

Natural and Anthropogenic Budgets of a Small Watershed in the Massif Central (France): Chemical and Strontium Isotopic Characterization of Water and Sediments

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(Received: 23 January 1996; in final form: 16 May 1996)

Abstract. A small watershed (160 km²) located in the Massif Central (France) has been chemically, isotopically and hydrologically studied through its dissolved load, bed sediments and soils. This watershed is underlain by basaltic bedrock and associated soils in which the vegetation is dominated mainly by meadows.

Dissolved concentrations of major ions (Cl, SO₄, NO₃, HCO₃, Ca, Na, Mg, K, Al and Si), trace elements (Rb and Sr) and strontium isotopes have been determined for two different hydrologic periods on the main stream of the Allanche river and its tributaries.

The major objectives of this study were to characterize the chemical and isotopic signatures of each reservoir occurring in the watershed. Changes in chemical and isotopic signatures are interpreted in terms of fluctuations of the different components inputs: rainwater, weathering products, anthropogenic addition.

Water quality may be influenced by natural inputs (rainwater, weathering processes) and anthropogenic additions (fertilizers, road salts, etc.). Precipitation serves as a major vehicle for dissolved chemical species in addition to the hydrosystem and, in order to constrain rain inputs, a systematic study of rainwaters is carried out over a one year period using an automatic collector. Corrections of rainwater addition using chloride as an atmospheric input reference were computed for selected elements and the ⁸⁷Sr/⁸⁶Sr ratio. After such corrections, the geochemical budget of the watershed was determined and the role of anthropogenic additions evaluated through the relationship between strontium isotopes and major and trace element ratios. Thus, 10% of Ca and Na originate in rainwater input, 40 to 80% in fertilizer additions and 15 to 50% in rock weathering

The cationic denudation rates for this watershed are around 0.3 g s⁻¹ km² during low water discharge and 0.6 g s⁻¹ km² in high water stage. This led to a chemical denudation rate of 5.3 mm/1000 years.

For solid matter, the normalization of chemical species relative to parent rocks shows the depletion or enrichment in soils and sediments. The use of K and Ca as mobile reference illustrates the weathering state of soils and sediments relative to parent rocks. This weathering state for bed sediments range from 15 to 45% for the K normalization and from 2 to 50% for the Ca normalization. For the soils, the weathering state ranges from 15 to 57% for the K normalization and from 17 to 90% for the Ca normalization.

Key words: Small watershed, Massif Central, France, dissolved load, strontium isotopes, rain water, anthropogenic inputs, erosion rates, weathering state.

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1. Introduction

The chemical weathering of rocks is one of the essential processes in the geochemical cycling of elements (Garrels and McKenzie, 1971; compilation in Berner and Berner, 1987 and Drever, 1988). During chemical weathering, rocks and primary minerals are transformed into solutes and secondary minerals which form, in some measure, soils and sediments. Superimposed on these processes, human activities also have an impact on the hydrological cycle of dissolved species (Meybeck, 1979; Etanchu and Probst, 1988).

This study is aimed at evaluating first the chemistry and isotopic characteristics of the dissolved load of a small watershed in order to understand, through the river water chemistry, the water-rock interaction and the agricultural pollution. River catchment is usually an unambiguous area for studying the supply of the dissolved river load (Edwards, 1973a, b; Miller and Drever, 1977; Likens et al., 1977). The second goal is to look at the multi-element chemistry of both soils and river bed sediments, and compare the behavior of chemical species during weathering relative to parental bedrock.

The surface waters of the Allanche river drainage basin (hereafter ALW) offer unusual opportunities for selected geochemical studies. The unusual aspects of this river are as follows. (1) It drains areas with one type of rock. (2) It is an inland basin in which atmospheric input can be characterized by local rains. (3) It is virtually unpolluted in the upland and agricultural activities increases toward lowland. So the chemical composition of waters in the upper part should be controlled by *rain water + water-rock interactions* and by *rain water + water-rock interactions + human activities* in the lower part of the watershed. This characteristic allows the quantification of each component. Soils and sediments are derived exclusively from weathering processes of basalts and their chemistry should provide information about element behavior during weathering.

2. Study Area, Geological and Geographical Considerations

The Allanche river flows through the Massif Central (France). The ALW has an area of 160 km² (Figure 1). The maximum altitude in the watershed is 1400 m above sea level and the relief between the two extreme sampling points is 340 m; the river is 29 km long from headwaters to the outlet. From its origin in the Cézallier area to its mouth in the Allagnon river (a tributary of the Allier river), the Allanche river flows through the volcanic terrains of the lava plateau. The Allanche river divides the Cantal stratified volcano and the Cézallier volcano (De Goër de Herve, 1972a; De Goër de Herve and Tempier, 1988; Brousse and Lefevre, 1990). Three volcanic cycles can be viewed : 8–5.4 Ma. (late Miocene); 5.4–3 Ma. (Pliocene) and 240 000–6000 BP. The ALW is underlain by alkaline basalt bedrock and the volcanic rocks on this watershed comprise two main types:

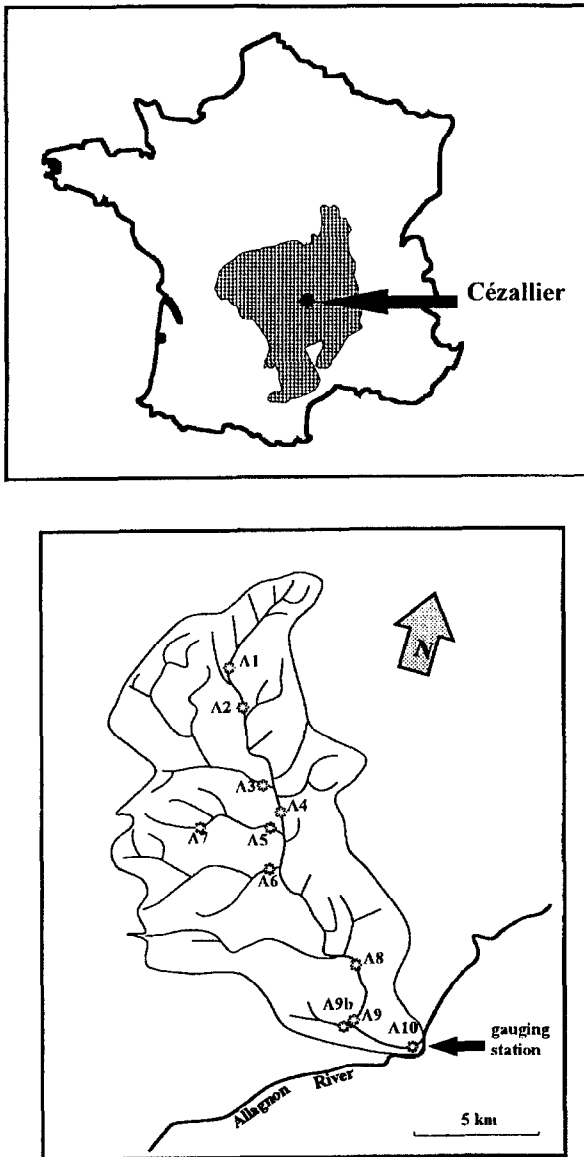


Figure 1. Location map of the Cézellier region and detailed map of the Allanche watershed (AWL) and of the different sampling points.

- Feldspathic basalts (De Goër de Herve, 1972a; De Goër de Herve and Tempier, 1988; Brousse and Lefevre, 1990) with SiO_2 close to 46–49%, low $\text{Na}_2\text{O} + \text{K}_2\text{O}$ (<5%). The main phase in these basalts is plagioclases (An 55–70) with normative nepheline, hyperstene and olivine.

- Basanites (nepheline or leucitic basalts), with SiO₂ around 41–45%, low Na₂O + K₂O (<5%), and with modal or normative nepheline or leucite. The ground mass includes clinopyroxene and plagioclase (An_{50–60}).

The basalt bedrock is overlain by a variable thickness of derived soils (De Goër de Herve, 1972a; De Goër de Herve and Tempier, 1988). The vegetation of this watershed is constituted mainly by meadows and agricultural activities which historically include cereal and bovine farming. The lower part of the AWL has been affected by the Würmian glaciation (De Goër de Herve, 1972b).

Data on rainwater amount and potential evapotranspiration are sparse in this area. However, total rain water amount is close to 1200–1500 mm y⁻¹ and total annual efficient rainwater amount is around 1000 mm y⁻¹. This led to a concentration factor resulting from the evapotranspiration of rainwater of close to 1.2 (De Goër de Herve and Tempier, 1988).

In ALW, the human activities are defined mainly as the result of agricultural activities (amendments with fertilizers; De Goër de Herve and Tempier, 1988).

3. Sampling and Analytical Methodology

3.1. STREAM DISCHARGE

No discharge measuring stations exist in the main part of the watershed except near the outflow. An appraisal of the discharge of the Allanche river and main streams was made at different sampling locations. Briefly, the methodology uses estimates of the cross-section of the stream bed, the water depth and an average flow velocity (Michell, 1970). Results are listed in Table I. Stream discharge ranges between 890 l s⁻¹ in May 1994 and 210 l s⁻¹ in September 1994 for the headwaters. For the outlet, the discharge ranges between 7950 l and 2600 l s⁻¹ for the two surveys, respectively. The last sampling point near the outlet is equipped with a river gauge and the results of our measurement and the river gauge can be compared. For the three sampling periods; the results of this study and the river gauge fluctuate by a factor ranging between 3 and 6%.

