Acidification processes and soil leaching influenced by agricultural practices revealed by strontium isotopic ratios

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Abstract

In natural river systems, the chemical and isotopic composition of stream- and ground waters are mainly controlled by the geology and water–rock interactions. The leaching of major cations from soils has been recognized as a possible consequence of acidic deposition from atmosphere for over 30 years. Moreover, in agricultural areas, the application of physiological acid fertilizers and nitrogen fertilizers in the ammonia form may enhance the cation leaching through the soil profile into ground- and surface waters. This origin of leached cations has been studied on two small and adjacent agricultural catchments in Brittany, western France. The study catchments are drained by two first-order streams, and mainly covered with cambisoils, issued from the alteration and weathering of a granodiorite basement. Precipitations, soil water- and NH_4 acetate-leachates, separated minerals, and stream waters have been investigated. Chemical element ratios, such as Ba/Sr, Na/Sr and Ca/Sr ratios, as well as Sr isotopic ratios are used to constrain the relative contribution from potential sources of stream water elements.

Based on Sr isotopic ratio and element concentration, soil water- and NH_4 acetate leaching indicates (1) a dominant manure/slurry contribution in the top soil, representing a cation concentrated pool, with low $^{87}Sr/^{86}Sr$ ratios; (2) in subsoils, mineral dissolution is enhanced by fertilizer application, becoming the unique source of cations in the saprolite. The relatively high weathering rates encountered implies significant sources of cations which are not accessory minerals, but rather plagioclase and biotite dissolution.

Stream water has a very different isotopic and chemical composition compared to soil water leaching suggesting that stream water chemistry is dominated by elements issued from mineral and rock weathering. Agriculture, by applications of chemical and organic fertilizers, can influence the export of major base cations, such as Na^+. Plagioclase dissolution, rather than anthropogenically controlled soil water, seems to be the dominant source of Na^+ in streams. However, Ca^{2+} in streams is mostly derived from slurries and manures deposited on top soils, and transferred into the soil ion-exchange pool and stream waters. Less than 10% of Na^+, 5–40% of Sr^{2+} and 20–100% of Ca^{2+} found in streams can be directly derived from the application of organic fertilizers.

1. INTRODUCTION

Acid deposition has been an important and increasing cause of soil acidification in Europe since the industrial revolution and, recently with the development of intensive

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livestock production and the resultant large emissions of ammonia. The acidification induced by acidic compounds produced by industrial activities has been widely investigated on natural and forested silicate catchments (Armbruster et al., 2003; Fernandez, 1985; Fernandez et al., 2003; Likens et al., 1998; Stoddard et al., 1999). Ammonium-based fertilizers have dramatic consequences on metal mobilization and plant uptake (Goulding and Blake, 1998) and represent the single most significant cause of soil acidification on most agricultural land (Ganev, 1992; Graham et al., 2002). The acidification phenomenon is not only localized on the topsoil, but propagates into the subsoil, which becomes more acid than the topsoil (Goulding and Annis, 1998). Soil acidification causes cation depletion and possible accelerated leaching of base cations from soils, thus increasing major base-cation (Ca^{2+}, Mg^{2+}, Na^+, K^+) concentrations and fluxes in soil solutions and surface waters (Driscoll et al., 2001; Johnson et al., 1991). This is attributable to ion-exchange reactions in the soil, which result in the loss of mineral cations from the soil by leaching while H^+ accumulates in the exchange complex (Barak et al., 1997; Graham et al., 2002; Sverdrup et al., 1994).

In silicate bedrock, the major sources of base cations and the most abundant minerals are plagioclase, potassic feldspar, biotite and muscovite (Goulding and Annis, 1998; Lasaga et al., 1994; Probst et al., 2000; Sverdrup and Warfvinge, 1995). Trace minerals such as apatite and calcite, have been identified as potential major sources of Ca in ground- and stream waters, in addition to Ca–plagioclase weathering (Aubert et al., 2002; Blum et al., 2002; Clow et al., 1997; Fernandez et al., 2003; Oliva et al., 2004; Sverdrup and Warfvinge, 1995; White et al., 1999). In soil chemistry, the major cation release, the Al production rate and the neutralization of acidity, all depend on the chemical weathering of soil minerals (Sverdrup, 1996). The soil zone, where the weathering is intense, has traditionally been considered as dominant in the weathering process and the export of solutes from catchments (Shand et al., 2007). But the export of solutes may be derived from less intense weathering of large volumes of rocks in the subsurface environment below the soil. The respective contribution of these two main zones is variable and is not clearly defined. However, some authors do not consider that soil acidification has an impact on the mineral weathering rates (Fernandez et al., 2003; Gbondo-Tugbawa and Driscoll, 2003; Sverdrup et al., 1995). The acidification process is rather associated with leaching of soil base cations from the exchange complex and the mobilization of toxic forms of aluminium, leading to a decrease of the soil base saturation (Dahlgren et al., 1990; Wright et al., 1988).

The strontium isotopic composition ($^{87}Sr/^{86}Sr$) has been extensively used in order to (i) determine the sources of Ca in stream- and ground waters in weathered environments (i.e. (Åberg and Jacks, 1987; Clow et al., 1997; Dupré et al., 1996; Gaillardet et al., 2003; Miller et al., 1993) and (ii) to investigate water–rock interactions during weathering processes and solute transport (i.e. (Bullen et al., 1996; Collerson et al., 1988; Franklyn et al., 1991; Johnson and Depaolo, 1997; Katz and Bullen, 1996; Neumann and Dreiss, 1995). More recently, several studies

have shown contamination of stream- and ground waters by agricultural activities based on the complex chemical and isotopic signatures of waters, soils, rocks and fertilizers (Böhlke and Horan, 2000; Nakano et al., 2005; Vitòria et al., 2004; Widory et al., 2004). Sr isotopic composition and concentration in runoff, soils, waters and biomass are primarily dependent on mixing between atmospheric inputs and mineral weathering sources, but also human-influenced sources, such as fertilizers. Strontium of all these sources may be included in the cation exchange pool and further interact with catchment soil solutions (Åberg et al., 1989; Bullen et al., 1996; Katz and Bullen, 1996). The $^{87}Sr/^{86}Sr$ ratio in waters will therefore be a function of the weatherable and exchangeable Sr signatures as well as hydrological processes (Åberg et al., 1989). It may be a powerful tool to discriminate between mineral and agricultural sources in catchments influenced by anthropogenic activities.

Brittany, western France, is an interesting place for studying the impact of agriculture on soil and water chemistry, quality and stability, because of the development of intensive agriculture since the late 1960's. This study has been conducted on a field area that has been previously studied in order to determine the variability of the transfer of nitrates from soil to stream waters through ground waters and to determine the respective hydrobiogeochemical compartments of the catchment (Legout et al., 2007, 2005; Martin et al., 2004; Ruiz et al., 2002a,b). A previous study focused on the determination of chemical weathering rates based on atmospheric inputs, mineral weathering and agricultural contributions (Pierson-Wickmann et al., in press). It indicated a direct relationship between high agricultural pressure and enhanced chemical weathering rates, which were much higher than in any other small granitic catchments. In this study, the Sr isotopic composition and major cation concentrations have been determined in the same two small granitic catchments, Kerbernez and Kerrien, located in western Brittany in order to determine the mineralogical sources of the high cation loads, induced by agricultural activities.

2. GEOLOGICAL SETTING AND HYDROLOGICAL CONTEXT

The Kerbernez and Kerrien catchments are located in south-western Brittany, France (47°57′ N–4°8′ W), roughly 550 km west of Paris (Fig. 1). Kerrien (0.095 km^2) and Kerbernez (0.120 km^2) are two adjacent first-order catchments, which consequently share the same lithological and climatic characteristics. The different catchment streams join a river 10 km before it flows into the Atlantic Ocean. The climate is oceanic. Mean annual precipitation and potential evapo-transpiration (calculated on the last decade) are 1161 and 616 mm, respectively (Legout et al., 2005; Ruiz et al., 2002a). The rainiest seasons are autumn and winter. Mean monthly temperatures reach a minimum in January (6.1 °C) and a maximum in July (17.6 °C) (Ruiz et al., 2002a).

The bedrock belongs to the Paleozoic leucogranodiorite of Plomelin (Béchennec et al., 1999).The granite is fractured and fissured, and is overlaid by weathered material, with a
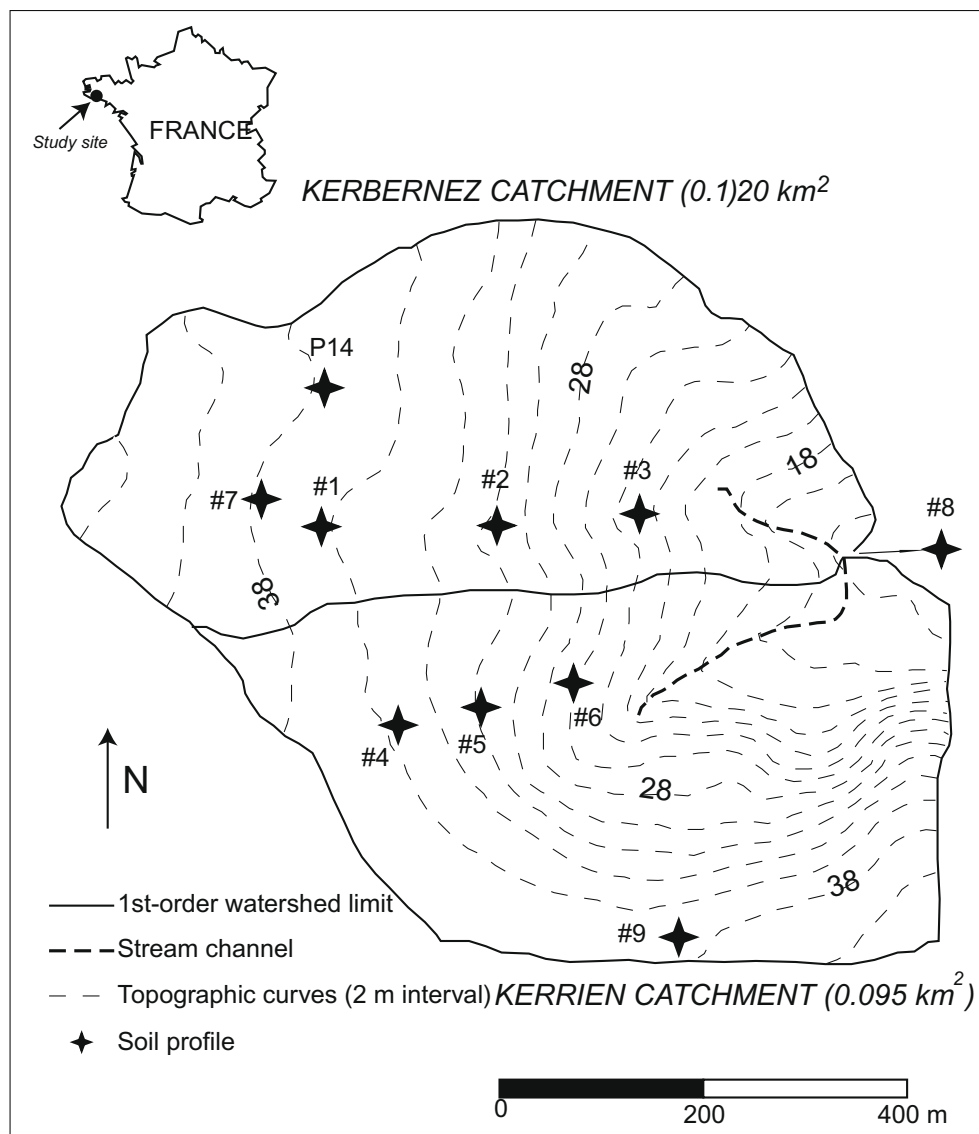
Fig. 1. Location map of Kerbernez and Kerrien catchments (Brittany, northwestern France), showing the different sampling sites (soils and streams). Stars represent soil profiles.

