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Anne Probst, Bruno Ambroise. Disturbance and resilience of a granitic critical zone submitted to acid atmospheric influence (the Ringelbach catchment, Vosges Mountains, France): Lessons from a hydrogeochemical survey in the nineties. *Journal of Hydrology*, 2019, 569, pp.77-92. 10.1016/j.jhydrol.2018.11.018 . hal-03510016

HAL Id: hal-03510016

<https://hal.science/hal-03510016v1>

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<https://doi.org/10.1016/j.jhydrol.2018.11.018>

To cite this version:

Probst, Anne and Ambroise, Bruno *Disturbance and resilience of a granitic critical zone submitted to acid atmospheric influence (the Ringelbach catchment, Vosges Mountains, France) : Lessons from a hydrogeochemical survey in the nineties.* (2018) Journal of Hydrology, 569. pp. 77-92. ISSN 0022-1694

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Disturbance and resilience of a granitic critical zone submitted to acid atmospheric influence (the Ringelbach catchment, Vosges Mountains, France): Lessons from a hydrogeochemical survey in the nineties

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A B S T R A C T

Keywords:

Acid precipitation
Sulfur
Streamflow
Major elements
Weathering
Catchment budgets

The chemistry of precipitations and stream waters in the critical zone of a small granitic catchment mainly covered by grassland has been investigated backward (period 1990–1997). Major elements concentrations, fluxes and budgets at annual and seasonal scales allowed evaluating the catchment response to variation trends in atmospheric deposition and hydrological patterns. Acid precipitation was efficiently buffered by soil cations exchange and mineral weathering processes, as attested by the dominance of Ca and HCO₃ in stream waters. A decrease of sulfate acidity in precipitation following clean air measures was accompanied by an increase of alkalinity and a decrease of sulfate in stream waters. Waters of short residence time from water-saturated areas in the valley bottom and rapid shallow circulations within slopes were a very effective diluted weathering end-member contributing to stream outlet in high flow conditions, whereas evapotranspiration from saturated areas and/or deep waters with long residence time influenced the stream water concentration pattern in low flow conditions.

Water discharge controlled the variations of the annual and seasonal budgets of major elements, except for nitrate and sulfate, mainly stored during summer. Soil legacy sulfate was mainly released during the first autumn stormflows, with high peak concentrations decreasing rapidly from 1990 to 1992 and disappearing afterwards. The output water flux was the main driver of the weathering rate in the acidification recovery period 1993–97, contrary to the first period 1990–92 when acidification was still under way, as attested by the weathering plateau (constant Si/ΣBC ratio). At that time, the intense weathering testifies the disturbance caused by acidification process. However, this critical zone was resilient enough to allow rapid and significant recovery over a few years following sulfur atmospheric abatement. For the future, the atmospheric nitrogen deposition pressure remains still challenging in a global change context, which argues for the necessity of long-term observatories.

1. Introduction

The very thin interface between atmosphere, vegetation, soil and bedrock at the earth surface, the so-called “critical zone” (Brantley et al., 2006), has been under the pressure of human activities for decades and even centuries, particularly in industrialized countries of the northern hemisphere (Wohl, 2013). Among these pressures, a lot of industrial activities such as coal burning have led to emissions of sulfur and nitrogen, which have largely contributed to acid precipitations (Smith et al., 2011). Atmospheric circulation may spread these gaseous emissions over hundreds of kilometres from the sources, resulting in long range atmospheric pollution (Chin et al., 2007). Acid compounds

have consequently been deposited on the ecosystems and led to disturbances such as soil and water acidification even in remote areas, particularly in northern Europe, North America and Asia (Ulrich, 1984; Probst et al., 1990b; Kreiser et al., 1995; Hettelingh et al., 2007; Pardo et al., 2011; Burns et al., 2016).

Soils and bedrocks undergo natural weathering processes driven by atmospheric CO₂, precipitation and temperature (White and Blum, 1995; Oliva et al., 2003). However, these processes are disturbed under the influence of strong acid (sulfuric and nitric) inputs by precipitations, resulting in enhanced silicate weathering and/or soil base cations depletion (Pačes, 1985; Amiotte Suchet et al., 1995). This disturbance is more obvious where (i) the buffering capacity of the weathering

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processes is low like in very sensitive areas of northern Europe (granitic areas with limited soil cover: Wright and Johannessen, 1980), and/or (ii) the acid inputs are very high due to regional coal burning sources like in north-eastern USA or the “Black Triangle” region in central Europe.

In the early eighties, the scientific communities have undertaken the hydrogeochemical survey of small catchments over the northern hemisphere to study these processes and quantify their intensity (Likens et al., 1977; Hornung et al., 1990; Davies et al., 1992). In France, the influence of acid atmospheric deposition has been particularly evidenced in the north-eastern region (Probst et al., 1990a; Party et al., 1995; Dambrine et al., 1998; Pascaud et al., 2016). Surface water acidification was demonstrated in the Ardennes and some sensitive parts of the Vosges Mountains (Février et al., 1999; Probst et al., 1990b; Kreiser et al., 1995), and forest decline was related to soil acidification, base cation depletion and aluminium toxicity (Landmann and Bonneau, 1995) as the initial step of the forest dieback observed in very polluted areas of other countries (Johnson and Siccama, 1983; Ulrich, 1984). The main concern about forest health has consequently focused European researches on biogeochemical cycles in small spruce forested catchments (Birkenes, Norway: Christophersen and Wright, 1981; Lysina, Czech Republic: Pačes et al., 1985; Plynlimon, UK: Durand et al., 1992; Strengbach, Vosges, France: Probst et al., 1992).

Over the last decades, recovery patterns from acidification have been detected in some places in Europe following clean air measures, but in a very variable way depending on pollution pressure and environmental characteristics (Dambrine et al., 2000; Evans et al., 2001; Marx et al., 2017). Moreover, few surveys have concerned catchments not covered by coniferous forests and with high weathering buffering capacity, since the influence of acid deposition was then more “hidden” and difficult to detect.

In parallel to these pollution-driven investigations initiated in the seventies, hydrologists have been particularly aware of the utility to set up long-term monitoring multidisciplinary research catchments to investigate processes, water pathways and contributing areas over a large range of climatic and geologic conditions (Ward, 1971; Swank and Crossley, 1988; Ambroise, 1994). Particularly, concentration/discharge relationships (Durum, 1953; Pinder and Jones, 1969; Feller and Kimmins, 1979), end-member mixing analysis (Miller and Drever, 1977; Hooper et al., 1990) as well as mass balance approach (Hornung et al., 1990), were frequently used because of their well-established performance to assess hydrochemical processes, water and elements sources, and weathering intensity, particularly in small catchments.

In France, one of these pioneer remote sites is the Ringelbach catchment (Vosges Mountains), which is mainly covered by grassland and has passively been under the influence of long range atmospheric pollution. A pluriannual hydrochemical survey was set up in the nineties with the objective to help understanding the hydrological functioning using geochemical tracers, as in other sites in Europe or USA (Hornung et al., 1990; Likens et al., 1977). This survey combined detailed hydrological data from various compartments of the critical zone and the associated chemical data. It allows (i) to set up hydrochemical budgets at time scales varying from season to year; (ii) to investigate and identify the water and element sources and pathways, and (iii) to compare the Ringelbach hydrochemical behavior to those of other sensitive silicate catchments with different vegetation cover submitted to the pressure of acid atmospheric inputs.

In a context of global change, it is a major concern today to get historical registrations by collecting and exploiting ancient databases. Such data mining at international level would help to reinforce hypotheses on processes acting in geosystems that are under anthropogenic pressures or in a recovery stage from these pressures. Particularly, it would help to model in a robust way these patterns and functioning under a large range of environmental conditions.

By investigating the nineties data set of the Ringelbach research catchment, the objectives of this paper are: (i) to characterize the

hydrochemical features, fluxes and budgets on annual and seasonal time steps at the catchment scale; (ii) to investigate the combined influences of hydrological conditions and atmospheric inputs on the critical zone response; (iii) to evaluate the disturbance of weathering processes and the resilience of the catchment to this disturbance during the nineties.

The key question is whether the disturbance of the critical zone by, and its resilience to, sulfuric acid atmospheric inputs were detectable over only a few years of survey.

2. Material and methods

2.1. Site description

The Ringelbach catchment is located at Soutzeren (Haut-Rhin) on the eastern side of the Vosges Mountains (NE France). It is a 0.36 km² research catchment, in which interdisciplinary studies on water cycle dynamics have been conducted since 1976 (Mercier, 1982; Ambroise, 1995, 2016; Baltassat et al., 2005; Schaffhauser et al., 2014; Lucas et al., 2017). It lies on a large south-facing versant, with elevation ranging from 1000 to 750 m and rather steep slopes (mean: 20°, maximum: 35°) (Fig. 1).

The climate is temperate mountainous, which is a transition between oceanic and semi-continental regimes. At 800 m, mean monthly temperatures range from 0 °C in January to 15.6 °C in July (Paul, 1982). Precipitation is rather well distributed all over the year, with a mean annual value of about 1230 mm.yr⁻¹ and a mean snowfall proportion of about 16% (Humbert, 1982). Snow cover is frequent between November and April, but usually lasts only a few days because of frequent thaws at this low altitude. Mean annual potential evapotranspiration is about 650 mm.yr⁻¹ (Fouché-Roguez, 1998).

The catchment exhibits a relatively complex 3-D geological structure resulting from both weathering and tectonics (Baltassat et al., 2005). Bedrock consists of Hercynian porphyroid granite (“*granite des crêtes*”) capped in its upper part (Hurlin and Heidenkopf summits) by a residual cover of Triassic sandstones (Fluck et al., 1978). The porphyroid granite is medium-grained, relatively homogeneous, rich in biotite, and made up of quartz, plagioclase, K-feldspar and amphibole. There is a truncated saprolite at the top of its ante-Triassic weathering profile (Wyns, 2012). The Triassic sandstone cover, which gently dips towards the north, is composed of relatively thick, hard medium-grained sandstone layers interstratified with a series of thinner beds of relatively fine, clayey and indurated sand. Faults define three main tectonic blocks (Heidenkopf, Hurlin and Bunker).

The superficial formations, which are usually a few meters deep only, are mostly regolith (granitic arena) covered by slope and colluvial deposits. Soils, which belong to the podzolic series, are characterized by a weak structure, a coarse texture (more than 70% of sand and gravel) and a high macroporosity. Soil water retention is low in mineral layers but much higher in the upper layers (up to 0.70 at saturation) because of their high organic matter content. The hydraulic conductivity is high at saturation (> 10⁻⁴ m/s), but decreases very rapidly as soon as the soil dries out a little (Ambroise and Viville, 1986; Viville et al., 1986; Reutenauer and Ambroise, 1992). No surface runoff is usually observed on slopes. The vegetation cover consists in extensively pastured dense grasslands and moorlands on granite and a pine forest on sandstone, representing about 80% and 20% of the area, respectively.

