Pirineos, **147-148**: 41 a 59, JACA; 1996

GEOCHEMISTRY OF THE SURFACE AND GROUND WATERS OF THE UPPER BASIN OF THE RIVER LLOBREGAT

A. FREIXES, M. MONTERDE, J. RAMONEDA

Servei Geològic de Catalunya, Institut Cartogràfic de Catalunya, Parc de Montjuic, 08038 - Barcelona.

RESUMEN.- En el presente estudio se presentan y discuten las principales características geoquímicas de las aguas superficiales y subterráneas de la Alta cuenca del río Llobregat hasta la entrada del río al embalse de La Baells. El conjunto de aguas analizadas presentan características muy contrastadas. Así, tanto en la subcuenca de las fuentes del Llobregat como en la del río Bastareny predominan las aguas bicarbonatadas cálcicas poco mineralizadas. En la subcuenca del río Arija, si bien las aguas del curso alto y las de los principales afluentes también son bicarbonatadas cálcicas, destaca el hecho de que en la confluencia con el río Llobregat el agua es sulfatada cálcica. La subcuenca del río Saldes es la que presenta una mayor heterogeneidad, con aguas bicarbonatadas cálcicas, cloruradas sódicas y sulfatadas cálcicas, las cuales provocan que en la confluencia con el río Llobregat el agua sea bicarbonatada-sulfatada sódico-cálcica. El análisis de componentes principales ha permitido sintetizar estas características de forma muy clara. Los resultados se interpretan, esencialmente, a partir de las litologías drenadas por los distintos cursos de agua.

SUMMARY.- In this workthe main geochemical characteristics of the surface and ground waters of the Upper basin of the River Llobregat are described and discussed. The water samples analysed reveal sharply contrasting characteristics. In both the Fonts del Llobregat and River Bastareny catchments, calcium bicarbonated waters with a low mineral content clearly predominate. However, in the catchment of the River Arija, although the waters of the upper course and the main tributaries are also calcium bicarbonated, it is worth noting that at the confluence with the River Llobregat calcium sulphated water is found. The catchment of the River Saldes shows a greater heterogeneity, with calcium bicarbonated, sodium chloridized and calcium sulphated waters, and thus at the confluence with the River Llobregat the water is sodium-calcium bicarbonated-sulphated. Principal components analysis enables us to arrive at a synthesis which clearly explains these characteristics. These results are fundamentally interpreted on the basis of the lithologies drained by the different watercourses.

RESUMÉ.- Cette étude présente et discute des principales caractéristiques géochimiques des eaux superficielles et souterraines du haut-bassin du fleuve Llobregat *(le point le plus en aval considéré se situe juste avant l'entrée du cours d'eau dans le lac de La Baells). L'ensemble des eaux analysées présente des caractéristiques trés contrastées. Dans les sous-bassins des sources du Llobregat et du Bastareny prédominent des eaux bicarbonatées calciques peu minéralisées. Dans les sousbassin de la rivière Arija, sur son cours supérieur ainsi que ses principaux affluents, les eaux sont également bicarbonatées calciques, exceptées celles de la confluence avec le Llobregat qui sont sulfatées calciques. Le sous-bassin de la riviere Saldes est celui qui présente la plus grande hétérogénéité, avec des eaux bicarbonatées calciques, chlorurées sodiques et sulfatées calciques. Ces dernières sont responsables du fait qu'à la confluence avec la Llobregat les eaux soient bicarbonato-sulfato sodico-calciques. L'analyse en composantes principales a permis de discriminer nettement ces caractéristiques. Ces résultats sont essentiellement expliqués à partir de la lithologie des différents bassins versants drainés.*

Key-words:

1. Introduction

When studying the chemical properties of the water of a river, it is essential to remember that its hydrogeochemical characteristics are the result of the spatial and temporal integration of all the water flows that carry rainwater to the river. It is therefore evident that one cannot seek to explain the chemistry of the water of a river by referring solely to the dissolution processes in the river-bed (WALLING and WEBB,1986). In fact, much of the interaction between rainwater and the substratum takes place in the ground (DREVER, 1982). A number of authors have undertaken to study the influence of lithology on the chemical quality of continental waters. In this respect, MEYBECK (1984) analyses the geochemical characteristics of waters with reference to lithology on the basis of the concentrations of the major elements and the ionic relationships Ca^{2+}/Mg^{2+}, Ca^{2+}/Na^{+} and SiO_2/Σcations.

Various studies have been made of the River Llobregat and its tributaries which have made it possible to define the main limnological characteristics of the basin as a whole (GONZALEZ et al. 1985; MUÑOZ and PRAT 1992, 1994; PRAT et al. 1984).

The aim of this work is to define the geochemical characteristics of the surface and ground waters of the Upper basin of the River Llobregat, and to attempt to establish a possible link with the lithological nature of the different catchments concerned, and also the role played by human activities.

This characterization has been based on the major elements. The sampling points extend from the sources of the Bastareny and Llobregat rivers, which provide the most important volumes of groundwater to the basin, to the entrance of the river to the Baells reservoir.

This research has been undertaken with the support of the Lucdeme Project: "Dynamics of degraded geosystems in mountainous areas: Upper Llobregat Basin. Evolutionary action of the natural and human processes of degradation. Quantification of these in order to propose guidelines for their control", and within the framework of the collaboration between the "Jaume Almera" Earth Sciences Institute of the C.S.I.C. and the Geological Survey of the Autonomous Government of Catalonia (FREIXES, 1988, 1989, 1990). Dr. Núria Clotet, the director and coordinator of the project, died while the research was in progress, and we dedicate this work to her memory.

2. Area studied

Geochemical analysis was undertaken in the Upper basin of the River Llobregat, that is to say, in the catchments of the Llobregat, Arija, Bastareny and Saldes rivers as far as the Baells reservoir (figure 1). This basin has been the focus of studies concerned with erosive processes and the quantification of the flux of solids into the river (CLOTET, 1984 a) and b); CLOTET and GALLART, 1986; BALASCH et al., 1992; CASTELLTORT, 1995).

In terms of its structure, the Upper basin of the River Llobregat is situated between two important geological units: the Cadí thrust sheet and the Southern Pyrenean unit. In the Cadí thrust sheet, situated further north, Palaeozoic and Tertiary materials can be observed in particular; although the proportion of Mesozoic materials is smaller, the garumnian facies can be found with important outcrops.

The Southern Pyrenean unit, situated to the south of the Cadí thrust sheet, is mainly composed of Mesozoic and Tertiary lithologies, with an important development of the garumnian materials.

The catchments of the Bastareny and the Llobregat rivers have mainly developed in material belonging to the Cadí thrust sheet. The River Bastareny, however, crosses the Southern Pyrenean unit from Bagà village, and from Guardiola de Bergadà village, where it meets the Llobregat river, the watercourse develops in the Cretaceous limestones of the South Pyrenean unit and flows to the Baells reservoir.

