

silicate catchment polluted by acid atmospheric inputs, Strengbach, France

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Abstract

This paper determines the weathering and atmospheric contributions of Ca in surface water from a small spruce forested silicate catchment (N–E France) receiving acid atmospheric inputs. The bedrock is a granite with K-feldspar and albite as dominant phases. The calcium content in plagioclase is low and the Ca/Na ratio in surface water is high, reflecting other sources of calcium from those expected from the weathering of major mineral phases. The biotite content is low. Only traces of apatite were detected while no calcite was found in spite of a major hydrothermal event having affected the granite. The strontium isotopic ratio $^{87}\text{Sr}/^{86}\text{Sr}$ and Sr content was used as a tracer of weathering and was determined in minerals and bulk bedrock, open field precipitation, throughfall, soil solution, spring and stream water. The Sr isotopic ratio of the reacting weathering end-member was predicted by simulating the alteration of the granite minerals by incorporating strontium into the water–rock interaction kinetic code KINDIS. In the early stages of water–rock interaction, K-feldspar and biotite strongly influence the isotopic composition of the weathering solution whereas, the Na-rich plagioclase appears to be the main long-term reactive weathering end-member. Approximately 50% of dissolved Sr in streamwater are atmospherically derived. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of exchangeable Sr in the fine fraction at 1-m depth from a soil profile indicate that the amount of exchangeable Sr seems essentially controlled by atmospheric inputs. The exception is the deep saprolite where weathering processes could supply the Sr (and Ca). Na-Plagioclase weathering obviously control the chemistry and the isotopic composition of surface waters. The weathering of trace mineral plays a secondary role, the exception is for apatite when plagioclase is absent. Our hydrochemical, mineralogical and isotopic investigations show that a major part of the strong Ca losses detected in catchment hydrochemical budgets that result from the neutralization of acid precipitation has an

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atmospheric origin. Consequently, in the long term, in such areas, the availability of such an exchangeable base cation might be strongly limited and surface waters consequently acidified.

Keywords: Strontium isotopes; Weathering; Modelling; Catchment; Granite; Acid inputs

1. Introduction

Rock weathering rates in catchments have been estimated by considering either a steady-state mass balance approach or the stoichiometry of weathering reactions according to field or experimental data (Velbel, 1985; Colman and Dethier, 1986; Giovanoli et al., 1988; Mast et al., 1990; Kirkwood and Nesbitt, 1991; Drever and Zobrist, 1992; Casey et al., 1993; Swoboda-Colberg and Drever, 1993; Blum et al., 1994). Over the last 20 years, catchment budget approach has been developed to determine the influence of acid atmospheric inputs on weathering rates (e.g., Likens et al., 1977; Paces, 1985; Probst et al., 1992a; Rice and Bricker, 1993). The neutralization of acid atmospheric inputs by weathering of the bedrock and soil minerals and/or by exchange reactions results in important losses of base cations from catchments (Paces, 1985). However, predicting the amount of nutrients originating from geochemical processes remains problematic, since the soil exchange complex is not in a steady-state in acid disturbed areas (Jacks et al., 1989; Probst et al., 1992a; El Gh'mari, 1995; Bailey et al., 1996). In forested areas on poorly buffered silicate terrains, the Ca/Na ratios are often found to be high in surface waters despite their low value in plagioclase. In some granitic sites, the importance of Ca in surface waters has been related to trace mineral weathering such as calcite (Mast et al., 1990; Clow et al., 1997).

Over the last 10 years, strontium isotopes have been used in environmental studies to distinguish between different sources of Sr within the ecosystem (i.e., Capo et al., 1998). Strontium 86 is non-radiogenic and ^{87}Sr is produced by decay of ^{87}Rb (half-life = $4.8 \cdot 10^{10}$ y). Thus, the ratio $^{87}\text{Sr}/^{86}\text{Sr}$ depends of the Rb/Sr ratio and age of the host rock and is changing with time. Most studies on monolithologic terrains use a two-component mixing equation to determine the respective contributions to the Sr in

streamwater from atmospheric inputs and bedrock weathering, or from weathering and exchange processes in soils (Miller et al., 1993). The models can be applied when the Sr isotopic compositions of the end-members are significantly different (Graustein and Armstrong, 1983). Weathering rates of Ca containing minerals can be estimated assuming that Sr and Ca have a similar geochemical behavior (Graustein, 1989; Jacks et al., 1989; Åberg, 1995; Åberg et al., 1989; Bailey et al., 1996; Clow et al., 1997).

The result of this method depends heavily on the choice of the weathering end-member. Some studies chose the bulk bedrock isotopic value or the Sr ratio of the leachate derived from batch bedrock dissolution experiments using strong acids. But, the isotopic values of such weathering end-members might not be adequate because the specific individual mineral weathering rates are not taken into account (Clow et al., 1997). Since these experimental conditions are far from field conditions, other authors chose to use organic acids in batch experiments (e.g., Wickman and Jacks, 1992). However, natural organic acids are principally concerned with the upper layers of the soils whereas in the deeper profiles from areas sensitive to acid inputs, bedrock weathering is mainly the result of mineral acid influence (Probst et al., 1990).

The main objective of the paper is to investigate the origin of Ca in a catchment receiving acid atmospheric inputs and where Ca dominates the surface water chemistry. For that purpose, the chemistry, the Sr isotopes and the mineralogy of the bedrock were first determined. Secondly, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and Sr contents of surface waters draining the catchment were characterized. Thirdly, the respective contributions of atmospheric and lithologic strontium were assessed. The weathering end-member was determined by simulating the bedrock dissolution using the specific mineral Sr characteristics as well as their dissolution rates in a geochemical model (KINDIS code, Madé et al., 1990, Richard, 1993). Finally, the

geochemical cycle and the hydrochemical budget of Sr and Ca are discussed on the basis of the potential sources of Sr.

2. Material and methods

2.1. Site description

The Strengbach forested catchment (80 ha) at Aubure is located on the eastern side of the Vosges massif (northeastern France), 58-km SW from Strasbourg. The elevation ranges from 883 m at the outlet to 1146 m at the catchment divide (Fig. 1). The slopes are rather steep. The climate is temperate oceanic mountainous, with monthly averages of daily mean temperature ranging from -2°C to 14°C . Westerly winds are dominant. The mean annual rainfall amount is about 1400 mm. Rainfall is spread all over the year, with the driest season in autumn;

Generally, snowfall season lasts 4 months per year (Probst et al., 1990).

