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# New methodological approach for deep penetrating geochemistry and environmental studies.

## Part 1 - On-site soil extraction of trace and rare earth elements

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### Abstract

The use of on-site soil extractions for direct quantification provides a fast and efficient method for environmental monitoring and mineral prospecting. In this study, an on-site extraction protocol was developed and tested on northern boreal soils using partial extractants: 0.01 M calcium chloride (CaCl<sub>2</sub>) and 0.43 M nitric acid (HNO<sub>3</sub>). CaCl<sub>2</sub> is commonly used as an extractant for mobile and directly available elements, while 0.43 M HNO<sub>3</sub> is used to extract also the reactive pool with the weakly bound elements from soil particle surfaces. These two extractants were chosen because they have (i) no specific constraints for electrochemical or spectrometric analysis for element quantification and (ii) are more environmentally friendly than the ones often used for mineral exploration; e.g., the aqua regia (AR) or mobile metal ions like Ionic leach<sup>TM</sup> (IL, ALS).

Extractions with HNO<sub>3</sub> offered the same patterns as those obtained with AR but with better contrast for anomalies, while the CaCl<sub>2</sub> results were very similar to those obtained with IL. Nevertheless, neither HNO<sub>3</sub> nor CaCl<sub>2</sub> was effective in mobilizing Au, W, or Sn due to their low concentrations. Our study demonstrated that on-site soil extractions with HNO<sub>3</sub> and CaCl<sub>2</sub> were potentially good candidates for the detection of REEs, such as Ce and La, and some trace elements, especially Cd, for both extractions, Co, Pb and U with HNO<sub>3</sub>, and Mn and Ni with CaCl<sub>2</sub>. This work highlights the potential of on-site extraction using partial extractants. This is a key step prior to the quantification of elements by on-site voltametric techniques.

### Introduction

On-site quantification of elements in soils using field analytical techniques offers great opportunities for environmental monitoring and mineral exploration. Both topics need the implementation of rapid and adaptable sampling strategies on site, which is not possible when the analyses are carried out through standard laboratory procedures, which take weeks before the analytical data are retrievable.

43 In mineral exploration, the surface geochemistry approach, known as deep penetrating geochemistry  
44 (DPG, Cameron et al., 2004) focuses on discriminating between endogenic and exogenic geochemical  
45 signals of elements in soils (Heberlein and Samson, 2010). Endogenic signals are composed of  
46 elements from the primary mineral matrix of the parent material of soil. Exogenic signals refer to  
47 labile elements transported from other sources, such as contamination, deep-seated/suboutcropping  
48 mineralization, and/or ions added through hydromorphic processes, which are unrelated to the soil  
49 parent materials. Elements from exogenic sources are mobile or potentially mobile and are found on  
50 mineral and organic constituent surfaces and/or in soil solutions. They can be detected only if they  
51 have anomalous concentrations compared to background concentrations. On-site surface  
52 geochemistry could guide exploration activities such as bedrock drilling in a dynamic way by allowing  
53 instantaneous identification of an underlying exploration target and prioritization of drilling when  
54 several targets are present. This would save time, reduce costs and be more environmentally friendly  
55 by reducing the amount of bedrock drilling.

56 To measure the exogenic component of elements, there is no direct analytical method available for  
57 metal concentration measurements. Full and direct element analyses, such as X-ray fluorescence  
58 (XRF), currently provide only the total element concentration and are insensitive to the binding type  
59 of elements to soil particle surfaces. Thus, extraction is required first to release the weakly bound  
60 component to the solution and then to enable quantification of these specific elements. When using  
61 partial extraction of soil samples for surface geochemical exploration or soil surveys, element  
62 quantification usually includes three steps: step 1—soil sampling and preparation; step 2—chemical soil  
63 extraction; and step 3—element quantification.

64  
65 Sampling and preparation (step 1) are crucial for the extraction and analysis of soil elements. Various  
66 studies have shown the effects of soil preparation on the solubility of major elements such as  
67 aluminium (Al), iron (Fe), manganese (Mn, Pérez et al. (2004)), trace elements (Berndt 1988; Gray  
68 and McLaren 2003; Száková *et al.* 2009; Vodyanitskii and Minkina 2020) and rare earth elements  
69 (REEs, Wang et al., 2001). Special care must also be taken to avoid element contamination, with  
70 adapted sampling and storage materials. Soils can be air- or freeze-dried but can also be directly used  
71 to prevent biases due to remoistening. Soil samples must be stored at cool temperatures after  
72 sampling to limit bacterial activity (ISO 18512 2007). Soils are then sieved a < 2 mm size fraction to  
73 remove larger particles, allowing extraction of elements from the fine soil fraction, the most reactive  
74 fraction of the soil. Sometimes, the fine earth is ground and sieved to a < 200 µm grain size fraction  
75 to ensure sample homogeneity. Regardless of soil preparation used, measurements are reported as  
76 “dry weight”, which refers to the absence of water in the soil matrix (dried at 105 °C), to compare the  
77 concentrations of soil solid constituents.

78

79 Soil extraction (step 2) aims to bring into solution elements to investigate one or several element  
80 compartments (or “pools”) in the soils. The main compartments containing elements in soils are (i)  
81 water soluble, (ii) organically bound metals, (iii) metals adsorbed on minerals and (iv) metals included  
82 in mineral matrices such as clays, other silicates, carbonates, amorphous and crystalline iron (Fe)  
83 and/or manganese (Mn) oxides (Chao 1984; Brummer 1986; Cameron *et al.* 2004). The water-soluble  
84 compartment corresponds to the "mobile" metal pool, while the organically bound metals and  
85 metals adsorbed on mineral compartments refer to a "potentially mobile" metal pool. The exogenic  
86 signal could be related to one or all of these compartments. The fourth compartment refers to the  
87 mineral matrix derived from the geological parent material of the soil and then to the endogenic  
88 signal.

89 Aqua regia digestion (AR, ISO 11466, 1995) is a strong partial extractant since AR does not totally  
90 dissolve silicates or oxides (Berrow and Stein, 1983). Despite this, AR is an efficient method for  
91 characterizing mainly the endogenic signal as it can extract up to 70 to 90% of metals (Alloway 1995)  
92 in mineral grains. It has proven to be an effective method for identifying endogenic signals in formerly  
93 glaciated regions, such as Northern Finland, where the soil parental material corresponds to  
94 heterogenous sediments transported by glacial processes (Koljonen, 1992; Salminen and Tarvainen,  
95 1995).

96 To capture the exogenic signal, specific partial extractions, such as the Mobile Metal Ion (MMI)  
97 extraction method, are required (Mann *et al.* 1998, 2000, 2005, 2012; Mann 2010). These methods  
98 are often developed by geochemical laboratories, and scarce information about these proprietary  
99 protocols is available. The MMI-M<sup>®</sup> method, developed by SGS (2022), uses strong ligands that detach  
100 loosely bound metal ions from the surfaces of soil particles. Ionic Leach<sup>™</sup> (IL), developed by the ALS  
101 laboratory (2013), is a static sodium cyanide leach using chelating agents such as ammonium  
102 chloride, citric acid and ethylenediaminetetraacetic acid (EDTA), which are buffered at pH 8.5. The IL  
103 method enables the liberation of weakly bound ions from soil particle surfaces. The presence of EDTA  
104 and cyanide enables metals to remain in solution, thus preventing readsorption on undigested  
105 mineral surfaces. MMI-M and ILs are thus widely used for mineral prospecting of gold (Au) and  
106 associated metals (Heberlein and Samson 2010).

