3	39.5%
CaO	2.9%
As	1 200 μg/g
Cd	19 μg/g
Cr	320 μg/g
Cu	350 μg/g
Hg	24 μg/g
Mn	600 μg/g
Ni	600 μg/g
Pb	1 120 μg/g
Se	88 μg/g
Zn	3 300 μg/g

A representative analysis of the fly ash produced from the plant is given in Table II. It should be noted that most of the values given in Table II are toward the upper end of the ranges given in Figure 1. As might be expected, this ash exhibits an acid reaction in water. The pH measured in the pond was consistently between 5.5 and 6.0.

Specie concentrations for most of the trace metals analyzed in the groundwater are given in Figures 6, 7, and 8 for three separate sampling days. Data are presented as distance profiles using the wells outlined previously. The groundwater surface elevation is also presented. The initial concentrations of metals in the pond were found to vary widely; it is assumed that these were mainly functions of the

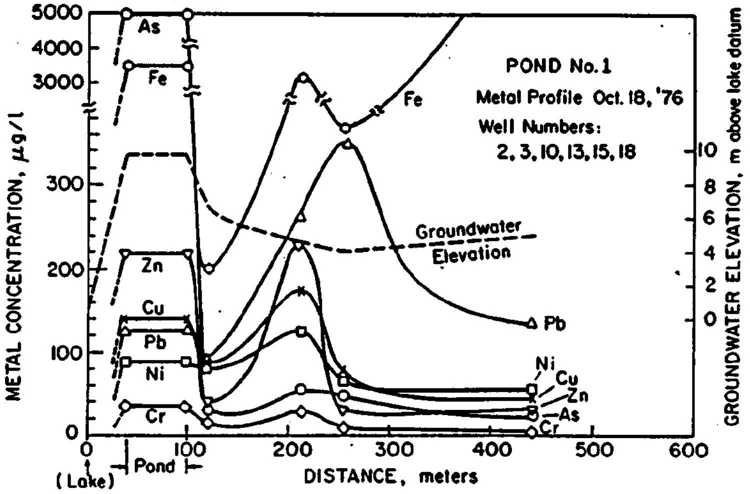

FIGURE 6. Trace metals as a function of distance for Pond 1, October 18, 1976.

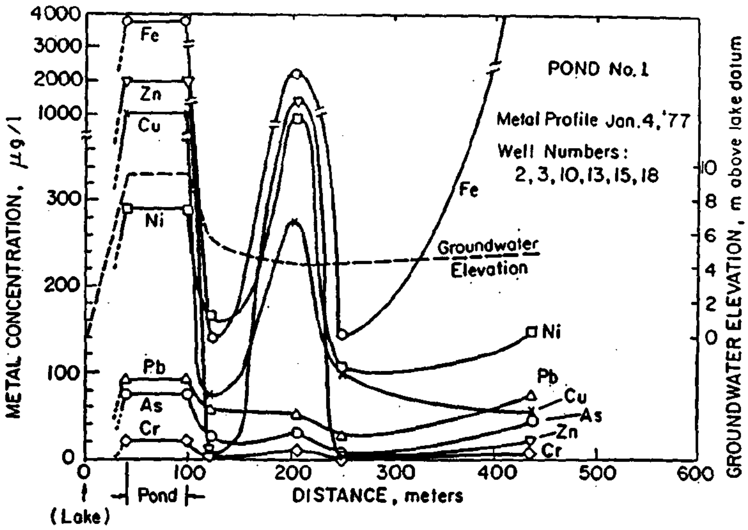

FIGURE 7. Trace metals as a function of distance for Pond 1, January 4, 1977.

fly ash loading rate. For all three sampling days, metals generally decreased rapidly with distance from the pond. This is true also for Wells 2 and 3, which are not plotted. Certain metals were consistently low: cadmium was not plotted since its concentration in the groundwater was generally less than 5 μg/l; chromium was also very low.

The October 18 and January 4 samples also show certain similarities in that virtually all the metals displayed sharp peaks at about 115 m from the pond (Well 18), which decreased at greater distances. No such peak was found on the March 3 date. These observations are difficult to explain unless the cycle and loading rates of the ash pond are taken into consideration. Figure 9 shows concentrations as a function of time for several of the metals analyzed. A sequence of significant events is also presented. From the beginning of the monitoring (July 1976) to the end of September, Pond 1 was allowed to dry and the ash was removed. Metal concentrations are uniformly low. Pond filling began at the end of

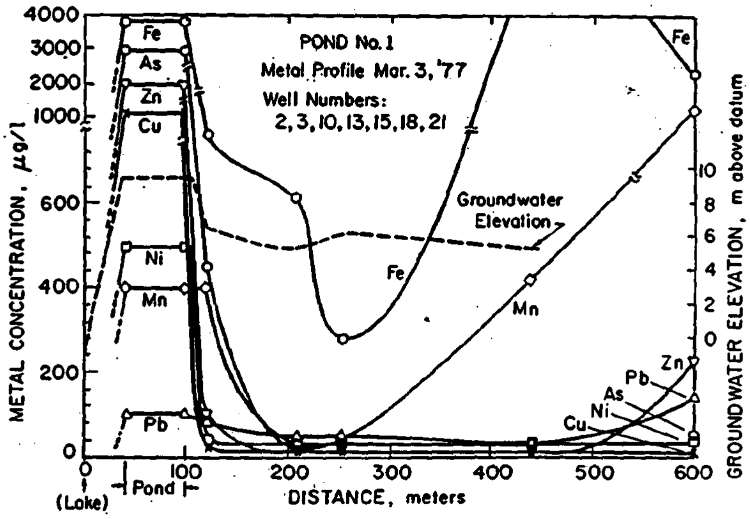

FIGURE 8. Trace metals as a function of distance for Pond 1, March 3, 1977.

September. Samples taken shortly thereafter (in October, Figure 6) at Well 18 show increases in filterable metals. Maintenance needs within the power station considerably reduced the generating capacity for several weeks during the next sampling interval. Unit 12 in particular is rated at 520 MW. Plant records of sluice water quantities to Pond 1 reflect the decreased activity. From October through December, an average of 5 300 m³/d (1.40 mgd) was pumped to the pond, as compared with an average of 10 800 m³/d (2.85 mgd) for periods when all units are on-line.

Plant capacity returned to normal on December 12, 1976. The next sampling day was January 4. Coincidentally, the interval between each activity (pond filling initiated and return of Units 12 and 3) and sampling day was approximately the same—21 to 23 days. It appears that groundwater concentrations of trace metals are significantly affected by normal plant operations. In the case of the pond filling, fly ash concentrations at the bottom, before the water volume has reached pond capacity, are larger than normal. The return to service of such a large amount of generating capacity brings about a similar increase in ash concentration. The effect in either case is similar. The uniformly low levels of trace metals for the March 3 sample date could perhaps be considered more indicative of a steady-state operation of the disposal system.

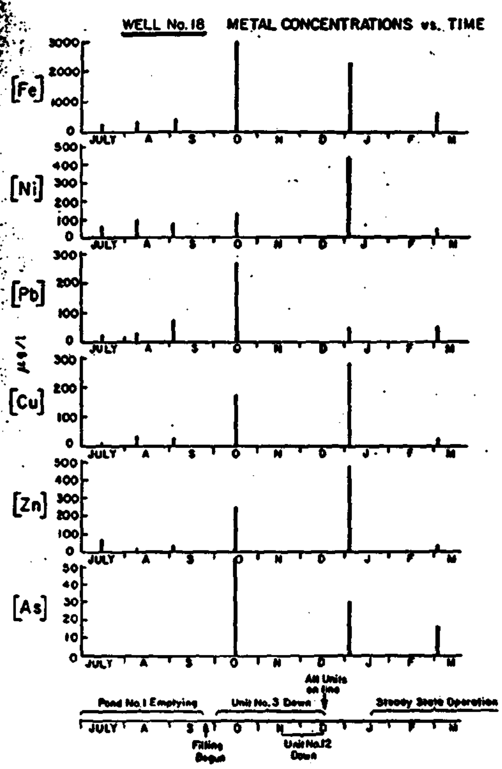

FIGURE 9. Trace metal concentrations at Well 18 (115 m from Pond 1) as a function of time. Scale at bottom depicts significant events which affected trace metal levels.

TABLE III. Macro-ionic composition of water at Wells 18, 13, and 15 (Jan. 4, 1977) (all values mg/l).

Specie	Well 18	Well 13	Well 15
Na^+	52	7.5	16.0
K^+	24	8.2	13.6
Ca^{2+}	424	96	166
Mg^{2+}	41	17	25
Alk (as $CaCO_3$)	8	80	478
SO_4^{2-}	1 250	210	28
Cl^-	65	2.5	7.5
Fe	2.25	0.14	—
Mn	1.48	0.03	0.60
Si	4.60	2.85	9.0
pH	7.0	6.9	6.5

The phenomenon described is further supported by an analysis of the travel time of groundwater from Well 10, adjacent to the pond, to Well 18, a distance of approximately 90 m.

The travel time can be estimated using Darcy's law and Dupuit's assumption that the hydraulic gradient is equal to the slope of the free surface.

Writing Darcy's law

$$\bar{v} = \frac{-kc'}{n}$$

where

$\bar{v}$ = seepage velocity
k = coefficient of permeability
i = hydraulic gradient
n = porosity

and substituting measured and previously determined values, ($k = 0.1$ cm/s, $i = 2.5 \times 10^{-2}$, and $n = 0.5$ for the medium sand),

$$\bar{v} = \frac{10^{-3}\ \text{cm/s} \times 2.5 \times 10^{-2}}{0.5} \times \frac{8.64 \times 10^{4}\ \text{sec}}{\text{day}}$$

$$\bar{v} = 4.3\ \text{m/d.}$$

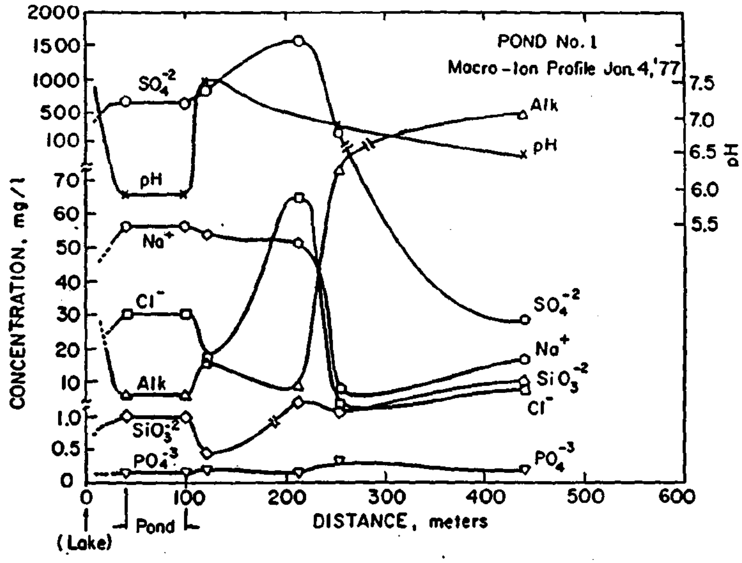

FIGURE 10. Major ionic components in groundwater for Pond 1, January 4, 1977.

Travel time is then

$$\frac{90}{4.3 \text{ m/d}} = 21 \text{ d.}$$

Figure 10 gives some of the major ionic species present in the groundwater on January 4. Results for other days were similar. The confluence of pond seepage with natural groundwater is clearly indicated. The dominant anion shifts from sulfate to carbonate. These values are given more precisely in Table III. Similar data exist for other sampling days. It should be noted that there were large amounts of both iron and manganese present in the natural groundwater outside of the influence of the ponds.

In order to analyze the data further, it is necessary to consider the results of the chemical analysis of soil samples. As indicated previously, soils were sieved, yielding fractions of several sizes. Each of these was analyzed for metals. Total metals were then computed by taking the weighted average of individual fractions. For all soil samples tested, the greatest concentration of metals was consistently associated with smallest-sized fraction. Specific data for a sample taken from Well 18 at the approximate groundwater level are given in Table IV. Although this interesting trend is to be expected for cases where adsorption is occurring, it is nevertheless of limited significance with respect to the total metals found in any sample. It was indicated previously that the D_{10} size was 0.16 to 0.18 mm. The smaller-sized fractions rarely composed more than 2% of the total sample and were normally much less.

