

The geochemical features of the Ter River watershed (NE Spain)

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RESUMEN

Características geoquímicas de la cuenca del río Ter. El objetivo de este trabajo ha sido conocer las distintas proporciones de los compuestos iónicos mayoritarios que definen el carácter geoquímico de cada punto de muestreo en la cuenca del río Ter. Se ha considerado la variación espacial y temporal de la composición relativa de estos compuestos. La forma de representar las distintas proporciones iónicas en diagramas de Piper y de Maucha sugerían un espectro de variación espacial característico para algunas subcuencas. La aplicación de técnicas estadísticas multivariantes (análisis discriminante) ha servido para agrupar las distintas subcuencas que presentaban las mismas características hidroquímicas. Se clasificó un total de 10 grupos de subcuencas, cuyo resultado revelaba diferencias geoquímicas entre sectores del tramo principal del río Ter y entre afluentes calcáreos poco y muy mineralizados. Algunos de los factores fisiográficos de la cuenca (litológicos y actividad humana diversa) ayudaban, también, a determinar el carácter geoquímico de cada subcuenca. El cloruro, el sodio y el potasio eran los iones que mejor relación guardaban con la actividad antropogénica. El resto de los iones estaba mucho más relacionado con las características litológicas y no presentaba correlación significativa con los cambios de caudal.

SUMMARY

The aims of this paper is to assess the different major ion proportions which define the chemical water type in each sampling-station of the river Ter watershed. Considerations of the relative abundance on the various major ionic constituents of the river is the main subject of discussion. The results show that application of multivariate statistical techniques may help in clustering the different watershed with similar chemical properties characterized by several abiotic factors. The spatial distribution of major dissolved ions has also been considered in addition to an approach to determining regional differences in solute levels of the river Ter during low flow conditions.

PALABRAS CLAVE: geoquímica, cuenca hidrográfica, compuestos iónicos mayoritarios, río Ter.

KEY WORDS: geochemistry, watershed, major ionic components, River Ter.

INTRODUCTION

The global salinity of fresh water is characterized by its total dissolved salt content.

Nevertheless, it would be more satisfactory to define salinity as the concentration of the major ions dissolved: sodium, potassium, magnesium, calcium, carbonates, bicarbonates, chlorides and sulphates.

GIBBS (1970) considers that the three main mechanisms controlling the chemical composition of the major dissolved salts of the fresh waters can be defined as atmospheric precipitation, rock dominance and the dissolution/precipitation processes. However, the chemical composition may also be supposed to depend on other intrinsic characteristics of the watershed, such as relief, vegetation, soils, composition of material in the basin and human activities

(Urbanization, agriculture and industry) (WEBB, 1976). An explanation of spatial variations in stream solute concentrations is more difficult because many environmental factors tend to vary simultaneously and have mutually reinforcing effects on stream chemistry (MEYBECK, 1979).

The effect of catchment characteristics on the concentration of dissolved ions in the Ter river has been studied in SABATER *et al.* (1987). The present paper is mainly devoted to a consideration of the relative abundance of the different major ionic constituents in so far as they determine the overall chemical features of a water type. Therefore, an assessment of the relative proportion of each of these ions is used to define the chemical water type at each sampling station. The studies of water composition at tributary and main channel

stations are thought to offer considerable scope for further understanding of stream solute behaviour in the study of the Ter basin.

STUDY AREA AND METHODS

The Ter is a typical mediterranean river running through the northern half of Catalonia (NE Spain). It has a mountain influence in the upper reaches, which results in strong variations in flow over the year. The average discharge is $25 \text{ m}^3/\text{s}$ at the mouth. The source of the Ter is in the Pyrenees mountains at 2400 m (a.s.l.). The river is 208 km long and has a drainage area covering 3010 km^2 . River water is poorly mineralized in the upper part, where the bedrock is siliceous and human occupation

