

Evidence of hydrological control of Sr behavior in stream water (Strengbach catchment, Vosges mountains, France)

Dominique Aubert^a, Anne Probst^{b,*}, Peter Stille^a, Daniel Viville^c

^aULP-Ecole et Observatoire des Sciences de la Terre (EOST)-CNRS, Centre de Géochimie de la Surface, UMR 7517, 1 rue Blessig, 67084 Strasbourg Cedex, France

^bLaboratoire des Mécanismes de Transferts en Géologie, UMR 5563, CNRS/Université Paul Sabatier, 38 rue des 36 Ponts, 31400 Toulouse, France

^cULP-CNRS, Centre d'Etudes et de Recherches Eco-Géographiques (CEREG), UMR 7007, 3 rue de l'Argonne, 67083 Strasbourg Cedex, France

Abstract

Strontium and particularly $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in stream water have often been used to calculate weathering rates in catchments. Nevertheless, in the literature, discharge variation effects on the geochemical behavior of Sr are often omitted or considered as negligible. A regular survey of both Sr concentrations and Sr isotope ratios of the Strengbach stream water draining a granite (Vosges mountains, France) has been performed during one year. The results indicate that during low water flow periods, waters contain lower Sr concentrations and less radiogenic Sr isotope ratios ($\text{Sr} = 11.6$ ppb and $^{87}\text{Sr}/^{86}\text{Sr} = 0.7246$ as an average, respectively) than during high water flow periods ($\text{Sr} = 13$ ppb and $^{87}\text{Sr}/^{86}\text{Sr} = 0.7252$ as an average, respectively). This is contrary to expected dilution processes by meteoric waters which have comparatively lower Sr isotopic ratios and lower Sr concentrations. Furthermore, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in stream water behave in 3 different ways depending on moisture and on hydrological conditions prevailing in the catchment. During low water flow periods (discharge < 9 l/s), a positive linear relationship exists between Sr isotope ratio and discharge, indicating the influence of radiogenic waters draining the saturated area during storm events. During high water flow conditions, rising discharges are characterized by significantly less radiogenic waters than the recession stages of discharge. This suggests a large contribution of radiogenic waters draining the deep layers of the hillslopes during the recession stages, particularly those from the more radiogenic north-facing slopes. These results allow one to confirm the negligible instantaneous incidence of rainwater on stream water chemistry during flood events, as well as the existence in the catchment of distinct contributive areas and reservoirs. The influence of these areas or reservoirs on the fluctuations of Sr concentrations and on Sr isotopic variations in stream water depends on both moisture and hydrological conditions. Hence, on a same bedrock type, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in surface waters can be related to flow rate. Consequently, discharge variations must be considered as a pre-requisite when using Sr isotopes for calculating weathering rates in catchments, particularly to define the range of variations of the end-members.

1. Introduction

Catchment studies often use a combination of hydrologic and chemical techniques to determine the processes controlling the chemistry of surface waters. The

analyses of temporal and spatial variations of major and minor element concentrations have proved to be efficient tools (e.g. Likens et al., 1977; Pionke and DeWalle, 1994; Rice and Bricker, 1995; Land and Öhlander, 1997; Idir et al., 1999). Nevertheless, their origin is often difficult to determine since multiple sources are possible for a given element. To solve this problem, Sr isotopes were first used by Gosz et al. (1983) and Graustein and Armstrong (1983) with the objective of estimating the importance of weathering and atmospheric inputs to the

* Corresponding author. Tel.: +33-5-6155-6113; fax: +33-5-6155-8138.

E-mail address: aprobst@cict.fr (A. Probst).

ecosystems. Rocks and minerals of the same age but with different Rb/Sr concentration ratios generally display various $^{87}\text{Sr}/^{86}\text{Sr}$ due to ^{87}Rb decay with time. Thus, the Sr isotope ratios in natural waters reflect the contribution of the different rock-forming minerals rather than the value of the whole bedrock itself (McNutt et al., 1990; Probst et al., 1992a, 2000; Bain and Bacon, 1994; Bailey et al., 1996), since the dissolution rate of different minerals is highly variable (Lasaga, 1984). The Sr isotope ratios in rainwater and streamwater are often significantly different. Consequently, Sr has frequently been used in catchment studies to differentiate Ca sources, since Sr and Ca behave similarly (Åberg and Wickman, 1987; Gosz and Moore, 1989; Jacks et al., 1989; Miller et al., 1993; Bailey et al., 1996; Clow et al., 1997; Probst et al., 2000). In addition to weathering processes, atmospheric deposition or cation exchange processes have been shown to greatly influence the behavior of Sr in surface waters (Graustein and Armstrong, 1983; Miller et al., 1993). However, despite many studies using Sr isotopes, the potential influence of discharge variations on the Sr isotope composition in streamwater has often been omitted or considered as negligible. Most studies have shown that there is little or no effect of flow rate on the Sr isotopic composition in river waters (Bain and Bacon, 1994; Bullen et al., 1994; Bailey et al., 1996; Négrel et al., 1997a; Bain et al., 1998). However, some authors have found significant differences between the Sr isotope ratios measured at low and high water flow in different sized basins (e.g. Palmer and Edmond, 1989; Åberg, 1995; Clow et al., 1997). Most of them have reported an inverse relationship between the discharge and the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in stream water. Only Négrel and Dupré (1993) for the Oubangui large scale basin and Krishnaswami et al. (1992) for some Himalayan rivers found that the most radiogenic waters were associated with the highest discharges. These variations were interpreted as the result of differences in the respective contributions of river waters draining silicate and carbonate terrains. Most of these studies have been investigated in catchments that cover many lithologies. Also the periods of sampling (monthly or longer intervals, excepting the works of Åberg and Wickman, 1987 and Bain et al., 1998) were usually insufficient to assess the degree to which discharge variations would influence the Sr isotope ratios of river waters.

The aim of this paper is to report the results of detailed investigations on Sr isotope ratios and Sr concentration in surface waters from a small granitic catchment (Vosges mountains, France) during one year, incorporating high and low water flow periods and several storm events. The objective is to determine the behavior of Sr in surface waters according to various moisture and hydrological conditions in order to appreciate the ability of this element to discriminate contributive areas or sources.

2. Geological settings

2.1. Site description

The Strengbach forested catchment (80 ha area) is located on the eastern part of the Vosges Mountains (North East of France), 58 km SW of Strasbourg (Fig. 1). The elevation ranges from 883 m at the outlet up to 1146 m at the catchment divide. The slopes are rather steep. The climate is temperate oceanic mountainous and westerly winds dominate. The monthly average daily mean temperature ranges from -2 to 14 °C (Probst et al., 1990), and mean annual rainfall is about 1400 mm (Probst and Viville, 1997) with rainfall spread all over the year. Nevertheless, most rainfall occurs in spring whereas the driest season is in autumn. Usually, the snowfall season lasts four months per year from December to April. The total runoff reached 853 mm for the 1986–1995 period (Probst et al., 1995a), which corresponds to a mean annual discharge of 21.7 l/s.

The bedrock is a base poor leucogranite (The Brézouard granite) aged 315 ± 7 Ma (Bonhomme, 1967). This granite is coarse-grained and has undergone hydrothermal alteration, which is particularly obvious on the south-facing slope of the catchment (Fig. 1, El Gh'Mari, 1995). Hydrothermal alteration has caused depletion of plagioclase, and precipitation of illite and hematite in the fractured granite (Table 1) (El Gh'Mari, 1995; Probst et al., 2000). At the upper margin of the catchment, a banded gneiss is in contact with the granite. The soils (here called, HP and PP, Fig. 1) belong to the brown acidic to ochreous podzolic soil series (Lefèvre, 1988). PP is located in the hydrothermally altered zone. These soils are rather deep (80 cm average), sandy and stony and lie on a saprolite, which can reach up to 10 m depth. They are described in detail by Fichter et al. (1998 a,b). The humus is an acid mull in PP and a moder in HP. Illuvial horizons of HP (ochreous podzolic soil) are enriched in organic compounds. In PP, pH values range between 3.7 in the surface horizon and 4.6 in the deepest one. In HP, pH is generally about 0.3 units higher than in PP. Both soils are very coarse-grained. The brown ochreous soil (PP) shows higher amounts of skeleton (> 2 mm) than the podzolic soil (HP). Clay contents decrease in both soils from upper to deeper horizons. At corresponding soil depths, the fine fraction (< 2 mm) of PP contains twice as much clay as the fine fraction of HP. Coarse sand (0.2–2 mm) represents at least half of the mineral fine fraction in both soils (Fichter et al., 1998a). The mineralogical characteristics of both soils are given in Table 1 (from Fichter, 1997). Quartz is very abundant in the shallowest horizons of both soils and its amount progressively decreases from upper to deeper horizons. Feldspars mainly occur in coarse fractions and are more abundant in HP than in PP. The plagioclase content is relatively stable in HP