3.2. MASTER VARIABLES MEASUREMENTS; WATERS AND SEDIMENTS SAMPLING

Electrical conductivity and water temperature were measured using a microprocessor conductivity meter WTW LF96 standardized to 20 °C. The pH was measured on site using an Ingold electrode and a Orion 250 pH-meter previously calibrated using standard buffers. All waters were collected in polyethylene bottles and filtered through precleaned 0.22 μm Teflon (PVDF) Millipore filters using a precleaned Nalgene filter apparatus. The filtrate was separated into three aliquots: 100 + 250 ml were acidified with twice distilled nitric acid and stored in precleaned polyethylene bottles for major cations analysis and strontium isotopes determination, 100 ml

were stored in polyethylene bottles, unacidified, for anion determination, and 100 ml were stored in polyethylene bottles, unacidified, for alkalinity determination.

Recent bed sediments were collected at the same sampling point as river water. Samples of sediments were collected with plastic spatulas and stored in polypropylene boxes. Soils were collected near the river water sampling points in the surrounding fields. The top 25 centimeters were collected and stored into plastic bags.

The concentration of the suspended matter (SM) was measured where it was possible (Table I). Results show large variations reflecting the inhomogeneities of the water masses in its SM concentration. Focusing on the sampling points in the headwaters and at the outlet, the SM ranges between 0.2 mg l^{-1} in September 1994 to 5.3 mg l^{-1} in May 1994 in the headwaters and between 0.7 mg l^{-1} in September 1994 and 3.4 mg l^{-1} in May 1994 and April 1995 for the outlet. However, the SM contents in April 1995 and May 1994 disagree with the fluctuation in the river discharge (7900 l s^{-1} in May 1994 and 2300 l s^{-1} in April 1995).

3.3. CHEMICAL AND ISOTOPIC ANALYSES OF THE DISSOLVED LOAD

Chemical analyses of water samples were performed by atomic absorption spectrometry (Ca, Na, K), colorimetry (Si), ion chromatography (Cl, SO_4 , NO_3), inductively coupled plasma mass spectrometry (Al, Mg, trace elements), HCl titration and Gran's method for HCO_3 .

Chemical separation and mass spectrometric procedures for strontium follow the standard method used at BRGM. Briefly, Sr was separated by using a cation exchange column (DOWEX AG50X8) with HCl 2N as eluant. Total blank for Sr is less than 0.5 ng for the whole chemical procedure. After chemical separation, 1/5 of the sample was loaded onto a single tungsten filament and analysed using a Finnigan MAT 262 multiple collector mass spectrometer. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are normalized to $^{86}\text{Sr}/^{88}\text{Sr}$ of 0.1194. An average internal precision of $\pm 10^{-6}$ (2σ) was obtained during this study. The reproducibility of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios measurement was tested through duplicate analyses of the NBS 987 standard and the mean value appears to be close to $0.710227 \pm 17 \cdot 10^{-6}$ (2σ of the mean; $n = 70$).

3.4. CHEMICAL ANALYSES OF SEDIMENTS, SOILS AND ROCKS

As previously described, recent bed sediments and soils were collected all around the watershed. All soils and sediments were oven-dried at 70°C and powdered prior to analysis. In order to obtain representative aliquots for analyses, samples were homogenized, quartered and dry-sieved through a $165 \mu\text{m}$ nylon mesh. Parent rock samples were collected and powdered prior to analysis.

All bulk samples were analyzed for major and trace elements by X-ray fluorescence energy dispersive spectrometry (XRF). The methodology has been previously described by Négrel (in press). Briefly, contents of major oxides and trace elements

were determined using 9g of pressed powder. The analytical program was calibrated using 20 reference standards. In addition, two certified reference materials (stream sediments GBW 07311; GBW 07306) were run to verify the calibration. Accuracy and reproducibility were determined by mean values and 1σ standard deviation of one selected in-house standard (stream sediments of Lot River, France). Results demonstrate that the X-ray instrument is both extremely precise and accurate for the analysed elements. On the basis of replicate analyses ($n = 19$ during this study), precision were better than $\pm 2\%$ for Fe_2O_3 , Sr, Zr and Ba; $\pm 5\%$ for SiO_2 , K_2O , CaO, TiO_2 and Rb; $\pm 10\%$ for Zn, Pb, Sn, La and Ce

4. Results

4.1. DISSOLVED LOAD

4.1.1. *Master Variables Along the Main Stream of the Allanche River*

The electrical conductivity is a useful indicator of the total content of ions and the total content of dissolved inorganic components. As Figure 2 illustrates, large variations are observed in the Allanche river samples collected from the main stream when C is plotted versus the river discharge. Two linear relationships can be calculated and the correlation coefficients are always greater than 0.96. The electrical conductivity increases (by a factor of 2 for the three surveys) with the river discharge (by a factor of 9–10 for the three surveys).

The pH increases with increasing discharge from the headwaters to the outlet. The values range from 7.45 (May 1994) and 7.75 (September 1994) in headwaters to 8.01 (May 1994) and 8.31 (April 1995) at the outlet of the river. The increase of the pH value could be related to the addition of fertilizer to the watershed as described in Berner and Berner, (1987).

4.1.2. *Chemical Elements Distribution and Sr Isotopic Variation Along the Main Stream of the Allanche River*

The order of cation abundance in the streamwater was $\text{Si} > \text{Mg} > \text{Na} > \text{Ca} > \text{K} > \text{Al}$ in the headwaters and $\text{Si} > \text{Mg} > \text{Ca} > \text{Na} > \text{K} > \text{Al}$ in the outlet for the survey carried out in May. This order became $\text{Si} > \text{Mg} > \text{Ca} > \text{Na} > \text{K} > \text{Al}$ in the headwaters and $\text{Si} > \text{Mg} > \text{Na} > \text{Ca} > \text{K} > \text{Al}$ in the outlet for the survey carried out in September 1994 and April 1995. For the anions, the order was $\text{HCO}_3 > \text{Cl} > \text{NO}_3 > \text{SO}_4$ both in the headwaters and at the outlet for the three surveys. The variations of the chemical species (Ca, Na, Mg, K, Si, Al, NO_3 , SO_4 , Cl, Rb, Sr) with the discharge in the samples collected from the Allanche main stream during the surveys of May 1994 and September 1994 can be classified as two populations. The first one encompasses the elements which exhibit an increase with increasing discharge along the Allanche river main stream. The second population includes elements which are invariant with the discharge along the course of the river. The regression equations and the

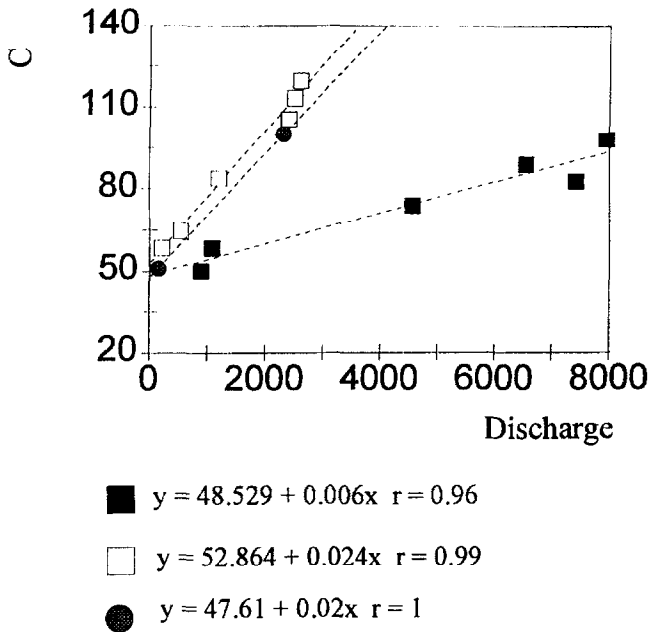


Figure 2. Plot of the electrical conductivity C (in $\mu\text{S}/\text{cm}$, normalized to 20°C) versus the discharge W (in l s^{-1}) for the May 1994 (closed squares), September 1994 (open squares) and April 1995 (shaded circles) surveys. Only samples collected from the main stream of the Allanche river are reported.

correlation coefficients are indicated in Table II. The first population includes Ca, Na, K, Mg, Si, Sr, HCO_3 , Cl, NO_3 and SO_4 . For these elements, the coefficient correlations are greater than 0.75 except for Sr during the survey of September 1994 because one point is clearly outside of the correlation. The increase of an element content with the discharge reflects the increase of the inputs of the different components which interacted with water. The second population include Al and Rb and no relationships can be seen as a function of discharge.

The $^{87}\text{Sr}/^{86}\text{Sr}$ fluctuations along the main stream of the Allanche river show an increase from the headwaters to the outlet for all the surveys ($R = 0.95$, respectively). The increase ranges between 0.00015 and 0.0003 and reflects the existence of at least two sources for Sr in the ALW.

4.2. CHEMISTRY OF PARENT ROCKS, SEDIMENTS AND SOILS

Analytical results obtained for seven parent rocks, 27 stream-bed sediments and 12 soils are given in Table III. Data for major elements are presented in oxydes form and are expressed in weight percentages, trace elements are expressed in ppm.

Table II. Equations of the linear relationships between the measured chemical species in the dissolved load of the Allanche main stream versus the discharge (1 s^{-1}). R is the correlation coefficient, X is the discharge. Only samples collected from the main stream of the Allanche river are reported.

