

Geochemical insights into spatial and temporal evolution of sediment at catchment scale (Egoutier stream, France)

Lauriane Ledieu, Anaëlle Simonneau, Olivier Cerdan, Philippe Négrel, Valérie Laperche, Cécile Grosbois, Fatima Laggoun-Défarge

► To cite this version:

Lauriane Ledieu, Anaëlle Simonneau, Olivier Cerdan, Philippe Négrel, Valérie Laperche, et al.. Geochemical insights into spatial and temporal evolution of sediment at catchment scale (Egoutier stream, France). Applied Geochemistry, 2020, 122, pp.104743. 10.1016/j.apgeochem.2020.104743. insu-02925859

HAL Id: insu-02925859 https://insu.hal.science/insu-02925859

Submitted on 31 Aug2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

GEOCHEMICAL INSIGHTS INTO SPATIAL AND TEMPORAL EVOLUTION OF SEDIMENT AT CATCHMENT SCALE (Egoutier stream, France)

L. Ledieu, A. Simonneau, O. Cerdan, P. Négrel, V. Laperche, C. Grosbois, F. Laggoun-Défarge

PII: S0883-2927(20)30235-3

DOI: https://doi.org/10.1016/j.apgeochem.2020.104743

Reference: AG 104743

To appear in: Applied Geochemistry

Received Date: 20 December 2019

Revised Date: 21 August 2020

Accepted Date: 21 August 2020

Please cite this article as: Ledieu, L., Simonneau, A., Cerdan, O., Négrel, P., Laperche, V., Grosbois, C., Laggoun-Défarge, F., GEOCHEMICAL INSIGHTS INTO SPATIAL AND TEMPORAL EVOLUTION OF SEDIMENT AT CATCHMENT SCALE (Egoutier stream, France), *Applied Geochemistry*, https://doi.org/10.1016/j.apgeochem.2020.104743.

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2020 Elsevier Ltd. All rights reserved.



1 GEOCHEMICAL INSIGHTS INTO SPATIAL AND TEMPORAL EVOLUTION OF SEDIMENT AT CATCHMENT 2 SCALE (Egoutier stream, France)

L. Ledieu¹, A. Simonneau¹, O. Cerdan², P. Négrel², V. Laperche², C. Grosbois³, F. Laggoun-Défarge¹

¹Univ. Orléans, CNRS, BRGM, ISTO, UMR 7327, F-45071, Orléans, France

²BRGM, 3 avenue Claude Guillemin, 45060 Orléans, France

³GéHCO, University of Tours, 37200 Tours, France

3

11 Abstract

12 The transfer and storage of chemical elements in particulate matter are controlled by physical, chemical and biological processes. Their dynamics are well understood, especially in environments 13 14 that show strong tectonic and/or geomorphic pressures, and are frequently reconstructed over centuries 15 or decades to evaluate climate change effects for example. However, observations carried out at high spatial and temporal resolutions are less common, particularly in lowland areas. The present study 16 aimed to better understand the links between earth surface processes, such as soil weathering and 17 erosion, by combining pedology, geochemistry and hydrology at a small catchment scale. It focuses on 18 the transfer of selected chemical elements (Ca, K, Ti, Fe, Mn, Rb and Sr) associated with particulate 19 20 erosion and transport. The first (topsoil) and last (subsoil) soil horizons from different soil profiles and stream bed-load sediments of the Egoutier catchment (8 km², Loiret, France) were studied. The 21 22 objective was to investigate the relationship between the weathering and erosion processes. The soils are developed on ancient alluvium as evidenced by their physical and chemical properties, which 23 clearly displayed a weathering profile from bedrock to topsoil layers. Ca, Fe and Rb showed migration 24 25 dynamics from the topsoils to the subsoils, whereas Mn appeared immobilized within topsoils. Enrichments of all investigated elements increased in bed-load sediments. Topsoil erosion is the main 26 source of sediment. However, Fe and Rb enrichments also highlight the remobilization of subsoils 27 28 during periods of enhanced precipitation. Furthermore, Fe and Rb enrichments show a selective 29 erosion of clay minerals. K and Sr contents evidence mineral break-up processes favoring mechanical erosion of all mineral phases. Moreover, their enrichments can be interpreted as the result of higher 30 erosion rates and deposition during high rainfall events. The same conclusion can be drawn for Mn 31 and Ca although their spatial variabilities depend on contributions from runoff in urban areas, as 32

rainwaters from anthropized areas supply Ca mineral phases and diluted Mn depleted bearing phasesfrom topsoil layers.

35

36 Keywords

37 Weathering, Erosion, Soil, Sediment, Geochemistry

38

39 1. Introduction

40 The Critical Zone (CZ) is defined as the thin layer of the Earth's surface and near-surface terrestrial 41 environment. This zone forms the link between rocks, soils, atmospheric gases and meteoric waters, which are the habitat of humanity and biodiversity (Anderson et al., 2007). The storage and transfer of 42 waters and chemical elements in these compartments are controlled by complex physical, chemical 43 and biological processes (Négrel et al., 2018a) leading to vertical and lateral heterogeneities of the CZ. 44 45 To better understand the behavior of this sensitive compartment, we need to combine disciplines such 46 as geochemistry, pedology and hydrology (Richter et al., 2015) and to evaluate the spatial and temporal evolutions of its physical and chemical properties (Pierret et al., 2018). 47

At catchment scale, some CZ compartments, such as soils, act as a sink with large capacities 48 of storage for many chemical elements (Kabata-Pendias and Pendias, 2001), while other 49 50 compartments, such as river bed-load sediments, are crucial vectors for element transport (Oelkers et al., 2011). As underlined by Nesbitt et al. (1980), in order to achieve full knowledge of sedimentary 51 cycle geochemistry, documentation about the behavior of chemical elements during weathering is 52 required. In the 19th century, soils were defined as dynamic sensitive systems responding to natural 53 54 environmental forcings, whose weathering mainly depends on climate forcing (Pickering, 1986; 55 Richter et al., 2015) and rainfall amounts (Defersha and Melesse, 2012), especially in tropical (Silva et 56 al., 2018; Yang and Zhang, 2019) and glacial (Bernasconi et al., 2008; Heindel et al., 2018; Marerro et 57 al., 2018) environments. Considering that soil elemental composition is also driven by the bedrock 58 composition (Pickering, 1986), detailed descriptions of weathering processes were done on specific bedrocks and/or mineral phases (Harriss and Adams, 1966; Johnson et al., 1968; Cleaves et al., 1970). 59

60 As strong links exist between chemical weathering and physical erosion (Emberson et al., 2016), integrated studies evaluating the geochemistry of bed-load sediments related to their direct bedrock or 61 62 soil sources thus started to be developed (Martin and Meybeck, 1979; Cullers et al., 1987; Cullers, 1988). Nevertheless, most of the studies were carried out at a global scale and encountered difficulties 63 making the link between weathering and erosion processes because of the complexity induced by the 64 potential interaction of different phenomena : absorption, retention, fractionation, transport, and 65 66 deposition (Bormann and Likens, 1967; Nesbitt et al., 1980; Cullers, 1988). As these processes can operate independently, together or sequentially (Butt, 1992), their respective effects are difficult to 67 distinguish. This is even more the case in environments with variable lithologies and a relationship 68 between surface and groundwaters (Bormann and Likens, 1967) where the contributions of the 69 different bedrocks and elemental cycles through groundwaters are hard to establish. 70

To assist in the characterization of soil and water geochemical cycles, the concept of 71 individual catchment units was defined (Likens and Cowan Jr, 1992). In a watershed ecosystem, 72 73 geochemical inputs have meterological and biological origins, while outputs have biological and 74 geological ones. The differences between the inputs and outputs therefore provide insight into 75 weathering and erosion dynamics (Bormann and Likens, 1967). Catchment outputs are linked to dissolved and particulate material originating from chemical and physical erosion (Nelson, 1973). At 76 77 catchment scale, multi-elemental chemistry analysis of water, soils and bed-load sediments, compared 78 to the bedrock signature (Cullers et al., 1988; Négrel and Deschamps, 1996; Grosbois et al., 2000) 79 become widely used. Given the crustal abundance of silicate rocks (Parker, 1967) and their weathering recycling role for atmospheric CO2 (Brady, 1991), riverine particulate transport associated to 80 weathered silicate bedrocks has recently received attention (Viers et al., 2009). Directly linked to their 81 82 geochemistry, sediment rates, textural and mineralogical characteristics are driven by soil erosion. 83 Because erosion rates are enhanced under strong topographic and anthropogenic forcings (Delmas et al., 2012), many studies have focused on mountainous (Gaillardet et al., 1999; Emberson et al., 2016) 84 or agricultural areas (Marshall and Bayliss, 1994; Grosbois et al., 2000; Cerdan et al., 2002). As a 85 result of increasing urbanization, urban geology has started to emerge as a discipline (Wilson and 86

Jackson Jr., 2016). Growing funds and legislative demands to improve knowledge of urban areas has
enabled the development of geochemical mapping in this kind of environment (Johnson and Ander,
2008). Nevertheless, only a few studies on erosion have been carried out in peri-urban areas (Rowntree
et al., 1991; Grau et al., 2008). Although subjected to rapid transformations, these anthropogenic zones
are nevertheless important actors in modifications of biogeochemical cycles (Douglas, 2012).

To evaluate the horizontal and lateral evolutions and transportability of chemical elements in 92 93 the sedimentary cycle, from bedrock to sediments, more information is needed. It is necessary to distinguish whether existing observations are ubiquitous or site-dependent, suggesting specific 94 95 controlling factors. The determination of the predominant controlling factors is possible by observing of weathering and erosion processes in small peri-urban catchments. Small watershed studies are 96 manageable (Nelson, 1973), present fewer variabilities (Likens and Cowans Jr, 1992) and avoid scale 97 effect smoothing, thus enabling high spatial and temporal characterization of the processes driving 98 biogeochemical cycles. 99

100 The present study was conducted at a small catchment scale (Egoutier, 8 km²) with 101 homogeneous bedrock to decipher weathering dynamics and the continuum of erosion processes and 102 to improve the understanding of particle evolution by the textural, mineralogical and geochemical 103 characterization of soil and sediments. Conducted on varying landscapes on hydromorphic sandy-clay 104 soils and on bed-load sediments derived from different rainfall events in a small stream, this research 105 defines forcing effects in a peri-urban lowland area. It allowed the source contributions to be 106 reconstructed and/or specific processes to be traced at a low temporal scale.

