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# 1 The response of Li and Mg isotopes to rain 2 events in a highly-weathered catchment

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## 12 **ABSTRACT**

13 Storms are responsible for up to ~50 % of total annual rainfall on tropical islands and result in rapid  
14 increases in discharge from rivers. Storm events are, however, notoriously under-sampled and their  
15 effects on weathering rates and processes are poorly constrained. To address this, we have  
16 undertaken high-frequency sampling of Quiock Creek catchment, a Critical Zone Observatory  
17 located in Guadeloupe, over a period of 21 days, encompassing several storm events. Chemical and  
18 isotopic (Li and Mg) analyses of different critical zone reservoirs (throughfall, soil pore water,  
19 groundwater and river water) were used to assess the interactions between rock, water and  
20 secondary minerals. The Li concentrations and  $\delta^7\text{Li}$  values of these different reservoirs range from  
21 14 to 95 nmol/kg and 1.8 to 16.8‰, respectively. After several rain events, the average  $\delta^7\text{Li}$  value  
22 (13.3‰) of soil solutions from the lower part of the soil profile (> ~150 cm below the surface) was  
23 unchanged, whereas in the upper part of the profile  $\delta^7\text{Li}$  values increased by ~2 - 4‰ due to  
24 increased contribution from throughfall. By contrast, the  $\delta^{26}\text{Mg}$  value of soil waters in the upper  
25 part of the soil profile were not significantly affected by the rain events with an average value of -  
26 0.90‰. The  $\delta^{26}\text{Mg}$  values of the different fluid reservoirs were generally close to the value of  
27 throughfall (~ -0.90‰), but higher  $\delta^{26}\text{Mg}$  values (up to -0.58‰) were measured in the deeper parts

28 of the soil profile, whereas groundwaters that have a long residence time had lower  $\delta^{26}\text{Mg}$  values  
29 (down to  $-1.48\text{‰}$ ). These higher and lower values are attributed to, respectively,  
30 adsorption/desorption of light Mg isotopes on/from the surface of clay minerals. The  $\delta^7\text{Li}$  value of  
31 the river waters was  $\sim 9.3\text{‰}$ , with a Li concentration of  $60\ \mu\text{mol/kg}$ , but during a storm these values  
32 decreased to, respectively,  $7.8\text{‰}$  and  $40\ \mu\text{mol/kg}$ . This change in  $\delta^7\text{Li}$  is consistent with an increased  
33 contribution of Li from the soil solution. Thus, even in highly weathered catchments, changes in  
34 hydrological conditions can have a significant impact on weathering processes and therefore the  
35 composition of river waters delivered to the ocean.

36

### 37 **KEYWORDS**

38 **Lithium isotopes; Magnesium isotopes; Tropical rivers; Weathering ; Critical Zone; Hydrology**

### 39 **HIGHLIGHTS**

- 40 • **Series of rain events reduces the  $\delta^7\text{Li}$  value of river waters in a tropical catchment**
- 41 • **Mg isotope composition of soil solutions is controlled by adsorption and desorption**  
42 **processes.**
- 43 • **Storm events have little effect on  $\delta^{26}\text{Mg}$  values because most of the Mg in the studied**  
44 **catchment is supplied by throughfall.**

45

46

## 47 **1. Introduction**

48 Weathering processes drive soil and landscape formation, soil nutrient cycling and control the  
49 delivery of chemical elements from the continents to the oceans (Gaillardet et al., 1999; Millot et  
50 al., 2002). The chemical composition of water compartments in the critical zone is also strongly  
51 influenced by hydrology (Maher, 2011); in some rivers element concentrations do not vary with  
52 discharge, so elemental fluxes are determined primarily by the water flux, whereas in other rivers,  
53 element concentrations decrease with increasing discharge indicating that dilution is the principal  
54 control and elemental fluxes remain constant (Godsey et al., 2009). Concentration-discharge  
55 relationships are controlled by various parameters, including: water saturation in the soil (Godsey  
56 et al., 2009); the interplay between fluid residence time, the thermodynamics and kinetics of water-  
57 rock interactions (Maher, 2011); exchange reactions (Clow and Mast, 2010); and mixing between  
58 different subsurface or surface water bodies (Calmels et al., 2011) (Bouchez et al., 2017). During  
59 extreme hydrological events such as storms, chemical weathering fluxes are likely to be highly  
60 dependent on changes in water residence time (Benettin et al., 2017), as well as on the mobilization  
61 of “old pockets” of subsurface/deep water that has a distinct chemical composition linked to its  
62 long residence time. However, even in small, relatively homogeneous catchments, sampling of  
63 rivers (e.g. weekly or monthly) provides only a snapshot of the water-rock interactions. Storm  
64 events are often undersampled although they can contribute up to 50% of the total annual water  
65 export over very short periods of time (Larsen and Simon, 1993). In areas where the hydrological  
66 cycle is highly variable, high-frequency sampling is thus needed to fully evaluate weathering fluxes  
67 and gain better insight into weathering processes and their relationship with catchment hydrology  
68 (Wohl et al., 2012; Flourey et al., 2017).

69 Isotopic tracers that are sensitive to chemical weathering processes can be used to help understand  
70 the controls on concentration-discharge relationships. Many studies have highlighted the potential  
71 of lithium (Li) and magnesium (Mg) isotopes for characterising the variety of weathering processes  
72 that occur in the natural environment (Teng et al., 2010; Pogge von Strandmann et al., 2012; Tipper  
73 et al., 2012). These isotope systems provide insight as to plant uptake (Bolou-Bi et al., 2012) and  
74 sources of dissolved solutes (Kisakurek et al., 2005; Weynell et al., 2017), as well as the importance

75 of mineral (trans)formations (Ryu et al., 2014; Ma et al., 2015). Li and Mg isotopes are also  
76 fractionated during the formation of secondary minerals (Opfergelt et al., 2012; Henchiri et al.,  
77 2014; Trostle et al., 2014; Clergue et al., 2015; Dellinger et al., 2015; Dessert et al., 2015; Henchiri  
78 et al., 2016; Chapela Lara et al., 2017) and are thus well suited for tracing water-rock interactions  
79 in weathering systems. Here, we investigate the Li and Mg isotope composition of fluids from a  
80 small catchment in Guadeloupe (Quiock Creek) during a stormy period of one month. Throughfall,  
81 soil solution, river waters and groundwater were sampled to assess the effects of hydrological  
82 changes on Li and Mg isotopes.

## 83 **2. Site description**

84 Quiock Creek catchment (16°17'N, 61°70'W) is located on Basse-Terre Island, the volcanic part of  
85 the Guadeloupe archipelago in the French West Indies (Figure A1), and covers an area of ~8  
86 hectares. The catchment is a Critical Zone Observatory (CZO), part of the Observatoire de l'Eau et  
87 de l'érosion aux Antilles (ObsERA), which is operated by INSU-CNRS (OZCAR, the French National  
88 Research Infrastructure of CZOs) and the Institut de Physique du Globe de Paris (IPGP), and is  
89 devoted to the study of weathering and erosion of volcanic islands under tropical climate  
90 conditions. Quiock Creek is a small tributary of the Bras-David River, which is located in primary  
91 tropical rainforest in the Guadeloupe National Park. Rainfall variation is high in Basse-Terre and  
92 varies with the strength of the Northeast trade winds and topography. The mean annual  
93 temperature and throughfall rate (the quantity of rainfall that reaches the ground having passed  
94 through the subaerial vegetation) are, respectively, 25 °C and 3079 mm.yr<sup>-1</sup>, and the rate of  
95 infiltration is relatively fast, ~0.1-1 mm.s<sup>-1</sup> (Guérin, 2015). Climate is characterised by two seasons:  
96 a dry season, from January to June, and a cyclonic wet season, from July to December. Wet seasons  
97 are associated with intense rainfall events initiated by tropical depressions and cyclones (Zahibo et  
98 al., 2007) that significantly contribute to the water budget. The rate of evapotranspiration is around  
99 63% (Clergue et al., 2015). The mean hourly discharge ranges between 9.9 m<sup>3</sup>/h and 10.3 m<sup>3</sup>/h over  
100 the course of the year (Clergue et al., 2015; Guérin, 2015), which is five times lower than the Bras-  
101 David river (~50.4 m<sup>3</sup>/h; Lloret et al., 2011). The subsurface of Quiock Creek catchment hosts an

102 unconfined aquifer (i.e. it is connected to the atmosphere) with a porosity of ~2% and a  
103 permeability of  $\sim 10^{-6}$  m/s (Guérin, 2015). During storm flow Quiock Creek discharge increases in  
104 proportion to the rainfall rate, whereas during drought flow the discharge decreases as a power  
105 law with time. This behaviour shows that the Quiock Creek aquifer acts as a non-linear filter  
106 between precipitation inputs and river discharge (Guérin, 2015), which suggests that Quiock Creek  
107 is mostly fed by groundwater. This is also supported by the fact that the creek flows throughout  
108 most of the year, even after long periods of drought (Guérin, 2015). In turn, the catchment is  
109 relatively unaffected by overland flow due to its smooth topography and the fast infiltration rate  
110 (Guérin, 2015).

111 Quiock Creek catchment is underlain by Pleistocene andesitic pyroclastic deposits that are usually  
112 covered by >15 meters of highly-weathered ferralitic regolith (Clergue et al., 2015). The deep  
113 regolith isolates groundwater and vegetation from the bedrock. The mineralogy, chemistry and  
114 resistivity of the regolith shows little variation with depth (Guérin, 2015). The bulk regolith is highly  
115 weathered and is composed of 95 wt.% of secondary mineral phases with clays (mostly halloysite  
116 and kaolinite) accounting for 70 wt.% of the secondary minerals; the remaining 30% mainly consists  
117 of Fe(III)-hydroxides and gibbsite (Buss et al., 2010). Primary minerals consist of quartz (0–8 wt%),  
118 feldspar (0–4 wt.%) and volcanic dust from Monserrat (~3 wt.%). The upper 30 cm of the profile is  
119 slightly enriched in quartz and feldspars (dominantly orthoclase) due to deposition of Saharan dust,  
120 the main terrestrial dust source to Guadeloupe (Buss et al., 2010; Clergue et al., 2015). The dust  
121 flux is highest between the months of June and October (Graham and Duce, 1979). The regolith is  
122 strongly depleted in soluble cations compared to the bedrock (Buss et al., 2010) and it supports a  
123 dense tropical rainforest that has a mean litter flux of  $7.8 \text{ t ha}^{-1} \text{ yr}^{-1}$ .

### 124 **3. Methodology**

#### 125 **3.1 Sample collection and elemental analyses**

126 A total of 55 water samples comprising throughfall, soil solution, river water and groundwater were  
127 collected in Quiock Creek catchment over a period of 21 days in October 2015 (Figure 1). Soil  
128 solution and groundwater reservoirs were emptied after sampling to remove the “stagnant” water

129 such that only “fresh” water was collected when they were next sampled. Soil solution reservoirs  
130 were emptied on 18/09/2015, 18 days before the first sampling date (Day 1, 06/10/2015), but the  
131 groundwater reservoirs were not emptied prior to the first sampling date. Temperature,  
132 conductivity and pH were directly measured in the field with a combined pH and conductivity probe  
133 (Hanna Instruments HI 98130;  $\pm 0.5^\circ\text{C}$  for temperature,  $\pm 2\%$  for conductivity, and  $\pm 0.01$  pH units  
134 for pH). Fluid samples were filtered at  $0.2\ \mu\text{m}$ -porosity through a cellulose acetate filter, and  
135 collected in 250 or 500 mL acid-cleaned HDPE bottles for cation analysis and in Milli-Q water ( $18.2$   
136  $\text{M}\Omega\ \text{cm}^{-1}\ \text{H}_2\text{O}$ ) washed 30 mL bottles for anion analysis. The cation samples were acidified to  $\text{pH} \approx$   
137 2 with distilled nitric acid. Alkalinity was determined by titration with 0.01 M HCl within 24 hours  
138 of sample collection.

139 Major and minor cation (Na, Ca, Mg, K, Al, B, Fe, Sr, Li) and silicon concentrations were measured  
140 by inductively-coupled plasma-source mass spectrometry (ICP-MS; Thermo X-Series II) at the  
141 National Oceanography Centre Southampton (NOCS). Analyses were calibrated using a set of  
142 synthetic multi-element standards prepared gravimetrically from high purity single element  
143 standard solutions. The certified standard reference material SLRS-6 (river water) and IAPSO  
144 seawater were analysed multiple times ( $n = 8$ ) alongside the samples to assess the accuracy of the  
145 analyses, which was within  $\pm 5\%$  of the certified values. Anion ( $\text{Cl}$  and  $\text{SO}_4$ ) concentrations were  
146 measured by ion chromatography (Dionex ICS2500) and calibrated using a set of synthetic multi-  
147 element standards prepared gravimetrically from high purity single element standard solutions.  
148 IAPSO seawater was analysed multiple times ( $n = 7$ ) alongside the samples to assess the accuracy  
149 of the analyses, which was within  $\pm 5\%$  of the certified values.

## 150 3.2 Li and Mg isotope analyses

151 For Li isotope analysis, an aliquot of each water sample equivalent to 20 ng of Li was dried down  
152 and re-dissolved in 0.2 M HCl and loaded onto a cation exchange column filled with BioRad AG50W-  
153 X12 cation exchange resin to separate Li from the sample matrix (James and Palmer, 2000). Lithium  
154 isotope ratios were determined by multi-collector inductively-coupled plasma-source mass  
155 spectrometry (MC-ICP-MS; Thermo Scientific Neptune Plus) using a sample-standard bracketing

156 technique (Flesch et al., 1973), at NOCS. The Li isotope composition of samples is expressed as  $\delta^7\text{Li}$   
157 (‰), which is given by:

$$\delta^7\text{Li} = \left[ \frac{\left( \frac{{}^7\text{Li}}{{}^6\text{Li}} \right)_{\text{sample}}}{\left( \frac{{}^7\text{Li}}{{}^6\text{Li}} \right)_{\text{L-SVEC}}} - 1 \right] \times 10^3 \quad \text{Eq. 1}$$

158 where L-SVEC is the Li isotope standard reference material (Flesch, 1973). The external  
159 reproducibility of the Li isotope analyses was assessed by repeated measurement of IAPSO  
160 seawater ( $\delta^7\text{Li} = 30.9 \pm 0.6\text{‰}$ ; ( $2\sigma$ ,  $n=27$ )), L-SVEC ( $\delta^7\text{Li} = 0.0 \pm 0.5\text{‰}$  ( $2\sigma$ ,  $n = 28$ )), and SLRS-6 river  
161 water ( $\delta^7\text{Li} = 23.6 \pm 0.7\text{‰}$  ( $2\sigma$ ,  $n = 3$ )).

162 For Mg isotope analysis, an aliquot of each water sample equivalent to 10  $\mu\text{g}$  of Mg was dried down  
163 and re-dissolved in 0.8 M  $\text{HNO}_3$  and loaded onto a cation exchange column filled with BioRad  
164 AG50W-X12 cation exchange resin to separate Mg from the sample matrix (Tipper et al., 2006b;  
165 Pogge von Strandmann, 2008). Magnesium isotope ratios were determined by MC-ICP-MS (Thermo  
166 Scientific Neptune Plus) using a sample-standard bracketing technique. The Mg isotope  
167 composition of samples is expressed as  $\delta^x\text{Mg}$  (where x is  $^{25}\text{Mg}$  or  $^{26}\text{Mg}$ ), which is given by:

$$\delta^x\text{Mg} = \left[ \frac{\left( \frac{{}^x\text{Mg}}{{}^{24}\text{Mg}} \right)_{\text{sample}}}{\left( \frac{{}^x\text{Mg}}{{}^{24}\text{Mg}} \right)_{\text{DSM-3}}} - 1 \right] \times 10^3 \quad \text{Eq. 2}$$

168 where DSM-3 is the Mg isotope standard (Galy et al., 2001). The external reproducibility of the  
169 measurements was determined by repeated analysis of IAPSO seawater ( $\delta^{26}\text{Mg} = -0.82 \pm 0.05\text{‰}$   
170 ( $2\sigma$ ,  $n = 18$ )), DSM-3 ( $\delta^{26}\text{Mg} = 0.00 \pm 0.07\text{‰}$  ( $2\sigma$ ,  $n = 27$ )), and SLRS-6 river water ( $\delta^{26}\text{Mg} = -1.22 \pm$   
171  $0.03\text{‰}$  ( $2\sigma$ ,  $n = 5$ )).

### 172 3.3 Hydrological measurements

173 Precipitation, discharge and water table data for the 21-day sampling period are shown in Figure 2.  
174 Additional data, for the period between 18/09/2015 (when the soil solution reservoirs were first  
175 emptied) and 06/10/2015 are given in the Appendix (Figure A2). Rainfall was measured using a  
176 tipping-bucket rain gauge. Discharge was measured using a Venturi Flume (19 x 26.6 x 250 cm)  
177 together with a pressure sensor (CS451, Campbell Scientific) that measured the water height (or

178 stage) to a precision of  $\pm 0.5$  mm (Guérin, 2015). Water table elevation is reported relative to the  
179 river elevation so a value of zero means that the water table is below the river elevation, but water  
180 is present. The water table elevation was determined with a pressure sensor (CS451, Campbell  
181 Scientific, precision  $\pm 5$  mm) connected to a data logger (CR800, Campbell Scientific, resolution  $\pm 1$   
182 mm) placed approximately 15 cm above the bottom of the piezometer.

## 183 4. Results

184 Sample terminology is described in Table 1. Temperature, pH, conductivity and alkalinity data are  
185 summarized in Table 2. Major and minor element and Total Dissolved Solids (TDS) concentrations  
186 are displayed in Table 3. Li and Mg isotope measurements are summarized in Table 4.

### 187 4.1 Hydrological data, in-situ measurements, alkalinity and TDS

188 Levels of discharge and precipitation in the catchment during the sampling campaign are shown in  
189 Figure 2. The year 2015 was drier than usual, with a mean throughfall input of  $\sim 2509$  mm in 2015  
190 compared to an average of  $3079$  mm/yr between 2011 and 2013 (Clergue et al., 2015). Similarly,  
191 the mean discharge in 2015 was  $\sim 5.2$  m<sup>3</sup>/h compared to  $\sim 10$  m<sup>3</sup>/h between 2011 and 2013. During  
192 the one-month period of this study,  $283.6$  mm of rain entered the catchment, corresponding to  
193  $12.5\%$  of the total annual rain input in 2015. A series of large rain events occurred starting on days  
194 4, 8, 11 and 19 of the sampling period (Figure 2). Three of these rain events noticeably increased  
195 the discharge in Quiock Creek (days 9, 11 and 19), and they also increased the elevation of the water  
196 table. Highest rainfall ( $92$  mm) occurred on day 19, generating a peak discharge of  $145$  m<sup>3</sup>/h.  
197 Because of previously dry conditions, the rainfall event on day 4 only triggered a small response in  
198 river discharge and water table (Figure 2).

199 The temperature of the river water samples ranged from  $23.7$  to  $25.5^\circ\text{C}$ , conductivity ranged from  
200  $35$  to  $56$   $\mu\text{S}/\text{cm}$ , pH ranged from  $4.9$  to  $5.6$ , TDS concentrations ranged from  $18$  to  $24$  ppm and  
201 alkalinity was  $<10$   $\mu\text{eq}/\text{L}$ . All of these parameters showed a slight tendency to decrease with  
202 increasing discharge. Groundwater samples by comparison had generally higher pH ( $4.8$  to  $6.5$ ),  
203 higher conductivity ( $48$  to  $109$   $\mu\text{S}/\text{cm}$ ) and a wider range of alkalinity ( $5$  to  $1108$   $\mu\text{eq}/\text{L}$ ) and TDS ( $21$

204 to 97 ppm) values. Groundwaters collected from Piezo 2 had lower pH, conductivity and alkalinity  
205 compared to other groundwater samples. Groundwaters collected on Day 1 generally had higher  
206 alkalinities compared to samples collected later in the sampling campaign, presumably because the  
207 groundwater reservoir had not been emptied prior to sample collection, allowing greater time for  
208 water-rock reactions. The temperature of the groundwater samples (24.1 to 25.9°C) was close to  
209 that of the river water samples. The soil solutions were characterised by generally lower pH (4.5 to  
210 5.5), TDS (15 to 25 ppm) and alkalinity (5 to 22 µeq/L) compared to the groundwater samples. The  
211 pH and conductivity of the throughfall samples were close to those of the soil solutions  
212 (respectively, 5.9 and 42 µS/cm), but the throughfall samples had higher alkalinity and lower TDS.

## 213 4.2 Composition of the dissolved load

214 The accuracy of the analyses for major ions can be estimated from the electrical balance (E.B., Eq.  
215 3) of the cations and anions (expressed in meq/L):

$$\text{Electrical Balance (E. B., \%)} = \frac{\text{Sum cations} - \text{Sum anions}}{\text{Sum cations} + \text{Sum anions}} \times 100 \quad \text{Eq. 3}$$

216 The electrical balance was within ±10% and for most samples it was within ±5% (Figure A3). This  
217 indicates that there is no significant contribution to the geochemical composition of the waters  
218 from any species not reported in Table 3 (Appelo and Postma, 2004). Additionally, TDS extrapolated  
219 from conductivity measurements made in the field were well correlated with TDS measurements  
220 made in the laboratory indicating that the chemical composition of the samples was preserved  
221 between collection and analysis (Figure A3).

222 The major ion compositions of catchment waters are plotted in a Piper diagram (Piper, 1953) in  
223 Figure 3. The two throughfall samples were chloride and sodium rich, showing a strong seawater  
224 influence, but they had higher Ca and K concentrations (18 - 21 µmol/kg for Ca and 31 - 67 µmol/kg  
225 for K) compared to rain water (3 - 8 µmol/L for Ca and 3 - 5 µmol/L for K; Dessert et al., 2015). Soil  
226 solutions were also chloride and sodium rich and their alkalinity (up to 22 µeq/L) and Mg content  
227 (11 - 43 µmol/kg) were variable. Quiock Creek samples contained higher proportions of Na and Cl  
228 compared to throughfall samples, and their chemical composition showed little variation  
229 throughout the sampling campaign. Groundwater samples contained proportionally higher calcium

230 and alkalinity than the other water samples and tend to become more enriched in chloride and  
231 sodium with decreasing distance from the river. The compositions of all of the samples were similar  
232 to those measured in 2012-2013 (Clergue et al., 2015) with the exception of the alkalinities of the  
233 soil solutions and Quiock Creek samples, which had higher alkalinity in 2012-2013 (11 - 66  $\mu\text{eq/L}$ ).  
234 Concentrations of TDS, Si, Li and Mg in Quiock Creek are plotted versus discharge in Figure 4. Most  
235 of these variables showed a linear, slightly inverse relationship with discharge (Q), in a log-log plot  
236 indicating that there is a power-law relationship (e.g. for Si,  $[\text{Si}] = aQ^b$ , where a and b are constants  
237 and b is the power-law exponent) between concentration and discharge (Godsey et al., 2009). A  
238 slope of 0 would indicate that concentrations remain constant despite changes in discharge (so-  
239 called “chemostatic behaviour”; Godsey et al., 2009), whereas a slope of -1 indicates that solute  
240 concentration become more dilute as discharge increases (concentration scales as  $1/Q$ ). All  
241 concentration-discharge plots had a slope of slightly less than zero (between -0.09 and -0.03)  
242 suggesting that Quiock Creek behaves almost chemostatically for most of the major elements.  
243 However, Li and Mg had a weaker relationship with discharge ( $R^2=0.23$  and  $0.47$ , respectively;  
244 Figure 4), and showed chemostatic behaviour only at low discharge.

### 245 4.3 Sea salt contribution

246 The chemical composition of river water was determined by inputs from several sources, including  
247 sea salt and dust delivered in precipitation. The contribution from sea salts can be assessed through  
248 analysis of the Cl content, assuming that all of the Cl in the river water comes from sea salt (Stallard  
249 and Edmond, 1981), and that Cl shows conservative behaviour in the weathering system. Thus, for  
250 Li:

$$[\text{Li}]_{\text{sea}} = \left(\frac{\text{Li}}{\text{Cl}}\right)_{\text{sea}} \times [\text{Cl}]_X \quad \text{Eq. 4}$$

251 where  $(\text{Li}/\text{Cl})_{\text{sea}} = 0.05$  (Dessert et al., 2015) and X is either the soil solution, groundwater, or river  
252 water. The fraction of Li derived from sea salt in the different fluid reservoirs is given in Table 5.

253 The sea salt contribution in throughfall was determined using the seawater Li/Na ratio and the  
254 sample Na concentration instead, because Cl was not determined for sample Th1 (Keene et al.,  
255 1986; Clergue et al., 2015). The majority of the Na, and most of the Mg, in all of the fluid reservoirs

256 (throughfall, soil solutions, groundwater and river water) has a marine origin, whereas Li was mainly  
257 provided by other sources.

## 258 4.4 Li and Mg, and their isotopes

### 259 4.4.1 [Li] and $\delta^7\text{Li}$

260 The Li concentration and Li isotope composition of the water samples are plotted in Figure 5A.  
261 Different critical zone reservoirs had very different dissolved Li concentrations ([Li]) and  $\delta^7\text{Li}$  values,  
262 and the overall range was, respectively, between 14 to 95 nmol/kg and 1.8 to 16.8‰. Throughfall  
263 contained relatively low [Li], averaging  $\sim 14$  nmol/kg, and had  $\delta^7\text{Li}$  values of  $\sim 13.3$ ‰. By contrast,  
264 the soil solutions (taken on Day 1 and Day 18, before and after rain events) generally had the highest  
265 Li concentrations of all of the reservoirs (29 to 95 nmol/kg), and lowest  $\delta^7\text{Li}$  values (1.8 to 10.4‰)  
266 (Figure 5A and Figure 6). Soil solution data were consistent with other measurements of soil  
267 solutions in Quioc Creek catchment ([Li] = 41-121 nmol/kg and  $\delta^7\text{Li}$  = 4.6 to 8.9‰; Clergue et al.,  
268 2015). [Li] and  $\delta^7\text{Li}$  were variable in the upper 300 cm of the soil profile, whereas [Li] increased with  
269 depth and  $\delta^7\text{Li}$  decreased with depth in the deeper part of the profile (>300 cm). There was little  
270 difference in either the Li concentration or the  $\delta^7\text{Li}$  value of soil solutions sampled before and after  
271 the rain events.

272 Groundwaters generally had highest  $\delta^7\text{Li}$  values (up to 21‰), but they had generally lower [Li] than  
273 the soil solutions (29 to 92 nmol/kg; Figure 5A and Figure 7A). Significantly higher Li concentrations  
274 ( $\sim 288$  to 3026 nmol/L) were found in shallow and deep groundwater in the Columbia River Basalts  
275 (Liu et al., 2015). Lithium concentrations increased towards the river whereas  $\delta^7\text{Li}$  values decreased  
276 from  $\sim 16$ ‰ 30 m away from the river channel to  $\sim 9$ ‰ close to the river (Figure 7B). The  
277 groundwater sample from Piezo 5 had much higher [Li] than the rest of the samples (92 nmol/kg  
278 compared to  $\sim 35$  nmol/kg at the adjacent sampling site, Piezo 6), but its  $\delta^7\text{Li}$  value was similar to  
279 samples recovered from Piezo 6. Whereas the Li concentrations in samples collected on different  
280 days were similar in all the piezometers, their  $\delta^7\text{Li}$  values varied by up to 4‰ (e.g. Piezo 3 and 4).  
281 By contrast, all of the groundwater samples from Piezo 6 had very consistent Li concentrations ( $35$   
282  $\pm 5$  nmol/kg;  $n = 3$ ) and  $\delta^7\text{Li}$  values ( $16.5 \pm 0.3$ ‰;  $n = 3$ ).

283 The Li content of the river waters (~55 nmol/kg) was generally lower than the soil solutions, and  
284 was also relatively low compared to the world's major rivers ([Li] = ~215 nmol/L; Huh et al., 1998)  
285 but comparable to other rivers draining basaltic tropical catchments (Henchiri et al., 2014).  $\delta^7\text{Li}$   
286 values (7.2 to 10‰) were similar to those measured in a previous sampling campaign in Quiock  
287 Creek ( $\delta^7\text{Li}$  = 8 to 9.3‰ (n = 4), (Clergue et al., 2015)) and other highly-weathered catchments (1-  
288 16‰; Dellinger et al., 2015 and references therein) and volcanic islands (e. g. Martinique  $\delta^7\text{Li}$  = 4.9  
289 to 20.6‰; Rad et al., 2013). However, Martinique rivers can be strongly affected by hydrothermal  
290 inputs (that have  $\delta^7\text{Li}$  = ~1.6‰; Rad et al., 2013), whereas Quiock Creek is not affected by  
291 hydrothermal inputs (Clergue et al., 2015). Li concentrations tended to slightly decrease with  
292 increasing discharge (Figure 4) but there was no relationship between discharge and  $\delta^7\text{Li}$  values  
293 (Figure A4). However, two samples (QC20 and QC21) measured during and a day after a storm event  
294 had relatively low [Li] and  $\delta^7\text{Li}$  ([Li] = ~40 nmol/kg and  $\delta^7\text{Li}$  = ~7.4‰).

#### 295 4.4.2 [Mg] and $\delta^{26}\text{Mg}$

296 The Mg concentration and Mg isotope composition of the catchment samples are plotted together  
297 in Figure 5B. The Mg concentrations of the two throughfall samples were similar (18  $\mu\text{mol/kg}$  and  
298 14  $\mu\text{mol/kg}$ ), but their corresponding  $\delta^{26}\text{Mg}$  values were slightly different (-0.97 and -0.84‰; Figure  
299 5B) but close to the value for seawater ( $-0.82 \pm 0.05\text{‰}$ ; Foster et al., 2010; Ryu et al., 2016). The  
300  $\delta^{26}\text{Mg}$  values of the throughfall samples are similar to values measured in rainwater in Guadeloupe  
301 ( $-0.87 \pm 0.05\text{‰}$  and  $-0.86 \pm 0.11\text{‰}$ ; Dessert et al., 2015), and in openfall precipitation in Puerto Rico  
302 ( $-1.10$  to  $-0.92\text{‰}$ ; Chapela Lara et al., 2017).

303 The concentration of Mg in the soil solutions (10 to 43  $\mu\text{mol/kg}$ ) was generally lower than the Mg  
304 concentration of throughfall, and the soil solutions generally have higher  $\delta^{26}\text{Mg}$  (-1.04 to -0.58‰;  
305 Figure 5B and Figure 6) compared to other reservoirs. The Mg concentrations were within the range  
306 of those previously measured in Quiock Creek catchment (11-32  $\mu\text{mol/L}$ ; Clergue et al. (2015)), and  
307 in soil solutions from Puerto Rico (6 to 68  $\mu\text{mol/L}$ ; Chapela Lara et al., 2017). There was no clear  
308 trend between [Mg] and depth, but  $\delta^{26}\text{Mg}$  values increased progressively from -1.04‰ at the  
309 surface to -0.65‰ at 1250 cm. This pattern of increasing soil solution  $\delta^{26}\text{Mg}$  with depth has also  
310 been observed in soil profiles from California (from -0.99‰ at the surface to -0.43‰ at the base of

311 the profile; Tipper et al., 2010) and Puerto Rico (from -0.78‰ at the surface to -0.22‰ at the base  
312 of the profile; Chapela Lara et al., 2017). Soil solutions sampled on Day 18 have higher [Mg] in the  
313 upper part of the profile, compared to the samples measured on Day 1, whereas in the deeper part  
314 of the profile there was no obvious change in [Mg]. The  $\delta^{26}\text{Mg}$  values of soil pore waters were  
315 generally identical within analytical uncertainty between Day 1 and Day 18.

316 Groundwaters sampled before and after significant rain events (Day 1 and 9) had the lowest  $\delta^{26}\text{Mg}$   
317 values (from -1.48 to -0.81‰) and the highest Mg concentrations (from 21 to 54  $\mu\text{mol}/\text{kg}$ )  
318 compared to any of the other Quiock Creek fluids (Figure 5B and Figure 7C and D). The range of  
319  $\delta^{26}\text{Mg}$  measured in the groundwaters was comparable with other reported groundwaters (-1.70 to  
320 0.23‰; Teng, 2017). There was no obvious change in groundwater Mg concentration with distance  
321 from the river channel, but [Mg] decreased by 10-23  $\mu\text{mol}/\text{kg}$  after the significant rain event on Day  
322 9, reaching values similar to the throughfall concentration. Similarly, there was no obvious change  
323 in  $\delta^{26}\text{Mg}$  with distance from the river channel (Figure 7D). However, three samples taken from  
324 piezometers 4 and 5 (Piezo 41, Piezo 49 and Piezo 51) had significantly lower  $\delta^{26}\text{Mg}$  (-1.48 to -  
325 1.07‰) compared to any of the other samples. The Mg concentrations and  $\delta^{26}\text{Mg}$  values of  
326 groundwaters from Piezo 6 (respectively, 21 to 27  $\mu\text{mol}/\text{kg}$  and -0.99 to -0.95‰) were relatively  
327 stable throughout the sampling period but the  $\delta^{26}\text{Mg}$  values of all of the other groundwater samples  
328 increased by 0.05 to 0.41‰ after the rainfall event, towards the value measured in throughfall.

329 Mg concentrations of samples from Quiock Creek ranged between 22 and 29  $\mu\text{mol}/\text{kg}$ .  $\delta^{26}\text{Mg}$  values  
330 showed a limited range, from -0.87 to -0.72‰, and there was no obvious relationship between  
331 either [Mg] or  $\delta^{26}\text{Mg}$  with discharge (Figure 4 and Figure A4) even at very high discharge. These  
332  $\delta^{26}\text{Mg}$  values were lighter than those measured in other Guadeloupe rivers (-0.59 and -0.43‰;  
333 Dessert et al., 2015), but within the range measured in the world's largest rivers (-0.52 to -1.70‰;  
334 Tipper et al., 2006b), and rivers in Puerto Rico (-0.57 to 0.01‰), with the exception of one sample  
335 ( $\delta^{26}\text{Mg} = -0.74‰$ ) that was sampled when discharge was extremely high (Chapela Lara et al., 2017).

## 336 5. Discussion

## 337 5.1 Sources of Li and Mg in Quiock Creek catchment

338 The isotope compositions of Mg and Li are plotted with sea salt-corrected elemental ratios (Mg/Ca  
339 and Li/Na, respectively) in Figure 8 and Figure 9 to help characterize the possible sources of Mg and  
340 Li in the catchment. The use of elemental ratios allows for better comparison between the fluids as  
341 they are unaffected by dilution and evaporation processes (Gaillardet et al., 1999). Mg and Ca are  
342 both soluble alkaline earth elements that are susceptible to uptake by plants. However, in volcanic  
343 settings, Mg is more likely to be incorporated into secondary clays or adsorbed on clay mineral  
344 surfaces (Tipper et al., 2006a, 2008). Figure 8 shows that the Mg/Ca ratios of different reservoirs of  
345 Mg in the catchment can be very variable but the Mg isotope composition of the river waters and  
346 most of the groundwaters is within the range of throughfall and sea salt, consistent with the  
347 estimates of sea salt contribution reported in Table 5. However, groundwater samples from Piezo  
348 41, Piezo 49 and Piezo 51 have much lower  $\delta^{26}\text{Mg}$  that cannot be explained by mixing between any  
349 of the potential Mg reservoirs analysed in this study. We investigate the possible causes of these  
350 low  $\delta^{26}\text{Mg}$  values in Section 5.3. Li and Na are both soluble alkali metals and are not essential  
351 nutrients, so they can be expected to act similarly during weathering. However, Na is generally not  
352 incorporated into secondary minerals whereas Li can be significantly enriched in clays and oxy-  
353 hydroxides (Sawhney, 1972; Millot et al., 2010; Dellinger et al., 2015). Figure 9 shows that most of  
354 the Quiock Creek fluids have Li/Na and  $\delta^7\text{Li}$  values that are intermediate between sea salts that  
355 have low Li/Na and high  $\delta^7\text{Li}$ , and Saharan dust or bulk soil that have much lower  $\delta^7\text{Li}$  and higher  
356 Li/Na (Clergue et al., 2015). However, many of the samples have higher  $\delta^7\text{Li}$  than predicted by  
357 simple binary mixing, which can likely be attributed to uptake of Li into secondary mineral phases  
358 (Huh et al., 1998; Huh et al., 2001; Rudnick et al., 2004; Kisakurek et al., 2005).

## 359 5.2 Controls on the Li and Mg isotope composition of throughfall and soil 360 solutions

### 361 *5.2.1 Li and Mg isotopes in throughfall*

362 The  $\delta^7\text{Li}$  values of the two throughfall samples (13 and 13.6‰) are much lower than that of sea salt  
363 ( $\delta^7\text{Li} = \sim 31\text{‰}$ ; Pogge von Strandmann et al. (2017)), suggesting that there is additional input of Li  
364 from a source with lower  $\delta^7\text{Li}$ . The source of this Li is most likely to be leaching of Saharan dust  
365 located on the canopy, which has  $\delta^7\text{Li} = -0.7\text{‰}$  (Clergue et al., 2015). Assuming that no fractionation  
366 of Li isotopes occurs during dust dissolution (Pistiner and Henderson, 2003; Wimpenny et al., 2010),  
367 then mass balance considerations indicate that approximately 50% of the Li in throughfall comes  
368 from Saharan dust, consistent with estimations of the sea salt contribution (44-48% of Li was  
369 derived from sea salt; Table 5). Note, however, that this estimate is specific to our sampling period,  
370 as at other times of the year, the dust contribution to the Li load may be lower (as low as 25%;  
371 Clergue et al. (2015)).

372 The  $\delta^{26}\text{Mg}$  values of the two throughfall samples differ by 0.13‰, just outside of the uncertainty of  
373 the analyses. This difference is unlikely to be due to differences in dust input, as no difference in  
374  $\delta^7\text{Li}$  is observed in the throughfall samples. The variation of  $\delta^{26}\text{Mg}$  in the throughfall could be due  
375 to differences in inputs of Mg from the canopy. While plants are overall enriched in heavy Mg  
376 isotopes compared to the soil solution, the transfer of Mg from the roots to the leaves fractionates  
377 Mg isotopes, such that the upper part of the plant has lower  $\delta^{26}\text{Mg}$  (Bolou-Bi et al., 2010; Bolou-Bi  
378 et al., 2012). Sample Th1 has lower  $\delta^{26}\text{Mg}$  and higher [K] compared to sample Th3 (Table 3); high  
379 concentrations of K in rainfall and throughfall are indicative of input of K from vegetation (Riotte et  
380 al., 2014). By contrast, vegetation inputs have little effect on  $\delta^7\text{Li}$  (Lemarchand et al., 2010; Clergue  
381 et al., 2015).

### 382 *5.2.2 Li isotopes in the soil solution*

383 Soil solution  $\delta^7\text{Li}$  decreases with depth (from 10.4 to 1.8‰) and the  $\delta^7\text{Li}$  value of bulk soil also  
384 decreases with depth (from 0.6 to -13.5‰; Clergue et al., 2015). The change in the  $\delta^7\text{Li}$  value of the  
385 bulk soil has been attributed to increased dust input to the upper part of the soil profile (Clergue et

386 al., 2015). In the soil solutions, however, the proportion of Li derived from sea salt does not  
387 decrease significantly with depth (Figure A5), suggesting that changes in  $\delta^7\text{Li}$  in the soil solution  
388 must be principally controlled by weathering processes rather than atmospheric inputs. However,  
389 in the upper part of the soil profile, the  $\delta^7\text{Li}$  value of the soil solution increases after the rain events,  
390 whereas the Li/Na ratio decreases (Figure 6 and Figure A5). This is consistent with increased input  
391 of Li from throughfall that has relatively high  $\delta^7\text{Li}$  and low Li/Na. Thus, the soil solution  $\delta^7\text{Li}$  in the  
392 upper part of the profile appears to be much more influenced by throughfall inputs compared to  
393 the deeper part of the soil profile.

### 394 *5.2.3 Mg isotopes in the soil solution*

395 In contrast to Li, almost all of the Mg in the soil solution is delivered by atmospheric inputs (Table  
396 5), which is consistent with the strong depletion of Mg in the soil of the catchment (Clergue et al.,  
397 2015). Nevertheless, the  $\delta^{26}\text{Mg}$  values of the soil solutions increase slightly with depth in the soil  
398 profile; this cannot be attributed to simple mixing between throughfall and Mg derived from the  
399 bulk soil (Figure 8), suggesting that Mg isotope fractionation must occur during weathering. As all  
400 of the Cl in the soil solution comes from throughfall, and Cl is conservative during water transfer  
401 into the soil, changes in the Mg/Cl ratio of the soil solution can be used to identify whether the soils  
402 are a source or a sink of Mg. Therefore, the decrease of Mg/Cl suggests that Mg is removed from  
403 the soil solution in the deeper part of the soil profile, this removal leading to an increase in  $\delta^{26}\text{Mg}$   
404 (Figure A6).

405 Magnesium may also potentially be affected by vegetation uptake. The soil solutions have much  
406 lower K/Na than the throughfall (Figure A5), which is indicative of uptake of K (and by analogy  
407 uptake of Mg) by plants (Jobbagy and Jackson, 2001). However, this appears to have limited impact  
408 on the  $\delta^{26}\text{Mg}$  value of the soil solutions, consistent with results from a previous study (Chapela Lara  
409 et al., 2017). Despite dense vegetation cover and tight nutrient cycles in tropical rainforests (Wood  
410 et al., 2009), the  $\delta^{26}\text{Mg}$  of soil solutions therefore appears to be unaffected by plant uptake, most  
411 likely because atmospheric inputs of Mg are high there. This is a major difference with more  
412 temperate mountainous areas where lower  $\delta^{26}\text{Mg}$  in soil water has been attributed to preferential  
413 uptake of the heavy Mg isotopes by plants (Uhlir et al., 2017).

414 The change in  $\delta^{26}\text{Mg}$  must reflect preferential incorporation of light Mg isotopes into secondary  
415 mineral phases, or preferential adsorption of light Mg isotopes, in the deeper part of the soil profile.  
416 In Guadeloupe, soils tend to be enriched in heavy Mg isotopes compared to the fluids (Opfergelt et  
417 al., 2012; Dessert et al., 2015), which suggests that secondary minerals are enriched in heavy, not  
418 light, Mg isotopes. However, several studies have shown that cation exchange can lead to  
419 preferential uptake of light Mg isotopes onto mineral surfaces, increasing the  $\delta^{26}\text{Mg}$  value of Mg  
420 that remains in solution (Jacobson et al., 2010; Opfergelt et al., 2012; Ma et al., 2015). Therefore, it  
421 seems likely that cation exchange occurs in the deepest part of the profile where the longer  
422 residence time of the water allows dissolved Mg to adsorb on the clay surfaces.

### 423 5.3 Weathering processes in groundwaters

424 The Li isotopic signature of groundwaters cannot be explained by simple mixing of Li from bulk soil  
425 or rock, and throughfall, as discussed in Section 5.1. The  $\delta^7\text{Li}$  value of the groundwaters (8 to 16.8‰)  
426 is significantly higher than the  $\delta^7\text{Li}$  value of the bulk soil ( $\delta^7\text{Li} = 2.9\text{‰}$  above 274 cm and  $-6.1\text{‰}$   
427 below 274 cm on average; Clergue et al., 2015) and, because primary minerals are almost totally  
428 absent from the soil (Buss et al., 2010), the  $\delta^7\text{Li}$  value of the groundwaters must be linked to  
429 dissolution and precipitation of secondary mineral phases. After a rain event, the Li/Na ratio of the  
430 groundwaters increases, whereas the  $\delta^7\text{Li}$  value of the groundwaters decreases (by 1.5 to 3.6‰ in  
431 Piezo 1, 2, 3 and 4; Figure 10). As this cannot only be attributed to input of Li from sea salt (Figure  
432 9), implying that a  $^6\text{Li}$ -enriched reservoir of Li in the catchment is contributing Li to groundwater  
433 during rain events, either through enhanced dissolution of secondary minerals - or through  
434 suppressed secondary mineral formation - during the time of the event itself, or through injection  
435 of previously isolated pockets of water enriched in  $^6\text{Li}$  through interactions with secondary minerals  
436 before the rain event.

437 To further explore the possibility of a change in the rate of secondary mineral dissolution during a  
438 rain event, the saturation states of the groundwaters with respect to different secondary mineral  
439 phases were calculated with the PHREEQC program (Parkhurst and Appelo, 2013) using the  
440 measured concentration data, field pH and temperature. PHREEQC calculates mineral stability in

441 terms of the saturation index (SI). If  $SI > 0$ , the solution is supersaturated and the mineral may  
442 precipitate, whereas if  $SI < 0$ , the mineral is likely to dissolve. The groundwater SI for the principal  
443 constituents of the soil, kaolinite (halloysite), gibbsite and goethite (Buss et al., 2010), are shown in  
444 the Appendix (Figure A7). All of these mineral phases are oversaturated in the Quiock Creek  
445 groundwaters, so changes in  $\delta^7\text{Li}$  are most likely controlled by changes in the rate of secondary  
446 mineral precipitation. After a rain event, the SI of all of the secondary mineral phases decreases,  
447 consistent with lower rates of secondary mineral precipitation and thus lower  $\delta^7\text{Li}$  (Figure A7).

448 The majority of the groundwater samples have a Mg isotope composition similar to the  
449 groundwaters sampled in Piezo 6 ( $\delta^{26}\text{Mg} = -0.95$  to  $-0.99\text{‰}$ ). The  $\delta^{26}\text{Mg}$  value of these  
450 groundwaters was invariant over time, suggesting that they have a long residence time and that  
451 they represent the baseflow contribution to Quiock Creek. Two samples, Piezo 41 and Piezo 51,  
452 have significantly lower  $\delta^{26}\text{Mg}$  values (respectively,  $-1.48$  and  $-1.33\text{‰}$ ). These samples contained  
453 'stagnant' water, as the piezometers were not emptied prior to sampling (see Section 3.1). The low  
454  $\delta^{26}\text{Mg}$  values could be linked to: (1) release of Mg to groundwater from solid phases; (2) uptake or  
455 release of Mg by plants; or (3) cation exchange with mineral surfaces. Because soils and bedrock  
456 tend to be enriched in heavy Mg isotopes in Guadeloupe (Figure 8), addition of Mg with low  $\delta^{26}\text{Mg}$   
457 cannot be attributed to dissolution of mineral phases, dismissing hypothesis 1. In support of  
458 hypothesis 2 above, these two samples have much lower K/Cl and higher Mg/Cl and Mg/K ratios  
459 compared to the other groundwater samples (Figure 11). Potassium is an essential nutrient that is  
460 highly concentrated in plant tissues (Bowen, 1979; Riotte et al., 2014). The potential effects of  
461 vegetation on K and Mg in groundwaters include leaching of leaves that increases the K content of  
462 throughfall relative to sea salt and slightly decreases  $\delta^{26}\text{Mg}$  due to preferential leaching of light Mg  
463 isotopes from the upper part of the plant (Bolou-Bi et al., 2010; Bolou-Bi et al., 2012); uptake of K,  
464 but not Mg, by plants; The two first patterns concur with analyses of soil solutions as discussed in  
465 Section 5.2.3, which suggests that groundwaters can be also affected by plant uptake. However,  
466 the lower K/Cl (Figure 11B) is inconsistent with reduced plant uptake which would have increased  
467 [K] relative to [Cl] (Jobbagy and Jackson, 2001). Therefore, it seems most likely that the low  $\delta^{26}\text{Mg}$   
468 groundwaters acquire Mg through cation exchange (hypothesis 3). As discussed in Section 5.2.3,

469 soil waters in the deeper part of the profile have relatively high  $\delta^{26}\text{Mg}$  values, which is consistent  
470 with preferential adsorption of lighter Mg isotopes (Ma et al., 2015). Thus, desorption of this Mg  
471 can be expected to enrich groundwaters in light isotopes. These 'stagnant' groundwater samples  
472 have high [Ca];  $\text{Ca}^{2+}$  has a higher ionic radius and a lower hydrated radius than  $\text{Mg}^{2+}$ , so it is  
473 preferentially adsorbed on clay surfaces (Udo, 1978; Appelo and Postma, 2004). As  $\text{Ca}^{2+}$   
474 concentrations increase with increasing residence time, previously adsorbed light Mg isotopes are  
475 released in groundwater, increasing the Mg concentration and reducing the  $\delta^{26}\text{Mg}$  value of the  
476 groundwater.

#### 477 5.4 Temporal variations in the Mg and Li isotopic compositions of Quiock 478 Creek waters

479 As the soils in Quiock Creek catchment are highly weathered, and as there is limited contact with  
480 the bedrock as the soils are thick, river waters can be expected to become more dilute during storm  
481 events. However, there was in fact little variation in element concentrations with discharge in this  
482 study, even though discharge varied by two orders of magnitude (Figure 4). At the highest  
483 discharge, [Li] and [Mg] were slightly lower (by ~25%) than expected for chemostatic behaviour,  
484 which implies that solute production is kinetically-limited at high discharge (Maher, 2011). This is  
485 consistent with the high permeability of the catchment ( $10^{-6}\text{m/s}$  or  $\sim 30\text{m/yr}$ ; Guérin, 2015), which  
486 means that water residence time is relatively short.

487 In contrast to previous studies conducted in Guadeloupe and Puerto Rico (both tropical  
488 catchments), we find no evidence for increased river water  $\delta^{26}\text{Mg}$  at low discharge, which has been  
489 attributed to an increased contribution of Mg from weathering from the deep saprolite at low flow  
490 (Dessert et al., 2015; Chapela Lara et al., 2017). This is likely related to the very high depletion of  
491 Mg and the absence of easily-weathered primary mineral phases in the soil (Buss et al., 2010). By  
492 contrast, the  $\delta^7\text{Li}$  value of the river water decreased by, on average, ~2‰ after the largest rain  
493 event and remained low afterwards. The decrease in  $\delta^7\text{Li}$  is most likely due to either input of Li from  
494 isolated pockets of soil solution with lower  $\delta^7\text{Li}$  that are flushed out during rain events, or to a  
495 decrease in rates of secondary mineral precipitation during the rain event itself.

496 On a first order, the Li isotope composition of Quiock Creek ( $\delta^7\text{Li}_{\text{QC}}$ ) is controlled by mixing between  
497 Li derived from the soil solution and Li derived from groundwater:

$$\delta^7\text{Li}_{\text{QC}} = \delta^7\text{Li}_{\text{Soil solution}} \times f_{\text{Soil solution}} + \delta^7\text{Li}_{\text{Groundwater}} \times f_{\text{Groundwater}} \quad \text{Eq. 5}$$

$$f_{\text{Soil solution}} + f_{\text{Groundwater}} = 1 \quad \text{Eq. 6}$$

498 where  $\delta^7\text{Li}_{\text{Soil solution}}$  and  $\delta^7\text{Li}_{\text{Groundwater}}$  are the average isotope composition of the soil solution and  
499 groundwater respectively, and  $f_{\text{Soil solution}}$  and  $f_{\text{Groundwater}}$  represent, respectively, the flux of Li derived  
500 from the soil solution and groundwater. Hence:

$$f_{\text{Soil solution}} = \frac{\delta^7\text{Li}_{\text{QC}} - \delta^7\text{Li}_{\text{Groundwater}}}{\delta^7\text{Li}_{\text{Soil solution}} - \delta^7\text{Li}_{\text{Groundwater}}} \quad \text{Eq. 7}$$

501 Assuming that  $\delta^7\text{Li}_{\text{Soil solution}} = 6.9 \pm 2.6\text{‰}$  and  $\delta^7\text{Li}_{\text{Groundwater}} = 13.2 \pm 3.2\text{‰}$ , we calculate that 52 to  
502 73% of the Li in Quiock Creek came from the soil solution before the storm, whereas after the storm  
503 this increased to 89 to 95%. Thus, the decrease in  $\delta^7\text{Li}$  was most likely due to increased input of Li  
504 from soil solution that has lower  $\delta^7\text{Li}$  and was flushed out during the rain event.

505 The response of other elements, for which isotope data are not available, to the storm event can  
506 also be assessed if the ratio of the concentration of that element, normalised to a conservative  
507 element (e.g., Cl), differs between the different weathering reservoirs. This is not the case for most  
508 of the elements analysed in this study, with the exception of Ca. Groundwaters have an average  
509 molar Ca/Cl ratio of  $697 \pm 535$ , whereas soil solutions have  $\text{Ca/Cl} = 11 \pm 8$ . We calculate that  $96 \pm$   
510 19% of the Ca in Quiock Creek came from soil solution before the storm event, and this did not  
511 change after the storm event ( $95 \pm 21\%$ ). Thus, as for Li, soil solutions are an important source of  
512 Ca in Quiock Creek water.

## 513 6. Conclusions

514 This study highlights that, even in a highly-weathered catchment that drains single lithology, there  
515 can be significant differences in the Li and Mg isotope compositions of different critical zone  
516 reservoirs. Isotope signals are strongly affected by atmospheric inputs of Mg and Li, but they are  
517 also controlled by interactions with soil and bedrock. Li isotope compositions are mostly influenced  
518 by preferential incorporation of  $^6\text{Li}$  into secondary minerals, whereas Mg isotope compositions

519 mainly reflect input of Mg from sea salts although adsorption or desorption of light Mg isotopes  
520 to/from mineral surfaces can occur in waters that have a relatively long residence time.  $\delta^7\text{Li}$  values  
521 of groundwaters can quickly decrease even after a single rain event and this is likely due to lower  
522 rates of precipitation of secondary minerals. A rapid decrease in  $\delta^7\text{Li}$  in Quiock Creek after a storm  
523 event is attributed to increased input of Li from soil solutions that have lower  $\delta^7\text{Li}$  compared to  
524 groundwater. Atmospheric inputs of Li increase the  $\delta^7\text{Li}$  of soil solutions after rain events only in  
525 the upper part of the soil profile.  $\delta^{26}\text{Mg}$  values show little change during hydrological events,  
526 because most of the Mg in Quiock Creek catchment is supplied by throughfall and Mg is not  
527 significantly impacted by plant uptake.

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# The response of Li and Mg isotopes to rain events in a highly-weathered catchment

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## Manuscript Figures 1-11

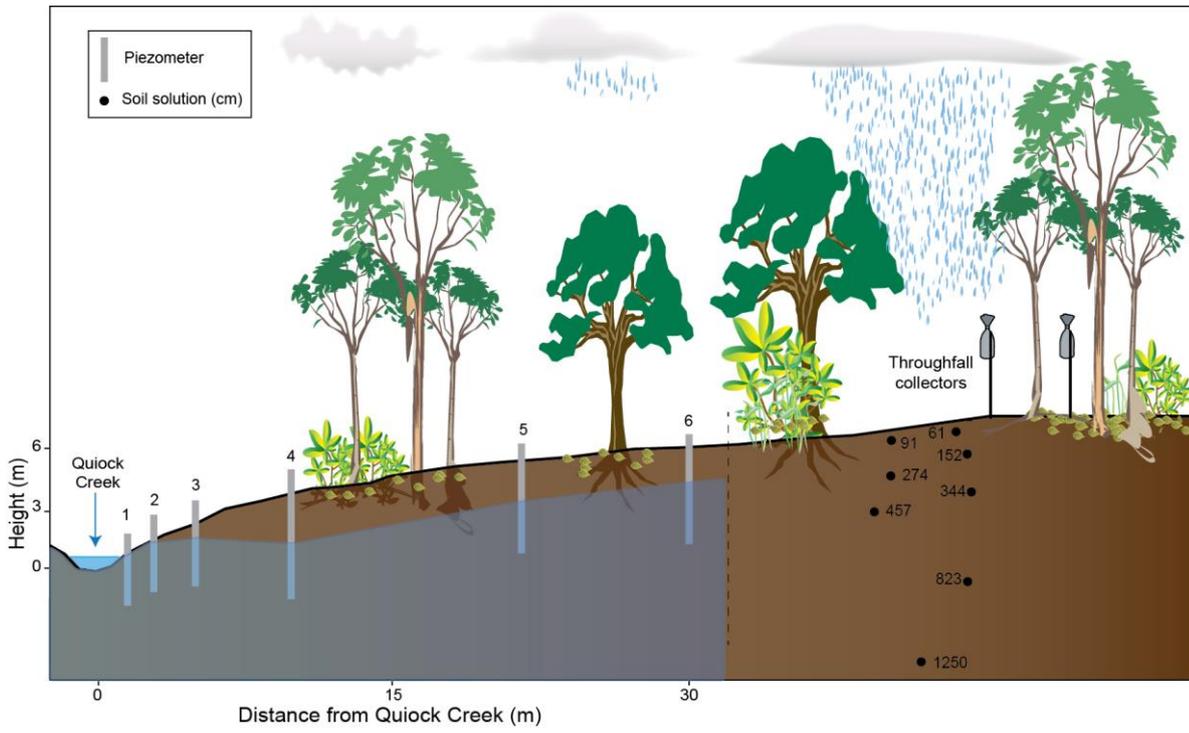


Figure 1. Schematic diagram showing the samples collected in Quiock Creek catchment. Depth of soil solution samples are shown as centimetres below the soil surface.

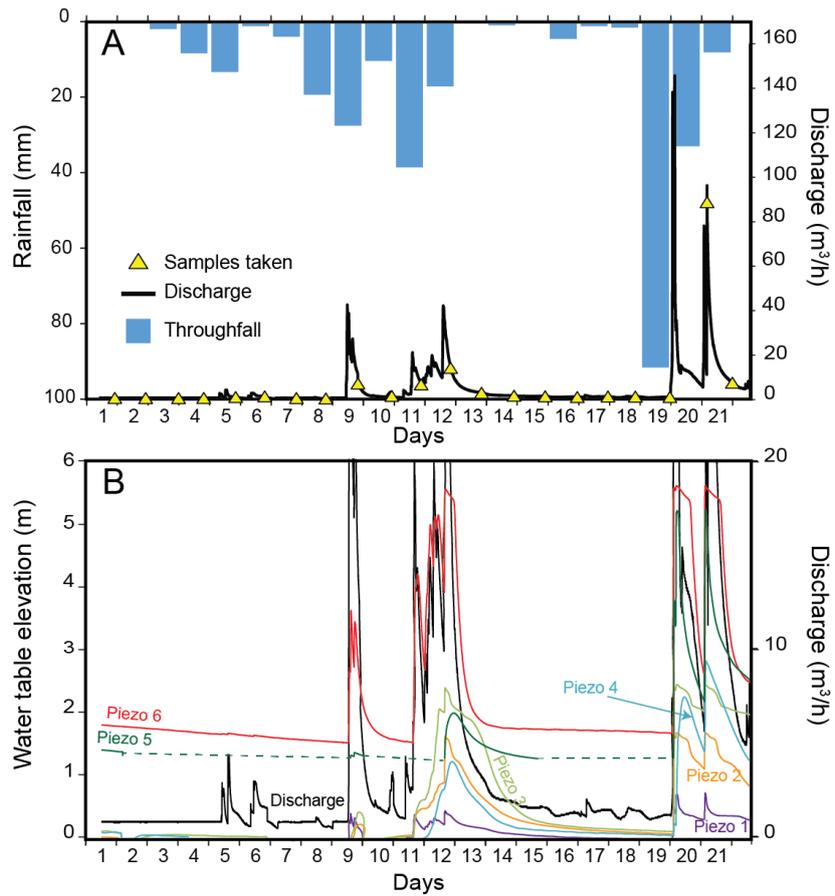


Figure 2. A. Precipitation and discharge of Quioc Creek. B. Water table elevation and discharge during the period of study. Data are from the ObsERA website (<http://webobsera.ipgp.fr/>).

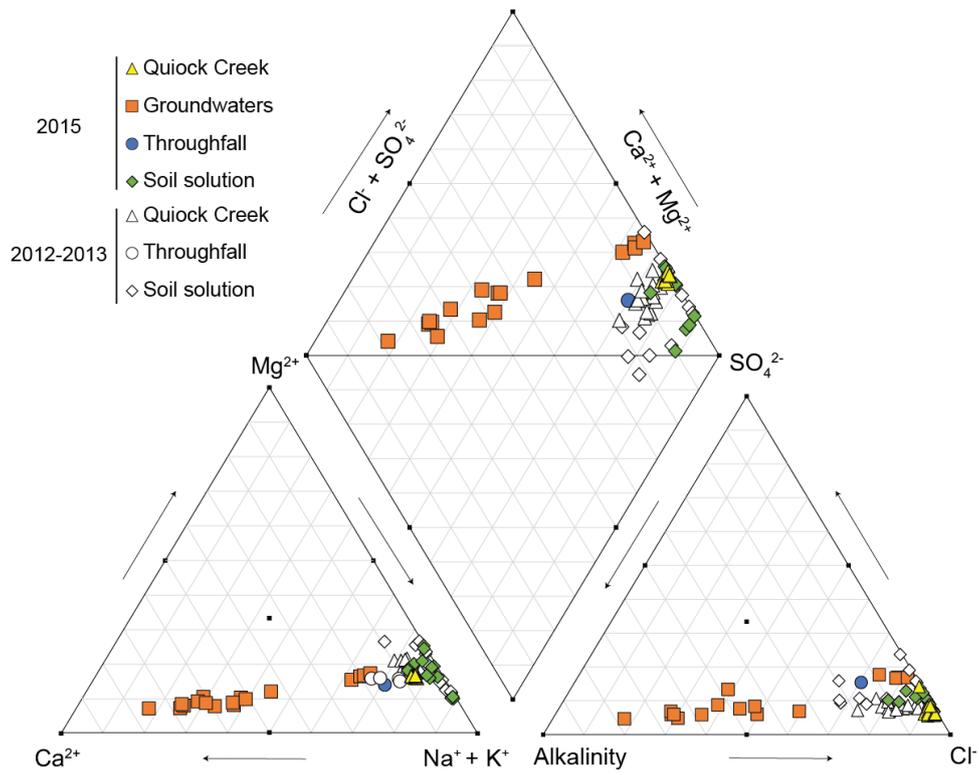


Figure 3. Piper diagram showing the relative abundance of anions and cations in samples from Quiock Creek catchment. Data for water samples collected in 2012-2013 (white symbols) are from Clergue et al. (2015).

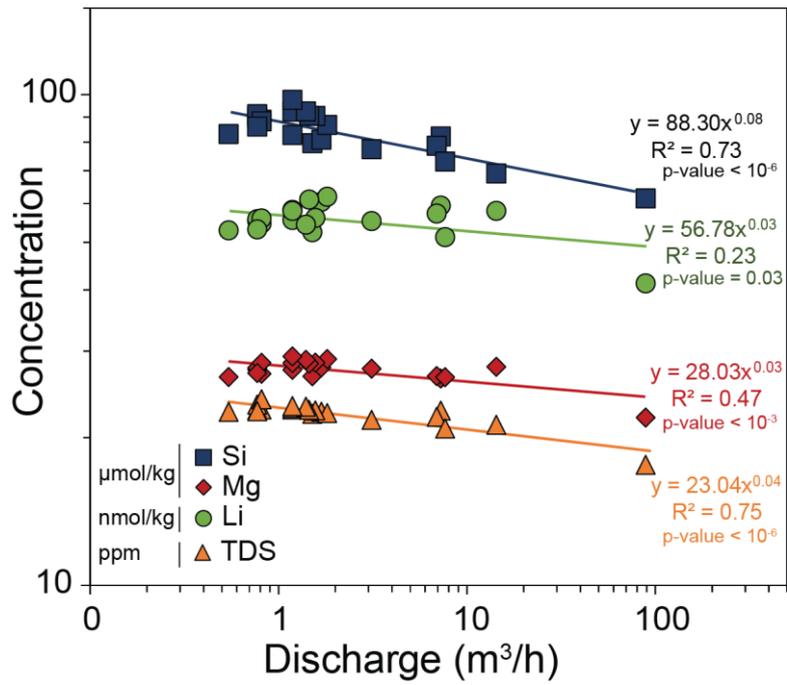


Figure 4. Si, Total Dissolved Solid (TDS), Mg and Li concentration in Quiock Creek as a function of discharge. Each coloured lines represents the power-law relationship between concentration and discharge.

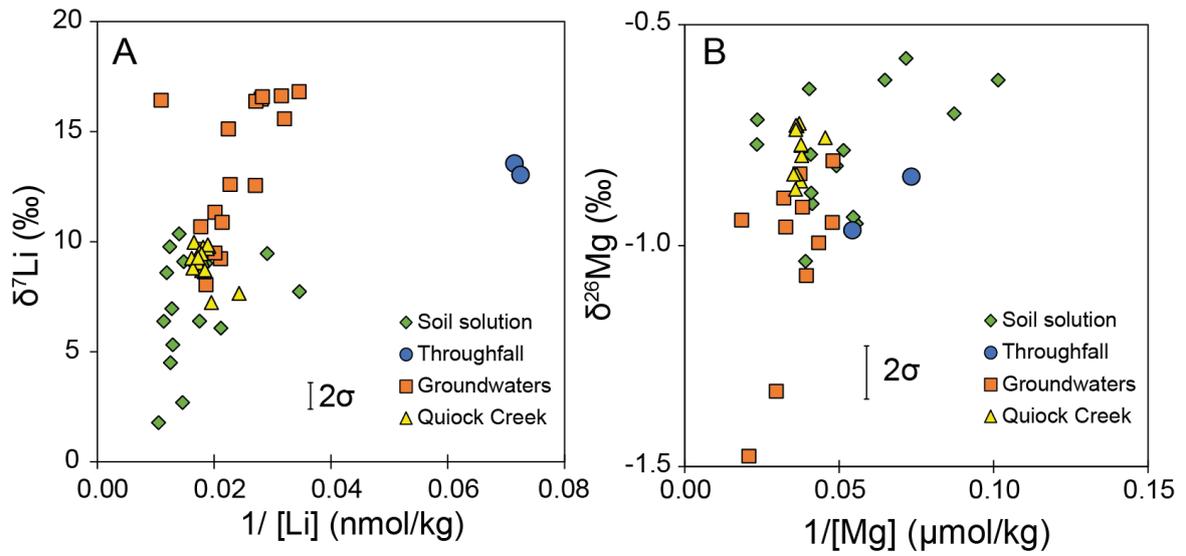


Figure 5. A. [Li] and  $\delta^7\text{Li}$  values of the dissolved load in Quiock Creek catchment. B. [Mg] and  $\delta^{26}\text{Mg}$  values of the dissolved load in Quiock Creek catchment. The error bars represent the external error ( $2\sigma$ ) of the isotopic compositions. The external error on the Li and Mg concentration are smaller than the symbols.

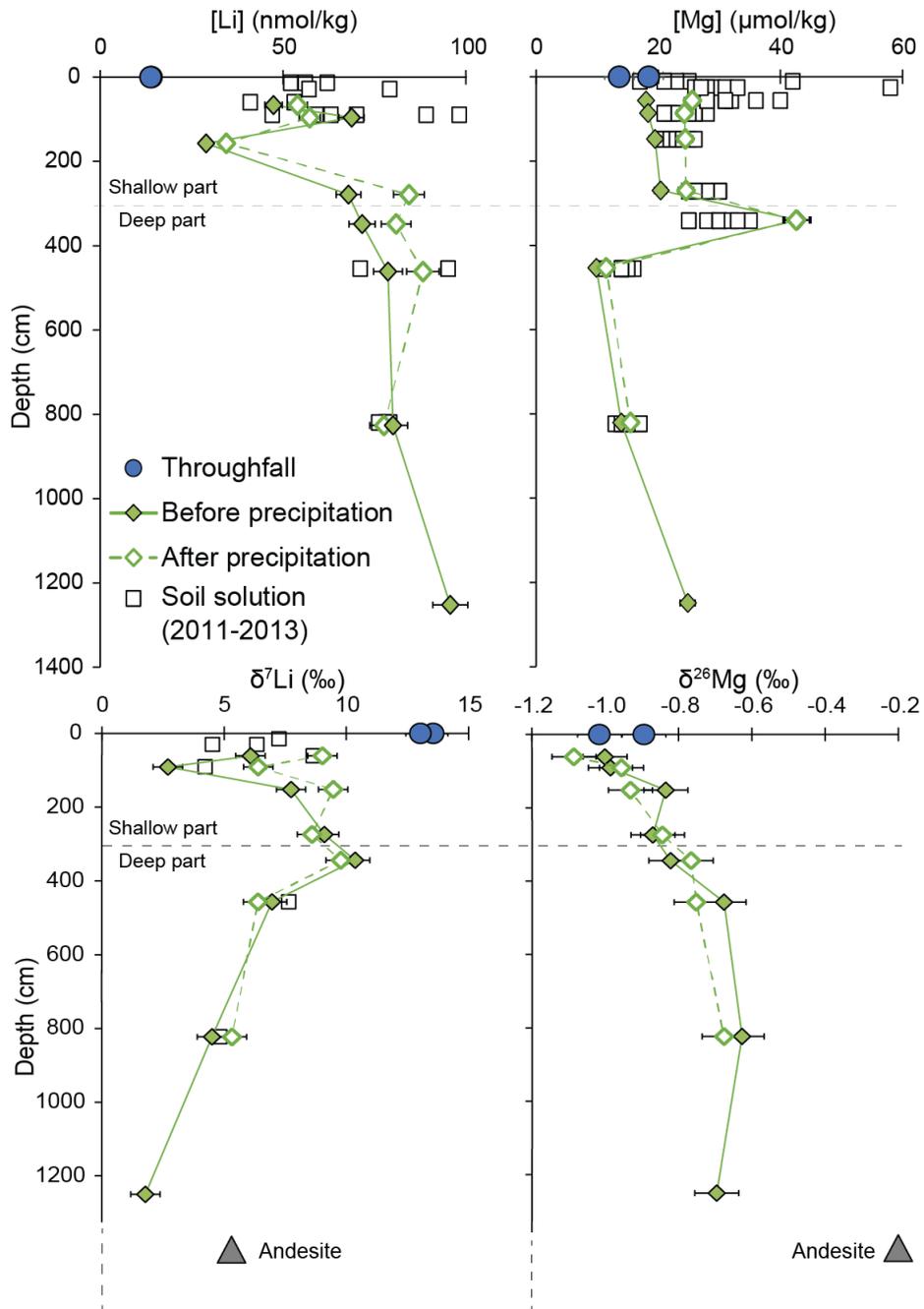


Figure 6. Li and Mg concentrations ( $\pm 5\%$ ) and isotope compositions of soil solutions taken before (Day 1) and after (Day 18) several rain events. Data for soil solution (collected in 2011-2013) are from Clergue et al. (2015),  $\delta^7\text{Li}$  and  $\delta^{26}\text{Mg}$  values for andesite are from Clergue et al. (2015) and Dessert et al. (2015).

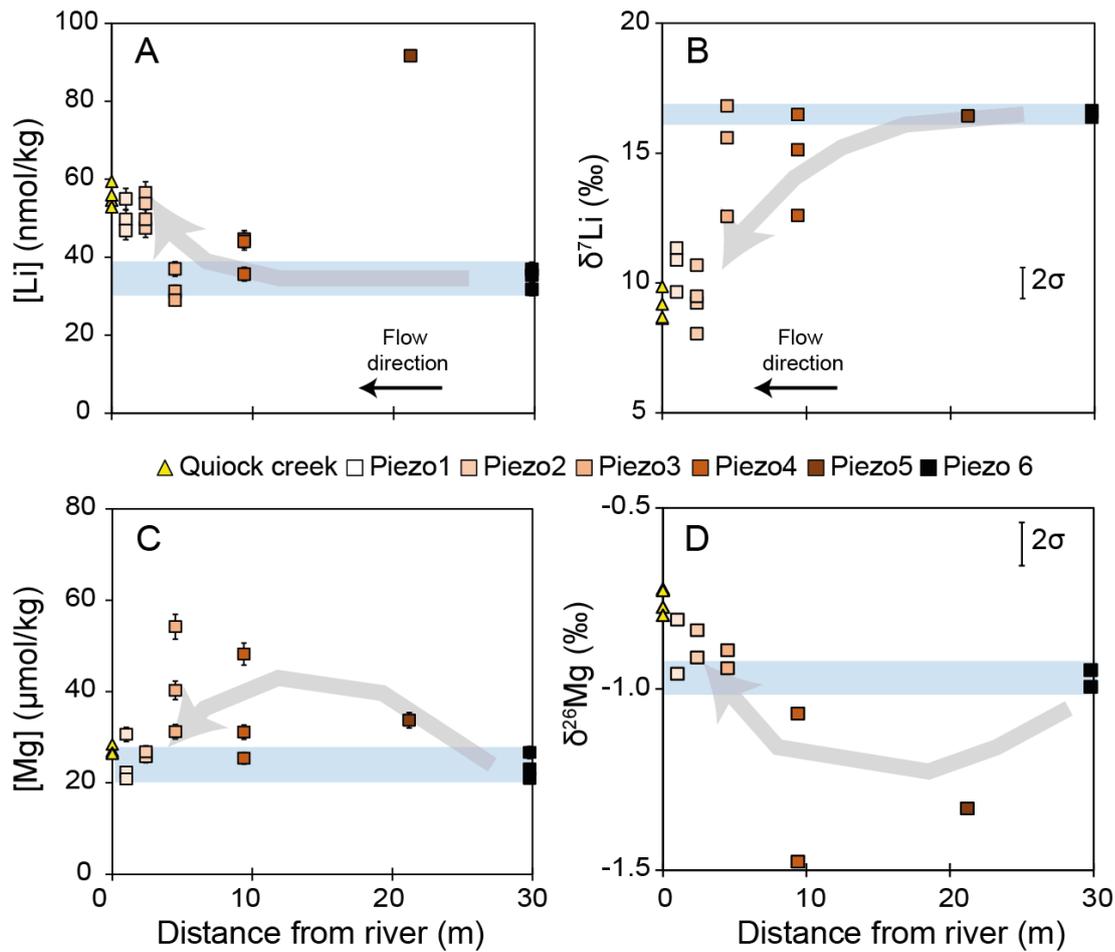


Figure 7. Evolution of groundwater [Li] and [Mg] ( $\pm 5\%$ ),  $\delta^7\text{Li}$  and  $\delta^{26}\text{Mg}$  versus distance to the river. Along this specific profile, groundwater from the Quiock Creek aquifer feeds Quiock Creek (Guérin, 2015). The blue shaded boxes highlight Piezo 6 samples likely represent river baseflow (see section 4.4.1). The grey shaded arrows show the general trend of the data points. Error bars show the external reproducibility of the isotope analyses ( $2\sigma$ ).

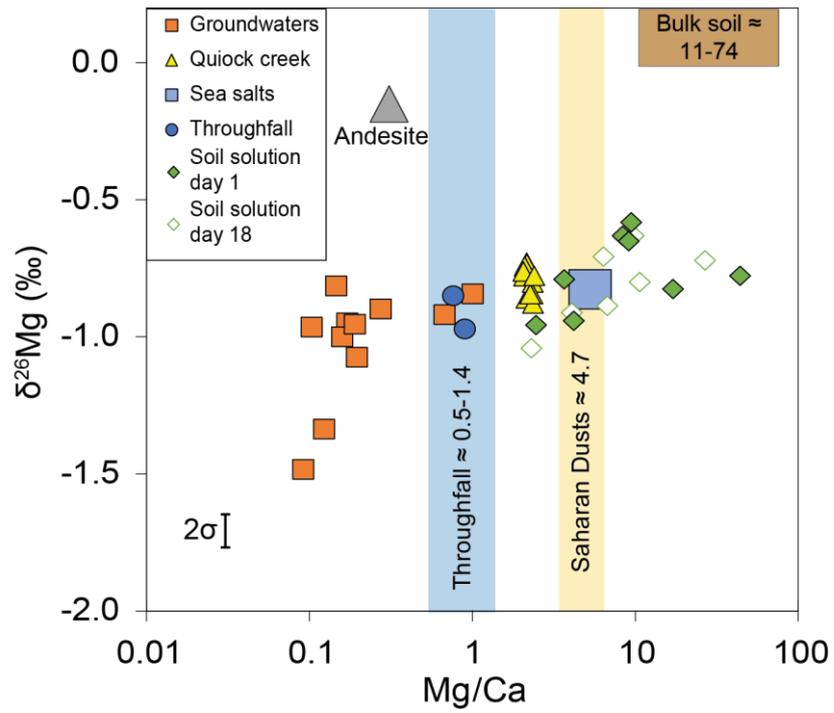


Figure 8.  $\delta^{26}\text{Mg}$  versus Mg/Ca for fluids in Quiock Creek catchment. Bedrock (andesite) and bulk soil  $\delta^{26}\text{Mg}$  are from Dessert et al. (2015) and Mg/Ca ratios used for throughfall (blue box), bulk soil (brown box) and Saharan dusts (yellow box) are from Clergue et al. (2015).

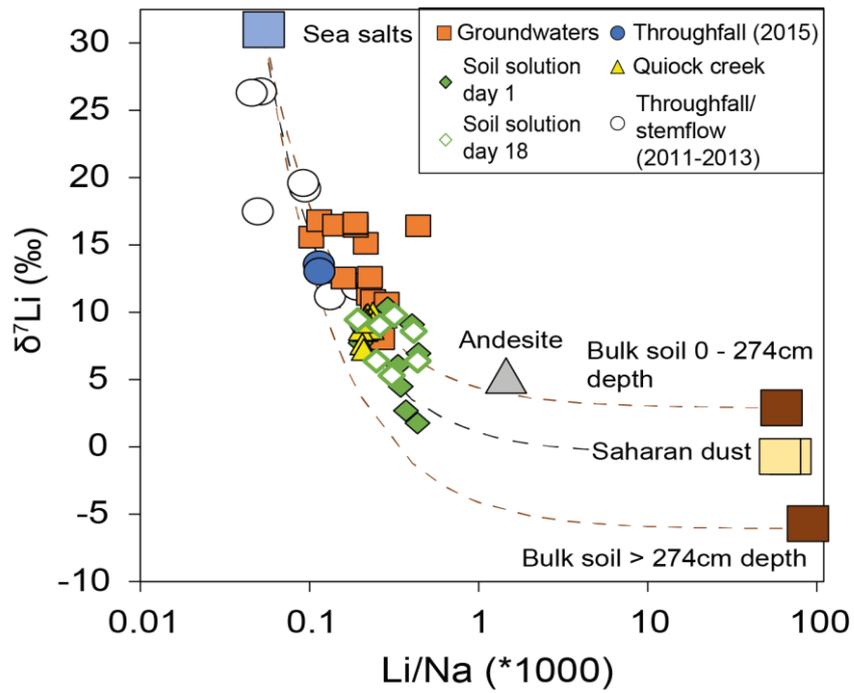


Figure 9.  $\delta^7\text{Li}$  versus  $\text{Li}/\text{Na}$  for all fluids from Quiock Creek catchment.  $\delta^7\text{Li}$  values for andesite, throughfall/stemflow (collected in 2011-2013), and bulk soils are from Clergue et al. (2015). Dashed lines represent the theoretical mixing trend between seawater and dust or bulk soils. The external error of the  $\delta^7\text{Li}$  values is smaller than the symbols.

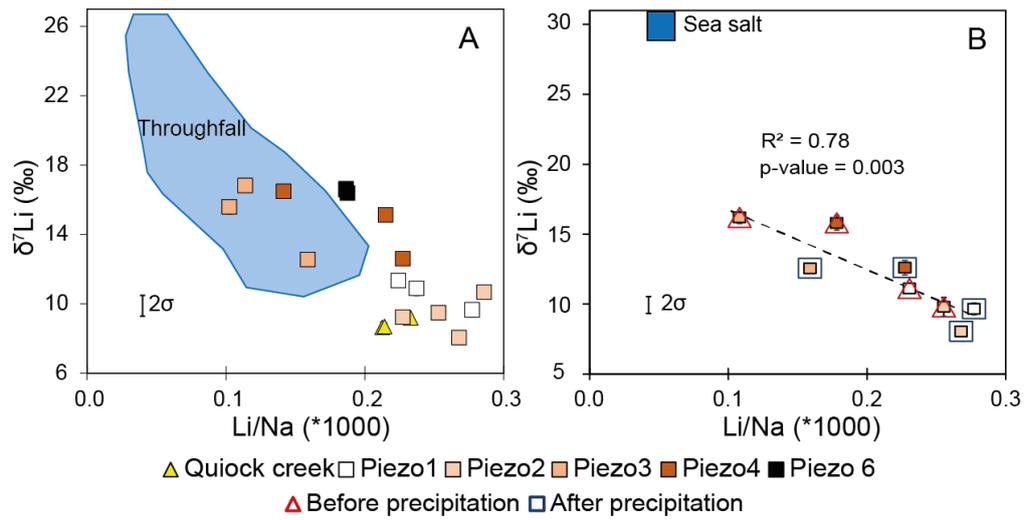


Figure 10. A. Relationship between  $\delta^7\text{Li}$  vs  $\text{Li/Na}$  for the dissolved load in groundwaters and Quiock Creek samples sampled on Day 1, 4, 8, and 9 (Piezo 5 is not shown). The blue shaded area shows the throughfall/stemflow composition (Clergue et al., 2015). B.  $\text{Li/Na}$  versus  $\delta^7\text{Li}$  in groundwaters before and after precipitation. The red open triangles show the average value for samples collected on Day 1 and 8 while the blue open squares show the values measured after a significant rain event at Day 9. The dashed line represents the linear evolution of  $\text{Li/Na}$  versus  $\delta^7\text{Li}$  before and after precipitation.

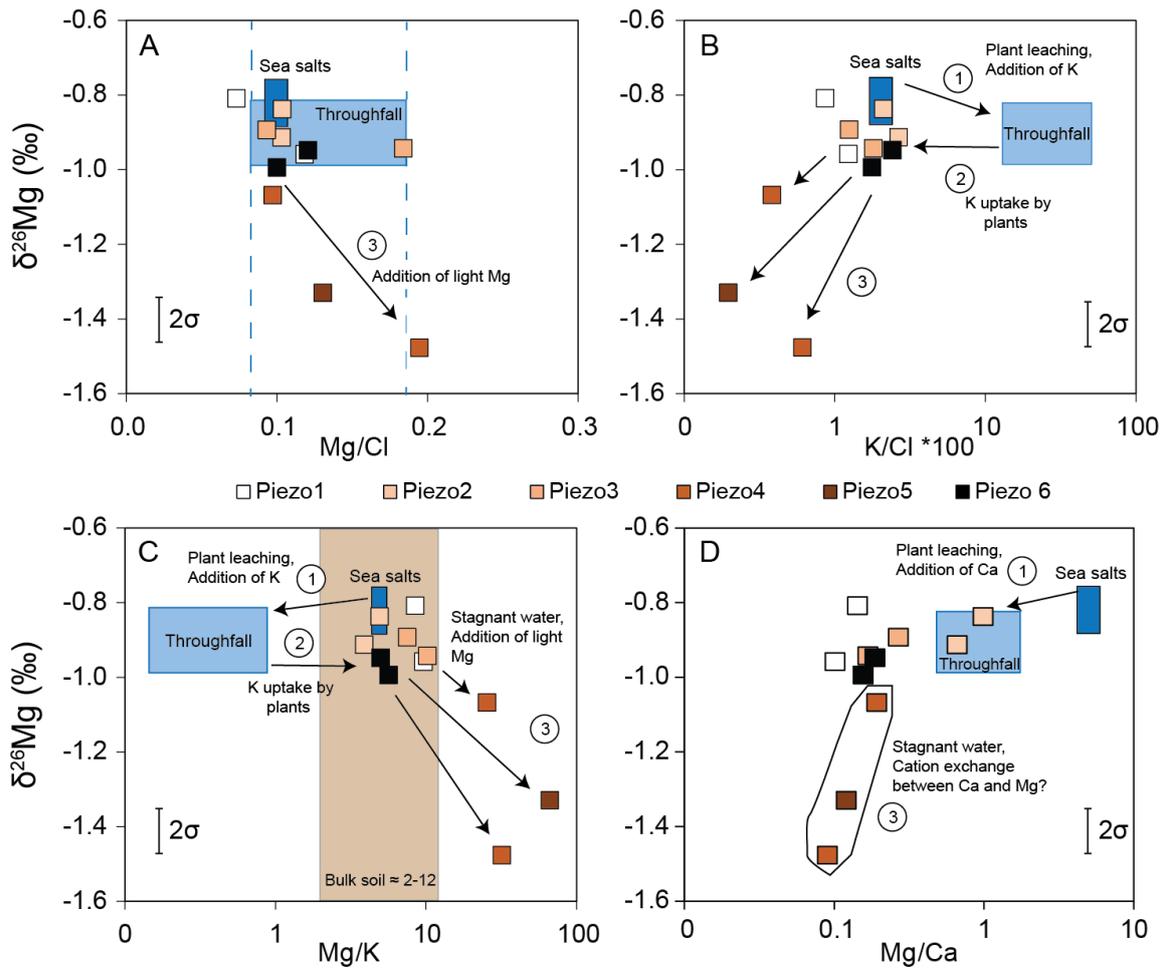


Figure 11. A. Relationship between  $\delta^{26}\text{Mg}$  vs Mg/Cl, B.  $\delta^{26}\text{Mg}$  vs K/Cl, C.  $\delta^{26}\text{Mg}$  vs Mg/K and D.  $\delta^{26}\text{Mg}$  vs Mg/Ca for the dissolved load in groundwaters. The light blue shaded box shows the throughfall composition while the dark blue shaded box shows the sea salt composition. The brown shaded box shows the composition range (Mg/K ratio) of bulk soil. Three different patterns are observed to explain change in K and Mg content together with  $\delta^{26}\text{Mg}$ .

# The response of Li and Mg isotopes to rain events in a highly-weathered catchment

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## Manuscript Tables 1-5

Table 1. Sample terminology.

| <b>Sample</b>    | <b>Description</b>       | <b>X</b>              | <b>Y</b>                      |
|------------------|--------------------------|-----------------------|-------------------------------|
| <b>L</b> X.Y     | Lysimeter/Soil solution  | Depth (61 to 1250 cm) | Collection day (1 or 18)      |
| <b>Th</b> X      | Throughfall              | Location              | -                             |
| <b>Piezo</b> X.Y | Piezometer/Groundwater   | Location (1 to 6)     | Collection day (1, 4, 8 or 9) |
| <b>QC</b> Y      | Quiock Creek/River water | -                     | Collection day (1 to 21)      |

Table 2. Field measurements and alkalinity data for Quiock Creek catchment samples. n.d = not determined, b.d = below detection limit. Discharge data are from the ObsERA website (<http://webobsera.ipgp.fr/>).

| Sample        | Day | Date       | Distance to river (m) | Temperature (°C) | pH  | Conductivity (µS/cm) | Alkalinity (µeq/L) |
|---------------|-----|------------|-----------------------|------------------|-----|----------------------|--------------------|
| Soil solution |     |            |                       |                  |     |                      |                    |
| L91.18        | 18  | 23/10/2015 | -                     | n.d              | 4.9 | n.d                  | b.d                |
| L152.1        | 1   | 06/10/2015 | -                     | n.d              | 5.2 | n.d                  | 18                 |
| L152.18       | 18  | 23/10/2015 | -                     | n.d              | 5.2 | n.d                  | 5                  |
| L274.1        | 1   | 06/10/2015 | -                     | n.d              | 4.9 | n.d                  | b.d                |
| L274.18       | 18  | 23/10/2015 | -                     | n.d              | 4.7 | n.d                  | b.d                |
| L344.1        | 1   | 06/10/2015 | -                     | n.d              | 4.8 | n.d                  | b.d                |
| L344.18       | 18  | 23/10/2015 | -                     | n.d              | 4.5 | n.d                  | b.d                |
| L457.1        | 1   | 06/10/2015 | -                     | n.d              | 5.5 | n.d                  | 22                 |
| L457.18       | 18  | 23/10/2015 | -                     | n.d              | 5.2 | n.d                  | 9                  |
| L823.1        | 1   | 06/10/2015 | -                     | n.d              | 5.1 | n.d                  | 8                  |
| L823.18       | 18  | 23/10/2015 | -                     | n.d              | 4.8 | n.d                  | b.d                |
| Throughfall   |     |            |                       |                  |     |                      |                    |
| Th1           | 11  | 16/10/2015 | -                     | 25.4             | 5.9 | 42                   | 67                 |
| Th3           | 11  | 16/10/2015 | -                     | 25.4             | 5.9 | 42                   | 28                 |
| Groundwaters  |     |            |                       |                  |     |                      |                    |
| Piezo 1.1     | 1   | 06/10/2015 | 1.0                   | 24.9             | 6.1 | 92                   | 597                |
| Piezo 1.4     | 4   | 09/10/2015 | 1.0                   | 24.8             | 6.5 | 77                   | 297                |
| Piezo 1.8     | 8   | 13/10/2015 | 1.0                   | 24.5             | 6.0 | 68                   | 254                |
| Piezo 2.1     | 1   | 06/10/2015 | 2.4                   | 25.3             | 5.6 | 49                   | 28                 |
| Piezo 2.4     | 4   | 09/10/2015 | 2.4                   | 25.9             | 5.3 | 60                   | 13                 |
| Piezo 2.8     | 8   | 13/10/2015 | 2.4                   | 24.6             | 4.9 | 48                   | 15                 |
| Piezo 2.9     | 9   | 14/10/2015 | 2.4                   | 24.6             | 4.8 | 49                   | 5                  |
| Piezo 3.1     | 1   | 06/10/2015 | 4.5                   | 24.5             | 6.3 | 105                  | 691                |
| Piezo 3.8     | 8   | 13/10/2015 | 4.5                   | 24.5             | 6.4 | 109                  | 529                |
| Piezo 3.9     | 9   | 14/10/2015 | 4.5                   | 24.7             | 5.8 | 72                   | 187                |
| Piezo 4.1     | 1   | 06/10/2015 | 9.4                   | 24.2             | 6.4 | 149                  | 1108               |
| Piezo 4.8     | 8   | 13/10/2015 | 9.4                   | 24.1             | 6.0 | 94                   | 566                |
| Piezo 4.9     | 9   | 14/10/2015 | 9.4                   | 24.4             | 5.6 | 65                   | 238                |
| Piezo 5.1     | 1   | 06/10/2015 | 21.2                  | 24.4             | 6.3 | 94                   | 579                |
| Piezo 6.1     | 1   | 06/10/2015 | 29.8                  | 24.2             | 5.7 | 65                   | 315                |
| Piezo 6.8     | 8   | 13/10/2015 | 29.8                  | n.d              | n.d | n.d                  | n.d                |
| Piezo 6.9     | 9   | 14/10/2015 | 29.8                  | 24.7             | 5.6 | 53                   | 214                |
| Sample        | Day | Date       | Discharge (m³/h)      | Temperature (°C) | pH  | Conductivity (µS/cm) | Alkalinity (µeq/L) |
| Quiock Creek  |     |            |                       |                  |     |                      |                    |
| QC1           | 1   | 06/10/2015 | 0.8                   | 25.5             | 5.5 | 53                   | b.d                |
| QC2           | 2   | 07/10/2015 | 0.8                   | 25.3             | 5.5 | 48                   | 1                  |
| QC3           | 3   | 08/10/2015 | 0.8                   | 25.5             | 5.6 | 52                   | 8                  |
| QC4           | 4   | 09/10/2015 | 0.8                   | 25               | 5.5 | 52                   | 7                  |
| QC5           | 5   | 10/10/2015 | 1.2                   | 25               | 5.6 | 49                   | 5                  |
| QC6           | 6   | 11/10/2015 | 1.5                   | 24.7             | 5.3 | 55                   | b.d                |
| QC7           | 7   | 12/10/2015 | 0.8                   | 24.9             | 5.3 | 56                   | b.d                |
| QC8           | 8   | 13/10/2015 | 0.5                   | 24.4             | 5.3 | 52                   | 10                 |
| QC9           | 9   | 14/10/2015 | 7.3                   | 24.7             | 5.1 | 48                   | 6                  |
| QC10          | 10  | 15/10/2015 | 1.7                   | 24.8             | 5.2 | 50                   | 3                  |
| QC11          | 11  | 16/10/2015 | 6.9                   | 24.5             | 5.1 | 48                   | 5                  |
| QC12          | 12  | 17/10/2015 | 14.3                  | 24.2             | 5.1 | 45                   | 1                  |
| QC13          | 13  | 18/10/2015 | 3.1                   | 23.7             | 5.2 | 46                   | 2                  |
| QC14          | 14  | 19/10/2015 | 1.8                   | 23.8             | 5.2 | 46                   | b.d                |
| QC15          | 15  | 20/10/2015 | 1.6                   | 23.9             | 5.2 | 47                   | 5                  |
| QC16          | 16  | 21/10/2015 | 1.2                   | 24.7             | 5.3 | 48                   | 7                  |
| QC17          | 17  | 22/10/2015 | 1.5                   | 25               | 5.5 | 48                   | 1                  |
| QC18          | 18  | 23/10/2015 | 1.4                   | 24.1             | 5.1 | 48                   | b.d                |
| QC19          | 19  | 24/10/2015 | 1.2                   | 24.2             | 5.2 | 47                   | 0.1                |
| QC20          | 20  | 25/10/2015 | 88.8                  | 24.3             | 4.9 | 35                   | b.d                |
| QC21          | 21  | 26/10/2015 | 7.7                   | 24.5             | 4.9 | 42                   | 0.4                |

Table 3. Concentrations of major and minor elements in soil solution, groundwater, throughfall and Quiock Creek itself. n.d = not determined, b.d = below detection limit. TDS\* = Total Dissolved Solids, calculated as the sum of cation, anion and Si concentrations in ppm.

| Sample               | μmol/kg         |                               |                 |                  |     |                  |                |      |     |     | nmol/kg |    | TDS* |
|----------------------|-----------------|-------------------------------|-----------------|------------------|-----|------------------|----------------|------|-----|-----|---------|----|------|
|                      | Cl <sup>-</sup> | SO <sub>4</sub> <sup>2-</sup> | Na <sup>+</sup> | Ca <sup>2+</sup> | Si  | Mg <sup>2+</sup> | K <sup>+</sup> | Al   | B   | Fe  | Sr      | Li |      |
| <i>Soil solution</i> |                 |                               |                 |                  |     |                  |                |      |     |     |         |    |      |
| L61.1                | n.d             | n.d                           | 142             | 7.5              | 86  | 18.0             | 3.0            | 5.3  | 2.4 | b.d | 53      | 47 | -    |
| L61.18               | n.d             | n.d                           | 207             | 11.3             | 67  | 25.6             | 4.5            | 6.7  | 3.6 | b.d | 76      | 54 | -    |
| L91.1                | n.d             | n.d                           | 185             | 4.5              | 92  | 18.3             | 3.1            | 3.3  | 1.5 | b.d | 19      | 69 | -    |
| L91.18               | 264             | 9.3                           | 230             | 6.1              | 68  | 24.2             | 4.1            | 3.9  | 2.1 | b.d | 21      | 57 | 19   |
| L152.1               | 206             | 11.7                          | 145             | 5.4              | 45  | 19.4             | 2.1            | 3.2  | 0.8 | b.d | 14      | 29 | 15   |
| L152.18              | 207             | 12.3                          | 179             | 3.7              | 52  | 24.4             | 1.9            | 4.6  | 1.0 | b.d | 13      | 34 | 15   |
| L274.1               | 244             | 12.5                          | 168             | 1.2              | 65  | 20.4             | 2.9            | 9.3  | 2.4 | b.d | 15      | 68 | 16   |
| L274.18              | 253             | 14.4                          | 204             | 2.4              | 78  | 24.5             | 3.6            | 9.4  | 2.8 | b.d | 21      | 84 | 18   |
| L344.1               | 388             | 15.0                          | 247             | 1.0              | 75  | 42.8             | 7.1            | 12.7 | 2.3 | b.d | 16      | 71 | 25   |
| L344.18              | 360             | 17.1                          | 255             | 1.6              | 87  | 42.6             | 7.8            | 11.4 | 2.4 | b.d | 18      | 81 | 24   |
| L457.1               | 184             | 11.4                          | 178             | 1.2              | 102 | 9.9              | 3.5            | 5.5  | 0.8 | b.d | 10      | 79 | 16   |
| L457.18              | 195             | 14.8                          | 202             | 1.8              | 106 | 11.5             | 3.8            | 5.3  | 1.0 | b.d | 13      | 88 | 17   |
| L823.1               | 264             | 16.6                          | 231             | 1.5              | 113 | 14.0             | 14.2           | 6.5  | 0.9 | b.d | 14      | 80 | 21   |
| L823.18              | 271             | 18.5                          | 253             | 1.6              | 106 | 15.4             | 15.3           | 6.6  | 1.0 | b.d | 14      | 77 | 21   |
| L1250                | n.d             | n.d                           | 220             | 2.8              | 153 | 24.8             | 34.9           | 1.8  | 0.9 | b.d | 12      | 95 | -    |
| <i>Throughfall</i>   |                 |                               |                 |                  |     |                  |                |      |     |     |         |    |      |
| Th1                  | n.d             | 7.1                           | 123             | 20.9             | 18  | 18.4             | 66.7           | 2.9  | 3.0 | 0.6 | 64      | 14 | -    |
| Th3                  | 144             | 15.4                          | 121             | 18.2             | 26  | 13.6             | 30.6           | 2.5  | 3.0 | 0.5 | 55      | 14 | 14   |
| <i>Groundwater</i>   |                 |                               |                 |                  |     |                  |                |      |     |     |         |    |      |
| Piezo 1.1            | 259             | 25.9                          | 222             | 302              | 58  | 30.6             | 3.2            | 2.5  | 1.5 | 3.7 | 232     | 50 | 62   |
| Piezo 1.4            | 278             | 23.0                          | 197             | 178              | 60  | 22.3             | 2.4            | 0.6  | 1.4 | 1.7 | 160     | 47 | 41   |
| Piezo 1.8            | 285             | 16.4                          | 198             | 145              | 68  | 20.8             | 2.5            | 0.9  | 1.4 | 0.2 | 151     | 55 | 37   |
| Piezo 2.1            | 255             | 29.8                          | 209             | 40               | 69  | 26.2             | 6.8            | 10.8 | 2.1 | 5.9 | 88      | 47 | 23   |
| Piezo 2.4            | 260             | 27.3                          | 198             | 32               | 68  | 25.8             | 5.9            | 3.9  | 1.9 | 3.2 | 119     | 56 | 21   |
| Piezo 2.8            | 261             | 27.1                          | 196             | 30               | 69  | 25.7             | 5.6            | 3.5  | 1.9 | 6.5 | 95      | 50 | 22   |
| Piezo 2.9            | 259             | 26.3                          | 201             | 27               | 64  | 26.8             | 5.5            | 9.7  | 2.0 | 5.3 | 100     | 54 | 21   |
| Piezo 3.1            | 295             | 35.1                          | 305             | 322              | 41  | 54.2             | 5.3            | 7.5  | 1.3 | 4.5 | 187     | 31 | 71   |
| Piezo 3.8            | 328             | 25.6                          | 254             | 284              | 41  | 40.3             | 3.9            | 3.0  | 1.3 | 2.4 | 179     | 29 | 60   |
| Piezo 3.9            | 335             | 18.6                          | 233             | 116              | 44  | 31.2             | 4.2            | 8.3  | 1.5 | 0.6 | 121     | 37 | 35   |
| Piezo 4.1            | 248             | 31.5                          | 252             | 534              | 40  | 48.2             | 1.5            | 1.1  | 2.3 | 0.2 | 99      | 36 | 97   |
| Piezo 4.8            | 269             | 20.0                          | 208             | 270              | 48  | 31.1             | 1.5            | 2.2  | 1.8 | 1.1 | 77      | 45 | 58   |
| Piezo 4.9            | 261             | 22.0                          | 194             | 132              | 48  | 25.4             | 1.0            | 2.1  | 1.4 | 4.2 | 51      | 44 | 35   |
| Piezo 5.1            | 259             | 25.4                          | 209             | 279              | 43  | 33.7             | 0.5            | 4.2  | 1.3 | 3.5 | 127     | 92 | 59   |
| Piezo 6.1            | 231             | 25.3                          | 197             | 148              | 43  | 23.0             | 4.1            | 1.8  | 1.7 | 2.2 | 90      | 37 | 39   |
| Piezo 6.8            | n.d             | n.d                           | 190             | 193              | 47  | 26.7             | 3.8            | n.d  | 1.9 | n.d | 133     | 35 | -    |
| Piezo 6.9            | 174             | 29.3                          | 170             | 112              | 48  | 20.9             | 4.2            | 11.9 | 2.4 | 2.8 | 85      | 32 | 31   |
| <i>Quiock Creek</i>  |                 |                               |                 |                  |     |                  |                |      |     |     |         |    |      |
| QC1                  | 334             | 10.0                          | 257             | 12.8             | 89  | 27.0             | 9.0            | 2.1  | 1.6 | 0.3 | 57      | 55 | 23   |
| QC2                  | 333             | 9.8                           | 258             | 13.1             | 90  | 27.5             | 6.2            | 2.0  | 1.6 | 0.2 | 67      | 55 | 23   |
| QC3                  | 336             | 9.6                           | 260             | 13.1             | 91  | 27.8             | 6.5            | 2.1  | 1.5 | 0.3 | 64      | 56 | 23   |
| QC4                  | 350             | 11.0                          | 261             | 14.0             | 88  | 28.4             | 6.7            | 2.5  | 1.7 | 0.3 | 79      | 56 | 24   |
| QC5                  | 326             | 13.5                          | 247             | 13.3             | 83  | 27.5             | 9.3            | 3.4  | 1.8 | 0.4 | 68      | 56 | 23   |
| QC6                  | 332             | 12.5                          | 241             | 12.7             | 80  | 26.7             | 8.3            | 3.4  | 1.8 | 0.4 | 64      | 52 | 22   |
| QC7                  | 335             | 11.0                          | 246             | 13.0             | 86  | 27.1             | 7.5            | 4.0  | 1.7 | 0.4 | 65      | 53 | 23   |
| QC8                  | 327             | 10.5                          | 240             | 13.0             | 83  | 26.6             | 7.5            | 3.0  | 1.7 | 0.4 | 64      | 53 | 23   |
| QC9                  | 328             | 11.3                          | 255             | 11.5             | 82  | 26.4             | 7.0            | 3.3  | 1.7 | 0.4 | 60      | 59 | 23   |
| QC10                 | 317             | 13.8                          | 255             | 13.6             | 81  | 27.8             | 8.1            | 4.9  | 1.9 | 0.7 | 78      | 60 | 23   |
| QC11                 | 319             | 10.7                          | 250             | 11.8             | 79  | 26.7             | 6.1            | 3.8  | 1.7 | 0.6 | 60      | 57 | 22   |
| QC12                 | 307             | 11.8                          | 249             | 12.1             | 69  | 27.9             | 4.9            | 3.8  | 1.8 | 0.6 | 66      | 58 | 21   |
| QC13                 | 321             | 9.3                           | 251             | 12.1             | 77  | 27.6             | 4.8            | 1.8  | 1.6 | 0.2 | 62      | 55 | 22   |
| QC14                 | 325             | 9.9                           | 261             | 13.1             | 87  | 28.9             | 5.4            | 1.8  | 1.6 | 0.2 | 75      | 62 | 22   |
| QC15                 | 326             | 9.9                           | 257             | 12.4             | 90  | 28.4             | 5.2            | 2.6  | 1.5 | 0.2 | 63      | 56 | 23   |
| QC16                 | 326             | 10.1                          | 262             | 12.8             | 92  | 28.4             | 5.4            | 1.8  | 1.5 | 0.2 | 66      | 58 | 23   |
| QC17                 | 328             | 10.1                          | 263             | 13.3             | 91  | 28.3             | 6.3            | 2.3  | 1.6 | 0.2 | 78      | 61 | 23   |
| QC18                 | 330             | 11.0                          | 271             | 12.6             | 92  | 28.8             | 6.5            | 2.6  | 1.6 | 0.4 | 58      | 54 | 23   |
| QC19                 | 330             | 10.4                          | 269             | 12.8             | 98  | 29.3             | 5.8            | 2.2  | 1.5 | 0.3 | 65      | 58 | 23   |
| QC20                 | 226             | 18.3                          | 201             | 10.9             | 61  | 22.0             | 4.8            | 8.0  | 2.0 | 1.5 | 56      | 41 | 18   |
| QC21                 | 297             | 13.2                          | 245             | 11.3             | 73  | 26.6             | 4.3            | 2.1  | 1.7 | 0.3 | 61      | 51 | 21   |

Table 4. Li and Mg isotope compositions in soil solution, groundwater, throughfall and Quiock Creek

itself. n.d = not determined.  $2\sigma$  is the internal uncertainty of the sample measurements.

| Sample               | $\delta^7\text{Li}$ (‰) | $2\sigma$ | $\delta^{25}\text{Mg}$ (‰) | $2\sigma$ | $\delta^{26}\text{Mg}$ (‰) | $2\sigma$ |
|----------------------|-------------------------|-----------|----------------------------|-----------|----------------------------|-----------|
| <i>Soil solution</i> |                         |           |                            |           |                            |           |
| L61.1                | 6.1                     | 0.5       | -0.53                      | 0.01      | -0.95                      | 0.00      |
| L61.18               | 9.0                     | 0.5       | -0.54                      | 0.03      | -1.04                      | 0.05      |
| L91.1                | 2.7                     | 0.2       | -0.50                      | 0.03      | -0.94                      | 0.05      |
| L91.18               | 6.4                     | 0.3       | -0.48                      | 0.01      | -0.91                      | 0.03      |
| L152.1               | 7.7                     | 0.5       | -0.42                      | 0.02      | -0.78                      | 0.04      |
| L152.18              | 9.5                     | 0.1       | -0.48                      | 0.04      | -0.88                      | 0.00      |
| L274.1               | 9.1                     | 0.1       | -0.46                      | 0.05      | -0.82                      | 0.04      |
| L274.18              | 8.6                     | 0.1       | -0.41                      | 0.03      | -0.79                      | 0.05      |
| L344.1               | 10.4                    | 0.5       | -0.41                      | 0.07      | -0.77                      | 0.06      |
| L344.18              | 9.8                     | 0.3       | -0.37                      | 0.01      | -0.72                      | 0.02      |
| L457.1               | 7.0                     | 0.1       | -0.32                      | 0.01      | -0.63                      | 0.01      |
| L457.18              | 6.4                     | 0.6       | -0.36                      | 0.03      | -0.70                      | 0.06      |
| L823.1               | 4.5                     | 0.1       | -0.30                      | 0.00      | -0.58                      | 0.02      |
| L823.18              | 5.3                     | 0.2       | -0.32                      | 0.03      | -0.63                      | 0.07      |
| L1250                | 1.8                     | 0.0       | -0.33                      | 0.01      | -0.65                      | 0.03      |
| <i>Throughfall</i>   |                         |           |                            |           |                            |           |
| Th1                  | 13.6                    | 0.2       | -0.50                      | 0.01      | -0.97                      | 0.02      |
| Th3                  | 13.0                    | 0.0       | -0.45                      | 0.00      | -0.84                      | 0.04      |
| <i>Groundwater</i>   |                         |           |                            |           |                            |           |
| Piezo 1.1            | 11.3                    | 0.1       | -0.52                      | 0.04      | -0.96                      | 0.06      |
| Piezo 1.4            | 10.9                    | 0.4       | n.d                        | n.d       | n.d                        | n.d       |
| Piezo 1.8            | 9.7                     | 0.2       | -0.43                      | 0.08      | -0.81                      | 0.04      |
| Piezo 2.1            | 9.2                     | 0.7       | -0.48                      | 0.02      | -0.91                      | 0.04      |
| Piezo 2.4            | 10.7                    | 0.1       | n.d                        | n.d       | n.d                        | n.d       |
| Piezo 2.8            | 9.5                     | 0.2       | n.d                        | n.d       | n.d                        | n.d       |
| Piezo 2.9            | 8.0                     | 0.1       | -0.43                      | 0.05      | -0.84                      | 0.06      |
| Piezo 3.1            | 15.6                    | 0.4       | -0.49                      | 0.01      | -0.94                      | 0.02      |
| Piezo 3.8            | 16.8                    | 0.0       | n.d                        | n.d       | n.d                        | n.d       |
| Piezo 3.9            | 12.6                    | 1.3       | -0.45                      | 0.00      | -0.89                      | 0.07      |
| Piezo 4.1            | 16.5                    | 0.5       | -0.78                      | 0.02      | -1.48                      | 0.01      |
| Piezo 4.8            | 15.1                    | 0.3       | n.d                        | n.d       | n.d                        | n.d       |
| Piezo 4.9            | 12.6                    | 0.3       | -0.56                      | 0.02      | -1.07                      | 0.01      |
| Piezo 5.1            | 16.4                    | 0.2       | -0.73                      | 0.09      | -1.33                      | 0.10      |
| Piezo 6.1            | 16.4                    | 0.3       | -0.51                      | 0.03      | -0.99                      | 0.05      |
| Piezo 6.8            | 16.6                    | 0.2       | n.d                        | n.d       | n.d                        | n.d       |
| Piezo 6.9            | 16.6                    | 0.3       | -0.48                      | 0.05      | -0.95                      | 0.04      |
| <i>Quiock Creek</i>  |                         |           |                            |           |                            |           |
| QC1                  | 8.6                     | 0.3       | -0.38                      | 0.01      | -0.72                      | 0.02      |
| QC2                  | 9.8                     | 0.4       | -0.38                      | 0.02      | -0.73                      | 0.05      |
| QC3                  | 9.2                     | 0.1       | -0.38                      | 0.01      | -0.73                      | 0.01      |
| QC4                  | 8.7                     | 0.2       | n.d                        | n.d       | n.d                        | n.d       |
| QC5                  | 9.1                     | 0.6       | n.d                        | n.d       | n.d                        | n.d       |
| QC6                  | 9.8                     | 0.1       | -0.44                      | 0.03      | -0.85                      | 0.06      |
| QC7                  | 9.7                     | 0.4       | n.d                        | n.d       | n.d                        | n.d       |
| QC8                  | 9.9                     | 0.1       | -0.41                      | 0.01      | -0.77                      | 0.02      |
| QC9                  | 9.2                     | 0.1       | -0.41                      | 0.06      | -0.80                      | 0.05      |
| QC10                 | 10.0                    | 0.2       | -0.38                      | 0.00      | -0.74                      | 0.03      |
| QC11                 | 9.5                     | 0.1       | n.d                        | n.d       | n.d                        | n.d       |
| QC12                 | 9.1                     | 0.1       | -0.45                      | 0.01      | -0.87                      | 0.01      |
| QC13                 | 8.8                     | 0.3       | -0.43                      | 0.01      | -0.84                      | 0.01      |
| QC14                 | 9.2                     | 0.3       | n.d                        | n.d       | n.d                        | n.d       |
| QC15                 | 9.5                     | 0.1       | n.d                        | n.d       | n.d                        | n.d       |
| QC16                 | 9.0                     | 0.2       | -0.43                      | 0.03      | -0.84                      | 0.03      |
| QC17                 | 8.8                     | 0.0       | n.d                        | n.d       | n.d                        | n.d       |
| QC18                 | 8.7                     | 0.1       | n.d                        | n.d       | n.d                        | n.d       |
| QC19                 | 9.3                     | 0.0       | n.d                        | n.d       | n.d                        | n.d       |
| QC20                 | 7.7                     | 0.2       | -0.40                      | 0.01      | -0.76                      | 0.03      |
| QC21                 | 7.2                     | 0.6       | -0.40                      | 0.06      | -0.77                      | 0.06      |

Table 5. Elemental contribution (%) of sea salts in Quiock Creek catchment fluids where  $(\text{Mg}/\text{Cl})_{\text{sea}} = 0.1$ ,  $(\text{Ca}/\text{Cl})_{\text{sea}} = 0.02$ ,  $(\text{K}/\text{Cl})_{\text{sea}} = 0.02$  and  $(\text{Na}/\text{Cl})_{\text{sea}} = 0.86$  (Dessert et al., 2015).

| X             | Amount derived from sea salt (%) |     |     |     |     |     |     |     |     |     |
|---------------|----------------------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
|               | Li                               |     | Mg  |     | Ca  |     | K   |     | Na  |     |
|               | Min                              | Max | Min | Max | Min | Max | Min | Max | Min | Max |
| Soil solution | 10                               | 33  | 85  | 100 | 76  | 100 | 35  | 100 | 83  | 100 |
| Throughfall   | 44                               | 48  | 77  | 100 | 13  | 16  | 4   | 9   | 94  | 100 |
| Groundwaters  | 13                               | 52  | 51  | 100 | 1   | 19  | 75  | 100 | 83  | 100 |
| Quiock Creek  | 24                               | 29  | 100 | 100 | 41  | 57  | 70  | 100 | 96  | 100 |

# The response of Li and Mg isotopes to rain events in a highly-weathered catchment

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## Appendix/ Supplementary Figures A1 -A7

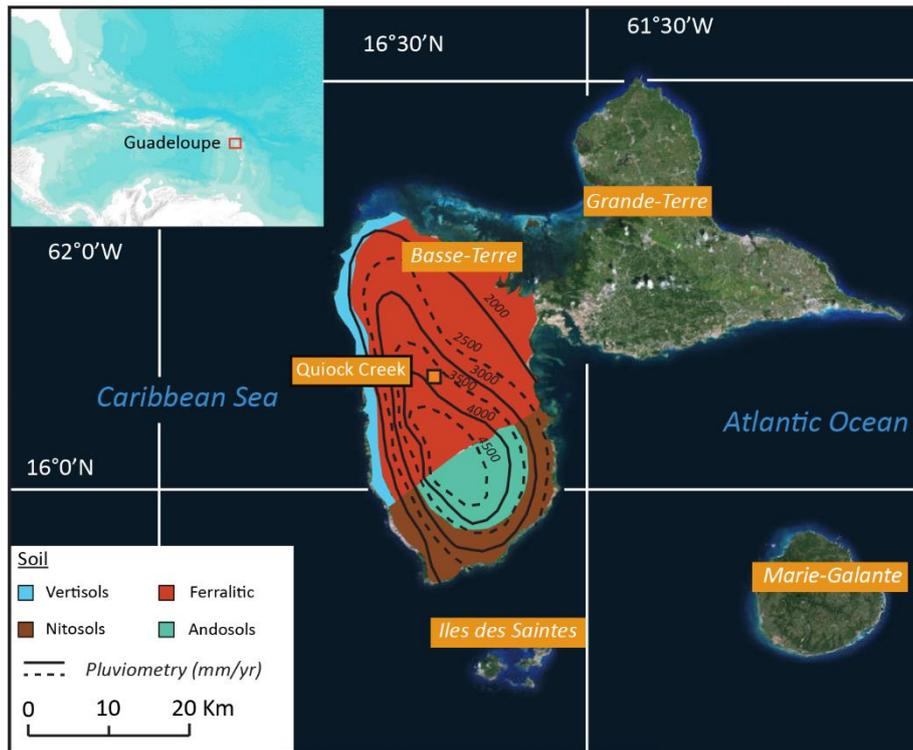


Figure A 1. Location of Quiock Creek catchment (orange square; 16°17'N, 61°60'W) in Guadeloupe with isohyets (adapted from Lloret et al., 2010) and simplified map of Guadeloupe soils (adapted from Colmeet-Daage and Bernard, 1979).

The hydrological conditions of Quiock Creek catchment since the soil solution reservoirs were first emptied is reported here. A description of these conditions is necessary to accurately interpret the soil solution and groundwater chemistry of the sample collected during the first day of the campaign. Briefly, during this period a relatively small input of rainfall entered the catchment (~36.4 mm over 18 days) and therefore the water table elevation decreased and discharge was relatively low (maximum of 12m<sup>3</sup>/h on 28/09/15). The water table in Piezo 1, 2 and 3 was below the river elevation at the beginning of the study.

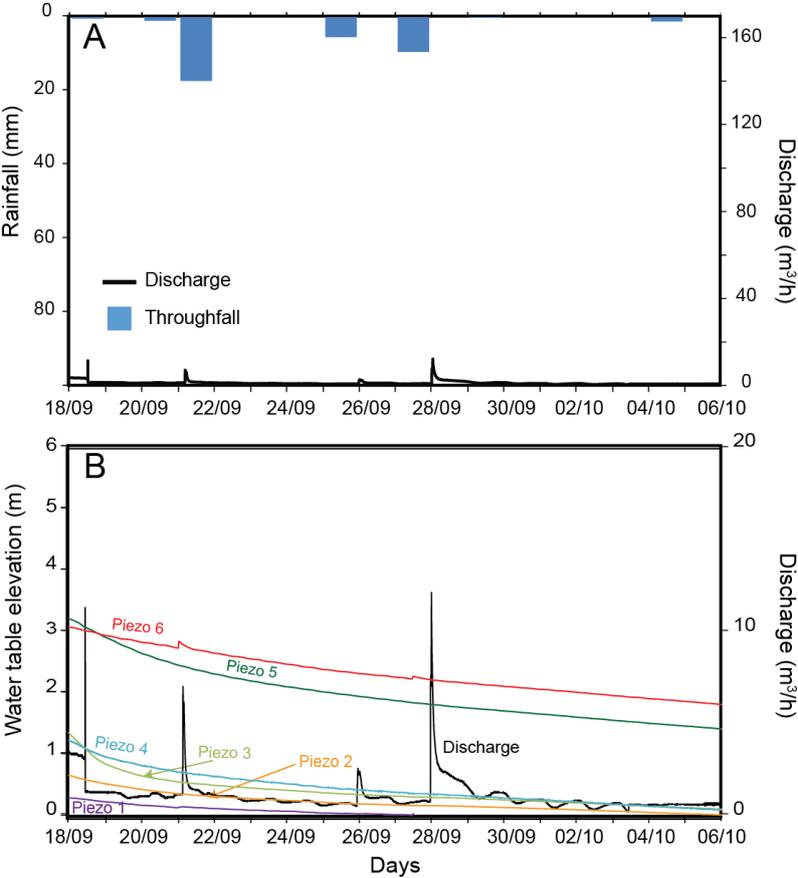


Figure A 2. A. Precipitation and discharge of Quiock Creek. B. Water table elevation and discharge from the 18/09/2015 until the beginning of the sampling campaign. All the discharge and water elevation data are from the ObsERA website (<http://webobsera.ipgp.fr/>).

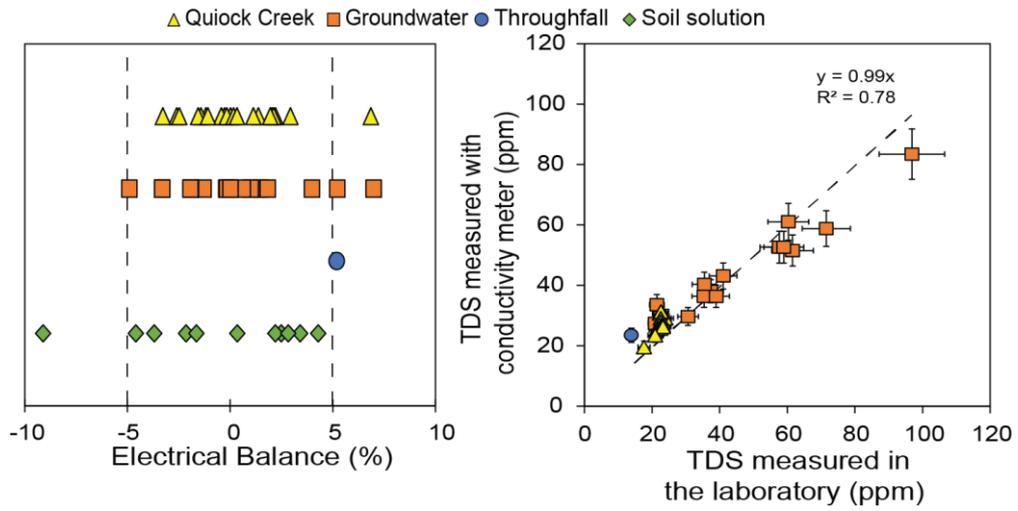


Figure A 3. (a) Electrical balance and (b) TDS measured using a conductivity meter vs TDS measured in the laboratory for Quiock Creek samples.

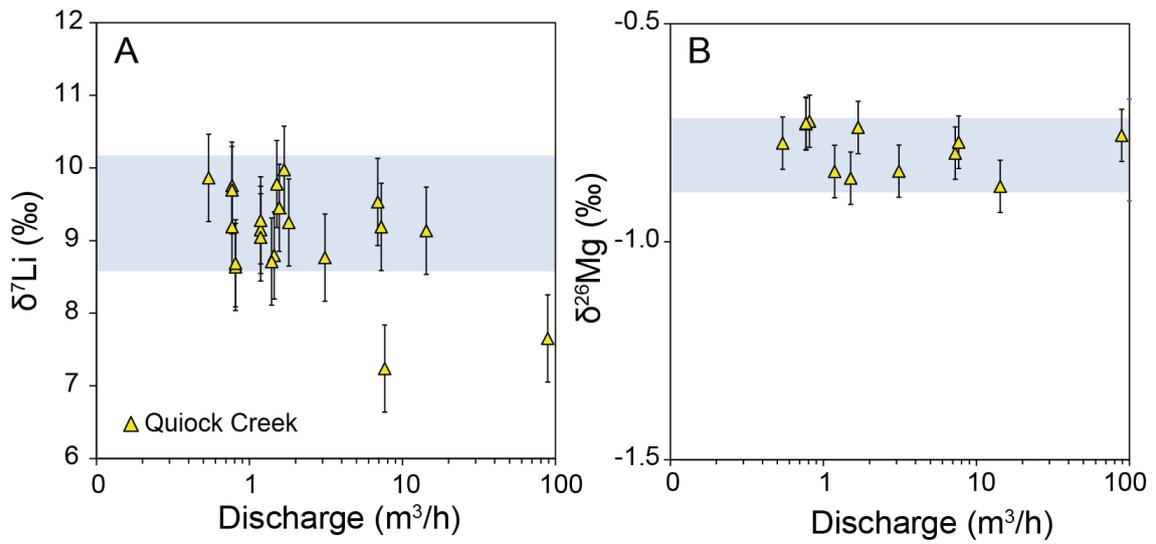


Figure A 4. A.  $\delta^7\text{Li}$  vs discharge. B.  $\delta^{26}\text{Mg}$  vs discharge. Blue shaded boxes show the range of  $\delta^7\text{Li}$  and  $\delta^{26}\text{Mg}$  measured before the storm (QC20 and QC21 excluded from the average). Error bars show the external error of the isotope measurements.

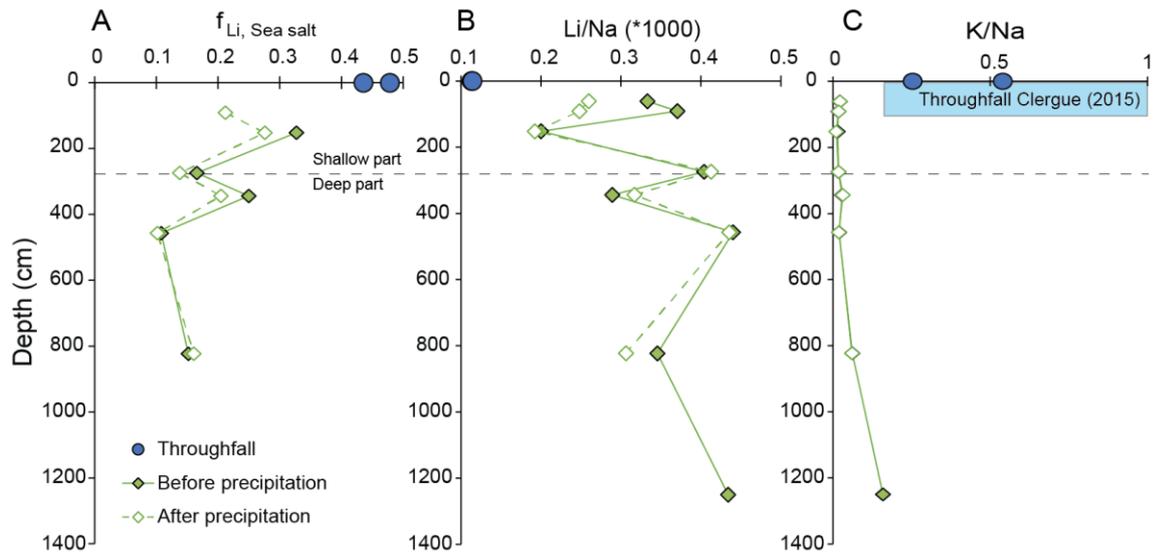


Figure A 5. A. Fraction of Li derived from sea salts in the soil solutions. B and C. Evolution of soil solution Li/Na and K/Na with depth before and after rainfall events. C. The blue shaded box shows the range of K/Na in throughfall samples measured by Clergue et al. (2015).

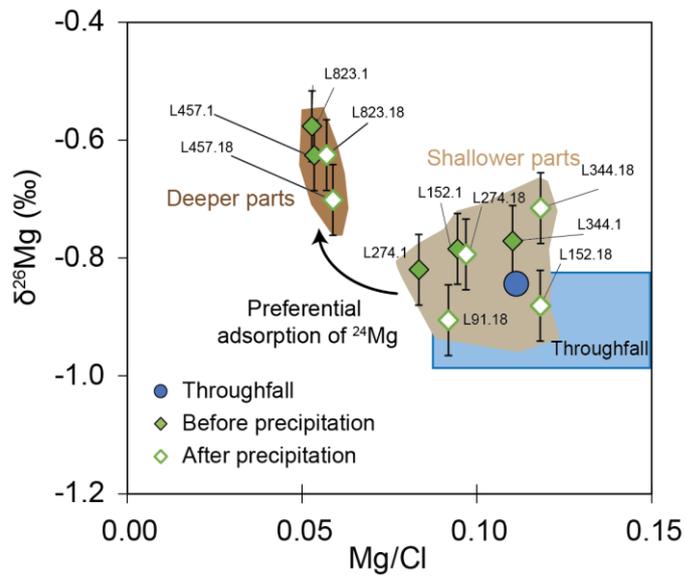


Figure A 6. Mg/Cl versus  $\delta^{26}\text{Mg}$  in the soil solution before and after rainfall events. The figure highlights the removal of Mg from the solution in the deeper part of the profile together with an increase of  $\delta^{26}\text{Mg}$ . The blue shaded box shows the throughfall/stemflow composition (Clergue et al., 2015).

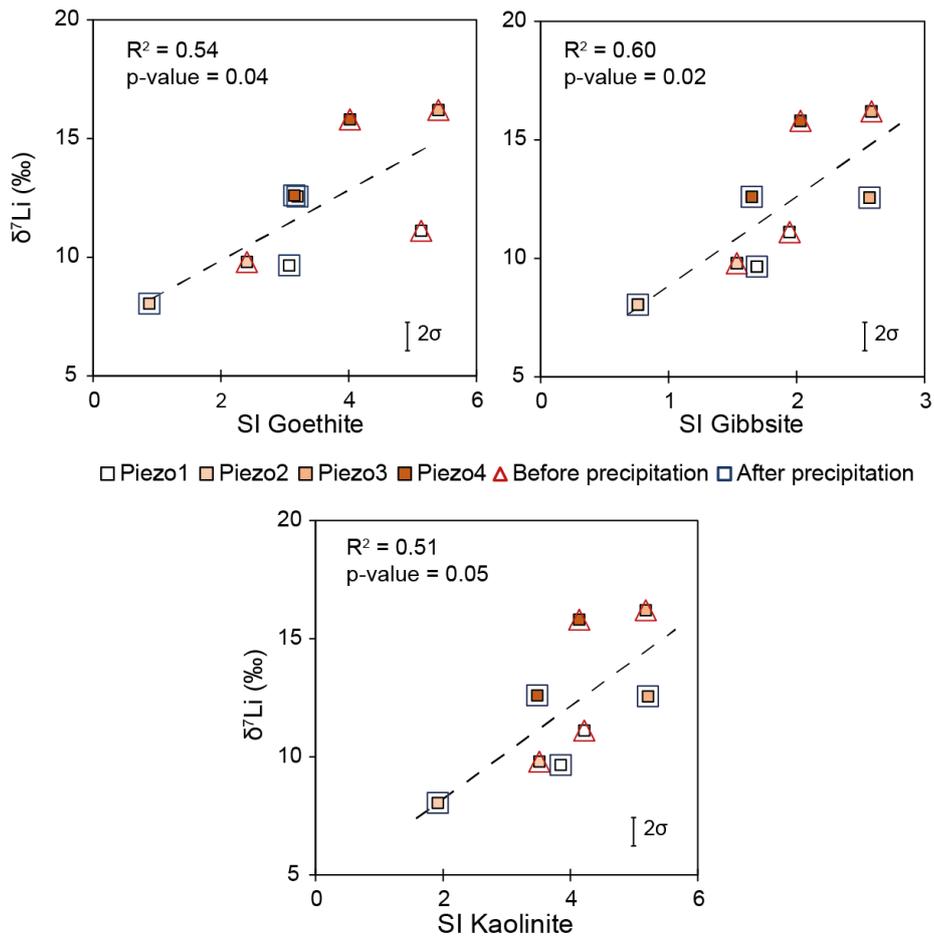


Figure A 7.  $\delta^7\text{Li}$  vs saturation index (SI) of goethite, gibbsite and kaolinite in groundwaters. The red open triangles show the average value for samples collected on Day 1, 4 and 8 while the blue open squares show the value measured after a significant rain event at Day 9.