Element	May 1994	September 1994	R coefficient
Ca	$Y = 54.3 + 0.013 X$	$Y = 120.1 + 0.034 X$	0.93/0.76
Na	$Y = 93.3 + 0.01 X$	$Y = 88.4 + 0.05 X$	0.96/0.99
Mg	$Y = 79.9 + 0.013 X$	$Y = 144.7 + 0.06 X$	0.93/0.97
K	$Y = 19.9 + 0.001 X$	$Y = 23.4 + 0.01 X$	0.91/0.97
Si	$Y = 162.7 + 0.01 X$	$Y = 244.8 + 0.04 X$	0.98/0.99
Al	$Y = 0.4 + 0.01 X$	$Y = 1.22 + 0 X$	-0.42/-0.65
HCO ₃	$Y = 398.8 + 0.05 X$	$Y = 141.5 + 0.35 X$	0.94/0.96
Cl	$Y = 46.3 + 0.005 X$	$Y = 46.2 + 0.024 X$	0.92/0.97
SO ₄	$Y = 12.6 + 0.01 X$	$Y = 17 + 0.01 X$	0.88/0.86
NO ₃	$Y = 21.7 + 0.02 X$	$Y = 34.2 + 0.001 X$	0.75/0.86
Rb	$Y = 0.03 + 0.001 X$	$Y = 0.07 + 0.001 X$	0.45/0.2
Sr	$Y = 0.56 + 0.001 X$	$Y = 0.85 + 0.001 X$	0.75/0.47
⁸⁷ Sr/ ⁸⁶ Sr	$Y = 0.70376 + 0.001 X$	$Y = 0.70382 + 0.001 X$	0.95/0.95

4.2.1. Parent Rocks

The chemical composition of seven representative basaltic rocks of the AWL were averaged (Table III) because the source rocks can be considered as rather homogeneous. The variation in the composition never exceeds 24%. For the major elements, the least variation is observed for Fe₂O₃ (4.8%) and SiO₂ (6.7%), and the greatest variation is found for K₂O (24%). The SiO₂ content average $46.80\% \pm 6.7\%$ which is consistent with the basaltic composition of the rocks (De Goër de Herve and Tempier, 1988). Except for Zn with a standard deviation close to 11%, all the trace elements exhibit a standard deviation greater than 15%. La and Ce have the greatest variation (22–24%), while Zr, Pb and Sr vary by 15–17% and Ba and Rb by 20%.

A comparison between our data and those from the same rock given by Chauvel (1982) and De Goër de Herve and Tempier (1988) are in good agreement for major and trace elements. The ⁸⁷Sr/⁸⁶Sr ratios given by Chauvel (1982) for the basanites range between 0.70338 and 0.70393. The mean value is 0.70366 ± 0.0002 .

4.2.2. Bed Sediments and Soils

The chemical compositions of bed sediments and soils fluctuate which may or may not be important (Table III). For major elements, Ca and K fluctuate the most (ranges 20–35%), whereas Fe₂O₃ and SiO₂ fluctuate least (ranges 5–16%). For trace species, the higher variations are observed for Pb and Rb (ranges 30–40%) and the lesser variations are observed for Zr and Ba (ranges 9–12%). Stream bed sediments and soils have generally TiO₂ greater than 2.8% which is higher than the

Table III. Major oxides (wt%) and trace elements (ppm) contents of parent rocks, bed sediments and soils collected on the AWL.

	SiO ₂	K ₂ O	CaO	TiO ₂	Fe ₂ O ₃	Zn	Pb	Rb	Sr	Zr	Ba	La	Ce
PARENT ROCKS													
AR04	41.17	2.39	10.09	2.73	13.04	107	42	68	1025	333	804	72	151
AR05	43.67	1.34	9.38	2.73	12.13	90	26	73	1200	353	1008	83	139
AR07	48.53	2.11	7.90	2.20	11.08	118	41	56	993	346	791	75	144
AR08	48.01	1.88	8.80	2.32	12.46	105	34	54	981	281	641	49	98
AR09	48.38	1.62	8.94	2.27	12.21	122	38	48	802	245	609	42	93
AR10	48.03	1.90	8.93	2.28	12.13	106	35	42	784	251	604	41	87
AR12	48.71	2.79	11.65	2.28	12.36	94	29	72	1029	354	819	59	131
Mean	46.80	2.00	9.37	2.42	12.20	108	35	59	972	309	753	57	121
sd	3.13	0.48	1.22	0.24	0.59	12	6	12	143	49	146	14	27
sd (%)	6.69	24.04	12.99	9.99	4.81	11	18	21	15	16	19	24	22
SEDIMENTS													
<i>May 1994</i>													
A2	43.73	1.15	3.3	2.43	11.76	127	27	94	383	348	655	86	176
A6	42.17	0.49	7.85	>2.8	12.63	128	34	28	577	274	583	35	88
A9	41.83	0.85	5.97	>2.8	12.83	124	53	44	582	311	645	41	98
A9 b	42.57	0.49	5.26	>2.8	13.14	116	19	34	499	298	564	40	91
A8.1	43.21	0.71	5.7	>2.8	13.47	175	31	48	541	344	660	45	105
A.10	43.22	0.83	5.21	2.08	11.85	120	52	49	618	249	686	44	98
<i>September 1994</i>													
A1.2	40.11	0.7	4.33	>2.8	13.92	147	19	32	469	313	657	47	97
A1.2 b	37.33	0.71	4.99	>2.8	13.66	133	30	34	513	374	649	45	108
A2.2	40.3	0.92	3.71	>2.8	13.03	130	35	69	437	362	687	72	141
A3.2	37.53	0.61	5.03	>2.8	13.13	142	27	35	542	310	653	43	98
A4.2	41.75	0.79	4.28	>2.8	12.66	157	48	52	485	335	643	60	128
A5.2	37.49	0.58	6.29	>2.8	11.42	100	19	27	527	313	603	37	91
A6.2	40.02	0.64	6.23	2.73	12.49	140	22	36	536	305	693	43	96
A7.2	38.58	0.65	4.15	>2.8	14.04	163	26	42	353	282	529	33	81
A8.2	42.28	0.73	5.84	2.65	12.73	168	28	48	615	310	673	48	100
A9.2	39.55	0.72	5.08	2.53	12.48	165	45	43	612	300	680	42	95
A9.2 b	39.83	0.61	6.28	>2.8	12.6	157	26	41	572	293	616	40	95
A10.2	37.94	0.73	5.67	2.49	13.01	189	30	50	624	309	682	50	101
<i>April 1995</i>													
A1.3 S	37.95	1.01	6.32	>2.8	13	132	46	33	558	450	653	48	109
A1.3 S2	32.68	0.73	6.86	>2.8	14.23	131	46	23	591	346	639	48	111
A8.3 S	38.22	1.05	6.57	>2.8	14.19	144	49	46	183	323	845	56	122
A8.3 S2	37.77	0.8	6.85	>2.8	12.61	141	71	33	536	294	459	48	122
A9.3	42.65	1.1	5.83	>2.8	13.33	183	52	58	580	306	872	47	101
A10.3 S1	37.8	0.86	6.16	2.74	12.3	150	38	52	637	327	580	47	105
A10.3 S2	46.2	1.36	9.03	>2.8	13.54	161	56	52	790	337	714	50	115
SOILS													
<i>September 1994</i>													
A1.2	32.59	0.55	5.02	>2.8	15.62	121	21	32	535	313	672	49	117
A2.2	38.43	0.87	3.07	>2.8	13.88	114	27	84	397	396	673	69	140
A9.2	42.18	1.00	4.60	2.74	13.68	150	32	58	505	317	837	51	109
A10.2	48.98	1.32	2.44	2.19	9.60	129	33	113	401	361	643	65	131
A8.2	36.24	0.44	2.86	>2.8	14.31	160	19	45	434	366	699	68	122
A9.2	37.97	0.68	4.06	2.77	12.35	142	47	50	379	308	610	48	110
A6.2	39.45	0.85	5.01	>2.8	12.94	110	30	47	511	299	646	51	107
A7.2	34.01	0.65	3.05	>2.8	14.15	185	19	38	238	270	505	34	87
A8.2 b	40.57	0.72	5.12	>2.8	14.23	119	35	72	403	345	673	59	123
<i>April 1995</i>													
A1.3 SOL	33.78	0.78	3.75	>2.8	13.13	46	33	42	403	327	576	45	115
A10.3	47.98	1.28	2.10	2.20	10.67	57	35	103	385	393	708	73	149
A10.3 b	42.72	1.14	2.85	1.93	8.87	137	48	82	398	338	597	63	123

parent rocks. Over all, no general trends can be observed between element contents in soils and bed sediments and the distance between the headwaters and the outlet of the Allanche river.

