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1 Influence of atmospheric deposits and secondary minerals on Li isotopes
2 budget in a highly weathered catchment, Guadeloupe (Lesser Antilles)

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11 weathering, mass balance

12 Abstract:

13 To better constrain Li dynamics in the tropics, we sampled critical zone compartments of a
14 small forested andesitic catchment in Guadeloupe (soils, parent rock, atmospheric dust,
15 plants, soil solutions, stream and rain waters). The aims of this study are to identify the origin
16 of Li in the different compartments and to better characterize the behavior of Li and its
17 isotopes during water-rock interaction in a highly cation-depleted soil. The Li isotope
18 signature ($\delta^7\text{Li}$) of throughfall samples varies between +11.2‰ and +26.4‰. As this is lower
19 than the seawater signature (31‰) and vegetation does not fractionate Li isotopes, our data
20 indicate that Saharan dust (-0.7‰) significantly contributes to the throughfall signature.

21 Li isotope composition measured in a 12.5 m deep soil profile varies from +3.9‰ near the
22 surface to -13.5‰ at 11 m depth. Compared to unweathered andesite (+5‰), the deep soil
23 signature is in agreement with preferential incorporation of light Li into secondary minerals. In
24 the top soil however, our results also emphasized that atmospheric deposition (wet and dry)

25 is a main source of Li to the soil. The decreasing $\delta^7\text{Li}$ with increasing depth is consistent with
26 a vertical gradient of incorporation of heavy atmospheric Li, this input being maximal near the
27 surface. At the catchment scale, throughfall and total atmospheric inputs (sea salts +
28 Saharan dust) provide 12.1 and 23.9 g Li.yr⁻¹ respectively to the Quiok Creek catchment.
29 These fluxes represent 34% and 67%, respectively, of Li exported at the outlet indicating that
30 atmospheric deposition is one of the main Li inputs to the critical zone. Li concentration and
31 isotopic mass balance at the catchment scale indicate that in addition to atmospheric
32 deposition, secondary mineral phase dissolution is a major solute source and that andesite
33 no longer participates in significant production of Li.

34 Introduction

35 The evolution of Earth's carbon cycle, climate and habitability is modulated by the
36 concentration of greenhouse gases in the atmosphere, in particular carbon dioxide (CO₂).
37 Over long time scales (10⁶ years), neutralization of atmospheric CO₂ by silicate weathering
38 partly controls the variation of atmospheric CO₂ content and thus helps regulate global
39 climate (Walker et al., 1981; Berner et al., 1995). The importance of chemical weathering in
40 controlling the long term evolution of the Earth's climate has stimulated the development of
41 proxies to constrain the weathering history of the continents.

42 Lithium (Li) and its isotopes have been shown to be sensitive to weathering intensity (Huh et
43 al., 2001; Pogge von Strandmann et al., 2010; Dellinger et al., 2015, Wang et al., 2015) and
44 thus Li seems to be a promising silicate weathering proxy. First, Li is mainly sourced from
45 chemical weathering of silicate rocks in surface waters (Kisakurek et al., 2005; Millot et al.,
46 2010a). In addition, Li is poorly involved in biological processes as it is not a nutrient
47 element. Therefore, its concentration in vegetation is very low and Li isotopes are not
48 fractionated by vegetation uptake (Lemarchand et al., 2010). Moreover, during chemical
49 weathering, Li isotopes are partitioned between secondary mineral and water compartments.
50 The difference between the seawater Li isotopic signature, about 30.8 ± 0.4 ‰ (compilation
51 by Rosner et al., 2007) and the upper continental crust value of 0 ± 2 (1 σ) ‰ (Teng et al.,
52 2004) reflects this partition. In general, the dissolved load in both rivers and soil solutions is
53 enriched in ⁷Li compared to corresponding river sediments and bedrock, confirming the
54 fractionation of Li isotopes during silicate weathering reactions (Huh et al., 2001, 1998;
55 Tomascak et al., 2003; Kisakurek et al., 2005; Pogge von Strandmann 2010; Wimpenny et
56 al., 2010a; Rad et al., 2013; Dellinger et al., 2015).

57 In this context, one of the key issues concerning the use of Li isotopes as weathering proxy
58 is to understand the Cenozoic increase of seawater $\delta^7\text{Li}$ (Misra and Froelich, 2012). Some
59 authors argue that this variation results of modification of $\delta^7\text{Li}$ of rivers as a consequence of

an increase of global denudation and weathering rates (Misra and Froelich, 2012; West et al., 2014; Pogge von Strandmann and Henderson, 2015). On the contrary, Vigier and Godderis (2015) argue for a stable $\delta^7\text{Li}$ during the Cenozoic but large change of the Li flux to the ocean during the Cenozoic.

Experimental studies pointed out that while no fractionation is observed during parent rock dissolution (Pistiner and Henderson, 2003; Wimpenny et al., 2010b), the isotopic contrast observed between solution and secondary mineral is due to the preferential incorporation of ^6Li in secondary minerals whereas ^7Li remains in the residual solution (Pistiner and Henderson, 2003; Wimpenny et al., 2010b; Vigier et al., 2008). It is yet unclear whether this fractionation depends on the nature of the secondary mineral involved (Millot and Girard, 2007; Pistiner and Henderson, 2003, Vigier et al., 2008) or is independent of the mineralogy (Li and West, 2014; Dellinger et al., 2014). Another parameter susceptible to influence the intensity of Li isotopic fractionation is the residence time of water in the subsurface environment (Liu et al., 2015).

Despite the abundance of riverine Li originating from weathering, atmospheric input can significantly contribute to the surface water Li budget (Lemarchand et al., 2010; Witherow et al., 2010). For instance, in the Strengbach catchment (Vosges Mountains, France), 25% of the Li exported at the outlet has an atmospheric origin. At the soil scale, two distinct behaviors of Li isotopes have been proposed. In soils with a high abundance of evolved secondary minerals (with high Al/Si ratio), the soil Li isotope signatures ($\delta^7\text{Li}$) are usually low values relative to the unweathered parent rock (Rudnick et al., 2004; Kisakurek et al., 2004; Huh et al., 2004; Liu et al., 2013). In contrast, the Li isotope composition of immature soils (i.e. rich in primary minerals) is not fractionated relative to bedrock samples (Huh et al., 2004; Lemarchand et al., 2010; Pogge von Strandmann et al., 2012). However, the interpretation of soil profiles is made difficult by the uncertainty about the contribution of atmospheric deposits, including marine aerosols (Pistiner and Henderson, 2003; Huh et al., 2004; Teng et al., 2010; Pogge von Strandmann et al., 2012) and atmospheric mineral dusts (Kisakurek et

87 al., 2004; Liu et al., 2013; Huh et al., 2004), both can shift the isotopic signature of the bulk
88 soil. Despite the fact that atmospheric inputs can significantly contribute to soil solutes (e.g.,
89 Widory et al., 2005; Millot et al., 2007), very little atmospheric data exists for non-traditional
90 stable isotope systems as pointed out by Millot et al. (2010b).

91 In order to better characterize Li atmospheric inputs and to investigate their influence on Li
92 isotopes as a weathering proxy, we analyzed here the Li isotopic fractionation in the Quiock
93 Creek catchment, a tributary of the already well-constrained Bras-David River basin
94 (monitored within the framework of the French Critical Zone Observatory) on the Caribbean
95 island of Guadeloupe. This study contributes to a coordinated effort to better constrain new
96 weathering isotopic proxies (Opfergelt et al., 2012; Dessert et al., 2015) and to quantify
97 weathering rates in Guadeloupe at different scales (Rad et al., 2006; Sak et al., 2010; Lloret
98 et al., 2011; Gaillardet et al., 2011; Ma et al., 2012; Dessert et al., 2015). In this study, we
99 measured Li fluxes and isotopic signatures of all the dissolved and solid compartments of the
100 small andesitic watershed of Quiock Creek. As is common for Caribbean islands, this
101 catchment is characterized by a high weathering intensity and relatively important
102 atmospheric inputs of both dust of Sahara origin and sea salts. In this context, we show that
103 atmospheric inputs of Li provide up to 67% of the Li exported at the outlet and that secondary
104 mineral weathering also contributes to the Li budget. We provide the first measurements of
105 $\delta^7\text{Li}$ for Saharan dust deposited in Guadeloupe. These values are crucial for the
106 determination of the global budget of Li in areas that are severely impacted by Saharan
107 dusts, such as the Caribbean region and Amazon basin.

108 1. Site description

109 The Quiock Creek catchment (16°17'N, 61°70'W) is located on Basse Terre Island, the
110 volcanic part of the Guadeloupe archipelago in the French West Indies (Figure 1). The study
111 site (area of 8ha) is located in the primary tropical rainforest of the Guadeloupe National Park
112 at an elevation ranging from 200 m to 350 m. Quiock Creek is a small tributary of the Bras-

David River monitored by the ObsErA observatory (INSU-CNRS CZO) dedicated to the study of weathering and erosion processes under tropical climatic conditions (Lloret et al., 2011; 2013; Dessert et al., 2015).

The Quiock Creek catchment has a wet tropical climate with two seasons: the dry season, from January to June, and the cyclonic wet season, from July to December. The mean annual temperature and precipitation rate measured on site for the last 2 years are 25 °C and 3500 mm yr⁻¹ respectively. The annual runoff ranges from 700 mm to 2800 mm with a mean annual value of 1130 mm. Evapotranspiration is high, around 63 %, which is typical for a tropical rainforest (Roche, 1982; Loescher et al., 2005, Lloret et al., 2011) and is likely due to the high frequency of low intensity short duration rainfalls and convective transport of evaporated moisture as shown to be the case in similar Caribbean tropical forests (Schellekens et al., 2000). Tropical storms and hurricanes also contribute significantly to the hydrology of the site (Zahibo et al., 2007). For instance, during hurricane Rafael (13-14 October 2012), 141 mm of rainfall in 48 h were measured on site, corresponding to 5% of the total annual rainfall.

The Quiock Creek catchment lies on Pleistocene andesitic pyroclastic deposits (Boudon et al., 1988) that are covered by a very thick ferrallitic soil (>15 m thick; Colmet-Daage and Bernard, 1979, IRD soil map; Buss et al., 2010). Although these deposits are not dated, the age of adjacent volcanic flows is 1.46 Myr before present (Samper et al., 2007). The soil profile of Quiock Creek consists of highly weathered volcanoclastic debris flows containing andesitic clasts at various stages of weathering (Buss et al., 2010; Sak et al., 2010; Ma et al., 2012). A previous study showed that secondary minerals are dominant and represent 95 wt.% of the bulk soil (Buss et al., 2010). Clays corresponding to kaolinite and dominantly halloysite, account for 70 wt.% of the mineralogy and non-clay secondary minerals are almost entirely Fe(III)-hydroxides (approx.. 19 wt.%) and gibbsite (concentration is highly variable along the profile). Primary minerals consist of quartz (0-8 wt.%), feldspar (0-4 wt.%) and cristobalite (mean of 3 wt.%) (Buss et al., 2010). Quartz and feldspars (dominantly

orthoclase) are primarily found in the upper 30 cm of the profile and, concomitantly, in several deeper levels but quartz content is otherwise very low and feldspar largely absent in the rest of the profile. The soil is highly depleted in soluble cations (Buss et al., 2010), but despite the high nutrient depletion of these soils, the tropical rainforest vegetation is dense and the mean litter flux is high ($7.8 \text{ t ha}^{-1} \text{ yr}^{-1}$, Rousteau, 2014) comparable to a similar rainforest in northeastern Puerto Rico (Weaver and Murphy, 1990).

