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Discussions

Chemical and U-Sr isotopic variations of stream and source waters at a small catchment scale (the Strengbach case; Vosges mountains; France)

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Abstract

This is the first comprehensive study dealing with major and trace element data as well as ^{87}Sr/^{86}Sr isotope and (^{234}U/^{238}U) activity ratios (AR) determined on the totality of springs and brooks of the Strengbach catchment. It shows that the small and more or less monolithic catchment drains different sources and streamlets with very different isotopic and geochemical signatures. Different parameters control the diversity of the source characteristics. Of importance is especially the hydrothermal overprint of the granitic bedrock, which was stronger for the granite from the northern than from the southern slope; also significant are the different meteoric alteration processes of the bedrock causing the formation of 0.5 to 9 m thick saprolite and above the formation of an up to 1 m thick soil system. These processes mainly account for springs and brooks from the northern slope having higher Ca/Na, Mg/Na, Sr/Na ratios but lower ^{87}Sr/^{86}Sr isotopic ratios than those from the southern slope. The chemical compositions of the source waters in the Strengbach catchment are only to a small extent the result of alteration of primary bedrock minerals and rather reflect dissolution/precipitation processes of secondary mineral phases like clay minerals.

The (^{234}U/^{238}U) AR, however, are decoupled from the ^{87}Sr/^{86}Sr isotope system and reflect to some extent the level of altitude of the source and, thus, the degree of alteration of the bedrock. The sources emerging at high altitudes have circulated through already weathered materials (saprolite and fractured rock depleted in ^{234}U) implying (^{234}U/^{238}U) AR < 1, which is uncommon for surface waters. Preferential flow paths along constant fractures in the bedrocks might explain the over time homogeneous U AR of the different spring waters. However, the geochemical and isotopic variations of stream waters at the outlet of the catchment are controlled by variable contributions of different springs depending on the hydrological conditions.

It appears that the (^{234}U/^{238}U) AR is an appropriate very important tracer for studying and deciphering the contribution of the different source fluxes at the catchment scale because this unique geochemical parameter is different for each individual spring

and at the same time remains unchanged for each of the springs with changing discharge and fluctuating hydrological conditions. This study further highlights the important impact of different and independent water pathways in fractured granite controlling the different geochemical and isotopic signatures of the waters.

1 Introduction

Large rivers carry erosion products from the different drainage areas and, therefore, are pathways of continental weathering products that finally enter the oceans. Thus, they fetch the various chemical and isotopical characteristics of the different drainage basins and therefore allow to elucidate erosion processes, derive erosion rates and to illustrate biogeochemical cycling of elements. Actually many of the major world rivers are well documented with major and trace element and isotope data on dissolved and suspended phases, which provide the different factors controlling chemical and physical denudation (Degens et al., 1991; Dupré et al., 2003; Gaillardet et al., 1999; Martin and Meybeck, 1979; Négrel et al., 1993). At the large catchment scale, the stream waters chemical composition is generally the result of mixing between phases derived from the different main lithologies (e.g., Bickle et al., 2006; Blum et al., 1998; Chabaux et al., 2001; Millot et al., 2003; Steinmann and Stille, 2009; Tipper et al., 2006; Zakharova et al., 2007). However, especially at the small catchment scale, the impact and the role of vegetation cover and soils on the chemical or isotopical evolution of erosion signals in waters have only seldom been observed and discussed (Cenki-Tok et al., 2009; Cidivini et al., 2011; Lemarchand, E. et al., 2010; Zakharova et al., 2007). In addition, determination of parameters controlling the chemical composition of superficial waters is important for a correct modeling of the future evolution of the ecosystems in response to external natural or anthropogenic forcing such as climate evolution and atmospheric pollution (trace metal depositions, acid rain etc.). Among these parameters water/rock interactions (including secondary phases such as clays), hydrological processes and biological activities play an important role in affecting mobilization, (re)cycling and fractionation of elements; their specific influences on weathering processes at the watershed scale remains a matter of discussion (Brantley et al., 2008).

Because natural systems are subject to complex and multiple reactions, the combination of different geochemical and isotopical tools is necessary to decipher the different natural processes. ^{87}Sr/^{86}Sr isotopic ratios and (^{234}U/^{238}U) AR have successfully been used in the discussion of hydrological and hydrochemical processes at the catchment scale (e.g. Riotte and Chabaux, 1999; Tricca et al., 1999; Aubert et al., 2002; Bagard et al., 2011; Bickle et al., 2005; Bonotto and Andrews, 2000; Chabaux et al., 2011; Durand et al., 2005; Schaffhauser et al., 2014). The Sr isotopic composition of e.g. a source water mainly reflects its origin and, thus, is a tool to discuss water-rock interactions. Alternatively, the value of the U activity ratios can reflect a strong constraint from minerals and rocks involved in the water-rock interactions. Indeed, in the case that the U system has been closed for approximately 1 million years, minerals and rocks are in secular equilibrium and activities of all parents and daughters from ^{238}U decay chain are identical and the (^{234}U/^{238}U) AR is equal to 1. However, this ratio can fractionate during chemical weathering when ^{234}U is more easily escaping into solution by the combined effects of (1) direct recoil of ^{234}Th near grain boundaries out of mineral and (2) preferential release from crystal lattices that are damaged by energetic α-decay (e.g. Bourdon et al., 2009; Chabaux et al., 2003, 2008; DePaolo et al., 2006, 2012; Osmond and Ivanovich, 1992 and reference therein). Therefore, natural waters (stream, spring, groundwaters, seawaters) are generally in excess of ^{234}U and have a (^{234}U/^{238}U) AR > 1 (Andrews and Kay, 1983; Camacho et al., 2010; Chabaux et al., 2003, 2008; Dosseto et al., 2008, 2012; Gryzmko et al., 2007; Osmond and Ivanovich, 1992; Paces et al., 2002; Pierret et al., 2012; Vigier et al., 2001, 2006). Consequently, (^{234}U/^{238}U) AR in superficial waters allow to trace river- flow patterns, and hydrological mixing (e.g., Chabaux et al., 2001; Durand et al., 2005; Maher et al., 2006; Osmond and 1982; Paces et al., 2002; Riotte et Chabaux, 1999).

In the present paper we focus on a small, more or less monolithic drainage basin, the experimental Strengbach catchment (Vosges mountains, NE France). Several studies have shown that the vegetation cover, the atmospheric deposition, the secondary minerals and the biological recycling play an important role in controlling the geochemical signatures of soil solutions (Brioshi et al., 2012; Lemarchand, E. et al., 2010, Lemarchand, D. et al., 2012; Prunier, 2008; Stille et al., 2006, 2009, 2011, 2012). However, soil solution contributions to the outlet can be variable; for instance, it represents 5 to 20 % for the Ca, depending on the type of vegetation or soil (Cenki Tok et al., 2009).

A previous U isotope study performed on waters from the Strengbach streamlet shows a decrease of the (^{234}U/^{238}U) AR from 1.02 to 0.96 when the discharge of the stream increases (Riotte and Chabaux, 1999). Such an isotopic evolution has been interpreted as mixing between a water body enriched in ^{234}U which weathered the granitic bed rock at secular equilibrium, and waters with a (^{234}U/^{238}U) AR below unity representing a mobilization of U from material that has already been weathered. Similarly, the streamlets ^{87}Sr/^{86}Sr isotope ratios collected during low flow periods have less radiogenic Sr isotope ratios than during high water flow periods (Aubert et al., 2002). These variations have been explained by important contributions of waters from the deep soil profile during the recession stage but also by the relative importance of waters coming from distinct distributive areas such as the opposite slopes or the saturated area of the catchment.

In order to define more precisely temporal and spatial variations of the hydrochemistry of the streamlet and the different springs and to evaluate the major and trace element sources and the processes controlling this element supply to the freshwaters, additional (^{234}U/^{238}U) AR, ^{87}Sr/^{86}Sr isotopic ratios and major and trace element concentrations were analyzed in the different source waters collected during two different hydrological seasons (2004–2006) and compared to those of the streamlet waters.

2 Site description

The Strengbach catchment is a small granitic watershed (80 ha) where meteorological, hydrological and geochemical data are recorded since 1986 (Observatoire

Hydro-Géochimique de l'Environnement; OHGE; http://ohge.u-strasbg.fr). The first studies were performed in order to understand the impact of acid rain on the forested ecosystem (Dambrine et al., 1991, 1992a, b; Probst et al., 1990, 1992a, b). The catchment is situated in the Vosges Mountains (NE France) at altitudes between 880 and 1150 m (a.m.s.l.) and has strongly inclined slopes (mean 15°; Fig. 1).

The climate is temperate oceanic mountainous (mean annual temperature of 6 °C; mean monthly temperature range from −2 to 14 °C) with an average rainfall of 1400 mm yr^{-1} (ranging between 890 and 1630 mm yr^{-1} over the period 1986–2006) and with snowfall during 2–4 month yr^{-1} (Probst and Viville, 1997; Viville et al., 2012; OHGE Data). The mean annual runoff for the same period is of 853 mm (26.9 $\mathrm{L\,s^{-1}\,km^{-2}}$) and ranges from 525 to 1147 mm over 1986–2006 (Ladouche et al., 2001; Probst and Vivile, 1997; OHGE data). The evapotranspiration (ETP) has been evaluated to be about 40 % on the site (Aubert, 2001; Probst et al., 1992).

The bedrock is mainly composed of a Hercynian base-poor granite (332 ± 2 Ma) (Boutin et al., 1995), with low Ca and Mg contents (less than 1 % for both); it suffered different degrees of hydrothermal alteration some 180 Ma ago (Fichter et al., 1998). In addition to the granite, which is strongly hydrothermally altered on the northern slope and comparatively weakly altered on the southern slope, small microgranite and gneiss bodies outcrop at the southern and northern slopes (Fig. 1) (El Gh'mari, 1995; Fichter et al., 1998). The gneiss is enriched in Mg mainly because of the presence of biotite and chlorite (El Gh'mari, 1995; Fichter, 1997). Hydrothermal processes caused the alteration and transformation of albite, K-feldspar and muscovite into fine-grained illite and quartz; biotite and albite disappeared to a large extend. The strongly altered granite (on the northern slope) is characterized by larger amounts of quartz, clays and Fe-oxydes, small amounts of apatite (< 1 %), and by higher Mg but lower Ca, K and Na contents than the less altered granite at the southern slope (El Gh'mari, 1995; Fichter et al., 1998). The soils are brown acidic to ochreous brown podzolic and are generally about 1 m thick. They are very coarse grained, sandy and rich in gravel (Fichter et al., 1998). The brown acidic soils are mainly located on the northern slope and are characterized by higher clay contents, lower K-feldspar, lower albite, higher cation exchange capacity (CEC), lower pH and lower organic matter content than the ochreous brown podzolic soils, which are mainly located on the southern slope (Fichter, 1997; Fichter et al., 1998). A sandy saprolite separates soil and granite. Its thickness varies between 1 and 9 m; on the southern slope it is generally thicker (El Gh'Mari, 1995) with the most important thickness in the depression zone near the four springs CS1 to CS4. The forest covers 90 % of the area and corresponds to about 80 % spruce (mainly *Piceas Abies L.*) and 20 % beech (*Fagus Sylvatica*). The catchment contains 10 different springs feeding the Strengbach streamlet (Fig. 1).

The catchment is situated in a remote area lacking direct industrial activities. Nevertheless, atmospheric pollution occurs in many forms (acidic deposition, O_3 pollution or as atmospheric dust deposition). The forestry has increased the proportion of spruce with especially dense spruce plots planted between 1890 and 1960. The site is well equipped for sampling of atmospheric depositions and spring and stream waters at the whole catchment scale.

For this study, the stream and the different springs of the catchment were collected at various hydrological periods with high and low water levels during a two years period (2004–2006) in order to obtain a precise chemical and isotopic signature of the different sources in this hydrological system (Fig. 1). Four springs were collected at the southern slope (CS1, CS2, CS3 and CS4). CS1 and CS3 are the deepest (up to 4 m depth) whereas CS2 and CS4 are both superficial springs. The springs SG, ARG, RH, BH, CS_3 and CS4 are located on the northern slope and the springs CS1, CS2, SH and RUZS emerge at the southern slope. The spring RUZS is situated in the humid zone at the bottom of the catchment near the outlet (saturated area, Fig. 1) and covered by dense grass vegetation. In addition rain (bulk precipitation) and throughfalls were collected using rain collectors and gutters, respectively.

3 Analytical procedures

The different spring waters were collected every 6 weeks during 2 years unless the springs were dry or under snow. The waters were collected in clean polyethylene (HDPE) bottles (250 mL for major element analysis and 1 L for isotope and trace element analysis) and filtered the same day through a 0.45 µm pore diameter membrane (Millipore ester cellulose, 142 mm diameter). Before, the HDPE bottles were washed with HCl 10 % (24 h contact) and then rinsed with MilliQ deionised water. The filtrated waters for trace element and U-Sr isotopic composition determinations were acidified with 250 µL of ultrapure HNO_3 13 M and then stored in a cold room at 5 °C.

The pH were measured just after filtration using a pHM210 MeterLab (Radiometer analytical) with an Mettler HA405-DXKS8 electrode and calibrated with standard buffer solutions (pH 4.00 and 7.00 at 25 °C). The precision of the pH measurement was ±0.02 units. The electrical conductivity and the alkalinity were determined respectively using a CDM210 MeterLab (radiometer analytical) with an CDC 745-9 electrode (precision 0.1 $\mu S\,cm^{-1}$) and with 716DMS Titrino (Metrohm; precision of 0.01meq L^{-1} – Acid/base titration, Gran method).

The major element contents were determined by Ionic chromatography, atomic absorption, colorimetry and ICP-AES and the trace element concentrations were determined by ICP-MS (Pierret et al., 2010; Chabaux et al., 2011). The analytical uncertainty of the determinations of the major cations and anions in solution (by atomic absorption and ionic chromatography Dionex, 4000 I) is ±2 %. The uncertainty on the major element concentrations such as Fe, Al, Mn and Si (by ICP-EAS, Jobin Yvon 124, at a precision of ±2 %) is 5 %, and that of the trace element concentrations (by ICP-MS, VG Plasma Quad; Thermo Electron) is ±5 %. The dissolved organic carbon (DOC) was determined using an organic carbon analyser (Shimatzu TOC-5000A) with an uncertainty of 5 to 10 %. The accuracy of the analysis was assessed by regular analysis of the SLRS-4 riverine standards.

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The Sr isotopic ratios were determined by thermo-ionisation mass spectrometry on a multi-collector VG-Sector mass spectrometer. Sr was extracted by standard procedures (Steinmann and Stille, 1997; Lhad Geagea et al., 2008; Clauer et al., 2009; Pierret et al., 2010). The routinely measured NBS 987 standard yield an average $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.71026 ± 0.00002 (2 s) for 10 determinations during the course of this study. The U isotope ratios were analysed on a TRITON Thermofinnigan mass spectrometer after separation and purification of U by anionic exchange chromatography (resin AG1X8, 200–400 mesh) following the classical technique used in the lab (e.g. Chabaux et al., 1997; Pelt et al., 2008; Pierret et al., 2012). During this study (2006–2008) the reproducibility of the U isotopic analyses was tested with the HU1 standard which yield an average value of 0.999 ± 0.004 (2σ) ($n = 27$). The analytical error for the ($^{234}\text{U}/^{238}\text{U}$) activity ratio is ±0.5 % (2σ).

4 Results

Previous studies performed on the Strengbach watershed mainly focused on the geochemical and isotopic variations of dissolved loads of the stream waters collected at its outlet. The new results (Tables 1 and 2) yield a first complete dataset of the spatial variability of major and trace element concentrations as well as Sr and U isotope ratios of the spring and streamlet waters emerging on the Strengbach watershed. The data also allow us to present the geochemical variability of the source as well as stream waters at the outlet of the watershed over the period 2004–2006, that is to say during two hydrologic cycles.

4.1 The major and trace element data

Among the spring and stream waters the pH, alkalinity, DOC, TDSw (total dissolved solids, Table 1), TDS-Ca (total dissolved solids-cation; Table 1) and conductivity are highly variable and range respectively from 5 to 6.85, from 0 to 0.16 meq L^{-1}, from

0.42 to 11.6 ppm, from 10.3 to 26.8 mgL^{-1}, from 3.87 to 9.05 mgL^{-1}, and from 13.2 to 60.3 µScm^{-1} (Table 1). The pH is well correlated with alkalinity and TDS-Ca, Ca/Na and relatively well with Mg/Na (Fig. 2). The range of variations of the major element concentrations at the watershed scale can be important but clearly depends on the chemical elements and the physico-chemical parameters. For the cation concentrations the variation at the watershed scale reaches about one order of magnitude for Mg, but only 20 to 30 % for Na concentrations. At the watershed scale, the most discriminating cation is Mg. SH and CS1 sources are marked by weakest Mg (and Ca) and the SG source by highest concentrations (Table 1). In addition, as illustrated by Ca/Na, Mg/Na, K/Na, Sr/Na and H_4SiO_4/Ca concentration ratios, the different springs are not only marked by different mean major element concentrations (2004–2006 period) but also by different elemental ratios (Fig. 3).