4.2.3. Normalization

One way to understand the chemical compositions of bed sediments and soils developed on some parent rocks is by the normalization of each chemical species X by the average value of the same species X in parent rock (Dennen and Anderson, 1962; Cullers *et al.*, 1988). For each elements, the enrichment factor EF values obtained by this normalization for the sediment and soil samples were averaged;

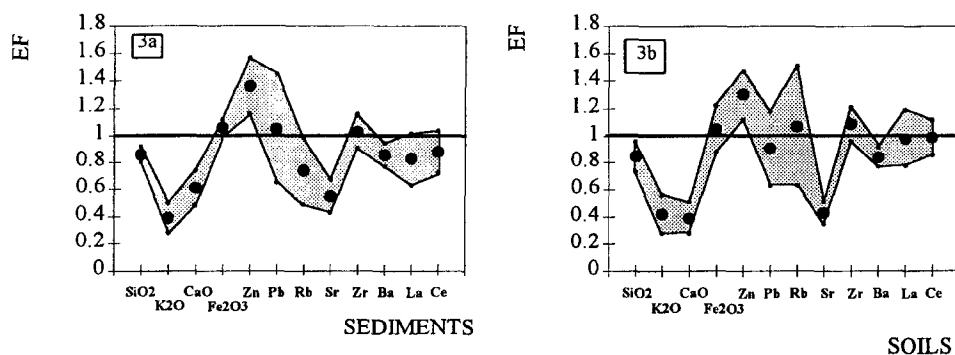


Figure 3. Graphs of elements vs. enrichment factor (EF) in (a) bed sediment samples and (b) soils collected over the AWL.

the results are presented graphically with the standard deviation in Figure 3a for sediments and Figure 3b for soils.

In term of major elements in the sediments (Figure 3a), Si and Fe have the lowest deviation from the unity line. Si exhibits the lowest depletion because this element is generally weakly mobilized during weathering but does decrease with an increasing degree of weathering (Middelburg *et al.*, 1988). Fe is weakly enriched, this is in agreement with the low mobilization of iron during weathering (Boust *et al.*, 1981; Middelburg *et al.*, 1988). Conversely, K and Ca exhibit the highest depletion; K decreases more rapidly than Ca implying that the K phases have a greater alteration rate than the Ca phases. An opposite behavior is generally found in granitic environments (Nesbitt *et al.*, 1980; Middelburg *et al.*, 1988). For minor and trace elements in sediments, Zn is enriched with a mean EF of 1.4 ± 0.2 . Depletion as well as enrichment is observed for lead. However, the behavior of Pb during weathering was generally not studied because of its pollutant origin, as we will see later. As previously shown by Middelburg *et al.* (1988), Rb is depleted in sediments compared to parent rocks but this depletion is less than that of K. Similarly, Sr is depleted in sediments and its EF is similar to that of Ca. Zr appears to be essentially immobile with respect to the weathering processes. Ba exhibits an EF close to 0.8, similar to that of Si. Finally, La and Ce have similar EF of near 0.6.

The EF pattern for the soils is presented in Figure 3b. This pattern is quite similar to that of sediments. Si and Fe have EF closest to those of sediments but the dispersion from the mean value is greater. This could reflect a different behavior in soil environments. We can suppose that in soils, Si and Fe are more weathered and concentrated resulting in greater Fe loss. K and Ca are depleted in soils with a similar EF. Zn is enriched as for sediments. Pb is enriched too but although it is depleted in sediments, in soils the dispersion from the mean value is greater. The largest discrepancy between soils and sediments is found for Rb. In soils, Rb

is enriched (whereas it is depleted in sediments) but the deviation from the mean value is surprisingly large ($0.6 < EF < 1.5$).

Furthermore, although K and Rb behave similarly in sediments, their behavior is opposite in soils. Zr and Sr in soils and in sediments behave similarly; the behavior of Sr is similar as Ca in soils. EF for La and Ce in soils are close to the unity whereas they were depleted in sediments.

5. Discussion

5.1. DISSOLVED LOAD

A general mass-balance equation for the sedimentary budget of the ALW can be written as follow (Drever and Hurcomb, 1986; Drever and Zobrist, 1992):

$$\begin{aligned} &\text{Rock weathering} + \text{Atmospheric input} + \text{Human activities input} \\ &= \text{Dissolved load} + \text{solid residue.} \end{aligned}$$

In ALW, the mobility of major elements such as Ca, Na, Mg, Cl, NO_3 , SO_4 can be influenced by fertilizers application (Meybeck, 1979; Etanchu and Probst, 1988) which constitute the main human input and resulting in an increase in the contents in river water. The bedrock can be considered as monolithologic and atmospheric inputs are derived mainly from rainfall.

As previously demonstrated, the dissolved load of the Allanche river increases as a function of discharge and Sr isotopic ratios and Cl content in the dissolved load collected from the Allanche river exhibit a good relationships in the three surveys (Figure 4). These relationships imply the existence of at least two components: (1) a first component with low Cl content and low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and (2) a component with high Cl content and high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. As we will see later, these two components can be related to rock weathering and to addition of fertilizers from the land.

The mass balance approach requires the determination of an output-input budget (Mast and Drever, 1990; Velbel, 1985). This consists of quantifying the inputs of chemical species as a result of rainfall, human activities and rocks weathering.

5.1.1. Atmospheric Inputs Correction: Methodology and Results

The aim of the atmospheric input correction is to quantify and subtract the portion of the elements carried by rainwater. Classically, for any element Z , the atmospheric contribution to a river (r) is estimated by reference to the Cl concentration in the river multiplied by the Z/Cl ratios in rainwater (rw) (Meybeck, 1983):

$$(Z)_{\text{rw}} = (\alpha\text{Cl})_r \times \left(\frac{Z}{\text{Cl}} \right)_{\text{rw}} \quad (1)$$

The quantification of atmospheric input due to rainwater requires the knowledge of the chemical composition of rainfall on the watershed (Likens *et al.*, 1977;

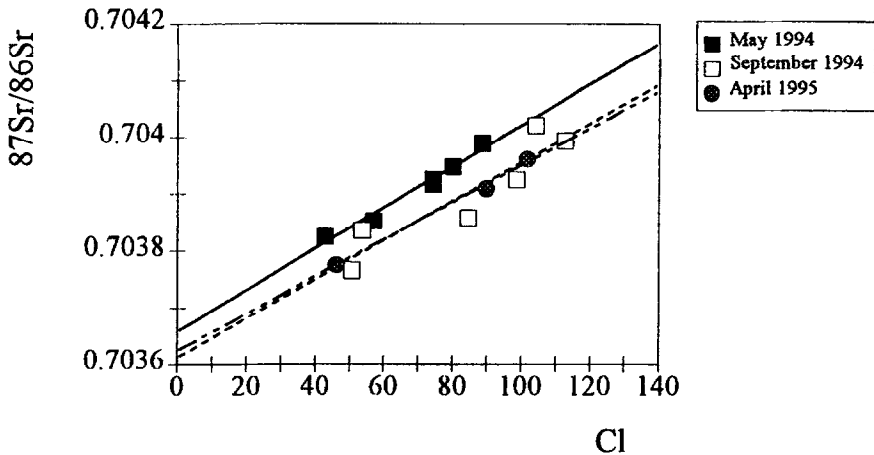


Figure 4. Relationship between the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and Cl contents in the Allanche river main stream for the May 1994, September 1994 and April 1995 surveys. Only samples collected from the main stream of the Allanche river are reported.

Meybeck, 1983) Monthly samples of precipitation since March 1994 were obtained from the Massif Central for chemical and isotopic analyses. Rainwaters are sampled with an automatic collector described elsewhere (Négreil and Roy, in preparation) and located 30 km eastward from the watershed. The analyses (averages) of precipitations (Négreil and Roy, in preparation) show that Ca and Na were the most abundant cations (9.4 and $14.1 \mu\text{moles l}^{-1}$, respectively) and Mg and Si were the least abundant cations (2.5 and $1.5 \mu\text{moles l}^{-1}$, respectively). The anions all had similar concentrations of Cl ($19.8 \mu\text{moles l}^{-1}$), SO_4 ($22.4 \mu\text{moles l}^{-1}$) and NO_3 ($25.6 \mu\text{moles l}^{-1}$). Trace elements such as Sr ($0.031 \mu\text{moles l}^{-1}$) and Rb ($0.005 \mu\text{moles l}^{-1}$) vary greatly but are only weakly abundant. The mean $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the rain (weighted by the Sr content) is close to 0.70972 .

Chloride ions in the atmosphere originate from seasalt and human activities; the release of Cl due to rock weathering has not been clearly demonstrated (excepted in the weathering of salty rocks; Meybeck, 1979). Furthermore, chloride ions behave conservatively through the hydrological cycle (Meybeck, 1979) and as a result they are used as a reference of atmospheric inputs in many unpolluted hydrosystems (Meybeck, 1983; Sarin *et al.*, 1989; Négreil *et al.*, 1993). However, chloride ions can also result from a wide range of human activities (domestic sewage, fertilizers, etc., Sherwood, 1989). For the mass balance equations, the highest concentrations of Cl ions issued from rainwaters must be determined. We use the method of Négreil *et al.* (1993) in which the mean weighted Cl content in the rainwater is multiplied by the concentration factor. For the ALW, around $20 \mu\text{mole l}^{-1}$ of Cl originates in rain water and the concentration factor is close to 1.2 which gives a maximum value of $25 \mu\text{mole l}^{-1}$ for Cl originating from rainwater inputs. If the Cl content

in the riverwater is greater than this value, the difference is attributed to human activities.

Rainwater input expressed as percentages of the total elemental content in the river water samples for the whole data base are listed in Table IV and plotted in Figure 5a with the standard deviation. The atmospheric inputs are dominated by Cl and K ($34 \pm 10\%$ and $18 \pm 8\%$, respectively) with lesser amounts of Ca, Na, Mg and Si (respectively, $9 \pm 4\%$, $11 \pm 4\%$, $2 \pm 1\%$ and $0.6 \pm 0.3\%$). As previously mentioned by Stauffer (1990), Si requires only a minimal atmospheric corrections because it is only found in trace quantities in rainwaters (0.5–1.1% of the total rainwater dissolved load, Négrel and Roy, in preparation). For trace elements, Rb exhibits the highest input by rainwater ($12 \pm 5\%$) and Sr the lowest input ($5 \pm 2\%$).