TABLE IV. Typical distribution of metals with soil grain size.

Boring 18 at Groundwater Interface (all values μg/g dry wt).

Size Range (mm)	As	Cd	Cr	Cu	Ni	Pb	Se	Zn
>0.841	6.3	0.10	36.7	28.1	40.6	25.1	26.1	65.4
0.425–0.841	4.8	0.14	12.7	15.5	25.0	8.6	19.1	28.7
0.250–0.425	3.4	0.11	13.6	12.6	20.0	8.6	12.0	26.7
0.149–0.250	3.9	0.32	10.2	12.6	36.5	9.9	15.8	30.8
0.075–0.149	6.0	0.09	76.5	19.4	16.8	16.4	22.3	65.6
<0.075	15.0	0.33	105.3	106.5	49.5	77.7	30.0	353.3

Figure 11 shows total metal concentrations in soils as a function of depth for several distances from Pond 1. Most of the metals display elevated soil concentrations at or beneath the groundwater level suggestive of bulk transport. Profiles at 340 m are outside of the area of influence of groundwater flow from the ponds; they appear to be much more uniform. The most prominent feature of Figure 11 is the elevated levels of metals at 150 m (Well 13) over other distances, particularly at the groundwater surface. Figure 12 presents this for a constant depth (groundwater interface) as a function of distance. All metals show elevations at a distance of 150 m from the pond, with the exception of nickel and copper. Arsenic shows a rather large rise in view of its consistently low levels in the groundwater.

The reasons for these increases are not obvious unless both the hydrologic characteristics of the site and the chemical interactions are considered. An examination of Figures 4 and 5 reveal the saddle point for the meeting of the two groundwater flows to be very close to Well 13, which is 150 m from Pond 1. This point will naturally move back-and-forth during the year, depending on pond cycling. There are significant changes in both soil composition and water quality (see Figure 9) that occur near this point. Tables IV and V give specific data which illustrate this change. In general, there are two attenuation mechanisms which can act to decrease soluble metal concentrations in the water: precipitate formation of an insoluble compound and adsorption onto local solid phases. The data of Tables IV and V suggest that both may be occurring in the groundwater.

Figure 13 gives some indication of the presence of chemical precipitates for copper, lead, nickel, and zinc. Here, known thermodynamic equilibrium data plus measured concentrations in the field have been applied to speciate metals according to distance, with the aid of the computer program MINEQL.[14]

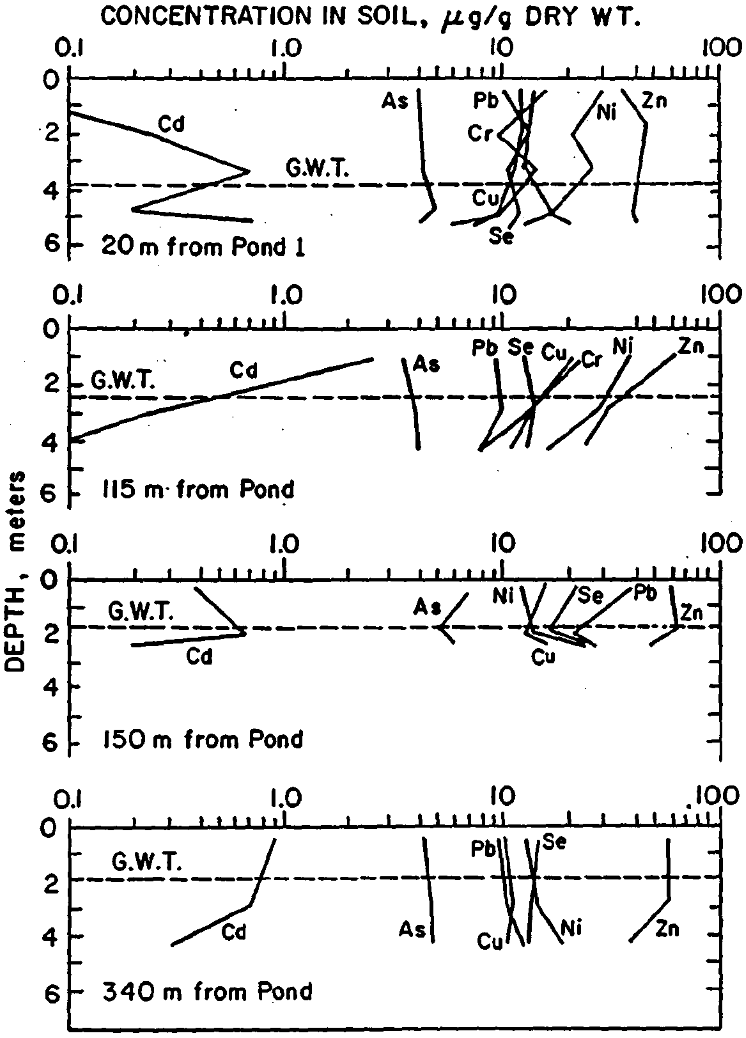

FIGURE 11. Depth profiles of trace metals in soil around Pond 1 for several distances.

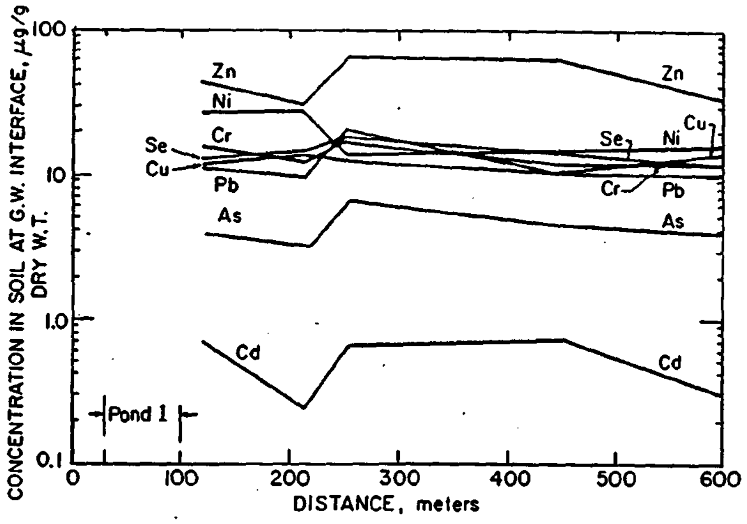

FIGURE 12. Trace metal concentrations in soil at the depth of the groundwater as a function of distance.

Total analytical metal concentrations are held constant for each case at the maximum levels found in the wells around Pond 1, simulating the movement of a pulse of metals through the soil, as suggested previously. Some interesting trends become evident when compared with Figure 12. For example, the formation of the basic copper carbonate (malachite, Figure 13) is favored for all distances from the pond. Copper concentrations measured in the soil show a uniform distribution, with only a slight elevation of the leachate with the natural groundwater at the zone of confluence.

In contrast, a lead carbonate does not precipitate until the groundwater inorganic carbon levels have increased substantially (Figure 13). Lead hydroxide, $Pb(OH)_2$, may precipitate in the vicinity of the pond due to slightly elevated pH levels. This pattern remarkably reflects the pattern actually found in the soil (as shown in Figure 12). Nickel (Figure 13) exists almost solely as the Ni^{2+} ion in both seepage and groundwater. Nickel ion is a comparatively nonreactive specie in this environment. Studies have shown that it does not adsorb readily onto oxide minerals until pH values of 8 to 9 are reached.[15] Thus, nickel concentrations in soil (Figure 12) show a sharp decrease at the confluence of pond seepage with natural groundwater. This is due to another attenuation mechanism—simple dilution. The anticipated behavior of zinc is given in Figure 13. Here, conditions favor the precipitation of zinc as the silicate throughout the seepage zone. Accordingly, zinc would be expected to accumulate in the immediate vicinity of the ash pond. Increases in the soil at further distances are probably due to adsorption (which is discussed in more detail below).

TABLE V. Soil iron and managanese concentrations at groundwater interface (μg/g dry wt)

Location No.	Mn	Fe
10	22.3	1 510
18	36.0	2 710
13	57.3	3 230
15	52.1	3 180
21	33.0	2 120

Although precipitation offers an explanation for the observed trends of certain metals, specific adsorption onto solid phases may also account for increased metal concentrations in soil. Amorphous oxides of manganese and iron that are present probably exert a major influence. Concentrations of iron and manganese in soil, given in Table V, show significant increases near the point of greatest metal shifts (Figure 12).

Parks[16] reports the zero point or charge (ZPC) of freshly precipitated iron hydroxide to be 8.5. Manganese dioxide has a ZPC of approximately 2.0. Accordingly, a major difference between these sorbing surfaces in the environment under discussion is that manganese oxides are negatively charged, while iron oxides are positively charged. Silica, which also would be negatively charged and is present to excess, sorbs comparatively little. James and Healy[17] attribute this to the low dielectric of silica, which effectively inhibits overcoming the solvation energy of hydrated metal ions.

Both arsenic and selenium possess an anionic chemistry under the groundwater conditions. They would be expected to adsorb readily onto the positive iron hydroxide surface. Other metals may adsorb onto the manganese. Figure 12 suggests that all of the metals except nickel (as noted above) adsorb to some extent, although the precipitation of lead and copper carbonates may also be important for these metals.

It appears that the elevated levels of iron and manganese at Well 13 are present natur-

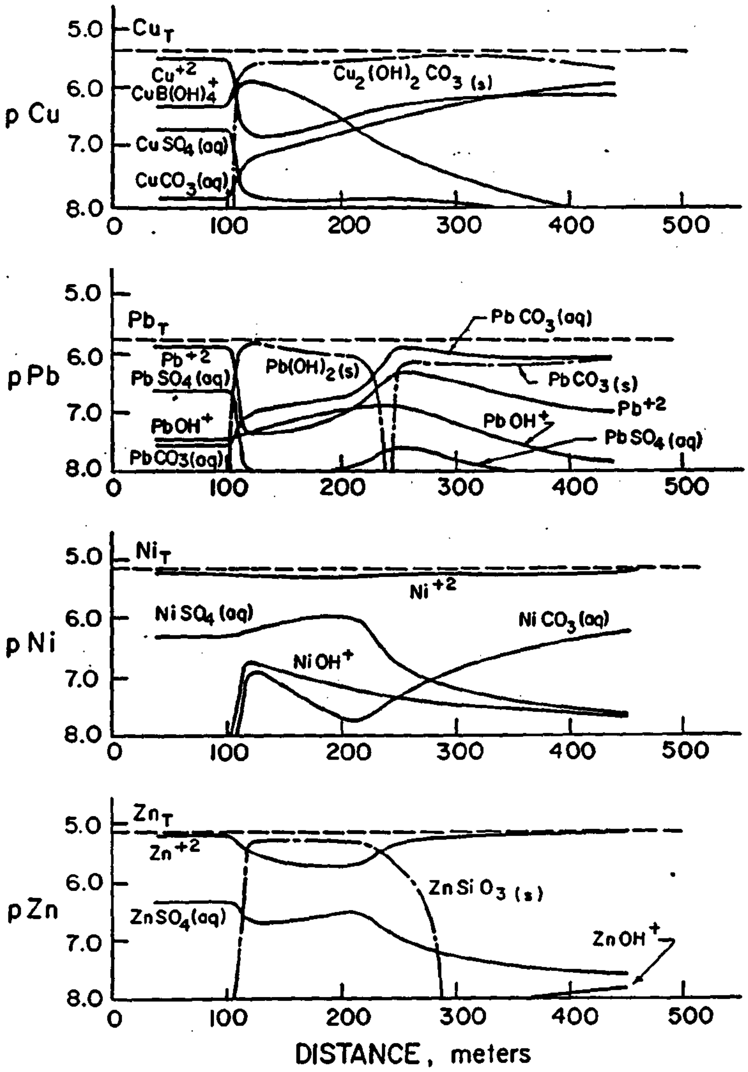

FIGURE 13. Dominant inorganic complexes for copper, lead, nickel, and zinc as determined by equilibrium calculations. Data for January 4, 1977.