One of the peculiarities of the Quiock Creek catchment is the input of both Saharan dust and volcanic ash. Montserrat volcano, located 86 km NW of Guadeloupe, erupted on July 18th 1995, after a century of quiescence and is still currently active. Since 1995, six ash fall episodes were recognized that had consequences in Guadeloupe (www.mvo.ms; activity report OVSG 2000). The two most important events took place in September 1996 and February 2010 and produced ash-fall deposits over Guadeloupe Island that were thicker than 1mm, corresponding to fluxes of about 100 g m^{-2} of ash each (OVSG and personal communication of J.C. Komorowski). The other exogenous input to the top soil comes from the Sahara desert. This flux, measured in Guadeloupe, is around $100 \text{ kg ha}^{-1} \text{ yr}^{-1}$ (J. Molinié, personal communication) and is consistent with literature values varying between 50 and $200 \text{ kg ha}^{-1} \text{ yr}^{-1}$ in the Caribbean basin (Glaccum and Prospero, 1980; Mahowald et al., 2006; Pett-Ridge et al., 2009). The Saharan dust deposits are mainly composed of mica/illite and quartz with lesser amounts of kaolinite, chlorite, montmorillonite, microcline, plagioclase, and calcite (Prospero et al., 1970; Glaccum and Prospero, 1980). These deposits contribute significantly to the formation of many soils in the Caribbean and Amazon Basin (Borg and Banner, 1996; Herwitz et al., 1996; Muhs et al., 2009; Pett-Ridge et al., 2009). In Guadeloupe, the dull aspect of quartz in the soil, characteristic of aerial transport, suggests that Saharan dust is likely the source of quartz to the soil profile, although chemical weathering of quartz can also alter grain surfaces and is known to occur in thick tropical soils (e.g. Schulz and White, 1999).

2. Sample collection

This study is based on the quantification and geochemical characterization of water fluxes entering, passing through and leaving the catchment. The precipitation rate above the canopy (openfall) was measured on site with a rain gauge in a clearing in the vicinity of the sampling site. The rain gauge measured events of minimum 0.2 mm of rainfall per hourly step. The throughfall flux was measured every two weeks for two years (06-2011 to 08-2013), using 22 collectors randomly positioned across the site. In this study, 131 water samples were collected: 13 rainfall samples, collected on site (RF-MF) or at the OVSG (RF-OVSG, 15 km southeast of the studied site), 51 throughfall and stemflow samples, 57 samples of Quiock Creek stream water and 35 soil solution samples. These samples were collected during contrasting hydrological periods. Throughfall, stemflow and rainwaters were sampled during six field trips between 2011 and 2013. Throughfall and rainwaters were collected in polypropylene bottles with a funnel located one meter above the ground in order to avoid contamination from soil particles. Three throughfall collectors were randomly positioned at the study site. Stemflow samples were collected from silicone gutters set around the trunks of two different trees. However, the sampling device caused Cl contamination thus the stemflow Cl concentration were not taken into account. Quiock Creek samples were collected manually once a month and more frequently during field trips. Soil solutions were sampled once a month from nested tension lysimeters (positioned between 15 and 823 cm depth) equipped with porous ceramic cups (see Buss et al., 2010).

For all water samples, pH and conductivity were measured on site or at the OVSG. After collection, non-filtered 20 mL aliquots were used for alkalinity measurements. The remaining water samples were filtered through 0.2 μm cellulose filters and divided in two aliquots stored in polypropylene bottles: one non-acidified for anion and silica determination and one acidified to 2% HNO_3 for cation and trace element analyses. Samples for Li isotope measurements were stored in polypropylene bottles previously washed with distilled 0.5N HNO_3 and acidified to 2% HNO_3 . Lithium isotopic compositions were measured on 19 selected water samples corresponding to 7 samples of throughfall and stemflow, 4 samples

of Quirock Creek stream water and 8 samples of soil solution corresponding to two sampling dates (October 26, 2012, and June 28, 2013).

Soil samples (n=23) down to 12.5 m depth were collected with a hand-auger during lysimeter installation in 2007 (Buss et al., 2010). As the auger did not encounter fresh andesite at the bottom of the profile; we analyzed andesite from Samper et al. (2007) (sample 04-GW-12) to characterize the unweathered parent rock. Ash from Montserrat volcano was collected at the OVSG during the February 2010 eruption. During a Saharan dust event in July 2013, we collected rainfall particulate matter by filtration on a 0.2 μm cellulose filter, which was then dried and stored in a Petri dish. Finally, 7 vegetation samples were analyzed (litter, branches and roots). Litter samples chosen for analysis correspond to the most productive period between the 10th and the 24th of June 2011. Lithium isotopic compositions were measured in all of these solid samples but only in 13 soil samples. Finally, Nd isotopic compositions were measured in 6 samples of the soil profile.

3. Analytical methods

3.1 Sample preparation for analyses

3.1.1 Solid sample digestion

Soil and vegetation samples were first dried in an oven (60°C) for 3 days and crushed in an agate mortar (soil samples) or in a ball mill (vegetation samples). For soils, volcanic ash and rocks, 100 mg of each sample was dissolved in a mixture of HNO_3/HF for 2 days at 120 °C. This mixture was then evaporated and dissolved twice in 2mL 6N HCl and finally stored in 1N HCl. Saharan dust samples collected on cellulose filters were treated with the same protocol but with an initial step of filter digestion in diluted 5N HNO_3 at 100°C for 1 day. Vegetation samples (about 0.5 g) were dissolved in 10 mL of HNO_3 in 50 mL Teflon beakers and digested in a DigiPREP block digestion system for 24h at room temperature and another 24h at 90°C. These samples were then evaporated at 60°C and dissolved once more in 16N

219 HNO₃ for 24h at 90°C. Finally, after evaporation, 0.5 mL HF/ H₃BO₃ were added to fully
220 dissolve phytoliths. These samples were then stored in 50 mL of 2N HNO₃.

221 3.1.2 Li and Nd purification

222 For Li isotopes, the evaporated volumes were calculated to reach 20 ng of Li in 1 mL. Water
223 samples were first evaporated to dryness and digested in HNO₃ to remove the organic
224 matter. Then the protocol is the same for water and solid samples. Lithium was separated
225 from the rest of the matrix by ion-exchange chromatography with a Biorad AG50X-12 resin
226 and a 0.2N HCl eluent following the protocol detailed in Dellinger et al. (2014) (modified from
227 James and Palmer, 2000).

228 The separation of Nd from the rest of the matrix is a two-step procedure (Richard et al.,
229 1976; Caro et al., 2006). The first step consists of separation of rare earth elements from the
230 rest of the matrix on TRU-Spec resin in 2N HNO₃ media. The second step consists of
231 separation on Ln-spec resin of the different rare earth elements in 0.25N HCl media. The
232 purified solution of Nd is then evaporated and dissolved in 3N HNO₃ for isotopic
233 measurement. The minimum quantity of Nd in purified solution is 50ng in 1 mL (50ppb).

234 3.2 Major and trace elements analyses

235 Base cations were measured by ICP AES (ThermoFisher iCap 6200 series) at the Institut de
236 Physique du Globe de Paris (IPGP). Anions in soil solutions were measured with a Dionex
237 DX 120 chromatograph at the IPGP and the OVSG/IPGP. Dissolved Li concentrations were
238 measured using HR-ICP-MS (Element II ThermoScientific) at IPGP. The limit of
239 quantification is estimated to be 20 ppt and the accuracy was controlled by repeated
240 measurement of the SLRS-5 standard with an external reproducibility of 3%. Trace elements
241 in solid samples were measured with an ICP-MS X series mass spectrometer (Thermo
242 Electron) at the Institut des Sciences de la Terre de Paris (ISTeP) of the University of Pierre
243 et Marie Curie (UPMC). We followed the bracketing method using rock standards BEN for
244 bracketing and BEN, GSN, BCR-2, BHVO2 and JB-2 to validate the measurements. The

standard values measured in this study are compared to the certified values to validate the data (Table 1S). Major element and Li concentrations in litter samples were measured by a calibration curve, such as for water samples. The accuracy of this measurement was checked by repeated analyses of a vegetation standard NIST SRM 1515 (apple leaves).

3.3 Li isotope analyses

Li isotope analyses were performed on the Neptune multicollector ICP-MS (Thermo Scientific) at IPGP using the Apex sample inlet system. The $\delta^7\text{Li}$ is calculated relative to the L-SVEC standard (Flesh et al., 1973) as follows:

$$\delta^7\text{Li} = \left(\frac{\left(\frac{^7\text{Li}}{^6\text{Li}}\right)_{\text{sample}}}{\left(\frac{^7\text{Li}}{^6\text{Li}}\right)_{\text{L-SVEC}}} - 1 \right) \times 1000 \quad (1)$$

Each sample was measured three times and bracketed before and after with the L-SVEC standard, which had the same concentration as the sample (within 10% error). This bracketing sequence yields five $\delta^7\text{Li}$ values which are averaged to give the $\delta^7\text{Li}$ of the sample. Three values are obtained using the average L-SVEC values of standard measured before and after the sample. Two supplementary values are obtained using the average value of two sample normalized by the L-SVEC which is measured between the two samples. In addition, IRMM-16 (Qi et al., 1997) and Spec-pure (Dellinger, 2013) Li standards are routinely measured at the beginning and during each sequence. The in-run precision, calculated from repeated measurements, is below 0.2 ‰. Indeed, the IRMM-16 standard isotopic composition we measured was $0.17 \pm 0.08 \text{ ‰}$ (2σ , $n=50$) and $94.42 \pm 0.12 \text{ ‰}$ (2σ , $n=19$) for the Li-SPEC standard. Typically, a solution of 20 ppb produces a signal of 8 V and the background was typically less than 50 mV (0.01 ng corresponding to 0.6% of the 20 ppb signal). The blank measured immediately before and after each sample and standard is subtracted. The method used corresponds to the measurement of 8 ratios of 12 seconds iteration time per sample or standard. The external reproducibility, based on repeated measurements of standards is below 0.5‰. The $\delta^7\text{Li}$ of the NASS-5 seawater standard was

measured at $+30.73 \pm 0.35\%$ (2σ) ($n=9$ separations and measurements) in good agreement with data from the literature (Millet et al. 2004; Rosner et al., 2007; Huang et al., 2010). A homemade standard, called SLC, corresponds to L-SVEC mixed into a multi-element matrix in order to reproduce the mean river composition and was measured at $-0.11 \pm 0.27\%$ (2σ) ($n=16$ separations and measurements). Standard basalt BHVO-2 samples were measured at $+4.33 \pm 0.43\%$ (2σ) ($n=6$, 6 separations), in good agreement with the data from the literature (Jeffcoate et al., 2004 ; Penniston-Dorland et al., 2012 ; Vlastelic et al., 2009 ; Dellinger, 2013). Finally, the procedural blank is lower than 0.05 ng of Li, negligible compared with the 20 ng of Li from the sample.

3.4 Nd isotope analyses

Nd isotope analyses were performed on the Neptune multicollector ICP-MS (Thermo Scientific) at IPGP using the Apex sample inlet system. The ϵ_{Nd} is calculated relative to the CHUR (Chondritic Uniform Reservoir) as follows:

$$\epsilon_{Nd} = \left(\frac{\frac{{}^{143}Nd}{{}^{144}Nd}_{sample}}{\frac{{}^{143}Nd}{{}^{144}Nd}_{CHUR}} - 1 \right) \times 10\,000 \quad (2)$$

The CHUR value is 0.512638 (Jacobsen and Wasserburg, 1980). The method used corresponds to the measurement of 100 ratios of 4 seconds iteration time per sample or standard. Mass interferences with Sm (144, 148 and 150) were corrected using ${}^{147}Sm/{}^{144}Sm = 4.83870$. The mass bias was corrected using the ${}^{146}Nd/{}^{144}Nd$ ratio of 0.72190. Each measurement was normalized to the NIST value certified as ${}^{143}Nd/{}^{144}Nd = 0.511418 \pm 6 \cdot 10^{-6}$ (Caro et al., 2006) which is measured every 3 samples. The external error is 0.18ϵ (2σ).