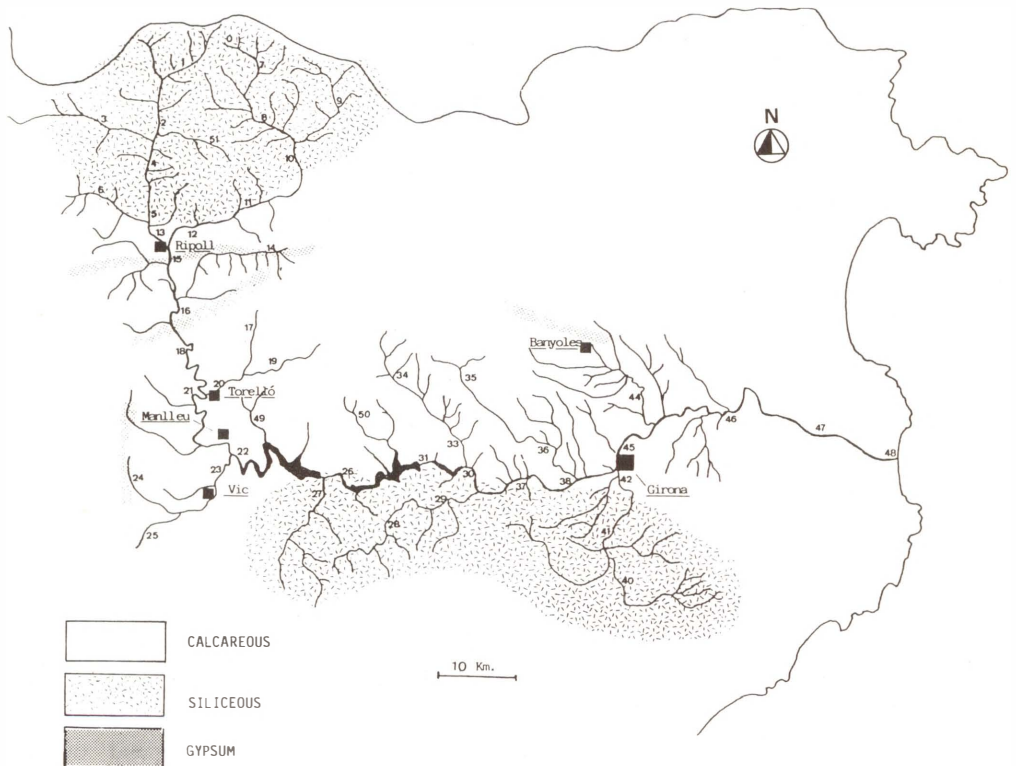


FIG. 1.: The location of the fifty one sampling sites along the catchment area of the Ter river. The main lithologic features are pictured. *Localización de los 51 puntos de muestreo en la cuenca hidrográfica del río Ter. Se representan las principales características litológicas.*

is low. Salinity and nutrient concentrations rapidly increase downstream, reaching high values in some polluted sites (SABATER & ARMENGOL, 1986). Reservoirs situated in the middle stretch bring about an improvement in water quality (PUIG *et al.*, 1987). In the lower stretch urban and industrial effluents increase pollution loadings. Tributary subbasins of the river Ter vary according to geochemical features (siliceous versus calcareous) and the extent of forest cover.

Fifty one sampling points throughout the hydrographic network of the Ter river were studied for a one-year period starting in October 1982. The samples were taken monthly and the following parameters were measured in the laboratory: calcium, magnesium, sodium and potassium by atomic absorption spectrometry; alkalinity by volumetric titration to pH 4.5; and sulphates and chlorides by ionic chromatography.

For the statistical processing of the data a Cluster analysis and Stepwise Discriminant analysis were carried out following the package of statistic programs BMDP, after logarithmic transformation so as to stabilize the variance.

RESULTS AND DISCUSSION

THE IONIC COMPOSITION OF THE WATER

Table I gives the summary statistics of the chemical variables used for R-mode cluster analysis (fig. 2). This analysis indicates that the major ions analysed in Ter river water can be divided into two basic groups: The group of components associated with the conductivity (alkalinity, calcium, magnesium and sulphate), and the group of ions which apparently seem to have less relationship with total dissolved ions (Chloride, sodium and potassium). This particular hydrochemical behaviour may be somewhat different under differing

hydrological conditions. The last parameter groups are clearly related to river discharge. This is demonstrated by the high correlation coefficient linking these parameters with average monthly water flow. These coefficients decrease in the following order: Chloride (-0.84); Sodium (-0.76) and Potassium (-0.43). The remaining ions in the first group are not always correlated significantly at $p < 0.01$. The concentrations of the second group probably represent the contribution of a number of sources: sedimentary rocks, saline soils, groundwater seepage, atmospheric precipitation, human activity, and so on.

A subset composed of bicarbonates, calcium and magnesium is distinguishable within the first group of components. Carbonate rocks are their main source. Since they do not show any obvious relationships with discharge, it is possible that the variations of concentrations of these ions are occasionally smoothed out by tributaries whose hydrographs differ from that of the rest of the Ter river.

During the entire period of the research the ionic composition of the water was that typical for most of the surface waters of our climatic zone; i.e., it was a calcium-hydrocarbonate one. The water is essentially rich in $\text{Ca}(\text{HCO}_3)_2$, mainly because of the geology of the catchment area of the river Ter. The hydrocarbonate represents 63% of

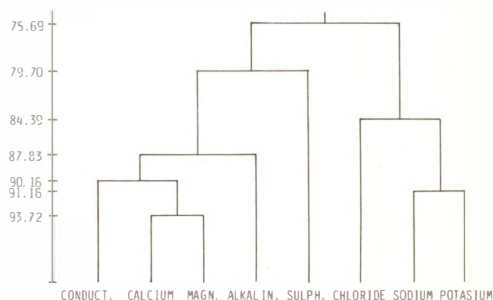


FIG. 2. Dendrogram of major ions derived from cluster analysis of the main ionic composition of the whole sampling points. *Dendrograma de los iones mayoritarios a partir del análisis de clasificación de la composición iónica del conjunto de puntos de muestreo.*