The valley bottom is partly water-saturated throughout the year, but the extent of the saturated areas varies largely, up to 8% of the catchment area, depending on groundwater storage (Ambroise, 1988, 2016). It is drained by three small streams, which can dry out locally and temporarily during some late summers. Stream discharge at the outlet ranges between less than 0.01 L.s⁻¹ and more than 100 L.s⁻¹, around a mean of about 7.4 L.s⁻¹ (i.e. 20.6 L.s⁻¹.km⁻² or 648 mm.yr⁻¹) (Humbert, 1982). Discharge is usually high in winter and low in summer and early autumn. Several springs are located along the

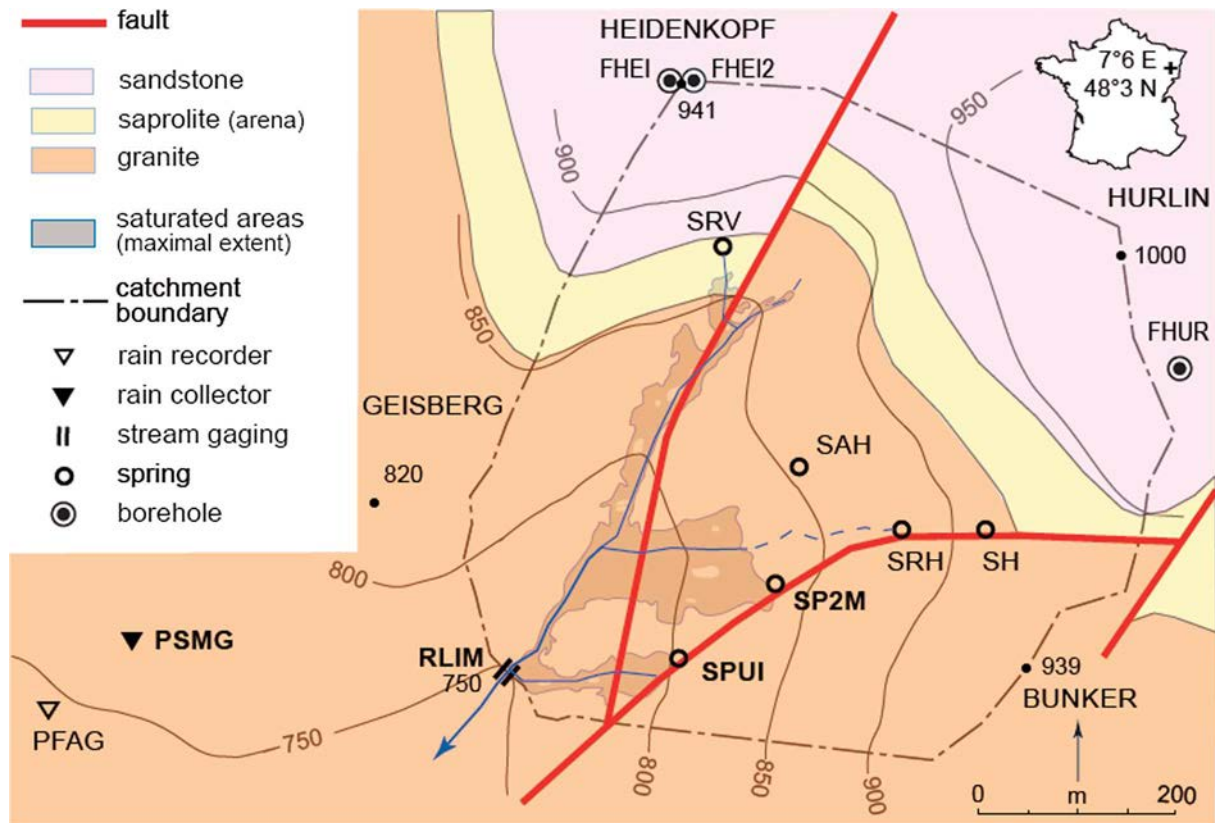


Fig. 1. Topographical and geological map of the Ringelbach catchment with location of the measurement and sampling sites.

sandstone/granite contact (SRV), along the fault Hurlin-Bunker (SH, SRH, SP2M, SPUI) and at midslope of the block Hurlin (SAH). Two of them, SPUI and, from May 1991 on, SP2M, are tapped for water supply outside the catchment (Fig. 1).

2.2. Water fluxes measurement and sampling

The study period extends from January 1990 to August 1997, including seven hydrological years (from September to August) usually beginning with very low flow conditions.

The main meteorological parameters were continuously recorded at the automatic weather station PSMG, and precipitation data at the nearby heated chart-recording (Précis Mécanique) rain gauge PFAG, both sites being in the close vicinity of the catchment (Fig. 1). According to data from Adjizian-Gérard (1994), a coefficient of 1.0325 has been applied to the PFAG data to determine the total precipitation amount at the catchment scale. Discharges at the catchment outlet, which is equipped with a very sensitive, carefully rated 26.5° V-notch weir, were obtained from continuously measured stream water levels (submerged ultrasonic SAB600/CR2M probe, OTT chart recorder). The two springs SPUI and SP2M, which are connected to the same water pipe, were gauged about weekly during the period 1990–1995, but much more irregularly in 1996 and 1997, to determine the total abstracted discharge, which remains limited to $1.75 \text{ L}\cdot\text{s}^{-1}$ by an overflow.

Bulk open field precipitation was collected in a polyethylene bucket at the site PSMG, and sampled about weekly (with cumulative samples over two or more weeks in case of too small amount). Stream water was sampled at the outlet about weekly. This resulted in 258 precipitation samples for the 305 weeks with significant amount and 348 stream water samples over the 404-weeks period, leading to similar good weekly sampling rates of 83 and 86%, respectively. The last sampling date was July 29, 1997. To ensure a complete hydrological year, the chemistry of August 1997 was estimated using data from periods with

similar conditions (August 1996 for precipitations, July 1997 for streamflow). All waters were sampled using polyethylene bottles.

Spring water at both SPUI and SP2M could not be sampled regularly during the study period (only 3 samples for SPUI in 1990, and 2 for SP2M in 1991). But, as for the other mentioned springs, chemical analyses (28 for SPUI, 27 for SP2M) are available over the whole range of spring discharge for the period 2001–2006 (Schaffhauser et al., 2014). Some analyses (Schaffhauser et al., 2014) are also available for water sampled in 2008–2010 at several depths within three boreholes drilled in 2005 in or near the upper part of the catchment (Fig. 1): FHUR and FHEI (150 m deep, granite aquifer), FHEI2 (70 m deep, sandstone aquifer).

2.3. Analytical techniques

Immediately after field sampling, water samples were filtered at the laboratory (using $0.45 \mu\text{m}$ Millipore cellulose acetate membrane) and kept in the dark at 4°C . Chemical analysis were performed rapidly: alkalinity by Gran's titration (Mettler apparatus); Cl, NO_3 and SO_4 by ion chromatography (Dionex apparatus); Na, K, Ca and Mg by atomic absorption spectrometry (Perkin-Elmer spectrometer); NH_4 and H_4SiO_4 by automatic colorimetry (Technicon apparatus). PO_4 was sometimes detected using first colorimetry technique, then ion chromatography, but in most cases concentrations were under the detection limit. NPOC was analyzed using a Shimadzu TOC 5000 analyzer. The detection limit for both cations C^+ and anions A^- concentrations was $0.001 \text{ mmol}\cdot\text{L}^{-1}$ (even lower for Mg). The analytical accuracy was better than $\pm 2\%$. The mean relative ionic balance $200 \cdot [\Sigma\text{C}^+ - \Sigma\text{A}^-] / [\Sigma\text{C}^+ + \Sigma\text{A}^-]$ was $\pm 5\%$ for precipitation waters and less than $\pm 10\%$ for stream and spring waters, ensuring the quality of the data.

2.4. Calculation of fluxes and budgets

The Ringelbach catchment exchanges no significant lateral or deep groundwater fluxes with its environment (Ambroise et al., 1996).

Element inputs by dry atmospheric deposits were assumed to be negligible between two rain events. Indeed, the catchment is located far from any local pollution sources and the vegetation is mainly composed of grassland with a limited forest cover. There is no significant exportation of biomass, and the permanent vegetation can be considered in a stationary state over the study period. Therefore, elements budgets were computed by subtracting from the input fluxes (open field precipitations) the total output fluxes (stream water at the outlet plus the abstracted water from the two tapped springs SPUI and SP2M). Same procedures as already applied in the nearby Strengbach catchment (Probst et al., 1992) have been used to estimate the associated element fluxes from measured water concentrations and fluxes.

For precipitation inputs, element fluxes for each sampling time step (between two sampling dates) have been calculated by simply multiplying the element concentrations by the corresponding water volume. For stream water output, the volume of water flow between two consecutive sampling dates was multiplied by the mean concentration of these two instantaneous samples. Constant concentrations in stream waters have been assumed within each time step to allow flux distribution before and after any needed intermediate date. Such an assumption of no significant chemistry variation within about weekly time steps may be rather crude for some periods, owing to the possible variability of both water fluxes and concentrations in case of a succession of storm events within the week. But the week has been considered as a time step short enough to get an accurate estimation of element fluxes over much longer periods (season, year) in such a small size catchment (Probst et al., 1992; Ferrant et al., 2013).

Because of lack of data, a specific procedure was used for estimating correctly the fluxes abstracted from the two tapped springs SPUI and SP2M, whose discharge and chemistry vary relatively slowly and regularly, with a variation range much larger for discharge than for concentrations. Daily spring discharges were interpolated from weekly measured instantaneous discharges using a simple daily water balance model (Ambroise, 2016). Daily spring concentrations were estimated from daily discharges using the significant loglinear relationships obtained for 2001–2006 spring samples (see below § 3.3.1). The resulting element fluxes of both springs were then mixed proportionally to their discharges to derive the element fluxes of abstracted spring water, taking also into account the overflow threshold.

All specific fluxes were then cumulated to estimate the total flux over a given period. Budgets were calculated considering the hydrological year, as well as the four well contrasted hydrological seasons identified for this catchment: autumn (September to November: rapid recharge of groundwater), winter (December to February: high flow conditions), spring (March to May: progressive depletion of groundwater), summer (June to August: low flow conditions, but with many thunderstorms).

All mean annual and seasonal concentration values are flux-weighted averages.

3. Results

3.1. Hydrological features

Annual water fluxes for the seven hydrological years 1990–97 are given in Table 1. Variations of daily precipitations and stream discharge are presented as online Supplementary data in Fig. EA-1. Mean annual values 1990–97 are 1162 mm.yr⁻¹ for precipitations, 548 mm.yr⁻¹ for stream discharge and 58 mm.yr⁻¹ for the abstracted spring discharge (*i.e.* as much as 10% of the total output discharge). As a whole, the period is slightly drier than mean long-term conditions (Humbert, 1982).

The study period appears particularly well suited for sampling and assessing the whole time variability of hydrogeochemical fluxes, as it corresponds to a sequence of contrasted hydrological years (driest:

1990–91, 1995–96; wettest: 1993–94, 1994–95). It includes long recession periods during both warm and cold seasons, and extremely low flows in August 1991 and 1992, when the stream (but not the tapped springs) dried out during a few days. It also includes some major hydrological events, usually occurring in winter, like the exceptional event of February 1990 ($P = 195$ mm), which combined snowmelt and heavy rainfall, or the major events of January 1995 ($P = 200$ mm) and February 1997 ($P = 110$ mm). Except during December 1990, snow-pack was neither significant nor lasting.

3.2. Chemical features of input and output water fluxes

The chemical composition of individual water samples and the associated water fluxes are given in Table EA-1 for precipitations and Table EA-2 for stream waters, and the corresponding correlation tables (between concentrations and parameters) in Table EA-3, as online Supplementary data.

3.2.1. Mean ion concentrations and relative abundances

Mean annual molar concentrations are given in Table 1.

Open field atmospheric precipitations are slightly acidic, with a mean pH of 4.9 (calculated from mean proton concentrations). NH₄, SO₄ and NO₃ are the dominant ions. The mean total dissolved salts (TDS) is 6.4 mg/L, which is within the range of values in precipitations measured in the nearby Strengbach catchment for the same period (Probst et al., 1992; 1995a). This value is also consistent with data from the MERA and RENECOFOR networks in charge of the long-term precipitations survey over France (Pascaud et al., 2016).

Stream waters at the outlet and abstracted spring waters (SPUI and SP2M) are circumneutral and dominated by Ca and HCO₃, as usually observed in surface waters draining granitic areas (Meybeck, 2003). All ions are more concentrated in abstracted spring water than in stream water. It is particularly true for NO₃. These results are in agreement with preliminary studies on water chemistry in the Ringelbach catchment (Fritz, 1982; Fritz et al., 1984; Probst et al., 1987; Alary, 1993; Redon, 2005).

For each water sample, the proportions of the chemicals with respect to the respective sum of anions or cations were calculated using concentrations expressed in meq.L⁻¹ and plotted in a Piper's diagram (Fig. 2).