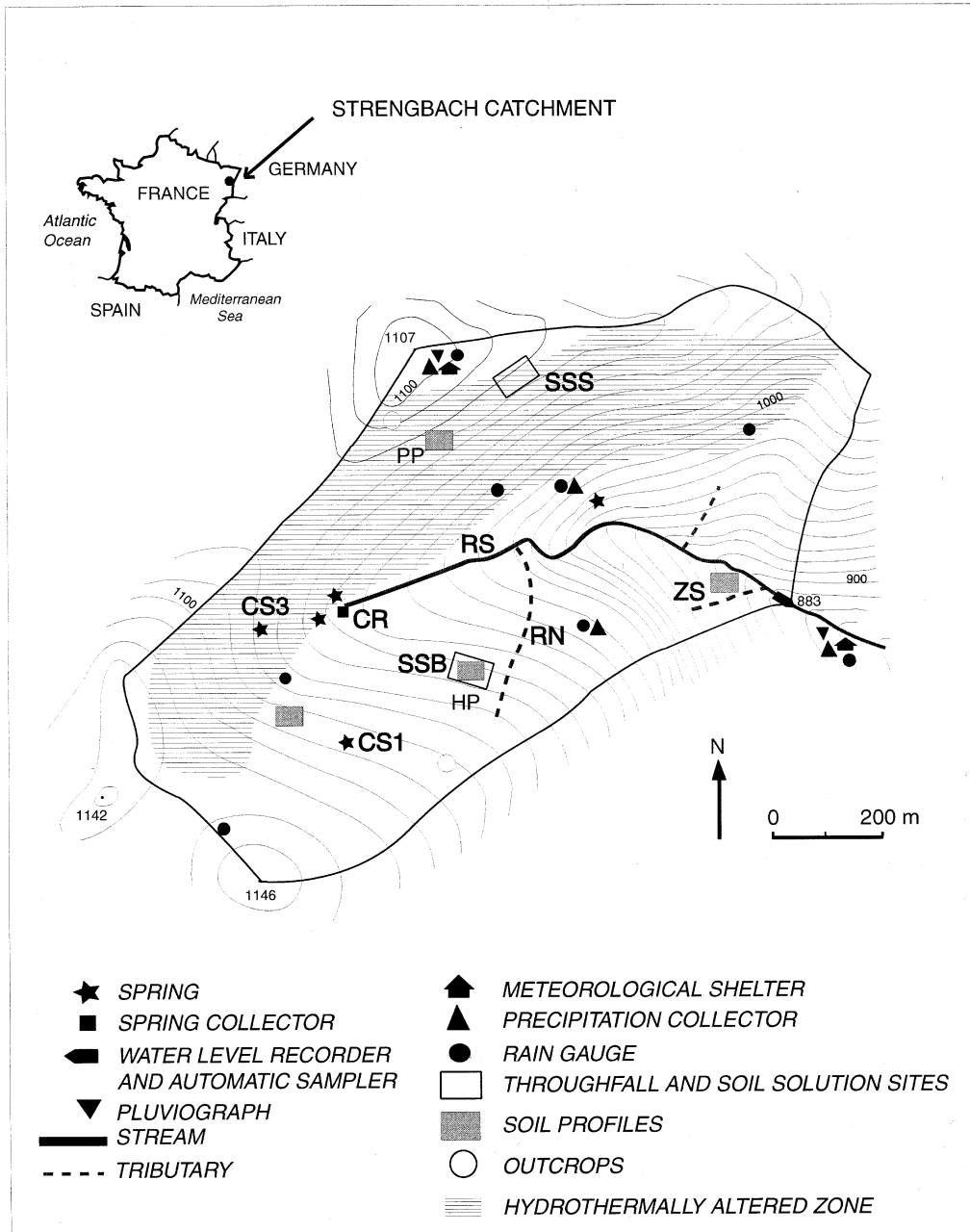


Fig. 1. Map of the Strengbach catchment and sampling locations.

whereas the upper part of PP profile (0–100 cm) is plagioclase depleted. White micas (muscovite) are more abundant in PP than in HP. The amounts of biotite in HP are small and no biotite was detected in PP (El Gh'Mari, 1995; Fichter et al. 1998a). Secondary minerals in the clay fraction are mainly interstratified illite-vermiculite or illite-smectite assemblages. Smectite is more stable in the confined environment of deep PP horizons (El Gh'Mari, 1995). Apatite is more abundant in the

brown ochreous soil (PP) than in the ochreous podzolic one (HP), particularly in the upper horizons.

A small saturated area with permanent moisture conditions, which only represents 2% of the total catchment area (Probst et al., 1990; Latron, 1990), occurs along the valley bottom near the outlet. This area can contribute significantly to stream water output, particularly during storm events (Idir et al., 1999; Ladouche et al., 2001). Forest covers 95% of the total area. Norway spruce

Table 1

Mineralogical characteristics of the fine fraction (<2 mm) of the brown ochreous soil (PP), the ochreous podzolic soil (HP) (% in weight, from Fichter, 1997) and of the two granite facies (hydrothermally altered or not) (% in volume, from El Gh'Mari, 1995 and Probst et al., 2000)

Samples	Depth (cm)	Quartz (%)	K-feldspar (%)	Plagioclase (%)	Clays + Micas (%)	Apatite (%)
HP soil	0–20	39.5	18.9	14.7	23.3	0.15
	20–40	36.5	20	13.6	27.7	0.1
	40–60	35.1	17.8	12.5	27.4	0.05
	60–80	31.7	15.9	13.4	31.3	0.1
	80–100	28.6	14.4	14.3	34.8	0.15
	100–120	29.5	14.7	11.8	38.6	0.27
	120–140	27.3	13.9	13.1	40.8	0.33
	140–160	22.7	14.8	16.6	40.9	0.4
	160–180	23.3	17.9	19.1	34.6	0.28
	180–200	20.9	12.7	20.2	30.5	0.39
PP soil	0–20	38.6	10.9	5.4	45.9	0.05
	40–60	27.3	5.6	7.5	55.9	0.21
	60–80	27.8	7	8.7	53.5	0.42
	80–100	27.4	8.9	8.1	53.2	0.43
	100–120	27.2	12.8	10.6	46.6	0.43
	120–140	22.1	10.7	16.4	47.6	0.54
	140–160	21.9	7.2	17.8	50.8	0.42
	160–180	26.9	12.6	15.9	45.8	0.41
Granite ^a		36	18	33	9	0.5
Hydrothermal altered granite ^b		53	23	1	13	0.5

^a From Probst et al., 2000.

^b From El Gh'Mari, 1995.

(*Picea abies* Karst.) dominates while mixed silver fir (*Abies alba* Mill.) and beech (*Fagus sylvatica* L.) are present over one third of the area.

2.2. Site equipment and sampling

The Strengbach catchment (Fig. 1) has been investigated since 1986 (see Probst et al., 1990 for further details) and has been previously monitored to study the effects of acid rain on a forested ecosystem, particularly on the hydrochemistry of surface waters and weathering (Probst et al., 1987, 1992a,b, 1995a,b). This site was progressively instrumented and many geochemical, mineralogical and biological studies have been performed (Dambrine et al., 1995; Fichter et al., 1998; Amiotte-Suchet et al., 1999; Idir et al., 1999; Riotte and Chabaux, 1999; Probst et al., 2000; Ladouche et al., 2001; Aubert et al., 2001).

Granite outcrop, soils (ochreous brown soils) and corresponding saprolite were sampled on the north-facing slope (HP) and the south-facing slope (PP) (Fig. 1).

As a routine, bulk open field precipitation is regularly collected (every 2 weeks) at 4 sites (Fig. 1) in polypropylene funnel collectors exposed at all times. During the snow season buckets are used. Throughfall is sampled using 2 m-long open gutters and soil solutions are collected at different depths using zero-tension lysimeter plates, both in a beech stand (SSB) and in an old spruce stand (SSS).

Four springs (among which CS1 and CS3) emerging at 4 m depth in the granite at the upper part of the basin are the main contributors to the stream. They flow into a general collector (CR), which is partly harnessed for drinking water supplies (representing 2% of the total runoff; Probst et al., 1992b). Stream water is controlled by an H-Flume notch weir and water level is monitored both by ultrasonic and mechanical limnigraphs. Stream water and spring water are collected weekly and stream water is also sampled more frequently during flood events by automatic samplers.

In the present study, two first order ephemeral tributaries are also sampled when they flow during the wet season. They drain two different areas: the first one (RN) is located close to the beech stand (north-facing slope), and the other one (ZS) drains the moisture area near the outlet.

2.3. Analytical techniques

Water samples were collected in polypropylene bottles and filtered in the laboratory using 0.45 µm Millipore HAWP membranes and then conserved at 4 °C. Base cations (Ca²⁺, Mg²⁺, Na⁺, K⁺) were analyzed by atomic absorption spectrometry and anions (NO₃⁻, Cl⁻, SO₄²⁻) by ion chromatography. Colorimetry was used to measure silica and NH₄⁺. Aluminium, Mn, Fe were

determined by ICP–AES and Rb and Sr by ICP–MS. Conductivity, alkalinity and pH were electrometrically analyzed (alkalinity by GRAN’s titration method).

$^{87}\text{Sr}/^{86}\text{Sr}$ was measured regularly in stream and spring water all over the period 1997–1998 and less frequently in other types of waters (precipitation, throughfall, soil solutions, tributaries).

The fine fraction (<2 mm) of the different soil samples and the bedrock were digested for 7 days in closed Savilex vessels containing a HF, HNO₃ and HClO₄ mixture. Strontium was separated from other ions using a cation exchange resin (AG 50W-X12, 200–400 mesh) with 1.5 and 4 N HCl as eluents. The total procedural blank was < 0.5 ng. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were determined on a VG Sector multicollector mass spectrometer. Strontium was deposited on a W filament with Ta₂O₅ as activator. Mass fractionation corrections were applied by normalizing the average $^{87}\text{Sr}/^{86}\text{Sr}$ ratios to the $^{86}\text{Sr}/^{88}\text{Sr}$ ratio of 0.1194. The accuracy of the $^{87}\text{Sr}/^{86}\text{Sr}$ analyses was evaluated by determining the NBS standard 987. A mean value of $^{87}\text{Sr}/^{86}\text{Sr} = 0.710258 \pm 13$ (\pm sigma mean, $n = 9$) was obtained over the period of study.