107 **2. Materials and methods**

108 *2.1 Study site and sampling*

109 The Egoutier stream is located in the Loire River basin near Orleans (Loiret, France, Fig. 1). The 110 Egoutier is a tributary of the Loire River draining a small catchment (27 km²) collecting pluvial and 111 sewage networks. In this study, we restricted the investigation area to the upstream part of the 112 catchment covering 8 km². It has a temperate climate, with an average annual rainfall in the area of

113	650 mm (Soucémarianadin and Verbèque, 2007). Depending on stormwaters and soil saturated runoff,
114	the location of the Egoutier source can vary according to the season and/or the rainfall regime. The
115	upstream eastern stream (dotted line, Fig. 1) is for instance only effective during periods of enhanced
116	precipitation. In the northern part, the stream is also fed by two sewage water effluents: one from a
117	Central Army Pharmacy (CAP, Fig. 1), and another from a psychiatric hospital (PH, Fig. 1).

118

119 [Figure 1]

Figure 1: Characteristics of the study site and location of the samples: types of soils and location of the soil surveys (A), land
 covers, location of the artificial supplies to the watercourse and of the bed-load sediment samples (B)

The mean slope gradient of the catchment is 0.5 %. The upstream to downstream substratum is composed of Sologne sands and clays (SSC), Orleanais sands (OS), Burdigalian fluvial deposits dated 21.5 to 16.3 Ma and Beauce limestone dated 23.3 to 21.5 Ma (Berger and Desprez, 1969, Fig. 1). The streambed is impermeable because of clay-rich subsoil horizons (Soucémarianadin and Verbèque, 2007; Fig. 1). Land cover is mainly forests (74 % of the total surface, Fig. 1) and anthropized areas with residential (12 %, Fig. 1), agricultural (7 %, Fig. 1) and industrial zones (4 %, Fig. 1). One pond (the Beulie pond) is present in the central part of the catchment area.

129 Soil surveys (yellow stars, Fig. 1) were conducted for each type of soil and under each land cover type. Following Soucémarianadin and Verbèque (2007), Redoxisol, Planosol and Brunisol 130 (French classification; Baize et al., 2009) cover 95 %, 4% and 1 % of the area, respectively. 13 soil 131 profiles were collected in April 2018 with a hand soil auger and the maximum depth was limited to the 132 133 homogeneous impermeable subsoil layer. Each horizon was described and sampled but only the top and bottom layers of each profile were analyzed (topsoil and subsoil, respectively). Bed-load 134 135 sediments (BLS) were collected from upstream to downstream all along the watercourse (orange 136 circles, Fig. 1), paying attention to each confluence. A total of 8 samples were collected in February and March 2017 and replicated in April 2018 (Fig. 1). 137

139 2.2 Quantification of chemical elements

140 Elemental concentration measurements of all collected samples (soils and BLS) were performed by X-Ray Fluorescence spectrometry (XRF) with a NITON XL3t980 GOLDD fitted with a 50 kV X-ray 141 tube (max. 50 kV, 100 µA, 2 W) with an Ag anode target excitation source and a Large Drift Detector 142 (LDD). As part of the standard set-up routine and to avoid contamination, the analyzer was initially 143 144 Energy calibrated using the embedded Silver target. Samples were dried at 50 °C during 48 hours, crushed in an agate mortar and sieved under 200 µm to have a homogeneous overview of the bulk 145 geochemistry. XRF sample cups with 10-15g of powder were analyzed through 6 µm Mylar films and 146 with an average analyzed spot diameter of 8 mm. The mining mode calibration done by the 147 148 manufacturer was used for all analyses and source count time was fixed at 90 seconds using the 3 filters of the pXRF in the laboratory (30 seconds for each filter). Three certified standards 149 150 (NIST2710a, NIST2711a, NIST2780) were used to verify the calibration and calculate correction factors (Table 1). Each sample was analyzed three times to determine the reproducibility of the 151 152 measurements (Table 1). In order to highlight different processes, only seven elements were selected in this study in relation with their particular behavior: soluble elements such as calcium (Ca), 153 potassium (K), strontium (Sr) and rubidium (Rb); an insoluble one: titanium (Ti); and two redox 154 sensitive ones: iron (Fe) and manganese (Mn). These elements enable mineral contributions to be 155 156 tracked as they are often associated to silicates (K, Rb, Ti), carbonates (Ca, Sr, Negrel and Grosbois, 1999), clays (K, Fe, Mn, Pickering, 1986), and metal oxi-hydroxides (Fe, Mn, Kabata-Pendias and 157 158 Pendias, 2001).

159	Table 1: Certified standards mean contents (mg/g) and % standard deviations (National Institute of Standards and
160	Technology), derived correction factors and % samples mean deviations

Element	ment Certified		Correction factors	Samples mean
	standards mean	deviations		deviations
	contents	(NIST2710a/		
	(NIST2710a/	NIST2711a/		
	NIST2711a/	NIST2780)		
	NIST2780)			
K	21.7 / 25.3 / 33.8	6.0 / 3.9 / 7.7	1.0 / 1.0 / 1.0	0.6
			100	
Са	9.6 / 24.2 / 1.9	4.7 / 2.5 / 10.3	0.8 / 1.0 / 0.7	0.5
Ti	3.1 / 3.2 / x	2.2 / 2.5 / x	0.8 / 1.1 / x	1.2
Fe	43.2 / 28.2 / 27.8	1.8 / 1.4 / 2.9	1.0 / 1.1 / 0.9	0.6
Mn	2.1 / 0.7 / 0.5	2.8 / 2.7 / 4.5	0.2 / 1.2 / 0.9	4.9
Rb	0.12 / 0.12 / x	2.6 / 0.5 / x	0.9 / 1.1 / x	1.4
Sr	0.26 / 0.24 / 0.22	2.7 / 4.1 / 8.3	0.8 / 1.1 / 0.9	1.7
	3			

161

Multivariate statistical analysis can provide precious informations about the correlations 162 between different variables (Zhang and Selinus, 1998; Reimann et al., 2002). A Principal Component 163 Analysis (PCA) was therefore conducted using XLSTAT with topsoil and subsoil layers geochemical 164 results to visualize any correlations between each chemical element and its distribution in the soil 165 166 sample set. Moreover, soil typologies, land cover and bedrock were represented as additional variables to see their potential effect on the distribution of chemical elements. The PCA had a p-value < 0.0001 167 at the Bartlett sphericity test, and a Kaiser-Meyer-Olkin sample adequacy of 0.437. Data set statistical 168 169 parameters are resumed in Table 2.

	К	Ca	Ti	Fe	Mn	Rb	Sr
Variables contribution to	26.9	0.1	5.9	28.7	17.2	8.6	12.6
F1							
Variables contribution to	5.0	31.6	14.8	5.5	1.6	27.1	14.4
F2							
Variables contribution to	30.9	8.4	17.2	10.0	7.7	0.2	25.6
F1 after varimax rotation					5		
Variables contribution to	3.8	18.0	1.2	29.1	14.2	33.6	0.1
F2 after varimax rotation			0	X			
p-value of the Shapiro-	0.289	0.031	0.032	0.120	0.002	0.590	0.050
Wilk test							

170 Table 2: Variables contribution (%) to the first (F1) and the second (F2) principal components of the PCA before and after the 171 varimax rotation, and the p-value of the Shapiro-Wilk test

172

Enrichment factors (EF) are traditionally used to evaluate chemical changes due to alteration-173 erosion processes (Ghadiri and Rose, 1991; Négrel and Deschamps, 1996; Négrel, 1999) and 174 contamination levels (Barbieri, 2016), or to highlight losses (nutrients, Palis et al., 1990). For soils-175 176 sediments, EF are calculated by dividing the element content in the eroded sediment by its content in the original soil (Barrows and Kilmer, 1963). Basic EF can be improved by a normalization with a 177 conservative element such as Al, Li, Sc, Zr, or Ti. This conservative element must show weak 178 variability within the sample set and should not be affected by weathering processes (Reimann and 179 Caritat, 2005). Moreover, it must be free from particle size effects and/or fractionation by any 180 processes. Ti is often a good candidate to carry out this normalization (Zr being another one). Here EF 181 182 were calculated as follows:



183

184 2.3 Mineralogical and textural analysis

Bulk mineralogy was determined by X-Ray Diffraction spectrometry (XRD) at ISTO laboratory on ten 185 186 samples (two topsoils, two subsoils and three BLS samples from each of the two surveys dating from 187 2017 and 2018, respectively, Fig. 1). The BLS sampled in 2017 were analyzed using a Thermo-Electron Bruker D8 Advance diffractometer, whereas the others were characterized using an INEL 188 diffractometer with a Debye-Scherrer configuration. The diagrams obtained were compared to the 189 characteristic diagrams of the ICDD (International Centre for Diffraction Data) PDF (Powder 190 191 Diffraction File). It allowed to identify the presence of mineral phases but this method was only 192 qualitative.

193 Textures were determined by granulometric analysis. For all samples, the moistened fraction 194 under 1.6 mm was analyzed by a laser particle sizer Mastersizer 3000. The relative percentages of four 195 grain-size classes were quantified: 0-2 µm as clay size fraction, 2-63 µm as silt size fraction, 63-196 200/250 µm as fine sand size fraction and 200/250-1600 µm as medium to coarse sand size fraction.

197 **3. Results**

198 *3.1 Soils and sediments geochemistry*

K and Fe were the most abundant elements in topsoils, with concentrations ranging from 15.7 to 23.8 mg/g and from 4.6 to 24.6 mg/g, respectively (median content of 19.0 and 13.8 mg/g, respectively; Fig. 2). Ca content did not exceed 9.4 mg/g (median content of 4.4 mg/g; Fig. 2) and was the lowest major element. Ti ranged from 5.2 mg/g to 8.6 mg/g (median content of 6.4 mg/g; Fig. 2). Considered as trace element because of its concentrations, Mn was the most abundant but also the most dispersed, with concentrations ranging from 0 to 1.24 mg/g (median content of 0.39 mg/g; Fig. 2). Sr was the

least abundant, with values between 0.05 and 0.07 mg/g (median content of 0.06 mg/g; Fig. 2) and Rb
ranged from 0.10 to 0.16 mg/g (median content of 0.13 mg/g; Fig. 2).

