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Isometric log-ratio co-ordinates and their simple use in water geochemistry

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ABSTRACT

This paper is designed to provide the reader with some guidelines towards understanding the importance of the log-ratio approach in geochemistry. An application example is presented with an analysis of the water chemistry from the Arno river basin (Tuscany, central Italy). Simple graphical alternatives are proposed using *ilr* (isometric log-ratio) transformation on compositional data (constrained support), which are generally used to build up molar-ratio diagrams. If the variables are suitably chosen from a geochemical standpoint, relationships among samples in space and time, as well as compositional changes attributable to different natural or anthropogenic processes, can be analysed on a sound statistical basis. Classical statistics can be applied to *ilr* diagrams to evaluate differences among groups of data, presence of outliers, or significant changes in time (monitoring). The final aim is to demonstrate that through simple principles of univariate or bivariate statistics, valuable results can be obtained, both from a geochemical and a statistical point of view. The approach can be extended to the analysis of different geochemical data matrices.

Key words: compositional data, molar-ratio diagrams, river geochemistry, simplex space

Coordenadas isométricas de tipo log-cociente y su aplicación en geoquímica de aguas

RESUMEN

El artículo presenta un esquema útil para que el lector perciba la importancia del método basado en log-cocientes en geoquímica. Las aplicaciones estudian muestras geoquímicas de agua de la cuenca del río Arno (Toscana, Italia central). Haciendo uso de la transformación ilr *(log-cociente isométrica) para datos composicionales, usada habitualmente para construir diagrams de cocientes molares, se proponen alternativas gráficas atractivas por su sencillez. Si las variables se seleccionan de forma apropriada desde una perspectiva geoquímica, es posible analizar sobre una base estadística consistente las relaciones entre muestras en el espacio y en el tiempo, así como las variaciones composicionales atribuibles a diversos procesos naturales o antrópicos.*

Palabras clave: datos composicionales, diagramas de cocientes molares, el símplex como espacio, geoquímica fluvial

VERSIÓN ABREVIADA EN CASTELLANO

Introducción

Los grandes ríos son agentes muy importantes del modelado del relieve. La mayoría de ellos han estado asociados con el desarrollo de la civilización y sus cuencas ocupan aproximadamente el 69% de la superficie emergida, transportando anualmente alrededor de 19 billones de toneladas de sedimento de las cuales aproximadamente del 20% va en forma de disolución (Gupta, 2007). Nuestro conocimiento acerca de estos ecosistemas, desde un punto de vista geoquímico, se ha incrementado significativamente con la consideración de las leyes naturales que gobiernan los procesos de meteorización, consumo de CO_2 *o contaminación. Sin embargo, los modelos propuestos hasta la fecha (tratamientos numéricos o gráficos) consideran los datos geoquímicos, usualmente concentraciones (mg/L o ppm), como pertenecientes al espacio muestral real. Este espacio muestral real es en el que se desarrollaron las estadísticas clásicas sobre la base de la geometría euclídea donde la escala es absoluta, no relativa. Sin embargo, las concentraciones son datos composicionales que contienen solo información relativa y forman parte de un total. Consecuentemente, la elección de cualquier método para investigar datos experimentales requiere la definición de las propiedades del espacio muestral donde poder definir modelos probabilísticos y estadísticos coherentes. En otras palabras, se debe introducir en dicho espacio muestral un concepto de distancia que debe ser coherente y consistente (Egozcue and Pawlowky-Glahn, 2006).*

La química de los ríos se caracteriza frecuentemente por un número de ratios elementales en lugar de concentraciones simples con el objeto de evitar la dependencia con respecto a procesos de disolución y evaporación. Este trabajo tiene como objetivo el proporcionar una alternativa válida a este tipo de enfoque mediante la aplicación de la transformación ilr *(isometric log-ratio) (Egozcue* et al.*, 2003) a las tres variables usadas en la construcción de los diagramas clásicos de ratios molares. En el espacio bidimensional así obtenido, todos los métodos de la estadística clásica pueden ser aplicados de modo que se puede evaluar la significación estadística de los resultados. Estos mismos resultados no se pueden obtener a partir de los diagramas de ratios molares ya que al compartirse el mismo denominador en los ejes X e Y (por ejemplo Ca/Na frente a* HCO_3*/Na), se genera un sesgo numérico (relaciones inducidas) en el marco euclídeo.*