TABLE I.: The mean annual chemical composition of the major ions of each sampling point (in meq/l). The conductivity (corrected to 25°C) in uS/cm. *Composición química anual media de los iones mayoritarios en cada*

EST.	COND.	CO ₃	CO ₃ H	SO ₄	Cl	Ca	Mg	Na	K
0	31.8	0.00	0.21	0.14	0.00	0.20	0.01	0.12	0.01
1	68.4	0.00	0.85	0.14	0.04	0.54	0.10	0.10	0.01
2	131.0	0.01	1.50	0.20	0.03	0.54	0.18	0.05	0.01
3	142.9	0.02	1.76	0.21	0.12	1.05	0.42	0.11	0.02
4	206.7	0.04	2.24	0.35	0.08	0.92	0.23	0.09	0.02
5	317.3	0.03	2.65	1.53	0.12	2.41	0.64	0.19	0.02
6	443.3	0.06	3.58	3.65	0.41	2.96	0.91	0.56	0.05
7	52.8	0.00	0.63	0.12	0.02	0.39	0.09	0.08	0.01
8	132.3	0.01	1.49	0.34	0.18	1.09	0.21	0.28	0.02
9	121.6	0.01	1.18	0.19	0.09	0.60	0.25	0.14	0.02
10	137.1	0.01	1.35	0.34	0.09	1.11	0.24	0.14	0.02
11	241.7	0.02	3.16	0.55	0.13	1.88	0.49	0.22	0.03
12	204.7	0.02	1.91	0.48	0.28	1.39	0.31	0.26	0.03
13	307.9	0.04	2.33	1.00	0.90	1.85	0.43	1.09	0.04
14	393.2	0.03	3.86	1.68	0.12	2.96	0.99	0.13	0.02
15	314.3	0.03	2.16	1.13	0.28	2.30	0.48	0.32	0.03
16	247.5	0.03	2.21	1.00	0.19	1.43	0.33	0.25	0.03
17	278.9	0.04	3.43	0.45	0.11	2.01	0.72	0.17	0.03
18	296.5	0.02	2.41	0.90	0.25	2.02	0.50	0.28	0.03
19	268.7	0.12	3.01	0.47	0.17	2.13	1.06	0.25	0.05
20	509.1	0.19	4.57	0.95	0.76	2.40	1.16	1.27	0.16
21	284.7	0.02	2.28	0.96	0.28	2.13	0.61	0.71	0.05
22	557.0	0.02	3.04	1.23	2.13	2.50	0.68	2.01	0.12
23	4194.9	0.25	9.37	7.64	43.40	6.08	2.96	31.28	1.34
24	1978.3	0.06	4.16	10.09	12.22	8.49	3.73	7.93	0.10
25	970.0	0.21	6.96	6.17	1.88	4.41	2.78	1.77	0.27
26	360.5	0.04	2.91	1.00	0.84	1.80	0.51	0.88	0.07
27	159.7	0.02	1.76	0.26	0.27	1.04	0.37	0.25	0.02
28	238.7	0.01	2.21	0.30	0.49	0.84	0.27	0.92	0.06
29	262.0	0.02	2.13	0.51	0.45	1.28	0.36	0.53	0.05
30	459.2	0.02	3.20	1.09	0.76	2.47	0.63	0.60	0.07
31	276.7	0.02	2.64	0.83	0.63	1.57	0.46	0.50	0.05
32	270.0	0.01	2.39	0.50	0.69	0.93	0.33	0.39	0.03
33	669.7	0.02	4.44	3.61	0.58	4.54	1.61	0.60	0.07
34	371.2	0.06	4.51	0.40	0.18	3.07	1.41	0.26	0.04
35	387.7	0.07	4.70	0.65	0.23	2.83	1.06	0.23	0.07
36	396.2	0.07	4.66	0.34	0.64	3.12	1.00	0.57	0.09
37	352.0	0.06	2.55	0.91	0.69	1.42	0.39	0.49	0.05
38	401.1	0.03	2.91	0.99	0.81	2.16	0.55	0.66	0.06
40	475.0	0.01	3.96	0.88	2.85	2.05	0.75	1.89	0.18
41	912.7	0.02	5.43	0.85	4.23	2.63	0.91	2.85	0.15
42	968.7	0.07	6.40	1.34	3.64	4.17	1.29	4.43	0.27
44	1224.0	0.03	5.10	10.99	2.06	9.61	2.14	1.89	0.14
45	492.4	0.01	3.15	2.16	0.92	2.49	0.55	0.87	0.16
46	611.4	0.02	3.63	2.52	1.31	3.42	0.74	1.35	0.14
47	683.6	0.02	3.62	3.39	1.56	3.10	0.67	1.37	0.14
48	2384.0	0.12	3.92	7.22	22.19	5.21	4.76	21.30	0.55
49	426.2	0.05	4.74	0.76	0.37	2.70	1.12	0.28	0.05
50	411.9	0.06	4.69	0.70	0.28	2.99	1.15	0.22	0.07
51	244.2	0.01	2.18	0.94	0.04	3.76	0.82	0.10	0.03

the total anions and calcium 60% of the total cations.