The hydrographic basin of the head of the River Llobregat is situated on the southern slopes of the Eastérn Pyrenees (figure 1); to the N-NW of the basin lies the Cadí-Moixeró range, to the N-NE the relieves of Tosa d'Alp, Puigllançada and PletaRoja, to the W-SW the Pedraforca massif and the ranges of Ensija and Serrat Negre, to the south the Baells reservoir, to the south-east the Catllaraàs range, to the east the col of Merolla and to the north-east the Barraca range. The total area of the basin is about 345 km^2.

The following is a description of the main catchments which contribute to the basin:

The **catchment of the River Arija** drains the waters of the western part of the Mogrony range, the relieves of Pedra Picada and Emperadora, the southern and eastern slopes of the Meranges range, the north-west area of the Tubau plains, the northern slopes of the Fajabranca range and the eastern slopes of the Catllaras range. The Arija system evolved principally in Tertiary materials, to be exact in marls, gypsums and limestone intercalations of the Ilerdian-Cuisian period (Sagnari formation), marls, red sandstones and limestones of the Cuisian period (Corones formation), marls and marly-calcareous material (Armàncies formation) and in Cuisian-Lutetian turbidites (Campdevànol formation); notwithstanding this, the highest part of the head is situated in Devonian limestones, in the foothills of the Mogrony range; it crosses Permian sandstones and lutites, as well as the entire group of Mesozoic materials formed by Buntsandstein sandstones and lutites, and limestones and arkosic sandstones of the Late Cretaceous; but above all, mention should be made of the versicoloured clays and Keuper evaporites (gypsums) which constitute an important outcrop crossed east to west by the River Arija just before Pobla de Lillet village.

The River Arija runs for 12.1 km before it joins the River Llobregat at Pobla de Lillet and its basin covers an area of 50.3 km^2.

The **catchment of the River Bastareny** is bordered to the north by the relieves of Moixeró, la Moixa and Molnells, to the W-NW by the Muga, Comabona and the Pedregosa ranges, and to the south by the Gisclareny range. The River Bastareny receives a notable volume of ground water through the Adou del Bastareny karstic system, whose main outflow points are the Adou spring and its own important overflow points, in addition to other permanent springs in the same system, such as the Bullidor de Sant Esteve spring and the Violí spring (FREIXES et al., 1995). The nature of the materials of the Bastareny basin is relatively comparable to that observed in the case of the River Arija. Tertiary materiais predominate throughout most of the watercourse from the Muga and Murcurols streams and from Adou spring. The lithological units are: marls and marlycalcareous material of the Sagnari formation (Ilerdian-Cuisian), marls, limestones and red sandstones of the Corones formation (Late Ilerdian-Early Cuisian), limestone and marly-calcareous materials of the Penya formation (Cuisian) and calcareous sandstones, marls and lutites of the Armàncies formation (Cuisian); the southern slopes of the relieves of La Moixa, Moixeró and Tosa d'Alp are also drained by tributaries of the

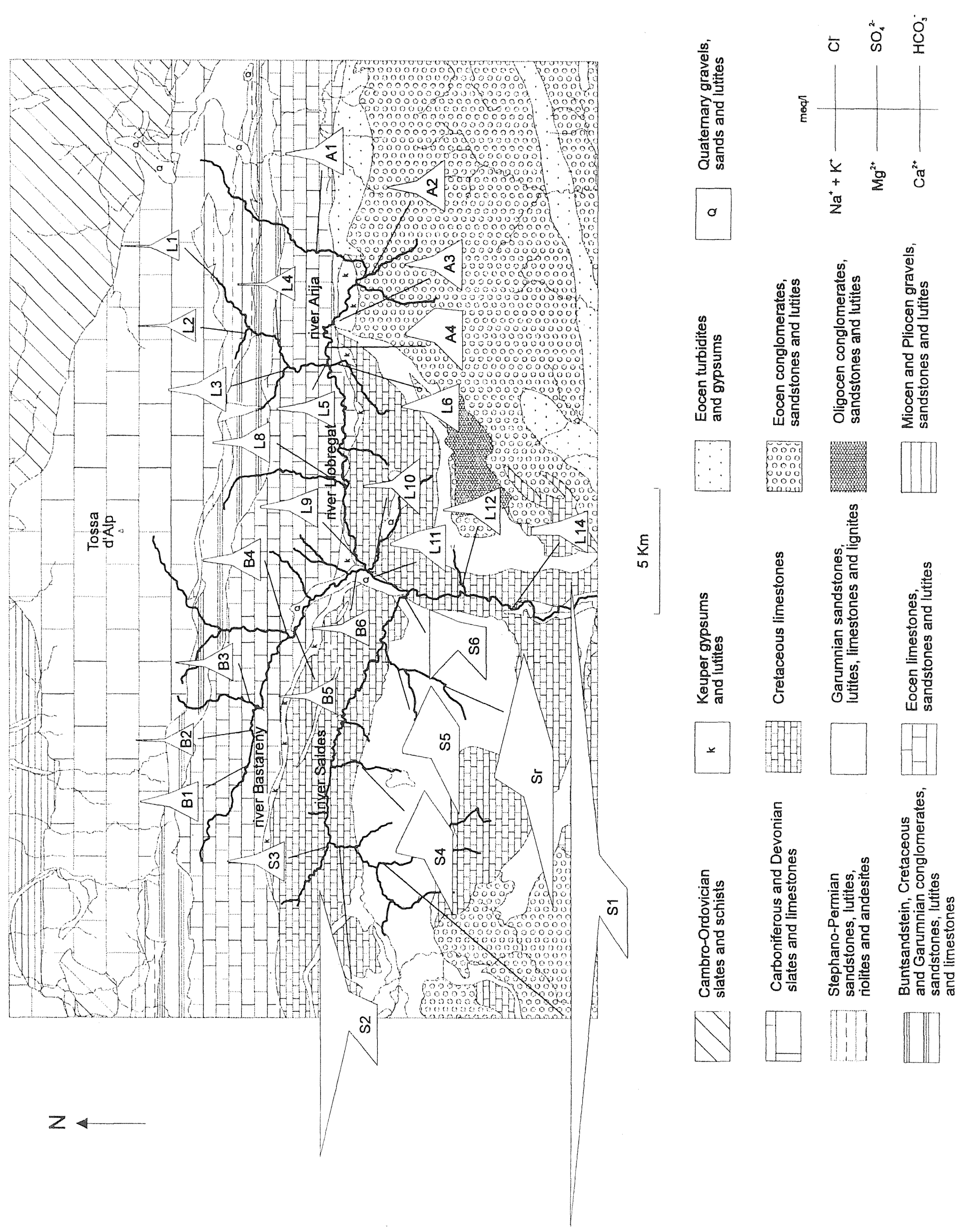


Fig. 1. Geological map of the Upper Llobregat basin, showing the location of the water points studied in the hydrographic network, with the corresponding Stiff diagrams.
Mapa geológico de la cuenca del Alto Llobregat, con la situación de los puntos estudiados en la red hidrográfica y los correspondientes diagramas de Stiff.

