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Temporal variation in dripwater chemistry in the Cueva del Pindal (Asturias, NW of Spain)

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ABSTRACT

The Pindal Cave (Asturias, NW of Spain) is hosted by limestones of the Barcaliente Formation 24 m above sea level and in close proximity (50 m) to the coastal sea cliffs. For eleven months, dripwater flow was collected in 153 discrete samples each representing integrated flow over 48 hours. Dripwater flow rate is compared with precipitation and the major element chemistry of dripwaters. Dripwater flow rates vary dramatically from sample to sample, typically lagging precipitation peaks by 1-3 days. Overall dripwater flow is highest in the wet winter season and lowest in the dry summer season. Concentrations of Ca vary dramatically from sample to sample and are highly positively correlated with the daily-weekly variations in dripwater flow. Mean Ca concentrations are comparable during summer and winter months, despite lower summer drip flow, probably because higher soil CO_2 during the summer growing season increases dissolution of host rock during infiltration, compensating for longer Ca residence times. Sr/Ca ratios and Mg/Ca ratios correlate inversely with dripwater flow rates, and together with Ca variations imply variable precipitation of calcite during aquifer throughflow. The concentration of Na in dripwaters reflects prevailing wind direction and transport of sea salt aerosols into the cave drainage basin and correlates with the NAO index, where as concentrations of K are influenced by biological uptake and episodic anthropogenic inputs.

Key words: Asturias, cantabrian coast, cave, dripwaters, hydrochemistry

Variaciones temporales en la hidroquímica de goteos en la Cueva del Pindal (Asturias, NO de España)

RESUMEN

La Cueva del Pindal (Asturias, NO de España) está enclavada en calizas de la Formación Barcaliente, a 24 m de altitud s.n.m. y muy próxima (50 m) a un acantilado marino. Durante once meses se recogieron 153 muestras discretas de aguas de goteo correspondientes a intervalos de 48 horas. La proporción de agua recogida se compara con los valores de precipitación y la de los elementos mayores de las aguas de goteo. Se aprecia que el flujo de agua varía drásticamente de una muestra a otra, con retrasos de entre 1 y 3 días con respecto a los picos de precipitación. El flujo total de agua de goteo en invierno, más húmedo, es superior al de verano, más seco. Las concentraciones de Ca varían drásticamente de unas a otras y presentan una alta correlación positiva con las variaciones diarias y semanales del flujo de agua de goteo. Las concentraciones medias de Ca son comparables durante los meses de verano e invierno, a pesar del descenso de flujo de goteo en verano. Esto sugiere que los mayores contenidos de CO_2 durante el verano aumentan la disolución de la caliza durante el proceso de infiltración, compensando así tiempos de residencia del Ca más largos. Las relaciones Sr/Ca y Mg/Ca muestran una correlación inversa con los valores de caudal de goteo, y junto con las variaciones de Ca sugieren una precipitación variable de calcita durante el tránsito de agua subterránea en el acuífero. La concentración de Na en las aguas de goteo refleja la influencia de la dirección de los vientos predominantes y el transporte de aerosoles salinos procedentes del mar hacia el interior de la cueva, y se correlaciona con el

índice NAO, mientras que las concentraciones de K están influidas por retención debido a procesos biológicos y por aportes antrópicos de carácter episódico.

Palabras clave: *Asturias, costa cantábrica, cueva, goteo, hidroquímica*

1. Introduction

The relation of dripwater chemistry with dripwater hydrology can provide useful constraints on sources of contaminants and flow pathways. In addition, dripwater chemistry may correlate with climatological variations that may be recorded in cave stalagmites and used for paleo-climatological studies (eg. Fairchild et al 2000; Hellstrom *et al.* 2000).

Here we describe a long term (11 month) monitoring of dripwater flow volume combined with collection of discrete 48 hour samples for analysis of major and minor element chemistry in cave dripwaters. This sample set enables us to examine the response of dripwater flow and chemistry to both episodic precipitation as well as longer seasonal oscillations in climate.