mean thickness of about 20 m and is slightly thicker in Kerbernez than in Kerrien (Legchenko et al., 2004). The principal minerals in the granodiorite are quartz, plagioclase (albite-oligoclase), K-Feldspar, muscovite and biotite. Secondary minerals, such as clays (i.e. kaolinite and illite) are also present in the granitic arena. After Béchennec et al. (1999), some accessory minerals include apatite, garnet and zircon. However, despite previous apatite observation (Béchennec et al., 1999), no apatite has been observed in our rock and soil samples.

Soils are mainly brown sandy loam (distric cambisol, FAO classification) developed on a granitic arena. Soil profiles were dug down to C or B/C horizon, finding the weathered granite (C-horizon) between 0.7 and 1.2 m below the soil surface (Legout et al., 2005). The C-contains sand (63%), silt (26%) and clay particles (11%). The B-horizon, a cambic horizon (BW), between 40 and 65 cm depth,

displays low organic carbon content (0.5 wt% C) and a higher content of silt particles (~64%) relative to sand (19%) and clays (17%). The upper horizons from 10 to 40 cm depth, corresponding to mineral horizons altered by human-related activities (Ap), are formed by micaceous sand and silt particles and display a higher organic carbon content (2.8 wt% C). The soil bulk density ranges from 1.3–1.5 g cm^{-3} (A and B horizons) to 1.7 g cm^{-3} (C-horizon). Soils are well drained except in the relatively narrow bottomlands where hydromorphic soils are found. Land use is mainly agricultural (77%). Most arable fields (43% of cultivated surface) grow maize and cereals alternately. They are farmed intensively, including importation of pig slurry and cattle manure: an average of 1300 kg/ha of ammonitrates, 40 m^3/ha of pig slurries and 20 kg/ha of manures are applied over a 10 years period (Appendix A). A large part of the grasslands (40% of the cultivated surface) are

grazed intensively by dairy cows (Ruiz et al., 2002a). Lime (CaOMg and local organogenic calcareous sands called Trez) was applied in 2002 and 2005.

An automatic weather station, located 500 m away from the catchments, recorded hourly rainfall and the different parameters required to calculate potential evapo-transpiration by the Penman formula. Catchment outlets were equipped with V-notch gauging stations for weekly discharge measurements. The monitoring period (studied in this paper) comprised four hydrological years, from 01/2001 to 12/2004, including two very contrasting years (2000–2001 and 2001–2002). The first year (from October 2000 to September 2001) was very wet, with a total precipitation of 1760 mm and a potential evapo-transpiration of 690 mm. The second year (from October 2001 to September 2002) was much drier, with a total precipitation of 986 mm and a potential evapo-transpiration of 697 mm (Martin et al., 2004). The catchments are characterized by the presence of shallow ground water developed perennially in the weathered granitic material, with the water table depth ranging from 2 to 8 m below the soil surface throughout the hydrological cycle.

3. SAMPLING AND ANALYTICAL PROCEDURES

3.1. Sampling and analyses

Stream- and rain water samples were collected monthly for the two first years, and then every 3 months from January 2001 to December 2004. Water samples were filtered in the field with 0.20 μm nylon Millipore filters and then stored in HNO_3 acidified and non-acidified vials, for cation and anion analyses, respectively, in the dark at less than 4 °C before analysis. All the analyses have been carried out in the Caren-Geosciences analytical and isotopic laboratories. Major and trace cation concentrations were determined using an Agilent Technologies™ HP4500 ICP-MS instrument (Bouhnik-Le Coz et al., 2001; Yeghicheyan et al., 2001). Experimental protocol of sampling, storage, and analysis has been previously described in Dia et al. (2000). Typical uncertainties including all error sources are <5% for all trace elements, whereas for major anions, the uncertainty lies between 2 and 5%, depending on the concentration levels. Dissolved organic carbon (DOC) concentrations were determined using a Shimadzu 5000 TOC analyzer with an accuracy estimated at ±5%.

Biotite, muscovite, plagioclase and K-Feldspar have been separated from the Plomelin leucogranodiorite using dense liquids and a Frantz isodynamic magnetic separator, and by handpicking under the binocular microscope. A bulk digestion, using HF and HNO_3, has been performed on each mineral fraction in order to determine their geochemical composition. The international standards SLRS-4, and CRPG Biotite Mica-Fe standard, ANRT K-Feldspar FK-N (Govindaraju, 1984, 1995) were used to check the validity and reproducibility of the results.

Soil samples were collected upland to downland in both Kerrien and Kerbernez catchments (Fig. 1). The soils were air-dried and sieved through a 2-mm sieve. Soil pH was measured, using 10 g of soil, after extraction in 20 mL of

0.01 M $CaCl_2$ (pH_{Ca}) by shaking for 30 min. Some soils were analyzed by bulk digestion, NH_4 acetate leaching and water leaching in order to determine the whole pool of cations in soils, the cations available for plants related to ion-exchange complex of the soil (NH_4 acetate leaching, NH_4Ac), and the cations leachable with water flowing through the soil, respectively. The maximum depth of soil samples in the recharge zone is 70 and 110 cm for Kerrien (#9) and Kerbernez (#7), respectively, corresponding to the C-horizon depth. Downland soils (#8) have been sampled at 20, 60, 90 and 120 cm depth.

The NH_4 acetate leaching procedure (NH_4Ac-leaching) consists of a mixing of 10 g of soil sample 100 mL of 1 M NH_4 acetate (pH = 7), then shaken for 30 min and centrifuged at 2900 rpm. The supernatant was filtered at 0.2 μm and then dried. The whole procedure was repeated twice, adding 40 mL NH_4 acetate each time. For water leaching procedure (H_2O-leaching), 10 g of soil sample were leached with 50 mL of deionized water (DI-H_2O), shaken for 20 h and then centrifuged at 2500 rpm. The supernatant solution has been filtered at 0.2 μm, and then acidified with HNO_3. All the final solutions were then analyzed by ICP-MS.

The Sr isotopic composition has been determined on stream waters, soil H_2O- and NH_4Ac-leaches of soils, bulk digest separated minerals and bulk digest soils. The solid material or solution was mineralized with an ultrapure HNO_3–HF mixture and HCl in Teflon vials, until the solution was perfectly clean. Strontium was isolated from the residue using a cation exchange column Bio-Rad Dowex® AG50-WX8, 200–400 mesh, resins for soil leachates and separated minerals, or Sr-SPEC resin (Eichrom® Industries) for rain and stream water samples, and 2 M HCl as the eluant. Strontium isotope ratios were measured using a Finnigan® MAT 262 thermal ionization mass spectrometer fitted with multicollector array consisting of five Faraday cups. Corrections for mass fractionation were made by normalizing $^{86}Sr/^{88}Sr$ to 0.1194. Standard reference material NBS 987 run over the period of analyses gave an average $^{87}Sr/^{86}Sr$ ratio of 0.710258 ± 0.00008 (2σ standard deviations, $n = 15$).

3.2. Calculations

The relative contribution of Sr from soil mineral weathering and fertilizers to waters is calculated using two mass balance equations, that must be satisfied (Eqs. (1) and (2)).

$$[Sr]_M = f \cdot [Sr]_A + (1 - f) \cdot [Sr]_B \qquad (1)$$

$$[Sr]_M \cdot (^{87}Sr/^{86}Sr)_M = f \cdot [Sr]_A \cdot (^{87}Sr/^{86}Sr)_A + (1 - f)$$
$$\cdot [Sr]_B \cdot (^{87}Sr/^{86}Sr)_B \qquad (2)$$

where [Sr] and $^{87}Sr/^{86}Sr$ represent the concentration of Sr and Sr isotopic composition, respectively, in each end-member and the mixture. A and B refer to two end-members, being separated minerals or animal manures and M refers to the 'water' mixture component, being waters, H_2O-leachates or NH_4Ac-leachates, and f represents the relative contribution of end-member A.

The different curves are calculated for the provisional weathering of end-members as well as for a range of $^{87}Sr/^{86}Sr$

ratios of soil leachates. On this diagram, various mixtures of two end-members define a hyperbola. The curvature of the mixing lines depends on the differences in Sr isotopic and Ca/Sr ratios of the end-members.

4. RESULTS

4.1. Solid phases: Soil profiles and separated minerals

Table 1 summarizes geochemical data obtained on bulk digestion of separated minerals from Plomelin leucogranodiorite, soil profile (P14) and manures. The H_2O-leaching and NH_4Ac-leaching are presented in Tables 2 and 3 for soil profiles. The combined information provided by the chemical and isotopic data, as well as a comparison with likely source rocks and separated minerals, allows the relative effects of alteration to be constrained.

