Chemical and U-Sr isotopic variations in stream and source waters of the Strengbach watershed (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 slope; also significant are the different meteoric alteration processes of the bedrock causing the formation of 0.5 to 9 meter thick saprolite and above the formation of an up to 1m 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 bedrock 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. Despite the fact that soils and vegetation cover have a great influence on the water cycle balance (evapotranspiration, drainage, runoff), the chemical compositions of waters are strongly modified by processes occurring in deep saprolite and bedrock rather than in soils along the specific water pathways.

Keywords: U activity ratios, Sr isotopes, spring and stream water chemistry, weathering, Strengbach catchment.

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. 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). The impact and the role of vegetation cover and soils on the chemical or isotopical evolution of erosion signals in waters of small catchments have very recently been discussed (Laudon et al., 2004; Cenki-Tok et al., 2009; Cidivini et al., 2011; Engstrom et al., 2010; Kohler et al., 2014; Lemarchand et al., 2010; Zakharova et al., 2007). Determination of parameters controlling the chemical composition of superficial waters is important for a correct modeling of the future evolution of 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). Indeed, when 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

78 equal to 1. However, this ratio can fractionate during chemical weathering when ^{234}U is more easily
79 released into solution by the combined effects of 1) direct recoil of ^{234}Th near grain boundaries out
80 of mineral and 2) preferential release from crystal lattices that are damaged by energetic α-decay
81 (e.g. Bourdon et al., 2009; Chabaux et al., 2003; 2008; DePaolo et al., 2006; 2012; Osmond and
82 Ivanovich, 1992 and references therein). Therefore, natural waters (stream, spring, groundwaters,
83 seawaters) are generally in excess of ^{234}U with ($^{234}U/^{238}U$) AR >1 (Andrews and Kay, 1983;
84 Camacho et al., 2010; Chabaux et al., 2003, 2008; Dosseto et al., 2008, 2012; Gryzmko et al., 2007;
85 Osmond and Ivanovich, 1992; Paces et al., 2002; Pierret et al., 2012; Vigier et al., 2001, 2006).
86 Consequently, ($^{234}U/^{238}U$) AR in superficial waters allow to identify river- flow patterns, and
87 hydrological mixing by tracing the sources of water and recording mixing between superficial and
88 groundwaters characterized by different U AR. Thus the ($^{234}U/^{238}U$) AR change along river flows
89 and in function of hydrological mixing (e.g., Chabaux et al., 2001; Durand et al., 2005; Maher et al.,
90 2006; Osmond and 1982; Paces et al., 2002; Riotte et Chabaux, 1999).
91 In the present paper we focus on a small, more or less monolithic drainage basin, the experimental
92 Strengbach catchment (Vosges mountains, NE France). Several studies have shown that the
93 vegetation cover, the atmospheric deposition, the secondary minerals and the biological recycling
94 play an important role in controlling the geochemical signatures of soil solutions (Brioshi et al.,
95 2012; Lemarchand et al., 2010; Lemarchand et al., 2012; Prunier, 2008; Stille et al., 2006, 2009,
96 2011, 2012). The impact of physico-chemical processes in soil on the chemical balance of waters at
97 the outlet is rather weak. For instance, the mean annual flux of Ca in soil solution at 60 cm depth
98 represents 5 to 20% of the annual flux at the outlet, depending on the type of vegetation or soil
99 (Cenki-Tok et al., 2009). Therefore, the chemical compositions of waters are mainly controlled by
100 interactions occurring with the deep saprolite and bedrock rather than with soils.
101 A previous U isotope study performed on waters from the Strengbach streamlet shows a decrease of
102 the ($^{234}U/^{238}U$) AR from 1.02 to 0.96 when the discharge of the stream increases (Riotte and
103 Chabaux, 1999). Such an isotopic evolution has been interpreted as mixing between a water body

104 enriched in ^{234}U, which is supposed to have interacted with a granitic bed rock at secular
105 equilibrium, and waters with a ($^{234}U/^{238}U$) AR below unity pointing to mobilization of U from
106 material that has already been weathered. Similarly, the streamlets $^{87}Sr/^{86}Sr$ isotope ratios collected
107 during low flow periods have low$^{87}Sr/^{86}Sr$ ratios than during high water flow events (Aubert et al.,
108 2002). The Sr signature at low discharge has been explained by important contributions of waters
109 from the deep soil profile during the recession stage, whereas higher $^{87}Sr/^{86}Sr$ isotope ratios at
110 higher discharge are due to important contributions of waters from the saturated area of the
111 catchment.
112 In order to define more precisely temporal and spatial variations of the hydrochemistry of the
113 streamlet and the different springs and to evaluate the major and trace element sources and the
114 processes controlling this element supply to the freshwaters, additional ($^{234}U/^{238}U$) AR. $^{87}Sr/^{86}Sr$
115 isotopic ratios and major and trace element concentrations were analyzed in the different source
116 waters collected during two different hydrological seasons (2004-2006) and compared to those of
117 the streamlet.
118

119 ## 2. Site description

120 The Strengbach catchment is a small granitic watershed (0.8 km^2) where meteorological,
121 hydrological and geochemical data are recorded since 1986 (Observatoire Hydro-Géochimique de
122 l'Environnement; OHGE; http://ohge.u-strasbg.fr). The first studies were performed in order to
123 understand the impact of acid rain on the forested ecosystem (Dambrine et al. 1991, 1992a,b; Probst
124 et al. 1990, 1992a, b). The catchment is situated in the Vosges Mountains (NE France) at altitudes
125 between 880 and 1150 m (amsl) and has strongly inclined slopes (mean 15°; Fig. 1).
126 The climate is temperate oceanic mountainous (mean annual temperature of 6°C; mean monthly
127 temperature range from –2 to 14°C) with an average rainfall of 1400 mm/yr (ranging between 890
128 and 1630 mm/yr over the period 1986-2006) and with snowfall during 2-4 month/yr (Probst and
129 Viville, 1997; Viville et al., 2012; OHGE Data). The mean annual runoff for the same period is of

853 mm (26.9 $Ls^{-1}km^{-2}$) 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). In addition, the northern sun-facing slope is characterized by a drier and slightly warmer climate with 10% less precipitation than observed for the southern slope. The soils are brown acidic to ochreous brown podzolic and are generally about 1 meter 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). The pedological differences are due to the different mineralogical compositions of the northern and southern bedrocks, and the different types of vegetation but also the different orientations of the slopes. Indeed, exposure and consequently rainfall and temperature influence the chemical weathering of soils and organic matter, the soil acidity and processes of clay formation (Egli et al., 2007; 2010).

156 A sandy saprolite separates soil and granite. Its thickness varies between 1 and 9 meters; on the
157 southern slope it is generally thicker (El Gh'Mari, 1995) with the most important thickness in the
158 depression zone near the four springs CS1, CS2, CS3 and CS4. The forest covers 90% of the area
159 and corresponds to about 80% spruce (mainly *Piceas Abies L.*) and 20% beech (*Fagus Sylvatica*).
160 The catchment contains 10 different springs feeding the Strengbach streamlet (Fig.1).
161 The catchment is situated in a remote area lacking direct industrial activities. Nevertheless,
162 atmospheric pollution occurs in many forms (acidic deposition, O_3 pollution or as atmospheric dust
163 deposition). Anthropogenic Pb has been identified in the atmospheric dust depositions and soils
164 (Lahd Geagea et al., 2008b; Stille et al., 2011). The forestry has increased the proportion of spruce
165 with especially dense spruce plots planted between 1890 and 1960. The site is well equipped for
166 sampling of atmospheric depositions and spring and stream waters at the whole catchment scale.
167 For this study, the stream and the different springs of the catchment were collected at various
168 hydrological periods with high and low water levels during a two years period (2004-2006) in order
169 to obtain a precise chemical and isotopic signature of the different sources in this hydrological
170 system (Fig. 1). The springs SG, ARG, RH, BH, CS_3 and CS_4 are located on the northern slope and
171 the springs CS_1, CS_2, SH and RUZS emerge at the southern slope (Fig. 1). The spring RUZS is
172 situated in the humid zone at the bottom of the catchment near the outlet (saturated area, Fig.1) and
173 covered by dense grass vegetation. In addition rain (bulk precipitation) and throughfalls were
174 collected using rain collectors and gutters, respectively.
175

176 ## 3. Analytical procedures

177 The different spring waters were collected every 6 weeks during 2 years unless the springs were dry
178 or under snow. The waters were collected in clean polyethylene (HDPE) bottles (250 ml for major
179 element analysis and 1 litter for isotope and trace element analysis) and filtered the same day
180 through a 0.45 μm pore diameter membrane (Millipore ester cellulose, 142 mm diameter). Before,
181 the HDPE bottles were washed with HCl 10% (24h contact) and then rinsed with MilliQ deionised

182 water. The filtrated waters for trace element and U-Sr isotopic composition determinations were
183 acidified with 250 μl of ultrapure HNO_3 13M and then stored in a cold room at 5°C.
184 The pH were measured just after filtration using a pHM210 MeterLab (Radiometer analytical) with
185 an Mettler HA405-DXKS8 electrode and calibrated with standard buffer solutions (pH 4.00 and
186 7.00 at 25°C). The precision of the pH measurement was ± 0.02 units. The electrical conductivity
187 and the alkalinity were determined respectively using a CDM210 MeterLab (radiometer analytical)
188 with an CDC 745-9 electrode (precision 0.1 μS/cm) and with 716DMS Titrino (Metrohm ; precision
189 of 0.01 meq/l – Acid/base titration, Gran method).
190 The major element contents were determined by ionic chromatography, atomic absorption,
191 colorimetry and ICP-AES and the trace element concentrations were determined by ICP-MS
192 (Pierret et al., 2010, Chabaux et al., 2011). The analytical uncertainty of the major cation and anion
193 determinations in solution (by atomic absorption and ionic chromatography Dionex, 4000 I) is ± 2
194 %. The uncertainty on the major element concentrations such as Fe, Al, Mn and Si (by ICP-EAS,
195 Jobin Yvon 124) is ±5%, and that of the trace element concentrations (by ICP-MS, VG Plasma
196 Quad; Thermo Electron) is ±5%. The dissolved organic carbon (DOC) was determined using an
197 organic carbon analyser (Shimadzu TOC-5000A) with an uncertainty of 5 to 10 %, The accuracy of
198 the analysis was assessed by regular analysis of the SLRS-4 riverine standards,
199 The Sr isotopic ratios were determined by thermo-ionisation mass spectrometry on a multi-collector
200 VG-Sector mass spectrometer. Sr was extracted by standard procedures (Steinmann et Stille, 1997;
201 Lahd Geagea et al., 2008a; Pierret et al., 2010). The routinely measured NBS 987 standard yield an
202 average $^{87}Sr/^{86}Sr$ ratio of 0.71026 ± 0.00002 (2s) for 10 determinations during the course of this
203 study. The U isotope ratios were analysed on a TRITON Thermofinnigan mass spectrometer after
204 separation and purification of U by anionic exchange chromatography (resin AG1X8, 200-400
205 mesh) following the classical technique used in the lab (e.g. Chabaux et al., 1997; Pelt et al., 2008,
206 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 ($^{234}U/^{238}U$) 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, from 0.42 to 11.6 ppm, from 10.3 to 26.8 mg/L, from 3.87 to 9.05 mg/L, and from 13.2 to 60.3 μS/cm (Table 1). The pH is well correlated with alkalinity and TDS-Ca (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 CS_1 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 and H_4SiO_4/Ca concentration ratios (Fig.3) but also the K/Na, Sr/Na, Mg/Ca ratios (not shown), the different springs are not only marked by different mean major element concentrations (2004-2006 period) but also by different elemental ratios.

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, CS_3, CS_4 and BH) and those from the southern slope (CS_1, CS_2, 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; table 1). 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).

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. 4, 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 concentrations (Fig. 4).

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. 6) 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 AR of the source waters when the altitude of the spring decreases. A similar behavior has been observed for waters from another small granitic watershed in the Vosges Mountain, the Ringelbach watershed (Schaffhauser et al., 2014). But in contrast to the Ringelbach catchment, where the U AR in the spring waters are above 1, one observed for the spring waters of the Strengbach cachtment U AR $\leq$1 except for BH source.

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, and H_4SiO_4/Na concentration ratios are neither rainwater nor throughfall controlled. Indeed rainwater and throughfall show rather large variations of their Ca/Na or Mg/Na ratios (throughfall: Ca/Na: 0.9-2.1; Mg/Na: 0.3-0.6) 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 throughfall cannot be a significant source of cation fluxes in the spring waters (Figs.7a and c and 13).

284 Therefore, chemical differences among the sources of the Strengbach watershed have to be
285 interpreted in terms of variations in the nature or in the intensity of water-rock interactions
286 occurring from one source to another or in the intensity of the interactions between different water
287 reservoirs. This interpretation is entirely consistent with the correlations observed for the spring
288 waters at the watershed scale between the alkalinity, TDSw and their pH (Fig. 2; Table 1), since
289 consumption of H^+ during silicate weathering increases pH and alkalinity. Thus, from these data it
290 appears, that the spring waters from the northern slope with higher total dissolved solid contents,
291 higher alkalinity and pH values (SG, CS4, CS3, RH with BH having the highest values) are more
292 involved in weathering reactions, or are subject to more intense weathering processes than spring
293 waters from the southern slope (especially SH, RUZS and CS1).
294 The geochemical signatures of the different springs can be generally linked to specific lithological
295 and mineralogical differences existing for the two hillsides of the catchment. This is particularly
296 obvious for the SG spring, which emerges near the top of the catchment, just below the gneiss,
297 whereas the other sources emerge within the granitic environment (Fig. 1). In comparison with the
298 granite, the gneiss has 4 to 5 times higher Mg concentrations due to important occurrences of biotite
299 and chlorite (El Gh'mari. 1995; Table 4). The Mg/Na and Mg/Ca elemental ratios are about 7.5
300 respectively 11 for the gneiss and range from 0.7 to 0.1 respectively 0.5 to 1.5 for the granite (El
301 Gh'Mari, 1995; Fichter, 1997; Table 4). Mg is also more concentrated in the gneiss-derived soils
302 (MgO : 0.9 to 1.4 wt.%), than in other soil profiles of the catchment (0.4 to 0.7 wt.%) (El Gh'Mari,
303 1995; Lefèvre, 1988; Table 4). Similarly, the Ca/Na ratios of the gneiss (0.71) and the
304 corresponding soils (0.7 to 9.2) are higher than those of the granite (0.2 to 0.6) or of the
305 corresponding soils (0.1 to 0.5) (El Gh'Mari, 1995; Fichter, 1997; Table 4). All these lithological
306 and pedological characteristics explain why the SG spring waters are more enriched in Mg and have
307 higher Mg/Ca, Mg/Na and Ca/Na ratios than the other springs (Fig. 3).
308 The variation of the chemical data of the other spring waters emerging from the granite might result
309 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; Prunier, 2008; Stille et al. 2009). 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; Table 4). 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, CS_2, CS_1, RUZS) are, like the corresponding rocks and soils (Aubert et al. 2002) (Fig. 7), more radiogenic with lower Sr concentrations than those from the northern slope (BH, RH, SG, CS_3, CS_4) (Fig. 4). 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. 8a,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