207 Similar variations in a higher range of concentrations were observed in the subsoils. Fe and K were still the two most abundant elements, with concentrations ranging from 17.8 to 42.8 mg/g and 208 from 14.7 to 21.4 mg/g, respectively (median content of 29.0 and 17.1 mg/g, respectively; Fig. 2). Ca 209 was still the least abundant varying from 2.5 to 10.8 mg/g (median content of 5.1 mg/g; Fig. 2), while 210 211 Ti concentrations ranged from 5.7 to 7.3 mg/g (median content of 6.1 mg/g; Fig. 2). Trace elements also presented similar variations to the topsoil samples. Mn was still the most dispersed element 212 ranging from 0 to 0.57 mg/g (median content of 0.19 mg/g; Fig. 2) but had the highest concentrated in 213 only two soil surveys (S9 and S12, Fig. 1). In other soil profiles, Rb presented higher concentrations, 214 between 0.15 and 0.21 mg/g (median content of 0.18 mg/g; Fig. 2). Sr was still the least abundant 215 216 element with ontents varying from 0.05 to 0.07 mg/g (median content of 0.06 mg/g; Fig. 2).

217

218 [Figure 2]

Figure 2: Median values (and standard deviation values) of iron, calcium, potassium, titanium, strontium, rubidium and
 manganese in topsoils (a) and subsoils (b) of each soil described in the catchment area and bed-load sediment samples (BLS,
 c). The typology of each soil is mentioned in figure 1.

222 The BLS samples showed different trends (Fig. 2). In 2017, Ca was the major element, with concentrations ranging from 2.7 to 130.0 mg/g (median content of 28.6 mg/g; Fig. 2) but also the most 223 224 dispersed. Ti concentrations were the lowest, varying from 1.1 to 8.2 mg/g (median content of 5.5 mg/g, Fig. 2). In these samples, K and Fe presented intermediate concentrations with values between 225 14.9 and 26.8 mg/g, and between 4.0 and 27.5 mg/g, respectively (median content of 23.2 and 16.9 226 227 mg/g, respectively; Fig. 2), whereas the trends of trace elements were the same as in soils. Mn presented the highest concentrations and scattering, ranging from 0 to 1.65 mg/g (median content of 228 229 0.24 mg/g; Fig. 2). Sr was the least abundant varying from 0.06 to 0.13 mg/g (median content of 0.08 230 mg/g; Fig. 2) and Rb ranged from 0.11 to 0.16 (median content of 0.13 mg/g; Fig. 2).

231 In 2018, concentrations were generally lower but in quite the same trends as observed in the 2017 campaign. Ca again presented the highest concentrations, between 1.5 and 82.7 mg/g (median 232 233 content of 9.4 mg/g; Fig. 2), Ti was again the least abundant, with concentrations between 0.4 and 6.6 mg/g (median content of 1.9 mg/g; Fig. 2), while K and Fe ranged between 14.4 and 26.7 mg/g, and 234 between 2.5 and 37.4 mg/g, respectively with a median content of 19.0 and 9.2 mg/g, respectively 235 (Fig. 2). Among the three trace elements, the concentrations of Mn were still the highest and the most 236 237 widely scattered, varying from 0.02 to 0.43 mg/g (median content of 0.11 mg/g; Fig. 2). The lowest 238 concentrations were again found in Sr, with between 0.042 and 0.11 mg/g (median content of 0.075 mg/g; Fig. 2), while the concentrations of Rb remained moderate, ranging between 0.073 and 0.13 239 mg/g (median content of 0.11 mg/g, Fig. 2). 240

241 3.2 Mineralogical composition

All the samples are made of quartz, albite and orthoclase, which is consistent with the geological 242 context in the catchment (e.g. fluvial deposits and sands). Smectite is found in all samples with the 243 exception of one topsoil sample (S7; Table 3) and one BLS sample, collected downstream the Beulie 244 245 pond (BLS-6; Table 3). Calcite and kaolinite are not evidenced in the soil profiles, but appear in the 246 composition of BLS samples (BLS-1 and 6b, respectively; Table 3). These two BLS samples were collected close to artificial drainage discharges into the watercourse of the Egoutier stream (Fig. 1). A 247 very low presence of micas or illite was suspected in the BLS sample analyzed with the Thermo-248 249 Electron diffractometer (BLS-1 collected in 2017) but given the overlapping of their peaks, the discrimination of their type could not be characterized. In the other samples, the presence of micas was 250 not evidenced but small amounts could be hidden behind other mineral peaks. No difference was 251 observed between the two years of sampling for any of the BLS samples except for sample BLS-1 in 252 which kaolinite was only detected in 2017 (Table 3). 253

254 Table3: Observed mineral species in selected samples of soil profiles and BLS (X: presence)

Soil	horizons	Quartz	Calcite	Albite	Orthoclase	Smectite	Kaolinite
profiles	or year of						

Journal Pre-proof								
/ BLS samples	campaign							
S2	A (topsoil)	X		X	X	X		
	C (subsoil)	X		X	X	X		
S7	A (topsoil)	X		X	X	<u>k</u>		
	C (subsoil)	X		X	X	X		
1	2017	X		X	X	X	X	
	2018	X		X	X	X		
6	2017	X		X	X			
	2018	X		X	X			
6b	2017	X	X	X	X	X		
	2018	X	X	X	X	X		

255

256 *3.3 Particle size characteristics*

257 In topsoils, the grain-size classes 2-63 µm (silt) and 200-1600 µm (medium to coarse sands) presented 258 the highest proportions and dispersion varied from 26 to 56 % and from 24 to 51 %, respectively 259 (average percentages of 38 and 37 %, respectively; Fig. 3). The clay size fraction (0-2 µm) was the 260 lowest ranging between 0 to 3 % (average percentage equal to 2 %; Fig. 3). 63-200 µm (fine sands) 261 particle size fraction presented intermediate proportions ranging between 18 and 30 % (average 262 percentage of 23 %; Fig. 3). Despite high proportions of the silt size fraction, most topsoils were 263 mainly made of coarse particles \geq 63 μ m in size. Only topsoils S3 and S10 had a major contribution of 264 fine particles (< 63 μ m; Fig. 3).

Subsoils presented different trends. The grain-size class 2-63 μ m (silt) had the highest and the most dispersed values, varying from 29 to 78 % (average percentage of 50 %; Fig. 3). Despite higher proportions than in topsoils, the clay size fraction (0-2 μ m) was still the least abundant, ranging between 1 and 8 % (average percentage of 3 %; Fig. 3). Coarser grain-size classes 63-200 and 200-1600 μ m ranged from 10 to 28 % and from 9 to 51 %, respectively (average percentages of 20 and 27 %, respectively; Fig. 3). Subsoils were also mainly made of fine particles (< 63 μ m) except for soils S5, S10, S11 and S12 which presented a major contribution of coarse particles (> 63 μ m; Fig. 3).

Particle size distributions in BLS showed different trends. In 2017, the grain-size classes 2-63 272 μ m (silt) and 200-1600 μ m (medium to coarse sands) presented the highest proportions and dispersion 273 varying from 16 to 79 % and from 1 to 73 %, respectively (average percentage of 42 and 35 %, 274 respectively; Fig. 3). Proportions of the clay size fraction (0-2 μ m) ranged between 1 and 12 % 275 (average percentage of 4 %; Fig. 3). The grain-size class 63-250 µm (fine sands) showed an 276 intermediate range between 6 and 35 % (average percentage of 19 %; Fig. 3). Textural characteristics 277 278 were very variable in BLS depending on the location of the samples in the watercourse and no systematic composition of fine ($< 63 \,\mu$ m) or coarse particles ($> 63 \,\mu$ m) appeared in a BLS sample set. 279

280

281

282 [Figure 3]

Figure 3: Proportion of the size fractions in (a) the topsoils, (b) the subsoils, (c) the bed-load sediments (BLS) of 2017 and (d)
the bed-load sediments (BLS) of 2018. The typology of each soil is mentioned in figure 1.

The sample set dating from 2018 was coarser. The highest contributions were only observed in the grain-size class 250-1600 μ m, ranging between 27 and 89 % (average percentage of 65 %; Fig. 3). The clay size fraction was the least abundant, varying between 0 and 1 % (average percentage of 0.1 %; Fig. 3), and was even absent in some samples in the upstream part of the watercourse and at the outlet (BLS-2, 3, 4 and 7, respectively; Fig. 3). Despite a high dispersion, medium proportions of the intermediate grain-size classes 2-63 µm and 63-250 µm were found, ranging from 6 to 43 % and from
4 to 49 %, respectively (average percentages of 18 and 16 %, respectively; Fig. 3).

292

293 4. Discussion

294 4.1 Vertical textural and geochemical soil variabilities: a weathering effect ?

4.1.1 Test of the bedrock uniformity

The presence of quartz, feldspar and clay minerals identified in soil samples (Table 3) is consistent with eroded material from granitic formations. Besides, SSC (i.e. Sologne Sands and Clays) and OS (i.e. Orleanais Sands) are ancient alluvia of the Loire River and thus correspond to detritic sediments resulting from the erosion of bedrocks from the Massif Central (Soucémarianadin and Verbèque, 2007). The fluvial origin of those bedrocks however involves a potential spatial heterogeneity in their deposits, particularly in the case of SSC (Soucémarianadin and Verbèque, 2007).

Soil chemical composition is driven by bedrock sources and weathering processes (Négrel et al., 2018b). To investigate elemental behavior during weathering at the catchment scale, potential bedrock heterogeinities should not be sources of textural and geochemical variabilities within soil profiles. Bedrock uniformity can be demonstrated by homogeneous rock sources. Ternary diagrams of major and trace elements with highly similar geochemical properties, against an insoluble one, were therefore plotted with bedrocks and Continental Crust compositions according to Parker, 1967.