2. Setting and Methods

Pindal cave is located to the East of Asturias (NW of Spain), 4° 30' W, 43° 23' N. The cave is 590 m long (314 m open to tourist use, where this study has been developed), and presents an E-W and 110° N (WNW-ESE) trending, showing important and well preserved Paleolithic paintings. The maximum altitude is located to the W (30 m above the sea, +6 m above the entrance) and the minimum altitude is located to the E (6 m above the sea level, -18 m under the entrance). The width of the cave ranges from 2 to 50 m, while the vertical distance from ceiling to bottom ranges from 1,5 m to 11 m (Obeso *et al.*, 1996). From a geological point of view, it is developed in Carboniferous bedrock, Barcaliente Limestone, with no documented dolomitization (Martínez García *et al.*, 1980). Previous geomorphological research in the area (Jiménez-Sánchez *et al.*, 2002 and 2004) showed that the landscape results from fluvial, mass wasting, karstic and marine processes with the outstanding presence of two erosion marine surfaces ("rasas"): Pimiango (125-170 m) and Pindal (50-64 m). The origin of the cave, developed in a karstic massif reaching its highest surface in Pindal Rasa, is mainly controlled by two sets of subvertical fractures trending E-W (F1), the bedding planes, dipping 70° to the North, and 3 joint systems.

On december 26, 2003 we deployed a battery-powered dripwater collector which collects all dripwater during each 48 hour period in discrete 1.5 L bottles. The array contains 24 bottles and is deployed for 48 day intervals. Upon collections, the volume of water is measured and two aliquots are retained for geochemical analysis. Because dripwaters are supersaturated with carbonate in atmospheric environments, calcite precipitates from stored samples, so samples are acidified to contain 0,005 % HNO_3 (tracepure) before analysis. Ca and Mg measurements for all samples were made using atomic absorption spectrometry using addition of $LaCl_3$ as a spectral release agent. Na and K analyses (to date completed for the period from Dec 26, 2003 through march 31, 3004) were made using atomic emission spectrometry. For

20% of the samples we also measured Sr using graphite furnace atomic absorption spectrometry. All analyses were made on a Perkin Elmer Analyst 300 at Williams College.

Dripwater flow and chemistry are compared with daily precipitation and temperature from the INM meteorological station at Llanes, Asturias, located on the coast 20 km to the west of Pindal cave. To compare drip data with the broader meteorological context, we use the regional daily North Atlantic Oscillation (NAO) derived from NCEP reanalysis data, retrieved from the archive of Dr. James Hurrell.

3. Results and Discussion

3.1 Drip flow rate

There is general seasonal correspondence between rainy winter months with high driprates and dry summer months with low driprate. However, drip is not a constant proportion of precipitation. A larger proportion of precipitation is converted to dripflow in the wetter months than in the drier summer months (correlation between infiltration efficiency and temperature is 0,75 and with total precipitation 0,63), probably due to greater evapotranspiration in summer months. Moderate precipitation events in the summer produce small increases in dripflow, whereas moderate precipitation events in the winter produce large increases in dripflow. Water storage in intermediate karst reservoirs, which are depleted in summer and early fall and renewed in mid fall (mid-october in this record), may also contribute. The lag between increased precipitation and increased dripflow is variable, between 1-3 days.

3.2 Sodium concentrations

The mean dripwater Na concentration is 38 ppm (range 35-42 ppm) and is comparable to that observed in marine rain from coastal regions (eg. Berner and Berner, 1996). We infer that Na is derived from sea salt delivered in rain and possibly also through dry aerosol deposition. Variations in Na concentrations in dripwater occur on timescale of weeks and are not correlated with dripwater flow rate (table 1). Rather Na variations are likely correlated to shifts in wind strength and intensity, with stronger northerly winds increasing Na concentrations by directing sea spray over the catchment area.