The data points of the different sources define linear trends with slopes different from each other (Fig. 3). The variation of the Ca/Na and Mg/Na ratios are much larger at the watershed scale than at the scale of a single spring. On the basis of the above data a clear distinction is possible between the spring waters from the northern slope (SG, RH, ARG, CS3, CS4 and BH) and those from the southern slope (CS1, CS2, SH and RUZS), the former being characterized by higher pH, alkalinity, conductivity TDSw and Ca/Na, K/Na and Mg/Na ratios than the latter (Figs. 2 and 3). In addition to the spatial variations, the chemical signatures of waters also show temporal variations. These are strongest for the most DOC enriched sources (RUZS, SH) and for the stream at the outlet (RS).

The Fe, U and DOC concentrations vary strongly in the different spring waters (Fig. 4). For some springs with high DOC concentrations (SH, BH, RUZS), U concentrations are correlated with dissolved organic carbon and Fe concentrations, whereas for the others (CS1, CS2, CS3, CS4, RH, ARG) no clear correlation are recognizable. Nevertheless, the later are characterized by large variations of U and Fe concentrations despite their low DOC contents (Fig. 4).

4.2 Sr and U isotope data

The $^{87}Sr/^{86}Sr$ isotopic composition values of the different spring waters are highly variable and range between 0.72206 (RH) and 0.72801 (SH) with an average Sr isotopic composition for the stream at the outlet of 0.72573 (Fig. 5, Table 1). The data show a clear relationship between the Sr isotopic signature and the geographical location in the watershed; the springs from the northern slope are characterized by lower $^{87}Sr/^{86}Sr$ ratios and higher Sr concentration (Fig. 5).

As shown in Fig. 6, the variation range of ($^{234}U/^{238}U$) AR in the source waters is much larger than that of the streamlets waters at the outlet. The U AR range from 1.112 (BH) to 0.819 (CS3); the average ($^{234}U/^{238}U$) AR for the stream at the outlet is 1.104. Among the 9 springs analyzed, 8 of them have unusual low ($^{234}U/^{238}U$) AR < 1. In addition, and to the best of our knowledge, these values are the lowest ever published before for superficial waters. Indeed, the U AR measured in world surface rivers or groundwaters have generally ($^{234}U/^{238}U$) > 1 (see introduction and citations therein).

In contrast to Sr isotopic compositions (Fig. 7) or chemical concentrations (Fig. 3) ($^{234}U/^{238}U$) AR of a single source do not significantly vary over the period 2004–2006 (Fig. 7). Finally, $^{87}Sr/^{86}Sr$ and $^{234}U/^{238}U$ AR of the source waters are not correlated with each other and in contrast to the Sr isotopic compositions or chemical concentrations (Fig. 6) there is no clear distinction between the U AR of the springs from the southern and northern slope. In the Strengbach watershed there is a clear increase of the U activity ratio of the source waters when the altitude of the spring decreases in the watershed, as also observed in another small granitic watershed in the Vosges Mountain, the Ringelbach watershed (Schaffhauser et al., 2014). But at the difference of the Ringelbach catchment, where the U activity ratios in the spring waters are above 1, in the Strengbach cachtment the U activity ratios of spring waters are ≤ 1 for all sources but one (i.e., BH).

5 Discussion

5.1 Geochemical and Sr isotopic characteristics of the spring waters

As shown in the result section, the chemical characteristics of the sources are marked by an important spatial variation with in particular a clear distinction between the springs from the northern and the southern slope (Fig. 3). It appears that the Ca/Na, Mg/Na, K/Na and Sr/Na concentration ratios are neither rainwater nor throughfall controlled. Indeed rainwater and throughfall show rather large variations of their Ca/Na, Mg/Na, K/Na or Sr/Na ratios (throughfall: Ca/Na: 0.9–2.1; Mg/Na: 0.3–0.6; K/Na: 0.6–0.9; Sr/Na: 0.02–0.07) and do not plot at one of the extremities of the correlations. Mass balance calculations show that the atmospheric input (including rain and througfalls) corresponds to various proportion of the exportation flux at the watershed scale, depending on type of element, as for example 2 %, 8 % or 19 % for Si, U or Sr respectively (Table 3).

Similarly, the observation of a clear increase of the Sr isotope ratios with increasing discharge towards values different from those of rainwater and/or throughfall Sr isotopic composition values (^{87}Sr/^{86}Sr ratios of 0.71110, 0.71327 and 0.71293 for rain, throughfall under spruces and throughfall under beeches respectively) implies that rainwater or througfall cannot be a significant source of cation fluxes in the spring waters (Figs. 7a and c and 13).

Therefore, chemical differences among the sources of the Strengbach watershed have to be interpreted in terms of variations in the nature or in the intensity of water-rock interactions occurring from one source to another or in the intensity of the interactions between different water reservoirs. This interpretation is entirely consistent with the correlations observed for the spring waters at the scale of the watershed between the alkalinity, TDSw and their pH, since consumption of H$^+$ during silicate weathering increases pH and alkalinity. Thus, from these data it appears, that the spring waters from the northern slope with higher total dissolved solid contents, higher alkalinity and pH values (SG, CS4, CS3, RH with BH having the highest values) are more involved in weathering reactions, or are subject to more intense weathering processes than spring waters from the southern slope (especially SH, RUZS and CS1).

The variation in the nature and/or intensity of the weathering fluxes carried by the different springs can be linked to specific lithological and mineralogical differences existing for the two hillsides of the Strengbach catchment. This is particularly obvious for the SG spring, which emerges near the top of the catchment, just under the banded gneiss, whereas the other sources emerge within the granitic environment (Fig. 1). In comparison with the granite, the gneiss has 4 to 5 times higher Mg concentrations due to important occurrences of biotite and chlorite (El Gh'mari, 1995). The Mg/Na and Mg/Ca elemental ratios are about 30 respectively 6 for the gneiss and range from 0.1 to 0.2 respectively 0.5 to 1 for the granite (El Gh'Mari, 1995; Fichter, 1997) (Table 1). Mg is also more concentrated in the gneiss-derived soils (0.60 to 0.81 wt.%), than in other soil profiles of the catchment (0.11 to 0.41 wt.%) (El Gh'Mari, 1995; Lefèvre, 1988). Similarly, the Ca/Na ratios of the gneiss (4.8) and the corresponding soils (0.3 to 4.6) are higher than those of the granite (0.19 to 0.25) or of the corresponding soils (0.06 to 0.4) (El Gh'Mari, 1995; Fichter, 1997) (Table 1). All these lithological and pedological characteristics easily explain why the SG spring waters are more concentrated in Mg and have higher Mg/Ca, Mg/Na and Ca/Na ratios than the other springs (Fig. 3).

The variation of the chemical data of the other spring waters emerging within the granitic environment might result from the specific characteristics of the two hillsides, which show different types and thicknesses of soils and saprolite and different degrees of hydrothermal alteration of the granitic bedrock (Lefèvre, 1988; Fichter, 1997; El Gh'Mari, 1998; see also geological setting). Indeed, the study of 13 weathering profiles from the whole Strengbach catchment point to important variations of the mineralogical composition of soils and bedrocks at the catchment scale (El Gh'Mari, 1995; Fichter, 1997; Aubert, 2001; Stille et al., 2009; Prunier, 2008). The soils from the northern slope are brown acidic and overlay a 0.5 to 4 m thick saprolite. At the southern slope, however, an ochreous podzolic soil type overlays a much thicker 4 to 9 m deep saprolite (El Gh'mari, 1995; Fichter et al., 1998). The bedrock from the northern slope was subjected to stronger hydrothermal alteration, which caused disappearance of albite and biotite, diminution of K-feldspar but an increase of quartz, clays and white mica contents and the occurrence of hematite (Bonneau, 1994; Fichter, 1997; El Gh'Mari, 1995). The hydrothermally strongly altered granite on the northern slope is characterized by generally higher Mg and lower Ca and Na contents than observed for the less altered granite on the southern slope (Fichter et al., 1998; El Gh'Mari, 1995). This could account for the comparatively higher Mg concentrations and Mg/Na ratios of the sources from the northern slope, but not for e.g. the higher Ca or K concentrations.

The ^{87}Sr/^{86}Sr ratios of springs from the southern slope (SH, CS2, CS1, RUZS) are, like the corresponding rocks and soils (Aubert et al., 2002) (Fig. 8), more radiogenic with lower Sr concentrations than those from the northern slope (BH, RH, SG, CS3, CS4) (Fig. 5). Thus, the Sr isotopic compositions of springs can be directly related to the signatures of the weathering profile and their geographical localization. But the mineral phases involved in the weathering processes and causing the geochemical characteristics of these superficial waters are still matter of discussion.

Based on Sr and Nd isotope ratios, Aubert et al. (2001) explained the isotopic signature of the Strengbach stream water by mixing of two isotopically different end-members: apatite and plagioclase. However, the Mg/Sr and Mg/Ca ratios of the waters cannot simply be explained by dissolution of apatite and plagioclase (Fig. 9a and b). In addition, biotite and muscovite have far too high Sr isotopic ratios (respectively 5.8 and 5.4; Aubert et al., 2001) and thus their contribution can be ignored. The clay fractions, extracted from the two weathering profiles at sites HP and VP (Prunnier, 2008) can represent an end-member able to explain the Sr isotopic composition as well as the Mg/Ca and Mg/Sr ratios of springs. In addition, the northern slope contains twice as much clay and especially more Mg-bearing smectite than those of the southern slope (Fichter et al., 1998; this study) which can explained why the springs for the northern slope are more radiogenic (Fig. 5a and b) with comparatively higher Mg/Ca and Mg/Sr ratios (Fig. 9a and b) than those from southern slopes, confirming the role play by clays.

Such an interpretation is consistent with results of numerical modeling, which indicates that precipitation/dissolution of more or less crystallized clay minerals (such as smectite) control the Mg concentrations and possibly the high Mg/Ca ratios in the source waters of the Strengbach watershed (Godderis et al., 2006, 2009). The same authors proposed that Mg^{2+} is controlled by smectites, Ca^{2+} by the dissolution of apatite and by smectite, and K^+ by smectite/illite precipitation and dissolution of K-feldspar. Interaction with clays might occur all along the circulation pathway of waters in soils, saprolite and in bedrock fractures. Recent studies in Mackenzie basin and Damma Glacier catchment confirm the importance of secondary mineral formation, especially montmorillonite in the control of chemical composition of stream at the watershed scale (Beaulieu et al., 2011; Hindshaw et al., 2011).

Thus, the variation of the current chemical compositions of the source waters in the Strengbach catchment possibly reflects dissolution/precipitation processes of secondary mineral phases like clay minerals. In such a model the generally low apatite-like Sr isotopic composition values of the source waters and comparatively high and not apatite-like Mg/Ca ratios can be explained by the fact that the Sr has not been remobilized by alteration of primary apatite but by weathering of secondary mineral phases, which integrated during an earlier stage of alteration and crystallization apatite-derived Sr. At this point we therefore propose that the alteration flux controlling the $^{87}Sr/^{86}Sr$ and Mg/Ca (resp Mg/Sr) variation in the sources is imposed by secondary minerals.

5.2 $^{234}U/^{238}U$ AR in spring waters

Observation of ($^{234}U/^{238}U$) AR < 1 in most of the spring and stream waters of the Strengbach catchment is unusual as river waters exhibit generally ^{234}U excess (e.g., Chabaux et al., 2003). Such U AR < 1 have already observed before for waters from the outlet of the Strengbach catchment (0.963 to 1.023) with a decrease of the U AR in the dissolved load when the discharge increases (Riotte et al., 1999). The authors explained this variation by the involvement of at least two different weathered end-members: a water body enriched in ^{234}U which weathered the granitic bedrock at secular equilibrium and a water with a U AR below unity representing mobilization of U from material that has already been weathered. Our study shows an even larger range of variation of the U AR among the different springs ranging from 0.819 (CS3) to 1.112 (BH) (Table 2).

The lack of correlation between (^{234}U/^{238}U) AR and ^{87}Sr/^{86}Sr isotopic composition or chemical values (Fig. 6a and b) show that AR are not simply lithology controlled.

The mechanisms classically involved to explain (^{234}U/^{238}U) AR > 1 in natural waters are linked to the recoil process associated to the decay of ^{238}U: (1) due to alpha recoil when ^{238}U decays to ^{234}Th, it can be ejected out of a grain into the fluid if the distance to the grain boundary is smaller than the recoil range of ^{234}Th (∼ 30 nm; DePaolo et al., 2006); the ^{234}Th decays then rapidly to ^{234}U (^{234}Th half-life is 24 days); (2) α-particles emitted during radioactive decay damage the crystal lattice of mineral grains and the recoil nuclide is subsequently easily mobilized out of the damaged site. As a consequence, the daughter nuclide ^{234}U is preferentially leached relative to the parent ^{238}U during weathering. Thus, natural waters with (^{234}U/^{238}U) AR < 1 most likely correspond to environments, which have already experienced a loss of ^{234}U.

In a first and simple approach one might interpret the U AR < 1 in the Strengbach source waters by circulation through already weathered soils. However, chemical flux balance calculations show that the annual U fluxes from the soils under spruces or beeches represent at maximum about 8 % or 22 %, respectively, of the annual U flux at the outlet (Table 3). At the same time, the U concentrations in the different springs can reach in average 0.345 ppm whereas it ranges only between 0.011 to 0.023 ppm (factor of 30 to 15 lower) in the deep soil solutions of the two experimental plots (Table 2). These two observations indicate that the U in the springs originates from circulations and interactions, which occurred below the soil horizons.

The relationship between the U AR and the altitude of the springs (Fig. 10) indicates that the springs from both slopes with the lower U AR (CS1, CS2, CS3, CS4) are located at higher altitude and circulate in zones where the saprolite reaches 7 to 9 m depth (El'Ghmari, 1995) than springs with high U AR. The spring BH, with the highest

U AR is located at the bottom of the watershed where the saprolite layer reaches less than 1.5 m thickness (Fig. 1). Also RUZS was taken at low altitude (950masl), but drains the whole wetland and, therefore, integrated an intermediate U AR. Thus, a possible scenario explaining the (^{234}U/^{238}U) AR of the spring waters is that BH like sources are closer to the "fresh" granite and reflect meteoric alteration of fresher rock material at secular equilibrium. CS1, CS3, CS2, CS4 and SH sources, by contrast, drain thicker saprolite profiles and/or less fresh granite and, therefore, their low AR may point to the mobilization of U from mineral phases whose outermost surfaces have already been depleted in ^{234}U due to previous water-rock interactions (old saprolite where the pool of excess ^{234}U has been exhausted). We therefore propose that the ^{234}U/^{238}U AR in the catchments spring waters can be interpreted as a function of water pathways. The sources emerging at high altitude, with AR $<$ 1, have circulated through already weathered horizons (saprolite, fractured bedrock depleted in ^{234}U, i.e., with U AR $<<$ 1), whereas the springs emerging at the bottom of the watershed have U AR $>$ 1 because of the interaction with fresher mineral phases. Therefore, U disequilibrium ratios can be a powerful tool to study the water pathways. These preferential flow paths cross more or less weathered materials implying various (^{234}U/^{238}U) AR for the corresponding springs.

This interpretation is in agreement with a granite leaching experiment under continuous flow through a reactor (Andersen et al., 2009). It is indeed shown that during the experiment (1200 h) there is a clear trend of variation of the U activity ratios in the outflowing waters, with (^{234}U/^{238}U) AR $>$ 1 at the beginning of the experiment and a minimal value of 0.9 after 650 to 700 h; then the AR increased up to 0.95. The values suggest that at the beginning of the experiment high exposure of fresh material promotes direct recoil of ^{234}U into water and potentially enhances preferential release of ^{234}U from damaged lattice sites. However, since there was no renewal of material, because the excess ^{234}U constitutes a finite pool of easy leachable ^{234}U, the (^{234}U/^{238}U) values become lower than unity when this pool is used up.

Similarly, the observed ($^{234}U/^{238}U$) AR < 1 in Strengbach springs might indicate that the rate of production of ^{234}U excess (by direct recoil and preferential release) is lower than the rate of renewal of material. This can be explained by continuous preferential water circulation along fractures (Le Borgne et al., 2007), in an old weathered mineral surface where the production of ^{234}U excess is supposed to be low.

However, the springs emerging at lower altitude (mainly BH and to a lesser extend RH), with ($^{234}U/^{238}U$) > 1, circulate through fresher granite where α-recoil tracks have direct contact with the outer mineral surfaces and thus with fresh mineral phases (Andersen et al., 2009).