Discusión y resultados

El caso de estudio considerado es la cuenca de drenaje del río Arno (Tocana, Italia central) que cubre una superficie de 8228 km^2 y tiene una elevación media de 353 m. El río Arno, con una longitud de 242 km, nace en la parte norte de los Apeninos a una elevación de 1650 m y desemboca al mar de Liguria, 10 km al este de Pisa y a 110 km de Florencia (Figura 1). La red de drenaje del Río Arno sigue una tendencia estructural NW-SE dando origen a la presencia de seis subcuencas principales que son de este a oeste: 1) Casentino (CA), 2) Chiana Valley (CH), 3) Sieve (SI), 4) Upper Valdarno (UV), 5) Middle Valdarno (MV) y 6) Lower Valdarno (LV) (Figura 1). Una gran base de datos con más de 500 casos se creó a partir de las campañas de muestreo que tuvieron lugar de febrero 2002 a julio 2005 de modo que se cubrieron cambios estacionales durante varios años. Los resultados permitieron la investigación de las contribuciones naturales y antrópicas en el quimismo del agua del río (Nisi et al., *2008).*

Con el objeto de proponer una alternativa a los diagramas de ratios molares para la investigación de la química del agua del río Arno, el primer paso consiste en la elección de las tres variables cuyo comportamiento conjunto ha de ser analizado. Para el propósito de esta investigación se han seleccionado las concentraciones de Ca^{2+}, HCO_3^- y Na^+ en mg/L. Subsecuentemente, se pueden determinar dos coordenadas ilr *(Egozcue* et al., *2003).*

En la Figura 2 se muestran todos los datos pertenecientes a las seis subcuencas. Sobre los ejes de las curvas de la estimación "kernel" de la densidad se puede verificar simultáneamente la forma de la distribución de frecuencia para cada coordenada. Como se puede apreciar, no se las puede describir en base a un modelo gausiano (Anderson-Darlin y Kolmogorov-Smirnov tests de normalidad, p *<0.01), revelando la posible presencia de fenómenos de mezcla.*

En la Figura 2 se muestra de modo evidente como para valores crecientes en el eje Y la contribución de las fuentes que suministran HCO_3^- y Ca^{2+} aumentan mientras que para valores decrecientes las fuentes que suministran Na^+ parecen ser relevantes. En el primer caso las muestras parecen estar determinadas por fenómenos naturales; en el segundo caso las muestras parecen estar afectadas por la intrusión de agua marina (Lower Valdarno) y por la contaminación. El ión Na^+ es uno de los iones más afectados por fuentes de contaminación (28% del total, Berner and Berner, 1996), incluyendo aguas residuales domésticas, minería de halita, salmuera industrial y sal usada en carreteras. Sales de sodio, tales como Na_2CO_3, Na_2SO_4, así como boratos de sodio, tales como zeolita sódica y Na_2CO_3, son extraídos y utilizados industrialmente como aditivos al agua, reemplazando Ca^{2+} y Mg^{2+} por Na^+ en aguas industriales y domésticas.

Las muestras de Casentino están caracterizadas por un valor medio del ratio Ca/Na, que es alrededor de 130 veces el ratio de Na/HCO_3. Este valor decrece hasta 33 para la cuenca Sieve, 15 para Upper Vardano, 9 para Chiana, 8 para el Lower Valdarno y 6 para el Middle Valdarno. Las muestras tomadas cerca de la desembocadura del río se caracterizan por un ratio Ca/Na que es cerca de 0.002 veces el de Na/HCO_3. Es importante destacar que los cambios más importantes en la química del agua se destacan comparando la subcuenca Casentino, donde está localizado el nacimiento del río y las otras subcuencas donde el efecto de la presión antrópica es alta (por ejemplo la ciudad de Florencia, está localizada en el Middle Valdarno).

