

Using dual-isotope data to trace the origin and processes of dissolved sulphate: a case study in Calders stream (Llobregat basin, Spain)

Neus Otero · Àngels Canals · Albert Soler

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Abstract Whereas most of the reported $\delta^{34}\text{S}$ values of dissolved sulphate are positive in the Llobregat basin, Calders stream, which is a tributary of the Llobregat River, is characterised by negative values. Stream waters, sampled monthly between 1997 and 1998, and quarterly in 1999, show an overall increase in $\delta^{34}\text{S}$ from -10‰ to 0‰ , coupled with an increase in Na and Cl concentration. On the other hand, the oxygen isotopic composition of dissolved sulphate, $\delta^{18}\text{O}$, displayed an opposite trend with a slight decrease, from $+9\text{‰}$ to $+6\text{‰}$. Detailed sampling up stream in November 2000 indicated that, contrary to most of the surficial waters of the Llobregat basin with a $\delta^{34}\text{S}_{\text{SO}_4}$ mainly controlled by evaporites, in Calders stream, sulphate is derived from pyrite oxidation. The dual-isotope approach, coupled with chemical data, allowed us to identify the contribution of ^{34}S -rich sulphate effluents from anthropogenic sources, while mixing models, calculated between natural and anthropogenic sources, enabled us to estimate their contribution. Sudden increases of $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ of dissolved sulphate in stream waters are believed to be caused by a sulphate reduction process related to oil spillage. The long-term enrichment in $\delta^{34}\text{S}$, coupled with a decrease in $\delta^{18}\text{O}_{\text{SO}_4}$, from Jan-97 to Aug-99, is interpreted as a progressive increase in the contribution of pig manure.

Keywords Sulphur · Oxygen · Isotopes · Water pollution · Fertilisers · Animal waste · River water

N. Otero (✉)

Grup d'Hidrogeoquímica, Departament de Geologia Ambiental, Institut de Ciències de la Terra "Jaume Almera", CSIC. C/Lluís Solé i Sabarís, s/n, 08028 Barcelona, Spain
e-mail: notero@ub.edu

À. Canals · A. Soler

Mineralogia Aplicada i Medi Ambient Research Group, Departament de Cristal·lografia, Mineralogia i Dipòsits Minerals, Facultat de Geologia Universitat de Barcelona, C/ Martí i Franquès, s/n, 08028 Barcelona, Spain

1 Introduction

Dissolved sulphate in river water can have different origins: those related to (a) bedrock as dissolution of evaporites or oxidation of reduced sulphur compounds; (b) air deposition, including marine aerosol and secondary sulphate formed via SO_2 oxidation; (c) rainwater; and/or (d) anthropogenic sources such as fertilisers, sewage and mine drainage. Several studies in river systems apply $\delta^{34}\text{S}$ as a tracer of natural or anthropogenic sources, in some cases reporting the relationship between sulphur isotopes and bedrock (Hitchon and Krouse 1972; Ivanov 1983; Longinelli and Edmond 1983; Cameron et al. 1995); others identify anthropogenic sources of pollution, such as air deposition (Williams et al. 1995; de Caritat et al. 1997; Fitzhug et al. 2001), or an unspecified anthropogenic source (Yang et al. 1996; Ardoni-Braccessi et al. 1998; Cortecci et al. 2002). Ingrid et al. (1997) and Mörth et al. (1999) applied sulphur isotopes to trace processes such as sulphate reduction. Moreover, since early work carried out by Longinelli and Cortecci (1970), an increasing number of studies have used the oxygen isotopic composition of dissolved sulphate, coupled with sulphur isotopes, to better characterise the sources of dissolved sulphate in surface water (Grasby et al. 1997; Robinson and Bottrell 1997; Karim and Vezier 2000).

In a previous article, Soler et al. (2002) reported differences between sulphur isotopic composition of natural and anthropogenic sources in the Llobregat River waters. These differences were great enough to consider $\delta^{34}\text{S}$ as a good tool to discriminate their different origins. The authors pointed out, however, that this tool can be more efficient when the studied area is small and/or there is a denser network since in both cases the inputs can be better constrained.

A study of hydrochemical parameters together with the sulphur and oxygen isotopic composition of dissolved sulphate in the Llobregat Basin was conducted over a period of 3 years at 31 sampling sites, with monthly samplings between Jan-97 and Dec-98, and quarterly samplings in 99. Results of hydrochemical data were reported in Otero et al. (2005) and Tolosana-Delgado et al. (2005). Data regarding the sulphur and oxygen isotopic composition of dissolved sulphate are summarised in Fig. 1. As for the sulphur data, two populations are defined; one—93% of the samples—has positive values with a mode of $+9\text{‰}$; the other is characterised by negative values, with a mode of -5‰ . Data of $\delta^{18}\text{O}_{\text{SO}_4}$ have a mode of $+11\text{‰}$, and do

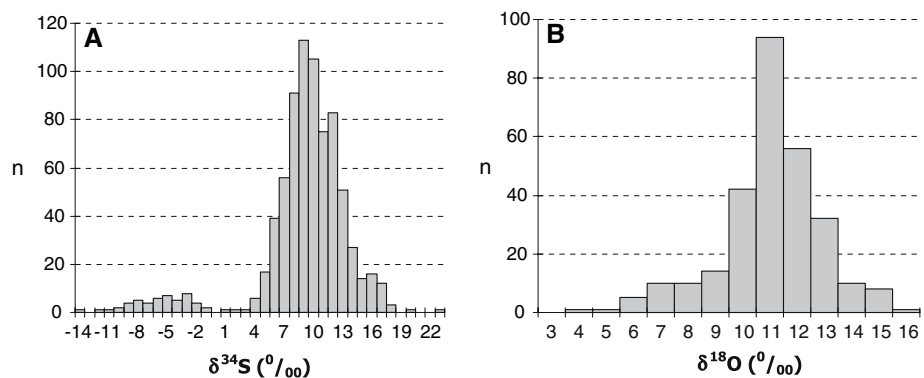


Fig. 1 Histograms of the isotopic composition of dissolved sulphate in the Llobregat River (**A**) $\delta^{34}\text{S}$, $n = 762$, (**B**) $\delta^{18}\text{O}$, $n = 239$

not show this bi-modal distribution, though the lower values of $\delta^{18}\text{O}$ correspond to samples with negative $\delta^{34}\text{S}$. The negative $\delta^{34}\text{S}$ -values correspond to samples from two small tributaries: Calders stream and Castellolí creek. Our study focussed on Calders stream, which is characterised by a sulphate concentration of around 50 ppm—a concentration ten times lower than most other tributaries of the Llobregat River. The isotopic data of the Calders site sampling, during the sampling period, show changes that at first sight do not appear to be seasonal. A decrease in $\delta^{18}\text{O}$ and increase in $\delta^{34}\text{S}$ of the dissolved sulphate resulted in values of $+7\text{‰}$ and 0‰ , respectively (Fig. 2). If these latter values have a natural origin, Calders stream is recovering its natural signature and before the sampling started must have been affected by some input characterised by negative values of sulphur. On the contrary, if negative values are natural, then this trend to positive values can be explained by the contribution of another sulphate source, either natural—an explanation that requires a change in the hydrology of the stream, e.g. increase of the pumping—and/or an anthropogenic source, in which case the stream is increasingly affected. The aim of the present study is to elucidate the origin of the singular values of this stream (negative for the sulphur and less positive for the oxygen) and to understand if their evolution indicates an increase or not of pollution.