At this point it is interesting to note that in a neighbored granite catchment (Ringelbach watershed) all the sources only display U AR > 1 (Schaffhauser, 2013; Schaffhauser et al., 2014). This small catchment located in the Vosges massif at altitudes between 750 and 1100 m (0.36 km^2) also consists of Hercynian granite capped in its upper part by residual Triassic sandstones (Schaffauser et al., 2014).

Plotting the U AR of springs of the both watersheds vs. alkalinity and pH (Fig. 11) one observes a pretty good correlation where springs with highest U AR are characterized by highest alkalinity and pH values. These two parameters can be considered to reflect the intensity of weathering and water/rock interactions, meaning that the waters from the Ringelbach watershed are characterized by more intense weathering. Only SG spring from the Strengbach catchment shows a slightly different behavior because it originates from a gneiss and not a granite body (see Sect. 5.1). The modeling of chemical composition of the waters from the Ringelbach catchment implies dissolution of primary minerals of granite and precipitation of secondary phases such as clays but no dissolution of clays (Schaffauser, 2013); this is in contrast to Strengbach catchment. Thus, we suggest that the waters with the lowest U AR correspond to less intense weathering in an already rock altered system with only few fresh primary mineral phases whereas higher U AR correspond to more intense weathering for waters circulating for example in fresher bedrock. In this way, the weathering history can be older in the Strengbach watershed than in Ringelbach watershed, which is consistent with the fact that Triassic sandstones still cover the granite in the Ringelbach catchment.

It is striking that the BH waters from Strengbach watershed plot in between the data from the Strengbach and Ringelbach watershed (Fig. 11a and b) and are characterized by the highest pH (6.7) and alkalinity despite the relatively high DOC content (2.27 ppm), which usually increases the acidity of solution. If we consider that the proton inputs due to atmospheric deposition or biological activity are homogeneous at the watershed scale, then the variation of pH in the different springs only reflects water/rock interactions and the consumption of protons by dissolution reactions. The high pH and alkalinity observed for the BH source are in this case consistent with the fact that its water has interacted with fresher bedrock; this further implies a stronger weathering intensity and higher dissolution rate of smectite along the pathway of this source water.

In such a scenario, the relationship observed between ($^{234}U/^{238}U$) AR and Mg/Ca ratios (Fig. 12) would indicate that the intensity or the nature of water reactions controlling the Ca-Mg budget of these waters, namely the dissolution/precipitation reactions of Mg- or Ca-smectites (see discussion in Sect. 5.1), would be clearly dependent on the weathering level of the saprolite/bedrock system. This is consistent with the fact that (1) smectite occurs along the weathering profile and even in deep weathering horizons (Fichter et al., 1998) and (2) the reactivity of secondary phases like smectite control the chemistry of Mg and Ca in streamwater (this study, Godderis et al., 2006, 2009). In addition, dissolution of clays implies an increase of Mg/Ca ratios in water (Fig. 9b). Thus, the relation between U AR and Ca/Mg ratios for the Strengbach springs reflects nothing else than the degree of alteration of the source rock being in contact with the waters: at low altitude the material is fresher, the weathering intensity is more important (higher pH and alkalinity) and thus causes higher Ca/Mg and U AR ratios in the waters than at higher altitudes.

5.3 Temporal variations of spring waters

The data obtained during 2 hydrological years allow for the analysis of the temporal variations of the springs (Fig. 3). The spring RUZS shows the largest variations, which can be explained by the fact that this spring, drains wetland (10 to 15 % of the whole catchment area) with fluctuations in the groundwater level and contributions.

The Sr isotopic compositions of single springs are correlated with discharge (Fig. 7a). In previous studies these variations have been interpreted by mixing of superficial (soil solution type) and deep (groundwater type) waters (Aubert et al., 2002). But, at the same time, the U AR show no temporal variation and, therefore, no relation with discharge (Fig. 7b).

Consequently, the U AR and Sr isotopic compositions are not correlated. Similarly, there is no correlation between U AR and geographical location and lithology (discussed in Sect. 5.2). In addition, the lack of temporal U AR variations indicates that the single springs are probably not the result of mixing of different waters. In the same way, the lack of correlation between discharge and DOC or NO_3, but also the majority of major and trace element concentrations suggests that the variation of chemical composition of spring waters cannot be explained by a simple variation of the contribution between different types of waters or as mixing between superficial waters (with high DOC, NO_3 concentrations for instance) and deep waters. At the same time, the lack of correlation between Sr isotopic compositions and concentrations for individual springs (Fig. 5a) confirms that the temporal variations of spring waters cannot simply be explained by mixing between two end-members (e.g. superficial and deep waters). The lack of variation of U AR of the individual springs with changing discharge (Fig. 7) during 2 years further suggests that the water pathways are the same whatever the hydrological conditions. Under these conditions, the water did not interact with new fresh material but rather with minerals having experienced at their surface a prior loss of ^{234}U from damaged lattice sites (Andersen et al., 2009). In such a fractured bedrock system, the water flow is often reduced to only a few main flow paths that control most of the hydrological response of the aquifer (Le Borgne et al., 2007). These preferential flow paths along constant fractures in the bedrocks might explain the over time homogeneous (^{234}U/^{238}U) AR of the different analyzed spring waters.

In contrast, there is a correlation between discharge and ^{87}Sr/^{86}Sr ratios for each single spring (Fig. 7b). When increasing discharge the Sr isotopic composition increases as well, whereas the Si concentrations and alkalinity decrease (Fig. 13).

Different Si concentration–discharge relationships have been observed in several catchments and three different types have been identified: type 1 when Si concentration decreases with discharge; type 2 when Si concentration remains constant and type 3 when Si concentration remains constant until a threshold in discharge is exceeded (Godsey et al., 2009; Maher, 2011). The springs from the Strengbach watershed belong to the type 1 which are explained by average residence times shorter than required to approach chemical equilibrium. Thus, the chemistry of waters could vary entirely as a function of the nature of subsurface flow paths and the global solute fluxes depend strongly on the geometry, relief, runoff and permeability of basins (Maher, 2011). In addition, the variation of the Sr isotopic compositions with discharge suggests that the source of Sr changes with changing hydrological condition; this confirms again that the temporal variation cannot be explained by a mixing process but possibly also by changing residence times of fluid and/or flow rate which according to Maher (2010) have an important impact on the weathering rates. This is in accordance with the hypothesis of preferential flow pathways through fractures for the water circulation in the basin.

In addition, modeling studies have shown that precipitation/dissolution process of secondary phases control the dissolved Si export in stream waters (Godderis et al., 2006; Beaulieu et al., 2011). Thus, the decrease of Si concentration with increasing discharge can be explained by a change in the ratio between dissolution and precipitation of clays (see also Sect. 5.2). We propose that at high discharge the water is undersaturated for clay precipitation (lower Si concentration) causing a more important contribution by dissolution of clays as implied by the higher Mg/Ca (see Sect. 5.1) and Sr isotopic ratios (Fig. 12c). Thus, in agreement with Maher (2011), our study confirms that hydrological properties limit the solute fluxes carried by rivers and physic-chemical conditions.

5.4 The chemical and isotopic signatures of the waters at the Strengbach outlet

The stream at the catchments outlet shows with increasing discharge increasing $^{87}Sr/^{86}Sr$ and decreasing alkalinity, pH, H_4SiO_4, and ($^{234}U/^{238}U$) AR (Fig. 14a–e). The important point is that the variation of U AR observed at the outlet (Fig. 14e) can only be explained by a change in the discharge contribution of the different springs because the U AR of single springs are constant with time (Fig. 7). When the discharge increases, the U AR values tend towards 0.95, which is close to the ($^{234}U/^{238}U$) AR of the spring from the saturated area (RUZS) (Figs. 6 and 14). Previous papers proposed that during storm event, the contribution of the small saturated zone could reach up to 30 % of the runoff (Idir et al., 1999; Ladouche et al., 2001). Similarly, the increase of the Sr isotopic composition with increasing discharge points to the important contribution of RUZS to the streamlet during high discharge events (Fig. 14d).

However, during the lowest discharge, the U AR of the stream at the outlet is > 1 (max. 1.023). These higher values can only be explained by a more important contribution of the spring BH from the northern slope which is the only one with a U AR > 1 (average: 1.103; Table 1; Fig. 14). Other parameters such as H_4SiO_4, pH and alkalinity confirm the important contribution of the BH spring to the streamlet during low discharge (Fig. 14). Similarly, the position of the RUZS spring with the low pH, alkalinity and silica concentrations (Fig. 14) confirms its important contribution during high discharge. But also the fact that the Sr isotopic composition of the stream at the outlet decreases with decreasing discharge is in accordance with a more important contribution of the less radiogenic springs from the northern (e.g. BH) (Fig. 14) than from the southern slope (Fig. 5).

6 Conclusion

The study shows that the small and more or less “monolithic” Strengbach catchment drains different sources and streams with very different isotopic and geochemical signatures. This heterogeneity is mainly linked up with:

- the nature of the bedrock (gneiss, more or less altered granite),
- the specific mineralogical composition and thickness of the substratum (soil, saprolite, bedrock),
- the degree of hydrothermal alteration: the bedrock granite from the northern slope is hydrothermally much more altered (less biotite, apatite and albite, more clays) and, therefore, the sources draining this slope have higher TDSw-, pH values, higher Ca, K, Mg concentrations and lower $^{87}Sr/^{86}Sr$ ratios than sources draining the southern slope,
- the water flow is probably controlled by pathways through main fractures, as it is generally the case in fractured granite systems.

This study has also shown, that there is an important decoupling between chemical composition on the one hand and the $^{87}Sr/^{86}Sr$ ratios and ($^{234}U/^{238}U$) AR on the other hand. The Sr isotopic compositions of the source waters are generally thought to be the result of alteration of primary mineral phases such as apatite. However, the low apatite-like Sr isotopic composition but comparatively high and not apatite-like Mg/Ca ratio cannot simply be derived from apatite dissolution; nevertheless, they might originate from alteration of a secondary mineral phase like clay minerals, which integrated during their formation an apatite-derived Sr isotopic composition from the solution. The dissolution and precipitation dynamics of secondary phases, especially clays such as montmorillonite, seem to control the mobility of Si, Ca or Mg and, therefore, emphasize the key role of the clays reactivity in the biogeochemical transfer of especially nutrient elements like Ca and Mg.

Different processes control the variation of the U AR. Springs at high altitude with U AR < 1, which is uncommon for surface waters, have circulated through already weathered bedrock (thick saprolite and fractured rock) and have interacted with already weathered surface minerals. These values are due to strong ^{234}U depletion during predating alteration processes of the bedrock granite. At the opposite, springs emerging at the bottom of the watershed have U AR > 1 because of interaction with fresher materials.

The lack of variation of U AR of the individual springs with changing discharge during 2 years suggests that the water pathways are the same whatever the hydrological conditions and that there is no interaction between the different source waters.

It appears that the (^{234}U/^{238}U) AR is a very important tracer for studying and deciphering the contribution of the different source fluxes at the catchment scale because this unique geochemical parameter is different for each individual spring and at the same time remains unchanged for each of the springs with changing discharge and fluctuating hydrological conditions. Without this parameter it would not have been possible to decipher the real contribution of the different water masses, especially that of the BH spring at low discharge conditions.

Thus all these observations converge toward the same functioning:

- The proportion of the contributions of the different springs to the stream at the outlet varies in function of the hydrological conditions; the variable contributions of the different sources carrying different geochemical signatures define the signature of the waters at the Strengbach outlet.
- During high flow events, the contribution of the saturated area (RUZS) to the streamlet increases.
- At low discharge, the contributions of springs from the northern slope become important (e.g. BH).

The U-Sr isotope study, combined with physico-chemical investigations of the waters offered the opportunity to better understand the processes causing the hydrochemical signature and its temporal variation in each of the individual springs and in the stream waters at the outlet of the small catchment. Indeed, this work points not only to the importance of investigate larger time intervals including one total or even two hydrological cycles but also the interest of geographically enlarged studies including several springs; punctual or only outlet observations will not allow for understanding of the complex functionning of a watershed.

The study further highlights the important impact of different and independent water pathways in fractured granite controlling the different geochemical and isotopic signatures of the waters.

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Table 1a. Chemical compositions of spring and stream waters, open field precipitation, througfalls under spruces (PL5) and beeches (PLH). The total dissolved solids (TDS_W) have been calculated from the concentrations of the major dissolved elements (cations, anions and silica) and are expressed in $mg\,L^{-1}$, as calculated for several watersheds (e.g., Gaillardet et al., 1999). Another parameter, called here TDS-Ca (= Ca + Mg + Na + K + SiO_2 + Fe) has been calculated as proposed by Zakharova et al. (2007) and reflects the silicate weathering.

	date	Discharge $L\,s^{-1}$	pH	Cond. $\mu S\,CM^{-1}$	Na^+ $mmol\,L^{-1}$	K^+ $mmol\,L^{-1}$	Mg^{2+} $mmol\,L^{-1}$	Ca^{2+} $mmol\,L^{-1}$	Alc $meq\,L^{-1}$	Cl^- $mmol\,L^{-1}$	NO_3^- $mmol\,L^{-1}$	SO_4^{2-} $mmol\,L^{-1}$
Spring Collector CR	12 Jul 2004		5.66	35.5	0.092	0.025	0.018	0.07	0.049	0.057	0.058	0.066
CR	28 Sep 2004		5.74	34.9	0.096	0.02	0.018	0.074	0.05	0.053	0.061	0.066
CR	2 Nov 2004		5.84	30.3	0.083	0.02	0.019	0.077	0.041	0.053	0.073	0.062
CR	13 Dec 2004		6.50	33.4	0.089	0.02	0.018	0.074	0.041	0.055	0.066	0.066
CR	24 Jan 2005		6.41	32.0	0.082	0.018	0.018	0.073	0.032	0.052	0.066	0.063
CR	29 Mar 2005		5.91	32.1	0.079	0.019	0.018	0.072	0.033	0.051	0.063	0.064
CR	3 May 2005		5.92	31.3	0.085	0.019	0.017	0.069	0.039	0.051	0.058	0.062
CR	31 May 2005		6.17	31.5	0.085	0.018	0.018	0.071	0.041	0.050	0.057	0.063
CR	11 Jul 2005		6.33	30.5	0.086	0.018	0.016	0.068	0.045	0.047	0.052	0.061
CR	22 Aug 2005		6.49	29.9	0.092	0.018	0.017	0.07	0.041	0.051	0.063	0.063
CR	3 Oct 2005		6.50	30.1	0.089	0.019	0.018	0.069	0.05	0.051	0.055	0.062
CR	7 Feb 2006		6.38	31.8	0.092	0.019	0.017	0.073	0.05	0.060	0.058	0.064
CR	3 Apr 2006		6.05	31.4	0.075	0.021	0.018	0.071	0.022	0.049	0.074	0.064
CR	10 Jul 2006		6.18	32.6	0.086	0.018	0.016	0.068	0.045	0.049	0.055	0.059
CR	21 Aug 2006		6.12	30.0	0.084	0.018	0.017	0.065	0.039	0.049	0.059	0.059
CR	2 Oct 2006		6.22	31.4	0.082	0.019	0.017	0.069	0.039	0.052	0.064	0.058
CR	22 May 2006		6.22	28.7	0.083	0.018	0.017	0.066	0.039	0.047	0.058	0.061
CR	Average		6.15	31.61	0.086	0.019	0.017	0.070	0.041	0.052	0.061	0.062
Spring CS1	12 Jul 2004	0.113	5.9	28.2	0.078	0.018	0.015	0.051	0.036	0.043	0.027	0.062
CS1	28 Sep 2004	0.148	5.82	26.8	0.078	0.014	0.016	0.053	0.035	0.037	0.029	0.061
CS1	13 Dec 2004	0.318	6.12	24.5	0.073	0.013	0.014	0.048	0.02	0.039	0.027	0.027
CS1	29 Mar 2005	1.156	5.22	25.2	0.067	0.014	0.014	0.044	0.008	0.04	0.035	0.061
CS1	3 May 2005	0.560	6.19	22.1	0.068	0.012	0.013	0.043	0.017	0.036	0.024	0.058
CS1	31 May 2005	0.268	6.33	24.0	0.072	0.014	0.014	0.051	0.035	0.036	0.022	0.057
CS1	11 Jul 2005	0.076	6.44	25.5	0.076	0.014	0.014	0.053	0.042	0.036	0.024	0.059
CS1	22 Aug 2005	0.110	6.40	24.4	0.079	0.014	0.015	0.055	0.043	0.037	0.029	0.061
CS1	3 Oct 2005	0.192	6.50	24.0	0.075	0.014	0.015	0.049	0.029	0.046	0.026	0.058
CS1	7 Feb 2006	0.165	6.05	25.1	0.081	0.015	0.014	0.053	0.038	0.041	0.027	0.06
CS1	3 Apr 2006	1.672	5.33	25.5	0.068	0.015	0.015	0.044	0.008	0.044	0.038	0.062
CS1	22 May 2006	0.349	6.10	22.1	0.072	0.013	0.014	0.045	0.022	0.036	0.028	0.058
CS1	10 Jul 2006	0.092	6.48	25.8	0.075	0.013	0.014	0.047	0.037	0.035	0.022	0.057
CS1	21 Aug 2006	0.658	6.02	25.8	0.071	0.014	0.014	0.046	0.018	0.04	0.032	0.056
CS1	2 Oct2006	0.635	5.85	25.7	0.071	0.013	0.014	0.044	0.014	0.044	0.033	0.057
CS1	Average		6.05	24.92	0.074	0.014	0.014	0.048	0.027	0.039	0.028	0.057