Note that the input of SO_4 and NO_3 in riverwater from rainfall cannot be calculated from the mass balance considerations because the contents of these two elements are too high relative to Cl and result in negative values in riverwater for these two elements.

5.1.2. *Budgets of Human Activities and Rock Weathering in the ALW; Sr Isotopes Constrains on Rock Weathering Processes*

When corrected from atmospheric inputs, Equation (1) shows that the dissolved load carried by the Allanche river is composed by the mixing of two components : rock weathering and human activities. After correction of the data for atmospheric inputs, the effect of human activities were examined for all of the samples collected in the ALW with multivariate regressions between elements/Sr ratios and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the river chemistry. Indeed, the input of fertilizers lead to variable levels of chemical species depending on the kinetic effects of dissolution of the elements of fertilizers. The Sr isotope ratios can be used to investigate the effects of the addition of fertilizers because this ratio is not fractionated by any of the above processes. The measured isotopic ratio of the fertilizers with deionized water is 0.7083 and the use of multivariate regressions between elements/Sr ratios and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios provides an estimate of the X/Sr ratios of fertilizers (R is the correlation coefficients). The best fit regression lines are obtained between Cl/Sr, Ca/Sr, Na/Sr, Mg/Sr, K/Sr and $^{87}\text{Sr}/^{86}\text{Sr}$:

$$\text{Ca/Sr} = 80 + 1.65 \text{ Cl/Sr} \quad R = 0.76 \text{ (a)}$$

$$\text{Na/Sr} = 102 + 1.85 \text{ Cl/Sr} \quad R = 0.85 \text{ (b)}$$

$$\text{K/Sr} = 201 + 0.3 \text{ Cl/Sr} \quad R = 0.80 \text{ (c)}$$

$$\text{Mg/Sr} = 140 + 2 \text{ Cl/Sr} \quad R = 0.85 \text{ (d)}$$

$$^{87}\text{Sr}/^{86}\text{Sr} = 0.70304 + 0.000004 \text{ Cl/Sr} \quad R = 0.7 \text{ (e)}$$

These correlations are considered excellent because the coefficient correlations are all greater than 0.7, whereas a coefficient greater than 0.4 is considered statistically significant. The lack of correlation of the Si/Sr, Rb/Sr and Al/Sr ratios

Table IV. Results expressed in % of Cl, Ca, Na, Mg, K, Si, Rb and Sr of rainwater, fertilizer and rock weathering input in the rivers of the AWL. Results of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the weathered basalts.

	% Cl rw	% Ca rw	% Na rw	% Mg rw	% K rw	% Sr rw	% Rb rw	% Si rw	% Cl f	% Ca f	% Na f	% Mg f	% K f	% Sr f	% Ca r	% Na r	% Mg r	% K r	% Sr r	% Rb r	% Si r	$^{87}\text{Sr}/^{86}\text{Sr}$	
May 94																							
September 94																							
A1	55%	17%	20%	3.6%	29%	8%	24%	1.2%	42%	44%	39%	43%	30%	4%	39%	41%	53%	41%	89%	78%	95%	0.70314	
A2	44%	16%	15%	3.2%	26%	6%	15%	1.0%	56%	74%	54%	69%	47%	5%	11%	30%	28%	27%	89%	85%	94%	0.70319	
A3	30%	8%	14%	2.4%	21%	6%	16%	0.9%	70%	70%	88%	91%	71%	9%	22%	1%	7%	8%	85%	84%	90%	0.70300	
A4	34%	14%	13%	2.5%	21%	6%	15%	0.9%	66%	80%	70%	75%	70%	7%	6%	18%	17%	21%	87%	85%	92%	0.70318	
A5	28%	7%	10%	1.6%	21%	5%	13%	0.6%	74%	71%	76%	75%	70%	9%	22%	14%	24%	9%	86%	87%	90%	0.70309	
A6	40%	11%	10%	2.1%	17%	7%	15%	0.8%	60%	67%	42%	53%	37%	7%	26%	47%	45%	46%	86%	85%	92%	0.70315	
A7	42%	16%	20%	2.5%	17%	10%	19%	0.9%	58%	81%	76%	58%	71%	9%	3%	4%	40%	12%	81%	81%	90%	0.70278	
A8	34%	11%	11%	2.1%	21%	8%	15%	0.7%	66%	77%	60%	70%	59%	8%	13%	29%	28%	21%	86%	85%	91%	0.70311	
A9	31%	8%	11%	1.8%	19%	5%	15%	0.7%	69%	62%	68%	65%	81%	8%	31%	24%	33%	20%	87%	85%	92%	0.70320	
A9 b	38%	12%	9%	2.1%	14%	7%	15%	0.7%	62%	74%	40%	57%	33%	7%	14%	51%	41%	53%	86%	85%	92%	0.70309	
A10	28%	6%	11%	1.6%	20%	5%	16%	0.7%	72%	60%	74%	69%	74%	9%	34%	15%	23%	6%	86%	84%	91%	0.70321	
September 94																							
A1.2	49%	11%	19%	2.1%	24%	5%	10%	0.8%	51%	41%	52%	35%	36%	3%	48%	28%	63%	40%	92%	90%	96%	0.70332	
A2.2	47%	10%	15%	2.0%	20%	4%	8%	0.7%	53%	42%	47%	37%	32%	3%	48%	37%	61%	48%	92%	92%	96%	0.70340	
A3.2	27%	5%	11%	1.4%	16%	4%	8%	0.7%	73%	51%	82%	64%	61%	7%	44%	7%	35%	24%	89%	92%	93%	0.70329	
A4.2	30%	5%	8%	1.1%	14%	4%	8%	0.7%	70%	47%	72%	55%	47%	6%	48%	17%	44%	40%	91%	92%	94%	0.70335	
A5.2	23%	5%	8%	1.1%	11%	3%	6%	0.5%	67%	61%	76%	61%	53%	7%	34%	16%	37%	36%	80%	94%	93%	0.70329	
A6.2	33%	6%	8%	1.3%	11%	4%	8%	0.5%	67%	48%	45%	44%	32%	6%	48%	47%	54%	57%	90%	92%	94%	0.70331	
A7.2	39%	12%	12%	1.3%	18%	5%	7%	0.7%	61%	72%	54%	34%	41%	6%	18%	33%	65%	40%	89%	93%	94%	0.70341	
A8.2	26%	6%	8%	1.2%	12%	5%	11%	0.8%	75%	68%	67%	61%	51%	10%	28%	24%	38%	37%	84%	89%	88%	0.70302	
A9.2	22%	6%	8%	1.1%	12%	3%	7%	0.6%	78%	81%	79%	67%	58%	7%	13%	13%	32%	31%	90%	93%	92%	0.70345	
A9b.2	32%	7%	8%	1.3%	10%	4%	10%	0.8%	68%	53%	40%	47%	32%	6%	41%	47%	51%	57%	80%	90%	94%	0.70345	
A10.2	24%	6%	8%	1.1%	12%	3%	8%	0.8%	76%	65%	66%	56%	52%	6%	30%	27%	43%	36%	90%	92%	93%	0.70352	
April 95																							
A1.3	54%	6%	13%	2.0%	9%	5%	19%	0.9%	46%	24%	30%	29%	11%	3%	69%	57%	69%	81%	93%	81%	97%	0.70334	
A8.3	26%	5%	7%	1.1%	13%	4%	10%	0.8%	72%	46%	49%	43%	49%	8%	49%	44%	50%	40%	90%	90%	94%	0.70337	
A10.3	29%	4%	6%	1.1%	11%	4%	10%	0.9%	75%	51%	55%	55%	49%	7%	45%	43%	44%	40%	89%	90%	93%	0.70338	

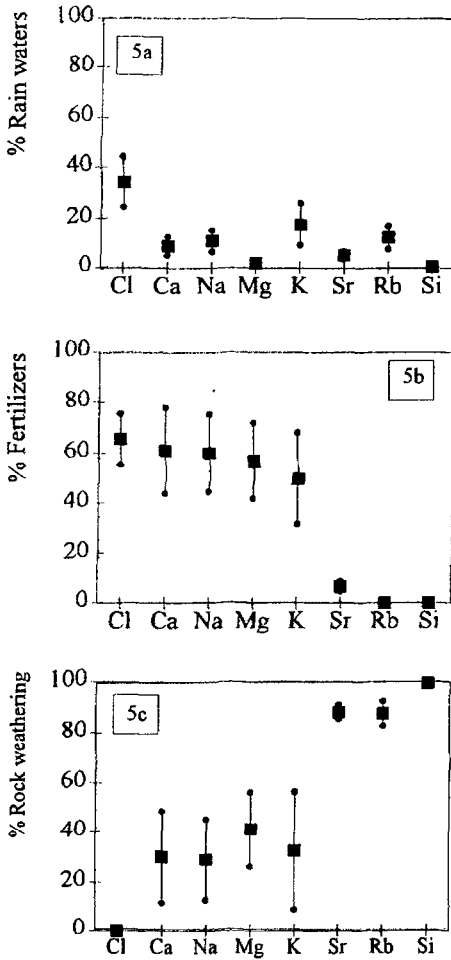


Figure 5. Average proportions of element origins with the standard deviation for the 25 samples collected on the ALW (main stream, tributaries) in the three surveys for the three assumed origins: rainwater (a), fertilizer (b) and rock weathering (c) input.

which have correlation coefficients lower than 0.4 implies that these elements are not mobilized by fertilizers. This is coherent for Si and Rb by the XRF analyse of total fertilizer which gives a level less than 5% for Si and around 15 ppm for Rb.