TABLE VI. Maximum increase of heavy metal over background concentration in soils (all concentrations $\mu g/g$).

Metal	Boring 13	Boring 21 (background)	Me_{13}/Me_{21}	Average Crustal Abundance ($\mu g/g$)	Source
As	6.5	3.83	1.7	1.8	18
Cd	0.66	0.30	2.20	0.2	19
Cr	17.0	12.8	1.33	100	18
Cu	13.4	15.4	0.87	40	19
Ni	14.9	17.6	0.85	80	20
Pb	20.7	9.50	2.18	13	18
Se	17.8	12.7	1.40	1	21
Zn	61.0	32.5	1.88	50	19

ally. These two oxides, however, are also major components of the surface of the fly ash. In view of the high solubilities of the metals under pond-water conditions, adsorption is the likely mechanism for the rapid attenuation of metal concentrations within the pond. The fact that this mechanism is unable to control the large pulses of metals which arise from operational variability suggests a more complex phenomenon may be occurring, in which kinetic factors may be important.

The extent of the accumulation of the trace metals in the soil around Pond 1 can be assessed through a comparison with background soil levels. Well 13 contained the maximum or near-maximum concentrations for each metal. Well 21 was located 500 m from the pond and is considered representative of background conditions. Table VI gives ratios of soluble metals in Well 13:background as well as average crustal abundances as reported in the literature. It is evident that accumulation of metals through precipitation and adsorption over background is occurring. If the increases shown are attributed to ash pond seepage, then this has taken place over a period of 2.5 years. It is not clear that the higher levels which exist are excessive in view of natural abundances, with the exceptions of arsenic and cadmium. The high selenium concentrations—even in the background samples—are as yet unexplained. Further increases in soil metals are possible. The problem becomes an interesting one to model.

The matter of metal concentrations which flow directly into the lake from the pond is one which must be addressed further. Analysis is difficult because the site layout leaves room for only one boring line between the ponds and the lake. At this time, it seems reasonable to assume metal attenuation patterns on the lake side of the pond, similar to those observed and described previously for the opposite side. Metal concentrations attenuate rapidly; however, short-term perturbations may create momentary large concentrations entering the lake water.

SUMMARY

For the fly ash disposal site studied, it has been found that trace metals are released into the groundwater. In general, the concentrations are low, although they are sensitive to the ash loading rates and procedures. Rapid attenuation occurred for most metals very close to the pond itself. Many of the components of fly ash, especially iron and manganese oxides, are effective metal scavengers once they are formed in the pond. These oxides are, however, unable to dampen the curious peaks of metals which were observed and were related to the operation of the ponds and the power plant. This suggests that at sudden increases in ash concentrations there is either insufficient time or unfavorable local conditions (such as low pH) for the oxides to exert controls. If this is the case, simple pH adjustment, using lime or limestone, in the pond to a more alkaline range should control metal release. Lime could elevate the pH, causing precipitation of insoluble hydroxides of trace metals and promoting the formation of the sorbing hydrous oxides. Little excess sludge would be produced because of the low alkalinity of the pond water. Limestone would produce more sludge, but would also bring about the formation of insoluble metal carbonates prior to their release into the groundwater.

The behavior of trace metals, once released into the groundwater, is dependent upon the site hydrologic characteristics and the water quality differences between seepage water and natural groundwater. In this study, metals were found to accumulate in the soil due to precipitation and adsorption onto the hydrous iron and manganese oxides.

If the accumulations of metals in soils is deemed to be a problem or if the filterable concentrations of metals in the water are considered too high even after remedial pH adjustment in the pond (for example, nickel is naturally very soluble in this environment and the Ni^{2+} ion shows little tendency toward adsorbing onto local solid phases), then there may be no alternative except to limit the extent and quantity of pond seepage. Natural or chemical lining materials could be used for such a purpose, although their presence makes the removal operation decidedly more difficult.

The ultimate answer to concern about heavy metal pollution from this type of nonpoint source lies in the proper siting of disposal facilities prior to their use.

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APPLICATION OF ULTRACLEAN SAMPLING AND ANALYTICAL TECHNIQUES TO AN INVESTIGATION OF THE IMPACT OF POWER-PLANT DERIVED HEAVY METALS ON GROUNDWATER, RIVERWATER, BOTTOM SEDIMENTS AND BENTHIC ORGANISMS

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ABSTRACT

As utility companies refit their oil-fired power stations for use with coal, they are attracting the attention of a concerned public. It becomes especially important, when operating under such close scrutiny, to conduct thoughtful environmental investigations with accurate analytic techniques. In one case, at a Massachusetts, U.S.A., power station, the routine trace metal analyses provided by private water-quality laboratories gave the impression that metal levels in stream and groundwaters adjacent to the plant were alarmingly high. This data, released by the utility company itself, resulted in extensive public criticism and costly effort for the utility and State of Massachusetts regulatory agencies.

The problem, however, was more perceived than real, as the present study, conducted later, showed. This investigation brought together ultra-clean sampling and handling techniques (borrowed from geochemical oceanographic practices) and interpretive concepts from aquatic geochemistry. Levels of metal enrichment in stream waters were revealed to be in fact much lower (eg. Cu, 2 ug/l) than implied by the evidently investigator-contaminated samples (eg. Cu, 20 ug/l) from previous work, underlining the importance of employing difficult but uncompromising procedures when dealing with metals in the aquatic environment. Furthermore, with accurate analyses at hand, the geochemist's "mixing diagram" concept allowed interpretation of the fate of the power-plant derived excess metals in the cooling-water discharge; excess dissolved copper, for instance, disappeared not due to reactions with particles, but rather due to simple and rapid dilution in the effluent-river mixing zone.

Examination of the relationships between various trace metal concentrations and parameters reflecting major processes controlling metal distributions (sediment grain size, labile iron and manganese concentrations) for bottom sediments from the adjacent Connecticut River revealed that natural processes largely explained the distribution of Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn associated with the acid leachable fraction of the sediments in all locations. While no anomalous metal concentrations were recognized amongst sediments, oligochaete worms living in the sediments beneath the cooling-water plume appeared to have accumulated more metal than those elsewhere. Because tissue metal levels were unrelated to sediment metal levels, it seems that the worms may respond more to the dissolved metal load than to the sediment burden.

Tight correlations are evident between metal concentrations determined by the author's techniques and a measure of the redox poise (COD) in groundwaters near [redacted] Relationships between parameters determined by the routine water-quality laboratories on duplicate samples, on the other hand, are characterized by the lack of correlations, suggesting that in the latter case sample handling methods were inappropriate, leading to unrepresentative concentration estimates. The correlations that appeared with the author's data, however, indicate that metal levels in the groundwater are controlled more by spatial variations in the redox poise than by pollutant (leachate) source strength.

INTRODUCTION

It is now well established in the academic geochemist's community that ultra-clean techniques are a necessary part of studies involving trace metals in the environment (Patterson and Settle, 1976; Bruland et al., 1979). Routine techniques, while appropriate for major ion studies, have now been shown inadequate to the task of accurate trace metal investigations. If contamination free procedures were to be uniformly employed in studies of waste-water discharges to the environment, one might expect quite a different picture to emerge concerning the levels and behavior of trace metals in receiving waters. Generally lower concentrations than those now perceived would be revealed, and with accurate analyses at hand, geochemical concepts could be brought to bear to produce conclusive interpretations of aquatic chemical phenomena. For example, one should expect to find correlations between the concentrations and distributions of minor elements, and parameters that reflect the operation of important physico-chemical processes. If they are not found, one should be suspicious that his approach (sampling design, analytical procedures) is somehow inappropriate to allow understanding of the environmental system. It is shown in this paper that there is a much greater potential for understanding when non-routine, state-of-the-art geochemical investigations, no more costly in time or finances, are applied to situations, than when routine "water-quality" practices are the sole source of information.

This study was done after an apparent problem had surfaced concerning the Mt. Tom Power Station, in Massachusetts, U.S.A., which underwent conversion to coal-firing in December, 1981. Routinely reported metal levels in groundwater, and a pre-conversion study (September '80) of metal levels in the adjacent Connecticut River (which has a low-water discharge of 7.5×10^4 liters/sec, compared to a power station cooling water discharge of 5.7×10^3 liters/sec), conducted by private water-quality laboratories hired by the utility company, seemed to reveal that dissolved metal levels were alarmingly high in the vicinity of the power station. For instance, dissolved copper concentrations downstream from the cooling water outfall were reported to be as high as 30 ug/l. Such levels were a cause of concern amongst citizens, in light of evidence that Atlantic salmon tend to avoid waters with copper concentrations as low as 4.0 ug/l (Sprague, 1964), and because a management plan was underway to reestablish the river a a spawning area for salmon. Fears were that copper levels in the river might increase still more, due to metal-rich leachate from new coal and flyash storage areas near the river.

In October 1981, the author conducted a study of the distribution of dissolved copper in the Connecticut River, near the power plant and in the mixing zone of the cooling water discharge (Fig. 1), for comparison to the September 1980 study. The latter investigation was done expressly by non-contaminating procedures and by sampling designed to allow interpretation of the behavior of copper in the mixing zone; the former study apparently was not intended to contain these elements of strategy. In February, 1982, the author obtained samples of groundwater, from observation wells located between unlined settling basins for bottom- and fly-ash slurries and the Connecticut River, that were duplicates of routine monitoring samples taken simultaneously by plant personnel. The comparison was intended to reveal any weaknesses in the methods used in the monitoring program. After obtaining them through a single pumping system, the two sets of samples were handled quite differently. In April, 1982, surface samples of the river, grab samples of underlying bottom sediments, and individually picked samples of benthic infauna (oligochaete worms) were obtained for assessment of possible impacts on natural metal distributions, after the first few months of coal use at the power plant.

RESULTS AND DISCUSSION

The Nature of Dissolved Metal Distributions in the Connecticut River

In October 1981, dissolved copper concentrations in the Connecticut River upstream from the power station occurred at about 2.4 ± 0.3 ug/l (mean of 18 samples taken from surface, mid-depth, and bottom waters at six sites; variation is one standard deviation from the mean; Table 1). Copper levels determined by the author during high river stage in April 1982 were not much different, having a mean of 2.0 ± 0.5 ug/l. These values may be directly contrasted with the upstream copper concentration, ca. 20 ug/l, reported by the private water-quality laboratory that obtained and analysed samples in September 1980 from similar upstream locations (Table 1). It would seem inescapably apparent that the higher 1980 level reflects sample contamination resulting from inappropriate handling, a conclusion that will be reinforced when other metals are discussed.

Comparison of copper levels in river water at the intake (sample 2), and those in the cooling water discharge at the outfall (sample 3) reveal the amount of copper added to river water as it passes through the power plant (Table 2). The dissolved copper concentration is approximately doubled, with plant-derived excesses on the order of 2.7 ug/l (ie. 4.7 - 2.0 = 2.7). Samples that would systematically represent the dilution of cooling waters as mixing occurred were taken from surface waters within the thermal plume. Samples were chosen so that they would span the 0 - 8.4 degrees Centigrade temperature anomaly range of the mixing-zone (Figure 1 and Table 2). Using sample temperature as a conservative index of the extent of dilution in the mixing zone, a mixing diagram may be constructed to examine the levels and reactivity of plant-derived dissolved copper in the plume (Fig. 2). Such mixing diagrams have been described and used by Waslenchuk (1982a,b) in investigations of the reactivity and fate of metals discharged with the cooling waters of the Millstone Nuclear Power Station on Long Island Sound, Connecticut, U.S.A. The well constrained linear relationship between the two parameters indicates that the power-station-induced copper anomaly disappears due to simple dilution, just as does the temperature anomaly. The excess copper, then, undergoes no discernable phase-change reactions during dilution, but is overwhelmingly diluted within 500 meters or so of the outfall, and is therefore probably quite innocuous.