2 Study area

Calders stream is a small catching of a 170 km^2 draining area that flows into the Llobregat River. For more information on the characteristics of the Llobregat River see Soler et al. (2002). Calders stream has an irregular flow linked to the irregular pluviometric regime in the area, with periods of drought, usually from June to

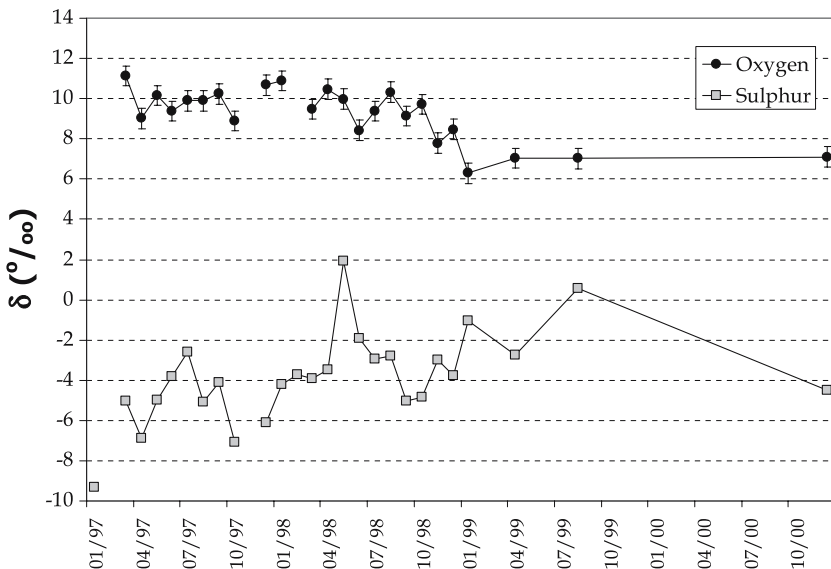


Fig. 2 Isotopic evolution of dissolved sulphate in the Calders stream throughout the sampling period

September, and rainy periods from October to February. The area has a sub-Mediterranean climate with an annual mean temperature of 14°C, mean rainfall of about 450 mm/year, and potential evapotranspiration larger than rainfall (740 mm/year). During the dry periods, the flow reaches minimum values and some sections of the river have ponded waters maintained by slow-flow. Figure 3 shows a simplified lithologic map of the Calders Basin. The major part of the basin consists of sandstone, conglomerates and clays of Middle Eocene age and in the northern part of the basin limestone and marls of Late Eocene age outcrop. The marls that the stream flows through contain disseminated pyrites. In the northern part of the map, there is a gypsum outcrop but it lies outside the drainage basin.

The Calders Basin has a population of 42 inhabitants per km². In the southern part of the basin, the main land use is forest and grassland; in the northeastern part, it is agriculture and pig farming, with a density close to 1,000 pigs/km² (Fig. 4). The latter activity increased 200% between 1989 and 1999. It is worth noting that pig manure is commonly spread on the fields as organic fertiliser. Therefore, important non-point sources of pollution in the northeastern area might be fertilisers and pig manure, though sewage cannot be discarded considering that the first sewage-treatment plant in the basin opened in April 99. Until then, sewage was discharged directly into the stream. Moreover, a point source of pollution in the area comes

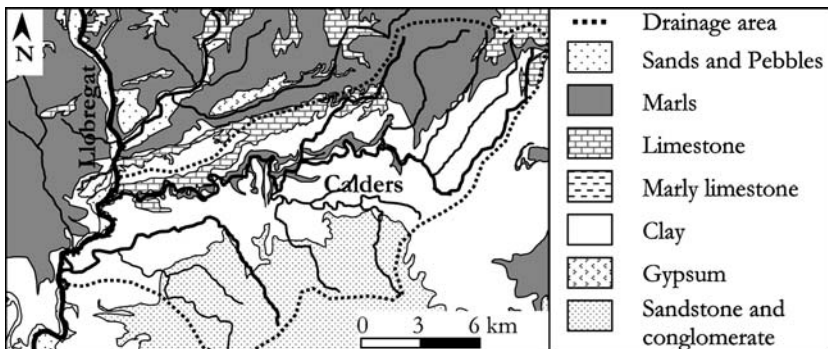


Fig. 3 Simplified lithologic map of the Calders Basin

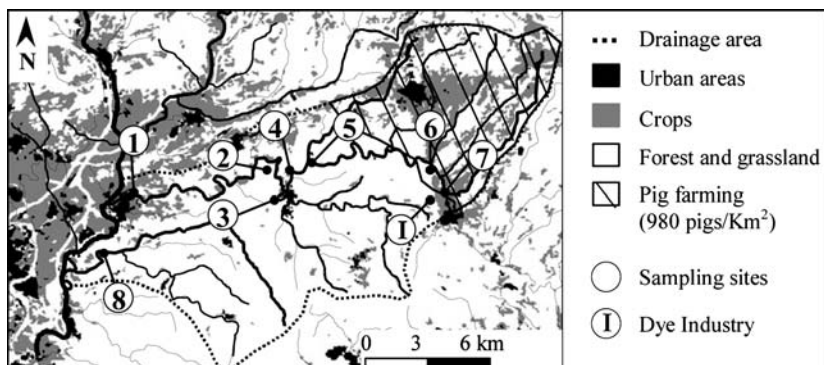


Fig. 4 Land uses and detailed sampling stations in the Calders Basin

from industrial activity located in the headwaters of the stream where a dye industry is located. In this area occasional oil spills occurred (see Fig. 4), the last took place on May 98 and “remediation” consisted of oil depression into the river. In Dec-00 the oil was still visible (Fig. 5); Viñals et al. (2002) analysed the extractable organic matter of the water and the results showed the presence of traces of mineral oil.

