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#### 1 Atmospheric contribution to cations cycling in highly weathered catchment, Guadeloupe

- 2 (Lesser Antilles)
- 3
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 Zone.

16

#### 17 Abstract:

The important fertilizing role of atmospheric dust, and particularly African dust, in tropical rainforests is increasingly recognized but still poorly quantified. To better evaluate dust input into the Caribbean basin, we sampled critical zone compartments of a small forested volcanic catchment in Guadeloupe (soils, parent rock, atmospheric dust, plants, soil solutions, stream and rain waters). The aims of this study are to track sources of cation nutrients (Ca, Mg, K, Sr) developed on highly weathered soil in the rainforest of Guadeloupe, to quantify plant recycling of these nutrients, and to identify constraints on regolith development and its associated nutrient pool.

In the Quiock Creek catchment, a large isotopic range of <sup>87</sup>Sr/<sup>86</sup>Sr and εNd values was observed despite
the small scale of observation. Sr isotopic composition of the dissolved load varied from 0.7084 in
rainfall to 0.7110 in soil solution, whereas it ranges between 0.7068 and 0.7153 for soil samples and
between 0.7096 and 0.7102 for plants. The Nd isotopic composition varied between -8.39 in nearsurface soil samples to 2.71 in deeper soil. All samples had an intermediate signature between that of
the bedrock endmember (<sup>87</sup>Sr/<sup>86</sup>Sr=0.7038; εNd=4.8) and the atmospheric endmember (sea salt:
<sup>87</sup>Sr/<sup>86</sup>Sr=0.7092 and Saharan dust: <sup>87</sup>Sr/<sup>86</sup>Sr=0.7187, εNd=-11.5).

The regolith was built on pyroclastic deposits, but, because of extreme leaching, the regolith has lost its original bedrock signature and inherited an exogenous atmospheric signature. Our results show that only the chemical weathering of the fresh near-surface minerals can provide nutrients to the ecosystem (first 30 cm). However, this dust weathering is too low to sustain the tropical forest ecosystem on its own. The cationic mass balance at the catchment scale, as well as the Sr isotopic signature, show that cation and Sr fluxes are of atmospheric origin only and that original bedrock no longer participates in nutrient cycles. The vegetation reflects the <sup>87</sup>Sr/<sup>86</sup>Sr of the dissolved pool of atmospheric Sr.

At the soil-plant scale, the cation-nutrient fluxes provided by vegetation (litter fall + leaf excretion) are major compared to input and output fluxes. The annual Ca, K, Sr and Mg fluxes within the vegetation are, respectively, 31, 28, 20 and 3 times greater than the exported fluxes at the outlet of the basin. The residence time of nutrients in the vegetation is 16 years for K and close to 45 years for Sr, Ca and Mg. These results emphasize the highly efficient vegetative turnover that dominates the nutrient cycle in the Quiock Creek catchment.

This first characterization of biogeochemical cycles in the Guadeloupean rainforest suggests that the
 forest community of Quiock Creek is sustained by a small near-surface nutrient pool disconnected from

- 47 the deep volcanic bedrock. We also demonstrated that, even with efficient nutrient recycling, Saharan
- 48 dust plays a significant role in maintaining ecosystem productivity in Guadeloupe over long-time scales.

#### 49 1. Introduction

50 The base cations calcium, potassium and magnesium, are nutrient elements essential for plant 51 development as they are building blocks of tissues and chlorophyll and have a number of metabolic 52 functions. They also play a major role in neutralizing soil acidity and maintaining biological activity. In ecosystems, base cations in soils and plants originate from in situ mineral weathering (e.g. Schlesinger, 53 54 1997). However, numerous studies have shown that, under specific circumstances, these elements can be provided by the atmosphere through precipitation or dust (e.g. Dahms, 1993; Hedin et al., 1994; 55 56 Kennedy et al., 1998). Forest ecosystems are generally poor in nutrients and many studies have 57 suggested that atmospheric deposits are significant sources of nutrients (e.g. Hedin and Likens, 1996; 58 Okin et al., 2004; Soderberg and Compton, 2007; Pett-Ridge, 2009; Yu et al., 2015; Schuessler et al., 59 2018). Nutrient depletion in soils is particularly high in tropical areas, where temperature and 60 precipitation combine to intensively leach nutrients from rocks and soil. In such contexts, the soil is 61 usually strongly impacted by atmospheric inputs (e.g. Whipkey et al., 2000; Kurtz et al., 2001; Poszna et al., 2002; Pett-Ridge et al., 2009b). Cation nutrients, essential for plants, are thus expected to be 62 63 strongly influenced by atmospheric inputs in highly weathered soils. Several studies conducted in Hawaii (Kennedy et al., 1998; Chadwick et al., 1999; Stewart et al., 2001), along chrono- and climato-64 65 sequence gradients, have shown that the more soils are leached, the more associated plants are 66 influenced by atmospheric inputs. Other studies conducted in tropical areas of Costa-Rica (Bern et al., 2005; Porder et al., 2006) have shown that the soil-nutrient pool could still be influenced by bedrock 67 68 weathering. The authors have suggested that rock-derived input was maintained by high erosion rates 69 or deep plant roots.

The transport of African dust into the Caribbean basin is relatively well documented, either by measuring contemporary fluxes (e.g. Prospero et al., 1981; Prospero 1999) or by studying Quaternary age geological limestone records found on the western Atlantic islands of Barbados, the Florida Keys, and the Bahamas (e.g. Muhs et al., 1990; 2007). However, the number of soil record studies examining the impact of Saharan dust inputs on nutrient cycling over pedogenic timescales of hundreds to

75 thousands of years is limited. Studies conducted in the Luquillo Mountains in Puerto Rico (Pett-Ridge 76 et al., 2009a; McClintock et al., 2015) have revealed that Saharan dust contributes significantly to 77 nutrient inputs into weathered soils. Recent studies (Dessert et al., 2015; Clergue et al., 2015; Fries et 78 al., 2019) have also tended to show that the soils of Guadeloupe can be strongly impacted by 79 atmospheric deposits. These few studies did not take into account internal nutrient cycles in the watershed (e.g. litterfall, leaf excretion) and did not focus on the influence of dust on plants. However, 80 81 the characterization of these cycles is important from the perspective of ecological theory and the 82 understanding of Earth's Critical Zone.

83 As it is impossible to directly measure the cation-nutrient flux between rock, soil and vegetation, base 84 cation cycles in forested ecosystems are not straightforward to characterize. Sr and its radiogenic 85 isotopes have been shown to be proxies for cation-nutrient cycling in the atmosphere-soil-plant system 86 (e.g. Capo et al., 1998; Bern et al., 2005; Belanger et al., 2012; Stille et al., 2012). As calcium has a hydrate ionic radius and an ionic charge similar to those of Sr, its behaviour can be deduced from the 87 88 <sup>87</sup>Sr/<sup>86</sup>Sr ratio. K and Mg chemistry differs from that of Ca and Sr, but these lithophile elements 89 ultimately originate from the same sources. Their behaviour can be inferred from Sr isotope data 90 combined with on site element flux calculations. The efficient use of Sr isotopes as a cation-nutrient cycle proxy necessitates that different Sr sources exhibit different <sup>87</sup>Sr/<sup>86</sup>Sr ratios. 91

92 In Guadeloupe, possible common sources of Sr and base cation nutrients (volcanic rock, sea salt and Saharan dust) differ in Sr isotopic signature. The <sup>87</sup>Sr/<sup>86</sup>Sr ratio of volcanic bedrock is between 0.70341 93 94 and 0.70382 (White and Patchett, 1984; White and Dupré, 1986). The signature of sea salt is 0.70917 (e.g. Dia et al., 1992) and the <sup>87</sup>Sr/<sup>86</sup>Sr mean ratio of Saharan dust is 0.71788 (Biscaye et al., 1974; 95 Grousset et al., 1988; Grousset et al., 1992; Rognon et al., 1996; Grousset et al., 1998; Pett-Ridge et al., 96 97 2009). We looked at Sr isotopes, Nd isotopes, and base cation nutrients to identify their sources. Like Sr, Nd isotope ratios are used to trace Nd sources, as they are not affected by biological and weathering 98 99 processes (e.g. Liu et al., 2013). The Nd signature in volcanic rock from Guadeloupe ranges from 3.02 100 to 5.05 (White and Patchett, 1984; White and Dupré, 1986) and the signature of Saharan dust varies between -10.5 and -14.5 (Grousset et al., 1992; Dia et al., 2006). Nd and Sr differ in their mobility (Nd
is less mobile than Sr) and are distributed differently in surface compartments, thus the comparison
between these two isotopic systems provides complementary information on constraints in the study
area.

In this study we report Sr isotope ratios in all compartments of a small catchment (rainfall, throughfall, 105 106 soil solution, bulk soil, unweathered rock, river water, litter and atmospheric dusts) and Nd isotope 107 ratios of soils and unweathered rock. The catchment is located in the tropical rainforest of Guadeloupe, 108 in the Caribbean (FWI). This area is covered by highly weathered soils built on mono-lithological 109 volcaniclastic deposits. Despite the poverty of the soils (Buss et al., 2010; Clergue et al., 2015), a dense 110 rainforest is developed on it (Rousteau et al., 1994, 1996). The aims of this study are to: 1) Track sources 111 of cation nutrients (Ca, Mg, K) of the rainforest of Guadeloupe developed on a highly weathered soil; 112 2) Quantify the vegetation recycling of cation nutrients; 3) Identify the origin of "rock-derived" cationnutrient pool in the soil and give constraints on regolith development. 113

114

#### 115 2. Site description

The studied catchment (16°17′N, 61°70′W) is located on Basse-Terre Island, the volcanic part of the Guadeloupe archipelago in the French West Indies (Fig. 1). The Quiock Creek drains a watershed of 8 ha, ranging from 200 m to 350 m in altitude, located in the primary tropical rainforest of the Guadeloupe National Park. The Quiock Creek catchment is monitored by the ObsErA observatory (OZCAR research infrastructure; Gaillardet et al., 2018) dedicated to the study of weathering and erosion processes under tropical climatic conditions (Clergue et al., 2015; Lloret et al., 2016; Fries et al., 2019; Guérin et al., 2019).

The climate on site is characterized by high mean annual temperature (25°C) and precipitation (3500 mmyr<sup>-1</sup>). The mean annual runoff is 1,130 mm. Evapotranspiration is high, between 60 and 70% (Clergue et al., 2015; Guérin et al., 2019) and tropical storms and hurricanes contribute significantly to the hydrology of the site (Zahibo et al., 2007).

127 Quiock Creek is covered by a very thick ferralitic soil (>15 m thick; Colmet-Daage and Bernard, 1979, 128 IRD soil map) built on Pleistocene andesitic pyroclastic deposits (Boudon et al., 1988). The regolith profile of Quiock Creek mainly consists of secondary minerals, with kaolinite/halloysite as the main 129 130 mineral (95% by weight of the bulk soil; Buss et al., 2010) and is highly depleted in mobile elements (Buss et al., 2010; Clergue et al., 2015). All these features are characteristic of a highly weathered soil. 131 Despite the high nutrient depletion of these soils, they support a tropical rainforest (Rousteau et al., 132 133 1996; Van Laere et al., 2016). This rainforest is characterized by three dominant species: Amanoa 134 caribaea Kr. and Urb. (Phyllanthaeae), Tapura latifolia Benth (Dichapetalaceae) and Dracryodes excelsa 135 Vahl (Burseraceae). The litter flux produced by this oldgrowth rainforest was determined each two 136 weeks using 10 litter traps of one square meter size each monitored for two years (2011–2013). Annual 137 litter flux reached 7.8 t.ha<sup>-1</sup>.yr<sup>-1</sup> of dry matter (Rousteau, 2014), comparable to the rainforest flux in northeastern Puerto Rico (Weaver and Murphy, 1990). The litter production is seasonal, with the 138 139 highest litter fall occurring in June-August (40% of the annual litter fall). Finally, the biomass measured on site is equal to 376.8 t.ha<sup>-1</sup> (Rousteau, 2014). 140

Atmospheric inputs to the watershed come in two forms: wet deposits and dry deposits. Wet deposits consist of rainfall, while dry deposits include sea salt aerosols, Saharan dust and volcanic ash. Because of the location of the study site in the heart of the National Park, anthropic contributions are negligible.

144 One of the peculiarities of the Caribbean is the major input of Saharan dust (SD) up to 100 kg.ha<sup>-1</sup>.yr<sup>-1</sup> measured in Guadeloupe (J. Molinié, personal communication) which is consistent with amounts 145 146 reported in the literature for the Caribbean basin (Glaccum and Prospero, 1980; Mahowald et al., 2006; 147 Pett-Ridge et al., 2009; Yu et al., 2015). Throughout the Caribbean region, Saharan dust is deposited on the ground or on the canopy by rain. These dust deposits are mainly composed of mica/illite and quartz 148 (Prospero et al., 1970; Glaccum and Prospero, 1980). For instance, in the Quiock Creek soil profile, the 149 150 dull aspect of quartz, characteristic of aerial transport, suggests that Saharan dust is likely the source 151 of quartz.

Another exogenous input to the top soil comes from the neighbouring volcano Soufriere Hills on Montserrat, located 86 km NW of Guadeloupe. It erupted on July 18, 1995, after a century of quiescence. Since 1995, six recognized ash fall episodes have impacted Guadeloupe (<u>www.mvo.ms</u>; activity report of OVSG 2000). The two most important events took place in September 1996 and February 2010 and produced ash-fall deposits on Guadeloupe that were thicker than 1 mm, corresponding to fluxes of about 50 to 100 g m<sup>-2</sup> of ash each (Cadelis et al., 2013; OVSG reports). The volcanic ashes were mainly composed of crystalline silica, mostly cristobalite (Baxter et al., 1999).

All these atmospheric sources (sea salt and dust) have been shown to highly impact soil in the Caribbean Basin (*e.g.* Borg and Banner, 1996; Herwitz et al., 1996; Muhs et al., 2009; Pett-Ridge et al., 2009; Opfergelt et al., 2012; Clergue et al., 2015; Dessert et al., 2015; Fries et al., 2019).

162

#### 163 3. Sample collection

All compartments of the watershed were sampled between 2011 and 2013. Water samples consisted of rainfall, throughfall, soil solution and river water, and solid samples consisted of soil, rock, litter and dust.

167 3.1. Water samples

168 We collected water samples during contrasting hydrological periods. River samples (QC, n=39) were 169 collected manually once a month and more frequently during six field trips. Rainfall (RF, n=9), and 170 throughfall (TF, n=48) were sampled during six field trips between 2011 and 2013. They both were 171 collected in polypropylene bottles with a funnel located one meter above the ground in order to avoid 172 contamination from soil particles. Rainfall were collected on site on the roof of the "Maison de la Forêt" 173 (RF-MF) or at the "Observatoire Volcanologique et Sismologique de Guadeloupe" (RF-OVSG). These 174 samples correspond to several rainfall events cumulated over 1 to 5 days, depending on the sample. 175 Throughfall waters were collected by three collectors randomly positioned in the Quiock Creek 176 catchment (collector n°1 to n°3) and were sampled every 1 to 5 days, depending on the sample. Soil solutions (SS) were sampled using nested tension lysimeters equipped with porous ceramic cups
located between 15 and 823 cm in depth (Buss et al., 2010). These soil solutions were sampled each
month and the sampling dates selected for isotopic measurement were 10-26-2012 and 06-28-2013.

180 Conductivity and pH were measured on site for the Quiock Creek samples and after collection at the OVSG for the other samples. For alkalinity measurements, non-filtered 20 mL aliquots were used. The 181 remaining water was filtered through 0.2 µm cellulose filters and divided into two subsamples. One 182 183 non-acidified aliquot was stored in polypropylene bottles and used for anion and silica analyses. The 184 second aliquot was acidified (2% HNO<sub>3</sub>), stored in polypropylene bottles and used for cation, trace element and Sr isotope measurements. Strontium isotopic compositions were measured on 26 185 186 selected samples corresponding to 3 samples of rainfall, 6 samples of throughfall, 4 samples of stream 187 water and 13 samples of soil solution.

188 3.2. Solid samples

We analyzed andesite (04-GW-12) and basalt (00-GU-44 and 03-GU-75) samples from Samper et al. 189 190 (2007) to characterize the unweathered parent rock (Fig. 1). A soil profile (n=27) was collected with a hand-auger down to 12.5 m depth during lysimeter installation in 2007 (Buss et al., 2010). We collected 191 192 Saharan dust during a dust event deposit on July 1 and 5, 2013. It corresponds to rainfall particulate 193 matter obtained by filtration on a 0.2 µm cellulose filter. The filter was then dried and stored in a Petri 194 dish. We also analysed 5 samples of litter, collected during one of the most productive periods 195 (between June 10 and 24, 2011). "Leaves 1" corresponds to a mixture of litter from different species 196 (collected in the same litter collector) whereas "Leaves 2" corresponds to Amanoa caribaea leaves only. "Branches 1" and "Branches 2" correspond to a mixture of branches collected in two different litter 197 collectors. Finally, "Roots" (April 2012) are from Amanoa caribaea. 198

199

200 4. Analytical methods and flux calculation

201 4.1. Solid sample digestion

202 Soil and litter samples were first dried in an oven (60°C) for 3 days and crushed in an agate mortar (soil 203 samples) or in a ball mill (litter samples). Soil and rock samples (100 mg) were dissolved in a mixture of HNO<sub>3</sub>/HF for 2 days at 120 °C. This mixture was then evaporated and dissolved twice in 2mL 6N HCl 204 205 and finally stored in 1N HCI. Saharan dust samples collected on cellulose filters underwent an initial step of filter digestion in diluted 5N HNO<sub>3</sub> at 100°C for 1 day and were treated with the same protocol 206 207 as for rock and soil samples. Litter samples (500 mg) were first dissolved in 10 mL of 16N HNO<sub>3</sub> in 50 208 mL Teflon beakers for 24h at room temperature and then digested in a DigiPREP block digestion system 209 for another 24h at 90°C. After an evaporation step at 60°C, the samples were dissolved once more in 210 16N HNO<sub>3</sub> for 24h at 90°C. Finally, after evaporation, 0.5 mL HF/ H<sub>3</sub>BO<sub>3</sub> were added to fully dissolve the 211 phytoliths. These samples were then stored in 50 mL of 2N HNO<sub>3</sub>.

212 4.2. Major and trace element analyses

We measured base cations by ICP AES (Thermofisher iCap 6200 series) at the Institut de Physique du Globe de Paris (IPGP). Anions in soil solutions were measured with a Dionex DX 120 chromatograph at the IPGP and the OVSG/IPGP. We quantified Sr concentrations using HR-ICP-MS (Element II ThermoScientific) at IPGP. The limit of quantification is 20 ppt and repeated measurement of the SLRS-5 standard lead to an external reproducibility of 3%.

218 Major elements in solid samples were measured by ICP AES (Thermofisher iCap 6200 series) at the 219 IPGP. Trace elements in solid samples were measured with an ICP-MS X series mass spectrometer (Thermo Electron) at the Institut des Sciences de la Terre de Paris (ISTeP) of the Université Pierre et 220 221 Marie Curie. We followed the bracketing method using BEN rock standards for bracketing and BEN, 222 GSN and LKSD2 to validate the measurements. The standard values measured in this study are compared to the certified values to validate the data (Table S1). We measured major element and Sr 223 224 concentrations in litter samples using a calibration curve, such as for water samples. The accuracy of 225 this measurement was checked by repeated analyses of a vegetation standard NIST SRM 1515.

226 4.3. Sr and Nd purification

Sr and Nd isotope analyses were performed on the Neptune multicollector ICP-MS (Thermo Scientific)
at IPGP using the Apex sample inlet system. A prior step of purification is needed in order to avoid a
matrix effect during measurement.

230 The separation of Sr from the rest of the matrix was automated for water samples with HPIC (High Performance Ion Chromatography) as fully described in Meynadier et al. (2006). Sr contained in 231 232 solubilized solid samples was separated from the rest of the matrix on Sr-Spec resin in 3N HNO<sub>3</sub> media. 233 The elution step was performed with milliQ H<sub>2</sub>O. The resin was replaced after each separation to avoid 234 memory effects. The purified solution of Sr was evaporated and dissolved in 0.05N HNO<sub>3</sub> for isotopic 235 measurement. The minimum amount required for Sr isotopic measurement is 50-100 ng Sr in 1 mL. 236 For Nd separation, a two-step procedure was applied (Richard et al., 1976; Caro et al., 2006). First, rare 237 earth elements were separated from the rest of the matrix on TRU-Spec resin in 2N HNO<sub>3</sub> media. Then,

The purified Nd solution was evaporated and dissolved in 3N HNO<sub>3</sub> for isotopic measurement. The
minimum amount required for Nd isotopic measurement is 50 ng Nd in 1 mL.

the separation of the different rare earth elements was performed on Ln-spec resin in 0.25N HCl media.

241 4.4. Sr and Nd isotope analyses

238

For Sr, the method used corresponds to the measurement of 100 ratios of 4 second iteration time per sample or standard. Mass interferences with Kr (84 and 86) were corrected using <sup>83</sup>Kr/<sup>84</sup>Kr and <sup>83</sup>Kr/<sup>86</sup>Kr, measured in the blank at the beginning of each session. Mass interference with Rb (87) was corrected using the <sup>85</sup>Rb/<sup>87</sup>Rb ratio measured in a low concentrated Rb solution (2.5 ppb) after Kr measurement. The mass bias was corrected using the <sup>86</sup>Sr/<sup>88</sup>Sr ratio of 0.1194. Each measurement was normalized to the NBS value certified as <sup>87</sup>Sr/<sup>86</sup>Sr = 0.71025, which was measured every 3 samples. The standard error based on repeated measurement of the NBS standard was 2% = 0.00001.

249 The εNd was calculated relative to the CHUR (Chondritic Uniform Reservoir) as follows:

250 
$$\epsilon Nd = \left(\frac{{}^{143}Nd/{}^{144}Nd_{Sample}}{{}^{143}Nd/{}^{144}Nd_{CHUR}} - 1\right) \times 10000$$
 (1)

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

257 4.5. Cation flux and residence time calculation

Elemental fluxes were obtained by multiplying the water/matter flux by the mean concentrations or determined from the following equations. Water fluxes were determined in Clergue et al. (2015). Throughfall water flux is 3079 mm yr<sup>-1</sup>. The Quiock Creek discharge ranges between 150 and 400 L min<sup>-1</sup> with a mean value of 172 L min<sup>-1</sup>, corresponding to a runoff of 1130 mm yr<sup>-1</sup>. Dry matter litter flux reaches 7.8 t ha<sup>-1</sup> yr<sup>-1</sup> (Rousteau 2014).

263 Throughfall elementary fluxes ( $F_{TF}$ ) are described by equation 2, where  $F_{EX}$  is the flux of cations exuded 264 by plants, and  $F_{RF}$  the rainfall flux.

$$265 \quad F_{TF} = F_{EX} + F_{RF} \tag{2}$$

266 The rainfall compartment is influenced by both sea salt aerosols ( $F_{SW}$ ) and Saharan dust leaching ( $F_{SD}$ ) 267 and  $F_{RF}$  is equal to:

$$F_{RF} = F_{SW} - F_{SD}$$
(3)

269 We consider that the flux of Cl in throughfall (F-Cl<sub>TF</sub>) is exclusively from rainfall.  $F_{RF}$  is determined from 270 the F-Cl<sub>TF</sub> and (X/Cl) rainfall ratios:

271 
$$F_{RF} = F - CI_{TF} \times (X/CI)_{RF}$$
 (4)

272 with Na/Cl<sub>RF</sub> = 0.63, Ca/Cl<sub>RF</sub> = 0.09, Mg/Cl<sub>RF</sub> = 0.09, K/Cl<sub>RF</sub> = 0.05 ; 1000Sr/Cl<sub>RF</sub> = 0.56 (mean mass ratio

273 determined from rainfall data; see following section)

and F<sub>EX</sub> is equal to:

275 
$$F_{EX} = F_{TF} - F_{RF}$$
 (5)

276 Assuming that all the CI flux in throughfall has a sea salt origin, we used F-Cl<sub>TF</sub> and X/Cl sea salt ratios

277 (Na/Cl<sub>sw</sub> = 0.86, Ca/Cl<sub>sw</sub> = 0.02, Mg/Cl<sub>sw</sub> = 0.10, K/Cl<sub>sw</sub> = 0.02, 1000Sr/Cl<sub>sw</sub> = 0.16 and mass ratio from 278 Brewer et al., 1975) to determine  $F_{sw}$  for each cation:

279 
$$F_{SW} = F - Cl_{TF} \times (X/Cl)_{SW}$$
 (6)

280 and  $F_{SD}$  is equal to:

$$281 \quad F_{SD} = F_{RF} - F_{SW} \tag{7}$$

The vegetation flux ( $F_{VEG}$ ) is described by equation 8, where  $F_{EX}$  is the flux of cations exuded by plants, and  $F_{LF}$  the litter fall flux.

$$284 \quad F_{VEG} = F_{EX} + F_{LF} \tag{8}$$

The standing stock of cations in the forest (Stock) is determined from biomass (376.8 t.ha<sup>-1</sup>; Rousteau et al., 2014) and mean cationic concentrations into plants. The residence time (T<sub>res</sub>) of each element in the vegetation is determined by the following equation:

$$288 \quad T_{res} = Stock / F_{VEG} \tag{9}$$

289

#### 290 **5. Results**

All the compartments of the catchment were characterized for their element concentrations and isotopic compositions. Table 1 presents results of major elements and Sr concentrations only in water samples for which Sr isotopic composition was measured. A full list of the concentrations of major cations we have used in this paper are taken from Clergue et al. (2015) of which the range in 295 concentrations, means and median values are summarized in Table 2. New trace element and isotopic

compositions for solid samples are presented in Table 3.

#### 297 5.1. Atmospheric samples

The pH of rainfall ranged from 4.1 to 5.7 (Clergue et al., 2015). The major cation in rainfall was Na, whose concentration varied between 41 and 165 µmol/L. The mean concentration of K, Ca and Mg were 4, 7 and 12 µmol/L, respectively. Sr concentration ranged from 9 and 39 nmol/L (Table 2S) and Sr isotopic composition varied between 0.70841 and 0.71029 (Fig. 2). These data were in agreement with previously published data in the Puerto Rican and Guadeloupean rainforests (Gioda et al., 2013; Dessert et al., 2015).

304 The concentrations of major elements in Saharan dust collected in Guadeloupe, were higher than those 305 in the soil samples (except for Al and Fe; see Clergue et al., 2015) and lower than in the rock samples 306 (Table 3). The average values for Ca (1830 ppm), Na (940 ppm) and K (5300 ppm) were lower than those 307 reported in the literature for dust samples collected in West Africa (> 2600 ppm for Ca and Na, > 9800 308 ppm for K; Moreno et al., 2006). Mg concentrations around 5200 ppm were in the range of those 309 reported in the literature (> 4600 ppm; Moreno et al., 2006). The concentration of Sr concentration 310 was around 50 ppm, 1.5 to 5 times lower than the values reported in the literature for dust samples 311 (Moreno et al., 2006) and 10 times higher than soil Sr concentrations. Concerning Sr isotopic data, the 312 dust samples were the most radiogenic of all samples collected on the site. The isotopic signature, 313 around 0.7187, is consistent with previous estimations and measurements (Biscaye et al., 1974; 314 Grousset et al., 1988; Grousset et al., 1992; Rognon et al., 1996) which gave a value of 0.7179 for 315 Saharan dust in the Caribbean (Pett-Ridge et al., 2009b).

316 5.2. Throughfall samples

The pH of the throughfall was slightly higher than that of the rainfall, ranging from 5.1 to 6.3 (Clergue
et al., 2015). The major cation in the throughfall was Na, whose concentration varied between 17 and
264 μmol/L (Table 2). Mean concentration of K, Ca and Mg were 39, 17 and 17 μmol/L respectively. Sr

concentration ranged from 8 and 136 nmol/L (Table S2) and Sr isotopic composition varied between
0.70953 and 0.70978 (Table 1, Fig. 2). These data were in agreement with the ranges published in the
literature for tropical rainforests (e.g. Forti and Neal, 1992; McDowell, 1998).

The K/Cl ratio in throughfall was ten times higher than the K/Cl ratio in rainfall, attesting to a strong enrichment of K in throughfall (Fig. 3). To a lesser extent, Sr, Ca and Mg were also enriched in throughfall. The enrichment of throughfall compared to rainfall indicates that these elements are partially released by plants. This exudation process has been largely described in the literature (Vitousek and Sanford, 1986; Dezzeo and Chacon, 2006).

Throughfall is slightly more radiogenic than sea salt (Fig. 2). This observation can be explained by a mixture in throughfall of sea salt Sr and Sr from Saharan dust leachates or plant exudates. It is impossible to distinguish between the two latter sources only on the basis of Sr isotopes.

#### 331 5.3. Litter samples

Major element concentrations in litter samples were very different from concentrations in the other 332 333 solid samples (Table 3). The most abundant element in the litter was Ca, with concentrations ranging 334 between 1 and 3%. This is more than 100 times the Ca concentration in the soil and is similar to the parent rock Ca concentration. The K concentration, intermediate between 0.1 and 1.1%, and the Mg 335 336 concentration, ranging between 0.2 and 0.6%, were also higher than the K and Mg concentrations in 337 the soil. These concentrations are consistent with values in the literature for litter samples (e.g. Liao et al., 2006; Riotte et al., 2014). Similarly, the Sr concentration in the litter varied from 80 to 200 ppm, 338 which is one or two orders of magnitude higher than the Sr concentration in the soil (up to 13 ppm). 339 340 The isotopic signature of the litter varied between 0.70966 and 0.71019 (Fig. 2). This signature differed from the <sup>87</sup>Sr/<sup>86</sup>Sr ratio of local bedrock, but was similar to that of samples of vegetation growing on 341 highly depleted volcanic soil as reported in the literature (Whipkey et al., 2000; Stewart et al., 2001; 342 343 Chadwick et al., 2009).

344 5.4. Soil solution samples

345 The soil solutions were acidic, with pH values ranging from 4.2 to 5.4. This can be explained by the low 346 cation content, which plays a key role in neutralizing the acidity of soil solutions. Na and Cl were the most abundant elements, with mean concentrations of 179 µmol/L and 199 µmol/L, respectively (Table 347 348 2). Average Mg, K and Ca concentrations were 24, 5 and 3 respectively. Sr concentrations in soil solutions ranged between 7 and 101 nmol/L (Table S2), and isotopic composition varied between 349 350 0.70996 and 0.71097 (Table 1). Soil solutions were more radiogenic than local rocks and sea salts, 351 attesting to an exogenous source of Sr in the soil solution (Fig. 2). In superficial soil horizons (up to 90 352 cm), Sr concentrations were systematically higher than in the deeper horizons (mean value of 53 and 353 16 nmol/L respectively). To a lesser extent, Ca and Mg were also slightly higher in superficial horizons 354 than in the deepest. On the contrary, K concentrations were constant over the entire soil profile.

355 Fig. 3 shows the cation concentrations normalized to Cl for all dissolved samples. Na/Cl ratios were 356 relatively homogeneous in all water samples and close to the sea salt ratio. In general, soil solutions 357 were depleted in nutrient cations compared to throughfall. This was particularly true for K, which was probably due to efficient K uptake by plant root systems and microorganisms in the first few 358 359 centimeters of soil. As previously noted, soil solutions of superficial horizons were slightly enriched in Sr, Ca and Mg compared to deeper soil solutions, which indicates a potential atmospheric source of 360 361 cations. It was even observed that the surface solutions were sometimes enriched in Mg with respect 362 to throughfall.

363 5.5. Soil and rock samples

The soil profile is characterized by a very high proportion of secondary minerals (95% wt. of secondary minerals and 70 %wt. of kaolinite and halloysite; Buss et al., 2010). The chemical composition of the soil indicated that it was highly depleted in mobile cations compared to unweathered rock in Guadeloupe (Table 3). For example, the Ca concentration varied from 23 to 306 ppm, which corresponds to about 100% depletion compared to volcanic rock, which contains 4.85% to 7.45% of Ca. Sr concentration in soil varied between 2 and 13 ppm and was very low compared to unweathered rock

370 (Table 3). To correct for dilution effects and volume change, Sr concentration in the soil samples was
 371 normalized to an immobile element (Ti). Fig. 4 presents mass transfer coefficient (τ) values for Sr:

372 
$$\tau Sr = [(Sr/Ti)_{soil} / (Sr/Ti)_{rock}] -1$$
 (10)

TSr was negative, representing the depletion of Sr in soil compared to unweathered rock. Sr had a
depletion rate of around 98 ± 2%. The soil profile was systematically less depleted in its first 15 cm and
at depths of 305 cm, 427 cm, 1219 cm and 1250 cm. These depths corresponded to horizons enriched
in quartz and K-feldspar.

The entire profile was more radiogenic (0.70677 - 0.71527) than the unweathered volcanic rock sampled in Guadeloupe (Fig. 2 and 4). Quartz horizons exhibited the highest Sr isotopic ratio. This observation attests of exogenic source(s) of Sr to the soil. The  $\varepsilon$ Nd of the profile varied between -8.39 and 2.44 and was different from unweathered rock ranging from 4.34 to 5.45 (Table 3). The Nd signature of the quartz horizons was very negative and attested again of an exogenic contribution of Nd to the profile.

383 5.6. Quiock Creek water samples

Conductivity in Quiock Creek ranged from 22.5 to 68.2 μS and pH was acidic, ranging from 4.3 to 5.9 (see Clergue et al., 2015). The major cation was Na, with a mean concentration of 234 μmol/L. Mean concentrations of K, Ca and Mg were 5, 10 and 29 μmol/L, respectively (Table 2). Sr concentration ranged from 35 and 70 nmol/L (Table S2) and Sr isotopic composition varied between 0.70922 and 0.70939.

389

#### 390 6. Discussion

391 6.1. Vegetation cycling

392 6.1.1. Impact of atmospheric deposits on the cation-nutrient budget

A key question is to what extent atmospheric deposition (wet and dry) impacts the forest's nutrient source. Many biogeochemical studies have shown that Sr, and particularly the <sup>87</sup>Sr/<sup>86</sup>Sr isotopic ratio, is a good tracer of ecosystem Ca sources (e.g. Capo et al., 1998; Bern et al., 2005; Belanger et al., 2012; Stille et al., 2012; Pett-Ridge et al., 2009a). K and Mg chemistry differs from Ca and Sr, but these lithophilic elements ultimately originate from the same sources. It is therefore possible to acquire some qualitative information on the cycles of these elements using Sr as a proxy.

399 The internal water cycle of our basin is relatively homogeneous from a Sr isotopic point of view, with a mean <sup>87</sup>Sr/<sup>86</sup>Sr ratio of 0.7097 for throughfall and 0.7104 for soil solutions (up to 12 meters deep; Fig. 400 2). This shows that the dissolved pool of Sr is dominated by sea salts (<sup>87</sup>Sr/<sup>86</sup>Sr value equal to 0.7092), 401 402 with a small influence of more radiogenic sources coming from Saharan dust leaching (Fig. 2). Note also 403 that the Sr isotopic composition of litter of 0.7099 is in the range of that of the dissolved pool of Sr. 404 This has already been well described in several studies, which have shown that vegetation exhibits the 405 signature of the exchangeable Sr pool (e.g. Kennedy et al., 1998; Poszwa et al., 2002). Our results 406 emphasize that atmospheric inputs contribute significantly to actively cycled Sr in the Quiock Creek 407 basin. This hypothesis is consistent with the literature for similar contexts with highly depleted volcanic soils and strong atmospheric input (e.g. Whiptkey et al., 2000; Stewart et al., 2001; Chadwick et al., 408 409 2009; Schuessler et al., 2018). As an example, Pett-Ridge et al. (2009a) reported that the proportions 410 of foliar Sr derived from sea salt and dust vary between 33% and 59% in the Puerto Rican rainforest. Similarly, in the Quiock Creek catchment, the <sup>87</sup>Sr/<sup>86</sup>Sr of litter is slightly more radiogenic than sea salt 411 412 aerosols, emphasizing the influence of Saharan Sr on the ecosystem.

Based on the Sr isotopic composition, the weathering of local volcanic rock seems not to contribute in the plant Sr pool. It can be deduced that this is also true for the Ca, K and Mg pools. This observation is consistent with the idea that tropical forests developed on highly nutrient-depleted soils derive their nutrients from superficial atmospheric sources and from litter recycling (Jordan, 1982). It may be for this reason that surface soil solutions are slightly less depleted in cations than deeper solutions (>91 cm; Fig. 3), reflecting the cationic inputs of throughfall, dust leaching/weathering and litter

419 remineralization. We also suggest that a little near-surface nutrient pool sustains the forest community

420 of Quiock Creek.

Tropical forests are largely described as dependent on atmospheric sources, as observed in this study,
but they are also known to recycle nutrients very efficiently. In the following section, we calculate the
vegetation fluxes in the catchment and estimate the cation-nutrient recycling fluxes.

424 6.1.2. Vegetation cycling at the soil-plant profile scale

Nutrients contained in plants are released during leaf excretion, litter leaching and litter decomposition. These bio-available elements are partly taken up by the vegetation from the soil solution and, therefore, are recycled. The proportion of nutrients recycled by plants depends on the amounts of available nutrients in the soil. As an example, the study by Holmden and Belanger (2010) shows that in a Boreal forest ecosystem, the proportion of recycled Ca from litter fall can represent from 80% and 90% of the annualized Ca inputs to the forest Ca cycle. The authors also note that the proportion of recycled Ca increases with decreasing weathering flux.

432 The internal-cationic fluxes calculated in the Quiock Creek catchment are summarized in Table 4 and Fig. 5. The vegetation flux (FVEG) varies between 8.4 kg.ha<sup>-1</sup>.yr<sup>-1</sup> for Na and 141.5 kg.ha<sup>-1</sup>.yr<sup>-1</sup> for Ca and 433 434 represents the biggest elemental flux, except for Na. These results are in agreement with those of the 435 review by Proctor et al. (1987) on primary rainforests and the study by McDowell (1998) in a Puerto Rican rainforest. For Ca, Mg and Sr, most of the vegetation flux is provided by litter fall. Concerning K, 436 its flux provided by leaf excretion (41.2 kg.ha<sup>-1</sup>.yr<sup>-1</sup>) is twice as abundant as the litter fall flux (20.9 kg.ha<sup>-1</sup>.yr<sup>-1</sup>) 437 438 <sup>1</sup>.yr<sup>-1</sup>). This confirms that canopy leaching is the main source of K for the top soil (e.g. McDowell 1998; 439 Riotte et al., 2014). Finally, the Na flux released by vegetation is relatively weak compared to rainfall 440 flux. Na is not a nutrient for plants and it exhibits conservative behaviour when rainwater passes 441 through the canopy. We note that for Sr, K, Ca, and, to a lesser extent Mg, plant recycling is highly efficient. The vegetation flux (FVEG) of Sr, K, and Ca are respectively, 20, 28 and 31 times greater than 442 443 flux exported at the outlet of the basin (FQC). The vegetation flux of Mg is 3 times greater than the flux

exported by the Quiock Creek. This vegetation turnover efficiency is related to the degree of soil
leaching and thus the nutrient pool derived from weathering minerals. In the tropical context of our
study, it is not surprising to observe such a high turnover, because of the nutrient paucity in soils. The
same range of solute turnover has been measured in the tropical watershed of Mule Hole in India
(Riotte et al., 2014), where vegetation recycling fluxes represented 10-15 times the exported fluxes.
More recently, in a tropical watershed in Sri Lanka, Schuessler et al. (2018) estimated this recycling
factor between 2 and 7 for Mg, 3 and 10 for Ca and 9 and 29 for K.

451 Rousteau et al. (2014) have shown that vegetation in the Quiock Creek catchment is at equilibrium with respect to carbon. If the ecosystem is close to equilibrium, the nutrient fluxes taken up would be equal 452 453 to FVEG (litter fall + leaf excretion). Numerous studies (e.g. Proctor, 1987) have shown that in tropical 454 rainforests, decomposition is invariably rapid and that litter turnover takes less than a year. Even though 455 we did not measure the decomposition rate of litter, our field observations confirm the speed of this 456 process. From the standing stocks of cations in the forest and the annual-cationic FVEG fluxes (Table 457 4), we determined the residence time (Tres) of each element in the vegetation. The element presenting 458 the shortest residence time in the vegetation is K, namely 16 years. This residence time is consistent with the 10 year period determined for K in Puerto Rican forest (McDowell 1998). This short residence 459 460 time is justified by the fact that K is one of the most important elements for plant metabolism (as a catalytic agent for carbohydrate synthesis and the transfer of other nutrients) and is abundantly 461 462 excreted by the leaves. For other elements, the residence time is slightly longer than those determined for K: 44.6 years for Sr, 44.9 for Ca, 45.7 for Mg and 48.2 for Na. These results highlight that vegetation 463 recycling dominates the nutrient cycle, and, in light of the Sr isotopic signature, we can deduce that 464 465 these nutrients have the particularity of being initially of atmospheric origin. Therefore, the Quiock 466 Creek ecosystem is sustained by a little near-surface nutrient pool, which seems disconnected from the deep bedrock. 467

468 Our study is a first step in the characterization of biogeochemical cycles at the plant-soil scale in the 469 Guadeloupean rainforest. To better characterize and quantify the nutrient recycling, it would be useful 470 for example, to study the seasonality of vegetation fluxes, investigate the N and P cycles, or use the

471 isotopic fractionations of the elements involved in these biogeochemical processes (Ca, Mg, Si, B,...).

- 472 6.2. Soil cation-nutrient pool and weathering
- 473 6.2.1. Origin of cation-nutrient pool in the soil

474 After studying geochemical cycles at the plant-soil scale, it is necessary to study the soil profile to475 determine whether soil is still able to provide nutrients to the forest.

476 In the entire soil profile (Fig. 2), the Sr isotopic signature of the solid phase is high relative to rock, 477 which is consistent with exogenous contributions of Sr. Fig. 6 presents the Sr isotopic signature of soil 478 as a function of the Sr depletion rate ( $\tau$ Sr). The more the sample is rich in Sr, the more the soil Sr 479 signature is radiogenic. This implies that the main source enriching the soil in Sr is more radiogenic than 480 bedrock. The two potential sources of Sr that could enrich the soil in radiogenic Sr are: 1) Sea salts with a signature of 0.70917 (Dia et al., 1992) or 2) Saharan dust with a signature of 0.7187 (this study). This 481 482 indicates that the soils are so leached that they have almost lost their original rock signature and have 483 inherited an exogenous atmospheric signature. As previously discussed (Section 5.5) at depths of 15, 30, 305, 427, 1219 and 1250 cm, the high <sup>87</sup>Sr/<sup>86</sup>Sr ratios (> 0.712) are correlated with the highest 484 485 primary mineral content (Quartz + Feldspar), which could correspond to different dust deposit horizons. All the other soil samples are not enriched in primary minerals but, nevertheless, are 486 characterized by Sr isotopic ratios that indicate a mixture of bedrock and exogenous atmospheric 487 488 sources. This indicates that Sr derived from atmospheric deposits is transferred to the soil exchangeable 489 pool and may be incorporated into secondary minerals. This recycled Sr in the soil exchangeable pool 490 could be taken up by plants and reinforces the hypothesis that the nutrients involved in the Quiock 491 Creek ecosystem are of atmospheric origin. This strong atmospheric influence on the soil profile has 492 been described in the study by Clergue et al. (2015), devoted to Li dynamic in the same catchment. The 493  $\delta^7$ Li measured in the soil profile also indicated that atmospheric deposition (wet and dry) was a main 494 source of Li in the bulk soil.

495 Because both wet and dry atmospheric deposits are sources of radiogenic Sr, it is not possible to discriminate between sea salt and Saharan sources in soil only on the basis of the <sup>87</sup>Sr/<sup>86</sup>Sr ratio. 496 Coupled with Sr isotopes, Nd isotopes are useful for identifying the different contributions to the soil 497 498 profile. For example, ENd of rock ranges from 4.34 to 5.45 (Table 3) and ENd of Saharan dust ranges from -10.5 to -14.5 (Grousset et al., 1992; Dia et al., 2006; Scheuvens et al., 2013; McClintok et al., 499 500 2015). Sea salt exhibits an extremely low Nd concentration and Saharan dust input seems to be the 501 only atmospheric contribution able to shift the isotopic composition of the soil. The Nd isotopic 502 composition of soil varies between -8.39 and 2.71 and could be explained by a mixture of rock and dust 503 endmembers. The quartz-feldspar horizons are characterized by very negative  $\epsilon$ Nd, indicating a strong 504 Saharan Nd contribution. The amount of quartz and Nd isotopes provide two independent proxies of 505 long-term dust additions to the soil profile. The superficial horizon (the first 30 centimetres) is a contemporary depositional surface while the other horizons attest to past deposition. The deepest 506 507 quartz horizons (305, 427, 792 and 1219-1250 cm) may represent paleo-surfaces of dust deposits, 508 interspersed between multiple events of volcanic deposition. The variable thickness of these horizons 509 may be partly explained by a physical soil mixing process resulting from bioturbation.

510 In Fig. 7, the soil samples are plotted in a two-component mixing diagram for <sup>87</sup>Sr/<sup>86</sup>Sr versus ɛNd. The 511 curvature of the different mixing lines depends on the Sr/Nd ratio of each endmember. The dotted curve represents the mixing line between the unweathered rock endmember ( $^{87}$ Sr/ $^{86}$ Sr = 0.7038,  $\epsilon$ Nd 512 = 4.8, Sr/Nd = 17.9; from this study and the andesite Nd content of 16 ppm from Taylor and McLennan 513 1985) and the Saharan endmember ( ${}^{87}$ Sr/ ${}^{86}$ Sr = 0.7187,  $\epsilon$ Nd = -11.5, Sr/Nd = 3.4; from this study and 514 515 Grousset et al., 1998). This mixing line cannot explain the isotopic composition of the soil samples, 516 indicating that dust is not mixed with fresh rock but with a Sr-depleted weathered rock. Four mixing lines with depleted rock endmembers are shown on Fig. 7. Their Sr/Nd ratios decreased from 10 to 0.1 517 518 in the most depleted case.

519 If we first consider soil horizons enriched in quartz-feldspar, this mixing model confirms that these 520 particular layers are strongly influenced by the dust endmember. It also emphasized that the 521 proportion of Saharan Sr in the soil decreases with depth, from 65% in the first 15 cm, to 20% in the 522 deepest quartz-feldspar horizons. Finally, our results show that the degree of rock depletion also increases with depth. Indeed, surface horizons (15 and 30 cm) can be explained by mixing of dust with 523 524 moderately depleted rock (10<Sr/Nd<5) whereas the deeper horizons involve a mixture with a very depleted rock (Sr/Nd<1). The superficial volcanic rock signature is inherited from the deposit of volcanic 525 526 ashes in Guadeloupe linked to very recent activity of neighbour volcano Soufriere Hills on Montserrat 527 (Baxter et al., 1999; Cadelis et al., 2013). The accumulation of Saharan dust in the upper soil is also 528 observed in quartz-diorite and volcaniclastic soils in Puerto Rico (McClintock et al., 2015), which is too 529 far from the volcanic arc of the Lesser Antilles to be impacted by recent ash deposits. In Puerto Rico, 530 the calculated soil dust content ranges between 0 and 8%, and Nd from dust in the upper 20 cm of soil 531 ranges between 0 and 92% (McClintock et al., 2015), which is consistent with what we have observed 532 in Guadeloupe.

533 If we now consider soil horizons non-enriched in quartz-feldspar, we note that their isotopic composition still reflects a slight influence of the dust endmember and that they have <sup>87</sup>Sr/<sup>86</sup>Sr ratios 534 535 close to those of rainfall or that are slightly more radiogenic. The rock Sr isotope signature in these horizons has been completely overprinted by the atmospheric signature (rainfall and dust-derived Sr). 536 537 The slight influence of dust on the Nd signature in the entire soil profile is clear evidence for the 538 mobilization of dust-derived Nd and its redistribution in the soil. This is especially the case for the horizons at depths of 61 and 91 cm, which do not contain quartz and felspar, but whose Sr and Nd 539 540 isotope signatures are strongly influenced by the dust endmember (25 to 35%). It is possible that the 541 Sr and Nd come from the leaching of Saharan minerals contained in the upper soil and that are 542 reincorporated into the deeper soil levels. Even if Nd mobility is much lower than Sr mobility, it seems to increase under extreme leaching conditions. This mobilization of dust-derived Nd into highly 543 544 weathered soil profiles has been observed in Puerto Rico, where the Nd isotope signature of Saharan 545 dust has been observed noted at depths of 2 and 3 m (Pett-Ridge et al., 2009b). Our mixing model 546 cannot explain all the data because of the influence of a third end-member, namely sea salt Sr derived from rainwater. Because sea salts are not a significant source of Nd, the addition of sea salts does not
influence the Nd isotopic composition of soil. Except for the dust horizons, andesitic and dust-derived
Sr have been leached extensively and the sea salt Sr signature dominates in the entire profile.

550 In the Quiock Creek catchment, we observe a strong impact of atmospheric sources on the evolution of the chemical composition of the soil with depth and with time. Elements are continuously provided 551 552 at the surface by fresh dust minerals on a highly depleted soil. Then, we observe a "reversed" 553 weathering profile, with the horizon the most enriched in primary minerals (Saharan and volcanic) and 554 having the strongest andesitic isotopic signature at the top of the soil profile. The impact of atmospheric sources on volcanic soil has been demonstrated in different tropical contexts. In a soil 555 556 chronosequence in Hawaii, it was shown that the older the soils, the bigger the impact of atmospheric inputs (Kennedy et al., 1998; Whiptkey et al., 2000; Kurtz et al., 2001; Chadwick et al., 2009). Saharan 557 558 dust was shown to affect soil composition in Puerto Rico (Pett-Ridge et al., 2009b; McClintock et al., 559 2015) and in Mount Cameroon (Dia et al., 2006). In Guadeloupe, Mg and Li isotopes reflect the influence of sea salt and dust on soil (Opfergelt et al., 2012; Clergue et al., 2015; Fries et al., 2019). Our 560 561 study supports these prior observations and the need to fully account for these inputs when studying 562 weathering and cation-nutrient cycling under tropical climatic conditions.

563 6.2.2. Does chemical weathering provide elements to the catchment flux?

564 The comparison between rainfall fluxes and output flux from Quiock Creek provides information on 565 processes taking place in the soil. Elementary budgets (output flux – input flux) are negative (Fig. 5). 566 This may mean that the catchment stores cation nutrients in the soil or in the vegetation. However, it 567 can also mean that for these elements, inputs from rainfall are underestimated. In fact, their mean 568 concentrations in rain are highly variable and hard to estimate. In any case, it means that these elements are not enriched as they move through the soil and thus there is no weathering flux for these 569 elements in the catchment. The Sr isotopic composition of Quiock Creek, which is close to the sea salt 570 571 aerosol signature, supports the idea that the Sr comes from atmospheric input only (Fig. 5). The fact

that the Quiock Creek <sup>87</sup>Sr/<sup>86</sup>Sr ratio is very different from the volcanic rock signature, indicates that 572 573 the local rock no longer contributes to the weathering flux. The absence of weathering flux in the 574 Quiock Creek catchment and its peculiar Sr isotopic composition are linked with the intense weathering 575 of the soil, which is highly depleted in major elements (Clergue et al., 2015). This situation is peculiar in Guadeloupe, as in all other catchments studied, the weathering flux is equivalent, or even twice as 576 high, as the rainfall flux (Dessert et al., 2015). This situation is also peculiar in the Caribbean, for 577 578 example in Puerto-Rico, where numerous catchments are surveyed by the USGS. In the Puerto-Rican 579 catchments, which are subject to the same climate and are covered by rainforest, soils are not as 580 depleted as in Guadeloupe (e.g. Ferrier et al., 2010). The Rio Icacos basin in Puerto Rico is the site of the highest measured chemical solute fluxes for a catchment on granodiorite (Turner et al., 2003). 581

582 Clergue et al. (2015) showed that in this catchment, part of the weathering flux of Li originates from 583 the main secondary mineral dissolution (i.e. kaolinite). Using the kaolinite dissolution rate (Carroll et 584 al., 1988), the authors showed that kaolinite dissolution can explain the weathering flux of Li measured on site. The same calculations were made for Mg and Sr, using the average concentration of those 585 586 elements in kaolinite. They show that kaolinite can provide Mg and Sr by dissolution, with a respective flux of 0.012 kg<sub>Mg</sub> ha<sup>-1</sup> yr<sup>-1</sup> and 0.002 kg<sub>sr</sub> ha<sup>-1</sup> yr<sup>-1</sup>. However, these fluxes are much lower than the 587 588 rainfall fluxes and consistent with the absence of measurable weathering flux for some major elements 589 and Sr.

In the Quiock Creek catchment, a large range of <sup>87</sup>Sr/<sup>86</sup>Sr and εNd values is observed despite the small scale of observation. Sr isotopic composition varies from 0.70677 in deep bulk soil samples to 0.71882 in dust samples. The Nd isotopic composition varies just as much, between -8.39 in near-surface soil samples to 2.71 in deeper soil (732 cm depth). For the Saharan dust endmember, we used a mean εNd value of -11.5, determined from the literature. These large isotopic ranges, coupled with major and trace elements, have helped to better understand nutrient dynamic in tropical ecosystems in Guadeloupe.

598 The regolith profile was built on pyroclastic deposits, but, because of extreme leaching, it has almost 599 lost its original andesitic signature and inherited an exogenous atmospheric signature. Only Saharan dust is likely to have influenced the Nd balance throughout the entire 12m-thick profile, while the Sr 600 balance is influenced by both Saharan dust and sea salt aerosols. Sr and Nd isotopes, combined with 601 602 mineralogy and mobile element concentrations in the regolith, argue for a multi-layered soil profile 603 which has been built by successive volcaniclastic episodes, separated by periods of dust deposition. 604 Deep horizons enriched in quartz-felspar are then interpreted as paleo-soils impacted by Quaternary 605 Saharan dust deposits, whereas the near-surface soil horizon is currently impacted by fresh dust 606 deposits. Our results show that only the chemical weathering of the near-surface fresh minerals can 607 provide nutrients to the ecosystem, the deeper regolith (> 30 cm) being nutrient depleted. However, 608 this dust weathering flux is too low to sustain the tropical forest ecosystem.

The cationic mass balance at the catchment scale and the Sr isotopic signature of Quiock Creek indicate that cation and Sr fluxes are of atmospheric origin. Thus, in this highly weathered catchment, the original andesitic bedrock no longer participates in the weathering fluxes of Quiock Creek. This conclusion leads us to question the notion of "bedrock" in catchment involving on a deep weathered formation. Is it still an andesitic bedrock or is it now a lateritic bedrock?

614 The dissolved Sr cycle at the catchment scale is mainly dominated by sea salts, with a small contribution

of Sr coming from the Saharan dust leaching. The vegetation exhibits the signature of the dissolved

616 pool of Sr, indicating that the nutrient pool derives from atmospheric inputs.

At the soil-plant scale, the cation-nutrient fluxes provided by vegetation (litter fall + leaf excretion) are major compared to input and output fluxes. The Ca, K, Sr and Mg fluxes each year in the vegetation are, respectively, 31, 28, 20 and 3 times greater than the exported fluxes at the outlet of the basin. The residence time of nutrients in vegetation is 16 years for K and close to 45 years for Sr, Ca and Mg. These results emphasize the highly efficient plant turnover that dominates the nutrient cycle in the Quiock Creek catchment.

This first characterization of biogeochemical cycles in a Guadeloupean forest suggests that the forest community of Quiock Creek is sustained by a small near-surface nutrient pool, disconnected from the deep andesitic bedrock.

626

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Fig. 1. The Quiock Creek catchment (16°17'N, 61°70'W) in the Guadeloupe National Park. The MF rain gauge is located in a clearing, on the roof of the "Maison de la Forêt", and the OVSG rain gauge is located on the roof of the observatory. The soil profile was sampled during lysimeter installation (see Buss et al., 2010).

Fig. 2. Sr isotopic composition of dissolved and solid samples collected in the Quiock Creek catchment.
Sea salt Sr isotopic ratio = 0.70917 (Dia et al., 1992); volcanic rock = 0.7038 (this study); Saharan dust
= 0.7187 (this study).

Fig. 3. Molar ratios (µmol/µmol ratios, except for the Sr/Cl ratio expressed in nmol/µmol) of dissolved
load in the different compartments of the Quiock Creek catchment. RF: rainfall, TF: throughfall, SS: soil
solution (above and below 91 cm depth), QC: Quiock Creek, SW: seawater/sea salt.

Fig. 4. Soil profiles. Quartz + feldspar content (from Buss et al., 2010), mass transfer coefficient (τ) for
Sr in soil samples relative to bedrock, and isotopic signature of Sr and Nd. τ is calculated considering Ti
to be immobile and illustrates the extreme depletion of Sr in the soil compared to unweathered rock
(values closed to -1).

Fig. 5. Cation fluxes in the Quiock Creek catchment expressed in kg/ha/yr. FSW is the sea salt flux, FSD
the Saharan dust leaching flux, FRF the rainfall flux, FTF the throughfall flux, FLF the litter fall flux, FEX
the leaf excretion flux and FQC the Quiock Creek flux.

Fig. 6. Sr mass transfer coefficient as a function of Sr isotopic ratio in soil samples. Sea salt Sr isotopic
ratio = 0.70917 (Dia et al., 1992); volcanic rock = 0.7038 (this study); Saharan dust = 0.7187 (this study).
Samples enriched in quartz-feldspar are symbolized by white square.

Fig. 7. Two-component mixing diagram of εNd vs. Sr isotopic ratio in soil samples. Horizon depths (cm)
are added and samples enriched in quartz-feldspar are symbolized by white squares. The solid lines

881 represent different mixing curves between a bedrock (fresh and depleted) end-member and a "Saharan 882 dust" end-member. The mixing proportions are expressed in % of dust Sr. The black dotted curve represents a mixture of fresh rock ( ${}^{87}$ Sr/ ${}^{86}$ Sr = 0.7038,  $\epsilon$ Nd = 4.8, Sr/Nd = 17.9) and dust ( ${}^{87}$ Sr/ ${}^{86}$ Sr = 883 884 0.7187, εNd = -11.5, Sr/Nd = 3.4). The other curves show a mixture between of depleted rock (<sup>87</sup>Sr/<sup>86</sup>Sr = 0.7038,  $\varepsilon Nd = 4.8$ , Sr/Nd varying from 10 to 0.1 for the most depleted rock) and dust. The samples 885 are explained by a mixture of Saharan dust and depleted rock. The soil horizons enriched in quartz-886 feldspar are strongly influenced by dust (20 to 65% of dust Sr). The near-surface horizon (first 30 cm) is 887 888 the most impacted by dust and can be explained by the mixing of dust with moderately depleted rock. 889 This emphasizes the contemporary, or very recent, deposition of both Saharan dust and volcanic ash in 890 Guadeloupe (recent volcanic activity of nearby Montserrat). The deeper quartz-feldspar horizons are 891 paleo-surfaces of dust deposits interspersed with volcanic deposits. With time, andesitic and dust-892 derived Sr has been leached extensively and the sea salt Sr signature dominates today in the entire 893 profile.





















## Tables\_Results

Table 1: Major element concentrations are from Clergue et al	. (2015). Sr concentrations and Sr isotopic
signature in water samples are new data.	

Sample name	Date dd/mm/yy	рН	<b>Na</b> µmol/L	Cl µmol/L	<b>Ca</b> µmol/L	<b>Mg</b> μmol/L	<b>K</b> μmol/L	<b>Sr</b> μmol/L	<sup>87</sup> Sr/ <sup>86</sup> Sr
Rainfall (RF)									
RF-OVSG	20/03/13	4.8	82	85	2	10	3	0.010	0.70918
RF-OVSG	04/04/13	5.1	76	88	7	13	9	0.015	0.70841
RF-OVSG	15/07/13	nda	96	nd	7	14	5	0.034	0.71029
Throughfall (TF)									
TF collector n°2	21/11/11	nd	25	27	6	4	18	0.121	0.70965
TF collector n°1	10/08/12	6.1	81	92	15	13	31	0.056	0.70978
TF collector n°3	21/03/13	5.6	71	64	6	7	13	0.015	0.70953
TF collector n°1	03/04/13	nd	155	168	14	19	26	0.048	0.70969
TF collector n°3	03/04/13	nd	154	158	14	18	27	0.043	0.70972
TF collector n°1	25/06/13	5.6	117	132	17	17	32	0.067	0.70968
Soil solution (SS) <sup>b</sup>									
GBD2_91	26/10/12	5.1	226	211	3	21	3	0.022	0.71070
GBD2_122	26/10/12	4.9	171	145	2	16	2	0.009	0.71097
GBD2_152	26/10/12	4.6	153	141	1	22	1	0.008	0.71063
GBD2_274	26/10/12	4.6	209	241	4	28	5	0.022	0.71020
GBD2_344	26/10/12	4.5	207	244	0	30	2	0.009	0.71094
GBD2_457	26/10/12	4.5	194	168	2	14	4	0.013	0.71004
GBD2_15	28/06/13	nd	118	130	2	21	2	0.039	0.71037
GBD2_30	28/06/13	5.4	147	150	1	27	2	0.034	0.71029
GBD2_61	28/06/13	4.8	126	163	12	31	4	0.063	0.70996
GBD2_91	28/06/13	5.3	194	207	3	25	2	0.020	0.71087
GBD2_274	28/06/13	4.7	161	221	2	26	2	0.017	0.71064
GBD2_457	28/06/13	5.4	159	167	2	14	3	0.010	0.71097
GBD2_823	28/06/13	nd	210	243	1	15	13	0.010	0.71022
Quiock Creek									
QC	23/04/12	nd	184	229	11	25	6	0.056	0.70939
QC	03/08/12	nd	248	271	9	29	5	0.052	0.70922
QC	26/10/12	4.7	254	271	8	30	4	0.048	0.70933
QC	21/03/13	4.8	211	274	15	32	3	0.046	0.70928

<sup>a</sup> nd=not determined.
 <sup>b</sup> For soil solution sample names GBD2\_X, X=depth in cm.

Table 2: Range of concentration in the different compartments (mean value/median value) from Clergue et al. (2015).

	K (µmol/L)	Na (µmol/L)	Mg (µmol/L)	Ca (µmol/L)	Cl (µmol/L)
RF* (n=13)	1 – 9 (4/3)	41 – 165 (89/79)	1 – 22 (12/11)	1 – 15 (7/7)	49 – 167 (92/85)
TF (n=48)	10 – 108 (39/32)	17 – 264 (117/102)	3 – 40 (17/17)	3 – 36 (17/16)	23 – 264 (125/99)
SS (n=75)	1 – 39 (5/3)	112 – 266 (179/182)	11 – 58 (24/25)	0.3 – 14 (3/2)	85 - 345 (199/203)
QC (n=57)	3 – 12 (5/5)	184 – 282 (234/239)	24 – 35 (29/29)	7 – 15 (10/10)	229 – 315 (272/274)
QC (n=57)	3 - 12(5/5)	184 - 282 (234/239)	24 - 35 (29/29)	7 – 15 (10/10)	229 - 315 (272/2

\*: MF + OVSG rainfall.

Sample name	Ca ppm	<b>K</b> ppm	<b>Mg</b> ppm	<b>Na</b> ppm	<b>Ti</b> ppm	Sr ppm	<sup>87</sup> Sr/ <sup>86</sup> Sr	εNd
Saharan Dust								
Saharan 1	1747	5474	5355	951	nd	52	0.71865	nd
Saharan 2	1918	5134	5059	930	nd	49	0.71882	nd
Vegetation Litter								
Leaves 1	30533	5087	5441	1356	nd	203	0 71010	nd
Leaves 2	10237	2302	1960	1857	nd	203 80	0.71019	nd
Branches 1	14234	1315	2730	581	nd	112	0.71010	nd
Branches 2	19254	1122	2750	504	nd	08	0.70900	nd
Branches 2	16410	1122	5676	2450	nd	90	0.70975	nd
Roots	10410	11590	5070	2439	na	24	0.70970	na
Soil <sup>a</sup>								
GBD2_15	306	1087	1977	681	8573	13	0.71293	-8.39
GBD2_30	147	643	1339	404	8873	9	0.71331	-7.57
GBD2_61	45	356	1189	356	7913	6	0.71065	-2.35
GBD2_91	43	455	1207	295	6894	6	0.71064	-3.66
GBD2_183	41	174	1287	444	7674	4	0.70840	<u>1.92</u>
GBD2_274	28	249	1043	248	7374	4	0.70893	0.74
GBD2_305	47	1026	1499	353	8033	12	0.71474	<u>-6.70</u>
GBD2_366	35	194	1068	344	8153	4	0.70964	1.19
GBD2_427	28	615	1262	158	10132	7	0.71496	-6.54
GBD2_610	34	326	1419	264	7314	4	0.71109	-0.21
GBD2_732	36	317	825	160	6834	2	0.70677	<u>2.71</u>
GBD2_792	43	621	880	278	5096	4	0.71125	-2.12
GBD2_914	29	321	1196	339	7074	4	0.71062	0.42
GBD2_1036	48	258	1234	347	6714	4	0.70877	nd
GBD2_1097	23	242	946	291	5995	3	0.70988	2.44
GBD2_1158	41	215	1341	324	9052	2	0.70764	nd
GBD2_1219	78	1276	1612	277	7674	12	0.71527	-1.89
GBD2_1250	60	971	1312	215	8273	12	0.71508	-0.97
Volcanic Rock <sup>b</sup>								
04GW12	48462	7308	9060	27328	5373	244	0 70388	5 4 5
00GU44	74521	5175	29483	20282	5466	331	0 70380	4 34
03GU75	68417	4325	26106	21669	5796	283	0.70385	4.67

Table 3: Chemical and isotopic (Sr and Nd) composition of soil, rock, Saharan dust and vegetation samples. Some Nd isotopic composition of soils (highlighted) and Ca, K, Mg, Na, Ti concentrations are from Clergue et al. (2015).

<sup>a</sup> for soil sample names GBD2\_X, X=depth in cm <sup>b</sup> rock samples from Samper et al. (2007).

	Na	Ca	Mg	K	Sr
Rainfall flux (FRF)	83.0	11.7	11.7	6.2	0.076
Sea Salt flux (FSW)	74.1	2.7	9.6	2.7	0.053
Saharan dust leaching flux (FSD)	8.9	9.0	2.1	3.5	0.023
Throughfall flux (FTF)	83.0	21.4	13.0	47.4	0.156
Sea Salt flux (FSW)	74.1	2.7	9.6	2.7	0.053
Saharan dust leaching flux (FSD)	8.9	9.0	2.1	3.5	0.023
Leaf excretion flux (FEX)	0.0	9.6	1.4	41.2	0.080
Vegetation flux (FVEG)	8.4	141.5	25.8	62.1	1.039
Litter fall flux (FLF)	8.4	131.9	24.4	20.9	0.959
Leaf excretion flux (FEX)	0.0	9.6	1.4	41.2	0.080
Vegetation Stock	405.1	6355.9	1180.1	1010.6	46.3
<b>Residence time (Tres)</b>	48.2	44.9	45.7	16.0	44.6
Quiock Creek flux (FQC)	60.9	4.5	8.0	2.2	0.051

Table 4: Elemental annual flux (kg.ha<sup>-1</sup>.yr<sup>-1</sup>), stock (kg.ha<sup>-1</sup>) and residence time (yr) in the Quiock Creek catchment.

Calculations are described by equations 2 to 9.

	Al	Ca	Fe	К	Mg	Na	Sr
	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Rock standards							
BEN certif <sup>1</sup>	53312	99071	89880	11534	79291	23594	1370
BEN (this study)	54289	99897	90935	11739	79269	23846	1655
	52140	95138	89888	11397	76588	23325	
GSN certif <sup>1</sup>	77665	17857	26250	38419	13868	27971	570
GSN (this study)	77987	17562	25798	35813	13629	26838	531
	77673	17467	25594	35454	13600	26723	554
	80519	17834	26123	37214	13770	27587	
Vegetation standard							
NIST_SRM 1515 (certif)	286	15260	83	16000	2700	24.4	25
NIST_SRM 1515 (this study)	283	14441	69	15216	2421	55	
	290	14349	73	15544	2478	57	
	283	14872	75	16102	2662	42	
	286	15014	76	16307	2682	42	

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

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

Table 2S : Sr concentration in throughfall, rainfall and Quiock Creek samples

Sample name	Date	Sr µmol/l	Sample name	Date	Sr µmol/l	Sample name	Date	Sr µmol/l
Throughfall								
TF col nº1	14/11/2011	0.136	TF col nº3	25/03/2013	0.041	QC	16/03/2012	0.064
TF col nº2	14/11/2011	0.129	TF col nº1	27/03/2013	0.070	QC	04/04/2012	0.057
TF col nº1	21/11/2011	0.025	TF col nº3	27/03/2013	0.049	QC	09/04/2012	0.058
TF col nº2	21/11/2011	0.121	TF col nº1	29/03/2013	0.070	QC	13/04/2012	0.058
TF col nº3	21/11/2011	0.038	TF col nº3	29/03/2013	0.050	QC	19/04/2012	0.070
TF col nº1	25/11/2011	0.035	TF col nº1	01/04/2013	0.018	QC	23/04/2012	0.056
TF col nº2	25/11/2011	0.026	TF col nº3	01/04/2013	0.016	QC	26/04/2012	0.056
TF col nº3	25/11/2011	0.035	TF col nº1	03/04/2013	0.048	QC	08/06/2012	0.054
TF col nº1	09/04/2012	0.012	TF col nº3	03/04/2013	0.043	QC	03/08/2012	0.052
TF col nº2	09/04/2012	0.067	TF col nº1	25/06/2013	0.067	QC	05/08/2012	0.053
TF col nº3	09/04/2012	0.037	TF col nº3	25/06/2013	0.062	QC	10/08/2012	0.053
TF col nº1	13/04/2012	0.126	TF col nº1	26/06/2013	0.048	QC	16/08/2012	0.050
TF col nº2	13/04/2012	0.076	TF col nº3	26/06/2013	0.036	QC	07/09/2012	0.050
TF col nº3	13/04/2012	0.049	TF col nº1	28/06/2013	0.043	QC	05/10/2012	0.050
TF col nº2	16/04/2012	0.027				QC	23/10/2012	0.049
TF col nº3	16/04/2012	0.023	Rainfall			QC	26/10/2012	0.048
TF col nº1	19/04/2012	0.119	RF-MF	03/08/2012	0.039	QC	30/11/2012	0.037
TF col nº2	19/04/2012	0.113	RF-MF	10/08/2012	0.034	QC	14/12/2012	0.035
TF col n°3	19/04/2012	0.109	RF-OVSG	20/03/2013	0.010	QC	18/01/2013	0.037
TF col nº1	23/04/2012	0.011	RF-OVSG	21/03/2013	0.011	QC	01/02/2013	0.037
TF col nº2	23/04/2012	0.010	RF-OVSG	27/03/2013	0.021	QC	01/03/2013	0.046
TF col nº3	23/04/2012	0.008	RF-OVSG	31/03/2013	0.009	QC	20/03/2013	0.045
TF col nº1	05/08/2012	0.031	RF-OVSG	01/04/2013	0.017	QC	21/03/2013	0.046
TF col nº2	05/08/2012	0.032	RF-OVSG	04/04/2013	0.015	QC	25/03/2013	0.042
TF col nº3	05/08/2012	0.038	RF-OVSG	15/07/2013	0.034	QC	29/03/2013	0.039
TF col nº1	10/08/2012	0.056				QC	01/04/2013	0.039
TF col nº2	10/08/2012	0.060	Quiock Creek			QC	03/04/2013	0.042
TF col nº3	10/08/2012	0.121	QC	14/10/2011	0.059	QC	24/05/2013	0.056
TF col nº1	16/08/2012	0.098	QC	10/11/2011	0.069	QC	21/06/2013	0.048
TF col nº2	16/08/2012	0.115	QC	23/11/2011	0.068	QC	25/06/2013	0.051
TF col nº3	16/08/2012	0.136	QC	09/12/2011	0.060	QC	26/06/2013	0.052
TF col nº1	21/03/2013	0.017	QC	06/01/2012	0.064	QC	28/06/2013	0.047
TF col nº3	21/03/2013	0.015	QC	03/02/2012	0.061	QC	02/07/2013	0.049
TF col nº1	25/03/2013	0.084						