Bastareny river: the Pradell, Molnells, Font del Faig and Gréixer streams, generally flowing N to S. The Pradell and Molnells streams have their own basin in Tertiary materials. The Font del Faig and Gréixer streams have their heads in Palaeozoic, Mesozoic and Garumnian materials (Devonian limestones, Carboniferous slates, Cretaceous limestones, and limestones, sandstones and lutites of the Garumnian period); however, the drainage channel of both these streams crosses the different Tertiary units. To be precise, the Gréixer stream rises in the southern foothills of Tosa d'Alp; the head is located in Devonian limestones and Carboniferous slates, and downstream it cuts through Stephano-Permian riolites, Buntsandstein sandstones and lutites, Cretaceous limestones (Santonian mid-Campanian) and materials of the garumnian facies (which is notably developed: conglomerates, sandstones, lutites and limestones); before reaching the Bastareny, the Gréixer stream cuts through Tertiary units: limestones of the Cadí formation and marly-calcareous materials, limestones and *marls of the Sagnari, Corones and Armàncies formations.*

The relief of the Cadí range is largely drained below the surface by the Adou del Bastareny karstic system. The karstified materials are mainly limestones and marly-calcareous of the Armàncies and Penya formations.

The River Bastareny runs 14.8 km to join the River Llobregat at Guardiola de Bergueda village; its basin covers an area of 79.2 km^2.

The **catchment of the River Saldes** is surrounded to the north by the Gisclareny range and the cliffs of Gresolet and La Bola, to the west by the Pedraforca massif, and to the south by the Ensija range and the cliffs of Vallcebre. The basin has mainly developed in Mesozoic and early Tertiary lithologies, which may be summarised as follows: versicoloured clays and Keuper evaporites, Cretaceous limestones (Santonian mid-Campanian) and limestones, conglomerates, sandstones and lutites with intercalations of Garumnian lignites.

The River Saldes, which flows into the River Llobregat at Collet, is 19.2 km long and has a basin of 102 km^2.

The **catchment of the sources of the River Llobregat** drains the southern slopes of the Barraca, Rus and Puigllançada ranges, the Catllaras range and the ranges of Colobre and Falgars. This catchment mainly receives groundwater flow originating from the karstic system that has been given the name of its main oufflow point: the Llobregat springs, the source of this river course. In this catchment, the river cuts through Palaeozoic, Mesozoic and Tertiary materials; the head is located mainly in Devonian limestones (Monell and Fontetes streams), while downstream the river crosses Permian sandstones and lutites, Buntsandstein conglomerates, sandstones and lutites,

Table 1. *Description of the stations sampled in each catchment of the Upper Llobregat.*

- CATCHMENT OF THE RIVER ARIJA:
  - .A1 = River Arija at Coll de Merolla. 3 samples 1988-89.
  - .A2 = Solls stream, which drains the northern slopes of the eastern sector of the Fajabranca range. 3 samples 1988-89.
  - .A3 = Junyent stream, which drains the northern slopes of the Fajabranca range (Puig Lluent) and the eastern part of the Catllaràs massif. 3 samples 1988-89.
  - .A4 = River Arija total. 24 samples 1588-89, 14 samples 1989-90.
- CATCHMENT OF THE RIVER BASTARENY:
  - .B1 = Murcurols stream, which drains the Murcurois terrace and the northern slopes of Estoselles. 3 samples 1988-89.
  - .B2 = L'Adou spring (spring of the river Bastareny). 24 samples 1988-89, 20 samples 1989-90.
  - .B3 = Font del Faig stream, which drains the terrace of the Font dei Faig, between the Moixeró peak and the col of Pendís, and the eastern sector of the Cap de la Boixassa. 3 samples 1988-89.
  - .B4 = River Gréixer, which drains the southern sector of the relief comprising the peaks of Moixeró, Penyes Altes de Moixeró, Pedró dels Quatre Batlles and Serrat Gran. 3 sam ples 1988-89.
  - .B5 = River Bastareny before Bagà village. 3 samples 1988-89.
  - .B6 = River Bastareny total. 24 samples 1988-89, 14 samples 1989-90.
- CATCHMENT OF THE RIVER SALDES:
  - .S1 = Salada stream, which drains the northern sector of the Ensija range. 3 samples 1988-89.
  - .S2 = Upper course of the River Saldes. 3 samples 1988-89.
  - .S3 = Gresolet stream, which drains the northern slopes of the Pedraforca massif, the cliffs of Gresolet and La Bola, and the southern slopes of the Pedregosa range. 3 samples 1988-89.
  - .S4 = Esquers stream, which drains the northern slopes of the Costa Freda cliffs and the range of Mata-Rodona. 3 samples 1988-89.
  - .Sr = Tributary of the Vallcebre stream at Cal Rodó, which drains the eastern slopes of the Conangle cliffs. 16 samples 1988-89.
  - .S5 = Vallcebre stream, which drains the ranges of Sant Joan, Boixeder and Serrat Negre and part of the range of MataRodona. 26 samples 1988-89.
  - .S6 = River Saldes total. 24 samples 1988-89, 14 samples 1989-90.
- CATCHMENT OF THE SOURCES OF THE RIVER LLOBREGAT:
  - .L1 = Llobregat springs. 24 samples 1988-89, 20 samples 1989-90.
  - .L2 = Monell stream, which drains the southern slopes of the Orriols and Rus hillocks, and the eastern slopes of Puig Llançada. 3 samples 1988-89.
  - .L3 = Molina stream, which drains Puig Roig and Montderm. 3 samples 1988-89.
  - .L4 = Combined waters of Llobregat spring and the stream of Monell. 3 samples 1988-89.
  - .L5 = Rivers Llobregat and Arija total. 24 samples 1988-89. 14 samples 1989-90.
  - .L6 = Regatell stream, which drains the northern sector of the Catllaràs massif. 3 samples 1988-89.
  - .L8 = Riutort, which rises at Col of Pal and drains the S and SW sectors of Puig Llançada. 3 samples 1988-89.
  - .L9 = River Llobregat total at Guardiola. 24 samples 1988-89, 14 samples 1989-90.
  - .L10 = Sant Julià de Cerdanyola stream, which drains the westem sector of the Catllaràs range. 3 samples 1988-89.
  - .L11 = Rivers Llobregat and Bastareny total. 23 samples 1988-89, 14 samples 1989-90.
  - .L12 = Malanyeu stream, which drains the Solana Gran and the southem slopes of the Malanyeu cliffs. 3 samples 1988-89
- UPPER LLOBREGAT BASIN TOTAL:
  - .L14 = River Llobregat just before Baells reservoir. 24 samples 1988-89, 14 samples 1989-90.