On the anion triangle, most precipitation samples are on the sulfate axis with a large variation of SO₄ abundance (from about 20 to 70% of the anionic charge), compensated by Cl + NO₃. Because some of them contain a significant proportion of HCO₃, the samples scatter rather largely. On the cation triangle, this is also observed for Ca and Mg proportions, with Ca varying from 5 to 70% of the cationic charge, while Mg is always lower than 10%. Protons and NH₄ represent between 60 and 95% of the total monovalent ions.

For surface waters (stream and abstracted spring waters), the cations spread is relatively narrow, the most important variation concerning Ca (between 40 and 60% of the cationic charge). On the opposite, the anions scatter largely, with a majority of samples having more than 80% HCO₃, but also with some samples dominated by SO₄ (more than 40% of the anionic charge). Consequently, in the synthetic diamond, samples are largely stretched along a gradient of complementary values from dominant acid anions (Cl + NO₃ + SO₄) to buffering HCO₃ ion.

Compared with stream waters, the granite spring waters are much more homogeneous, with shorter linear scatters. The lower springs (SPUI, SP2M, SAH) are concentrated in the buffering HCO₃ end-member (more than 60% of the anionic charge), while the upper ones (SH, SRH) are relatively enriched in acid anions, particularly Cl + NO₃. Slightly lower Ca + Mg and SO₄ proportions distinguish SP2M from SPUI tapped waters. Sandstone waters from both the SRV spring and FHEI2 borehole are similar, in between precipitations and the less

Table 1

Flux-weighted mean and standard deviation for major elements concentrations in precipitations and output water fluxes over the period 1990–97 (7 hydrological years) in the Ringelbach catchment. pH values are computed using annual mean H concentrations. Note the shorter (6 hydrological years 1991–97) reference period for spring SP2M tapped from May 1991 on.

Hydrological year (September-August)	Flux _{H₂O} mm.yr ⁻¹	pH	NH ₄	Na	K	Mg	Ca	H mmol.L ⁻¹	HCO ₃	Cl	NO ₃	SO ₄	Si	TDS mg.L ⁻¹
Precipitations														
mean annual	1162.2	4.91	0.0402	0.0130	0.0056	0.0025	0.0089	0.0128	0.0076	0.0173	0.0320	0.0165	0.0014	6.45
standard deviation	235.3	0.12	0.0176	0.0025	0.0016	0.0006	0.0030	0.0032	0.0063	0.0030	0.0136	0.0030	0.0005	2.10
Stream														
mean annual	548.4	6.85	0.0011	0.0791	0.0265	0.0365	0.0695	0.0001	0.1647	0.0395	0.0025	0.0408	0.1295	34.52
standard deviation	228.2	0.09	0.0001	0.0045	0.0018	0.0059	0.0106	0.0000	0.0503	0.0092	0.0009	0.0092	0.0059	3.14
SPUI spring														
mean annual	38.0	7.22	0.0010	0.1070	0.0564	0.0604	0.0892	0.0001	0.3456	0.0320	0.0235	0.0257	0.2016	55.25
standard deviation	9.4	0.01	0.0000	0.0013	0.0010	0.0021	0.0036	0.0000	0.0135	0.0004	0.0001	0.0001	0.0017	1.25
SP2M spring														
mean annual*	23.2	7.14	0.0010	0.1050	0.0479	0.0419	0.0623	0.0001	0.2545	0.0280	0.0340	0.0183	0.1961	47.05
standard deviation*	3.4	0.02	0.0000	0.0017	0.0008	0.0012	0.0017	0.0000	0.0089	0.0000	0.0010	0.0002	0.0026	0.92

*: Values for the 6 hydrological years 1991–97.

buffered samples of stream water. Waters from the granite boreholes are very concentrated in HCO₃ and Ca + Mg (more than 80%), but with a Mg proportion much higher in FHUR than in FHEI.

These patterns are consistent with the preliminary investigations done in the eighties for precipitations and stream waters (Probst et al., 1987) and with more recent data on spring waters (Schaffhauser et al., 2014).

● PSMG ● RLIM ● SPUI ● SP2M ● SRH ● SH ● SAH ● SRV ● FHEI2 ● FHEI ● FHUR

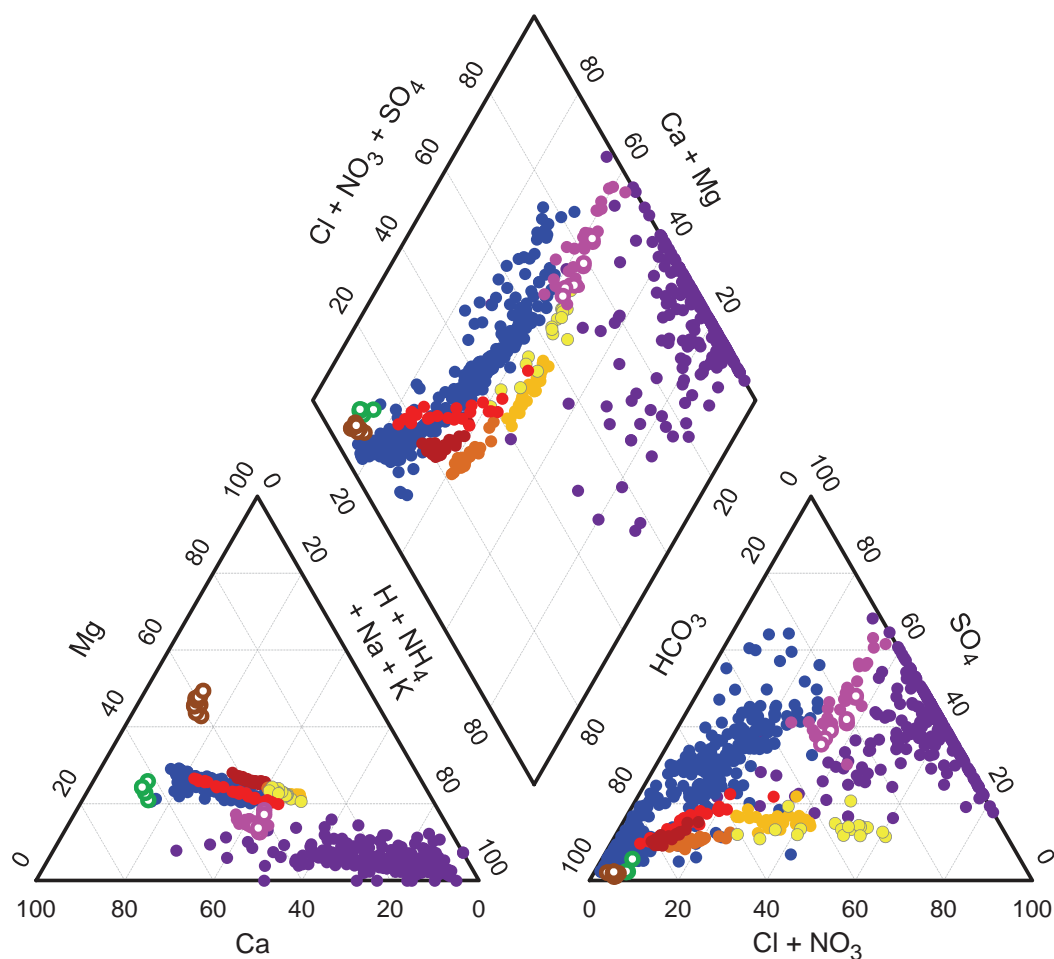


Fig. 2. Piper's diagram of water samples in the Ringelbach catchment: 1990–1997 precipitations (PSMG) and stream (RLIM) (this study); 2001–2006 granite (SPUI, SP2M, SRH, SH, SAH) and sandstone (SRV) springs; 2008–2010 granite (FHUR, FHEI) and sandstone (FHEI2) boreholes [data from Schaffhauser et al., 2014]. All percentages are computed using concentrations expressed in meq.L⁻¹.

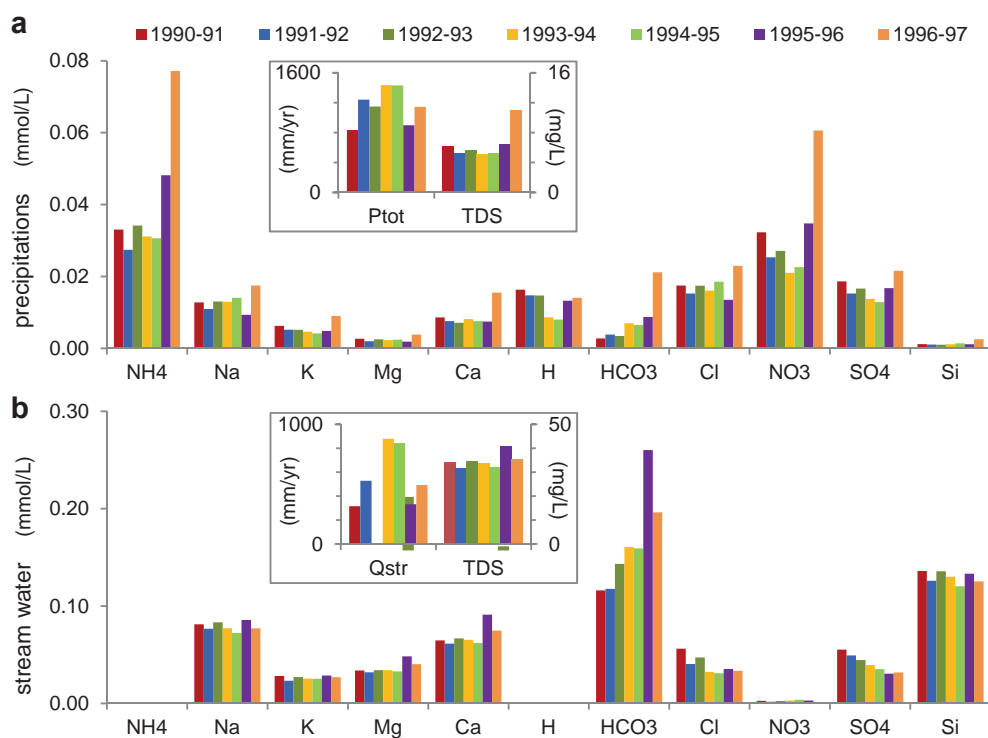


Fig. 3. Variations of annual water fluxes and flux-weighted mean TDS and element concentrations in precipitations (a) and stream waters (b) during the period 1990–97 (7 hydrological years) in the Ringelbach catchment. P_{tot} : total catchment precipitation amount; Q_{str} : discharge at the outlet. Note different scales on ordinate axis.

3.2.2. Trends in annual mean concentrations

The inter-annual concentration variability depends on the elements (Table 1). In precipitations, the variation coefficient is maximal for HCO_3 (83%) and greater than 40% for NH_4 , NO_3 and H_4SiO_4 , but it is lower than 20% for Cl and SO_4 . In stream water, the variability is reduced, from more than 30% for HCO_3 and NO_3 to less than 7% for NH_4 , Na, K and H_4SiO_4 .

In precipitations, a marked change in the variation trend is observed for most elements (Fig. 3). During the first five years 1990–95, annual mean concentration was rather constant for a large set of elements (NH₄, Na, Mg, Ca, Cl), whereas it increased for HCO_3 and decreased for some others (H, NO_3 and SO_4 , and, to a lesser extent, K). As a consequence, acidity decreased (from pH 4.8 to pH 5.1). During the last two years 1995–97, concentration of H, NH_4 , HCO_3 , NO_3 and SO_4 increased. The highest concentration was observed in 1996–97 for all elements except H.

In stream water, similar variation patterns are observed (Fig. 3). During the first period 1990–95, annual mean concentration of Na, K, Mg, Ca and Si remained rather constant, whereas it increased for HCO_3 and decreased for SO_4 (and to a lesser extent, Cl). During the second period 1995–97, concentration increased for Ca, Mg and HCO_3 , but the increase was more obvious in 1995–96. As shown for SO_4 and HCO_3 in Fig. 4, all elements also exhibited intra-annual cycles with significant seasonal variations in concentration.