336 be ignored. The clay fractions, extracted from the two weathering profiles at sites HP and VP
337 (Prunier, 2008) can represent an end-member able to explain the Sr isotopic composition as well as
338 the Mg/Ca and Mg/Sr ratios of springs. The springs, bulk soils and clays from the southern slope
339 show higher $^{87}Sr/^{86}Sr$ ratios than those from the northern slope. Clay fraction contents in weathering
340 profiles from northern slope are twice as big as those from the southern slope. This suggests that the
341 impact of clay on the chemical composition of springs and streams is more important on the
342 northern than the southern slope. This also explains why the springs from the northern slope are
343 more radiogenic (Fig. 4a and b) with comparatively higher Mg/Ca and Mg/Sr ratios (Fig. 8a and b)
344 than those from southern slope.
345 Such an interpretation is consistent with results of numerical modeling, which indicates that
346 precipitation/dissolution of more or less crystallized clay minerals (such as smectite) control the Mg
347 concentrations and possibly the high Mg/Ca ratios in the source waters of the Strengbach watershed
348 (Godderis et al. 2006; 2009). The same authors proposed that Mg^{2+} is controlled by smectites, Ca^{2+}
349 by the dissolution of apatite and by smectite, and K^+ by smectite/illite precipitation and dissolution
350 of K-feldspar. Interaction with clays might occur all along the circulation pathway of waters in
351 soils, saprolite and in bedrock fractures. Recent studies in the Mule Hole watershed, Mackenzie
352 basin and Damma Glacier catchment confirm the importance of secondary mineral formation,
353 especially montmorillonite in the control of chemical composition of stream water at the watershed
354 scale (Violette et al., 2010; Beaulieu et al., 2011; Hindshaw et al., 2011).
355 Thus, the variation of the current chemical compositions of the source waters in the Strengbach
356 catchment possibly reflects dissolution/precipitation processes of secondary mineral phases like
357 clay minerals. In such a model the low apatite-like Sr isotopic composition values of the source
358 waters and comparatively high and not apatite-like Mg/Ca ratios can be explained by the fact that
359 the Sr has not been remobilized by alteration of primary apatite but by weathering of secondary
360 mineral phases, which integrated during an earlier stage of alteration and crystallization apatite-

361 derived Sr. At this point we therefore propose that the alteration flux controlling the $^{87}Sr/^{86}Sr$ and
362 Mg/Ca (resp Mg/Sr) variation in the sources is imposed by secondary minerals.
363
364 **5.2. $^{234}U/^{238}U$ AR in spring waters**
365 Observation of ($^{234}U/^{238}U$) AR < 1 in most of the spring and stream waters of the Strengbach
366 catchment is unusual as river waters exhibit generally ^{234}U excess (e.g., Chabaux et al., 2003). U AR
367 < 1 have already been observed for waters from the outlet of the Strengbach catchment (0.963 to
368 1.023) with a decrease of the U AR in the dissolved load when the discharge increases (Riotte et al.,
369 1999). The authors explained this variation by the involvement of different weathered end-
370 members: a water body enriched in ^{234}U which weathered the granitic bedrock at secular
371 equilibrium and waters with a U AR below unity representing mobilization of U from material that
372 has already been weathered. Our study shows an even larger range of variation of the U AR among
373 the different springs ranging from 0.819 (CS3) to 1.112 (BH) (Table 2). The lack of correlation
374 between ($^{234}U/^{238}U$) AR and $^{87}Sr/^{86}Sr$ isotopic compositions or chemical values (Fig. 5a and b) show
375 that AR are not simply lithology controlled.
376 The mechanisms classically involved to explain ($^{234}U/^{238}U$) AR >1 in natural waters are linked to the
377 recoil process associated to the decay of ^{238}U: 1) due to alpha recoil when ^{238}U decays to ^{234}Th, it can
378 be ejected out of a grain into the fluid if the distance to the grain boundary is smaller than the recoil
379 range of ^{234}Th (~30 nm; DePaolo et al., 2006); the ^{234}Th decays then rapidly to ^{234}U (^{234}Th half-life is
380 24 days); (2) α - particles emitted during radioactive decay damage the crystal lattice of mineral
381 grains and the recoil nuclide is subsequently easily mobilized out of the damaged site. As a
382 consequence, the daughter nuclide ^{234}U is preferentially leached relative to the parent ^{238}U during
383 weathering. Thus, natural waters with ($^{234}U/^{238}U$) AR < 1 most likely correspond to environments,
384 which have already experienced a loss of ^{234}U.
385 One might simply suggest that the U AR < 1 in the Strengbach source waters are the results of
386 circulation through already weathered soils, supposedly having U AR<1 due to previous

387 weathering. However, chemical flux balance calculations show that the annual U fluxes from the
388 soils under spruces or beech trees represent at maximum about 8% or 22%, respectively, of the
389 annual U flux at the outlet (Table 3). At the same time, the U concentrations in the different
390 springs can reach on average 0.345 ppb whereas they range only between 0.011 to 0.023 ppb
391 (factor of 30 to 15 lower) in the deep soil solutions of the two experimental plots (Table 2). In
392 addition, ($^{234}U/^{238}U$) AR determined on soil solutions from depths between 5 and 70 cm, range from
393 0.899 and 0.945 under spruces and from 0.953 to 1.194 under beech trees (Prunier, 2008) whereas
394 they are significantly low for some spring waters (0.82). This indicates that circulations and
395 interactions in the saprolite and bedrock (below the soil) control the U isotopic signature in
396 spring and stream waters.
397 The relationship between the U AR and the altitude of the springs (Fig. 9) indicates that the springs
398 from both slopes with the lower U AR (CS1, CS2, CS3, CS4) are located at higher altitude and
399 circulate in zones where the saprolite reaches 7 to 9 m depth (El'Ghmari, 1995) than springs with
400 high U AR. The spring BH, with the highest U AR is located at the bottom of the watershed where
401 the saprolite layer reaches less than 1.5 m thickness (Fig. 1). Also RUZS was taken at low altitude
402 (950masl), but drains the whole wetland and, therefore, integrated an intermediate U AR. Thus, a
403 possible scenario explaining the ($^{234}U/^{238}U$) AR of the spring waters is that BH like sources are
404 closer to the "fresh" granite and reflect meteoric alteration of fresher rock material at secular
405 equilibrium, CS_1, CS_3, CS_2, CS_4 and SH sources, by contrast, drain thicker saprolite profiles and/or
406 less fresh granite and, therefore, their low AR may point to the mobilization of U from mineral
407 phases whose outermost surfaces have already been depleted in ^{234}U due to previous water-rock
408 interactions (old saprolite where the pool of excess ^{234}U has been exhausted). We therefore propose
409 that the $^{234}U/^{238}U$ AR in the catchments spring waters can be interpreted as a function of water
410 pathways. The sources emerging at high altitude, with AR<1, have circulated through already
411 weathered horizons (saprolite, fractured bedrock depleted in ^{234}U, i.e., with U AR <<1), whereas the
412 springs emerging at the bottom of the watershed have U AR>1 because of the interaction with

413 fresher mineral phases. Therefore, U disequilibrium ratios can be a powerful tool to study the water
414 pathways. These preferential flow paths cross more or less weathered materials implying various
415 ($^{234}U/^{238}U$) AR for the corresponding springs.
416 This interpretation is in agreement with a granite leaching experiment under continuous flow
417 through a reactor (Andersen et al., 2009). It has indeed been shown that during the experiment
418 (1200 hours) there is a clear trend of variation of the U AR in the outflowing waters, with
419 ($^{234}U/^{238}U$) AR >1 at the beginning of the experiment and a minimal value of 0.9 after 650 to 700
420 hours; then, the AR increased up to 0.95. The values suggest that at the beginning of the experiment
421 high exposure of fresh material promotes direct recoil of ^{234}U into water and potentially enhances
422 preferential release of ^{234}U from damaged lattice sites. However, since there was no renewal of
423 material, because the excess ^{234}U constitutes a finite pool of easy leachable ^{234}U, the ($^{234}U/^{238}U$)
424 values become lower than unity when this pool is used up.
425 Similarly, the observed ($^{234}U/^{238}U$) AR <1 in Strengbach springs might indicate that the rate of
426 production of ^{234}U excess (by direct recoil and preferential release) is lower than the rate of renewal
427 of material. This can be explained by continuous preferential water circulation along fractures (Le
428 Borgne et al., 2007), on old weathered mineral surfaces where the production of ^{234}U excess is
429 supposed to be low.
430 However, the springs emerging at lower altitude (mainly BH and to a lesser extend RH), with
431 ($^{234}U/^{238}U$) >1, circulate through fresher granite where α-recoil tracks have direct contact with the
432 outer mineral surfaces and thus with fresh mineral phases (Andersen et al., 2009).
433 At this point it is interesting to note that in a neighboured granite catchment (Ringelbach watershed)
434 all the sources only display U AR >1 (Schaffhauser, 2013; Schaffhauser et al., 2014). This small
435 catchment located in the Vosges massif at altitudes between 750 and 1100m (0.36 km^2) also
436 consists of Hercynian granite capped in its upper part by residual Triassic sandstones (Schaffauser
437 et al., 2014).

Plotting the U AR of springs of the both watersheds versus alkalinity and pH (Fig. 10) one observes a 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 section 5.1). The modeling of chemical composition of the waters from the Ringelbach catchment implies mainly dissolution of primary granite minerals and precipitation of secondary phases such as clays (Schaffauser, 2013). Ringelbach stream waters present higher alkalinity, pH (Fig. 10) and also conductivity, K, Mg, Si and Ca concentrations (not show) than spring and stream waters from Strengbach watershed, which might point to higher dissolution processes. Thus, we suggest that the waters with the lowest U AR correspond to less intense weathering in an already rock altered system with only a few fresh and 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 might be older for the Strengbach watershed than the Ringelbach watershed. This may be related to 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. 10a 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 variations of pH in the different springs only reflect 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 secondary phases such as smectite along the pathway of this source water.

464 In such a scenario, the relationship observed between ($^{234}U/^{238}U$) AR and Mg/Ca ratios (Fig. 11)
465 would indicate that the intensity or the nature of water reactions controlling the Ca-Mg budget of
466 these waters, namely the dissolution/precipitation reactions of Mg- or Ca-smectites (see discussion
467 in 5.1), would be clearly dependent on the weathering level of the saprolite/bedrock system. This is
468 consistent with the fact that 1) smectite occurs along the weathering profile and even in deep
469 weathering horizons (Fichter et al., 1998) and 2) the reactivity of secondary phases like smectite
470 control the chemistry of Mg and Ca in streamwater (this study, Godderis et al., 2006; 2009). In
471 addition, dissolution of clays implies an increase of Mg/Ca ratios in water (Fig. 8b). Thus, the
472 relation between U AR and Mg/Ca ratios for the Strengbach springs reflects nothing else than the
473 degree of alteration of the source rock being in contact with the waters: at low altitude the material
474 is fresher, the weathering intensity is more important (higher pH and alkalinity) and, thus, causes
475 higher Mg/Ca and U AR ratios in the waters than at higher altitudes.
476
477 **5.3. Temporal variations of spring waters**
478 The data obtained during 2 hydrological years allow for the analysis of the temporal variations of
479 the springs (Fig. 3). The spring RUZS shows the largest variations, which can be explained by the
480 fact that this spring drains wetland (10 to 15 % of the whole catchment area) with fluctuations in the
481 groundwater level and contributions.
482 The Sr isotopic compositions of single springs are correlated with discharge (Fig. 6a). In previous
483 studies these variations have been interpreted by mixing of superficial (soil solution type) and deep
484 (groundwater type) waters (Aubert et al., 2002). But, at the same time, the U AR show no temporal
485 variation and, therefore, no relation with discharge (Fig. 6b).
486 Consequently, the U AR and Sr isotopic compositions are not correlated. Similarly, there is no
487 correlation between U AR and geographical location and lithology (discussed in section 5.2). In
488 addition, the lack of temporal U AR variations indicates that the single springs are probably not the
489 result of mixing of different waters. In the same way, the lack of correlation between discharge and

490 DOC or NO_3, but also the majority of major and trace element concentrations suggests that the
491 variation of chemical composition of spring waters cannot be explained by a simple variation in the
492 contribution between different types of waters or as mixing between superficial waters (with high
493 DOC, NO_3 concentrations for instance) and deep waters. At the same time, the lack of correlation
494 between Sr isotopic compositions and concentrations for individual springs (Fig. 4a) confirms that
495 the temporal variations of spring waters cannot simply be explained by mixing between two end-
496 members (e.g. superficial and deep waters). The lack of variation of U AR in the individual springs
497 with changing discharge (Fig. 6) during 2 years further suggests that the water pathways are the
498 same whatever the hydrological conditions. Under these conditions, the water did not interact with
499 new fresh material but rather with minerals having experienced at their surface a prior loss of ^{234}U
500 from damaged lattice sites (Andersen et al., 2009). In such a fractured bedrock system, the water
501 flow is often reduced to only a few main flow paths that control most of the hydrological response
502 of the aquifer (Le Borgne et al., 2007). These preferential flow paths along constant fractures in the
503 bedrocks might explain the homogeneous ($^{234}U/^{238}U$) AR of the different spring waters with time.
504 In contrast, there is a correlation between discharge and $^{87}Sr/^{86}Sr$ ratios for each single spring (Fig.
505 6b). With increasing discharge the Sr isotopic composition increases as well, whereas the Si
506 concentrations and alkalinity decrease (Fig. 12).
507 Different Si concentration-discharge relationships have been observed in several catchments and
508 three different types have been identified: type 1 when Si concentration decreases with discharge;
509 type 2 when Si concentration remains constant and type 3 when Si concentration remains constant
510 until a threshold in discharge is exceeded (Godsey et al.. 2009; Maher. 2011). The springs from the
511 Strengbach watershed belong to the type 1 which are explained by average residence times shorter
512 than required to approach chemical equilibrium. Thus, the chemistry of waters could vary entirely
513 as a function of the nature of subsurface flow paths and the global solute fluxes depend strongly on
514 the geometry, relief, runoff and permeability of basins (Maher. 2011). In addition, the variation of
515 the Sr isotopic compositions with discharge suggests that the source of Sr changes with changing

516 hydrological condition; this confirms again that the temporal variation cannot be explained by a
517 mixing process but possibly by changing residence times of fluid and/or flow rate which according
518 to Maher (2010) have an important impact on the weathering rates. This is in accordance with the
519 hypothesis of preferential flow pathways through fractures for the water circulation in the basin.
520 In addition, modeling studies have shown that precipitation/dissolution process of secondary phases
521 control the dissolved Si export in stream waters (Godderis et al., 2006; Violette et al., 2010;
522 Beaulieu et al., 2011). Thus, the decrease of Si concentration with increasing discharge can be
523 explained by a change in the ratio between dissolution and precipitation of clays (see also chapter
524 5.2). We propose that at high discharge the water is undersaturated for clay precipitation (lower Si
525 concentration) causing a more important contribution by dissolution of clays as implied by the
526 higher Mg/Ca (see chapter 5.1) and Sr isotopic ratios (Fig. 11c). Thus, our study confirms that
527 hydrological properties limit the solute fluxes carried by rivers and physico-chemical conditions.
528

529 **5.4. The chemical and isotopic signatures of the waters at the Strengbach outlet**

530 The stream at the catchments outlet shows with increasing discharge increasing $^{87}Sr/^{86}Sr$ and
531 decreasing alkalinity, pH, H_4SiO_4, and ($^{234}U/^{238}U$) AR (Fig. 13a-e). The important point is that the
532 variation of U AR observed at the outlet (Fig. 13e) can only be explained by a change in the
533 discharge contribution of the different springs because the U AR of single springs are constant with
534 time (Fig. 6). When the discharge increases, the U AR values tend towards 0.95, which is close to
535 the ($^{234}U/^{238}U$) AR of the spring from the saturated area (RUZS) (Figs. 6 and 14). Previous papers
536 proposed that during storm events, the contribution of the small saturated zone could reach up to 30
537 % of the runoff (Idir et al., 1999; Ladouche et al., 2001). Similarly, the increase of the Sr isotopic
538 composition with increasing discharge points to the important contribution of RUZS to the
539 streamlet during high discharge events (Fig. 13d).
540 However, during the lowest discharge, the U AR of the stream at the outlet is > 1 (max. 1.023).
541 These higher values can only be explained by a more important contribution of the spring BH from

