Sulphur and strontium isotope composition of Llobregat river (NE of Spain): natural versus anthropogenic tracers in stream waters

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The dissolved sulphate in fluvial water come from natural and anthropogenic sources. The most important natural source is the dissolution of sulphur-bearing minerals from the bedrock (sulphides and sulphates) and at a lesser extent from rainwater. The anthropogenic supply is carried out in several ways, among them, mining activity, fertilizers, industrial activities and urban sewage. On the other hand, when a specific type of bedrock with a characteristics $^{87}Sr/^{86}Sr$ ratio is exposed to circulating groundwater, the isotopic composition of strontium taken into solution will be related to that of the bedrock. This $^{87}Sr/^{86}Sr$ ratio should persist in the water after it reaches the surface, unless it has become mixed with other groundwaters containing dissolved strontium having different isotopic compositions. Therefore the $^{87}Sr/^{86}Sr$ ratio of water in stream is determined primarily by the isotopic characteristics, total strontium concentrations, and relative amounts of the groundwaters that contribute to it. Within a drainage basin that has sufficiently varied bedrock, it should be possible to use the $^{87}Sr/^{86}Sr$ ratio as a tracer of water provenance (Fisher and Stueber, 1976).

The Llobregat is a typical Mediterranean river located in the NE of Spain (Fig. 1), with a length of 156.5km, drainage area of 4948.4 km^2, and a mean discharge of 100 m^3/s. The rainfall distribution is markedly seasonal. Although the upland course is developed in the relatively unpolluted eastern Pyrenees zone, in the lowland the Llobregat flows through one of the most industrialized, agricultural and densely populated areas of the Mediterranean region and in the middle land tertiary sedimentary materials are used for agricultural purposes mainly.

Surface water samples were collected along the Llobregat river and from six of its tributaries. All samples were collected in June 1997, following a period of minimal rainfall, when the contribution of the base flow to a stream's discharge was at the

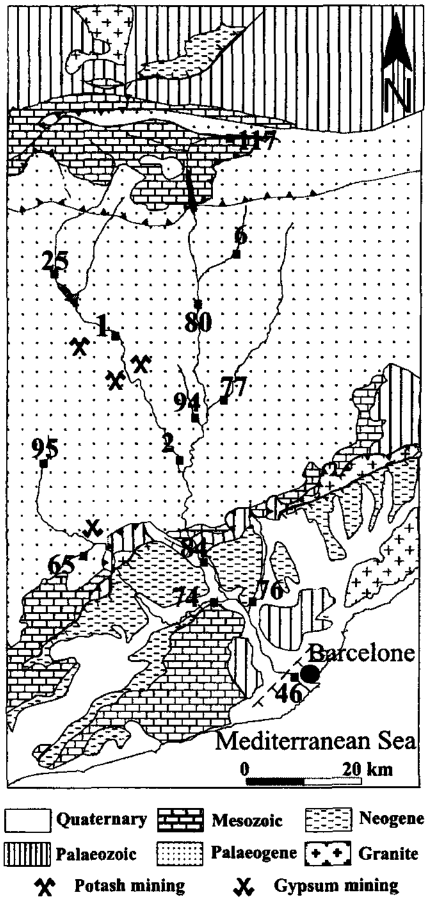

FIG. 1. Sampling localities for the Llobregat system. Sample stations as in Table 1.

TABLE 1. Chemical, mineralogical and isotopic data for the Llobregat system. Locations are plotted in Fig. 1