Other ions are only important in particular places along the river. Sulphates constitute on the average 24% of the sum

total of anions, and chlorides only 13%. Among cations, magnesium is 20%, sodium 18% and potassium 2%.

To illustrate the differences in relative importance of these ions at each sampling

site they were plotted on a Piper trilinear diagram (fig.3). This diagram confirms the spectrum of variation in the ionic proportion of the river Ter waters and defines the chemical water type. The water type is also noted in table I, which gives the summary statistics of each major ion used for further analysis. Most watershed stations have alkaline-earth bicarbonate waters. The majority of the Ter basin stations plot in the lower left corner of the cation triangle, indicating that the dominant cation is calcium (more than 50%), with sodium and potassium accounting for 10 to 45 and usually less than 30 per cent magnesium. The sampling stations also tend to plot in the

lower left of the anion triangle; but in this case, within the bicarbonate-rich area; there are two point distribution trends (fig.3). There is a dispersion of points from the field occupied in the lowermost corner of the triangle, where it contains waters with greater than 85% bicarbonates, to waters containing more sulphates and chlorides. The sampling points with a greater chloride proportion are those that have undergone the greatest degree of anthropogenic alteration as a result of urban/industrial inputs. In the other side, the sampling points with sulphate-rich waters are due, basically, to geochemical inputs. All fresh water, which is primarily derived from atmospheric

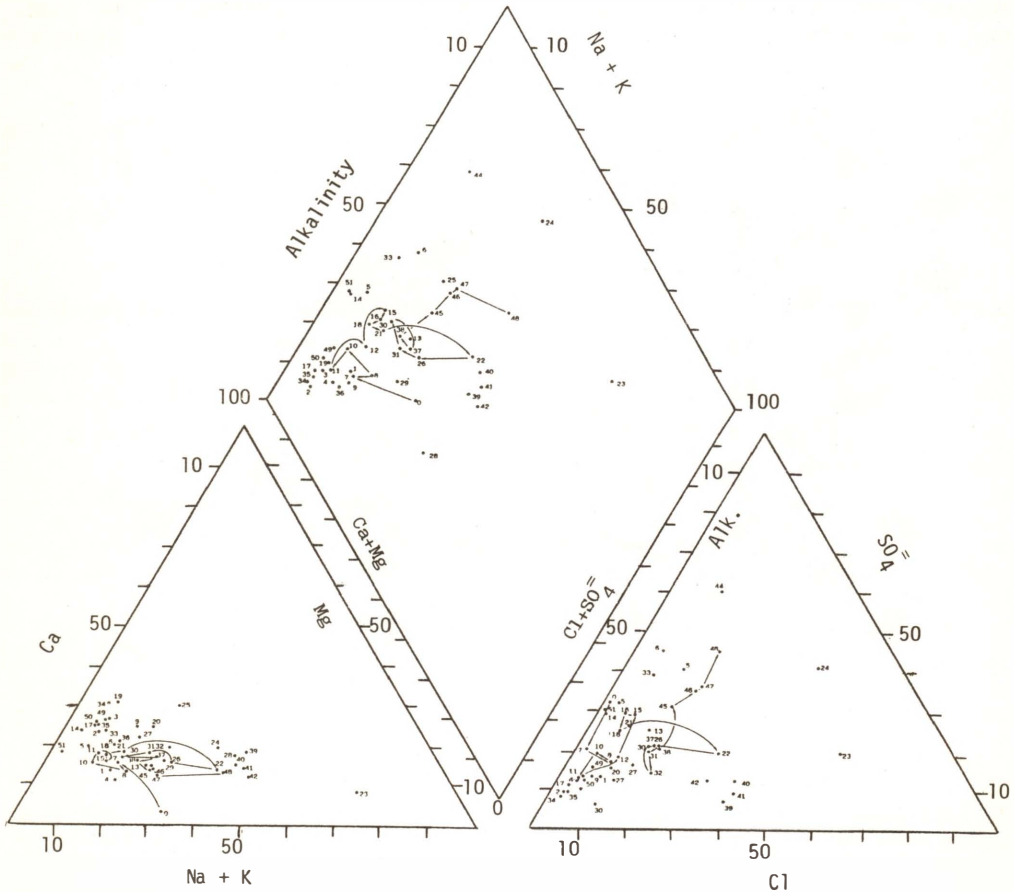


FIG. 3. Relative major ion proportions of each samplingpoints plotted on a Piper trilinear diagram. The arrows indicate the direction of the Ter river channel. *Representación en un diagrama trilineal de Piper de la proporción relativa de los iones mayoritarios en cada punto de muestreo. Las flechas indican el sentido del canal del río Ter.*

precipitation, exhibits an alkaline-earth bicarbonate composition unless influenced by soil, bedrock, or exogenous inputs to the drainage basin. Thus, natural waters will tend to scatter in the lower left corner of the anion triangle. On the upper diamond-shaped portion of the diagram fresh water points lie along the left, whereas the most saline waters are plotted to the right.