542 the northern slope which is the only one with a U AR>1 (average: 1.103; Table 1; Fig.14). Other
543 parameters such as H_4SiO_4, pH and alkalinity confirm the important contribution of the BH spring
544 to the streamlet during low discharge (Fig. 13). Similarly, the position of the RUZS spring with the
545 low pH, alkalinity and silica concentrations (Fig. 13) confirms its important contribution during
546 high discharge. But also the fact that the Sr isotopic composition of the stream at the outlet
547 decreases with decreasing discharge is in accordance with a more important contribution of the less
548 radiogenic springs from the northern (e.g. BH) (Fig. 13) than from the southern slope (Fig. 4).
549

550 **6. Conclusion :**

551 The study shows that the small Strengbach catchment drains different sources and streams with very
552 different isotopic and geochemical signatures. This heterogeneity is mainly related to:
553 - the parent material (gneiss, more or less hydrothermally altered granite) and the degree of their
554 weathering. This is confirmed by the fact that the sources draining the northern slope
555 (hydrothermally much more altered) have higher TDSw-, pH values, higher Ca, K, Mg
556 concentrations and lower $^{87}Sr/^{86}Sr$ ratios than sources draining the southern slope.
557 - the water flow is probably controlled by pathways through main fractures, as it is generally the
558 case in fractured granite systems.
559 This study has also shown, that there is an important decoupling between chemical composition on
560 the one hand and the $^{87}Sr/^{86}Sr$ ratios and ($^{234}U/^{238}U$) AR on the other hand. The Sr isotopic
561 compositions of the source waters are generally thought to be the result of alteration of primary
562 mineral phases such as apatite. However, the low apatite-like Sr isotopic composition but
563 comparatively high and not apatite-like Mg/Ca ratio cannot simply be derived from apatite
564 dissolution; however, they might originate from alteration of secondary mineral phases like clay
565 minerals, which integrated during their formation an apatite-derived Sr isotopic composition. The
566 dissolution and precipitation dynamics of secondary phases, especially clays such as
567 montmorillonite, seem to control the mobility of Si, Ca or Mg and, therefore, emphasize the key

568 role of the clays reactivity in the biogeochemical transfer of especially nutrient elements like Ca and
569 Mg.
570 Different processes control the variation of the U AR. Springs at high altitude with U AR<1 have
571 circulated through already weathered bedrock (thick saprolite and fractured rock) and have
572 interacted with already weathered surface minerals. These uncommon values for surface waters are
573 due to strong ^{234}U depletion during predating alteration processes of the bedrock granite. At the
574 opposite, springs emerging at the bottom of the watershed have U AR >1 because of interaction
575 with fresher materials.
576 The lack of variation of U AR in the individual springs with changing discharge during 2 years
577 suggests that the water pathways are the same whatever the hydrological conditions and that there is
578 no interaction between the different source waters.
579 It appears that the ($^{234}U/^{238}U$) AR is a very important tracer for studying and deciphering the
580 contribution of the different source fluxes at the catchment scale because this unique geochemical
581 parameter is different for each individual spring and at the same time remains unchanged for each
582 of the springs with changing discharge and fluctuating hydrological conditions. Without this
583 parameter it would not have been possible to decipher the real contribution of the different water
584 masses, especially that of the BH spring at low discharge conditions.
585 Thus all these observations converge toward the same functioning:
586 - The proportion of the contributions of the different springs to the stream at the outlet varies in
587 function of the hydrological conditions; the variable contributions of the different sources carrying
588 different geochemical signatures define the signature of the waters at the Strengbach outlet.
589 - During high flow events, the contribution of the saturated area (RUZS) to the streamlet increases.
590 - At low discharge, the contributions of springs from the northern slope become important (e.g.
591 BH).
592 The U-Sr isotope study, combined with physico-chemical investigations of the waters offered the
593 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 to 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.

Acknowledgements

We thank Daniel Million, Sophie Gangloff, Sylvain Bénarioumlil and René Boutin for technical assistance. We would like to warmly acknowledge Yves Goddéris and Yann Lucas for discussion about modeling. The manuscript benefit from constructive reviews from Stephan SK Köhler and an anonymous reviewer. The Observatoire Hydro-Géochimique de l'Environnement OHGE is financially supported by INSU-CNRS, as well as by the REALISE network. This work has been funding by EC2CO INSU CNRS program, and by 7th PCRD EU program (SoilTrec program). This is an EOST contribution.