The same reach of the river was sampled again in April 1982 (Fig. 1), to determine if the first few months of coal-fired operation had any measurable effect on riverine water-quality. Since cooling water composition is independent of the fuel firing the plant, the study was not concerned with mixing behavior of metals in the plume so much as with the levels of metals in the water column near the west bank. If substantial amounts of metal-rich leachate from the coal storage area and the settling basins were entering the river via groundwater, it was supposed that maximum impact would occur along the western shore. The river was at high stage, however, so that impacts would tend to be minimized by dilution, anywhere that they might occur. While the data (Table 1) would therefore not represent a worse-case or even an average-case of metal loading into the stream, they are instructive when compared to the 1980 data reported by the private water-quality laboratory. [Note that we are comparing data from a low river stage to a high stage, hence some differences might be expected; however, it was shown earlier that at least for copper the seasonal variation was small.]

It is clear that the levels obtained by the author's ultraclean methods for each metal, except iron (the concentration of which is 10 to 100 times greater than the others), are substantially lower than those obtained by routine "handbook" methods (specifically, "Standard Methods", APHA, 1975). I posit again that the higher levels reflect sample contamination; metal concentrations in contaminated samples were elevated by factors between 4 (for Ni) and 50 (for Cd), with a factor of 10 being the most common. It seems possible that the practice of measuring trace metal concentrations by techniques not specifically designed to avoid the various sources of contamination is widespread, hence one should use great caution when evaluating the analytical findings of waste-water investigations. Furthermore, the water-quality laboratories responsible for providing such services should undertake a self-examination to determine if samples for trace metal analyses are being handled appropriately. The governmental regulatory agencies overseeing environmental monitoring studies should also look inwards to determine if their expertise includes an understanding of the requirements for non-contaminating metal analysis.

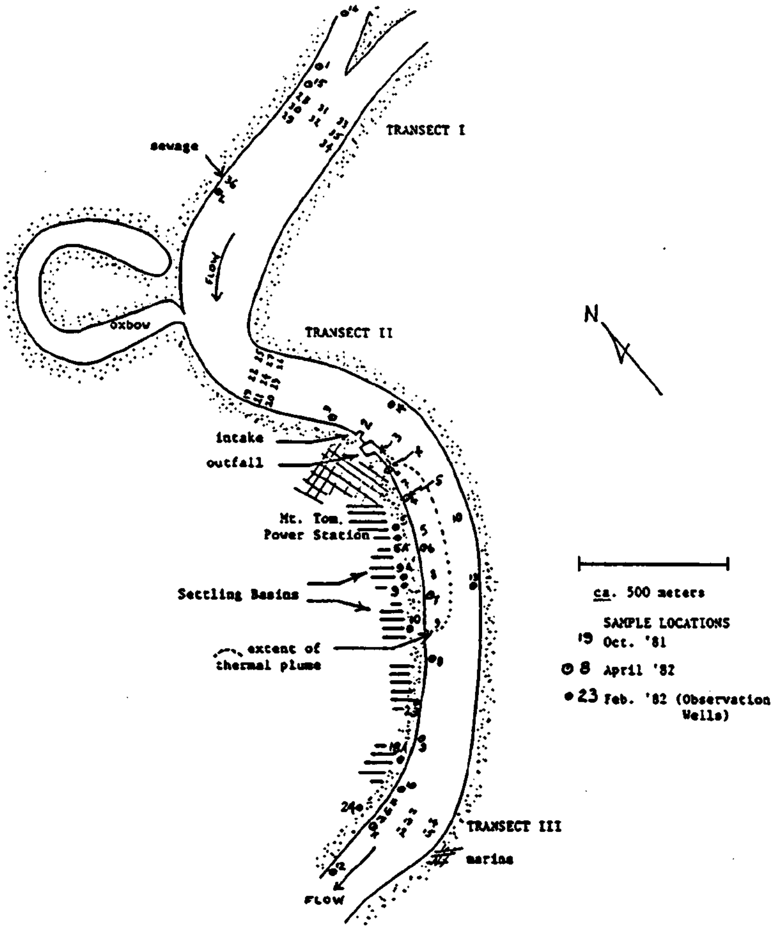

FIGURE 1. THE STUDY AREA IS A FOUR KILOMETER REACH OF THE CONNECTICUT RIVER, NEAR NORTHAMPTON, MASSACHUSETTS.

The April 1982 survey showed that cooling water was a source of plant-derived iron, nickel, and zinc, and possibly a weak source for copper, to the river. In each case, samples from the nearshore area downstream from the outfall, alongside the settling basins (samples 7, 8, and 9, Figure 1), contained metals at concentrations similar to upstream areas. Hence, dilution of cooling water was rapid, and leachate seepage caused no measurable effect on riverine metal solute concentrations.

TABLE 1. DISSOLVED TRACE METAL CONCENTRATIONS REPORTED FOR VARIOUS SAMPLING PERIODS, BY THE AUTHOR AND BY A PRIVATE WATER-QUALITY LABORATORY.

OCTOBER, 1981 (rising river stage, near low-flow) - THIS STUDY

Location	[Cu]ug/l
upstream	2.4 ± 0.3
plume, at outfall	4.7
mixing zone	(see Table 2)

APRIL, 1982 (high flow) - THIS STUDY

Location*	[Cd] ug/l	[Cu] ug/l	[Fe] mg/l	[Mn] ug/l	[Ni] ug/l	[Zn] ug/l
upstream (1,3,14,15,16)	0.03**	2.0±0.5	0.21±0.4	14.0±1.1	0.8±0.3	3.2±0.3
plume, at outfall (4)	0.03**	2.2	0.29	14.1	1.2	7.9
mixing zone (7,8,9)	0.04	2.3±0.4	0.19±1.3	16.8±1.6	0.8±0.2	3.4±0.4

SEPTEMBER, 1980 (rising stage, near low-flow) - PRIVATE WATER-QUALITY LABORATORY

Location***	[Cd]	[Cu]	[Fe]	[Mn]	[Ni]	[Zn]
upstream (6 samples)	1.2±0.2	<10-30****	0.16±.05	45±10	23±7	40±27
mixing zone (3 samples)	1.8±0.7	25±5	0.27±.05	57±12	25±5	37±6

* actual samples in parentheses; see Figure 1

** at detection limit

*** Sample locations are similar to those of the author. The cooling water discharge at the outfall was not sampled. However, these mixing zone samples had temperature anomalies of about 4.0°C above ambient, indicating about 50% dilution of the heated effluent.

**** Three samples reported at ≤ 10 ug/l, three others at 10-30 ug/l, mean of 20 ug/l.

TABLE 2. DISSOLVED COPPER CONCENTRATIONS IN THE COOLING-WATER PLUME

Sample	Temp (°C)	[Cu]ug/l
3	20.4	4.7
1	19.5	4.3
6	18.9	3.8
7	17.4	4.2
4	16.7	3.6
8	14.5	2.8
2 (intake)	12.0	2.0
Ambient*	12.0	2.2

* mean of all samples outside the detectable thermal anomaly, including the upstream samples of Table 1, one sample adjacent to the plume and 8 samples from a transect across the river about 1/2 km downstream from the detectable thermal plume. The latter 9 samples ranged between 1.8 and 2.8 ug Cu/l, with a mean and standard deviation of 2.3 ± 0.4 ug/l.

Factors Controlling Metal Levels in Bottom Sediments

Considering that synoptic sampling of riverwater may not allow detection of the impact of long term seepage of leachate-enriched groundwater through river bottom sediments, the concentrations of metals associated with the acid-leachable fraction of bottom sediments were also measured (Table 3). Sediment samples were taken beneath the surface water sample locations of Figure 1. Because heavy metals preferentially accumulate in fine-grained bottom sediments with great surface areas in association with ionically active clay and oxyhydroxide surfaces (Jenne, 1968; de Groot et al., 1971; Waslenchuk, 1975), it was necessary to account for this natural phenomenon when interpreting the distribution of heavy metals in the inhomogeneous fluvial deposit of the study area. To this end, leachable metal concentrations were normalized to the weight percent of silt and clay (ie. the sediment fraction with less than 53 micrometers grain size).

The causative relationship between sediment grain size and labile trace metal concentrations is best reflected by the plots of leachable manganese and leachable chromium concentrations versus weight percent of clay and silt in Figure 3. Similar, but less well constrained relationships were obtained for all other metals. The goodness of inter-relationships between metals and proportions of fine sediments is very obvious in the highly significant correlations of Table 4. Notice that particularly high correlations were realised between most metals and % fines, and between most metals and iron or manganese. Plots of manganese vs. lead, iron vs. manganese, and iron vs. copper (Figure 4) visually attest the high correlation coefficients of Table 4, and illustrate very well the control exerted by Fe and Mn oxyhydroxide grain coatings on other trace metal distributions. The absence of obvious outliers in all such plots is taken as strong evidence that the processes controlling metal distributions in the sediments are uniformly operating everywhere in the study area, implying also the absence of localized contaminant accumulations.

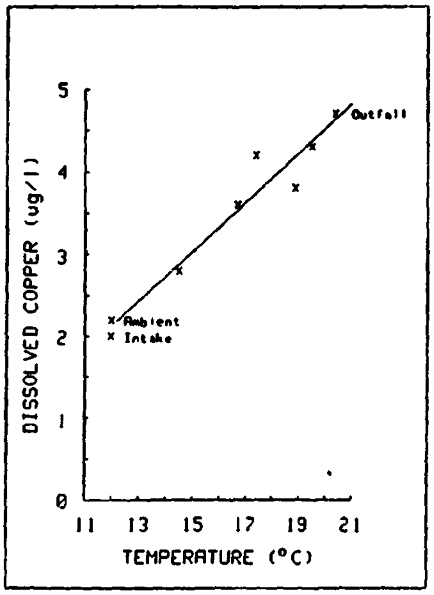

FIGURE 2. MIXING BEHAVIOR OF DISSOLVED COPPER IN THE COOLING WATER PLUME

TABLE 3. LEACHABLE METAL CONCENTRATIONS IN CONNECTICUT RIVER BOTTOM SEDIMENTS COLLECTED NEAR THE MT. TOM POWER STATION. (μg/g dry wt.)

SAMPLE	Cd	Cr	Cu	Fe (mg/g)	Mn	Ni	Pb	Zn
16	0.39	30.3	11.94	3.88	485.58	4.26	23.63	26.72
1	<0.004	0.45	0.24	0.29	62.25	0.93	1.09	3.34
15	0.12	11.7	2.47	1.12	300.13	0.77	10.39	8.42
2	0.12	3.3	10.52	0.91	74.71	1.98	10.61	27.41
3	0.04	2.9	9.09	2.67	246.40	3.11	13.06	34.24
14	0.16	23.6	12.10	3.69	354.52	4.85	22.81	46.26
4	0.05	9.9	16.19	3.90	398.43	7.48	18.60	38.09
5	0.09	6.9	9.72	2.15	103.54	3.52	9.82	28.22
6	0.02	1.2	3.06	0.26	51.12	0.62	1.84	4.36
7	0.10	12.9	14.94	3.10	182.18	4.32	14.06	33.58
13	0.03	3.9	4.96	2.42	125.16	2.73	9.21	23.20
8	0.05	17.8	15.02	3.80	206.42	3.26	13.13	33.29
9	0.11	18.0	5.32	1.48	71.43	6.41	9.27	20.47
10	0.03	4.5	2.11	1.06	43.91	1.66	4.66	11.27
11	0.01	10.8	5.18	2.40	230.67	2.34	12.12	22.50
12	0.01	10.5	7.75	1.95	159.90	2.78	16.00	34.00