SPATIAL VARIATIONS

The spatial variations of the relative chemical composition at each sampling site is illustrated in figure 4 by ionic proportion diagrams (Maucha diagrams). They also show a more or less continuous trend from

calcium dominance to sodium or magnesium relative dominance in cations, and similarly, from highly bicarbonate-dominated waters to chloride-dominated waters in the anions. The conductivity increases from less than 100 uS/cm to more than 1000 uS/cm because of salt accumulation from soil washing and also because of human activity leading to an increase in chloride, sodium and potassium. Most of the parameters (alkalinity, calcium, chloride, sodium and sulphate) are highly correlated to the distance from the mouth.

To establish the broad relationships between water types and the sampling points more clearly, a nonhierarchical cluster analysis was performed on the hydrochemical data. A Stepwise

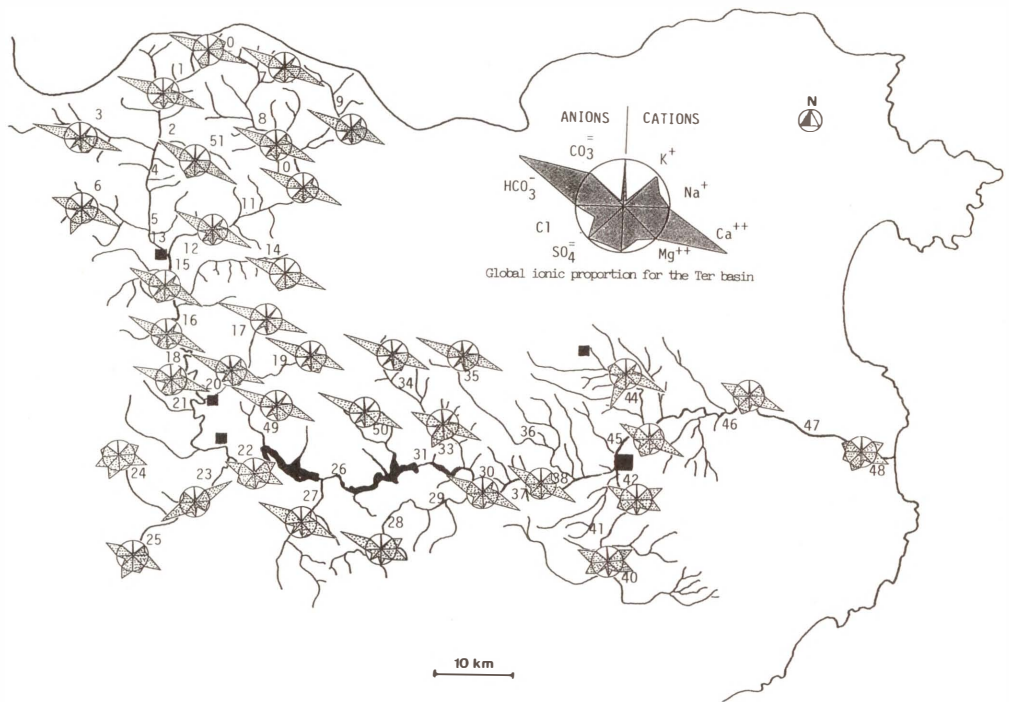


FIG. 4. The average ionic proportion diagram for the Ter river for each sampling point throughout the basin. These diagrams are divided into two fields (anions and cations). Each field represents 100% of either anions or cations. The shaded area in each sector is proportional to the equivalents per cent of that ion. The circumference of the circle represents 25%. The diagram located at the top-right of the figure shows the relative chemical composition for the Ter basin from the mean annual data. *Diagrama de proporción iónica media de cada punto de muestreo en la cuenca del río Ter. Los diagramas se dividen en dos campos (aniones y cationes), representando cada uno de ellos el 100% de unos u otros. El área sombreada en cada sector es proporcional a los equivalentes por ciento de cada ion. La circunferencia del círculo representa el 25%. El diagrama de la parte superior derecha muestra la composición química relativa de la cuenca del Ter según los datos anuales medios.*

Discriminant Analysis program was run in order to classify the different stations according to the average values of the chemical composition of the major ions dissolved in water. The results reveal differences along the river and distinguish mainly between the siliceous watersheds and the calcareous ones.

The goal of this stepwise analysis is to obtain the least variation within the groups and the greatest one among each other. Ten classified groups of sampling stations have resulted in an iterative way from nine discriminant functions. The different sampling points around the group center are plotted in the space defined by the two first canonical axes resulting from this analysis. The first axis accounts for 79% and the second axis explains 13% of the total

variance. The first canonical variable is the linear combination of variables entered that best discriminates among the groups and the second canonical variable is the next best linear combination orthogonal to the first one.