4. Results

4.1 Major and trace element concentrations

4.1.1 Water samples

293 Major element and Li concentration data are presented in Table 1 for samples for which Li
 294 isotopic composition was measured. Concentrations of major elements and Li in all the other
 295 samples measured during this study are presented in Table 3S. All samples have low pH
 296 ranging from 3.6 for a stemflow sample to 6.3 for a throughfall sample. Stemflow samples
 297 have the highest major element concentrations. The later are probably due to organic matter
 298 leaching from the tree surface during the water flow. Along this sinuous pathway, strong
 299 interactions between water and tree surface take place and can induce water evaporation,
 300 contributing thereby also to increase concentrations. Li concentrations vary between 2 and
 301 20 nmol.L⁻¹ in rainfall (RF) and throughfall (TF). The median Li concentration in rainfall (5
 302 nmol.L⁻¹) is lower than in throughfall (7 nmol.L⁻¹). These concentrations are in the low range
 303 of the literature data for volcanic island (Louvat et al., 1997; Pistiner and Henderson, 2003;
 304 Pogge von Strandmann, 2006, 2010). In comparison, stemflow waters have higher Li
 305 contents (29 to 66 nmol.L⁻¹). Soil solution (SS) is the dissolved compartment with the highest
 306 Li concentrations between 41 and 121 nmol.L⁻¹ (mean [Li]_{SS}= 77 nmol.L⁻¹). Finally Quiock
 307 Creek (QC) samples have Li concentrations ranging between 38 and 72 nmol.L⁻¹ (with a
 308 mean value of [Li]_{QR}= 56 nmol.L⁻¹). For RF and TF samples, Cl concentrations are well-
 309 correlated with Na concentrations (Figure 2, $r^2=0.97$) and plot close to the dilution line of
 310 seawater. This indicates that both Na and Cl in RF and TF originate mostly from sea salt and
 311 are not influenced by the vegetation. The molar Li/Cl ratios of RF and TF, ranging from 4 10⁻⁵
 312 to 13 10⁻⁵, are higher than the seawater ratio (Figure 3) and thus show that sea salts are not
 313 the only source of Li in the rain. The Li/Cl ratios measured in RF and in TF have similar
 314 ranges, but are higher in the soil solutions and the Quiock Creek water samples. Dessert et
 315 al. (2015) demonstrated that Cl behaves conservatively in Basse-Terre watersheds,
 316 therefore our observation indicates that in addition to rain, another source contributes lithium
 317 to soil solutions and to Quiock Creek. Moreover, Li/Cl ratios in soil solution samples are more
 318 variable than in Quiock Creek samples. The fact that Quiock Creek integrates solutes

derived from a larger surface area and over a longer time-scale than the soil solution compartment could explain this observation.

4.2.2 Soil, rock and vegetation samples

Table 2 reports major element and trace element concentrations together with Li isotopic composition in Saharan dust, volcanic ash, litter, soil and rock samples. Saharan dust has the highest Li concentration of this sample set with a mean Li content of 18.5 ppm. This value is in agreement with those found in the literature (Moreno et al., 2006; Trapp et al., 2010). The Li concentration in the local andesite is 12 ppm, also in good agreement with the characteristic range for andesite in the literature (Magna et al., 2004; Schuessler et al., 2009; Halama et al., 2009). Montserrat volcanic ash has the same Li concentration as andesite, consistent with the andesitic origin. In vegetation samples, the Li concentration is low and relatively constant in all plant compartments with a mean Li concentration of 0.3 ppm, consistent with values found in the literature (Lemarchand et al., 2010; Vetter et al., 2005). Soil samples have Li contents between 5 and 15 ppm. To correct for dilution effects and volume change, Li concentrations in soil samples are normalized to an immobile element (Ti) and to a mobile element (Na). In Figure 4a and 4b mass transfer coefficient (τ) values are presented for major elements and Li :

$$\tau = [(X/Ti)_{\text{soil}} / (X/Ti)_{\text{andesite}}] - 1 \quad (3)$$

and represents the depletion of X (element of interest) in the soil compared to the andesite. If τ is <0 , X is depleted in the soil relative to the andesite and if τ is >0 , X is enriched in the soil relative to the andesite (Brimhall and Dietrich, 1987). Figure 4a shows that Li and other soluble elements are depleted in the soil relative to andesite. However Li is less depleted ($\tau = -0.6$) in the soil than the major elements ($\tau < -0.85$, where $\tau = -1.0$ indicates total depletion). Moreover, Li/Na ratios in the soil profile compared to the ratio in andesite (4c) shows that Li is less depleted than Na. These observations indicate that Li is lost from the bedrock during water rock interaction in agreement with its soluble behavior, but is less mobile than the other

soluble elements reflecting its incorporation into secondary minerals. Additionally, Li and other mobile elements are notably less depleted in the bottom 15 cm of the soil profile and at 305 cm, 427 cm, 1219 cm and 1250 cm depth.

4.2 Nd and Li isotope compositions

Nd isotopes in the soil displayed ϵ_{Nd} values between -8.39 and 2.71 (Table 2). The very negative values of ϵ_{Nd} are very different from values characteristic for andesite (Figure 4), implying that an exogenous source contributes to Nd budget in the soil. Indeed, these particular values are close to ϵ_{Nd} of Saharan dust. Two soil depths exhibit the Saharan dust-like Nd signature: the most superficial at 15 cm depth and the 305 cm depth. These depths correspond to levels enriched in quartz and feldspar, which are also less depleted in mobile elements and Li. The presence of quartz associated with the relatively higher concentrations of mobile elements and the isotopic signature of Nd provide independent lines of evidence for dust layers at discrete depths well below the soil surface. The only way to explain dust mineral inputs below about 1 meter depth is if the soil profile developed from a bedrock profile that comprising multiple episodes of volcanic deposition, with quiet periods of dust deposition in between. Zones of dust within the profile thus represent soil paleo-surfaces.

Li isotope signatures in all compartments studied in the catchment are displayed in Figure 5. Throughfall samples have the highest δ^7Li , ranging between +11.2 and +26.4‰. Li isotopic compositions measured in two distinct throughfall samples from the same date are similar, demonstrating the robustness and significance of δ^7Li values. The δ^7Li values of Montserrat volcanic ash are +4.7‰ close to the value of andesite (Halama et al., 2009; Magna et al., 2006; Schuessler et al., 2009). The measured Saharan dust δ^7Li is -0.7‰ consistent with their crustal origin and mineralogy. This value is slightly lower than the δ^7Li of the mean continental crust, which is 0 ± 2 (1 σ) ‰ (Teng et al., 2004; Liu and Rudnick, 2011) probably due to the predominance of secondary minerals in these dust samples (70% of mica/illite, kaolinite, chlorite; Glaccum and Propero, 1980) enriched in the light Li isotope. Vegetation

$\delta^7\text{Li}$ is found to vary between +3.6 and +8.7‰, a range that is higher than the one reported by Lemarchand et al. (2010). Li isotope signatures in the solid soil profile are highly variable and can be separated into two zones (Figure 5). The shallower zone, between the surface and 274 cm depth, with a mean signature of $+2.9 \pm 0.9\text{‰}$, exhibits no variation as a function of depth. In the deeper zone, between 274 cm and 1097 cm depth, the Li signature decreases regularly with depth from +0.6 to -13.5‰, reaching one of the lowest $\delta^7\text{Li}$ values ever reported in the literature for soil samples (Pistiner et al., 2003; Rudnick et al., 2004; Huh et al., 2004; Lemarchand et al., 2010; Pogge von Strandmann et al., 2012; Liu et al., 2013). Li isotope signatures in the solid soil are systematically more negative than in andesites. Soil solution $\delta^7\text{Li}$ varies between +4.6 and +8.9 ‰ with no trend with depth. The measured $\delta^7\text{Li}$ of andesite is consistent with values reported for andesite in the literature (Halama et al., 2009; Magna et al., 2006; Schuessler et al., 2009). Quiock Creek water samples have a relatively constant $\delta^7\text{Li}$ value of $+8.2 \pm 0.6\text{‰}$, close to the soil solution value, suggesting that Quiock Creek Li is essentially supplied by the soil solution. The Quiock Creek $\delta^7\text{Li}$ falls in the low range reported in the literature for rivers draining volcanic rock (Rad et al., 2013; Henchiri et al., 2014).

4.3 Water budget

The mean annual rainfall is 3500 mm yr^{-1} (ObsErA database). The yearly average throughfall flux varies significantly between the two years studied: 3530 mm yr^{-1} for the first year (June 2011 to June 2012) and 2990 mm yr^{-1} for the second year (June 2012 to June 2013). We used a sliding average to estimate a mean throughfall flux of $3079 \pm 660 \text{ mm yr}^{-1}$.

Unlike throughfall, stemflow flux cannot be accurately estimated because of the difficulty in determining the water interception surface of the trees. The discharge of the catchment was measured ten times in the Quiock Creek and was found to vary between 150 and 400 L.min^{-1} . In order to determine a more precise discharge, Cl is used as a conservative element (Dessert et al., 2015). We considered that the flux of Cl that enters the catchment is leaving it

without significant loss. As we know the throughfall flux, the median throughfall Cl concentration ($100 \mu\text{mol L}^{-1}$) and the mean Cl concentration in RQ ($272 \mu\text{mol L}^{-1}$), we can infer the discharge. The calculated discharge is 1130 mm yr^{-1} , corresponding to a flow of 172 L min^{-1} , which is consistent with the values episodically measured in the catchment.

5. Discussion

We have shown that the various compartments in the Quiock Creek catchment have distinct Li concentrations and isotopic signatures. Here, we first discuss and quantify the influence of atmospheric inputs to the Li budget in the catchment. Then we examine their importance at both the profile and catchment scales. Finally, we propose a sequence of events describing the evolution of the soil profile over time based on the Li isotope signatures.

5.1 The role and fate of atmospheric inputs

The results presented above show that the Li/Cl ratio of rainfall and throughfall are higher than the Li/Cl ratio in seawater (Figure 3) indicating that sea salts are not the only source of Li in the rainwater. Other possible sources of Li to rainwater include the dissolution of atmospheric dust or an anthropogenic source (Millot et al., 2010b). Influence of anthropogenic Li can be discarded because of the absence of nuclear activity and fertilizers in the National Park of Guadeloupe. Moreover, fertilizers are typically characterized by extremely high $\delta^7\text{Li}$ (up to 215‰ determined by Negrel et al. (2009)) due to synthetic Li additive derived from a ^7Li -rich reagent (Qi et al., 1997). As $\delta^7\text{Li}$ of Quiock rainwaters exhibit a maximum value of +26.4‰, the additive source must have a Li signature lower than that of seawater. Saharan dust and the remobilization of local and volcanic dusts from Montserrat are therefore the best candidates to provide Li by leaching in the atmosphere followed by deposition via rainfall. This is consistent with the pristine character of the Quiock Catchment. The relationship between $\delta^7\text{Li}$ and Li/Na value in throughfall and stemflow (Figure 6a) confirms that, at first order, Li in throughfall results from a mixture of sea salts and dissolved mineral dust. Considering the scarcity of volcanic events able to spread andesite in the

atmosphere, the direction of the major winds and the high and regular flux of Saharan dusts reaching Guadeloupe (*i.e.* 100 kg.ha⁻¹.yr⁻¹), Saharan dusts are considered as the major additional source of Li to the rainwater. In order to calculate the proportion of Li from each source in the throughfall samples, we use Na as the best tracer for sea salt contribution in rainfall and throughfall (Keene et al., 1986; Negrel and Roy, 1998; Basak and Alagha, 2004; Rastogi and Sarin, 2005). Considering the seawater Li/Na ratio (Li/Na_{SW}), it is possible to calculate the proportion of sea salt Li (Li_{SW}) in rainwater and throughfall as follows:

$$Li_{SW} = Na_{TF} \times \left(\frac{Li}{Na}\right)_{SW} \quad (4)$$

Where Na_{TF} is the concentration in the sample (throughfall or stemflow). In Figure 6b, the Li isotopic signature is plotted as a function of the proportion of Li coming from sea salts. The addition of Li from dusts is thus accompanied by a decrease in the Li isotopic signature. One peculiar data point exhibits a Li seawater proportion of 98% and a Li isotopic composition of +17.5‰, which may be related to the unusually (and unexplained) lower Na and Cl concentrations measured in this sample.

In order to calculate the Li mass balance at the catchment scale (see section 5.3), we assess the mean integrated δ⁷Li value of throughfall because the mean δ⁷Li of the individual samples might not be representative of the catchment integrated δ⁷Li value due to the large variability and paucity of throughfall data. In order to assess this mean integrated δ⁷Li value, we calculate the mean proportion of Li derived from sea salts in all throughfall samples collected (n=48) during our study with Equation (3). The mean proportion of Li in rain coming from sea salts is 75% with the remaining 25% derived from Saharan dust. We then compute the mean throughfall signature as a mixture between 25% of Saharan dust (δ⁷Li_{SD} = -0.7‰) and 75% of sea salts (δ⁷Li_{SS} = +31‰) assuming no fractionation of δ⁷Li during mineral and sea salt dissolution. It is interesting to note that the calculated mean throughfall signature is +23.1‰, similar to the data reported by Millot et al. (2010b) for rainfall measured on the French Atlantic coast.

5.2 Using $\delta^7\text{Li}$ to interpret soil profile development

In the entire soil profile, the Li isotopic signature of the solid phase is low relative to andesite consistent with the preferential incorporation of ^6Li into secondary minerals during weathering processes. Figure 7 presents the Li isotopic signature of the soil as a function of τ_{Li} . As previously discussed (Section 4.2) at 15, 305, 488, 1219 and 1250 cm depths, the relatively high proportions of Li and other mobile elements (Figure 4), the higher primary mineral content (10% of quartz and microcline, Buss et al., 2010) and the Nd isotope signatures suggest that horizons of Saharan dust increase the local Li/Ti ratio at these depths. At 792 cm, we observe that the Ti concentration is abnormally low and thus, at this particular depth, the high Li/Ti ratio seems to be controlled by Ti depletion rather than by Li enrichment.

For soil samples, according to the behavior of Li isotopes during chemical weathering, the simplest hypothesis for the decrease in $\delta^7\text{Li}$ with depth is that the fractionation of Li isotopes is related to its depletion in the soil. Figure 7 shows that this is not the case as no relationship between τ_{Li} and the Li isotopic signature of the soil is observed (Figure 7). In Figure 7, we exclude samples impacted by dust deposition because their normalized Li content is not only derived from weathering processes but is also influenced by dust input or anomalous Ti concentrations. Most of the soil samples cluster around $\tau_{\text{Li}} = -0.6$ while a very large decrease of the $\delta^7\text{Li}$ with depth is observed (from +3.9‰ at the top of the profile to -13.5‰ at depth). The -13.5‰ value of $\delta^7\text{Li}$ found at the base of the profile is one of the lowest values of $\delta^7\text{Li}$ in bulk soil ever published (Rudnick et al., 2004; Kisakurek et al., 2004; Huh et al., 2004; Liu et al., 2013).

A “batch” fractionation model similar to the one described in Bouchez et al. (2013) can be applied to interrogate the range of soil $\delta^7\text{Li}$ measured. This water-mineral interaction model, adapted from Johnson et al. (2004), considers that congruent dissolution of an initial rock leads to an initial solution ($\delta^7\text{Li}_{\text{rock}}$) from which secondary phases precipitate. The model assumes an isotopic equilibrium between the residual solution ($\delta^7\text{Li}_{\text{diss}}$) and the precipitated

solid phase ($\delta^7\text{Li}_{\text{sec}}$). It is assumed that the main process fractionating Li isotopes is the formation of secondary phases that preferentially incorporate ^6Li .

$$\delta^7\text{Li}_{\text{sec}} = \frac{\alpha_{\text{sec-diss}} \times \delta^7\text{Li}_{\text{rock}} + 1000 f_{\text{Li}} \times (\alpha_{\text{sec-diss}} - 1)}{\alpha_{\text{sec-diss}} (1 - f_{\text{Li}}) + f_{\text{Li}}} \quad (5)$$

The parameters of the model are the fractionation factor ($\alpha_{\text{sec-diss}}$) and the proportion of Li incorporated into secondary phases ($1 - f_{\text{Li}}$). $\alpha_{\text{sec-diss}}$ is expressed as follow:

$$\alpha_{\text{sec-diss}} = \frac{\delta^7\text{Li}_{\text{sec}} + 1000}{\delta^7\text{Li}_{\text{diss}} + 1000} \quad (6)$$

$$1 - f_{\text{Li}} = \frac{(\text{Li}/\text{Ti})_{\text{sec}}}{(\text{Li}/\text{Ti})_{\text{initial rock}}} \quad (7)$$

In order to link the model with field data we make the following approximation:

$$1 - f_{\text{Li}} \approx -\tau_{\text{Li}} \quad (8)$$

This approximation assumes that the soil only contains secondary minerals, which is reasonably consistent with the mineralogy of the soil samples (Buss et al., 2010). The fraction of Li not incorporated into secondary minerals (f_{Li}) is fixed as the value measured in the soil profile and we fit the fractionation factors ($\alpha_{\text{sec-diss}}$) needed to the soil profile data (Figure 7).

The $\delta^7\text{Li}$ and the f_{Li} values of the deepest soil samples (having the most negative Li isotope signature) can be modelled with a fractionation factor ($\alpha_{\text{sec-diss}}$) between 0.970 and 0.973, in the low range of the fractionation factors in the literature (Li and West, 2014). Some authors showed that $\alpha_{\text{sec-diss}}$ can vary depending on the nature of the secondary mineral formed. For instance, Millot and Girard (2007) reported a $\Delta^7\text{Li}_{\text{solution-rock}}$ value of 7.1‰ for Li adsorption onto kaolinite and a $\Delta^7\text{Li}_{\text{solution-rock}}$ value of 24.8‰ for gibbsite in agreement with values reported by Pistiner and Henderson (2003). The fractionation factor values ($\alpha_{\text{sec-diss}}$ from 0.993 to 0.998) needed to fit the shallow profile data (Figure 7) are very low and not consistent with literature values for the secondary minerals found in the Quiock profile.

498 Figure 7 shows that the batch equilibrium model provides a reasonable fit to the soil Li
499 composition of the deeper part of the profile (610 cm to 1158 cm) with fractionation factors
500 for gibbsite and kaolinite. However, the changes in $\alpha_{\text{sec-diss}}$ necessary to explain the $\delta^7\text{Li}$
501 variations along the profile are not consistent with the mineralogy, which is largely invariant
502 with depth. Li and West (2014) have argued against a relationship between Li isotope
503 fractionation factors and secondary phases. They propose instead that fractionation factors
504 are linked to the mean annual temperature of a site. William and Hervig (2005) experiments
505 suggested that high temperature Li fractionation by clays depended on crystal size. These
506 results were obtained under simulated hydrothermal conditions (300°C and 100 MPa) which
507 do not correspond to our conditions. There are no data on the influence of crystal size under
508 supergene conditions and since the crystal size on site is unknown we cannot its influence.

509 The variation of $\delta^7\text{Li}$ in the profile could instead result from the surficial input of one or
510 several additional Li sources with higher $\delta^7\text{Li}$. The two possible candidates for this source of
511 high $\delta^7\text{Li}$ are atmospheric (Saharan dust and seasalt) inputs and vegetation. The $\delta^7\text{Li}$ of
512 Saharan dust is -0.7‰ and may vary in the upper continental crust signature range between
513 0 and +4‰ (Teng et al., 2004; Liu and Rudnick, 2011). It is clear that this source of Li is not
514 sufficiently enriched in ^7Li to explain the isotopic signature of the upper part of the profile.
515 Vegetation has a Li isotopic signature varying between +3.6 and +8.7 ‰ that could provide
516 supplementary ^7Li to the soil (see Section 5.3). Organic carbon concentration in the soil
517 profile (Lloret, 2010) indicates that less than 1g.kg^{-1} of organic matter is preserved in the soil
518 lower than 20 cm depth. If we assume that the Li concentration is the same in both organic
519 matter and vegetation, 1g kg^{-1} of organic matter corresponds to only 0.3 ppb of Li which is
520 too low to influence the Li isotopic signature of the soil (approx. 5 ppm).

521 High soil $\delta^7\text{Li}$ values in the upper part of the profile can therefore only be explained by input
522 of Li from throughfall that has a signature of around 23‰ and thus can provide a positive $\delta^7\text{Li}$
523 source to the soil profile. Such influence of atmospheric input on soil profiles has already
524 been described in the literature for Li isotopes in Hawaii (Huh et al., 2004; Pistiner and

Henderson, 2003), in Iceland (Pogge von Strandmann et al., 2012), in South Carolina (Rudnick et al., 2004, Teng et al., 2010) and for Mg isotopes in Puerto Rico (Chapela-Lara et al., 2014). However, a recent study conducted in Hawaii states that atmospheric inputs of Li do not impact solid soil (Ruy et al., 2014). Li isotope signatures in the Quiock profile suggest that the Li of andesitic origin in the soil is progressively replaced by atmospheric Li, creating a gradient of atmospheric influence from the top soil to the deep soil. The non-erratic decrease of the soil Li isotopic signature from surface to deeper horizons is another evidence for atmospheric Li diffusion coming from the surface.

To conclude, in the deeper soil away from atmospheric influence, Li isotope are a good proxy for weathering degree of soils because in this highly weathered regime, Li depletion is associated with very low $\delta^7\text{Li}$ (one of the lowest values reported in the literature) as a result of intense weathering. However, at the surface, the influence of atmospheric inputs becomes more and more important and soil samples have $\delta^7\text{Li}$ that mimics the source rock but are depleted in Li compared to the source rock due to intense weathering. Therefore, surface soil $\delta^7\text{Li}$ does not only reflect the high weathering degree (Li depletion) of soil samples as a significant part of their Li is of marine origin. This shows that in environments characterized by high precipitation rates and highly weathered soils, river suspended sediments sourced from the erosion of top soil will have a Li depletion associated to a $\delta^7\text{Li}$ signature higher than predicted value because of reincorporation of atmospheric lithium in secondary minerals. This observation has important implications for using $\delta^7\text{Li}$ as solid weathering product as a fingerprint for past weathering regimes. It also shows that at least for Li, chemical weathering is not a simple mass loss of rock material but the result of an exchange with the atmosphere (Bouchez and Gaillardet, 2014).

5.3 Li budget at the catchment scale

5.3.1 Li fluxes in the Quiock Creek catchment

Water and solid flux quantification and mean Li concentrations and isotopic compositions of the different compartments, allow us to calculate the fluxes of Li that enter and leave the Quiock Creek catchment. Taking into account the litter flux ($7.8 \text{ t ha}^{-1} \text{ yr}^{-1}$) and the Li concentration in litter ($0.3 \pm 0.087 \text{ ppm}$), it is possible to determine the amount of Li provided to the soil by vegetation decay ($F_{\text{VEG}} = 18.7 \pm 1.2 \text{ g.yr}^{-1}$) (Figure 8). This flux is relatively high despite the fact that Li is not a plant nutrient and has no known physiological role. However Rousteau (2014) showed that the vegetation is at steady-state with respect to carbon, *i.e.*, the rate of carbon uptake is equal to the flux of carbon loss by vegetation. We hypothesize that the organic Li sub-cycle is also at steady state. As the $\delta^7\text{Li}$ of vegetation is similar to that of the soil solution, it appears that no fractionation occurs during Li uptake by vegetation. Thus, we conclude that the litter flux does not influence the Li mass balance at the watershed scale despite the flux of Li cycled through vegetation.

By combining the throughfall water flux (3079 mm over a surface of 8 ha) and its median Li concentration (7 nmol L^{-1}) we calculate the total flux of dissolved atmospheric Li of $12.1 \text{ g Li yr}^{-1}$ (or $1724 \text{ mmol Li.yr}^{-1}$) (Figure 8). At the watershed scale, the dissolved yield of Li is $1.5 \text{ g Li ha}^{-1} \text{ yr}^{-1}$. The Li atmospheric flux in the Quiock Creek catchment is twice the value measured in the volcanic Islands of La Réunion (Louvât et al., 1997) and of Azores Archipelago (Pogge von Strandmann et al., 2010) which are both characterized by lower precipitation rate. As 75% of the atmospheric flux to the Quiock Creek catchment comes from sea salts, the sea salt input is $F_{\text{SS}} = 9.1 \text{ g Li yr}^{-1}$ and the remaining dissolved Li, derived from leaching of the Saharan dust provides 3 g Li yr^{-1} (F_{SDdis}) (Figure 8). The flux of Saharan dust that reaches the catchment is estimated to be $100 \text{ kg ha}^{-1} \text{ yr}^{-1}$ (Molinié, personal communication). The Li concentration of the dust was measured as 18.5 ppm and thus Saharan dust provides $14.8 \text{ g Li yr}^{-1}$ (F_{SD}). Therefore, only a fifth of this flux ($F_{\text{SDd}} = 3 \text{ g Li.yr}^{-1}$) is dissolved in throughfall and the remainder reaches the soil in its solid form ($F_{\text{SDs}} = 11.8 \text{ g Li.yr}^{-1}$). Depending on whether the particulate Li will be dissolved once deposited, we can

estimate that the input of Li from the atmosphere to the Quiock Creek watershed is between 12.1 g Li yr⁻¹ (no dissolution of solid dust in the soil) to 23.9 g Li yr⁻¹ (total dissolution of dust).

As the Quiock Creek water flux is 1130 mm over a surface area of 8 ha and the mean Li concentration is 56 nmol L⁻¹, the dissolved Li flux at the outlet of the catchment is 5.1 mol Li yr⁻¹ or 35.7 g Li yr⁻¹ (F_{QC}). The atmosphere contributes between 34% (no dissolution of solid dust in the soil) and 67% (total dissolution of dust) of the Li exported, depending on the atmospheric flux considered. These values are higher than those reported by Lemarchand et al. (2010) and highlight the importance of Li atmospheric inputs in this environment.

5.3.2 Characterization of the weathering flux of Li

The calculated fluxes show that atmospheric inputs do not account for all of the Li exported. The weathering flux (F_{wea}) and its isotopic composition (δ⁷Li_{wea}) can be estimated using a box model based on two assumptions:

- The catchment is at steady-state, consequently the input flux of Li to the catchment is equal to the output Li flux and no Li is stored within the catchment.
- All the Li in this catchment is exported in a dissolved form. In other word, we neglect the export of Li by suspended matter which has never been observed even during flood events.

We consider two extreme scenarios in order to determine the lower and upper bounds for the weathering fluxes of Li and for the Li isotopic signature of the weathering flux.

In the first scenario, we assume that the fraction of Li from the atmospheric dust that was not dissolved during deposition (75% of the total dust input) can still contribute to an “internal” source of Li to the soil solution and creek compartments (Hypothesis 1):

$$F_{SS} + F_{SD} + F_{wea} = F_{QC} \quad (9)$$

$$F_{SS} \delta^7Li_{SS} + F_{SD} \delta^7Li_{SD} + F_{wea} \delta^7Li_{wea} = F_{QC} \delta^7Li_{QC} \quad (10)$$

Where $F_{SS} = 9.1 \text{ g Li yr}^{-1}$ and $F_{SD} = 14.8 \text{ g Li yr}^{-1}$ are the Li inputs fluxes of sea salt and of Saharan dust respectively. F_{QC} is the Li flux at the output of the catchment. $\delta^7\text{Li}_{SS}$, $\delta^7\text{Li}_{SD}$ and $\delta^7\text{Li}_{QC}$ are the Li isotopic signature of sea salts, Saharan dust and Quiock Creek respectively. The resultant Li weathering flux, F_{wea} is $11.8 \text{ g Li yr}^{-1}$ with an isotopic composition of 3.6‰.

In the second scenario we consider only the flux of dissolved Li that comes from the throughfall as atmospheric input (Hypothesis 2):

$$F_{TF} + F_{wea} = F_{QC} \quad (11)$$

$$F_{TF} \delta^7\text{Li}_{TF} + F_{wea} \delta^7\text{Li}_{wea} = F_{QC} \delta^7\text{Li}_{QC} \quad (12)$$

F_{TF} and $\delta^7\text{Li}_{TF}$ are the flux and isotopic signature of throughfall. Here the resulting weathering flux, F_{wea} of $23.6 \text{ g Li yr}^{-1}$ with an isotopic composition of 1.4‰.

This exercise shows that the weathering flux of Li constitutes between 33% (Hypothesis 2) and 66% (Hypothesis 1) of the Li exported at the outlet of the Quiock Creek catchment. The isotopic composition of this Li weathering flux varies between 1.4‰ (Hypotheses 2) and 3.6‰ (Hypotheses 1). These signatures are not necessarily the signature of the solid phase from which the Li originates. Indeed, the Li weathering flux (F_{wea}) is the combined result of the flux of Li released by dissolution (D) of the lithogenic source and the flux of precipitation (P) of Li-bearing secondary minerals (Figure 8). While dissolution does not fractionate Li isotopes, precipitation of Li-bearing secondary minerals is accompanied by a fractionation ($\Delta_{diss-sec}$). Thus we can write:

$$D - P = F_{wea} \quad (13)$$

$$D \delta^7\text{Li}_{LS} + P (\delta^7\text{Li}_{QC} - \Delta_{diss-sec}) = F_{wea} \delta^7\text{Li}_{wea} \quad (14)$$

Combining and rearranging these equations gives:

$$\delta^7\text{Li}_{LS} = ((F_{wea} \delta^7\text{Li}_{wea} - P (\delta^7\text{Li}_{QC} - \Delta_{diss-sec})) / (F_{wea} + P)) \quad (15)$$

623 In these equations $\delta^7\text{Li}_{\text{LS}}$ is the Li isotopic signature of the lithogenic source of dissolved Li
 624 and varies between -13.5‰ (the most negative soil Li signature) and 5‰ (fresh andesite),
 625 which are the endmember values of materials at the site that could provide Li by weathering.
 626 $\Delta_{\text{diss-sec}}$ is set at 20‰ consistently to $\Delta_{\text{diss-sec}}$ values reported for similar context (Kisakurek et
 627 al., 2004 ; Rudnick et al., 2004 ; Dellinger et al., 2015). These calculations show that if $P=0$
 628 (no precipitation of Li-bearing secondary minerals), then $\delta^7\text{Li}_{\text{LS}}$ is equal to $\delta^7\text{Li}_{\text{wea}}$. If $P>0$,
 629 $\delta^7\text{Li}_{\text{LS}}$ is necessarily lower than $\delta^7\text{Li}_{\text{wea}}$ regardless of which hypothesis is taken into account.
 630 As $\delta^7\text{Li}_{\text{wea}}$ is lower than the andesite value, in any case $\delta^7\text{Li}_{\text{LS}}$ is lower than the andesite
 631 signature. The only lithological source of Li with a signature lower than andesite in the soil is
 632 secondary minerals. This result thus indicates secondary mineral dissolution occurs in the
 633 Quiock Creek catchment. This process has already been described in Guadeloupe for major
 634 elements and Mg isotopes (Dessert et al., 2015).

635 The main secondary mineral on site is the kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) in which Li^+ in
 636 incorporated with Mg^+ , both replacing Al^{3+} (Tardy et al., 1972). The dissolution constant of
 637 kaolinite regarding Al is $10^{-17.2} \text{ mol}_{\text{Al}}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$ (Carroll et al., 1988). Considering $10 \text{ m}^2/\text{g}$ for the
 638 kaolinite specific surface, it corresponds to $10^{-4.7} \text{ mol}_{\text{Al}}\cdot\text{g}_{(\text{kaolinite})}^{-1}\cdot\text{an}^{-1}$. We make the
 639 approximation that the soil is mostly composed by kaolinite. With a Li/Al ratio of $2.6 \cdot 10^{-4}$
 640 measured on site, it leads to $5.2 \cdot 10^{-9} \text{ mol}_{\text{Li}}\cdot\text{g}_{(\text{kaolinite})}^{-1}\cdot\text{an}^{-1}$. At Quiock Creek (8 ha), it signifies
 641 that the soil can at least release $29 \text{ g}_{\text{Li}}/\text{yr}$ which is in very good agreement with the
 642 weathering Li flux measured on site (11.8 to $23.6 \text{ g}_{\text{Li}}/\text{an}$). This first order calculation supports
 643 the idea that secondary mineral dissolution occurs on Quiock Creek catchment, as shown by
 644 Li isotopes. Considering a mean weathering flux of $15 \text{ g}_{\text{Li}}\cdot\text{yr}^{-1}$, it would take 400 000 years to
 645 deplete all the Li of the 10 m deep soil (which contains $6000 \text{ kg}_{\text{Li}}\cdot\text{ha}^{-1}$).

646 As reported in Section 5.2, secondary minerals in the soil have incorporated Li derived from
 647 atmospheric inputs. Thus a primary part of the weathering flux comes from the atmosphere.
 648 This demonstrates that in a river draining highly weathered soils, even corrected for present-
 649 day atmospheric inputs, the weathering flux include elements of atmospheric origin.

Moreover it implies that processes involving Li isotopes cannot be simply envisaged as two step processes (dissolution of parent rock without fractionation and precipitation of secondary minerals with fractionation) but in some contexts it is important to integrate a third process which is the dissolution of secondary minerals.

5.3.3 Implication for the use of Li isotopes as weathering proxy

The Quiock Creek watershed, characterized by thick soils, low physical erosion rate and high chemical flux compared to physical erosion, is characteristic of a transport-limited context. In an earlier study, Huh et al. (2001) proposed that this context is characterized by low isotopic Li signature in the dissolved phase of rivers, as a consequence of equilibrium reactions between water and clays. On the contrary, in weathering-limited settings (characterized by thin soils and high physical erosion rate), Huh et al. (2001) proposed that dissolved load of river exhibit high $\delta^7\text{Li}$ as a result of kinetic reactions. Later studies have shown that, in the context of Iceland, the most weathering-limited context is associated with the lower $\delta^7\text{Li}$ (Pogge von Strandmann et al., 2006; Vigier et al., 2009). In the present study, we found particularly low Li isotopic signature associated with a transport-limited context. We explain this observation by secondary mineral dissolution, which produces low isotopic Li signature. The intermediate weathering regime, which is the most common context, leads to high $\delta^7\text{Li}$ values (up to 36.2‰ in the Azores (Pogge von Strandmann et al., 2010) and to 30‰ in the Columbia river basalt (Liu et al., 2015)). These observations in basaltic catchment, lead to a bell-curved relationship between weathering regime and $\delta^7\text{Li}$ signature of dissolved load, as proposed in Dellinger et al. (2015) for the Amazon Basin. In this bell-curved relationship, lower $\delta^7\text{Li}$ are associated with extremely high and low weathering intensity while higher $\delta^7\text{Li}$ are associated to intermediated weathering intensity (Dellinger et al., 2015).

Our study on the Quiock Creek catchment shows also that in a tropical context, despite the high influence of atmospheric inputs (rich in heavy isotopes), the river exhibits a very low $\delta^7\text{Li}$. This observation is consistent with the model proposed by Wanner et al. (2014)

676 suggesting influence of secondary mineral dissolution to explain the lower values of $\delta^7\text{Li}$ in
677 the Cenozoic seawater.

678 Conclusion

679 In the Quiock Creek catchment, a large range of $\delta^7\text{Li}$ values is observed despite the small
680 scale of observation. Li isotopic composition varies from -13.5‰ in the deepest bulk soil
681 sample to +26.4‰ in throughfall water samples. This large range is explained by several
682 water-rock interaction processes.

683 Li and major element concentrations and Li isotopic compositions of throughfall samples
684 attest that sea salts are not the only source of Li in throughfall. At the first order, Li in
685 throughfall results from a mixture of Li derived from sea salts and Li derived from the
686 leaching of Saharan dust which is the main atmospheric terrestrial dust source to
687 Guadeloupe. It is therefore essential to characterize these atmospheric inputs to close the
688 mass balance at all scales of this catchment study.

689 Silicate weathering is usually considered to be the main source of Li in rivers but in the
690 Quiock Creek, atmospheric inputs account for 34 to 67% of Li exported at the outlet of the
691 catchment. These observations can be explained by the high precipitation rate and the
692 location of Guadeloupe in the Saharan dust corridor. In addition, the very high cation-
693 depleted soils are likely to provide a smaller amount of Li in comparison to less weathered
694 soils. Our work reinforces the need to accurately characterize the Li isotopic signature of
695 atmospheric inputs.

696 Nd isotopes combined with mineralogy and mobile element concentrations in the soil argue
697 for a multi-layered soil profile which has been built by successive volcanoclastic episodes,
698 separated by periods of dust deposition. Li isotopes are not affected by the multi-step soil
699 formation but rather by weathering processes in the soil. The high variability of $\delta^7\text{Li}$ in the soil
700 combined with the invariant Li content and the absence of mineralogical variation along the
701 soil profile attest to the incorporation of atmospheric Li into the bulk soil. The Li isotopic

composition decreases from the top to the bottom of the profile where atmospheric influence is probably minimal. In the deeper part of the profile (610-1250 cm), the isotopic fractionation factor is estimated to be between 0.970 and 0.973, consistent with values reported in the literature. In the shallower part of the profile (15-610 cm), a batch equilibrium model suggests that theoretical solution (calculated as in equilibrium with the present-day solid phase) is more influenced by atmospheric inputs compared to present-day soil solutions (sampled on site). Our results indicate that atmospheric inputs have had a significant influence on the soil formation. However, present-day soil solutions are more influenced by lithogenic Li than atmospheric inputs, implying that a change in the weathering regime has occurred between the past formation of the soil and the present day.

Despite the fact that Li is not a nutrient, the passive Li flux through vegetation is important. As vegetation does not seem to fractionate Li isotopes, this sub-cycle has little influence on the Li budget at the catchment scale.

The Li mass balance at the catchment scale highlights the importance of secondary mineral phase dissolution to solute export. Thus, in this highly weathered catchment, andesite does not participate in the weathering Li flux to the Quiock Creek.

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1014 Figures captions:

1015 Figure 1: The Quiock Creek catchment (16°17'N, 61°7'0'W) in the National Park of
1016 Guadeloupe. SS : soil solutions, TF : throughfall and SF : stemflow. The soil profile was
1017 sampled during lysimeter installation. The rain gauge is located in a clearing on the roof of
1018 the “Maison de la forêt”.

1019 Figure 2: Cl concentrations ($\mu\text{mol L}^{-1}$) plotted as a function of Na concentrations ($\mu\text{mol L}^{-1}$) in
1020 rainwater samples (RF) collected on site (RF-MF) and at the OVSG (RF-OVSG), and in
1021 throughfall (TF) samples. The seawater dilution line (dashed) and the linear regression line
1022 (solid) between Na and Cl for throughfall samples are shown.

1023 Figure 3: Li/Cl molar ratios for throughfall, rainfall, Quiock Creek and soil solution samples.
1024 The dashed line represents the sea water Li/Cl ratio.

1025 Figure 4: Mass transfer coefficients (τ) for Li and major elements (a.) and Li/Na wt. ratios (b.)
1026 in soil samples as functions of depth relative to andesite. τ is calculated considering Ti to be
1027 immobile (Square for Li, black diamond for Mg, triangle for K, black point for Na and open
1028 diamonds for Ca). ϵNd (c.) of the bulk soil and quartz + feldspar content (d.) are also shown.

1029 Figure 5: Lithium isotopic compositions measured in all compartments of the Quiock Creek
1030 catchment. Error bars, smaller than 0.5‰, are contained in the data points.

1031 Figure 6: $\delta^7\text{Li}$ plotted as a function of the Li/Na molar ratio in throughfall and stemflow
1032 samples. The star represents the sea salt signature. Andesite and Saharan dust signatures
1033 are also shown. 6b: Li isotopic compositions plotted as a function of the proportion of Li
1034 coming from marine sea salts in throughfalls samples. The sea water isotopic composition is
1035 also shown.

1036 Figure 7: Li isotopic composition of soil samples as a function of τ_{Li} . Straight lines represent
1037 the evolution of $\delta^7\text{Li}$ vs τ_{Li} predicted by the batch equilibrium model. The depth for each soil
1038 sample is indicated.

1039 Figure 8: Fluxes of Li and Li isotopic compositions of compartments in the Quiock Creek
1040 catchment. Fluxes, indicated in italics, were measured on site. Sea salt flux (F_{ss}) and flux of
1041 Saharan dust dissolved in throughfall (F_{SDd}) were calculated from the chemical composition
1042 of throughfall (Section 5.1). The Saharan dust flux that reaches the soil in the solid phase
1043 (F_{SDs}) is also calculated in Section 5.1. Fluxes in red are computed with a steady state box
1044 model in Section 5.3. $\delta^7\text{Li}_{\text{wea}}$ is the isotopic signature of the weathering flux (F_{wea}). The
1045 weathering flux can be divided in two fluxes: the dissolution Li flux (D) of the lithogenic
1046 source of Li ($\delta^7\text{Li}_{\text{LS}}$) and the precipitation flux (P) which is accompanied by fractionation (Δ).

1047

Figure1

Figure2

Figure3

Figure 4

Figure5

Figure6

a.

b.

Figure 7

Figure8

Table 1: Cation, anion and Li concentrations and Li isotopic compositions of throughfall, stemflow, Quiock Creek and soil solution.

Sample name	Date	T	C	pH	Cl	Na	Si	K	HCO ₃	Mg	SO ₄	Ca	NO ₃	Li	δ ⁷ Li
		°C	μS		μmol/L	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L	nmol/L	‰
<i>Throughfalls</i>															
TF collector n°1	10/08/2012			6.1	92	81	43	31	nd ¹	13	16	15.0	2	4	17.5
TF collector n°1	03/04/2013			nd	168	155	< ²	26	nd	19	15	14.5	<	8	26.4
TF collector n°3	03/04/2013			nd	158	154	<	27	nd	18	15	14.1	<	7	26.3
TF collector n°1	25/06/2013			5.6	132	117	36	32	nd	17	16	16.9	<	11	19.2
<i>Stemflow</i>															
SF tree n°1	14/11/2011			nd	nd	316	nd	167	nd	106	17	143.6	<	29	19.6
SF tree n°2	18/11/2011			nd	nd	235	nd	131	nd	63	33	104.5	5	31	11.2
SF tree n°1	09/04/2012			3.6	nd	347	69	172	nd	103	24	149.0	<	66	11.9
<i>Quiock Rill</i>															
QC 1	23/04/2012	nd	nd	nd	229	184	109	6	37	25	15	10.5	<	42	9.3
QC 2	21/03/2013	22.6	43	4.8	274	211	112	3	28	32	13	14.9	<	45	7.9
QC 3	03/04/2013	22.6	39	4.6	249	217	112	5	34	28	15	12.1	<	38	8.3
QC 4	25/06/2013	24.2	38	nd	246	185	130	5	39	27	13	10.9	<	nd	8.0
<i>Soil solution³</i>															
GBD2 30	26/10/2012			4.8	169	166	nd	3.2	nd	26	15	1.4	5	57	4.6
GBD2 61	26/10/2012			4.8	164	147	nd	5.1	nd	31	19	10.7	26	53	8.7
GBD2 457	26/10/2012			4.5	168	194	nd	3.7	nd	14	13	1.9	<	68	8.9
GBD2 15	28/06/2013			nd	130	118	nd	1.6	nd	21	12	1.9	25	nd	7.3
GBD2 30	28/06/2013			5.4	150	147	nd	2.2	44	27	18	1.4	5	nd	6.4
GBD2 91	28/06/2013			5.3	207	194	nd	1.6	43	25	12	3.1	15	47	4.3
GBD2 457	28/06/2013			nd	165	153	nd	2.3	53	14	12	1.2	<	75	7.7
GBD2 823	28/06/2013			nd	242	204	nd	12.7	nd	14	15	0.6	<	79	4.9

¹ nd = not determined
² < = below detection (1.6 μmol L⁻¹ for nitrates)
³ For soil solution sample names GBD2 X, X = depth in cm.

Table 2: Major, Li and Ti concentrations and Li isotopic (‰) compositions of soil, andesite, dust and vegetation samples.

	Al	Fe	Mg	K	Na	Ca	Ti ¹	Li ²	$\delta^7\text{Li}$	ϵNd
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	‰	
<i>Soil</i>										
GBD2_15	127354	96625	1977	1087	681	306	8573	11	2.7	-8.39
GBD2_30	103613	76592	1339	643	404	147	8873	8	3.9	
GBD2_61	155323	108098	1189	356	356	45	7913	7	2.8	-2.35
GBD2_91		90709	1207	455	295	43	6894	8		
GBD2_122		102804	1391	236	341	32	5336	5		
GBD2_152		102783	1564	292	452	51		6		
GBD2_183	153174	96955	1287	174	444	41	7674	6	1.5	1.92
GBD2_213		71214	1062	184	302	31	7374	5		
GBD2_244		85988	1326	226	347	51	7314	6		
GBD2_274	152976	79742	1043	249	248	28	7374	6	3.7	
GBD2_305	146994	106781	1499	1026	353	47	8033	15	3.0	-6.70
GBD2_366		92165	1068	194	344	35	8153	7		
GBD2_488	171413	116157	1262	615	158	28	10132	11	0.6	
GBD2_549	116900	80691	1041	164	209	26		7		
GBD2_610	162376	99738	1419	326	264	34	7314	7	0.6	
GBD2_671		58583	1041	491	309	42	6175	8		
GBD2_732	223894	80125	825	317	160	36	6834	5	-2.2	2.71
GBD2_792	161720	64526	880	621	278	43	5096	7	-4.1	
GBD2_853		80504	954	409	272	36	6654	6		
GBD2_914	162935	97945	1196	321	339	29	7074	6	-8.9	
GBD2_975	137066	93726	949	177	423	36	7374	5		
GBD2_1036		84111	1234	258	347	48	6714	5	-12.5	
GBD2_1097	159502	97153	946	242	291	23	5995	5	-13.5	2.44
GBD2_1158	146488	152338	1341	215	324	41	9052	9	-10.8	
GBD2_1219	135472	100878	1612	1276	277	78	7674	17	-8.8	
GBD2_1250	143788	100181	1312	971	215	60	8273	12	-10.5	
<i>Andesite</i>										
04GW12	95806	52600	9060	7308	27328	48462	5373	12	5.3	3-5 ³
<i>Montserrat dust</i>										
DMS 2010	84241	40537	15107	9406	26261	41158	3136	13	4.7	
<i>Saharan dust</i>										
SD 1	46151	23727	5355	5474	951	1747		20	-0.7	-10/-14 ⁴
SD 2	39693	20216	5059	5134	930	1918		17	-0.7	
<i>Vegetation</i>										
Root	464	252	1645	2839	2331	7284		345	4.3	

Branch	362	191	1728	4353	1921	11600	198	3.6
Litter 1	174	130	1930	2246	1828	10165	324	8.7
Litter 2	233	146	1960	2302	1857	10237	232	7.6
Litter 3	19606	328	5435	5106	2933	9993	413	7.4

¹ Ti concentrations in soil samples are from Buss et al. (2010).

² Li concentrations in vegetation given in ppb.

³ Nd signature from White and Dupré (1986).

⁴ Nd signature from Grousset et al. (1992).

Table 1S: ICP AES (for major elements) and ICP MS (for Li and Zr) analyses of rock and vegetation standard reference materials.

	Al	Ca	Fe	K	Mg	Na	Li
	ppm	ppm	ppm	ppm	ppm	ppm	ppm
<i>Rock standards</i>							
BEN certif ¹	53312	99071	8988	11534	789	23594	13
BEN (this study)	54289	99897	90935	11739	79269	23846	15
	5214	95138	89888	11397	76588	23325	
GSN certif ¹	77665	17857	2625	38419	138	27971	55
GSN (this study)	77987	17562	25798	35813	13629	26838	54.6
	77673	17467	25594	35454	136	26723	56.1
	80519	17834	26123	37214	1377	27587	50.9
BCR-2 certif ²	71471	50857	966	14853	2154	23445	9
BCR-2 (this study)	72353	50762	93866	13885	21555	22619	9.96
BHVO-2 certif ²	71471	81429	8638	4315	4338	16471	5
BHVO-2 (this study)	7056	7895	8321	3957	42096	15813	5.1
	73674	82099	87389	4184	44552	16492	4.4
JB-2 certif ³	77267	70683	100299	3487	28103	1506	8
JB-2 (this study)	77245	70136	95777	3058	2739	14046	8.9
							7.9
<i>Vegetation standard</i>							
NIST_SRM 1515 (certif)	286	15260	83	16000	2700	24	
NIST_SRM 1515 (this study)	283	14441	69	15216	2421	55	305 ⁴
	290	14349	73	15544	2478	57	
	283	14872	75	16102	2662	42	
	286	15014	76	16307	2682	42	

¹ Recommended values of GSN, BEN are taken from CRPG certificate of analyse (<http://helium.crpq.cnrs-nancy.fr/SARM/pages/geostandards.html#>).

² Recommended values of BHVO-2 and BCR-2 are taken from USGS certificate of analyses (http://crustal.usgs.gov/geochemical_reference_standards/).

³ JB2 is a GSJ (Geological Survey of Japan) reference rock standards (http://georem.mpch-mainz.gwdg.de/sample_query.asp).

⁴ Vegetation Li concentration in ppb

Table 3S: Cation, anion and Li concentrations of throughfall, stemflow, Quiock Creek (QC) and soil solution (GBD2_L) samples.

Sample name	Date	T	C	pH	Na	Cl	Si	K	Ca	Mg	Alc	SO ₄	NO ₃	Li
		°C			μmol/L	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L	nmol/L
<i>Throughfall</i>														
TF collector n°1	14/11/2011	nd ¹	nd	nd	213	nd	nd	108	28	32	nd	nd	nd	20
TF collector n°2	14/11/2011	nd	nd	nd	177	nd	nd	50	30	29	nd	nd	nd	16
TF collector n°1	21/11/2011	nd	nd	5.49	21	23	nd	11	5	4	nd	7.5	4.6	3
TF collector n°3	21/11/2011	nd	nd	5.8	71	78	nd	34	8	8	nd	13.0	8.0	5
TF collector n°1	25/11/2011	nd	nd	nd	36	nd	nd	26	8	7	nd	nd	nd	6
TF collector n°2	25/11/2011	nd	nd	nd	26	nd	nd	22	8	5	nd	nd	nd	3
TF collector n°3	25/11/2011	nd	nd	nd	57	nd	nd	35	8	6	nd	nd	nd	4
TF collector n°1	09/04/2012	nd	nd	nd	124	nd	36	61	23	23	nd	nd	nd	3
TF collector n°2	09/04/2012	nd	nd	nd	124	nd	31	62	26	23	nd	nd	nd	13
TF collector n°3	09/04/2012	nd	nd	nd	125	nd	nd	42	16	17	nd	nd	nd	11
TF collector n°1	13/04/2012	nd	nd	nd		nd	42	94	35	40	nd	nd	nd	20
TF collector n°2	13/04/2012	nd	nd	nd		nd	39	68	34	31	nd	nd	nd	16
TF collector n°3	13/04/2012	nd	nd	nd	180	204	47	68	33	29	nd	21.9	<	16
TF collector n°2	16/04/2012	nd	nd	nd	100	119	15	30	14	13	nd	13	<	9
TF collector n°3	16/04/2012	nd	nd	nd		107	15				nd	13	<	7
TF collector n°1	19/04/2012	nd	nd	nd	199	nd	32	57	29	29	nd	nd	nd	13
TF collector n°2	19/04/2012	nd	nd	nd	215	nd	27	52	30	35	nd	nd	nd	13
TF collector n°3	19/04/2012	nd	nd	nd	254	nd	38	47	25	35	nd	nd	nd	13
TF collector n°1	23/04/2012	nd	nd	nd	17	nd	8	17	5	4	nd	nd	nd	3
TF collector n°2	23/04/2012	nd	nd	nd	19	nd	36	14	5	4	nd	nd	nd	3
TF collector n°3	23/04/2012	nd	nd	nd	25	nd	7	10	3	3	nd	nd	nd	3
TF collector n°1	05/08/2012	nd	nd	6.02	83	93	35	33	8	10	nd	12.3	<	5
TF collector n°2	05/08/2012	nd	nd	5.96	72	84	34	21	10	9	nd	9.5	<	<
TF collector n°3	05/08/2012	nd	nd	6.18	89	89	49	22	11	9	nd	11.5	<	<
TF collector n°1	10/08/2012	nd	nd	6.08	81	92	43	31	15	13	nd	15.5	1.6	4
TF collector n°2	10/08/2012	nd	nd	6.33	74	88	47	30	18	14	nd	13.7	1.2	4
TF collector n°3	10/08/2012	nd	nd	5.65	104	94	73	31	31	17	nd	16.6	5.1	4
TF collector n°1	16/08/2012	nd	nd	6.05	196	224	44	41	25	25	nd	28.3	4.4	13
TF collector n°2	16/08/2012	nd	nd	6.29	238	259	67	56	30	28	nd	28.1	<	18
TF collector n°3	16/08/2012	nd	nd	6.19	264	264	81	57	36	32	nd	29.4	6.7	17
TF collector n°1	21/03/2013	nd	nd	5.74	71	67	< ²	16	5	7	nd	7.6	<	4
TF collector n°3	21/03/2013	nd	nd	5.6	71	64	<	13	6	7	nd	8.1	<	<
TF collector n°1	25/03/2013	nd	nd	nd	nd	nd	34	nd	nd	nd	nd	nd	nd	13
TF collector n°3	25/03/2013	nd	nd	5.76	152	150	48	62	19	20	nd	18.6	<	9
TF collector n°1	27/03/2013	nd	nd	5.09	177	211	44	78	24	28	nd	17.2	<	<
TF collector n°3	27/03/2013	nd	nd	nd	193	182	66	52	21	23	nd	20.3	<	<
TF collector n°1	29/03/2013	nd	nd	5.73	167	190	31	70	25	27	nd	25.0	<	<
TF collector n°3	29/03/2013	nd	nd	5.75	196	178	55	52	20	23	nd	28.0	<	<
TF collector n°1	01/04/2013	nd	nd	5.5	43	44	<	16	6	6	nd	6.8	<	2
TF collector n°3	01/04/2013	nd	nd	5.49	48	42	<	18	6	6	nd	7.7	<	2
TF collector n°1	03/04/2013	nd	nd	nd	155	168	<	26	14	19	nd	15.1	<	8

TF collector n°3	03/04/2013	nd	nd	nd	154	158	<	27	14	18	nd	15.1	<	7
TF collector n°1	25/06/2013	nd	nd	5.58	117	132	36	32	17	17	nd	15.5	<	11
TF collector n°3	25/06/2013	nd	nd	5.63	164	177	<	43	21	26	nd	21.5	<	13
TF collector n°1	26/06/2013	nd	nd	5.94	83	99	<	23	11	12	nd	9.9	<	6
TF collector n°3	26/06/2013	nd	nd	5.83	91	99	750	21	12	11	nd	10.3	<	4
TF collector n°1	28/06/2013	nd	nd	5.74	66	74	<	16	11	11	nd	9.5	<	5
<i>Stemflow</i>														
SF tree n°1	14/11/2011	nd	nd	nd	316	pol	nd	167	144	106	nd	17.5	<	29
SF tree n°2	18/11/2011	nd	nd	nd	235	pol	nd	131	104	63	nd	33.5	4.6	31
SF tree n°1	09/04/2012	nd	nd	3.55	347	pol	69	172	149	103	nd	23.8	<	66
<i>Rainfall</i>														
RF-MF 1	09/04/2012	nd	22.59	5.3	69	86	nd	3	8	8	nd	10	<	<
RF-MF 2	13/04/2012	nd	nd	nd	137	167	nd	5	10	17	nd	15	<	<
RF-MF 3	16/04/2012	nd	nd	4.93	87	110	nd	3	4	11	nd	11	<	<
RF-MF 4	19/04/2012	nd	nd	nd	165	nd	nd	6	11	22	nd		nd	9
RF-MF 5	23/04/2012	nd	nd	nd	69	73	nd	1	1	1	nd	8	<	<
RF-MF 6	03/08/2012	nd	nd	4.93	65	55	nd	3	15	10	nd	4	<	6
RF-MF 7	10/08/2012	nd	nd	5.65	48	54	nd	1	15	10	nd	6	<	<
RF-OVSG 1	20/03/2013	nd	nd	4.77	82	85	nd	3	2	10	nd	7.4	<	4
RF-OVSG 2	21/03/2013	nd	nd	4.51	71	75	nd	4	4	10	nd	8.0	<	<
RF-OVSG 3	27/03/2013	nd	nd	nd	127	133	nd	5	7	16	nd	12.1	<	<
RF-OVSG 4	31/03/2013	nd	nd	4.69	41	49	nd	2	3	5	nd	5.8	4.2	<
RF-OVSG 5	01/04/2013	nd	nd	4.09	121	131	nd	4	4	15	nd	10.9	3.0	<
RF-OVSG 6	04/04/2013	nd	nd	5.14	76	88	nd	9	7	13	nd	7.4	<	4
<i>Quiock Creek</i>														
QC	21/06/2011	25	nd	5.67	261	nd	nd	5	10	29	27.2	nd	<	nd
QC	08/07/2011	24.1	34.3	5.51	2016	nd	nd	7	13	24	25.2	nd	<	nd
QC	19/08/2011	24.1	38	5.3	213	nd	nd	6	12	25	28.4	nd	<	nd
QC	16/09/2011	24.1	nd	4.65	247	nd	nd	4	9	28	26.9	nd	<	nd
QC	14/10/2011	23.8	29	5.5	241	nd	nd	4	10	28	28.4	nd	<	68
QC	08/11/2011	23.9	22.49	4.85	226	nd	nd	5	10	26	67.5	nd	<	nd
QC	08/11/2011	24	33.3	4.98	227	nd	nd	5	10	26	73.8	nd	1.8	nd
QC	09/11/2011	24.1	31	5.45	234	nd	nd	5	10	27	43.1	nd	1.5	nd
QC	09/11/2011	nd	nd	nd	237	nd	nd	4	10	27	nd	nd	1.6	nd
QC	10/11/2011	23.5	31.5	5.48	212	nd	nd	5	10	25	49.3	nd	1.8	41
QC	10/11/2011	23.8	31.4	5.55	222	nd	nd	5	10	26	88.2	nd	1.6	nd
QC	11/11/2011	23.8	33.8	5.3	235	nd	nd	4	10	28	48.9	nd	1.6	nd
QC	12/11/2011	23.4	36.5	5.38	239	nd	nd	4	9	28	44.4	nd	1.8	nd
QC	14/11/2011	23.3	31.7	5.38	244	nd	nd	4	9	28	44.8	nd	1.5	nd
QC	15/11/2011	23.3	34.1	5.13	246	nd	nd	4	9	29	33.4	nd	1.6	nd
QC	16/11/2011	23	53.6	5.3	244	nd	nd	4	9	29	26.2	nd	1.9	nd
QC	18/11/2011	23.3	33.3	5.38	249	nd	nd	7	11	29	13.8	nd	1.5	nd
QC	21/11/2011	21.8	32.4	5.35	207	nd	nd	4	9	30	12.5	nd	1.9	nd
QC	23/11/2011	23.2	33.4	5.56	247	nd	nd	4	8	29	23.4	nd	1.6	48
QC	09/12/2011	23	68.2	5.56	218	nd	nd	4	9	27	nd	nd	<	59
QC	06/01/2012	22.5	32.5	4.95	233	nd	135	5	9	29	26.6	nd	1.6	63

QC	03/02/2012	21.6	38	5.15	239	nd	152	5	8	30	nd	nd	1.8	72
QC	16/03/2012	21.6	49.8	4.75	254	nd	148	7	10	31	7.2	nd	<	72
QC	04/04/2012	22.8	nd	nd	245	298	162	6	9	28	40.5	12.1	<	62
QC	09/04/2012	22.3	48.1	5.2	218	282	149	8	10	29	34.1	14.0	<	60
QC	13/04/2012	23	45.9	5.31	258	298	142	9	10	30	nd	13.0	<	62
QC	19/04/2012	22.5	42.7	5.49	199	nd	nd	7	14	31	29.7	nd	6.1	47
QC	23/04/2012	nd	nd	nd	184	229	109	6	11	25	37.0	15.5	<	42
QC	26/04/2012	23.7	42.5	5.22	220	nd	nd	6	10	26	38.0	nd	3.4	55
QC	08/06/2012	23.8	51	5.54	262	nd	nd	4	8	30	37.0	nd	1.8	61
QC	03/08/2012	24.3	45	nd	248	271	303	5	9	29	41.6	13.5	<	54
QC	05/08/2012	24.9	25.8	5.12	234	257	278	5	10	27	nd	13.2	<	50
QC	10/08/2012	24.2	46.1	5.9	237	253	268	5	9	28	30.7	13.3	<	54
QC	16/08/2012	24.3	47.4	5.2	253	275	300	5	8	29	34.4	13.1	<	60
QC	07/09/2012	23.7	30.9	4.34	264	nd	nd	3	7	30	31.1	nd	1.6	65
QC	05/10/2012	23.8	38.6	4.63	243	nd	nd	4	8	28	9.2	nd	1.6	56
QC	23/10/2012	23.6	40.3	4.9	250	269	300	5	10	29	36.4	12.4	<	59
QC	26/10/2012	24	40	4.65	254	271	304	4	8	30	23.3	11.8	<	60
QC	30/11/2012	23.4	41.8	5.03	263	nd	nd	12	9	30	8.0	nd	<	63
QC	14/12/2012	22.3	44.7	4.92	264	nd	nd	6	9	31	43.3	nd	<	60
QC	18/01/2013	nd	nd	5.06	269	nd	nd	6	9	32	33.6	nd	<	62
QC	01/02/2013	21.9	30.6	5.23	264	nd	152	8	10	32	28.4	nd	<	58
QC	01/03/2013	21.1	51.3	5.45	258	nd	177	5	10	32	9.2	nd	<	71
QC	20/03/2013	22.1	49	5.22	282	315	151	10	13	35	24.4	13.8	<	59
QC	21/03/2013	22.6	43	4.78	211	274	112	3	15	32	27.5	12.9	<	45
QC	25/03/2013	23.3	44	4.92	258	283	167	7	11	30	13.4	12.9	<	57
QC	26/03/2013	nd	nd	nd	208	nd	nd	4	11	29	nd	nd	<	nd
QC	27/03/2013	nd	nd	5.26	251	276	161	7	11	30	24.8	12.1	<	nd
QC	29/03/2013	23	43	5.32	250	279	153	8	11	30	23.9	14.5	<	49
QC	01/04/2013	22.2	40	4.57	224	263	129	5	12	28	17.2	12.9	<	40
QC	03/04/2013	22.6	39	4.6	217	249	112	5	12	28	33.6	14.7	<	38
QC	24/05/2013	23.4	38.8	5.29	203	265	145	3	9	28	31.1	11.9	<	nd
QC	21/06/2013	23.9	43	nd	209	288	148	3	10	30	40.0	11.3	<	59
QC	25/06/2013	24.2	38	nd	185	246	130	5	11	27	39.2	12.7	<	nd
QC	26/06/2013	23.9	39.4	5.1	189	260	133	3	11	28	65.6	12.1	<	47
QC	28/06/2013	24	40.5	5.17	200	275	144	3	9	30	29.7	11.7	<	52
QC	02/07/2013	23.6	40.3	5.27	202	277	147	3	10	30	11.1	11.6	<	51

Soil solution³

GBD2 15 L	08/07/2011	nd	nd	4.82	117	103	nd	3.8	2.85	21	nd	20.3	27.4	52
GBD2 61 L	08/07/2011	nd	nd	4.79	131	135	nd	3.5	8.63	28	nd	31.0	6.8	41
GBD2 91 L	08/07/2011	nd	nd	4.93	245	241	nd	4.3	4.46	28	nd	14.3	31.9	98
GBD2 457 L	08/07/2011	nd	nd	4.83	204	205	nd	3.7	0.25	11	nd	11.4	<	95
GBD2 823 L	08/07/2011	nd	nd	4.68	252	259	nd	14.0	0.88	13	nd	16.8	<	78
GBD2 30 L	16/03/2012	nd	nd	5.2	170	143	nd	14.1	4.68	29	nd	18.8	5.3	nd
GBD2 61 L	16/03/2012	nd	nd	4.64	125	149	nd	5.9	13.63	32	nd	26.6	16.6	nd
GBD2 91 L	16/03/2012	nd	nd	4.99	237	229	nd	3.6	3.09	22	nd	15.0	20.3	121
GBD2 457 L	16/03/2012	nd	nd	5.28	266	197	nd	38.8	6.65	16	nd	19.1	<	112

GBD2 823 L	16/03/2012	nd	nd	4.88	243	256	nd	13.8	1.93	17	nd	18.0	<	105
GBD2 91 L	26/04/2012	nd	nd	5.16	216	230	nd	3.5	4.01	26	nd	12.7	17.3	59
GBD2 457 L	26/04/2012	nd	nd	4.88	188	182	nd	6.0	3.62	15	nd	16.5	<	101
GBD2 823 L	26/04/2012	nd	nd	4.61	211	252	nd	14.1	1.94	17	nd	15.3	<	116
GBD2 15 L	08/06/2012	nd	nd	4.96	112	124	nd	4.2	3.29	25	nd	14.1	19.8	56
GBD2 91 L	08/06/2012	nd	nd	5.02	228	232	nd	3.2	3.88	26	nd	12.6	17.4	70
GBD2 457 L	08/06/2012	nd	nd	5.09	184	182	nd	4.8	2.93	14	nd	15.8	<	95
GBD2 823 L	08/06/2012	nd	nd	4.78	211	247	nd	13.9	4.42	15	nd	15.0	<	108
GBD2 15 L	05/10/2012	nd	nd	4.82	129	101	nd	4.1	2.50	23	nd	10.5	72.9	62
GBD2 30 L	05/10/2012	nd	nd	4.49	182	213	nd	5.4	2.24	28	nd	13.3	7.6	79
GBD2 91 L	05/10/2012	nd	nd	4.49	243	237	nd	4.3	3.36	23	nd	11.0	26.5	89
GBD2 457 L	05/10/2012	nd	nd	4.4	195	176	nd	4.9	1.99	14	nd	14.3	<	nd
GBD2 823 L	05/10/2012	nd	nd	5	244	257	nd	16.7	0.40	14	nd	16.1	<	97
GBD2 15 L	26/10/2012	nd	nd	4.57	112	85	nd	1.8	1.49	17	nd	13.0	33.1	48
GBD2 30 L	26/10/2012	nd	nd	4.75	166	169	nd	3.2	1.45	26	nd	14.8	5.0	57
GBD2 61 L	26/10/2012	nd	nd	4.49	147	164	nd	5.1	10.72	31	nd	19.5	25.8	53
GBD2 91 L	26/10/2012	nd	nd	5.14	226	211	nd	2.8	2.74	21	nd	11.0	17.4	63
GBD2 457 L	26/10/2012	nd	nd	4.46	194	168	nd	3.7	1.86	14	nd	13.2	<	68
GBD2 91 L	21/06/2013	nd	nd	nd	173	182	nd	1.9	2.53	21	57.5	11.6	<	49
GBD2 457 L	21/06/2013	nd	nd	nd	153	165	nd	2.3	1.20	14	52.8	11.7	<	75
GBD2 823 L	21/06/2013	nd	nd	nd	204	242	nd	12.7	0.65	14	nd	15.3	<	79
GBD2 15 L	28/06/2013	nd	nd	nd	118	130	nd	1.6	1.85	21	nd	12.4	25.0	nd
GBD2 30 L	28/06/2013	nd	nd	5.35	147	150	nd	2.2	1.36	27	43.9	17.5	5.5	nd
GBD2 91 L	28/06/2013	nd	nd	5.28	194	207	nd	1.6	3.13	25	43.3	11.8	15.3	47
GBD2 457 L	28/06/2013	nd	nd	5.41	159	167	nd	2.9	1.52	14	38.0	12.1	2.6	71
GBD2 823 L	28/06/2013	nd	nd	nd	210	243	nd	13.4	0.97	15	29.7	15.6	<	76

¹ nd = not determined

² < = below detection (1.6 $\mu\text{mol L}^{-1}$ for nitrates)

³ For soil solution sample names GBD2 X, X = depth in cm.