Cretaceous arkosic sandstones (Coniacian-Early Santonian) and also an important Garumnian outcrop with limestones, conglomerates, sandstones and lutites (Clot del Moro). In the final course, running to la Pobla de Lillet village, it crosses Tertiary marly-calcareous materials, limestones and marls of the Sagnari, Corones and Armàncies formations.

In the course from la Pobla de Lillet to Guardiola de Berguedà villages, the River Llobregat crosses the turbidites of the Campdevànol formation, Jurassic and Cretaceous limestones and Keuper versicoloured clays and evaporites.

Between Llobregat springs and the Baells reservoir the river runs for 14.7 km, and its basin covers an area of 113.2 km^2 (this figure does not include the areas of the catchments of the main tributaries).

The average volume of water in the River Llobregat where it passes the Collet station is 167.5 hm^3 (average taken over the period 1975-1990) (JUNTA D'AIGÜES, 1995).

3. Methodology

In order to make a geochemical characterization of the waters of the Upper Llobregat basin, samples were taken at 29 points dotted among the four catchments between June 1988 and December 1990 (table 1, figure 1). Of these 29 points, there were 11 from which samples were taken fortnightly during the 1988-89 cycle and then monthly during the 1989-90 cycle: these were the two main karstic springs (L1- Llobregat springs and B2-Adou del Bastareny spring), the totals for each catchment (A4-River Arija catchment total, L5-rivers Llobregat and Bastareny total, L9-sources of the River Llobregat catchment total, B6-River Bastareny catchment total, L11-rivers Llobregat and Bastareny total, S6-River Saldes catchment total and L14-Upper Llobregat basin total), and the two most noteworthy inflows from a geochemical point of view (S5-Vallcebre stream, tributary of the River Saldes, and Sr-stream at Cal Rodó, tributary of the Vallcebre). Three samples were taken from each of the remaining points during the same period.

With each sampling the water temperature, conductivity, pH and alkalinity (TAC) were measured in the field. The remaining major ions (calcium, magnesium, chlorides, sodium, potassium and sulphates), the nitrates and the total hardness (TH) were analysed in the laboratory using Standard Methods methodology.

To present the geochemical characteristics, we have used modified Stiff diagrams and tables with the basic statistics (mean, deviation and range) corresponding to each point where water was sampled.

4. Results and discussion

4.1. *Geochemical characteristics*

4.1.1. Catchment of the River Arija (figure 1; table 2)

Both the middle course of the river (A1) and the two main tributaries (A2 and A3) contain calcium bicarbonated water with a relatively low level of mineralization. On the other hand, water from the point representing the total of the catchment (A4) is calcium sulphated, with significantly higher concentrations of chlorides, sodium, calcium, magnesium and sulphates than water from the aforementioned points; thus the global mineralization of the water, expressed as electrical conductivity, is also markedly higher. This is due to the fact that in its lower course the River Arija crosses evaporitic levels (Keuper gypsums in this case) which bring about a change in its geochemical characteristics. Since the gypsums are much more soluble than the limestone materials, the water at point A4 is more highly mineralized than at the remaining catchment stations.

4.1.2. Catchment of the River Bastareny (figure 1; table 3)

The geochemical characteristics of the water from the points studied are very homogeneous: all the samples are calcium bicarbonated with a low level of mineralization. The only barely appreciable differences are found in the concentration of sulphates, which is higher at B1 (Murcurols stream) and B4 (River Gréixer) than at the remaining sampling points. This is explained by the passage of these two tributaries through substrata with more soluble materials, in this case Keuper gypsums. In this catchment the role of the ground waters is very important, due to the volume of water they bring to the river (15-18 hm^3 a year) and to the geochemical characteristics, clearly calcium bicarbonated, they give the water. In fact, the main inflow to the catchment comes from the Adou karstic system, which drains into the River Bastareny through several permanent outlets (three of which are of special importance: the Adou spring (B2), the Bullidor de Sant Esteve spring and the Violí spring), and through numerous overflow points of a temporary nature (Freixes et al., 1995). There are other springs belonging to small hydrogeological units that are totally independent of the Adou karstic system; the most important of these are the Faig spring and the Bullidor de la Llet spring, which drain into the area of the Font del Faig stream (B3).

4.1.3. Catchment of the River Saldes (figure 1; table 4)

The most notable feature is the great geochemical heterogeneity of the different tributaries of the River Saldes, clearly linked with the different lithological substrata that make up the catchment. The waters of the Salada stream (S1) are sodium chloridized with high concentrations of sulphates and potassium, and they impose these characteristics on the water in the upper course of the river (S2); it is therefore clear that this stream drains highly soluble evaporitic material, where sodium chloride salts (halites) are present. The Gresolet stream (S3), which drains terrain which is basically limestone and marly-calcareous, provides calcium bicarbonated waters with a low level of mineralization and relatively high sulphate levels. The water of the Esquers- (S4), Vallcebre (S5) and Cal Rodó (Sr) streams is calcium sulphated and highly mineralized, originating in Keuper and Garumnian gypsums.

The extremely diverse geochemical characteristics of these main tributaries have the effect that the water of the lower course of the river (S6), just before it joins the River Llobregat, is sodium-calcium chloridized-sulphated with a high level of mineralization (giving conductivity readings of between 700 and 1,700 µS/cm at 20° C).

4.1.4. Catchment of the sources of the River Llobregat (figure 1; table 5)

All the water from the points included in this catchment is calcium bicarbonated with a low level of mineralization, except for that of the Regatell stream (L6) and the River Llobregat after the confluence with the River Bastareny just outside Guardiola de Berguedà village (L11), which have a comparatively higher concentration of sulphates, due to their passage through Keuper evaporitic materials. Karstic waters also play a very important role in this catchment: the most significant in terms of volume are the waters that come from the karstic system of Llobregat springs (L1), which provide some 25 hm^3 a year; there are also some notable springs related to the streams of Monell, la Molina, Riutort and Sant Julià de Cerdanyola, although these are considerably smaller in volume.

4.1.5. Upper Llobregat basin total: River Llobregat just before the Baells reservoir (figure 1; table 6)

Overall, the water that arrives at the Baells reservoir (L14) is calcium bicarbonated with a relatively low level of mineralization (between 300 and 700 µS/cm at 20° C) and of some significance with respect to chloride, sodium and sulphate concentrations. At all events, the mineralization of the water at this point is higher than upstream; this is due, at least in part, to the fraction of water in the River Saldes which flows into the River Llobregat (although before joining the River Llobregat part of the water in the River Saldes is channeled to Berga to supply industries), and also to its passage through Keuper gypsums.