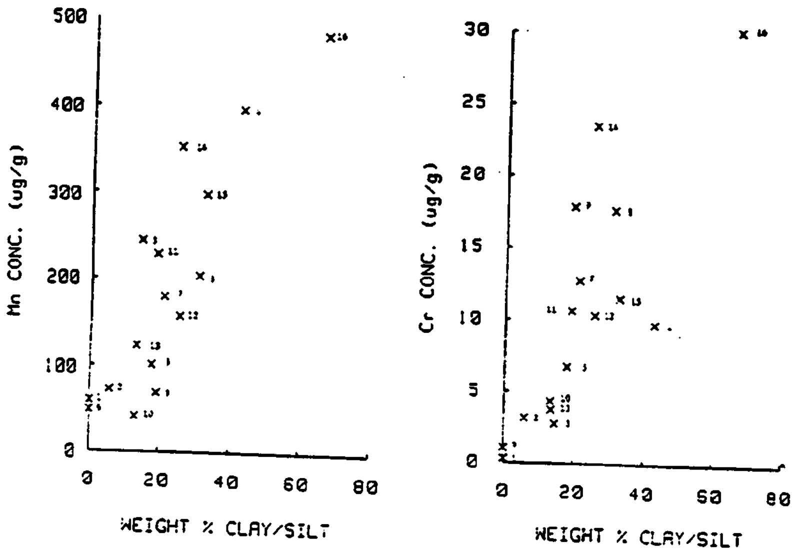

FIGURE 3. CONCENTRATIONS OF LEACHABLE MANGANESE (a), AND LEACHABLE CHROMIUM (b), ASSOCIATED WITH BOTTOM SEDIMENTS, NORMALIZED TO THE PROPORTION OF FINE SEDIMENTS (53 microns) IN THE SAMPLES

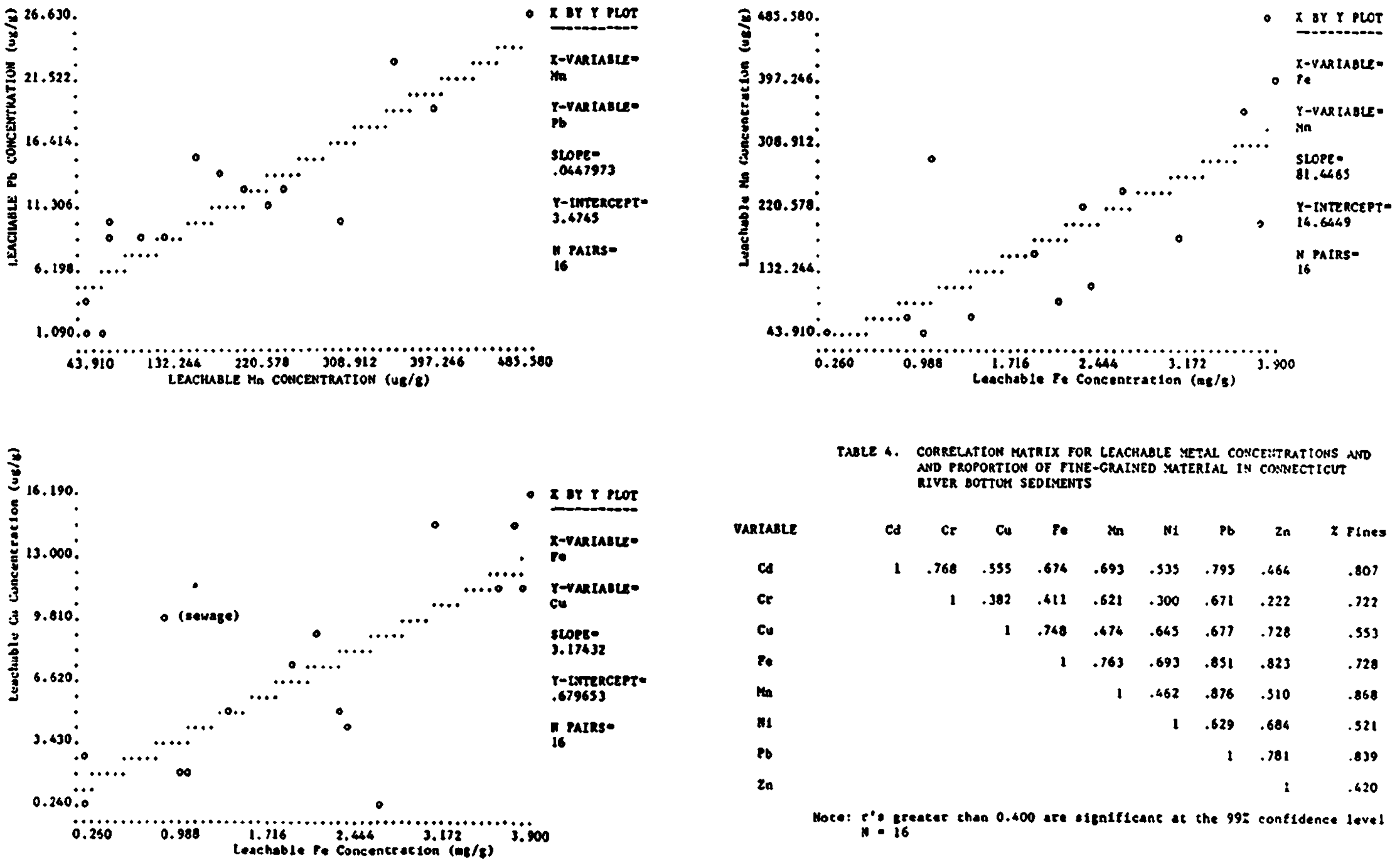

FIGURE 4. INTER-RELATIONSHIPS BETWEEN (a) MANGANESE AND LEAD, (b) IRON AND MANGANESE, (c) IRON AND COPPER, IN LABILE FRACTION OF SEDIMENTS

TABLE 4. CORRELATION MATRIX FOR LEACHABLE METAL CONCENTRATIONS AND AND PROPORTION OF FINE-GRAINED MATERIAL IN CONNECTICUT RIVER BOTTOM SEDIMENTS

VARIABLE	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn	% Fines
Cd	1	.768	.555	.674	.693	.535	.795	.464	.807
Cr		1	.382	.411	.621	.300	.671	.222	.722
Cu			1	.748	.474	.645	.677	.728	.553
Fe				1	.763	.693	.851	.823	.728
Mn					1	.462	.876	.510	.868
Ni						1	.629	.684	.521
Pb							1	.781	.839
Zn								1	.420

Note: r's greater than 0.400 are significant at the 99% confidence level
N = 16

Metal Levels in Benthic Organisms

An alternative indicator of the long term impact of any metal-rich leachate entering the river might be the body burden of metals in benthic infauna. One of the dominant groups of organisms in the study area sediment were oligochaete worms, which occurred in densities on the order of 10 individuals per 10^3 cm^3 of sediment. The measured concentrations in dried tissue are reported in Table 5.

TABLE 5.
METAL CONCENTRATIONS IN OLIGOCHAETE SAMPLES FROM CONNECTICUT RIVER SEDIMENTS NEAR THE MT. TOM POWER STATION (ug/g dry wt.)

SAMPLE	[Cd]	[Cr]	[Cu]	[Pb]	[Zn]
16	0.65	3.27	21.65	4.68	267.54
1	1.55	14.67	28.65	16.51	678.20
15		(barren)			
2	28.36	105.86	nd	272.03	nd
3	10.81	84.53	17.35	187.78	2897.37
14	< 0.1	11.29	12.98	< 0.29	321.30
4	2.90	20.87	9.72	17.88	nd
5		(barren)			
6	1.58	110.67	619.29	44.81	3190.11
7	0.79	20.91	75.95	14.02	494.76
13	0.54	23.57	56.58	11.70	354.06
8	8.73	15.45	100.10	32.87	1567.86
9	2.91	18.61	138.80	27.35	404.88
10	2.20	8.43	96.13	11.48	603.54
11	1.26	< 2.57	29.54	5.68	475.02
12	0.83	9.88	20.01	7.34	126.63

nd = not determined due to insufficient sample

Samples 16, 1, 3, 14, 13 and 12 may be considered to reflect background conditions. For each metal, these ambient samples establish a relatively wide range of natural metal burdens, which mostly bracket all other concentrations encountered. Such a wide range unfortunately limits the usefulness of the infauna as bioaccumulation indicators.

However, some observations are of interest. As for sediment samples there is a high degree of correlation in metal vs. metal relationships (Table 6), indicating that, to a first approximation, body burdens of metals in worms were controlled by processes that operated uniformly throughout the study area. Of particular interest is the good correlation between Cd and Pb; both are environmentally noteworthy because they have relatively high volatility. Good correlations among Cu, Cr, and Zn probably also reflect their similar biogeochemistries.

TABLE 6. CORRELATION MATRIX FOR METALS IN OLIGOCHAETE SAMPLES

VARIABLE	Cd	Cr	Cu	Pb	Zn
Cd	1	.646	-.052	.935	.625
Cr		1	.730	.785	.903
Cu			1	.069	.637
Pb				1	.737
Zn					1

Note: r's above 0.623 are significant at the 99.9% confidence level
N = 14

A statistical treatment of the data alone is insufficient when potential anomalies are the point of concern. A direct examination of the data does reveal some trends that suggest worms adjacent to the power station were exposed to anomalous metal levels. The evidence is not dramatic, but samples from the area of expected impact often had metal levels at the upper end of the ranges encountered. Samples 6 and 8 each had relatively high levels of four of the five metals. Copper was enriched in samples 6,7,8,9, and 10, all from the zone of influence of the cooling water plume.

The metal enrichments in worm tissue may reflect accumulation of plant-derived metals from the dissolved state, since the superjacent cooling water plume is characterized by dissolved copper, iron, nickel and zinc anomalies (Figure 2 and Table 1). Oligochaete body burdens and sediment burdens of trace metals are not correlated, therefore it is apparent that these worms do not principally obtain metals from ingestion of bottom sediment. [Note that it would have been of interest to seek correlations between metal levels in worm tissue and dissolved metal levels in sediment interstitial waters. This was not done, but might have provided an indication of the route of metal assimilation by oligochaetes, and might have pointed to areas of leachate seepage.] One curiosity of the study is sample 2, which was located immediately downstream from the discharge of sewage from a treatment facility in Easthampton; metal levels in sediments and worms were clearly anomalous with respect to all other samples, and the dissolved copper concentration in a water sample taken from there in October 1981 was much elevated also (6.7 ug/l near the sewage outfall, compared to 4.7 ug/l at the power station outfall and 2.0 ug/l in ambient water).

Distribution of Trace Metals in Groundwaters

The observation wells that were sampled are located in floodplane deposits between the power station settling basins and the Connecticut River (Fig. 1). One might anticipate that trace metal concentrations in the groundwaters would be importantly controlled by, inter alia, the source strength of natural and unnatural (coal and flyash leachate) contributions, and by the prevailing oxidation-reduction poise. Redox conditions would largely control the partitioning of redox-active iron and manganese compounds, of which the oxidized forms are highly insoluble and the reduced forms are quite soluble. Newly precipitated oxyhydroxides of either metal in oxygenated waters have high surface activity (Parks, 1967), and can cause adsorption or co-precipitation of most other metals; dissolution of iron and manganese precipitates in response to more reducing conditions would then liberate other metals to the dissolved phase. Under still more reduced conditions, each metal may precipitate as a more or less insoluble sulfide mineral phase, reducing the solute concentrations. If a settling basin were contributing substantial amounts of metals to groundwater, anomalously high metal concentrations should have occurred in observation wells hydraulically below that particular source. However, the basis for establishing what is anomalous due to source strength must recognize the influence of redox variations on metal concentrations.

The author's analyses of groundwater samples taken in February 1982 (Table 7), reveal that concentrations of each metal varied by more than a factor of 10 from well to well. Iron and manganese, which are particularly reactive, had still greater variability. Some wells (eg. OW9A) had high concentrations of many metals, but since OW24 (a control sample, since the well is not hydraulically below the leachate sources) often also had relatively high metal concentrations, a high metal level apparently does not clearly signal the nearby presence of a strong leachate source. The strong odor of H_2S emanating from sample OW9A, and weakly from some others, however, indicated that redox variations might have played an important role in establishing dissolved metal distributions. The chemical oxygen demand (COD) of the samples was routinely measured by a private water quality laboratory (whose samples were duplicates of the author's), and provided a crude measure of the concentration of reducing agents in the samples. As seen in the correlation matrix of Table 8, cadmium, copper, iron, and manganese concentrations co-vary strongly (at greater than 98% significance level) with COD. The correlations suggest that, in the absence of remarkable outliers from the metal vs. COD relationships, metal levels in groundwater can be largely explained in terms of the prevailing redox chemistry, and that high metal concentrations do not necessarily indicate localized pollutant inputs. No significant correlations were found for nickel, lead, and zinc with respect to COD, perhaps because the latter parameter is a poor reflection of redox conditions, because power plant leachate does substantially affect these metals, or because artifacts were introduced in the handling of the samples. It would seem necessary, for purposes of unambiguous interpretation of the impact of coal use on groundwaters, to examine such relationships over time, however, and with a more exacting indicator of oxidation potential (such as careful electrode measurements of Eh, or analysis of oxidized and reduced forms of some redox active couples such as sulfur, nitrogen, or arsenic species).