Table 1a. Continued.

	date	Discharge $L\,s^{-1}$	pH	Cond. $\mu S\,CM^{-1}$	Na^+ $mmol\,L^{-1}$	K^+ $mmol\,L^{-1}$	Mg^{2+} $mmol\,L^{-1}$	Ca^{2+} $mmol\,L^{-1}$	Alc $meq\,L^{-1}$	Cl^- $mmol\,L^{-1}$	NO_3^- $mmol\,L^{-1}$	SO_4^{2-} $mmol\,L^{-1}$
Spring CS2	12 Jul 2004	0.482	5.56	34.6	0.091	0.018	0.018	0.068	0.046	0.051	0.054	0.066
CS2	28 Sep 2004	0.535	5.58	34.4	0.094	0.018	0.019	0.07	0.048	0.052	0.058	0.064
CS2	13 Dec 2004	1.446	6.44	31.9	0.086	0.017	0.018	0.071	0.037	0.055	0.063	0.063
CS2	3 May 2005	2.500	6.23	28.8	0.078	0.016	0.017	0.067	0.037	0.05	0.05	0.06
CS2	31 May 2005	1.117	6.30	30.2	0.082	0.017	0.017	0.07	0.04	0.05	0.055	0.061
CS2	11 Jul 2005	0.246	6.27	30.5	0.087	0.016	0.017	0.067	0.042	0.049	0.054	0.06
CS2	22 Aug 2005	0.450	6.47	29.5	0.093	0.017	0.017	0.069	0.047	0.049	0.061	0.063
CS2	7 Feb 2006	0.678	6.24	32.3	0.092	0.019	0.018	0.069	0.047	0.055	0.06	0.062
CS2	22 May 2006	1.364	6.28	28.7	0.084	0.017	0.018	0.067	0.036	0.051	0.061	0.06
CS2	3 Apr 2006	7.156	6.04	31.2	0.073	0.018	0.018	0.073	0.031	0.049	0.067	0.064
CS2	10 Jul 2006	0.389	6.5	32.6	0.087	0.018	0.017	0.067	0.043	0.047	0.056	0.059
CS2	21 Aug 2006	2.978	6.3	33.1	0.084	0.017	0.018	0.068	0.039	0.056	0.063	0.058
CS2	2 Oct 2006	3.800	6.3	32.3	0.082	0.023	0.018	0.072	0.05	0.048	0.065	0.057
CS2	Average		6.19	31.55	0.086	0.018	0.018	0.069	0.042	0.051	0.059	0.061
Spring CS3	13 Dec 2004	0.265	6.65	36,00	0.097	0.022	0.017	0.083	0.051	0.05	0.071	0.071
CS3	29 Mar 2005	0.480	6.11	35.7	0.09	0.022	0.017	0.084	0.047	0.05	0.073	0.072
CS3	3 May 2005	0.408	6.42	33.6	0.094	0.021	0.017	0.083	0.052	0.051	0.067	0.069
CS3	31 May 2005	0.246	6.24	34.1	0.094	0.021	0.016	0.08	0.053	0.049	0.064	0.068
CS3	11 Jul 2005	0.089	6.31	32.9	0.091	0.02	0.015	0.077	0.05	0.047	0.056	0.065
CS3	22 Aug 2005	0.086	6.52	31.7	0.097	0.021	0.016	0.08	0.054	0.049	0.062	0.07
CS3	3 Oct 2005	0.181	6.58	33.1	0.096	0.022	0.016	0.079	0.054	0.05	0.065	0.068
CS3	7 Feb 2006	0.164	6.53	33.9	0.098	0.022	0.015	0.078	0.054	0.051	0.064	0.068
CS3	3 Apr 2006	1.222	6.22	33.4	0.084	0.021	0.017	0.082	0.044	0.048	0.074	0.067
CS3	22 May 2006	0.229	6.42	32.2	0.093	0.021	0.016	0.078	0.051	0.048	0.068	0.068
CS3	10 Jul 2006	0.109	6.55	35.6	0.092	0.02	0.016	0.078	0.055	0.047	0.057	0.066
CS3	21 Aug 2006	0.268	6.44	33,00	0.095	0.021	0.016	0.078	0.05	0.048	0.07	0.066
CS3	2 Oct 2006	0.445	6.40	36.5	0.094	0.021	0.017	0.082	0.051	0.05	0.08	0.065
CS3	Average		6.41	33.98	0.093	0.02	0.016	0.080	0.051	0.05	0.07	0.07
Spring CS4	13 Dec 2004	0.314	6.58	35.70	0.096	0.024	0.020	0.078	0.05	0.056	0.071	0.071
CS4	3 May 2005	0.427	6.30	30.40	0.085	0.021	0.017	0.070	0.04	0.051	0.062	0.062
CS4	31 May 2005	0.268	6.29	32.70	0.089	0.021	0.018	0.072	0.04	0.050	0.062	0.064
CS4	11 Jul 2005	0.121	6.39	33.60	0.094	0.021	0.018	0.075	0.06	0.051	0.059	0.064
CS4	22 Aug 2005	0.170	6.68	31.90	0.097	0.022	0.019	0.077	0.06	0.052	0.064	0.065
CS4	7 Feb 2006	0.213	6.45	34.30	0.100	0.027	0.017	0.073	0.06	0.054	0.065	0.066
CS4	3 Apr 2006	0.265	5.69	32.50	0.080	0.024	0.019	0.070	0.02	0.054	0.088	0.059
CS4	22 May 2006	0.309	6.37	31.80	0.092	0.022	0.018	0.073	0.05	0.050	0.070	0.065
CS4	10 Jul 2006	0.157	6.60	35.50	0.092	0.021	0.018	0.073	0.06	0.050	0.055	0.064
CS4	21 Aug 2006	0.462	6.47	33.20	0.091	0.024	0.018	0.070	0.05	0.050	0.071	0.060
CS4	2 Oct 2006	0.772	6.50	33.50	0.087	0.024	0.018	0.070	0.05	0.054	0.065	0.061
CS4	Average		6.39	33.19	0.091	0.02	0.02	0.07	0.049	0.05	0.07	0.06

Table 1a. Continued.

	date	Discharge $L\,s^{-1}$	pH	Cond. $\mu S\,CM^{-1}$	Na^+ $mmol\,L^{-1}$	K^+ $mmol\,L^{-1}$	Mg^{2+} $mmol\,L^{-1}$	Ca^{2+} $mmol\,L^{-1}$	Alc $meq\,L^{-1}$	Cl^- $mmol\,L^{-1}$	NO_3^- $mmol\,L^{-1}$	SO_4^{2-} $mmol\,L^{-1}$
Spring BH	2 Feb 2004	nd	6.60	36.50	0.089	0.024	0.040	0.087	0.06	0.058	0.090	0.071
BH	12 Jul 2004	0.388	6.78	34.50	0.088	0.014	0.034	0.074	0.14	0.033	0.014	0.061
BH	28 Sep 2004	0.450	6.79	42.10	0.100	0.029	0.042	0.095	0.16	0.066	0.039	0.062
BH	13 Dec 2004	1.241	6.76	41.20	0.092	0.024	0.042	0.090	0.09	0.061	0.074	0.074
BH	7 Mar 2005	0.690	6.63	38.80	0.088	0.024	0.041	0.087	0.07	0.061	0.077	0.073
BH	29 Mar 2005	3.000	6.66	37.30	0.086	0.025	0.038	0.083	0.09	0.057	0.055	0.073
BH	3 May 2005	2.095	6.64	32.60	0.082	0.014	0.035	0.080	0.11	0.046	0.028	0.066
BH	31 May 2005	1.049	6.44	32.00	0.080	0.011	0.033	0.076	0.09	0.046	0.025	0.063
BH	11 Jul 2005	0.130	6.72	31.00	0.086	0.016	0.032	0.075	0.13	0.033	0.015	0.053
BH	22 Aug 2005	0.637	6.76	34.00	0.089	0.029	0.038	0.087	0.15	0.056	0.023	0.052
BH	3 Oct 2005	0.724	6.79	38.10	0.100	0.042	0.042	0.091	0.15	0.067	0.036	0.058
BH	3 Apr 2006	5.450	6.46	36.80	0.081	0.023	0.036	0.076	0.07	0.048	0.066	0.069
BH	22 May 2006	1.264	6.62	31.70	0.084	0.016	0.035	0.075	0.11	0.039	0.025	0.064
BH	10 Jul 2006	0.278	6.85	36.40	0.086	0.023	0.036	0.082	0.16	0.039	0.020	0.054
BH	21 Aug 2006	3.261	6.40	29.80	0.086	0.020	0.036	0.078	0.10	0.049	0.047	0.062
BH	2 Oct 2006	3.155	6.74	35.60	0.087	0.020	0.037	0.081	0.10	0.048	0.057	0.066
BH	Average		6.67	35.53	0.09	0.02	0.037	0.082	0.11	0.05	0.04	0.06
Spring RUZS	28 Sep 2004	0.206	6.28	18.30	0.089	0.006	0.010	0.036	0.06	0.020	0.000	0.030
RUZS	13 Dec 2004	0.299	5.77	26.30	0.093	0.005	0.015	0.051	0.01	0.046	0.002	0.002
RUZS	29 Mar 2005	1.300	5.82	26.00	0.084	0.013	0.015	0.050	0.02	0.052	0.004	0.071
RUZS	3 May 2005	1.190	5.94	16.00	0.058	0.002	0.010	0.040	0.04	0.004	0.000	0.042
RUZS	31 May 2005	0.525	5.90	13.20	0.038	0.002	0.009	0.042	0.03	0.021	0.000	0.013
RUZS	11 Jul 2005	0.057	6.44	13.40	0.053	0.004	0.009	0.035	0.04	0.008	0.000	0.019
RUZS	22 Aug 2005	0.390	6.04	28.80	0.119	0.018	0.016	0.060	0.04	0.092	0.001	0.059
RUZS	3 Oct 2005	0.284	6.10	24.70	0.100	0.013	0.013	0.048	0.03	0.051	0.006	0.057
RUZS	20 Mar 2006	1.140	5.75	32.20	0.090	0.020	0.021	0.066	0.02	0.062	0.050	0.070
RUZS	3 Apr 2006	3.395	5.59	29.50	0.082	0.019	0.017	0.056	0.01	0.053	0.029	0.068
RUZS	18 Apr 2006	2.805	5.55	24.60	0.078	0.015	0.015	0.049	0.01	0.047	0.027	0.063
RUZS	22 May 2006	0.139	6.44	15.30	0.063	0.005	0.011	0.041	0.06	0.010	0.020	0.026
RUZS	10 Jul 2006	0.036	6.72	20.30	0.060	0.004	0.016	0.063	0.12	0.009	0.002	0.011
RUZS	21 Aug 2006	0.501	6.10	44.00	0.098	0.005	0.011	0.046	0.03	0.032	0.000	0.054
RUZS	2 Oct 2006	1.457	6.22	21.20	0.088	0.006	0.012	0.042	0.04	0.042	0.000	0.045
RUZS	Average		6.03	23.96	0.079	0.01	0.01	0.05	0.04	0.04	0.01	0.04
Spring RH	12 Jul 2004	0.160	5.89	46.50	0.092	0.030	0.036	0.103	0.06	0.060	0.119	0.080
RH	28 Sep 2004	0.200	6.03	50.50	0.098	0.031	0.040	0.116	0.07	0.060	0.158	0.076
RH	2 Nov 2004	2.030	6.34	41.20	0.089	0.031	0.035	0.105	0.06	0.073	0.112	0.080
RH	13 Dec 2004	0.434	6.54	44.70	0.091	0.030	0.035	0.103	0.05	0.069	0.111	0.111
RH	24 Jan 2005	2.098	6.21	39.70	0.084	0.028	0.031	0.091	0.03	0.066	0.085	0.080
RH	7 Mar 2005	0.430	6.34	39.80	0.087	0.028	0.031	0.090	0.03	0.063	0.093	0.081
RH	29 Mar 2005	1.062	6.23	40.30	0.083	0.028	0.031	0.090	0.04	0.058	0.087	0.081
RH	3 May 2005	0.907	6.26	38.20	0.082	0.027	0.030	0.090	0.04	0.058	0.079	0.081
RH	31 May 2005	0.515	6.40	38.80	0.082	0.024	0.030	0.089	0.05	0.054	0.086	0.076
RH	11 Jul 2005	0.324	6.53	41.10	0.086	0.027	0.031	0.096	0.05	0.055	0.095	0.075
RH	22 Aug 2005	0.313	6.61	39.50	0.090	0.029	0.034	0.100	0.07	0.055	0.107	0.075
RH	3 Oct 2005	0.138	6.56	40.80	0.088	0.030	0.033	0.098	0.07	0.057	0.098	0.076
RH	7 Feb 2006	0.313	6.28	38.50	0.086	0.028	0.030	0.089	0.05	0.060	0.080	0.081
RH	3 Apr 2006	2.130	6.30	41.90	0.085	0.030	0.031	0.090	0.04	0.054	0.107	0.074
RH	22 May 2006	0.492	6.39	37.20	0.085	0.028	0.030	0.088	0.05	0.050	0.094	0.075
RH	10 Jul 2006	0.213	6.55	42.20	0.086	0.028	0.031	0.093	0.07	0.053	0.082	0.077
RH	21 Aug 2006	1.244	6.40	60.30	0.090	0.029	0.032	0.095	0.06	0.054	0.119	0.067
RH	2 Oct 2006	1.078	6.48	42.40	0.088	0.032	0.033	0.098	0.06	0.059	0.115	0.071
RH	Average		6.35	42.42	0.087	0.03	0.03	0.10	0.05	0.06	0.10	0.08

Table 1a. Continued.