3 Methodology

In order to characterise the water chemistry and the isotopic signature of dissolved sulphate different sites for river-water analyses were chosen. Samples from Calders stream at the confluence with the Llobregat River (site 1, Fig. 3) were collected monthly between Jan-97 and Jan-99; two more samples were collected in Apr-99 and Aug-99 at the same site. A detailed sampling up waters was conducted in Dec-00; sampling locations are shown in Fig. 3. In addition, waters from a pristine stream, with similar geology, located near Calders stream (site C-8), and the dye industry located in the headwaters (C-I), were sampled. Sampling site C-6, where the oil was depressed, was further sampled in Mar-99, and in Jul-01.

Physicochemical parameters (pH, temperature and dissolved O_2) were measured in situ. Prior to analysis, samples were filtered with a Millipore® filter of 0.45 μm pore size. Major anions (Cl^- , NO_2^- , NO_3^- , SO_4^{2-} and PO_4^{3-}) were analysed by HP Liquid Chromatography and HCO_3^- was measured by titration. Concentration of Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Sr^{2+} and B was determined by ICP-OES and the total organic carbon (TOC) was determined by the combustion method.

Isotopic characterisation includes deuterium and oxygen of water, as well as sulphur and oxygen of dissolved sulphate. Furthermore, the $\delta^{34}\text{S}$ of the total organic sulphur from the solid residue at site C-6 was also determined. The δD and $\delta^{18}\text{O}$ of water were obtained by H_2 and CO_2 equilibrium, respectively, and Isotope Ratio Mass Spectrometry (IRMS) with a Delta S Finnigan Mat. For sulphur and oxygen isotopic analysis, the dissolved sulphate was precipitated as BaSO_4 by the addition of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$. The sulphur isotopic composition was determined with an Elemental Analyser (Carlo Erba 1108) coupled with an IRMS (Delta C Finnigan Mat) and the oxygen isotopic composition was analysed with a Thermo-Chemical Elemental Analyser (TC/EA Thermo-Quest Finnigan) coupled with an IRMS (Delta C Finnigan Mat). In order to determine the sulphur isotopic composition of total



Fig. 5 Sampling site 6, showing depressed oil

organic sulphur in the residue at site C-6, the sample was filtered with a Millipore® filter of 0.45 µm pore size and the residue was dried and analysed by EA-IRMS. Notation is expressed in terms of δ per mil relative to the Vienna Standard Mean Ocean Water (V-SMOW) and Vienna Canyon Diablo Troilite (V-CDT) standards. The isotope ratios were calculated using international and internal laboratory standards. Reproducibility of the samples calculated from standards systematically interspersed in the analytical batches is $\pm 1.5\%$ for δD , $\pm 0.2\%$ for $\delta^{18}O_{H_2O}$, $\pm 0.2\%$ for $\delta^{34}S$, and $\pm 0.5\%$ for $\delta^{18}O_{SO_4}$. All chemical and isotopic analyses were prepared at the Mineralogia Aplicada i Medi Ambient research group laboratory and analysed at the Serveis Científicotècnics of Universitat de Barcelona.

4 Results

4.1 Monthly sampling 97–99

Results of the chemical analyses of the 3-year sampling are shown in Table 1. In a ternary diagram (Fig. 6) most samples are HCO_3 –Ca–Mg-type; some are HCO_3 –Ca-type. Although there are no great changes in the major ion content, a clear increase in Na and Cl is detected throughout the sampling period. Major ion time-evolution does not show seasonal variations, and no clear correlation is observed between them, except for Na–Cl and Ca–Sr. As for minor elements such as NH_4 , NO_3 , B, TOC and PO_4 , no correlation is observed between them or with other elements. The only clearly seasonal variation observed during the sampling period was seen in PO_4 with maximum concentration in August and January–February.

Isotopic composition of water and dissolved sulphate is shown in Table 2. Results of δD and $\delta^{18}O$ fit with the local meteoric water line, except for two samples (Jun and Jul-98), which seem to be affected by evaporation processes. The low flow during the summer of 1998, when precipitation was 40% lower than the mean annual value, can account for a minimum or negligible flow in some transects of the river, where evaporation may have taken place. The $\delta^{34}S$ shows an overall increase from -10% to 0% , with a break on May 98, when a maximum $\delta^{34}S$ of $+2\%$ was reached (Fig. 2). In contrast, the oxygen isotopic composition of dissolved sulphate, $\delta^{18}O_{SO_4}$, displays an opposite trend with a slight decrease, from $+9\%$ to $+6\%$ (Fig. 2). There is no clear seasonal variation in either $\delta^{34}S$ or $\delta^{18}O$. Coupling chemical and isotopic data, the increase in Cl (from 97 to 99) is associated with an increase in $\delta^{34}S$, and a slight decrease in $\delta^{18}O$, though there is no linear correlation.

4.2 Detailed sampling December 2000

Chemical results of the detailed sampling are shown in Table 3, and represented in a ternary diagram (Fig. 6) and Stiff diagrams (Fig. 7). Calders stream waters show a downstream evolution from HCO_3 –Ca-type at C-7 to HCO_3 –Ca–Na-type at C-6, C-5 and C-4; and finally HCO_3 –Ca–Mg-type at C-3, C-2 and C-1. The sample from the pristine creek (C-8) is SO_4 –Ca-type, and the Dye Industry water (C-I) is Na–Cl-type. From site C-7, at the headwaters, to site C-6 there is a sudden increase in Na and Cl contents, which is progressively diluted downstream. Sulphate concentration decreases from C-7 to C-6 but increases at C-5 and then is progressively diluted

