

Hydrochemistry of northwest Spain ponds and its relationships to groundwaters

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ABSTRACT

We built a classification system for lentic ecosystems and groundwaters in South-East León based on degree of mineralization and composition of major ions. In the ponds with the softest water (< 5 mEq/L), chlorides and bicarbonates were the main mineralizing anions. In contrast, in more highly mineralized ponds (> 5 mEq/L), all major ions were at comparable proportions. In these more mineralized shallow lakes, more sulphates could be found compared to less mineralized waters in the region. Independently of the level of mineralization, calcium was the predominant cation, although shallow lakes with lower mineral content favoured sodium over magnesium. The intense summer evaporation and the filling in autumn of ponds which had completely dried out and remained dry during the summer triggered changes not only in the mineral content, but also in the ionic composition of the water, with an increase in the concentrations of all ions in autumn. Overall mineralization and alkalization were the two chief factors shaping the chemical variability of groundwater in our region. The length of flows discharging into groundwater-influenced areas shaped the general features of the wetlands studied, so that the degree of mineralization of the water in any given lake was determined in large measure by the geographical position. Thus, the greater length of flows in southerly areas of the study zone led to an increase in the more highly mineralized shallow lakes of the salinity of groundwater and of surfacing groundwater. Nonetheless, a substantial number of the ponds investigated are apparently linked to the aquifers under the "raña" formations. The chemical make-up of the water in these bodies is to some extent related to precipitation in the form of rain or in other forms and is apparently little influenced by groundwater. Hence the ponds are made up of slightly mineralized sheets of water, and can be tracked to discharges from brief surfacing groundwater flows. A link to deeper regional flows can be identified by the presence of comparatively more mineralized water bodies. Overall, outflows do not correspond to the chemical pattern of groundwaters, suggesting a more complex explanation for the hydrology of the study area.

Keywords: water mineralization, ponds, groundwater, relative ion composition.

RESUMEN

Se realizó una tipificación de los sistemas leníticos y del agua subterránea en el sureste de la provincia de León basada en su grado de mineralización y composición iónica mayoritaria. En las lagunas más dulces (<5 mEq/L) cloruro y bicarbonato fueron los aniones con mayor peso en la mineralización. Por el contrario, en las lagunas más mineralizadas (>5 mEq/L) las proporciones de los aniones mayoritarios fueron muy semejantes, con un incremento de sulfato respecto a las aguas menos mineralizadas. Con independencia del nivel de mineralización, el calcio fue el catión predominante, aunque la disminución del contenido mineral favoreció al sodio sobre el magnesio. La intensa evaporación producida durante el verano y el llenado en otoño de las lagunas que permanecieron secas en el periodo anterior provocaron cambios no sólo en el contenido mineral, sino también en la composición iónica del agua, con aumento de las concentraciones de todos los iones en otoño. La mineralización global y la alcalinización fueron los dos procesos más importantes que marcaron la variabilidad hidroquímica del agua subterránea. La longitud del flujo de descarga en las áreas bajo la influencia del agua subterránea ha condicionado las características de los humedales estudiados, de modo que el nivel de mineralización del agua ha estado determinado en buena medida por su posición geográfica. Es así que el aumento de la longitud de flujo hacia el sur del área de estudio ha determinado un incremento de la concentración salina del agua subterránea y de su manifestación en superficie, en formaciones palustres más mineralizadas. No obstante, una parte importante de las lagunas estudiadas aparecen ligadas a los acuíferos de rañas y el carácter hidroquímico de sus aguas está relacionado, en parte, con el agua meteórica y aparece poco influenciado por el agua subterránea. Constituyen, por tanto, láminas de agua poco mineralizada, identificándose como descargas de flujos subterráneos cortos. La conexión con flujos regionales más profundos se reconocen como lagunas que comparativamente son altamente mineralizadas. Sin embargo, estas descargas no tienen correspondencia con el quimismo de las aguas subterráneas, lo que otorga una cierta complejidad al comportamiento hidrológico observado en el área de estudio.

Palabras clave: mineralización del agua, lagunas, agua subterránea, composición iónica relativa.

INTRODUCTION

It is accepted that the chemical composition of surface waters is controlled by three main factors, i.e. the underlying geology, the atmospheric precipitation and the balance between evaporation and the precipitation of salts. Gibbs (1970) proposed a descriptive model including these three factors, which has later been challenged (Kilham, 1990; Eilers *et al.*, 1992). Opponents to Gibbs' model observe substantial deviations from the distribution of surface waters predicted using his model (Gibbs 1970). Eilers *et al.* (1992), for instance, point out that factors such as local geological variations, soil type and water flow patterns can lead to considerable chemical variability in small shallow lakes. Especially in arid and semi-arid regions, groundwater together with rainfall water and surface run-off may play a leading part in the formation of zones that can become wetlands (Rey Benayas, 1990).

The physical and chemical composition of the water in shallow lakes is considerably variable over both time and space. With regard to space, there are crucial interactions between topography, lithology (or rock formations) and hydro-geological processes. The wetlands that depend primarily on groundwater are discharge areas related to systems of flows, whether these are local, at intermediate spatial scales or regional (Toth, 1971, 1972, 1999; Custodio & Llamas, 1976). The differing types of flow will determine shapes, salinities and habitats offered by these wetlands. The groundwater flows are responsible for transporting and dispersing soluble material in discharge areas (González Bernáldez & Rey Benayas, 1992). The flow length and the groundwater residence time in the aquifer will give rise to a geochemical gradient, observed as directional variability among the various discharge (or outflow) zones along the length of one single aquifer (González Bernáldez *et al.*, 1989; Rey Benayas *et al.*, 1990a, 1990b; Rey Benayas, 1991; González Bernáldez & Rey Benayas, 1992).

More generally, the chemical composition of water in wetlands is the outcome of lithological, climatic, biological or human factors and of geochemical processes interacting in the aquifers

and across the catchment (González Bernáldez *et al.*, 1989; Rey Benayas, 1991; Robledano *et al.*, 1991; González Bernáldez & Rey Benayas, 1992; González Bernáldez *et al.*, 1993; Llamas, 1993; Suso & Llamas, 1993). Topography and lithology act directly upon hydro-geological processes, influencing the genesis and hydro-chemical functioning of the wetland. Both these factors may create alternating inflow and outflow areas, thus leading to the confluence of groundwater flows of different mineralization (Rey Benayas, 1991; González Bernáldez & Rey Benayas, 1992).

Seasonal fluctuations in the total volume of water in the system will have an impact on water chemical composition. Hence, water chemistry may vary solely as a function of volume over the course of the year and even from year to year, as weather does (Vangenechten *et al.*, 1981a; Montes *et al.*, 1982a, 1982b; Meintjes *et al.*, 1994; Quesada *et al.*, 1995).

Studies on the hydrochemistry of wetland ecosystems are relatively scarce and often descriptive accounts which are part of wider-ranging works covering biological aspects of these ecosystems (Borrego & García-Gil, 1994; Cirujano, 1995; Da Fonseca *et al.*, 1999; Álvarez-Cobelas *et al.*, 2005; Dodson *et al.*, 2005; Peralta & Fuentes, 2005; Serrano *et al.*, 2004). One useful contribution to the analysis of the processes governing chemical changes in shallow lakes comes from the work carried out by Vangenechten *et al.* (1981a, 1981b) on pools in Belgium.

Several studies have been conducted across the Iberian Peninsula on the hydrogeologic processes in aquifers and subsurface groundwaters and the influence of those processes on ionic composition and biota of aquatic ecosystems (Custodio & Llamas, 1983; Rey Benayas *et al.*, 1990a, 1990b; Rey Benayas, 1991; González Bernáldez *et al.*, 1993; Rey Benayas & Scheiner, 1993). A broader snapshot view of the chemistry (mineralization and trophic state) of some Spanish ponds, particularly in the region of Castilla y León can be found in Alonso & Comelles (1987). More recently, Alonso (1998) proposed a typology for classifying ponds in Spain, which uses both environmental parameters and crustacean assemblages.

The main aims of the present study were:

- To provide a complete classification and typology of the systems of ponds and groundwaters in the South-East of León, based on their mineralization and the identity of their main ions.
- To identify spatial patterns of the chemistry of groundwaters, relating these to the spatial patterns of surfacing groundwater chemistry in the form of ponds.