	date	Discharge L s^{-1}	pH	Cond. µS CM^{-1}	Na^+ mmol L^{-1}	K^+ mmol L^{-1}	Mg^{2+} mmol L^{-1}	Ca^{2+} mmol L^{-1}	Alc meq L^{-1}	Cl^- mmol L^{-1}	NO_3^- mmol L^{-1}	SO_4^{2-} mmol L^{-1}
Spring SG	12 Jul 2004	0.030	6.94	54.90	0.095	0.021	0.078	0.118	0.16	0.043	0.142	0.082
SG	28 Sep 2004	0.032	6.16	59.40	0.103	0.023	0.082	0.125	0.12	0.050	0.187	0.086
SG	13 Dec 2004	0.007	6.61	52.80	0.094	0.026	0.072	0.111	0.11	0.060	0.137	0.137
SG	29 Mar 2005	0.064	6.27	44.30	0.074	0.019	0.060	0.095	0.08	0.037	0.125	0.080
SG	3 May 2005	0.030	6.58	46.50	0.085	0.020	0.067	0.106	0.11	0.046	0.122	0.082
SG	31 May 2005	0.007	6.47	48.10	0.087	0.021	0.066	0.107	0.12	0.045	0.127	0.080
SG	11 Jul 2005	0.025	6.31	51.40	0.093	0.023	0.064	0.115	0.12	0.044	0.145	0.080
SG	22 Aug 2005	0.010	6.65	47.30	0.091	0.025	0.073	0.117	0.14	0.042	0.138	0.076
SG	3 Oct 2005	0.024	6.67	49.70	0.092	0.025	0.072	0.112	0.14	0.049	0.134	0.082
SG	22 May 2006	0.014	6.68	47.90	0.090	0.021	0.070	0.111	0.11	0.040	0.160	0.079
SG	3 Apr 2006	0.101	6.17	43.30	0.072	0.019	0.060	0.091	0.07	0.034	0.149	0.071
SG	21 Aug 2006	0.031	6.55	23.80	0.087	0.020	0.070	0.110	0.10	0.042	0.166	0.075
SG	2 Oct 2006	0.034	6.77	51.00	0.087	0.021	0.071	0.112	0.11	0.050	0.169	0.076
SG	Average		6.49	47.13	0.088	0.02	0.069	0.109	0.11	0.04	0.15	0.084
Spring SH	28 Sep 2004	0.033	5.02	21.80	0.084	0.016	0.007	0.023	0.00	0.049	0.004	0.033
SH	2 Nov 2004	2.252	5.24	18.10	0.078	0.013	0.008	0.025	0.00	0.053	0.007	0.046
SH	13 Dec 2004	0.074	5.23	22.00	0.083	0.017	0.009	0.028	0.00	0.051	0.012	0.012
SH	24 Jan 2005	2.000	5.29	20.60	0.075	0.015	0.009	0.028	0.00	0.051	0.016	0.045
SH	29 Mar 2005	1.280	5.00	24.10	0.074	0.019	0.010	0.031	0.00	0.048	0.023	0.045
SH	3 May 2005	0.324	5.05	20.20	0.072	0.019	0.008	0.025	0.00	0.048	0.009	0.035
SH	31 May 2005	0.027	5.56	18.80	0.076	0.017	0.007	0.024	0.01	0.045	0.009	0.038
SH	22 Aug 2005	0.231	5.16	19.50	0.075	0.016	0.008	0.031	0.01	0.039	0.015	0.033
SH	3 Oct 2005	0.278	5.25	19.70	0.080	0.019	0.008	0.025	0.01	0.049	0.008	0.038
SH	7 Feb 2006	0.260	5.30	23.80	0.087	0.022	0.009	0.031	0.01	0.053	0.019	0.053
SH	3 Apr 2006	5.711	5.36	20.80	0.068	0.014	0.008	0.024	0.01	0.044	0.019	0.039
SH	22 May 2006	0.125	5.45	18.20	0.076	0.018	0.007	0.024	0.01	0.043	0.012	0.041
SH	21 Aug 2006	0.554	5.60	15.40	0.077	0.013	0.008	0.026	0.01	0.045	0.005	0.042
SH	2 Oct 2006	0.883	5.61	18.50	0.076	0.011	0.007	0.022	0.01	0.051	0.004	0.040
SH	Average		5.29	20.11	0.077	0.02	0.008	0.026	0.01	0.05	0.01	0.04
Outlet RS	2 Feb 2004	nd	6.19	30.10	0.083	0.020	0.024	0.069	0.03	0.056	0.059	0.068
RS	12 Jul 2004	4.58	6.66	29.20	0.081	0.016	0.020	0.060	0.07	0.044	0.026	0.059
RS	28 Sep 2004	5.45	6.53	32.60	0.090	0.018	0.024	0.070	0.07	0.053	0.044	0.061
RS	2 Nov 2004	59.30	6.38	30.10	0.084	0.020	0.025	0.073	0.04	0.057	0.068	0.063
RS	13 Dec 2004	12.00	6.49	34.30	0.088	0.019	0.025	0.075	0.04	0.061	0.061	0.062
RS	24 Jan 2005	42.60	6.38	33.10	0.083	0.021	0.025	0.073	0.03	0.057	0.068	0.067
RS	7 Mar 2005	8.37	6.25	32.40	0.085	0.019	0.023	0.070	0.03	0.057	0.059	0.068
RS	21 Mar 2005	78.50	6.14	32.40	0.079	0.022	0.024	0.071	0.03	0.055	0.075	0.063
RS	29 Mar 2005	48.70	6.22	31.90	0.079	0.020	0.022	0.068	0.03	0.056	0.059	0.065
RS	3 May 2005	22.70	6.31	28.00	0.076	0.015	0.021	0.063	0.05	0.044	0.038	0.060
RS	31 May 2005	11.10	6.40	28.60	0.078	0.013	0.021	0.065	0.05	0.044	0.038	0.058
RS	11 Jul 2005	3.85	6.51	28.20	0.080	0.014	0.020	0.063	0.07	0.041	0.028	0.056
RS	22 Aug 2005	6.88	6.52	29.00	0.089	0.020	0.023	0.069	0.07	0.056	0.032	0.057
RS	3 Oct 2005	14.00	6.56	29.10	0.085	0.022	0.022	0.065	0.06	0.057	0.035	0.057
RS	28 Nov 2005	4.70	6.16	32.20	0.089	0.020	0.024	0.070	0.06	0.059	0.049	0.067
RS	7 Feb 2006	8.05	6.44	33.20	0.089	0.021	0.024	0.075	0.04	0.057	0.059	0.071
RS	20 Mar 2006	22.97	6.52	32.10	0.084	0.022	0.023	0.068	0.03	0.056	0.060	0.067
RS	3 Apr 2006	127.50	5.70	30.50	0.076	0.024	0.020	0.064	0.02	0.052	0.072	0.061
RS	22 May 2006	10.70	6.45	28.00	0.082	0.017	0.022	0.064	0.05	0.045	0.041	0.062
RS	10 Jul 2006	3.60	6.45	30.10	0.084	0.017	0.021	0.064	0.07	0.046	0.033	0.057
RS	21 Aug 2006	22.40	6.01	22.90	0.098	0.005	0.012	0.047	0.04	0.030	0.001	0.056
RS	2 Oct 2006	15.50	6.30	31.60	0.083	0.019	0.022	0.067	0.04	0.052	0.057	0.059
RS	Average		6.34	30.44	0.084	0.018	0.022	0.067	0.05	0.05	0.05	0.06
atmopsheric inputs	Average data											
Rain	2004–2006		5.21	15.73	0.011	0.004	0.002	0.005	0.01	0.012	0.038	0.016
Throughfalls spruces	2004–2006		5.18	34.11	0.048	0.069	0.011	0.027	0.01	0.058	0.074	0.041
Througfalls beeches	2004–2006		5.75	23.14	0.026	0.074	0.006	0.010	0.04	0.029	0.033	0.022

Table 1b. Chemical compositions of spring and stream waters, open field precipitation, througfalls under spruces (PL5) and beeches (PLH). The total dissolved solids (TDS_W) have been calculated from the concentrations of the major dissolved elements (cations, anions and silica) and are expressed in $mg\,L^{-1}$, as calculated for several watersheds (e.g., Gaillardet et al., 1999). Another parameter, called here TDS-Ca (= Ca + Mg + Na + K + SiO_2 + Fe) has been calculated as proposed by Zakharova et al. (2007) and reflects the silicate weathering.

	date	Discharge $L\,s^{-1}$	DOC ppm	H_4SiO_4 $mmol\,L^{-1}$	Al ppm	Mn ppm	Fe ppm	Ba ppb	Rb ppb	Sr ppb	U ppb	TDSw $mg\,L^{-1}$	TDS-ca $mg\,L^{-1}$
Spring Collector CR	12 Jul 2004		0.47	0.157	0.02	0.01	0.01	79.56	3.02	10.12	0.24	21.35	6.44
CR	28 Sep 2004		0.45	0.157	0.05	0.01	0.00	84.00	3.44	11.03	0.23	21.52	6.49
CR	2 Nov 2004		0.78	0.132	0.06	0.01	0.00	66.00	3.18	11.66	0.24	21.13	6.32
CR	13 Dec 2004		0.53	0.145	0.04	0.01	0.00	74.75	3.07	11.21	0.24	21.16	6.32
CR	24 Jan 2005		0.64	0.13	0.03	0.01	0.00	78.23	2.77	12.63	0.18	19.92	6.03
CR	29 Mar 2005		0.68	0.119	0.07	0.01	0.01	66.43	2.61	12.49	0.19	19.75	5.96
CR	3 May 2005		0.6	0.129	< 0.01	0.00	0.05	73.47	2.42	10.12	0.14	19.64	6.00
CR	31 May 2005		0.63	nd	< 0.01	0.00	0.02	78.79	2.90	12.35	0.05	19.55	5.96
CR	11 Jul 2005		0.44	0.152	< 0.01	0.00	0.04	83.05	2.82	11.40	0.15	19.37	5.93
CR	22 Aug 2005		0.5	0.159	0.05	0.01	0.01	74.37	2.85	10.21	0.23	20.39	6.15
CR	3 Oct 2005		0.53	0.153	0.02	0.01	0.01	75.77	3.09	11.33	0.17	20.29	6.10
CR	7 Feb 2006		0.62	0.154	0.04	0.01	0.01	76.68	3.03	11.00	0.22	21.19	6.30
CR	3 Apr 2006		0.84	0.114	0.06	0.01	0.01	60.27	2.86	11.86	0.20	19.63	5.91
CR	10 Jul 2006		1.67	0.148	0.02	0.01	0.01	69.84	2.67	10.23	0.16	19.43	5.90
CR	21 Aug 2006		0.59	0.137	nd	nd	nd	nd	nd	nd	nd	19.15	5.74
CR	2 Oct 2006		0.72	0.133	0.07	0.01	0.02	65.32	2.79	10.70	0.37	19.62	5.91
CR	22 May 2006		0.66	0.133	0.04	0.01	0.00	64.88	2.85	10.18	0.24	19.21	5.76
CR	Average		0.67	0.140	0.04	0.01	0.01	73.21	2.90	11.16	0.20	20.14	6.07
Spring CS1	12 Jul 2004	0.113	0.7	0.158	0.02	0.230	0.006	11.19	2.79	8.09	0.31	16.35	5.01
CS1	28 Sep 2004	0.148	0.62	0.154	0.08	0.220	0.000	12.00	2.79	7.83	0.24	16.04	4.95
CS1	13 Dec 2004	0.318	0.87	0.145	0.11	0.026	0.005	11.11	2.69	7.71	0.37	11.52	4.55
CS1	29 Mar 2005	1.156	nd	0.120	0.19	0.037	0.002	14.73	2.52	8.81	0.38	14.14	4.27
CS1	3 May 2005	0.560	0.74	0.133	0.03	0.006	0.098	12.78	2.38	7.70	0.25	13.50	4.25
CS1	31 May 2005	0.268	0.74	0.138	< 0.01	0.003	0.043	13.84	2.79	11.50	0.14	14.90	4.72
CS1	11 Jul 2005	0.076	0.64	0.157	0.03	0.004	0.029	13.84	2.85	9.54	0.19	15.85	4.89
CS1	22 Aug 2005	0.110	0.61	0.158	0.03	0.003	0.020	11.67	2.78	8.84	0.24	16.62	5.05
CS1	3 Oct 2005	0.192	0.66	0.151	0.04	0.023	0.000	12.66	2.78	8.73	0.15	15.27	4.69
CS1	7 Feb 2006	0.165	0.85	0.153	0.06	0.020	0.006	11.68	2.77	8.36	0.30	16.21	5.02
CS1	3 Apr 2006	1.672	1.75	0.113	0.26	0.044	0.015	17.94	2.98	8.54	0.53	14.64	4.37
CS1	22 May 2006	0.349	0.74	0.135	0.06	0.026	0.004	11.83	2.63	7.16	0.33	14.29	4.40
CS1	10 Jul 2006	0.092	0.48	0.153	0.01	0.021	0.000	10.29	2.48	7.72	0.18	14.89	4.55
CS1	21 Aug 2006	0.658	0.76	0.133	0.10	0.030	0.000	12.48	2.55	7.86	0.44	14.30	4.45
CS1	2 Oct2006	0.635	0.78	0.135	0.12	0.032	0.000	14.07	2.75	8.31	0.51	14.24	4.33
CS1	Average		0.781	0.142	0.07	0.048	0.015	12.81	2.70	8.45	0.30	14.85	4.63

Table 1b. Continued.

	date	Discharge $L s^{-1}$	DOC ppm	H_4SiO_4 $mmol L^{-1}$	Al ppm	Mn ppm	Fe ppm	Ba ppb	Rb ppb	Sr ppb	U ppb	TDSw $mg L^{-1}$	TDS-ca $mg L^{-1}$
Spring CS2	12 Jul 2004	0.482	0.48	0.157	0.02	0.01	0.00	71.89	2.64	10.03	0.24	20.33	6.06
CS2	28 Sep 2004	0.535	0.42	0.155	0.06	0.01	0.00	76.00	3.00	10.14	0.20	20.72	6.23
CS2	13 Dec 2004	1.446	0.58	0.138	0.05	0.01	0.00	70.15	2.78	10.70	0.26	20.13	6.01
CS2	3 May 2005	2.500	0.74	0.124	< 0.01	0.00	0.05	72.40	2.29	10.00	0.13	18.44	5.64
CS2	31 May 2005	1.117	0.57	0.131	< 0.01	0.00	0.16	72.40	2.41	12.42	0.05	19.29	6.01
CS2	11 Jul 2005	0.246	0.54	0.149	< 0.01	0.00	0.05	71.34	2.28	10.03	0.20	19.21	5.87
CS2	22 Aug 2005	0.450	0.46	0.157	0.05	0.00	0.01	75.93	2.66	10.25	0.27	20.50	6.09
CS2	7 Feb 2006	0.678	0.51	0.151	0.03	0.01	0.01	79.16	2.76	11.43	0.18	20.63	6.17
CS2	22 May 2006	1.364	0.63	0.128	0.05	0.01	0.00	71.20	2.58	10.29	0.25	19.30	5.80
CS2	3 Apr 2006	7.156	0.88	0.107	0.06	0.01	0.00	59.98	2.45	10.60	0.18	19.65	5.81
CS2	10 Jul 2006	0.389	0.36	0.146	< 0.01	0.01	0.00	69.31	2.50	10.57	0.13	19.31	5.89
CS2	21 Aug 2006	2.978	0.55	0.134	0.06	0.01	0.00	70.57	2.54	10.76	0.30	19.65	5.84
CS2	2 Oct 2006	3.800	0.59	0.129	0.05	0.01	0.00	75.40	2.78	11.63	0.32	20.41	6.19
CS2	Average		0.562	0.139	0.04	0.01	0.02	71.98	2.59	10.68	0.21	19.81	5.97
Spring CS3	13 Dec 2004	0.265	0.44	0.159	0.01	0.00	0.15	20.39	4.10	10.85	0.25	22.99	7.08
CS3	29 Mar 2005	0.480	nd	0.142	0.03	0.00	0.00	24.44	3.99	13.44	0.21	22.81	6.80
CS3	3 May 2005	0.408	0.52	0.153	< 0.01	0.00	0.02	23.42	3.73	10.95	0.16	22.53	6.83
CS3	31 May 2005	0.246	0.5	0.154	< 0.01	0.00	0.02	25.55	3.88	11.65	0.07	22.10	6.69
CS3	11 Jul 2005	0.089	0.45	0.156	< 0.01	0.00	0.01	24.49	3.64	9.82	0.20	20.83	6.43
CS3	22 Aug 2005	0.086	0.53	0.164	< 0.01	0.00	0.00	22.18	4.06	10.47	0.27	22.32	6.75
CS3	3 Oct 2005	0.181	0.4	0.163	0.03	0.00	0.00	23.15	4.12	10.69	0.20	22.33	6.73
CS3	7 Feb 2006	0.164	0.51	0.164	0.01	0.00	0.01	22.60	4.12	11.15	0.21	22.28	6.70
CS3	3 Apr 2006	1.222	0.89	0.126	0.03	0.01	0.01	22.05	0.50	10.71	0.24	21.87	6.55
CS3	22 May 2006	0.229	0.54	0.152	0.01	0.00	0.00	16.86	3.31	8.27	0.17	22.09	6.57
CS3	10 Jul 2006	0.109	0.41	0.158	< 0.01	0.00	0.00	19.80	3.75	10.30	0.13	21.38	6.51
CS3	21 Aug 2006	0.268	0.5	0.159	0.01	0.00	0.00	21.18	3.94	10.57	0.31	22.03	6.62
CS3	2 Oct 2006	0.445	0.6	0.151	0.02	0.00	0.00	22.52	4.22	11.92	0.37	22.83	6.78
CS3	Average		0.52	0.15	0.01	0.00	0.02	22.20	3.64	10.83	0.21	22.18	6.70
Spring CS4	13 Dec 2004	0.314	0.66	0.152	0.04	0.01	0.00	127.41	3.21	12.10	0.26	23.00	6.85
CS4	3 May 2005	0.427	0.70	0.128	< 0.01	0.00	0.06	127.77	2.69	11.15	0.17	20.07	6.13
CS4	31 May 2005	0.268	0.64	0.141	< 0.01	0.00	0.01	137.35	2.86	12.25	0.09	20.68	6.29
CS4	11 Jul 2005	0.121	0.52	0.156	< 0.01	0.00	0.06	145.87	2.53	11.05	0.21	21.47	6.59
CS4	22 Aug 2005	0.170	0.61	0.163	0.04	0.00	0.01	154.38	2.93	12.11	0.29	22.69	6.75
CS4	7 Feb 2006	0.213	0.66	0.161	0.01	0.01	0.00	149.91	3.12	12.40	0.14	22.41	6.74
CS4	3 Apr 2006	0.265	1.20	0.105	0.09	0.02	0.01	96.46	2.78	10.66	0.24	20.41	6.12
CS4	22 May 2006	0.309	0.74	0.142	0.07	0.01	0.00	133.26	3.20	11.43	0.24	21.85	6.43
CS4	10 Jul 2006	0.157	0.41	0.155	0.01	0.00	0.00	148.84	2.78	11.76	0.17	21.43	6.40
CS4	21 Aug 2006	0.462	0.73	0.145	0.05	0.01	0.00	119.00	2.94	11.10	0.30	21.09	6.36
CS4	2 Oct 2006	0.772	1.00	0.140	0.07	0.01	0.58	115.10	3.19	11.92	0.45	21.33	6.85
CS4	Average		0.72	0.14	0.04	0.01	0.07	132.30	2.93	11.63	0.23	21.49	6.50