Table 1 Results of chemical data of the 3-year sampling

Site	Date	pH	Cond ($\mu\text{s}/\text{cm}$)	Na (ppm)	K (ppm)	Mg (ppm)	Ca (ppm)	Sr (ppm)	B (ppm)	NH ₄ (ppm)	Cl (ppm)	NO ₃ (ppm)	SO ₄ (ppm)	HCO ₃ (ppm)	TOC (ppm)
C-1	Jun 97	8.4	570	21	4.4	37	58	0.6	0.05	0.15	27	1.4	53	244	4.05
C-1	Jul 97	8.4	553	18	3.8	30	68	0.8	0.07	0.26	22	4.4	55	294	2.95
C-1	Aug 97	8.4	561	19	3.3	39	60	0.7	0.04	0.21	24	1.8	51	293	3.26
C-1	Sep 97	8.4	500	21	4.0	39	58	0.7	0.05	0.29	29	2.4	53	283	3.12
C-1	Oct 97	8.6	627	22	2.0	38	56	0.6	0.05	0.00	28	2.5	60	292	2.95
C-1	Nov 97	8.4	635	24	3.1	38	77	0.7	0.04	0.11	53	5.2	68	—	2.58
C-1	Dec 97	8.2	527	16	3.1	31	102	1.7	0.12	0.05	41	5.2	58	341	2.26
C-1	Jan 98	7.5	698	24	2.9	32	71	0.7	0.08	0.02	42	6.8	93	349	3.20
C-1	Feb 98	8.5	677	23	3.2	31	80	1.0	0.07	0.13	26	8.4	53	241	2.65
C-1	Mar 98	8.2	669	24	3.3	34	72	0.9	0.08	0.04	30	3.2	61	311	3.02
C-1	Apr 98	8.3	751	32	3.6	34	72	0.9	0.09	0.04	48	2.6	43	289	3.52
C-1	May 98	8.1	630	27	3.0	34	61	0.7	0.07	0.26	37	1.0	54	304	2.49
C-1	Jun 98	8.0	578	26	3.7	32	44	0.6	0.06	0.00	38	0.7	58	253	2.49
C-1	Jul 98	8.0	539	29	4.9	35	40	0.6	0.06	0.05	46	1.3	65	246	4.90
C-1	Aug 98	8.1	508	29	5.0	32	44	0.6	0.08	0.17	43	0.5	53	255	4.01
C-1	Sep 98	8.2	601	27	3.8	38	50	0.6	0.06	0.07	32	0.2	59	270	3.50
C-1	Oct 98	8.2	585	29	3.9	34	55	0.6	0.07	0.04	39	0.5	60	271	3.25
C-1	Nov 98	8.0	692	40	4.7	36	66	0.6	0.07	0.05	44	1.3	40	312	2.61
C-1	Dec 98	8.0	723	39	4.9	38	74	0.7	0.08	0.20	72	4.0	102	324	2.13
C-1	Jan 99	8.3	755	29	5.7	30	100	1.1	0.04	0.14	41	31.0	66	295	3.28
C-1	Apr 99	8.0	640	36	4.8	38	61	0.7	0.08	0.07	51	2.9	70	240	3.34
C-1	Aug 99	7.8	610	33	6.3	35	64	0.8	0.13	0.09	42	3.0	66	271	6.77

(-) Not determined; NO₂ and CO₃ are below the detection limit

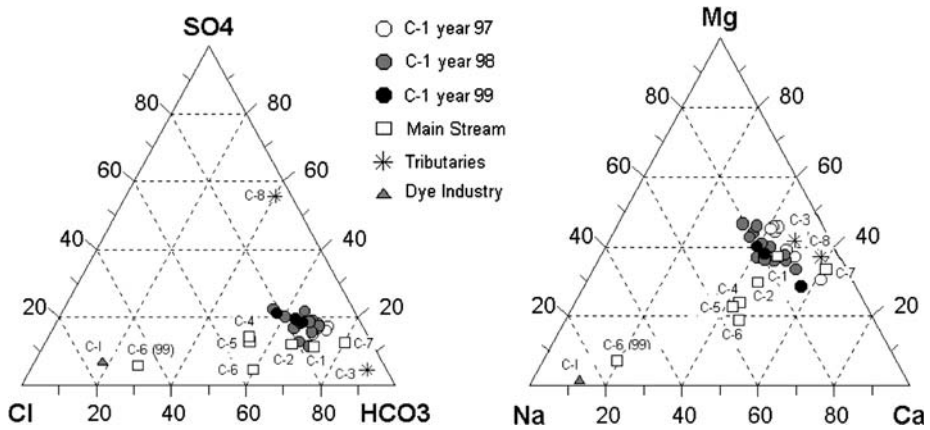


Fig. 6 Ternary diagrams of the 3-year sampling and the detailed sampling

down waters. Regarding minor elements, PO_4 is not detected, NO_3 contents are variable although they increase downstream, and NH_4 and TOC reach a maximum at C-6 and decrease down waters.

Table 2 Results of the isotopic composition of water and dissolved sulphate of sampling site C-1

Site	Date	$\delta^{18}\text{O}$ (‰)	δD (‰)	$\delta^{34}\text{S}_{\text{SO}_4}$ (‰)	$\delta^{18}\text{O}_{\text{SO}_4}$ (‰)
C-1	Jan 97	–	–	–9.3	–
C-1	Feb 97	–	–	–	–
C-1	Mar 97	–	–	–5.0	11.1
C-1	Apr 97	–	–	–6.9	9.0
C-1	May 97	–	–	–5.0	10.2
C-1	Jun 97	–6.0	–40.6	–3.8	9.4
C-1	Jul 97	–6.5	–40.0	–2.6	9.9
C-1	Aug 97	–6.2	–39.8	–5.1	9.9
C-1	Sep 97	–6.3	–40.7	–4.1	10.2
C-1	Oct 97	–6.4	–40.8	–7.1	8.9
C-1	Nov 97	–6.8	–43.5	–	–
C-1	Dec 97	–6.8	–41.4	–6.1	10.7
C-1	Jan 98	–6.8	–42.9	–4.2	10.9
C-1	Feb 98	–7.8	–48.9	–3.7	–
C-1	Mar 98	–6.7	–39.7	–3.9	9.5
C-1	Apr 98	–6.2	–39.1	–3.5	10.5
C-1	May 98	–6.1	–38.1	1.9	10.0
C-1	Jun 98	–4.5	–35.7	–1.9	8.4
C-1	Jul 98	–5.1	–35.3	–3.0	9.4
C-1	Aug 98	–5.7	–36.4	–2.8	10.3
C-1	Sep 98	–5.5	–35.7	–5.0	9.1
C-1	Oct 98	–6.2	–40.3	–4.8	9.7
C-1	Nov 98	–6.4	–41.5	–3.0	7.8
C-1	Dec 98	–6.6	–41.0	–3.8	8.5
C-1	Jan 99	–7.5	–44.3	–1.0	6.3
C-1	Apr 99	–6.1	–38.7	–2.7	7.0
C-1	Aug 99	–5.5	–34.2	0.6	7.0