It is of interest to consider a comparison between the author's analytical results and those of the private water-quality laboratory to whom duplicate samples were delivered (Table 7). Differences abound, but a common observation is that the author's concentrations are greater for Cd, Cu, Fe, and Ni. This is probably a reflection of the different handling procedures for the two sets of samples; the author immediately filtered the samples (with ultra clean apparatus) to preclude repartitioning of dissolved and particulate metal species during storage, whereas the other set of samples was not filtered until the day after sampling. In the latter case, precipitation of oxides (with accompanying ion-exchange reactions) might have occurred in the oxygen poor waters during storage in an oxygenated environment, causing removal of metals from solution. Other artifacts could also have arisen, such as dissolution of metal sulfide mineral phases (augmenting the dissolved metal load) and adsorption of metal ions to the walls of the storage bottles. All these effects, together with contamination from impure materials, would tend to render the eventual analytic determinations unrepresentative of the natural chemistry of the solutes. As evidence that the latter sample set was handled inappropriately, and that the results were therefore compromised, it may be noted that of the correlations in the author's data (Table 8), only one significant correlation is found in the other data set (COD - Cd, r=0.772).

TABLE 7. DISSOLVED TRACE METAL CONCENTRATIONS IN GROUNDWATERS (INCLUDING A TEST OF CONTAMINATION DUE TO PUMPING APPARATUS)

SAMPLE	pH	COD	Cd µg/l	Cu µg/l	Fe mg/l	Mn mg/l	Ni µg/l	Pb µg/l	Zn µg/l
OW5	(6.9)	(12)	84.3 (2)	62.5 (15)	0.09 (.59)	3.08	nd (95)	4.03 (<10)	63.2 (12)
OW5A	(6.9)	(12)	8.69 (1)	3.75 (11)	13.5 (14.6)	4.81	143. (11)	4.35 (<10)	32.5 (43)
OW9A	(7.0)	(32)	97.9 (8)	65.5 (12)	7.21 (3.8)	4.35	102. (20)	21.3 (70)	<0.80 (19)
OW9	(6.3)	(8)	5.72 (<1)	22.7 (1)	0.78 (.033)	0.06	102. (22)	14.1 (60)	10.7 (11)
OW10	(6.5)	(8)	2.39 (4)	19.3 (8)	2.93 (2.0)	1.77	36.9 (18)	56.1 (70)	5.78 (15)
OW23	(6.2)	(1)	11.6 (1)	8.15 (8)	<0.002 (10)	0.02	167. (106)	2.53 (10)	9.74 (9)
OW18A	(6.6)	(1)	13.6 (2)	20.1 (15)	1.14 (.48)	0.18	21.2 (22)	17.9 (<10)	39.4 (19)
OW24	(7.1)	(16)	8.69 (2)	45.7 (9)	2.33 (.16)	1.33	5.46 (28)	36.6 (30)	19.6 (35)
DIRECT RIVER			nd	3.00	0.25	0.05	3.01	nd	2.97
PUMPED RIVER			nd	3.85	0.30	0.07	4.45	nd	38.5

nd - not determined for these samples

Values in parentheses are results reported by a private water-quality laboratory for duplicate samples.

TABLE 8. CORRELATION MATRIX FOR METALS AND C.O.D. IN GROUNDWATERS

VARIABLE	COD	Cd	Cu	Fe	Mn
COD	1	.695	.726	.455	.707
Cd		1	.845	.050	.560
Cu			1	-.172	.349
Fe				1	.802
Mn					1

Note: r's above 0.443 are significant at the 98% confidence level
N = 8

Finally, the use of a non-ultraclean pumping system for sampling constituted a source of error which was common to both sets of samples. The pump had a plastic diaphragm, but it and the rubber hose used were not handled in a way to avoid introducing contamination to samples. In order to assess the potential for sample contamination, the pumping system was used to obtain a river water sample at the end of the day of sampling wells. Riverwater was allowed to flush through the system for about 5 minutes, then riverwater was sampled directly (by submerging a collection bottle), and from the water pumped through the system. All metal concentrations in the river water increased as a result of passing through the pump system; zinc concentration increased dramatically! While such changes may not occur quantitatively with each use of the pump, the experiment does point to the potential for contamination by non-ultracleaned apparatus.

METHODS

Of fundamental importance to a study of trace metals in natural waters is the observation of ultra-clean procedures. All sources of metal contamination must be avoided, since metals occur in the samples at such low concentrations. The sources of contamination that may plague an investigation have been documented by Patterson and Settle (1976), whose quality-control procedures have set a much needed standard. The day to day operations in a laboratory concerned with ultrapurity in trace analysis have been described by Mitchell (1973), among others.

The methods used in this study are slightly modified variants of those in the works referred to above. Briefly, all materials used in the sampling, storage, handling, and analysis of samples were non-metallic, and were extensively cleaned prior to use (with the exception of the grab sampler used for sediment collection, and the pumping system used for groundwater sampling). All plastic bottles, filtration apparatus, filter membranes, pipettes, etc. are cleaned in three stages; for three days in each case, the materials are soaked in concentrated HCl, 2N HNO_3, and 0.5% ultrapure HNO_3, with several rinses by progressively purer water between stages. Cleaning, and sample handling upon return to the laboratory, are carried out in a Class 100-A Ultraclean Laboratory, which provides a metal-free, positive pressure environment of micro-filtered air. At the purest stage, cleaning acids are diluted with, and reagents are made up with, distilled deionized water that is further purified by sub-boiling distillation in a quartz still. Significant reductions in reagent and procedural blanks are obtained as reward for these efforts. All critical ultracleaned equipment is taken into the field double-bagged in similarly cleaned plastic bags (separately sealed). Whenever an operator handles this equipment, he wears polyethylene gloves, which are changed often to avoid cross-contamination with uncleaned materials that must also handled.

Surface water samples taken from a vessel are collected from the bow while the vessel eases forward into undisturbed areas; the surface film is avoided by plunging the collection bottle quickly to about 0.5 meter depth. Samples are pumped from depth through ultracleaned plastic tubing with a portable peristaltic pump. Water samples are filtered immediately in closed apparatus, through ultraclean 0.4 micron Nuclepore membranes, and are then preserved with purified HCl. The acid used is reagent grade concentrated HCl that is doubly distilled at sub-boiling temperatures in a Teflon apparatus (the final normality of the purified HCl is less than that of the original concentrated acid; acidification at the rate of 2 ml purified acid per one liter of sample results in a satisfactory final pH, less than 2). The amount of time that any ultracleaned equipment is out of its bag, exposed to potentially contaminating aerosols is kept to a minimum. Sediment samples must often be obtained with a steel grab, as in this study. The undisturbed interior of the mass collected was quickly sub-sampled. The sampler was free of loose, rusty material. Preferably, a more highly controlled sample should be taken with a plastic coring device that preserves the original layering of the sediment as much as possible, so that the surficial sediments can be preferentially sub-sampled to better reflect recent phenomena.

Water samples that contained more than a few parts per billion of a metal of interest were analyzed directly by graphite-furnace atomic absorption spectrometry. For those with lower metal levels, preconcentrations were accomplished either by careful sub-boiling evaporation or by organic chelation/solvent extraction. In the former case, 15 ml of sample were evaporated to near dryness, 2 ml of purified HNO_3 were added to aid in the destruction of organic compounds, and that was evaporated to dryness. The residue was taken up in 1 ml of 1N HNO_3, providing a 15:1 concentration for AAS determination. Alternatively, greater concentration factors were achieved by chelating up to 200 ml of sample with a combined APDC-DDDC solution, extracting the complex into a few milliliters of Freon, and back extracting metals into a 7N HNO_3 phase. The final phase was evaporated to dryness, and the residue was taken up as before. This technique is a minor modification of that described in detail by Bruland et al. (1979). Calibration is done with standards made up in quartz-distilled water, and for each new sample type encountered, calibration is checked against standard additions (which may necessarily supplant distilled water standards, especially where preconcentration produces an interfering matrix).

The labile fraction of metals associated with sediments were dissolved with 5% HCl (purified) after an H_2O_2 treatment to destroy organics (Skougstad et al., 1979). All manipulations were done in quartz beakers, under a laminar-flow clean bench/fume hood. Metals associated with oligochaetes were brought into solution by successive concentrated HNO_3 digests, each time bringing the solution to near dryness, until a white residue was obtained. Subsequently, 1 ml of 30% H_2O_2 was added and evaporated to dryness, and the residue was taken up in 1N HNO_3. Analytical determinations for metals in sediments and worms were done by flameless AAS.

SUMMARY AND CONCLUSIONS

1) At the Mt. Tom Power Station, cooling waters discharged to the Connecticut River contained about twice the ambient riverine concentrations of copper, iron, nickel, and zinc. The excess copper contributed by the condenser system was ideally diluted as the cooling water plume mixed into the river; copper anomalies disappeared at the samme rate as temperature anomalies in the mixing zone. Ambient conditions prevailed again within some 500 meters downstream from the outfall.

2) The concentrations and distributions of metals associated with labile phases of bottom sediments were largely accounted for by natural phenomena. No anomalies could be discerned when trace metal concentrations were normalized to sediment textural quality (proportion of fine-grained sediment), or to concentration of geochemically important iron and manganese phases. Evidently, leachate from the coal and flyash stored on the adjacent riverbank has not measurably affected metal levels in riverine sediments.

3) The concentrations of trace metals in oligochaete worm tissues from ambient samples span a wide range, hence oligochaetes seem to be poor indicators of unnatural bioaccumulation. While usually within the range of ambient levels, some metal concentrations were persistently high in oligochaetes from sediments beneath the metal-enriched cooling water plume. The lack of correlations between sediment and worm metal levels suggest that the organisms are affected by the metals of the dissolved phase rather than of the sediments.

4) Dissolved metal levels in groundwater samples from observation wells near the coal and flyash storage areas were substantially higher than those in the river, but also varied widely. A control well had intermediate metal levels. The concentrations of several elements were highly correlated to the chemical oxygen demand of the groundwater (a crude reflection of the redox poise of samples). The absence of obvious outliers in such relationships may indicate that metal levels are controlled more by the redox state of the aquifer than by pollutant source strength. Contamination of groundwaters by leachate may be recognizable only through extended monitoring of metal levels and their relationships to parameters reflecting major physical-chemical processes.

5) For each compartment studied, geochemically reasonable relationships were recognized in the data generated by ultraclean analytical techniques and chemically sound sample handling methods. The data obtained by others, using common, routine methods inappropriate for trace metal investigations, was characterized by a lack of meaningful inter-relationships. The latter methods were shown to result in sample contamination, where natural levels were obscured by additions of ten-fold quantities of metals.

6) This paper calls for a reconsideration of techniques used in waste-water monitoring programs, on the part of water-quality laboratories and governmental regulatory agencies, in light of the possibly widespread problems revealed here, and the promise of more conclusive interpretations that may come from state-of-the-art geochemical practices.