4.1.1. Separated minerals

The separated minerals from the Plomelin granodiorite (Table 1) present different Sr isotopic ratios, ranging from 0.708 to 0.727 for most minerals and 0.999 for muscovite. The relatively low $^{87}Sr/^{86}Sr$ ratio of the Na–plagioclase is consistent with the relatively low Rb content (17 ppm). However, because of the difficulty of collecting enough material, the Sr isotopic composition of the biotite was not determined, but is presumably much more radiogenic than any other minerals, even muscovite, because of its high K concentration. For the following discussion, the $^{87}Sr/^{86}Sr$ ratio of the biotite is estimated at 3.21, assuming that the minerals are contemporaneous and considering the Sr concentrations of separated minerals and their $^{87}Sr/^{86}Sr$ ratios and the biotite Sr concentrations (plagioclase, K-feldspar and muscovite correlation presents a R^2 coefficient of 0.999). The $^{87}Sr/^{86}Sr$ of plagioclase and K-Feldspar bracket that of stream waters (Tables 4 and 5) and most of soil horizons (Tables 1–3), with a value of 0.7084 for the Na–plagioclase and 0.7186 for the K-feldspar.

4.1.2. Soil profiles

4.1.2.1. Bulk digest soils.
Taking into account the pH_{Ca} in all samples (Table 3), Kerbernez soils are considered as strongly acid soils, while Kerrien soils are slightly acid soils. Variations of geochemical parameters with soil depth are shown in Fig. 2, summarizing the H_2O-leaching and bulk digest analyses.

In bulk digest soils (Table 1), the concentrations of Sr, Rb, Na, Ca, Mg and K remain fairly constant in the three upper horizons, between 10 and 50 cm. However, in the two deeper horizons (between 75 and 105 cm), these concentrations increase by 30–100%, indicating a more significant pool of mineral cations in the deeper less weathered soil. The higher K concentrations in the bulk digest of the deeper horizons suggest a remaining source of K in these horizons. However, Ba does not display any variation in concentration with increasing depth in the whole soil profile as well as Ca/Sr ratio which slightly varies from 34 to 44. The bulk Sr isotopic composition is relatively radiogenic, ranging from 0.72351 to 0.72746.

In order to better determine the influence of K-host minerals versus the biotite or muscovite high $^{87}Sr/^{86}Sr$ minerals, the $^{87}Sr/^{86}Sr$ versus the reciprocal Sr concentration is plotted in Fig. 3. A significant correlation ($R^2 = 0.68$ for all bulk digest soils analyzed; $R^2 = 0.98$ for all soils except the alterite at 105 cm depth) is produced for the bulk digest soils, indicating a mixture between two end-members. One of the end-members can be interpreted as including K-feldspar since it is almost directly included in the correlation curve (Fig. 4). The other end-member is unknown. It could correspond to another mixed end-member between a highly radiogenic biotite ($\sim$24%) and hog manure ($\sim$76%) (Table 6).

4.1.2.2. Water soluble cations in soils.
For the soil H_2O-leachates (Table 2, Fig. 2), the different cation concentrations and Sr isotopic composition are more variable with soil depth than for bulk digest soils. Sr and Ca concentrations display an obvious monotonous, decrease with increasing soil depth. This decrease in Sr and Ca concentrations does not mimic that of bulk digest soil, with a Ca/Sr

Table 1
Bulk digestion of soil, separated minerals and manures: Major and trace element concentrations (mg/kg), Sr isotopic composition, and element ratios.

	Sample	Depth (cm)	Na	Ca	Mg	K	Ba	Fe	Sr	Rb	Rb/Sr	Ba/Sr	Ca/Sr	Ca/Na	$^{87}Sr/^{86}Sr$
Mineral	Muscovite	–	4733	35	5144	n.d.	364	11747	19.4	442	22.7	18.7	1.8	0.01	0.98892
	Biotite	–	652	2124	47422	87327	828	20240	2.2	1036	463	370	949	3.26	n.d.
	K-feldspar	–	29741	7032	96	n.d.	1162	1084	324	279	0.9	3.6	21.6	0.24	0.71864
	Plagioclase	–	89763	33600	251	5514	70	4873	489	17.1	0.03	0.14	68.7	0.37	0.70845
Bulk digest soil	P14	10	12027	4356	2503	27360	342	19705	101	173	1.7	3.4	43.0	0.36	0.72592
		20	11455	3698	2369	28797	358	17046	99	180	1.8	3.6	37.2	0.32	0.72717
		50	11662	3230	2751	26905	340	19932	95	171	1.8	3.6	33.9	0.28	0.72746
		75	16955	4856	4867	35568	355	30043	128	199	1.5	2.8	37.8	0.29	0.72351
		105	20772	6385	5001	39110	360	21113	144	220	1.5	2.5	44.4	0.31	0.72611
Manure	S4LB a	–	2724	42584	11271	12164	39.6	2340	63.6	10.0	0.2	0.6	670	0.001	0.70939
	S4LB b	–	2786.	43022	11519	12359	39.3	2362	64.0	10.2	0.2	0.6	672	0.001	0.70939
	S1LB	–	3531	35884	14206	15156	35.8	2346	73.6	13.1	0.2	0.5	488	0.001	0.70962

n.d.: not determined. Concentrations determined on dry matter.

Table 2
Major and trace element concentrations (µg/g), Sr isotopic composition, and element ratios of soil H$_2$O-leachates of Kerrien and Kerbernez catchment soils.

Catchment	Horizon	Soil depth (cm)	Na	Ca	Mg	K	Ba	Fe	Sr	Rb	Rb/Sr	Ba/Sr	Ca/Sr	Ca/Na	^{87}Sr/^{86}Sr
Kerrien Soil #9	OA	20	2936	6756	943	4061	3.4	882	36.4	8.4	0.2	0.1	186	2.30	0.70963
	A	60	3799	4035	1063	3576	17.1	6470	27.8	21.2	0.8	0.6	145	1.06	0.71333
	B	70	3888	1909	310	2465	5.0	1250	21.2	8.5	0.4	0.2	90	0.49	0.71181
Kerbernez Soil #7	OA	20	2183	5382	1252	7428	5.7	2125	22.1	12.8	0.6	0.3	243	2.46	0.71022
	A	70	1453	2425	661	6342	1.9	344	9.8	5.2	0.5	0.2	248	1.67	0.71047
	B	110	1544	1002	995	8447	20.4	7471	7.4	22.0	3.0	2.8	135	0.65	0.71841
Soil #8	OA	20	2897	7274	4040	13075	123.5	32771	49.4	135.2	2.7	2.5	147	2.51	0.72213
	A	60	2573	3787	819	1849	12.1	2266	18.2	9.7	0.5	0.7	208	1.47	0.71254
	B	90	3883	2260	767	291	2.8	415	14.0	1.4	0.1	0.2	162	0.58	0.71160
	C	120	2615	201	176	1431	6.4	477	2.4	4.7	2.0	2.7	85	0.08	0.72615
Soil P14	OA	10	2673	4805	2160	19158	17.3	8423	26.8	33.6	1.2	0.6	179	1.80	0.71181
	A	20	2954	6710	2495	18313	27.4	12409	37.4	47.3	1.2	0.7	179	2.27	0.71214
	AB	50	2375	3843	1841	9835	24.8	16363	25.4	41.7	1.6	1.0	151	1.62	0.71391
	B	75	1560	1702	513	6024	4.1	2248	12.1	9.9	0.8	0.3	141	1.09	0.70949
	C	105	5293	313	258	6075	4.9	1472	3.3	12.2	3.7	1.4	95	0.06	0.72981

ratio much higher and more variable in H$_2$O-leachates, ranging from 85 to 248. The high Ca/Sr ratio in H$_2$O-leachates relative to bulk digest soils is mostly explained by a higher Sr loss than Ca loss, varying with depth. Indeed, the upper horizons release much more Sr than the deeper and less altered horizons (C-horizon or granitic arena), by a factor 2–20. A similar behaviour is observed for Ca, with a larger release factor range from 4 to 36 which explains the very high Ca/Sr in the top soil. In general, the higher cation losses are encountered in the soil sampled at the catchment outlet (#8). Potassium is the main cation released from soil during H$_2$O-leaching, representing 30–70% of the cations. However, K decreases dramatically in the A and B horizons, becoming unchanged in the deeper horizons, under the alteration front.

In general, the solubility and dissolution rate of plagioclase makes it a major contributor of Na$^+$ and a major source of Ca^{2+} ions to weathering solutions. It induces a Ca/Na ratio close to that of congruent dissolution of plagioclase in soil solutions and river waters. The Ca/Na ratio in H$_2$O-leachates and stream waters of both Kerbernez and Kerrien is larger than the ratio in the plagioclase, indicating either the presence of an additional source of Ca^{2+} or a sink of Na$^+$. The progressive decrease with depth in Sr^{2+} and Ca^{2+} contents in H$_2$O-leaching experiments (Fig. 2) suggests a more significant labile stock of Ca^{2+} and Sr^{2+} in the surface soil horizons.

The variation of ^{87}Sr/^{86}Sr ratios in leachates is neither monotonous, nor correlated to Sr concentration decrease with increasing soil depth. In the upper three horizons

Table 3
Major and trace element concentrations (µg/L), pH$_{Ca}$, Sr isotopic composition, and element ratios of NH$_4$Ac-leaching solution of Kerrien and Kerbernez catchments.