The atmospheric circulation in the Iberian peninsula is strongly affected by the pressure gradient between the Icelandic Low pressure system and the Azores High pressure system. Stronger than average pressure gradients are defined as North Atlantic Oscillation (NAO) positive phase, weaker than average pressure gradients as NAO negative phaseSwings from one phase to another produce large changes in the wind behavior over the Atlantic and the heat and moisture transport between the Atlantic and the neighboring continents.

We compared variations in Na and NAO indexes for the time span of our studies. There is a modest correlation between Na concentrations and the NCEP daily NAO index which is consistent with the NAO influence on winter storm tracks and wind directions (Fig. 3).

3.3 Potassium concentrations

The mean K concentration in dripwaters is 0,320 ppm (range 0,22 to 0,8 ppm). If we assume that all Na is derived from sea salt then based on the K/Na ratio in seawater (0,036) we would expect K concentrations of 1,36 ppm, four times higher than observed cave dripwaters. We infer that a significant portion of sea salt K may have been taken up in biomass (and subsequently removed from the site by haying or livestock removal). The K variations are not correlated with Na variations or dripflow and most may reflect changes in the efficiency of biological uptake. However, a dramatic increase in K concentrations for a week in March likely represents an anthropogenic addition to the drainage area, either from fertilization or biomass burning which are important ways to reintroduce K in the system (Berner and Berner, 1996).

3.4 Calcium concentrations

The mean Ca concentration is 57 ppm but Ca varies widely (43-93 ppm) (Figs. 4 and 5). There are significant rapid (daily scale) variations in Ca which in the wet winter season are strongly

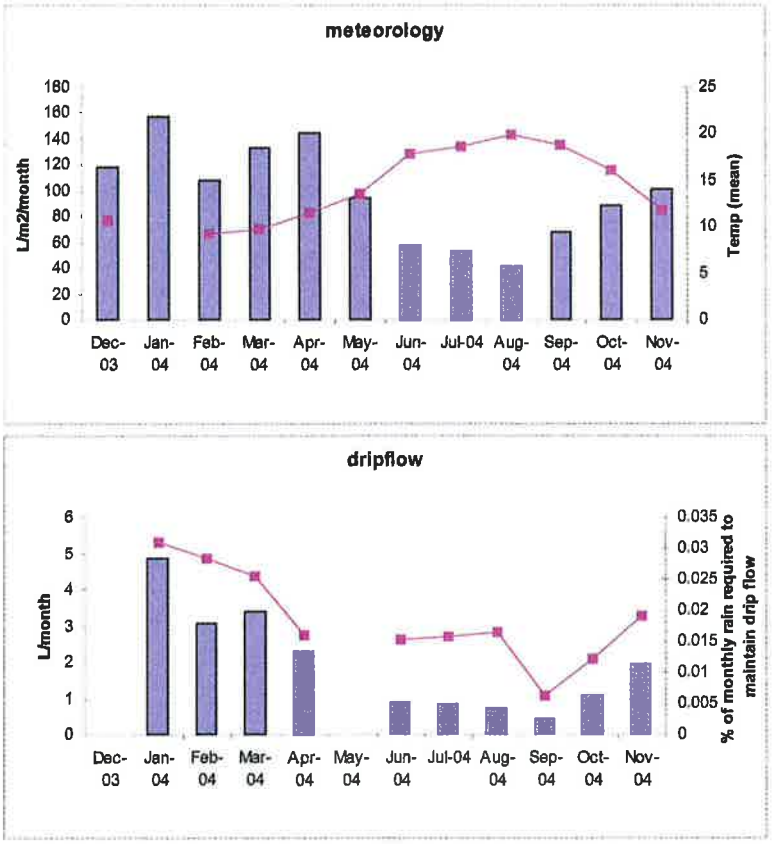

Figure 1. Monthly average precipitation and temperature (INM station at Llanes) compared with dripflow. We calculate the proportion of precipitation falling in L/m² area which would be required to account for the monthly total dripflow (this is not an attempt to constrain the actual catchment area contributing flow to this drippoint but to index the hydrological mass balance)