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AERIAL INPUTS OF CADMIUM, COPPER, LEAD, AND MANGANESE INTO A FRESHWATER POND IN THE VICINITY OF A COAL-FIRED POWER PLANT

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Abstract. Cadmium, Cu, Mn, and Pb were analyzed in bulk precipitation for 21 mo at a 2 ha pond, located 5.5 km northwest of an 83 MW coal-fired power plant in South Carolina. No significant changes in mean concentrations of the four metals in bulk precipitation were observed after installation of modern electrostatic precipitators on the stacks of the power plant, which had previously been equipped with mechanical cyclone collectors for removal of fly ash. Hence, fly ash from stack emissions was apparently not a major source of aerially deposited trace metals at the pond site. Annual inputs of the four metals in bulk precipitation at the pond were similar to values reported for other rural areas in North America. Enrichment factors, with Mn as a reference element, indicated that Cd, Cu, and Pb in bulk precipitation were not derived from soil or crustal material. Cadmium, Cu, and Pb were enriched in all samples of bulk precipitation relative to their abundances in local soils, and were most enriched during autumn and winter. A multiple regression procedure suggested that wetfall was the primary mode of aerial deposition of Cd and Cu, whereas both wetfall and dryfall were important modes of aerial deposition of Pb.

1. Introduction

Quantitative assessments of atmospheric inputs of trace elements to lentic systems have only recently emerged. Because of the present rates of anthropogenic mobilization of certain trace elements into the atmosphere (Bertine and Goldberg, 1971), determination of aerial inputs should be an integral part of investigations of trace metal budgets for both lakes and watersheds. Trace substances released into the atmosphere can be transported considerable distances (Bertine and Goldberg, 1977; Winchester and Duce, 1977), and atmospheric deposition of certain trace elements in natural systems has increased considerably, even in remote regions far removed from sources of pollution (Hirao and Patterson, 1974; Schlesinger *et al.*, 1974; Elias *et al.*, 1976). In this study, concentrations of Cd, Cu, Mn, and Pb in bulk precipitation (dryfall + wetfall; Whitehead and Feth, 1964) at a small freshwater pond (Skinface Pond) were measured to estimate atmospheric inputs of these elements into the pond and to determine the relation of trace element composition of bulk precipitation to emissions from a nearby coal-fired power plant.

Skinface Pond is a 2 ha, softwater impoundment located near Jackson, South Carolina, approximately 5.5 km northwest of the 484-D power plant on the nearby U.S. Department of Energy's Savannah River Plant (33° 14′ N, 81° 47′ W). On an annual basis, the region has no prevailing wind direction and receives an average of

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approximately 120 cm of rainfall (Langley and Marter, 1973). Detailed hydrological, biological, and meteorological descriptions of the area have been given by Langley and Marter (1973). The 484–D plant is an 83 MW coal-fired power plant of the pulverized wet bottom type with four 38 m stacks. The plant has operated since 1952 and burns approximately 2.6×10^5 metric tons of bituminous coal per year. Prior to 1976, fly ash produced by plant operations was removed with mechanical cyclone collectors that had a maximum efficiency of about 75%. Horton *et al.* (1977) estimated that approximately 3.6×10^8 kg of fly ash were released from the stacks during the 23 yr of operation from 1952 to 1975. Electrostatic precipitators were installed on each of the four stacks during late 1975 and early 1976 and are estimated to be more than 99% efficient at removing fly ash from stack emissions (Horton *et al.*, 1977).

Small (submicron) fly ash particles are highly enriched with many trace elements (Block and Dams, 1975a, 1975b; Kaakinen *et al.*, 1975; Klein *et al.*, 1975; Block *et al.*, 1976) and can be transported considerable distance in the atmosphere before deposition (Parungo *et al.*, 1978). Increased concentrations of certain trace elements in soils surrounding coal-fired power plants have been detected (Klein and Russell, 1973; Horton *et al.*, 1977). Horton *et al.* (1977) studied total concentrations of 29 trace elements in soil in relation to distance from the 484–D power plant and found elevated concentrations of Ba, Be, Cu, Hg, Mn, Se, and Sr near the stacks. Because total concentrations of Cd in soil were below detection limits of the analytical methods employed by Horton *et al.* (1977), they did not determine whether soil concentrations of Cd had been affected by stack emissions. Horton *et al.* (1977) found no impact of stack emissions on concentrations of Pb in soil.

2. Methods

Bulk precipitation samples for trace metal analyses were obtained with two collectors placed approximately 100 m apart on Skinface Pond. Collectors were located in open areas devoid of overhanging or nearby vegetation. Each collector was constructed by inverting the top one-half of a 25 l polyethylene carboy equipped with a polyethylene funnel to drain directly into a 4 l Erlenmeyer glass flask. The flask and bottom section of the carboy were enclosed in a protective plywood housing to prevent both damage to the collectors and solar illumination of the bulk precipitation samples. Tops of the collectors were situated 1.5 to 2.0 m above the pond surface, dependent upon pond water level.

Bulk precipitation was collected from July 1975 to April 1977. Collection periods varied in duration from less than 0.1 to 18.0 days. The mean duration of sampling periods was 6.0 days. At the beginning of each sampling period, cleaned collector tops, funnels, and flasks were placed at each station. Two milliliters of redistilled, concentrated HNO_3 were added to each flask at the beginning of each collection period to prevent biological activity and adsorptive losses of metals. Amount of rainfall during

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each sampling period was estimated to the nearest 0.01 cm with a Taylor Clear-Vu rain gage located at the pond. Each bulk precipitation collector yielded approximately 600 ml of sample per centimeter of rainfall. Volumes of samples obtained with collectors were highly correlated with rain gage readings ($r^2 > 0.99$).

After collection, samples of bulk precipitation were taken to the laboratory and acidified to 2% of volume with redistilled HNO_3. Samples were then stored in polyethylene bottles that had been washed in Contrad 70 solution (American Hospital Supply Co., McGaw Park, Illinois) and were refrigerated at 4°C until analysis. Procedural blanks were included with each pair of samples to assess contamination from container walls and nitric acid solution.

Concentrations of Cd, Cu, Mn, and Pb were determined with a Perkin-Elmer model 306 atomic absorption spectrophotometer equipped with an HGA-2100 flameless atomizer. To reduce the probability of sample contamination, analyses were performed directly on acidified rainfall samples, without preconcentration, with sample injection volumes of 10 to 50 μl (Lindberg *et al.*, 1977). Measured concentrations were corrected for blank concentration values prior to data analysis. Data analysis was conducted with the Statistical Analysis System (Barr *et al.*, 1976).

3. Results and Discussion

3.1. METAL CONCENTRATIONS IN BULK PRECIPITATION

Total rainfall at the pond during the 21 mo study was 240 cm, of which 175 cm (73%) were sampled and analyzed. Fifty-six pairs of bulk precipitation samples were collected. For 13 of the pairs, one of the two samples was discarded because of obvious contamination, usually caused by insects or avian feces. Hence, 43 sample pairs and 13 single samples were included in the analysis. Concentrations of each metal were highly correlated ($n = 43$, $P < 0.01$) between the two collector sites; correlation coefficients (r) were 0.93, 0.79, 0.93, and 0.96 for Cd, Cu, Mn, and Pb, respectively. There were no significant differences in metal concentrations between the two sites, except for Pb, which was significantly higher at one site (paired t-test, $P < 0.01$). However, the mean difference in Pb concentrations between collectors (1.0 μg l^{-1}) was small relative to the range of Pb concentrations observed, and the data for the two sites were averaged. Further data analyses will pertain to these average concentration estimates.

Twenty-nine of the 56 sample collections contained wetfall from one rainfall event, 17 contained wetfall from two rainfall events, and five contained wetfall from three or more rainfall events. Number of rainfall events for five sample collections could not be determined with certainty. Mean concentrations of Cd, Cu, Mn, and Pb did not differ significantly between samples containing wetfall from one rainfall event and those containing wetfall from two or more rainfall events.

Concentrations of each of the four metals in bulk precipitation varied considerably among sampling periods. Concentration (μg l^{-1}) ranges for the 56 sample collections were: Cd, 0.06–20.8; Cu, 0.3–17.5; Mn, 0.1–48.4; and Pb, 0.4–37.3. Other investigators have reported ranges exceeding two orders of magnitude for trace metal conc in samples of wetfall or bulk precipitation (Drozdova and Makhon' Schlesinger *et al.*, 1974; Merritt, 1976). Van der Sloot and Luten (1976) p frequency histogram of V concentrations in wetfall from a Dutch provinc positively skewed and approximately lognormal. In this study, frequency di of all four metals exhibited positive and highly significant ($P < 0.01$) ske kurtosis. Frequency distributions of Cu and Pb did not differ significantly lognormal distribution, whereas Cd and Mn distributions did ($P < 0.01$, KSL-

Concentrations of Cd, Cu, Mn, and Pb in bulk precipitation were correlated (Table I). Trace metal concentrations in bulk precipitation sa sometimes negatively correlated with amount of precipitation (Schlesinger *et*

TABLE I

Correlation coefficients (*r*) between concentrations of Cd, Cu, Mn, and Pb in bulk precipitation at Skinface Pond. Simple correlation coefficients are given above the diagonal and partial correlation coefficients adjusted for amount of rainfall are given below the diagonal. One and two asterisks (*) indicate significance at the 5 and 1% levels, respectively.

	Cd	Cu	Mn	Pb
Cd	–	0.53**	0.31*	0.23
Cu	0.47**	–	0.35**	0.50**
Mn	0.22	0.27*	–	0.53**
Pb	0.14	0.44**	0.47**	–

because of dilution of metal-containing dryfall which is washed out of the collector as rainfall continues (Gascoyne, 1977). Sequential sampling dur rainstorm also shows decreasing metal concentrations in wetfall as a stor (Ter Harr *et al.*, 1967; van der Sloot and Luten, 1976), due to washout and metal-containing aerosols and particulates from the atmosphere during r and Franey, 1977). Concentrations of Cd, Cu, Mn, and Pb in bulk pre Skinface Pond were significantly and negatively correlated with amoun however, amount of wetfall only accounted for about 10% of the variat concentrations. Believing that correlations observed between concentra study might be spurious because of simultaneous and equivalent dilution metals in the dryfall component in individual samples, I computed partial adjusted for amount of rainfall, among concentrations of the four metals. amount of rainfall decreased the strength of all correlations be concentrations, but did not generally diminish the significance of the correl I). Thus, dilution of dryfall by wetfall was only partly responsible for th between metal concentrations.

consumption (Struempler, 1976). However, Chow and Earl (1970) associated the dramatic annual cycle of Pb concentration in atmospheric aerosols in the San Diego area with seasonal changes in meteorological conditions. Generalizations concerning factors causing seasonal differences should, therefore, be considered warily. Increased atmospheric levels of crustally derived elements such as Mn during warm periods have been associated with agricultural practices which increase dispersal of soil particles into the atmosphere (Cryer, 1976; Swank and Henderson, 1976).

Electrostatic precipitators, installed on the stacks of the 484–D power plant during late 1975 and early 1976, should have reduced fly ash emissions from more than 25% (with mechanical collectors) to less than 1% of total fly ash production by weight (Horton *et al.*, 1977). To determine if reduction of fly ash emissions had any effect on trace metal content of bulk precipitation at Skinface pond, samples of bulk precipitation collected from July through November 1975 were grouped ($n = 11$ collections) and compared to samples collected during the same time interval in 1976 ($n = 18$ collections), after operation of electrostatic precipitators had begun. Mean concentrations ($\mu g\ l^{-1}$) in bulk precipitation collected before (1975) and after (1976) installation of electrostatic precipitators were, respectively, Cd, 0.49 and 0.59; Cu, 2.2 and 2.6; Mn, 2.8 and 3.1; Pb, 7.8 and 10.1. Analysis of covariance, with amount of wetfall as a covariate, indicated that concentrations did not differ significantly between the two time intervals ($P > 0.50$ for all tests). Reduction of fly ash emissions at the 484–D power plant had no apparent effect on the trace metal composition of bulk precipitation at Skinface Pond.