The regular decreasing trend observed in stream water for sulfate over the whole period is compensated by the increase in alkalinity (Figs. 3 and 4). Moreover, high concentration peaks of SO_4 occurred after the summer dry season between 1990 and 1992, but with a decreasing intensity over time. Such peaks were no longer observed afterwards (except a very limited one in 1995), and were reduced to minor autumn fluctuations. During the first three years, and particularly in 1991, summer stream discharge was much lower than in the following years (Fig. 4).

3.3. Relationships between concentrations and water fluxes

3.3.1. Main correlations and patterns

In precipitations, concentrations of NH_4 , NO_3 and SO_4 , TDS and the electrical conductivity EC exhibit the most significant positive correlations,

as well as Na and Cl (Tab. EA-3a). In stream water, TDS, EC and pH are mainly positively related with Ca, Mg, Na and HCO_3 , whereas H_4SiO_4 is significantly correlated to Na, and K to Cl (Tab. EA-3b). Correlations involving SO_4 are weak or not significant, except a negative one with NPOC. On the opposite, NPOC is positively related with pH, EC, Mg, Ca and HCO_3 , because of increasing concentrations during low flow conditions.

Even if some linear correlation coefficients are low or not significant, concentrations of most elements tend to increase with decreasing bulk precipitation amount and, more obviously, with decreasing instantaneous discharge (Tab. EA-3, Fig. 5). Indeed, these relationships, which are negative except for SO_4 (Fig. 5d), are not linear but of either power- or loglinear-type, as already observed in many catchments (Durum, 1953; Feller and Kimmins, 1979). Despite some rather large scatters in low flow conditions, they are highly significant for major cations (Fig. 5a, b), HCO_3 and H_4SiO_4 (Table 2). These relationships allow estimating the quasi-asymptotic minimal concentrations that would be observed for $Q = 250 \text{ L}\cdot\text{s}^{-1}$, a realistic estimation of the maximal discharge possible in this catchment (see DWEM in Table 2). The abstracted waters of both springs SPUI and SP2M have also strong negative loglinear relationships with discharge for Ca, Mg, Na, K, HCO_3 , H_4SiO_4 and TDS (Table 2).

The concentration-discharge relationships for SO_4 and HCO_3 show marked but different contrasts between the two periods 1990–1992 and 1993–1997. For HCO_3 , both point scatters overlap in high flows, but the 1990–1992 scatter is more spread and less concentrated in low flows, leading to two negative power-type concentration-discharge relationships with different parameters and significance (Fig. 5c). On the opposite, for SO_4 (Fig. 5d), the power-type relationship with discharge is significant for the second period only and is positive, while the 1990–92 point scatter is largely spread for all discharge, with a lot of samples of SO_4 concentration above $0.060 \text{ mmol}\cdot\text{L}^{-1}$.

3.3.2. End-member mixing diagrams

As examples of the highly significant relationships observed between concentrations of major elements in stream water (Tab. EA-3b), Ca, Mg and SO_4 were considered in mixing diagrams (Fig. 6). The Ca vs Mg diagram (Fig. 6a) includes the diluted water end-member DWEM,

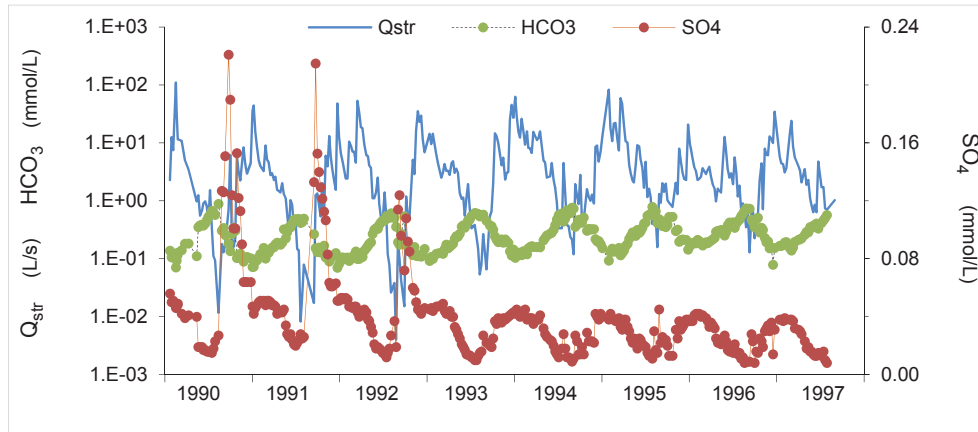


Fig. 4. Evolution of instantaneous discharge and SO_4 and HCO_3 concentrations of stream water samples during the period 1990–1997. Note the log scale for HCO_3 and discharge Q_{str} .

which is assumed to correspond to the estimated possible minimal concentrations (Table 2). It includes also other water types that could potentially influence the stream water composition: (i) open field precipitations (this study), (ii) spring and borehole waters from sandstone (SRV, FHEL2) and granite (others) aquifers (Schaffhauser et al., 2014).

A highly significant positive linear relationship was found between Ca and Mg in stream water (Eq. (1)), which can be considered as passing through the origin:

$$[\text{Ca}] = 2.017[\text{Mg}] - 0.004 \quad R^2 = 0.95; n = 348; p < 0.001 \quad (1)$$

with concentrations [Ca] and [Mg] in mmol.L^{-1} .

As both are strongly negatively related to discharge also, following a discharge dilution pattern, a concentration decrease by a factor 5 was observed from low to high water flow conditions. Each of all springs follows a similar linear trend (see equations on Fig. 6a), but with much shorter variation ranges than for stream. The relatively long pattern of the shallow spring SAH, which is located at mid-slope of the granite block Hurlin capped by sandstone (Fig. 1), overlaps the stream pattern, while the four overlapping springs located along the main fault (SH, SRH, SP2M, SPUI) are slightly enriched in Mg. On the opposite, the sandstone spring SRV has a very short and less concentrated pattern,

and is relatively enriched in Ca. The precipitations are less concentrated, with a much more spread scatter, and therefore a less significant positive linear relationship. All stream and spring linear regression lines can be considered as passing through the origin, indicating a rather constant Ca/Mg ratio over the whole concentration ranges. Similarly, significant linear relationships of quasi proportionality were observed in Mg/Na vs Ca/Na spring graphs also (Schaffhauser et al., 2014).

Concerning SO_4 , two contrasted power-type relationships with Ca (see equations in Fig. 6b) are observed above and below a SO_4 concentration threshold of about $0.060 \text{ mmol.L}^{-1}$ (Fig. 6b). For most samples, which are below this threshold, the relationship is negative whereas for samples above this threshold (mostly the 1990–1992 autumn samples), the relationship is positive. This is related with decreasing concentrations of both SO_4 and Ca with increasing discharge for the formers and the reverse for the latter ones. The maximal autumn concentrations of both elements tend also to decrease from 1990 to 1992 towards the general pattern. Each year, it was in early autumn (September-October) that the highest concentrations were observed, with then a progressive decrease towards the high flow end-member of the general pattern, which was reached again in late autumn

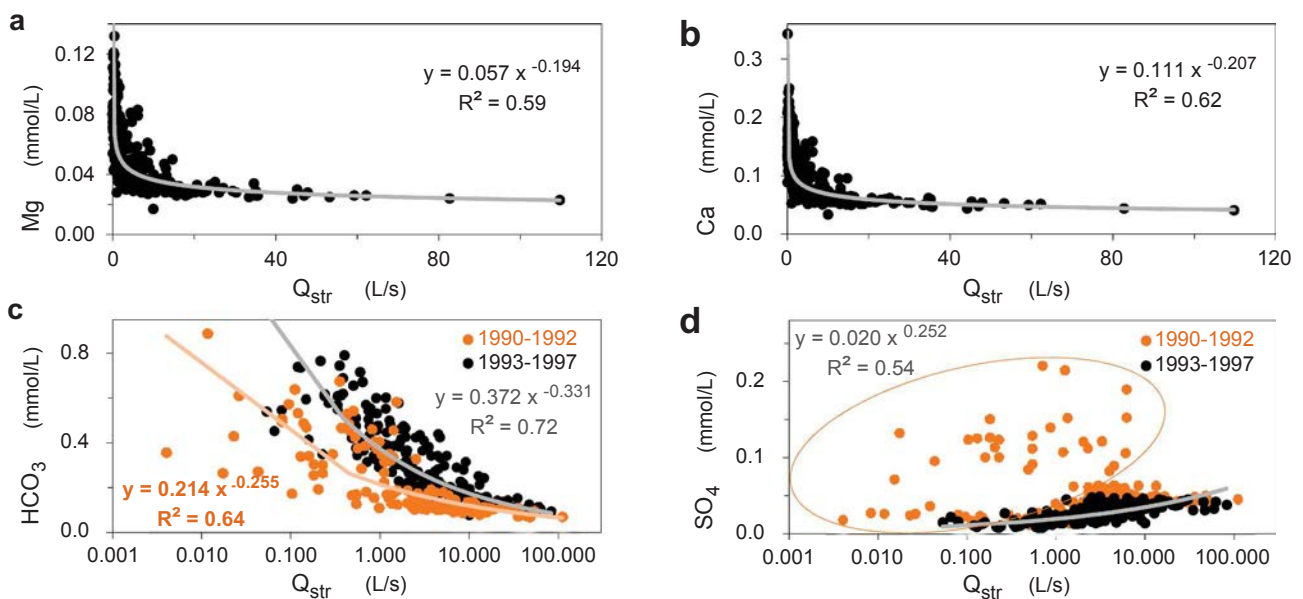


Fig. 5. Relationships between element concentration and instantaneous discharge in stream waters: (a) Mg; (b) Ca; (c) HCO_3 ; (d) SO_4 . Graphs (c), (d): separated regressions for the two periods 1990–1992 and 1993–1997; ellipse: 1990–1992 autumn samples. Note different scales on the axis.

Table 2

Relationships between element concentrations [C] and instantaneous discharge Q in stream and tapped spring waters. Power-type: RLIM stream, 1990–1997 water samples. Loglinear: SPUI and SP2M springs, 2001–2006 water samples (Schaffhauser et al., 2014). R^2 : coefficient of determination; N: number of samples. NH_4 detection limit: $0.001 \text{ mmol.L}^{-1}$. Bold: $R^2 \geq 0.64$; underlined: $0.64 > R^2 \geq 0.36$. DWEM: estimated concentrations of the stream Diluted Water End-Member.

Regression [C] vs Q Q in L.s^{-1}	NH_4	Na	K	Mg	Ca	H mmol.L^{-1}	HCO_3	Cl	NO_3	SO_4	Si	TDS mg.L^{-1}
power-type: $[C] = b Q^a$												
RLIM stream (N = 348)	significance level: $p < 0.05, 0.01, 0.001$ for $R^2 > 0.011, 0.019, 0.031$, respectively											
R^2	–	<u>0.497</u>	0.011	<u>0.592</u>	<u>0.620</u>	<u>0.466</u>	<u>0.543</u>	0.049	–	0.079	0.262	<u>0.648</u>
power a	0.000	–0.082	–0.023	–0.194	–0.207	0.262	–0.266	0.113	–	0.105	–0.035	–0.135
coefficient b	0.001	0.096	0.026	0.057	0.111	$7.E-05$	0.290	0.023	–	0.029	0.138	46.803
DWEM ($Q_{\text{max}} = 250 \text{ L.s}^{-1}$)		0.061	0.023	0.019	0.035		0.067				0.113	22.210
loglinear: $[C] = a \text{Log}_{10}(Q) + b$												
SPUI spring (N = 28)	significance level: $p < 0.05, 0.01, 0.001$ for $R^2 > 0.140, 0.229, 0.346$, respectively											
R^2	–	0.817	0.922	0.930	0.959	0.169	0.946	0.348	0.017	0.017	0.846	0.954
slope a	–	–0.012	–0.009	–0.019	–0.033	$2.E-05$	–0.124	0.003	–0.001	–0.001	–0.015	–11.417
intercept b	0.001	0.104	0.054	0.056	0.081	$6.E-05$	0.314	0.033	0.023	0.026	0.198	52.342
SP2M spring (N = 27)	significance level: $p < 0.05, 0.01, 0.001$ for $R^2 > 0.145, 0.237, 0.357$, respectively											
R^2	–	0.736	0.672	0.783	0.734	0.153	0.775	0.014	0.351	0.285	0.903	0.798
slope a	–	–0.023	–0.010	–0.016	–0.022	$4.E-05$	–0.116	0.001	0.013	–0.003	–0.034	–11.943
intercept b	0.001	0.093	0.043	0.034	0.051	$9.E-05$	0.194	0.028	0.041	0.017	0.178	40.818

(November). Similar relationships with SO_4 are observed for Mg, Na and, to a lesser extent, K (not shown).