The bedrock is the base-poor Brézouard leucogranite. This 2-mica granite is coarse grained and has undergone hydrothermal alteration, which is most obvious on the south-facing slope. At the upper margin of the basin, a banded gneiss lies in contact with the granite. Brown acid soils have developed on the south-facing slope, where soil solutions were collected. Ochreous brown to podzolic soils cover the north-facing slope; these soils are rather deep (60 to 80 cm), sandy and stony, and lie on a saprolite, which can reach 10 m depth in places. The valley bottom is occupied by a saturated area with permanent moisture conditions, representing 2% of the basin area (Probst et al., 1990). Forest cover is rather homogenous and complete; Norway spruce (*Picea abies* Karst.) dominates while mixed silver fir (*Abies alba* Mill.) and beech (*Fagus sylvatica* L.) cover 1/3 of the area. Symptoms of forest decline began

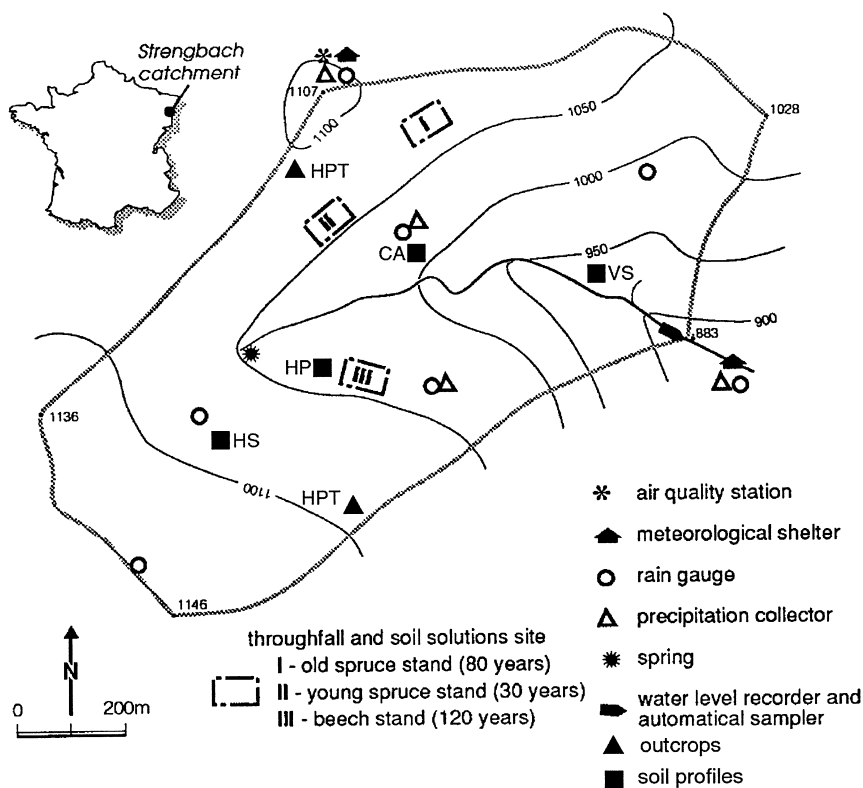


Fig. 1. Location map of the study area showing the sampling sites.

in the early 1980s and spruce yellowing has been related to magnesium deficiencies (Landmann et al., 1987) as observed at several other European sites (Ulrich, 1984). Crown thinning affects both white fir and spruce; the mean level of needle loss is about 30 %.

2.2. Site equipment, sampling and analytical work

The Strengbach catchment has been monitored since 1986. The catchment equipment has been detailed in Probst et al. (1990). As a routine, bulk precipitation is collected fortnightly at four sites in PVC funnel collectors exposed at all times to atmospheric deposition (for snow episodes, buckets are used); throughfall (using replicate 2-m-long open gutters) and soil solution at different depths (using zero-tension lysimeter plates) are sampled fortnightly in three spruce stands of various ages and in a beech stand (Fig. 1). Because mature spruces are dominant in this basin, the results presented here mainly concern throughfall and soil solution from the instrumented old stand. Four springs, emerging at about 4-m depth in the granite at the upper part of the basin, are the main contributors to the stream and are partly utilised for drinking water supplies (for 2% of the total annual runoff, Probst et al. 1992a). Streamwater is controlled by an H-Flume type weir and water level is monitored by ultrasonic and mechanical limnigraphs (for details see Probst et al., 1990, 1992a). Streamwater and springwater are generally sampled at least weekly and more frequently during flood events (using automatic samplers). Samples are stored in polyethylene bottles and filtered in the laboratory (0.45 μm Millipore membrane).

All waters are analysed in the laboratory as follows: pH, conductivity and alkalinity electrometrically (the latter by Gran titration); sodium, potassium, calcium, magnesium by atomic absorption spectrometry; ammonium and silica by colorimetry; aluminum by ICP-AES; nitrate, chloride and sulphate by ion chromatography.

Sr concentration and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were measured in open field precipitation, throughfall, soil solution, springwater and streamwater during specific hydrological periods occurring in various seasons, including low and high water flow conditions (Table 1). Sr contents and Sr isotopic compositions were also determined for the constituent minerals of fresh bedrock as well as for the whole bedrock. Mineral separation was from the 100–200 μm fraction of the granite using a combination of magnetic separation (for muscovite and biotite), heavy liquids and handpicking techniques under optical microscope (quartz, plagioclase and K-spar). Finally, once separated, each mineral phase was checked using X-ray diffraction and chemical analysis on STEM. Hence, the purity of the mineral separation is considered reliable. Moreover, crushed fresh bedrock (HPT) was in contact with a 1 N HCl solution for 15 days as a batch leaching experiment.

The silicate samples were spiked with a ^{84}Sr tracer and subsequently digested with HF, HNO_3 and HClO_4 for 5–7 days in closed Savillex vials, dried and treated with 6 N HCl for several hours. The Sr of both the digested silicate and water samples was separated from other ions using AG 50 W-X12 (200–400 mesh) cation exchange resin and 1.5 N and 4 N HCl as eluents. The total procedural blank for the lab procedure was < 1.5 and < 0.5 ng for Sr of silicate and water samples, respectively. Sr iso-

Table 1

Chemical composition (% oxides) of the granitic bedrock from different profiles in the Strengbach catchment
L.I.: Loss on ignition.

%	SiO_2	Al_2O_3	MgO	CaO	Fe_2O_3	Mn_3O_4	TiO_2	Na_2O	K_2O	P_2O_5	Sum	L.I. 100°C	L.I. 1000°C	CaO ^a
HPT	73.8	14.13	0.24	0.37	1.08	0.02	0.16	3.68	5.05	0.27	98.63	0.12	0.77	0.061
VS	73.7	14.01	0.25	0.35	1.12	0.02	0.18	2.67	6.05	0.26	99.78	0.17	1.16	0.45
HP	73.3	14.40	0.26	0.23	0.64	0.01	0.16	2.03	6.14	0.25	99.00	0.26	1.64	−0.06
HS	73.8	14.40	0.51	0.08	1.36	0.02	0.15	0.26	6.55	0.16	99.70	0.41	2.52	−0.11
CA	74.4	13.94	0.39	0.29	1.41	0.02	0.16	0.08	5.84	0.22	98.93	0.30	2.18	0.00

^aRepresents the amount of calcium of the bedrock corrected for apatite.

topic ratios and concentrations were analyzed on a VG Sector multicollector mass spectrometer. Strontium was deposited on W single filaments with Ta₂O₅ as activator. The NBS 987 standard yielded an ⁸⁷Sr/⁸⁶Sr value of 0.71027 ± 1 (2σ mean, n = 18).

Rock and saprolite chemistry was investigated using classical methods of ICP-AES and XRF. The mineral abundance in granite was determined by point counting on several thin sections under an optical microscope. Exchangeable cations were extracted from the < 2 mm-size fraction of soils and saprolite using 1-M ammonium chlorite (NH₄Cl) in a 1/10 solid-solution ratio.