Sample	Sulphate (ppm)	$\delta^{34}S$ (‰)	$^{87}Sr/^{86}Sr$ (water)	Sr water (ppm)	$^{87}Sr/^{86}Sr$ (filter)	Sr filter (ppm)	Filter mineralogy	Main bed rock
1	78		0.70818	1.6	0.70968	24.5	Q, Ill, Chl, Ca, Do, Fld	Oligocene (C,Sa,S,H)
2	153	10.7	0.70846	2.1	0.71154	104.2	Q, Ill, Chl, Ca, Do, Fld	Oligocene (C,Sa,S,H)
6			0.70849	1.0	0.71139	24.3	Q, Ill, Chl, Ca, Do, Fld	Eocene-Oligocene (C, M)
25	83	12	0.70795	1.3	0.70908	9.8	Q, Chl, Ca	Oligocene (C,S)
46	870	12.2	0.70944	2.9	0.70908	21.4	Q, Ill, Chl, Ca, Do, Fld, Gy, Hal	Holocene (Co, Cl)
65	286		0.70804	2.6	0.70844	14.3	Q, Ill, Ca	Triassic (C) and Eocene (M,C)
74	430	10.1	0.70824	3.9	0.71013	32.7	Q, Ill, Chl, Ca, Do, Fld,	Miocene (S,C)
76	207	10.2	0.70882	1.3	0.70917	34.9	Q, Ill, Chl, Ca, Do, Fld	Miocene (S,C)
77	573		0.70859	5.9	0.70934	36.9	Q, Ill, Chl, Ca, Do, Fld	Oligocene (C,S,M)
80	120		0.70869	0.5	0.71352	5.6	Q, Ill, Chl, Ca, Do, Fld	Oligocene (C,Sa,S,H)
84	150	9.3	0.70842	2.2	0.71070	2.2	Q, Ill, Chl, Ca, Do, Fld	Triassic (C) and Eocene (M,C)
94	67		0.70834	1.8	0.70866	1.4	Q, Ill, Chl, Ca, Do, Fld	Oligocene (C,Sa,S,H)
95	707	9	0.70844	7.5	0.70891	32.4	Q, Ill, Chl, Ca, Do, Fld	Oligocene (C,Sa,S)
117	26	8.4	0.70869	0.2	0.71150	17.9	Q, Ill, Chl, Ca, Fld	Devonian (C)

Abbreviations: C.- carbonates; Sa,. Sandstones; S.- sulphates; H.- halides; M.- marls; Cl.- clays, Co.- conglomerates.

maximum. Prior to analysis, each water sample was passed through 0.45μ Millipore® membrane, which also were analysed by means of strontium and X-ray diffraction. Strontium concentrations, $^{87}Sr/^{86}Sr$ ratios and $\delta^{34}S$ were determined by standard mass spectrometric methods. Sub-sets of these samples have been used for TOC, major and trace element analysis (Table 1). From all these data mass balance equations were used to calculate the amount of each element that originated from different tributaries.

The dissolution of evaporites plays an important role in the chemistry of the Llobregat. One of the Llobregat tributaries, the Cardener river, flows through marine sulphates and halides (sodium and potassium salts) of Eocene age, and it has geochemical characteristics from this bedrock (Sr, Ca, Na, K, Mg, SO_4^{2-}, Cl^-, $^{87}Sr/^{86}Sr$) different of the rest of the river. In this evaporite sub-basin, potash-mining activity exist since Neolithic times and tailings are exposed to rainwater, although a salt collector was built at the beginning of 90ths. The geochemical characteristics of the Llobregat River change after the input of the Cardener River to the Cardener characteristics.

The $\delta^{34}S$-values of dissolved sulphate in the studied waters vary from 8.4 to 12.2‰. These values are significantly lighter than the values of sulphates from the bedrocks. The fertilisers and soaps used in the region contributed to the water a dissolved sulphate with $\delta^{34}S$-value range from 2 to 11.3‰ and 10.6 to 13‰ respectively. The $\delta^{34}S$ values found in water dissolved sulphate indicates that the most part of the sulphate is not natural and mainly corresponds to the anthropogenic inputs of sulphate in this area (fertilisers and soaps).

Strontium isotope ratios of waters strongly correlate with the bedrock however all of them are low and are compatible with carbonates, sulphates, low-rubidium or young rocks. Thus sample 117 from a location with Devonian limestone bedrock has a $^{87}Sr/^{86}Sr$ ratio in accordance with it. Samples 95 and 77 have higher strontium contents and the main bedrock is composed of Eocene-Oligocene age sulphates. The Sr isotope ratio of the solid material in the filters are always more radiogenic than waters, except for sample 46, located within the delta area, where water composition coincides with the Sr isotope ratio of seawater.

Because the difference between the sulphur isotopic composition of natural and anthropogenic sulphate is large, the isotopic composition of the dissolved sulphate in Llobregat fluvial waters can be used to discriminate between the different origins. As the strontium isotopes trace the natural sources of this element as they seems exclusively related to the isotopic composition of the bed-rocks, sulphur versus strontium isotope diagrams provide information about the amount of anthropogenic contribution in the system.