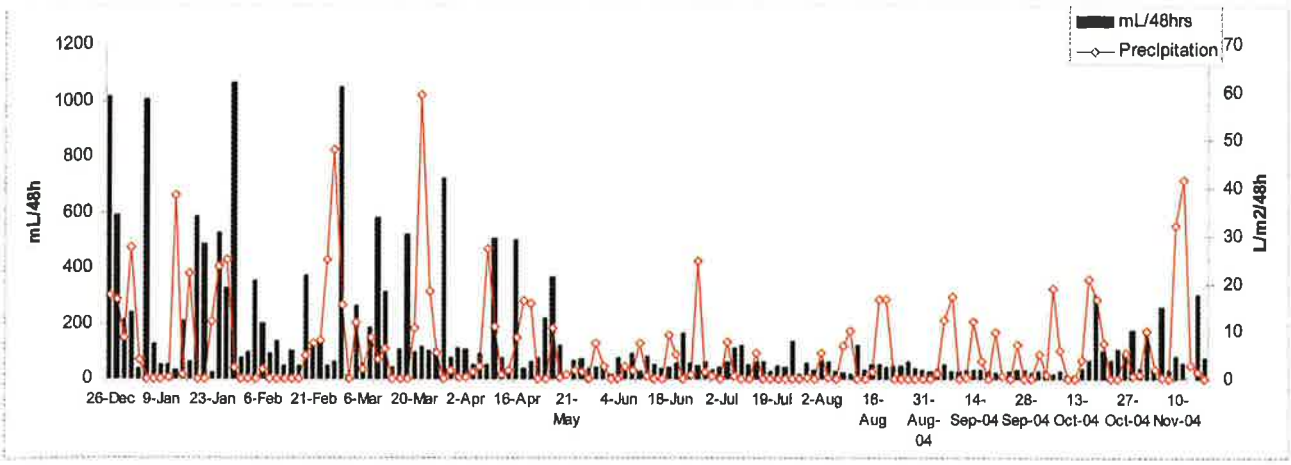

Figure 2. Dripwater flow and precipitation (48 hour cumulative) at Llanes

	Ca	Mg	K	Na	Mg/Ca	Sr	Sr/Ca
Dec-April (wet)	0,85	0,28	-0,31	0,06	-0,60	0,55	-0,79
May-Oct (dry)	0,43	0,45	NA	NA	-0,08	0,12	-0,54
Full year	0,57	0,17	NA	NA	-0,46	-0,07	-0,75

Table 1. Correlations of elemental concentrations and ratios with dripwater flow rate

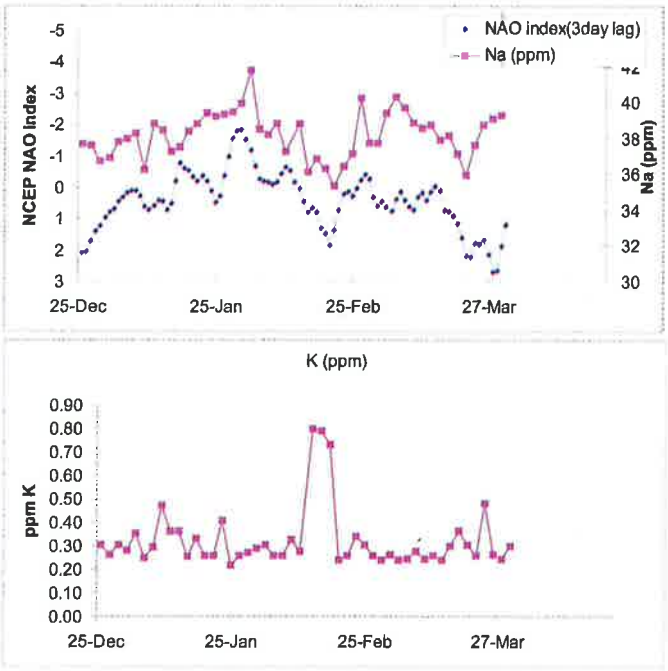

Figure 3. Variation of sodium and potassium concentrations over time, compared with NCEP NAO index. The NAO index is plotted with a 3 day lag to account for transit time of dripwater