(–) Not determined

Table 3 Results of chemical data of the detailed sampling

Site	Date	pH	Cond ($\mu\text{S}/\text{cm}$)	Na (ppm)	K (ppm)	Mg (ppm)	Ca (ppm)	Sr (ppm)	B (ppm)	NH ₄ (ppm)	Cl (ppm)	NO ₃ (ppm)	SO ₄ (ppm)	HCO ₃ (ppm)	TOC (ppm)
C-7	Dec-00	8.2	905	8.9	2.7	30.3	89.7	0.9	0.04	<0.1	19	1.0	50	—	—
C-6	Dec-00	7.2	1029	110.2	10.8	31.2	122.7	0.9	0.13	12.2	175	<0.5	31	502.4	27.8
C-5	Dec-00	8.4	1383	99.0	12.8	33.5	103.3	1.8	0.26	0.3	128	<0.1	92	370.4	5.1
C-4	Dec-00	8.5	1244	83.2	10.6	31.9	95.0	1.4	0.20	0.1	121	0.9	71	348.7	3.7
C-2	Dec-00	8.0	1064	56.1	6.7	34.9	87.5	0.9	0.16	0.3	67	6.3	54	353.1	3.4
C-1	Dec-00	8.2	820	32.3	5.1	39.3	79.9	0.8	0.08	<0.1	49	2.2	64	377.5	1.8
C-3	Dec-00	7.5	791	17.1	2.9	39.7	76.7	0.2	0.13	0.8	12	0.5	40	353.7	2.9
C-8	Dec-00	8.3	533	3.5	2.9	11.7	31.4	0.1	<0.025	0.1	4	0.2	61	64.2	5.8
C-1	Dec-00	8.8	7270	1131.5	89.4	10.9	139.5	0.2	0.20	18.5	1576	<0.5	277	—	—
C-6	Mar-99	—	—	633.0	36.4	32.6	144.6	1.1	0.18	—	898	<0.1	107	—	42.1

(-) Not determined; NO₂, PO₄ and CO₃ are below the detection limit

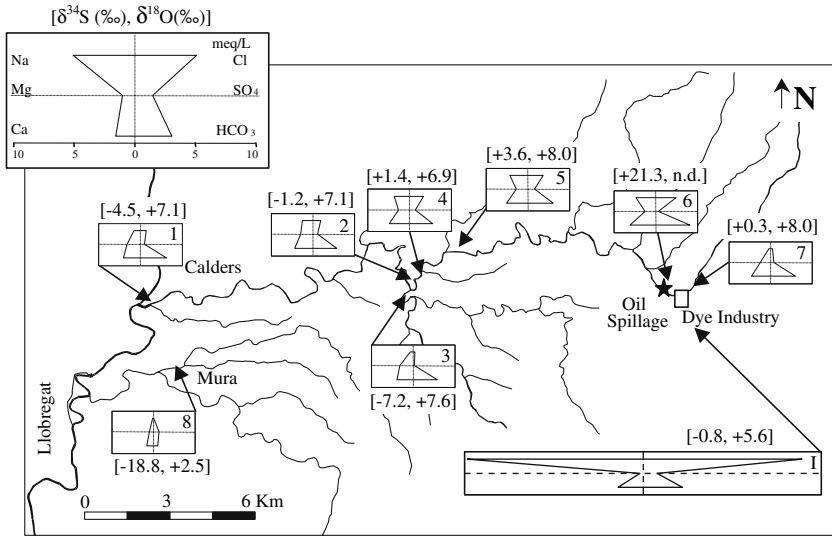


Fig. 7 Stiff diagrams and $\delta^{34}\text{S}$ – $\delta^{18}\text{O}$ of the detailed sampling

Table 4 shows the isotopic composition of water and dissolved sulphate. As occurred for the long-term sampling of site 1, δD and $\delta^{18}\text{O}$ match with the local meteoric water line, except for the sample from the Dye Industry, and those collected at site C-6, which follow an evaporation line. At the industry, evaporation processes can occur due to the closed system used and samples of site C-6 receive the industry effluents. Regarding sulphur isotopes (Fig. 7), the initial value at C-7 is $+0.3\text{‰}$ and there is a drastic $\delta^{34}\text{S}$ enrichment up to $+21\text{‰}$ at site C-6 which is followed by a strong diminution at site C-5, with a $\delta^{34}\text{S} = +3.6\text{‰}$. From that point on, the isotopic composition progressively decreases downstream, down to -4.5‰ at the confluence with the Llobregat River. The sulphur isotopic composition of C-6R (oil spillage solid residue) is -1.1‰ . $\delta^{18}\text{O}$ at C-6 was not determined, however the site was sampled before and after the Dec-00 sampling, with values of $+11.3$ and $+9.3$, respectively (Table 4). From the headwaters to the confluence with the Llobregat

Table 4 Results of the isotopic composition of water and dissolved sulphate of the detailed sampling

Site	Date	$\delta^{18}\text{O}$ (‰)	δD (‰)	$\delta^{34}\text{S}_{\text{SO}_4}$ (‰)	$\delta^{18}\text{O}_{\text{SO}_4}$ (‰)
C-7	Dec-00	-7.5	-48.1	0.3	8.0
C-6	Dec-00	-4.7	-34.4	21.3	–
C-5	Dec-00	-7.4	-48.6	3.6	8.0
C-4	Dec-00	-7.4	-48.7	1.4	6.9
C-2	Dec-00	-7.3	-46.7	-1.2	7.1
C-1	Dec-00	-6.9	-44.5	-4.5	7.1
C-3	Dec-00	-7.1	-41.2	-7.2	7.6
C-8	Dec-00	-5.7	-36.5	-18.8	2.5
C-I	Dec-00	-6.0	-42.0	-0.8	5.6
C-6	Mar-99	-2.5	-40.0	12.3	11.3
C-6	Jul-01	–	–	6.9	9.3

(–) Not determined

River the $\delta^{18}\text{O}$ shows a slight decrease, practically negligible considering analytical error. Coupling chemical with isotopic data a positive linear correlation between Cl and $\delta^{34}\text{S}$ is observed for samples C-5, C-4, C-2, C-1 and C-3 (Fig. 8), and a similar correlation is detected between Na and $\delta^{34}\text{S}$.