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613

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	date	Discharge	pH	Cond.	Na^{+}	K^{+}	Mg^{2+}	Ca^{2+}	Alc	Cl^{-}	NO_3^{-}	SO_4^{2-}	DOC	H_4SiO_4	Al	Mn	Fe	Ba	Rb	Sr	U	TDSw	TDS-ca
		l/s		µS/cm	mmol/l	mmol/l	mmol/l	mmol/l	meq/l	mmol/l	mmol/l	mmol/l	ppm	mmol/l	ppm	ppm	ppm	ppb	ppb	ppb	ppb	mg/l	mg/l
Spring Collector CR	12/07/04		5.66	35.5	0.092	0.025	0.018	0.07	0.049	0.057	0.058	0.066	0.47	0.157	0.02	0.01	0.01	79.56	3.02	10.12	0.24	21.35	6.44
CR	28/09/04		5.74	34.9	0.096	0.02	0.018	0.074	0.05	0.053	0.061	0.066	0.45	0.157	0.05	0.01	0.00	84.00	3.44	11.03	0.23	21.52	6.49
CR	02/11/04		5.84	30.3	0.083	0.02	0.019	0.077	0.041	0.053	0.073	0.062	0.78	0.132	0.06	0.01	0.00	66.00	3.18	11.66	0.24	21.13	6.32
CR	13/12/04		6.50	33.4	0.089	0.02	0.018	0.074	0.041	0.055	0.066	0.066	0.53	0.145	0.04	0.01	0.00	74.75	3.07	11.21	0.24	21.16	6.32
CR	24/01/05		6.41	32.0	0.082	0.018	0.018	0.073	0.032	0.052	0.066	0.063	0.64	0.13	0.03	0.01	0.00	78.23	2.77	12.63	0.18	19.92	6.03
CR	29/03/05		5.91	32.1	0.079	0.019	0.018	0.072	0.033	0.051	0.063	0.064	0.68	0.119	0.07	0.01	0.01	66.43	2.61	12.49	0.19	19.75	5.96
CR	03/05/05		5.92	31.3	0.085	0.019	0.017	0.069	0.039	0.051	0.058	0.062	0.6	0.129	< 0.01	0.00	0.05	73.47	2.42	10.12	0.14	19.64	6.00
CR	31/05/05		6.17	31.5	0.085	0.018	0.018	0.071	0.041	0.050	0.057	0.063	0.63	nd	< 0.01	0.00	0.02	78.79	2.90	12.35	0.05	19.55	5.96
CR	11/07/05		6.33	30.5	0.086	0.018	0.016	0.068	0.045	0.047	0.052	0.061	0.44	0.152	< 0.01	0.00	0.04	83.05	2.82	11.40	0.15	19.37	5.93
CR	22/08/05		6.49	29.9	0.092	0.018	0.017	0.07	0.041	0.051	0.063	0.063	0.5	0.159	0.05	0.01	0.01	74.37	2.85	10.21	0.23	20.39	6.15
CR	03/10/05		6.50	30.1	0.089	0.019	0.018	0.069	0.05	0.051	0.055	0.062	0.53	0.153	0.02	0.01	0.01	75.77	3.09	11.33	0.17	20.29	6.10
CR	07/02/06		6.38	31.8	0.092	0.019	0.017	0.073	0.05	0.060	0.058	0.064	0.62	0.154	0.04	0.01	0.01	76.68	3.03	11.00	0.22	21.19	6.30
CR	03/04/06		6.05	31.4	0.075	0.021	0.018	0.071	0.022	0.049	0.074	0.064	0.84	0.114	0.06	0.01	0.01	60.27	2.86	11.86	0.20	19.63	5.91
CR	10/07/06		6.18	32.6	0.086	0.018	0.016	0.068	0.045	0.049	0.055	0.059	1.67	0.148	0.02	0.01	0.01	69.84	2.67	10.23	0.16	19.43	5.90
CR	21/08/06		6.12	30.0	0.084	0.018	0.017	0.065	0.039	0.049	0.059	0.059	0.59	0.137	nd	nd	nd	nd	nd	nd	nd	19.15	5.74
CR	02/10/06		6.22	31.4	0.082	0.019	0.017	0.069	0.039	0.052	0.064	0.058	0.72	0.133	0.07	0.01	0.02	65.32	2.79	10.70	0.37	19.62	5.91
CR	22/05/06		6.22	28.7	0.083	0.018	0.017	0.066	0.039	0.047	0.058	0.061	0.66	0.133	0.04	0.01	0.00	64.88	2.85	10.18	0.24	19.21	5.76
CR	Average		6.15	31.61	0.086	0.019	0.017	0.070	0.041	0.052	0.061	0.062	0.67	0.140	0.04	0.01	0.01	73.21	2.90	11.16	0.20	20.14	6.07
Spring CS1	12/07/04	0.113	5.9	28.2	0.078	0.018	0.015	0.051	0.036	0.043	0.027	0.062	0.7	0.158	0.02	0.230	0.006	11.19	2.79	8.09	0.31	16.35	5.01
CS1	28/09/04	0.148	5.82	26.8	0.078	0.014	0.016	0.053	0.035	0.037	0.029	0.061	0.62	0.154	0.08	0.220	0.000	12.00	2.79	7.83	0.24	16.04	4.95
CS1	13/12/04	0.318	6.12	24.5	0.073	0.013	0.014	0.048	0.02	0.039	0.027	0.027	0.87	0.145	0.11	0.026	0.005	11.11	2.69	7.71	0.37	11.52	4.55
CS1	29/03/05	1.156	5.22	25.2	0.067	0.014	0.014	0.044	0.008	0.04	0.035	0.061	nd	0.120	0.19	0.037	0.002	14.73	2.52	8.81	0.38	14.14	4.27
CS1	03/05/05	0.560	6.19	22.1	0.068	0.012	0.013	0.043	0.017	0.036	0.024	0.058	0.74	0.133	0.03	0.006	0.098	12.78	2.38	7.70	0.25	13.50	4.25
CS1	31/05/05	0.268	6.33	24.0	0.072	0.014	0.014	0.051	0.035	0.036	0.022	0.057	0.74	0.138	< 0.01	0.003	0.043	13.84	2.79	11.50	0.14	14.90	4.72
CS1	11/07/05	0.076	6.44	25.5	0.076	0.014	0.014	0.053	0.042	0.036	0.024	0.059	0.64	0.157	0.03	0.004	0.029	13.84	2.85	9.54	0.19	15.85	4.89
CS1	22/08/05	0.110	6.40	24.4	0.079	0.014	0.015	0.055	0.043	0.037	0.029	0.061	0.61	0.158	0.03	0.003	0.020	11.67	2.78	8.84	0.24	16.62	5.05
CS1	03/10/05	0.192	6.50	24.0	0.075	0.014	0.015	0.049	0.029	0.046	0.026	0.058	0.66	0.151	0.04	0.023	0.000	12.66	2.78	8.73	0.15	15.27	4.69
CS1	07/02/06	0.165	6.05	25.1	0.081	0.015	0.014	0.053	0.038	0.041	0.027	0.06	0.85	0.153	0.06	0.020	0.006	11.68	2.77	8.36	0.30	16.21	5.02
CS1	03/04/06	1.672	5.33	25.5	0.068	0.015	0.015	0.044	0.008	0.044	0.038	0.062	1.75	0.113	0.26	0.044	0.015	17.94	2.98	8.54	0.53	14.64	4.37
CS1	22/05/06	0.349	6.10	22.1	0.072	0.013	0.014	0.045	0.022	0.036	0.028	0.058	0.74	0.135	0.06	0.026	0.004	11.83	2.63	7.16	0.33	14.29	4.40
CS1	10/07/06	0.092	6.48	25.8	0.075	0.013	0.014	0.047	0.037	0.035	0.022	0.057	0.48	0.153	0.01	0.021	0.000	10.29	2.48	7.72	0.18	14.89	4.55
CS1	21/08/06	0.658	6.02	25.8	0.071	0.014	0.014	0.046	0.018	0.04	0.032	0.056	0.76	0.133	0.10	0.030	0.000	12.48	2.55	7.86	0.44	14.30	4.45
CS1	02/10/06	0.635	5.85	25.7	0.071	0.013	0.014	0.044	0.014	0.044	0.033	0.057	0.78	0.135	0.12	0.032	0.000	14.07	2.75	8.31	0.51	14.24	4.33
CS1	Average		6.05	24.92	0.074	0.014	0.014	0.048	0.027	0.039	0.028	0.057	0.781	0.142	0.07	0.048	0.015	12.81	2.70	8.45	0.30	14.85	4.63
Spring CS2	12/07/04	0.482	5.56	34.6	0.091	0.018	0.018	0.068	0.046	0.051	0.054	0.066	0.48	0.157	0.02	0.01	0.00	71.89	2.64	10.03	0.24	20.33	6.06
CS2	28/09/04	0.535	5.58	34.4	0.094	0.018	0.019	0.07	0.048	0.052	0.058	0.064	0.42	0.155	0.06	0.01	0.00	76.00	3.00	10.14	0.20	20.72	6.23
CS2	13/12/04	1.446	6.44	31.9	0.086	0.017	0.018	0.071	0.037	0.055	0.063	0.063	0.58	0.138	0.05	0.01	0.00	70.15	2.78	10.70	0.26	20.13	6.01
CS2	03/05/05	2.500	6.23	28.8	0.078	0.016	0.017	0.067	0.037	0.05	0.05	0.06	0.74	0.124	< 0.01	0.00	0.05	72.40	2.29	10.00	0.13	18.44	5.64
CS2	31/05/05	1.117	6.30	30.2	0.082	0.017	0.017	0.07	0.04	0.05	0.055	0.061	0.57	0.131	< 0.01	0.00	0.16	72.40	2.41	12.42	0.05	19.29	6.01
CS2	11/07/05	0.246	6.27	30.5	0.087	0.016	0.017	0.067	0.042	0.049	0.054	0.06	0.54	0.149	< 0.01	0.00	0.05	71.34	2.28	10.03	0.20	19.21	5.87
CS2	22/08/05	0.450	6.47	29.5	0.093	0.017	0.017	0.069	0.047	0.049	0.061	0.063	0.46	0.157	0.05	0.00	0.01	75.93	2.66	10.25	0.27	20.50	6.09
CS2	07/02/06	0.678	6.24	32.3	0.092	0.019	0.018	0.069	0.047	0.055	0.06	0.062	0.51	0.151	0.03	0.01	0.01	79.16	2.76	11.43	0.18	20.63	6.17
CS2	22/05/06	1.364	6.28	28.7	0.084	0.017	0.018	0.067	0.036	0.051	0.061	0.06	0.63	0.128	0.05	0.01	0.00	71.20	2.58	10.29	0.25	19.30	5.80
CS2	03/04/06	7.156	6.04	31.2	0.073	0.018	0.018	0.073	0.031	0.049	0.067	0.064	0.88	0.107	0.06	0.01	0.00	59.98	2.45	10.60	0.18	19.65	5.81
CS2	10/07/06	0.389	6.5	32.6	0.087	0.018	0.017	0.067	0.043	0.047	0.056	0.059	0.36	0.146	< 0.01	0.01	0.00	69.31	2.50	10.57	0.13	19.31	5.89
CS2	21/08/06	2.978	6.3	33.1	0.084	0.017	0.018	0.068	0.039	0.056	0.063	0.058	0.55	0.134	0.06	0.01	0.00	70.57	2.54	10.76	0.30	19.65	5.84
CS2	02/10/06	3.800	6.3	32.3	0.082	0.023	0.018	0.072	0.05	0.048	0.065	0.057	0.59	0.129	0.05	0.01	0.00	75.40	2.78	11.63	0.32	20.41	6.19
CS2	Average		6.19	31.55	0.086	0.018	0.018	0.069	0.042	0.051	0.059	0.061	0.562	0.139	0.04	0.01	0.02	71.98	2.59	10.68	0.21	19.81	5.97
Spring CS3	13/12/04	0.265	6.65	36,00	0.097	0.022	0.017	0.083	0.051	0.05	0.071	0.071	0.44	0.159	0.01	0.00	0.15	20.39	4.10	10.85	0.25	22.99	7.08
CS3	29/03/05	0.480	6.11	35.7	0.09	0.022	0.017	0.084	0.047	0.05	0.073	0.072	nd	0.142	0.03	0.00	0.00	24.44	3.99	13.44	0.21	22.81	6.80
CS3	03/05/05	0.408	6.42	33.6	0.094	0.021	0.017	0.083	0.052	0.051	0.067	0.069	0.52	0.153	< 0.01	0.00	0.02	23.42	3.73	10.95	0.16	22.53	6.83
CS3	31/05/05	0.246	6.24	34.1	0.094	0.021	0.016	0.08	0.053	0.049	0.064	0.068	0.5	0.154	< 0.01	0.00	0.02	25.55	3.88	11.65	0.07	22.10	6.69
CS3	11/07/05	0.089	6.31	32.9	0.091	0.02	0.015	0.077	0.05	0.047	0.056	0.065	0.45	0.156	< 0.01	0.00	0.01	24.49	3.64	9.82	0.20	20.83	6.43
CS3	22/08/05	0.086	6.52	31.7	0.097	0.021	0.016	0.08	0.054	0.049	0.062	0.07	0.53	0.164	< 0.01	0.00	0.00	22.18	4.06	10.47	0.27	22.32	6.75
CS3	03/10/05	0.181	6.58	33.1	0.096	0.022	0.016	0.079	0.054	0.05	0.065	0.068	0.4	0.163	0.03	0.00	0.00	23.15	4.12	10.69	0.20	22.33	6.73
CS3	07/02/06	0.164	6.53	33.9	0.098	0.022	0.015	0.078	0.054	0.051	0.064	0.068	0.51	0.164	0.01	0.00	0.01	22.60	4.12	11.15	0.21	22.28	6.70
CS3	03/04/06	1.222	6.22	33.4	0.084	0.021	0.017	0.082	0.044	0.048	0.074	0.067	0.89	0.126	0.03	0.01	0.01	22.05	0.50	10.71	0.24	21.87	6.55
CS3	22/05/06	0.229	6.42	32.2	0.093	0.021	0.016	0.078	0.051	0.048	0.068	0.068	0.54	0.152	0.01	0.00	0.00	16.86	3.31	8.27	0.17	22.09	6.57
CS3	10/07/06	0.109	6.55	35.6	0.092	0.02	0.016	0.078	0.055	0.047	0.057	0.066	0.41	0.158	< 0.01	0.00	0.00	19.80	3.75	10.30	0.13	21.38	6.51
CS3	21/08/06	0.268	6.44	33,00	0.095	0.021	0.016	0.078	0.05	0.048	0.07	0.066	0.5	0.159	0.01	0.00	0.00	21.18	3.94	10.57	0.31	22.03	6.62
CS3	02/10/06	0.445	6.40	36.5	0.094	0.021	0.017	0.082	0.051	0.05	0.08	0.065	0.6	0.151	0.02	0.00	0.00	22.52	4.22	11.92	0.37	22.83	6.78
CS3	Average		6.41	33.98	0.093	0.02	0.016	0.080	0.051	0.05	0.07	0.07	0.52	0.15	0.01	0.00	0.02	22.20	3.64	10.83	0.21	22.18	6.70
Spring CS4	13/12/04	0.314	6.58	35.70	0.096	0.024	0.020	0.078	0.05	0.056	0.071	0.071	0.66	0.152	0.04	0.01	0.00	127.41	3.21	12.10	0.26	23.00	6.85
CS4	03/05/05	0.427	6.30	30.40	0.085	0.021	0.017	0.070	0.04	0.051	0.062	0.062	0.70	0.128	< 0.01	0.00	0.06	127.77	2.69	11.15	0.17	20.07	6.13
CS4	31/05/05	0.268	6.29	32.70	0.089	0.021	0.018	0.072	0.04	0.050	0.062	0.064	0.64	0.141	< 0.01	0.00	0.01	137.35	2.86	12.25	0.09	20.68	6.29
CS4	11/07/05	0.121	6.39	33.60	0.094	0.021	0.018	0.075	0.06	0.051	0.059	0.064	0.52	0.156	< 0.01	0.00	0.06	145.87	2.53	11.05	0.21	21.47	6.59
CS4	22/08/05	0.170	6.68	31.90	0.097	0.022	0.019	0.077	0.06	0.052	0.064	0.065	0.61	0.163	0.04	0.00	0.01	154.38	2.93	12.11	0.29	22.69	6.75
CS4	07/02/06	0.213	6.45	34.30	0.100	0.027	0.017	0.073	0.06	0.054	0.065	0.066	0.66	0.161	0.01	0.01	0.00	149.91	3.12	12.40	0.14	22.41	6.74
CS4	03/04/06	0.265	5.69	32.50	0.080	0.024	0.019	0.070	0.02	0.054	0.088	0.059	1.20	0.105	0.09	0.02	0.01	96.46	2.78	10.66	0.24	20.41	6.12
CS4	22/05/06	0.309	6.37	31.80	0.092	0.022	0.018	0.073	0.05	0.050	0.070	0.065	0.74	0.142	0.07	0.01	0.00	133.26	3.20	11.43	0.24	21.85	6.43
CS4	10/07/06	0.157	6.60	35.50	0.092	0.021	0.018	0.073	0.06	0.050	0.055	0.064	0.41	0.155	0.01	0.00	0.00	148.84	2.78	11.76	0.17	21.43	6.40
CS4	21/08/06	0.462	6.47	33.20	0.091	0.024	0.018	0.070	0.05	0.050	0.071	0.060	0.73	0.145	0.05	0.01	0.00	119.00	2.94	11.10	0.30	21.09	6.36
CS4	02/10/06	0.772	6.50	33.50	0.087	0.024	0.018	0.070	0.05	0.054	0.065	0.061	1.00	0.140	0.07	0.01	0.58	115.10	3.19	11.92	0.45	21.33	6.85
CS4	Average		6.39	33.19	0.091	0.02	0.02	0.07	0.049	0.05	0.07	0.06	0.72	0.14	0.04	0.01	0.07	132.30	2.93	11.63	0.23	21.49	6.50
Spring BH	02/02/04	nd	6.60	36.50	0.089	0.024	0.040	0.087	0.06	0.058	0.090	0.071	1.70	0.137	0.03	0.00	0.02	62.52	2.42	10.28	0.06	25.63	7.55
BH	12/07/04	0.388	6.78	34.50	0.088	0.014	0.034	0.074	0.14	0.033	0.014	0.061	2.68	0.143	0.02	0.00	0.06	57.83	1.67	8.85	0.11	22.68	6.51
BH	28/09/04	0.450	6.79	42.10	0.100	0.029	0.042	0.095	0.16	0.066	0.039	0.062	2.43	0.154	0.05	0.01	0.04	68.00	3.59	10.69	0.07	28.51	8.40
BH	13/12/04	1.241	6.76	41.20	0.092	0.024	0.042	0.090	0.09	0.061	0.074	0.074	1.51	0.145	0.02	0.00	0.02	67.18	2.94	11.10	0.05	27.11	7.79
BH	07/03/05	0.690	6.63	38.80	0.088	0.024	0.041	0.087	0.07	0.061	0.077	0.073	1.39	0.137	< 0.01	0.00	0.01	67.22	2.40	12.22	0.04	25.85	7.54
BH	29/03/05	3.000	6.66	37.30	0.086	0.025	0.038	0.083	0.09	0.057	0.055	0.073	1.58	0.123	0.03	0.00	0.01	63.55	2.68	11.97	0.04	24.92	7.30
BH	03/05/05	2.095	6.64	32.60	0.082	0.014	0.035	0.080	0.11	0.046	0.028	0.066	1.89	0.123	< 0.01	0.02	0.03	67.08	1.91	10.11	0.07	22.72	6.60
BH	31/05/05	1.049	6.44	32.00	0.080	0.011	0.033	0.076	0.09	0.046	0.025	0.063	2.09	0.134	< 0.01	0.01	0.04	66.01	1.44	9.81	0.07	21.12	6.24
BH	11/07/05	0.130	6.72	31.00	0.086	0.016	0.032	0.075	0.13	0.033	0.015	0.053	2.91	0.144	< 0.01	0.05	0.05	66.01	1.89	9.57	0.11	21.48	6.52
BH	22/08/05	0.637	6.76	34.00	0.089	0.029	0.038	0.087	0.15	0.056	0.023	0.052	3.92	0.136	0.07	0.07	0.01	76.46	4.06	11.82	0.15	25.35	7.68
BH	03/10/05	0.724	6.79	38.10	0.100	0.042	0.042	0.091	0.15	0.067	0.036	0.058	3.69	0.138	0.08	0.00	0.06	77.72	4.69	12.05	0.11	27.70	8.75
BH	03/04/06	5.450	6.46	36.80	0.081	0.023	0.036	0.076	0.07	0.048	0.066	0.069	1.37	0.120	0.03	0.00	0.01	59.17	2.65	9.79	0.05	23.10	6.76
BH	22/05/06	1.264	6.62	31.70	0.084	0.016	0.035	0.075	0.11	0.039	0.025	0.064	2.09	0.115	0.03	0.00	0.03	62.10	2.47	9.46	0.08	22.38	6.51
BH	10/07/06	0.278	6.85	36.40	0.086	0.023	0.036	0.082	0.16	0.039	0.020	0.054	3.10	0.147	0.04	0.00	0.02	59.41	3.04	10.50	0.13	24.40	7.15
BH	21/08/06	3.261	6.40	29.80	0.086	0.020	0.036	0.078	0.10	0.049	0.047	0.062	2.16	0.139	0.04	0.00	0.03	57.21	2.58	10.11	0.11	23.45	6.88