Table 1b. Continued.

	date	Discharge $L\,s^{-1}$	DOC ppm	H_4SiO_4 $mmol\,L^{-1}$	Al ppm	Mn ppm	Fe ppm	Ba ppb	Rb ppb	Sr ppb	U ppb	TDSw $mg\,L^{-1}$	TDS-ca $mg\,L^{-1}$
Spring BH	2 Feb 2004	nd	1.70	0.137	0.03	0.00	0.02	62.52	2.42	10.28	0.06	25.63	7.55
BH	12 Jul 2004	0.388	2.68	0.143	0.02	0.00	0.06	57.83	1.67	8.85	0.11	22.68	6.51
BH	28 Sep 2004	0.450	2.43	0.154	0.05	0.01	0.04	68.00	3.59	10.69	0.07	28.51	8.40
BH	13 Dec 2004	1.241	1.51	0.145	0.02	0.00	0.02	67.18	2.94	11.10	0.05	27.11	7.79
BH	7 Mar 2005	0.690	1.39	0.137	< 0.01	0.00	0.01	67.22	2.40	12.22	0.04	25.85	7.54
BH	29 Mar 2005	3.000	1.58	0.123	0.03	0.00	0.01	63.55	2.68	11.97	0.04	24.92	7.30
BH	3 May 2005	2.095	1.89	0.123	< 0.01	0.02	0.03	67.08	1.91	10.11	0.07	22.72	6.60
BH	31 May 2005	1.049	2.09	0.134	< 0.01	0.01	0.04	66.01	1.44	9.81	0.07	21.12	6.24
BH	11 Jul 2005	0.130	2.91	0.144	< 0.01	0.05	0.05	66.01	1.89	9.57	0.11	21.48	6.52
BH	22 Aug 2005	0.637	3.92	0.136	0.07	0.07	0.01	76.46	4.06	11.82	0.15	25.35	7.68
BH	3 Oct 2005	0.724	3.69	0.138	0.08	0.00	0.06	77.72	4.69	12.05	0.11	27.70	8.75
BH	3 Apr 2006	5.450	1.37	0.120	0.03	0.00	0.01	59.17	2.65	9.79	0.05	23.10	6.76
BH	22 May 2006	1.264	2.09	0.115	0.03	0.00	0.03	62.10	2.47	9.46	0.08	22.38	6.51
BH	10 Jul 2006	0.278	3.10	0.147	0.04	0.00	0.02	59.41	3.04	10.50	0.13	24.40	7.15
BH	21 Aug 2006	3.261	2.16	0.139	0.04	0.00	0.03	57.21	2.58	10.11	0.11	23.45	6.88
BH	2 Oct 2006	3.155	1.83	0.142	0.03	0.00	0.18	63.68	2.98	11.11	0.10	24.46	7.20
BH	Average		2.27	0.14	0.03	0.01	0.04	65.07	2.71	10.59	0.08	24.43	7.21
Spring RUZS	28 Sep 2004	0.206	9.05	0.103	0.24	0.03	0.46	20.00	1.33	5.01	0.35	11.08	4.49
RUZS	13 Dec 2004	0.299	2.47	0.154	0.07	0.01	0.11	26.24	1.08	7.77	0.11	7.81	4.95
RUZS	29 Mar 2005	1.300	2.83	0.121	0.10	0.01	0.04	31.80	2.31	9.16	0.14	14.85	4.93
RUZS	3 May 2005	1.190	6.00	0.048	< 0.01	0.15	0.18	29.81	0.45	6.86	0.38	9.63	3.47
RUZS	31 May 2005	0.525	9.38	0.045	< 0.01	0.21	0.23	28.75	0.40	7.63	0.42	6.67	3.11
RUZS	11 Jul 2005	0.057	7.24	0.027	0.01	0.20	0.20	25.55	0.68	5.71	0.44	7.72	3.22
RUZS	22 Aug 2005	0.390	6.74	0.079	0.15	0.15	0.01	40.86	3.73	10.28	0.26	17.48	6.30
RUZS	3 Oct 2005	0.284	6.39	0.108	0.18	0.00	0.12	35.36	2.70	8.29	0.31	14.60	5.23
RUZS	20 Mar 2006	1.140	3.27	0.150	0.08	0.01	0.03	43.19	2.90	10.70	0.12	19.05	6.11
RUZS	3 Apr 2006	3.395	3.00	0.116	0.14	0.01	0.03	41.64	2.10	8.53	0.23	16.15	5.38
RUZS	18 Apr 2006	2.805	3.07	0.108	0.13	0.01	0.05	36.96	2.06	8.43	0.22	14.87	4.82
RUZS	22 May 2006	0.139	8.20	0.040	0.21	0.02	0.24	26.57	1.08	6.34	0.46	11.04	3.82
RUZS	10 Jul 2006	0.036	10.96	0.101	0.16	0.02	0.14	19.80	0.99	9.92	0.49	13.20	4.66
RUZS	21 Aug 2006	0.501	7.26	0.086	0.16	0.02	0.13	30.40	1.06	7.42	0.33	12.87	4.74
RUZS	2 Oct 2006	1.457	6.31	0.121	0.16	0.02	0.03	27.07	1.48	7.21	0.37	12.33	4.34
RUZS	Average		5.94	0.09	0.11	0.06	0.11	31.71	1.64	8.16	0.31	12.73	4.65
Spring RH	12 Jul 2004	0.160	0.58	0.144	0.02	0.00	0.00	136.18	3.73	14.71	0.18	29.01	8.38
RH	28 Sep 2004	0.200	0.60	0.146	0.05	0.00	0.00	163.00	4.15	16.33	0.14	32.28	9.18
RH	2 Nov 2004	2.030	0.88	0.133	0.06	0.00	0.00	144.44	4.57	16.08	0.19	28.98	8.40
RH	13 Dec 2004	0.434	0.82	0.141	0.05	0.00	0.00	129.97	3.80	14.95	0.16	31.14	8.33
RH	24 Jan 2005	2.098	0.89	0.124	0.07	0.00	0.00	136.78	3.46	15.43	0.15	24.74	7.50
RH	7 Mar 2005	0.430	0.76	0.136	0.03	0.00	0.00	124.00	3.52	16.33	0.13	24.91	7.55
RH	29 Mar 2005	1.062	0.84	0.117	0.06	0.00	0.00	126.12	3.41	15.84	0.14	25.08	7.44
RH	3 May 2005	0.907	0.88	0.127	< 0.01	0.01	0.04	132.03	3.36	14.05	0.14	24.64	7.40
RH	31 May 2005	0.515	0.74	0.129	< 0.01	0.00	0.07	128.83	3.45	13.60	0.07	24.44	7.27
RH	11 Jul 2005	0.324	0.62	0.138	< 0.01	0.00	0.04	140.55	3.54	15.45	0.16	25.84	7.76
RH	22 Aug 2005	0.313	0.73	0.143	0.05	0.00	0.00	144.26	3.80	15.20	0.25	27.92	8.13
RH	3 Oct 2005	0.138	0.75	0.145	0.04	0.00	0.01	145.49	3.93	15.56	0.19	27.60	8.02
RH	7 Feb 2006	0.313	0.90	0.144	0.02	0.00	0.01	129.12	3.58	13.95	0.16	25.09	7.47
RH	3 Apr 2006	2.130	0.95	0.105	0.06	0.00	0.01	131.03	3.44	13.28	0.19	25.63	7.56
RH	22 May 2006	0.492	0.81	0.129	0.04	0.00	0.00	127.92	3.86	13.44	0.20	25.13	7.39
RH	10 Jul 2006	0.213	0.60	0.139	0.01	0.00	0.00	118.81	3.41	13.85	0.10	25.87	7.64
RH	21 Aug 2006	1.244	0.87	0.135	0.05	0.00	0.00	134.40	3.51	14.42	0.23	27.07	7.87
RH	2 Oct 2006	1.078	0.88	0.132	0.05	0.00	0.00	145.20	3.81	15.73	0.28	27.76	8.09
RH	Average		0.78	0.13	0.04	0.00	0.01	135.45	3.69	14.90	0.17	26.84	7.85

Table 1b. Continued.

	date	Discharge L s^{-1}	DOC ppm	H_4SiO_4 mmol L^{-1}	Al ppm	Mn ppm	Fe ppm	Ba ppb	Rb ppb	Sr ppb	U ppb	TDSw mg L^{-1}	TDS-ca mg L^{-1}
Spring SG	12 Jul 2004	0.030	0.94	0.128	0.02	0.00	0.02	122.70	5.22	12.65	0.03	37.60	9.73
SG	28 Sep 2004	0.032	0.80	0.141	0.02	0.01	0.01	147.00	5.75	14.35	0.02	39.36	10.36
SG	13 Dec 2004	0.007	1.03	0.142	0.02	0.02	0.03	119.83	6.37	13.46	0.01	39.68	9.50
SG	29 Mar 2005	0.064	0.84	0.122	0.03	0.00	0.01	115.78	4.22	13.57	0.01	29.40	7.80
SG	3 May 2005	0.030	0.82	0.127	< 0.01	0.01	0.01	138.42	4.44	12.75	0.01	32.34	8.70
SG	31 May 2005	0.007	1.02	0.127	< 0.01	0.03	0.09	132.03	5.24	13.10	0.02	32.83	8.89
SG	11 Jul 2005	0.025	1.39	0.136	0.02	0.03	0.04	149.07	5.54	14.20	0.02	34.48	9.32
SG	22 Aug 2005	0.010	nd	0.123	0.07	0.03	0.10	151.52	6.55	15.41	0.08	35.62	9.71
SG	3 Oct 2005	0.024	1.71	0.134	0.04	0.00	0.04	138.88	6.24	14.48	0.04	35.45	9.45
SG	22 May 2006	0.014	0.79	0.124	0.02	0.00	0.01	112.00	5.44	13.42	0.03	34.75	9.12
SG	3 Apr 2006	0.101	0.94	0.112	0.02	0.01	0.00	120.89	3.89	10.92	0.01	28.68	7.57
SG	21 Aug 2006	0.031	0.99	0.131	0.02	0.00	0.01	134.10	4.57	13.51	0.02	33.96	8.98
SG	2 Oct 2006	0.034	0.82	0.137	0.02	0.00	0.07	148.10	5.11	14.73	0.01	35.35	9.19
SG	Average		1.01	0.13	0.02	0.01	0.03	133.97	5.28	13.66	0.02	34.32	9.05
Spring SH	28 Sep 2004	0.033	9.78	0.144	0.44	0.04	0.25	20.00	4.38	3.71	0.34	9.16	3.99
SH	2 Nov 2004	2.252	3.34	0.134	0.22	0.02	0.06	19.00	4.02	4.42	0.30	10.58	3.64
SH	13 Dec 2004	0.074	3.47	0.148	0.24	0.03	0.07	22.11	3.89	4.77	0.26	8.13	4.08
SH	24 Jan 2005	2.000	2.23	0.129	0.19	0.02	0.03	20.13	3.07	5.02	0.18	11.05	3.76
SH	29 Mar 2005	1.280	4.65	0.121	0.27	0.03	0.14	20.08	4.97	5.72	0.24	11.46	4.14
SH	3 May 2005	0.324	7.21	0.092	0.03	0.21	0.35	20.23	5.17	4.30	0.33	9.46	4.00
SH	31 May 2005	0.027	4.15	0.124	0.03	0.30	0.48	26.62	3.59	4.53	0.37	10.32	4.10
SH	22 Aug 2005	0.231	9.63	0.114	0.40	0.30	0.03	18.32	4.13	4.99	0.56	10.17	3.89
SH	3 Oct 2005	0.278	6.16	0.137	0.28	0.03	0.18	21.52	5.55	4.86	0.42	10.35	4.04
SH	7 Feb 2006	0.260	2.80	0.154	0.23	0.04	0.03	28.94	4.11	5.39	0.27	13.08	4.45
SH	3 Apr 2006	5.711	3.31	0.106	0.28	0.02	0.03	19.32	2.97	4.08	0.29	10.15	3.39
SH	22 May 2006	0.125	3.55	0.117	0.29	0.02	0.06	11.00	4.11	4.12	0.36	10.55	3.71
SH	21 Aug 2006	0.554	4.01	0.130	0.25	0.03	0.06	20.56	2.97	4.39	0.43	10.18	3.66
SH	2 Oct 2006	0.883	3.77	0.134	0.24	0.02	0.00	20.60	2.95	4.29	0.48	9.86	3.31
SH	Average		4.86	0.13	0.24	0.08	0.13	20.60	3.99	4.61	0.35	10.32	3.87
Outlet RS	2 Feb 2004	nd	1.85	0.131	0.05	0.01	0.02	67.31	2.41	10.46	0.14	19.99	6.15
RS	12 Jul 2004	4.58	1.99	0.132	0.02	0.01	0.05	57.08	1.76	9.07	0.19	18.29	5.52
RS	28 Sep 2004	5.45	1.80	0.140	0.06	0.01	0.04	69.00	2.96	11.50	0.15	20.77	6.29
RS	2 Nov 2004	59.30	1.55	0.134	0.05	0.01	0.02	71.65	3.19	11.05	0.12	21.07	6.35
RS	13 Dec 2004	12.00	1.13	0.143	0.03	0.01	0.02	68.76	2.59	11.10	0.08	20.90	6.49
RS	24 Jan 2005	42.60	1.30	0.133	0.03	0.00	0.01	78.96	2.64	12.29	0.08	20.96	6.36
RS	7 Mar 2005	8.37	1.10	0.135	0.02	0.00	0.02	69.00	2.43	13.16	0.07	20.36	6.16
RS	21 Mar 2005	78.50	1.63	0.121	nd	nd	nd	nd	nd	nd	nd	20.29	6.18
RS	29 Mar 2005	48.70	1.28	0.122	0.03	0.00	0.01	74.63	2.74	12.00	0.08	19.58	5.94
RS	3 May 2005	22.70	1.99	0.104	< 0.01	0.02	0.05	70.27	2.08	10.03	0.13	17.84	5.48
RS	31 May 2005	11.10	1.78	0.119	< 0.01	0.01	0.03	68.14	1.95	13.35	0.12	17.60	5.45
RS	11 Jul 2005	3.85	1.85	0.134	< 0.01	0.03	0.04	70.27	2.35	10.65	0.18	17.99	5.52
RS	22 Aug 2005	6.88	2.92	0.127	0.06	0.07	0.01	68.03	3.14	10.04	0.22	19.91	6.24
RS	3 Oct 2005	14.00	2.73	0.130	0.07	0.00	0.04	69.48	3.37	11.16	0.23	19.21	6.07
RS	28 Nov 2005	4.70	1.20	0.143	nd	nd	nd	nd	nd	nd	nd	21.08	6.21
RS	7 Feb 2006	8.05	1.20	0.143	0.03	0.00	0.02	74.11	2.66	11.50	0.08	21.48	6.55
RS	20 Mar 2006	22.97	1.22	0.131	nd	nd	nd	nd	nd	nd	nd	20.06	6.16
RS	3 Apr 2006	127.50	1.64	0.111	0.09	0.02	0.01	73.05	2.96	10.86	0.14	18.93	5.82
RS	22 May 2006	10.70	1.72	0.115	0.07	0.01	0.03	65.82	2.80	10.44	0.15	18.97	5.75
RS	10 Jul 2006	3.60	1.59	0.135	0.03	0.01	0.03	59.80	2.59	9.68	0.17	18.85	5.79
RS	21 Aug 2006	22.40	7.03	0.089	0.05	0.01	0.03	70.00	2.45	10.54	0.18	13.23	4.71
RS	2 Oct 2006	15.50	1.59	0.134	0.05	0.01	0.00	71.59	2.59	10.62	0.17	19.65	5.96
RS	Average		1.91	0.128	0.04	0.01	0.03	69.31	2.61	11.03	0.14	19.41	5.96
atmopsheric inputs	Average data												
Rain	2004–2006		1.01	0.000	0.01	0.01	0.01	3.77	1.47	0.85	0.01		
Throughfalls spruces	2004–2006		8.80	0.003	0.10	0.31	0.02	9.34	13.99	3.37	0.01		
Througfalls beeches	2004–2006		6.42	0.005	0.02	0.02	0.03	11.41	28.70	1.02	0.00		

Table 2. Sr isotopic compositions and U activity ratios for spring waters, outlet, rain, througfalls and clays (Prunnier, 2008) from the Strengbach watershed. Clays SS: clays from a soil profile located in the southern slope and under beeches, and clays NS: clays from a soil profile located in the northern slope and under spruces.