5 Discussion

5.1 Bedrock values

Available $\delta^{34}\text{S}$ of disseminated pyrite in marls from the area have a range of -11‰ to -28.8‰ (Pierre et al. 1994; Urquiola, 1994). Besides the presence of this sulphide, several sulphate sources are described, such as gypsum-nodules derived from

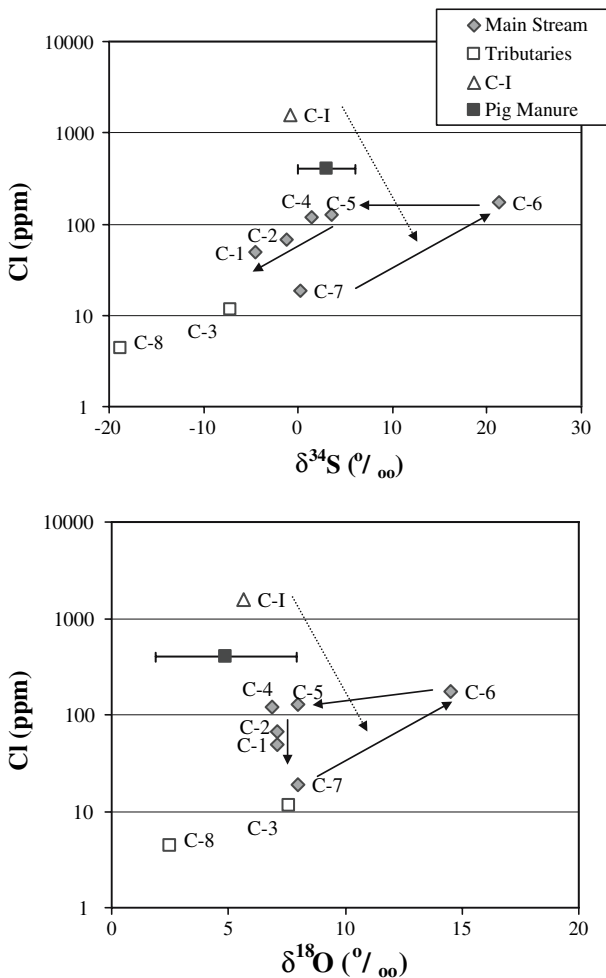


Fig. 8 Cl vs. $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ diagram, showing the main stream (solid arrows indicate the downstream evolution), the tributaries and the Dye Industry (dashed arrow indicates where the industry effluents joins)

sulphide oxidation with $\delta^{34}\text{S} = -23\text{‰}$ to -15‰ and $\delta^{18}\text{O} = -1\text{‰}$ to $+6\text{‰}$ ($n = 6$), or gypsum in sandstones and crusts. These cluster in two groups, one with a mean value of $\delta^{34}\text{S} = +22\text{‰}$ and $\delta^{18}\text{O} = +12\text{‰}$ ($n = 11$), in agreement with the composition of Tertiary marine sulphates, and the other with an average value ($n = 8$) of $\delta^{34}\text{S} = -8\text{‰}$ and $\delta^{18}\text{O} = +6\text{‰}$ (Pierre et al. 1994; Urquiola 1994).

Despite the wide range of bedrock sulphate values, pristine water from Mura stream, a tributary located in an area with no human activity, is SO_4 -Ca-type and has a $\delta^{34}\text{S} = -18\text{‰}$ and a $\delta^{18}\text{O} = +2.5\text{‰}$ (site 8, Fig. 7), values in accordance with the literature data for gypsum-nodules derived from pyrite oxidation in marls and with sulphate produced by present day sulphide oxidation of disseminated pyrite in marls. Although these two sources cannot be distinguished because their isotopic composition coincides, we can conclude that negative $\delta^{34}\text{S}$ values are natural and obtained by leaching of bedrock.

Both $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ of dissolved sulphate in Calders stream have higher values than those from C-8. The difference for $\delta^{34}\text{S}$ can be up to 40‰ , with a minimum of 10‰ . The difference in $\delta^{18}\text{O}$ is lower, around 5‰ . The first possible explanation to justify these differences is their geological background or an anthropogenic contribution. Water from Mura stream is SO_4 -Ca-type whereas Calders stream is HCO_3 -Ca-type, however, in an area with the same bedrock Vitòria et al. (2003a) and Otero et al. (2006) found HCO_3 -Ca-type groundwater, and $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values similar to those of C-8, in agreement with the oxidation of disseminated pyrite in marls. Therefore, the input of anthropogenic sources existing in the area can account for these differences in isotopic values. The anthropogenic contribution is supported by the presence of NO_3^- , TOC, and NH_4^+ in Calders waters, and also by the coupled increase of $\delta^{34}\text{S}$ with Cl and Na concentrations observed at the monthly sampling of this stream throughout the sampling period (Fig. 8).

5.2 Anthropogenic sources

Following land uses, the main non-point sources are fertilisers, pig manure, and sewage. Besides, there is a point source of pollution at the dye industry located between site C-7 and site C-6. Vitòria et al. (2003a) provide a comprehensive isotopic characterisation of fertilisers, including those widely used in the Llobregat Basin, whose mean $\delta^{34}\text{S}$ value is $+5.3\text{‰}$ and $\delta^{18}\text{O}$ is $+12.3\text{‰}$. Sewage waters in the Llobregat Basin ($n = 15$) have sulphur isotopic values ranging from $+9.5\text{‰}$ to $+13.2\text{‰}$, and oxygen isotopic values from $+9.8\text{‰}$ to $+10.8\text{‰}$ (Otero 2004). Cravotta (1997) presented six sulphur isotopic values of pig manure ranging from -0.9‰ to $+5.8\text{‰}$, with a mean value of $+3.7\text{‰}$. Two samples analysed for this study gave values of $\delta^{34}\text{S} = 0\text{‰}$ and $+5\text{‰}$, both within the range found by Cravotta. To our knowledge, no data reports in the literature are available for $\delta^{18}\text{O}$ of pig manure dissolved sulphate, except for one, $+5.6\text{‰}$, offered by Otero et al. (2003). However, this can be estimated through the analysis of groundwater polluted beyond doubt by pig manure. This is the case of the area studied by Vitòria (2004), Vitòria et al. (2003b) and Otero et al. (2006) where the $\delta^{18}\text{O}_{\text{SO}_4}$ ranges from $+3.8\text{‰}$ to $+6\text{‰}$ ($n = 20$).