Table 2. *Geochemical characteristics of the waters of the River Arija catchment.*

		COND (µS 20°)	pH	Cl^- (mg/l)	Na^+ (mg/l)	k^+ (mg/l)	Ca^{2+} (mg/l)	Mg^{2+} (mg/l)	HCO_3^- (mg/l)	SO_4^{2-} (mg/l)	NO_3^- (mg/l)	n
	mean	400	8.21	3.2	4.0	1.1	72.9	13.9	233	43.4	1.4	
A1	deviation	99.1	0.16	0.4	1.1	0.2	10.6	7.6	46.2	17.1	1.1	3
	range	286-462	8.02-8.30	2.7-3.4	3.3-5.2	0.9-1.3	61-81	5.8-20.9	182-271	24.2-57.0	0.2-2.3	
	mean	439	8.32	2.9	2.9	0.6	83.4	13.2	259	54.5	0.8	
A2	deviation	20.8	0.08	1.0	1.1	0.1	4.2	2.9	28.2	21.0	0.8	3
	range	426-463	8.22-8.37	2.2-4.1	2.0-4.1	0.5-0.6	79-86	10.7-16.3	227-276	42.0-78.7	0.0-1.6	
	mean	452	8.20	2.9	4.0	0.8	86.8	11.0	232	73.5	0.8	
A3	deviation	66.6	0.12	0.2	1.8	0.2	11.6	2.3	19.8	44.2	0.5	3
	range	377-505	8.10-8.34	2.7-3.1	2.4-6.0	0.6-0.9	79-100	8.5-13.1	210-248	32.5-120.3	0.4-1.4	
	mean	777	8.22	10.0	11.7	2.1	160.1	25.8	201	325	1.1	
A4	deviation	137.5	0.14	3.1	3.1	0.8	36.2	8.8	27.5	123.4	0.8	38
	range	560-1042	7.78-8.52	4.9-15.6	4.1-17.2	1.0-5.1	110-229	12.2-60.1	154-280	135-638	0.0-3.9	

Table 3. *Geochemical characteristics of the waters of the River Bastareny catchment.*

		COND (µS 20°)	pH	Cl^- (mg/l)	Na^+ (mg/l)	k^+ (mg/l)	Ca^{2+} (mg/l)	Mg^{2+} (mg/l)	HCO_3^- (mg/l)	SO_4^{2-} (mg/l)	NO_3^- (mg/l)	n
	mean	358	8.31	2.7	2.4	0.8	68.8	11.3	181	64.7	0.5	
B1	deviation	46.0	0.09	1.7	1.3	0.2	7.5	1.6	25.8	29.9	0.2	3
	range	312-404	8.21-8.38	1.3-4.6	1.4-3.9	0.5-0.9	60-73	10.2-13.1	161-210	42.0-98.6	0.3-0.6	
	mean	253	7.92	1.8	1.7	0.3	51.5	6.6	174	14.1	1.0	
B2	deviation	19.0	0.13	1.1	0.9	0.1	4.5	1.8	15.2	3.2	0.7	44
	range	212-287	7.72-8.24	0.7-5.3	0.7-4.0	0.2-0.6	45-65	3.2-9.5	150-215	9.7-24.3	0.0-4.5	
	mean	294	8.48	2.2	1.1	0.5	62.5	8.7	178	23.5	1.8	
B3	deviation	31.0	0.05	0.4	0.4	0.1	14.3	4.4	24.5	7.9	1.6	3
	range	263-325	8.44-8.54	1.8-2.6	0.8-1.5	0.4-0.6	48-77	4.3-13.1	155-204	18.4-32.6	0.6-3.6	
	mean	385	8.35	5.3	5.2	0.8	71.3	10.9	196	53.7	2.9	
B4	deviation	72.9	0.02	2.4	1.8	0.3	16.4	1.0	18.2	24.0	1.8	3
	range	327-467	8.34-837	3.5-8.0	3.4-6.9	0.4-1.1	60-90	9.7-11.7	183-217	39.0-81.4	1.2-4.7	
	mean	287	8.46	2.4	1.5	0.4	58.6	6.0	167	26.4	1.4	
B5	deviation	26.2	0.06	0.3	0.2	0.1	6.5	2.1	25.3	5.5	1.0	3
	range	259-311	8.40-8.51	2.1-2.7	1.4-1.7	0.3-0.5	51-64	3.7-7.5	144-194	21.5-32.3	0.7-2.5	
	mean	309	8.44	4.4	4.0	0.7	59.2	9.3	191	34.4	1.9	
B6	deviation	22.2	0.12	1.8	1.5	0.2	4.4	2.0	11.5	9.0	0.7	38
	range	263-360	8.24-8.79	1.3-10.8	1.7-8.0	0.3-1.3	51-72	6.1-16.3	170-226	24.3-77.0	0.5-3.7	

Table 4. *Geochemical characteristics of the waters of the River Saldes catchment.*

		COND (µS 20º)	pH	Cl^- (mg/l)	Na^+ (mg/l)	k^+ (mg/l)	Ca^{2+} (mg/l)	Mg^{2+} (mg/l)	HCO_3^- (mg/l)	SO_4^{2-} (mg/l)	NO_3^- (mg/l)	n
	mean	3161	8.30	1994	1260	35.2	178.3	17.6	175	439.3	0.5	
S1	deviation	210.9	0.10	1046.6	600.8	17.0	49.8	10.1	28.8	207.9	0.6	3
	range	3000-3400	8.19-8.38	957-3050	745-1920	16.6-50.0	135-233	10.7-29.2	145-203	243-657	0.0-1.1	
	mean	2650	8.36	833	518	14.4	137.9	9.9	196	284.6	1.4	
S2	deviation	905.3	0.04	444.1	285.5	5.1	26.8	4.1	32.2	98.5	0.3	3
	range	1616-3300	8.33-8.40	403-1290	247-816	8.8-18.6	117-168	7.3-14.6	173-233	181-378	1.2-1.7	
	mean	349	8.38	2.9	2.0	0.6	69.7	7.2	179	53.8	0.7	
S3	deviation	16.1	0.07	1.0	0.5	0.2	5.7	0.6	27.3	3.6	0.5	3
	range	332-364	8.33-8.46	2.0-3.9	1.6-2.5	0.4-0.8	64-75	6.6-7.8	160-210	50.5-57.6	0.4-1.3	
	mean	973	8.24	2.8	11.2	0.7	222.9	19.1	170	495.6	0.2	
S4	deviation	205.9	0.09	1.5	5.0	0.1	50.8	4.9	37.9	146.5	0.2	3
	range	830-1209	8.15-8.32	1.7-4.5	7.8-16.9	0.6-0.9	176-277	13.4-21.9	128-201	398-664	0.0-0.4	
	mean	1065	8.23	4.8	18.3	2.1	244.8	25.2	231	535	2.7	
S5	deviation	135.3	0.09	1.1	4.9	0.9	34.6	8.2	38.6	109.5	1.2	26
	range	704-1336	8.07-8.41	1.3-6.7	9.9-28.0	0.8-3.8	152-301	12.2-51.0	194-399	275-774	0.8-4.9	
	mean	1613	8.00	3.8	7.3	1.5	440.4	42.3	249	974.4	2.5	
Sr	deviation	517.8	0.13	1.0	1.6	0.7	90.0	14.0	33.6	221.3	1.0	16
	range	928-2082	7.67-8.31	1.1-4.7	4.8-10.8	0.6-3.1	224-568	14.6-68.0	214-362	407-1281	1.3-5.3	
	mean	1148	8.26	208.3	146.2	6.1	119.3	4.8	188	202.5	1.3	
S6	deviation	230.4	0.13	79.3	53.4	2.3	18.8	4.3	29.4	44.6	0.7	38
	range	731-1681	7.95-8.48	81-387	57-260	2.4-11.8	80-172	7.3-24.3	144-310	105-302	0.0-3.1	