Catchment	Horizon	pH$_{Ca}$	Na	Ca	Mg	K	Ba	Sr	Rb	Rb/Sr	Ba/Sr	Ca/Sr	Ca/Na	^{87}Sr/^{86}Sr
Kerbernez	#1 – O	4.77	14.9	1000	110.5	393	4.4	6.0	1.3	0.21	0.73	166	67.2	0.70936
	#1 – AO	4.88	12.4	442	59.7	365	2.3	2.4	1.1	0.45	0.97	1845	35.5	0.70943
	#1 –A	4.92	13.7	408	52.8	406	2.4	2.1	1.1	0.52	1.11	190	29.9	0.70924
	#2 – O	4.39	18.3	675	79.6	311	3.3	4.2	1.3	0.31	0.78	161	36.9	0.70929
	#2 – AO	4.33	13.9	501	71.8	197	2.5	2.9	1.2	0.40	0.87	172	36.0	0.70929
	#2 –A	4.25	11.9	178	33.3	149	1.4	0.9	0.9	0.96	1.46	188	14.9	0.70952
	#3 – O	4.49	20.3	845	58.6	207	4.7	5.0	1.2	0.23	0.94	168	41.6	0.70936
	#3 –A	4.77	18.2	519	40.5	146	4.5	3.4	0.9	0.25	1.29	150	28.5	0.70938
Kerrien	#4 – O	5.37	28.4	2000	134.7	320	3.6	13.7	1.4	0.10	0.26	146	70.5	0.70925
	#4 – AO	5.24	26.1	1102	89.9	178	3.3	7.3	1.1	0.15	0.45	151	42.1	0.70922
	#4 –A	5.26	21.3	556	54.5	199	3.7	4.6	0.8	0.18	0.79	119	26.1	0.70947
	#5 – O	5.21	28.0	1443	59.0	207	4.9	9.9	1.2	0.12	0.49	145	51.6	0.70944
	#5 – AO	4.91	23.2	840	38.6	109	4.4	5.9	1.2	0.21	0.74	141	36.2	0.70916
	#5 –A	5.10	13.7	371	27.3	103	4.6	3.0	1.0	0.34	1.53	123	27.2	0.70943
	#6 – O	6.51	19.3	2579	132.4	173	5.0	18.0	0.9	0.05	0.28	143	133.3	0.70921
	#6 – AO	5.99	20.7	1672	110.6	191	3.1	13.0	1.3	0.10	0.24	128	80.8	0.70936
	#6 – A	6.27	18.5	826	54.6	186	3.6	9.6	1.2	0.13	0.37	86	44.5	0.70918

Table 4
Major and trace element concentrations (μg/L), Sr isotopic composition, and element ratios of stream water at the Kerbernez catchment outlet.

date	pH	Na	Ca	Mg	K	Ba	Sr	Rb	DOC (mg/L)	Rb/Sr	Ba/Sr	Ca/Sr	Ba/Ca	Ca/Na	$^{87}Sr/^{86}Sr$
17/01/2001	6.5	25620	16570	10440	4290	24.1	161.5	4.8	2.29	0.030	0.149	102.6	0.0015	0.647	
14/02/2001	5.89	24620	15520	10450	4005	24.1	162.6	4.7	1.90	0.029	0.148	95.4	0.0016	0.630	
14/03/2001	6.32	24853	16528	11278	3825	24.9	163.6	4.6	4.93	0.028	0.152	101.0	0.0015	0.665	
11/04/2001	5.88	23190	15090	10440	3899	24.0	165.8	4.6	2.85	0.028	0.145	91.0	0.0016	0.651	0.71104
09/05/2001	5.94	22140	13990	10320	3359	26.2	165.8	4.4	1.32	0.026	0.158	84.4	0.0019	0.632	
06/06/2001	6.02	24350	13970	10250	4326	27.4	164.2	5.4	2.14	0.033	0.167	85.1	0.0020	0.574	0.71113
04/07/2001	6.2	25400	18250	12380	4201	28.4	171.3	5.2	2.27	0.031	0.166	106.5	0.0016	0.719	
01/08/2001	6.09	25050	16420	10090	4010	24.5	161.3	5.0		0.031	0.152	101.8	0.0015	0.655	
29/08/2001		23950	16770	10310	4645	23.6	163.1	5.7	2.91	0.035	0.145	102.8	0.0014	0.700	
26/09/2001	6.79	24180	15090	11460	4602	24.3	168.4	5.3	1.87	0.031	0.144	89.6	0.0016	0.624	
16/10/2001	6.59	25310	15940	11460	4329	29.8	177.5	5.1	1.27	0.029	0.168	89.8	0.0019	0.630	
14/11/2001	5.94	24310	14930	10810	4158	28.5	164.1	4.8	1.06	0.029	0.174	91.0	0.0019	0.614	
18/12/2001	5.94	26820	17020	12200	4556	29.2	190.7	5.1	0.99	0.027	0.153	89.3	0.0017	0.635	0.71118
16/01/2002	5.78	25860	14950	11740	4218	29.1	173.3	4.9	1.71	0.028	0.168	86.3	0.0019	0.578	
14/02/2002	5.63	26660	16320	11580	4212	28.7	172.7	4.8	1.62	0.028	0.166	94.5	0.0018	0.612	
13/03/2002	5.89	23270	7018	7180	1690	12.5	80.2	1.6	0.76	0.020	0.156	87.5	0.0018	0.302	
17/04/2002		27510	15080	11680	4685	28.8	164.3	4.8	1.40	0.029	0.175	91.8	0.0019	0.548	
12/06/2002	6.06	25220	15930	11260	6284	27.1	171.8	5.9	3.32	0.034	0.158	92.7	0.0017	0.632	
11/09/2002	6.37	25150	14670	11070	4779	30.9	175.3	5.2		0.030	0.176	83.7	0.0021	0.583	0.71115
20/11/2002	5.99	27656	15981	11432	4967	27.4	164.8	5.1		0.031	0.166	97.0	0.0017	0.578	
18/03/2003	5.73	24225	13641	10145	4129	25.4	149.3	4.3		0.029	0.170	91.4	0.0019	0.563	
09/07/2003	5.99	24293	15361	11064	6854	28.4	160.2	5.1		0.032	0.177	95.9	0.0019	0.632	
15/10/2003	6.2	25676	14935	11801	5119	29.4	162.0	5.4		0.033	0.182	92.2	0.0020	0.582	
03/03/2004	5.99	23004	12390	9847	3884	26.7	144.5	4.4		0.030	0.184	85.7	0.0022	0.539	
03/06/2004	5.83	20957	11723	8716	3313	30.0	159.1	4.3		0.027	0.188	73.7	0.0026	0.559	
07/09/2004	6	23628	12736	9603	4616	28.0	156.4	5.3		0.034	0.179	81.4	0.0022	0.539	
14/12/2004	6.02	22653	13117	9401	4373	27.3	155.2	5.0		0.032	0.176	84.5	0.0021	0.579	

(between 20 and 60 cm depth), the $^{87}Sr/^{86}Sr$ ratios are much less radiogenic (0.70963–0.71391) than in deeper horizons (0.71160–0.72981). The dramatic increase in $^{87}Sr/^{86}Sr$ ratios and mineralogical composition of the soil horizon indicate that location of the weathering front is about cm-depth. This implies that in the upper horizons the leached and altered minerals remain relatively non-radiogenic compared to the bulk digest samples. However, the A-horizon of soil #8 samples in the hydromorphic zone reveals a pretty high $^{87}Sr/^{86}Sr$, close to that of bulk digest samples, suggesting a more intense alteration releasing radiogenic strontium.

In order to define the respective sources implied in the H$_2$O-leaching, potential mixing lines have been defined between the rain water and radiogenic sources (biotite, bulk digest soil) or unradiogenic sources (manure, plagioclase) (Fig. 4). Table 6a summarizes the minimum and maximum percentages of each end-member allowing to explain the $^{87}Sr/^{86}Sr$ ratios of soil leachates. In Fig. 4a, the mixing curves represent the potential evolution during the H$_2$O-leaching experiments. None of these mixing curves explains alone the soil H$_2$O-leaching compositions, except the leaching of the deepest horizons which are in good agreement with biotite dissolution and do not seem to require any other contribution (curve 1). For the other shallower soil leachates, biotite and bulk digest soil (curve 5) produce too high isotopic ratios, while plagioclase and manure produce slightly too low isotopic ratios (curve 2). The $^{87}Sr/^{86}Sr$ ratio of upper H$_2$O-leaching reflects the contribution of Sr^{2+} from two opposite sources: relatively low $^{87}Sr/^{86}Sr$

from plagioclase and/or hog manures and higher $^{87}Sr/^{86}Sr$ from biotite and/or bulk digest soils. Neither the Sr isotopic ratios, nor the element ratios indicate a K-Feldspar contribution, which is confirmed through the bulk digest analyses (see next section). Four mixing lines (curves 6, 7, 8, 9) between the two radiogenic (biotite and bulk digest soil) and the two less-radiogenic end-members (manure and plagioclase) are also drawn. The evolution during H$_2$O-leaching experiments can be modelled as a curve (curves 3 and 4, Fig. 4a) which originates from the rain water end-member and is mixed with these four mixing curves (6–9). Curve 3 presents a $^{87}Sr/^{86}Sr$ ratio similar to the streams, by contrast curve 4 presents a higher $^{87}Sr/^{86}Sr$ ratio than streams. However, both curves represent a large part of the H$_2$O-leaching experiments. Higher $^{87}Sr/^{86}Sr$ indicate a predominant biotite contribution (deepest soils), whilst lower $^{87}Sr/^{86}Sr$ indicate a predominant plagioclase and/or hog manure contribution (top soils). The connection between rain water and mixing curves 6–9, including the H$_2$O-leaching and stream compositions, define four potential mixing values (A, B, C and D in Fig. 3a) of the low- and high-radiogenic end-members on curves 6–9.

Using plagioclase as the non-radiogenic end-member implies a higher biotite or bulk digest soil contribution up to a factor 10 as compared to a mixing with hog manure. This is explained by a relatively high major cation concentration in hog manure as compared to plagioclase. Whatever the low end-member, the biotite contribution seems significant as regards the quantities of manures and slurries

Table 5
Major and trace element concentrations (µg/L), Sr isotopic composition, and element ratios of stream waters at the Kerrien catchment outlet.