The computation of the proportion for an element Z ($Z = \text{Ca}, \text{Na}, \text{Mg}, \text{K}$ and Sr) carried by fertilizers was made by reference to the excess $(\text{Cl})_{\text{ex}}$ following Equation (2). The calculation requires the X/Cl ratios of the fertilizers (f) which are derived from the relationships (a) to (e).

$$(\text{Z})_f = (\text{Cl})_{\text{ex}} \times \left(\frac{\text{Z}}{\text{Cl}} \right)_f. \quad (2)$$

The results are summarized in Table IV and are expressed in percentages of the riverwater content uncorrected for atmospheric inputs. As for rainwater input, the 25 samples collected on the ALW (main stream, tributaries) in the three surveys were averaged and presented in Figure 5b.

The averaged fertilizer inputs is similar for all the major elements excepted Si which is not transported by fertilizers. Ca, Na, Mg and K exhibit a mean proportion close to 60% with a range of around 40–80%. For trace elements, Rb is not carried out by fertilizers; Sr shows a mean value of around $7 \pm 2\%$. No trends are observed when the proportions of each elements are plotted versus the distance between headwaters and the outlet.

The effects on overall rock weathering are summarized in Table IV and Figure 5c. The redistribution of major elements produced by rock weathering is similar for Ca, Na, Mg and K (mean value 15–50%) whereas Si is entirely linked with weathering (99%). Trace elements such as Sr and Rb are produced by weathering with a range of around 90%. Some constrains on the weathering conditions can be given by the Sr isotopes systematic. The $^{87}\text{Sr}/^{86}\text{Sr}$ values for the weathered basalts resulting from the mass balance calculations are summarized in Table IV. Notwithstanding the propagate errors on these data (0.005), the fluctuations in the different sampling points on the AWL are not noticeable. The mean values are close to 0.7033 ± 0.0003 in May 1994 ($n = 11$); 0.7031 ± 0.0001 in September 1994 ($n = 11$) and 0.70325 ± 0.0002 in April 1995 ($n = 3$). Note that these values are included in the range of the bedrock (0.70366 ± 0.0002 ; Chauvel, 1982) excepted in September 1994. The main conclusion is the evidence of the great homogeneity of the bedrock of the AWL through the steadiness of Sr isotopes. The $^{87}\text{Sr}/^{86}\text{Sr}$ reflect the weathering of the lower radiogenic phases (mainly plagioclases) and the discrepancies between the surveys may represent an increase or a decrease of the proportions of the low radiogenic weathered phases with regard to the hydrologic events.

5.1.3. *Anthropogenic and Natural Exportation Rates, Weathering and Overall Erosion Processes in the ALW*

The cationic exportation rates ω (in g s^{-1}) due to rock weathering and fertilizers addition can be calculated as follows:

$$\omega = \Sigma X^+ \times W, \quad (3)$$

where ΣX^+ represents the sum of Ca, Na, Mg, K, Si, Rb and Sr expressed in g l^{-1} , W is the discharge measured at the sampling points expressed in l s^{-1}

Because NO_3 and SO_4 concentrations cannot be computed, the anion exportation rates for both cations and anions for fertilizers cannot be investigated. The fertilizer exportation rate in May 1994 (Figure 6a) increases gradually from the headwaters to the river mouth except between 20 and 25 km from the headwaters where the exportation rate is constant after which it increases substantially towards the outlet.

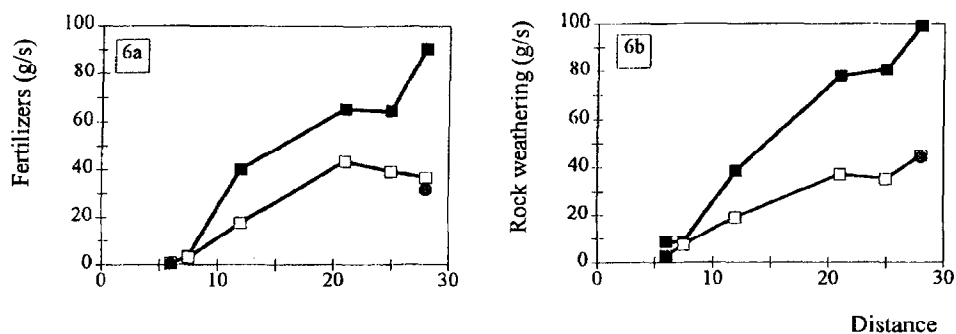


Figure 6. Cations exportation rates ω (in g s^{-1}) for fertilizers (a) and rock weathering (b) in the Allanche river for the May 1994, September 1994 and April 1995 surveys. The legend is the same as Figure 4.

In September 1994, the exportation rate ω for fertilizers (Figure 6a) increases gradually from the headwaters for 20 km and then decreases slightly. The two April 1995 points plot close to the September 1994 data. Rock weathering rates ω in May 1994 fluctuate in the same manner as the fertilizers exportation rates for the same period (gradual increase, constant evolution between 20 and 25 km and then a substantial increase towards the outlet). A similar fluctuation profile is found for the September 1994 data, but with lower values. The two April 1995 data points are one again consistent with the September 1994 values. No trends are observed when the exportation rates for rocks weathering is plotted against the altitude.

If each sampling point along the Allanche river is considered to be a sub-basin, then the fertilizer and rock weathering exportation rates ω calculated at the different sampling points can be normalized by the area of each sub-basins as follow:

$$\omega = (\Sigma X^+ \times W) / S (\text{g s}^{-1} \text{ km}^2), \quad (4)$$

where ΣX^+ represents the sum of Ca, Na, Mg, K, Si, Rb and Sr expressed in g l^{-1} , W is the discharge measured at the sampling points expressed in l s^{-1} , S is the area of each sub-basins in km^2 .

The anthropogenic products exportation rate ω (Figure 7a) for May 1994 increases rapidly between the headwaters and 12 km (from $0.04 \text{ g s}^{-1} \text{ km}^2$ to $0.62 \text{ g s}^{-1} \text{ km}^2$), decreases gradually between 12 and 25 km ($0.62 \text{ g s}^{-1} \text{ km}^2$ to $0.45 \text{ g s}^{-1} \text{ km}^2$) and finally increases towards the river mouth ($0.6 \text{ g s}^{-1} \text{ km}^2$). In September 1994, ω increases gradually between the headwaters and 21 km ($0.09 \text{ g s}^{-1} \text{ km}^2$ to $0.31 \text{ g s}^{-1} \text{ km}^2$) and thereafter shows a weak decrease toward the river mouth ($0.23 \text{ g s}^{-1} \text{ km}^2$). Note that the fluctuations of the ω rate are different for the two surveys. This could be related to both the hydrologic period and the time passed since the fertilizers were spread. The April 1995 values mimic the September 1994 values.

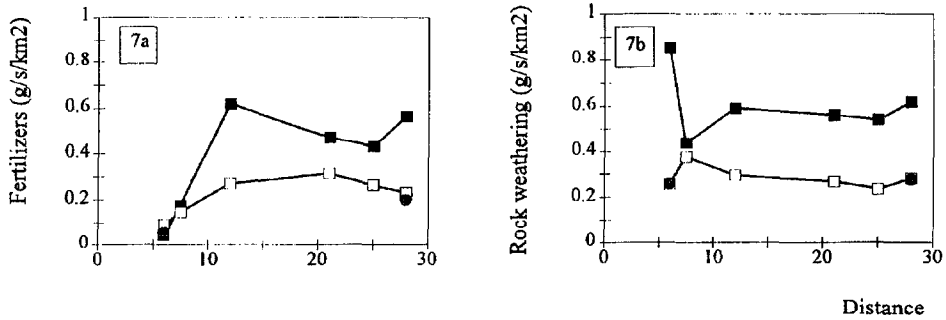


Figure 7. Fertilizer (a) and rock weathering (b) exportation rates ϖ normalized by the area of each sub-basin in the Allanche river for the May 1994, September 1994 and April 1995 surveys. The legend is the same as Figure 4.

The area-normalized rock weathering exportation rates (Figure 7b), for May 1994, decrease rapidly between the headwaters and 5 km, increase slightly and then remain stable until the outlet. In September 1994, ϖ increases between headwaters and 5 km and then the ϖ evolution remains stable until the outlet. Similar ϖ values are observed in April 1995 as were found from September 1994.

Note that the discrepancies in the ϖ rates between the two extreme points (May 1994 and September 1994–April 1995) is a maximum in the headwaters region (70%), a minimum at the second sampling point (14%) and subsequently levels off until the outlet (around 50–55%).

The total cationic denudation rates for the ALW over the studied periods are $0.62 \text{ g s}^{-1} \text{ km}^2$ in May 1994, $0.29 \text{ g s}^{-1} \text{ km}^2$ in September 1994 and $0.28 \text{ g s}^{-1} \text{ km}^2$ in April 1995 at the outlet of the watershed. From these values, an estimate of the specific chemical erosion fluxes can be calculated. Our two surveys in May and September 1994 are consistent with this classification. Based on this annual variation, we calculate a specific chemical erosion flux for the basaltic bedrock of around $14 \text{ t y}^{-1} \text{ km}^2$. This value is in agreement with the specific chemical erosion fluxes obtained on different drainage basins from different areas (Berner and Berner, 1987; Meybeck, 1987; Summerfield and Hulton, 1994; Gaillardet *et al.*, 1995).