correlated with driprate (eg. december 2003- march 2004, correlation is 0,85; table 1). Dry season Ca concentrations are modestly correlated with driprate (0,43). On the seasonal scale, despite a pronounced drop in dripflow in summer months the average Ca concentration is about the same over the course of the year. The rapid daily oscillations in Ca concentration likely reflect the extent of prior $CaCO_3$ precipitation in upper cavities during aquifer throughflow; during high flow periods, these cavities are probably saturated with water and hence no degassing or $CaCO_3$ precipitation occurs, whereas during lower flow periods degassing in these cavities leads to precipitation of $CaCO_3$. Superimposed on this high frequency pattern, seasonal changes in temperature and vegetation likely increase soil CO_2 and dissolution of host rock in the summer, maintaining high dripwater Ca in summer months despite higher expected rates of $CaCO_3$ precipitation during aquifer throughflow. Further analyses of $CaCO_3$ supersaturation on the samples will evaluate this hypothesis.

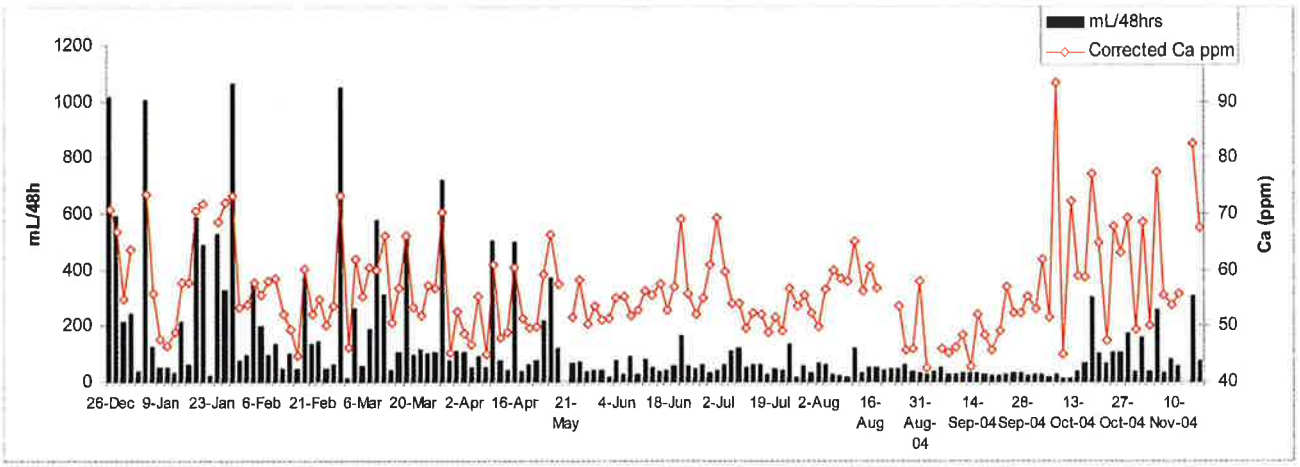

Figure 4. Temporal variation in dripwater Ca compared with dripwater flow changes