Following analysis of the variation in the concentration of some major ions in the water along the course of the River Llobregat, certain observations may be made:

It can be noted that the concentration of sulphates shows a marked increase at the point corresponding to la Pobla de Lillet village (L5), at the station situated just after Guardiola de Berguedà village (L11) and just before the reservoir (L14); in the first case, this increase is mainly due to the incorporation of water from the River Arija and possibly to the effect of a certain volume of waste water. In the second case, the increase in the concentration of sulphates coincides with the river's passage through Guardiola, which suggests the incorporation of a significant fraction of waste water; furthermore, it should be pointed out that at this sampling point the water from the River Bastareny, which has a low sulphate content, has already joined the River Llobregat. Finally, the increase detected just before the reservoir appears to be attributable to the volume of water from the River Saldes which has joined the River Llobregat.

The concentration of chlorides shows a notable increase at la Pobla de Lillet (L5) and, particularly, just before the reservoir (L14). The first increase

Table 5. *Geochemical characteristics of the waters of the sources of the River Llobregat catchment.*

		COND (μS 20°)	pH	Cl^- (mg/l)	Na^+ (mg/l)	k^+ (mg/l)	Ca^{2+} (mg/l)	Mg^{2+} (mg/l)	HCO_3- (mg/l)	SO_4 2- (mg/l)	NO_3- (mg/l)	n
	mean	231	7.91	1.8	1.2	0.3	49.5	4.6	167	7.0	2.0	
L1	deviation	13.6	0.12	0.5	0.3	0.1	4.1	1.4	6.2	1.3	0.7	44
	range	207-273	8.69-8.18	1.0-3.5	0.8-2.0	0.2-0.6	43.59	1.7-7.0	157-178	4.3-10.0	0.3-4.2	
	mean	243	8.44	1.9	1.4	0.5	55.5	1.9	153	12.2	2.5	
L2	deviation	24.2	0.05	0.8	0.7	0.1	4.6	0.5	9.0	4.0	1.4	3
	range	216-262	8.39-8.48	1.3-2.8	0.9-2.2	0.4-0.7	51-60	1.5-2.5	143-160	8.7-16.5	1.7-4.1	
	mean	397	8.01	3.1	3.2	1.8	77.1	11.3	212	53.5	0.4	
L3	deviation	26.9	0.21	1.0	0.6	0.4	4.8	1.2	7.5	9.8	0.4	3
	range	378-428	7.78-8.18	2.1-4.1	2.7-3.8	1.4-2.0	73.82	10.5-12.6	204-218	44.3-63.8	0.0-0.8	
	mean	251	8.48	3.2	2.2	0.6	56.5	2.8	160	12.4	2.1	
L4	deviation	22.5	0.10	0.6	0.9	0.1	3.4	1.0	3.2	3.4	1.3	3
	range	226-269	8.38-8.58	2.8-3.8	1.5-3.2	0.5-0.7	53-64	1.7-3.6	157-164	9.2-16.0	1.3-3.6	
	mean	352	8.23	7.1	5.7	1.0	70.9	7.4	188	58.0	2.2	
L5	deviation	63.0	0.18	4.1	3.0	0.4	11.2	2.1	16.3	29.7	1.3	38
	range	255-493	7.56-8.52	2.7-21.0	2.1-17.0	0.4-2.2	55-100	3.6-11.2	165-251	25.0-165.5	0.0-5.1	
	mean	457	8.37	3.9	4.3	1.2	89.2	13.2	211	98.1	0.7	
L6	deviation	41.7	0.07	0.7	1.2	0.1	2.8	2.5	14.2	27.7	0.3	3
	range	412-494	8.30-8.44	3.2-4.6	3.3-5.6	1.2-1.3	87-92	10.9-15.8	198-226	70.2-125.6	0.5-1.0	
	mean	349	8.45	3.0	2.6	0.9	70.1	7.6	193	42.0	1.6	
L8	deviation	22.7	0.03	0.6	0.5	0.3	6.2	2.4	27.7	0.7	0.2	3
	range	325-370	8.42-8.47	2.5-3.7	2.0-3.0	0.7-1.2	63-75	4.9-9.0	172-225	41.2-42.4	1.4-1.7	
	mean	373	8.45	7.2	6.1	1.1	74.3	9.3	200	65.9	1.2	
L9	deviation	39.1	0.15	3.0	2.3	0.4	8.5	2.3	20.7	20.2	0.8	38
	range	279-436	8.15-8.82	2.7-15.3	2.8-12.0	0.6-2.0	58-90	4.9-16.0	164-239	35.0-106.2	0.0-3.2	
	mean	448	8.45	4.9	3.2	2.0	99.6	4.2	256	44.2	9.8	
L10	deviation	17.6	0.03	0.4	1.1	0.3	10.3	2.7	13.0	5.3	3.9	3
	range	428-459	8.42-8.47	4.4-5.3	2.0-4.1	1.7-2.2	88-108	2.2-7.3	242-267	40.7-50.3	7.0-14.2	
	mean	452	8.36	6.1	5.6	1.1	92.6	11.5	207	100.5	2.7	
L11	deviation	111.7	0.22	2.6	2.7	0.5	27.5	4.2	19.8	57.1	1.2	37
	range	278-676	8.01-8.94	2.1-11.9	2.1-12.0	0.4-2.5	35-152	5.3-24.3	175-253	29.3-217.6	0.3-6.3	
	mean	422	8.36	3.0	3.2	0.8	86.6	7.4	209	81.9	0.2	
L12	deviation	23.4	0.12	0.5	0.2	0.2	2.2	1.6	13.4	5.3	0.2	3
	range	405-449	8.29-8.50	2.7-3.6	3.0-3.3	0.6-0.9	85-89	5.6-8.8	195-222	77.1-87.6	0.0-0.4	