Introduction

Large rivers are important components of continental landform modelling. Most of them have been associated with the growth and development of civilization and their basins occupy about 69% of the land area, transporting an estimated 19 billion tonnes of material annually, about 20% of it in solution (Gupta, 2007). Our knowledge about these ecosystems, particularly from a geochemical point of view, has increased considerably in recent years, including a greater understanding of natural laws governing weathering phenomena, consunption of CO_2 and the effects of pollution. Until now, however, most of the analyses and models proposed (numerical or graphical treatments) consider geochemical data, usually concentrations expressed as mg/L or ppm as pertaining to the real sample space. This space is the one in which classical statistics was developed on the basis of Euclidean geometry, where the scale is absolute rather than relative, but concentrations are compositional data, containing only relative information, and form part of a whole. Consequently, the choice of any method to investigate sample data requires a definition of the properties of the sample space, in which reliable probabilistic and statistical models can be defined. In other words, the concept of distance in the sample space should be defined and properly applied.

Since John Aitchison introduced the log-ratio method for the statistical analysis of compositional data in the early 1980s a lot of progress has been made in several fields. Nowadays there are different strategies, all of them based on log-ratios of parts (Egozcue and Pawlowsky-Glahn, 2006).

River chemistry is often characterized by a number of elemental ratios rather than single concentrations in order to avoid dependence on dilution and evaporation processes. This paper aims to provide a valid simple alternative to this type of approach by applying the *ilr* transformation (Egozcue *et al.,* 2003) to the three variables used to build up classical molar-ratio diagrams. In the two dimensional obtained space all the methods of classical statistics can be applied, thus allowing an assessment of the significance of the results. The same outcome cannot be obtained in molar-ratio diagrams since the sharing of the same denominator on the *x* and *y* axes (for example Ca/Na versus HCO_3/Na) generates a numerical bias (induced relationships) in the Euclidean framework.

River-water geochemistry

The dissolved chemical constituents of river water derive mainly from the weathering of silicates and carbonates and the dissolution of evaporates from a source region, and also precipitation. As far as the major elements are concerned (excluding Cl^- and Na^+), the supply from the atmosphere is in general unlikely to be significant in comparison to the input from chemical weathering of the source region. Even the contribution of Na^+ through rainfall is likely to be restricted to regions near the sea. On a global scale, a large number of samples are characterized by the dominance of Ca^{2+} and HCO_3^- in the cation and anion budget, indicating that a major source of dissolved elements in water is carbonate weathering, contributing about half of the dissolved solids in rivers (Meybeck, 1987). The main constituents affected by pollution are Cl^-, SO_4^{2-}, Na^+, and thus about 30% of their concentration can be considered as arising from anthropogenic sources (Maybeck, 1979; Berner and Berner, 1996), whilst a lesser effect is detectable for Ca^{2+} and Mg^{2+}. The weathering of silicate rocks in the source region is another important source of major ions in river water. Silicate weathering is studied for many reasons, including its role in drawing-down atmospheric CO_2. Both carbonate and silicate weathering consume CO_2, although on the million-year time scale CO_2 consumed by carbonate weathering will be released back into the atmosphere during carbonate deposition and hence silicate weathering is the net sink of atmospheric CO_2. The importance of this phenomenon was stressed by Raymo and Ruddiman (1992), who discussed the role of the origin and evolution of the Himalayas since the beginning of the Cenozoic in enhancing silicate weathering rates, thus increasing CO_2 draw-down from the atmosphere.