The chemical denudation rate which is obtained using a mean density for the bedrock (2700 kg m^3 in this case) gives a value of $5.3 \text{ mm } 1000 \text{ y}^{-1}$ for the AWL. This value is in the same order of magnitude as that calculated by Miller and Drever (1977) for the Absaroka Mountains river ($6.6 \text{ mm } 1000 \text{ y}^{-1}$) underlain by andesitic rocks. However, the rate given by Miller and Drever (1977) was calculated without an atmospheric input correction.

5.2. SOLID MATTER: SEDIMENTS AND SOILS

The composition of bed sediments and soils reflects the composition of parent rocks and the phases genetically linked with the weathering of parent rocks (clays, altered phases, etc.). Stream sediments move gradually further from their source. Superimposed on this process, weathered or unweathered minerals moved from the soils into the streams. Bed sediments and/or soils may or may not be quite different from the parent rocks depending on the degree of weathering. We have seen previously that some elements in soils and/or sediments can be similar in concentration to the unaltered rocks but in general, they are variably enriched or depleted relative to the basalt bedrock (Figures 3a and 3b). However, this enrichment or depletion can be explained by a decrease (or by an increase) in the proportion of the minerals which contain the chemical elements.

Therefore, as emphasized by Nesbitt *et al.* (1980), the use of ratios of elements is useful in the study of weathering profiles or weathering suites of materials. However, soils and sediments behave in an open system and the choice of a reference is one of the most important assumptions in this calculation. Two approaches can be developed using either an immobile element or a mobile element as a reference. Dennen and Anderson (1962) have shown the tendency of several elements in various rocks (granitic to volcanic) to be relatively enriched or depleted, or to remain unchanged in a rock as it weathers. The sequence of enriched elements include Fe, Zr and K; Si and Ti for unchanged elements and Ca was depleted. Several studies have chosen immobile elements (Ti, Zr, etc.) as a reference (Nesbitt, 1979; Middelburg *et al.*, 1988). In this study, we have chosen the mobile element approach and we selected Ca and K as the elements for the normalization on the basis of their high solubility (EF close to 0.6 and 0.4, respectively) and their presence in the two main phases in the basalt bedrock: Ca plagioclase and K phases (feldspars are present in the ground mass).

The binary correlations between the X/K and X/Ca ratios (X being Si, Ca or K, Fe, Zn, Pb, Rb, Sr, Zr, Ba, La and Ce) for parent rocks, bed sediments and soils show linear relationships for numerous elements (Figures 8a and 8b). The regression equations and the correlation coefficients are indicated in the graphs. These relationships represent the evolution of the samples between two extreme end members. One unaltered end member is represented by the fresh basalts and an altered end member is represented by clays and altered phases. The position of each sample along these linear relationships reflects its degree of weathering. The variation of 7 elements can be explained by this model and among these elements, Si, Zr, Ce, La, Fe and Zn are normally considered as immobile (Cullers *et al.*, 1988). Only Ba is generally a mobile element (Nesbitt *et al.*, 1980). A surprising observation is the existence of two sets of relationships between the same series of elements using Ca and K as normalization. This implies that Si, Fe, Zn, Zr, Ba, La and Ce are being partitioned between the two main phases (and/or the K and Ca family of phases).

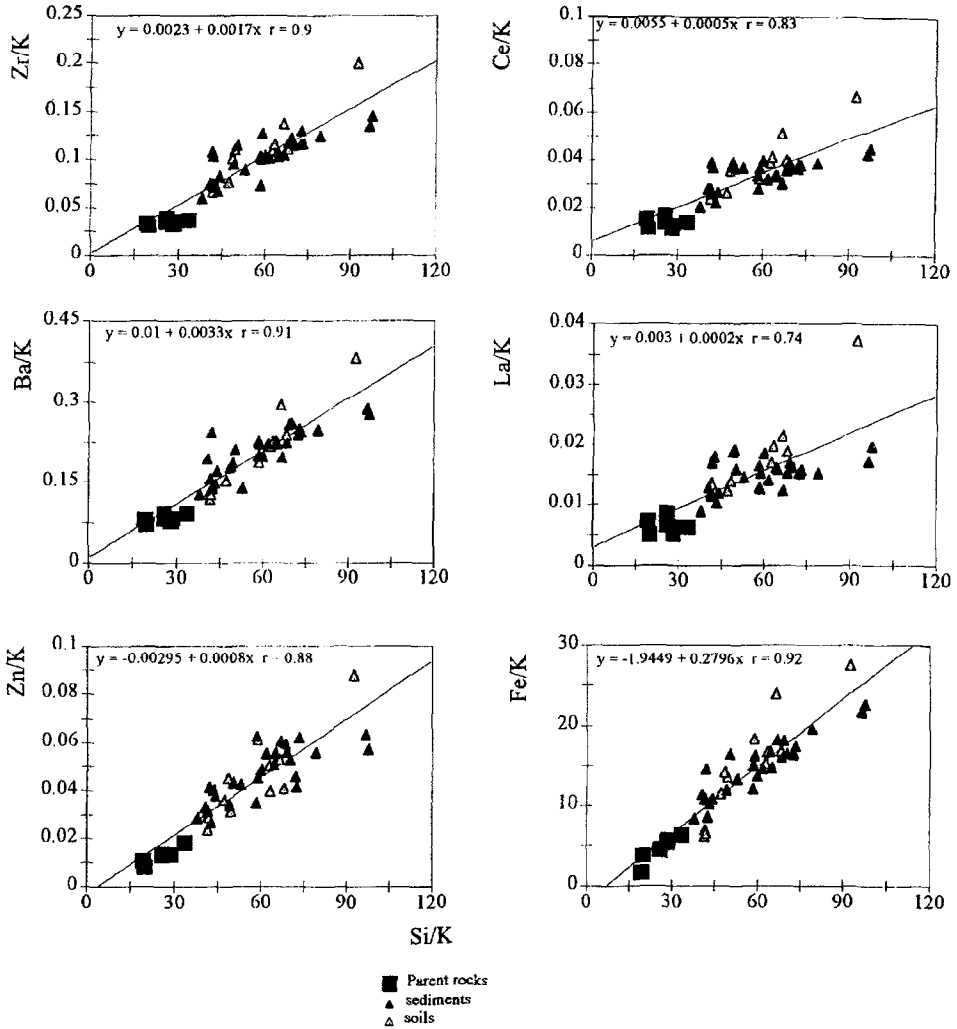


Figure 8(a).

However, when Ca and Sr are normalized to K, they are linearly correlated together but no relationships can be viewed with the other ratios. In the Ca/K versus Sr/K relationship (not shown), the fresh rocks, do not constitute a pure end-member. The samples are distributed linearly on both side of the fresh rocks. Nesbitt *et al.* (1980) noted that these elements are mobile during weathering of fresh rocks and are later refixed in clays. Samples are located on a linear weathering line on both side of the parent rocks. Furthermore, Ca/Si versus Sr/Si ratios (not shown) show a clear linear relationship between the unaltered end member represented by the fresh basalts and an altered end member, whereas K/Si versus both Ca/Si or

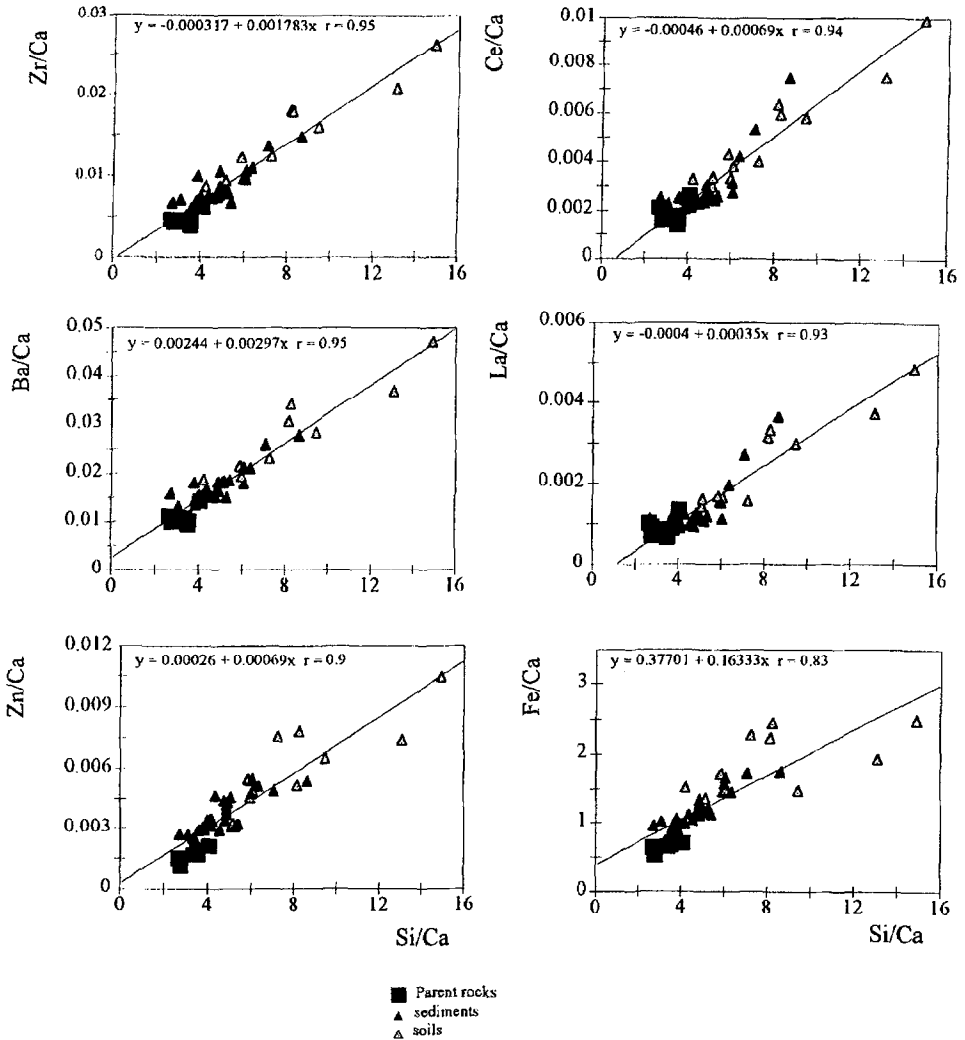


Figure 8(b). Linear relationships between the X/K versus Si/K ratios (a) and X/Ca versus Si/Ca ratios (b) for parent rocks (closed squares), bed sediments (closed triangles) and soils (shaded triangles) on the AWL. X = Zr, Ba, Zn, Ce, La, and Fe.