Moreover, $\text{Ca} + \text{Mg}$ is very significantly related to HCO_3 but even more to $\text{HCO}_3 + \text{SO}_4$ in stream water over the whole period:

$$[\text{Ca} + \text{Mg}] = 0.772[\text{HCO}_3] + 0.097 \quad R^2 = 0.85; n = 348; p < 0.0001 \quad (2)$$

$$[\text{Ca} + \text{Mg}] = 0.933[\text{HCO}_3 + \text{SO}_4] + 0.021 \quad R^2 = 0.98; n = 348; p < 0.0001 \quad (3)$$

with concentrations expressed in meq.L^{-1} .

3.4. Element fluxes and balances

3.4.1. Annual inputs and outputs

Annual fluxes of water and major elements as well as inter-annual means and standard deviations in precipitation, stream and abstracted

spring waters, are presented in Table 3.

Precipitation inputs are within the range of open field element fluxes measured over the same period in other nearby forested mountainous catchments that are also under the pressure of long range atmospheric pollution (Black Forest: Feger et al., 1990; Vosges: Probst et al., 1992, 1995a, 1995c). Except in 1996–97, annual fluxes of K, Mg, Ca, HCO_3 , SO_4 , H_4SiO_4 and TDS follow the variations of annual precipitation amounts, with particularly low fluxes in the dry 1995–96 year. Na and Cl fluxes are linearly related to increasing water fluxes during the first four years 1990–94. The total flux of nitrogen compounds (NH_4 and NO_3) increased over the period, with no important reduction in the dry 1995–96 year. On the opposite, very high fluxes were observed in 1996–97, while the precipitation amount was average. They exceeded the mean fluxes over the other years by a factor of 1.4–2.0 for most elements, and even by 2.2 for H_4SiO_4 , 2.3 for NO_3 and NH_4 , and 3.8 for HCO_3 .

Stream outputs of all elements are very significantly related with

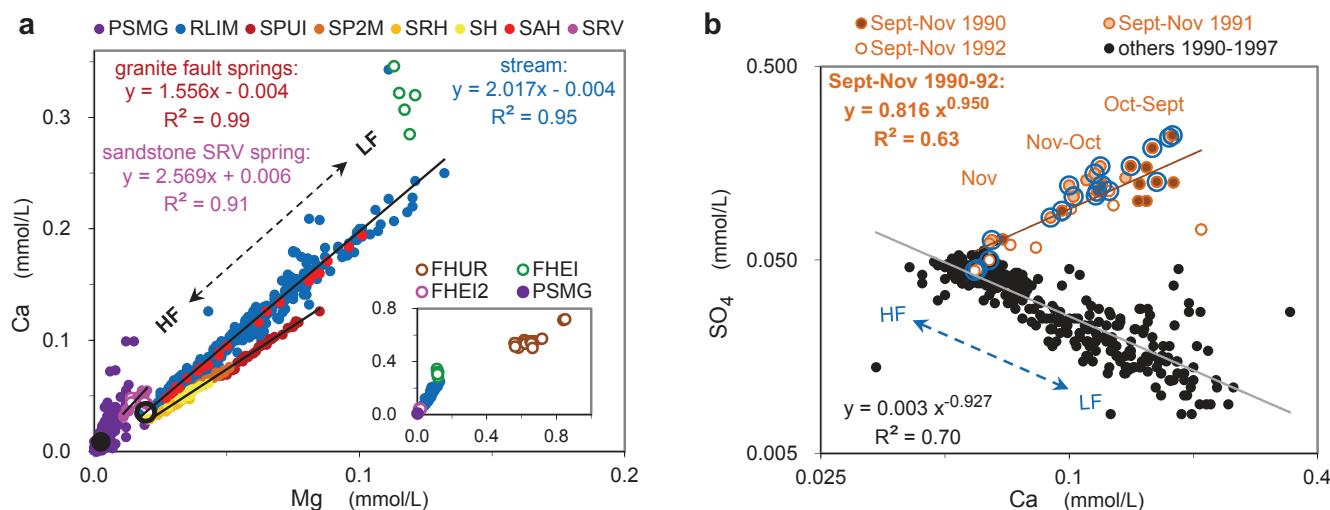


Fig. 6. Relationships between element concentrations in stream waters during the period 1990–1997: (a) Ca vs Mg, with also precipitations; (b) SO_4 vs Ca, with separate regressions for 1990–1992 autumn samples and all others 1990–1997. HF, LF: high, low flow conditions. In (a): solid black circle: mean values in precipitations P_{tot} ; empty black circle: estimated diluted water end-member DWEM in stream water; graph with also 2001–2006 spring and 2008–10 borehole samples (from Schaffhauser et al., 2014). In (b): 1990–1992 autumn samples (brown symbols); large empty blue circle: storm event; others: recession period; note log axes. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 3

Annual input and output fluxes and balances of water and major elements for the 7 hydrological years 1990–97 in the Ringelbach catchment. P_{tot} : catchment precipitation input; Q_{str} : stream water output; Q_{spr} : abstracted spring water output; Q_{tot} : total surface water output. STD: standard deviation. Note that the annual water balance $P_{\text{tot}} - Q_{\text{tot}}$ can be considered as an estimation of annual evapotranspiration.

Hydrol. year (Sept.-August)	H ₂ O mm.yr ⁻¹	NH ₄	Na	K	Mg	Ca	H	HCO ₃ kg.ha ⁻¹ .yr ⁻¹	Cl	NO ₃	SO ₄	H ₄ SiO ₄	TDS
Precipitations input													
1990–91	834.6	4.978	2.453	2.041	0.543	2.877	0.138	1.407	5.171	16.717	14.952	0.954	52.229
1991–92	1240.1	6.134	3.128	2.531	0.606	3.784	0.184	2.896	6.712	19.471	18.190	1.255	64.892
1992–93	1148.1	7.078	3.451	2.309	0.706	3.272	0.170	2.415	7.110	19.301	18.334	1.148	65.293
1993–94	1436.5	8.069	4.290	2.603	0.801	4.685	0.125	6.150	8.192	18.744	19.025	1.593	74.276
1994–95	1432.8	7.914	4.632	2.343	0.851	4.354	0.116	5.715	9.433	20.072	17.750	1.915	75.097
1995–96	897.9	7.797	1.924	1.703	0.411	2.683	0.120	4.787	4.309	19.356	14.457	1.001	58.550
1996–97	1145.1	15.941	4.601	4.029	1.073	7.132	0.162	14.771	9.309	43.024	23.748	2.840	126.630
mean annual	1162.2	8.273	3.497	2.509	0.713	4.112	0.145	5.449	7.177	22.383	18.065	1.530	73.852
STD	235.3	3.560	1.067	0.736	0.219	1.521	0.027	4.471	1.964	9.164	3.058	0.671	24.639
Stream output													
1990–91	315.1	0.063	5.889	3.467	2.593	8.163	0.000	22.315	6.272	0.512	16.710	41.205	107.190
1991–92	528.5	0.097	9.315	4.813	4.099	13.014	0.001	37.936	7.575	0.582	24.980	64.000	166.413
1992–93	447.5	0.084	8.562	4.746	3.713	11.986	0.001	39.103	7.495	0.681	19.123	58.378	153.872
1993–94	880.3	0.168	15.614	8.802	7.312	23.080	0.001	86.219	10.146	1.606	33.278	110.070	296.298
1994–95	843.7	0.152	14.062	8.385	6.738	20.972	0.001	81.972	9.273	1.947	28.519	97.533	269.554
1995–96	331.6	0.068	6.524	3.708	3.891	12.123	0.000	52.631	4.161	0.628	9.729	42.466	135.930
1996–97	492.2	0.091	8.723	5.193	4.826	14.754	0.001	58.906	5.848	0.306	15.067	59.279	172.993
mean annual	548.4	0.103	9.813	5.588	4.739	14.870	0.001	54.154	7.253	0.895	21.058	67.562	186.036
STD	228.2	0.041	3.672	2.147	1.703	5.306	0.000	23.559	2.046	0.622	8.239	26.443	70.059
Springs output													
1990–91	29.6	0.005	0.738	0.654	0.434	1.060	0.000	6.288	0.329	0.445	0.714	5.787	16.455
1991–92	67.0	0.012	1.624	1.383	0.857	2.085	0.000	12.477	0.730	1.138	1.480	12.786	34.572
1992–93	61.9	0.011	1.505	1.280	0.797	1.946	0.000	11.645	0.668	1.067	1.354	11.826	32.098
1993–94	79.3	0.014	1.910	1.628	1.004	2.441	0.000	14.591	0.868	1.346	1.754	15.064	40.621
1994–95	71.3	0.013	1.720	1.464	0.903	2.198	0.000	13.147	0.778	1.213	1.571	13.557	36.565
1995–96	49.0	0.009	1.217	1.035	0.656	1.607	0.000	9.666	0.520	0.838	1.069	9.504	26.120
1996–97	50.5	0.009	1.252	1.071	0.680	1.663	0.000	9.980	0.544	0.842	1.124	9.798	26.961
mean annual	58.4	0.011	1.424	1.216	0.762	1.857	0.000	11.114	0.634	0.984	1.295	11.189	30.485
STD	16.7	0.003	0.390	0.325	0.189	0.457	0.000	2.740	0.182	0.302	0.352	3.096	8.034
Total output													
1990–91	344.7	0.068	6.627	4.121	3.027	9.223	0.001	28.603	6.602	0.957	17.424	46.992	123.645
1991–92	595.6	0.110	10.939	6.196	4.956	15.099	0.001	50.413	8.306	1.720	26.460	76.786	200.985
1992–93	509.4	0.095	10.067	6.026	4.510	13.932	0.001	50.748	8.163	1.748	20.477	70.204	185.970
1993–94	959.6	0.182	17.525	10.430	8.316	25.522	0.001	100.811	11.013	2.952	35.032	125.134	336.918
1994–95	915.0	0.165	15.782	9.850	7.641	23.170	0.001	95.119	10.050	3.160	30.091	111.090	306.119
1995–96	380.5	0.077	7.741	4.743	4.547	13.731	0.000	62.297	4.681	1.466	10.798	51.971	162.050
1996–97	542.7	0.100	9.974	6.264	5.506	16.416	0.001	68.886	6.391	1.148	16.191	69.077	199.955
mean annual	606.8	0.114	11.237	6.804	5.500	16.727	0.001	65.268	7.887	1.879	22.353	78.750	216.520
STD	242.6	0.043	4.015	2.420	1.863	5.697	0.000	25.665	2.194	0.855	8.532	29.136	76.991
Balance (input – output)													
1990–91	489.9	4.910	-4.174	-2.080	-2.484	-6.346	0.137	-27.196	-1.431	15.760	-2.472	-46.039	-71.416
1991–92	644.6	6.024	-7.811	-3.665	-4.350	-11.315	0.183	-47.517	-1.594	17.750	-8.269	-75.530	-136.093
1992–93	638.8	6.982	-6.617	-3.717	-3.804	-10.660	0.170	-48.333	-1.053	17.553	-2.143	-69.056	-120.677
1993–94	477.0	7.886	-13.235	-7.827	-7.516	-20.837	0.124	-94.661	-2.821	15.792	-16.007	-123.540	-262.642
1994–95	517.8	7.749	-11.150	-7.507	-6.790	-18.815	0.115	-89.403	-0.617	16.913	-12.341	-109.175	-231.022
1995–96	517.3	7.720	-5.816	-3.040	-4.135	-11.048	0.120	-57.509	-0.372	17.890	3.659	-50.969	-103.501
1996–97	602.4	15.841	-5.373	-2.235	-4.433	-9.284	0.162	-54.115	2.918	41.876	7.557	-66.237	-73.325
mean annual	555.4	8.159	-7.740	-4.296	-4.788	-12.615	0.144	-59.819	-0.710	20.505	-4.288	-77.221	-142.668
STD	71.2	3.558	3.294	2.389	1.754	5.235	0.027	24.064	1.787	9.465	8.460	28.920	75.439

annual discharge. Annual exportations are the highest during the wettest years 1993–94 and 1994–95, and the lowest during the driest years 1990–91 and 1995–96. H, NO₃ and NH₄ outputs only are always very low and not directly related with annual discharge. Output fluxes are in the lower range of fluxes usually exported in similar granitic mountainous catchments (as example: Strengbach and Mont-Lozère: [Probst et al., 1995a, 1995c](#)). H₄SiO₄ and HCO₃ are the most exported compounds, representing 36% and 29% of the total exported TDS, respectively.