STUDY AREA

The ponds and wells selected for the study are located within the Douro Basin, in the South-Western quarter of the Province of León (Spain). They are scattered over an area of some 2,400 square kilometres delimited by the River Orbigo to the West and the River Cea to the East. In this region, the ponds and wells are distributed over two sectors separated by the River Esla. Ten of the ponds and twenty-four of the wells selected are in the Western sector, or Leonese “Páramo” district. Seventeen ponds and thirty wells are sited in the Eastern sector (Fig. 1), in the “Payuelo” district.

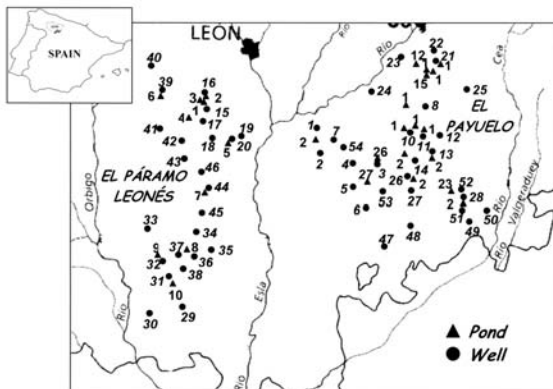


Figure 1. Geographical location of the ponds and wells studied in the Páramo (left) and Payuelo (right) districts in León (Spain). Numbers identifying ponds are the same as those used in Table 1. *Localización geográfica de las lagunas y pozos estudiados en las Comarca del Páramo (izquierda) y del Payuelo (derecha) en la provincia de León (España). Los números de las lagunas se corresponden con los indicados en la Tabla 1.*

The rocky formations in the study area are primarily Miocene clays, which in the river valleys are overlain by Quaternary terraces. The areas between the main rivers are covered by “rañas”, making up the highest grounds of the Douro Basin. These “rañas” are extensive formations of relatively thin (about 1.5 to 3 metres) Plio-Quaternary deposits made up of boulders and quartzite gravel bound up in a sandy clay matrix, lying directly on top of clayey Tertiary sediments. This lithological pattern has led to a variety of aquifer systems. Also, a deeper hydrological unit, the “Esla-Valderaduey” can be distinguished, defined on Tertiary detritic deposits and which functions as a heterogeneous and anisotropic aquifer, being partly or totally confined. A more superficial unit can also be made out, the “Raña Aquifers”, which are relatively independent “hanging” aquifers which are easily replenished. The study area has a scattered abundance of ponds, whose origins and properties are linked to a greater or lesser degree to hydrogeological factors. Table 1 shows morphometric and geographical characteristics of the study ponds, together with details on water permanence.

METHODS

Water samples were collected from ponds once every season between 1994 and 1995. Water temperature, pH, dissolved oxygen, Redox, turbidity and conductivity were measured *in situ*. Concentrations of nitrates, ammonia and chlorides were measured using selective electrodes; while alkalinity, total suspended solids (TSS), phosphates, total phosphorus, nitrites and sulphates concentrations were measured according to protocols in Standard Methods (APHA, 1989). Calcium, magnesium, sodium, potassium, total and dissolved iron and total and dissolved manganese were determined using ICP (Inductive Coupled Plasma Atomic Emission Spectroscopy).

The sampling of groundwater from the 54 wells was performed in the summer of 1996. Sampling was by pumping from wells that had a pump, while from the rest of wells, a weighted pail was lowered into the water for sample

Table 1. Morphometric and geographical characteristics and water permanence in the ponds studied in South-East León. *Características morfológicas, geográficas y de permanencia del agua de las lagunas estudiadas en el sureste de León.*

Ponds	Altitude (m)	Area (Ha)	Maximun Depth (m)	Persistence (*)
1-Chozas de Arriba (a)	890	2.7	110	3
2-Chozas de Arriba (b)	890	5.4	250	5
3-Chozas de Arriba (c)	890	5.7	150	4
4-Monte	870	0.6	100	2
5-Rey	860	2.5	200	4
6-Villadangos	940	9.2	150	5
7-La Mayor (Páramo)	840	0.6	100	3
8-Sta Cristina del Páramo	800	0.05	200	4
9-Melgan	789	2.2	150	4
10-Zotes del Páramo	782	1.3	200	5
11-Villaverde la Chiquita	940	1.8	130	4
12-Valdepolo	925	1.2	100	4
13-Laguneta 1	940	0.4	70	3
14-Laguneta 2	940	0.2	60	3
15-Sentiz	940	4.7	180	5
16-Mayor	900	3.1	80	2
17-Del Redos	900	1.0	180	4
18-Espino	900	1.7	100	3
19-Estorrubio	900	0.8	150	2
20-Campana	880	0.7	120	2
21-Surco	890	0.2	100	3
22-Burgo Ranero	878	1.4	100	4
23-Bercianos del Real Camino	855	0.6	150	5
24-Grande	830	16.2	200	4
25-Balastrea	800	2.7	150	3
26-Villamarco	840	1.7	150	3
27-Seca	810	3.0	200	3

(*)1.- Ephemeral (1-2 months)

2.- Very temporary (2-6 months)

3.- Temporary (6-9 months)

4.- Semipermanent (9-12 months)

5.- Permanent

collection. Temperature, pH, conductivity, total alkalinity, calcium, magnesium, sodium, potassium, chloride, sulphates, nitrates and phosphates were analysed. The same analytic techniques were used for groundwater as for surface water.

In order to establish the relationships of latitude with physical and chemical characteristics of surface and ground waters, a regression analysis was performed. Variables were first checked for normality through the Kolmogorov-Smirnoff test. Those variables that did not fit the Kolmogorov-Smirnoff distribution were transformed by use of the expression $\log(x+0.001)$. A Principal Component Analysis (PCA) was performed for the set of physical and chemical

variables measured in the water from the ponds and a similar analysis was also done for groundwater. All variables were logarithmically transformed $\log(x+0.01)$, with the exception of pH. All the analyses were performed using the Statistica version 6.0 statistical package.

With an aim to mapping the spatial variation trends in the study zone for the main hydro-chemical variables, a trend surface analysis was undertaken. This kind of analysis allows to map on a plane spatial variation trends in quantitative variables (Davis, 1973). The "Kriging interpolation" method used is suited to data with heterogeneous distributions. To carry out this analysis the program Surfer version 7.0 was used.

Table 2. Means and range of variation of conductivity and total anion content in the ponds studied. *Media y rango de variación de la conductividad y del contenido de aniones totales en las lagunas estudiadas.*

Ponds	Total Anions (mEq/L)		Conductivity ($\mu\text{S}/\text{cm}$)	
	Average	Rank	Average	Rank
16 Mayor	1.60	1.29-1.91	145	102-189
4 Chozas de Arriba (c)	1.66	1.14-2.44	172	144-200
2 Chozas de Arriba (a)	1.87	1.01-4.18	217	120-458
1 Villadangos	1.90	1.19-3.13	184	112-292
3 Chozas de Arriba (b)	1.98	1.12-3.33	193	131-286
11 Villaverde la Chiquita	1.98	1.38-2.67	195	149-272
21 Surco	2.26	1.52-2.69	215	143-282
6 Rey	2.97	2.51-3.46	292	250-338
14 Laguneta 2	3.14	1.60-6.43	302	156-572
5 Monte	3.69	2.35-6.24	389	250-650
13 Laguneta 1	3.82	2.41-7.27	373	218-592
18 Espino	3.89	2.80-4.63	335	260-378
15 Sentiz	3.99	2.71-5.39	401	304-546
12 Valdepolo	4.21	2.94-6.52	404	250-574
9 Melgan	4.60	3.11-5.28	433	280-490
20 Campana	4.62	2.36-8.41	427	102-818
19 Estorrubio	5.47	3.53-8.87	507	348-798
22 Burgo Ranero	5.56	5.05-6.75	532	464-606
23 Bercianos del Real Camino	5.65	3.94-7.58	521	322-768
17 Del Redos	5.93	2.92-9.03	562	287-888
10 Zotes del Páramo	6.01	4.13-9.40	495	377-694
8 Sta Cristina del Páramo	7.75	3.17-17.85	670	312-1478
25 Balastrea	8.79	6.05-14.94	805	638-1302
24 Grande	12.89	5.69-27.26	934	534-1614
26 Villamarco	13.61	11.28-17.98	1153	958-1508
7 La Mayor (Páramo)	20.70	10.02-48.44	1788	957-3860
27 Seca	32.79	11.50-85.55	2325	560-5750

RESULTS

Description of Ponds on the Basis of Water Mineralization

Table 2 gives the mean and the range of variation in conductivity and total anion content for each of the study ponds. These average values, obtained from seasonal sampling, were distributed over a wide range: conductivity ranged 145-2325 $\mu\text{S}/\text{cm}$, while mineralization calculated from the total anion content ranged 1.60-32.79 mEq/L.