Table 6. *Geochemical characteristics of the River Llobregat just before the Baells reservoir (globalization point of the Upper Llobregat basin).*

		COND (μS 20°)	pH	Cl^- (mg/l)	Na^+ (mg/l)	k^+ (mg/l)	Ca^{2+} (mg/l)	Mg^{2+} (mg/l)	HCO_3- (mg/l)	SO_4 2- (mg/l)	NO_3- (mg/l)	n
	mean	533	8.37	18.3	21.5	1.3	88.3	15.5	219	118.8	1.4	
L14	deviation	102,8	0.12	5.8	7.0	0.5	15.1	5.9	26.1	40.7	0.6	38
	range	295-688	8.08-8.68	9.7-42.3	9.5-35-8	0.7-2.7	47-120	6.8-29.2	142-276	55.6-182.5	0.0-2.6	

is due to the addition of water from the River Arija and to a certain volume of waste water, while the second increase is very probably due to the addition of water from the River Saldes at the Baells reservoir.

There is a relatively low concentration of nitrates throughout the entire course of the River Llobregat, although a certain increase is detected where the river flows through Guardiola (L11), due in all probability to discharges from the town. Finally, the conductivity variations indicate the overall effect of the River Arija, possible traces of pollution of human origin at la Pobla de Lillet and Guardiola, and the result of a volume of water from the River Saldes entering the River Llobregat shortly before the Baells reservoir.

4.2. *The principal components analysis (PCI) in order to synthesize the geochemistry results for the upper Llobregat*

In order to obtain an overall picture of the geochemistry of the surface and ground waters of the Upper Llobregat basin, a PCA has been conducted with the mean values of all the samples taken at each station. Nine of the variables analysed have been included (conductivity, chlorides, sodium, potassium, calcium, magnesium, bicarbonates, sulphates and nitrates), for 29 statistical units corresponding to the 29 sampling stations. Due to the fact that factor 1 accounts for 50.3% of the variability and factor 2 accounts for 29.1 %, the discussion is centred on the factorial plane defined by these two axes.

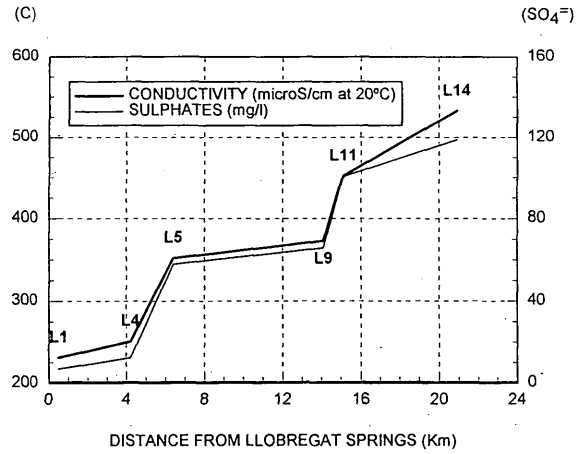


Fig. 2. Variation in conductuvity and sulphate concentrations along the River Llobregat, from its source to the Baels reservoir.

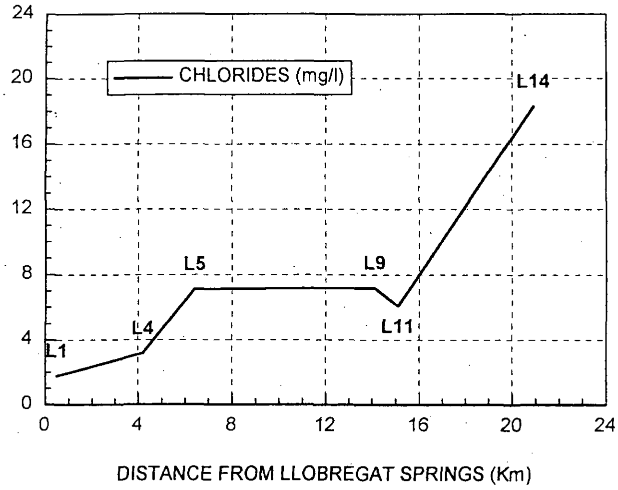


Fig. 3. Variation in chloride concentrations along the River Llobregat, from its source to the Baels reservoir.

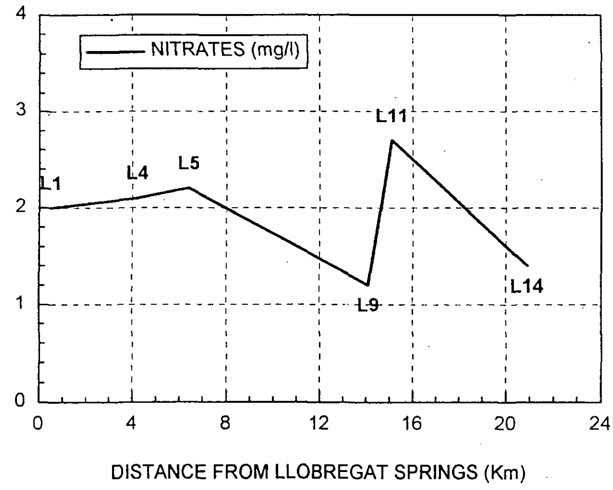


Fig. 4. Variation in nitrate concentrations along the River Llobregat, from its source to the Baels reservoir.

In the space of the variables (figure 5a), the chloride, sodium and potassium ions form one group, and the sulphates, calcium and magnesium ions form another, with very little correlation between the two. Conductivity is situated in the middle, and this is the variable which carries most weight in defining factor 1. This result indicates that in some waters the conductivity is basically determined by the chloride, sodium and potassium variables, while in others it is the sulphate, calcium and magnesium ions which play a dominant role in mineralization. Overall, it is shown that in the Upper Llobregat basin the variability of the geochemical characteristics of the waters is mainly determined by differences in the concentrations of these two groups of ions.

In the space of the statistical units (figure 5b) the sampling points are distributed so that four groups are outlined:

- S1 and S2, notable for the high concentrations of chlorides, sodium and potasium.

- Sr, S5, A4 and S4, notable for the high levels of sulphates and calcium

- S6, which due to its special geochemistry (calcium-sodium chloridized-sulphated water) occupies an intermediate position on the factorial plane.

-The fourth group is formed by all the points of the sources of the River Llobregat catchment, those of the Bastareny catchment and the stations A1, A2 and A3 of the Arija catchment. Their significant characteristics are the typically calcium bicarbonated waters.