BH	02/10/06	3.155	6.74	35.60	0.087	0.020	0.037	0.081	0.10	0.048	0.057	0.066	1.83	0.142	0.03	0.00	0.18	63.68	2.98	11.11	0.10	24.46	7.20
BH	Average		6.67	35.53	0.09	0.02	0.037	0.082	0.11	0.05	0.04	0.06	2.27	0.14	0.03	0.01	0.04	65.07	2.71	10.59	0.08	24.43	7.21
Spring RUZS	28/09/04	0.206	6.28	18.30	0.089	0.006	0.010	0.036	0.06	0.020	0.000	0.030	9.05	0.103	0.24	0.03	0.46	20.00	1.33	5.01	0.35	11.08	4.49
RUZS	13/12/04	0.299	5.77	26.30	0.093	0.005	0.015	0.051	0.01	0.046	0.002	0.002	2.47	0.154	0.07	0.01	0.11	26.24	1.08	7.77	0.11	7.81	4.95
RUZS	29/03/05	1.300	5.82	26.00	0.084	0.013	0.015	0.050	0.02	0.052	0.004	0.071	2.83	0.121	0.10	0.01	0.04	31.80	2.31	9.16	0.14	14.85	4.93
RUZS	03/05/05	1.190	5.94	16.00	0.058	0.002	0.010	0.040	0.04	0.004	0.000	0.042	6.00	0.048	< 0.01	0.15	0.18	29.81	0.45	6.86	0.38	9.63	3.47
RUZS	31/05/05	0.525	5.90	13.20	0.038	0.002	0.009	0.042	0.03	0.021	0.000	0.013	9.38	0.045	< 0.01	0.21	0.23	28.75	0.40	7.63	0.42	6.67	3.11
RUZS	11/07/05	0.057	6.44	13.40	0.053	0.004	0.009	0.035	0.04	0.008	0.000	0.019	7.24	0.027	0.01	0.20	0.20	25.55	0.68	5.71	0.44	7.72	3.22
RUZS	22/08/05	0.390	6.04	28.80	0.119	0.018	0.016	0.060	0.04	0.092	0.001	0.059	6.74	0.079	0.15	0.15	0.01	40.86	3.73	10.28	0.26	17.48	6.30
RUZS	03/10/05	0.284	6.10	24.70	0.100	0.013	0.013	0.048	0.03	0.051	0.006	0.057	6.39	0.108	0.18	0.00	0.12	35.36	2.70	8.29	0.31	14.60	5.23
RUZS	20/03/06	1.140	5.75	32.20	0.090	0.020	0.021	0.066	0.02	0.062	0.050	0.070	3.27	0.150	0.08	0.01	0.03	43.19	2.90	10.70	0.12	19.05	6.11
RUZS	03/04/06	3.395	5.59	29.50	0.082	0.019	0.017	0.056	0.01	0.053	0.029	0.068	3.00	0.116	0.14	0.01	0.03	41.64	2.10	8.53	0.23	16.15	5.38
RUZS	18/04/06	2.805	5.55	24.60	0.078	0.015	0.015	0.049	0.01	0.047	0.027	0.063	3.07	0.108	0.13	0.01	0.05	36.96	2.06	8.43	0.22	14.87	4.82
RUZS	22/05/06	0.139	6.44	15.30	0.063	0.005	0.011	0.041	0.06	0.010	0.020	0.026	8.20	0.040	0.21	0.02	0.24	26.57	1.08	6.34	0.46	11.04	3.82
RUZS	10/07/06	0.036	6.72	20.30	0.060	0.004	0.016	0.063	0.12	0.009	0.002	0.011	10.96	0.101	0.16	0.02	0.14	19.80	0.99	9.92	0.49	13.20	4.66
RUZS	21/08/06	0.501	6.10	44.00	0.098	0.005	0.011	0.046	0.03	0.032	0.000	0.054	7.26	0.086	0.16	0.02	0.13	30.40	1.06	7.42	0.33	12.87	4.74
RUZS	02/10/06	1.457	6.22	21.20	0.088	0.006	0.012	0.042	0.04	0.042	0.000	0.045	6.31	0.121	0.16	0.02	0.03	27.07	1.48	7.21	0.37	12.33	4.34
RUZS	Average		6.03	23.96	0.079	0.01	0.01	0.05	0.04	0.04	0.01	0.04	5.94	0.09	0.11	0.06	0.11	31.71	1.64	8.16	0.31	12.73	4.65
Spring RH	12/07/04	0.160	5.89	46.50	0.092	0.030	0.036	0.103	0.06	0.060	0.119	0.080	0.58	0.144	0.02	0.00	0.00	136.18	3.73	14.71	0.18	29.01	8.38
RH	28/09/04	0.200	6.03	50.50	0.098	0.031	0.040	0.116	0.07	0.060	0.158	0.076	0.60	0.146	0.05	0.00	0.00	163.00	4.15	16.33	0.14	32.28	9.18
RH	02/11/04	2.030	6.34	41.20	0.089	0.031	0.035	0.105	0.06	0.073	0.112	0.080	0.88	0.133	0.06	0.00	0.00	144.44	4.57	16.08	0.19	28.98	8.40
RH	13/12/04	0.434	6.54	44.70	0.091	0.030	0.035	0.103	0.05	0.069	0.111	0.111	0.82	0.141	0.05	0.00	0.00	129.97	3.80	14.95	0.16	31.14	8.33
RH	24/01/05	2.098	6.21	39.70	0.084	0.028	0.031	0.091	0.03	0.066	0.085	0.080	0.89	0.124	0.07	0.00	0.00	136.78	3.46	15.43	0.15	24.74	7.50
RH	07/03/05	0.430	6.34	39.80	0.087	0.028	0.031	0.090	0.03	0.063	0.093	0.081	0.76	0.136	0.03	0.00	0.00	124.00	3.52	16.33	0.13	24.91	7.55
RH	29/03/05	1.062	6.23	40.30	0.083	0.028	0.031	0.090	0.04	0.058	0.087	0.081	0.84	0.117	0.06	0.00	0.00	126.12	3.41	15.84	0.14	25.08	7.44
RH	03/05/05	0.907	6.26	38.20	0.082	0.027	0.030	0.090	0.04	0.058	0.079	0.081	0.88	0.127	< 0.01	0.01	0.04	132.03	3.36	14.05	0.14	24.64	7.40
RH	31/05/05	0.515	6.40	38.80	0.082	0.024	0.030	0.089	0.05	0.054	0.086	0.076	0.74	0.129	< 0.01	0.00	0.07	128.83	3.45	13.60	0.07	24.44	7.27
RH	11/07/05	0.324	6.53	41.10	0.086	0.027	0.031	0.096	0.05	0.055	0.095	0.075	0.62	0.138	< 0.01	0.00	0.04	140.55	3.54	15.45	0.16	25.84	7.76
RH	22/08/05	0.313	6.61	39.50	0.090	0.029	0.034	0.100	0.07	0.055	0.107	0.075	0.73	0.143	0.05	0.00	0.00	144.26	3.80	15.20	0.25	27.92	8.13
RH	03/10/05	0.138	6.56	40.80	0.088	0.030	0.033	0.098	0.07	0.057	0.098	0.076	0.75	0.145	0.04	0.00	0.01	145.49	3.93	15.56	0.19	27.60	8.02
RH	07/02/06	0.313	6.28	38.50	0.086	0.028	0.030	0.089	0.05	0.060	0.080	0.081	0.90	0.144	0.02	0.00	0.01	129.12	3.58	13.95	0.16	25.09	7.47
RH	03/04/06	2.130	6.30	41.90	0.085	0.030	0.031	0.090	0.04	0.054	0.107	0.074	0.95	0.105	0.06	0.00	0.01	131.03	3.44	13.28	0.19	25.63	7.56
RH	22/05/06	0.492	6.39	37.20	0.085	0.028	0.030	0.088	0.05	0.050	0.094	0.075	0.81	0.129	0.04	0.00	0.00	127.92	3.86	13.44	0.20	25.13	7.39
RH	10/07/06	0.213	6.55	42.20	0.086	0.028	0.031	0.093	0.07	0.053	0.082	0.077	0.60	0.139	0.01	0.00	0.00	118.81	3.41	13.85	0.10	25.87	7.64
RH	21/08/06	1.244	6.40	60.30	0.090	0.029	0.032	0.095	0.06	0.054	0.119	0.067	0.87	0.135	0.05	0.00	0.00	134.40	3.51	14.42	0.23	27.07	7.87
RH	02/10/06	1.078	6.48	42.40	0.088	0.032	0.033	0.098	0.06	0.059	0.115	0.071	0.88	0.132	0.05	0.00	0.00	145.20	3.81	15.73	0.28	27.76	8.09
RH	Average		6.35	42.42	0.087	0.03	0.03	0.10	0.05	0.06	0.10	0.08	0.78	0.13	0.04	0.00	0.01	135.45	3.69	14.90	0.17	26.84	7.85
Spring SG	12/07/04	0.030	6.94	54.90	0.095	0.021	0.078	0.118	0.16	0.043	0.142	0.082	0.94	0.128	0.02	0.00	0.02	122.70	5.22	12.65	0.03	37.60	9.73
SG	28/09/04	0.032	6.16	59.40	0.103	0.023	0.082	0.125	0.12	0.050	0.187	0.086	0.80	0.141	0.02	0.01	0.01	147.00	5.75	14.35	0.02	39.36	10.36
SG	13/12/04	0.007	6.61	52.80	0.094	0.026	0.072	0.111	0.11	0.060	0.137	0.137	1.03	0.142	0.02	0.02	0.03	119.83	6.37	13.46	0.01	39.68	9.50
SG	29/03/05	0.064	6.27	44.30	0.074	0.019	0.060	0.095	0.08	0.037	0.125	0.080	0.84	0.122	0.03	0.00	0.01	115.78	4.22	13.57	0.01	29.40	7.80
SG	03/05/05	0.030	6.58	46.50	0.085	0.020	0.067	0.106	0.11	0.046	0.122	0.082	0.82	0.127	< 0.01	0.01	0.01	138.42	4.44	12.75	0.01	32.34	8.70
SG	31/05/05	0.007	6.47	48.10	0.087	0.021	0.066	0.107	0.12	0.045	0.127	0.080	1.02	0.127	< 0.01	0.03	0.09	132.03	5.24	13.10	0.02	32.83	8.89
SG	11/07/05	0.025	6.31	51.40	0.093	0.023	0.064	0.115	0.12	0.044	0.145	0.080	1.39	0.136	0.02	0.03	0.04	149.07	5.54	14.20	0.02	34.48	9.32
SG	22/08/05	0.010	6.65	47.30	0.091	0.025	0.073	0.117	0.14	0.042	0.138	0.076	nd	0.123	0.07	0.03	0.10	151.52	6.55	15.41	0.08	35.62	9.71
SG	03/10/05	0.024	6.67	49.70	0.092	0.025	0.072	0.112	0.14	0.049	0.134	0.082	1.71	0.134	0.04	0.00	0.04	138.88	6.24	14.48	0.04	35.45	9.45
SG	22/05/06	0.014	6.68	47.90	0.090	0.021	0.070	0.111	0.11	0.040	0.160	0.079	0.79	0.124	0.02	0.00	0.01	112.00	5.44	13.42	0.03	34.75	9.12
SG	03/04/06	0.101	6.17	43.30	0.072	0.019	0.060	0.091	0.07	0.034	0.149	0.071	0.94	0.112	0.02	0.01	0.00	120.89	3.89	10.92	0.01	28.68	7.57
SG	21/08/06	0.031	6.55	23.80	0.087	0.020	0.070	0.110	0.10	0.042	0.166	0.075	0.99	0.131	0.02	0.00	0.01	134.10	4.57	13.51	0.02	33.96	8.98
SG	02/10/06	0.034	6.77	51.00	0.087	0.021	0.071	0.112	0.11	0.050	0.169	0.076	0.82	0.137	0.02	0.00	0.07	148.10	5.11	14.73	0.01	35.35	9.19
SG	Average		6.49	47.13	0.088	0.02	0.069	0.109	0.11	0.04	0.15	0.084	1.01	0.13	0.02	0.01	0.03	133.97	5.28	13.66	0.02	34.32	9.05
Spring SH	28/09/04	0.033	5.02	21.80	0.084	0.016	0.007	0.023	0.00	0.049	0.004	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	02/11/04	2.252	5.24	18.10	0.078	0.013	0.008	0.025	0.00	0.053	0.007	0.046	3.34	0.134	0.22	0.02	0.06	19.00	4.02	4.42	0.30	10.58	3.64
SH	13/12/04	0.074	5.23	22.00	0.083	0.017	0.009	0.028	0.00	0.051	0.012	0.012	3.47	0.148	0.24	0.03	0.07	22.11	3.89	4.77	0.26	8.13	4.08
SH	24/01/05	2.000	5.29	20.60	0.075	0.015	0.009	0.028	0.00	0.051	0.016	0.045	2.23	0.129	0.19	0.02	0.03	20.13	3.07	5.02	0.18	11.05	3.76
SH	29/03/05	1.280	5.00	24.10	0.074	0.019	0.010	0.031	0.00	0.048	0.023	0.045	4.65	0.121	0.27	0.03	0.14	20.08	4.97	5.72	0.24	11.46	4.14
SH	03/05/05	0.324	5.05	20.20	0.072	0.019	0.008	0.025	0.00	0.048	0.009	0.035	7.21	0.092	0.03	0.21	0.35	20.23	5.17	4.30	0.33	9.46	4.00
SH	31/05/05	0.027	5.56	18.80	0.076	0.017	0.007	0.024	0.01	0.045	0.009	0.038	4.15	0.124	0.03	0.30	0.48	26.62	3.59	4.53	0.37	10.32	4.10
SH	22/08/05	0.231	5.16	19.50	0.075	0.016	0.008	0.031	0.01	0.039	0.015	0.033	9.63	0.114	0.40	0.30	0.03	18.32	4.13	4.99	0.56	10.17	3.89
SH	03/10/05	0.278	5.25	19.70	0.080	0.019	0.008	0.025	0.01	0.049	0.008	0.038	6.16	0.137	0.28	0.03	0.18	21.52	5.55	4.86	0.42	10.35	4.04
SH	07/02/06	0.260	5.30	23.80	0.087	0.022	0.009	0.031	0.01	0.053	0.019	0.053	2.80	0.154	0.23	0.04	0.03	28.94	4.11	5.39	0.27	13.08	4.45
SH	03/04/06	5.711	5.36	20.80	0.068	0.014	0.008	0.024	0.01	0.044	0.019	0.039	3.31	0.106	0.28	0.02	0.03	19.32	2.97	4.08	0.29	10.15	3.39
SH	22/05/06	0.125	5.45	18.20	0.076	0.018	0.007	0.024	0.01	0.043	0.012	0.041	3.55	0.117	0.29	0.02	0.06	11.00	4.11	4.12	0.36	10.55	3.71
SH	21/08/06	0.554	5.60	15.40	0.077	0.013	0.008	0.026	0.01	0.045	0.005	0.042	4.01	0.130	0.25	0.03	0.06	20.56	2.97	4.39	0.43	10.18	3.66
SH	02/10/06	0.883	5.61	18.50	0.076	0.011	0.007	0.022	0.01	0.051	0.004	0.040	3.77	0.134	0.24	0.02	0.00	20.60	2.95	4.29	0.48	9.86	3.31
SH	Average		5.29	20.11	0.077	0.02	0.008	0.026	0.01	0.05	0.01	0.04	4.86	0.13	0.24	0.08	0.13	20.60	3.99	4.61	0.35	10.32	3.87
Outlet RS	02/02/04	nd	6.19	30.10	0.083	0.020	0.024	0.069	0.03	0.056	0.059	0.068	1.85	0.131	0.05	0.01	0.02	67.31	2.41	10.46	0.14	19.99	6.15
RS	12/07/04	4.58	6.66	29.20	0.081	0.016	0.020	0.060	0.07	0.044	0.026	0.059	1.99	0.132	0.02	0.01	0.05	57.08	1.76	9.07	0.19	18.29	5.52
RS	28/09/04	5.45	6.53	32.60	0.090	0.018	0.024	0.070	0.07	0.053	0.044	0.061	1.80	0.140	0.06	0.01	0.04	69.00	2.96	11.50	0.15	20.77	6.29
RS	02/11/04	59.30	6.38	30.10	0.084	0.020	0.025	0.073	0.04	0.057	0.068	0.063	1.55	0.134	0.05	0.01	0.02	71.65	3.19	11.05	0.12	21.07	6.35
RS	13/12/04	12.00	6.49	34.30	0.088	0.019	0.025	0.075	0.04	0.061	0.061	0.062	1.13	0.143	0.03	0.01	0.02	68.76	2.59	11.10	0.08	20.90	6.49
RS	24/01/05	42.60	6.38	33.10	0.083	0.021	0.025	0.073	0.03	0.057	0.068	0.067	1.30	0.133	0.03	0.00	0.01	78.96	2.64	12.29	0.08	20.96	6.36
RS	07/03/05	8.37	6.25	32.40	0.085	0.019	0.023	0.070	0.03	0.057	0.059	0.068	1.10	0.135	0.02	0.00	0.02	69.00	2.43	13.16	0.07	20.36	6.16
RS	21/03/05	78.50	6.14	32.40	0.079	0.022	0.024	0.071	0.03	0.055	0.075	0.063	1.63	0.121	nd	nd	nd	nd	nd	nd	nd	20.29	6.18
RS	29/03/05	48.70	6.22	31.90	0.079	0.020	0.022	0.068	0.03	0.056	0.059	0.065	1.28	0.122	0.03	0.00	0.01	74.63	2.74	12.00	0.08	19.58	5.94
RS	03/05/05	22.70	6.31	28.00	0.076	0.015	0.021	0.063	0.05	0.044	0.038	0.060	1.99	0.104	< 0.01	0.02	0.05	70.27	2.08	10.03	0.13	17.84	5.48
RS	31/05/05	11.10	6.40	28.60	0.078	0.013	0.021	0.065	0.05	0.044	0.038	0.058	1.78	0.119	< 0.01	0.01	0.03	68.14	1.95	13.35	0.12	17.60	5.45
RS	11/07/05	3.85	6.51	28.20	0.080	0.014	0.020	0.063	0.07	0.041	0.028	0.056	1.85	0.134	< 0.01	0.03	0.04	70.27	2.35	10.65	0.18	17.99	5.52
RS	22/08/05	6.88	6.52	29.00	0.089	0.020	0.023	0.069	0.07	0.056	0.032	0.057	2.92	0.127	0.06	0.07	0.01	68.03	3.14	10.04	0.22	19.91	6.24
RS	03/10/05	14.00	6.56	29.10	0.085	0.022	0.022	0.065	0.06	0.057	0.035	0.057	2.73	0.130	0.07	0.00	0.04	69.48	3.37	11.16	0.23	19.21	6.07
RS	28/11/05	4.70	6.16	32.20	0.089	0.020	0.024	0.070	0.06	0.059	0.049	0.067	1.20	0.143	nd	nd	nd	nd	nd	nd	nd	21.08	6.21
RS	07/02/06	8.05	6.44	33.20	0.089	0.021	0.024	0.075	0.04	0.057	0.059	0.071	1.20	0.143	0.03	0.00	0.02	74.11	2.66	11.50	0.08	21.48	6.55
RS	20/03/06	22.97	6.52	32.10	0.084	0.022	0.023	0.068	0.03	0.056	0.060	0.067	1.22	0.131	nd	nd	nd	nd	nd	nd	nd	20.06	6.16
RS	03/04/06	127.50	5.70	30.50	0.076	0.024	0.020	0.064	0.02	0.052	0.072	0.061	1.64	0.111	0.09	0.02	0.01	73.05	2.96	10.86	0.14	18.93	5.82
RS	22/05/06	10.70	6.45	28.00	0.082	0.017	0.022	0.064	0.05	0.045	0.041	0.062	1.72	0.115	0.07	0.01	0.03	65.82	2.80	10.44	0.15	18.97	5.75
RS	10/07/06	3.60	6.45	30.10	0.084	0.017	0.021	0.064	0.07	0.046	0.033	0.057	1.59	0.135	0.03	0.01	0.03	59.80	2.59	9.68	0.17	18.85	5.79
RS	21/08/06	22.40	6.01	22.90	0.098	0.005	0.012	0.047	0.04	0.030	0.001	0.056	7.03	0.089	0.05	0.01	0.03	70.00	2.45	10.54	0.18	13.23	4.71
RS	02/10/06	15.50	6.30	31.60	0.083	0.019	0.022	0.067	0.04	0.052	0.057	0.059	1.59	0.134	0.05	0.01	0.00	71.59	2.59	10.62	0.17	19.65	5.96
RS	Average		6.34	30.44	0.084	0.018	0.022	0.067	0.05	0.05	0.05	0.06	1.91	0.128	0.04	0.01	0.03	69.31	2.61	11.03	0.14	19.41	5.96
atmospheric 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	1.01	0.000	0.01	0.01	0.01	3.77	1.47	0.85	0.01		
Throughfalls spruces	2004-2006		5.18	34.11	0.048	0.069	0.011	0.027	0.01	0.058	0.074	0.041	8.80	0.003	0.10	0.31	0.02	9.34	13.99	3.37	0.01		
Througfalls beeches	2004-2006		5.75	23.14	0.026	0.074	0.006	0.010	0.04	0.029	0.033	0.022	6.42	0.005	0.02	0.02	0.03	11.41	28.70	1.02	0.00		