Date	pH	Na	Ca	Mg	K	Ba	Sr	Rb	DOC (mg/L)	Rb/Sr	Ba/Sr	Ca/Sr	Ba/Ca	Ca/Na	$^{87}Sr/^{86}Sr$
17/01/2001	6.7	20140	11520	7617	6533	26.4	101.3	6.0	2.89	0.059	0.261	113.7	0.0023	0.572	
14/02/2001	6.02	19850	11840	7500	5815	25.8	99.9	5.5	2.88	0.055	0.258	118.5	0.0022	0.596	
14/03/2001	6.16	20110	11027	7996	4433	27.3	103.8	4.4	3.12	0.043	0.263	106.2	0.0025	0.548	
11/04/2001	5.9	18880	11380	7582	4705	27.3	104.5	4.8	2.30	0.046	0.261	108.9	0.0024	0.603	0.71123
09/05/2001	6.04	19250	11330	7976	4407	30.2	113.4	4.9	1.99	0.043	0.266	99.9	0.0027	0.589	
06/06/2001	6.23	21010	10940	8336	5535	31.0	113.2	5.8	2.53	0.052	0.274	96.6	0.0028	0.521	0.71139
04/07/2001	6.45	21480	13270	9948	4338	27.2	112.2	5.1	2.49	0.045	0.242	118.3	0.0020	0.618	
01/08/2001	6.33	19710	9184	7842	2684	23.0	98.4	3.7		0.037	0.234	93.3	0.0025	0.466	
29/08/2001	8.11	20430	10110	8668	4973	26.1	109.6	5.8	3.99	0.053	0.239	92.2	0.0026	0.495	
26/09/2001	6.96	21750	10990	9226	6690	22.2	111.5	8.6	9.08	0.077	0.199	98.6	0.0020	0.505	
16/10/2001	7.23	22570	11070	9429	4100	22.0	115.4	5.4	4.32	0.047	0.191	95.9	0.0020	0.490	
14/11/2001	5.99	23870	11960	9875	4526	19.6	113.3	4.9	2.42	0.043	0.173	105.6	0.0016	0.501	
18/12/2001	6.15	24260	13410	10990	4904	21.8	121.4	4.8	2.04	0.040	0.179	110.5	0.0016	0.553	0.71141
16/01/2002	6.01	23940	11620	10280	4191	25.5	119.1	4.4	3.06	0.037	0.214	97.6	0.0022	0.485	
14/02/2002	5.94	23220	12160	9368	4389	30.3	118.5	4.6	3.01	0.039	0.256	102.6	0.0025	0.524	
13/03/2002	6.3	23810	20600	8216	4104	30.5	103.1	5.7	1.56	0.056	0.296	199.8	0.0015	0.865	0.71133
17/04/2002		25610	13170	9757	5759	35.2	128.1	5.5	1.63	0.043	0.275	102.8	0.0027	0.514	
12/06/2002	6.47	21660	12540	8333	6660	28.7	119.7	6.0	12.84	0.050	0.240	104.8	0.0023	0.579	
11/09/2002	6.51	nd	9855	8585	2504	23.7	103.5	3.1		0.030	0.229	95.2	0.0024	–	0.71146
20/11/2002	6.22	18994	10186	6750	5132	24.5	88.8	4.6		0.051	0.276	114.7	0.0024	0.536	
18/03/2003	5.88	19954	10240	7258	5302	26.3	93.0	4.4		0.048	0.283	110.1	0.0026	0.513	
09/07/2003	6.71	19798	7882	7477	2570	17.0	81.4	3.7		0.045	0.209	96.9	0.0022	0.398	
03/03/2004	5.93	19774	9861	7501	4858	26.6	97.9	4.6		0.047	0.271	100.7	0.0027	0.499	
03/06/2004	6.04	17527	7852	6175	3163	24.3	95.3	4.2		0.044	0.255	82.4	0.0031	0.448	
07/09/2004	6.51	20393	7301	6374	3583	14.8	76.7	4.2		0.055	0.192	95.2	0.0020	0.358	
14/12/2004	6.25	20015	9848	7751	4495	18.1	100.1	4.3		0.043	0.181	98.3	0.0018	0.492	

applied on the field (Appendix A). Since the end-member Sr concentrations and isotopic ratios are known, the source contributions can be converted into mass of material needed to be weathered or leached in order to explain a mean Sr^{2+} concentration of 20 µg/L in soil leaching solution (Table 6b). The biotite pool needed to explain soil leaching chemistry is far too large, from 179 to 2146 mg for 1 L of solution. This would be even worse to explain stream water chemistry which presents much higher Sr^{2+} concentrations. Even if the mass of manure implicated in the computation is high, it is in good agreement with the annual loads on the field (Appendix A) and seems the most reliable explanation, especially for the leachates displaying low Sr isotopic ratios.

By plotting the $^{87}Sr/^{86}Sr$ ratios versus Ca/Sr ratios, the soil leaching solutions present clearly a higher Ca/Sr ratio than that of separated minerals, except biotite (Fig. 4b), indicating a high manure contribution with a high Ca/Sr ratio, relative to granite minerals. The element ratios (Rb/Sr, Ba/Sr and Ca/Sr) are in good agreement with these observations (Fig. 5). The top soil H_2O-leachings present the larger range of Ba/Sr and Rb/Sr values, remaining below those of muscovite. Moreover, the soil H_2O-leachings are also enriched in Rb, compared to soil NH_4Ac-leaching. The deepest soil leachings present relatively high Ba/Sr, and Rb/Sr ratios which confirm the weathering of biotite and/or muscovite.

4.1.2.3. NH_4Ac exchangeable cations. Soils are leached using an NH_4Ac solution to investigate the soil ion-exchange pool (Table 3). The concentrations of leached cations are higher in the top soils than in the deeper soils by a factor of about 3 for Sr, 1.5 for Rb and K, 2–3 for Ca, Mg and Ba. The soils from Kerrien release more cations than those from Kerbernez, by a factor 2 in average.

The cation exchangeable pool has low and extremely homogeneous $^{87}Sr/^{86}Sr$ ratios, ranging from 0.70916 to 0.70952. This signature remains lower than those of river waters (~0.711), bulk digest soils and minerals, except plagioclase (0.70845). It is comparable to that of manure (~0.70950). This monotonous $^{87}Sr/^{86}Sr$ ratio in NH_4Ac-leachates strongly suggest that the topsoil, which is enriched in clay minerals, is more influenced by a non-radiogenic source, such as manures. Indeed, since manure is about 10-fold less concentrated in Sr than plagioclase, a Sr isotopic ratio close to that of manure implies that Sr in the exchangeable pool results from manure for at least 90%, considering a simple and pure mixing between the two end-members manure and plagioclase. These results suggest that the water moving through the soil, and then reaching the stream waters is not strongly influenced by manure, as proposed by several authors (Åberg et al., 1989; Bullen et al., 1996; Katz and Bullen, 1996). On the contrary, in deeper soils the low $^{87}Sr/^{86}Sr$ ratios in the NH_4Ac-leachates, different from those of stream waters and some soil H_2O-leachates suggests that the cation exchangeable component does not influence directly the surface soil solution. The cations ratios indicate a higher influence of mineral weathering, including biotite, muscovite or K-feldspar (Fig. 5), explained by the saturation of the cation exchange sites on the clay minerals for example.
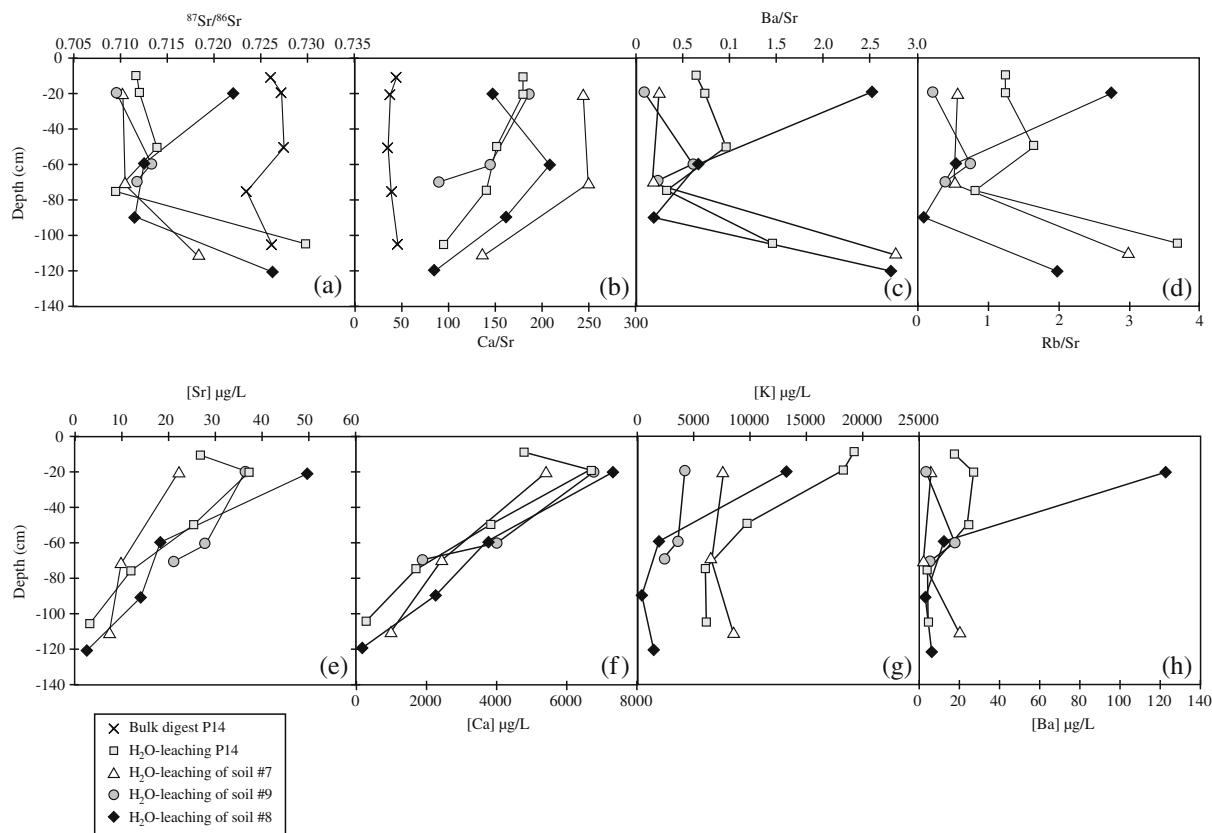
Fig. 2. Variations with soil depth of (a) $^{87}Sr/^{86}Sr$, (b) Ca/Sr ratio, (c) [Sr], (d) [K], (e) [Na], (f) [Ca] and (g) [Mg] for soils #7, #8 and #9 from Kerbernez and Kerrien.