In order to assess the contribution of these different sources, the isotopic composition of dissolved sulphate is represented in a $\delta^{34}\text{S}$ vs. $\delta^{18}\text{O}$ diagram. Figure 9 shows values of the detailed sampling together with the bedrock sulphate and the main anthropogenic sources, represented with their mean values and their standard

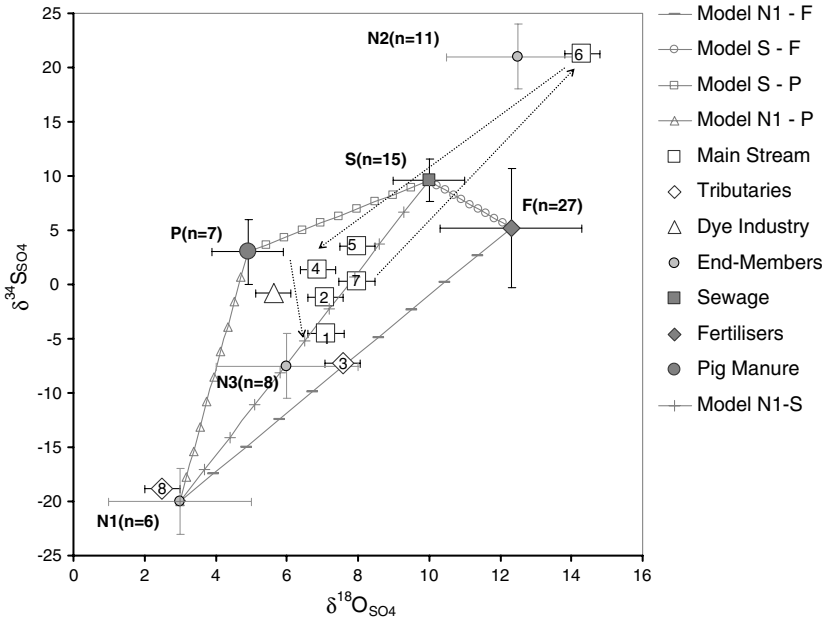


Fig. 9 $\delta^{34}\text{S}_{\text{SO}_4}$ vs. $\delta^{18}\text{O}_{\text{SO}_4}$ diagram showing values of the detailed sampling (arrows indicate downstream evolution). The bedrock sulphate sources (N1 = sulphate from pyrite oxidation, N2, N3 = sulphate in sandstones and crusts) and main anthropogenic inputs (F = Fertilisers, S = Sewage, P = Pig manure) are represented. The symbol corresponds to the mean value and the error bars to the standard deviation. Mixing models are calculated between the end-members considered, see explanation in text

deviation. Mixing models are calculated and only negative values are considered as natural due to the reasons explained in the previous section.

5.3 Detailed sampling

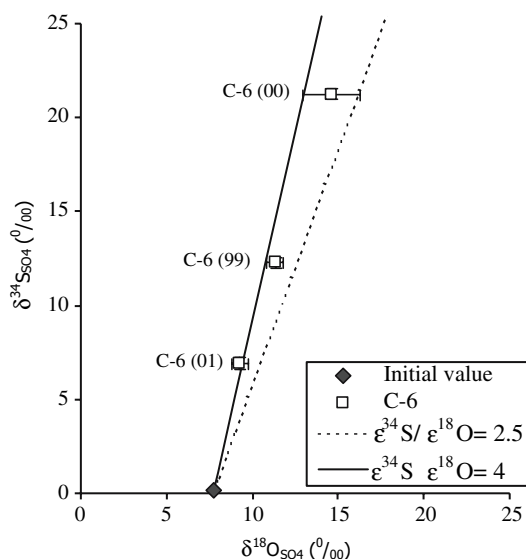
The sample of a tributary located in an area with no agricultural activity (C-3) is $\text{HCO}_3\text{-Ca-Mg}$ -type and has a $\delta^{34}\text{S} = -7.2\text{‰}$ and $\delta^{18}\text{O} = +7.6\text{‰}$. This value differs from that of site C-8, suggesting another input of sulphate, which can be either natural or anthropogenic. A village of 665 inhabitants, with no sewage-treatment plant at the time of sampling, discharged its sewage effluents directly into the tributary. Taking into account the high NH_4 concentration and the isotopic values, a mix between natural sources (N1) and sewage can explain the water chemistry and isotopic values of this sample.

Regarding the mainstream evolution, initial values from site C-7 are far from those of the pristine water of site C-8. According to the isotopic data, the $\delta^{34}\text{S}$ of this sample could be interpreted as a mix between N1 and N2; however, this does not explain the chemistry of the waters. Another possible mix is between natural sulphate, sewage and agricultural sources—fertilisers and pig manure, which in this area is known to be spread over the fields. Downstream, at site C-6, there is a drastic chemical and isotopic change, with an increase of Na and Cl, coupled with a substantial enrichment in $\delta^{34}\text{S}$ values. A dye industry is located between site C-7 and site C-6 and the contribution of its effluents could account for the increase in Na and Cl

values. A contribution of 10% in volume of water coming from the Dye Industry (C-I) and 90% of water from C-7 can be estimated by the Cl and Na concentrations. However, this proposed mixture should have a SO_4 concentration of 60 ppm and a $\delta^{34}\text{S}$ of $+0.2\text{‰}$, yet the measured SO_4 concentration is half that value, and the $\delta^{34}\text{S}$ is $+21\text{‰}$. Sulphate reduction mechanisms could account for such an increase of the isotopic signature, coupled with a lowering of sulphate concentration. As described in Sect. 2, at this sampling site oil spillage took place in May 98 and in Dec-00 part of the oil was still visible (Fig. 5). The presence of the oil can promote sulphate reduction processes at that site, because oil reduces O_2 availability. Although the value of $\delta^{18}\text{O}$ at C-6 was not determined, two other samples were analysed both before and after Dec-00, verifying that these values can be reached by sulphate reduction processes. Considering an initial value obtained with a mix of 10% from C-I and 90% from C-7, and following the enrichment ratios—between $\epsilon\delta^{34}\text{S}/\epsilon\delta^{18}\text{O}$ of 2.5 and of 4—in sulphate reduction processes (Mizutani and Rafter 1973) the values for C-6 of Mar-99 and Jul-01 plot between these two lines (see Fig. 10). Therefore, we can estimate the $\delta^{18}\text{O}$ of C-6 at the Dec-00 sampling using these ratios, obtaining a mean calculated value of $\delta^{18}\text{O} = +14 \pm 2\text{‰}$. Sample C-6 has a high ammonium and TOC content, and although C-I also has a high-ammonium content, according to the mix derived from the Na and Cl values, a 10% contribution from the dye industry cannot account for the observed NH_4 value. On the other hand, the reducing environment in the area, evidenced by the sulphur isotopic values and the lowering in sulphate concentration, can also explain the high TOC and NH_4 and the absence of NO_3 .