K and Ca are soluble major elements concentrated in different mineral phases and with different geochemical behaviors. By being mainly hosted in K-feldspar (Beaucaire and Michard, 1982), K can trace silicate weathering (Négrel et al., 2018a). Ca is concentrated in plagioclases and Kfeldspar (Beaucaire and Michard, 1982) and is highly mobile (De Vos et al., 2006). These elements were thus plotted with Ti contents, a weathering resistant element (Cornu et al., 1999), to trace detrital phase rock sources and the weathering effects. Ti and K contents in soil samples were distributed between granite and shist end-members (Fig. 4) suggesting different contributions from the Loire

315 River alluvial formations. These variations can, however, be the result of weathering as soil samples showed Ca losses compared to bedrock sources, implying Ca leaching (Fig. 4). The weathering of 316 317 chemical elements within soil profiles results in the concentration of Ti in weathering products, because of its resistance to those processes (Milnes and Fitzpatrick, 1989). No significant 318 differentiation was observed between topsoil and subsoil samples (Fig. 4), highlighting low 319 weathering rates. Moreover, K mobility can be affected by different processes such as plant uptake 320 321 (Kuhlmann et al., 1985) and release (Laskowski et al., 1995), and/or affinity with secondary clay minerals (Négrel et al., 2018a). In this context, the spread towards schist parent material (Fig. 4) can 322 323 be explained by heterogeneities in the spatial weathering effects. These variabilities can be linked to different weathering rates according to soil type and/or different biological weathering depending on 324 325 land cover. Since K and Ca play a role in plant biological cycles (Boyle and Voigt, 1973; Poszwa et al., 2000;), their contents clearly showed different migration trends between topsoil and subsoil 326 samples depending on land cover (Fig. 4). 327

The same ternary diagram was constructed with trace elements (Rb and Sr) having similar 328 behaviors to those of K and Ca during geochemical processes (Huntley and Hancock, 2001; Kabata-329 Pendias and Pendias, 2001; Négrel et al., 2018a). As in the first diagram Ti contents showed 330 enrichment compared to bedrock compositions and no significant differences between topsoil and 331 subsoil samples (Fig. 4), evidencing low weathering rates. Sr and Rb showed the same ranges in 332 333 granite and in subsoil samples but enrichment and depletion, respectively, in topsoil. However, this suggests quite different cycles to those of K and Ca. Rb losses in topsoil could be the result of strong 334 incorporation in secondary clay minerals (Négrel et al., 2018a) that are present in higher proportions in 335 subsoil samples (3.3, Fig. 3). Despite being a plant nutrient, Rb migration presented similar trends 336 337 according to land cover type, possibly linked to the low remobilization of its bound mineral (Kuhlmann et al., 1985). Sr is assumed to be removed at the same rates as Ca during weathering but is 338 preferentially incorporated in clay minerals (Nesbitt et al., 1980). Moreover its release from detrital 339 340 feldspar is slow (De Vos et al., 2006) and it can be strongly fixed in organic matter (Kabata-Pendias

and Pendias, 2001). These factors can explain the good differentiation between topsoil and subsoil samples and confirm that geochemical variations resulted from weathering processes.

343 [Figure 4]

344 345 Figure 4: Major (Ca, K, Ti) and trace elements (Rb, Sr) signatures of the soil investigated compared to bedrock and Continental Crust (CC) compositions according to Parker, 1967

Both diagrams show a principal granitic source (Fig. 4), corresponding to the soil mineralogical composition (*3.2*, Tab. 2) and to the geological bedrock signature of the upstream part of the Loire River catchment area. Ti enrichments highlight low weathering rates and Ca, K, Rb and Sr dispersion shows different behaviors associated with the biological cycle of nutrients and weathering. It suggests low lateral variabilities but the absence of vertical ones created by bedrock heterogeneities.

351

352 4.1.2 Homogeneity of the soil characteristics

The catchment area is mainly covered by neutral Redoxisol (Soucémarianadin and Verbèque, 2007) characterized by hydromorphic conditions because low permeabilities are observed in the subsoil leading to the presence of a temporary perched water table (Baize et al., 2009). Water table variations within soil profiles imply redox reactions modifying soil components mobility (Favrot and Vizier, 1994). Moreover, clays (particles < 63μ m) are subjected to illuviation processes from topsoil to subsoil layers (Pollet, 2009).

359 To confirm that soil geochemical variations reflect soil weathering, we investigated the Ti contents because Ti-bearing minerals are frequently found in sedimentary rocks as detrital phases 360 361 resulting from erosion of magmatic rocks (Milnes and Fitzpatrick, 1989). Moreover, because Ti resists weathering, Ti content is used to understand soil genesis (Kabata-Pendias and Pendias, 2001) and to 362 estimate the degree of weathering (Cornu et al., 1999). In our case, mean Ti content was 6.4 mg/g 363 364 (Fig. 5), which is a slightly higher than but in the same order of magnitude as the median content 365 measured in European top- and subsoil layers (5.7 mg/g; De Vos et al., 2006). Likewise, Ti content ratios between topsoil and subsoil were similar between soil profiles developed on SSC (i.e. Sologne 366

367 Sands and Clays, [Ti] topsoil / [Ti] subsoil ratio of 1.03, Fig. 5) and European soils (equals to 1.02; De Vos et al., 2006; Reimann et al., 2014a; Reimann et al., 2014b). Lower enrichments of Ti in topsoils 368 369 are therefore consistent with a slow weathering of these soils. Conversely, profiles developed on OS (i.e. Orleanais Sands) had a mean [Ti] topsoil / [Ti] subsoil ratio of 0.95 (Fig. 5), due to higher 370 concentrations of Ti in the suboil, already demonstrated by Larue and Etienne (2000) who documented 371 higher Ti contents in OS than in SSC. Following Reimann and De Caritat (2000), this difference can 372 373 lead to Ti-rich "geogenic" dust in deeper soil horizons. Furthermore, the depth at which the subsoil occurred was deeper in OS (from 48 to 90 cm with a mean value of 71 cm) than in SSC (from 22 to 65 374 375 cm with a mean value of 39 cm). This greater depth of the OS soil profiles could thus balance the enrichment of Ti in topsoil layers. In spite of different bedrock signatures, Ti contents at the Egoutier 376 377 scale showed low variability and were quite similar in all soil profiles.

378

379 [Figure 5]

Figure 5: Proportions of titanium in top- and subsoils developed on (a) Sologne sands and clays (SSC) and (b) Orleanais sands
 (OS). Differences in fine grain-size fraction proportions between top- and subsoils

382 In Redoxisol profiles, clay contents derive from pre-existing minerals but the weathering of initial minerals is far from complete (Righi and Meunier, 1995). Montmorillonite-type smectite is for 383 384 instance a secondary mineral formed by the weathering of feldspar in neutral to alkaline conditions where poor drainage occurs (Pickering, 1986). The clay contents in topsoil and subsoil samples 385 (illustrated by the 0-63 μ m subsoil / 0-63 μ m topsoil ratio, Fig. 5) can therefore highlight 386 heterogeneities inherited from the underlying fluvial deposits or the degree of soil weathering. 387 388 Depending on the soil types investigated, three trends of the 0-63 μm topsoil / 0-63 μm subsoil ratio were observed (Fig. 5). The Redoxisol 0-63 µm topsoil / 0-63 µm subsoil ratio ranged between 1.00 389 and 1.73 (mean value of 1.39, Fig. 5). The Planosol 0-63 µm topsoil / 0-63 µm subsoil ratio was the 390 highest with a mean value of 1.83 and the Brunisol one was the lowest, at 0.51 (Fig. 5). These results 391 392 suggest both low weathering and illuviation processes, and low heterogeneities in the clay contents 393 within Redoxisol profiles but an enrichment in clays in subsoil and in topsoil within the Planosol and

Brunisol ones, respectively (Fig. 5). These observations are consistent with the vertical dynamic of these types of soils: although Planosol and Brunisol are both hydromorphic, Planosols are characterized by high textural differentiation while Brunisols are not (Baize et al., 2009). In this context, the smectite (Table 3) was formed by the weathering of primary minerals and the soil vertical dynamics controls its migration from topsoil to subsoil layers.

399 Given the uniformity of bedrocks and the processes influencing the soil characteristics (4.1), it 400 can be concluded that the different textural and geochemical characteristics of the soils evidence the 401 effects of homogeneous low weathering rates at the catchment scale.

402

403 *4.2 Geochemical signature of the weathering processes*

404 4.2.1 Factors having an impact on soil geochemistry

405 Pedogenesis starts with bedrock alteration, but climate, soil organisms, vegetation and time distinguish 406 the different horizons with specific geochemical signatures (Sucharovà et al., 2012). The first principal component of the PCA explained 40 % of the total variance, the second 30 % and the third one, only 407 10 %. Around 70 % of the signal distribution was thus explained by two principal directions (Fig. 6). 408 409 The first one results from K and Fe distribution while the second only from Ca and Rb distribution (Table 2). The PCA was therefore considered as being representative with two principal directions 410 411 which were enough to explain the observed variations between top- and subsoil layers. Moreover, 412 despite showing a high variability, PCA results support observations already made (see §4.1).

Three main behaviors were identified. K, Sr and Ti were not specific to topsoil or subsoil samples, suggesting homogeneity of those elements at the profile scale, whereas Ca, Rb and Fe were only found in subsoil samples. On the contrary, Mn presented a specificity to topsoil layers (Fig. 6).

416 Compared to European soil signatures (De Vos et al., 2006), K (topsoil set), Ti and Fe (subsoil
417 set) contents were similar. However, the investigated soils were less concentrated in K (subsoil
418 samples), Sr, Ca, Fe (topsoil set) and Mn, but richer in Rb.

K and Sr contents seem to be influenced by the same phenomena (Fig. 6) and these differences with European trends could be due to low weathering rates, few interactions with secondary minerals and/or a mineral phase effect, rather than to lithology effects. Indeed, the mineralogical composition (quartz, albite, orthoclase and smectite) of the soil horizons does not vary according to soil type, land cover and/or bedrock. However, as seen in part *4.1.2*, Ti presented an independent behavior influenced by bedrock types (Fig. 6), which could explain the higher concentrations than in European soils.

425 Rb, Fe and Mn were not influenced by soil type, bedrock or land cover type, while Ca seemed to be linked with the latter (Fig. 6). Given the geological context of the Egoutier catchment, calcite and 426 427 plagioclase are the two main bearing phases of Ca (Négrel and Grosbois, 1999) and low contents of Ca could therefore be partly explained by the virtual absence of calcite at the catchment scale (Table 3). 428 429 Ca is highly soluble (De Vos et al., 2006), mostly under low pH conditions (Bailey et al., 1996). Topsoils pH values ranged between 6.5 and 8.3 (median value of 7.1, Soucémarianadin and Verbèque, 430 2007) suggesting than Ca leaching was not the main process involve in its distribution. Ca is a crucial 431 element for the mineral nutrition of trees (Drouet and Herbauts, 2008) and this could explain why Ca 432 was mainly representative of subsoil samples and influenced by land cover types (Fig. 6). Rb is mainly 433 hosted by K-feldspar (Beaucaire and Michard, 1982) and shows strong affinity with clay minerals 434 after weathering (Négrel et al., 2018a). Higher trends than European soils can thus be linked with the 435 granitic sources of the fluvial bedrocks providing high supplies in K-feldspar and sandy-clay soils 436 437 offering high stocks of secondary minerals. Regarding Fe, its depletion in topsoil compared to the European soils can be caused by its high mobility in Redoxisol because of redox reactions (Pollet, 438 2009). Dissimilarities in Mn contents can be correlated with the mineralogical and physicochemical 439 440 characteristics of the investigated soils.