4.1.3. Organic, mineral and chemical fertilizers

In addition to soils and rocks, major cations may be also released from anthropogenic materials, such as organic and mineral fertilizers, especially in Brittany. The main applied fertilizers are animal manures, NPK fertilizers and NH_4NO_3. Only hog manures have been analyzed for Sr isotopic composition for this study, because of the low Sr concentration of the other materials. An average $^{87}Sr/^{86}Sr$ ratio of 0.7079 for NH_4NO_3 applied in Brittany is given in the literature (Widory et al., 2004). NPK(S) fertilizers have about the same range of $^{87}Sr/^{86}Sr$ ratio (0.7072–0.7079) than ammonitrates (Riou, 1995). Hog manures (data from Widory et al. (2004), and this study, Table 1) present high Ca, Mg and K concentrations. The Sr concentration of bulk digest manure is about 63–73 ppm. Hog manures sampled in Brittany show quite homogenous $^{87}Sr/^{86}Sr$ ratios of 0.7094–0.7096. In the following discussion, the range of $^{87}Sr/^{86}Sr$ ratios includes data from this study and from Widory et al. (2004). Moreover, the hog manures are characterized and discriminated by much higher Ca/Sr than any other minerals or bulk digest soil.

4.2. Stream waters

The chemical and Sr isotopic composition of stream waters from both Kerrien and Kerbernez catchments are presented in Tables 4 and 5.

4.2.1. Major element chemistry

Stream waters from Kerrien and Kerbernez catchments display about the same major cation distribution (Tables 4 and 5). Sodium is the dominant major cation in both Kerrien and Kerbernez stream waters. Ranging from 17 to 27 mg/L, Na represents about from 42 to 54% of the total major cation content. Calcium is the second in importance (19–30%), and is about twice less concentrated than Na. However, Kerrien stream waters display a deficit of major cation relative to Kerbernez stream waters, over the same time period, of 10–50%, depending on the sampling date.

4.2.2. Strontium concentrations and $^{87}Sr/^{86}Sr$ ratios

Between 01/2001 and 12/2004, Kerbernez stream waters show a Sr concentration ranging from 145 to 190 μg/L (excepting one value at 80 μg/L), whereas the range of Sr concentration for Kerrien stream waters is 77–128 μg/L. Moreover, the Sr concentration in Kerrien streams shows the lowest value during the year 2003–2004. The $^{87}Sr/^{86}Sr$ ratios of stream waters present an extremely narrow range of variation, whatever the hydrological conditions (Fig. 3a), with a value of 0.71113 ± 0.00006 ($n = 4$) for Kerbernez and 0.71136 ± 0.00009 for Kerrien ($n = 5$). In spite of the low number of $^{87}Sr/^{86}Sr$ ratios, their variation does not reflect any range of hydrological conditions, or seasonal variations. The Sr content of open field bulk precipitation is rather low, 2–20 μg/L, with a $^{87}Sr/^{86}Sr$ ratio of 0.70892 ± 0.00001
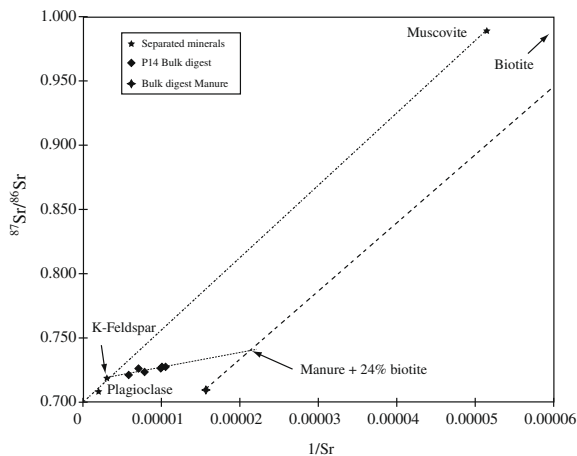
Fig. 3. Variations of $^{87}Sr/^{86}Sr$ ratio with (a) Sr concentration and (b) Ca/Sr ratio in stream waters of Kerrien and Kerbernez. Hog manures include data from this study and from Widory et al. (2004). Mixing curves represent a mixture (Table 6) between (1) biotite and rain water, (2) plagioclase and rain water. Curves (3 and 4) represent a mixing between rain water on one hand and a second mixing between manure or plagioclase and biotite. (3 and 4) represent two different contributions of biotite. Other mixing curves represent a mixture between (5) bulk digest soil and rain water, (6) manure and biotite, (7) plagioclase and biotite, (8) manure and bulk digest soil, (9) plagioclase and bulk digest soil. Here are the proportion of biotite or bulk digest soil for mixing with plagioclase or manure: (A) 24% biotite or 17% bulk digest soil, (B) 32% biotite or 65% bulk digest soil, (C) 2% biotite or 7% bulk digest soil, (D) 21% biotite or 55% bulk digest soil. Chemical composition of rain waters is available in Appendix B.

(Appendix A). This ratio is close to that of seawater, which is supported by the vicinity of the Atlantic Ocean.

4.2.3. Cation budgets

The various human-made inputs, such as fertilizers, have a range of Sr contents (3–1500 ppm) with an isotopic ratio ranging from 0.7079 to 0.7109 (Négrel, 1999; Widory et al., 2004; Table 1). An empirical estimation of cations released from the manure and slurry mineralization can be calculated through an annual mass balance. This computation is based on a hydrological water-balance. The precipitation average over a 5-year period (2000–2005) is 1235 mm, with potential evapo-transpiration of about 50% (Martin et al., 2004)). Such evapo-transpiration allows the infiltration of 500 L of rain water per m^2. The slurries and manures are applied at an average rate of 3–5 m^3/ha and 0.5–3.0 T/ha (Appendix A), respectively, on Kerrien and Kerbernez. Knowing the anthropogenic contribution, we used the cation concentrations presented in Appendix C, assuming that slurry contains between 10 and 30% of solids (Nicholson et al., 1999). Knowing the concentration of Na$^+$ (2.7–4.5 g/kg), Ca^{2+} (20–43 g/kg) and Sr^{2+} (0.06–0.10 g/kg) in slurries, the total mineralization of these organic matter releases between 1.2 and 14 mg/L of Ca^{2+} between 0.2 and 1.4 mg/L of Na$^+$ and between 4 and 30 µg/L of Sr^{2+} in streams. Considering the cation concentrations in stream waters in Kerrien and Kerbernez catchments, the organic

fertilizer mineralization explains from 5 to 40% of the Sr^{2+} pool, and less than 10% of the Na$^+$ pool. However, the slurry mineralization releases from 20 to 100% of the Ca^{2+} encountered in stream waters.

5. DISCUSSION

5.1. Systematics in soil profiles

There are three possible sources of Sr^{2+} to soil water: (1) Sr^{2+} released from mineral weathering within the soil zone through incongruent or congruent dissolution, (2) Sr^{2+} delivered via atmospheric aerosols dissolved in rainfall and (3) Sr^{2+} delivered by additional material applied on soil, such as fertilizers. All these sources are also considered for the other major cations (Ca, Na, Mg). Furthermore, the different cations can either be released into the soil mobile water and leave the soil, or can constitute a reservoir with an intermediate mobility in the clay fraction (cation exchange pool). In order to characterize the most reliable source of Sr and other basic cations in soil water, and then in streams, element concentrations and element ratios such as Ba/Sr, Rb/Sr, Ca/Sr and Sr isotope ratios ($^{87}Sr/^{86}Sr$) have been used as tracers. Ba, Rb and Sr occur in various minerals which have a different weathering susceptibility. In this studied granitic environment, the main carrier of Ca, Sr and Na is the Na–Ca-plagioclase, while the main carrier of Rb, Mg and K is biotite, and then muscovite (Table 1). K-feldspar is an intermediate between these two end-member concentrations.

First, trace minerals enriched in Ca, such as apatite and epidote, may be considered as an important source of Ca^{2+} in stream waters (Blum et al., 2002; Oliva et al., 2004). Moreover, several authors found that disseminated calcite can have a similar effect than apatite, in controlling the chemical composition of surface and ground waters in crystalline rocks (Blum et al., 1998; Clow et al., 1997; Jacobsen and Blum, 2000; Weyer et al., 2008; White et al., 1999). The control of trace minerals may also be highlighted through Sr isotope composition (Taylor et al., 2000). Indeed, during early stages of weathering, the $^{87}Sr/^{86}Sr$ ratios of soil solutions can be controlled by the presence of reactive phases, rather than that of major minerals. However, their influence is limited once the steady-state is reached. Generally, apatite is non-radiogenic (Probst et al., 2000), and thus has a $^{87}Sr/^{86}Sr$ ratio generally lower than other silicate minerals (Aubert et al., 2001). Dissolution of apatite would be in line with the low Sr isotopic ratios of plagioclase or manure. However, several arguments allow us to rule out the accessory mineral hypothesis as a major source of Ca. (1) Neither apatite nor calcite has been observed in the granite thin sections, nor with XRD analyses, nor binocular observation. (2) Weathering is advanced and does not seem to represent an early stage. Furthermore, the Ca and Sr decrease with depth in the H$_2$O-leaching, and to a lesser extent in the bulk digest, does not agree with a potential source related to accessory minerals which have no reason to be located in the upper part of the soils. (3) The extremely high cation concentrations and weathering rates as compared to catchments investigated elsewhere (White
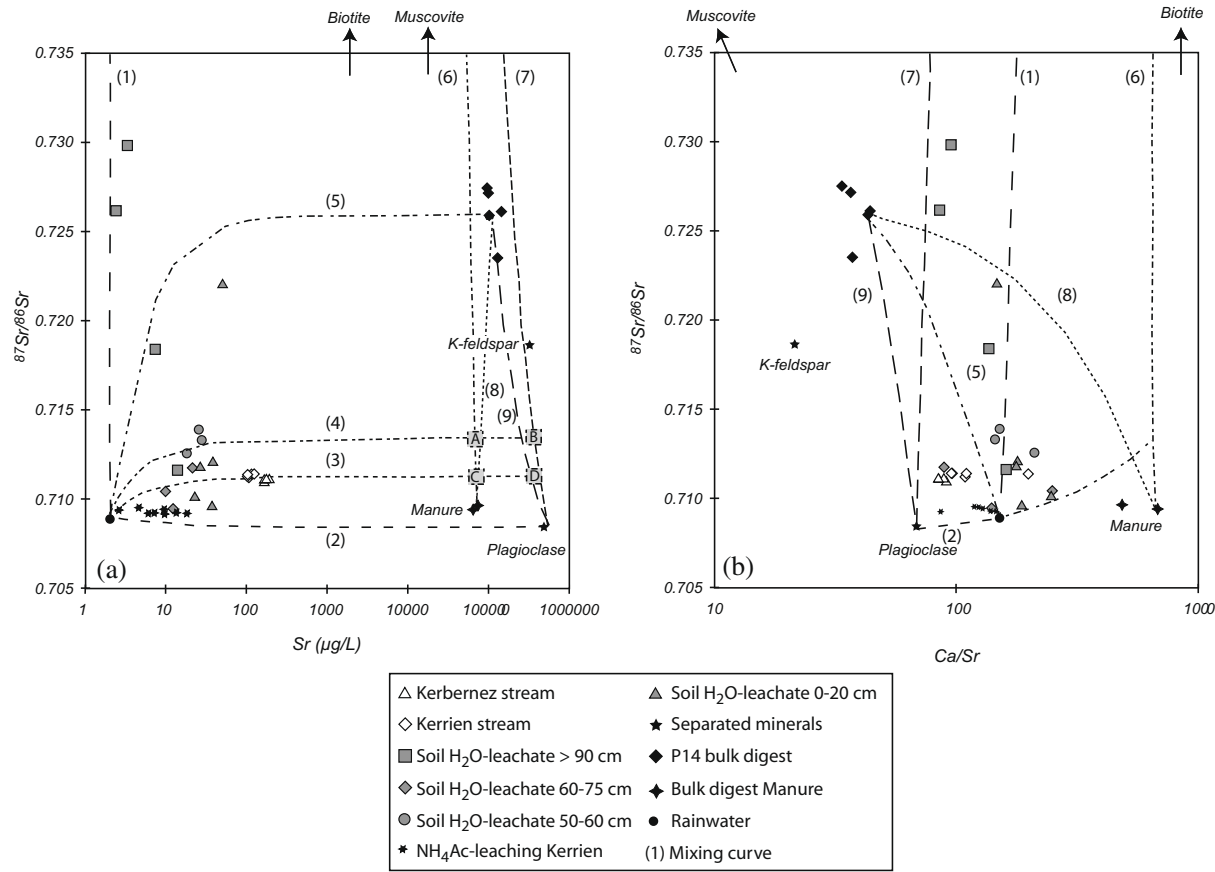
Fig. 4. Variations of $^{87}Sr/^{86}Sr$ ratio with 1/Sr for bulk digest soils, compared to separated minerals. Two correlation curves are drawn (1) between plagioclase, K-feldspar and muscovite ($R^2 = 0.9989$), and (2) between biotite and manure.