Samples	date	^{87}Sr/^{86}Sr	2sigma	^{234}U/^{238}U	2sigma	altitude (m)
Spring CS1	28 Sep 2004	0.72573	0.00002	0.880	0.001	1080
CS1	13 Dec 2004	0.72656	0.00004	0.875	0.005	1080
CS1	29 Mar 2005	0.72780	0.00001	0.892	0.003	1080
CS1	22 May 2006	0.72650	0.00001	0.886	0.002	1080
CS1	Average	0.72665		0.883		
Spring CS2	3 May 2005	0.72546	0.00001			1055
CS2	11 Jul 2005	0.72376	0.00001			1055
CS2	22 May 2006	0.72544	0.00001	0.875		1055
CS2	2 Oct 2006	0.72515	0.00001			1055
CS2	Average	0.72495		0.875		
Spring CS3	13 Dec 2004	0.72325	0.00002	0.823	0.003	1098
CS3	29 Mar 2005	0.72328	0.00001	0.827	0.003	1098
CS3	11 Jul 2005	0.72314	0.00002			1098
CS3	22 May 2006	0.72325	0.00001	0.819	0.004	1098
CS3	Average	0.72323		0.823		
Spring CS4	3 May 2005	0.72490	0.00002	0.866	0.003	1050
CS4	11 Jul 2005	0.72375	0.00001			1050
CS4	22 May 2006	0.72353	0.00001	0.867	0.002	1050
CS4	2 Oct 2006	0.72548	0.00001			1050
CS4	Average	0.72442		0.867		
Spring BH	12 Jul 2004	0.72262	0.00002	1.106	0.005	915
BH	13 Dec 2004	0.72289	0.00002	1.1	0.003	915
BH	29 Mar 2005	0.72359	0.00001	1.101	0.003	915
BH	3 May 2005	0.72340	0.00001	1.1	0.003	915
BH	31 May 2005	0.72319	0.00001	1.112	0.003	915
BH	11 Jul 2005	0.72279	0.00001	1.101	0.003	915
BH	22 Aug 2005	0.72287	0.00001	1.106	0.003	915
BH	3 Oct 2005	0.72307	0.00001	1.105	0.003	915
BH	22 May 2006	0.72334	0.00002	1.099	0.004	915
BH	Average	0.723084		1.103		

Table 2. Continued.

Samples	date	^{87}Sr/^{86}Sr	2sigma	^{234}U/^{238}U	2sigma	altitude (m)
Spring RUZS	13 Dec 2004	0.72700	0.00002	0.945	0.004	950
RUZS	29 Mar 2005	0.72665	0.00001	0.941	0.003	950
RUZS	22 May 2006	0.72669	0.00001	0.949	0.003	950
RUZS	Average	0.72678		0.945		
Spring RH	28 Sep 2004	0.72206	0.00008	0.996	0.003	980
RH	13 Dec 2004	0.72240	0.00002	0.991	0.004	980
RH	29 Mar 2005	0.72257	0.00002	0.993	0.005	980
RH	22 May 2006	0.72242	0.00001	0.991	0.004	980
RH	Average	0.72236		0.993		
Spring SG	28 Sep 2004	0.72353	0.00002	0.91	0.004	1093
SG	13 Dec 2004	0.72328	0.00007	0.93	0.003	1093
SG	29 Mar 2005	0.72352	0.00002	0.923	0.004	1093
SG	22 May 2006	0.72354	0.00002	0.927	0.002	1093
SG	Average	0.72347		0.923		
Spring SH	28 Sep 2004	0.72749	0.00003	0.916	0.003	1050
SH	13 Dec 2004	0.72720	0.00009	0.915	0.003	1050
SH	29 Mar 2005	0.72801	0.00002	0.914	0.004	1050
SH	3 May 2005	0.72798	0.00001			1050
SH	22 May 2006	0.72720	0.00001	0.911	0.004	1050
SH	2 Oct 2006	0.72752	0.00001			1050
SH	Average	0.72757		0.914		
Outlet RS	29 Mar 2005	0.72573	0.00002	0.939	0.003	883
RS	22 May 2006	0.72520	0.00001	0.974	0.004	883
RS	Average	0.72547		0.957		
atmopsheric inputs	Average					
Rain	2004–2006	0.7111		1.175		
Throughfalls spruces	2004–2006	0.71290		1.079		
Througfalls beeches	2004–2006	0.71620		0.953		
clays SS under beeches	35 cm depth	0.872847	0.00002	1.26	0.003	
clays SS under beeches	95 cm depth	0.767439	0.00001	1.074	0.002	
clays NS under spruces	35 cm depth	0.830034	0.00001	1.094	0.002	
clays NS under spruces	95 cm depth	0.802886	0.00001	nd		

Table 3. Elementary fluxes for rain, throughfalls and outlet in the Strengbach catchments. The rain corresponds to open field precipitations, the throughfalls have been collected under spruces (80 % of the forest cover) and beeches (20 % of the forest cover). The chemical composition of throughfalls results of (wet and dry atmospheric deposition) + (biological excretion = biological leaching). In order to estimate the atmosphere-derived fluxes (input fluxes) we applied for every element a specific corrective factor Cb (1) Ulrich et al. (1983); (2) Dambrine et al. (1998); (3) Thimonier et al. (2008), (4) Berger et al. (2008). The global atmospheric input has been calculated considering the catchment area as 15 % of clearing and 85 % of forest, the formula is then: $F_{\text{atm}} = 0.15.\ F_{\text{rain}} + 0.85F_{\text{througfall(corrected)}}$. The outlet fluxes correspond to the catchment export fluxes (b).

2004–2006	water fluxes (mm)	Na fluxes $\text{mg}\,\text{m}^{-2}\,\text{yr}^{-1}$	K fluxes $\text{mg}\,\text{m}^{-2}\,\text{yr}^{-1}$	Mg fluxes $\text{mg}\,\text{m}^{-2}\,\text{yr}^{-1}$	Ca fluxes $\text{mg}\,\text{m}^{-2}\,\text{yr}^{-1}$	Si fluxes $\text{mg}\,\text{m}^{-2}\,\text{yr}^{-1}$	Sr fluxes $\mu\text{g}\,\text{m}^{-2}\,\text{yr}^{-1}$	U fluxes $\mu\text{g}\,\text{m}^{-2}\,\text{yr}^{-1}$
rain – F_{rain}	1247	306	219	56	256	5	1.1	7.6
throughfall – $F_{\text{througfall}}$	1070	1041	3037	256	1034	101	2.4	12.6
biological contribution to throughfalls Cb (1.2.3.4)		**0.2**	**0.9**	**0.3**	**0.25**	**0.1**	**nd**	**nd**
Atmospheric contribution to throughfall – $F_{\text{througfall(corrected)}}$		**833**	**304**	**179**	**776**	**91**	**nd**	**nd**
global atmospheric input (a)	1096	754	291	161	697	78	1.1 to 2.4	7.6 to 12.6
outlet fluxes (b)	850	1634	608	456	2276	3008	8.8	113
rain-corrected outlet fluxes (c)	850	1328	388	399	2019	3003	7.7	105
(wet + dry atmos. deposits) -corrected outlet fluxes (d)	850	880	317	295	1579	2929	7.7 to 6.6	105 to 101

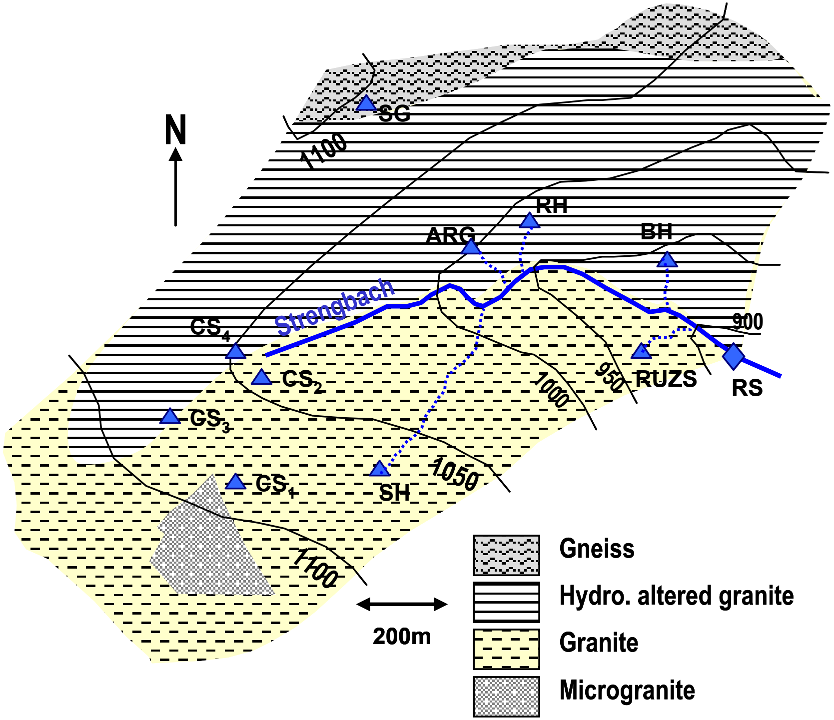

Fig. 1. Map of the Strengbach catchment showing the principal lithological units and the location of the 10 studied springs (SG, RH, ARG, BH, CS1, CS2, CS3, CS4, SH, RUZS). RS corresponds to the Strengbach stream at the outlet of the studied catchment.

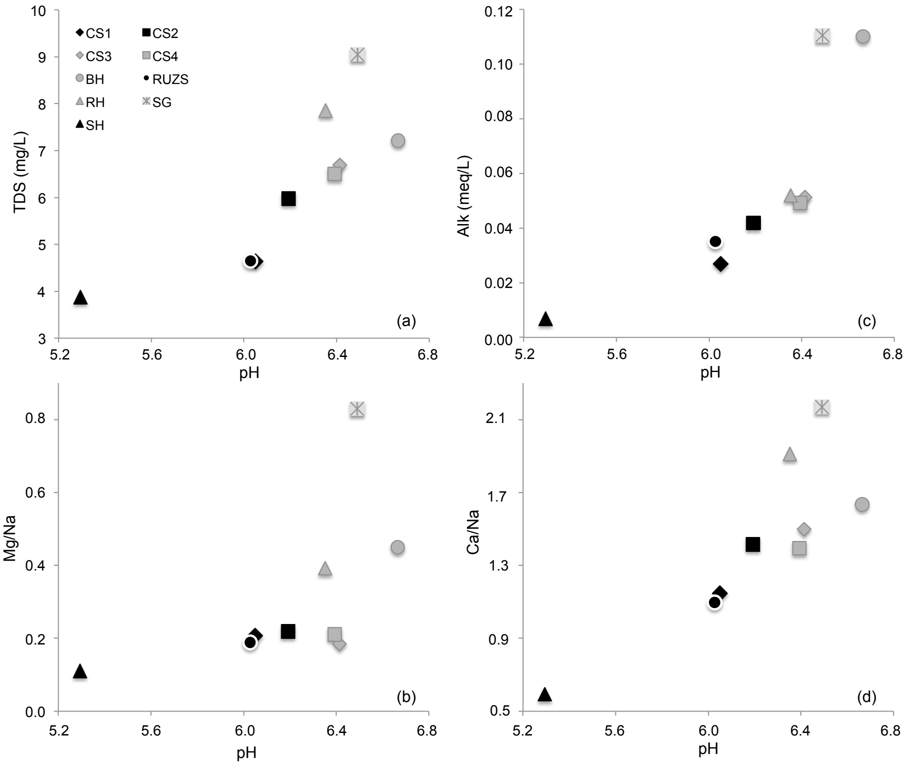

Fig. 2. Physico-chemical characteristics of the different source waters of the Strengbach watershed (average values of period 2004–2006). **(a)** pH vs. TDSw; **(b)** pH vs. Mg/Na, **(c)** pH vs. Alk and **(d)** pH vs. Ca/Na.

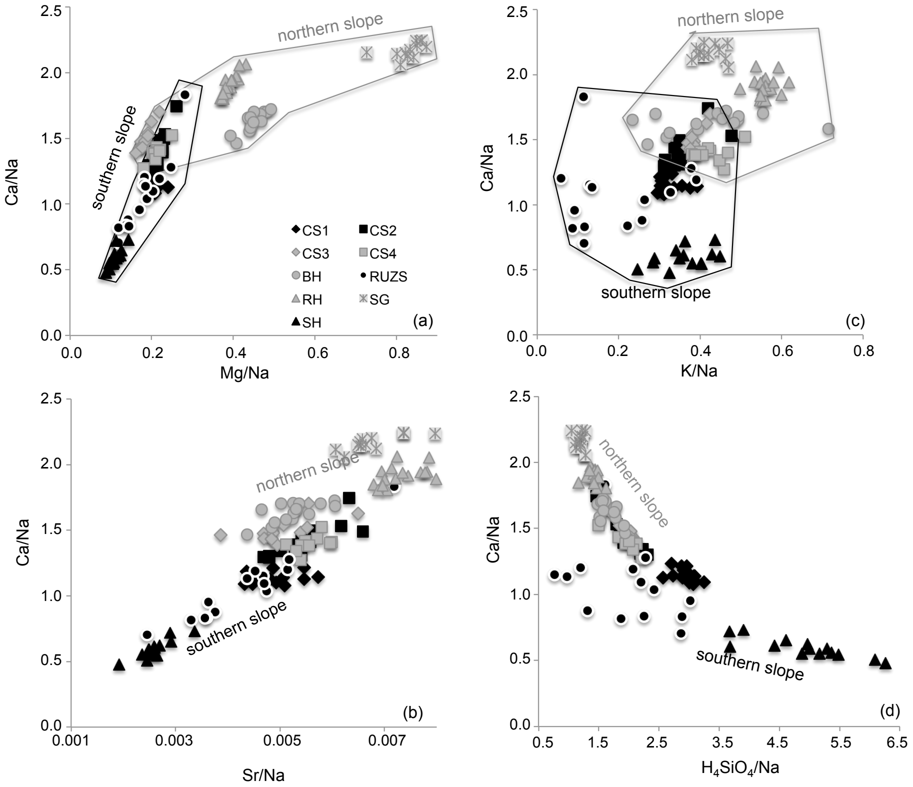

Fig. 3. Major element concentration ratios of the 9 different individual source waters of the Strengbach watershed. **(a)** Ca/Na vs. Mg/Na; **(b)** Ca/Na vs. K/Na; **(c)** Ca/Na vs. Sr/Na and **(d)** Ca/Na vs. $Si(OH)_4$/Ca. In each diagram the spring waters from the southern slope show different compositions than those from the northern slope.

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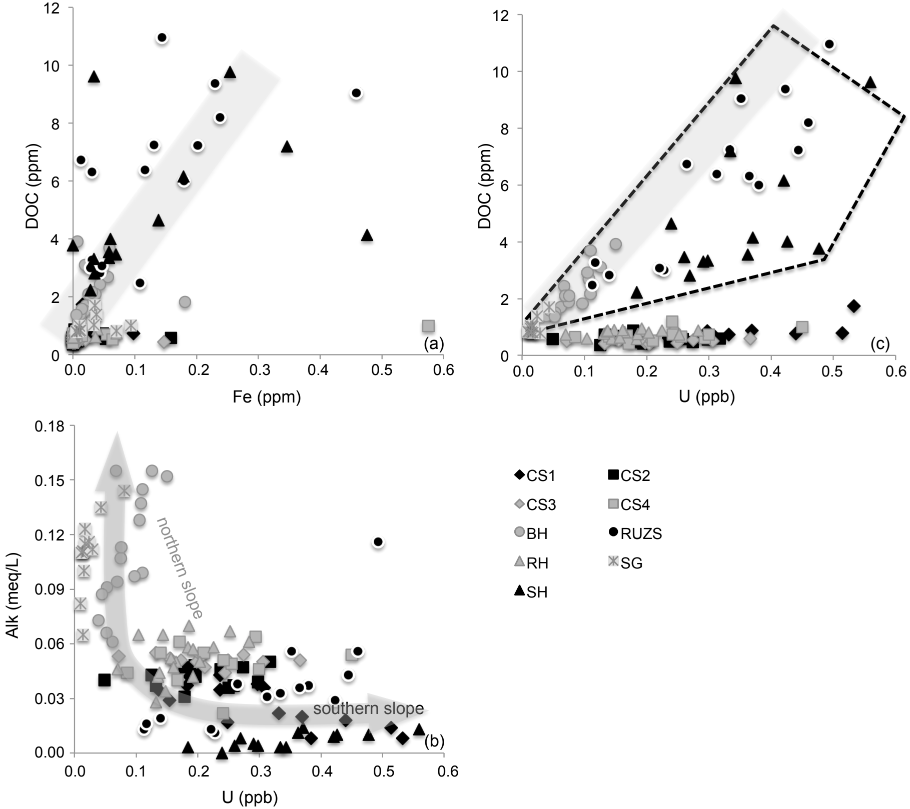

Fig. 4. Relationships between **(a)** DOC (ppm) vs. Fe (ppm), **(b)** Alk (meq L^{-1}) vs. U (ppb) and **(c)** DOC (ppm) and U (ppb). DOC: dissolved organic carbon. Some springs (BH, SH, RUZS, SG) show relationship between Fe, DOC and U concentrations whereas for the others (CS1, CS2, CS3, CS4, RH) the U concentrations show a large variation whereas the DOC concentrations remain low.