441 [Figure 6]

442

Figure 6: PCA of the geochemistry and characteristics of the soil horizons

443 Surprisingly, couples of chemical elements known to follow the same trends during 444 weathering, biochemical and redox processes, such as Ca/Sr (Bailey et al., 1996), K/Rb (Huntley and

Hancock, 2001) and Fe/Mn (Kabata-Pendias and Pendias, 2001) were not observed. In our case, the
observed chemical elements distribution was mainly driven by parent mineral composition, weathering
resistance, potential interaction with secondary phases, or the inherent dynamic of hydromorphic
sandy-clay soils, leading to these dissimilarities. Only Ca, and particularly Ti were slightly influenced
by study-case parameters, such as land cover and bedrock.

4

451 4.2.2 Behavior of the chemical elements in the soil profiles

452 Numerous chemical processes occur during weathering: dissolution, hydration, hydrolysis, oxidation, reduction and carbonatization (Kabata-Pendias and Pendias, 2001), implying changes in mineral 453 chemical composition by the leaching of alkaline/alkaline earth cations. Parent minerals therefore tend 454 455 to disappear depending on their weathering resistance, while secondary ones are created (Oludare, 456 2017). Comparing soil elemental composition with the parent material, Kabata-Pendias and Pendias (2001) highlighted element mobility during pedogenic processes. As bedrock was not sampled during 457 the present survey, the geochemistry of one selected subsoil was taken as representative of the local 458 459 geochemical background. The S8 profile subsoil layer (Fig. 1) was thus chosen since its composition was representative of all soil profiles. The enrichment factors (EF, Eq. 1) were therefore calculated 460 461 both using S8 composition as a reference, and considering Ti as a conservative element. EF should be used with caution since the behavior and weathering of some chemical elements in soil profiles can 462 reflect fractionation through uptake by plants, bonded to organic material or forming new minerals 463 (Sucharovà et al., 2012). For instance, Reimann and Caritat (2000) suggested that EF mainly reflect 464 the relative solubility of elements. In this study, EF were therefore considered as reflecting both the 465 fractionation and continuity of near-surface processes: weathering and erosion. To visualize general 466 elemental behaviors at catchment scale, boxplots of calculated EF were constructed (Fig. 7). To 467 468 distinguish retention, fractionation or illuviation processes causing these observations, elemental contents were normalized to fine grain-size particles (0-63 µm) as follows: 469

Eq. 2

70
$$[El]_{Norm} = [El]_{sample} / (0 - 63 \,\mu m)$$

⁴⁵⁰

With $[El]_{sample}$ the elemental concentration of each sample in $\mu g/g$ and $(0 - 63 \ \mu m)$ the percentage of this grain-size fraction. Normalized contents were represented as binary plots (Fig. 8). Given the uncertainties on micas low presence and type, their potential role in the geochemical effects of weathering is not discussed. Three behaviors were distinguished in topsoil layers (Fig. 7).

K and Sr presented a mean EF of 1.1 (Fig. 7), confirming no enrichment in topsoil layers, 475 which is consistent with European trends (De Vos et al., 2006; Reimann et al., 2014a; Reimann et al., 476 477 2014b). K and Sr are highly mobile elements (De Vos et al., 2006) whose main parent minerals are different: K-feldspar for K (Négrel and Grosbois, 1999) and plagioclase and K-feldspar for Sr (Blum 478 479 and Erel, 1997), respectively. K-feldspars are more resistant than plagioclases to weathering processes (Goldich, 1938) but Sr release from detrital feldspars is a slow process (De Vos et al., 2006). Even if 480 Sr is known to be incorporated in clay minerals (Kabata-Pendias and Pendias, 2001), cations with low 481 hydration energy, such as K^+ , are preferentially fixed by clays (Sawhney, 1972). Despite that, 482 preferential incorporation of K in subsoil clay minerals can be balanced by high rates of K released in 483 484 topsoil layers by decomposing leaf litters (Laskowski et al., 1995). Similarly, Sr mobility can be limited by its strong interaction with organic matter mainly contained in topsoils (Kabata-Pendias and 485 Pendias, 2001). K and Sr normalized contents were linear and showed similar evolutions (Fig. 8). 486 Nevertheless, a phase effect illustrates their interaction with clay minerals in subsoil layers (Fig. 8). 487

488 Fe, Ca and Rb presented mean EF lower than 1 (Fig. 7), illustrating a depletion of these 489 elements in topsoil samples, also consistent with European trends, except for Rb (De Vos et al., 2006; 490 Reimann et al., 2014a; Reimann et al., 2014b). On the one hand, results reflected the effect of redox reactions on Fe vertical distribution (Favrot and Vizier, 1994) and its strong interactions with clay 491 minerals (Pollet, 2009). Indeed, in spite of the weak mobility of Fe (Négrel and Deschamps, 1996), its 492 493 solubility is favored in saturated hydromorphic soils, as is its precipitation as oxi/hydroxydes and/or its 494 adsorption on clay minerals (Kabata-Pendias and Pendias, 2001), mostly located in subsoil layers (Fig. 495 3). Fe normalized contents evidenced a low differentiation between topsoil and subsoil layers (Fig. 8) confirming the combination of secondary minerals precipitation and its adsorption on clays. On the 496 497 other hand, the results plotted in Fig. 7 demonstrate Ca and Rb leaching by weathering of their

498 primary minerals. The high variability of EF for Ca (Fig. 7) can be explained by different mean values according to land cover types: 0.28 in topsoil layers under coniferous forests, 0.42 in those under 499 500 hardwood forests, and 1.15 in those under agricultural parcels. These differences suggest liming of 501 agricultural parcels given the importance of Ca for soil exchange complexes (Drouet and Herbauts, 2008), favouring nutrient availability (Holland et al., 2018). Furthermore, Ca leaching appeared higher 502 503 in topsoil layers under coniferous forests which might be the result of a typical soil acidification 504 (Hornung, 1985). Nevertheless, normalization demonstrates a matrix effect responsible for higher contents in subsoil layers (Fig. 8). Negatively-charged clay surfaces can adsorb divalent ions more 505 506 strongly than monovalent ones (De Vos et al., 2006). The distribution of Ca is thus also driven by 507 interactions with secondary phases. Rb distribution is driven by a combination of unaltered K-508 feldspars in topsoil, highlighted by K distribution, and illuviation of clay minerals to subsoil layers confirmed by the absence of phase effect after normalization (Fig. 8). This could elucidate the 509 difference with European top-/subsoil ratios where a constant Rb content is observed at profile scale 510 (De Vos et al., 2006). 511

Mn presented a mean EF of 3.3, demonstrating a high enrichment in topsoil layers. This is 512 consistent with previous results but not with constant European trends (De Vos et al., 2006). Soluble 513 and exchangeable, Mn^{2+} are dominant cations under strongly acidic conditions, and are immobilized in 514 neutral to basic soils (Adam and Beaugelin-Seiller, 2005; De Vos et al., 2006). The soil profiles in the 515 516 Egoutier catchment have a mean pH value of 7.35 (Soucémarianadin and Verbèque, 2007), Mn could thus form insoluble oxides under oxidizing conditions (De Vos et al., 2006), which cannot be 517 destabilized afterwards. It could explain the difference with the Fe pattern. Moreover, normalization 518 with fine grain-size particles (0-63 µm, Eq. 2) highlighted low differences between topsoil and subsoil 519 520 layers concentrations (Fig. 8), suggesting a behavior slightly influenced by phase effects.

521 [Figure 7]

Figure 7: Enrichment factors (EF) calculated for topsoil samples and for the two bed-load sediment (BLS) sample sets dating
 from 2017 and 2018

524 Weathering processes have variable consequences with respect to local climate, mineralogic 525 and pedogenic characteristics of the studied site. Moreover, the element distribution demonstrated 526 different influencing factors. Some elements presented low mobility because of biological supplies (K) or immobilization by redox reactions (Mn) and organic matter fixation (Sr), while others showed high 527 mobility induced by high leaching rates (Fe, Ca, Rb) enhanced by redox reactions (Fe), illuviation 528 processes (Rb) and soil acidification (Ca). In spite of low weathering rates and variable mobilities, all 529 530 the investigated elements are at least slightly subjected to leaching processes and interactions with 531 secondary mineral phases, except strongly immobilized ones.

532

533 *4.3 Geochemical impact of erosion processes*

4.3.1 Behavior of the geochemical elements in the bed-load sediment

Suspended particulate matter carried by streams and rivers is the result of rock and soil erosion 535 536 processes. Particles are therefore composed of selected resistant primary minerals and secondary phases, controlling the transport and deposition dynamics of associated elements over continental 537 areas (Viers et al., 2009) and controlling the behaviors of these elements in the sedimentary cycle 538 539 (Nesbitt et al., 1980). Grain size distribution and elemental sediment contents (Defersha and Melesse, 2012) represent two key parameters to decipher these kinds of patterns. To visualize erosion effects on 540 elemental behaviors at catchment scale, boxplots of bed-load sediments EF were compared to topsoil 541 ones (Fig. 7). Moreover to distinguish selective erosion, transport or deposition processes causing 542 543 these observations, elemental contents normalized to fine grain-size particles (0-63 μ m, Eq. 2) were 544 represented as binary plots (Fig. 8).