The chalcophilic elements Cd, Cu, and Pb are generally much more concentrated on submicron fly ash particles, which are less efficiently removed from stack emissions by electrostatic precipitators, than on larger fly ash particles (Natusch *et al.*, 1974), whereas Mn is lithophilic and not enriched in fly ash relative to coal or slag (Kaakinen *et al.*, 1975; Klein *et al.*, 1975; Block *et al.*, 1976). Because Cd, Cu, and Pb are presumably not discharged as vapors, they are released from stacks equipped with modern precipitators only in the very smallest fly ash fractions (Klein *et al.*, 1975). Since the most metal-enriched fraction of the fly ash is not retained, it might be argued that electrostatic precipitators have little impact on amounts of certain chalcophilic elements released from the stacks. However, this argument is not supported by other investigations. Schwitzgebel *et al.* (1975) determined budgets of 27 trace elements in three coal-fired power plants, including one plant equipped with modern electrostatic precipitators ('Station II') and another equipped with mechanical cyclone collectors ('Station III'). Percentages of elemental mass in coal discharged from the stacks were; Cd, < 3.8 and 41; Cu, 0.8 and 29; Pb, 7.5 and 65; Mn, 1.2 and 13, respectively, for Stations II and III. According to these observations, installation of modern electrostatic precipitators at the 484–D plant should have reduced emissions of these elements to about 10% of quantities released when mechanical collectors were used. In relation to other sources of atmospheric trace metals, the 484–D power plant is apparently a minor contributor of Cd, Cu, Mn, and Pb to the Skinface Pond locality.

Enrichment factors (EF) were used to assess possible origins of Cd, Cu, and Pb in bulk precipitation at Skinface Pond. Manganese was used as the reference element for EF because it is a major trace component of uncontaminated soils and sediments and is not enriched in the atmosphere relative to soil or crustal abundances (Zoller *et al.*, 1974b; Duce *et al.*, 1975; Struempler, 1976; Andren and Lindberg, 1977; Weiss *et al.*, 1978). Although high levels of Mn in dryfall and atmospheric dust can occur near point sources of industrial use (Ayling and Bloom, 1976; Beavington, 1977), there are no known industrial sources of Mn pollution near the study area. With Mn as a reference element, the EF for any other element, X, in bulk precipitation (bp) is

$$EF = \frac{[X]_{bp}/[Mn]_{bp}}{[X]_{soil}/[Mn]_{soil}}.$$

The frequency distributions of the ratios, $[X]_{bp}/[Mn]_{bp}$, for Cd, Cu, and Pb exhibited significant positive skewness; therefore, median values of these ratios were used for calculation of EF. For the denominators of the expressions for Cu and Pb, elemental abundances in representative samples of regional soils were employed (Horton and McMinn, 1977). Because Horton and McMinn reported a 'less than' value for Cd concentration, data from Bowen (1966) for world average soils were used for Cd concentration in the denominator of the expression for Cd. An element having continental dust or soil as a principal atmospheric source should have an EF near unity for bulk precipitation. An EF substantially greater (10×) than 1 for an element in bulk precipitation suggests existence of nonsoil sources of that element for the atmosphere. Because certain natural processes can cause atmospheric enrichment over soil or crustal abundances (Duce *et al.*, 1975), occurrence of an EF substantially greater than 1 does not prove anthropogenic origin of the element in question. Since mean concentrations of Mn and Pb in bulk precipitation varied seasonally, EFs were calculated for each season.

EFs for Cd, Cu, and Pb in bulk precipitation indicated substantial enrichment relative to soil abundances and greatest enrichment during autumn and winter (Table III). In fact, Cd, Cu, and Pb were enriched in all 56 sample collections relative to their abundances in soils. These elements in bulk precipitation at Skinface Pond are clearly not derived from crustal material.

Enrichment of Cd, Cu, and Pb in atmospheric aerosols or precipitation has been reported by a number of investigators (Zoller *et al.*, 1974a; Duce *et al.*, 1975; Struempler, 1976; Andren and Lindberg, 1977; Herron *et al.*, 1977; Wallace *et al.*, 1977; Weiss *et al.*, 1978). While there can be little question that atmospheric Pb is derived primarily from automobile emissions (Chow and Earl, 1970, Lazrus *et al.*, 1970; Hirao and Patterson, 1974; Elias *et al.*, 1975), the major sources of atmospheric Cd and Cu are more obscure. On a local basis, elevated aerial deposition of Cd and Cu can sometimes be related to point sources such as smelters (Beavington, 1977; Van Loon and Beamish, 1977; Andersen *et al.*, 1978) or industrial operations (Ayling and Bloom 1976). However, natural sources may still account for much of the atmospheric Cd and Cu on a global scale. Similarity between polar regions of EF of enriched metals and comparison

TABLE III

Median values of enrichment factors of Cd, Cu, and Pb in bulk precipitation at Skinface Pond.

Season	Enrichment factor Cd	 Cu	 Pb
Autumn	2230	57	192
Winter	2360	72	160
Spring	820	21	67
Summer	590	24	151

of EF to the relative volatilities of these metals has led Duce *et al.* (1975) to hypothesize that the enriched metals are derived from natural sources and that a vapor phase is involved in their release. Enrichment factors for Cd, Cu, and Pb in bulk precipitation at Skinface Pond paralleled the relative volatilities of these elements (Cd > Pb > Cu) as given by Bertine and Goldberg (1971); however, this could indicate preferential volatilization during either natural or anthropogenic processes.

3.2. RELATIVE IMPORTANCE OF WETFALL AND DRYFALL

Samples collected in this study were a composite of wetfall and dryfall that had accumulated in the collectors prior to wash-off by rain. Relative importance of wetfall and dryfall inputs was assessed for each metal with the multiple regression equation

$$Y_m = b_0 + b_1 X_1 + b_2 X_2,$$

where Y_m = total input (μg m^{-2}) of metal m during the collection period, X_1 = wetfall during the collection period (cm), and X_2 = duration of period of dryfall deposition prior to wash-off by rain (to nearest 0.1 day).

Only samples for which X_2 was accurately known were used ($n = 42$). The coefficient b_1 estimates wetfall input of trace metal m (μg m^{-2}) per centimeter of rain, and coefficient b_2 estimates rate of dryfall deposition (μg m^{-2} day^{-1}). The intercept (b_0) should be near zero if all important effects have been accounted for by the regression model. Multiple regressions were statistically significant for Cd, Cu, and Pb; however, predictability was low (Table IV). The coefficient b_1 was positive for all four metals,

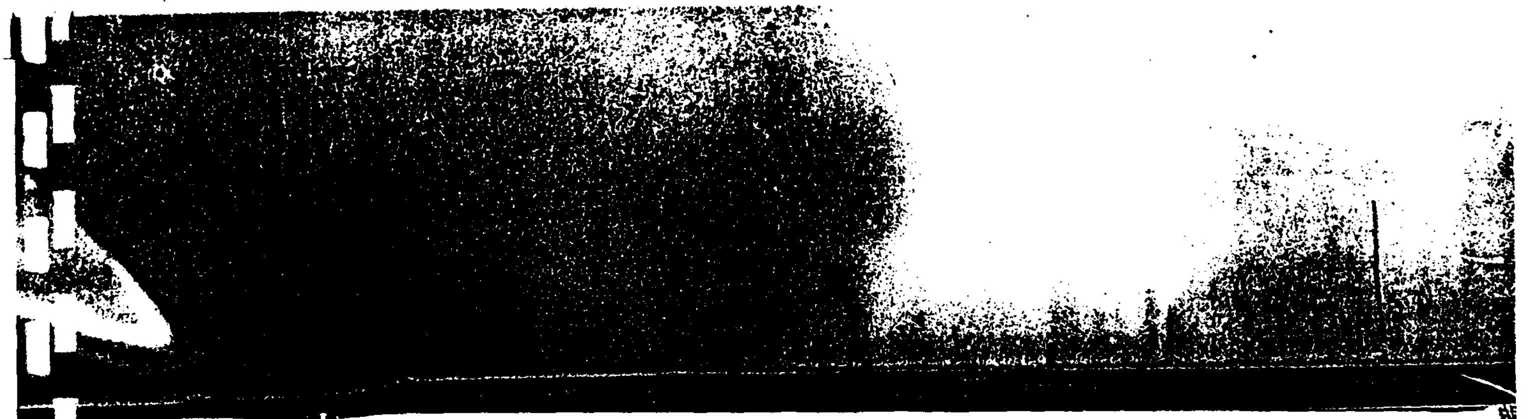
TABLE IV

Results of multiple regressions of metal input (μg m^{-2}) during a collection period on amount of wetfall (cm) and duration of dryfall deposition (days). The regression equation is given in the text. *P* indicates probability of a significant overall regression.

Element	P	b_0	b_1	b_2	r^2
Cd	<0.01	9.50*	4.22**	−0.87	0.29
Cu	<0.01	19.2	13.0**	3.19	0.22
Mn	0.22	40.9	2.99	6.71	0.07
Pb	<0.01	11.5	33.1**	15.7*	0.34

*$P(b_i \neq 0) \leq 0.05$

**$P(b_i \neq 0) \leq 0.01$.



1975) to hypothesize
a vapor phase is
ilk precipitation at
(Cd > Pb > Cu) as
ferential volatiliza-

i dryfall that had
importance of wetfall
regression equation

i period, X_1 = wetfall
od of dryfall deposition

= 42). The coefficient
centimeter of rain, and
. The intercept (b_0)
ior by the regression
1, Cu, and Pb; however,
for all four metals,

collection
ion (days).
oility of a

	r^2
7	0.29
9	0.22
1	0.07
7	0.34

---

indicating a direct relationship between metal input and amount of wetfall. The coefficient b_2 was positive for all metals studied except Cd, but differed significantly from zero only for Pb. An intercept significantly different from zero was found only for Cd. The poor predictability of the regression model as an estimator of metal input was probably due to the multiplicity of factors that influence chemical composition and deposition rate of wetfall and dryfall. However, importance of both wetfall and dryfall as aerial inputs of Pb was indicated. Importance of wetfall also was suggested for Cd and Cu, whereas neither amount of wetfall nor period of dryfall deposition was significantly associated with total Mn inputs. Logarithmic transformation of metal inputs (Y_m) did not improve predictability of the regression model.

The importance of dryfall relative to wetfall as a mode of elemental deposition apparently increases with decreasing total rainfall and/or increasing atmospheric pollution (c.f., Whitehead and Feth, 1964; Likens *et al.*, 1967; Peirson *et al.*, 1973; Servant, 1975; Galloway and Likens, 1976; Swank and Henderson, 1976; Krey and Toonkel, 1977). The area surrounding Skinface Pond receives considerable rainfall (~120 cm yr^{-1}) and is rural with little nearby industry. Hence, results of the multiple regression analyses support the above contention: wetfall appears to be the primary mode of trace metal deposition at the pond site.

METAL INPUTS IN BULK PRECIPITATION

Data from samples collected during 1976 were used to estimate annual inputs of Cd, Cu, Mn and Pb in bulk precipitation at Skinface Pond. A total of 130.7 cm of rainfall was recorded at the pond during 1976. Of this, 113.2 cm (87%) were sampled and analyzed. Total inputs of the four trace metals were calculated by summing products of concentrations and precipitation volumes. Weighted, seasonal mean concentrations from Table II were used as estimates of trace metal concentrations in bulk precipitation not analyzed. Because of the inefficiency of bulk collectors in sampling dry deposition (Galloway and Likens, 1976), these estimates should be regarded as conservative.

Estimated inputs of Cd, Cu, Mn, and Pb in bulk precipitation at Skinface Pond were surprisingly similar to inputs reported for other North American rural sites (Table V)

TABLE V

Annual inputs of Cd, Cu, Mn, and Pb in wetfall and bulk precipitation at various rural localities in North America.

Location	Sample[a] type	Annual input (mg m^{-2}) Cd	Cu	Mn	Pb	Reference
Skinface Pond, South Carolina	B	0.68	3.0	3.0	8.4	This study
Lake Superior	B	0.67	4.5	–	7.9	Swanson (1976)
Walker Branch Watershed, Tennessee	W	0.51	–	2.3	6.7	Lindberg *et al.* (1979)
Chadron, Nebraska	W	0.12	1.8	2.1	1.9	Struempler (1976)

[a] B = bulk precipitation; W = wetfall.

and were only slightly higher (~30%) than inputs in wetfall at nearby (≈ 350 km NW) Walker Branch Watershed. Similarity of trace metal inputs among Skinface Pond and other rural localities further indicates that fly-ash-related inputs of these trace metals at the pond are minor.

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