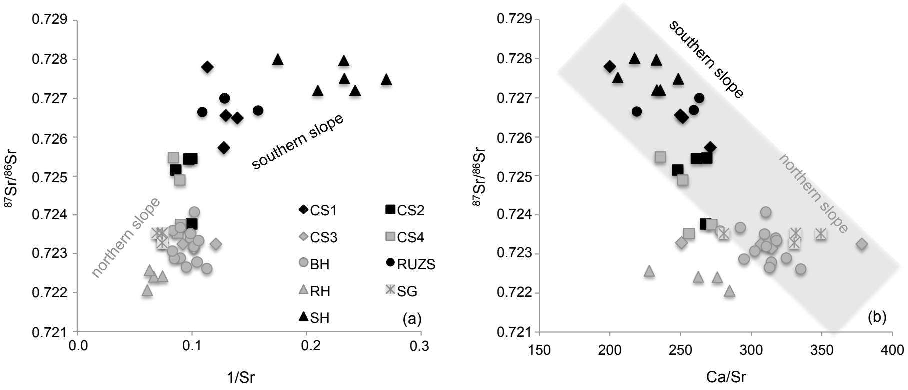

Fig. 5. Relationships between $^{87}Sr/^{86}Sr$ isotope ratios and **(a)** 1/Sr (ppb), **(b)** Ca/Sr (ppb ppb^{-1}), The isotope ratios allow a clear distinction between northern and southern slope sources.

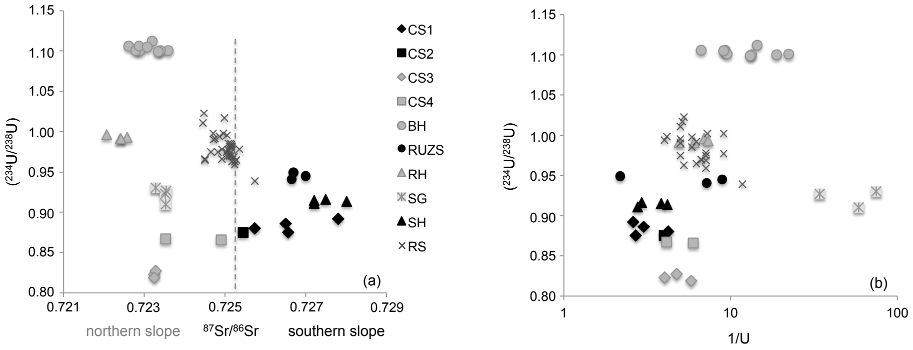

Fig. 6. Relationship between (^{234}U/^{238}U) AR and **(a)** 1/U and, **(b)** ^{87}Sr/^{86}Sr. In contrast to Sr isotopic compositions, the U AR of springs do not allow to distinguish between the northern and southern slopes.

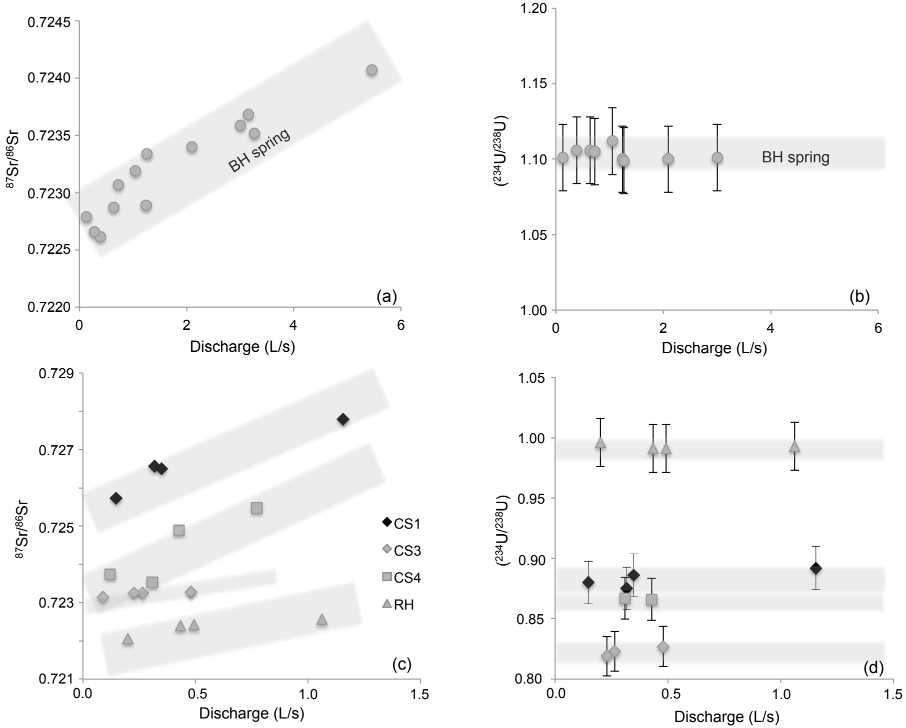

Fig. 7. $^{87}Sr/^{86}Sr$ vs. discharge and $(^{234}U/^{238}U)$ AR vs. discharge for respectively BH spring (**a** and **b**) and for 3 other springs (CS1, RH3 and CS4; **c** and **d**) from the Strengbach watershed.

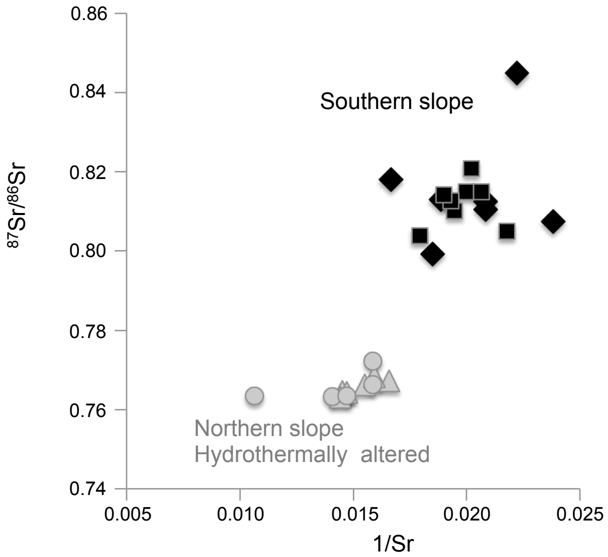

Fig. 8. Variations of $^{87}Sr/^{86}Sr$ vs. 1/Sr for the soil and saprolite samples from the Strengbach watershed. The data show a clear difference between the samples from the northern slope and those from the southern slope (Aubert, 2001; Stille et al., 2009; Prunier, 2008).

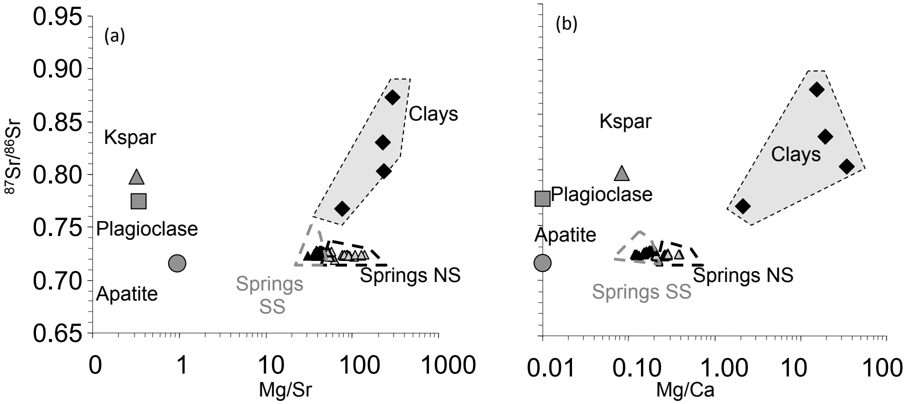

Fig. 9. (a) $^{87}Sr/^{86}Sr$ vs. Mg/Ca and **(b)** $^{87}Sr/^{86}Sr$ vs. Mg/Si for the spring waters (NS = northern slope and SS = southern slope), primary minerals of the granite (Aubert et al., 2001) and clays from soils (Prunier, 2008).

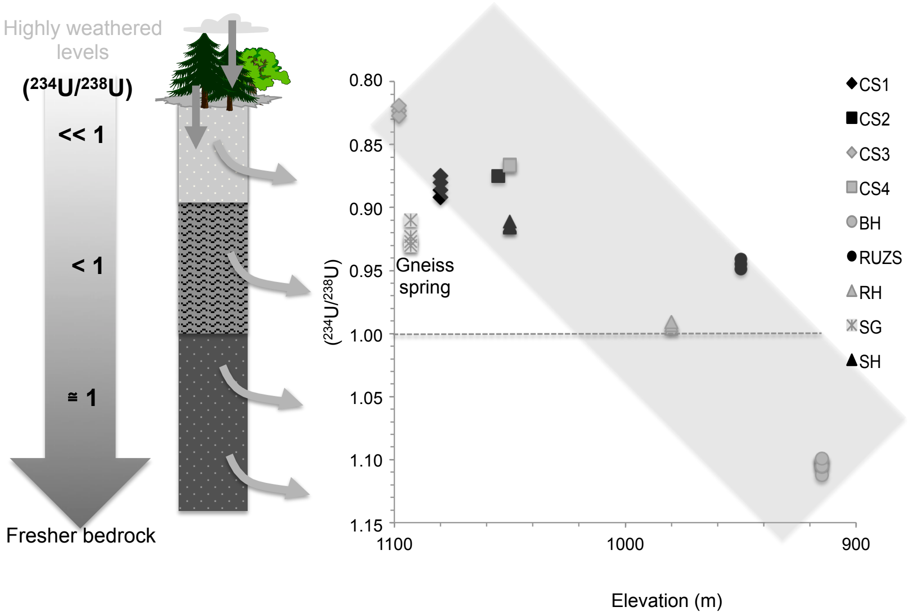

Fig. 10. Variations of (^{234}U/^{238}U) activity ratios vs. elevation in the springs from the Strengbach watershed. At catchment scale we observe relation between U AR and the altitude of source of the springs.

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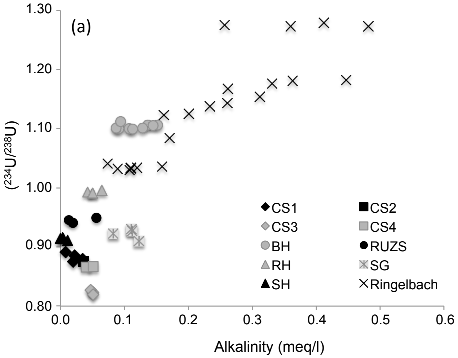

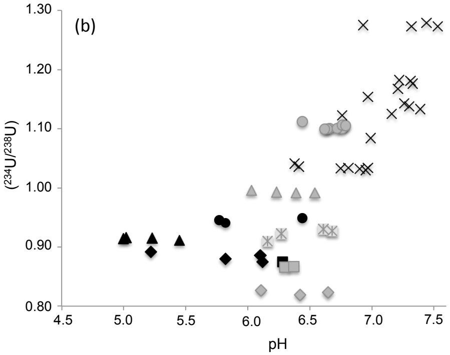

Fig. 11. Variations of (^{234}U/^{238}U) activity ratios vs. **(a)** alkalinity and **(b)** pH in the springs from the Strengbach and Ringelbach (Shaffauser et al., 2014) watersheds.

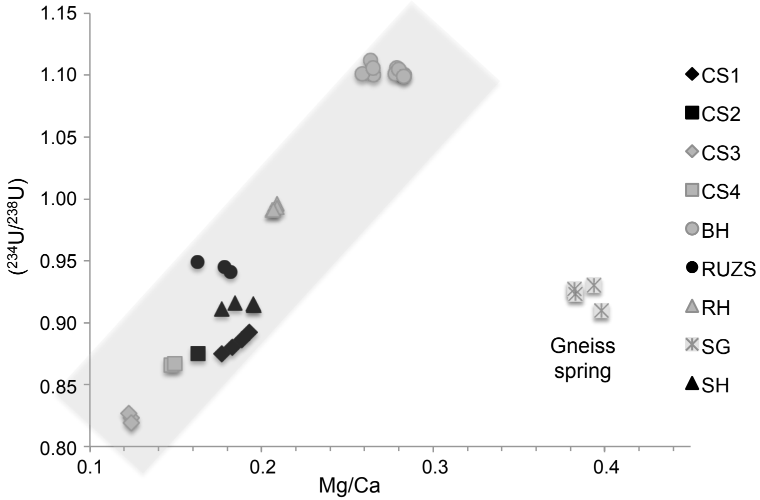

Fig. 12. Variations of $(^{234}U/^{238}U)$ activity ratios vs. Mg/Ca ratio in the springs from the Strengbach watershed. At catchment scale we observe a clear relation between U AR and the Mg/Ca ratio of the springs.

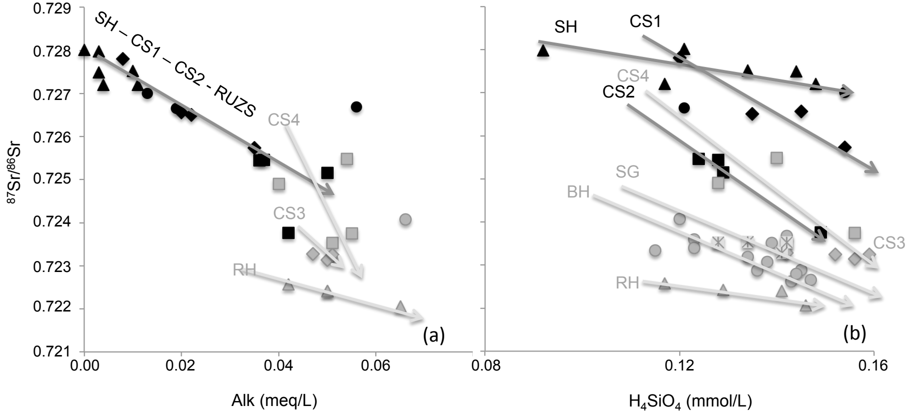

Fig. 13. Variations of $^{87}Sr/^{86}Sr$ vs. **(a)** alkalinity and **(b)** Si concentration for the springs from the Strengbach watershed. For each individual spring we observe a relation between $^{87}Sr/^{86}Sr$ and alkalinity or Si content.

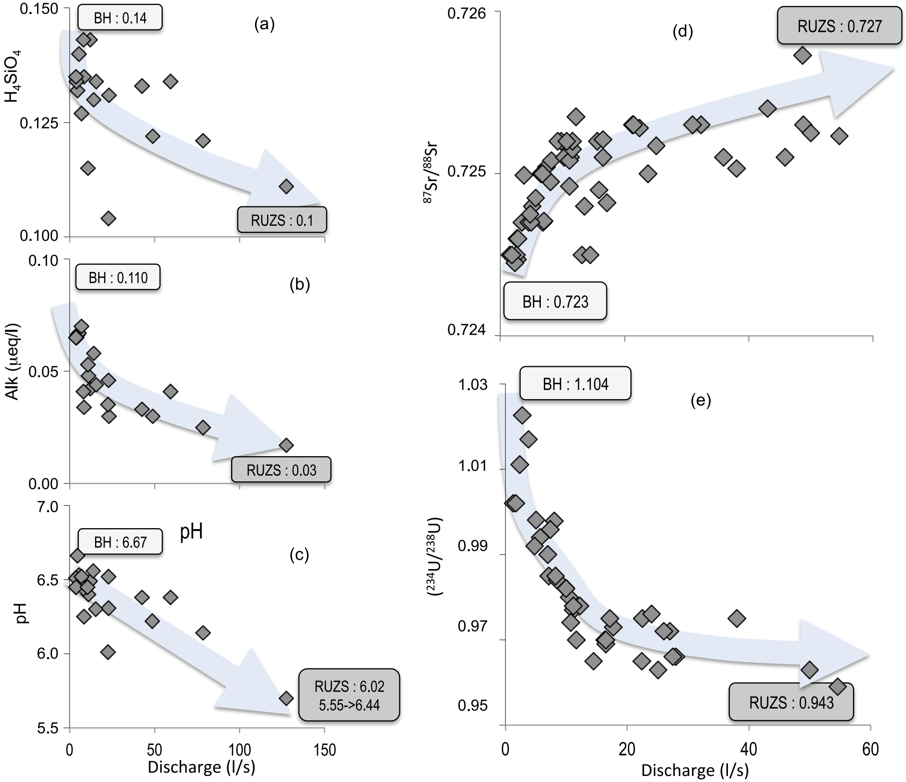

Fig. 14. Variation of **(a)** H_4SiO_4 concentration, **(b)** alkalinity, **(c)** pH, **(d)** $(^{234}U/^{238}U)$ AR and **(e)** $^{87}Sr/^{86}Sr$ vs. discharge for the Strengbach stream at the outlet, for the 2004–2006 studied period (additional data from Riotte et al. (1999) and Aubert et al. (2002) for respectively U AR and Sr isotopic compositions).