545 Firstly, all the investigated elements except for Mn presented higher EF in BLS than in topsoil546 layers (Fig. 7).

547 Mn contents were similar in topsoil, in BLS and in subsoil layers after normalization (Fig. 8), 548 evidencing a behavior resulting from phase effects. Mn lower enrichments in BLS are therefore due to 549 dilution by other mineral phase supplies. Ghadiri and Rose (1991) demonstrated that eroded sediments

550 generally present higher contents in chemical elements than soils. Erosion processes can destabilize aggregates in soils, but aggregates can also be formed directly in streams. However, the proportions of 551 552 this second type of aggregate appear to be less (Ghadiri and Rose, 1991). Higher EF for Fe, K, Ca, Rb and Sr in BLS could imply, for instance, a phase effect by selective erosion of secondary clay minerals 553 as these minerals fixed the weathered chemical elements and are preferentially transported by runoff. 554 However, that does not explain the large enrichments in Ca. Higher BLS contents could also be linked 555 556 with a preferential deposit of coarser particles (Fig. 3) made of K-feldspars and plagioclases (Tab. 2), rich in K, Rb and Ca, Sr, respectively. Although clay minerals are more prone to be exported by 557 erosion, the transport of other mineral phases can be facilitated by break-up processes (Anderson et al., 558 2007) and a matrix effect should also be considered as it changes the mineral phases composing each 559 particle size fractions. 560

Secondly, all the chemical elements except Fe presented mean EF higher than 1 in BLS 561 compared to subsoil layers (Fig. 7). Apart from K, these results are consistent with European stream 562 563 sediments (De Vos et al., 2006). K and Sr followed similar dynamics with mean EF of 2.6 and 2.4 in 2017, 5.8 and 5.4 in 2018, respectively (Fig. 7) testifying to K and Sr contents in BLS and higher 564 inputs in 2018. Besides, Négrel (1999), demonstrated that Sr is subject to depletion in sediments 565 because of the presence of K-feldspars, but Sr contents can also be caused by detrital feldspars (De 566 Vos et al., 2006). Moreover, K and Sr associated with both unaltered feldspars and clay minerals seem 567 568 to have the same sensitivity to erosion. While no phase effect was observed between the two years of sampling, K and Sr demonstrated different BLS particle sizes. The difference observed with European 569 soils for K contents could therefore be explained both by low weathering rates and high feldspar 570 content within the Egoutier catchment. 571

The Rb behavior in BLS was similar to that of K and Sr but enrichments were lower with mean EF of 1.1 and 2.3 in 2017 and 2018, respectively (Fig. 7). The same Rb contents in BLS and in topsoil in 2017 after normalization (Fig. 8) evidenced its enrichment in sediments by a selective erosion of clay minerals. Moreover, Négrel and Deschamps (1996) observed Rb depletion in sediments compared to the average contents of basaltic parent rocks while Négrel (1999) observed Rb

enrichment in sediments compared to the average contents of granitic parent rocks. The Rb mean EF close to 1 in 2017 (Fig. 7) and the same evolution for K suggest the contribution of additionnal topsoil layers supplied by almost unaltered K-feldspar from the erosion of granitic bedrocks.

580 [Figure 8]

- 581 Figure 8: Evolution of the chemical elements between soils and bed-load sediments (BLS) normalized by fine grain-size
- 582

particles (0-63 µm, Eq. 2)

Fe enrichments in BLS remained below 1 (mean EF of 0.9 and 0.5, respectively, Fig. 7) suggesting its depletion in BLS compared to subsoil layers. Indeed, lower Fe contents in sediments were already demonstrated by Négrel (1999) and seem to be caused by higher proportions of Kfeldspar. Despite the selective erosion of clay minerals, leading to higher enrichments in BLS than in topsoil (Fig. 7), the dilution of Fe contents suggests that topsoil layers are the main contributors to BLS.

Ca presented very high enrichments in BLS with mean EF of 9.2 in 2017 and 16.2 in 2018, respectively (Fig. 7). These values are surprising given the absence of carbonaceous phases (Table 3) and the leaching of this element in soils. The highest enrichments were observed on the release of rainwaters from anthropized areas (sample 6b) and of the PH sewage waters (sample 3), respectively. These enrichments could therefore be due to anthropogenic supplies, and more particularly to runoff on artificial surfaces made of calcareous gravels. Besides, calcite was observed in sample 6b (Table 3).

595 Natural fractionation of the investigated elements appears to be driven both by weathering and 596 erosion. The combination of these two processes was moreover already demonstrated by Reimann and 597 De Caritat (2005). On the one hand, erosion induced variations of the mineral phases occurring in each 598 grain-size fraction, except for highly insoluble minerals; on the other hand, supplying layers and 599 selective erosion explained variations in element contents (K, Sr, Rb and Fe). Other elements, such as 600 Mn, seem to remain independent from preferential erosion: diluted in BLS (Mn), or artificially added 601 by the runoff on anthropized areas (Ca).

602

603 4.3.2 Annual variability of bed-load sediment geochemistry

Erosion and deposition processes depend on numerous local factors such as rainfall intensity, 604 infiltration, runoff rates, soil properties and soil surface conditions (Defersha and Melesse, 2012). 605 These factors differed throughout the two years of sampling, especially the amount of rain. Only 0.8 606 mm of rain fell 48 hours before the field campaign in 2017, while 7.3 mm fell before the 2018 607 campaign. This difference enables visualization of erosion rates, potential selectivity as well as 608 609 transportation and deposition variabilities at low temporal scales to be visualized. To evidence the geochemical influence and spatial variabilities of rain amounts, binary plots with the enrichment 610 factors (EF) of elements with different observed behaviors were constructed (Fig. 9). 611

612 [Figure 9]

613 Figure 9: Evolution of geochemical enrichment factors (EF) between 2017 and 2018 bed-load sediment (BLS) sample sets

614 Globally, no difference was observed for Mn mean enrichments between the 2017 and 2018 sample sets (Fig. 7), demonstrating quite similar supplies in Mn oxides during erosion, as topsoil 615 layers were the main source of BLS. However, this observation depends on rainwater flow paths, as 616 shown by the spatial evolution of Mn EF: all the samples presented increasing EF in 2018 except those 617 collected at sewage and stormwater outfalls (BLS-1, 3, 5 and 6b, Fig. 9). Topsoil supplies to BLS were 618 thus locally diluted where runoff from urban areas contributed. The Mn geochemical signature thus 619 appeared constant at catchment scale but was mainly driven by topsoil contributions to BLS, which 620 were highly dependent on permeable areas. 621

622 Contrary to Mn, EF calculated for the 2018 sample set were always higher for all the other
623 elements investigated (Fig. 7 and 9), highlighting the strong covariation between element contents and
624 rainfall amounts.

The mean EF for K and Sr were more than twice as high in BLS dating from 2018 than those from 2017 (Fig. 7), evidencing higher inputs. Samples collected in 2018 presented a coarser composition (Fig. 3), confirming higher feldspar erosion rates and deposition. Moreover, these differences were not linked with a potential phase effect (Fig. 8) supporting K and Sr incorporation in

629 different mineral phases and break-up processes explaining their presence in all grain-size fractions. 630 Nonetheless, K EF spatial evolution showed the highest increases where fewer fine grain-size particles 631 deposited (BLS-2, 3, 4 and 7, Fig. 9 and 3), suggesting influence of longer fine particle (< 63 μ m) 632 transportation distances in 2018. Likewise, 2018 Sr EF decreased only on both sides of the pond 633 (BLS-5 and 6, Fig. 9), where the proportions of fine grain-size particles declined the least (Fig. 3).

The Rb evolution in BLS was quite similar but lower than K and Sr, with mean EF that were 634 twice as high in 2018 as in 2017 (Fig. 7). Strongly incorporated in K-feldspar as in clay minerals, the 635 2018 increase was due to enhanced particle supplies and selective erosion of clay. Its presence in the 636 two mineral phases is evidenced by well differentiated Rb contents between topsoil and subsoil layers, 637 not resulting from higher contents of clay minerals (Fig. 8). Moreover, its spatial evolution was quite 638 similar to that of K and Sr ones, with the highest increases in the coarser samples of 2018 (BLS-2, 3, 4 639 and 7, Fig. 9). EF for Rb in 2018 may thus evidence the contribution of subsoil layers and coarser 640 deposits in transportation zones because of higher rainfall. 641

Fe presented a higher EF in 2018 than in 2017, both locally (Fig. 9) and at catchment scale (Fig. 7), but the increase was lower than that of Rb. Fe is mainly hosted by clay minerals from subsoil layers. Like Rb, 2018 enrichments could be the result of selective erosion of clay minerals combined to higher contributions from the Fe-rich layer as 2018 BLS had a coarser composition (Fig. 3) and Fe dynamic was not due to phase effects (Fig. 8).

647 Ca behaves similarly to Fe but the higher mean EF observed in 2018 is driven by a phase 648 effect (Fig. 8), reflecting higher supplies by the runoff on anthropized areas due to rain amounts, and 649 the concentration of Ca in one particular grain-size fraction. These effects are visible in the local 650 evolution of Ca EF: samples collected from urban rainwater contributions presented a higher increase 651 in Ca (BLS-1 and 3, Fig. 9) and in the coarser grain-size fraction (250-1600 μ m, Fig. 3). This 652 evolution was not observed in sample 6b, highlighting more transportation in 2018, as the highest 653 increase in Ca was shown at the catchment outlet (Fig. 9).

654 sediment influenced The geochemistry is also by both depletion and the transportation/deposition dynamic of selected grain-size fractions and mineral phases. Therefore, rain 655 656 amounts drive the supplying quantities but also the sources of particles within soil profiles and in the catchment. Deviations of each element from their mean EF (Fig. 7) evidence high deposition zones 657 and input heterogeneities. These differences are linked with the pond and the impermeable urban areas 658 659 for some elements (Mn, Ca).

660

661

662 **5. Conclusions**

663 Despite a bedrock fluvial origin and low chemical variations according to land cover and bedrock 664 types, the small scale of the Egoutier catchment allows a good visualization of silicate weathering and 665 erosion processes, as well as stream transportation and deposition dynamics. Enrichment factor (EF) 666 calculation was a useful tool to understand both the fractionation and continuity of these near-surface 667 processes as soil geochemical profiles were not well differentiated.

In the case of low weathering rates, except chemical elements that were strongly immobilized, because of redox reactions for example, most of the elements are only slightly subjected to leaching. However, slow weathering enabled the identification of different forcing factors. Egoutier catchment hydromorphic soils are strongly controlled by redox reactions, but the main characteristic driving the specific elemental distribution within soil profiles is necessarily the weathering resistance of primary minerals. Combined to that, some characteristics, such as plant uptake and release, play ubiquitous roles, while others, such as illuviation processes or soil acidification, are site-dependent.