From the criteria by Alonso (1998), which have been used for Spanish ponds, we drew up a classification scheme for our ponds on the basis of total mineralization. Sixteen of the twenty-seven ponds fell into a “very low mine-

ralization” group (< 5 mEq/L). Moreover, for seven of these ponds, the mean concentration of total anions was less than 2.5 mEq/L.

In most of these low mineralization ponds, chlorides were the predominant fraction. Thus, on average for this group, the order of concentration of ions was $\text{Cl}^- > \text{alkalinity} > \text{SO}_4^{2-}$. With regard to cations, calcium predominated, followed by sodium and magnesium (Table 3). In the group made up of the eleven most heavily mineralized ponds (> 5 mEq/L), the mean total anion concentration was greater than 10 mEq/L in four systems, reaching a maximum of 32.8 mEq/L. The average proportions of the predominant anions were very similar in this group. Sulphates were strikingly more abundant in this group than in the less mineralized shallow lakes. Calcium

Table 3. Percentages (mEq/L) of the main ions in ponds of the South-East of León, in the Spanish freshwater ponds and as an average for freshwater world-wide (Conway, 1942). *Porcentajes (mEq/L) de los iones mayoritarios en las lagunas del SE de la provincia de León, en las lagunas españolas y en el promedio de aguas dulces de todo el planeta (Conway, 1942).*

	CO ₃ H ⁻	SO ₄ ⁼	Cl ⁻	Ca ⁺⁺	Mg ⁺⁺	Na ⁺	K ⁺
Freshwater ponds (SE León)	40	13.7	46.3	54.1	17.2	24	4.7
Mineral freshwater ponds (SE León)	33.3	31.2	35.5	50.8	23.1	22.4	3.7
Mean composition of waters of the world	73	16	10	63	17.5	16	3
Spanish freshwater ponds	53.5	23.8	22.3	38.9	18.2		42
Spanish mineral freshwater ponds	18.3	43.2	38.6	36.5	20.5		49

Table 4. Mean, maximum and minimum concentrations and standard deviations for the various ions and of the total of anions in the two salinity groups (<5 mEq/L and >5 mEq/L). *Concentraciones media, máxima, mínima y desviación estándar de los diferentes iones y del total de aniones en los dos grupos de mineralización (< 5 mEq/L, > 5 mEq/L).*

		CO ₃ H ⁻ mEq/L	SO ₄ ⁼ mEq/L	Cl ⁻ mEq/L	Ca ⁺⁺ mEq/L	Mg ⁺⁺ mEq/L	Na ⁺ mEq/L	K ⁺ mEq/L	Total anions mEq/L
Freshwater ponds	Mean	1.20	1.39	0.41	1.52	0.48	0.67	0.13	3.01
	S.D.	1.02	0.66	0.46	0.57	0.41	0.27	0.08	1.14
	Max.	2.62	2.62	1.50	2.57	1.26	1.22	0.31	4.62
	Min.	0.52	0.31	0.02	0.72	0.25	0.17	0.03	1.60
Mineral freshwater pond	Mean	3.79	3.55	4.05	5.05	2.30	2.23	0.37	11.38
	S.D.	1.70	4.48	3.71	3.19	1.67	2.24	0.29	8.56
	Max.	7.07	14.60	13.20	12.19	6.24	7.96	0.96	32.79
	Min.	1.07	0.27	0.83	2.37	0.45	0.63	0.09	5.47

was once again the main cation, while the percentages for magnesium and sodium were very similar (Table 3). Table 4 shows the mean, maximum and minimum concentrations and standard deviation for the various ions and of total anions in the two mineralization groups of ponds.

In the group of ponds with the least mineralized water, calcium, and to a lesser extent magnesium, were the cations most strongly involved in alkalinity. However, the correlations with this variable, although significant, were not very strong (Table 5). In contrast, in the most mineralized group, the lack of significance in the correlation values (Table 5) highlighted the relative unimportance of these two cations for the alkalinity of such environments with a greater ion content.

As for chlorides, in waters with low mineralization Chozas and Villadangos, at the Northern edge of the study area, stand out for their relatively high concentrations, of about 1 mEq/L, yet with mean conductivities below 225 µS/cm. In ponds with an ion content in excess of 5 mEq/L, a noteworthy dispersion in chloride levels was

observed. The influence of water flow patterns on chloride concentration was particularly strong in those ponds in this group with the highest dissolved salt content (e.g. La Seca and La Mayor). In these environments during autumn, when the basins that had dried out completely during the summer were gradually filling up again, the chloride concentrations were seven times those measured in spring, with concentrations of 35 mEq/L and 20 mEq/L, respectively. Correlations between chlorides and all cations with the exception of potassium, were very strong and higher than those observed in the low mineralization group of ponds, although correlations in this group were also significant. The correlation between chlorides and sodium was especially strong in both mineralization groups (Table 5).

As for sulphates, the two groups were also clearly different. Variability was considerable within each group. The effects of seasonal drought on the levels of this anion were remarkable, especially in the most mineralized group. In Santa Cristina, Villamarco and La Seca the concentra-

Table 5. Correlations between anions and cations, calculated separately for the two salinity groups (<5 mEq/L and >5 mEq/L) (* p<0.05, ** p<0.01, *** p<0.001). *Correlaciones entre aniones y cationes, calculadas por separado para los dos grupos de salinidad establecidos (<5 mEq/L, >5 mEq/L)*

	TOTAL ANIONS < 5 mEq/L			TOTAL ANIONS > 5 mEq/L		
	Alkalinity	Cl ⁻	SO ₄ ⁼	Alkalinity	Cl ⁻	SO ₄ ⁼
Ca ⁺⁺	0.695***	0.653***	0.468***	0.009	0.903***	0.973***
Mg ⁺⁺	0.562***	0.473***	0.503***	0.219	0.938***	0.900***
Na ⁺	0.206	0.824***	0.286*	0.179	0.980***	0.878***
K ⁺	-0.228	0.109	0.489***	0.322*	0.477**	0.373*
Conductivity	0.582***	0.826***	0.500***	0.120	0.959***	0.942***

tions of sulphates in autumn were 600, 100 and 15 times higher, respectively, than those measured in spring. In La Seca, the maximum concentration reached was 48 mEq/L. In the low mineralization group of shallow lakes, the greatest correlations noted for this anion were with magnesium, potassium and calcium. As the concentration of salts grew, there was a considerable increase in the associations of all cations with sulphates, with the exception of potassium (Table 5).

In the softer waters, chlorides had the greatest impact of all anions on mineralization, as inferred from correlations of anions with conductivity. In contrast, in the wetlands with high content of dissolved salts, chlorides and sulphates showed similarly high correlations with conductivity. This is an expression of their major role in the mineralization of these wetland systems, considerably more important than that of bicarbonates (Table 5).

As was the case for anions, the concentrations of all cations were strongly affected by seasonal fluctuations in the volume of water, with changes being of greater magnitude in the most highly mineralized ponds. Calcium, sodium and potassium were the cations which underwent in the greater number of shallow lakes a large increase in autumn. The most extreme situation was observed in La Seca, where the concentration of sodium increased five-fold and the concentration of potassium, nine-fold compared to the values observed in spring. Similarly, calcium underwent a twelve-fold increase in Santa Cristina. The increased salinity brought with it a greater involvement of chlorides and sulphates in calcium, magnesium and sodium dynamics, as implied by the correlation values. Moreover, increased salinity led to the disappearance of the links between calcium-magnesium and alkalinity which could be seen in the softer waters (Table 5).

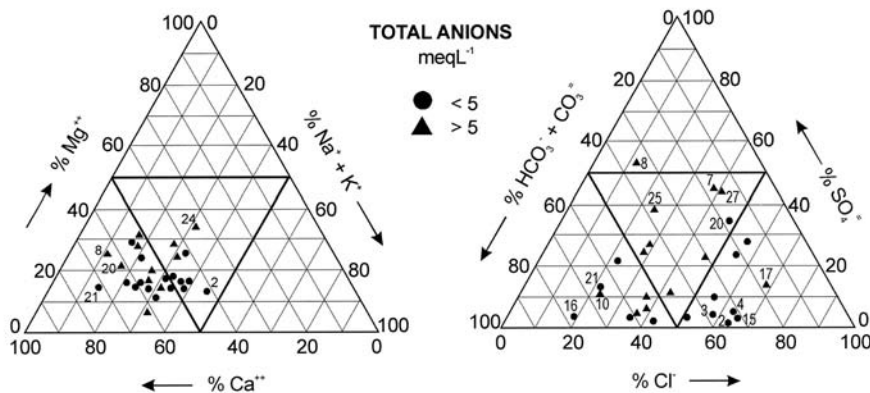


Figure 2. Piper diagrams showing mean concentrations for anions and cations in the water of ponds in the study area (León, Spain). Numbers identifying ponds are as those used in Figure 1. *Diagramas de Piper obtenidos a partir de las concentraciones medias de aniones y cationes de las lagunas estudiadas. Los números se corresponden con los indicados en la Figura 1.*

Relative Ion Composition of Ponds

The analysis of the triangle of anion composition obtained from yearly means showed that in the least mineralized waters chloride was the predominant ion, followed in importance by bicarbonate (Fig. 2). Among the more mineralized ponds, a greater spread was observed in the relationships of ions. In these bodies, water ionic composition was dominated by bicarbonate, although in binary mixtures. Furthermore, in the environments with extreme mineralization (> 20 mEq/L), such as La Mayor (7) and La Seca (27), the dominant anions were sulphates and chlorides, and alkalinity was less important (Fig. 2). The only lagoon of sulphate type was Santa Cristina (8), with mineralization following the order: $\text{SO}_4^- > \text{alkalinity} > \text{Cl}^-$.

With regard to the cation triangle, the greater part of the ponds predominantly had calcium-type water, without any clear trend related to level of mineralization. Only nine water bodies fell into

the group, with binary mixtures, primarily calcium-sodium or calcium-magnesium (Fig. 2).

Fluctuations of water level over the annual cycle impacted concentrations of anions and cations and their relative proportions. In spring, the majority of the most mineralized ponds could be classified as of bicarbonate type, while those with the smallest salt content, bicarbonate and chloride types were equally prevalent. This pattern was maintained in summer, although the relative contribution to total salt content of sulphates decreased. In autumn, the low mineralization ponds were mostly of the chloride type, while the majority of the most mineralized were of the bicarbonate and sulphate types, or of some binary combination of these two anions. In winter, although the bicarbonate and sulphate types held their place among the high mineralization ponds, as did the chloride type among the softest, a relatively balanced anion composition was present, with water of binary types being frequent: bicarbonate-sulphate, sulphate-chloride and sulphate-bicarbonate.

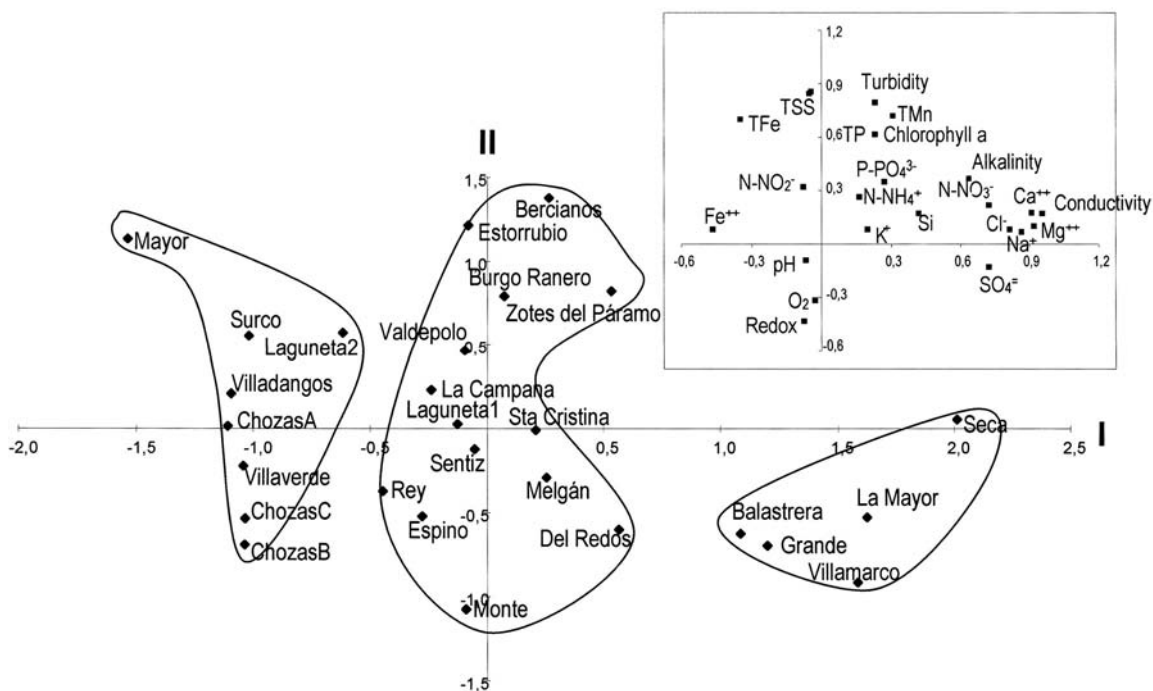


Figure 3. Diagrams showing the ordering of physical and chemical variables and of ponds on the plane defined by the first two axes of the Principal Component Analysis. The groups of ponds emerging from the classification analysis are shown. *Diagramas de ordenación de las variables físico-químicas y de las lagunas en el plano definido por los dos primeros ejes del Análisis de Componentes Principales. Se señalan los grupos de lagunas obtenidos en el análisis de clasificación.*

Overview of the physical and chemical characteristics of ponds

As a first step for establishing the relationship between water chemical composition of ponds and groundwater chemical composition, ponds were characterized according to their water chemistry. To do this, a principal component analysis was carried out, using the seasonal dataset of physical and chemical variables.

The first component in the analysis explained 30.35 % of the total variability and clearly defined a mineralization gradient associated with the majority ions (Ca^{++} , Mg^{++} , Na^+ , Cl^- , SO_4^- , alkalinity) and conductivity (Fig. 3). Associated to this gradient, an ordering was also found according to nitrate concentration. The nitrates in our ponds, in the light of their relatively high solubility, is likely linked to leaching from soils and pollution by fertilizers.

Moreover, the second axis, which explained 17.03 % of total variance, established a tendency related to lake trophic state and water turbidity due to suspended particles, both organic and inorganic, carrying associated nutrients and in particular phosphorus. At the extreme positive end of this axis were iron and manganese

(Fig. 3), which are often adsorbed to organic molecules or to inorganic particles such as clays which are resuspended in these shallow systems through the action of wind and rain or by bioturbation. This contribution to the water of substantial quantities of reduced materials, such as organic matter, also led to low oxygen concentrations and marginally acid conditions.

The principal component analysis (PCA) was carried out by using the seasonal data of the different variables. However, we have represented the average coordinates for each pond, calculated from those corresponding to the four seasons, in order to obtain a more precise ordination of sites. Furthermore, groups were classified more accurately by an analysis of the classification in which the variables were the mean coordinates of the first two axes.

Three groups of ponds were distinguished across the mineralization gradient (Fig. 3): of low, medium and high mineralization, and mean conductivity values of 212, 432 and 1401 $\mu\text{S}/\text{cm}$, respectively.

At the positive end of the gradient of eutrophication defined by the second axis, a group of ponds (El Estorrubio, Bercianos del Real Camino, Burgo Ranero and Zotes) were distin-

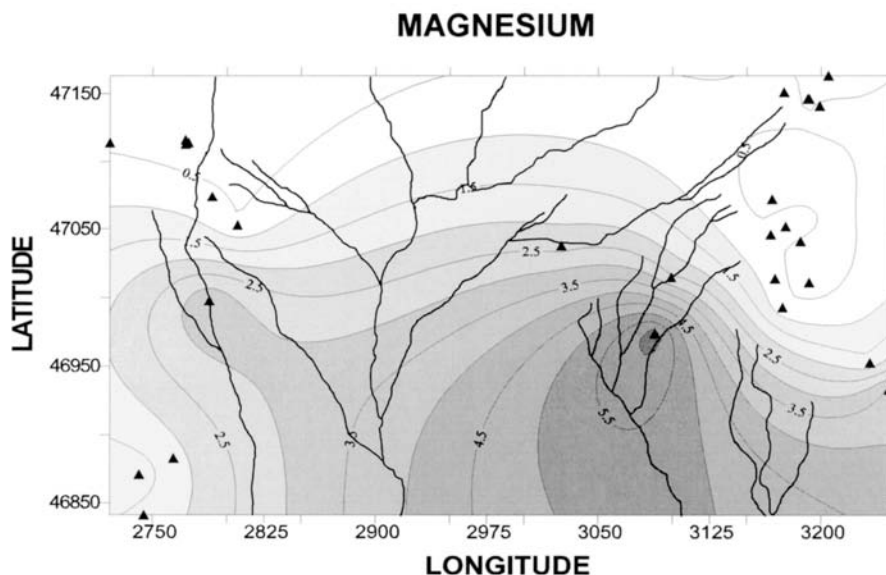


Figure 4. Spatial variation in the concentration of magnesium (mEq/L) in the ponds. *Variación espacial de la concentración de magnesio (mEq/L) de las lagunas.*

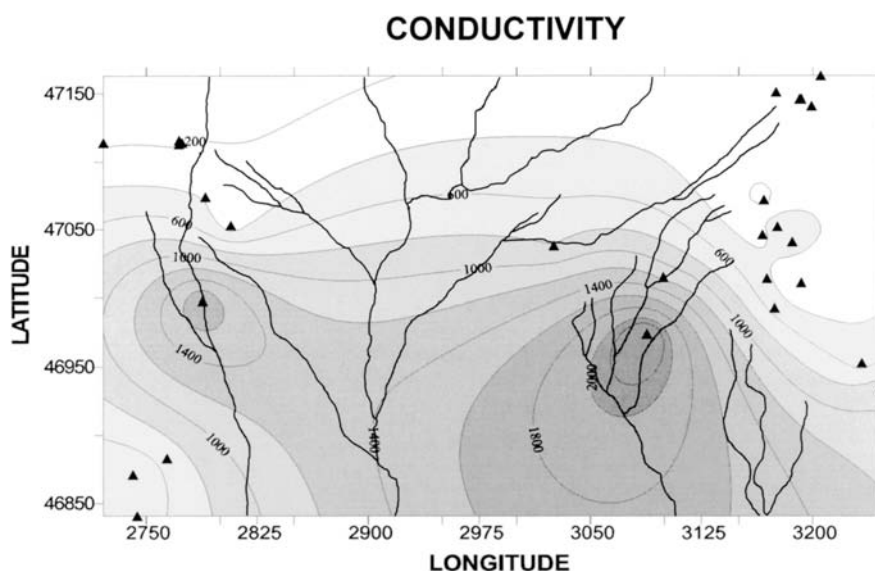


Figura 5. Spatial variations in conductivity ($\mu\text{S}/\text{cm}$) in the ponds. *Variación espacial de la conductividad ($\mu\text{S}/\text{cm}$) de las lagunas.*

guished (Fig. 3) as of high turbidity during the summer. In some cases (i.e. El Estorrubio and Bercianos del Real Camino), high turbidity is maintained throughout the year due to the clayed nature of the substrate. Furthermore, during summer some of the ponds were considerable reduced in volume. This, combined with a large increase in the growth of macrophytes or phytoplankton, lead to a large concentration of orga-

Table 6. Pearson's correlation coefficients between latitude and mineralization-related variables of studied ponds and between latitude and the first PCA axis (* $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$). *Valores del coeficiente de correlación de Pearson de las variables relacionadas con la mineralización del agua de las lagunas y el primer eje del ACP con la latitud. (* $p < 0,05$, ** $p < 0,01$, *** $p < 0,001$).*

Variables	Latitude
Conductivity	-0.51**
pH	-0.29
Alkalinity	-0.62***
Chloride	-0.18
Sulphate	-0.58**
Total Anions	-0.55**
Magnesium	-0.66***
Calcium	-0.53**
Sodium	-0.26
Potassium	-0.46*
PCA I	-0.51**

nic suspended solids, together with an increase in nutrients both in dissolved and particulate form (phosphorus, iron and manganese).

Relationships of latitude with water chemical composition in ponds

To investigate any possible influence of geographical location on the ion composition and mineralization of ponds, correlations were calculated between latitude and mean concentration of the main ions, conductivity and pH. The ordering of the ponds with respect to the first axis of the PCA was also included as a dependent variable in this analysis. Pearson's correlation coefficients from this analysis are shown in Table 6.

A significant negative correlation between latitude and the concentration of most dissolved salts was noted, as well as with the first axis of the PCA. Therefore, a spatial pattern was identified in the water mineral composition of wetland systems of the South-East of León, with a general tendency for higher total salt concentration towards the South. However, chlorides, sodium and pH were not dependent upon the geographical location of the water bodies.

Figures 4, 5, 6 and 7 map the trend for spatial variation over the area studied of the variables

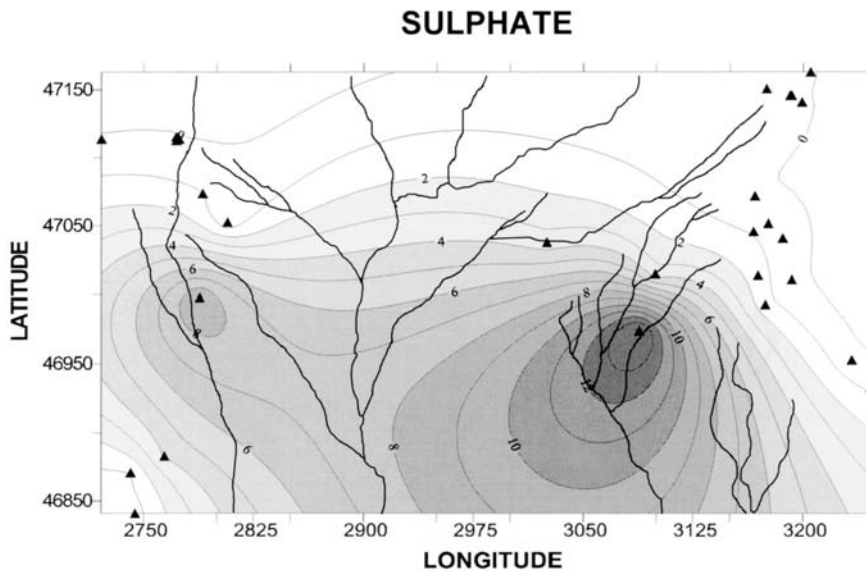


Figura 6. Spatial variation in the concentration of sulphate (mEq/L) in the ponds. *Variación espacial de la concentración de sulfato (mEq/L) de las lagunas.*

best correlating with latitude, which were magnesium, conductivity, sulphates and alkalinity. The geographical models derived from the mean annual values for the first three variables, and especially so for conductivity and sulphates, were essentially coincident. Water of lower ion content (< 2.5 mEq/L or $250 \mu\text{S}/\text{cm}$) were found in the ponds located in the Northern areas of the study zone, while between the rivers Esla and Cea, the increased mineralization ($2300 \mu\text{S}/\text{cm}$, 33 mEq/L) shown by trend surfaces converges from both the North-West and the North-East towards intermediate latitudes (Fig. 4, 5 and 6).

Characterization of groundwaters from their chemical composition

In the PCA conducted to establish variability trends affecting chemical composition of groundwaters, the first factor explained 46.79 % of the total variance. This factor was strongly correlated with sodium, chlorides, conductivity and sulphates. It may therefore be interpreted as an overall mineralization axis, i.e. a linear combination of almost all the principal ions making up salinity. On the second axis, explaining 12.53 % of the total variance, greatest contributors were pH and

Table 7. Factor loadings of the chemical variables measured in groundwater for the first three axes of the Principal Component Analysis. *Factores de carga de las variables químicas medidas en el agua subterránea para los tres primeros ejes del Análisis de Componentes Principales.*

Variables	Factor I	Factor II	Factor III
Calcium	0.521	0.616	0.128
Magnesium	0.511	0.638	0.009
Sodium	0.901	0.023	0.071
Potassium	0.029	0.031	0.804
Alkalinity	0.335	0.744	0.147
Chloride	0.859	-0.047	-0.421
Sulphate	0.679	0.508	0.164
pH	-0.241	0.746	-0.064
Conductivity	0.784	0.572	0.130
Nitrate	0.654	0.362	0.110
Phosphate	0.078	0.059	0.817

total alkalinity, although correlations with calcium and magnesium were also significant. Thus, this second axis can be linked with alkalization of groundwaters. A gradient of nutrient enrichment was defined from the third PCA axis (explaining 11.68 % of variance), since orthophosphate and potassium were the better correlated variables (Table 7).

The more common types of groundwater from the point of view of relative ion composition were those of a hard (calcium) type (Fig. 8).

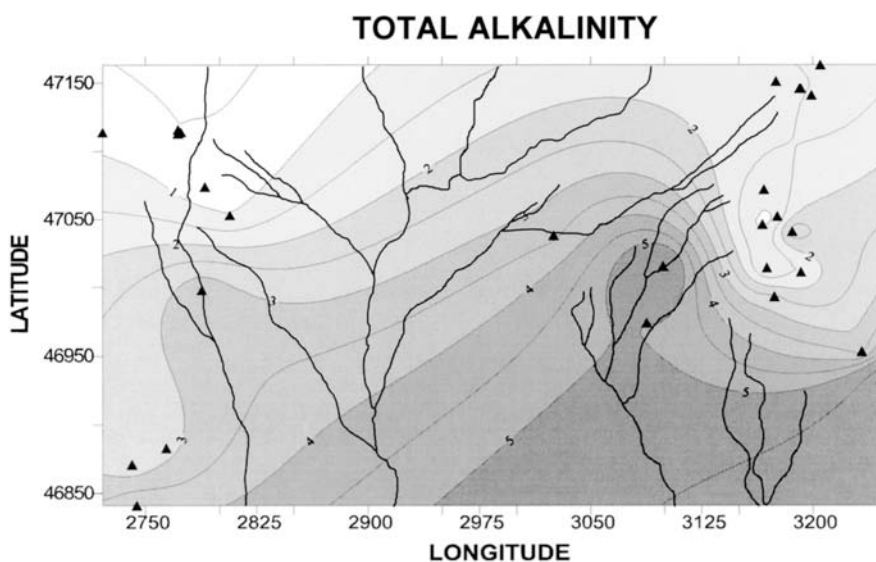


Figura 7. Spatial variation in total alkalinity (mEq/L) in the ponds. *Variación espacial de la alcalinidad total (mEq/l) de las lagunas.*

Nonetheless, sodium and magnesium on occasion were relatively abundant, i.e. 40-50 % in some wells, generally located in Southern parts of the study zone. A good example of this are the more mineralized groundwaters in the Southern edge of the Páramo area (well no. 30) with a relatively major contribution of sodium (36 %) in the cationic triangle. In these waters, sodium together with substantial amounts of $\text{HCO}_3^- + \text{CO}_3^{2-}$ (43 %), indicate slight alkalization due to aging of the groundwater.

With respect to anions, binary mixtures were frequent, with a larger contribution from bicarbonates and chlorides than from sulphates (Fig. 8). Moreover, chlorides were clearly predominant (65-97 % of total anions) in the low mineralization waters (110-480 $\mu\text{S}/\text{cm}$). This agrees with the typology for the ponds of the zone.

Relationships of groundwater chemical composition with latitude

In groundwater, the variables most strongly associated with latitude were the concentrations of magnesium, sulphate, conductivity and sodium, and total alkalinity (Table 8). As regards the PCA axes, the strongest correlation was for the second component (alkalinization),

although the relationship between latitude and the first (overall mineralization) was also significant (Table 8). Thus, a decrease in latitude and the consequent increase in the distance covered by groundwater flows and hence in the time they spend in contact with the substrate lead to increases in those physical and chemical parameters indicating greater mineralization and related to aging of groundwater.

The trend followed by mineralization in the area lying between the rivers Esla and Órbigo was particularly significant (Fig. 9). Salt concentration in groundwaters here increased as it flowed from the North of the study area, with low mineralization (conductivity between 100 and 250 $\mu\text{S}/\text{cm}$), to the South, with maxima for conductivity around 1000 $\mu\text{S}/\text{cm}$ (Fig. 9) through surface formations called “rañas”. Moreover, the clearly more alkaline pH and greater presence of magnesium and sodium relative to calcium towards the South suggests a mechanism for mineralization is operating, perhaps through the slow aging of the groundwater in the North-South direction. This tendency was not so apparent on the left bank of the river Esla. In this area, dominated by the “raña” formations of the Esla-Cea hydro-geological unit, groundwater increased in mineralization from

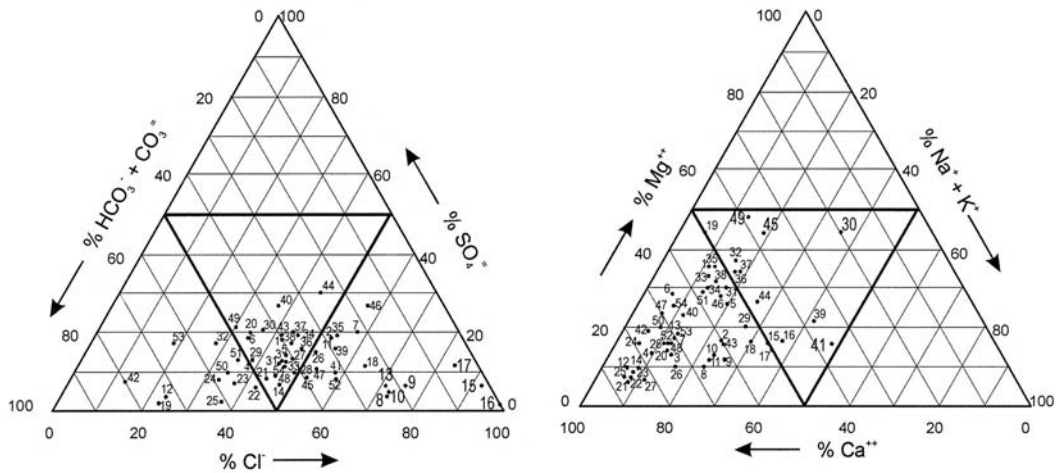


Figure 8. Piper diagrams (anions and cations) for groundwaters in the study area. Numbers identifying wells are as those used in Figure 1. *Diagramas de Piper (aniones y cationes) para el agua subterránea en el área de estudio. Los números se corresponden con los indicados en la Figura 1.*

the North-East to the south-west, in a direction perpendicular to the isopiezometric contours. However, the highest conductivities (1300-1400 $\mu\text{S}/\text{cm}$), accompanied by high concentrations of calcium and sulphates, were observed at intermediate latitudes, probably coinciding with the surfacing of deeper and more heavily mineralized regional flows (Fig. 9).

Also, a strong association was identified between latitude and alkalinity of groundwaters, whether expressed as an individual variable or as the second PCA axis. The pattern of spatial variation was similar to that observed for conductivity. Alkalinization of groundwater in areas on the right bank of the river Esla increased gradually from North to South (Fig. 10). By contrast, pat-

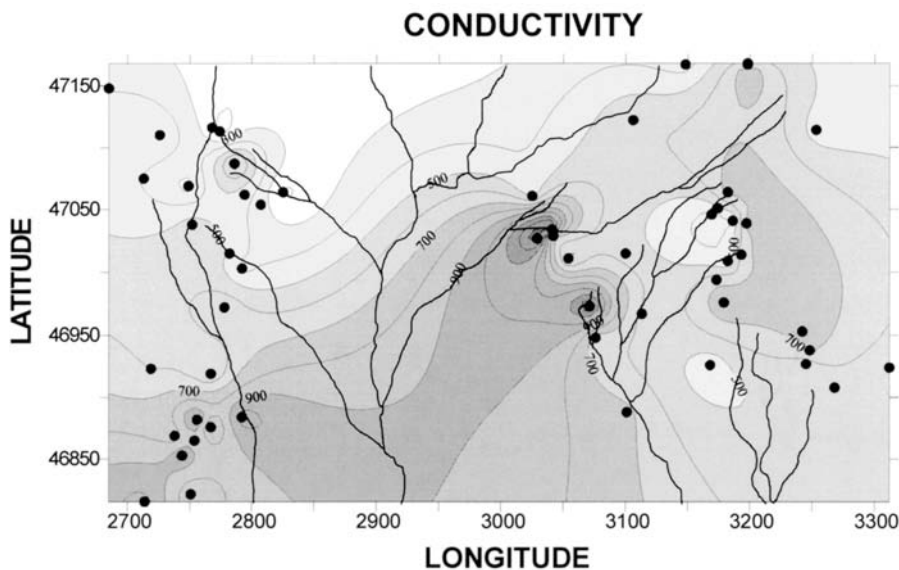


Figure 9. Spatial variation in groundwater conductivity ($\mu\text{S}/\text{cm}$) in the study area. *Variación espacial de la conductividad ($\mu\text{S}/\text{cm}$) del agua subterránea en el área de estudio.*

Table 8. Pearson's correlation coefficients between latitude and mineralization-related variables of groundwaters and between latitude and the PCA axes (* $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$). *Valores del coeficiente de correlación de Pearson de las variables relacionadas con la mineralización del agua subterránea y los ejes del ACP con la latitud. (* $p < 0,05$, ** $p < 0,01$, *** $p < 0,001$).*

Variables	Latitude
Conductivity	-0.472***
pH	-0.318*
Alkalinity	-0.462***
Chloride	-0.177
Sulphate	-0.539***
Magnesium	-0.731***
Calcium	-0.259
Sodium	-0.439***
Potassium	0.109
Nitrate	-0.347**
Phosphate	0.103
PCA I	-0.344*
PCA II	-0.517***
PCA III	0.19

terms of spatial change in alkalinity on the left bank of the Esla were more complex, with maximum values at intermediate latitudes (Fig. 10), which on occasion coincided with intensely mineralized water from the regional aquifer, largely overlain by the “raña” formations.

Relationships between water chemical composition of ponds and groundwater chemical composition

Table 9 shows results of the regression analysis of pond water and groundwater chemical composition.

In general terms, the chemistry of the wetland systems and the pattern of mineralization of the groundwaters followed similar trends. However, for all variables for which the correlation was significant, some ponds (Mayor(P), Villamarco, Seca and Grande) stood out as systems of higher mineralization than the groundwater. Similarly, some ponds (e.g. Mayor, Villaverde, Villadangos, Campana, Monte and Surco), did not fit the regression model, being of relatively low mineralization as compared to the groundwater (Fig. 11).

DISCUSSION

Water mineralization was the main factor grouping shallow lakes of the South-East of León. Ponds with low saline content (< 5 mEq/L) showed major departures in majoritary ion proportions compared to the average of freshwaters worldwide (Conway, 1942) and also compared to

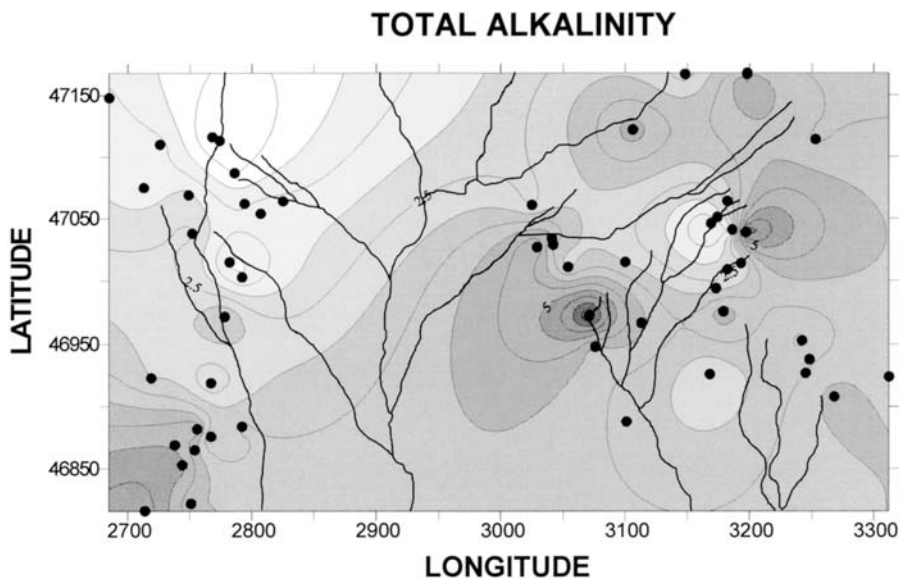


Figure 10. Spatial variation in groundwater alkalinity (mEq/L) in the study area. *Variación espacial de la alcalinidad (mEq/L) del agua subterránea en el área de estudio.*

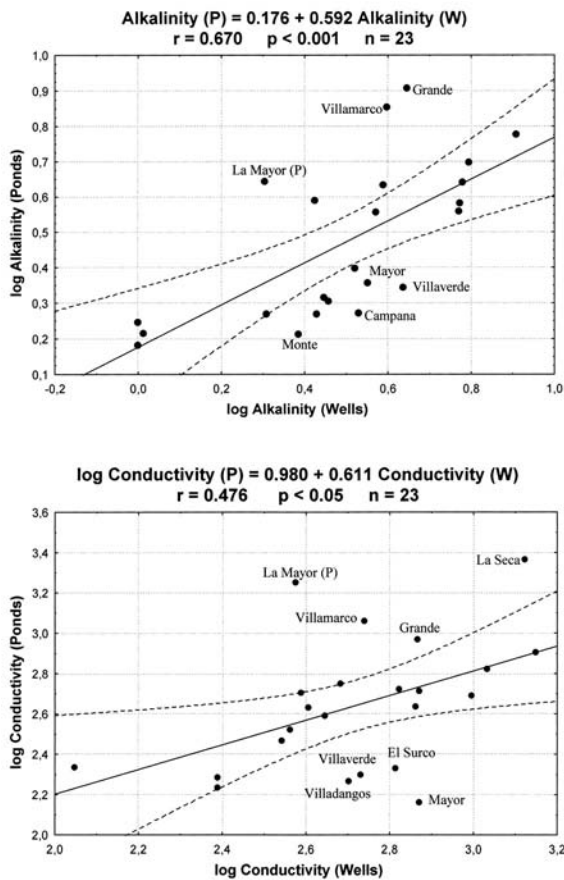


Figure 11. Regression models for alkalinity and conductivity of water in ponds against that in groundwaters. *Modelos de regresión de la alcalinidad y de la conductividad de las lagunas con el agua subterránea.*

the averages for freshwater bodies in Spain (Alonso, 1998) (Table 3). Low mineralization waters in the South-East of León were on average relatively impoverished in bicarbonates and sulphates, but richer in chlorides. Sulphates were not dominant over chlorides in any of the study ponds. Sulphate dominance over chlorides is taken as an indication of continentality in poorly mineralized lakes (Alonso, 1998). The ponds in our study were essentially of chloride type and only secondarily of bicarbonate type. Chloride dominance in combination with low mineralization is unusual. It is well known that low total mineralization is associated with dominance by bicarbonates and calcium, with other ions gaining in importance as salinity increases (Custodio & Llamas, 1983; Alonso & Comelles, 1987).