The abstracted spring water output amounts to 11% of the stream discharge in mean. When compared to stream water outputs, it appears as relatively depleted in SO₄ but enriched in Na, K, Mg, HCO₃, H₄SiO₄ and TDS, and even strongly in NO₃. The relative inter-annual flux variability of output fluxes is much lower in springs than in the stream

for all elements except Cl, for which they are similar.

The resulting total output is therefore slightly different from that of stream water, but falls within the range of fluxes measured in other silicate catchments in the Vosges and the Massif Central ([Probst et al., 1995c](#)). Annual total exportation flux of H₄SiO₄ ($78.75 \pm 29 \text{ kg.ha}^{-1}.\text{yr}^{-1}$ in mean) is significantly related with the annual total water output flux:

$$F_{\text{H}_4\text{SiO}_4} = 0.12 Q_{\text{tot}} + 6.24 \quad R^2 = 0.99; \quad n = 7; \quad p < 0.001 \quad (4)$$

with $F_{\text{H}_4\text{SiO}_4}$ in $\text{kg.ha}^{-1}.\text{yr}^{-1}$ and Q_{tot} in $\text{mmH}_2\text{O.yr}^{-1}$.

Annual mass balance indicates a net exportation of most elements, but a net annual storage of N compounds (NH₄ and NO₃) over the period. Most net annual fluxes are well related with the annual total water output flux. Between the driest and wettest years (1990–91 and 1993–94, respectively, with a precipitation ratio of 1.7), the net

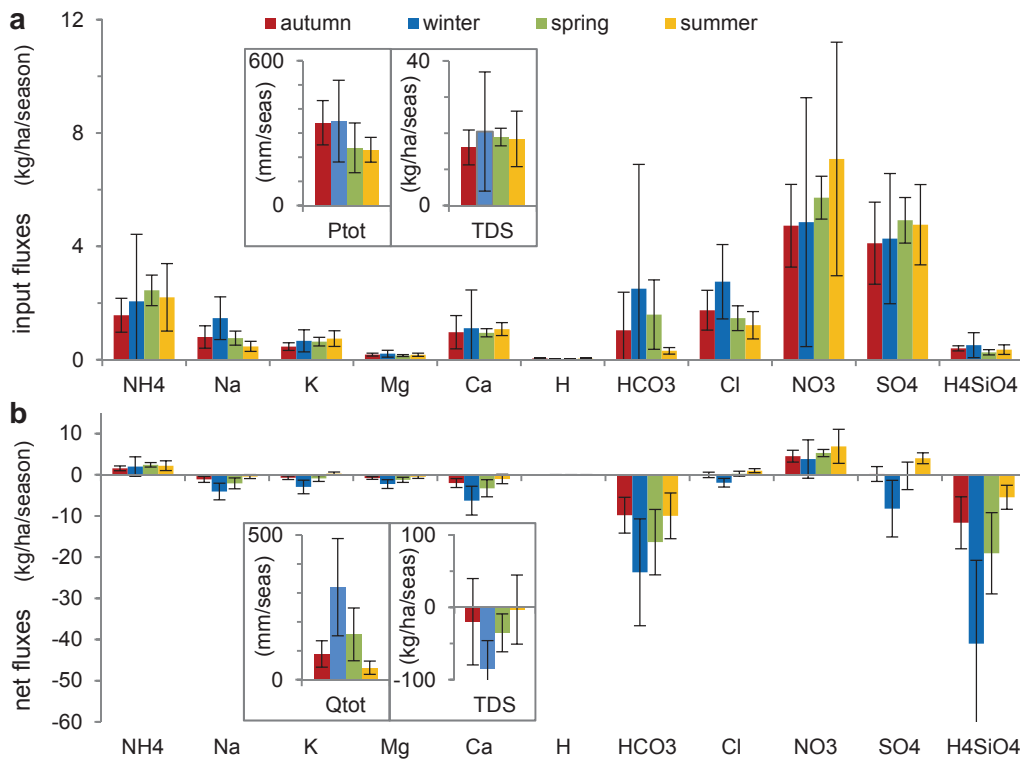


Fig. 7. Inter-annual means and standard deviations of seasonal fluxes of water and major elements over the 1990–97 period in the Ringelbach catchment: (a) precipitation inputs; (b) mass balance (input–output). P_{tot} : total catchment precipitation amount; Q_{tot} : total water output. Variation bar: mean \pm 1 standard deviation.

exportation is increased by a factor of 2.7 to 3.7 for Na, K, Ca, Mg, HCO_3 and H_4SiO_4 , and even 6.5 for SO_4 . Nitrogen storage is very high in 1996–97 and minimal in 1990–91. Chloride budget is well-balanced. Sulfate is exported on average, but its net output flux is not related with the total water output flux. Sulfate net exportation was maximum in 1993–94 and 1994–95, whereas a net storage occurred in 1995–96 and 1996–97. Bicarbonate and H_4SiO_4 present by far the highest net exportation fluxes (42% and 54% of the net exported TDS, respectively), since their inputs by precipitation are very low or negligible with respect to outputs, except in 1996–97 for HCO_3 .

3.4.2. Seasonal inputs and outputs

Mean seasonal fluxes and balances of water and elements and their variability are given in Table EA-4 (as online Supplementary data) and Fig. 7.

In precipitations, mean seasonal element fluxes vary according to the season (Fig. 7a). Fluxes of some elements, such as Na, Cl and HCO_3 , are related with seasonal precipitation amounts. For other ions, particularly SO_4 , NO_3 and NH_4 , input fluxes are the most important in spring and summer, when precipitations amount is the lowest. Standard deviations are very large, particularly in winter for most elements and also in summer for NO_3 .

Seasonal mass balances (Fig. 7b) indicate a net exportation for most elements whatever the season. Net fluxes are related with total water output for Na, K, Mg, Ca, HCO_3 and H_4SiO_4 , as already observed on the annual basis (Table 3). Net exportations are maximal in winter and spring, and minimal in summer. This is particularly true for H_4SiO_4 with a flux even two times higher in winter than in spring. Chloride budget is well-balanced, with a small exportation in winter and a small storage in summer, but these mean values are lower than standard deviations. On the opposite, nitrogen compounds (NH_4 , NO_3) are stored whatever the season, with a trend of highest storage in summer and, to a lesser extent, in spring. Sulfate mass balance exhibits a contrasted pattern, with a well-balanced budget in autumn and spring, a significant loss in winter (high flow conditions) and a storage in summer (low flow conditions).

4. Discussion

4.1. Origin of the elements and role of hydrology on chemical fluxes

The influence of long range atmospheric pollution on the composition of Ringelbach precipitations is attested by their slight acidity and the presence of some strongly related dominant compounds such as NH_4 , SO_4 and NO_3 . This is consistent with observations made during the study period in most remote sites surveyed in northern France and Europe (Probst et al., 1990a, 1995c; Rogora et al., 2006; Sicard et al., 2007; Smith et al., 2011). The persistent and correlated concentration trends observed for Ca and Mg, and for Na and Cl indicate a common origin, which is mainly continental for the formers and marine for the latter (Probst et al., 1990a, 1995b; Dambrine et al., 1995; Pascaud et al., 2016). Indeed, the continental origin of part of Ca is indicated by its positive relationship with NO_3 and SO_4 due to the influence of Ca-enriched pollution particles (Pascaud et al., 2016). Seasonal fluxes also confirm the marine origin of Na and Cl (mainly in winter) and the continental/anthropogenic origin of N and S compounds (mainly in spring and summer).

The annual input fluxes for Na, K, Ca, Cl and SO_4 are as a whole related with the precipitation amount, with values that are high for wet years (1994–95) and low for dry years (1990–91 and 1995–96), even though the highest input fluxes are observed in 1996–97 with an average precipitation amount. Particularly, for anthropogenic ions such as NH_4 and NO_3 , the mean concentrations are almost double the whole period averages. On the opposite, SO_4 did not evolve in the same proportion contrary to what is observed in previous years. The very rainy period of the second half of February 1997 ($P = 191$ mm) alone is responsible for these particular year increases. It represents 16% of the annual precipitations, but more than 25% of the annual fluxes for all elements (except H), and even 42% for NH_4 and 59% for HCO_3 . High natural inputs of Ca and HCO_3 derived from carbonate particles originating Sahara dust (Dambrine et al., 1995; Probst et al., 1995c), usually occurring in February–March, may contribute to significant annual fluxes enrichment. Indeed, such events were identified in 20–23/12/1996 and 19–23/01/1997. However, during the period of the major

specific February 1997 event, no Saharan dust event was clearly detected, the air masses originating from the west. A local/regional anthropogenic input could be evoked since it was also detected in the nearby Strengbach observatory catchment (Pierret et al., 2018, in press).

The decreasing trend observed in precipitation concentrations for acidic compounds over the study period has mainly to be related with the decreasing trend in SO₂ emission observed in the industrial countries of the northern hemisphere (Smith et al., 2011; Rice et al., 2014; Pascaud et al., 2016). As a consequence, annual H concentrations decreased by about 25% over the period, mainly because of H reduction in both winter and spring precipitations. The decrease is of 35%, when not considering the very dry year 1990–91 and the particular year 1996–97. The acidity decrease at the beginning of the period is explained by the decrease in both sulfur and oxidized nitrogen, while its increase back to the initial value in the last two years might be mainly related with some increase in nitrogen pollution (Fig. 3). However, trends for nutrient nitrogen are less obvious to identify because of multiple N sources and N transformation processes in the atmosphere, as observed in survey networks (Pascaud et al., 2016). This evolution is consistent with the general pattern observed in France and Europe, showing a switch from sulfur to nitrogen as dominant pollutant (Coddeville et al., 2016; Marx et al., 2017).