2.3. Modelling

In order to estimate the isotopic ratio ⁸⁷Sr/⁸⁶Sr of the weathering end-member, a modified kinetic model, the KINDIS Code (Madé et al., 1990), has been used to simulate the behavior of Sr isotopes during weathering processes (Fritz et al., 1992; Richard, 1993). The equation used in the KINDIS code to account for the dissolution rate of a particular mineral has the general following form (Madé et al., 1990):

$$v_{\text{dm}} = k_{\text{dm}} S_m a_{\text{H}^+}^n \left(1 - \frac{Q_m}{K_m} \right) \quad (1)$$

where v_{dm} is the dissolution rate for the mineral, k_{dm} is a dissolution rate constant determined experimentally, S_m is the surface of contact between the mineral and the solution, a_{H^+} is the activity of the proton in the solution, n is a real exponent with a value between 0 and 1 in acid solutions, and $(1 - (Q_m)/(K_m))$ corresponds to the departure from chemical equilibrium for the mineral, where Q_m is the ion activity product of reaction at given state of the system and K_m is the equilibrium solubility product of this mineral, respectively.

The isotopic version of the KINDIS code (Richard, 1993) defines a ⁸⁷Sr/⁸⁶Sr value and Sr content for each reacting mineral and for the aqueous phase. The aqueous phase is defined in the model by the sum of the concentrations of the three isotopes ⁸⁶Sr, ⁸⁷Sr and ⁸⁸Sr. The ⁸⁴Sr is negligible for purposes of the model.

A smectite has been allowed to precipitate during the simulation since it is the main clay mineral found

in the Strengbach catchment. The Sr isotopic ratio at the end of the simulation was assessed to represent that of the weathering end-member.

2.4. Calculation

The proportion x of the end-member A in the mixture M of A and B was calculated following Miller et al. (1993) using $\Delta^{87}\text{Sr}$ of each sample.

$$x = \frac{\Delta^{87}\text{Sr}_M - \Delta^{87}\text{Sr}_B}{\Delta^{87}\text{Sr}_A - \Delta^{87}\text{Sr}_B} \quad (2)$$

$\Delta^{87}\text{Sr}$ was calculated after the equation in Graustein (1989) as follows.

$$\Delta^{87}\text{Sr} = \left[\left(\frac{{}^{87}\text{Sr}}{{}^{87}\text{Sr} + {}^{86}\text{Sr}} \right)_{\text{sample}} - \left(\frac{{}^{87}\text{Sr}}{{}^{87}\text{Sr} + {}^{86}\text{Sr}} \right)_{\text{standard}} \right] \times 100 \quad (3)$$

The standard reference is the sea water isotopic ratio 0.70923 (Depaolo and Igram, 1985).

3. Results and discussion

3.1. Mineralogy and chemistry of the bedrock

The chemical and mineralogical compositions of five samples of the bedrock are given in Tables 1 and 2. The Brézouard granite (315 ± 7 Ma, Bonhomme, 1967) in the Strengbach catchment is a

Table 2
Mineralogical composition (%) of the same samples of granitic bedrock as in Table 1

%	Sampling sites				
	HPT	VS	HP	HS	CA
Quartz	36	32	32	37	46
Orthoclase	22	29	31	33	5
Albite	33	21	19	2	0
Muscovite	3	15	12	7	12
Biotite ^a	6	0	0	0	0
Sericite	0	3	6	21	37
Apatite ^b	0.5	0.6	0.6	0.3	0.3

^aPartially weathered into chlorite.

^bEstimated after total bedrock chemical analysis.

peraluminous leucogranite generally consisting of quartz, Na-rich plagioclase (An 6), and K-feldspar as major phases (Table 2, samples HPT, VS, and HP). Muscovite, biotite (partially transformed into chlorite) and apatite are present in minor amounts. The Brézouard granite has undergone hydrothermal alteration 183.9 ± 4 Ma ago (El Gh'mari, 1995), which resulted in the partial transformation of feldspar, biotite and muscovite into small-sized hydrothermal illites and quartz (Table 2, sample CA, HS). The hydrothermal altered bedrock, which contains less Na, and Ca (Table 1, CA, HS) mainly affects the southern slope. Therefore, the bedrock containing K-feldspar and plagioclase dominates in the catchment. No traces of calcite have been found in spite of a careful search using cathode luminescence on polished thin sections from the different bedrocks.

The mean total porosity of the granite (determined by weight of saturated cylindrical pieces of bedrock) varies between 2.3% and 10 % within the catchment (El Gh'mari, 1995). The lower porosity values are associated with hydrothermal alteration, which has precipitated minerals such as quartz and white mica into the crack spaces. The higher porosity values are associated with modern weathering, which increases the porosity by chemical and mechanical processes, producing important microfissuring features within the feldspar. The mean value of total porosity is 9%, which indicates that the major part of the bedrock is affected by weathering at ambient temperature.

STEM observations show that K-feldspar and albite have dissolution etch-pits on their surface, but albite much more (El Gh'mari et al., 1993) so reflecting the fact that K-feldspar is less reactive than plagioclase (Tardy, 1969; Fritz and Tardy, 1976). The main secondary mineral products in the clay fraction ($< 2 \mu\text{m}$) of the saprolite is illite, smectite and interstratified smectite–chlorite whereas it is predominantly regularly interstratified smectite–illite in the soils; smectite is formed from the weathering of biotite in the saprolite; kaolinite accounts for less than 5% of the clay fraction and is essentially located in feldspar cracks; muscovite is partly transformed into lath shaped illites as a result of hydrothermal alteration. Biotite is considerably more weathered than muscovite: the cleavage is open, the sheets are highly fractured and Fe–Ti oxides are present. Apatite is seemingly less affected by weath-

ering than plagioclase: no pits are observed on the surface. However, in thin section, this mineral appears highly fractured; this suggests that calcium could be supplied by the dissolution of apatite, particularly in places where the plagioclase is absent as a result of hydrothermal alteration (El Gh'mari et al., 1993).

3.2. Sr isotopic composition of the solid phases

The Sr content and isotopic composition of both the bedrock and its constituent minerals are given in Tables 3 and 4. Muscovite is the most radiogenic ($^{87}\text{Sr}/^{86}\text{Sr} = 7.496$) whereas plagioclase is the least radiogenic ($^{87}\text{Sr}/^{86}\text{Sr} = 0.742$) among the major mineral phases. The relatively high $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the plagioclase is consistent with its high Rb content (122 ppm), with regard to the age of the granite. The Sr content and $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of biotite are less precise because of the difficulty of collecting enough material due to the alteration of the biotite to chlorite. Because apatite is very scarce, it could not

Table 3
 $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratio, Sr content (ppm), dissolution rate constants (K_{dm} mol/m² year) and effective surface area (S_{m} : m² by kilogramme of water by considering an average diameter of cracks of 0.2 mm) values assigned to the simulations using KINDIS. The Sr data are measured values of the minerals from the Brézouard granite in the Strengbach catchment

	Sr (ppm)	$^{87}\text{Sr}/^{86}\text{Sr}$	k_{dm} (mol/m ² year)	S_{m} (m ²)
Quartz	–	–	$5.0 \cdot 10^{-7\text{a}}$	3.15
K-spar	102.73	0.782738 ± 5	$10^{-4.0\text{b}}$	2.14
Plagioclase	45.58	0.742029 ± 5		3.21
albite			$3.8 \cdot 10^{-4.0\text{b}}$	
anorthite			$1.76 \cdot 10^{-1.0\text{c}}$	
Biotite ^d	7.00	5.4	$4.4 \cdot 10^{-4.0\text{e}}$	0.58
Muscovite	4.44	7.496365 ± 7	$3.16 \cdot 10^{-7.0\text{f}}$	0.29
Apatite	500 ^g	0.709 ^h	$1.0 \cdot 10^{-4.0\text{i}}$	0.04

^aMurphy and Helgeson (1989).