Table 9. Pearson's correlation coefficients between variables measured in groundwaters and in the water in ponds in the study zone (* $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$). *Valores del coeficiente de correlación de Pearson entre las variables medidas en el agua subterránea y en el agua de charcas y lagunas (* $p < 0,05$, ** $p < 0,01$, *** $p < 0,001$).*

Variables	r
Conductivity	0.476*
pH	0.098
Alkalinity	0.670***
Chloride	0.012
Sulphate	0.685***
Magnesium	0.674***
Calcium	0.530**
Sodium	0.324
Potassium	0.139

As Alonso (1998) pointed out, lightly mineralized chloride waters are not frequent, especially in closed basins. The only significant instances of this type of lakes are lightly mineralized pools in arid zones. On the other hand, the dominance of chlorides in relatively soft waters might also be due to pollution (Hutchinson, 1957). In the studied ponds it is quite unlikely that there is any major discharge of urban waste water, because they are located in an area clearly dominated by agriculture. Thus, it is more likely that the unusual typology of our ponds is the result of the intensive application of fertilizers, which may interfere with salinity through the addition of chlorides or sulphates, causing a decrease in the relative importance of bicarbonates (Procházková & Blazka, 1989).

In the more heavily mineralized ponds (> 5 mEq/L) in the South-East of León, the proportions of the three main anions were very similar. However, their mean proportions of anions were very different from world averages (Table 3). The higher participation of sulphates as mineralization increases agrees with results reported by Alonso (1998) for Spanish ponds as a whole. Despite this, sulphate was not a dominant anion in the group of water bodies studied here.

Aside from mineralization, in the system of shallow lakes in the South-East of León, calcium was the main cation, as for the average of waters worldwide (Conway, 1945) and for fresh-

water ponds in Spain (Alonso, 1998) (Table 3). Nevertheless, any decreases in mineral content favoured sodium over magnesium. Potassium was the scarcest cation in our shallow lakes and its low correlation with all anions demonstrates its minor role in the mineralization of these ecosystems. The occasional increase in potassium concentrations in some ponds during the autumn, coinciding with their filling up, suggests increases from soil leaching and the consequent contribution from runoff.

The correlation analysis of cations against anions of water in ponds in this study helped to better understand ionic dynamics and the influence of mineralization on ionic concentrations. Chlorides and bicarbonates were the anions of greatest weight in the mineralization of the water ecosystems with the softest waters. However, ponds with higher concentration of salts had comparatively less bicarbonates and the main fraction of the anions was made up of strong acids, chlorides and sulphates. Thus chlorides and sulphates were proportionally more abundant in these systems. Furthermore, in more mineralized ponds, the contributions of calcium and magnesium to alkalinity were comparatively lower, while chlorides and sulphates increased their role in the dynamics of calcium and magnesium. Hence, in the more strongly mineralized waters, the main factor in the dynamics of calcium and magnesium is not related to the carbonate-bicarbonate system, but rather to the processes of oxidation of organic matter affecting sulphate concentration, together with the concentration effect due to intense evaporation during the summer. Similarly, outflows from aquifers may be a major source of mineralization (Llamas, 1984; González Bernáldez, 1987), in which groundwater flows may have long residence times. Groundwater influences on mineralization are likely in the high mineralization, albeit not saline ponds, such as La Seca. Regardless of the degree of mineralization, the strong association between chlorides and sodium, which were the two more highly correlated ions, suggests sodium chloride largely accounts for chloride concentrations.

In almost all ponds, and particularly in the more mineralized, the water regime had a very

significant influence on ionic concentrations. It is known that ion concentrations change with water level fluctuations. Malmer noted a considerable increase in the concentrations of sodium, magnesium, calcium, chlorides (Malmer, 1962) and sulphates (Malmer, 1960, 1961, 1962) in lakes in southern Sweden as a consequence of summer droughts. Similarly, Vangenechten *et al.* (1981a) described an increase in the concentrations of calcium, magnesium and sulphates during the filling period of acid moorland pools in Belgium.

The data reported here demonstrate that intense summer evaporation, and especially the filling up in autumn of ponds which had remained empty over the summer, led to changes not only in mineral content but also in the water ionic composition. These changes were particularly noteworthy in the more heavily mineralized ecosystems and, unlike what Vangenechten *et al.* (1981a) observed, involved increases in the concentrations of all anions and cations in autumn. These authors contended that if water level change from evaporation and refilling was the sole process explaining variations in ionic concentrations, a proportional increase in all ions would be expected associated with intense evaporation. However, when the lake bottom has become dry, a differential response to solubilization among the ions is observed upon refilling of the lake and rewetting of the lake sediment (Vangenechten *et al.*, 1981a). Observations during the present study confirm this idea, since the ionic proportions did not remain constant and greatest increases were found in sulphates.

Changes in water ion content during the system refilling could be due to the resolubilization of salts precipitated during summer. Resolubilization occurs according to the differing levels of solubility of each ion. To this is added the saline contribution from runoff (Alonso, 1998). Moreover, the substantial increase in sulphate concentrations could have been due to the oxidation of lake sediments during the dry-out (Gorham, 1956, 1957; Malmer, 1960, 1961, 1962). However, in ponds such as La Seca or Villamarco, the burning of vegetation could have contributed to the striking increase in sulphate concentrations in water as pond filled up.

The water chemical composition of ponds of the Leonese "Páramo" and "Payuelo" districts allows to infer features of the hydrology of the area. The length of discharge flows in ground-water-influenced areas turned out to be a major factor shaping the characteristics of the wetlands studied. Indeed, their greater or lesser mineralization was determined at large by their geographical location. Longer residence times or paths of flow may have favoured greater solubilization of minerals from the substrate and more intense ion exchange and consequently higher levels of mineralization of the water. Overall, mineralization and alkalization were the two main processes impinging hydro-chemical variability of groundwater in the study area. Both these two processes showed a tendency to increase with increases of the distance covered by groundwater flows, thus leading to longer contact times with the substrate. However, ponds may depend on both surface aquifers and connections with deeper and more extensive aquifers. The extent to which this is so is still matter of speculation.

Some of the pond complexes studied here are recharge areas because of their impermeable materials, soil and rock. This is the case of La Mayor in the village of Villamuñío. This very shallow body of water is ephemeral and always dries out in summer. Because it is very shallow, this pond has a high surface to volume ratio, and thus filling and emptying of the basin takes place very rapidly and fluctuations of water level are closely linked to the seasonal balance between precipitation and evaporation. However, many of the ponds in the area studied are linked to "raña" aquifers, which are free aquifers easily refilled through rainwater infiltration which they receive directly. The impermeability of the alluvial deposits or "rañas" underlying these wetlands allow the existence of "hanging" layers of water over the regional aquifer. The impermeable deposits overlie the zone in which the more strongly mineralized regional aquifer is located. Therefore, the hydro-chemical nature of water in these ecosystems is more related to rainwater than to groundwater and the influences of deep ground-

water are masked by those of the "rañas". Thus, most ponds in the hydrological complexes in Valdepolo and Villamuñío, together with ponds in the upper "Páramo", are water bodies with little mineralization which are influenced by linear discharges from short groundwater flows. The chemical composition of waters in these ponds is not very different from the initial chemical composition of the infiltrating water. On the other hand, changes in the chemical composition of water in the study ecosystems are in proportion to the time remaining underground (Toth, 1966; González Bernáldez *et al.*, 1987; González Bernáldez & Montes, 1989; Wassen *et al.*, 1989; Rey Benayas *et al.*, 1990a). In the region delimited by the rivers Esla and Orbigo the increase of the flow length towards the South lead to an increased overall mineralization of groundwater. These more alkaline sub-regional flows show up on the surface forming more heavily mineralized groups of ponds in the lower "Páramo", for instance at Santa Cristina, Melgán or Zotes del Páramo.

The connection with deeper regional flows in the Esla-Valderaduey region, emerging in the zones where Miocene formations contact more superficial Pliocene deposits (the "rañas"), shows as comparatively more mineralized outflows which form ponds, such as La Seca, Grande, Villamarco and Mayor on the Páramo region. The higher mineralization of these ponds waters is caused by long residence time of regional flows leading to modified, strongly mineralized groundwater, through ion exchange and solubilization of geological minerals (Fernández Uría *et al.*, 1985). Despite this, the chemical composition of outflows does not match the groundwater chemistry, suggesting other factors are operating in the complex hydrology of the study area

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