675 Influencing factors during erosion processes have more complex consequences. Firstly, as 676 already known, a selection of depleted particles occurs favoring a prefential erosion of fine grain-sizes, such as clay minerals. However, modifications of mineral grain sizes through disaggregation or break-677 up processes can encourage the erosion of other mineral phases. Beyond that, the main factors 678 679 controlling sediment geochemistry erosion particle are rates. sources, and stream

transportation/deposition dynamics. Logically, more depleted particles are supplied to sediments during periods of higher rainfall. This leads to higher enrichments in every chemical element except those mainly contained in topsoil, because subsoil layer particles also contribute to bed-load sediments (BLS) when soils are saturated and higher contributions of urban rainwaters buffered topsoil supplies to BLS. Moreover, longer transportation distances of fine grain-size particles lead to local enrichments of elements carried by coarser particles. Furthermore, caution must be taken concerning some elements which can be artificially supplied in this kind of peri-urban stream.

BLS geochemistry results thus from the combination of textural and mineralogical selectivity 687 during erosion, but also from sources within soil profiles and waterflow equilibrium between 688 deposition and transportation, which are directly dependent on the characteristics of rainfall events. 689 Therefore, BLS EF scattering highlights different soil profile sensitivities to erosion and sedimentary 690 dynamic variations along the watercourse. These observations provide useful information to 691 understand and predict sediment behavior and associated geochemistry. It could therefore be 692 interesting to conduct similar studies on suspended particle geochemistry correlated with more 693 detailed pluviometric characteristics than just rain amounts. A better characterization will allow 694 geochemical modeling to be applied to erosion processes and river particulate transportation. The peri-695 696 urban context of this watershed also allows the same application for the geochemistry of contaminants, supplied by sewage water inputs and urban stromwater runoff. 697

698

699 Acknowledgments

700 This work and the PhD grant of L. Ledieu were funded by the Région Centre Val de Loire (France) and are part of the Academic Initiative Project MOSAIC led by A. Simonneau. This work was also 701 supported by a grant overseen by the French National Research Agency (ANR) as part of the 702 "Investments d'Avenir" Programme LabEx VOLTAIRE, 10-LABX-0100. This study benefited from 703 collaboration with the GéhCO laboratory and J-P. Bakyonoo is warmly thanked for his help during 704 705 analysis. We are grateful to P. Penhoud for analytical and technical support in XRD analysis. L. 706 Baude, H. Alphonse and S. Picault are thanked for the sampling authorization at the G. Daumézon hospital and in the town of Semoy. We acknowledge F. Romain and S. Valdelièvre for their support 707 708 during the soil survey.

709

710 **References**

- Anderson, S.P., Von Blanckenburg, F., White, A.F., 2007. Physical and Chemical Controls on the
 Critical Zone. Elements 3 No. 5, 315-319.
- 713 Bailey, S.W., Hornbeck, J.W., Driscoll, C.T., Gaudette H.E., 1996. Calcium inputs and transport in a
- base-poor forest ecosystem as interpreted by Sr isotopes. Water Resources Research 32 No. 3, 707-
- 715 719.
- 716 Baize, D., Girard, M.C. Beaudou A.G., Poss R., 2009. Référentiel pédologique 2008. Quae, Versailles.
- Barbieri, M., 2016. The Importance of Enrichment Factor (EF) and Geoaccumulation Index (Igeo) to
 Evaluate the Soil Contamination. Journal of Geology and Geophysics 5 No. 237, 1-4.
- Barrows, H.L., Kilmer, V.J., 1963. Plant Nutrient Losses from Soils by Water Erosion. Advances in
 agronomy 15, 303-316.
- Beaucaire, C., Michard, G., 1982. Origin of dissolved minor elements (Li, Rb, Sr, Ba) in superficial
 waters in a granitic area. Geochemical Journal 16 No. 5, 247-258.
- 723 Berger, G., Desprez, N., 1969. Carte de France (1/50 000), "Orléans (363)". BRGM, Orléans.
- 724 Bernasconi, S. M., Biglink Project Members, 2008. Weathering, soil formation and initial ecosystem
- evolution on a glacier forefield: a case study from the Damma Glacier, Switzerland. Mineralogical
- 726 Magazine 72 No. 1, 19-22.
- Blum, J.D., Erel, Y., 1997. Rb-Sr isotope systematics of a granitic soil chronosequence: The
 importance of biotite weathering. Geochimica et Cosmochimica Acta 61 No. 15, 3193-3204.
- 729 Bormann, F. H., Likens, G. E., 1967. Nutrient cycling. Science 155 No. 3761, 424-429.
- Bowen, H.M., Dymond, J.A., 1955. Strontium and barium in plants and soils. Proceedings of the
 Royal Society of London. Series B-Biological Sciences 144 No. 916, 355-368.
- Boyle, J. R., Voigt, G. K., 1973. Biological weathering of silicate minerals. Plant and Soil 38 No. 1, 191-201.
- 734 Brady, P. V., 1991. The effect of silicate weathering on global temperature and atmospheric CO2.
- Journal of Geophysical Research: Solid Earth 96 No. B11, 18101-18106.
- Butt, C. R. M., 1992. Physical weathering and dispersion. In Handbook of Exploration Geochemistry
 4, 97-113. Elsevier Science BV.
- 738 Cerdan, O., Le Bissonnais, Y., Couturier, A., Bourennane, H., Souchère, V., 2002. Rill erosion on
- cultivated hillslopes during two extreme rainfall events in Normandy, France. Soil & Tillage Research67, 99-108.
- Cleaves, E. T., Godfrey, A. E., Bricker, O. P., 1970. Geochemical balance of a small watershed and its
 geomorphic implications. Geological Society of America Bulletin 81 No. 10, 3015-3032.
- Cornu, S., Lucas, Y., Lebon, E., Ambrosi, J.P., Luizão, F., Rouiller, J., Bonnay, M., Neal, C., 1999.
 Evidence of titanium mobility in soil profiles, Manaus, central Amazonia. Geoderma 91 No. 3-4, 281295.
- Cullers, R.L., Barrett, T., Carlson, R., Robinson, B., 1987. Rare-earth element and mineralogic
 changes in Holocene soil and stream sediment: a case study in the wet mountains, Colorado, U.S.A..
 Chemical Geology 63, 275-297.
- Cullers, R., 1988. Mineralogical and chemical changes of soil and stream sediment formed by intenseweathering of the Danburg granite, Georgia, U.S.A.. Lithos 21, 301-314.

- Delmas, M., Pak, L.T., Cerdan, O., Souchère, V., Le Bissonnais, Y., Couturier, A., Sorel, L., 2012.
 Erosion and sediment budget across scale: A case study in a catchment of the European loess belt.
- 753 Journal of Hydrology 420, 255-263.

Defersha, M.B., Melesse, A.M., 2012. Effect of rainfall intensity, slope and antecedent moisture
 content on sediment concentration and sediment enrichment ratio. Catena 90, 47-52.

De Vos, W., Tarvainen, T., Salminen, R., Reeder, S., De Vivo, B., Demetriades, A., Pirc, S., Batista,
M.J., Marsina, K., Ottesen, R.T., O'Connor, P.J., Bidovec, M., Lima, A., Siewers, U., Smith, B.,
Taylor, H., Shaw, R., Salpeteur, I., Gregorauskiene, V., Halamić, J., Slaninka, I., Lax, K., Gravesen,
P., Birke, M., Breward, N., Ander, E.L., Jordan, G., Duris, M., Klein, P., Locutura, J., Bel-lan, A.,
Pasieczna, A., Lis, J., Mazreku, A., Gilucis, A., Heitzmann, P., Klaver, G., Petersell, V., 2006.
Geochemical Atlas of Europe: Part 2: Interpretation of geochemical maps, additional tables, figures,

- 762 maps, and related publications. Geological Survey of Finland.
- Douglas, I., 2012. Peri-urban ecosystems and societies: Transitional zones and contrasting values. In
 The peri-urban interface, 41-52. Routledge.
- Drouet, T., Herbauts, J., 2008. Evaluation of the mobility and discrimination of Ca, Sr and Ba in forest
 ecosystems: consequence on the use of alkaline-earth element ratios as tracers of Ca. Plant and soil,
- 767 302 No. 1-2, 105-124.
- 768 Emberson, R., Hovius, N., Galy, A., Marc, O., 2016. Chemical weathering in active mountain belts769 controlled by stochastic bedrock landsliding. Nature Geoscience 9 No. 1, 42.
- Favrot, J., Vizier, J.F., 1995. Solums à caractères hydromorphes. Référentiel pédologique, 181-189.
- Gaillardet, J., Dupré, B., Allègre, C. J., 1999. Geochemistry of large river suspended sediments:
 silicate weathering or recycling tracer?. Geochimica et Cosmochimica Acta, 63 No. 23-24, 4037-4051.
- Ghadiri, H., Rose, C.W., 1991. Sorbed chemical transport in overland flow: II. Enrichment ratio
 variation with erosion processes. Journal of Environmental Quality 20 No. 3, 634-641.
- Goldich, S.S., 1938. A study in rock-weathering. The Journal of Geology 46 No. 1, 17-58.
- Grau, H.R., Hernandez, M.E., Gutierrez, J., Gasparri, N.I., Casavecchia, E.E., Flores-Ivaldi, E.E.,
 Paolini, L., 2008. A Peri-Urban Neotropical Forest Transition and its Consequences for Environmental
 Services. Ecology and Society 13 No. 1.
- Grosbois, C., Négrel, Ph., Fouillac, C., Grimaud, D., 2000. Dissolved load of the Loire River:
 chemical and isotopic characterization. Chemical Geology 170, 179-201.
- Guo, L., Lin, H., 2016. Critical zone research and observatories: Current status and future
 perspectives. Vadose Zone Journal 15 No. 9.
- Harriss, R. C., Adams, J. A., 1966. Geochemical and mineralogical studies on the weathering of
 granitic rocks. American Journal of Science 264 No. 2, 146-173.
- Heindel, R.C., Lyons, W.B., Welch, S.A., Spickard, A.M., Virginia, R.A., 2018. Biogeochemical
 weathering of soil apatite grains in the McMurdo Dry Valleys, Antarctica. Geoderma 320, 136-145.
- Holland, J. E., Bennett, A. E., Newton, A. C., White, P. J., McKenzie, B. M., George, T. S., Pakeman,
- 788 R. J., Bailey, J. S., Fornara, D. A., Hayes, R. C., 2018. Liming impacts on soils, crops and biodiversity
- in the UK: a review. Science of the Total Environment 610, 316-332.
- Hornung, M., 1985. Acidification of soils by trees and forests. Soil use and management 1 No. 1, 24-27.