^bHelgeson et al. (1984).

^cLasaga (1984).

^dPartly weathered into chlorite.

^eAcker and Bricker (1992).

^fLin and Clemency (1981).

^gData from Blum et al. (1994).

^hAssigned value equal to the zero $^{87}\text{Rb}/^{86}\text{Sr}$ intercept of the isochron determined on the Brézouard granite (Bonhomme, 1967).

ⁱHull and Hull (1987).

Table 4

$^{87}\text{Sr}/^{86}\text{Sr}$ ratio and Sr concentrations (ppm) of the Brézouard granite: HPT is from the Strengbach catchment of the present study area and the data from Bonhomme (1967) is outside the catchment area

Bedrock	Sr (ppm)	$^{87}\text{Sr}/^{86}\text{Sr}$
HPT ^a	42	0.83838 ± 1
HPT ^b	40.7	0.8328
HPT ^c	0.013	1.024997 ± 10
Bonhomme (1967)	65.8	0.795 ± 2

^aMeasured outcrop of the Brézouard granite in the Strengbach catchment.

^bRecalculated from mineral abundances and individual mineral measurements.

^cLeaching from batch experiment with HCl 1N during 15 days.

be accurately isolated for isotopic analysis. Consequently, in the weathering simulations, the Sr content of the apatite was taken from the literature (Blum et al., 1994). The $^{87}\text{Sr}/^{86}\text{Sr}$ value was assumed to be equal to the zero $^{87}\text{Rb}/^{86}\text{Sr}$ intercept for the Brézouard granite isochron (Bonhomme, 1967), i.e., 0.709.

The Sr content and the isotopic ratio of the bulk rock were both measured and calculated according to the Sr isotopic ratio and the abundance of each rock-forming mineral. Despite of the uncertainties on some radiogenic mineral isotopic value (particularly for biotite), the measured and calculated values of the rock are consistent (Table 4). This provides a quality check in mineral separation. The strontium isotopic ratio in leachates from the batch experiment of granite dissolution using strong acid is higher than the bulk bedrock value, probably because of specific and uncompleted mineral dissolution. On the contrary, the elemental Sr concentration in leachate is low and closer to the value found in surface waters.

3.3. Chemical and isotopic composition of surface waters

The chemical and Sr isotopic compositions of surface waters are given in Table 5. They reflect a range of hydrological conditions (from high water flow, i.e., February 1990, to very low water flow, i.e., September 1989 or September 1992) as well as seasonal variations (Winter, Spring and Summer/

Autumn). These samples represent the typical chemical characteristics determined by 10 years of chemical data record in the Strengbach catchment (Probst et al., 1995a).

Open field bulk precipitation is rather dilute and acidic (mean annual TDS = 5 mg/l and mean pH = 4.5). The chemistry is dominated by elements originating from atmospheric pollution (H^+ , NH_4^+ , NO_3^- , and SO_4^{2-}) (Probst et al., 1990, 1992a). The Sr content in open field precipitation is very low (0.4 to 1.7 ppb), while the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio varies from 0.7097 to 0.7114 (Table 5). These $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are close to, but slightly higher than, the Sr isotopic ratio of seawater ($^{87}\text{Sr}/^{86}\text{Sr} = 0.7092$; Depaolo and Igram, 1985). Some dust derived from local terrestrial sources (presence of loess in the nearby Alsace plain) contributes some radiogenic Sr to the precipitation. The highest Sr isotopic ratio, Sr and Ca contents correspond to a spring period (Table 5) when pollutants are generally the most concentrated.

Throughfall is 5 to 10 times more concentrated than open field precipitation, particularly for acid compounds. The Sr content of throughfall varies between 0.8 and 11.7 ppb, while the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio varies between 0.7121 and 0.7130 (Table 5). These Sr isotopic ratios are higher than those of open field rainwater sampled during the same period, reflecting contributions to throughfall from radiogenic sources such as dry deposits and vegetation, as found elsewhere (Graustein and Armstrong, 1983; Gosz and Moore, 1989). Like open field precipitation, the April 1990 sample is the most concentrated and has one of the most radiogenic Sr ratios (Table 5). This is consistent with the previous reported observation of influence of dry fallout, particularly in the upper part of the catchment during winter and spring (Probst et al., 1992a). Under spruce forest, the importance of Sr from dry fallout before leaching had already been indicated (Graustein and Armstrong, 1983; Gosz and Moore, 1989).

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of soil solutions in autumn period varies between 0.7212 and 0.7297 (Table 5). Such high values indicate the influence of soil-mineral weathering. Soil solution is acid and enriched in aluminum, nitrate and sulphate (Table 5) down to a depth of 60 cm (Dambrine et al., 1995a). Although the Sr and Ca concentrations in soil solutions increase regularly with depth as a result of

Table 5
Chemical and isotopic compositions of open field precipitation (OFP), throughfall (under spruce TFS, under beech TFB), soil solutions (LYS) at various depths, springwaters (SP) and streamwaters (SW) in the Strengbach catchment. Major elements and silica are expressed in $\mu\text{moles/l}$, strontium in ppb. Sr/Ca is expressed as a molar ratio