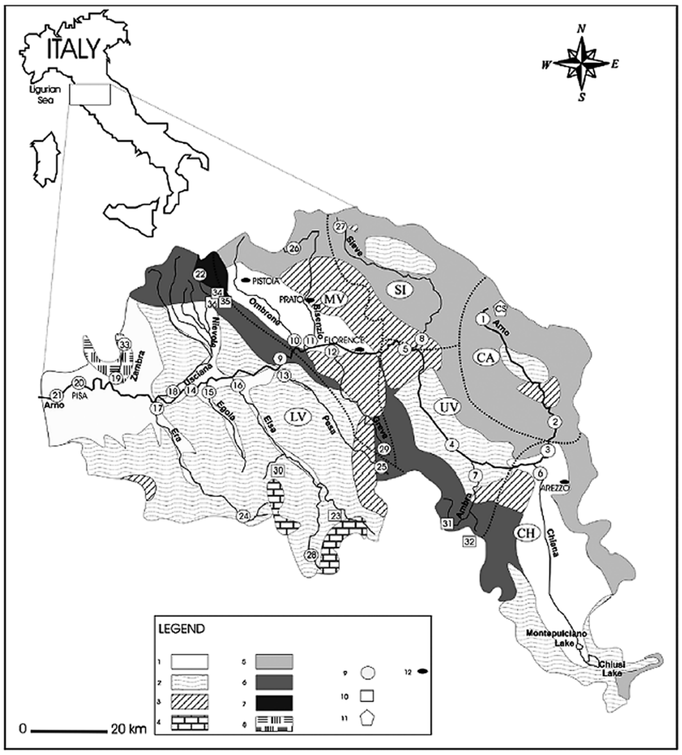

Figure 1. Schematic geological map of the Arno Basin. The catchment area is divided into six sub-basins by dashed lines as follows: Casentino (CA), Chiana Valley (CH), Sieve (SI), Upper Valdarno (UV), Middle Valdarno (MV), Lower Valdarno (LV). Legend: 1 = alluvial deposits; 2 = calys, sands and conglomerates of continental, lacustrine and marine environments; 3 = chaotic shaly rocks with calcareous and ophiolitic olistolitus; 4 = dolomitic and evaporitic rocks; 5 = turbiditic sandstones (Cervarola formation); 6 = turbiditic sandstones (Macigno formation); 7 = turbiditic sandstones (Modino formation); 8 = Paleozoic formations; 9 = running-water samples; 10 = thermal-water samples; 11 = rock samples; 12 = towns (Nisi *et al.,* 2008).

The hydrographic catchment area of the Arno river (Tuscany, central Italy) covers a surface of 8228 km² with an average elevation of 353 m. The headwaters of the 242 km-long river are in the Northern Apennines at a height of 1650 m.a.s.l. and flows into the Ligurian Sea 10 km west of Pisa and 110 km from Florence inland. The annual rainfall pattern is typical of the Mediterranean area, with low regime in summer and two peaks of precipitation during the winter (in December and February). Mean annual rainfall values range from 600 mm, mainly in the lowlands, up to 3000 mm on the Apennine ridge. The out-cropping rocks are predominantly folded and faulted Mesozoic and Tertiary sedimentary units resulting from the formation of the Apennine chain. A subsequent extensional tectonic phase produced a NW-SE oriented horst-and-graben system, made up of Cretaceous to Paleogene allochtonous units belonging to the Ligurian, Sub-Ligurian and Tuscan Domains, which have been subject to overthrusting, mostly during the Early Miocene (Nisi *et al.,* 2008).

The drainage network of the Arno river follows NW-SE trending structures, creating six main sub-basins, from east to west: 1) Casentino (CA), 2) Chiana Valley (CH), 3) Sieve (SI), 4) Upper Valdarno (UV), 5) Middle Valdarno (MV) and 6) Lower Valdarno (LV) (Fig. 1). A large database composed of more than 500 cases was built up of samples collected from February 2002 to July 2005, thus covering seasonal changes for several years. The results have allowed researchers to study natural and anthropogenic contributions to riverwater chemistry (Nisi *et al.,* 2008).