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887

888 Table 1: Chemical compositions of spring and stream waters, open field precipitation, througfalls
889 under spruces (PL5) and beeches (PLH). The total dissolved solids (TDS_W) have been calculated
890 from the major dissolved elements concentrations (cations, anions and silica) and are expressed in
891 mg/L. as calculated for several watersheds (e.g.. Gaillardet et al., 1999). Another parameter, called
892 here TDS-Ca (=Ca+Mg+Na+K+SiO_2+Fe) has been calculated as proposed by Zakharova et al.
893 (2007) and reflects the silicate weathering.

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Samples	date	$^{87}Sr/^{86}Sr$	2sigma	$^{234}U/^{238}U$	2sigma	altitude (m)
Spring CS1	28/09/04	0.72573	0.00002	0.880	0.001	1080
CS1	13/12/04	0.72656	0.00004	0.875	0.005	1080
CS1	29/03/05	0.72780	0.00001	0.892	0.003	1080
CS1	22/05/06	0.72650	0.00001	0.886	0.002	1080
CS1	**Average**	**0.72665**		**0.883**		
Spring CS2	03/05/05	0.72546	0.00001			1055
CS2	11/07/05	0.72376	0.00001			1055
CS2	22/05/06	0.72544	0.00001	0.875		1055
CS2	02/10/06	0.72515	0.00001			1055
CS2	**Average**	**0.72495**		**0.875**		
Spring CS3	13/12/04	0.72325	0.00002	0.823	0.003	1098
CS3	29/03/05	0.72328	0.00001	0.827	0.003	1098
CS3	11/07/05	0.72314	0.00002			1098
CS3	22/05/06	0.72325	0.00001	0.819	0.004	1098
CS3	**Average**	**0.72323**		**0.823**		
Spring CS4	03/05/05	0.72490	0.00002	0.866	0.003	1050
CS4	11/07/05	0.72375	0.00001			1050
CS4	22/05/06	0.72353	0.00001	0.867	0.002	1050
CS4	02/10/06	0.72548	0.00001			1050
CS4	**Average**	**0.72442**		**0.867**		
Spring BH	12/07/04	0.72262	0.00002	1.106	0.005	915
BH	13/12/04	0.72289	0.00002	1.1	0.003	915
BH	29/03/05	0.72359	0.00001	1.101	0.003	915
BH	03/05/05	0.72340	0.00001	1.1	0.003	915
BH	31/05/05	0.72319	0.00001	1.112	0.003	915
BH	11/07/05	0.72279	0.00001	1.101	0.003	915
BH	22/08/05	0.72287	0.00001	1.106	0.003	915
BH	03/10/05	0.72307	0.00001	1.105	0.003	915
BH	22/05/06	0.72334	0.00002	1.099	0.004	915
BH	**Average**	**0.723084**		**1.103**		
Spring RUZS	13/12/04	0.72700	0.00002	0.945	0.004	950
RUZS	29/03/05	0.72665	0.00001	0.941	0.003	950
RUZS	22/05/06	0.72669	0.00001	0.949	0.003	950
RUZS	**Average**	**0.72678**		**0.945**		
Spring RH	28/09/04	0.72206	0.00008	0.996	0.003	980
RH	13/12/04	0.72240	0.00002	0.991	0.004	980
RH	29/03/05	0.72257	0.00002	0.993	0.005	980
RH	22/05/06	0.72242	0.00001	0.991	0.004	980
RH	**Average**	**0.72236**		**0.993**		
Spring SG	28/09/04	0.72353	0.00002	0.91	0.004	1093
SG	13/12/04	0.72328	0.00007	0.93	0.003	1093
SG	29/03/05	0.72352	0.00002	0.923	0.004	1093
SG	22/05/06	0.72354	0.00002	0.927	0.002	1093
SG	**Average**	**0.72347**		**0.923**		
Spring SH	28/09/04	0.72749	0.00003	0.916	0.003	1050
SH	13/12/04	0.72720	0.00009	0.915	0.003	1050
SH	29/03/05	0.72801	0.00002	0.914	0.004	1050
SH	03/05/05	0.72798	0.00001			1050
SH	22/05/06	0.72720	0.00001	0.911	0.004	1050
SH	02/10/06	0.72752	0.00001			1050
SH	**Average**	**0.72757**		**0.914**		
Outlet RS	29/03/05	0.72573	0.00002	0.939	0.003	883
RS	22/05/06	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 2: Sr isotopic compositions and U AR for spring waters, outlet, rain, througfalls and clays (Prunier, 2008) from the Strengbach watershed. Clays SS: clays from a soil profile located on the southern slope and under beeches, and clays NS: clays from a soil profile located on the northern slope and under spruces.

2004-2006	water fluxes	Na fluxes	K fluxes	Mg fluxes	Ca fluxes	Si fluxes	Sr fluxes	U fluxes
	(mm)	mg/m2/yr	mg/m2/yr	mg/m2/yr	mg/m2/yr	mg/m2/yr	µg/m2/yr	µg/m2/yr
rain - F_{rain}	1247	306	219	56	256	5	1.1	7.6
throughfall - $F_{througfall}$	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 - $F_{througfall(corrected)}$		*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

Table 3: Elementary fluxes for rain, throughfalls and outlet in the Strengbach catchment. 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 includes wet and dry atmospheric deposition and 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: $F_{atm} = 0.15\ F_{rain} + 0.85\ F_{througfall(corrected)}$. The outlet fluxes correspond to the catchment export fluxes (b).

Soils under spruces - Northern slope (1)

depth	SiO2	Al2O3	MgO	CaO	Fe2O3	MnO	TiO2	Na2O	K2O	P2O5	Mg/Ca	Mg/Na	Ca/Na	muscovite	Quartz	K-Feld	plagio	apatite	Smectite	amorph	smectite (%)	OM	pH	Clays	CEC
cm	%	%	%	%	%	%	%	%	%	%				%	%	%	%	%	%	%	in clay fract.	%		%<2µm	cmol/kg
10	72.74	17.84	0.51	0.06	1.92	0.04	0.24	0.62	5.70	0.22	7.56	1.34	0.18	42.2	38.6	10.9	5.4	0.05	3.7	0.68	19.7	7.5	3.7	22.2	15.49
50	64.82	20.71	0.66	0.15	2.43	0.04	0.32	0.85	5.60	0.43	3.65	1.27	0.35	50.1	27.3	5.6	7.5	0.21	5.8	1.09	19.8	9.2	4.4	20.3	11.98
70	65.89	20.59	0.65	0.28	2.12	0.03	0.22	0.99	5.59	0.52	1.95	1.07	0.55	47.5	27.8	7	8.7	0.42	6	1.11		7	4.4	15.8	10.37
90	66.10	20.44	0.70	0.28	2.04	0.02	0.20	0.92	5.71	0.43	2.10	1.24	0.59	45.4	27.4	8.9	8.1	0.43	7.8	0.89		6.3	4.5	12.5	9.78
110	67.17	19.82	0.61	0.30	2.40	0.03	0.20	1.22	5.90	0.47	1.71	0.81	0.47	40.2	27.2	12.8	10.6	0.43	6.4	0.9	27.1	5.1	4.6	8.1	9.79
130	65.25	21.10	0.58	0.39	1.84	0.02	0.22	1.87	5.81	0.49	1.26	0.50	0.40	42.5	22.1	10.7	16.4	0.54	5.1	0.87		5.7	4.7	6.9	9.23
150	65.68	21.82	0.59	0.32	1.86	0.02	0.20	2.04	5.63	0.42	1.52	0.47	0.31	46.5	21.9	7.2	17.8	0.42	4.3	0.7		5.3	4.7	5.1	8.68
170	69.31	20.18	0.60	0.31	1.50	0.03	0.17	1.81	5.77	0.35	1.64	0.54	0.33	39.4	26.9	12.6	15.9	0.41	6.4	0.54		3.8	4.7	4.2	9.76
190	67.17	19.22	0.70	0.28	1.79	0.01	0.27	1.35	5.81	0.32	2.10	0.85	0.40	34.2	25.9	15.5	11.6	0.39	10.2	0.46		6.2	4.6	5.3	15.19
210	68.03	19.31	0.64	0.31	1.42	0.01	0.24	1.37	6.23	0.33	1.73	0.75	0.44	34	25.9	17.9	11.8	0.44	8.5	0.41	47.8	5.6	4.6	5.2	13.94

Soils under beeches - Southern slope (1)

depth	SiO2	Al2O3	MgO	CaO	Fe2O3	MnO	TiO2	Na2O	K2O	P2O5	Mg/Ca	Mg/Na	Ca/Na	muscovite	Quartz	K-Feld	plagio	apatite	Smectite	amorph	smectite (%)	OM	pH	Clays	CEC
cm	%	%	%	%	%	%	%	%	%	%				%	%	%	%	%	%	%	in clay fract.	%		%<2µm	cmol/kg
4	74.45	14.21	0.33	0.18	1.21	0.01	0.33	1.90	4.77	0.25	1.54	0.28	0.18	18.9	39.5	18.9	14.7	0.15	4.4	0.54	14.7	12	4.0	13.3	7.86
15	72.52	15.87	0.34	0.13	1.27	0.01	0.31	1.85	5.41	0.22	2.23	0.30	0.13	23.9	36.5	20	13.6	0.1	3.8	0.41		6.7	4.1	11.6	7.7
35	69.10	15.98	0.35	0.10	2.16	0.04	0.29	1.70	4.96	0.60	2.99	0.34	0.11	23.1	35.1	17.8	12.5	0.05	4.3	2.14		12.3	4.6	10.7	8.00
52.5	66.96	17.53	0.40	0.13	2.52	0.05	0.31	1.81	4.98	0.45	2.65	0.36	0.14	26.3	31.7	15.9	13.4	0.1	5	2.7	22.2	11.9	4.8	8.7	5.02
77.5	65.03	18.61	0.47	0.16	2.85	0.06	0.30	1.91	4.96	0.57	2.46	0.40	0.16	28.7	28.6	14.4	14.3	0.15	6.1	2.89		10.9	4.8	6.3	4.24
100	66.10	18.82	0.55	0.22	2.39	0.08	0.36	1.67	5.24	0.40	2.14	0.53	0.25	31	29.5	14.7	11.8	0.27	7.6	1.63	27.7	7.7	4.8	4.2	4.08
122.5	65.25	19.48	0.56	0.26	1.96	0.08	0.29	1.83	5.34	0.42	1.83	0.50	0.27	33.4	27.3	13.9	13.1	0.33	7.4	1.22		7.5	4.8	3.1	3.6
150	63.54	20.46	0.55	0.32	2.72	0.11	0.28	2.22	5.52	0.45	1.45	0.40	0.28	33.8	22.7	14.8	16.6	0.4	7.1	1.43		6	4.9	2.5	2.6
177.5	64.82	19.35	0.48	0.26	2.85	0.10	0.24	2.47	5.48	0.41	1.56	0.32	0.20	28.1	23.3	17.9	19.1	0.28	6.5	1.17		5.2	4.9	1.8	2.12
177.5	65.89	18.31	0.45	0.29	2.83	0.10	0.28	2.44	5.36	0.44	1.30	0.30	0.23	24	25.3	19.5	19	0.33	6.5	1.19		5.1	4.9	1.6	1.79
200	62.25	20.22	0.55	0.33	3.73	0.15	0.33	2.59	5.04	0.52	1.39	0.34	0.25	31.9	20.9	12.7	20.2	0.39	7.4	1.48	19.8	6.2	4.9	2.1	1.79

Soils - Gneiss (2)

depth	SiO2	Al2O3	MgO	CaO	Fe2O3	MnO	TiO2	Na2O	K2O	P2O5	Mg/Ca	Mg/Na	Ca/Na	muscovite	Quartz	K-Feld	plagio	apatite
cm	%	%	%	%	%	%	%	%	%	%				%	%	%	%	%
30	62.84	15.25	1.00	0.20	5.72	0.15	0.77	0.42	3.44	0.43	4.22	3.87	0.92	nd	nd	nd	nd	nd
65	69.61	15.20	1.35	0.13	5.27	0.09	0.71	0.38	3.93	0.24	8.77	5.77	0.66	nd	nd	nd	nd	nd
135	68.00	15.41	1.22	0.09	5.99	0.09	0.70	0.25	4.23	0.23	11.44	7.93	0.69	nd	nd	nd	nd	nd
175	71.88	15.61	1.02	0.24	3.11	0.04	0.56	0.05	4.71	0.23	3.59	33.16	9.24	nd	nd	nd	nd	nd
225	64.97	16.11	0.86	0.12	9.26	0.16	0.59	0.10	4.69	0.19	6.05	13.98	2.31	nd	nd	nd	nd	nd

Bedrock - average value (1), (2), this study

	SiO2	Al2O3	MgO	CaO	Fe2O3	MnO	TiO2	Na2O	K2O	P2O5	Mg/Ca	Mg/Na	Ca/Na	muscovite	Quartz	K-Feld	plagio	apatite
cm	%	%	%	%	%	%	%	%	%	%				%	%	%	%	%
Northern slope	75.38	14.50	0.45	0.29	1.38	0.03	0.19	0.98	6.19	0.31	1.31	0.75	0.57	29	49	19	2	0.5
Southern slope	74.13	14.32	0.26	0.36	0.98	0.01	0.18	2.87	5.70	0.33	0.61	0.15	0.24	13	34	30	22	0.5
Gneiss	65.08	17.95	2.55	0.20	7.59	0.07	0.89	0.55	4.13	0.12	10.63	7.54	0.71	nd	nd	nd	nd	nd

Table 4: Chemical and mineralogical compositions of soils and bedrocks from the Strengbach watershed. (1): Fichter, 1997, (2): El Gh'Mari, 1995.

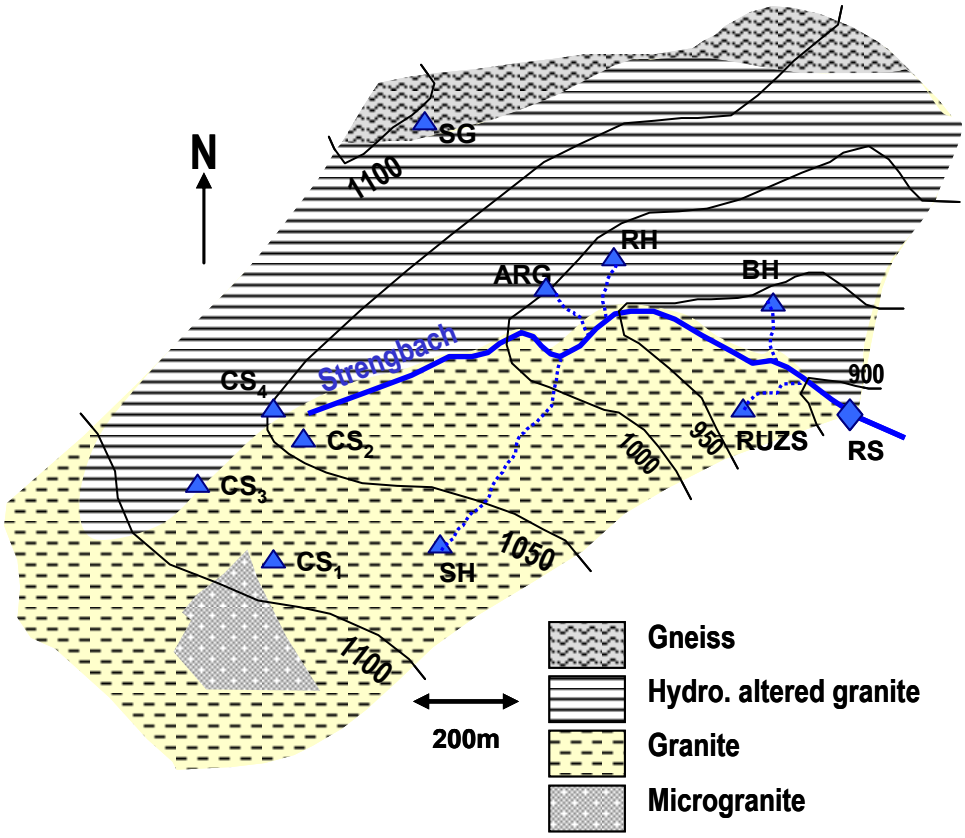


Fig. 1: Map of the Strengbach catchment showing the principal lithological units and the location of the 10 studied springs (SG, RH, ARG, BH, CS1, CS2, CS3, CS4, SH, RUZS). RS corresponds to the Strengbach stream at the outlet of the studied catchment.