Nature of the sample	Reference	Sampling date	pH	Na ⁺	K ⁺	NH ₄ ⁺	Mg ²⁺	Ca ²⁺	HCO ₃ ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Al ³⁺	H ₄ SiO ₄	⁸⁷ Sr/ ⁸⁶ Sr	Sr	Sr/Ca
Open field precipitation	OFP	Sep. 89	4.22	3	2	67	2	8	0	7	53	46	n.d.	< 1	0.709650 ± 20	1.1	1.57E-03
	OFP	Dec. 89	5.08	16	1	8	2	2	0	19	5	8	n.d.	< 1	0.709635 ± 31	0.4	2.28E-03
	OFP	Feb. 90	5.10	8	2	5	< 1	2	0	11	9	5	n.d.	< 1	0.710106 ± 27	0.5	2.85E-03
	OFP	Apr. 90	4.12	19	3	64	4	12	0	24	58	40	n.d.	< 1	0.711386 ± 12	1.7	1.62E-03
	OFP	Sep. 92	4.69	13	1	16	2	5	0	13	19	12	n.d.	< 1	0.710347 ± 24	0.6	1.37E-03
Throughfall	TFS	Sep. 89	3.91	34	75	144	17	75	0	57	215	144	n.d.	5	0.712091 ± 6	8.6	1.31E-03
	TFS	Dec. 89	4.28	55	45	53	9	31	0	74	91	91	n.d.	2	0.712271 ± 13	4.2	1.55E-03
	TFS	Feb. 90	4.70	33	14	7	3	5	0	43	16	11	n.d.	< 1	0.711945 ± 18	0.8	1.83E-03
	TFS	Apr. 90	3.71	72	82	180	26	94	0	78	213	237	n.d.	5	0.712477 ± 7	11.7	1.42E-03
	TFS	Sep. 92	4.99	30	42	17	5	19	3	42	40	27	< 1	< 1	0.712986 ± 11	1.6	9.61E-04
Soil solutions	TFB	Sep. 92	6.03	17	69	4	2	7	19	26	16	20	< 1	2	0.712378 ± 13	0.9	1.47E-03
	LYS	Sep. 92	4.14	17	108	74	1	11	0	100	51	37	7	20	0.721220 ± 13	1.5	1.56E-03
	LYS	Sep. 92	4.16	26	73	59	4	14	0	90	44	49	20	17	0.727876 ± 11	2.4	1.96E-03
	LYS	Sep. 92	4.29	41	27	8	6	20	0	98	88	55	45	58	0.722708 ± 9	2.6	1.48E-03
	LYS	Sep. 92	4.44	45	50	10	7	33	0	93	181	61	37	71	0.722329 ± 8	4.3	1.49E-03
Springwaters	LYS	Sep. 92	5.01	64	119	4	8	40	0	24	24	62	28	41	0.729651 ± 9	5.3	1.51E-03
	SP	Sep. 89	6.38	93	21	< 1	21	84	73	49	29	90	n.d.	165	0.724079 ± 13	13.1	1.78E-03
	SP1 ^a	Dec. 89	5.16	77	18	< 1	25	80	12	43	64	98	3	137	0.727106 ± 9	13.6	1.95E-03
	SP1 ^a	Feb. 90	5.25	71	17	< 1	24	76	0	42	61	99	5	128	0.727513 ± 10	13.3	2.00E-03
	SP3	Dec. 90	6.20	98	26	< 1	19	93	49	47	62	94	n.d.	163	0.722911 ± 5	12.1	1.48E-03
	SP1	Sep. 91	6.17	93	18	< 1	25	77	34	48	57	91	n.d.	166	0.725525 ± 11	12.2	1.81E-03
	SP2	Sep. 91	6.41	93	20	< 1	22	78	46	46	49	88	n.d.	165	0.724771 ± 9	12.2	1.79E-03
	SP3	Sep. 91	6.34	96	24	< 1	17	79	51	43	42	87	n.d.	168	0.722823 ± 11	10.6	1.53E-03
	SP4	Sep. 91	6.25	96	25	< 1	21	83	69	47	39	88	n.d.	171	0.723228 ± 10	13.2	1.82E-03
	SP5	Sep. 91	6.28	97	29	< 1	37	107	36	69	70	117	n.d.	147	0.722486 ± 10	16.2	1.73E-03
	SP	Sep. 92	6.30	95	22	< 1	21	83	44	47	48	88	n.d.	166	0.724392 ± 6	12.3	1.69E-03
	SW	Sep. 89	6.53	91	12	< 1	28	85	67	54	8	96	n.d.	145	0.724062 ± 12	13.5	1.81E-03
	SW ^a	Dec. 89	6.54	112	97	1	41	117	60	167	49	117	n.d.	143	0.724754 ± 9	17.5	1.71E-03
	SW ^a	Dec. 89	6.27	102	51	2	31	93	33	135	28	98	n.d.	122	0.724940 ± 10	13.6	1.67E-03
	SW ^a	Feb. 90	5.60	67	31	< 1	27	85	15	53	57	95	n.d.	100	0.724937 ± 9	12.6	1.69E-03
SW ^a	Feb. 90	6.38	68	29	< 1	27	100	57	53	52	82	n.d.	102	0.722506 ± 5	13	1.48E-03	
SW	Sep. 91	6.53	93	27	< 1	29	83	71	64	13	92	n.d.	147	0.724608 ± 14	13.3	1.83E-03	
SW	Sep. 92	6.50	93	25	< 1	30	89	56	63	18	97	n.d.	144	0.724487 ± 6	13.5	1.73E-03	

^aFlood events.

continuous weathering and/or evapotranspiration processes, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of these solutions show an irregular evolution, which probably mimics variations in the soil mineralogy with depth as mentioned by Bain and Bacon (1994). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is particularly high for the samples at 10 cm and 70 cm depth. At 10 cm depth, this high value can be attributed to the high content of K and Rb rich K-feldspar and white micas since there is no biotite (Fichter, 1997). Bullen et al. (1997) have proposed that significant quantities of radiogenic Sr may be leached from K-feldspar during weathering of granitoid. However, because the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and Sr contents of the soil solutions represent only one sampling period, the variations observed need to be confirmed before they are discussed further.

The chemistry of spring water and stream water is very similar. pH is circumneutral but sulphate dominates bicarbonate (Probst et al., 1987, 1992a). In these poorly buffered freshwaters, sodium is significantly related to silica (Probst et al., 1995b) (see Table 5 and Fig. 2) and calcium is dominant as indicated by $\text{Ca}/\text{Na} = 1.75$ (expressed as a molar ratio based on net catchment mass balance discharge fluxes). The Sr isotopic ratio and Sr content of springs and streamwaters (Table 5) are representative of exceptional and average hydrological situations, which is clearly indicated by the large variations in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio from 0.7225 to 0.7275. During the autumn period (September 1992), the Sr content of springs and streamwaters is much higher than the

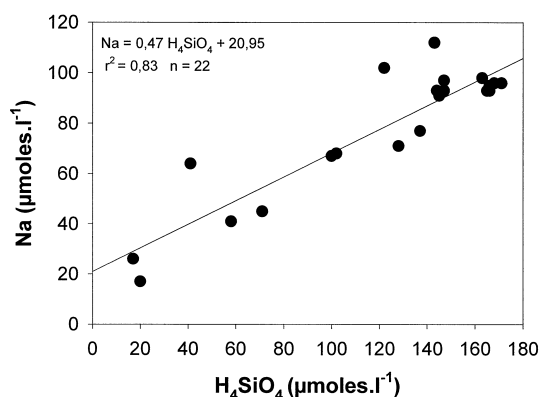


Fig. 2. Relationship between Na and H_4SiO_4 in surface waters (soil solution, stream and spring waters) from the Strengbach catchment.

Sr content of soil solutions whereas the Sr isotopic ratio is in the range of magnitude but lower than the Sr isotopic ratio of the deepest soil solution.

The increase of Sr concentration with depth in soil solution reflects the relative importance of bedrock weathering by comparison to atmospheric inputs. The high $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the deepest soil water during the low flow period (September 92), is due to the weathering of the major mineral phases of the granite that have high Sr isotopic ratios. Therefore, one would expect that during low water flow periods surface waters should have high Sr isotopic ratios. On the contrary as seen in Table 5, during high water flows the surface waters are generally more radiogenic. This is contrary to the observations of Clow et al. (1997) for a silicate catchment in the Rocky Mountains. Three possible explanations are: (i) the effective weathering end-member for the whole catchment is not so radiogenic; (ii) during high water flow periods, the contribution of radiogenic waters from the upper soil horizons is important. The stream water then reflects a three-component mixing between non-radiogenic atmospheric waters, relatively radiogenic shallow waters and significantly more radiogenic waters from upper soil horizons; (iii) Various areas in the catchment can significantly contribute to streamflow during high flow periods, as observed for the small moistened area during storm events (Idir et al., 1999). The Sr isotopic ratios of the waters draining these areas during high flow periods could be different from that measured in the studied soil although that kind of soil is well represented in the catchment.