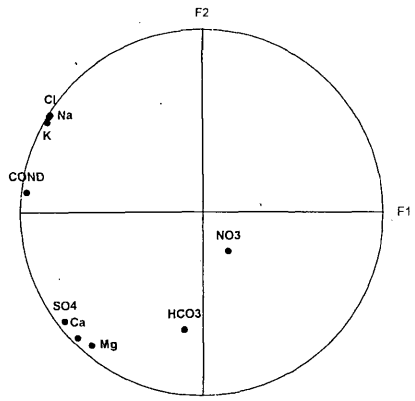
These four groups show the different types of water that determine the geochemistry of the River Llobregat where it flows into the Baells rsservoir, and the distribution of these types among the catchments.

This PCA therefore provides an effective synthesis of the geochemical characteristics of the waters drained by the River Llobregat in its upper course.

5. Conclusions

The results obtained show that waters of sharply contrasting chemical characteristics flow into the Upper Ltobregat basin. For although calcium bicarbonated waters with a low level of mineralization predominate in the basin as a whole, calcium sulphated and even sodium chloridized waters are of considerable importance in the basins of the Saldes and Arija rivers.

In all cases, there is a very close relationship between the chemical quality of the water and the lithology of the basin drained. In this respect, mention should be made of the role of the Keuper gypsums in the mineralization of the water in the lower course of the River Arija, and of the Garumnian and Keuper gypsums in the mineralization of the Esquers, Vallcebre and Cal Rodó streams in the catchment of the River Saldes. At other points the water



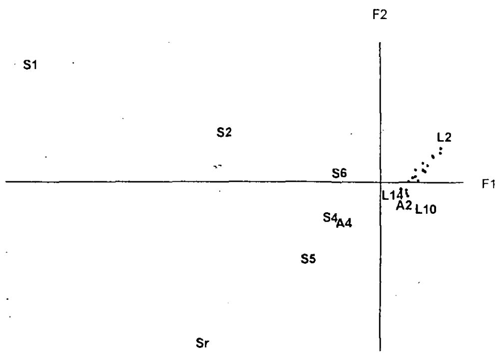


Fig. 5. Principal Components Analysis (PCA) with the mean chemical data from each of the water points sampled; a) space of the variables; b) space of the stadistical units, in wich the cluster of pionts situated between L14 and L12 represents all the points in the River Bastareny catchment (B1-B6), all those of the sources of the River Llobregat catchment except the Sant Julià de Cerdanyola stream (L10), the River Arija at Col of Merolla and the Junyet stream (A1 and A3),and the Gresolet stream (S3).

contains a certain concentration of sulphates (although considerably weaker than at the aforementioned points), which can also be linked with evaporitic facies in the basin, although the area covered by these is relatively small; this would be the case of the Murcurols stream at the head of the River Bastareny, the Junyent stream in the Arija catchment and the Regatell and Malanyeu streams, which are tributaries of the River Llobregat.

The types of elements analysed make it difficult to evaluate the effects of human activity on the chemical quality of the waters. At all events, the concentrations of sulphates and chlorides appear to show evidence of certain urban waste discharges at Pobla de Lillet and Guardiola de Bergueda.

References

BALASCH, J.C., CASTELLTORT, X., LLORENS, P., GALLART, F. (1992): Hydrological and sediment dynamics network design in a Mediterranean mountainous area subject to gully erosion. *Erosion and Sediment Transport Monitoring Programmes in River Basins* (Proceedings of the Oslo Symposium) IAHS Publ. no. 210: 433-442.

CASTELLTORT, F.X. (1995): Erosió, transport i sedimentació fluvial com a integració dels processos geomorfològics d'una conca (Conca de Cal Rodó, Alt Llobregat). *Doctoral Thesis, Faculty of Geology, University of Barcelona.*

CLOTET, N. (1984 a)): La dinàmica geomorfològica actual responsable del subministrament de cabals sòlids en una conca muntanyosa: la conca de La Baells (Alt Llobregat). *Doctoral Thesis, Faculty of Geology, University of Barcelona.*

CLOTET, N. (1984 b)): La Conca de la Baells (Alt Llobregat): Els processos geomorfològics actuals responsables del subministrament de sòlids i balanç previ de sediments. *Acta Geològica Hispànica,* 19(3): 177-191.

CLOTET, N.; GALLART, F. (1986): Sediment yield in a mountainous basin under high Mediterranean climate. *Z. Geomorph. N.F.* 60: 205-216.

DREVER, J.I. (1982): *The Geochemistry of Natural Waters.* Prentice-Hall Inc., 387 pp. New Jersey.

FREIXES, A. (1988): Geoquímica de les aigües superficials i subterrànies de la conca de l'Alt Llobregat (I). *Informe Servei Geològic,* 11 pp.

FREIXES, A. (1989): Geoquímica de les aigües superficials i subterrànies de la conca de l'Alt Llobregat (II). *Informe Servei Geològic, 16* pp.

FREIXES, A. (1990): Evolución de las aguas superficiales y subterráneas: implicaciones ecológicas de la cuenca. *Jornadas Sobre Investigaciones en el Ambito del Proyecto Lucdeme,* Málaga.

FREIXES, A.,RAMONEDA, J., MONTERDE, M. (1995): El sistema càrstic de l'Adou del Bastareny (Carst Experimental de ReferÈncia). EU *Project Report Human Capital and Mobility,* 15 pp.

GONZALEZ, G., MILLET, X., PRAT, N., PUIG, M.A. (1985): Patterns of macroinvertebrate distribution in the Llobregat river basin (NE Spain). *Verh. Internat. Verein. Limnol.,* 22: 2081-2086.

JUNTA D'AIGÜES (1995): Anuari de dades hidrològiques (Hydrological data yearbook) 1987-88 / 1988-89 / 1989-90. *Autonomous Government of Catalonia.* 473 PP

MEYBECK, M. (1984): *Les fleuves et le cycle geochimique des elements.* Thèse de Doctorat d'Etat, Université Pierre et Marie Curie, Paris.

MUÑOZ, I., PRAT, N. (1992): Cambios en la calidad del agua de los ríos Llobregat y Cardener en los últimos 10 años. *Tecnologia del Agua,* 91: 17-23.

MUÑOZ, I.; PRAT, N. (1994): A comparison between different biological water quality indexes in the Llobregat Basin (NE Spain). *Verh. Internat. Verein. Limnol.* 25: 1945-1949.

PRAT, N., PUIG, M.A., GONZALEZ, G., TORT, M.F., ESTRADA, M. (1984): Llobregat. In *Ecology of European Rivers,* ed. by B.A. WHITTON. Blackwell Scientifc Publications, Oxford.

WALLING, D.E., WEBB, B.W. (1986): Solutes in River Systems. In *Solute Processes,* ed. by S. T. TRUDGILL, John Wiley & Sons, Chichester.