Downstream from site C-6, stream waters show a decrease in Na and Cl contents, with values of 30 and 50 ppm respectively at the last sampling site, whereas isotopic values decrease drastically down to -4.5‰ at C-1. Note that we are mixing end members with similar SO_4 concentration but substantial differences in $\delta^{34}\text{S}$ values (Fig. 9). The evolution of the isotopic values from site C-6 to C-4, show a trend towards the value for pig manure. This is supported by the Cl vs. $\delta^{18}\text{O}$ diagram

Fig. 10 $\delta^{18}\text{O}_{\text{SO}_4}$ vs. $\delta^{34}\text{S}_{\text{SO}_4}$ showing samples of site C-6 and enrichment ratios from Mizutani and Rafter (1974). Initial values considered are a mixture of 10% from C-I and 90% from C-7. The Dec-00 $\delta^{18}\text{O}$ value of C-6 is estimated as the mean between the calculations with the two enrichment ratios



(Fig. 8), since there is a linear correlation for C-6, C-5 and C-4 that tends to the $\delta^{18}\text{O}$ of pig manure (from +3.6‰ to +5.6‰). In this section several tributaries draining areas with intensive pig farming join the main stream. Downstream from site C-4 to the confluence with the Llobregat River (site C-1) the isotopic values tend to the ones of C-3, indicating a dilution with waters similar to those of C-3. This is again supported by the linear correlation between Cl and $\delta^{18}\text{O}$ for samples C-4, C-2, C-1 and C-3 (Fig. 8).

Detailed sampling downstream evolution shows the influence of the dye industry and pig manure in the upper part of the drainage area as well as the contribution of waters similar to C-3 near the confluence with the Llobregat River. In addition, this has also allowed us to detect the occurrence of a sulphate reduction process at site C-6. Although, it is difficult to quantify the contribution of each source, due to the coinciding values of some inputs, we can estimate a minimum contribution of 50% of dissolved sulphate from anthropogenic sources (Fig. 9).

5.4 Monthly sampling from 1997 to 2000

Regarding the monthly sampling of site C-1 from 97 to 99, the statistical analysis of the hydrochemical data of the entire Llobregat Basin published by Otero et al. (2005) and Tolosana-Delgado et al. (2005) indicates that the Calders stream has a low, but detectable, anthropogenic influence, evidenced by the presence of NH_4 , NO_3 , B, TOC and/or PO_4 . Results of the $\delta^{34}\text{S}$ vs. $\delta^{18}\text{O}$ are shown in Fig. 11, together

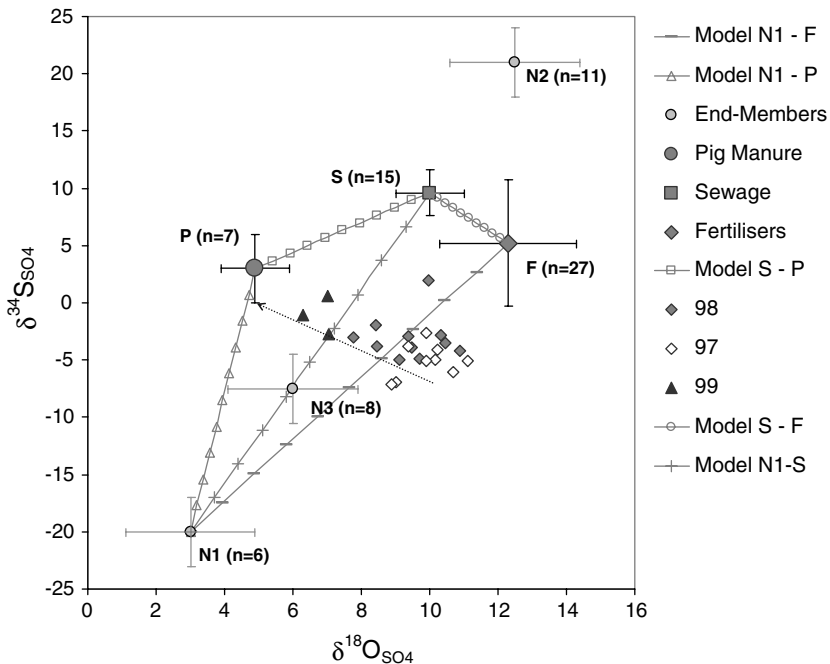


Fig. 11 Results of $\delta^{34}\text{S}$ vs. $\delta^{18}\text{O}$ of the monthly sampling of site C-1, the arrow illustrates the time evolution. The bedrock values and the main anthropogenic inputs are represented as described in Fig. 9

with the inputs previously described. Initial values of the sampling period can be explained by a mix between sulphate from sulphide oxidation and another sulphate source with a positive sulphur isotopic composition, either natural or anthropogenic. Although a clear linear correlation does not exist between Cl and/or Na as $\delta^{34}\text{S}$, a net increase in these variables supports the option of the anthropogenic influence. Moreover, a mix between natural sulphates from the bedrock cannot explain the isotopic evolution throughout the sampling period. For example, in a mix between N1 and N2, increasing $\delta^{34}\text{S}$ must be coupled with increasing $\delta^{18}\text{O}$ -values, yet the observed trend has an opposite behaviour, with a decrease in $\delta^{18}\text{O}$ as $\delta^{34}\text{S}$ increases. This tendency points to pig manure as the most likely input to explain the observed evolution. Regarding the sudden increases of $\delta^{34}\text{S}$ of dissolved sulphate in stream waters, such as those observed in Mar-98 (Fig. 2), these could have been caused by sulphate reduction processes influenced by the oil spillage. Finally, the Nov-00 sampling shows that the stream seems to be recovering its negative, and therefore natural, $\delta^{34}\text{S}$ values, coupled with slightly lower Na and Cl concentrations, indicating a lesser influence of pollution sources. The mixing models calculated, using the dual-isotope approach, allowed us to quantify the contribution of the anthropogenic sources as follows: a minimum of 50% of sulphate is linked to the anthropogenic sources, mainly fertilisers, sewage and pig manure. This percentage is in agreement with the one estimated with the detailed sampling.

6 Conclusions

The dual-isotope approach coupled with chemical data, and the results of the detailed sampling, showed the following: (a) the negative $\delta^{34}\text{S}$ -values in the area have a natural origin: sulphate derived from pyrite oxidation; (b) detailed sampling allows us to identify the influence of the dye industry effluent and pig manure in the upper part of the stream as well as the occurrence of sulphate reduction processes at site C-6; (c) sudden increases of $\delta^{34}\text{S}$ of dissolved sulphate in stream waters are believed to have been caused by oil spillage; and (d) the time evolution from 97 to 99 in a $\delta^{34}\text{S}$ vs. $\delta^{18}\text{O}$ diagram shows a trend that cannot be a mix between two natural sources since the increase in $\delta^{34}\text{S}$ must be coupled to an increase in $\delta^{18}\text{O}$, and oxygen values decrease. This trend can only be explained by a major influence of pig manure, which is replacing chemical fertilisers. The contribution of sulphate from anthropogenic sources is estimated to be in the order of 50%.

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