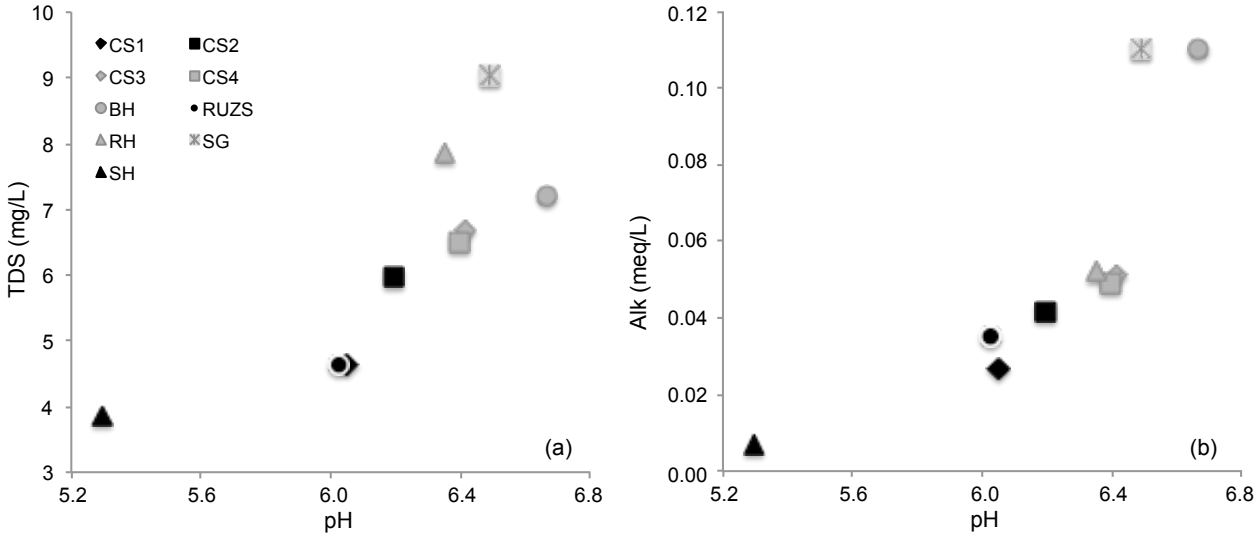


Fig. 2: Physico-chemical characteristics of the different source waters of the Strengbach watershed (average values for the period 2004-2006). a) pH vs TDSw and b) pH vs Alk.

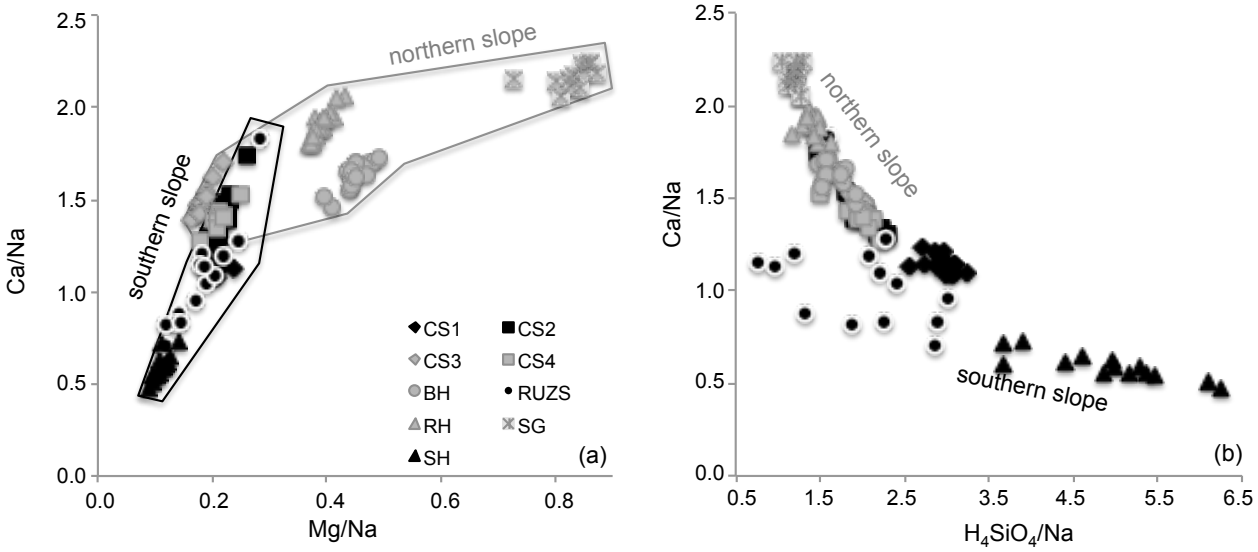
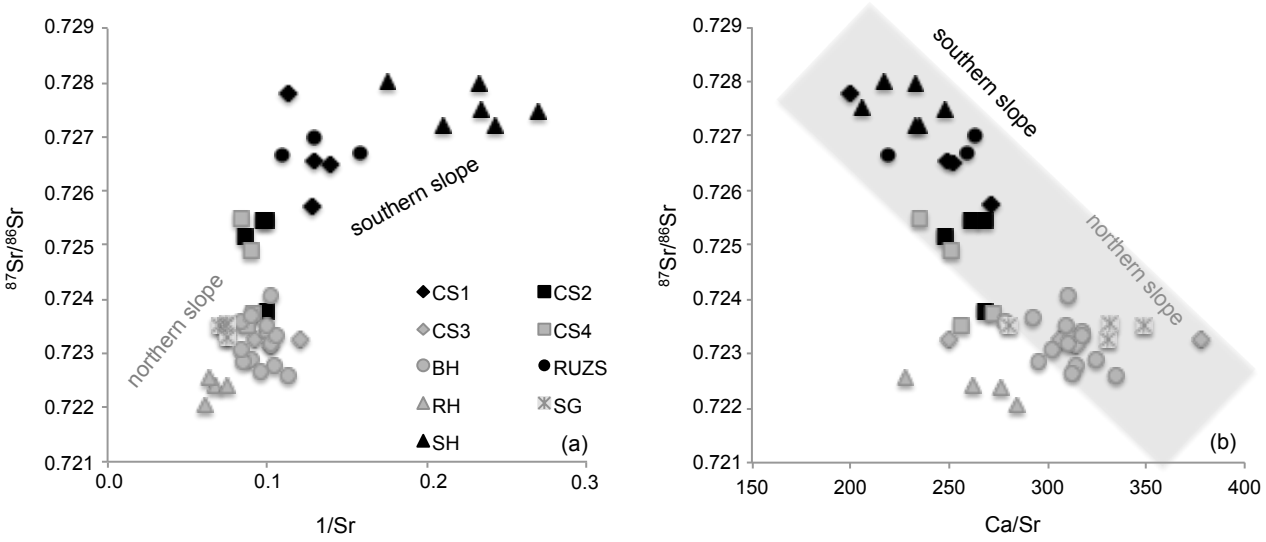


Fig. 3: Major element concentration ratios of the 9 different individual source waters of the Strengbach watershed. a) Ca/Na vs Mg/Na and b) Ca/Na vs $Si(OH)_4$/Ca. In each diagram the spring waters from the southern slope show different compositions than those from the northern slope.



944

945 Fig. 4: Relationships between $^{87}Sr/^{86}Sr$ isotope ratios and a) 1/Sr (ppb); b) Ca/Sr (ppb/ppb). The

946 isotope ratios allow a clear distinction between northern and southern slope sources.

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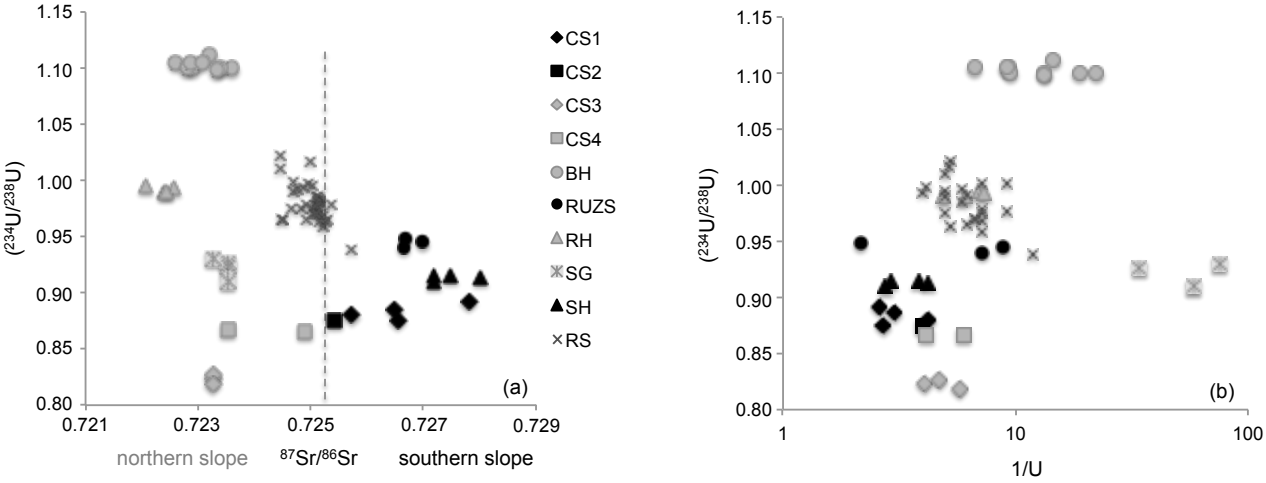


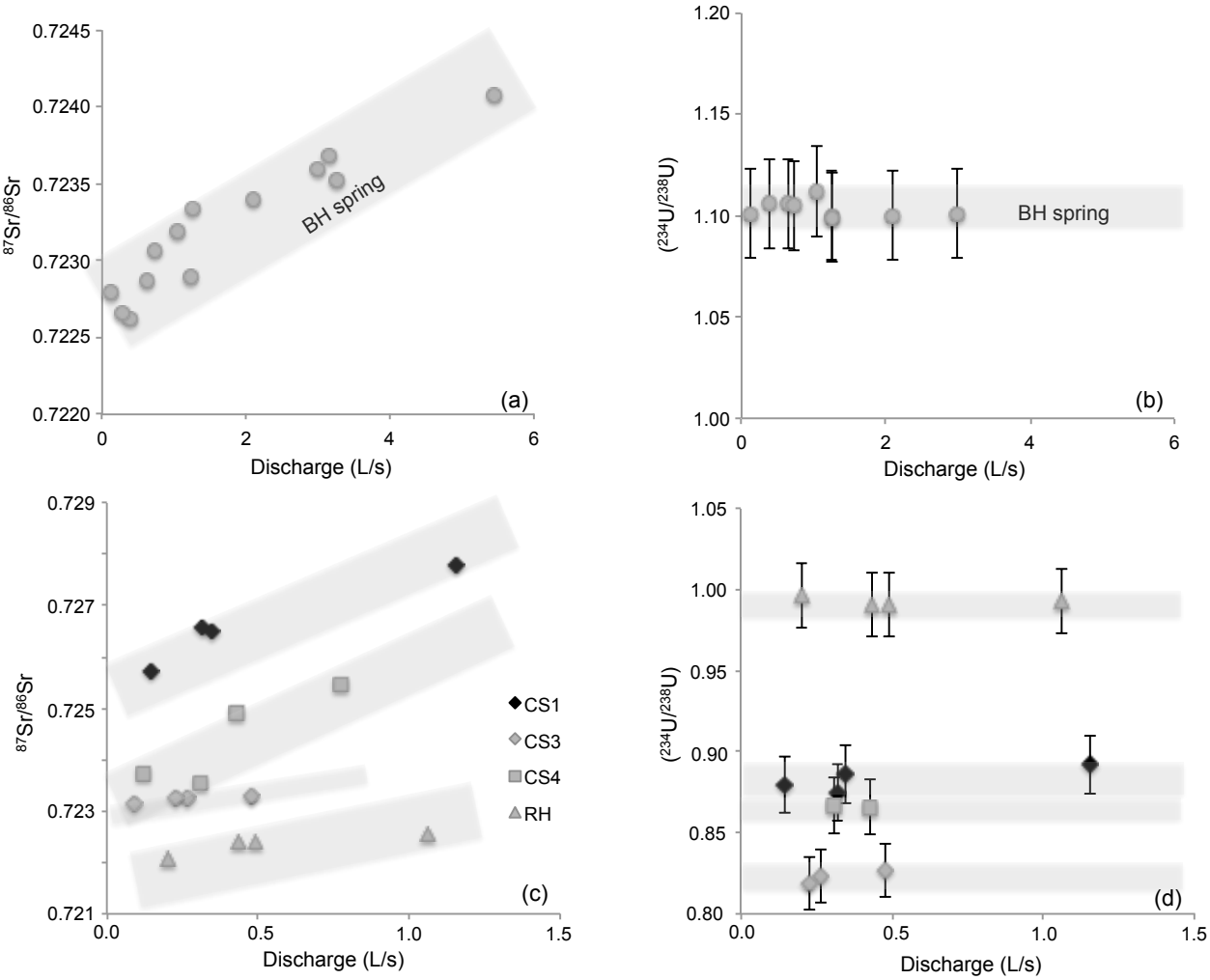
949

950 Fig. 5: Relationship between ($^{234}U/^{238}U$) AR and a) 1/U and, b) $^{87}Sr/^{86}Sr$. In contrast to Sr isotopic

951 compositions, the U AR of springs do not allow to distinguish between the northern and southern

952 slopes.

953



954

955 Fig. 6: $^{87}Sr/^{86}Sr$ and ($^{234}U/^{238}U$) AR vs discharge for the springs BH, CS1, CS3, CS4 and RH from

956 the Strengbach watershed.

957

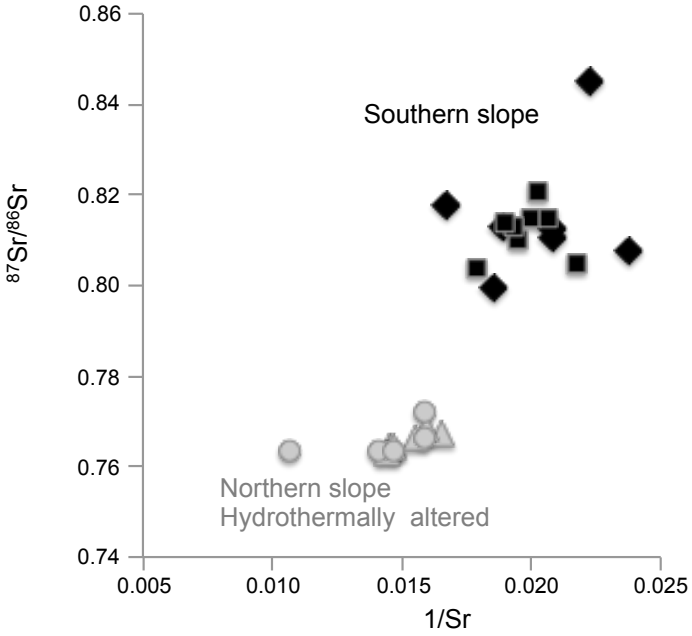


Fig. 7: $^{87}Sr/^{86}Sr$ vs 1/Sr for the soil and saprolite samples from the Strengbach watershed. The samples from the northern slope and those from the southern slope are clearly different (Aubert, 2001; Stille et al., 2009 ; Prunier, 2008).

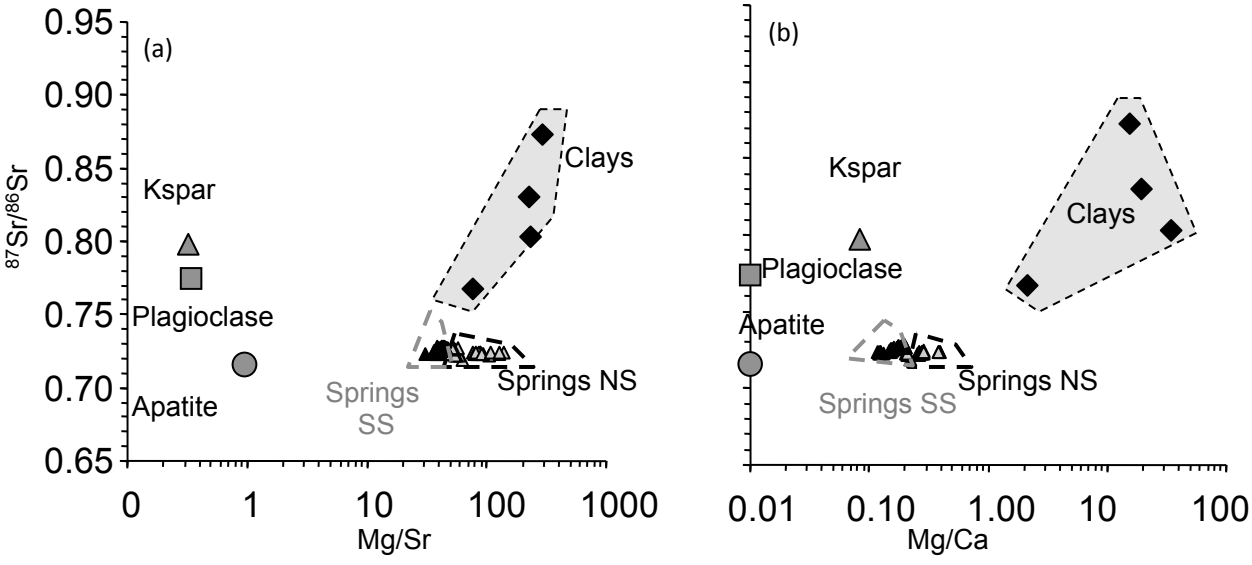
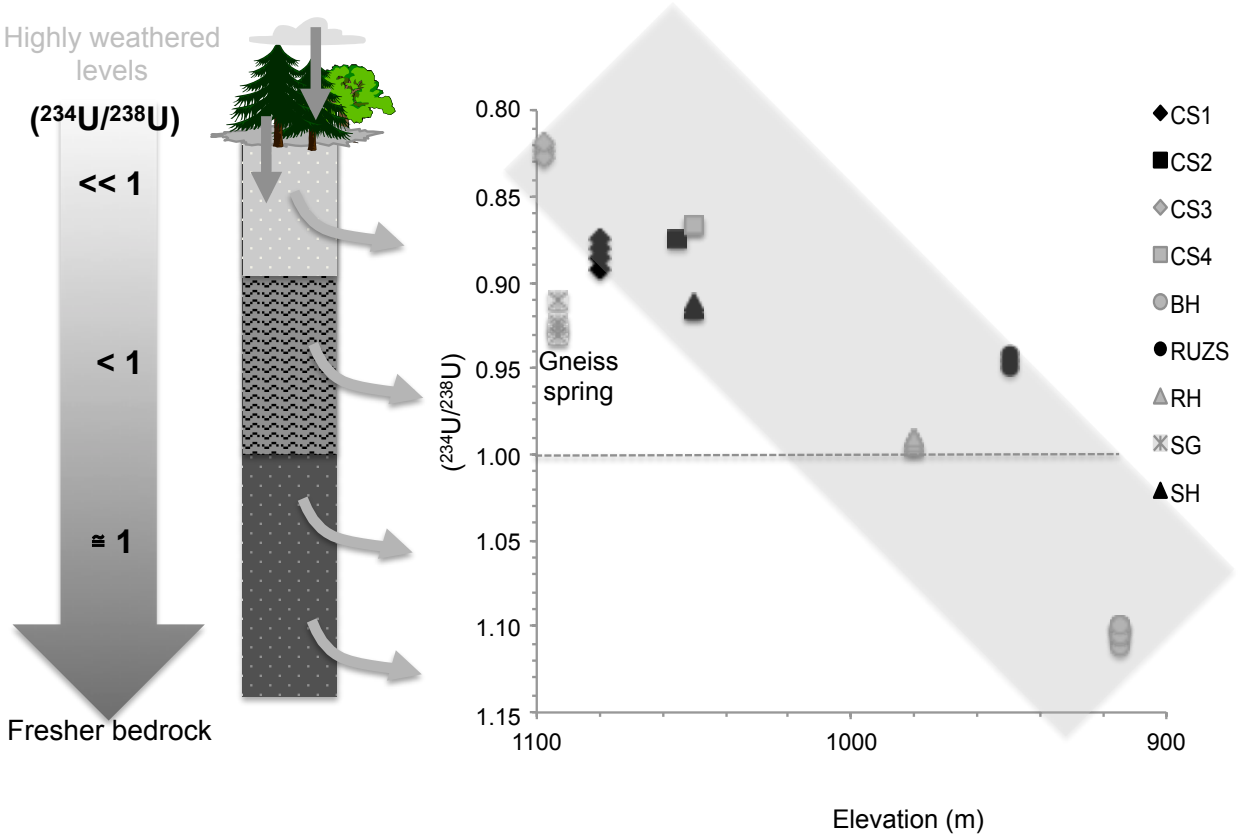


Fig. 8: $^{87}Sr/^{86}Sr$ vs Mg/Ca (a) and Mg/Si (b) for the spring waters (NS = northern slope and SS=southern slope), primary minerals of the granite (Aubert et al.. 2001) and clays from soils (Prunier, 2008).

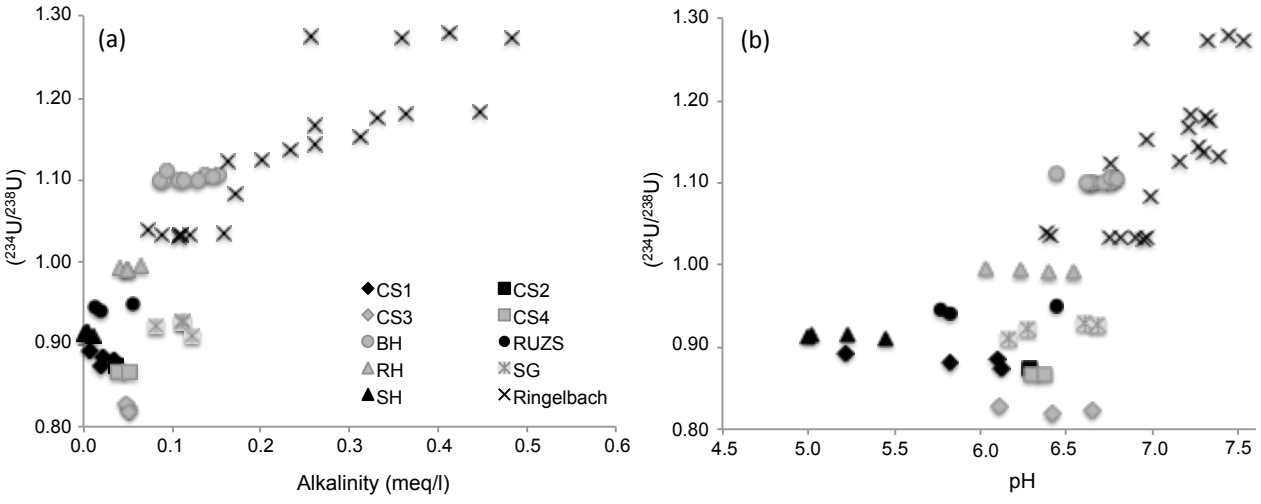


969

970 Fig. 9: ($^{234}U/^{238}U$) AR of springs vs elevation. The U AR increase with decreasing altitude at the

971 catchment scale.

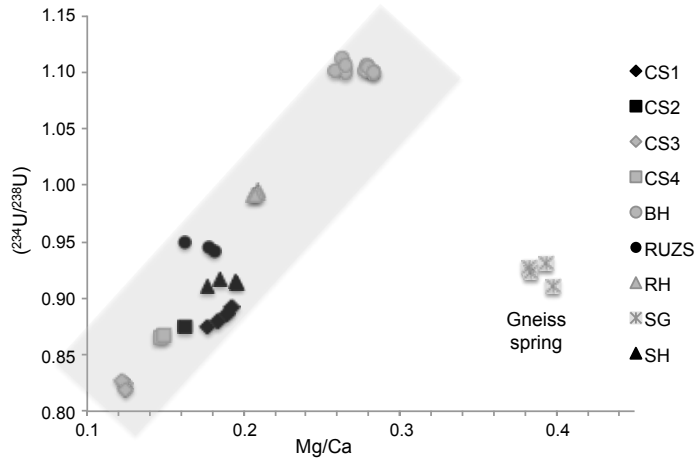
972



973

974 Fig.10: Variations of ($^{234}U/^{238}U$) AR vs a) alkalinity and b) pH in the springs from the Strengbach

975 and Ringelbach (Shaffauser et al., 2014) watersheds.



976

977 Fig. 11: Variations of ($^{234}U/^{238}U$) AR vs Mg/Ca ratio in the springs. The U AR are positively
978 correlated with the Mg/Ca ratios.

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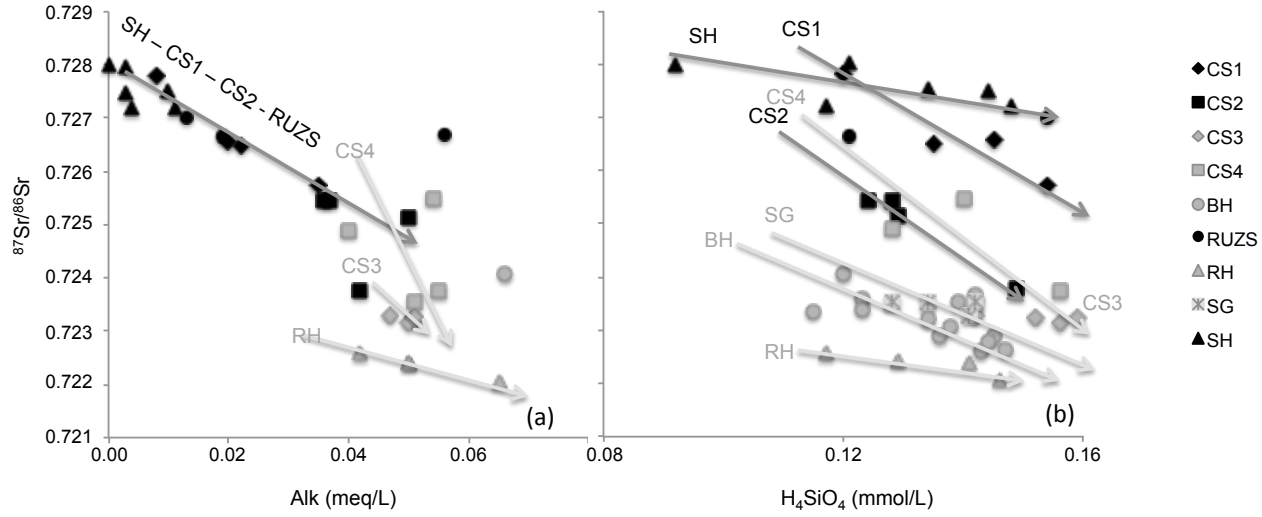
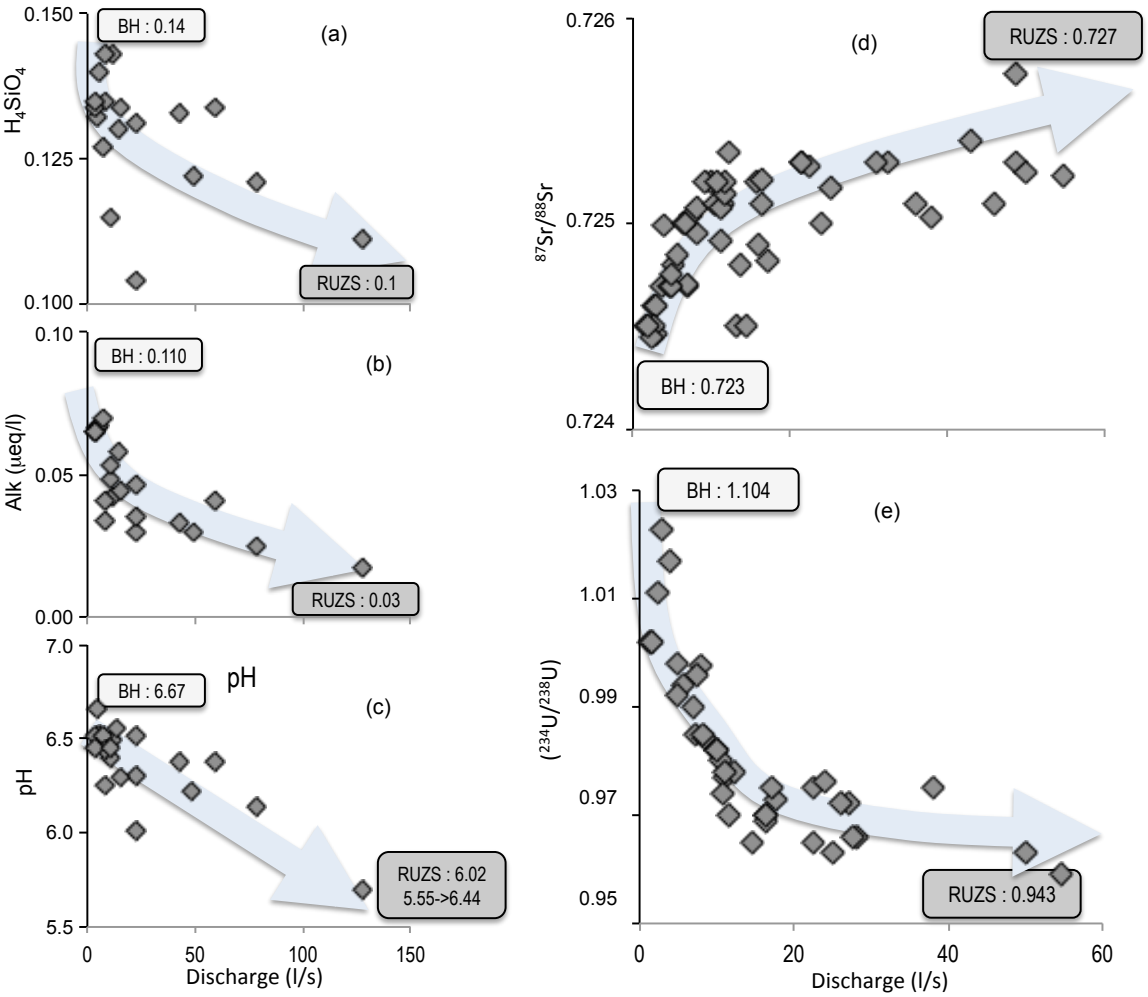


980

981 Fig. 12: $^{87}Sr/^{86}Sr$ vs alkalinity (a) and Si concentrations (b) for the springs from the Strengbach
982 watershed. For each of the individual spring the $^{87}Sr/^{86}Sr$ ratios decrease with increasing alkalinity
983 and Si content.

984



985

986 Fig. 13: H_4SiO_4 concentration (a), alkalinity (b), pH (c), ($^{234}U/^{238}U$) AR (d) and $^{87}Sr/^{86}Sr$ (e) vs
987 discharge at the outlet for the 2004-2006 period (additional data from Riotte et al. (1999) and
988 Aubert et al., (2002)).

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