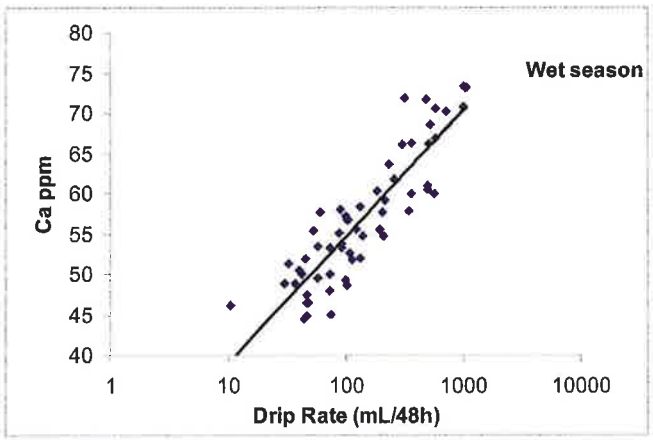

Figure 5. Winter wet season relationship between dripflow and Ca concentrations

3.5 Magnesium concentrations

Magnesium concentrations in cave dripwaters average 5,6 ppm (range 3,8 to 7,4). Based on the Mg/Na ratio of seawater (0,11) and Na values of dripwater, a high proportion of Mg could originate from sea salt (75%) rather than the limestone host rock. However, the Mg concentration in dripwaters is much more variable than that of Na, Mg concentrations do not covary with Na, and the calculated nonseasalt Mg contribution in dripwater correlates highly with total Mg (0,96). This suggests that dripwater Mg concentrations are controlled primarily by their removal from dripwaters during aquifer throughflow rather than by variations in their supply to dripwaters through sea salts. Mg shows limited covariation with driprate in winter months (0,24) and a stronger correlation with driprate in summer months (0,45). Mg/Ca ratios are inversely correlated with driprate (-0,46 over the whole year), especially in the wet months (-0,60), largely driven by the Ca variations. The shift towards low Mg/Ca ratios at high driprates is consistent with the hypothesis of $CaCO_3$ precipitation in cavities en route to the cave. Because Mg partitioning in calcite has a Kd <<1, then precipitation of $CaCO_3$ increases the Mg/Ca ratio in the residual dripwater. At high flow, there is limited $CaCO_3$ precipitation in upper cavities which maintains low Mg/Ca ratios. Further modeling will evaluate this mechanism.

3.6 Strontium

Among the limited Sr analyses completed, the mean concentration is 272 ppb (range 253-307 ppb). Based on seawater Sr/Na ratios and dripwater Na concentrations, roughly 10% of the Sr content can be attributed to sea salt Sr and the remainer is likely from host rock dissolution. As was the case for Mg, Sr removal during aquifer throughflow appears to be the most important control on the Sr concentration in dripwaters. In the winter (wet) months, Sr shows a correlation factor of 0,55 with driprate, but the correlation is negligible in dry months (Table 1). The Sr/Ca ratio is highly inversely correlated with driprate throughout the year (-0,79 in winter months, -0,75 overall). As was the case for Mg/Ca, the shift towards low Sr/Ca ratios at high driprates is consistent with the hypothesis of $CaCO_3$ precipitation in cavities during aquifer throughflow. Because Sr partitioning in calcite has a Kd<<1, then precipitation of $CaCO_3$ increases the Sr/Ca ratio in the residual dripwater so at high flow, there is limited $CaCO_3$ precipitation in upper cavities which maintains low Sr/Ca ratios.

4. Conclusions

Concentrations of Ca vary dramatically from sample to sample and are highly positively correlated with the daily-weekly variations in dripwater flow. Mean Ca concentrations are comparable during summer and winter months, despite lower summer drip flow, probably because higher soil CO_2 during the summer growing season increases dissolution of host rock during infiltration, compensating for longer Ca residence times.

The data indicate that significant variations in the Mg/Ca and Sr/Ca ratios of dripwater arise even in a purely limestone host rock. Previous studies of Mg/Ca and Sr/Ca variations focused

on mixed dolostone-limestone host rock in which high (low) Mg/Ca ratios were inferred to result from longer (shorter) water residence times due to the slower dissolution kinetics of dolostone relative to limestone. However, in this coastal karst system with low Mg content in host rocks and 75% of Mg from sea salt aerosols, the inverse correlation between Sr/Ca ratios or Mg/Ca ratios dripwater flow rates most likely arises due to variable precipitation of calcite during aquifer throughflow.

The concentration of Na in dripwaters reflects prevailing wind direction and transport of sea salt aerosols into the cave drainage basin and correlates with the NAO index, whereas concentrations of K are influenced by biological uptake and episodic anthropogenic inputs.

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