et al., 2001, 1999) imply extremely significant sources (see Section 5.3). Accessory minerals, even if they might contribute to the cation fluxes, do not play a major role in the investigated agricultural catchments.

Second, the influence of some silicate minerals, such as biotite or K-feldspar is accompanied by the contribution of manure, as suggested by bulk digest soils. This can be interpreted as the fact that manure and biotite bear a relatively similar weathering rate, which might be more important than K-feldspar. The triangular diagram plotting Rb/Sr, Ba/Sr and Ca/Sr/500 (Fig. 5) suggests that bulk digest soils are influenced by mineral sources, such as Biotite and K-Feldspar, but do agree with the potential influence of a mixture of biotite + manure. Overall, these results suggest that a large fraction of K-minerals remains to weather in soil particles. The succession of weathering reaction suggested by chemical tracers implies that K-mineral biotite is the less resistant mineral and the

Table 6
(a) Percentage of radiogenic end-members (biotite or bulk digest soil), mixed with either manure or plagioclase required to explain the Sr isotopic ratio of stream waters (from Fig. 4a). (b) Mass (in mg) of biotite, plagioclase, hog manure or bulk digest soil required to explain the concentration of 20 μg Sr/L of soil H$_2$O-leachates.

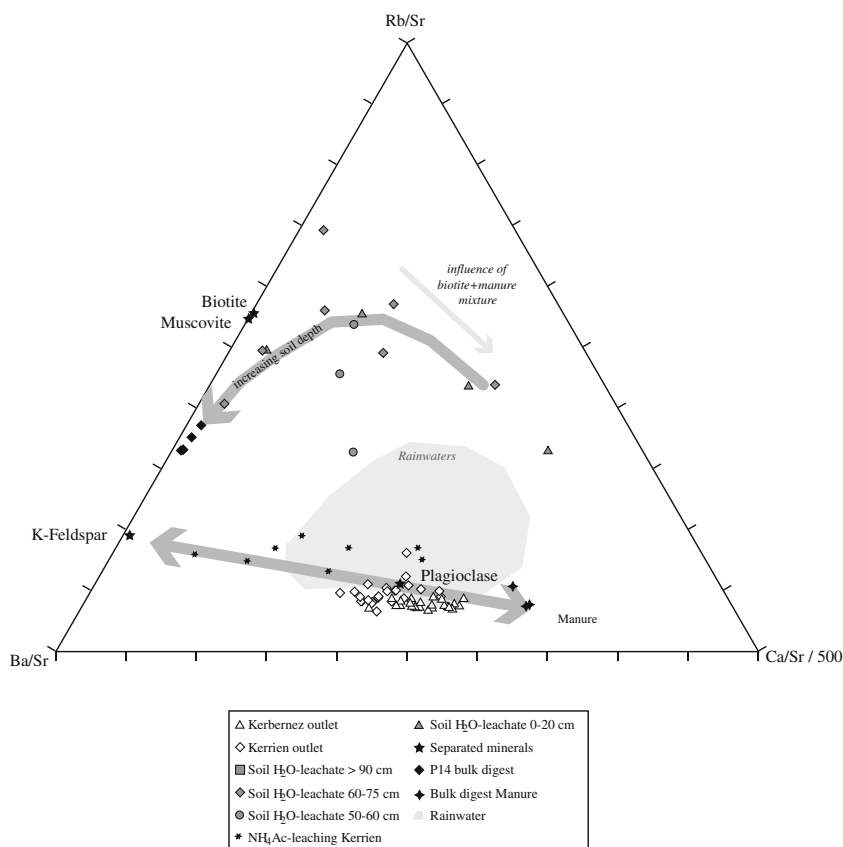|	Mixed with Hog manure		Mixed with plagioclase	
	Minimum	Maximum	Minimum	Maximum
(a)				
% Biotite	2	24	21	32
% Bulk digest soil	7	17	55	65
(b)				
Mass of Biotite	179	2146	1878	2861
Mass of bulk digest soil	18	28	89	105
	Mixed with biotite		Mixed with bulk digest soils	
Mass of manure	227	292	247	277
Mass of plagioclase	28	32	14	18

Fig. 5. Triangular diagram plotting Rb/Sr – (Ca/Sr)/500 – Ba/Sr for separated minerals, bulk digest soils, NH_4Ac- and H_2O–soil leachates, bulk digest manures and stream waters.

first to dissolve as observed in the deep soil profile, and in the saprolite (>70 cm). Biotite constitutes with manure, which is almost completely stored in the exchangeable phase, the main source of Sr^{2+} in the soil, both of them constituting a first phase of Sr^{2+} mobilization, prior to K-feldspar. A more intensive weathering, encountered in the mid-soil profile, allow the plagioclase dissolution to be a major source of elements into soil leaching solution, avoiding any major anthropogenic contribution. The plagioclase dissolution products seem to be removed from the soil itself through solution export to stream. The K-feldspar is more resistant relative to Sr isotopes, which explains that no clear contribution has been observed in soil leaching whilst it is the major source of the soil itself, as revealed by bulk digest analyses. As weathering continues, K-feldspar should become the dominant source, with muscovite which seems to be the more resistant mineral relative to Sr isotopes.

Fig. 6 summarizes all the observations and conclusions of this study. The soil leaching of different soil horizons demonstrated the influence of three different phases on the labile phase chemistry:

(1) In the top soil (0–20 cm), the manure contribution predominates and represents a high labile phase generating high major cation concentration and relatively low ^{87}Sr/^{86}Sr ratios in soil leaching solutions.

(2) In the mid-soils (20–70 cm), almost no influence of plagioclase is observed in the Sr isotopic composition of bulk digest soils. On the contrary, plagioclase signature is evident from H_2O-leaching. This can be interpreted as the fact that plagioclase is particularly labile and is not 'kept' in the soil neither in the solid nor in the exchangeable phase. Manure and plagioclase with a comparable low ^{87}Sr/^{86}Sr ratio, and a more radiogenic phase (such as bulk digest soil and/or biotite) control most of the geochemical isotopic and elemental tracers. The cations seem to be inherited from a slow weathering of the granitic rock.

(3) In the deep soil horizons and saprolite itself, a unique contribution may be revealed, with a high ^{87}Sr/^{86}Sr ratio, enriched in K, such as biotite or even muscovite. The weathering of such K-host mineral phases may occur below the alteration front, where the weathering processes are the most active, as suggested previously by Pavich (1986). The concomitance of high application rates of fertilizers, mineral dissolution chemical signature, and fertilizer influence on the chemistry on the surface soil, suggests that soil acidification induced by the use of fertilizers may enhance the mineral weathering in the deeper soil layers. This is contrary to some authors (Fernandez et al., 2003; Gbondo-Tugbawa and Driscoll, 2003; Sverdrup et al., 1995).
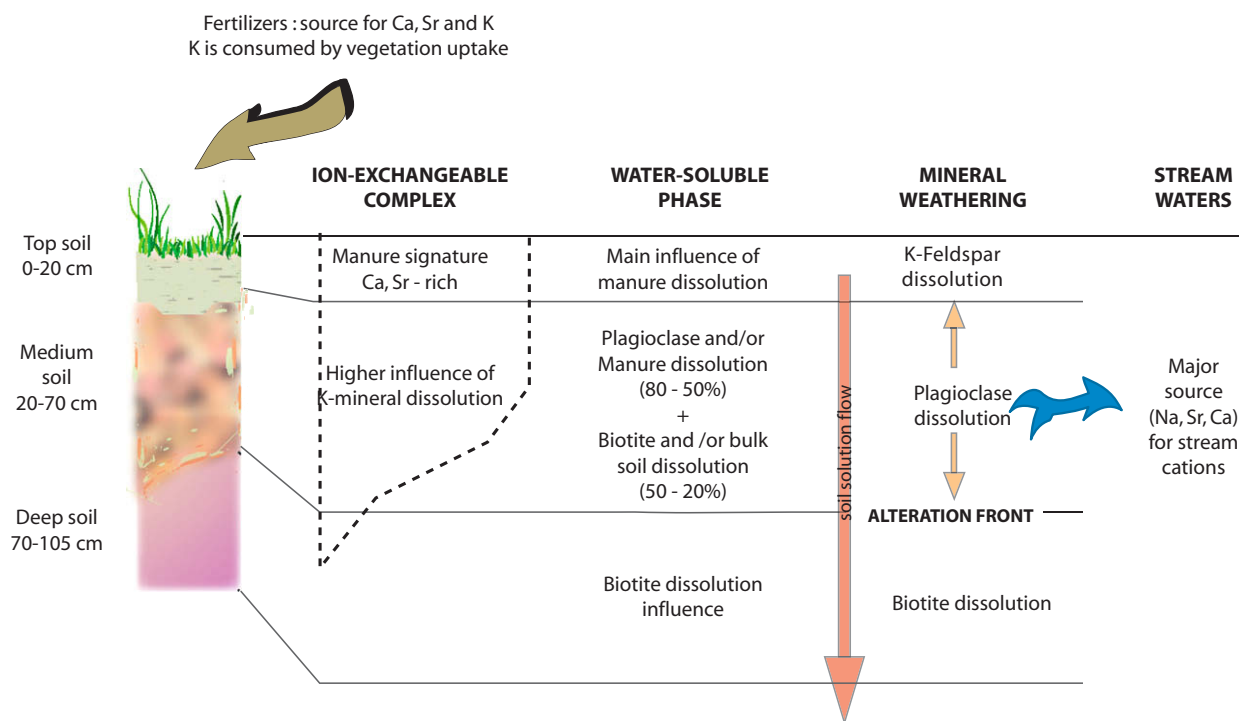
Fig. 6. Synthetic cartoon showing the evolution of cation release with depth depending on the exchangeable, labile and mineral fraction in a soil profile.

5.2. Acquisition of the chemical signature in stream waters

In anthropogenic catchments, mineral and organic fertilizers applied on soil at varying rates can alter the geochemistry of soil, ground- and stream waters. Stream chemistry is relatively sensitive to human activities, and especially agriculture, which induces rapid changes in cation release (Flintrop et al., 1996). Indeed, in the previous section we have shown that manure-derived Sr^{2+} was included in the exchangeable phase of the soil. The stream waters show definitely different geochemical characteristics from soil waters. Dissolved cation concentrations of both Kerrien and Kerbernez stream waters (Tables 4 and 5) are extremely high as compared to those found in small catchments under temperate climate conditions and on granite and granodiorite basements (Stutter et al., 2006; White and Blum, 1995). Such high cation concentrations are encountered in tropical environments where chemical weathering rates are extremely pronounced (Oliva et al., 2003; White and Blum, 1995). Stutter et al. (2002) suggested from catchment investigation in Great Britain that agricultural practices increased the Na concentrations. Na is also the dominant basic cation in both Kerbernez and Kerrien catchments. Stream waters display very high cation concentrations which are induced by (1) the KCl addition, K being largely consumed by the vegetation which requires another cation to electrically equilibrate the waters. (2) NH_4 derived from the manure addition, which acts as an acid addition since it is rapidly transformed to NO_3 in the soil (Van Miegroet and Cole, 1984). This large acidification process leads to the very high concentrations in the stream waters observed in Kerrien and Kerbernez catchments.

In the $^{87}Sr/^{86}Sr$ vs Ca/Sr diagram (Fig. 4b), the $^{87}Sr/^{86}Sr$ ratios of stream waters are specifically closer to those of soil layers dominated by mineral weathering rather than those dominated by hog manure leaching. Furthermore in the Fig. 5, there is a clear evidence that the stream waters are directly related to the plagioclase dissolution which appears as the dominant reaction. This implies that in both catchments, Na is the dominant weathering-derived cation in streams. The previous result is consistent with the low Ca/Na ratios in minerals (0.37 for Na–plagioclase) and soil (0.31). However, the Ca/Na ratios in streams are in average 0.60 for Kerbernez and 0.53 for Kerrien, respectively. Such high Ca/Na ratios, higher than that of plagioclase, have been interpreted as the result of accessory mineral dissolution (apatite or calcite) (Aubert et al., 2002; Blum et al., 2002; Clow et al., 1997; Jacobsen and Blum, 2000; Oliva et al., 2004; White et al., 1999). Here, these high Ca/Na ratios may be explained, with the lack of significant accessory minerals, either by the differential contribution of biotite (Ca/Na = 3.26), or mineralization of hog manure (Ca/Na = 10–15). The streams display Sr/Na and Ca/Na ratios ranging between those of plagioclase and biotite, whilst the manure influence is much more sensitive in the soil leaching which have much higher ratios. Although the manure influence is clear in the upper soil leaching, the high Ca/Na ratios of streams do not seem to result from agriculture product contribution. Compared to rain waters and soil leaching experiment, stream waters have relatively high Si concentration, positively correlated to Na and Mg (not shown here). This confirms that a large part of Na and Mg is directly inherited from silicate mineral weathering, respectively from Na–plagioclase and biotite, in the different soil layers, and the saprolite.

5.3. Cation solute budget

In this section, the respective role of the manure and mineral contribution to the total budget is addressed. It is important to recognize that the cation and Sr sources and contributions are estimates. Errors involved in the simple mass balance and two end-members mixtures approach include those associated with the measurements of water in a weekly scale and water chemistry on a monthly scale. However, based on a 11-year dataset, Likens et al. (1977) concluded that 1–3 years of measurements are adequate to characterize the magnitude of loss or gain of base cations, except K^+ which displays a high variability in annual inputs. However, the cation budget estimation gives a clear confirmation that (1) most of the Na and Sr budgets are not related to manure addition, and (2) the dissolved calcium in streams cannot be explained only by a water–rock interaction, but also implies the partial mineralization of manures and slurries. The fertilizer-derived Ca^{2+} pool stored in soil profile can be leached at the same time than other cations, such as Na^+ or Sr^{2+}. The main difference is that Na^+, and in a lesser extent Sr^{2+}, dissolved in streams is mostly controlled by the dissolution of Na–plagioclase (hydrolysis) in the soil, rather than any agricultural inputs.

Several environmental problems have been pointed out concerning the impact of organic and chemical fertilizers on surface and ground waters, with increasing dissolved nitrate concentrations for example. These concerns are not only confined to water quality, but also to ecology, with decreasing species diversity and increased productivity (Seitzinger and Kroeze, 1998). In Brittany, where base cations are largely exported from agricultural catchments compared to more natural catchments, the chemical weathering of silicate minerals is not the only contributor to this cation exportation. Indeed, soils may also be an important contributor, through its ion-exchange complex and its leaching by acidification process. Soil acidification, through atmospheric or agricultural deposition, can lead to irreversible decrease in clay activity with decreasing pH. Stability and cation exchange capacity of soil under temperate climate and under agricultural pressure might be a continuous and enhancing environmental concern for the next decades. Indeed, soil acidification by N-fertilizers can have significant impact on chemical aspects of soil quality, in particular on the partitioning of Al into solid phases. In addition to decreasing alkalinity, dissolved element fluxes exported by surface waters have been highlighted in a few studies devoted to agriculture impacts on chemical weathering, on a local scale (Collins and Jenkins, 1996; Pierson-Wickmann et al., in press; Semhi et al., 2000) or large scale (Perrin et al., 2008; Raymond and Cole, 2003; West and Mcbride, 2005). And in addition to cation loss by acidification, a counter effect of liming, to prevent acidification, is the loss and export of organic matter in the dissolved fraction of soil, which goes directly into streams. The increase in dissolved organic matter is also another environmental concern.

6. CONCLUSION

The chemistry of soil and stream waters was monitored in two small, adjacent, granitic catchments in Brittany, France, to evaluate the potential sources of cation solutes in the streams of both catchments. The results demonstrate that Ca^{2+} and Na^+ are the dominant weathering-derived solutes in streams. Such high concentrations mainly result from agricultural pressure. Our study investigates the origin of these solutes, analyzing Sr isotopic ratios and cation concentration ratios in the different rock minerals, soil leaching, stream water and manure chemical composition.

Soil leaching indicates a clear gradient with depth. The top soil leaching presents high cations concentrations that can mainly be related to manure addition. In the soil middle section, the cations derive from both manure addition and mineral dissolution, especially plagioclase. In the deeper part of the profile, below the soil, very low concentrations are observed with radiogenic strontium isotopic ratios which clearly indicate biotite dissolution. Finally, a mineral weathering sequence can be defined: (1) In the fresh rock, the first mineral dissolved is biotite. (2) Plagioclase dissolution is the second reaction: it appears as the dominant mechanism in the soil leaching, which in turn results from a high degree of the rock weathering. (3) K-feldspar (and probably muscovite) is the last mineral to be dissolved. In the profile investigated, the feldspar signature is dominant when the soil is entirely dissolved. It indicates that K-feldspar dissolution has not still occurred in the soil profile.

Stream waters present highly homogeneous concentrations and Sr isotopic ratios in regards to soil leaching and chemical composition or mineral composition. Several cation ratios indicate that the plagioclase hydrolysis is the dominant cation source. An influence of biotite dissolution is also observed, although less important than that of the plagioclase. It confirms that plagioclase dissolution products are not stored in the soil profile, as is the case for biotite, but are rapidly exported from the catchment. Slurries and manures remain a significant source of Ca^{2+}, and potentially Sr^{2+}, in soils. However, most of Ca^{2+} resulting from the organic fertilizer mineralization is stored in the soil ion-exchange complex.

A cation budget is computed from the chemical analysis of all the different sources. It indicates that if the Ca^{2+} originates from the manure, other cations like Mg^{2+}, Sr^{2+} and especially Si^{4+} and Na^+ which are the dominant cations in stream waters derive from mineral dissolution. The soil acidification induced by agriculture allows the mobilization of cations stored in soil layers (Ca^{2+}, Sr^{2+}). It enhances the rock weathering and accelerates plagioclase dissolution. The large cation export induced by agricultural pressure should be considered as a potential mechanism that could lead in term to soil destabilisation and agriculture productivity decrease.

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.gca.2009.05.051.

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