Log-ratio approach and water geochemistry

In most geochemical surveys water samples are collected from a defined area and their composition is often monitored in time or space. Most geochemical processes affecting water involve chemical reactions that govern the cycles of the elements. The partition of the elements into different geological materials (for example water and rocks/sediments) is well described by the *Law of Mass Action*, first formulated in 1863 (Guldberg and Waage, 1899). In the general case of a reaction at equilibrium expressed for example by

$$CaCO_3(calcite) + H^+ \leftrightarrow Ca^{2+} + HCO_3^- , \tag{1}$$

the Law of Mass Action takes the form

$$\frac{(Ca^{2+})\,(HCO_3^-)}{(CaCO_3)\,(H^+)} = K \tag{2}$$

where the components in parentheses are in the appropriate units of concentration. It is easy to verify that Equation 2 has an equivalent logarithmic condition which encourages the idea that a sensible way to identify patterns in compositional data sets is to search for log-ratios. According to Aitchison (Aitchison, 1986; 1999), the log-ratio approach may be the correct way to describe the proportionality law underlying the partition of the elements in geological materials. How we can use this approach to investigate water chemistry in a simple way?

Water chemical composition is often analysed by considering binary diagrams with ratios characterized by the same denominator. These graphics are often called molar-ratio diagrams. Examples of applications can be found in Gaillardet *et al.* (1999) for the world's most important rivers. Elemental ratios are in general preferred rather than concentrations because intensive parameters allow a comparison between rivers draining areas of high runoff and rivers draining arid areas. Moreover, since most ratios fluctuate over several orders of magnitude a logarithmic scale is preferred in their use. This approach in the treatment of compositional data corresponds to the application of the *alr* transformation (Aitchison, 1986). The *alr* co-ordinates are given by two components of the composition, which are divided by the remaining component (generally Na^+) and logarithms taken. This approach is, however, only a first approximation to the management of constrained data with classical statistics. In fact the *alr* co-ordinates cannot be mapped onto orthogonal axes because they are actually at 60° (Egozcue and Pawlowsky-Glahn, 2005). Their correct use is possible only if a metric is defined in that space, thus modifying methods of calculating the inner products and distances (Buccianti and Magli, 2011).

A better approach is to transform the three variables of the molar ratios by using *ilr* co-ordinates. Calculation of these co-ordinates is more complex and there are different rules on how to generate them (Egozcue *et al.,* 2003). A simpler approach is based on the use of balances, a particular form of co-ordinates that represent the relative variation of two groups of parts. From the mathematical point of view the co-ordinates of the samples are defined within an orthogonal system of axes. Thus, any statistical analysis can be applied.

Example application: the Arno river basin

With the aim of establishing an alternative to molar-ratio diagrams, the first step is to choose three variables whose behaviour must be analysed jointly. For the purpose of our investigation we chose Ca^{2+}, HCO_3^- and Na^+ concentrations in mg/L. Subsequently, two *ilr* co-ordinates were determined as follows (Egozcue *et al.,* 2003):

$$ilr(1) = \frac{1}{\sqrt{2}} \ln \frac{Ca^{2+}}{HCO_3^-} , \tag{3}$$

$$ilr(2) = \frac{1}{\sqrt{6}} \ln \frac{Ca^{2+} \times HCO_3^-}{(Na^+)^2} . \tag{4}$$

All the data pertaining to the six sub-basins are set out in Figure 2. On the axes the Kernel density estimation curves allow us to verify simultaneously the shape of the frequency distribution for each co-ordinate. As can be seen, they cannot be described by using a Gaussian model (Anderson-Darling and Kolmogorov-Smirnov test for normality, $p < 0.01$), revealing the possible presence of mixture phenomena.

Sources of Na^+ are in general given by feldspar, rock-salt, zeolites and atmosphere. The element is

