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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 Aug 2020

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Journal Pre-proof

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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>.

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

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10
11 **Abstract**

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

33 rainwaters from anthropized areas supply Ca mineral phases and diluted Mn depleted bearing phases
34 from 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,
42 which are the habitat of humanity and biodiversity (Anderson et al., 2007). The storage and transfer of
43 waters and chemical elements in these compartments are controlled by complex physical, chemical
44 and biological processes (Négre et al., 2018a) leading to vertical and lateral heterogeneities of the CZ.
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
47 temporal evolutions of its physical and chemical properties (Pierret et al., 2018).

48 At catchment scale, some CZ compartments, such as soils, act as a sink with large capacities
49 of storage for many chemical elements (Kabata-Pendias and Pendias, 2001), while other
50 compartments, such as river bed-load sediments, are crucial vectors for element transport (Oelkers et
51 al., 2011). As underlined by Nesbitt et al. (1980), in order to achieve full knowledge of sedimentary
52 cycle geochemistry, documentation about the behavior of chemical elements during weathering is
53 required. In the 19th century, soils were defined as dynamic sensitive systems responding to natural
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
59 bedrocks and/or mineral phases (Harriss and Adams, 1966; Johnson et al., 1968; Cleaves et al., 1970).

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

71 To assist in the characterization of soil and water geochemical cycles, the concept of
72 individual catchment units was defined (Likens and Cowan Jr, 1992). In a watershed ecosystem,
73 geochemical inputs have meteorological 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
76 dissolved and particulate material originating from chemical and physical erosion (Nelson, 1973). At
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
80 recycling role for atmospheric CO₂ (Brady, 1991), riverine particulate transport associated to
81 weathered silicate bedrocks has recently received attention (Viers et al., 2009). Directly linked to their
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
84 al., 2012), many studies have focused on mountainous (Gaillardet et al., 1999; Emberson et al., 2016)
85 or agricultural areas (Marshall and Bayliss, 1994; Grosbois et al., 2000; Cerdan et al., 2002). As a
86 result of increasing urbanization, urban geology has started to emerge as a discipline (Wilson and

87 Jackson Jr., 2016). Growing funds and legislative demands to improve knowledge of urban areas has
88 enabled the development of geochemical mapping in this kind of environment (Johnson and Ander,
89 2008). Nevertheless, only a few studies on erosion have been carried out in peri-urban areas (Rowntree
90 et al., 1991; Grau et al., 2008). Although subjected to rapid transformations, these anthropogenic zones
91 are nevertheless important actors in modifications of biogeochemical cycles (Douglas, 2012).

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

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 (Soucémariadin 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]

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

122 The mean slope gradient of the catchment is 0.5 %. The upstream to downstream substratum is
123 composed of Sologne sands and clays (SSC), Orleanais sands (OS), Burdigalian fluvial deposits dated
124 21.5 to 16.3 Ma and Beauce limestone dated 23.3 to 21.5 Ma (Berger and Desprez, 1969, Fig. 1). The
125 streambed is impermeable because of clay-rich subsoil horizons (Soucémariadin and Verbèque,
126 2007; Fig. 1). Land cover is mainly forests (74 % of the total surface, Fig. 1) and anthropized areas
127 with residential (12 %, Fig. 1), agricultural (7 %, Fig. 1) and industrial zones (4 %, Fig. 1). One pond
128 (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
130 cover type. Following Soucémariadin and Verbèque (2007), Redoxisol, Planosol and Brunisol
131 (French classification; Baize et al., 2009) cover 95 %, 4% and 1 % of the area, respectively. 13 soil
132 profiles were collected in April 2018 with a hand soil auger and the maximum depth was limited to the
133 homogeneous impermeable subsoil layer. Each horizon was described and sampled but only the top
134 and bottom layers of each profile were analyzed (topsoil and subsoil, respectively). Bed-load
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
137 and March 2017 and replicated in April 2018 (Fig. 1).

138

139 *2.2 Quantification of chemical elements*

140 Elemental concentration measurements of all collected samples (soils and BLS) were performed by X-
141 Ray Fluorescence spectrometry (XRF) with a NITON XL3t980 GOLDD fitted with a 50 kV X-ray
142 tube (max. 50 kV, 100 μ A, 2 W) with an Ag anode target excitation source and a Large Drift Detector
143 (LDD). As part of the standard set-up routine and to avoid contamination, the analyzer was initially
144 Energy calibrated using the embedded Silver target. Samples were dried at 50 °C during 48 hours,
145 crushed in an agate mortar and sieved under 200 μ m to have a homogeneous overview of the bulk
146 geochemistry. XRF sample cups with 10-15g of powder were analyzed through 6 μ m Mylar films and
147 with an average analyzed spot diameter of 8 mm. The mining mode calibration done by the
148 manufacturer was used for all analyses and source count time was fixed at 90 seconds using the 3
149 filters of the pXRF in the laboratory (30 seconds for each filter). Three certified standards
150 (NIST2710a, NIST2711a, NIST2780) were used to verify the calibration and calculate correction
151 factors (Table 1). Each sample was analyzed three times to determine the reproducibility of the
152 measurements (Table 1). In order to highlight different processes, only seven elements were selected
153 in this study in relation with their particular behavior: soluble elements such as calcium (Ca),
154 potassium (K), strontium (Sr) and rubidium (Rb); an insoluble one: titanium (Ti); and two redox
155 sensitive ones: iron (Fe) and manganese (Mn). These elements enable mineral contributions to be
156 tracked as they are often associated to silicates (K, Rb, Ti), carbonates (Ca, Sr, Negrel and Grosbois,
157 1999), clays (K, Fe, Mn, Pickering, 1986), and metal oxi-hydroxides (Fe, Mn, Kabata-Pendias and
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	Certified standards mean contents (NIST2710a/ NIST2711a/ NIST2780)	Certified standard deviations (NIST2710a/ NIST2711a/ NIST2780)	Correction factors	Samples mean deviations
K	21.7 / 25.3 / 33.8	6.0 / 3.9 / 7.7	1.0 / 1.0 / 1.0	0.6
Ca	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

161

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

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*

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

172

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

$$EF = \frac{\left(\frac{[Ei]}{[Ti]} \right)_{\text{sample}}}{\left(\frac{[Ei]}{[Ti]} \right)_{\text{reference}}} \quad \text{Eq. 1}$$

184 2.3 Mineralogical and textural analysis

185 Bulk mineralogy was determined by X-Ray Diffraction spectrometry (XRD) at ISTO laboratory on ten
 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-
 188 Electron Bruker D8 Advance diffractometer, whereas the others were characterized using an INEL
 189 diffractometer with a Debye-Scherrer configuration. The diagrams obtained were compared to the
 190 characteristic diagrams of the ICDD (International Centre for Diffraction Data) PDF (Powder
 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

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

205 least abundant, with values between 0.05 and 0.07 mg/g (median content of 0.06 mg/g; Fig. 2) and Rb
206 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
208 were still the two most abundant elements, with concentrations ranging from 17.8 to 42.8 mg/g and
209 from 14.7 to 21.4 mg/g, respectively (median content of 29.0 and 17.1 mg/g, respectively; Fig. 2). Ca
210 was still the least abundant varying from 2.5 to 10.8 mg/g (median content of 5.1 mg/g; Fig. 2), while
211 Ti concentrations ranged from 5.7 to 7.3 mg/g (median content of 6.1 mg/g; Fig. 2). Trace elements
212 also presented similar variations to the topsoil samples. Mn was still the most dispersed element
213 ranging from 0 to 0.57 mg/g (median content of 0.19 mg/g; Fig. 2) but had the highest concentrated in
214 only two soil surveys (S9 and S12, Fig. 1). In other soil profiles, Rb presented higher concentrations,
215 between 0.15 and 0.21 mg/g (median content of 0.18 mg/g; Fig. 2). Sr was still the least abundant
216 element with contents varying from 0.05 to 0.07 mg/g (median content of 0.06 mg/g; Fig. 2).

217

218 [Figure 2]

219 *Figure 2: Median values (and standard deviation values) of iron, calcium, potassium, titanium, strontium, rubidium and*
220 *manganese in topsoils (a) and subsoils (b) of each soil described in the catchment area and bed-load sediment samples (BLS,*
221 *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
223 concentrations ranging from 2.7 to 130.0 mg/g (median content of 28.6 mg/g; Fig. 2) but also the most
224 dispersed. Ti concentrations were the lowest, varying from 1.1 to 8.2 mg/g (median content of 5.5
225 mg/g, Fig. 2). In these samples, K and Fe presented intermediate concentrations with values between
226 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
227 mg/g, respectively; Fig. 2), whereas the trends of trace elements were the same as in soils. Mn
228 presented the highest concentrations and scattering, ranging from 0 to 1.65 mg/g (median content of
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
 232 2017 campaign. Ca again presented the highest concentrations, between 1.5 and 82.7 mg/g (median
 233 content of 9.4 mg/g; Fig. 2), Ti was again the least abundant, with concentrations between 0.4 and 6.6
 234 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
 235 between 2.5 and 37.4 mg/g, respectively with a median content of 19.0 and 9.2 mg/g, respectively
 236 (Fig. 2). Among the three trace elements, the concentrations of Mn were still the highest and the most
 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
 239 mg/g; Fig. 2), while the concentrations of Rb remained moderate, ranging between 0.073 and 0.13
 240 mg/g (median content of 0.11 mg/g, Fig. 2).

241 3.2 Mineralogical composition

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

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

<i>Soil profiles</i>	<i>horizons or year of</i>	Quartz	Calcite	Albite	Orthoclase	Smectite	Kaolinite

<i>/ BLS</i> <i>samples</i>	<i>campaign</i>						
S2	A (topsoil)	X		X	X	X	
	C (subsoil)	X		X	X	X	
S7	A (topsoil)	X		X	X		
	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 $\geq 63 \mu\text{m}$ in size. Only topsoils S3 and S10 had a major contribution of
264 fine particles ($< 63 \mu\text{m}$; Fig. 3).

265 Subsoils presented different trends. The grain-size class 2-63 μm (silt) had the highest and the
266 most dispersed values, varying from 29 to 78 % (average percentage of 50 %; Fig. 3). Despite higher
267 proportions than in topsoils, the clay size fraction (0-2 μm) was still the least abundant, ranging
268 between 1 and 8 % (average percentage of 3 %; Fig. 3). Coarser grain-size classes 63-200 and 200-
269 1600 μm ranged from 10 to 28 % and from 9 to 51 %, respectively (average percentages of 20 and 27
270 %, respectively; Fig. 3). Subsoils were also mainly made of fine particles (< 63 μm) except for soils
271 S5, S10, S11 and S12 which presented a major contribution of coarse particles (> 63 μm ; Fig. 3).

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

280

281

282 [Figure 3]

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

285 The sample set dating from 2018 was coarser. The highest contributions were only observed in
286 the grain-size class 250-1600 μm , ranging between 27 and 89 % (average percentage of 65 %; Fig. 3).
287 The clay size fraction was the least abundant, varying between 0 and 1 % (average percentage of 0.1
288 %; Fig. 3), and was even absent in some samples in the upstream part of the watercourse and at the
289 outlet (BLS-2, 3, 4 and 7, respectively; Fig. 3). Despite a high dispersion, medium proportions of the

290 intermediate grain-size classes 2-63 μm and 63-250 μm were found, ranging from 6 to 43 % and from
291 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 ?*

295 4.1.1 Test of the bedrock uniformity

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

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

308 K and Ca are soluble major elements concentrated in different mineral phases and with
309 different geochemical behaviors. By being mainly hosted in K-feldspar (Beaucaire and Michard,
310 1982), K can trace silicate weathering (Négrel et al., 2018a). Ca is concentrated in plagioclases and K-
311 feldspar (Beaucaire and Michard, 1982) and is highly mobile (De Vos et al., 2006). These elements
312 were thus plotted with Ti contents, a weathering resistant element (Cornu et al., 1999), to trace detrital
313 phase rock sources and the weathering effects. Ti and K contents in soil samples were distributed
314 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
316 showed Ca losses compared to bedrock sources, implying Ca leaching (Fig. 4). The weathering of
317 chemical elements within soil profiles results in the concentration of Ti in weathering products,
318 because of its resistance to those processes (Milnes and Fitzpatrick, 1989). No significant
319 differentiation was observed between topsoil and subsoil samples (Fig. 4), highlighting low
320 weathering rates. Moreover, K mobility can be affected by different processes such as plant uptake
321 (Kuhlmann et al., 1985) and release (Laskowski et al., 1995), and/or affinity with secondary clay
322 minerals (Négrelet et al., 2018a). In this context, the spread towards schist parent material (Fig. 4) can
323 be explained by heterogeneities in the spatial weathering effects. These variabilities can be linked to
324 different weathering rates according to soil type and/or different biological weathering depending on
325 land cover. Since K and Ca play a role in plant biological cycles (Boyle and Voigt, 1973; Poszwa et
326 al., 2000;), their contents clearly showed different migration trends between topsoil and subsoil
327 samples depending on land cover (Fig. 4).

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

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

343 [Figure 4]

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

346 Both diagrams show a principal granitic source (Fig. 4), corresponding to the soil
347 mineralogical composition (3.2, Tab. 2) and to the geological bedrock signature of the upstream part
348 of the Loire River catchment area. Ti enrichments highlight low weathering rates and Ca, K, Rb and Sr
349 dispersion shows different behaviors associated with the biological cycle of nutrients and weathering.
350 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

353 The catchment area is mainly covered by neutral Redoxisol (Soucémariadin and Verbèque, 2007)
354 characterized by hydromorphic conditions because low permeabilities are observed in the subsoil
355 leading to the presence of a temporary perched water table (Baize et al., 2009). Water table variations
356 within soil profiles imply redox reactions modifying soil components mobility (Favrot and Vizier,
357 1994). Moreover, clays (particles < 63µm) are subjected to illuviation processes from topsoil to
358 subsoil layers (Pollet, 2009).

359 To confirm that soil geochemical variations reflect soil weathering, we investigated the Ti
360 contents because Ti-bearing minerals are frequently found in sedimentary rocks as detrital phases
361 resulting from erosion of magmatic rocks (Milnes and Fitzpatrick, 1989). Moreover, because Ti resists
362 weathering, Ti content is used to understand soil genesis (Kabata-Pendias and Pendias, 2001) and to
363 estimate the degree of weathering (Cornu et al., 1999). In our case, mean Ti content was 6.4 mg/g
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
366 ratios between topsoil and subsoil were similar between soil profiles developed on SSC (i.e. Sologne

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

378

379 [Figure 5]

380 *Figure 5: Proportions of titanium in top- and subsoils developed on (a) Sologne sands and clays (SSC) and (b) Orleanais sands*
381 *(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
383 initial minerals is far from complete (Righi and Meunier, 1995). Montmorillonite-type smectite is for
384 instance a secondary mineral formed by the weathering of feldspar in neutral to alkaline conditions
385 where poor drainage occurs (Pickering, 1986). The clay contents in topsoil and subsoil samples
386 (illustrated by the $0-63 \mu m_{subsoil} / 0-63 \mu m_{topsoil}$ ratio, Fig. 5) can therefore highlight
387 heterogeneities inherited from the underlying fluvial deposits or the degree of soil weathering.
388 Depending on the soil types investigated, three trends of the $0-63 \mu m_{topsoil} / 0-63 \mu m_{subsoil}$ ratio
389 were observed (Fig. 5). The Redoxisol $0-63 \mu m_{topsoil} / 0-63 \mu m_{subsoil}$ ratio ranged between 1.00
390 and 1.73 (mean value of 1.39, Fig. 5). The Planosol $0-63 \mu m_{topsoil} / 0-63 \mu m_{subsoil}$ ratio was the
391 highest with a mean value of 1.83 and the Brunisol one was the lowest, at 0.51 (Fig. 5). These results
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

394 Brunisol ones, respectively (Fig. 5). These observations are consistent with the vertical dynamic of
395 these types of soils: although Planosol and Brunisol are both hydromorphic, Planosols are
396 characterized by high textural differentiation while Brunisols are not (Baize et al., 2009). In this
397 context, the smectite (Table 3) was formed by the weathering of primary minerals and the soil vertical
398 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
407 component of the PCA explained 40 % of the total variance, the second 30 % and the third one, only
408 10 %. Around 70 % of the signal distribution was thus explained by two principal directions (Fig. 6).
409 The first one results from K and Fe distribution while the second only from Ca and Rb distribution
410 (Table 2). The PCA was therefore considered as being representative with two principal directions
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).

413 Three main behaviors were identified. K, Sr and Ti were not specific to topsoil or subsoil
414 samples, suggesting homogeneity of those elements at the profile scale, whereas Ca, Rb and Fe were
415 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.

419 K and Sr contents seem to be influenced by the same phenomena (Fig. 6) and these differences
420 with European trends could be due to low weathering rates, few interactions with secondary minerals
421 and/or a mineral phase effect, rather than to lithology effects. Indeed, the mineralogical composition
422 (quartz, albite, orthoclase and smectite) of the soil horizons does not vary according to soil type, land
423 cover and/or bedrock. However, as seen in part 4.1.2, Ti presented an independent behavior influenced
424 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
426 to be linked with the latter (Fig. 6). Given the geological context of the Egoutier catchment, calcite and
427 plagioclase are the two main bearing phases of Ca (Négre and Grosbois, 1999) and low contents of Ca
428 could therefore be partly explained by the virtual absence of calcite at the catchment scale (Table 3).
429 Ca is highly soluble (De Vos et al., 2006), mostly under low pH conditions (Bailey et al., 1996).
430 Topsoils pH values ranged between 6.5 and 8.3 (median value of 7.1, Soucémariadin and Verbèque,
431 2007) suggesting that Ca leaching was not the main process involved in its distribution. Ca is a crucial
432 element for the mineral nutrition of trees (Drouet and Herbauts, 2008) and this could explain why Ca
433 was mainly representative of subsoil samples and influenced by land cover types (Fig. 6). Rb is mainly
434 hosted by K-feldspar (Beucaire and Michard, 1982) and shows strong affinity with clay minerals
435 after weathering (Négre et al., 2018a). Higher trends than European soils can thus be linked with the
436 granitic sources of the fluvial bedrocks providing high supplies in K-feldspar and sandy-clay soils
437 offering high stocks of secondary minerals. Regarding Fe, its depletion in topsoil compared to the
438 European soils can be caused by its high mobility in Redoxisol because of redox reactions (Pollet,
439 2009). Dissimilarities in Mn contents can be correlated with the mineralogical and physicochemical
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

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

450

451 4.2.2 Behavior of the chemical elements in the soil profiles

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

$$470 \quad [EI]_{\text{Norm}} = [EI]_{\text{sample}} / (0 - 63 \mu\text{m}) \quad \text{Eq. 2}$$

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

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

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
491 reactions on Fe vertical distribution (Favrot and Vizier, 1994) and its strong interactions with clay
492 minerals (Pollet, 2009). Indeed, in spite of the weak mobility of Fe (Négre and Deschamps, 1996), its
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)
496 confirming the combination of secondary minerals precipitation and its adsorption on clays. On the
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
499 according to land cover types: 0.28 in topsoil layers under coniferous forests, 0.42 in those under
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,
502 2008), favouring nutrient availability (Holland et al., 2018). Furthermore, Ca leaching appeared higher
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
505 contents in subsoil layers (Fig. 8). Negatively-charged clay surfaces can adsorb divalent ions more
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
509 confirmed by the absence of phase effect after normalization (Fig. 8). This could elucidate the
510 difference with European top-/subsoil ratios where a constant Rb content is observed at profile scale
511 (De Vos et al., 2006).

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

521 [Figure 7]

522 *Figure 7: Enrichment factors (EF) calculated for topsoil samples and for the two bed-load sediment (BLS) sample sets dating*
523 *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)
527 or immobilization by redox reactions (Mn) and organic matter fixation (Sr), while others showed high
528 mobility induced by high leaching rates (Fe, Ca, Rb) enhanced by redox reactions (Fe), illuviation
529 processes (Rb) and soil acidification (Ca). In spite of low weathering rates and variable mobilities, all
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*

534 4.3.1 Behavior of the geochemical elements in the bed-load sediment

535 Suspended particulate matter carried by streams and rivers is the result of rock and soil erosion
536 processes. Particles are therefore composed of selected resistant primary minerals and secondary
537 phases, controlling the transport and deposition dynamics of associated elements over continental
538 areas (Viers et al., 2009) and controlling the behaviors of these elements in the sedimentary cycle
539 (Nesbitt et al., 1980). Grain size distribution and elemental sediment contents (Defersha and Melesse,
540 2012) represent two key parameters to decipher these kinds of patterns. To visualize erosion effects on
541 elemental behaviors at catchment scale, boxplots of bed-load sediments EF were compared to topsoil
542 ones (Fig. 7). Moreover to distinguish selective erosion, transport or deposition processes causing
543 these observations, elemental contents normalized to fine grain-size particles (0-63 μm , 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 topsoil
546 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
551 aggregates in soils, but aggregates can also be formed directly in streams. However, the proportions of
552 this second type of aggregate appear to be less (Ghadiri and Rose, 1991). Higher EF for Fe, K, Ca, Rb
553 and Sr in BLS could imply, for instance, a phase effect by selective erosion of secondary clay minerals
554 as these minerals fixed the weathered chemical elements and are preferentially transported by runoff.
555 However, that does not explain the large enrichments in Ca. Higher BLS contents could also be linked
556 with a preferential deposit of coarser particles (Fig. 3) made of K-feldspars and plagioclases (Tab. 2),
557 rich in K, Rb and Ca, Sr, respectively. Although clay minerals are more prone to be exported by
558 erosion, the transport of other mineral phases can be facilitated by break-up processes (Anderson et al.,
559 2007) and a matrix effect should also be considered as it changes the mineral phases composing each
560 particle size fractions.

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

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

577 enrichment in sediments compared to the average contents of granitic parent rocks. The Rb mean EF
578 close to 1 in 2017 (Fig. 7) and the same evolution for K suggest the contribution of additional topsoil
579 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)*

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

589 Ca presented very high enrichments in BLS with mean EF of 9.2 in 2017 and 16.2 in 2018,
590 respectively (Fig. 7). These values are surprising given the absence of carbonaceous phases (Table 3)
591 and the leaching of this element in soils. The highest enrichments were observed on the release of
592 rainwaters from anthropized areas (sample 6b) and of the PH sewage waters (sample 3), respectively.
593 These enrichments could therefore be due to anthropogenic supplies, and more particularly to runoff
594 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

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

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
615 sample sets (Fig. 7), demonstrating quite similar supplies in Mn oxides during erosion, as topsoil
616 layers were the main source of BLS. However, this observation depends on rainwater flow paths, as
617 shown by the spatial evolution of Mn EF: all the samples presented increasing EF in 2018 except those
618 collected at sewage and stormwater outfalls (BLS-1, 3, 5 and 6b, Fig. 9). Topsoil supplies to BLS were
619 thus locally diluted where runoff from urban areas contributed. The Mn geochemical signature thus
620 appeared constant at catchment scale but was mainly driven by topsoil contributions to BLS, which
621 were highly dependent on permeable areas.

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.

625 The mean EF for K and Sr were more than twice as high in BLS dating from 2018 than those
626 from 2017 (Fig. 7), evidencing higher inputs. Samples collected in 2018 presented a coarser
627 composition (Fig. 3), confirming higher feldspar erosion rates and deposition. Moreover, these
628 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 ($< 63 \mu\text{m}$)
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).

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

642 Fe presented a higher EF in 2018 than in 2017, both locally (Fig. 9) and at catchment scale
643 (Fig. 7), but the increase was lower than that of Rb. Fe is mainly hosted by clay minerals from subsoil
644 layers. Like Rb, 2018 enrichments could be the result of selective erosion of clay minerals combined
645 to higher contributions from the Fe-rich layer as 2018 BLS had a coarser composition (Fig. 3) and Fe
646 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 ($250\text{-}1600 \mu\text{m}$, 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 The sediment geochemistry is also influenced by both depletion and the
655 transportation/deposition dynamic of selected grain-size fractions and mineral phases. Therefore, rain
656 amounts drive the supplying quantities but also the sources of particles within soil profiles and in the
657 catchment. Deviations of each element from their mean EF (Fig. 7) evidence high deposition zones
658 and input heterogeneities. These differences are linked with the pond and the impermeable urban areas
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.

668 In the case of low weathering rates, except chemical elements that were strongly immobilized,
669 because of redox reactions for example, most of the elements are only slightly subjected to leaching.
670 However, slow weathering enabled the identification of different forcing factors. Egoutier catchment
671 hydromorphic soils are strongly controlled by redox reactions, but the main characteristic driving the
672 specific elemental distribution within soil profiles is necessarily the weathering resistance of primary
673 minerals. Combined to that, some characteristics, such as plant uptake and release, play ubiquitous
674 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 preferential erosion of fine grain-sizes,
677 such as clay minerals. However, modifications of mineral grain sizes through disaggregation or break-
678 up processes can encourage the erosion of other mineral phases. Beyond that, the main factors
679 controlling sediment geochemistry are erosion rates, particle sources, and stream

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

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

698

699 **Acknowledgments**

700 This work and the PhD grant of L. Ledieu were funded by the Région Centre Val de Loire (France)
701 and are part of the Academic Initiative Project MOSAIC led by A. Simonneau. This work was also
702 supported by a grant overseen by the French National Research Agency (ANR) as part of the
703 “Investments d’Avenir” Programme LabEx VOLTAIRE, 10-LABX-0100. This study benefited from
704 collaboration with the GéhCO laboratory and J-P. Bakyonoo is warmly thanked for his help during
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
707 hospital and in the town of Semoy. We acknowledge F. Romain and S. Valdelièvre for their support
708 during the soil survey.

709

710 **References**

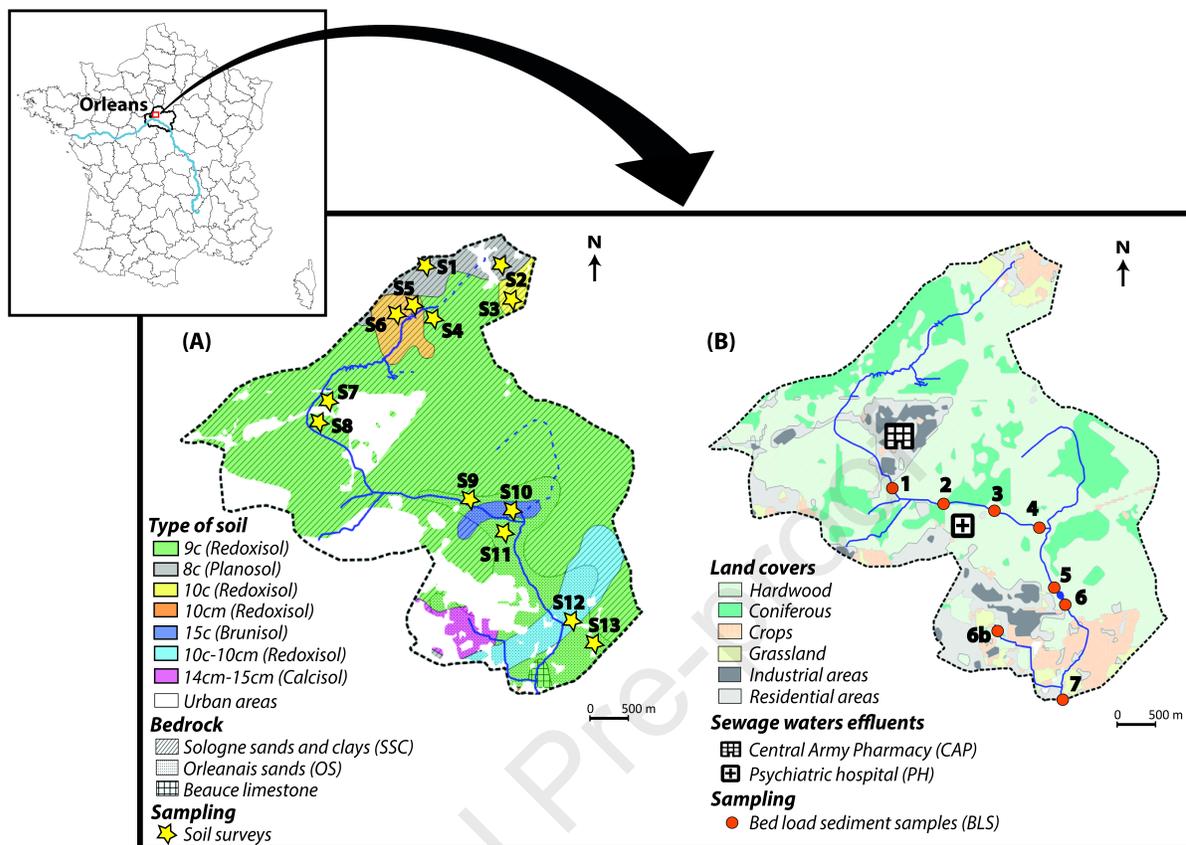
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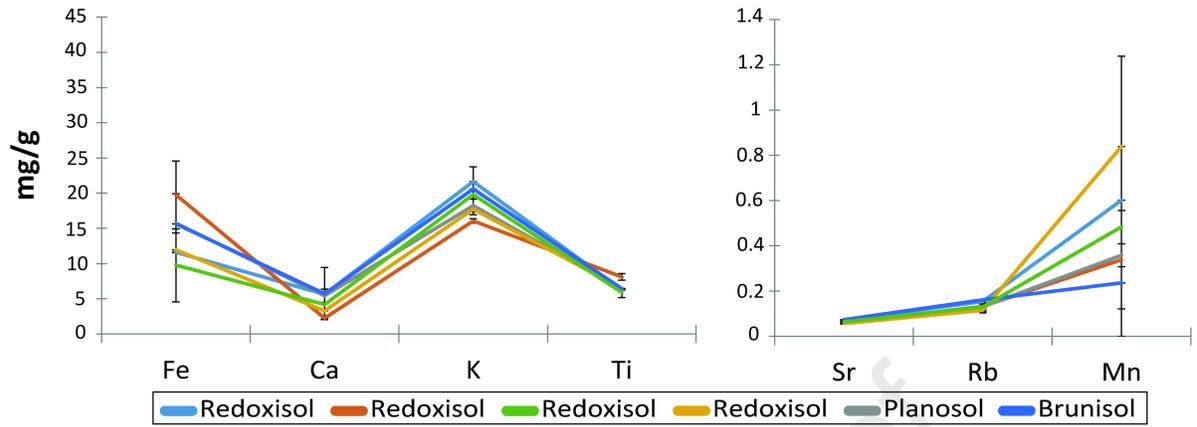
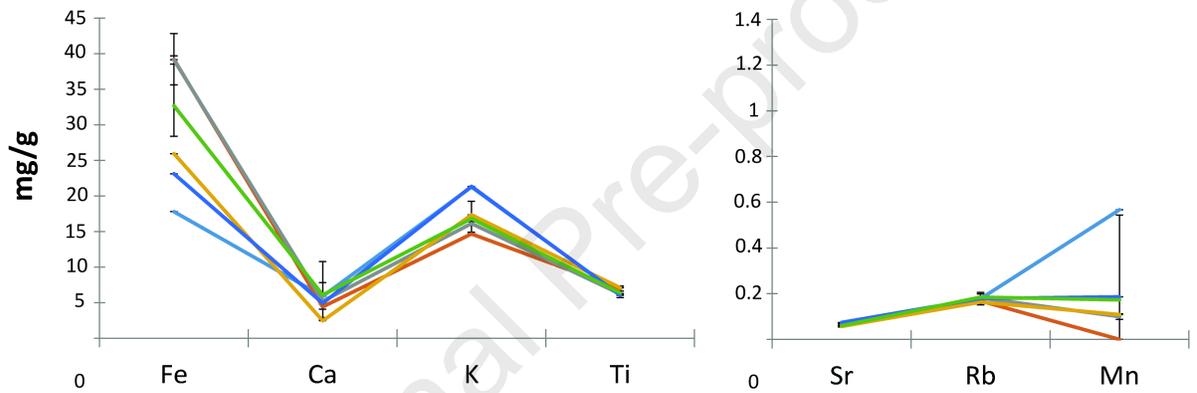
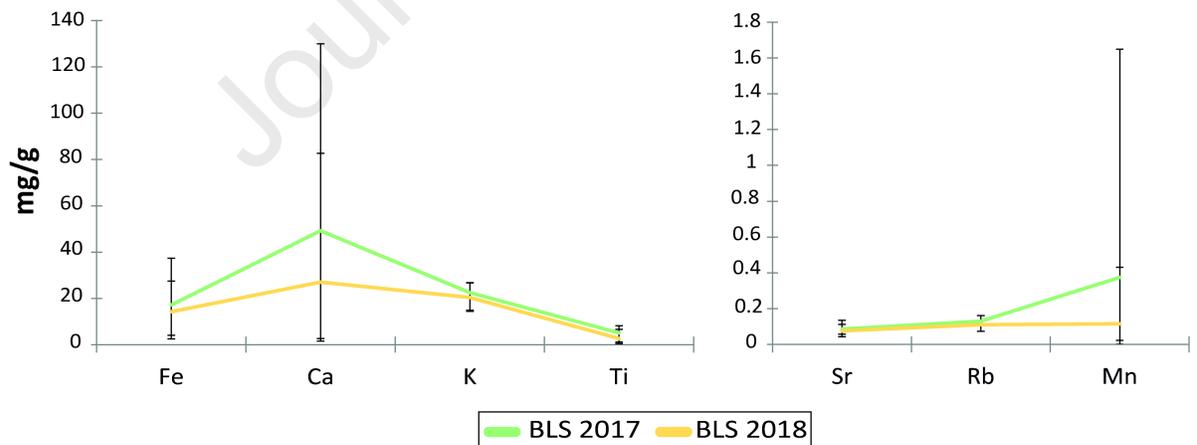
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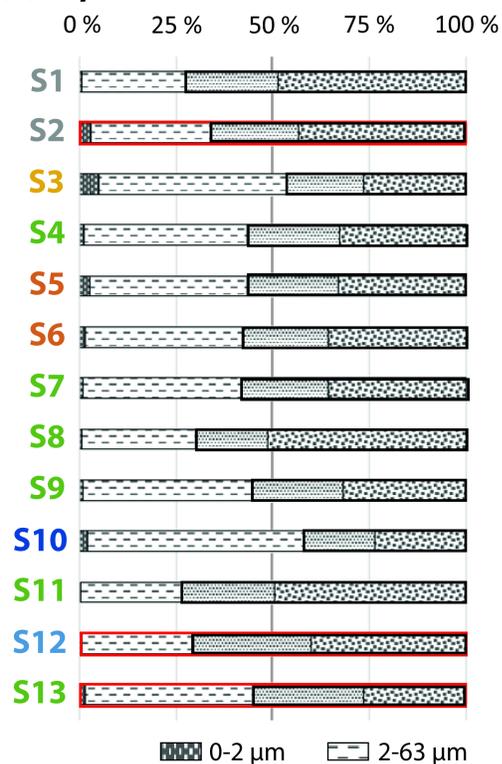
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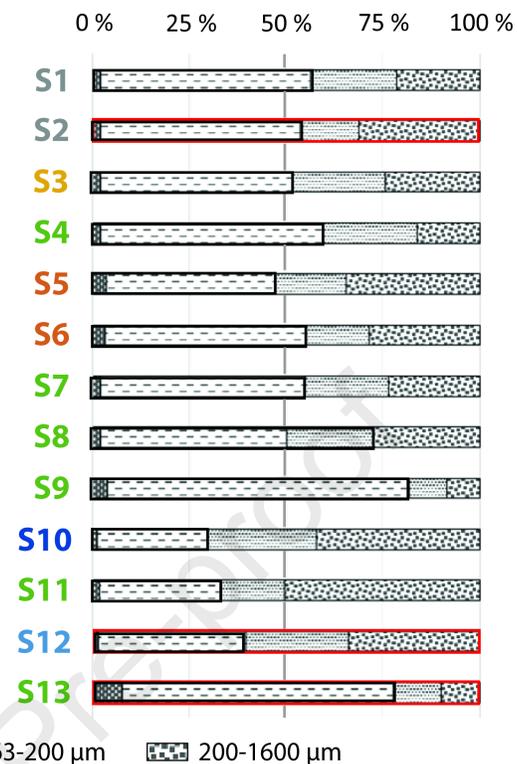
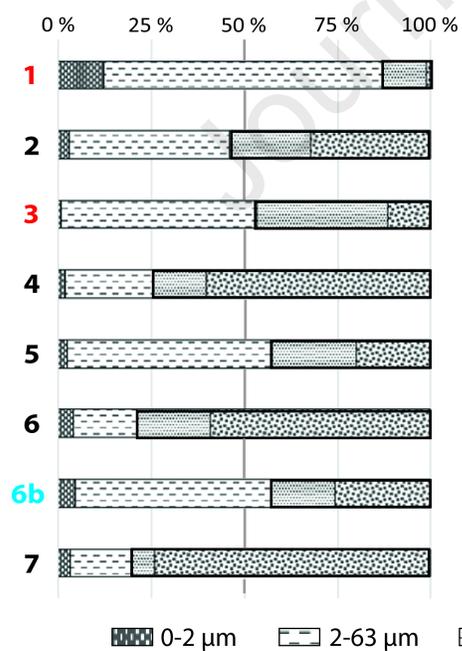
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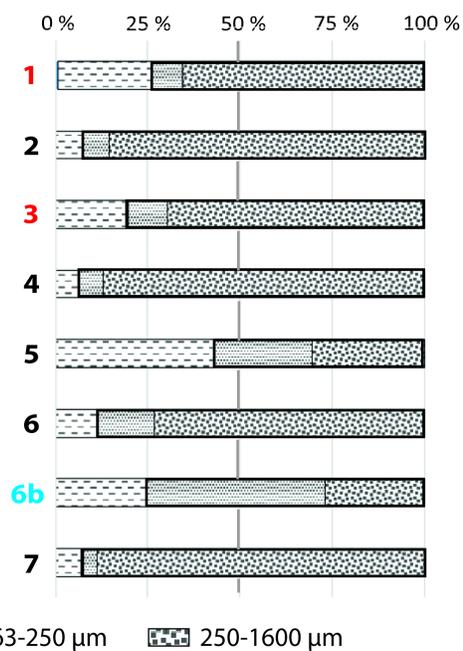
(a) Topsoils**(b) Subsoils****(c) Bed load sediments**

(a) Topsoils

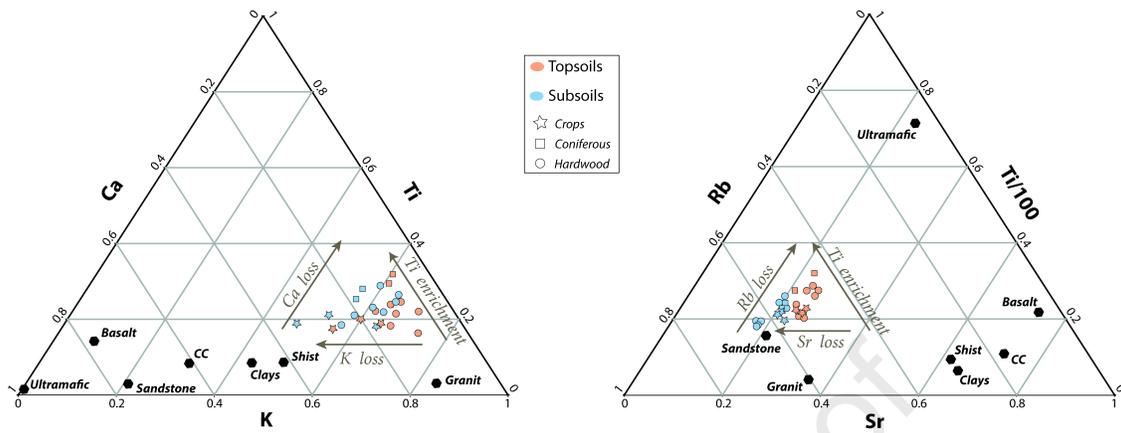
Redoxisol Redoxisol Redoxisol Redoxisol Planosol Brunisol
Agricultural parcels

(b) Subsoils**(c) Bed load sediment of 2017**

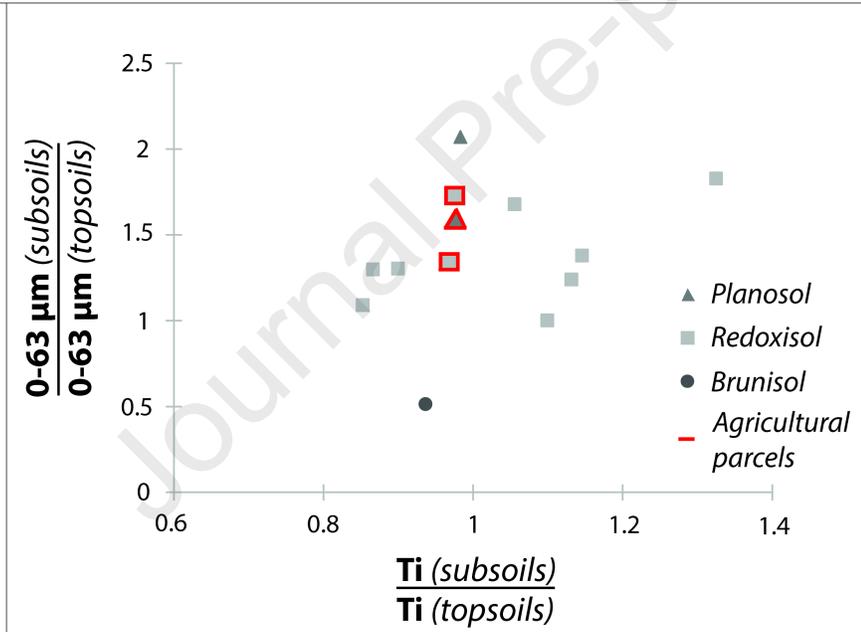
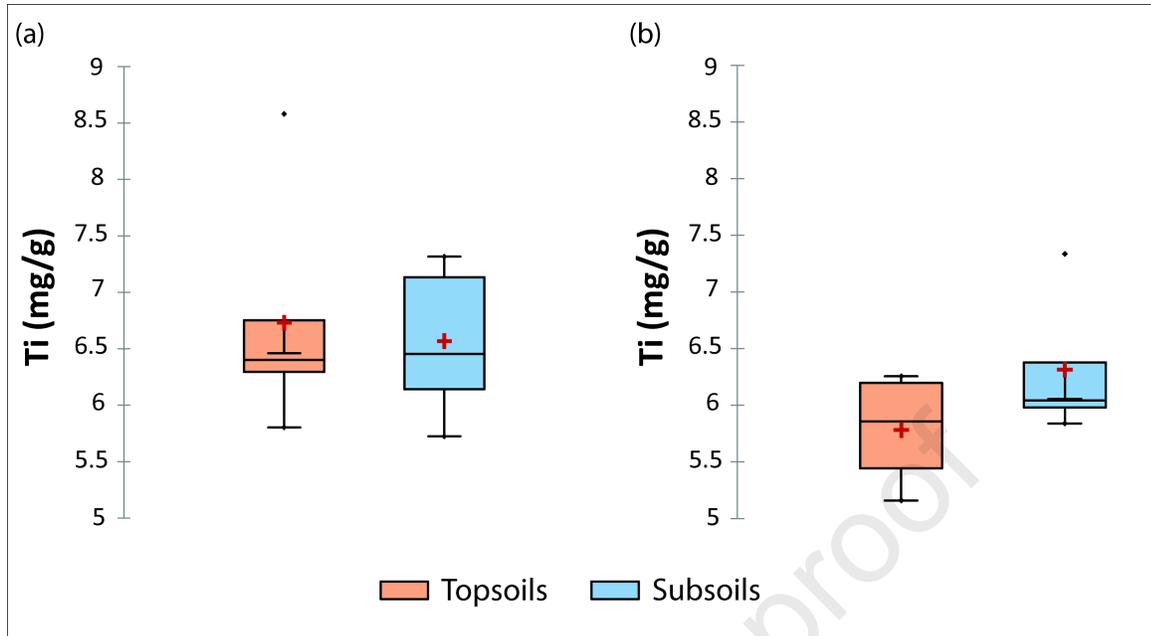
Sewage waters drainage Urban stormwaters drainage

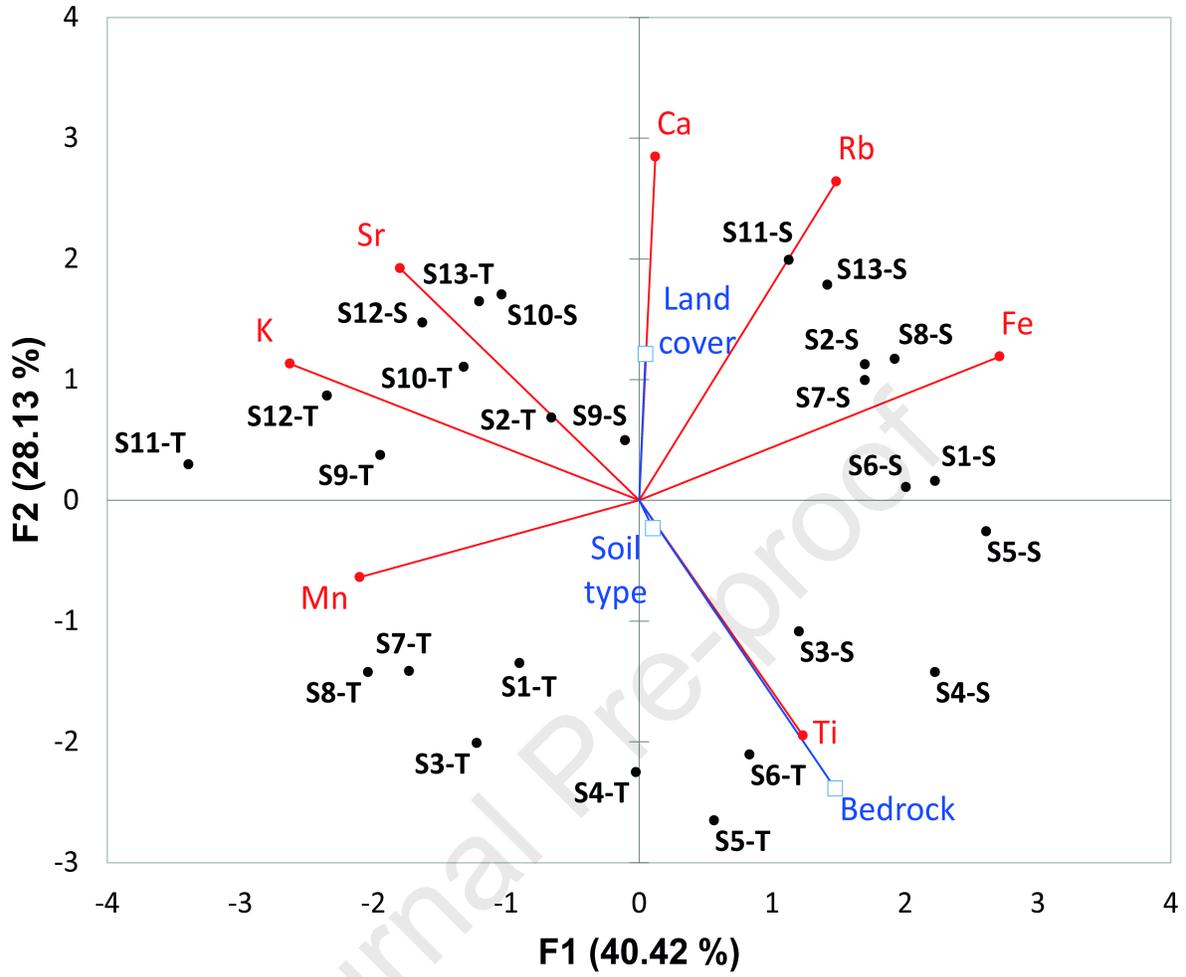
(d) Bed load sediment of 2018

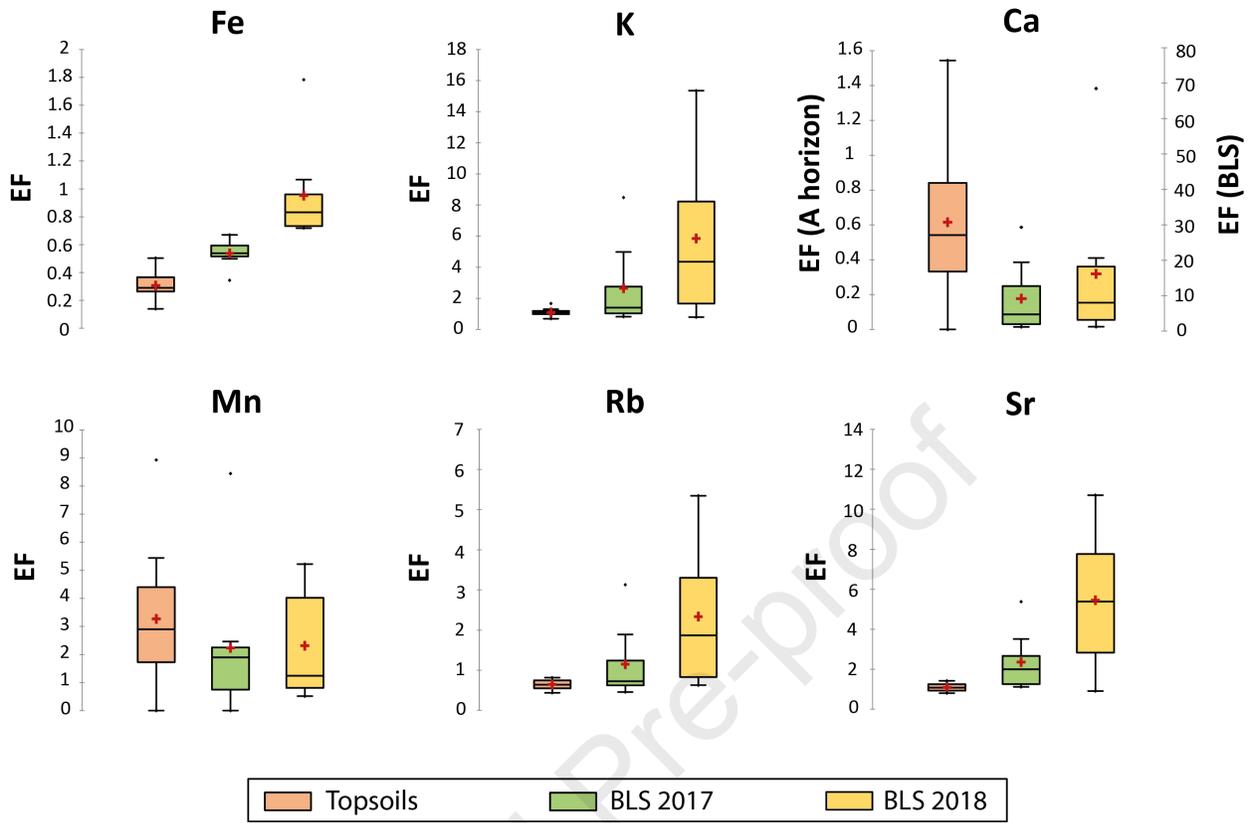
Sewage waters drainage Urban stormwaters drainage

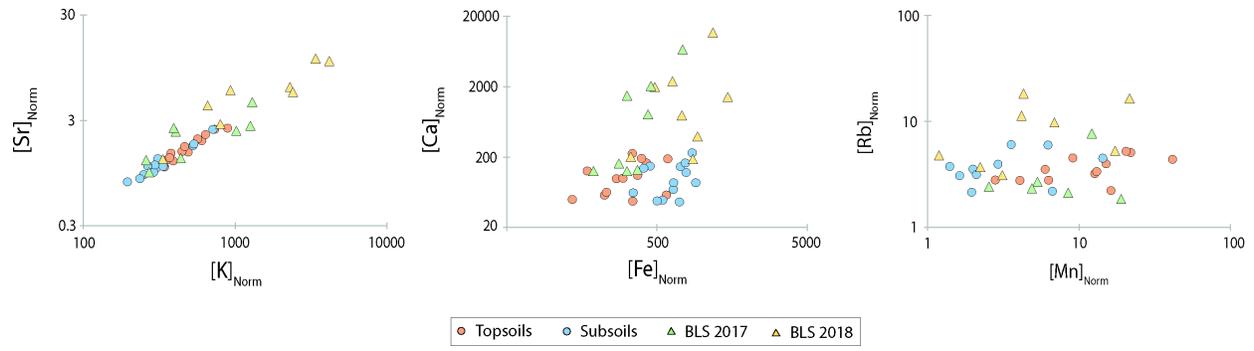


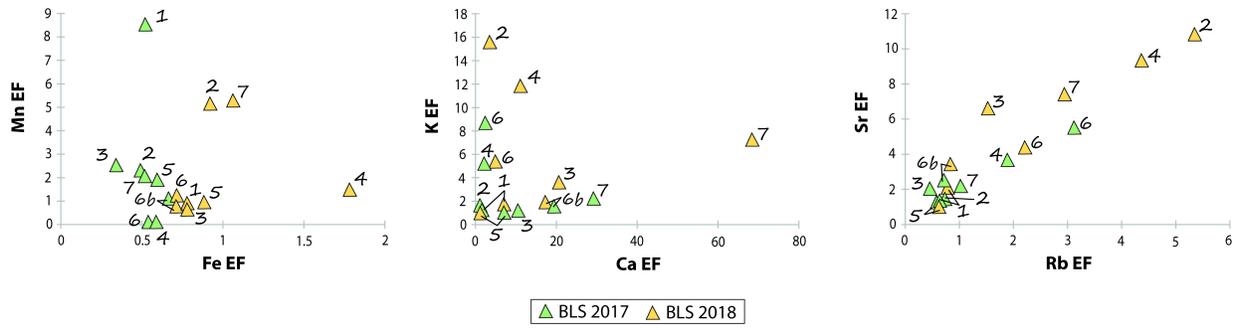
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Highlights

- 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

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Declaration of interests

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:

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