- Huntley, D.J., Hancock, R.G.V., 2001. The Rb contents of the K-feldspar grains being measured in
 optical dating. Ancient TL 19 No. 2, 43-46.
- Johnson, C. C., Ander, E. L., 2008. Urban geochemical mapping studies: how and why we do them.
 Environmental Geochemistry and Health 30 No. 6, 511.
- Johnson, N. M., Likens, G. E., Bormann, F. H., Pierce, R. S., 1968. Rate of chemical weathering of
 silicate minerals in New Hampshire. Geochimica et Cosmochimica Acta 32 No. 5, 531-545.
- Kabata-Pendias, A., Pendias, H., 2001. Trace Elements in Soils and Plants. CRC Press, London, NewYork, Washington D.C..
- Kuhlmann, H., Claassen, N., Wehrmann, J., 1985. A method for determining the K-uptake fromsubsoil by plants. Plant and Soil 83, 449-452.
- Larue, J-P., Etienne, R., 2000. Les Sables de Lozère dans le Bassin parisien : nouvelles interpétations.
 Géologie de la France 2, 81-94.
- Laskowski, R., Berg, B., Johansson, M-B., McClaugherty, C., 1995. Release pattern for potassium
 from decomposing forest needle and leaf litter. Long-term decomposition in a Scots pine forest. IX.
 Canadian Journal of Botany 73, 2019-2027.
- Likens, G. E., Cowan Jr, J. H., 1992. The ecosystem approach: its use and abuse. Ecology Institute.
- 808 Marrero, S.M., Hein, A.S., Naylor, M., Attal, M., Shanks, R., Winter, K., Woodward, J., Dunning, S.,
- 809 Westoby, M., Sugden, D., 2018. Controls on subaerial erosion rates in Antarctica. Earth and Planetary
- 810 Science Letters 501, 56-66.
- Marshall., D.C.W., Bayliss, A.C., 1994. Flood estimation for small catchments. Institute of
 Hydrology.
- Martin, J-M., Meybeck, M., 1979. Elemental mass-balance of material carried by major world rivers.
 Marine Chemistry 7, 173-206.
- Milnes, A.R., Fitzpatrick, R.W., 1989. Titanium and zirconium minerals. Minerals in soil
 environments, 1131-1205.
- Négrel, Ph., 1997. Multi-element chemistry of Loire estuary sediments: anthropogenic vs. natural
 sources. Estuarine, Coastal and Shelf Science 44 No. 4, 395-410.
- Négrel, Ph., 1999. Geochemical study of a granitic area-the Margeride Mountains, France: chemical
 element behavior and 87Sr/86Sr constraints. Aquatic Geochemistry 5 No. 2, 125-165.
- Négrel, Ph., Deschamps, P., 1996. Natural and anthropogenic budgets of a small watershed in the Massif
 Central (France): chemical and strontium isotopic characterization of water and sediments. Aquatic
 Geochemistry 2 No. 1, 1-27.
- Négrel, Ph., Grosbois, C., 1999. Changes in chemical and 87Sr/86Sr signature distribution patterns of
 suspended matter and bed sediments in the upper Loire river basin (France). Chemical Geology 156
 No. 1-4, 231-249.
- Négrel, Ph., Pauwels, H., Chabaux, F., 2018a. Characterizing multiple water-rock interactions in the
 critical zone through Sr-isotope tracing of surface and groundwater. Applied Geochemistry 93, 102-
- 829 112.
- 830 Négrel, Ph., Ladenberger, A., Reimann, C., Birke, M., Sadeghi, M., the GEMAS Project Team, 2018b.
- B31 Distribution of Rb, Ga and Cs in agricultural land soils at European continental scale (GEMAS):
 B32 Implications for weathering conditions and provenance. Chemical Geology 479, 188-203.

- Nelson, D. J., 1973. Measurement and sampling of outputs from watersheds. In Analysis of temperate
 forest ecosystems, 257-267. Springer, Berlin, Heidelberg.
- Nesbitt, H.W., Markovics, G., Prict, R.C., 1980. Chemical processes affecting alkalis and alkaline
 earths during continental weathering. Geochimica et Cosmochimica Acta 44 No. 11, 1659-1666.
- Oelkers, E.H., Gislason, S.R., Eiriksdottir, E.S., Jones, M., Pearce, C.R., Jeandel C., 2011. The role of
 riverine particulate material on the global cycles of the elements. Applied Geochemistry 26, S365S369.
- 840 Oludare, F.V., 2017. Effects of Weathering and Erosion on the Geochemistry Of Rocks And Soils.
 841 International Journal of Scientific Research in Science and Technology 3 No. 6, 74-80.
- Palis, R.G., Okwach, G., Rose, C.W., Saffigna, P.G., 1990. Soil erosion processes and nutrient loss. 1.
 The interpretation of enrichment ratio and nitrogen loss in runoff sediment. Soil Research 28 No. 4,
 623-639.
- Parker, R.L., 1967. Composition of the earth's crust. In data of geochemistry. United StatesGovernment Printing Office.
- Pickering, W.F., 1986. Metal ion speciation—soils and sediments (a review). Ore Geology Reviews 1
 No. 1, 83-146.
- 849 Pierret, M.C., Cotel, S., Ackerer, P., Beaulieu, E., Benarioumlil, S., Boucher, M., Boutin, R., Chabaux,
- 850 F., Delay, F., Fourtet, C., Friedmann, P., Fritz, B., Gangloff, S., Girard, J-F., Legtchenko, A., Viville,
- 851 D., Weill, S., Probst, A., 2018. The Strengbach catchment: A multidisciplinary environmental sentry
- for 30 years. Vadose Zone Journal 17 No. 1.
- Pollet, E., 2009. Vademecum des sols hydromorphes. Office national de l'eau et des milieu
 aquatiques,.
- Poszwa, A., Dambrine, E., Pollier, B., Atteia, O., 2000. A comparison between Ca and Sr cycling in
 forest ecosystems. Plant and Soil 225 No. 1-2, 299-310.
- Reimann, C., de Caritat, P., 2000. Intrinsic flaws of element enrichment factors (EFs) in
 environmental geochemistry. Environmental Science & Technology 34 No. 24, 5084-5091.
- Reimann, C., Filzmoser, P., Garrett, R. G., 2002. Factor analysis applied to regional geochemical data:
 problems and possibilities. Applied geochemistry 17 No. 3, 185-206.
- 861 Reimann, C., de Caritat, P., 2005. Distinguishing between natural and anthropogenic sources for
- 862 elements in the environment: regional geochemical surveys versus enrichment factors. Science of the
- 863 Total Environment 337 No. 1-3, 91-107.
- Reimann, C., Birke, M., Demetriades, A., Filzmoser, P., O'Connor, P. (Eds.), 2014a. Chemistry of
 Europe's Agricultural Soils Part A: Methodology and Interpretation of the GEMAS dataset.
 Geologisches Jahrbuch (Reihe B). Schweizerbarth, Stuttgart 528 pp.
- Reimann, C., Birke, M., Demetriades, A., Filzmoser, P., O'Connor, P. (Eds.), 2014b. Chemistry of
 Europe's Agricultural Soils Part B: general background information and further analysis of the
 GEMAS dataset. Geologisches Jahrbuch (Reihe B). Schweizerbarth, Stuttgart 352 pp.
- 870 Richter, D.D., Bacon, A.R., Brecheisen, Z., Mobley, M.L., 2015. Soil in the Anthropocene. IOP
 871 Conference Series: Earth and Environmental Science 25 No. 1.
- 872 Richter, D.D., Billings, S.A., 2015. 'One physical system': Tansley's ecosystem as Earth's critical
 873 zone. New Phytologist 206 No. 3, 900-912.

- Righi, D., Meunier, A., 1995. Origin of clays by rock weathering and soil formation. In Origin and
 mineralogy of clays. Springer, Berlin.
- 876 Rowntree, K.M., Ntsaba, M.M, Van B. Weaver, A., 1991. Changing patterns of erosion in a peri-urban
 877 catchment, Maseru, Lesotho. International Association of Hydrological Sciences Publications No. 203.
- 878 Sawhney, B.L., 1972. Selective sorption and fixation of cations by clay minerals: a review. Clays and clay
 879 minerals 20 No. 2, 93-100.
- 880 Silva, S.H.G., Hartemink, A.E., dos Santos Teixeira, A.F., Inda, A.V., Guilherme, L.R.G., Curi, N.,
- 881 2018. Soil weathering analysis using a portable X-ray fluorescence (PXRF) spectrometer in an
- Inceptisol from the Brazilian Cerrado. Applied Clay Science 162, 27-37.
- Soucémarianadin L., Verbèque, B., 2007. Notice explicative de la carte des sols de Orléans (1/50 000).
 Chambre d'argriculture du Loiret, Orléans.
- 885 Sucharovà, J., Suchara, I., Hola, M., Marikova, S., Reimann, C., Boyd, R., Filzmoser, P., Englmaier,
- P., 2012. Top-/bottom-soil ratios and enrichment factors: what do they really show?. Applied
 Geochemistry 27 No. 1, 138-145.
- Viers, J., Dupré, B., Gaillardet, J., 2009. Chemical composition of suspended sediments in World
 Rivers: New insights from a new database. Science of the total Environment 407 No. 2, 853-868.
- Wilson, M. C., & Jackson, L. E., 2016. Urban geology: An emerging discipline in an increasingly
 urbanized world. Earth magazine March 2016, 34-41.
- Yang, J.L., Zhang, G.L., 2019. Si cycling and isotope fractionation: Implications on weathering and
 soil formation processes in a typical subtropical area. Geoderma 337, 479-490.
- 894 Zhang, C., Selinus, O., 1998. Statistics and GIS in environmental geochemistry—some problems and
- solutions. Journal of Geochemical Exploration 64 No. 1-3, 339-354.



















Highlights

- Geochemical effects of silicate weathering and erosion continuum processes
- Hydromorphic soils slow weathering allows detailed forcing factors visualizing
- Particles sources, erosion selectivity, disaggregation and rates drive sediment geochemistry
- Stream transportation/deposition dynamic controls sediment geochemistry temporal evolution
- Sediment geochemistry is modified by stormwaters contributions from urban areas

Declaration of interests

 \boxtimes The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: