

Strontium isotope compositions of river waters as records of lithology-dependent mass transfers: the Garonne river and its tributaries (SW France)

K. Semhi ^a, N. Clauer ^{a,*}, J.L. Probst ^b

^a *Centre de Géochimie de la Surface (CNRS / ULP), Ecole et Observatoire des Sciences de la Terre, 1 rue Blessig, 67084 Strasbourg, France*

^b *Laboratoire des Mécanismes de Transfert en Géologie (CNRS / UPS), 38 rue des 36 Ponts, 31400 Toulouse, France*

Abstract

The relation of lithology in the drainage basin to the dissolved load of the Garonne river and its main tributaries, in southwestern France, was evaluated by determining $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, and concentrations of major and trace elements during a 2-year-long survey. In the upper drainage basin, the Garonne river waters were isotopically varied at two observation points: 0.71131 ± 0.00030 (2σ) for 84 ± 18 ppb (2σ) and 0.71272 ± 0.00044 for 86 ± 10 ppb, respectively. In the lower drainage basin, the Garonne river waters were isotopically identical at three observation points at 0.71020 ± 0.00024 for 125 ± 22 ppb. By contrast, the tributaries (Lot, Truyère, Aveyron, Ariège, Gers and Salat) are widely varied in their $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and Sr concentrations from 0.70836 ± 0.00049 to 0.71058 ± 0.00057 , and from 18 ± 8 to 280 ± 116 ppb.

The Sr isotope ratios and concentrations suggest a dominant supply of two reservoirs of Sr, one of which is with low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and high Sr contents that is typically characteristic of carbonate rocks, and the other with high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and low Sr concentrations that is characteristic of felsic rocks. Locally as in the Lot waters draining the Massif Central and within the Pyrénées mountains, a third source of Sr from mafic rocks may be involved. Mass-balance calculations based on the mean $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and contents of the dissolved Sr, and on the mean discharges integrating the 2-year survey, suggest that contribution of the silicate reservoir amounts 3–8% of the total dissolved Sr flux. Mass-balance calculations also suggest that variation in the supply of Sr from either of the two major reservoirs does not exceed the analytical uncertainty at about $\pm 5\%$.

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of HCl and NH_4Cl leachates of suspended loads of the Garonne river are different from that of the associated dissolved Sr. This leaching-related supplementary Sr represents less than 10% of the total amount of Sr transported by the Garonne waters. The Sr isotope characteristics of the leachates are probably records of an intermediate pedogenic episode in the weathering-erosion process occurring in the Garonne drainage basin.

Keywords: Mass transfer; River dissolved load; River particulate load; Sr isotopes; Elemental flux; Garonne river

* Corresponding author. Tel.: +33-88-35-8575; fax: +33-88-36-72-35.
E-mail address: nclauer@illite.u-strasbg.fr (N. Clauer).

1. Introduction

Chemical weathering and mechanical denudation constitute complementary processes of continental erosion of rocks. This combined effect is constrained by many external factors such as climate, topography, lithology, and also by kinetic parameters of hydrolysis/dissolution processes involving the minerals. These processes that release a range of chemical elements, were examined in many studies from local, regional and global perspectives (e.g. Garrels and Mackenzie, 1971; Stallard and Edmond, 1983; Meybeck, 1986; Berner, 1994; Berner and Berner, 1996; Drever, 1994). The released chemical elements are subsequently carried to the world ocean by rivers, which represent a major vector in the global mass transfers occurring at the surface of the Earth. Strontium has been widely used to quantify such transfers, because its major sources in continental runoffs are isotopically distinguishable and the Sr isotopic composition of the runoff differs substantially from that of hydrothermal fluxes at the oceanic ridges (Brass, 1975; Clauer, 1976; Spooner, 1976, and many others since). Sr has proved useful as a major tracer of the processes modifying the surface of the Earth (e.g. Wadleigh et al., 1985; Palmer and Edmond, 1992). Runoff with Sr from silicic rocks can be found with $^{87}\text{Sr}/^{86}\text{Sr}$ ratios higher than 0.715 (e.g. Negrel et al., 1993; Semhi, 1996), and that from carbonate rocks would have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios close to 0.708–0.709 (e.g. Brookins et al., 1969; Fisher and Stueber, 1976; Burke et al., 1982; Goldstein and Jacobsen, 1987).

Studies of the erosion fluxes of major rivers such as the Congo and Amazon have outlined difficulties to assess the whole mass budgets of the erosion-weathering processes occurring in their drainage basins (Gaillardet et al., 1995, 1997; Dupré et al., 1996). Limited analyses without information of potential seasonal and annual fluctuations of Sr in the river regimes is just one cause of such difficulties. An additional cause of the difficulties may be traced to the fact that the Sr carried by the rivers may be adsorbed on the particulate matter or even trapped in soluble mineral phases such as carbonates, sulphates or oxides.

Previous studies of some samples from Garonne river and its six tributaries by Bowins et al. (1993a,b) addressed on temporal and spatial variations of

Garonne river, from which they concluded that the Sr in the Garonne river derived from the top of the soil cover with a K- and Rb-mineral suite containing radiogenic Sr and from the bottom (bedrock) with plagioclase lacking in radiogenic Sr. Our contribution deals with a larger data base and we have used not only the Sr concentrations and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of a great number of samples, spatially and temporally varied, but also the major chemistry data of the waters and the data on Sr adsorbed on suspended sediments. Thus, we present a comprehensive and different model that traces the various sources of dissolved constituents in the waters of the Garonne river, and follows their variations over a 2-year period of time. Tracing experiments were made previously (e.g. Eastin and Faure, 1970; Peterman and Whetten, 1972; Palmer and Edmond, 1992), but the new aspects we have addressed here, are (1) estimation of long-term fluctuations on mass-transfer models of weathering-erosion processes on major rock lithologies, and (2) evaluation of the effect of Sr adsorbed on particulate loads on the budget of dissolved Sr in the Garonne waters.

2. Description of the Garonne hydrologic system and drainage basin

The Garonne river drains an area of 52,000 km² in southwestern France, covering the triangular Aquitaine basin bounded by the Massif Central highlands to the northeast, the Pyrénées mountains to the south, and the Atlantic Ocean to the west (Fig. 1). The outcropping lithologies of the western Massif Central consist mainly of carbonate-rich marine sediments, mostly of Jurassic age, and of Tertiary and Quaternary volcanics. The outcropping rocks of the Pyrénées mountains consist of pre-Jurassic schists, gneisses and granites, overlain by Mesozoic marine limestones. The core of the Pyrénées mountains includes Precambrian granites. The surface of the Aquitaine basin was flooded several times by western oceans during the Oligo-Miocene; each retreat of the ocean waters was followed by depositions of brackish limestones and molasse-type rocks on top of the marine carbonates in transitional continental environments.

During the period of this study (1989–1992), the discharge of the Garonne river at the upstream sta-

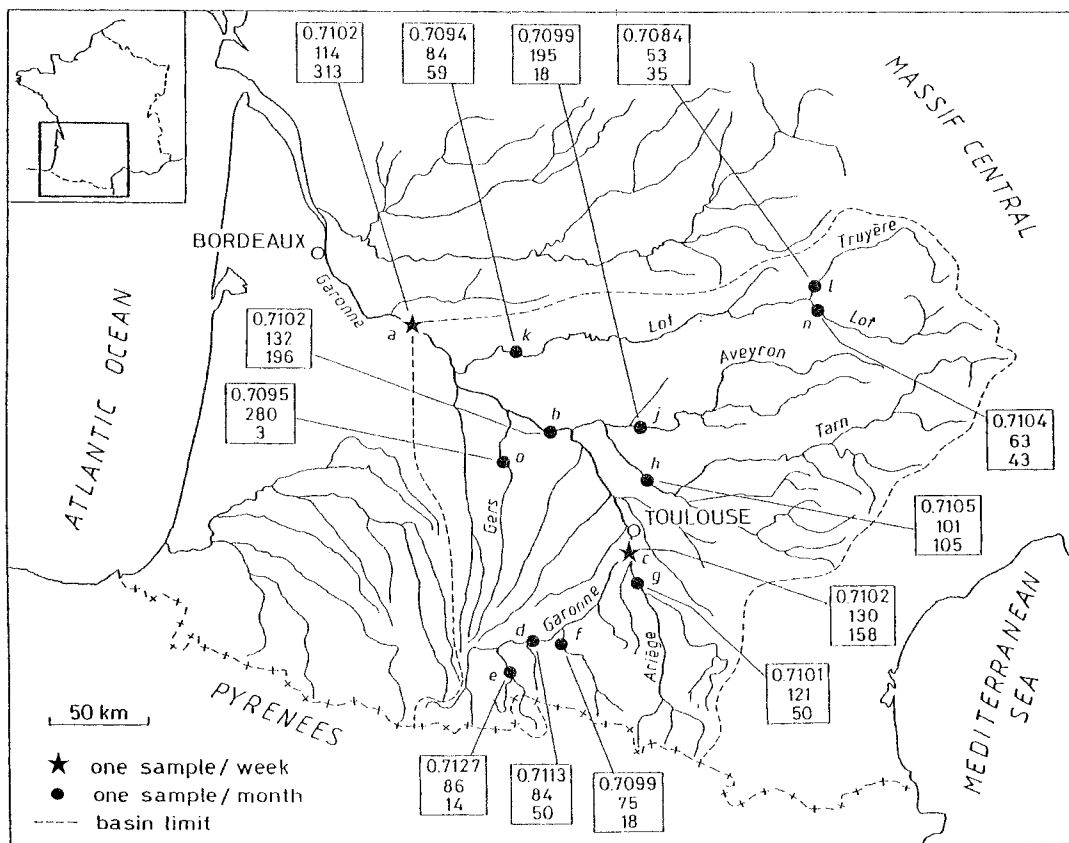


Fig. 1. Geographical sketch of the Garonne basin and location of the sampling stations. The average values of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, the Sr concentrations (in ppb) and the discharges (in m^3/s) measured in the Garonne and tributary waters during the 1990–1992 period are given in the boxes.

tion near Portet (station c on Fig. 1) ranged from 30 to 1890 m^3/s with a yearly average of 134 m^3/s , whereas the discharge at the La Réole downstream station (station a on Fig. 1) ranged from 52 to 4790 m^3/s with a yearly average of 403 m^3/s . The upper part of the Garonne river and its major tributary the Ariège in the Pyrénées mountains, supply about 32% of the total discharge of the Garonne river at its outlet. A large number of tributaries draining the Massif Central collectively contribute about 62% of the total Garonne discharge. The remainder of the total discharge comes from the Lanemezan area that is underlain by molassic sediments, whereas the small rivers draining the molassic sediments in the centre of the basin amount the remainder 5–6%. When compared to the interannual discharge (1910–

1992) of the Garonne river (Probst and Tardy, 1985), the survey period (1989–1992) corresponds to a dry episode. The mean discharge of the Garonne during that period is 34% lower than the interannual value corresponding to the 1910–1992 period. The year 1989 was the one with the greatest hydrological deficit that was observed during the last decade.

3. Sample description and analytical procedure

3.1. Dissolved material

The waters of the Garonne river were collected at five stations, one of which is at La Réole located

approximately 60 km southeast of Bordeaux (station a on Fig. 1), and the others further upstream at Lamagistère, Portet, Valentine and Plan d'Arem (stations b, c, d and e on Fig. 1, respectively). Water samples were also collected from three tributaries emerging from Pyrénées mountains. These samples constitute waters from the Ariège river near Lacroix Falgarde (station g on Fig. 1), the Gers river near Layrac (station o on Fig. 1), and the Salat river approximately 1 km from its confluence with the Garonne river (station f on Fig. 1). Tributaries from Massif Central were also sampled: the Tarn river near Montauban (station h on Fig. 1), the Aveyron river near Loubéjac (station j on Fig. 1), the Lot river near Villeneuve (station k on Fig. 1) and in its upper part before the confluence with the Truyère stream (station n on Fig. 1). Samples were also collected in the Truyère stream (station l on Fig. 1). Sampling was carried out periodically from May 1990 to August 1992 (Table 1). Up to 118 samples were collected, filtered through a Millipore HAWP 047-00 filter of 0.45 μm pore size, consisting in an ester of cellulose (nitrate + acetate) filter, acidified with 0.1 ml of HCl 4N and stored in acid-washed polyethylene bottles. Approximately 100 ml of each water sample was analyzed for the Sr concentration and

$^{87}\text{Sr}/^{86}\text{Sr}$ ratio with the remainder kept for major element analyses (both anions and cations). By convention in the continuation of this work, the dissolved elements belong to this filtered water, knowing that colloidal components that were not studied separately, may have a significant influence.

The Sr concentrations were determined within an accuracy of 1% on a Plasma Quad ICP-MS equipped with an ultrasonic nebulizer, using the isotope-dilution method with an enriched ^{84}Sr spike. For determination of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, the Sr was purified by standard cation-exchange procedure and the ratios were measured on a VG-354 mass spectrometer. Both were measured at the Department of Geology at Mc Master University (Canada). The reproducibility was verified by periodic determinations of the NBS 987 standard. The average $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of this standard for 10 determinations during the course of the study was 0.710212 ± 0.000024 ($2\sigma m$), and the precision for a single run was 0.0015% (two standard errors of the mean: $2\sigma m$). All $^{87}\text{Sr}/^{86}\text{Sr}$ ratios reported were normalized to a NBS 987 $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.71023.

The concentrations of major cations (Ca, Mg, Na and K) were determined by atomic absorption on a spectrometer Hitachi Z 8200 with an air-C₂H₂

Table 1

Average concentrations of the major dissolved elements of the Garonne river and its main tributaries during the 1990–1992 period a, b, c, d, e, k, l, n stand for the different sampling stations; for explanation, see text. The individual values are available upon request.

Station	mmol/l								
	Na	K	Mg	Ca	HCO ₃	Cl	NO ₃	SO ₄	SiO ₂
<i>Garonne</i>									
a	0.432	0.061	0.271	1.194	2.200	0.451	0.211	0.211	0.061
b	0.325	0.049	0.288	1.160	2.242	0.357	0.203	0.195	0.092
c	0.282	0.045	0.177	1.213	2.138	0.299	0.207	0.192	0.090
d	0.074	0.018	0.075	0.737	1.358	0.056	0.028	0.121	0.078
e	0.077	0.019	0.047	0.633	1.151	0.049	0.017	0.107	0.081
<i>Lot</i>									
k	0.208	0.046	0.227	0.932	1.966	0.203	0.102	0.114	0.103
n	0.165	0.036	0.268	0.636	1.623	0.151	0.049	0.076	0.102
l	0.180	0.036	0.106	0.166	0.490	0.132	0.045	0.035	0.158
Tarn	0.367	0.050	0.339	0.924	1.974	0.381	0.165	0.176	0.067
Aveyron	0.291	0.097	0.390	1.216	2.488	0.362	0.228	0.217	0.125
Ariège	0.220	0.033	0.132	1.036	1.840	0.210	0.139	0.169	0.087
Gers	0.497	0.092	0.340	1.933	3.034	0.781	0.522	0.332	0.086
Salat	0.089	0.018	0.112	0.726	1.421	0.057	0.024	0.120	0.082

gaseous mixture at the Centre de Géochimie de la Surface of the University of Strasbourg (France). La was added (0.5%) to the sample for the Ca and Mg analyses. These measurements were made with an accuracy of 1 $\mu\text{mol/l}$. The major anion (NO_3 , Cl and SO_4) concentrations were determined by liquid-ion chromatography on a Dionex chromatograph 4000I equipped with columns AG11 and AS11, using NaOH as eluant. The overall detection limit was 1 $\mu\text{mol/l}$. The alkalinity was measured by titration with 0.02 H_2SO_4 . The total analytical precision varied between 1 and 2%.

3.2. Particulate material

Samples of suspended sediments were collected during a flooding event (June 1992) at La Réole (station a). One sample (SL_1) was taken shortly before flooding, a second (SL_2) during the rising stage and a third (SL_3) during the falling stage. The sample volumes varied between 25 and 50 l. The particulate matter was concentrated by ultracentrifugation at 8000 rot/min during 90 min and the resulting suspension was split into four equivalent parts. One of these was analyzed by X-ray diffraction, and by transmission electron microscopy (TEM) and scanning electron microscopy (SEM) for mineralogical identification. A second split was leached with 1N HCl for 15 min at room temperature, following the method of Clauer et al. (1993). This fraction was used to determine separately the concentration and isotope composition of the Sr trapped in the soluble and silicate mineral phases of the suspended loads. A third split of the suspended loads was treated with NH_4Cl to determine the cation-exchange capacity of the particulate material. Ammonium chloride is known to remove exchangeable cations of clay material, preserving soluble calcite. The remaining split was saved untreated. Leaching by HCl and NH_4Cl may help to identify the contributions of the adsorbed, soluble and residual silicate matter, i.e. to differentiate in the river transport the elements belonging either to the chemical weathering, or to the mechanical erosion of the continental surfaces (Sayles and Mangelsdorf, 1977).

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of Sr separated from the leachates and residues of the particulate matter, and

of the untreated equivalents, as well as the corresponding dissolved loads during the flooding event, were determined on a VG Sector thermo-ionisation mass spectrometer with six collectors at the University of Strasbourg. The Sr separation was accomplished by using a cation-exchange procedure described by Schaltegger et al. (1994). The external reproducibility of the $^{87}\text{Sr}/^{86}\text{Sr}$ determinations was controlled by analyzing the standard NBS 987. During the course of the study, the mean $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 64 measurements averaged 0.710258 ± 0.000028 (2σ). As for the dissolved Sr, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were normalized to the NBS 987 value of 0.71023.

4. Results

4.1. Elemental compositions of the dissolved loads

The Na contents of the Garonne waters from the upstream side are relatively lower than those from the downstream side (Table 1). Many of these waters have Na/Cl molar ratios of approximately 1, but several were found with ratios that are clearly either lower than 1 as for some waters from downstream side, or higher than 1 as for some upstream waters (Fig. 2). The cause or causes of either Na-enrichment or Na-depletion relative to Cl are not clear. But in the absence of any evaporite deposits in the basin,

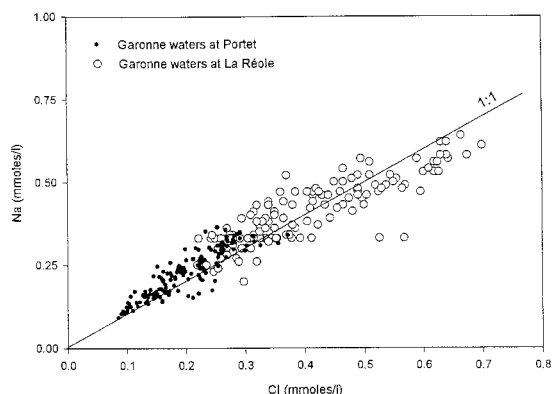


Fig. 2. Relationship between the Na and Cl concentrations (in mmol/l) measured upstream and downstream the Garonne river during the 1989–1992 period.

agricultural or communal pollution could have some important role in making the waters from the lower watershed to be lower than 1 in Na/Cl molar ratios. The trends in the Na/Cl relationship make evident that the influence of marine aerosols either from the Atlantic Ocean on the Mediterranean Sea is minimal. Marine aerosol input to the total dissolved constituents of the Garonne river, which is draining the basin for the most part more than 50 km away from the coast, is also considered to be small in light of the study of Ulrich et al. (1994) that has shown that precipitations occurring in lands more than 50 km away from the sea have very little marine aerosol inputs.

A comparison between the Ca and Sr contents of the waters from different tributaries of the Garonne river, shows that the Lot, Ariège and Tarn rivers have similar Ca/Sr ratios in the range between 500 and 1000, whereas the Gers and Aveyron tributary rivers have widely scattered ratios between 250 and 1000 (Fig. 3). The data suggest that the Lot, Ariège and Tarn have similar sources for these two elements, whereas the Gers and Aveyron have widely

varied sources. For the same elements, Garonne upstream waters have similar Ca/Sr ratios between 620 and 850, whereas the waters downstream have a much wider range of values from 480 to 1030 after the confluence of the Ariège river, and they become somewhat less after the confluence of the Lot (Semhi, 1996). The Ca/Sr ratios of the Garonne river seem to be influenced by the contributions of the tributaries.

Dissolved elements in river waters are generally derived from principally two lithological sources, carbonate and silicate-crystalline rocks. To provide information about the source of the elements dissolved in the Garonne-river waters, relationships among Sr and such elements that distinguish silicate sources (Na, K) from carbonate rocks (Ca, Mg) were examined. Comparison of the Ca/Na and Sr/Na ratios yields best-fit trends with high correlation coefficients of 0.90 for the Tarn, 0.96 for the Ariège and 0.78 for the Gers waters, whereas these ratios are more or less scattered for the waters of the Garonne river (Fig. 4A). The Mg/K and Sr/K ratios give similar best-fit trends with high correla-

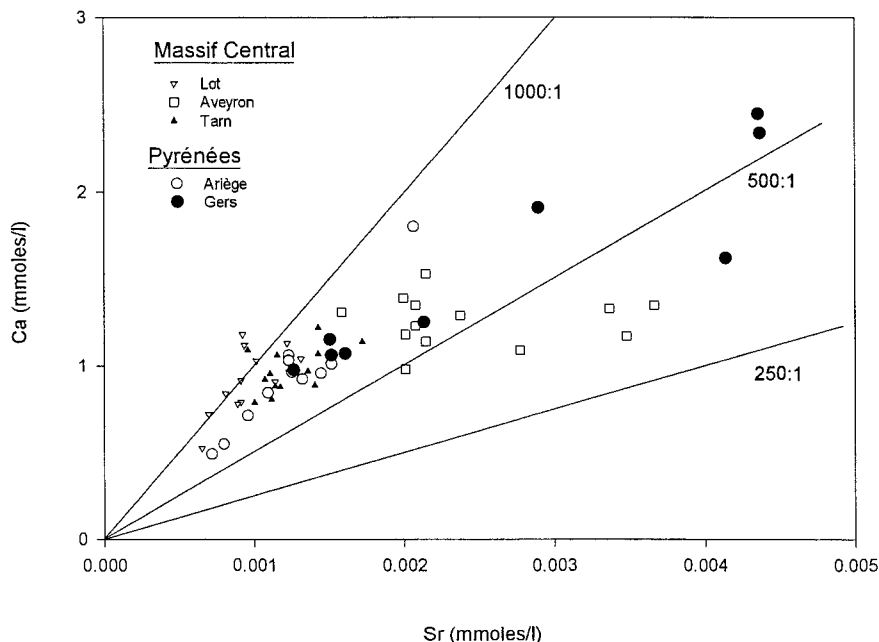


Fig. 3. Relationship between the Ca and Sr concentrations (in mmol/l) measured in the waters of the main tributaries of the Garonne river during the 1990–1992 period.

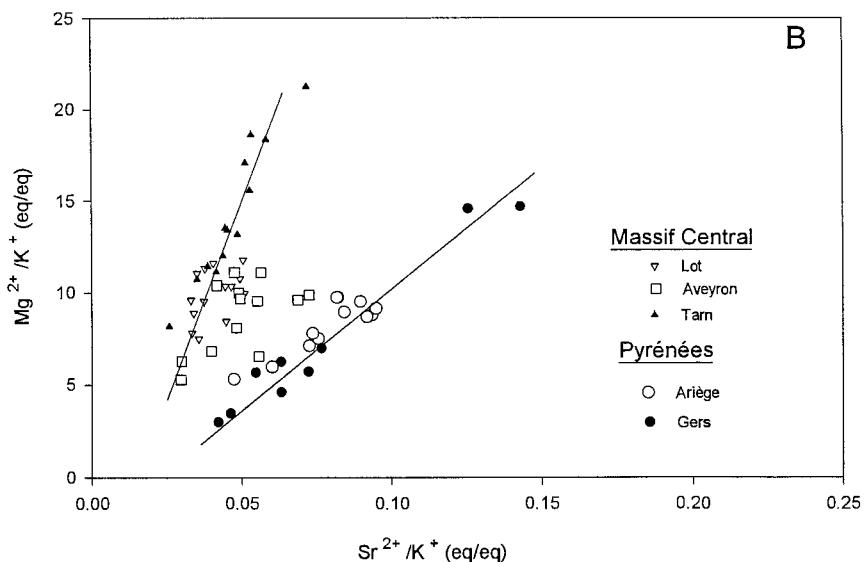
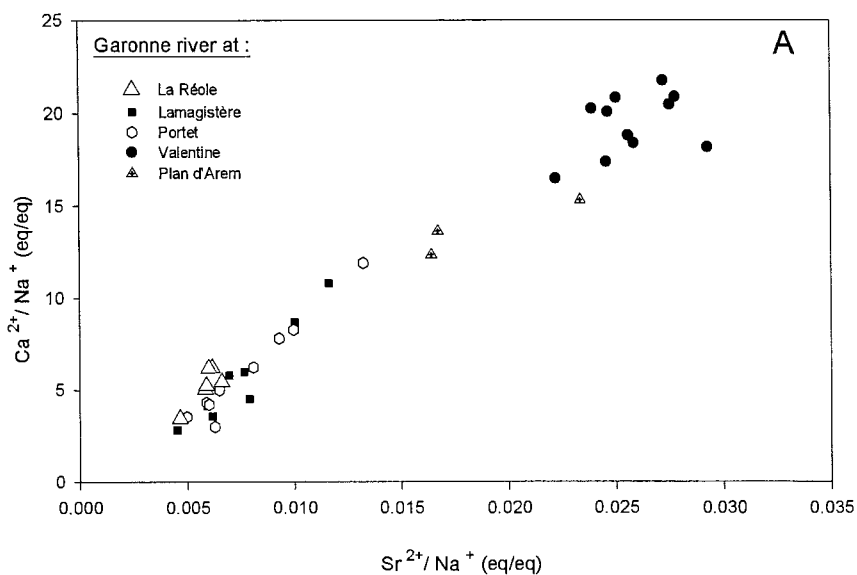


Fig. 4. Variations of ionic $\text{Ca}^{2+}/\text{Na}^+$ ratios versus ionic $\text{Sr}^{2+}/\text{Na}^+$ ratios observed in the Garonne waters (A) and ionic $\text{Mg}^{2+}/\text{K}^+$ ratios versus ionic $\text{Sr}^{2+}/\text{K}^+$ ratios observed in the main tributary waters (B) during the 1990–1992 period. The ionic $\text{Ca}^{2+}/\text{Na}^+$, $\text{Sr}^{2+}/\text{Na}^+$, $\text{Mg}^{2+}/\text{K}^+$ and $\text{Sr}^{2+}/\text{K}^+$ ratios are in eq/eq.

tion coefficients of 0.96 for the Tarn, 0.92 for the Ariège, 0.98 for the Gers and 0.59 for the Aveyron waters (Fig. 4B). Such high correlation coefficients suggest that the Garonne river and its tributaries are mainly supplied by two major reservoirs: a carbonate

one with high Ca/Na and Sr/Na ratios and a Mg–Fe poor crystalline silicate one with low Ca/Na and Sr/Na ratios. The streams from Massif Central have a trend in the Mg/K vs. Sr/K diagram that is different from those from the Pyrénées mountains.

Table 2

Discharge (m^3/s), concentration of dissolved Sr (ppb) and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in waters of the Garonne river and its tributaries during the 1990–1992 period

Errors and averages are at 2σ level.

Station	Year/ month	$^{87}\text{Sr}/^{86}\text{Sr}$	Sr (ppb)	Discharge (m^3/s)
<i>Garonne</i>				
La Réole				
(a)	91/09	0.710031	113	120
(a)	91/11	0.710171	107	469
(a)	92/01	0.710303	124	
(a)	92/02	0.710097	115	344
(a)	92/03	0.710675	123	316
(a)	92/12	0.709938	112	318
Average ^a	($n = 6$)	0.71021 ± 0.00026	114 ± 7	313 ± 125
Lamagistère				
(b)	90/07	0.710322	124	65
(b)	90/08	0.710393	104	81
(b)	90/11	0.710256	105	174
(b)	91/04	0.710430	126	533
(b)	91/05	0.710120	133	331
(b)	91/10	0.709962	144	86.5
(b)	91/11	0.709784	149	111
(b)	92/03	0.710148	173	183
Average ^a	($n = 8$)	0.71022 ± 0.00022	132 ± 23	196 ± 161
Portet				
(c)	90/07	0.710556	115	47
(c)	90/08	0.710508	96	61
(c)	90/11	0.710623	100	120
(c)	91/04	0.710246	134	257
(c)	91/05	0.710047	142	617
(c)	91/06	0.710433	79	130
(c)	91/10	0.710216	185	37.5
(c)	91/11	0.710025	115	67.6
(c)	92/03	0.710015	170	82.7
Average ^a	($n = 9$)	0.71018 ± 0.00024	130 ± 35	158 ± 184
Valentine				
(d)	90/05	0.711365	67.98	142
(d)	90/06	0.711397	83.98	30.1
(d)	90/07	0.711261	111	20
(d)	90/09	0.711345	113	5.3
(d)	90/10	0.711870	74	44.6
(d)	90/11	0.711136	94	14
(d)	91/04	0.711283	88	76.2
(d)	91/05	0.711456	79	138
(d)	91/10	0.711083	118	24
(d)	91/11	0.710716	117	36.7
(d)	92/02	0.710960	109	17.8
Average ^a	($n = 11$)	0.71131 ± 0.00030	84 ± 18	50 ± 48
Plan d'Arem				
(e)	91/10	0.712362	89	16
(e)	91/11	0.713246	71	5
(e)	92/02	0.712902	87	20
Average ^a	($n = 3$)	0.71272 ± 0.00044	86 ± 10	14 ± 7

Table 2 (continued)

Station	Year/ month	$^{87}\text{Sr}/^{86}\text{Sr}$	Sr (ppb)	Discharge (m^3/s)
<i>Lot</i>				
Villeneuve				
(k)	90/07	0.710070	80	15
(k)	90/08	0.709960	81	11
(k)	90/10	0.709150	115	14
(k)	90/11	0.709470	61	74.3
(k)	91/04	0.709550	71	96
(k)	91/05	0.709150	56	17
(k)	91/10	0.709010	108	13
(k)	91/11	0.709340	89	42
(k)	92/03	0.709040	100	50
(k)	92/04	0.709380	98	240
(k)	92/05	0.709170	82	55
(k)	92/06	0.709680	73	151
(k)	92/07	0.709550	81	26
(k)	92/08	0.709220	108	24
Average ^a	($n = 14$)	0.70941 ± 0.00033	84 ± 18	59 ± 65
Upstream Lot				
(n)	91/10	0.710400	67	6
(n)	91/11	0.709940	55	6.8
(n)	92/03	0.710030	67	75.3
(n)	92/04	0.710260	53	67
(n)	92/06	0.710380	64	70.5
(n)	92/07	0.710990	62	84.6
(n)	92/08	0.710700	63	12
(n)	92/09	0.710500	80	20
Average ^a	($n = 8$)	0.71044 ± 0.00034	63 ± 8	43 ± 34
Truyère				
(l)	91/10	0.709060	53	6.8
(l)	91/11	0.708570	55	9.6
(l)	92/03	0.708440	52	13
(l)	92/04	0.708000	54	105
(l)	92/06	0.708450	52	119
(l)	92/07	0.709240	48	20
(l)	92/08	0.708950	51	4
(l)	92/09	0.709350	53	2
Average ^a	($n = 8$)	0.70836 ± 0.00049	53 ± 3	35 ± 50
<i>Aveyron</i>				
Loubéjac				
(j)	90/07	0.709401	243	2.22
(j)	90/08	0.709660	208	6.9
(j)	90/11	0.710270	182	12.2
(j)	91/04	0.710677	139	4.18
(j)	91/05	0.709691	188	27
(j)	91/06	0.709220	295	19.1
(j)	91/10	0.708919	305	1.06
(j)	91/11	0.709720	188	25.08
(j)	92/03	0.710025	176	21.8
(j)	92/05	0.709940	182	28.8
(j)	92/07	0.710500	175	60
(j)	92/08	0.708900	321	4
Average ^a	($n = 12$)	0.70991 ± 0.00057	195 ± 60	18 ± 16

Table 2 (continued)

Station	Year/ month	$^{87}\text{Sr}/^{86}\text{Sr}$	Sr (ppb)	Discharge (m^3/s)
<i>Tarn</i>				
Montauban				
(h)	90/07	0.709654	125	19.7
(h)	90/08	0.709631	125	35.9
(h)	90/11	0.709664	84	74.3
(h)	91/04	0.710431	101	173
(h)	91/05	0.710919	94	144
(h)	91/06	0.710347	103	87.2
(h)	91/10	0.709834	123	43
(h)	91/11	0.709636	119	34.1
(h)	92/03	0.710683	88	72.1
(h)	92/04	0.710870	100	72.1
(h)	92/05	0.710910	98	385
(h)	92/07	0.711030	97	189
(h)	92/08	0.709910	151	37.6
Average ^a (n = 13)		0.71058 ± 0.00057	101 ± 19	105 ± 100
<i>Ariège</i>				
Lacroix Falgarde				
(g)	90/05	0.710698	83	67.6
(g)	90/06	0.709989	127	31.2
(g)	90/08	0.709760	133	21.8
(g)	90/09	0.710675	84	21.8
(g)	90/10	0.711145	70	17.8
(g)	90/11	0.710330	96	30.4
(g)	91/04	0.710140	110	91.4
(g)	91/05	0.710580	108	55.7
(g)	91/10	0.709930	116	25
(g)	91/11	0.709970	108	78.5
(g)	92/04	0.709810	181	119
(g)	92/05	0.710650	129	39.7
Average ^a (n = 12)		0.71014 ± 0.00044	121 ± 29	50 ± 32
<i>Gers</i>				
Layrac				
(o)	90/07	0.710009	133	0.9
(o)	90/08	0.709668	187	0.9
(o)	90/10	0.710584	111	1.5
(o)	90/11	0.709482	383	7.2
(o)	91/04	0.709397	254	10.5
(o)	91/05	0.709397	382	3.6
(o)	91/10	0.710327	132	1.8
(o)	91/11	0.710084	141	2.1
(o)	92/03	0.709399	363	2.3
Average ^a (n = 9)		0.70951 ± 0.00045	280 ± 116	3 ± 3
<i>Salat</i>				
(f)	91/10	0.709730	111	10.8
(f)	91/11	0.709830	84	21.7
(f)	92/05	0.709970	62	29.9
(f)	92/07	0.709970	62	20.4
(f)	92/09	0.709900	87	8.3
Average ^a (n = 5)		0.70988 ± 0.00010	75 ± 20	18 ± 8

^aAverage taking the discharge into account.

This difference may be due to a change in the dolomite-to-calcite ratio of the two regions. However, the Sr concentrations should be negatively related to the Mg concentrations, in this case, which is not. We therefore tend to attribute the difference to a dominance of a basaltic lithology in the Massif Central mountains. The Aveyron waters seem to be different from the other tributaries in their Mg/K–Sr/K relationship. This suggests that its waters derive from more complex mixed sources beyond carbonate and Mg–Fe poor crystalline rocks.

4.2. Isotopic compositions and contents of the dissolved Sr

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and the Sr concentrations of waters of the Garonne river and its tributaries are given in Table 2. These waters show temporal variations in the Sr isotope ratios and concentrations. The Tarn river shows the most variations in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios from 0.70963 to 0.71103, whereas the Salat river shows the least from 0.70973 to 0.70997.

The Sr concentrations like the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of each individual river also vary temporally. The variations in these two parameters for each tributary but the Lot river, tend to bear a recognizable relationship (Fig. 5), while the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and the $1/\text{Sr}$ are approximately positively correlated for the waters of the Tarn, Aveyron, Gers and Ariège rivers. Of the four, Tarn has a poor correlation ($R^2 = 0.55$) com-

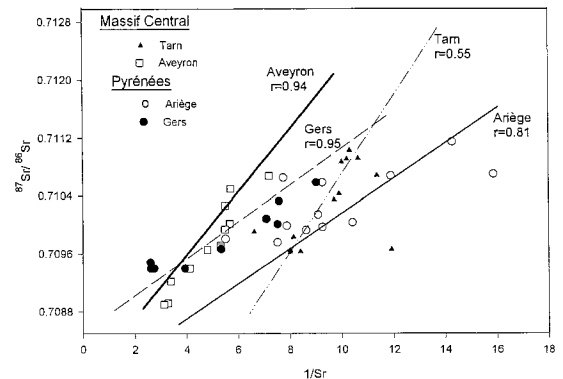


Fig. 5. An $^{87}\text{Sr}/^{86}\text{Sr}$ versus $1/\text{Sr}$ mixing diagram of the dissolved loads in two rivers from Massif Central and two from Pyrénées mountains.

pared to the others (R^2 better than 0.81). The two parameters remain unrelated to each other for the Lot. Where the correlations are good, they do not bear the same slopes. Where the correlation is poor, such as that for the Tarn river, or lacking such as that for the Lot river, the dissolved Sr derived from more than two sources. The variations in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for the Lot may be described in terms of mixing in varied proportions of Sr from a carbonate rock source, an alkali-rich Mg-poor silicate crystalline rock source, and a basaltic rock source (Fig. 6). The Massif Central lies to the northeast of the possible drainage basin of the Lot river. It is probable to have Sr coming to the drainage basin from the Massif Central, but this Sr has been added to the Lot river especially in the downstream region, as a groundwater addition.

The linear relationship in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and reciprocal of the Sr concentrations can be defined in terms of mixing of two components, one with high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and low Sr concentrations that characterizes Sr deriving from an alkali-rich and Fe-Mg-poor silicate rocks and the other with low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and high Sr concentrations deriving from carbonate dissolution. This indication of mixing

from the Sr data is also suggested by the major ion variations. The fact that the Sr contents and isotopic compositions of the two Pyrenean river waters display parallel arrays that have a different slope than those of the two Massif Central rivers may be due to the fact that the end-members are probably different among the areas, as outlined hereunder in the case of the Lot river.

Preliminary Sr isotope mass-balance calculations for the Garonne river reveal that in its upper region near the Pyrénées, one of the sources of Sr is from basic and ultrabasic crystalline rocks. This is illustrated by the October–November 1991 and February 1992 data for the waters collected at Plan d’Arem (station e) and Valentine (station d). Between these two stations of the Garonne river lies a tributary river. Sr isotope mass balance calculations from the 1991 data for the two stations imply that the tributary delivers Sr with $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.7071–0.7068 to the Garonne river. Similar calculations for the 1992 data suggest that the Garonne receives Sr with $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.7033 from the same tributary. Such low ratios imply that basic to ultrabasic rocks of the Pyrenées mountains may contribute to the Sr isotopic composition of the Garonne waters,

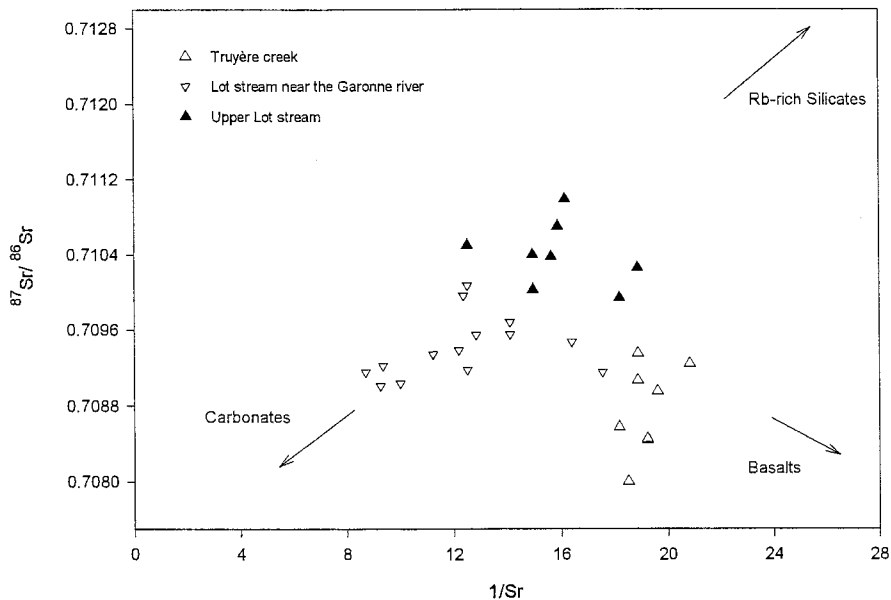


Fig. 6. An $^{87}\text{Sr}/^{86}\text{Sr}$ versus $1/\text{Sr}$ mixing diagram of the dissolved loads from waters of the Lot stream and its Truyère tributary.

contributing to the fact that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the waters may be quite varied over a longer period of survey.

4.3. Budget of dissolved Sr in the river waters

Knowledge of the seasonal discharge variations of the Garonne river and of the concentrations of the dissolved Sr at different sampling stations along the river allowed both to calculate the amounts of dissolved Sr transferred towards the ocean at given periods, and to evaluate the accuracy of these calculations. During November 1991, for instance, the water samples taken at the stations a–e, contained varied amounts of dissolved Sr, ranging from 0.4 g/s at Plan d'Arem (station e) through progressive downstream increase to 50.2 g/s at La Réole (station a). Although the amount of dissolved Sr transferred by the Garonne river progressively increases downstream, it cannot be accounted by addition of contributions by the tributaries. For example, the Sr was 16.5 g/s in November 1991, whereas that of the Lot and the Gers tributaries that join the Garonne river downstream of the Lamagistère station, were 3.7 and 0.3 g/s, respectively. Hence, the total Sr flux in the Garonne river after the confluence with the Lot should amount 20.5 g/s. This amount is less than the 50.2 g/s of Sr found to be carried by the Garonne river at La Réole. The discrepancy may mean that either the budget correlations are faulty, or that an additional supply of Sr, such as by aquifers, small tributaries or artificial reservoirs, must be taken into account in this part of the basin. The unbalance in the Sr budget is further evident if one takes the average amounts of Sr transferred by the Garonne river during the 2-year survey with 35.5 g/s at La Réole and with 25.9 g/s at Lamagistère and contrasts with the mean supplies of Sr by the Lot and Gers rivers for the same period with 5.4 and 0.8 g/s, respectively. Unless some major contribution could be attributed to the stream near the confluence with the Lot, which was not investigated in this study, the Sr budget remains sharply unbalanced. The systematic discrepancies suggest that the overall Sr budgets are difficult to balance. Among the possible reasons for such unbalanced budgets, one may consider some uncertainties in the determinations of discharge val-

ues, unless some discarded supplies have a more determining influence than expected.

4.4. Fluxes of dissolved Sr in the waters

The Sr concentrations and isotopic ratios of the different river waters were compared to the monthly discharges during the 2-year (1990–1992) survey period. For nearly all rivers, except the Gers for which the discharges are substantially lower than the others (Fig. 7), the Sr contents do not relate to discharges. On the other hand, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the dissolved Sr are positively well correlated with the discharges, except for the Gers waters for which the relationship is negative (Fig. 8). The Gers river is known to be temporarily supplied during summer time by waters of the Cap de Luz and Orédon artificial reservoirs located in the Pyrénées mountains, which are conveyed by the Neste canal. The chemistry of the Gers waters is consequently biased by these supplies, especially in summer time, when the discharge is low. For the Ariège, Lot, Tarn and possibly the Aveyron, it looks like the silicic end-member dominates during the high-water stages and the carbonate end-member during the low stages, suggesting that hydrology is the controlling factor of their Sr transfers. But this relationship between the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the dissolved Sr and the discharge is only confirmed for the Garonne waters at the sampling stations b and d (Fig. 9). The contents and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the dissolved Sr seem, therefore, not to be only monitored by the seasonal variations of the water discharges.

No clear relationships could be established between the concentrations or $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the dissolved Sr in the different river waters of the Garonne basin, and their discharges. This signifies that the seasonal variations of these parameters, are also monitored by some other parameters and that budget calculations based on limited samplings may neglect the Sr fluxes. This is discussed later through mass-balance calculations based on different Sr contents and discharge volumes.

4.5. Mineralogic and Sr isotopic compositions of the particulate loads

The suspended sediments transported by the Garonne river at La Réole (station a) consist mainly

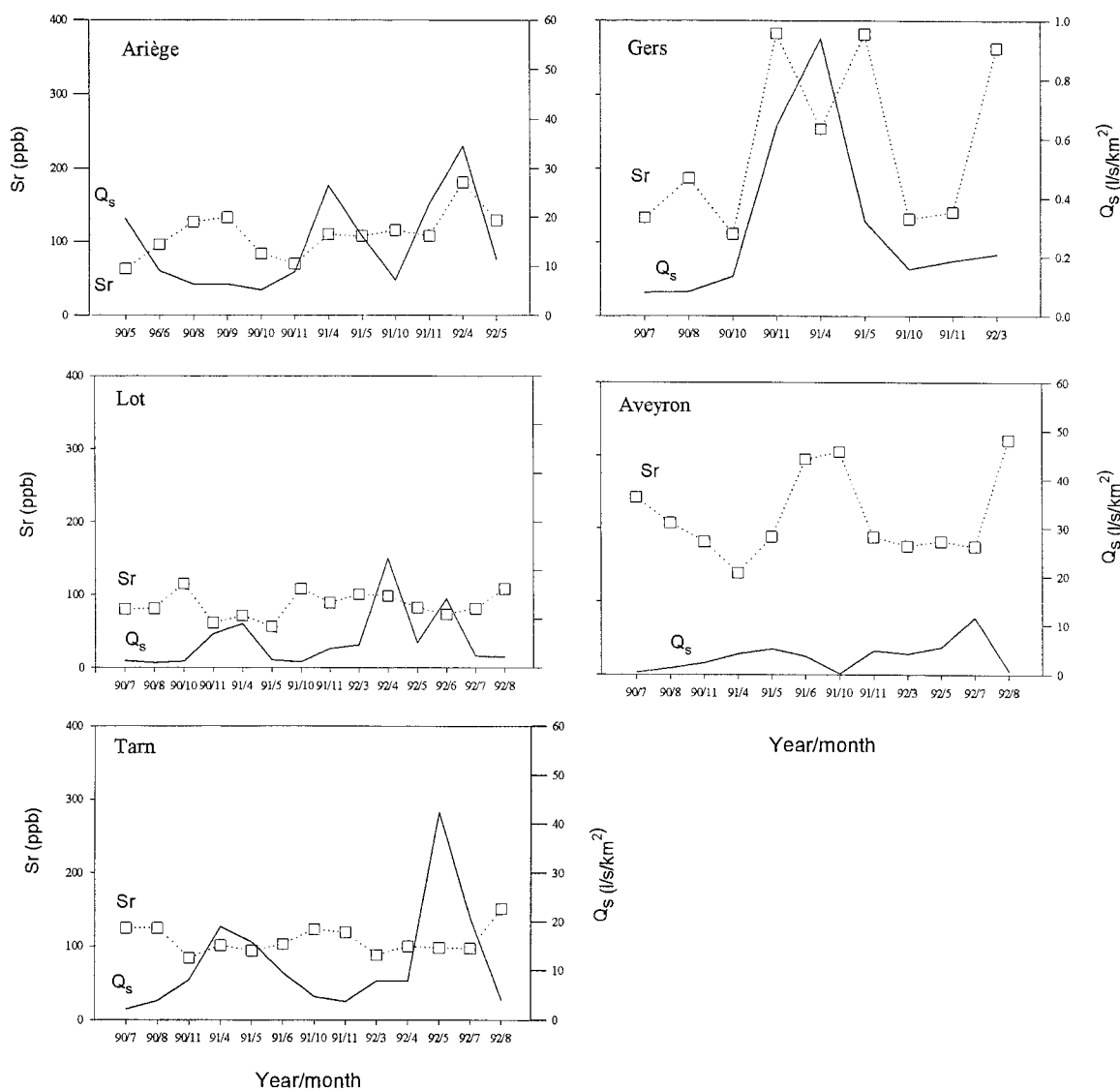


Fig. 7. Seasonal variations of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios combined with the seasonal variations of the specific discharge Q_s (in $\text{l}/\text{km}^2/\text{s}$) observed in the main tributaries of the Garonne river during the 1990–1992 period.

of clay particles (40–50%) and fine quartz grains (40%). The clay fraction contains 35–50% of mixed-layer illite/smectite (I/S), 25–35% of illite, 10–15% of kaolinite and 10–15% of chlorite (Table 3). The amounts of I/S and chlorite increase during the rising stage of the flood event as already shown by Probst and Bazerbachi (1986), whereas the amounts of kaolinite and illite decrease. Calcite has

been detected in accessory amounts (< 10%). Apatite, zircon and rutile were also identified in trace concentrations.

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the dissolved loads during the flood event of June 1992 range from 0.71003 to 0.71040; the lowest value corresponds to the sample taken after the maximum. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the particulate loads range from 0.71869 to 0.72054,

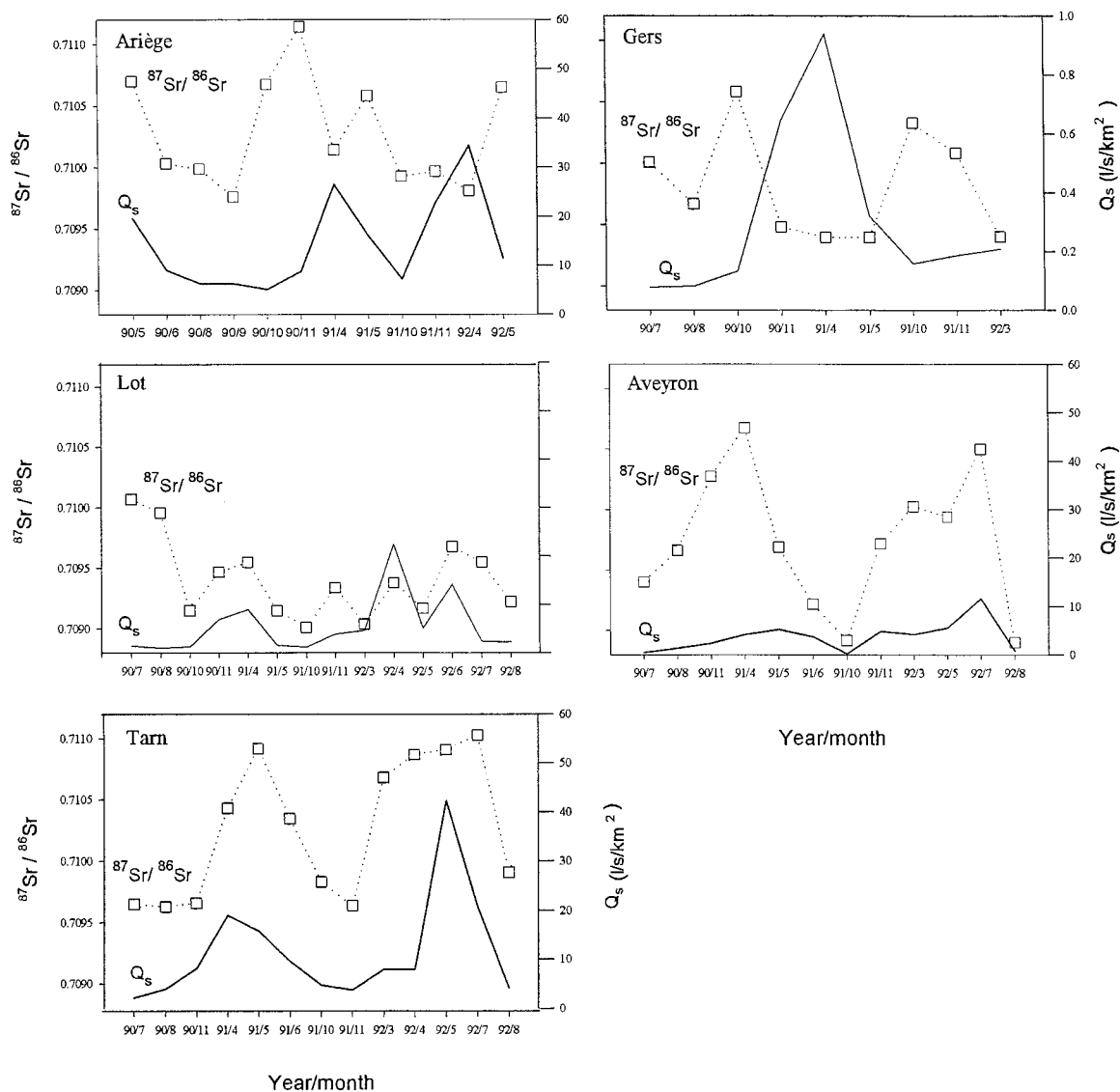


Fig. 8. Seasonal variations of the Sr concentrations combined with the seasonal variations of the specific discharge Q_s (in $l/km^2/s$) observed in the main tributaries of the Garonne river during the 1990–1992 period.

suggesting occurrences of minerals enriched with Rb, and consequently in radiogenic ^{87}Sr , including I/S and illite. Leaching of the particulate loads with 1N HCl increased their $^{87}Sr/^{86}Sr$ ratio to 0.72355–0.72559, with corresponding $^{87}Sr/^{86}Sr$ ratios of the leachates at 0.70982–0.71012. The NH_4Cl treatment increased the $^{87}Sr/^{86}Sr$ ratio of the residual silicate material to about 0.72023–0.72390, which was sys-

tematically below the $^{87}Sr/^{86}Sr$ ratio of the residue after HCl leaching. The leachates after NH_4Cl treatment yield $^{87}Sr/^{86}Sr$ ratios slightly above that of the HCl leachates at 0.70961–0.71393, further confirming that leaching of clay-type material with dilute (1N) HCl does not remove preferentially radiogenic ^{87}Sr (Table 4). The $^{87}Sr/^{86}Sr$ ratios of the HCl and NH_4Cl leachates and those of the HCl and

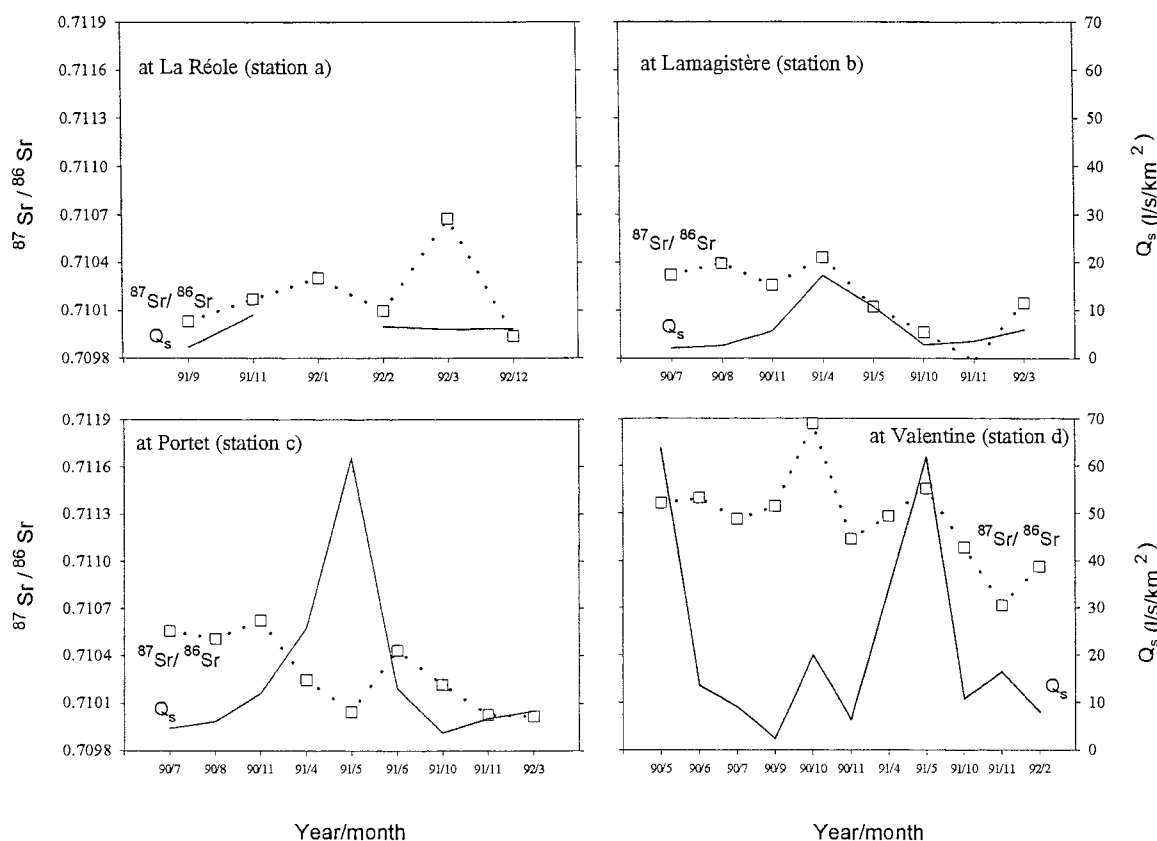


Fig. 9. Seasonal variations of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio combined with the seasonal variations of the specific discharge Q_s (in $\text{l}/\text{km}^2/\text{s}$) observed in the Garonne waters during the 1990–1992 period.

Table 3

Mineral composition of the suspended loads from Garonne waters during the 1992 flooding event at the starting (SL_1), rising (SL_2) and decreasing stages (SL_3)

Mixed layer stands for mixed layer illite/smectite.

Samples	Major minerals (%)				
	Quartz	Clays	Microcline	Plagioclase	Calcite
SL_1	41	47	2	4	6
SL_2	40	51	0	3	6
SL_3	40	39	3	4	14

	Clay minerals (%)			
	Kaolinite	Illite	Chlorite	Mixed layer
SL_1	12	34	11	43
SL_2	10	26	14	51
SL_3	15	34	14	37

NH_4Cl residues appear slightly different, indicating removal of different Sr by the two experiments. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the leachates are also different from those of the dissolved Sr loads, implying that neither the Sr of the soluble mineral phases nor that adsorbed onto the silicate particles originated from Garonne waters. This Sr was most probably incorporated in crystallizing minerals or adsorbed on clay particles in the soils, during a pedogenic episode. Mass-balance calculations showed that 82–94% of the total Sr carried by the Garonne waters was dissolved (Table 4), that 1–3% was adsorbed (leached by NH_4Cl) onto particles, that 1–4% was trapped in soluble minerals (leached by HCl), and that the remainder (5–14%) was trapped in insoluble minerals.

Table 4

$^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the dissolved (S), and the untreated particulate loads (U), the leachates (L) and residues (R) of Garonne waters during the 1992 flooding event with 1N HCl and 1N NH_4Cl , L/U in % = amount of leachate relative to untreated; L/(U + S) = amount of leached strontium relative to the budget of the waters; S/(U + S) = amount of dissolved strontium relative to the whole Sr budget of the waters; U/(U + S) = amount of particulate strontium relative to the whole Sr budget of the waters.

Samples	Dissolved loads				Particulate load HCl experiment				NH ₄ Cl experiment					
	S	U	L	R	L/U	L/(U + S)	S/(U + S)	U/(U + S)	L	R	L/U	L/(U + S)	S/(U + S)	U/ U + S
	$^{87}\text{Sr}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$	%	%	%	%	$^{87}\text{Sr}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$	%	%	%	%
SI ₁	0.71032 ± (6)	0.72044 ± (5)	0.70982 ± (6)	0.72503 ± (5)	24,50	4	82	14	0.71393 ± (20)	0.72023 ± (9)	15,42	3	83	14
SI ₂	0.71040 ± (5)	0.72054 ± (5)	0.71012 ± (7)	0.72559 ± (6)	20,05	2	87	11	0.71071 ± (13)	0.72390 ± (10)	19,49	2	88	10
SI ₃	0.71003 ± (6)	0.71869 ± (6)	0.70957 ± (6)	0.72355 ± (6)	23,62	1	94	5	0.70961 ± (8)	0.72222 ± (7)	19,38	1	94	5

5. Discussion

Accurate modelling of Sr transfer from any drainage basin to the ocean needs detailed information about the isotopic compositions and amounts of Sr dissolved in the river waters, of Sr adsorbed on the solid mineral phases, and of Sr trapped in soluble mineral phases. Special attention is given here to (1) an evaluation of the relative contribution of reservoirs for the dissolved Sr, and (2) an assessment of variations of these contributions relating to the discharge volumes of the tributaries and Sr concentrations of the waters.

5.1. Isotopic compositions and concentrations of the dissolved Sr

The Garonne river flows conceptually over two major rock lithologies that differ in their Sr contents and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. All rivers from the Pyrénées mountains except the Gers, have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios very close to 0.710 or higher (Garonne at Plan d'Arem and at Valentine). The Sr concentrations are about 100 ppb, ranging from 75 to 121 ppb. Whatever their origin, the Gers waters have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.7095 and high Sr concentrations of about 280 ppb, which are characteristic of a carbonate lithology. But because of its low discharge, the influence of the Gers is negligible on the Sr budget of the Garonne river downstream. With the exception of the Tarn river, the waters draining the Massif Central, have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios lower than 0.710 and Sr concentrations between 84 and 195 ppb. The mean values for the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, Sr concentrations and discharges for the 2-year survey period are given in Fig. 1. A reason for the Sr isotopic and content variations in the tributaries of the Garonne river could be that the bedrocks in the tributary drainage basins consisting of carbonate rocks, are varied in their Sr compositions and Sr contents. The variations could be within a single unit or among different units in the stratigraphic sequence.

A detailed study of the Sr concentrations and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the different waters in the Garonne basin also reveals that during the 2-year survey, there is no clear relationship between discharge and Sr contents or $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, and that all the tributaries, but Salat, yield varied $^{87}\text{Sr}/^{86}\text{Sr}$ ratios with

varied Sr concentrations. The Salat had nearly constant $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.7099 but varied Sr concentrations. On the other hand, the Garonne waters at each individual station had nearly constant $^{87}\text{Sr}/^{86}\text{Sr}$ ratios but varied Sr concentrations. The tributaries are not only varied in their $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and Sr concentrations, but also varied in their discharges. With such variations, budget calculation is difficult. The Garonne river flow could be differentiated into segments, one consisting of stations c, b and a with identical $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of about 0.7102, and the other of stations e and d with $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.7127 and 0.7113, respectively. The near constancy of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios from stations c–a is remarkable, because the tributaries that add water to the Garonne between these stations, are varied in their $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and Sr concentrations. These tributaries emerge either from the Massif Central from the Pyrénées mountains. Station c or any point upstream the Garonne receives input from any major tributary from the Massif Central. This suggests that if one takes into account the Sr budget integrating the 2-year survey, the input of the Massif Central rivers is not modifying significantly the Sr contents and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the Garonne waters. This could be due to the relative discharges of the different rivers. It may also be mentioned that in November 1991, the discharge of the Garonne river increased downstream progressively with 5 m³/s at Plan d'Arem (station e), 37 m³/s at Valentine (station d), 68 m³/s at Portet (station c), 111 m³/s at Lamagistère (station b) and 469 m³/s at La Réole (station a). Thus, in November 1991, the discharge from station c to station b increased by a factor of 1.6. Contrary to this increase in November 1991, the available data show that the discharge decreased by a factor of 2 between the same two stations in May 1991. Such variations can only be explained by connections to either near surface aquifers that may supply or subtract waters, or artificial regulations by man-made reservoirs. In view of such an apparent loss of waters by an unknown or undefinable avenue of transfer, mass budgeting is difficult to construct.

5.2. Isotopic compositions of the Sr adsorbed on particles and trapped in soluble mineral phases

The amounts of Sr trapped in soluble minerals and adsorbed on the silicate particulate loads repre-

sent 2–5% of the total Sr dissolved in the Garonne waters during a flood event. Despite their importance for understanding the weathering-erosion processes occurring in a drainage basin, such relatively small amounts should not significantly alter budget calculations of total-Sr transfers in the Garonne drainage basin. Also, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the “particulate” Sr that may be added to the dissolved Sr, either by desorption or by dissolution of the soluble minerals, may deviate slightly from $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the dissolved Sr, indicating a different origin. In fact, such differences in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are probably quite small in most cases, as it is here, because intermediate reservoirs such as a pedogenic profile certainly yield Sr contents and isotopic compositions that remain close to that of the outcropping rocks. We have therefore decided not to take into account the Sr concentrations and the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of both the adsorbed component and the soluble mineral phase in the calculations that were made to estimate the changing contributions of the major reservoirs of Sr for the dissolved phase.

5.3. Origin of the Sr dissolved in the river waters

If it is assumed that the dissolved Sr of the different river waters studied here, is mainly from two sources, the contribution of each reservoir to the budget of the dissolved Sr can be calculated by using a simple mixing equation (Eq. (1)). This equation takes into account the average discharge, Sr concentration and $^{87}\text{Sr}/^{86}\text{Sr}$ ratio at steady-state volumes for each tributary. The two main reservoirs considered here are silicate- and carbonate-dominated. We have neglected the volcanics of the Massif Central that contribute mainly to the Lot river and to a lesser extent to the final budget. The mass-balance equations applied to the amount of Sr delivered by each of the two reservoirs (subscripts 1 and 2) to the Garonne river or to one of its tributaries (subscript t) are formulated as:

$$C_t Q_t R_t = C_1 Q_1 R_1 + C_2 Q_2 R_2 \quad (1)$$

where C is the average Sr concentration (in ppb), Q the average discharge (in m^3/s) and R the average $^{87}\text{Sr}/^{86}\text{Sr}$ ratio. The mass balance applied to the discharge is given as:

$$Q_t = Q_1 + Q_2 \quad (2)$$

Thus, the amount of Sr supplied by the two reservoirs to the Garonne waters follows the equations:

$$F_1 = Q_1 C_1 \quad (3)$$

$$F_2 = Q_2 C_2 \quad (4)$$

The Sr concentrations of the silicate (C_1) and carbonate (C_2) reservoirs were estimated by using the correlations between the $^{87}\text{Sr}/^{86}\text{Sr}$ and $1/\text{Sr}$ ratios as:

$$[\text{Sr}] = a / ({}^{87}\text{Sr}/{}^{86}\text{Sr} - b) \quad (5)$$

The Sr concentrations are given in Table 5. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio at 0.7256 determined for the particulate residue, after leaching with dilute HCl of the suspended load of the Garonne waters, was thought to be the most representative of the Sr isotopic composition of the silicic reservoir. For the Sr isotopic composition of the carbonate reservoir, the lowest $^{87}\text{Sr}/^{86}\text{Sr}$ ratios found in the waters of the Aveyron stream at about 0.7090 may be the most appropriate. This value also corresponds to values reported by Albarède and Michard (1987) on nearby surface waters representative of carbonate drainage basins. The following equations, where the discharges of both sources are expressed as:

$$Q_1 = \frac{Q_t(C_t R_t - C_2 R_2)}{(C_1 R_1 - C_2 R_2)} \quad (6)$$

$$Q_2 = Q_t - Q_1 \quad (7)$$

may be used from Eq. (1). The calculations based on average values integrating the 2-year survey, show

Table 5

Concentration of dissolved Sr supplied by the silicate (C_1) and the carbonate (C_2) reservoirs, estimated on the basis of the equation ${}^{87}\text{Sr}/{}^{86}\text{Sr} = a1/\text{Sr} + b$

a and b are given in the legend.

	a	b	Silicate reservoir C_1 ($\mu\text{g}/\text{l}$)	Carbonate reservoir C_2 ($\mu\text{g}/\text{l}$)
<i>Massif Central</i>				
Aveyron river	0.00045	0.70755	25	310
Tarn river	0.00020	0.70834	12	303
<i>Pyrénées</i>				
Ariège river	0.00015	0.70890	9	1500
Gers river	0.00017	0.70889	10	1545

that the silicate reservoir represents between 3% and 8% of the total flux of Sr dissolved in the river waters (Table 6), the lowest contribution being for the Gers and the highest for the Tarn. The calculations outline also the fact that the contribution of the silicic reservoir to the global discharge is higher for the Ariège and Gers rivers draining the Pyrénées mountains, at about 93% and 82%, respectively, than for the Aveyron and Tarn rivers coming from Massif Central, for which it is 39% and 69%, respectively (Table 6). This is certainly to be related to larger outcropping areas of carbonated rocks in the Massif Central than in the Pyrénées mountains (Etchanchu,

1988), as well as to the “basaltic” Sr supply mentioned earlier but not considered in the calculation, which reduces the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the dissolved Sr.

Taking the maximum and minimum discharge volumes together with the corresponding Sr concentrations and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, of the four above mentioned rivers that were measured during the 2-year survey, the amount of Sr supplied by the silicic reservoir to the Aveyron waters would increase from 5% to 7% when the discharge is maximum and to almost 0% when minimum. This was suggested earlier in comparing discharge and $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of

Table 6

Estimated contributions of the silicate (Q_1 , F_1) and carbonate (Q_2 , F_2) reservoirs to the waters and the Sr fluxes of the main tributaries Q_t = mean discharge of the main tributaries measured during the 1990–1992 period; F_t = mean flux of Sr measured in the main tributary waters during 1990–1992 period; Q_1 = discharge input by the silicate reservoir; F_1 = flux of Sr released by the silicate reservoir; Q_2 = discharge input by the carbonate reservoir; F_2 = flux of Sr released by the carbonate reservoir. – stands for unrealistic negative values by the code.

Rivers	Area (km ²)	Q_t (m ³ /s)	F_t (mg/km ² /s)	Silicate reservoir				Carbonate reservoir			
				Q_1 (m ³ /s)	Q_1 (%)	F_1 (mg/km ² /s)	F_1 (%)	Q_2 (m ³ /s)	Q_2 (%)	F_2 (mg/km ² /s)	F_2 (%)
<i>Based on average Sr contents, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and discharges</i>											
Aveyron	5170	18	0.667	7	40	0.035	5	11	60	0.63	95
Tarn	9100	105	1.165	73	69	0.096	8	32	31	0.36	92
Ariège	3450	50	1.753	46	93	0.121	7	4	7	1.63	93
Gers	1195	3	0.802	2.8	82	0.024	3	0.2	18	0.60	97
<i>Based on maximum discharge and corresponding Sr contents and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios</i>											
Aveyron	5170	60	2.031	28	47	0.14	7	32	53	1.89	93
Tarn	9100	385	4.15	271	70	0.36	9	114	30	3.79	91
Ariège	3450	119	6.24	105	88	0.27	4	14	12	5.96	96
Gers	1195	10.5	2.23	8.83	84	0.074	3	1.67	16	2.16	97
<i>Based on minimum discharge and corresponding Sr contents and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios</i>											
Aveyron	5170	1.06	0.063	0.020	2	0.00009	< 1%	1.04	98	0.062	99.8
Tarn	9100	20	0.27	12	61	0.016	6	8	39	0.254	94
Ariège	3450	17.8	0.36	17	96	0.044	12	0.73	4	0.32	88
Gers	1195	0.9	0.1	0.83	92	0.007	7	0.07	8	0.09	93
<i>Based on maximum Sr contents and corresponding $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and discharges</i>											
Aveyron	5170	–	–	–	–	–	–	–	–	–	–
Tarn	9100	105	0.62	19.63	52	0.025	4	18	48	0.598	96
Ariège	3450	50	6.24	105	88	0.275	4	14	12	5.969	96
Gers	1195	3	2.31	5.45	82	0.046	2	1.75	24	2.26	98
<i>Based on minimum Sr contents and corresponding $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and discharges</i>											
Aveyron	5170	4.18	0.11	2.51	60	0.012	11	1.67	40	0.10	89
Tarn	9100	74.3	0.68	56	75	0.073	11	18	25	0.61	89
Ariège	3450	17.8	0.36	17	96	0.044	12	0.73	4	0.32	88
Gers	1195	1.5	0.14	1.4	93	0.011	8	0.098	7	0.13	92

the river waters (Fig. 8). In the case of the Tarn river, the contributions of the silicic reservoir are smaller, whereas in the cases of the Ariège and Gers rivers, they are higher (Table 6). Additional calculations were made in taking the highest and the lowest Sr concentrations, as well as the corresponding $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and discharges of the waters of the same rivers. The calculations indicate that the contribution of the silicic reservoir is at the lowest for the waters with the maximum Sr concentration in the waters of the Aveyron river, and at 11% for the minimal Sr concentration, instead of 5% for the average Sr concentrations (Table 6). For the Tarn river, the values shift from 4% to 11% for minimum and maximum Sr concentrations, respectively, instead of 8% for the average value. The variations are similar for the two other rivers when comparing the contribution of the silicic Sr to the average, minimum or maximum dissolved Sr concentrations. Comparison of the Sr supplies to the river waters from two main reservoirs on the basis of average, maximum and minimum Sr contents and discharges emphasizes that the variations are similar. The differences range within 10% at the most, amounting to insignificant difference considering the uncertainties of the parameters used in the calculations. In other words, it seems on the basis of the calculations made here, that the uncertainty of mass-transfer calculations based on a limited sampling, is of about $\pm 5\%$ in large drainage basins. This assumption may not be verified in the case of small catchments: Riotte and Chabaux (1999), for instance, reported differential behaviors of Sr and U dissolved in the waters of a small stream originating in the Vosges mountains, when sampled during normal discharge and flood episodes.