3.4. Ca as analog of Sr

The seasonal variation in the molar Sr/Ca ratio in open field precipitation ranges from $1.4 \cdot 10^{-3}$ to $2.9 \cdot 10^{-3}$ (Table 5). The lowest ratio corresponds to a dry period whilst the highest occurs during an important winter hydrological event. In throughfall, the molar Sr/Ca ratio varies between 1 and $1.8 \cdot 10^{-3}$ that is always lower than the molar ratio in respective open field precipitation. These ratios are lower, and the range wider, than that found by Åberg et al. (1989) in a coniferous Swedish watershed (molar Sr/Ca from $1 \cdot 10^{-2}$ to $2 \cdot 10^{-2}$). The ratio be-

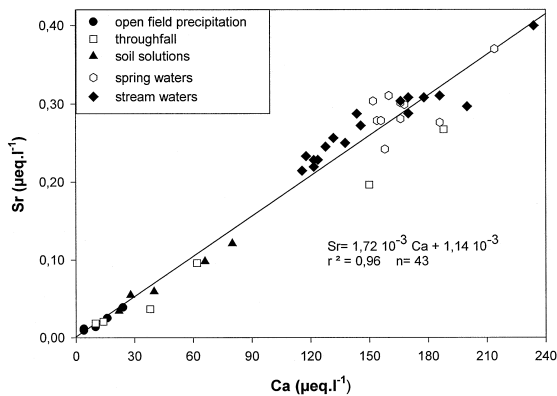


Fig. 3. Relationship between Sr and Ca in waters from the Strengbach catchment.

tween Sr in open field precipitation and Sr in throughfall follows the same pattern as the corresponding Ca ratio. This could indicate that Sr and Ca have a similar behavior with respect to atmospheric inputs and foliage leaching. The molar Sr/Ca ratio in soil solutions is relatively constant (around $1.5 \cdot 10^{-3}$) with depth in the soil profile, except in the -10 cm horizon where the Sr/Ca ratio is higher than that measured in throughfall during the same period (Sr/Ca = $0.97 \cdot 10^{-3}$). We have no data to calculate this ratio in biomass, but we suggest that spruce foliage has a lower ratio than wood, this latter being closer to soil solution as already concluded by Elias et al. (1982). In streamwater, the Sr/Ca ratio is rather constant (around $1.7-1.8 \cdot 10^{-3}$). It drops to $1.5 \cdot 10^{-3}$ during a very high flow event. The Sr/Ca ratio in spring water falls almost within the same range. During the low water flow period (September 1992), the Sr/Ca ratio was higher in spring and stream water than in soil solutions. At the catchment scale, the relationship between Sr and Ca in surface waters is linear and very significant (Fig. 3), supporting the hypothesis that Sr can be used to trace the origin of Ca.

3.5. Sr geochemical cycle during the autumn period

3.5.1. Determination of the Sr isotopic ratio of the weathering end-member

Mineral weathering rates can be determined using Sr because the Sr concentration and $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of each rock forming mineral is unique (McNutt et

al., 1990; Fritz et al., 1992; Probst et al., 1992b; Bain and Bacon, 1994, as examples), as well as their dissolution rates (Lasaga, 1984). Thus, Blum et al. (1994) have determined the relative rates of Sr dissolution from silicate minerals. They observed also variations of these rates with different times of exposure of the weathered surface.

The isotopic ratio of the weathering end-member was estimated by simulating the interaction between the minerals of the Brézouard granite and acid solutions (open field precipitation, throughfall or soil solution, Fig. 4) using the KINDIS geochemical code (Madé et al., 1990; Richard, 1993). The main benefit of this way of determining the isotopic ratio of the weathering end-member is that it combines the specific dissolution rates, the isotopic ratio and Sr content of the different rock-forming minerals. Apatite was considered in the simulations because trace minerals (such as calcite) are thought to greatly influence the weathering processes in some cases (Mast et al., 1990; Velbel, 1992; Sverdrup and Warfvinge, 1993; Clow et al., 1997). The mineral composition of the granite sample HPT was used in the simulations. It contains plagioclase and is the most able to release calcium (Tables 1 and 2). If one considered the hydrothermally altered granite (CA), the water-

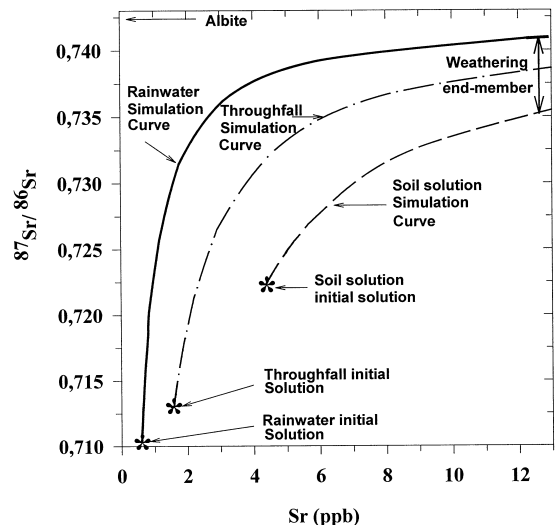


Fig. 4. $^{87}\text{Sr}/^{86}\text{Sr}$ vs. Sr simulations of the interaction between the minerals of the Brézouard granite and open field precipitation, throughfall and soil solution using the KINDIS model (Madé et al., 1990; Richard, 1993).

rock interaction would have been constrained by a very low porosity of the bedrock and by the absence of plagioclase that is not representative of the main catchment conditions.

The dissolution rate constants used are listed in Table 3, together with the surface area values. The surface area for each mineral has been calculated according to the methods of Helgeson and Murphy (1983), and Steefel and Lasaga (1994), by considering the surface of the mineral in contact with 1 kg of water in a network of cracks. According to the observations on thin sections of the granite, the mean diameter of the cracks was taken as 0.2 mm.

Field constants are not available for all the considered minerals in the literature and these values can be different from one study site to another (White et al., 1996). The natural kinetic rate constants may be two order of magnitude lower than those based on experimental rates. Thus, mixing field and experimental data can lead to an unrealistic weathering range. In the simulations, experimental dissolution constants are preferred to field values because the range of mineral weathering fits with our field observations. The Sr isotopic ratio of the weathering end-member can be accurately simulated since it depends on the relative mineral weathering rates. Nevertheless, the times calculated in the simulations can not be at all related to field reality.

For all simulations (Fig. 4), the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio increases very rapidly during the early stages of the interaction between the initial solutions (0.710, 0.712, 0.722 of, respectively, rainwater, throughfall or soil solution) and the granite. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the weathering solution reaches a plateau between 0.736 and 0.742 depending on the initial solution chosen in the simulation. At this stage, muscovite reaches saturation. Thereafter, clay mineral precipitates, i.e., the smectite considered by the model. The rapid initial increase of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio mainly results from the dissolution of radiogenic minerals (mainly K-feldspar and biotite). While muscovite is abundant, its dissolution rate and Sr content are low. Thus, despite a high Sr isotopic ratio (Fritz et al., 1992; Probst et al., 1992b; Richard, 1993), the contribution of this mica to weathering is small. With increasing dissolution, the solution reaches saturation with respect to biotite and K-feldspar (around 0.745). On a long-term, the weathering end-member is then char-

acterized mainly by the Sr isotopic value of the plagioclase ($^{87}\text{Sr}/^{86}\text{Sr} = 0.742$). The simulations indicate that the dissolution of apatite does not seem to influence to a significant degree the Sr isotopic ratio of the weathering solution. Indeed, in case of a strong influence, the simulated Sr isotopic ratio would have dropped because this mineral is non-radiogenic (Fig. 4). Then as a whole, the contribution of apatite remains small because of its very low abundance in the granite.