The mean annual open field proton input flux (0.144 kmol·ha⁻¹·yr⁻¹) is much lower than that registered in the previous ten or twenty years for instance in forested sites in the Vosges (1.17 kmol·ha⁻¹·yr⁻¹; Probst et al., 1995c) and the Czech Republic (more than 5 kmol·ha⁻¹·yr⁻¹; Pačes, 1985; Dambrine et al., 1993), if taking into account dry deposition. The incoming acidity (mean precipitation pH = 4.9) is buffered within the critical zone by soil cations exchange and weathering processes (mean stream water pH = 6.8), as attested by the strong relationships observed between silica, alkalinity and base cations, despite relatively low mean total weathering fluxes (803 kmol_{Si}·ha⁻¹·yr⁻¹). This results in calcium-bicarbonate dominance in stream and abstracted spring waters (Probst et al., 1987). Strong links between Si and Na and their corresponding budgets demonstrate the dominant weathering of plagioclases (Drever, 1982). Nitrates originating from deposition by precipitations are not exported. They are consumed by vegetation or other biological organisms and transformed by biogeochemical processes such as denitrification due to microbial activity within soils. This is especially the case in the hydromorphic water-saturated valley bottom, which acts as a major specific biogeochemical reactor (Cirimo and McDonnell, 1997) within the critical zone. This is particularly true in summer, as evidenced by the higher N summer storage (Fig. 7). In view of the uncertainty in the calculated fluxes, the equilibrated Cl mass balance is consistent with a dominant marine origin.

As shown on the Ca vs Mg mixing diagram (Fig. 6a), base cations in stream water cannot be explained by a simple conservative mixing between two clearly identified water types of constant chemistry, particularly regarding the considered abstracted springs which exhibit a similar dilution pattern as stream waters. The position of the well-defined linear stream water pattern between deep waters from granite (FHUR and FHEI) and sandstone (FHEI2, consistent with the SRV spring pattern), indicates the influence of some mixing of these components. Indeed, in very low flow conditions, the regression lines of stream and granitic springs do not pass through the two borehole clusters, far from each other. Especially for the very little transmissive FHUR, borehole waters, which are much more concentrated than spring waters and whose chemistry results from very long interaction times with bedrock (Lucas et al., 2017), appear to be about disconnected from the more superficial and mobile waters supplying springs. Rather than being limited by a not yet identified “concentrated end-member”, the higher spring concentrations probably depend mainly on actual residence times under the constraint of following the regression line expressing local water-rock interactions. Indeed, as soon as the groundwater

residence time increases, and as long as the bedrock is not yet depleted in weatherable minerals, weathering processes become more efficient (Drever, 1982). This is consistent with spring waters that are more concentrated (TDS, base cations, HCO₃) downslope (SPUI) than mid- and upslope (SP2M, SRH and SH) (Table 1) (Schaffhauser et al., 2014). This also explains the contrast in water chemistry between these granite springs and the SRV spring draining sandstone, which has a buffering capacity of weathering lower than granite (as shown in other places in the Vosges: Probst et al., 1999). There is also some differentiation among the granitic springs. On one hand, the waters of the midslope SAH spring draining a granite block covered by sandstone overlap stream waters, thus suggesting a same origin and dilution pattern. On the other hand, the four fault springs (SH, SRH, SP2M, SPUI) define a unique linear regression line also passing through the origin, but a little more tilted in direction of the FHUR cluster. This suggests similar water-rock interactions along the granitic slope, but with weathering intensity increasing downslope (Schaffhauser et al., 2014).

Nevertheless, the whole bundle of regression lines (stream and spring waters) converging to the origin through most precipitations samples and their flux-weighted mean suggest the flux-weighted mean precipitation chemistry to be their possible common “diluted water-end-member”. In reality, this point would never be reached, as the precipitation chemistry changes as soon as water reaches the soil. Therefore, the minimal possible concentrations derived from [C] vs Q relationships (Table 2) provide practically a good estimate of the stream DWEM. It may correspond to precipitations water having had a very little interaction time with soils before reaching the stream, because of rapid surface or subsurface flows and/or short pathways. Indeed, it is very close to, and in between, the most diluted samples of both the upslope granite SH and SRH springs and the sandstone SRV spring.

Water-saturated areas that are directly connected to the stream in the valley bottom are the only permanent interface between atmospheric, surface and subsurface waters (Ambroise, 2004). Consequently, they may have a huge influence on hydrogeochemical transfers to the stream because of their highly reactive responses to both local precipitations and evapotranspiration (Ambroise, 2016). Precipitations on them have an about proportional diluting effect on stream water, as they rapidly provide to the stream outlet water fluxes that are little concentrated for some elements because of very short interaction time with the saturated soil. Nevertheless, during hydrological events, they were also shown to strongly influence the relative contribution of some key concentrated elements, like carbon, as demonstrated in the nearby Strengbach catchment (Idir et al., 1999; Ladouche et al., 2001). The drainage water of these areas in the Ringelbach was not sampled during high flow, but we can suppose that its composition is not so far from the DWEM end-member, and may contribute actively to the major elements dilution in stream waters.

Inversely, evapotranspiration from these areas may generate marked inverse daily oscillations of stream discharge and concentrations in late spring and summer (Fritz et al., 1984). Because the concentrations relationships in stream water pass through the origin (Fig. 6a), this proportional concentrating effect of evapotranspiration may help explain that stream concentrations for low discharges, mainly observed in the warm season, reach much higher values than in the sampled granitic springs. It may also help explain the rather large dispersion observed on [C] vs Q graphs in mid and low flows, because of sampling during recession periods that are more or less influenced by evapotranspiration (Fig. 5). As a result, despite their small variable extent, these areas may control variations in stream water discharge and chemistry during storm events and large parts of the warm season. However, we cannot exclude as another concentrated end-member a not yet sampled contribution of some granitic deep waters to sustain discharge of the stream and SAH spring during very low water conditions.

The intensity of the catchment drainage plays a major role in the variations of the output fluxes (Table 3). The highest annual concentrations in stream waters for most ions are observed in 1995–96

with the lowest annual discharge (Fig. 3). For all elements, drainage variations also govern the inter-annual variations of seasonal exportations by stream and abstracted spring waters (Fig. 7). As classically found in most surveyed streams, the intra-annual cycles observed for all elements are mainly due to changing dilution-concentration processes in relation with variations in hydrological fluxes (Feller and Kimmins, 1979). For elements originating from weathering like Na, Mg, Ca and HCO₃, the most significant relationships with stream discharge are observed during very rainy events, when dilution processes by rain-water contribution is the most obvious. Strong relationships with discharge are also observed for Ca, Mg, NO₃, K, HCO₃, H₄SiO₄ and TDS for the two tapped springs (SPUI and SP2M), indicating a strong buffering influence of silicate weathering processes.

Like for most other elements, the drainage intensity influences sulfur leaching, as indicated by its major exportation during the wet 1993–94 and 1994–95 years. The major control of SO₄ output flux by total discharge is indicated by the significant linear relationship for the four last autumns 1993–1996 (Eq. (5)):

$$F_{\text{SO}_4}^{\text{autumn}} = 0.039 Q_{\text{tot}} - 0.830 \quad R^2 = 0.995; \quad n = 4; \quad p < 0.01 \quad (5)$$

with $F_{\text{SO}_4}^{\text{autumn}}$ in kg.ha⁻¹.season⁻¹ and Q_{tot} in mm_{H₂O}.season⁻¹.

However, the singular seasonal pattern of sulfate with a net release in winter and a net storage during summer cannot be related with the well distributed precipitation inputs over the year (Fig. 7). Rice and Bricker (1995) also noted that the stream water concentrations of atmospherically derived components, particularly sulfate, increased in winter when the water table was above the regolith-bedrock interface and stream discharge consisted primarily of shallow groundwater from the regolith. Other processes should have influenced sulfates during the three first autumns (1990–1992) since SO₄ output fluxes were much higher (by a decreasing factor of 3.4, 2.6 and 1.35, respectively) than those predicted by the above relationship (see § 4.2). The progressive lowering of near-surface water tables in summer allows reduced sulfur stored in peatland or hydromorphic soils to be oxidized due to addition of atmospheric oxygen or oxygen-saturated water (Clark et al., 2012). This could have occurred in the Ringelbach valley bottom during the very dry 1990–1992 summers resulting in a dramatic shrinking of water-saturated areas.

4.2. Disturbance and resilience to acidification: weathering influence

The very significant relationship between Ca + Mg and HCO₃ concentrations (Eq. (2)) in output fluxes over the whole study period indicates that Ca + Mg outputs are mainly controlled by weathering processes. However, this relationship is still improved when considering HCO₃ + SO₄ (Eq. (3)), instead of HCO₃ alone, particularly during the beginning of the period (1990–1992, *i.e.* the brown points isolated in Fig. 6d). This testifies that the acidification processes led to soil base cation depletion. Calcium and Mg were released particularly during autumn in association with high SO₄ exportation (Fig. 6), following summer period of intense mineralization processes in soils. The acidification led to a loss of alkalinity compensated by strong acid anions (*i.e.* mainly sulfates), as also demonstrated for a set of small streams draining coniferous forests in the Vosges mountains during that period (Probst et al., 1995d). The sulfates produced and/or stored in the valley bottom were then easily leached by the first summer/autumn storm events, when connected water-saturated areas are the main, if not the only, area contributing to storm flow. This might explain the highly concentrated SO₄ release in summer/autumn, by desorption of sulfates accumulated in soils during the last decades, when sulfur deposition was much higher (CITEPA, 2017). Such a mechanism was also described in other granitic catchments in the Vosges and other critical zones impacted by sulfur pollution (Probst et al., 1992; Marx et al., 2017), as well as in cambisols (similar to those found in the Ringelbach catchment) at sites of reduced acid deposition (Alewell and Matzner, 1993).

Wetland and soil waters provide environmental memories of inherited pollutant sulfates (Marx et al., 2017). Indeed, since the Ringelbach bedrock does not contain any sulfur, the switch of sulfur mass balance from negative to positive values between the first and last years, argues for the decreasing desorption of sulfates provided by precipitations and accumulated in soils (Rice et al., 2014). As stated above, the dry conditions observed in autumn might have influenced the sulfur release by the first autumnal floods (Aherne et al., 2006), but they are not the only influencing factor since the driest autumn 1992 was not followed by a major sulfur flood release. Indeed, with respect to the autumn SO₄ fluxes estimated using the 1993–96 regression (Eq. (5)), the observed relative excess ratio decreased from 3.4 to 1.35 between 1990 and 1992. This decreasing autumnal S release until 1992 as well as the absence of SO₄ autumnal peaks afterwards, indicate that sulfur storage/adsorption in soils became no more dominant from 1993 on (Fig. 4). This trend suggests that the sulfate amount in soils has significantly decreased following the locally measured decrease in sulfate and proton deposition, in accordance with the global trend in France but also in Europe and North America (Pascaud et al., 2016; Smith et al., 2011; Rice et al., 2014). It can be interpreted as a testimony of soil resilience against sulfate excess, as observed in other sites highly impacted by acid rain (Dambrine et al., 1995; Probst et al., 1995c; Marx et al., 2017). Indeed, this release of excess sulfate from soils in 1990–93 occurred earlier than in some other European sites (Vuorenmaa et al., 2017) and led to autumnal stream water concentrations ranging between 0.221 mmol.L⁻¹ during the first flood events and 0.045 mmol.L⁻¹, which corresponds to the highest concentrations of the “normal” seasonal cycles observed in the latest years 1992–1997 (Fig. 6b).

The decreasing proton and sulfate inputs by precipitations and the lower SO₄ desorption decreased the depletion of Ca and Mg from soils after 1992. From 1993 on, the Ca release pattern is consistent with a resilient process mainly through weathering of granitic minerals, and is then related to simple dilution by precipitations (Table 3).

To evaluate the capacity of the critical zone to buffer the acidity input, the annual so-called acidification rate AR [eq.eq⁻¹] was calculated using HCO₃ and SO₄ fluxes in total output water (Table 3):

$$AR = (F_{\text{HCO}_3} + F_{\text{SO}_4}) / F_{\text{HCO}_3} \quad (6)$$

with fluxes F_{HCO_3} and F_{SO_4} in eq.ha⁻¹.yr⁻¹. The higher the AR value above one, the lower the buffering capacity of the critical zone. The acidification rate decreased very significantly and loglinearly over the study period from 1.95 to 1.23 (Fig. 8a), indicating the progressive acidification recovery of the Ringelbach critical zone, tending to 1.0 when sulfate pool in soils will be almost depleted. This can be related to the decreasing trend of sulfate acidic precipitation inputs in the catchment (Fig. 3) and the efficient response of the soil/bedrock in terms of weathering processes *s.l.* (*i.e.* including exchange processes) (Bricker et al., 2003; Pačes, 1985). It is worth noting that the 1995–96 AR value is slightly lower than expected from the fitted loglinear curve (Fig. 8a). This indicates a higher buffering response for this dry year, because of both an even lower acid input by precipitations (Table 3) and a longer water residence time enhancing weathering reactions (Fig. 3).