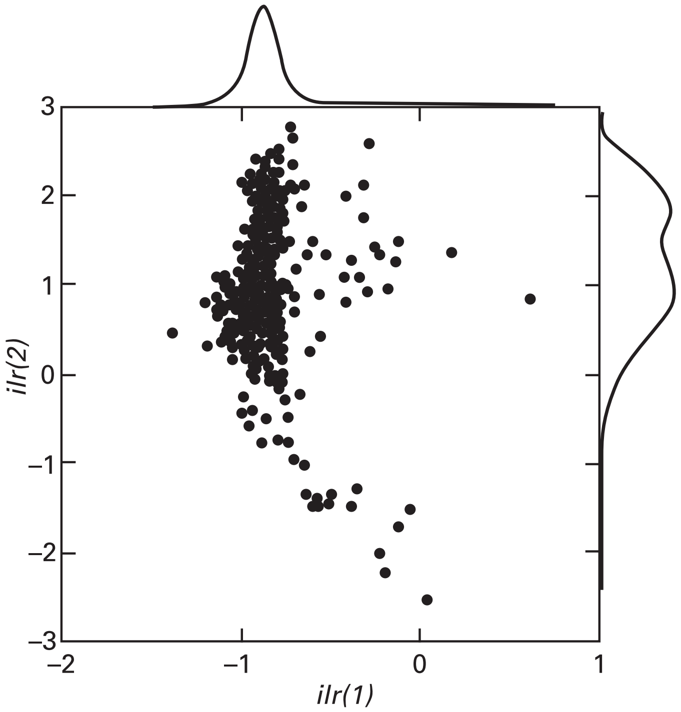

Figure 2. Isometric log-ratio co-ordinates obtained using Ca^{2+}, Na^+ and HCO_3^- for the dissolved phase of the Arno river water. Kernel density estimation curves are reported on the axes.

contributed by processes of dissolution and cation exchange, whilst concentration limits are attributable to the kinetics of silicate weathering. Sources of Ca are carbonate, gypsum, feldspar, pyroxene and anfibole. Dissolution is the main process contributing to the introduction of Ca^{2+}, whilst concentration limits are due to calcite solubility. Sources of HCO_3^- are carbonates and organic matter and the concentration is governed by weathering and CO_2 equilibrium processes.

Within this framework the *ilr(1)* co-ordinate describes the balance cations/anions characterizing carbonate equilibria (Meybeck, 1987). On the *x* axis the zero value corresponds to $Ca/HCO_3 = 1$. The *ilr(2)* co-ordinate describes the balance between the sources of Ca^{2+} and HCO_3^- (carbonate equilibria) in comparison to that of Na (silicate weathering, sea water contribution, pollution). On the *y* axis the zero value corresponds to $Ca/Na = Na/HCO_3$.

Most of the world's rivers have values of Ca/Na between 1 and 3, whilst the values for average crustal continental rocks are close to 0.6. Due to the higher solubility of Na compared to Ca, lower Ca/Na molar ratios may be expected in the dissolved load of rivers draining silicates. Chemical analyses of small rivers draining only carbonates, once corrected for atmospheric inputs, report Ca/Na ratios close to 50 and Na/HCO_3 close to 0.008 (Gaillardet *et al.,* 1999). In Figure 2 it is evident that towards the top of the *y* axis the contribution of sources contributing HCO_3^- and Ca^{2+} increases while towards the bottom sources contributing Na^+ appear to be more important. In the former case samples appear to be dominated by natural phenomena whilst in the latter samples can be affected by sea-water intrusion (Lower Valdarno) as well as pollution. According to Berner and Berner (1996), pollution is one of the greatest contributers of Na^+ ions (28% of the total), including domestic sewage, mining of halite, industrial brines and road salt. Sodium salts, such as Na_2CO_3, Na_2SO_4 and Na-borate are mined and used industrially in water softners as sodium zeolite and Na_2CO_3, replacing Ca^{2+} and Mg^{2+} with Na^+ in industrial and domestic water.

Samples from Casentino (CA) are characterized by a median value of Ca/Na about 130 times that of Na/HCO_3. This value decreases to 33 for the Sieve basin, 15 for the Upper Valdarno, 9 for the Chiana, 8 for the Lower Valdarno and 6 for Middle Valdarno. Samples collected near the mouth of the river are characterized by a Ca/Na ratio about 0.002 times that of Na/HCO_3. It is important to note that the most important changes in water chemistry are revealed when comparing the Casentino sub-basin, where the headwater of the river is located, with the other sub-basins, where the effect of anthropogenic pressure is higher; the city of Florence, in fact, is located in the Middle Valdarno. Due to the high variability of the data from the different sub-basins, the results of the non-parametric statistical test used to compare medians are not significant. Within this context, data from Casentino (Fig. 3) are characterized by lower variability, thus representing the more pristine and homogeneous condition of the area. Data from the Lower Valdarno, on the other hand, are affected by high variability and the Kernel frequency distribution of the *ilr* co-ordinates shifts from normal (Casentino) to multimodal (Kolmogorv-Smirnov test and Anderson-Darling test for normality, $p < 0.01$). Here the results indicate the presence of more sources contributing to the chemical elements, consequently revealing the action of mixture phenomena.