3. Results

3.1. Hydrological pattern

The annual precipitation (October 1997–September 1998) reached 1050 mm, indicating that this hydrological period was slightly dry compared to the 10a average period of measurement (Probst and Viville,

1997). The stream discharge variations and the corresponding rainfall amount for the studied period are shown in Fig. 2. Four major flood events can be identified. The high water flow period occurred between mid October and May. A first major flood event occurs during mid October, with a peak of discharge of 23 l/s occurring within the first hours of the precipitation. Then after a rapid decrease, the discharge increases again for a week without any corresponding precipitation. This is a consequence of the delayed response of water contributions from the upper basin hillslopes (Probst et al., 1995b; Ladouche et al., 2001). During winter and spring, 3 important flood events occurred. The most important one took place from the end of December 1997 to mid-January 1998, when precipitation was associated with snowmelt. The mean daily discharge reached 70 l/s at peak flow. The 2 following events occurred between March 1998 and the middle of May 1998 with a mean daily discharge of 40 l/s. In contrast to the first one, these 3 flood events are characterized by prevailing wet conditions and by significant precipitation (> 100 mm). The third flood event was mainly associated with snowmelt. The low water flow period began in mid May. Only a few storm events occurred during that period and have no significant effect on stream discharge which remained most of the time below 5 l/s until the end of the year. The discharge always remained above 9 l/s during the high water flow period (except the first 15 days of February) and reached a maximum of 8.5 l/s during summertime. Consequently, the value of 9 l/s has been chosen as the limit between the high water flow and the low water flow period.

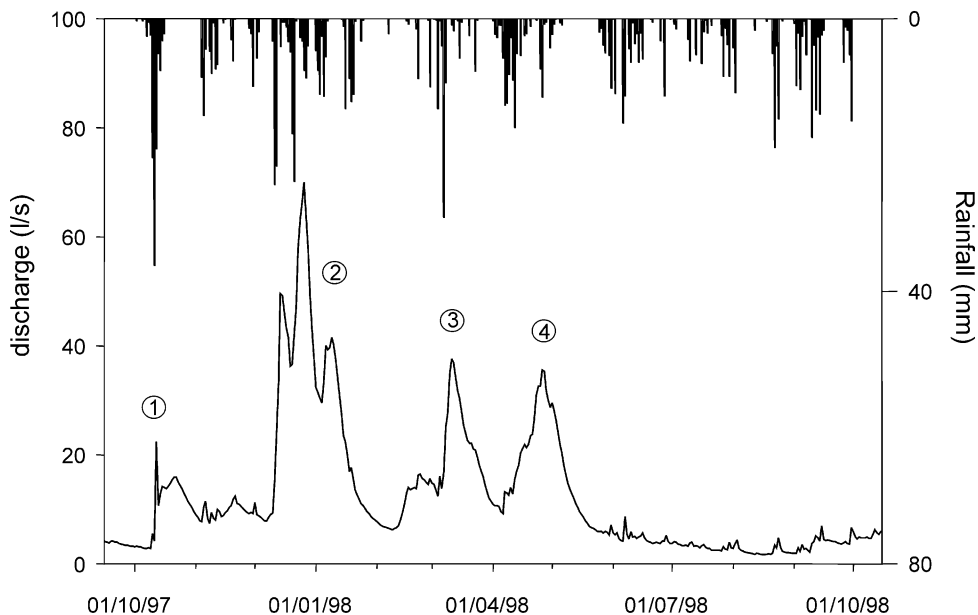


Fig. 2. Hydrograph and hietogram for the September 1997 to October 1998 period.

3.2. Chemical and isotopic pattern of surface waters

3.2.1. Sr concentration and Sr isotopic ratios in surface waters

The characteristics of the surface waters and particularly their respective Sr concentrations and Sr isotopic ratios are presented in Table 2 and in Fig. 3. Open-field precipitation displays the lowest Sr content; the less dilute rainwater seldom reaches 2 ppb Sr. The Sr isotope ratio ranges in between 0.7103 and 0.7129 with a mean value of 0.7115 ($n = 4$). This value is in agreement with the value found by Probst et al. (2000) for this site; however, it is higher than that of seawater ($^{87}\text{Sr}/^{86}\text{Sr} = 0.7092$, Depaolo and Ingram, 1985) and slightly lower than the mean value of bulk precipitation ($^{87}\text{Sr}/^{86}\text{Sr} = 0.715$) found by Åberg et al. (1989) in central Sweden during 1 year of sampling. The highest Sr isotope ratios are typical of spring and autumnal precipitation when atmospheric pollutants and dust are generally more concentrated. Throughfall is 5–10 times more concentrated in Sr than open field precipitation. Most of the time, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of throughfall is close to, but generally higher, than that of corresponding open field precipitation. It suggests the importance of dry deposition as also mentioned by Gosz and Moore (1989) and Probst et al. (2000). Cycling through trees is also an important component enhancing concentrations in throughfall and needs to be considered for mass balance. In both stands, the Sr concentration in soil solution increases regularly with depth. Nevertheless, Sr is generally more concentrated, but less radiogenic, in the solutions from soils developed on hydrothermally altered granite (SSS, spruce stand, south-facing slope,

Table 1) than in those from soils developed on less hydrothermally altered granite (SSB, beech stand, north-facing slope, Table 2). The exception is for soil solution at 10 cm depth under spruce (Fig. 3), which exhibits the highest Sr isotope ratio probably in relation to the importance of radiogenic minerals in the shallower horizons (Fichter et al., 1998a,b). Spring water and stream water fall in the same range of Sr concentration (10–16 ppb, Table 2) and of Sr isotope ratio (0.7240–0.7263). This indicates that the Sr isotopic composition of stream water is imported early in the upper part of the catchment (Aubert et al., 1999). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in streamwater are significantly more radiogenic than those in precipitation (Fig. 2) and are similar to those measured before in the same stream (Riotte and Chabaux, 1999; Tricca et al., 1999; Probst et al., 2000).

The first order tributary draining the north-facing slope (RN) and the drain from the saturated area (ZS) (see Fig. 1 and Table 2) are more concentrated in Sr and more radiogenic than the main stream at the outlet (RS). RN is characterized by a high Sr isotope ratio in agreement with what is observed for soil solutions draining the beech stand from the same slope.

3.2.2. Trends in Sr and major element concentration in stream waters

Fig. 4 represents the trend in Sr content, base cations and silica in relation to rainfall amount and discharge variations in stream water all over the year. As a whole, Sr concentrations range between 10 and 14.5 ppb. Nevertheless, significantly higher concentrations can be observed during the high water flow period (11.5–14.5

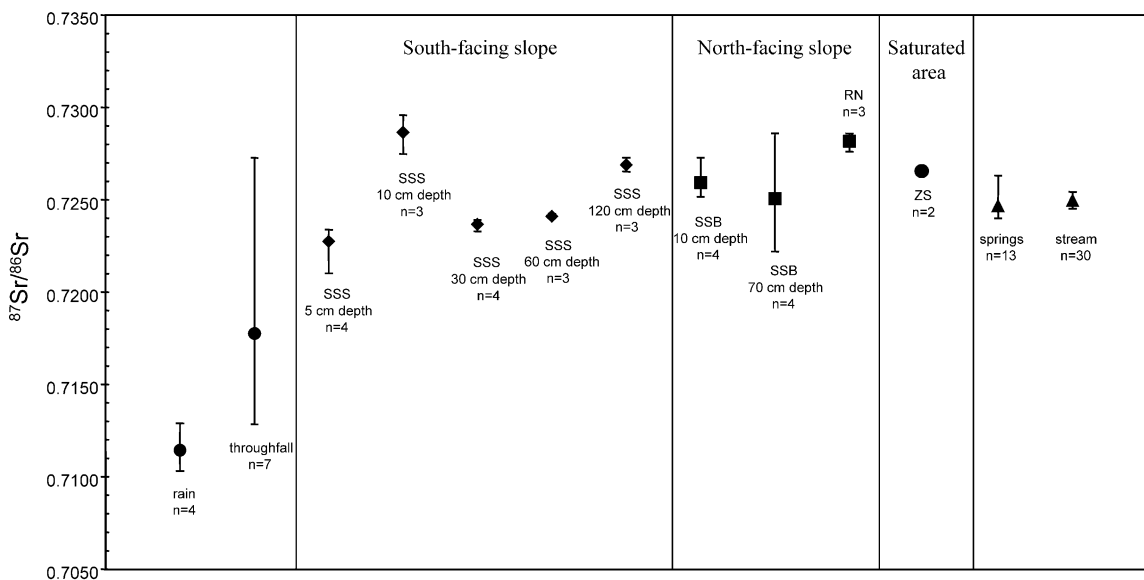


Fig. 3. $^{87}\text{Sr}/^{86}\text{Sr}$ in waters collected in the Strengbach catchment. Bars represent the range of ratios and the symbol is the average ratio measured for each water type (see Fig. 1 for sampling point locations).

Table 2

Sr content and Sr isotope ratios in the surface waters of the Strengbach catchment during the period September 1997–October 1998 (TFB : throughfall under beech, TFS : throughfall under spruce, SSB : soil solutions under beech, SSS : soil solutions under spruce)

Type of solution	Sample name	Na concentration ($\mu\text{mol/l}$)				Silica concentration ($\mu\text{mol/l}$)				Sr concentration (ppb)				$^{87}\text{Sr}/^{86}\text{Sr}$				ANC			
		Min	Max	Mean	Med ^a	Min	Max	Mean	Med	Min	Max	Mean	Med	Min	Max	Mean	Med	Min	Max	Mean	Med
Open field precipitation	OFP	4	40	13 (n=26)	9	0	3	<1 (n=26)	<1	0.2	2.2	0.8 (n=26)	0.64	0.7103	0.7129	0.7114 (n=4)	0.7105	-303	39	-42 (n=26)	-28
Throughfall	TFB	7	154	38 (n=25)	21	0	15	4 (n=25)	3	0.4	3.3	1.39 (n=25)	1.21	0.7133	0.7273	0.7172 (n=4)	0.7143	-366	328	1	19
	TFS	18	312	65 (n=27)	38	1	13	5 (n=27)	5	1	18.7	4.6 (n=27)	3.03	0.7128	0.7273	0.7186 (n=3)	0.7156	-534	82	-68	-34
Soil solutions	SSB																				
	10 cm	18	52	41 (n=25)	43	24	172	91 (n=25)	75	0.8	3.4	1.5 (n=25)	1.53	0.7252	0.7273	0.7259 (n=4)	0.7257	-48	99	-6 (n=25)	-6
	70 cm	18	59	41 (n=11)	43	5	113	70 (n=11)	90	0.9	4.1	1.8 (n=11)	1.28	0.7222	0.7286	0.7251 (n=4)	0.7247	-88	28	-42 (n=11)	-55
	SSS																				
	5 cm	21	70	50 (n=22)	49	21	218	89 (n=22)	85	1.3	8.9	4 (n=22)	3.49	0.7210	0.7234	0.7227 (n=4)	0.7233	-227	-24	-134 (n=22)	-121
	10 cm	34	81	62 (n=21)	69	27	206	119 (n=21)	129	1.3	6.2	4.3 (n=21)	4.54	0.7274	0.7296	0.7286 (n=3)	0.7289	-285	-53	-185 (n=21)	-209
	30 cm	48	81	61 (n=22)	61	36	141	95 (n=22)	99	2.6	5	4 (n=22)	3.99	0.7233	0.7239	0.7237 (n=4)	0.7237	-235	-74	-149 (n=22)	-148
60 cm	49	79	63 (n=17)	62	84	160	122 (n=17)	126	3.4	7	4.7 (n=16)	4.71	0.7240	0.7242	0.7241 (n=3)	0.7241	-190	-63	-132 (n=17)	-128	
120 cm	49	65	58 (n=5)	57	158	185	167 (n=5)	165	4.8	10.7	7.8 (n=5)	7.82	0.7265	0.7273	0.7269 (n=3)	0.7269	-279	-80	-183 (n=5)	-171	
Spring collector	CR	74	103	93 (n=58)	94	132	178	155 (n=58)	155	10	16	12.9 (n=58)	12.7	0.7240	0.7263	0.7247 (n=14)	0.7246	13	66	41 (n=58)	41
Tributaries	ZS	28	109	81 (n=18)	89	54	157	111 (n=18)	108	4.8	20.5	9.8 (n=18)	7.92	0.7264	0.7266	0.7265 (n=2)	-	23	129	54 (n=18)	41
	RN	-	-	-	-	128	185	164 (n=7)	166	7.2	33.4	22.8 (n=7)	25.17	0.7275	0.7286	0.7279 (n=3)	0.7276	-	-	-	-
Main stream	RS	81	95	89 (n=58)	89	129	160	142 (n=58)	140	10	14.4	12.4 (n=58)	12.36	0.7245	0.7253	0.7249 (n=27)	0.7251	27	119	51 (n=58)	47

^a Med : median.

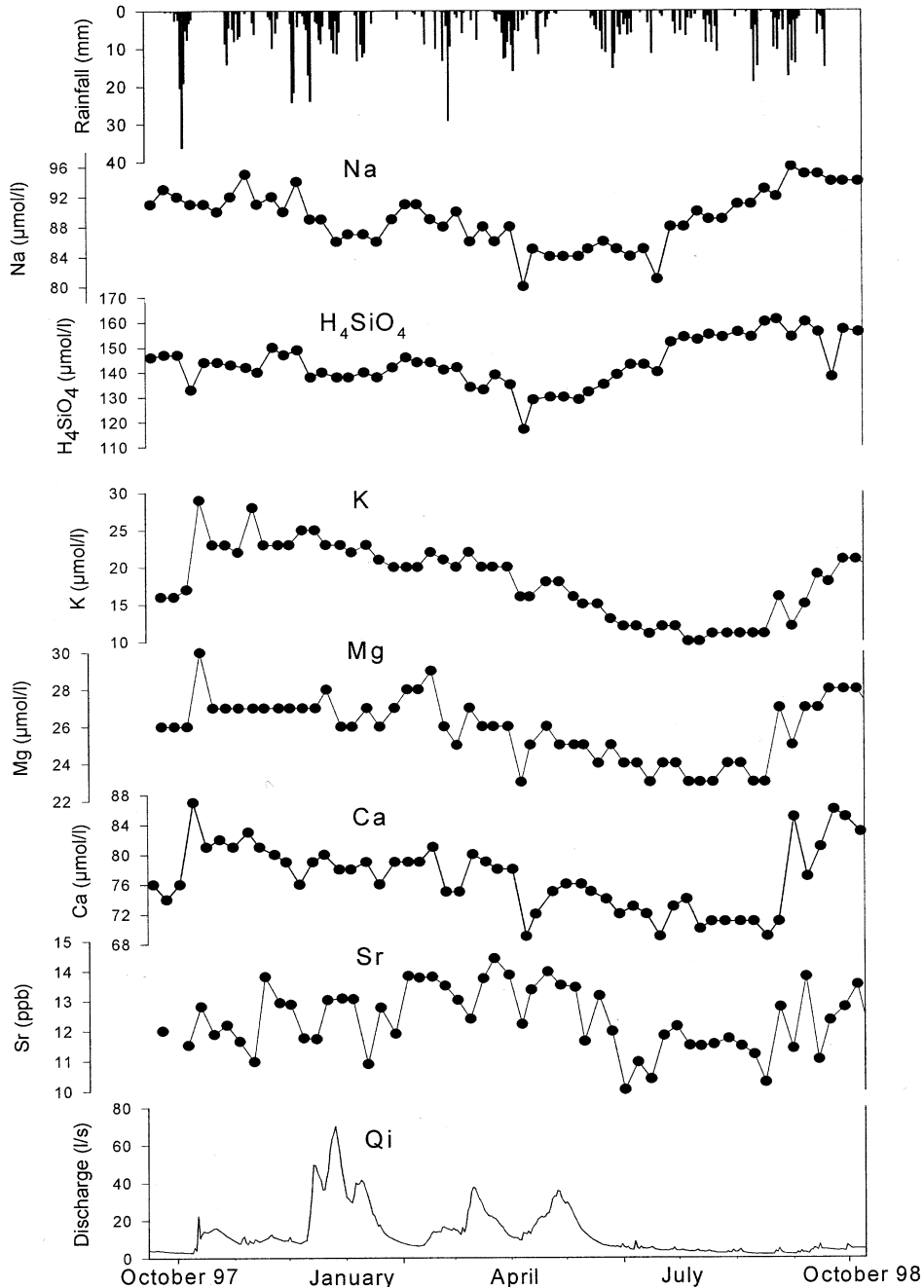


Fig. 4. Trends in precipitation, discharge and concentration for Na, H_4SiO_4 , K, Mg, Ca and Sr (period September 1997–October 1998).

ppb) compared to the low water flow period (10–13 ppb). This is contrary to the expected dilution process by meteoric waters (low Sr concentration and low Sr isotope ratio) that is frequently reported in the literature (e.g. Åberg et al., 1989; Palmer and Edmond, 1989; Négrel and Dupré, 1993; Bain et al., 1998). The highest Sr concentration is recorded at the end of March just after the second major flood event when the soil moist-

ure is high, notably in the upper part of the catchment. After the last main flood event (May 1998), Sr concentration decreases significantly; it reaches its lowest value (10 ppb) at the beginning of June and it fluctuates around values of 11.5–12 ppb during the dry period. Afterwards, by September 1998 with the occurrence of the first flood events, the Sr content increases again together with Ca, Mg and K (Fig. 4), probably as a

result of soil leaching. These latter elements have been considered to be involved in the biological cycle and in exchange processes (Probst et al., 1990). Ca and Sr are commonly assumed to have a similar geochemical behavior in surface waters (Jacks et al., 1989; Åberg et al., 1990; Wickman and Jacks, 1993; Bailey et al., 1996; Clow et al., 1997). In the Strengbach catchment a positive linear relationship is observed between Ca and Sr in all water types (Probst et al., 2000). Nevertheless, Ca and Sr are not significantly related in streamwater over the one year period of measurements, contrary to silica and Na, which mainly originate from albite weathering. For all base cations and silica, except Sr, the maximum dilution is observed during the snowmelt period (April) because of the importance of subsurface flow (Stottemyer et al., 1997). Afterwards, Na and Si concentrations increase during the early beginning of the low water flow period and reach values around 155 and 95 $\mu\text{mol l}^{-1}$ respectively (Fig. 4), in relation to the increasing importance of the weathering solution. In contrast, Sr, Ca, Mg and K concentrations continue to decrease because of biomass uptake (Probst et al., 1990).

3.2.3. Variation in Sr isotope ratios

The trend of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in stream water over the sampling period follows, as a whole, the same pattern as the Sr concentration (Figs. 4 and 5). The Sr isotopic composition is significantly higher during the high water flow period ($0.7250 < ^{87}\text{Sr}/^{86}\text{Sr} < 0.7254$, except during a dry episode in February, $^{87}\text{Sr}/^{86}\text{Sr} = 0.7248$) than during the low water flow period ($0.7245 < ^{87}\text{Sr}/^{86}\text{Sr} < 0.7248$, apart from one storm event in September 1998, $^{87}\text{Sr}/^{86}\text{Sr} = 0.7249$). Fig. 5 also shows the temporal evolution of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in springwater.

Springwater (CR) is, as a whole, less radiogenic than streamwater, except for one storm event sample in December 1997. Though less springwater samples are available, the fluctuations of the Sr isotope ratio in springwater are similar to those of streamwater.

During winter and spring, each major flood event (1,2,3,4) is characterized first by a slight decrease of the Sr isotope ratios with rising discharge. Then, the highest Sr isotope ratio is reached after the peak flow (Fig. 5).

As shown by the general positive relationships between discharge and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (Fig. 6), overall the higher the discharge, the higher the Sr isotope ratio in streamwater. In the Strengbach, 3 different positive relationships of $^{86}\text{Sr}/^{87}\text{Sr}$ versus discharge can be distinguished according to moisture and hydrological conditions (Fig. 6):

- during the low water flow period:
 - a linear significant relationship (open squares) for streamwaters sampled during the dry season (discharge lower than 9 l/s) (1): $^{87}\text{Sr}/^{86}\text{Sr} = 7.23 \times 10^{-5} * Q + 0.7244$, $r^2 = 0.72$, $n = 12$
- during the high water flow period:
 - a first hyperbolic relationship (black circles) corresponding to streamwater sampled during the rising stages of the discharge (2): $^{87}\text{Sr}/^{86}\text{Sr} = (0.7255 \times Q) / (1.39 \times 10^{-2} + Q)$, $r^2 = 0.85$, $n = 8$.
 - a second hyperbolic relationship (open circles) which corresponds to the samples collected during the decreasing stage of the discharge (3): $^{87}\text{Sr}/^{86}\text{Sr} = (0.7255 \times Q) / (4.3 \times 10^{-3} + Q)$, $r^2 = 0.83$, $n = 10$.

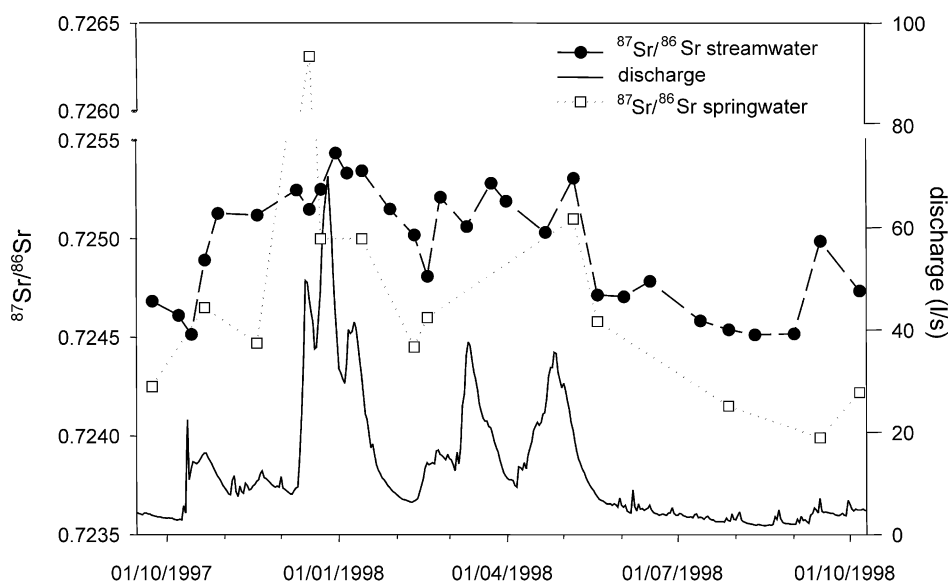


Fig. 5. Temporal evolution of Sr isotope composition in streamwater (black circles) and in springwater (open squares).

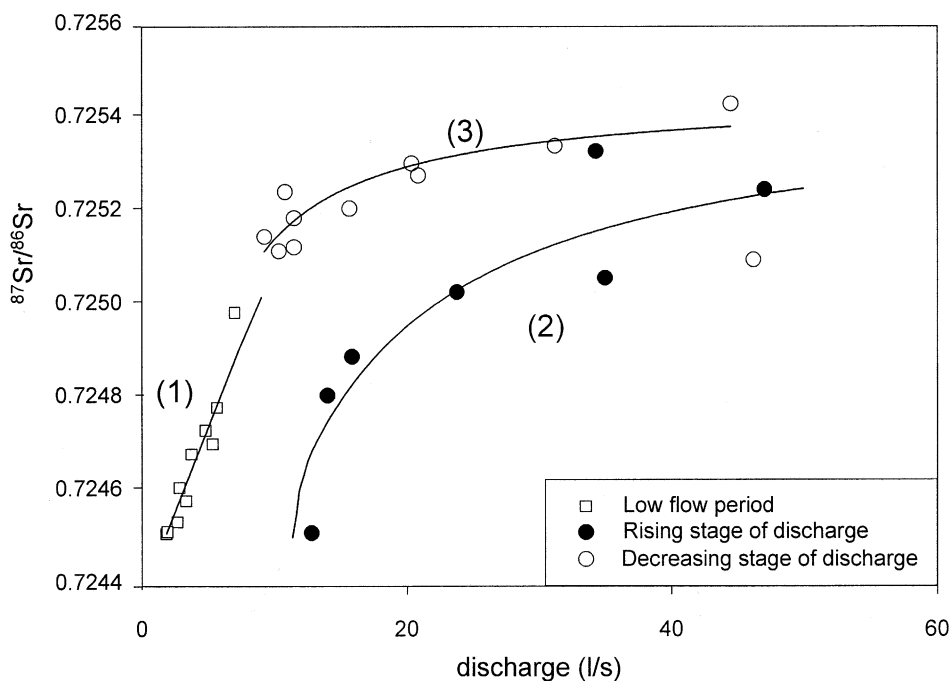


Fig. 6. Relationships between the Sr isotope ratios and discharge according to hydrological conditions.

Thus, all over the high discharge period, the rising flows (2) display lower Sr isotopic ratios than the waters of equivalent decreasing discharge (3) (hysteresis pattern). This suggests a significant contribution of waters with more radiogenic Sr from the hillslopes during recession periods.

3.3. Specific Sr behavior during flood events

The specific behavior of Sr has been investigated for the first two consecutive flood events of the hydrological year (1, 2 Figs. 2 and 7). The first flood (October 1997) is generated by heavy rainfall (about 80 mm for 3 days) and is characteristic of a flood occurring after prevailing dry conditions in the catchment (Fig. 5). This pattern corresponds to the instantaneous response of the small saturated area connected to the stream to a significant rainfall amount (Probst et al., 1995a,b; Idir, 1998). The second flood event (December 1997–January 1998) takes place during a more humid period and reaches higher discharges. Fourteen samples covering this period have been analyzed (Fig. 7).

The first two samples (1, 2), collected before the first flood event, correspond to base flow conditions. During the whole storm flow period, the range of Sr concentration is relatively large: between 11 ppb (sample 12) and close to 14 ppb (samples 6 and 14). No obvious relationship can be identified between the Sr concentration and the discharge.

Fig. 7 shows that the Sr isotope ratio varies in a cyclical manner in relation to discharge variations, in both events. The first stage of each rising flow goes together with a slight decrease of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (Fig. 7, samples 3 and 8), corresponding to a dilution process by meteoric waters. Then, for the first flood event ($P > 50$ mm), rainfall stops whereas the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio increases strongly with increasing discharge and reaches values characteristic of the high water flow period. The second event presents the same pattern, however, the range of variation is less important. The highest $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (0.7254) is recorded during the middle of the flood event (sample 10), just after the highest peak of discharge, which unfortunately could not be sampled. Then, the Sr isotope ratio decreases becoming less and less radiogenic during the recession stage of the discharge. The period between these two specific events (samples 6 and 7, Fig. 7) is characterized by stable Sr isotope ratios around 0.7252.

4. Discussion

In the Strengbach catchment, the chemistry of the stream water is mainly determined upstream since spring water shows the same ranges of Sr content and of Sr isotopic ratios (Probst et al., 2000). Moreover, the temporal evolution of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in spring water varies in the same way, that is to say, the lowest Sr isotope ratios are recorded during the low water flow period.

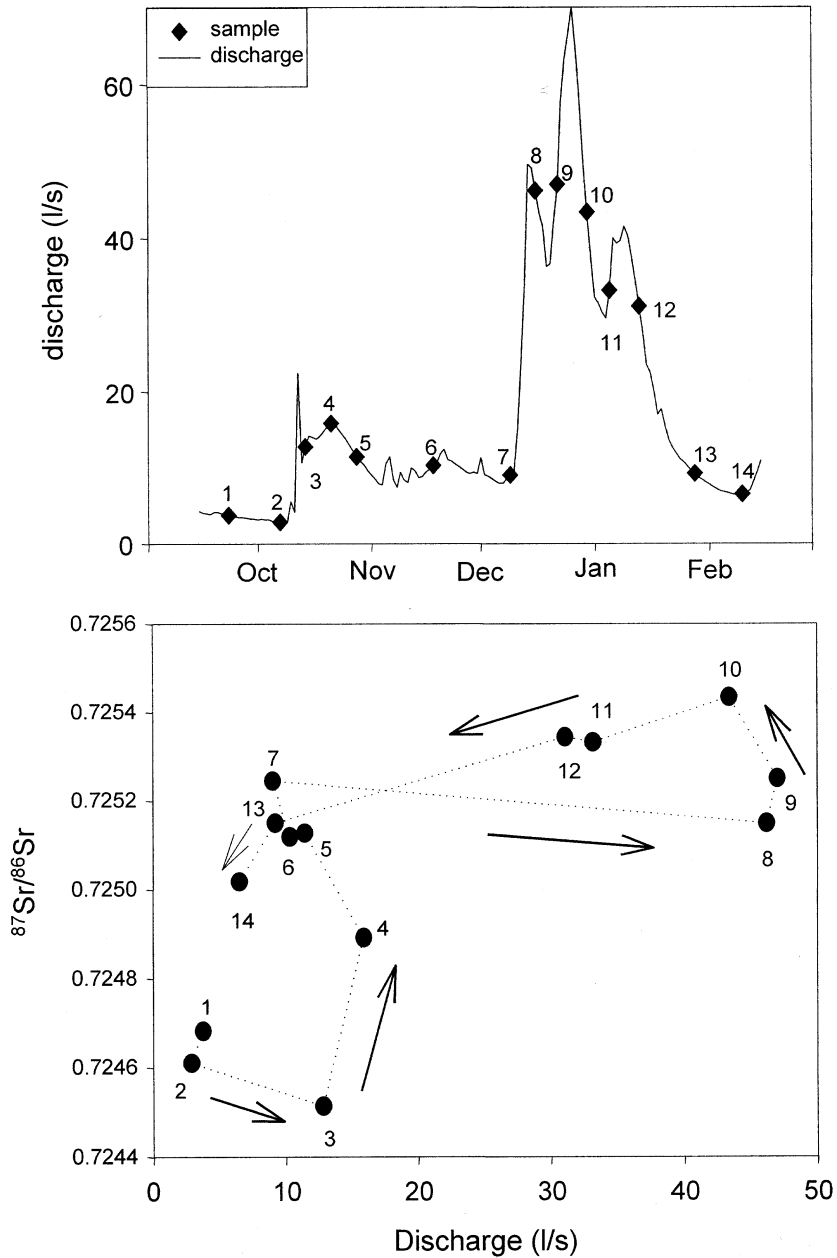


Fig. 7. Relationship between $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in streamwater and discharge during two consecutive flood events.

Thus, as a whole, the expected dilution phenomenon by meteoric waters (with low Sr concentrations and relatively non-radiogenic Sr) does not occur during the high water flow period. This is contrary to the results from Négrel et al. (1997b) for the Zagat River (Massif Central, France), Clow et al. (1997) for a stream water on granitoid rocks and Åberg (1995) for a stream in Central Sweden. These results are also opposite to what has generally been observed in most of the small silicate catchments where little or no change in stream water

$^{87}\text{Sr}/^{86}\text{Sr}$ ratios versus discharge has been detected (Bain and Bacon, 1994; Bullen et al., 1994; Bailey et al., 1996; Négrel et al., 1997a; Bain et al., 1998). However, this is in agreement with the results from Négrel and Dupré (1993) for a large scale basin (Oubangui river), where the variations were related to different bedrock weathering contributions.

In the granitic Strengbach catchment, depending on prevailing moisture and hydrological conditions, various end-members or contributive areas (upper or deeper soil

profiles, north and south-facing slopes, saturated area) can be invoked to explain such variations of Sr isotopic composition. During the low water flow period, stream water mainly originates from the springs (such as CS3) and tributaries from the south-facing slope, which are as well as soil solutions and soil material somewhat less radiogenic than that of the north-facing slope (Tables 2 and 3). Low Sr isotope ratios in streamwater were also observed after dry conditions in winter (February 1998). In contrast, during the high water flow conditions, the contribution of the waters draining the north-facing slope becomes significantly more important, as a result of the recharge of the significant reservoir of water located in the thick glacial deposits (Latron, 1990). This is indicated by the more radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in soil solution (SSB), tributary RN, spring water CS1 and the solid material from profile HP (Fig. 1, Table 2). In this catchment, silica has been identified as a good chemical tracer of stream water origin during storm events (Idir et al., 1999) as in other small catchments (Pionke et al., 1993; Rice and Bricker, 1995). The significant negative linear relationship which links silica (or Na, not shown) and $^{87}\text{Sr}/^{86}\text{Sr}$ on one hand, and ANC (acid neutralization capacity) and $^{87}\text{Sr}/^{86}\text{Sr}$ on the other hand, in spring waters (Fig. 8 a, b) means that during base flow conditions, the weathering of albite (Na and Si rich mineral) and apatite (low Sr isotopic composition) is the main process explaining the low Sr isotopic ratio and the high silica content (Probst et al., 2000; Aubert et al., 2001). Particularly, this suggests the importance of the contribution of the deep waters draining the southern hillslope to the streamwater, as indicated by the chemical

and isotopic characteristic of CS3 (spring water from the southern hillslope). In contrast, during the high water flow conditions, the high Sr isotope ratio linked to the low silica or low Na concentration indicates the major contribution of waters draining the north-facing slope (Table 2). This is clearly indicated by the behavior of CS1 if comparing the isotopic values between low and high discharge conditions (Fig. 8a and b). Indeed Idir et al. (1999) and Ladouche et al. (2001) have demonstrated from DOC, silica and O isotopes that even during storm events only a very small amount of rainwater (2–10%) contributes to the storm runoff. They have also identified the waters draining the deep hillslopes as the major contributors to the stream flow and consequently, to the spring waters.

The higher Sr, Ca, K and Mg concentrations measured in streamwater during the high water flow period reinforces the suggestion that the influence of rainwater which is Ca and Sr poor (Probst et al., 2000) is weak. Moreover, the significantly lower values from May to September (vegetation activity period) is due to biomass uptake. In contrast, silica and Na are not involved in biomass activity and the observed patterns are the result of simple dilution/concentration phenomenon. Elements released out of the Strengbach catchment originate from mineral weathering or exchange processes in the soil/saprolite (Probst et al., 1992b). Strontium which is often used as a proxy for Ca seems to behave in a similar way to the other nutrients (Ca, Mg, K). Nevertheless, Elias et al. (1982) or Poszwa (2000) in the Strengbach catchment demonstrated that Sr and Ca could behave differently through biomass uptake, Sr/Ca decreases between stem to leaf indicating that Ca would be preferably transported to the foliage. This is confirmed by the significantly lower Sr/Ca ratio found in throughfall compared to bulk precipitation. Hence, throughfall seems to be influenced by the canopy leaching of biomass characterized by a much lower Sr content (Bailey et al., 1996).

During base flow conditions, the positive linear relationship between $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and discharge is linked to the obvious influence of the waters draining the saturated area, which are more radiogenic (Table 2). During this period, rainfall is mainly intercepted, evaporated, partly used by the biomass or contributes to reload the soil moisture. Only the small saturated area reacts to rainfall events as shown by Ladouche et al. (2001), and thus contributes noticeably radiogenic water to the stream flow. During the particular event occurring after the base flow conditions, the regular rise of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios with increasing discharge is probably the result of a mixture of water originating from the saturated area and from the more radiogenic deep layers of the hillslopes (Table 3).

Concerning the following flow event, the pattern is similar, however, the $^{87}\text{Sr}/^{86}\text{Sr}$ is more radiogenic and the lower range of variation is due to antecedent humid conditions. Before the flood event, the contribution of

Table 3
Sr content and Sr isotope composition of the fine fraction (< 2 mm) of the two studied soil profiles: north-facing slope (HP) and south-facing slope (PP)

Soil profile	Depth (cm)	Sr concentration (ppm)	$^{87}\text{Sr}/^{86}\text{Sr}$	2 σ mean
HP	5	42	0,807495	+/- 11
	20	48	0,812474	+/- 11
	45	60	0,817961	+/- 10
	70	48	0,810361	+/- 10
	100	54	0,799300	+/- 10
	150	53	0,812912	+/- 10
	220	45	0,844925	+/- 10
PP	5	41	0,778157	+/- 11
	30	59	0,790507	+/- 9
	60	62	0,794886	+/- 8
	90	58	0,799916	+/- 11
	120	55	0,808044	+/- 11
	180	44	0,816873	+/- 7
Bedrock	–	42	0,838386	+/- 10

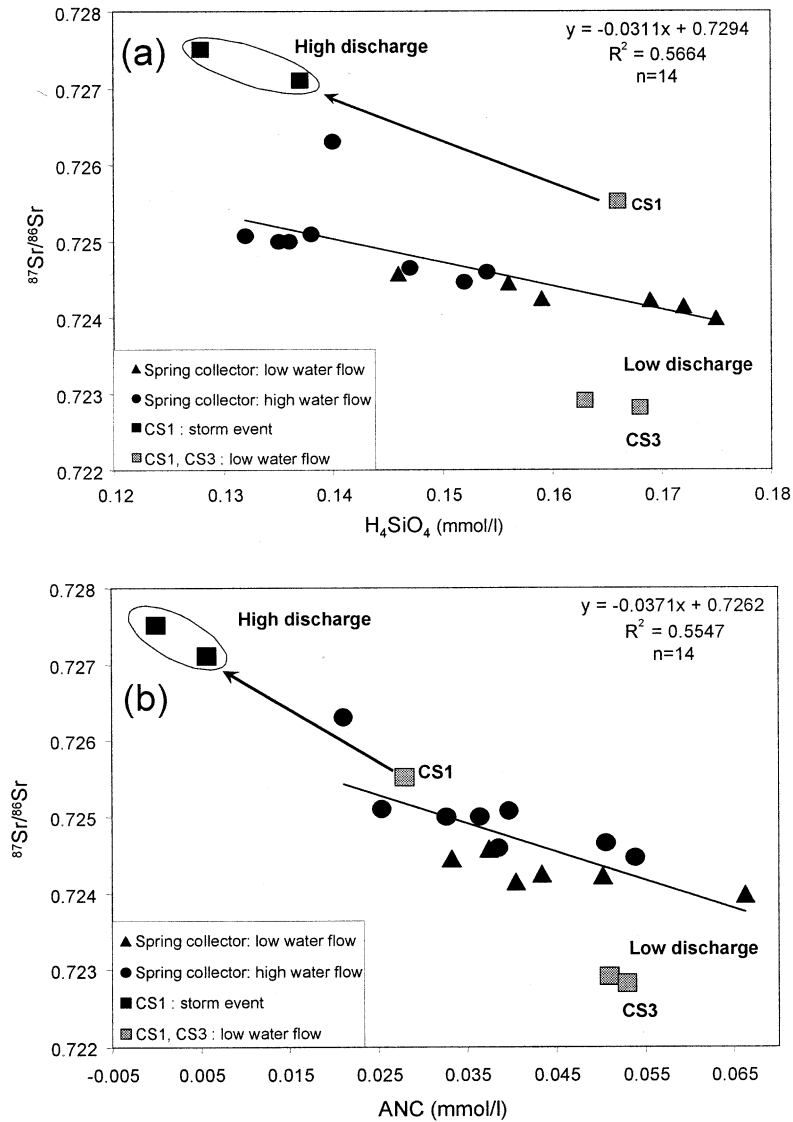


Fig. 8. Relationship between $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and H_4SiO_4 concentration (a), and between $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and ANC (b) in spring waters (data for CS1 and CS3 are from Probst et al., 2000).

water draining the north-facing slope is rather important. Water storage is also larger and the $^{87}\text{Sr}/^{86}\text{Sr}$ probably more homogeneous within the whole catchment. The occurrence of more radiogenic waters during the decreasing stages of discharge suggests the significant contribution of waters originating from the deep layers of the northern hillslopes by piston flow process, as already shown using silica and DOC (Idir et al., 1999; Ladouche et al., 2001). Afterwards, the proportion of waters draining the south-facing slope becomes more and more important as indicated by the decrease of the $^{87}\text{Sr}/^{86}\text{Sr}$.

The north-facing slope and the south-facing slope do not provide waters with the same Sr isotopic composition to the stream, which can be explained in terms of

weathering processes within the Strengbach catchment. The first hypothesis that can be formulated to explain the different behavior on both slopes is that the weathering rates of the different minerals are not the same due to inhomogeneous water/rock ratio or soil moisture, for example. But these phenomena are hard to check in the field. What is mostly probable is that the minerals do not contribute to the same extent to the Sr isotopic composition of the surface waters first, because Sr is not congruently released through mineral weathering since each mineral dissolves at a different rate to the other, and second, because the proportion of the minerals in the granite is different from one slope to another (El Gh'Mari, 1995, Probst et al., 2000). Moreover the

minerals are not uniformly distributed in the weathering profiles. Fichter et al. (1998a,b) show that the soil profile located on the south-facing slope (PP) that has undergone a strong hydrothermal event is substantially depleted in plagioclase compared to soils located on the opposite slope (north-facing one, HP) (see Table 1). Plagioclase is one of the most weatherable minerals of the bedrock and seems to contribute to a large part to the Sr isotopic ratio of the stream water (Probst et al., 2000). Thus, where plagioclase content is greatly depleted, increasing contribution of the leaching of accessory Sr-bearing minerals like apatite which has a low $^{87}\text{Sr}/^{86}\text{Sr}$ ratio compared to plagioclase (0.716 and 0.742, respectively; Aubert et al., 2001; Probst et al., 2000) would consequently decrease the Sr isotopic composition of the weathering solutions. The more radiogenic Sr ratio of the HP soil profile (north-facing slope) compared to PP (south-facing slope) is in agreement with this pattern. Moreover, the PP soil profile lays on the hydrothermally altered granite which is highly fractured, even at a mineral scale (El Gh'Mari, 1995). This fracturing certainly enhances the weathering of minerals thanks to greater surface contact between mineral and solution, and thus favors the release of Sr from apatite which is the most weatherable mineral in this granite facies (Aubert et al., 2001).

During dry conditions, waters draining the south-facing slope mainly contribute to streamwater. This suggests that the granitic weathering end-member ratio is not homogeneous contrary to the study of Bain et al. (1998) in a Scottish catchment. Its relative importance varies according to moisture conditions and consequently, in the function of the different contributive areas involved. Thus, as mentioned by Bain and Bacon (1994) caution must be exercised if using the Sr isotope ratio method (as analog to Ca) for calculating Ca budgets or weathering rates because the sources of Sr (i.e. weathering) may not be constant even for a silicate bedrock end-member. Graustein (1988) and Bailey et al. (1996) also suggested that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of weathering in a granite body is hard to determine since Sr isotopic ratios can differ from site-to-site, mineral-to-mineral and also with time. Consequently, in the case of both small and large scale basin approaches, it is necessary to discuss the respective contributions of bedrock weathering in term of ranges of $^{87}\text{Sr}/^{86}\text{Sr}$ end-members rather than absolute values.

5. Conclusion

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio and Sr content regularly measured over one year of sampling at the stream outlet of the granitic Strengbach catchment clearly show variations between 0.7242 and 0.7256, and between 10 and 14.5 ppb, respectively. These values are significantly higher during the high water flow period compared to the low

water flow period, suggesting that both isotope ratio and Sr concentration depend on the hydrological and moisture conditions in the catchment. Rainwater, which is Sr poor and less radiogenic has no noticeable influence on the Sr isotopic composition of streamwater since the more the catchment is water-saturated, the more the surface waters are radiogenic and Sr enriched. During flood events, the rising discharge is usually characterized by lower Sr isotope ratios as compared with the decreasing flows. These differences have been explained by the important contribution of waters from the deep soil profile during the recession stage but also by the relative importance of waters from distinct contributive areas such as the opposite slopes and the saturated area of the catchment. Those areas provide waters with specific Sr isotope composition and Sr concentration in relation to the mineralogical compositions of the weathering profiles developed on a granite which has more or less undergone hydrothermal alteration. The respective contribution of the drainage waters is thus a function of the moisture and hydrological conditions prevailing in the catchment.

For the first time, this study clearly shows that, even on an homogeneous granitic bedrock, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the streamwater vary with discharge. In consequence, it contradicts the established statement that flow rate has no effect on Sr isotopic composition in river waters. Thus, it is recommended that extreme hydrological conditions be considered when using Sr isotopes as a tracer to determine the weathering end-member in catchments because the range of variations can be important and can trigger incorrect calculations of weathering rates, both in small or large scale basins involving different rocks.

Acknowledgements

The authors are particularly grateful to S. Richard from the CEREG (Centre d'Etudes et de Recherches Eco-Géographiques) who participated in the field sampling and to D. Tisserant and B. Kiefel who helped in Sr isotopic analyses, Y. Hartmeier, D. Million and G. Krempf who helped with part of the chemical analyses of the major elements at the CGS (Centre de Géochimie de la Surface). P. Shand and an anonymous reviewer are gratefully acknowledged for their constructive reviews.

This research has been supported by the Région Alsace within the framework of the IFARE (Institut Franco-Allemand de Recherche pour l'Environnement) and D. Aubert benefits from a MRT (Ministère de la Recherche et de la Technologie) grant.

References

- Åberg, G., 1995. The use of natural strontium isotopes as tracers in environmental studies. *Water, Air, Soil Pollut.* 79, 309–322.

- Åberg, G., Wickman, F.E., 1987. Variations of $^{87}\text{Sr}/^{86}\text{Sr}$ in water from streams discharging into the Bothnian Bay, Baltic sea. *Nordic Hydrol.* 18, 33–42.
- Åberg, G., Jacks, G., Hamilton, P.J., 1989. Weathering rates and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios: an isotopic approach. *J. Hydrol.* 109, 65–78.
- Åberg, G., Jacks, G., Wickman, T., Hamilton, P.J., 1990. Strontium isotopes in trees as an indicator for calcium availability. *Catena* 17, 1–11.
- Amiotte-Suchet, P., Aubert, D., Probst, J.L., Gauthier-Lafaye, F., Probst, A., Andreux, F., Viville, D., 1999. $\delta^{13}\text{C}$ pattern of dissolved inorganic carbon in a small granitic catchment: the Strengbach case study (Vosges Mountains, France). *Chem. Geol.* 159, 129–145.
- Aubert, D., Probst, A., Stille, P., 1999. Strontium behaviour in surface waters and soils of a small granitic catchment under acid input influence: the Strengbach catchment case study (Vosges mountains, North-Eastern France). *J. Conf. Abstr., EUG 10*, March 28th–April 1st, 1999, *Terra Abstr.*, 4(1), 558.
- Aubert, D., Stille, P., Probst, A., 2001. REE fractionation during granite weathering and removal by waters and suspended loads: Sr and Nd isotopic evidence. *Geochim. Cosmochim. Acta* 65, 387–406.
- Bailey, S.W., Hornbeck, J.W., Driscoll, C.T., Gaudette, H.E., 1996. Calcium inputs and transport in a base-poor forest ecosystem as interpreted by Sr isotopes. *Water Resour. Res.* 32, 707–719.
- Bain, D.C., Bacon, J.R., 1994. Strontium isotopes as indicators of mineral weathering in catchments. *Catena* 22, 201–214.
- Bain, D.C., Midwood, A.J., Miller, J.D., 1998. Strontium isotopes ratios in streams and the effect of flow rate in relation to weathering in catchment. *Catena* 32, 143–151.
- Bonhomme, M., 1967. Ages radiométriques de quelques granites des Vosges moyennes. *Bull. Carte géol. Als. Lorr* 20, 101–106.
- Bullen, T.D., Shanley, J.B., Clark, S., 1994. Sr and Pb isotopes as surrogate tracers of water flowpaths in a forested catchment. *EOS, Trans. AGU*, 75 (16), Spring Meet. Suppl., 144.
- Clow, D.W., Mast, M.A., Bullen, T.D., Turk, J.T., 1997. Strontium 87/strontium 86 as a tracer of mineral weathering reactions and calcium sources in an alpine/subalpine watershed, Loch Vale, Colorado. *Water Resour. Res.* 33, 1335–1351.
- Dambrine, E., Ranger, J., Nys, C., Bonneau, M., 1995. Cycling and budgets of acidity and nutrients in Norway spruce stands in north-eastern France and the Erzgebirge (Czech Republic). In: Landmann, G., Bonneau, M. (Eds.), *Forest Decline and Atmospheric Deposition Effect in the French Mountains*, part 3. Springer, Berlin, pp. 233–258.
- Depaolo, D.J., Ingram, B.L., 1985. High resolution stratigraphy with strontium isotopes. *Science* 227, 938–941.
- El Gh'Mari, A., 1995. Etude minéralogique, pétrophysique et géochimique de la dynamique d'altération d'un granite soumis aux dépôts atmosphériques acides (bassin versant du Strengbach, Vosges, France): mécanismes, bilans et modélisations. PhD Thesis, Université Louis Pasteur, Strasbourg.
- Elias, R.W., Hiraou, Y., Patterson, C.C., 1982. The circumvention of the natural biopurification of calcium along nutrient pathways by atmospheric inputs of industrial lead. *Geochim. Cosmochim. Acta* 46, 2561–2580.
- Fichter, J., 1997. Minéralogie quantitative et flux d'éléments minéraux libéré par altération des minéraux des sols dans deux écosystèmes sur granite (bassin versant du Strengbach, Vosges). PhD Thesis, Univ. Henri Poincaré, Nancy I.
- Fichter, J., Turpault, M.P., Dambrine, E., Ranger, J., 1998a. Localization of base cations in particle size fractions of acid forest soils (Vosges Mountains, N-E France). *Geoderma* 82, 295–314.
- Fichter, J., Turpault, M.P., Dambrine, E., Ranger, J., 1998b. Mineral evolution of acid forest soils in the Strengbach catchment (Vosges Mountains, N-E France). *Geoderma*, 82 315–340.
- Gosz, J.R., Moore, D.I., 1989. Strontium isotope studies of atmospheric inputs to forested watersheds in New Mexico. *Biogeochem.* 8, 115–134.
- Gosz, J.R., Brookins, D.G., Moore, D.I., 1983. Using Sr isotope ratios to estimate inputs to ecosystems. *Bioscience* 33, 23–30.
- Graustein, W.C., 1988. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios measure the sources and flow of strontium in terrestrial ecosystems. In: Rundel, P.W., Ehleringer, J.R., Nagy, K.A. (Eds.), *Stable Isotopes in Ecological Research. Ecological Studies*, Vol. 68. Springer, New York, pp. 491–512.
- Graustein, W.C., Armstrong, R.L., 1983. The use of strontium-87/strontium-86 ratios measure atmospheric transport into forested watersheds. *Science* 219, 289–292.
- Idir, S., 1998. Etude géochimique des crues du bassin versant du Strengbach (Vosges): origine des écoulements et contribution aux flux d'éléments majeurs dissous exportés. PhD Thesis, Univ. Louis Pasteur.
- Idir, S., Probst, A., Viville, D., Probst, J.L., 1999. Contribution des surfaces saturées et des versants aux flux d'eau et d'éléments exportés en période de crue: traçage à l'aide du carbone organique dissous et de la silice. Cas du petit bassin versant du Strengbach (Vosges, France). *Cp. Rd. Acad. Sci.* 328, 89–96.
- Jacks, G., Åberg, G., Hamilton, P.J., 1989. Calcium budgets for catchments as interpreted by strontium isotopes. *Nordic Hydrol.* 20, 85–96.
- Krishnaswami, S., Trivedi, J.R., Sarin, M.M., Ramesh, R., Sharma, K.K., 1992. Strontium isotopes and rubidium in the Ganga-Brahmaputra river system: weathering in the Himalaya, fluxes to the Bay of Bengal and contributions to the evolution of oceanic $^{87}\text{Sr}/^{86}\text{Sr}$. *Earth Planet Sci. Lett.* 109, 243–253.
- Ladouche, B., Probst, A., Viville, D., Idir, S., Baqué, D., Loubet, M., Probst, J.L., Bariac, T., 2001. Hydrograph separation of stormflow components using isotopic, chemical and hydrological approaches (Strengbach, France). *J. Hydrol.* 242 (3-4), 255–274.
- Land, M., Öhlander, B., 1997. Seasonal variations in the geochemistry of shallow groundwater hosted in granitic till. *Chem. Geol.* 143, 205–216.
- Lasaga, A.C., 1984. Chemical kinetics of water rock interactions. *J. Geophys. Res.* 89, 4009–4025.
- Latron, J., 1990. Caractérisation géomorphologique et hydrologique du bassin versant du Strengbach (Aubure), Mémoire de maîtrise, UFR de géographie, CEREG, Univ. Louis Pasteur, Strasbourg I.
- Lefèvre, Y., 1988. Les sols du bassin d'Aubure (Haut-Rhin): caractérisation et facteurs de répartition. *Ann. Sci. For.* 45, 417–422.

- Likens, G.E., Bormann, F.H., Pierce, R.S., Eaton, J.S., Johnson, N.M., 1977. Biogeochemistry of a Forested Ecosystem. Springer, New York.
- McNutt, R.H., Frappe, S.K., Fritz, P., Jones, M.G., MacDonald, I.M., 1990. The $^{87}\text{Sr}/^{86}\text{Sr}$ values of Canadian shield brines and fracture minerals with applications to groundwater mixing, fracture history, and geochronology. *Geochim. Cosmochim. Acta* 54, 205–215.
- Miller, E.K., Blum, J.D., Friedland, A.J., 1993. Determination of soil exchangeable cation loss and weathering rates using Sr isotopes. *Nature* 362, 438–441.
- Négrel, P., Dupré, B., 1993. Temporal variations of Sr isotopic ratios, major and trace elements composition of the Oubangui River Basin: implications for the source of material. *Grands Bassins Fluviaux*, Paris, pp. 181–198.
- Négrel, P., Fouillac, C., Brach, M., 1997a. Occurrence of mineral springs in the stream channel of the Allier River (Massif Central, France): chemical and Sr isotope constraints. *J. Hydrol.* 203, 143–153.
- Négrel, P., Fouillac, C., Brach, M., 1997b. A strontium isotopic study of mineral and surface waters from the Cézallier (Massif Central, France): implications for mixing processes in areas of disseminated emergences of mineral waters. *Chem. Geol.* 135, 89–101.
- Palmer, M.R., Edmond, J.M., 1989. The strontium isotope budget of the modern ocean. *Earth Planet Sci. Lett.* 92, 11–26.
- Pionke, H.B., DeWalle, D.R., 1994. Streamflow generation on a small agricultural catchment during autumn recharge: I. Non stormflow periods. *J. Hydrol.* 163, 1–22.
- Pionke, H.B., Gburek, W.J., Folmar, G.J., 1993. Quantifying stormflow components in a pennsylvanian watershed when ^{18}O input and storm conditions vary. *J. Hydrol.* 148, 169–187.
- Poszwa, A., 2000. Utilisation des isotopes du strontium pour évaluer la dynamique des éléments minéraux dans des écosystèmes forestiers sous climat boréal, tempéré et tropical. PhD Thesis, Univ. Henri Poincaré, Nancy.
- Probst, A., Viville, D., 1997. Bilan hydrogéochimique du petit bassin versant forestier du Strengbach à Aubure (Haut-Rhin). In: *Rapport Scientifique Activités de Recherche, 5e Réunion du Conseil de Direction Scientifique Ifare/DFIU, Conseil de l'Europe, 30/04/1998*, pp. 59–66.
- Probst, A., Dambrine, E., Viville, D., Fritz, B., 1990. Influence of acid atmospheric inputs on surface water chemistry and mineral fluxes in a declining spruce stand within a small granitic catchment (Vosges massif, France). *J. Hydrol.* 116, 101–124.
- Probst, A., El Gh'Mari, A., Aubert, D., Fritz, B., McNutt, R., 2000. Strontium as a tracer of weathering processes in a silicate catchment polluted by acid atmospheric inputs, Strengbach, France. *Chem. Geol.* 170 (1–4), 203–219.
- Probst, A., Fritz, B., Ambroise, B., Viville, D., 1987. Forest influence on the surface water chemistry of granitic basins receiving acid precipitation in the Vosges massif, France. *Proceedings of the Vancouver symposium, August 1987, Internat. Assoc. of Hydrol. Sci. (IAHS)* 167, 109–120.
- Probst, A., Fritz, B., Stille, P., 1992. Consequence of acid deposition on natural weathering processes: field studies and modelling. In: Kharaka, Y. K., Maest, A. S., (Eds), *Proc. of the 7th Internat. Symp. Water Rock Interaction, WRI7*, 13–18 July, Park City, Utah (USA), Vol. 1, A. A. Balkema, Rotterdam, pp. 581–584. .
- Probst, A., Fritz, B., Viville, D., 1995a. Mid-term trends in acid precipitation, streamwater chemistry and elements budgets in the Strengbach catchment (Vosges mountains, France). *Water Air Soil Pollut.* 79, 39–59.
- Probst, A., Lelong, F., Viville, D., Durand, P., Ambroise, B., Fritz, B., 1995b. Comparative hydrochemical behavior and elements budgets of the Aubure (Vosges Massif) and Mont Lozère (Massif Central) spruce forested catchments. In: Landmann, G., Bonneau, M. (Eds.), *Forest Decline and Atmospheric Deposition Effect in the French Mountains, Part 3*. Springer, Berlin, pp. 203–225.
- Probst, A., Viville, D., Fritz, B., Ambroise, B., Dambrine, E., 1992b. Hydrochemical budgets of a small forested granitic catchment exposed to acid deposition: The Strengbach catchment case study (Vosges massif, France). *Water Air Soil Pollut.* 62, 337–347.
- Rice, K.C., Bricker, O.P., 1995. Seasonal cycles of dissolved constituents in streamwater in two forested catchments in mid-Atlantic region of the eastern USA. *J. Hydrol.* 170, 137–158.
- Riotte, J., Chabaux, F., 1999. ($^{234}\text{U}/^{238}\text{U}$) Activity ratios in freshwaters as tracers of hydrological processes: The Strengbach watershed (Vosges, France). *Geochim. Cosmochim. Acta* 63, 9. 1263-1275.
- Stottlemyer, R., Troendle, C.A., Markowitz, D., 1997. Change in snowpack, soil water, and streamwater chemistry with elevation during 1990, Fraser Experimental Forest, Colorado. *J. Hydrol.* 195, 114–136.
- Tricca, A., Stille, P., Steinmann, M., Kiefel, B., Samuel, J., Eikenberg, J., 1999. Rare earth elements and Sr and Nd isotopic compositions of dissolved and suspended loads from small river systems in the Vosges Mountains (France), the river Rhine and the groundwater. *Chem. Geol.* 160, 139–158.
- Wickman, T., Jacks, G., 1993. Base cation nutrition for pine stands on lithic soils near Stockholm, Sweden. *Appl. Geochem.*, Suppl. 2, pp. 199–202.