These ten resulting groups of stations are represented all over a map of the Ter basin (fig. 5) and are the following:

Group 1. This group is made up of the most mineralised sites of the Ter basin: 23, 24 and 48. These points have the highest annual mean concentration of chloride (912.4 mg/l), of sodium (463.7 mg/l), of potassium (26 mg/l) and of magnesium (46.4 mg/l). Both sites 23 and 24 are located in the same watershed (in the Gurri river), which drains a region highly affected by intense human land-use, such as

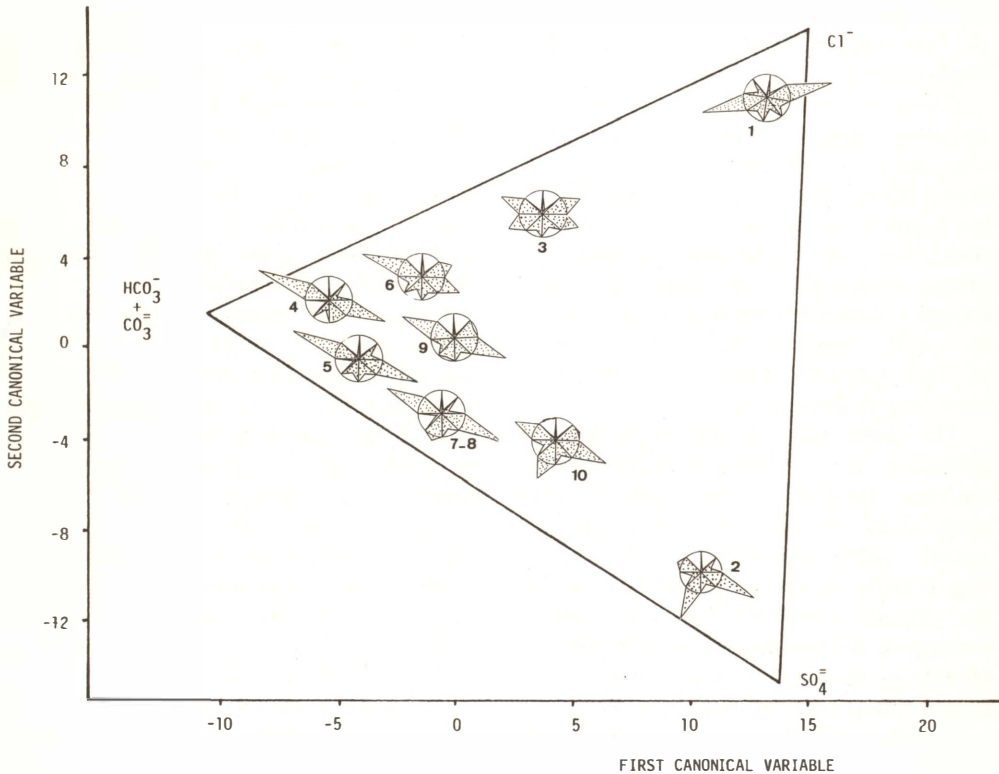


FIG. 5. Each one of the global ionic proportion diagrams, concerning the ten water-type groups classified, are plotted in the new space defined by the two first canonical axes that result from another Stepwise Discriminant Analysis (see text). *Se representan los diagramas de proporciones iónicas globales en el nuevo espacio definido por los dos primeros ejes canónicos resultantes del análisis discriminante paso a paso (ver texto).*

industrialization and agriculture, and the waste waters of Vic city with 40,000 inhabitants approximately. Finally, station 48 is situated in the Ter rivermouth at 1.5 km from the sea. During the summer, this point is influenced by sea water. According to the ionic proportion of each major ion, this group is a sodium and chloride water type which represents 71% and 71.4% of the total cations and anions respectively.

Group 2. This group is made up by the stations 44 (in the Terri river) and 25 (on the tributary of the headwater of the Gurri river). The two watersheds drain over an area of gypseous substratum. The annual mean concentration of sulphates is 412.8 mg/l, that of calcium is 140.4 mg/l, and the mean annual alkalinity values are the highest of the Ter basin (5.5 meq/l). This group is an alkaline-earth sulphate water type because sulphate exceeded bicarbonate as the major ion (63% and 25% respectively).

Group 3- This group is made up by the sampling points situated at the same watershed in the Onyar river basically. Other points, 20 in Ges river after Torelló town, and 22 in the middle stretch of the Ter river after reservoirs are also confined in this group. All these points show a high mean annual of chloride (101.6 mg/l) and sodium (60 mg/l). Therefore, there is clear evidence of anthropogenic alteration of the water chemistry in these localities.

The water type in the Onyar basin is classified as calcium-bicarbonate/sodium chloride because it has almost equal proportions of the two anions and two cations (40% and 48% of chloride and bicarbonate respectively; and both sodium and calcium with 41%). This watershed has undergone a high degree of anthropogenic alterations as a result of urban/agricultural inputs into its small volume flow.

Group 4. All the sites that make up this group (17, 19, 33, 34, 35, 36, 49 and 50) are located in calcareous watersheds. All of these (Ges, Fornes, Gorgues, Brugent and Llémna streams) drain the left side of the

Ter basin. These watersheds have high annual mean alkalinity values (4.2 meq/l) and high calcium concentrations (52 mg/l). The water type of this group is alkaline-earth bicarbonate, where calcium (65%) and magnesium (25%) are the dominant cations and bicarbonate (80%) is the dominant anionic constituent, because most of these streams drain dolomite-rich terrains.

Group 5. This group deals with sampling points located in headwaters and site 27, situated in the Riera Major stream, all of them draining terrains composed predominantly of silicate minerals and a very low percentage of carbonate minerals. This group is typified by very low dissolved loads and all river water samples are very soft with mean annual alkalinity values (1.3 meq/l) and calcium (14.9 mg/l). All these watersheds are essentially non-urbanized and have minimal agricultural or industrial land uses. The water type of this watershed group is alkaline-earth bicarbonate with the calcium and bicarbonate ions accounting for 70 to 78 per cent of the total ionic constituents of the samples. The concentrations of the latter ions were low in all headwater sites because they are underlain by Precambrian terrains.

Group 6. The sampling-points that make up this group (12, 13, 28, 29) receive waters that also drain siliceous soils but present more dissolved solid concentrations than group 5, because these points are underlain by evident and continuous anthropogenic contaminated loadings. The annual mean sodium concentrations (13.1 mg/l) and chloride concentrations (14.4 mg/l) were greater than magnesium (3.8 mg/l) and sulphate (10.1 mg/l) levels respectively. This feature is typical of urbanized or heavily farmed watersheds.

The water chemistry of this group tends to reflect the substratum characteristics of Paleozoic-carbonate in the Riera d'Osor (sites 28 and 29) or of Precambrian-silicate terrains at the sites 12 and 13 in the Ter and Freser headwaters respectively. Therefore,

Table II. Generalized catchment lithology and chemistry of the Ter River Basin, and water-type grouping determined from Stepwise Discriminant Analysis (see text). *Grupos de características litológicas y químicas generales y tipos de agua de la cuenca del río Ter determinados por un análisis discriminante paso a paso (ver texto).*

Group number	sampling points	water type	lithology	Bicarbonate %	land use	Total Dissolved Solids mg/l
1	23, 24 48	sodium chloride	calcareous & marls silts	11	high	668
2	44	alk-sulph.	conglom. & sands	25	high	220
3	40, 41 42, 22	alk. bicarb. sodium-chlor.	silic. sands & conglom.	48	high	136
4	17, 19, 33 34, 35, 36 49, 50	alkaline bicarbonate	calcareous & dolomite	80	low-moderate	72
5	1, 2, 3 4, 7, 8 9, 10, 27	alkaline bicarbonate	Schists & slates crystal. rocks	78	low	21
6	12, 13 28, 29	alkaline bicarbonate	congl. & sands crystal. rocks	72	moderate	42
7	14, 51	bic., sulph.	conglomerates dolom. & gypsums	65	low	75
8	15, 16 18, 21	alkaline bicarbonate	conglomerates calcareous	65	moderate-high	
9	26, 30, 31 32, 37, 38	alkaline bicarbonate	conglomerates sandstones	63	moderate	62

these waters will be typified as alkaline-earth bicarbonate water type; but within an intermediate position between the Precambrian watersheds (group 5) and others, which drain carbonate-rich terrains with moderately dissolved loads.

Group 7. This group is made up by the sites in watersheds draining calcareous rich areas (site 14 in the Riera de Vallfogona and 51 in Segadell stream). However, site 5 is also included in this group but is located in a siliceous watershed (Freser river) close to Campdevànol town. The total dissolved load is lesser than the remaining calcareous basins. All these sites are typified as alkaline- earth bicarbonate / sulphate water type. The mean annual calcium concentration is 61.1 and the sulphate one is

66.2 mg/l. Both the Segadell and the Riera de Vallfogona basins drain an area of chalk lithology.

Group 8. This group is established by the sampling points (15, 16, 18 and 21) located in the high middle stretch of the river Ter, just after the Freser river entrance. This group presents moderate mean annual chloride (8.5 mg/l) and sodium (6.5 mg/l) concentrations. The water chemistry of these stations is weakly affected by agricultural and urban land use activities. Its water type is classified as alkaline-earth bicarbonate.

Group 9. The sampling points (26, 30, 31, 32, 37 and 38) which constitute this group are located in the Ter river just below the reservoirs. These reservoirs have a strong regulatory effect on the lower sector of the

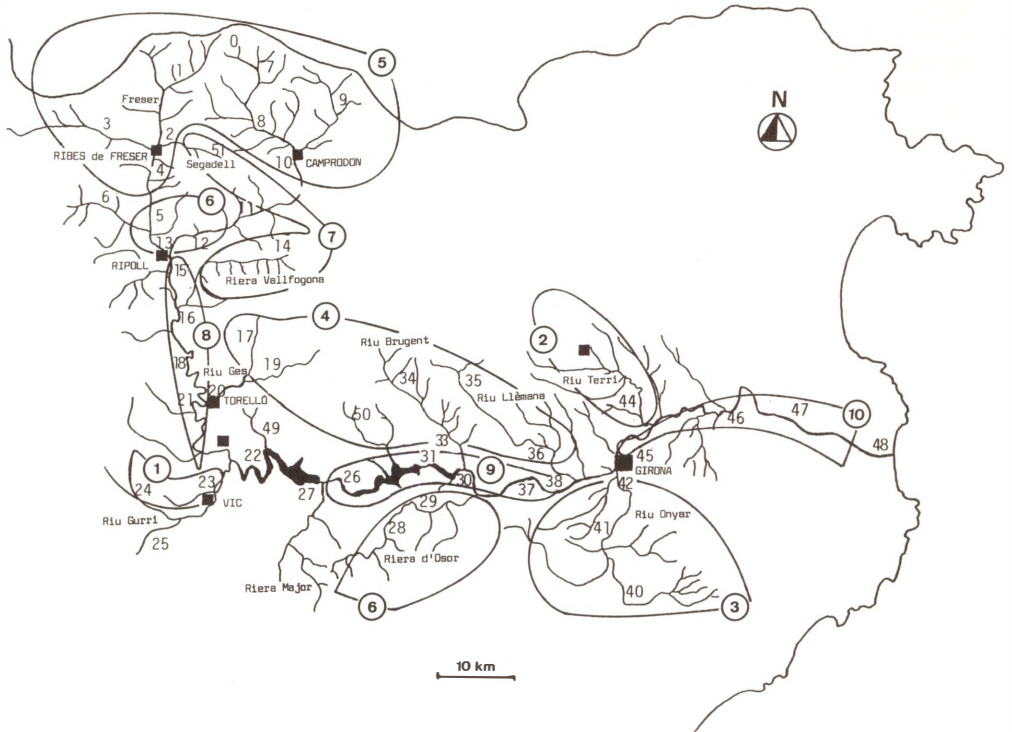


FIG. 6. The ten area-groups of sampling stations resulting from Stepwise Discriminant Analysis are represented all over the Ter basin (see text). *A partir del análisis discriminante paso a paso se obtuvieron diez grupos de puntos de muestreo, los cuales se representan a lo largo de toda la cuenca del Ter (ver texto).*

Ter, but the changes in major ion concentrations were not substantial in comparison to those observed in other compounds (e.g. nutrients) (PUIG *et al.* 1987). In this respect, just below reservoirs sulphates and chloride decreased in concentration whereas bicarbonates increased slightly. Moreover, the mean total dissolved ion concentrations and specific conductance decreased significantly from 550 to 450 uS/cm. This group is classified as alkaline-earth bicarbonate water type with the calcium and bicarbonate ions accounting for 60% to 62% of the total ionic constituents (table II).

Group 10. This is a group of sampling points (45, 46 and 47) situated in the low stretch of the Ter river between Girona city and the river mouth. The intense urban and industrial activity which occurs in this area brings about an increase in chloride and sodium concentrations. The mean annual sodium with respect to the preceding group

changes from 14.7 to 27.5 mg/l and chloride from 23.6 to 44.7 mg/l downstream. However, the water type remains on alkaline-earth bicarbonate.

As a result of the different classified groups, each one of their ionic proportions are plotted in the new space defined by the two first canonical axes that result from another Stepwise Discriminant Analysis (fig.6), but based only on relative values of major ions of each defined group. The first and second axis explains 56% and 34% respectively. The water chemistry data for each group are summarized in table II.

TEMPORAL VARIATIONS

There is a general trend in all sampled stations towards a notable drop in conductivity levels during discharge flow events. This descent of conductivity has been verified by several authors (WALLING & WEBB, 1980; WEBB &

WALLING, 1983; ÀVILA & RODÀ, 1984). Nevertheless, there is a broad range of response when the different linear regression coefficients between the discharge variations and conductivities, or each of the major ions, are represented for each watershed (EDWARDS, 1973).

Therefore, the concentration-discharge relationships associated with individual ions reveal considerable variation in response both between particular solute species and individual stations. For example, chloride and sodium concentrations tend to be more strongly diluted with increasing flow than calcium or magnesium levels, and it has been noted in several sampling points. The latter ions generally exhibit a relatively limited range in their temporal fluctuations. Potassium levels in many tributaries of the upper Ter basin increase during high streamflow. A similar response has been recorded by several authors (HILL, 1980; ÀVILA & RODÀ, 1984). It may be explained by the importance of the leaching

of the vegetation, as a source of this ion during storm runoff events (LIKENS *et al.*, 1977).

WEBB & WALLING (1983) stressed that none of the major ions showed the same response pattern between headwater watersheds (less mineralized waters) and downstream sites, where the river has more inertia (i.e. the water river changes produced are not so sudden).

MCNEELY (1979) considers that the water chemistry composition in watersheds subjected to human activities vary according to seasonal changes. At several sites of the river Ter basin there occur parameters (chloride, sodium, sulphate and potassium) which show a significantly negative correlation with the volume flow. However, the pattern behaviour of these major ions is different at the sampling stations below reservoirs and in the polluted sites. In the latter sites, there are strong fluctuations of the parameters during low flow periods.

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