Sr/Si ratios are not linearly correlated. Ca and Sr are correlated because they are linked to the same phases (mainly plagioclases, Nesbitt *et al.*, 1980).

Surprisingly, Rb cannot be modeled by the two sets of mixing lines, a behavior for which we have no explanation at this time. Moreover, Rb and K seem to behave separately. Pb is also a problem and cannot be explained by the two sets of lines. However, for this element, another end-member should be considered as we will see later.

These two mixing trends can be used to define the weathering state of each sample of bed sediment and soil with respect to the parent rocks. Assuming that the evolution between two extreme end-members represents a binary mixture, the following equation can be applied (Faure, 1988):

$$X_m/Y_m = \alpha X_a/Y_a + (1 - \alpha)X_b/Y_b, \quad (5)$$

where X and Y are two chemical species, m is the mixture, a and b are the two components involved in the mixing and α is the proportion of a in $a + b$ and $1 - \alpha$ is the proportion of b in $a + b$.

After characterization of the end-members, the calculation of α and $1 - \alpha$ is possible. The first end-member is represented by parent rocks and the X_a/Y_a ratios correspond to the averaged value of the seven representative basalt samples (see Section 4.3.1). The second end-member corresponds to the altered phases. The X_b/Y_b ratios are empirically determined using the X/K and X/Ca sets of graphs (Figures 8a and 8b) and the divergence of bed sediments and soils from the fresh basalts can be computed using Equation (5). Each set of values for a particular site were averaged and Table V summarizes the percentage of divergence from the parent rocks for the bed sediments and the soils. Note that two values are given for some points. These values represent the minimum and the maximum because more than one sample was computed with this model.

On the Allanche river main stream, the mean weathering state ranges between 15 to 45% using the K normalization and between 2 to 49% using the Ca normalization. However, in using the K normalization, the fluctuation in the minimum and maximum values remains more or less stable along the river but the fluctuation for the Ca normalization shows considerable variations. At the same location, the discrepancy between the two extreme values is close to 17% at the headwaters (A1) for both the K and Ca normalizations. Note that the calculation using the K normalization exhibits a weathering state higher than the Ca normalization. The K normalization range is 23–40% whereas the Ca one is 7–25%. At the outlet (A10), the discrepancy between the two extreme values is close to 27% for the K normalization and 13% for the Ca one. Thus, the weathering state of the K bearing phases seems to be consistently higher than the weathering state of Ca bearing phases.

On the tributaries, the mean weathering state is higher for the K normalization (range 38–58%) and lower for the Ca normalization (range 1–23%) compared to values on the Allanche river and the discrepancy never exceeds 13% between the different values for the two normalizations.

For soils, large fluctuations are observed in the Ca normalization (range 17–90%) but no trends are evident with respect to the location of the samples (e.g. altitude, distance from the top of the bassin, etc.). For the K normalization, with the exception of one point (sample A3), the values fluctuate between 15 and 57%. Note that the samples located near the outlet show less divergence from the parent rocks for the K bearing phases and greater divergence for the Ca bearing phases.

Table V. Chemical divergence from parents rocks expressed in % according to Equation (5) for bed sediments and soils. n is the number of collected samples.

	K normalization	Ca normalization
SEDIMENTS		
A1 (n = 5)	23 ± 7 / 40 ± 3	7 ± 6 / 25 ± 9
A2 (n = 2)	25 ± 15 / 32 ± 12	38 ± 5 / 49 ± 11
A3	46 ± 3	17 ± 7
A4	39 ± 8	29 ± 5
A5 (n = 2)	43 ± 6 / 47 ± 4	6 ± 4 / 12 ± 7
A6 (n = 2)	43 ± 4 / 56 ± 7	1 ± 4 / 9 ± 5
A7	38 ± 10	23 ± 14
A8 (n = 3)	24 ± 6 / 39 ± 7	6 ± 6 / 15 ± 7
A9 (n = 3)	19 ± 5 / 41 ± 3	10 ± 5 / 17 ± 8
A9b (n = 2)	45 ± 5 / 58 ± 6	9 ± 6 / 13 ± 6
A9r	42 ± 5	15 ± 7
A10 (n = 4)	13 ± 2 / 40 ± 8	2 ± 3 / 15 ± 8
SOILS		
A1 (n = 3)	32 ± 6 / 57 ± 11	18 ± 10 / 30 ± 10
A2	35 ± 13	51 ± 11
A3	90 ± 23	57 ± 12
A5	40 ± 4	26 ± 6
A6	43 ± 7	17 ± 5
A7	37 ± 10	38 ± 19
A9	23 ± 2	23 ± 7
A9b	43 ± 9	20 ± 5
A10 (n = 3)	15 ± 6 / 19 ± 8	46 ± 5 / 90 ± 5

The weathering state is generally higher for the K bearing phases than for the Ca bearing phases, possibly as a result of the preferential weathering of K bearing phases with regard to the Ca bearing phases. This is in agreement with our results for the dissolved load in which K from rock weathering fluctuates significantly more than Ca.

Comparatively, bed sediments collected on the main stream of the Allanche river and soils have a similar weathering state for the K and Ca normalization. Conversely, the weathering state is higher in bed sediments collected on the tributaries for the K normalization than in associated soils and an inverse observation can be made for the Ca normalization.

Lead case. We have seen above that lead cannot be explained by the two sets of evolution lines. Figure 9 shows the relationships between the Pb/K versus Si/K ratios. From this figure and comparison with the K and Ca normalizations, we can estimate the evolution line from weathering processes. The deviation of several points from this line must be related to lead enrichment in sediments and soils.

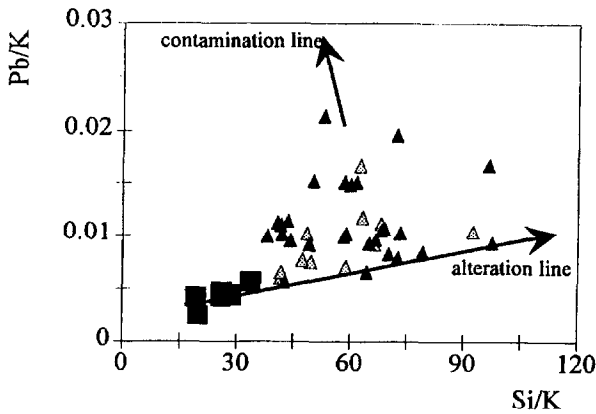


Figure 9. Relationship between Pb/K and Si/K ratios in parent rocks (closed squares), bed sediments (closed triangles) and soils (shaded triangles) samples collected over the AWL. The lack of correlation is caused by atmospheric deposition of lead.

Evidence of lead enrichment in lake sediments has been showed by Flegat *et al.* (1989) and atmospheric deposition of lead is a major contributor used to explain this enrichment (Miller and Friedland, 1994). Lead contents in the atmosphere have been increasing for several years due to human activities and lead released in the atmosphere can be transported thousands of kilometres and deposited onto soil surfaces. The atmospheric deposition of lead occurs by both rainfall and dry deposition. Lead deposited at the surface may be retained in the organic horizon of soils or redistributed in the soil profile. Finally, lead can be released into streams by erosion processes.

Lead contents in precipitations over the Massif Central are currently being studied (Roy and Négrel, in preparation). On the basis of 15 months of total precipitations, a lead deposition flux of about $4.3 \text{ mg m}^{-2} \text{ y}^{-1}$ is estimated on the AWL and this flux could explain the observed enrichment.

Acknowledgements

This work was financially supported by the BRGM (Bureau de Recherche Géologiques et Minières) research Program S20 (on Isotopes in hydrosystems). Thanks are due to Michel Brach for technical assistance in physico-chemical analyses and samples collection. We thank the TIMS team managed by C. Guerrot and the ICP-MS team managed by A. Cocherie which provided Sr isotopes analyses and traces element analyses. Discussions with L. Aquilina, J. L. Pinault and J. C. Baubron were extremely beneficial. We appreciate valuable comments and English improvements from R. Stevenson. Dr M. Meybeck and an anonymous reviewer are acknowledged for their helpful comments on the original manuscript.

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