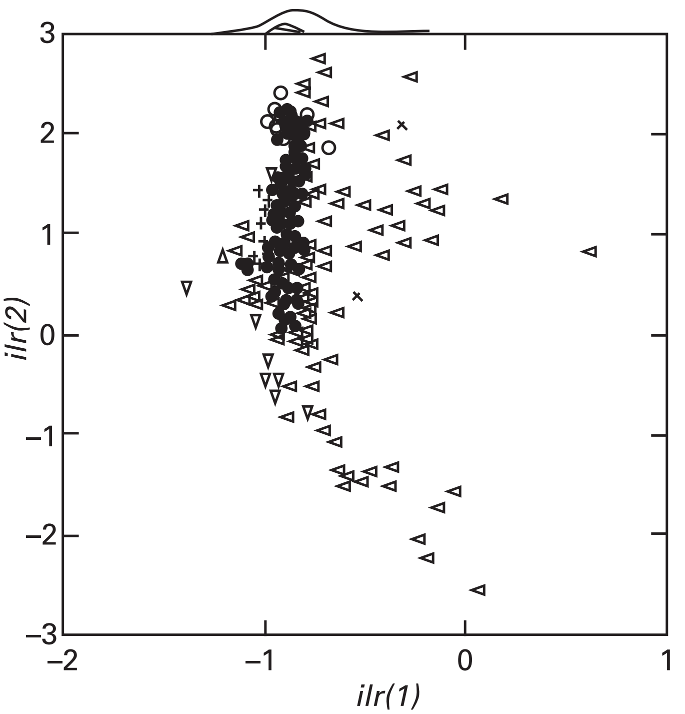

Figure 3. Isometric log-ratio co-ordinates obtained using Ca^{2+}, Na^+ and HCO_3^- for the dissolved phase of the Arno river water. Data are divided into sub-basins by different symbols (o = Casentino, × = Chiana, + = Upper Valdarno, Δ = Sieve, ∇ = Middle Valdarno, ◁ = Lower Valdarno). Kernel density estimation curves for each sub-basin are reported on the axes.

Conclusions

Compositional data are the heart of quantitative geochemistry and the large majority of publications making use of such data consider an unrestricted sample space to investigate their variability. The use of log-ratios has opened new paths in the investigation of natural phenomena in geochemistry for two main reasons: firstly, they describe the proportionality laws governing the partition of chemical elements in natural matrices, and secondly, standard statistical approaches are suitable for their description, making it possible to test models and assess the significance of the results.

The main aim of the paper is to demonstrate that it is also possible to obtain reliable results starting from simple binary diagrams and basic statistics. A valid alternative to the classical molar-ratio diagrams by using *ilr* transformation is proposed. We applied it to the three variables usually combined in common-denominator ratios. Our example application concerned the water chemistry of the Arno river basin (Tuscany, central Italy). The way to build up the *ilr* co-ordinates was guided by geochemical principles in order to facilitate interpretation. From this point of view, the balance approach, managing the relative variation of two groups of parts, was used to good end. Quantitative results indicate that there are important changes in the water geochemistry in the Arno river basin, from Casentino, the more pristine area, downriver towards the other sub-basins, where Na^+ derives from different sources, the mixing of which is a complex process. The approach can be applied to the investigation of other *ilr* co-ordinates in water chemistry; for example the use of Ca^{2+}, Mg^{2+} and HCO_3^- or Ca^{2+}, Mg^{2+} and SO_4^{2-} may be useful in the presence of carbonate or sulphate rocks. The application in the exploration of other geological matrices is also recommended.

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