In addition, two other ratios computed from total output data were compared (Fig. 8b): (i) the Si/ΣBC ratio between the annual molar Si flux and the sum ΣBC of the equivalent fluxes of base cations (Ca, Mg, Na, K), which is an indicator of the intensity of the weathering processes *s.l.*, and (ii) the SO₄/HCO₃ ratio of annual molar fluxes, which is an indicator of the acidification status of the critical zone. During the first three years 1990–1993 with acidification conditions (SO₄/HCO₃ values exceeding 0.25), the Si/ΣBC ratio remains almost constant at a maximum value of about 0.44, independently of the varying acidification and drainage intensity (Fig. 8b). This so-called “weathering plateau” at 0.44 indicates that both weathering and soil exchange processes are proportionally enhanced (joined increases of Si and base

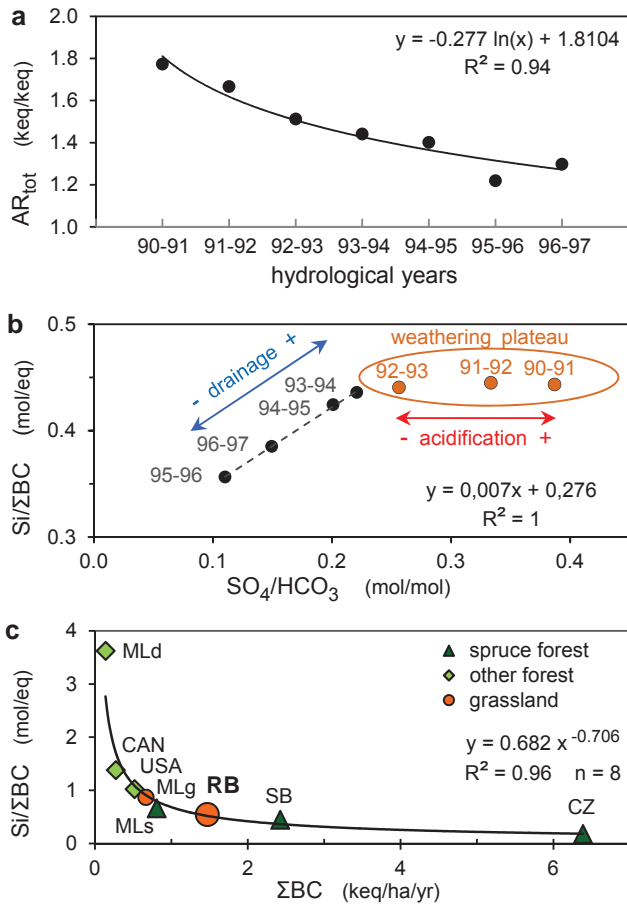


Fig. 8. Acidification recovery and weathering conditions during the period 1990–97 in the Ringelbach catchment: (a) annual trend for the acidification rate AR_{tot} in total output water; (b) relationship between annual flux ratios $Si/\Sigma BC$ (with ΣBC = sum of base cations equivalent fluxes) and SO_4/HCO_3 in total output water; (c) relationship between mean annual flux ratios $Si/\Sigma BC$ and ΣBC in total exportation fluxes for a set of small research catchments on crystalline bedrock with different vegetation cover submitted to a large range of pollution pressure: Vosges/F: RB (Ringelbach, grassland: this study), SB (Strengbach, spruce forest: Probst et al., 1995b); Massif Central/F: Mont-Lozère catchments (Durand et al., 1992): MLs (spruce forest), MLg (grassland), MLd (beech forest); CZ (Vysoca Pec/Black Triangle/CZ, damaged spruce forest: Pačes, 1985); USA (Cone Pond/NH, spruce-fir forest: Hyman et al., 1998); CAN (Edelweiss Creek/BC, mixed forest: Hudson and Golding, 1997).

cations fluxes regarding proton inputs). Indeed, recent experiments have demonstrated that non-crystalline soil phases can provide significant Ca and Mg amounts and compensate soil base cations depletion (Van der Heijden et al., 2017). In granitic bedrocks, some trace minerals like apatite can also be dissolved in more acid conditions and contribute to higher Ca release without silica (Probst et al., 2000). In contrast, during the last four years 1993–97 (with SO_4/HCO_3 values lower than 0.25), both ratios vary along a perfect positive linear relationship (see equation on Fig. 8b), in the same way as the annual discharge. At the temperature conditions prevailing in the catchment, and as soon as the critical zone has recovered from acidification process, the catchment drainage remains the main driver of the weathering processes of silica minerals, as already suggested for silicate areas by White and Blum (1995) and Millot et al. (2002). Moreover, this study also evidences that acidification increased silica flux together with an enhanced base cations release, a result that was put forward as an hypothesis, but which was not possible to detect by Oliva et al. (2003) using a dataset of silicate catchments distributed worldwide. Nonetheless, the resulting weathering in the Ringelbach catchment is low, according to the low mean total exportation of silica ($819 \text{ mol}_{Si} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$) and base cations

($1950 \text{ eq} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$) over the whole period.

The relative acidification status of the Ringelbach catchment was also evaluated by expressing the mean $Si/\Sigma BC$ ratio as a function of the mean base cations flux ΣBC in total exportation. A highly significant power-type curve could be fitted when using data from a set of well monitored small crystalline catchments representing a large range of acidification conditions (Fig. 8c). On this remarkable relationship, the Ringelbach catchment (mainly covered by grassland, with a small pine forest on the top) occupies a middle position, just a little above the nearby spruce-forested Strengbach catchment in the Vosges mountains and below the grassland and spruce catchments from the less air-polluted Massif Central in France. It is far from both extreme conditions: on the upper end, remote catchments covered by mixed deciduous forests receiving low pollution input (Massif Central, USA, Canada); on the lower end, the very acidified spruce-forested damaged catchment near major pollution sources (“Black Triangle” in Czech Republic), where soil base cations depletion is very strong. It is worth noting that nearby catchments in both the Vosges and Massif Central exemplify the specific acidifying effect of spruce forest cover. Indeed, spruce cover enhances dry deposition of acid atmospheric inputs and their effects on the critical zone, such as base cation depletion (Landmann and Bonneau, 1995).

Long-lasting acid precipitation inputs linked to sulfur emission have indeed impacted this remote mountain catchment and disturbed its biogeochemical behavior. However, this catchment demonstrated a strong capacity of resilience within a few years of reduced sulfur inputs, because of the significant acidity buffering efficiency of both soil cation exchange capacity and granite weathering. Such a resilience might be less obvious or efficient elsewhere in case of lower buffering capacity by silicate weathering or much higher strong acid inputs and sulfate storage in soils, like in the “Black Triangle” (Marx et al., 2017) or in other sites of Europe (Prechtel et al., 2001). In France, this was the case in more sensitive critical zones, where critical loads have been exceeded (Party et al., 1995; Probst et al., 1995d; Février et al., 1999; Moncoulon et al., 2004, 2007). The capacity of resilience against nitrogen acid deposition, whose impact is nowadays largely spread over remote areas also (Rogora et al., 2006), still needs to be assessed. But the associated mechanisms are much more difficult to identify, and the resilience more hazardous to predict for this element, because of its speciation, its complex cycle and its strong modifications and interactions within the critical zone, the so-called “nitrogen cascade” (Galloway et al., 2003).

5. Conclusions

This study aimed at investigating the buffering response of a granitic mountainous grassland critical zone (North-Eastern part of France) in the nineties, in a context of decreasing acid precipitation inputs and considering the influence of various hydrochemical conditions. Following clean air measures, the acidity of open field precipitations decreased in relation with the decrease of sulfur and oxidized nitrogen compounds originating from long range transboundary pollution. The moderate incoming acidity was efficiently neutralized by weathering processes, as indicated by the dominance of base cations, alkalinity and silica in stream waters. Like in most European countries, the inverse trends (increasing for alkalinity, decreasing for sulfates) observed in output fluxes expressed the response of the critical zone to the sulfate and protons decrease in precipitations. The soil inheritance of the impact of this pollution during previous decades and of the critical zone disturbance was attested by the sulfur release associated to high base cation depletion during the first years of the period, particularly with autumn flood flows following dry summers.

The increased water residence time during dry years and the bedrock richness in weatherable minerals (granite vs sandstone) explained the higher buffering efficiency. A constant weathering rate was evidenced when acidification was still obvious. The weathering buffering rate of the Ringelbach critical zone fitted with the remarkable curve

obtained using a worldwide set of remote sites representing a large range of acid atmospheric inputs and resulting base cations depletion. Acid inputs have thus disturbed the weathering rate *s.l.* consistently with other places from the Vosges in an intermediate position between very lowly and highly impacted sites, regarding the intensity of the acid deposition. Acidification recovery was regular over the period and it occurred earlier than in some other European sites, as attested by the absence of autumn peaks of sulfate release after 1992. The annual discharge was a key factor regulating silica and base cations fluxes at the seasonal scale and at the annual scale, following acidification recovery.

Finally, the contributing areas of springs and stream waters act as open reactors, whose output water chemistry is controlled by three main processes, which appear to have each about proportional effect on the concentrations of base cations: weathering through water-rock interactions depending on residence time, diluting effect by precipitation input or water from shallow soil and surface saturated areas, concentrating effect by evapotranspiration output. As a result, base cations concentrations of both springs and stream move up and down along proportionality lines, like a “yo-yo”, in response to varying hydrological conditions between low and high flows during the year. In the warm season, the range of this “yo-yo” behavior is amplified towards higher concentrations in low flow conditions by the concentrating effect of evapotranspiration and/or by contribution from deep waters of long residence time draining granite.

In a context of global warming and changes in atmospheric pollution patterns, the increasing occurrence of much drier conditions and/or strong hydrological events in the critical zone may delay or accelerate the release in stream water of sulfur and nitrogen from soils and sensitive areas, where S and N storage is still significant. The increase of nitrogen deposition at the end of the study period leading to a net storage of nitrogen compounds, indicated that it might be of major concern for the critical zone in a context of global change for the future. This highlights the necessity to perform long-term surveys of the critical zone to identify key processes and the influence of such strong driving factors on output fluxes and mass balances, to detect changes in pollution patterns and provide strong validation data for modelling predictions.

Acknowledgments

This research has been funded by the French programs “*Bassins de Recherche Vosgiens*” (Ministère de la Recherche et de la Technologie, 1990-96), Action “*Eau-Sol-Plante*” (Programme Environnement du CNRS, 1990-94) and “*Programme National de Recherche en Hydrologie*” (ECCO/PNRH, 2004-06). The authors initiated this study in 1990, when they were at the Centre de Géochimie de la Surface (CGS/CNRS, Strasbourg) and the Centre d’Études et de Recherches Éco-Géographiques (CEREG/ULP-CNRS, Strasbourg), respectively. Jean-Luc PROBST (head of the analytical laboratory in the CGS at that time) is thanked for facilitating the analytical survey. The authors also warmly thank Richard BRAUN and André WAEFFLER (CEREG) for their field work (weekly data collection and water sampling), as well as Yvette HARTMEIER, Gérard KREMPP and Daniel MILLION (CGS) for their laboratory work (chemical analyses). Preliminary results were presented in the master theses of Claire ALARY (1993) and Baptiste REDON (2005) prepared under their supervision.

Appendix A. Supplementary data

Supplementary data to this article (Tables EA-1 to EA-4, Figure EA-1) can be found online at <https://doi.org/10.1016/j.jhydrol.2018.11.018>.

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