The simulations (Fig. 4) indicate that the isotopic ratio of the weathering end-member is in between 0.73629 (value given by the interaction of the soil solution and the granite) and 0.74203 (value of the plagioclase, which is close to the result of the rain-water/granite interaction). This way of estimating the isotopic value of the weathering end-member is preferable to using the value found in leaching experiments with strong acids (Miller et al., 1993) or to the whole bedrock value (Graustein and Armstrong, 1983). It accounts for the specific dissolution and volumetric abundance of each mineral, and for their respective isotopic ratio and Sr content in the rock. As shown in Table 4, both the Sr isotopic ratio of the leachate (reflecting the interaction between crushed granite and HCl 1N) and that of the bulk bedrock are much higher (Table 4) than the value given by the simulation. Hence, we can suppose that the isotopic ratios of the weathering end-member thus determined in literature may be very often overestimated (Clow et al., 1997).

3.5.2. Respective contribution of atmospheric and lithologic Sr in the solutions

The throughfall Sr isotopic ratio was used to represent the “atmospheric end-member” because this catchment is mainly spruce forest and then dry deposits are important (Probst et al., 1990). The KINDIS modelling yielded the “weathering end-member”. Each solution measured along the water pathway is then defined as a mixing between the atmospheric end-member and the weathering end-member. The $^{87}\text{Sr}/^{86}\text{Sr}$ value of the atmospheric end-member is 0.71299 and the $^{87}\text{Sr}/^{86}\text{Sr}$ of the weathering end-member is in the range 0.73629–0.74220.

Using Eq. (2), the results for the period of September 1992 are presented in Fig. 5. The contri-

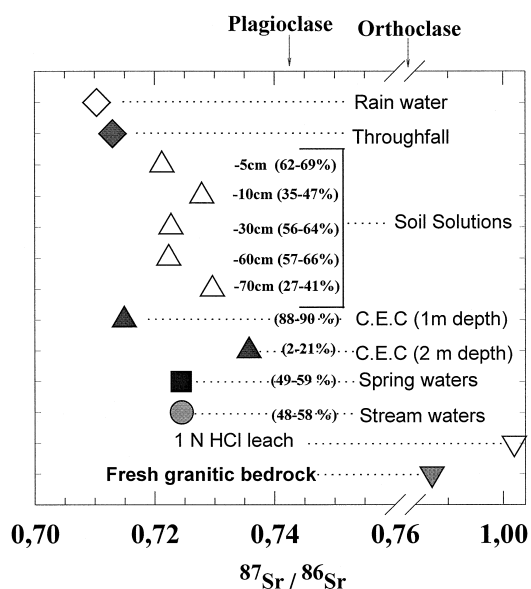


Fig. 5. Proportions of atmospheric inputs in the surface waters and in the exchangeable fraction of a soil profile from the Strengbach catchment as calculated according to $\Delta^{87}\text{Sr}$ values. $^{87}\text{Sr}/^{86}\text{Sr}$ is indicated for the granitic bedrock, the leachate, the plagioclase and the K-feldspar.

bution of the atmospheric Sr to the stream and spring water represents 49% or 58% depending on the weathering end-member value (Fig. 5). The soil solution values correspond to variable mixings, which show that between 27% to 69% of Sr originates from the atmosphere. The weathering end-member contribution is generally less than 50%, except at 10 cm depth or at 70 cm where it can reach 53–65% and 59–73%, respectively. These results differ from literature data (Miller et al., 1993) that indicate that weathering is the major component in surface waters. Nevertheless, in the study by Miller et al. (1993), the bedrock is anorthosite that should clearly be more rapidly weathered than the Brézouard granite. In addition, on the other hand the isotopic ratio of the weathering end-member chosen by Miller et al. (1993) and determined by acid leaching of the bedrock, might be too high leading to the overestimation of the weathering contribution. However, one must be aware that the Sr isotopic value of the weathering end-member can change with time of exposure. Sr released from recently exposed rock surfaces would have higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratio than Sr

from rocks exposed to longer periods of time (White et al., 1996; Bullen et al., 1997). Thus, these calculated values in soil must be considered as indicative.

In the present study, the cation exchange pool was not considered an end-member. Rather it is assumed to reflect a mixing between cations of atmospheric and lithologic origin. We measured the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio and the amount of exchangeable Sr to identify the proportions of atmospheric and of lithologic inputs using Eqs. (2) and (3). This was done in the soil and the saprolite where the amount of exchangeable Ca in the fine fraction (< 2 mm) was the most important in comparison to the other profiles of the catchment (El Gh'mari, 1995; profile VC, Table 1). In the profile VC, the Ca content increases in the deeper saprolite. The results (Table 6) indicate that the exchangeable Sr at 1-m depth is less radiogenic and is very close to the value found for throughfall. In contrast, at 2 m depth, the Sr isotopic ratio of the solution is closer to the value of the plagioclase and closer to the value given by the simulation using the KINDIS model. Thus, at 1-m depth, the atmospheric contribution represents 90% of the exchangeable Sr whereas at 2 m depth, only 2% to 21% would be of atmospheric origin (Fig. 5).

3.6. Sr and Ca catchment budget

The catchment hydrochemical budget (inputs minus outputs) represents the net contribution of both chemical weathering and soil exchangeable cation depletion. The Sr mass balance as an analogue of Ca can be tentatively described.

The fluxes are calculated from the Sr content in waters (Table 5) and the water fluxes as described in Probst et al. (1992a), (1995a). Contrary to Ca, biological uptake of Sr can not be calculated because there is no data. No changes occurred concerning

Table 6
 $^{87}\text{Sr}/^{86}\text{Sr}$ and concentration of exchangeable Sr in the saprolite fine fraction from the VS profile

Depth (m)	$^{87}\text{Sr}/^{86}\text{Sr}$	Sr (meq/100g)	Sr/Ca
1	0.714930 ± 7	0.398×10^{-3}	1.04×10^{-3}
2	0.735765 ± 16	0.232×10^{-3}	1.30×10^{-4}

forest management and the biomass uptake is assumed to be constant. Because the contribution of Sr dry deposition could not be accurately assessed, throughfall has been chosen as almost representative of catchment inputs. As far as we know, the net atmospheric inputs of Ca represent 85 % of throughfall inputs (Probst et al., 1992a). Mass balance (Fig. 6) indicates that the output of Sr represents more than four times the inputs. Therefore, as already stated for Ca the discrepancy between inputs and outputs indicates that the net losses of Sr are from exchange and weathering processes in soils and saprolite. The depletion of the exchangeable pool has been related to the neutralization of acid atmospheric inputs (Probst et al., 1992a). Ca mass balance as calculated by Probst et al. (1995b) indicated $32 \text{ kg ha}^{-1} \text{ a}^{-1}$ net losses of dissolved Ca. Strontium isotopic determinations (mean percentages, Fig. 5) can be used to partition the Ca budget and to determine Ca from atmospheric and mineral weathering inputs. The estimations (Fig. 5) indicate that about 50% of the Sr leached out of the catchment is from silicate weathering. Thus, as shown on Fig. 6, weathering supplies about $15 \text{ kg ha}^{-1} \text{ a}^{-1}$ Ca. The remainder is from atmospheric inputs that would be provided mainly by the way of exchange processes in the upper soil profile (89% as a mean). An important part of the Sr outputs is then likely composed of exchangeable strontium but partitioning