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the dissolved Sr in the river waters appears to record precisely the contribution of the silicic reservoir to the discharge of the different streams studied here, and thus, allows estimation of the theoretical $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (R0) representing river water draining exclusively the carbonate reservoir. This R0 ratio was found to be 0.7088 for the Aveyron water, which is close to the 0.7090 chosen for the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the carbonate reservoir. But the R0 status similarly estimated were found to be 0.7055 and 0.6968 for the Gers and Ariège waters, respectively. The estimated value for

the Gers is far too low for a supply from a sedimentary carbonate reservoir, unless it integrates some signature from the Pyrénées mountains because of the man-made water supply during low-discharge periods, and that for the Ariège is unrealistic. These abnormally low isotopic values favor the idea already suggested, that some Sr in the Garonne river derived from a source with low $^{87}\text{Sr}/^{86}\text{Sr}$ ratio possibly from a basic to ultrabasic crystalline source rock in the Pyrénées mountains.

6. Conclusion

The Sr contents and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the dissolved loads in the Garonne river waters and in those of its tributaries are controlled by the contribution of two major sources characteristic of carbonate rocks with high Sr concentrations and low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and silicic rocks with low Sr concentrations and high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. Mass-balance calculations based on mean discharges, Sr concentrations and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of waters collected during a 2-year survey, suggest that the silicic reservoir contributes between 3% and 8% of the total dissolved Sr of the river waters. In using maximum and minimum discharges, or maximum and minimum Sr contents in the waters, the supply of Sr from either reservoir are similar, suggesting that the differences, which are within 10% at the most, could represent the basic uncertainty of such calculations. In addition, the results suggest that the uncertainty of mass-transfer calculations based on a limited sampling, is at the least $\pm 5\%$, in the large drainage basin of the Garonne river. It could also be shown that the silicate reservoir contributes more to the discharge of the rivers originating in the Pyrénées mountains (80–90%), than to that of the rivers originating in the Massif Central (40–70%).

A detailed study of the suspended load of the Garonne river collected during a flood event, showed that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of Sr adsorbed on the silicate material and leached with dilute NH_4Cl , or the Sr trapped in soluble mineral phases, such as carbonates or oxides, and leached with dilute HCl , are different from that of the concomitant dissolved Sr. These differences strongly suggest that none of the Sr associated with the particulate loads but exter-

nal to the silicate minerals, has its origin in the Garonne waters. This supplementary Sr represents less than 10% of the total amount of Sr transported by the Garonne river, which means that it has only a minor influence on the dissolved Sr budget calculations. However, it most probably records an intermediate pedogenic episode in the overall weathering-erosion process occurring in the Garonne drainage basin.

Acknowledgements

The authors would like to thank sincerely J. Gaillardet (IPG Paris), J.I. Drever (University of Wyoming, USA) and an anonymous reviewer for thorough and improving comments of the script. F. Chabaux (EOST, Strasbourg) and T. Toulkeridis (University of Quito, Ecuador) are also thanked for constructive discussions during the final draft of the script, and S. Chaudhuri (Kansas State University, USA) for improvement of the English text, as well as Y. Hartmeier, G. Krempp, D. Million, D. Tisserant, J. Samuel and R. Rouault of the Centre de Géochimie de la Surface (CNRS-ULP) for technical assistance during the study. The data are part of the PhD dissertation of the first author. Thanks are also due to R.J. Bowins for the Sr isotope and concentration determinations of the waters performed at Mc Master University; all other analyses were made by the first author in Strasbourg. The study was funded by the Program DBT (INSU-CNRS)/Project ONT Garonne and, thanks to R.H. McNutt (Mac Master University Canada), by a NERC funding in Canada. The authors are grateful to A. Bazerbachi (Compagnie Générale des Eaux de Toulouse), to H. Etcheber (DGO Bordeaux), and to the Agence de Bassin Adour Garonne for collection of the river-water samples.

References

- Albarède, F., Michard, A., 1987. Evidence of slowly changing $^{87}\text{Sr}/^{86}\text{Sr}$ in runoff from freshwater limestones of southern France. *Chem. Geol.* 64, 55–65.
- Berner, R.A., 1994. Geocarb II; a revised model of atmospheric CO_2 over phanerozoic time. *Am. J. Sci.* 294, 56–91.
- Berner, E.K., Berner, R.A., 1996. *Global environment, Water, Air and Geochemical Cycles*. Prentice, Upper Saddle River, NJ 07458, 376 pp.
- Bowins, R.J., Mc Nutt, R.H., Probst, J.L., 1993a. A soil-based model for highly correlated time-series variation of Sr vs $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in river water: data from two rivers in France, extended abstract. *Proceeding 3rd International Symposium IAGC Geochemistry of the Earth Surface*, University Park, PA, USA, August 1–6.
- Bowins, R.J., Mc Nutt, R.H., Probst, J.L., 1993b. Seasonal variations in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the Agronne river system Southern France. *Geol. Soc. Am.* 25 (6), 415.
- Brass, G.W., 1975. The effect of weathering on the distribution of strontium isotopes in weathering profiles. *Geochim. Cosmochim. Acta* 39, 1647–1654.
- Brookins, D.G., Chaudhuri, S., Dowling, P.L., 1969. The isotopic composition of strontium in Peterman Limestone, Eastern Kansas. *Chem. Geol.* 4, 439–444.
- Burke, G.W., Denison, R.E., Hetherington, E.A., Koepnick, R.B., Nelson, H.F., Otto, J.B., 1982. Variation of seawater $^{87}\text{Sr}/^{86}\text{Sr}$ throughout Phanerozoic time. *Geology* 10, 516–519.
- Clauer, N., 1976. *Géochimie isotopique du strontium des milieux sédimentaires* 43 Sciences Géologiques Mémoires, Strasbourg, 256 pp.
- Clauer, N., Chaudhuri, S., Kralik, M., Bonnot-Courtois, C., 1993. Effects of experimental leaching on Rb–Sr and K–Ar isotopic systems and REE contents of diagenetic illite. *Chem. Geol.* 103, 1–16.
- Drever, J.I., 1994. The effect of land plants on weathering rates of silicate minerals. *Geochim. Cosmochim. Acta* 58, 2325–2332.
- Dupré, B., Gaillardet, J., Rousseau, D., Allegre, C.J., 1996. Major and trace elements of river-borne material. The Congo basin. *Geochim. Cosmochim. Acta* 60, 1301–1321.
- Eastin, R., Faure, G., 1970. Seasonal variation of the solute content and the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the Olentangy and Sioto rivers at Columbus, Ohio. *Ohio J. Sci.* 70, 170–179.
- Etchanchu, D., 1988. *Géochimie des eaux du bassin de la Garonne. Transfert de matières dissoutes et particulaires vers l'océan Atlantique*. Thèse de 3ème cycle, Toulouse, 156 pp.
- Fisher, R.S., Stueber, A.M., 1976. Strontium isotopes in selected streams within the Susquehanna river basin. *Water Resour. Res.* 12, 1061–1068.
- Gaillardet, J., Dupré, B., Allègre, C.J., 1995. A global geochemical mass budget applied to the Congo basin rivers, erosion rates and continental crust composition. *Geochim. Cosmochim. Acta* 59, 3469–3485.
- Gaillardet, J., Dupré, B., Allègre, C.J., Negrel, P., 1997. Chemical and physical denudation in the Amazon river basin. *Chem. Geol.* 142, 141–173.
- Garrels, R.M., Mackenzie, F.T., 1971. *Evolution of Sedimentary Rocks*. W.W. Norton and Co., New York, 397 pp.
- Goldstein, S.J., Jacobsen, S.B., 1987. The Nd and Sr isotopic systematics of river water dissolved material: implication for the sources of Nd and Sr in seawater. *Chem. Geol.* 66, 245–272, (Isotope Section).
- Meybeck, M., 1986. Composition chimique des ruisseaux non pollués en France. In: *Chemical Composition of Headwater Streams in France*, 39 Sciences Géologiques Bulletin, Strasbourg, pp. 3–78.
- Negrel, P., Allegre, J.C., Dupré, B., Lewin, E., 1993. Erosion

- sources determined by inversion of major and trace element ratios and strontium isotopic ratios in river water: the Congo basin case. *Earth Planet. Sci. Lett.* 120, 59–76.
- Palmer, M.R., Edmond, J.M., 1992. Controls over the strontium isotope composition of river water. *Geochim. Cosmochim. Acta* 56, 2099–2111.
- Peterman, Z.E., Whetten, J.T., 1972. $^{87}\text{Sr}/^{86}\text{Sr}$ variation in Columbia river bottom sediments as a function of provenance. *Mem. Geol. Soc. Am.* 135, 29–36.
- Probst, J.L., Bazerbachi, A., 1986. Transports en solution et en suspension par la Garonne supérieur. *Sci. Géol. Bull.* 39, 79–98.
- Probst, J.L., Tardy, Y., 1985. Fluctuations hydroclimatiques du bassin d'Aquitaine au cours des 70 dernières années. *Rev. Geol. Dyn. Geogr. Phys.* 26, 59–76.
- Riotte, J., Chabaux, F., 1999. ($^{234}\text{U}/^{238}\text{U}$) activity ratios in freshwaters: tracing hydrological processes or bed-rock weathering? Case of the Strengbach watershed (Vosges France). *Geochim. Cosmochim. Acta* 63 (9), 1263–1275.
- Sayles, F., Mangelsdorf, P.C., 1977. The equilibration of clay minerals with seawater: exchange reactions. *Geochim. Cosmochim. Acta* 41, 951–960.
- Schaltegger, U., Stille, P., Rais, N., Piqué, A., Clauer, N., 1994. Neodymium and strontium isotopic dating of diagenesis and low-grade metamorphism of argillaceous sediments. *Geochim. Cosmochim. Acta* 58, 1471–1481.
- Semhi, K., 1996. Erosion et transferts de matières sur le bassin versant de la Garonne-Influence de la sécheresse. PhD thesis, Univ. Strasbourg, 200 pp.
- Spooner, E.T.C., 1976. The strontium isotopic composition of seawater, and seawater–oceanic crust interaction. *Earth Planet. Sci. Lett.* 31, 167–174.
- Stallard, R.F., Edmond, J.M., 1983. Geochemistry of the Amazon: 2. The influence of geology and weathering environment on the dissolved load. *J. Geophys. Res.* 88, 9671–9688.
- Ulrich, E., Lanier, M., Schneider, A., 1994. RENECOFOR-Dépôts atmosphériques et concentrations des solutions du sol (sous réseau CATAENAT). Office National des Forêts, Département des Recherches Techniques, 165 pp.
- Wadleigh, M.A., Veizer, J., Brooks, C., 1985. Strontium and its isotopes in Canadian rivers, fluxes and global implications. *Geochim. Cosmochim. Acta* 49, 1727–1730.