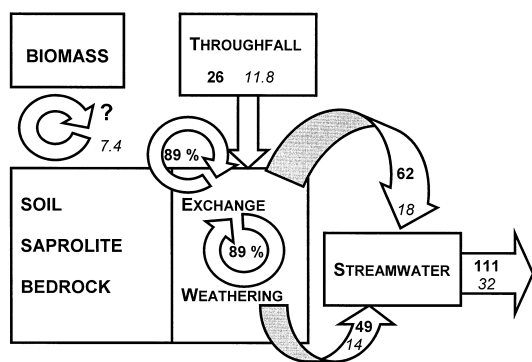


Fig. 6. Hydrochemical budget for Sr ($\text{g ha}^{-1} \text{ a}^{-1}$, bold) and Ca ($\text{kg ha}^{-1} \text{ a}^{-1}$, italic) in the Strengbach catchment according to Probst et al. (1995a) and to Sr isotopes (present study). The percentages represent the proportions of weathering inputs to the exchangeable fraction in the deep saprolite and of atmospheric inputs to the exchange fraction in the upper soil horizons, respectively.

atmospheric and weathering inputs of exchangeable Ca at the catchment scale still needs to be performed. Apatite could supply part of the exchangeable Ca where plagioclase is absent.

These values are consistent and greater in amount than Ca weathering contribution calculated using PROFILE simulations (Sverdrup and Warfvinge, 1993) or isovolumetric balances. Both indicate less than $5 \text{ kg ha}^{-1} \text{ a}^{-1}$ of Ca (El Gh'mari, 1995) at the catchment scale, and less than $1 \text{ kg ha}^{-1} \text{ a}^{-1}$ at the stand scale in the studied soil (Dambrine et al., 1995b). However, it goes against some conventional wisdom that Ca is essentially a weathering production in silicate catchments. The granite considered in the simulations is the most Ca-enriched, and then these results are probably maximum values for Ca weathering in this area.

The most important consequence of this result is that this catchment is not in a steady state at least for Ca and Sr. The neutralization of acid atmospheric inputs leads to the strong depletion of the exchangeable pool and explains the base cation losses ($2.8 \text{ keq ha}^{-1} \text{ a}^{-1}$, Probst et al., 1992a,b, 1995b). At present, the proton input to the ecosystem is less important related to the decrease in SO_2 emission, however, it is also linked to a decrease of base cation (and more particularly calcium) input (Probst et al., 1995a). Given that atmospheric inputs supply an important part of exchangeable calcium, such an ecosystem with a very low buffering capacity is particularly vulnerable with regard to forest nutrition and surface water quality.

4. Conclusions

Previous investigations on hydrochemical budgets have suggested that high losses of cations (particularly Ca) out of the granitic Strengbach catchment result from a combination of exchange and weathering processes to neutralize acid atmospheric inputs. The present paper aimed to partitioning the origin of Ca into atmospheric and weathering sources using Sr as an analog.

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and Sr contents measured in open field precipitation, throughfall, soil solutions, surface waters, bedrock and rock forming minerals suggest that Sr in surface waters results from the mixing between an atmospheric source and weather-

ing. Soil solutions, spring and streamwaters are characterized by a Sr isotopic ratio intermediate between the Sr ratios of atmospheric precipitation and bedrock. Ca and Sr behave similarly at the catchment scale.

The presence of low Ca content plagioclase in the granite and of a high Ca/Na ratio in surface waters necessitated careful investigation of the weathering processes and in particular with regard to the trace minerals. STEM investigations indicate that albite and biotite are intensively weathered contrary to K-feldspar, muscovite and quartz. Apatite is also partially weathered. No trace of calcite could be detected.

To partition sources of Ca, the difficulty comes from the determination of the reactive end-member. The weathering end-member was determined using Sr isotopes in a kinetic geochemical model (KINDIS Code) that allows to take into account the specific mineral weathering rates of each rock forming mineral (major and trace). In the simulations, K-feldspar and biotite weathering influences significantly the Sr isotopic ratio of the weathering solution on a short time scale. When the time of exposure between the minerals and the solution increases, the isotopic composition of the weathering solution steadies to the value of Na-plagioclase. The importance of plagioclase weathering in the Strengbach catchment can be confirmed by the significant positive relationship between sodium and silica in surface waters. In contrast, apatite weathering was found to play a minor role on the isotopic and chemical composition of the simulated weathering solution.

The mixing equations between atmospheric and weathering sources show that about 50% of the Sr is atmospherically derived at the catchment scale. The exception is in the surface horizons of the soils, where radiogenic minerals are concentrated and where organic acids can enhance the weathering processes as well as in the deep soil profiles where plagioclase is still present. The $^{87}\text{Sr}/^{86}\text{Sr}$ of the exchangeable Sr at 1-m depth in a soil profile of the catchment approximates that of the throughfall. At 2-m depth, this ratio is close to the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the plagioclase, i.e., to the weathering end-member determined by the KINDIS model.

Weathering inputs provide about $15 \text{ kg ha}^{-1} \text{ a}^{-1}$, i.e., 50% of the Ca released out of the catchment.

Hence, a major part of the losses of Ca detected in catchment budgets and previously interpreted to result from depletion of the exchange pool to neutralize acidic inputs, is atmospherically derived. Nevertheless, this atmospheric contribution mainly concerns the upper soil profile. A contribution of Ca from apatite weathering in the soils where plagioclase are absent is however possible.

These results go against some conventional wisdom that exchangeable Ca is assumed to originate essentially from weathering. This study aims to put emphasize on the importance of determining the accurate weathering end-member by taking into account the relative mineral weathering rates; it should however be stressed that there are still major problems in the estimation of natural reactive surface areas. Also, further investigations are needed of natural kinetic rate constants of the minerals, as well as changes in strontium isotopic ratio in minerals all as a function of weathering, exchange processes on non-stable secondary products, and about the potential non-stoichiometric release of strontium from complex silicate phases. These geochemical researches must be undertaken in addition to improvement in hydrochemical modelling to take into account the recharge of drainage solutions by macropore flow in open systems. Finally, the relative importance of the different contributive areas in catchments particularly during periods of high water flow needs further investigations.

Despite some uncertainties, our results can allow to better understand the base cation sources in similar areas that are base cation limited. The acid atmospheric inputs provoke the depletion of exchangeable pool and the availability of these forest nutrients might be strongly constrained, and surface waters consequently acidified. Detailed investigations are recommended to determine the relative importance of weathering and exchangeable pool to Ca budgets in such catchments where trace minerals can only partially explain the high Ca/Na ratio in surface waters.

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