107 For environmental monitoring, soil extractions were also used to release elements into solution to  
108 estimate their concentration. This is done for various applications, including the quantification of  
109 available nutrients (mobile and potentially mobile) contributing to ecosystem functioning (Rieuwerts  
110 *et al.* 1998) or labile elements as contaminants if they are present in excessive amounts. The available  
111 fraction can be subdivided into two pools: the “directly available pool” and the “reactive pool”  
112 (Peijnenburg *et al.* 2007; Römkens *et al.* 2009). The “directly available pool” corresponds to the  
113 mobile fraction present in the soil solution. The extractants commonly used in environmental studies  
114 are water or neutral salt solutions. A 0.01 M solution of calcium chloride (CaCl<sub>2</sub>) is one of the most  
115 suitable methods for estimating of the concentration of dissolved elements present in soil pore water

116 (Novozamsky *et al.* 1993; Houba *et al.* 1996, 2000). This method offers the advantage of having a  
117 concentration close to the salt concentration in the soil solution. Additionally, using  $\text{Ca}^{2+}$  as the  
118 dominant divalent cation improved the extraction ability of other cations present in the soil solution.  
119 Degryse *et al.* (2003) showed that the Cd and Zn concentrations in soil solutions of different European  
120 topsoil samples can be predicted with a  $\text{CaCl}_2$  extraction. The "reactive pool" corresponds to the  
121 "potentially available" fraction. It includes the elements that are bound to organomineral complexes  
122 in soils (Qu *et al.* 2019) and can be quickly released in soil solution. Diluted strong extractants such as  
123 a 0.43 M solution of nitric acid ( $\text{HNO}_3$ ) are particularly adaptable for the characterization of the  
124 reactive pool (Römken *et al.* 2009; Peijnenburg *et al.* 2007; ISO 17586 2016).  $\text{HNO}_3$  is buffered at pH  
125 0.5, where only elements adsorbed on organo-mineral complexes are extracted instead of the  
126 elements included in the soil matrix, also called the "inert pool" (van Vart and Harmsen 2016). More  
127 than 90% of reactive elements can be extracted via 0.43 M  $\text{HNO}_3$  extraction, even if their  
128 concentrations can be slightly overestimated by the dissolution of hydrous oxide or underestimated  
129 for elements with a high affinity for organic matter (Groenenberg *et al.* 2017). These two methods  
130 could then be used for releasing the exogenic geochemical component of mineral soil into solution.

131

132 Finally, metal quantification (step 3) depends on the target elements. Inductively coupled plasma-  
133 mass spectrometry (ICP-MS) remains the method of choice because elemental quantification can  
134 reach very low concentrations ( $\text{ng}\cdot\text{kg}^{-1}$ ) for a broad range of elements in solution (Smith and Cresser  
135 2003). However, two main types of field quantification methods are possible for soils:

136 - The quantification of many elements can be performed with limited or no soil preparation, but  
137 the approach is limited to analysing total concentrations. Nevertheless, caution must be taken of the  
138 grain size distribution of the soil material because it may cause severe biases in terms of  
139 quantification. Total quantification can be directly performed with portable spectroscopic devices  
140 such as portable X-ray spectrometry (pXRF, Sarala (2016); Ravensari *et al.*, (2020)) and portable laser-  
141 Induced breakdown spectroscopy (pLIBS; Cremers and Chinni, (2009). For example, Sarala *et al.*  
142 (2015) and Lemiere *et al.* (2020) demonstrated the effectiveness of pXRF for in situ analysis of till, Ah  
143 and Bh horizons.

144 - The other approach is on-site elemental quantification from soil solutions. The quantification  
145 could be performed directly on natural water in soils (pore water) or on soil extraction. Nonetheless  
146 simple and adaptable protocols for soil extraction must be both achieved and directly analysed on  
147 site. They are therefore not commonly used in exploration or environmental contexts. For on-site  
148 quantification, innovative protocols used pXRF analysis for copper (Cu), manganese (Mn), nickel (Ni),  
149 lead (Pb), uranium (U) and zinc (Zn) in preconcentrated natural water (Tiihonen *et al.* 2021, 2022) and  
150 for specific Au quantification in solutions of digested soil (Lintern 2018). The recent analytical  
151 development of total reflection XRF (tXRF) also offers the possibility of direct quantification of  
152 elements in water samples (ISO 20289 2018). Yehia *et al.* (2019) showed the potential of using a

153 photometer and voltammeter for the detection of arsenic (As) and Cu anomalies in water. Zeiner et  
154 al. (2020) recently worked on titrimetric and photometric methods after on-site acetic acid soil  
155 extraction, but the limits of detection were relatively high for some elements: for titrimetry,  
156 approximately 60 mg.l<sup>-1</sup> [Cu, Ni, and Zn], and for photometry, between 0.04 [Zn] and 0.1 [Cu, Ni] mg.l<sup>-1</sup>.  
157 Electrochemical probes could then offer promising methods for metal soil solution quantification  
158 (Chao, 1984; Lintern et al., 1988), but they need to be adapted for on-site use.

159

160 On-site soil element quantification could offer great opportunities for environmental monitoring and  
161 mineral exploration. This approach would allow for adaptable sampling strategies in the field, which  
162 is not possible with laboratory analysis. In this study, we tested a new methodological approach  
163 combining (i) soil extraction (ii) with elemental quantification using voltammetric techniques, both of  
164 which were achieved on site. The aim of the first part of this study was to validate the effectiveness  
165 of the chosen extraction protocols. The second part of the study focused on field quantification with  
166 a highly sensitive (ng.l<sup>-1</sup>) electrochemical probe and was discussed by Hackel et al. (Accepted in  
167 GEEA).

168 For both parts, we applied two selective extractions to fresh mineral B-horizon soil samples: 0.43 M  
169 HNO<sub>3</sub> and 0.01 M CaCl<sub>2</sub>. These extractions were chosen because (i) these reactants are suitable for  
170 field extraction, (ii) they are suitable for elemental analysis with electrochemical probes, and (iii) they  
171 are more environmentally friendly than most of the extractants used for elemental quantification in  
172 the context of DPG. Soil samples were collected near and above the Au-Co mineralization site located  
173 at the Rajapalot project in northern Finland. First, field protocols were validated by comparing them  
174 to the standard protocols achieved in the laboratory on air-dried soil samples. The elemental  
175 extractability of soil samples by HNO<sub>3</sub> and CaCl<sub>2</sub> was then compared with that of standard extraction  
176 methods: AR for pseudototal quantification and IL for the detection of anomalous concentrations of  
177 MMI. Trace and REE anomaly locations in Rajapalot were then discussed to emphasize on-site  
178 extraction and quantification in soil surveys.

179

## 180 **Materials and methods**

### 181 **Experimental site and sample collection**

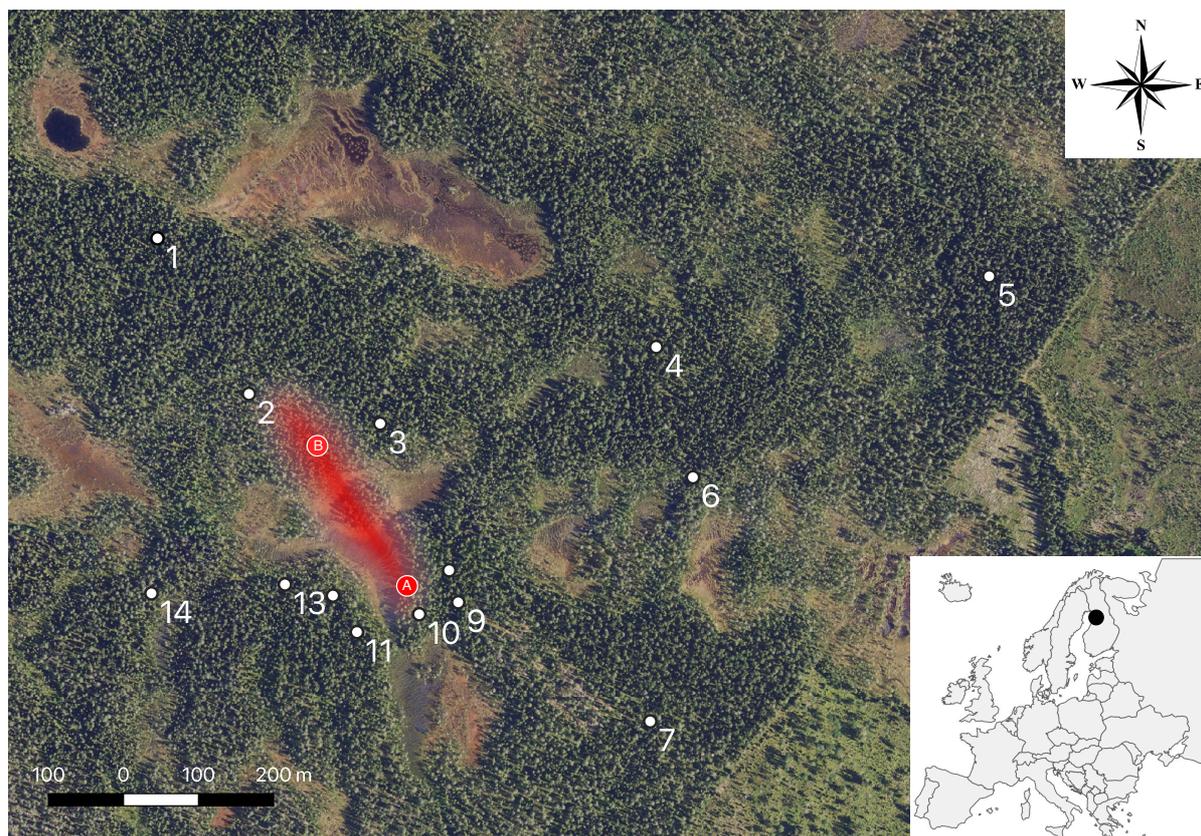
182 The soil samples were collected at the Rajapalot project, 30 km west of Rovaniemi (66.45° N, 24.75°  
183 E) in the Palaeoproterozoic Peräpohja Belt in southern Finnish Lapland (Cook and Hudson 2018;  
184 Ranta 2018; Mawson Resources Limited 2020). The main mineralization at the study site, the Raja  
185 prospect, is a “K-Fe type” with high-grade Au-Co sulfide mineralization first drilled by Mawson  
186 Resources Ltd. in 2016. It is an isoclinally folded package of amphibolite-facies metamorphosed rocks  
187 (Cook and Hudson 2018; Mawson 2018b; Cook 2019; Geological Survey of Finland 2020; Mawson  
188 Resources Limited 2020). Drill core lithogeochemistry indicates three stacked discontinuous lateral

189 mineralized horizons varying from 1 to 40 m in thickness. The stack of mineralized horizons plunges at  
190  $36 \pm 2^\circ$  in depth towards the NW ( $335 \pm 3^\circ$ ) from 40 m depth and approximately 240 m (Points A and  
191 B, respectively, in Erreur ! Source du renvoi introuvable.) to a known depth of 550 m (Mawson 2018a,  
192 2019). The maximum ground surface projected footprint is then 150 m by 500 m (Mawson Resources  
193 Limited 2020). The maximum grades reported at Raja are  $20 \text{ g.t}^{-1}$  for Au and  $1193 \text{ g.t}^{-1}$  for Co,  
194 including a multielement association of As, Bi, Mo, Ni, W, S, Se, and Te (Cook 2019; Mawson  
195 Resources Limited 2020). Overlying the crystalline bedrock basement, the weathered bedrock is  
196 characterized by glacial sediments and sandy till. The till cover was eroded by a subglacial meltwater  
197 corridor running across the northern part of the sampling area. Ancylus Lake sediments occur at  
198 elevations of 210–215 metres above sea level. (Sarala 2014). Furthermore, postglacial peatland  
199 deposits 0 to 10.2 m in thickness (median 4.4 m, based on the bottom of till data) are common in the  
200 topographic depressions. The site is occupied by a natural boreal forest dominated by Norway spruce  
201 (*Picea abies*), Scots pine (*Pinus sylvestris*) and downy birch (*Betula pubescens*).

202

203 Fourteen soil profiles were sampled from the forested soils around and above the subcropping and  
204 deep-lying Raja deposit (Erreur ! Source du renvoi introuvable.). These sampling sites were selected  
205 based on an airborne electromagnetic survey, ground-measured apparent resistivity and total  
206 magnetic intensity, and geological data (Middleton *et al.* 2021). The soil profiles were mostly of the  
207 Podzol type (IUSS Working Group WRB (2015), **Supp. Data 1**) and were composed of an organic O-  
208 horizon (with a thickness ranging from 5-20 cm), a poorly developed organo-mineral horizon “Ah”  
209 (with a thickness ranging from 1-10 cm), and an eluvial leached and bleached horizon “E”- with a  
210 (thickness ranging from 0-30 cm) overlying an illuvial spodic horizon “BP”- (with a thickness ranging  
211 from 30-60 cm; this horizon is referred to as B-horizon in the following text for the convenience of  
212 readers). From each profile, the upper B-horizon was collected at depths varying from 12 to 45 cm.

213



214

215 **Figure 1.** Aerial view of the Rajapalot sampling site.

216 Each sampling site is numbered and identified by a white circle. Forests are in shades of green, and mires are in brown shades. The vertical  
 217 projection of the concealed mineralization is represented by a red line, with point A corresponding to the maximum ore elevation at 40 m  
 218 depth and point B at approximately 240 m depth from the surface.

219

## 220 Pretreatment and extraction protocols

221 The fourteen fresh B-horizon samples were sieved directly on-site through a 2-mm mesh. Two  
 222 extraction methods were used in the field for fresh soil samples and in the laboratory for air-dried soil  
 223 samples: 0.43 M HNO<sub>3</sub> extraction and 0.01 M CaCl<sub>2</sub> extraction. The extractant solutions were  
 224 prepared from concentrated HNO<sub>3</sub> (70%, purified by redistillation, ≥99.999% trace metal basis) and  
 225 CaCl<sub>2</sub>·2H<sub>2</sub>O (>99%, American Chemical Society Standard Reagent). For each type of extraction, the soil  
 226 was mixed with an extraction solution at a 3:30 weight-to-volume (g:ml) ratio. Then, they were  
 227 shaken for 2 hours on an Intelli RM-2L rotator mixer (ELMI). After 30 min of decantation, the  
 228 suspensions were filtered through 0.45 μm Acrodisc syringe filters with a PES Supor® membrane. Six  
 229 extraction replicates were processed simultaneously in the field and three in the laboratory for each  
 230 B-horizon sample. Blank samples (empty samples, n=3) were subjected to the same procedure. Three  
 231 replicates of field extractions were directly analysed on-site by electrochemical stripping techniques:  
 232 square wave anodic stripping voltammetry for the simultaneous detection of Pb and Zn and linear  
 233 scan-cathodic stripping voltammetry for the detection of Co and Ni (Hackel *et al.* Accepted in GEEA).  
 234 Three replicates for both field and laboratory extractions were kept at 4 °C until ICP-MS analyses.

235 The field soil moisture content was determined on-site by air-drying ~ 10 g of fresh soil for at least 24  
 236 h until a constant weight of 0.01 g was reached (called “field moisture” expressed as % weight  
 237 content, wt%). The leachates and the remainder of the < 2 mm screened sample material were stored  
 238 at 4 °C until preparation and analysis were carried out in the laboratory. The preparation involved air-  
 239 drying at ambient temperature for a minimum of 24 h before laboratory extraction. The soil moisture  
 240 content was also determined from the air-dried fine soil aliquot before oven-drying for 24 h at 105 °C.  
 241 The difference in mass between laboratory air-dried and oven-dried moisture was called the “soil  
 242 moisture at 105 °C” – wt% (Erreur ! Source du renvoi introuvable.).

243

244 **Table 1.** Physicochemical properties of the sampled BP horizons.

245 Soil field moisture and soil moisture at 105 °C are expressed as weight content (wt%), the granulometry in volume fraction (vol%), cationic  
 246 exchange capacity (CEC) in cmol<sup>+</sup>/kg, and total organic carbon (TOC) in mg of C/100 mg of soil (%).

Soil	Sampling depth <i>cm</i>	Soil field moisture <i>wt%</i>	Soil moisture at 105 °C <i>wt%</i>	Granulometry ( $\mu\text{m}$ )					pH <sub>w</sub>	CEC <i>cmol<sup>+</sup>.kg<sup>-1</sup></i>	TOC <i>%</i>
				<2 <i>vol%</i>	2-20 <i>vol%</i>	20-50 <i>vol%</i>	50-200 <i>vol%</i>	200-2000 <i>vol%</i>			
1	20-30	13.8	0.9	0.9	5.6	9.4	22.1	62.0	4.9	0.7	0.5
2	50-55	25.4	1.1	1.2	7.5	15.2	38.4	37.7	4.8	1.3	1.2
3	13-26	21.8	1.2	1.3	9.9	15.1	38.2	35.5	4.3	3.1	0.6
4	15-25	21.9	3.1	1.5	9.1	14.2	31.6	43.6	4.8	0.9	1.9
5	25-30	33.0	2.0	3.5	17.1	17.6	30.3	31.6	4.9	1.2	1.0
6	25-35	23.1	1.0	0.7	4.0	5.3	10.8	79.2	4.8	1.2	0.6
7	25-35	13.0	0.3	1.1	5.3	7.6	25.4	60.7	5.1	0.2	0.4
8	20-30	5.9	0.7	0.9	5.0	6.2	17.5	58.0	4.8	0.4	0.8
9	30-40	11.4	0.9	1.3	7.2	9.7	29.0	52.8	4.5	1.0	0.9
10	25-35	21.1	2.1	1.5	8.7	12.9	39.8	37.1	5.4	0.5	0.5
11	20-30	13.6	1.6	2.1	11.5	16.5	38.7	31.2	4.5	1.6	1.7
12	30-35	34.5	3.0	1.7	9.9	18.8	39.1	30.4	4.8	0.7	1.5
13	13-24	22.7	2.1	1.7	9.4	16.4	39.4	33.1	4.7	0.7	1.2
14	15-30	16.8	1.5	1.2	7.3	14.3	46.6	30.6	4.8	1.0	1.0

247

## 248 Physicochemical and mineralogical soil analyses

249 All physicochemical analyses of the upper B-horizon samples were performed on air-dried -2 mm  
 250 screened fractions (Erreur ! Source du renvoi introuvable.). The particle size distribution of the 2-mm  
 251 fraction was determined via laser diffraction technique using the Fraunhofer mode (Mastersize  
 252 3000, Malvern). A few milligrams of the sample medium were added to a 600 ml cuvette with  
 253 deionized water and 2 g.l<sup>-1</sup> sodium-hexametaphosphate (laser obturation of 5 to 10%). Then, the  
 254 samples were dispersed prior to analysis with a stirring speed of 2500 rpm and a 60 s ultrasonic  
 255 dispersion. The pH<sub>water</sub> of the 2-mm fraction was measured with a PHM210 (MeterLab) pH meter  
 256 after mixing 10 g of soil and 50 ml of ultrapure water (ISO 10390 2005) for one hour. The effective  
 257 cation exchange capacity (CEC) and saturation rate (S/T) were determined following the ISO 23470  
 258 (2018) protocol using a hexaminecobalt(III) chloride solution (2:40 w:v). The CEC was measured

259 with a spectrophotometer, at 472 nm and exchangeable calcium (Ca), magnesium (Mg), potassium (K)  
260 and sodium (Na) concentrations were quantified using an AAS Varian SpectrAA 800 Zeeman. Then, an  
261 aliquot (~ 50 g) of the air-dried 2-mm fraction was ground using a mixer mill MM200 (Retsch) and  
262 PTFE grinding jar and balls. Total organic carbon (TOC) was measured on a pulp aliquot with a CHN  
263 Analyzer ThermoFlash EA 1112 and using a low organic carbon soil standard OAS (Cat No B2152).  
264 Mineralogical analyses were also performed on the pulp aliquots using a X-ray diffraction (XRD,  
265 Brucker) with a Co K  $\alpha$ -radiation source.

266

### 267 **ICP–MS analysis of the CaCl<sub>2</sub>, HNO<sub>3</sub>, AR and IL extractions**

268 Sixty elements were analysed by ICP-MS at the ALS laboratory (Prague, Czech Republic) on each field  
269 and laboratory soil sample replicate (n=3) after CaCl<sub>2</sub> and HNO<sub>3</sub> extractions and also on blanks (**Supp.**  
270 **Data 2**). The lower limits of quantification (LOQs) were between 0.4 and 40  $\mu\text{g.l}^{-1}$  for the extracted  
271 CaCl<sub>2</sub> and between 2.0 and 200  $\mu\text{g.l}^{-1}$  for HNO<sub>3</sub>. For each element, the content in the fine soil fraction  
272 was calculated as the dry mass equivalent at 105 °C to compare the field and laboratory results. The  
273 raw ICP–MS data and the relative standard deviation (%RSD) for each element are presented in  
274 Supplementary Data **3** and **4**, respectively. The data with average RSD higher than 25% had been  
275 considered uncertain.

276 AR and extraction were also performed on all B-horizon soil samples following the procedures of the  
277 ALS (ALS Global, 2013, 2021). For AR, the soil samples were dried at 60 °C and sieved at 180  $\mu\text{m}$ . The  
278 fraction under 180  $\mu\text{m}$  was then analysed after AR digestion with supertrace ICP–MS analysis (ALS  
279 method ME–MS41L). Fifty-two elements were determined with detection limits of 0.04  $\text{mg.kg}^{-1}$  for  
280 trace elements and up to 100  $\text{mg.kg}^{-1}$  for major elements (**Supp. Data 2**). For the ILs, the soil samples  
281 were not dried or sieved prior to leaching. Elements from the soil samples were extracted with  
282 sodium cyanide, ammonium chloride, citric acid and EDTA at pH 8.5 and analysed with ICP–MS (ALS  
283 method ME–MS23). A sample-to-reagent ratio of 1:1 was used, allowing very low detection limits  
284 (from 0.02  $\mu\text{g.kg}^{-1}$  to 0.2  $\text{mg.kg}^{-1}$ ) for the sixty-two elements analysed (**Supp. Data 2**). The data quality  
285 was monitored for each procedure using standards (GBM908-10 and OREAS46 for AR and OREAS217,  
286 SRM-19 and SRM-21-B-1 for IL) and duplicates.

287

### 288 **Statistical analysis**

289 The similarities between the B-horizon soil samples according to their physicochemical properties  
290 and pseudototal concentrations (after AR digestion) of major and trace REEs were first studied via  
291 hierarchical clustering (Euclidean distance and Ward method of aggregation). Distance matrices  
292 computed for each category of variables were then compared to each other using a Mantel test of  
293 correlation, which was used to determine whether distances between the 14 soil samples were  
294 correlated between the categories (Legendre and Legendre 2012).

295 Principal component analyses (PCA) were performed to determine the differences between the  
296 extraction methods and to identify the characteristic chemical patterns of each method. The  
297 similarity of patterns for element concentrations was assessed by coinertia analysis. They were based  
298 on the crossing of two PCAs containing the same number of rows. They were carried out using the  
299 "coinertia" function. A Monte Carlo test with the "randtest" function was then conducted to  
300 determine whether the coinertia was significant, and whether there was a common structure  
301 between the two datasets. All these analyses were performed using R software (R Development Core  
302 Team, version 4.4.1) and the vegan version 2.5-7 (Oksanen *et al.* 2020) and ade4 version 1.7-18 (Dray  
303 and Dufour 2007) packages. A threshold of  $p \leq 0.05$  was considered significant.

304 The pairwise Wilcoxon test and Spearman rank correlation ( $r_s$ ) were used to compare the field and  
305 laboratory soil extractions with  $\text{HNO}_3$  and  $\text{CaCl}_2$  (XLStat 2020.1.3). Log-ratio variance was performed  
306 to determine the relationships between element concentrations obtained via the same method  
307 extraction, using R software following the methodology of Van den Boogaart and Tolosona-Delgado  
308 (2013).

309

## 310 **Results and discussion**

### 311 **Mineralogy and physicochemical properties of B-horizons and correlation with their pseudototal** 312 **concentrations**

313 All B-horizon soil samples had low effective CEC (almost all samples  $<2 \text{ cmol}^+.\text{kg}^{-1}$ ) and similar  
314 mineralogy when compared to each other (Erreur ! Source du renvoi introuvable. and **Supp. Data 5**).  
315 The main mineral phases detected by XRD were quartz, feldspar (albite, labradorite, and microcline),  
316 amphiboles (tremolite and ferrogedrite), chlorite, muscovite, vermiculite, and talc. The soil samples  
317 at site 5 differed from those at other sites, with a probable presence of upalite (a mineral belonging  
318 to the phosphuranylite group), which suggests the presence of U at this location. Half of the samples  
319 also contained poorly crystallized aluminosilicates. Small differences were observed between  $\text{pH}_w$   
320 (4.3 to 5.4), carbon content (TOC between 0.4 and 1.9%) and granulometry ( $>70\%$  of fine and coarse  
321 sand for all B-horizon samples, except at site 5, which had a value of only 60%). The soil B-horizons  
322 have very similar physicochemical properties, and correlations were observed with the distributions  
323 of the pseudototal major elemental concentrations of Al, Ca, K, Fe, Mg, Na, P, S and Ti determined  
324 via AR digestion (dPhysico vs. dMajors:  $p = 0.002$ ; **Supp. Data 6**). Notable differences were observed  
325 for the pseudototal concentrations of Fe and Mg between sites 5 and 6 compared to the other  
326 sampling sites. The upper B-horizons at sites 5 and 6 had higher Fe concentrations ( $>85 \text{ g}.\text{kg}^{-1}$  versus  
327  $<53 \text{ g}.\text{kg}^{-1}$ ) and lower Mg concentrations ( $<5 \text{ g}.\text{kg}^{-1}$  versus  $>9 \text{ g}.\text{kg}^{-1}$ ) than did the other sampling  
328 locations. The observed differences could be caused by the heterogeneity of the soil parental  
329 material, such as the different nature of deposits during glacial events, the liberation of soil when ice  
330 melts during postglacial events (Whalen and Sampedro 2009) and/or the topography, which control

331 the intensity of podzolization processes such as the illuviation of Fe, Al and organic matter.  
332 Nonetheless, no correlation was shown between physicochemical properties and pseudototal trace  
333 element and REE concentrations (dPhysico vs. dTraces-REE:  $p = 0.839$ ). The concentrations of trace  
334 elements and REEs were thus not directly related to the physicochemical properties of the sampled  
335 soils.

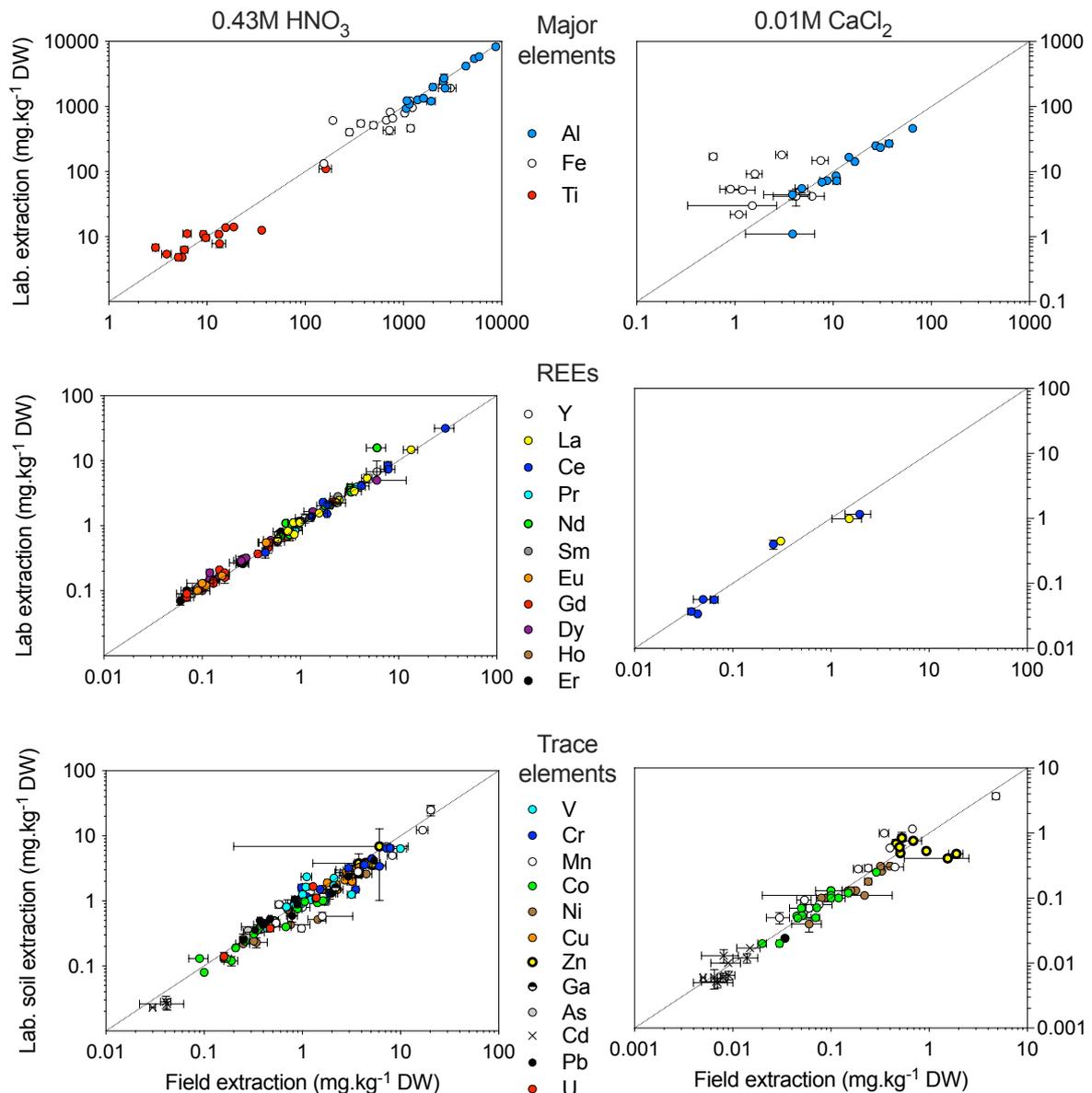
336

### 337 **Comparison between field and laboratory soil extractions: effect of fresh versus dry soil extractions**

338 As expected, the concentrations of elements extracted with  $\text{HNO}_3$  were much greater than those  
339 extracted with  $\text{CaCl}_2$ . Less than half of the elements quantified after  $\text{HNO}_3$  extraction were extracted  
340 and quantified with  $\text{CaCl}_2$  due to the lower extraction efficiency of this leach (**Supp. Data 3**). Some  
341 elements, such as Ag, Sn and W, were not quantifiable with either method. The concentrations were  
342 too low, and/or the limit of quantification of ICP/MS was too high. Thus, we cannot discuss the  
343 efficiency of the methods on these elements.

344 By using  $\text{HNO}_3$  for soil extraction in the field and in the laboratory, twenty-six elements were  
345 quantified (**Figure 2**, left column). Three major elements (Al, Fe and Ti), eleven REEs (Ce, Dy, Er, Eu,  
346 Gd, Ho, La, Nd, Pr, Sm and Y) and twelve trace elements (As, Cd, Co, Cr, Cu, Ga, Mn, Ni, Pb, U, V and  
347 Zn) were quantified in the fourteen B-horizon samples. A good correlation ( $0.75 < r_s < 0.9$ ) was found  
348 between the field and laboratory results for one major element (**Al**), all REEs (**Ce, Dy, Er, Eu, Ho, Gd,**  
349 **La, Nd, Pr, Sm and Y**) and eight trace elements (**As, Co, Cr, Cu, Mn, Ni, Pb** and U). The correlation is  
350 strong for the elements listed in bold ( $r_s > 0.9$ ). Nonetheless, the Al, Co, Cr, Cu and Ni ( $p < 0.05$ )  
351 concentrations were nonetheless slightly greater in the field extractions, while the La ( $p < 0.05$ ) and  
352 Dy, Er and Nd ( $p < 0.01$ ) concentrations were slightly lower. There were weak correlations for Fe and Ti  
353 (for values  $< 100 \text{ mg.kg}^{-1}$ ), and for Cd, Ga, V and Zn ( $r_s < 0.75$ ) concentrations between both  
354 extractions, including a significantly greater field extraction for Cd and Zn ( $p < 0.05$ ).

355 By using  $\text{CaCl}_2$  for soil extractions both in the field and laboratory, ten elements were quantified: Al  
356 and Fe for major elements; Ce and La for REEs; and Cd, Co, Mn, Ni, Pb, and Zn for trace elements  
357 (**Figure 2**, right column). A very strong correlation was found between the field and laboratory results  
358 for **Al, Co, and Mn** ( $r_s > 0.9$ ), and a strong correlation was observed for Ce, La and Ni ( $0.75 < r_s < 0.9$ ).  
359 However, the Al and Ni concentrations were slightly higher with the field extraction (such as using  
360  $\text{HNO}_3$ ), in contrast to the Mn concentration ( $p < 0.01$ ; higher extraction concentration in the laboratory  
361 than in the field). All Cd concentrations were of the same order of magnitude, with very low  
362 concentrations (approximately  $0.005\text{-}0.02 \text{ mg.kg}^{-1}$ ) close to the LOQs, which can explain the low  
363 correlation for all the protocols used. Lead was detected in too few samples to be discussed. There  
364 was no correlation for the Fe and Zn contents using  $\text{CaCl}_2$  extractions in either the field or the  
365 laboratory analytical data ( $r_s = 0.554$ ).



367

368 **Figure 2.** Comparison of element concentrations (expressed in  $\text{mg.kg}^{-1}$  of dry weight) between field and  
 369 laboratory extractions using 0.43 M  $\text{HNO}_3$  and 0.01 M  $\text{CaCl}_2$  solutions.

370 Each element is represented by the mean  $\pm$  standard deviation of replicate analyses ( $n=3$ ) for each sampling site. Note the logarithmic  
 371 scales of the x- and y-axes.

372

373 Similar element concentration ranges were obtained with both extractions in the field and in the  
 374 laboratory, except for Fe, Ti ( $<100 \text{ mg.kg}^{-1}$ ), Mn and Zn. Differences in the quality of extractions  
 375 between field and laboratory preparations, such as for Fe and Zn, are partly explained by the higher  
 376 %RSD observed for field soil extractions (**Supp. Data 3**), which meant lower precision of field  
 377 extraction compared to that performed in the laboratory. The drying protocol and subsequent rapid  
 378 remoistening could also affect the solubility of some elements and subsequently impact the  
 379 extraction yield. Bartlett and James (1980) showed that Mn solubility and exchangeability increased if  
 380 the soil was previously dry. Drying of soil may cause solubilization of organic matter with the  
 381 formation of organic acid and subsequently increase surface acidity. Iron close to and/or bound to

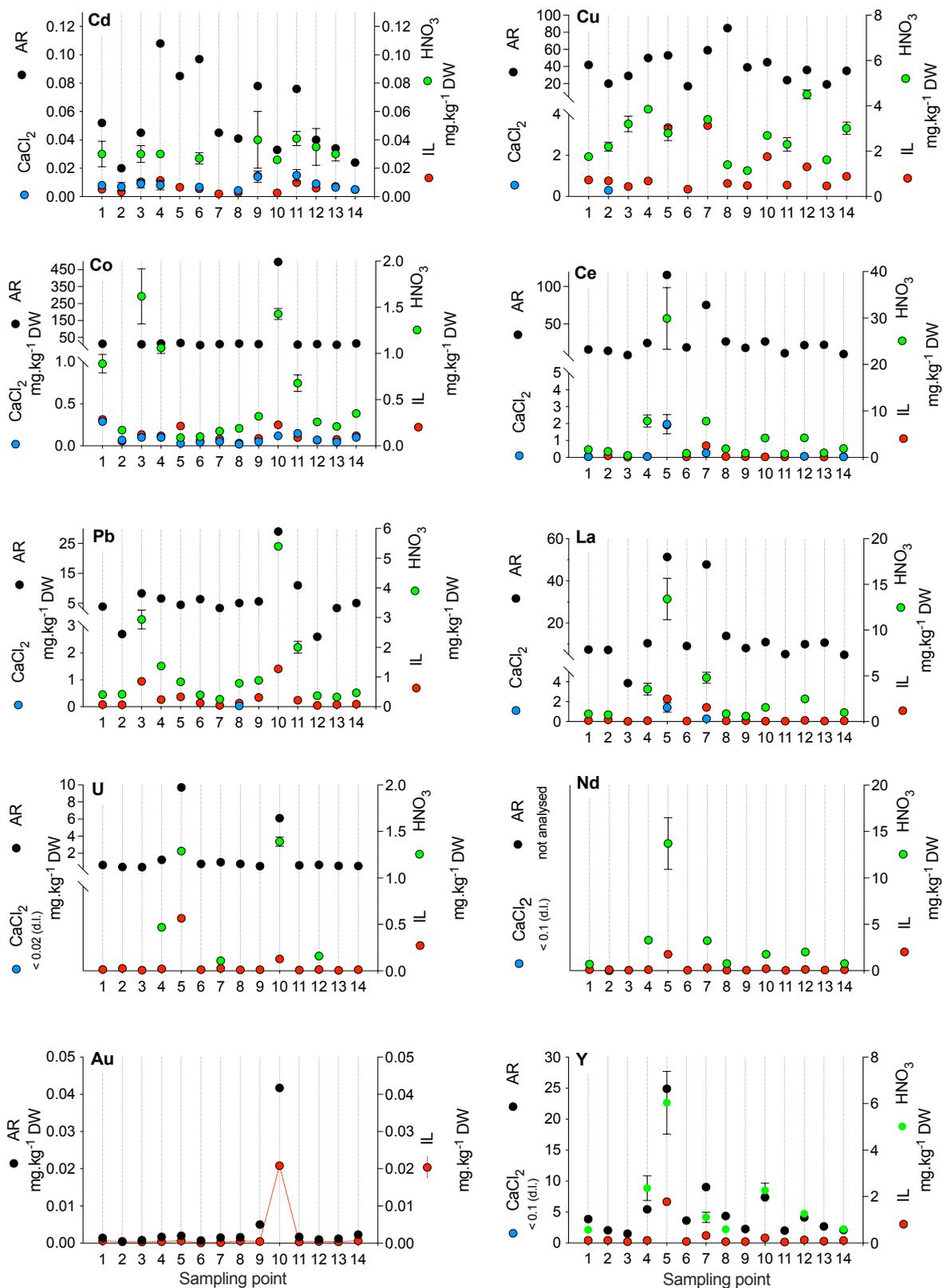
382 organic matter was then solubilized at the same time. Nonetheless, it may concern only small  
383 quantities of elements (few mg.kg<sup>-1</sup> for Fe and µg.kg<sup>-1</sup> for Mn), and it is mainly observed with the  
384 CaCl<sub>2</sub> extraction, which extracts low element concentrations. The CaCl<sub>2</sub> method extracts only the  
385 most easily exchangeable fraction, and it seems that the soil drying step increased the proportion of  
386 mobilized Fe and Mn.

387

### 388 **Field extraction for on-site anomalous detection of elements**

389 The HNO<sub>3</sub> and CaCl<sub>2</sub> extractions performed on the fourteen fresh soil B-horizon samples were  
390 compared with the two main classical laboratory methods: (i) AR extraction used for pseudototal  
391 quantification and (ii) IL extraction used for the detection of mobile metal ions (Erreur ! Source du  
392 renvoi introuvable. and **Supp. Data 7**). Twenty elements were studied: three major elements (Al, Fe  
393 and Ti), thirteen trace elements (As, Au, Cd, Co, Cr, Cu, Ga, Mn, Ni, Pb, U, V and Zn) and four REEs (La,  
394 Ce, Nd and Y). All elements were measured with the four methods, except for Al and Nd which were  
395 not analysed by IL and AR extraction. Higher element concentrations were always obtained with AR  
396 extractions regardless of what the element was (**Figure 3**). For some sampling sites, the element  
397 concentrations were much higher than those at most of the other sampling sites (Erreur ! Source du  
398 renvoi introuvable.). They could then be considered as anomalous concentrations. After AR  
399 extraction, Mn (525 mg.kg<sup>-1</sup> at site 4; **Figure 1** and **Supp. Data 7**), Ce and La (75-112 mg.kg<sup>-1</sup> for Ce  
400 and 47-51 mg.kg<sup>-1</sup> for La at sites 5 and 7) and Y (25 mg.kg<sup>-1</sup> at site 5); Au, As, Pb and Co (0.04, 19, 29  
401 and 496 mg.kg<sup>-1</sup>, respectively, at site 10); and U (9 and 6 mg.kg<sup>-1</sup>, at sites 5 and 10) were particularly  
402 effective. Close behaviours were found between elements, such as for REEs (Ce-La-Y), and Au with As,  
403 Co and Pb (**Supp. Data 8**). Furthermore, consistent behaviours were also observed for Cu and U with  
404 REEs and Co with U.

405 High values were also detected using IL extraction for Au (site 10) and U (sites 5 and 10). In addition,  
406 higher values were detected for Co (sites 1, 5 and 10), Cu (sites 5 and 7), Mn (sites 5, 9 and 11) and  
407 REEs (Ce, La, Nd and Y at sites 5 and 7). The results obtained with the IL confirmed the higher  
408 elemental ion concentrations and close behaviours observed with the AR extraction of Au and Co at  
409 site 10 (**Figure 3** and **Supp. Data 8**). This sampling site was one of the closest to the Au-Co  
410 mineralization site (Point A, **Figure 1**). Lead and U were highly extracted with AR and IL, and As was  
411 highly extracted with AR at site 10. Lead and As are usually associated with Au deposits and serve as  
412 pathfinders in conventional geochemical exploration (Tolessa and Pohl 1999). Ionic leaching also  
413 highlighted close behaviours between Cu, U and REEs, based on higher values of Cu-U-REE at site 5,  
414 Cu-REE at the site 7 and Cu-U at the site 10 (**Figure 3**). The mobility of REEs was strongly correlated  
415 with U and Cu because of their high affinity for dissolved organic matter (McLennan and Taylor 1979;  
416 Steinmetz *et al.* 2017).



417

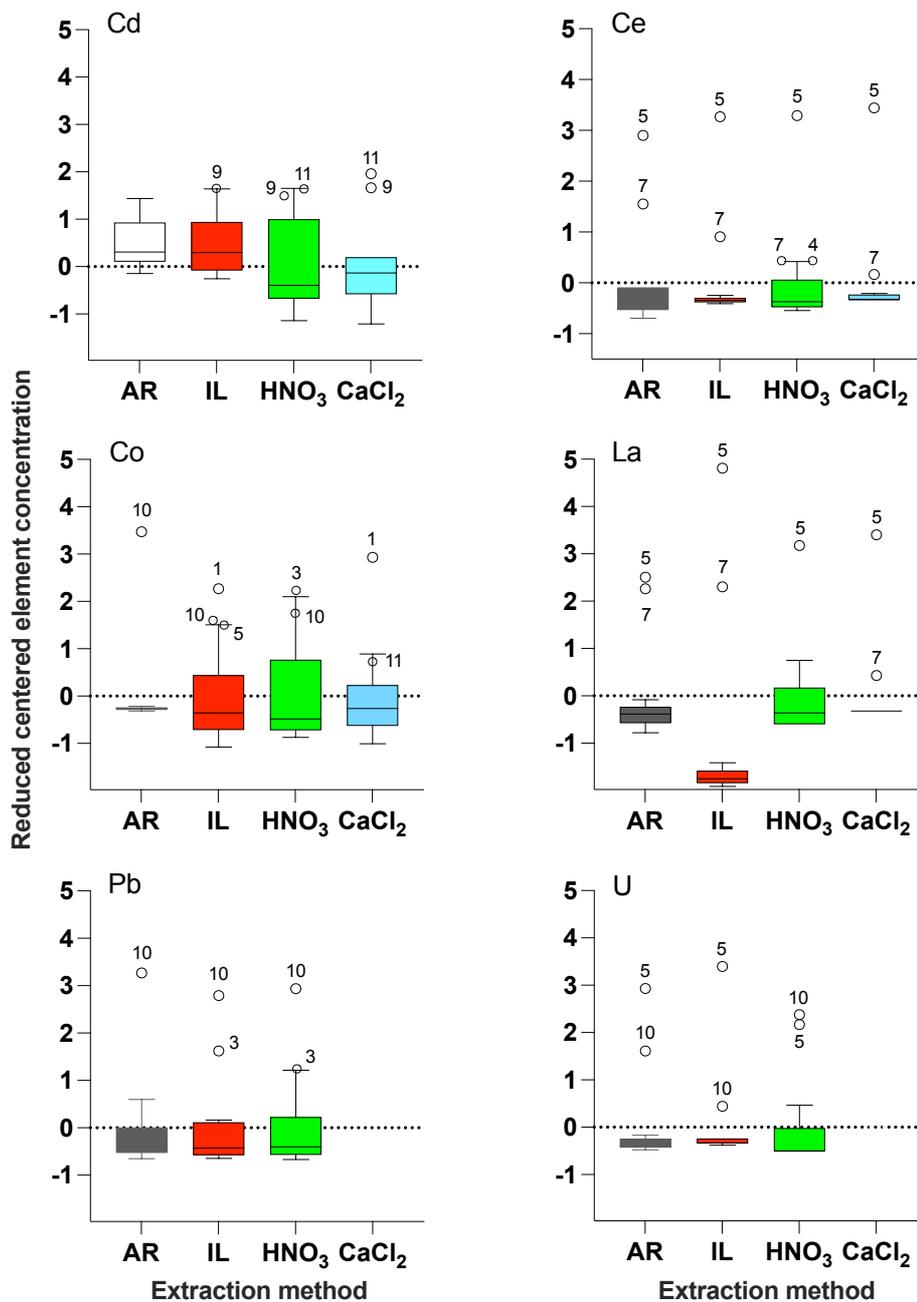
418 **Figure 3.** Comparison plot of concentrations of trace elements (Au, Cd, Co, Cu, Pb, and U) and REEs (La, Ce, Nd  
 419 and Y) in different finished soil samples, measured in solutions of 0.43 M HNO<sub>3</sub> (in green), 0.01 M CaCl<sub>2</sub> (in  
 420 blue), aqua regia (AR; in black), and ionic leach (IL; in red).

421 Elements were organized relative to their pseudo-total content and the location of anomalies. Other elements  
 422 are presented in Supp. Data 6. The locations of the sampling sites are shown in Figure 1.

423

424 The measured concentrations of *on-site CaCl<sub>2</sub> extraction* followed the same trend as those of AR and  
425 IL for Cd, Ce and La (**Figure 3**). These elements were mainly in the soil solution or loosely bound to  
426 organo-mineral soil exchangeable complexes and were then easily extractable with salts such as  
427 CaCl<sub>2</sub>. This is particularly true for Cd, which is highly mobile in acidic soils (Adriano 2001). The CaCl<sub>2</sub>  
428 extraction revealed the close behaviour of Ce and La (a correlation already observed with the AR and  
429 IL extractions) but also their high mobility/availability. The manganese and Ni concentrations were  
430 also correlated between the CaCl<sub>2</sub> and IL extractions ( $0.623 < r_s < 0.863$ ). The mobility of Mn and Ni  
431 were clearly related to Fe, Cd and Pb (Figure 5). For Co, there were correlations at some sampling  
432 sites but not enough to reach a specific correlation between CaCl<sub>2</sub> and IL. However, other elements,  
433 such as As (LOQ < 0.05 mg.kg<sup>-1</sup>), Au (< 0.025 mg.kg<sup>-1</sup>), and U (< 0.03 mg.kg<sup>-1</sup>), were not extracted by  
434 CaCl<sub>2</sub> or were below the LOQ. These elements have a high affinity for organomineral complexes  
435 (McBride and Blasiak 1979; Wang 1984; Groenenberg *et al.* 2017; Larsson *et al.* 2017) and are poorly  
436 extractable with weak leaching. The poorer LOQ of CaCl<sub>2</sub> extraction compared to that of IL (for  
437 example, 30 µg.kg<sup>-1</sup> against 0.02 µg.kg<sup>-1</sup> for Au) limits the use of CaCl<sub>2</sub> extraction for the detection of  
438 elements that are not easily exchangeable and are present in low concentrations in the soil solution.  
439 Our results suggested that CaCl<sub>2</sub> could be a good environmentally friendly substitute for ILs for an on-  
440 site detection of the most mobile trace elements and REEs (CaCl<sub>2</sub> vs. IL:  $p = 0.045$ ). Nevertheless, it  
441 cannot replace pseudototal quantification (CaCl<sub>2</sub> vs. AR:  $p = 0.076$ ), and is not suitable for the  
442 determination of Au and elements with low extractable capacity, such as As and U, and/or less mobile  
443 elements, such as Ti.

444  
445 The on-site HNO<sub>3</sub> results were correlated with the AR (HNO<sub>3</sub> vs AR:  $p = 0.037$ ). Strong similarities of  
446 high values were shown for Cd, Ce, Pb and U (**Figures 3 and 4**). For Cd, the concentrations extracted  
447 using HNO<sub>3</sub> or AR were very similar. This suggests that HNO<sub>3</sub> extraction can closely estimate the  
448 pseudototal amount of the target element (Adriano, 2001) for values higher than 0.02 mg.kg<sup>-1</sup> (which  
449 represents the LOQ of Cd for HNO<sub>3</sub>) and/or when pseudototal Cd concentrations correspond mainly  
450 to mobile Cd. REEs, Pb and U were also highly extracted by HNO<sub>3</sub>, which was expected, given that  
451 they are normally lightly adsorbed onto the organomineral complexes of soil and that they are  
452 geochemically reactive elements in soil (Groenenberg *et al.* 2017). Land *et al.* (1999) showed that  
453 suspended particulate matter in stream water draining Swedish podzol was enriched in light-REEs  
454 such as Ce and La, which migrated with the help of organic matter. Our results also confirm that a  
455 significant portion of these light REEs are available. For Co, the correlation observed between HNO<sub>3</sub>  
456 and AR (**Figure 5**) was mainly due to the anomalous quantity at site 10 (**Figure 1**). Additional sampling  
457 sites are needed to determine the correlation between these two methods. The extractions of other  
458 elements, such as As, Cr, Fe, Ga, Ni, Ti and Zn, by HNO<sub>3</sub> and AR were different. Extractions by HNO<sub>3</sub>  
459 highlighted the correlation of Fe-Mn with Ti, V, Ni and Cd, and to lesser extend with Co and Pb (**Figure**  
460 **5**). These elements are then related to one or more Fe mineral sources.



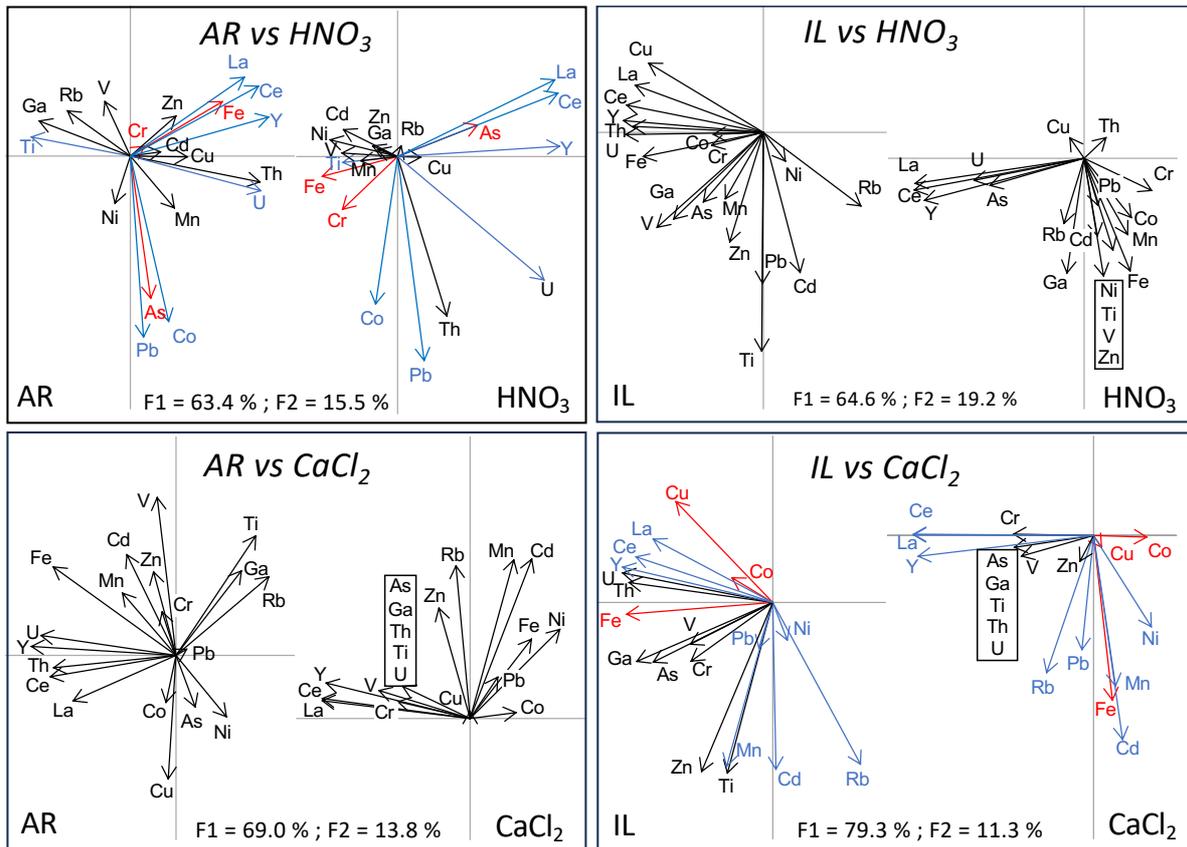
461

462 **Figure 4.** Box and whisker plots for cobalt (Co), cerium (Ce), lead (Pb) and uranium (U) after CaCl<sub>2</sub> and HNO<sub>3</sub>  
 463 extractions in the field and Ionic Leach (IL) and aqua regia (AR).

464 The Y-axis was normalized to the reduced centred values (z) for each extraction method, calculated as  $z = (\bar{x} - \mu) / \sigma$  where  $\bar{x}$  is the mean of  
 465 each point and  $\mu$  and  $\sigma$  are the mean and the standard deviation of the 14 sampling sites, respectively.  
 466

467 In contrast, extractions by HNO<sub>3</sub> not correlated with IL (HNO<sub>3</sub> vs. IL:  $p = 0.063$ ), although there were  
 468 some similarities between the two extractions for mobile elements such as Cd, U and REEs (Ce, La,  
 469 Nd, and Y). Similarities were also observed for Co (sites 1, 10 and 14), Cu (sites 5, 7, 19 and 12), Mn  
 470 (site 11), and Ti (site 3) after HNO<sub>3</sub> and IL extraction.

471 It appeared that when higher values were detected with AR and confirmed by IL, HNO<sub>3</sub> extraction fit  
 472 well with both extractants (such as Ce, Co, La, Pb, U and Y). HNO<sub>3</sub> is a promising environmentally  
 473 friendly leach for the detection of anomalous concentrations of some elements with higher



474

475 **Figure 5.** Comparison between elements extracted in the field by  $\text{CaCl}_2$  and  $\text{HNO}_3$  and in the laboratory by Ionic Leach (IL) and aqua regia (AR).  
476

477 The figures plot the variables (elements) in a common space by coupling two PCAs with a coinertia analysis. The blue arrows indicate that the element concentrations are positively correlated with the two extraction methods, while the red arrows indicate that the concentrations diverge between the two extraction methods (either negative correlation or no correlation).  
478  
479  
480

481 extraction efficiencies than those of ILs and  $\text{CaCl}_2$ . As a partial extractant it also clearly improves the  
482 signal of anomalies in comparison to a nonselective leacher such as AR (Cameron et al., 2004; Mann,  
483 2010). However, Au, which is the strategic element associated with Rajapalot, could not be quantified  
484 by the  $\text{HNO}_3$  solution because its concentration was too low to be detected with ICP-MS (LOQ 0.13  
485  $\text{mg.kg}^{-1}$ ; this value was two times greater than the highest value observed by AR extraction). In this  
486 case, pathfinders of Au such as Co and Pb must be used.

487 AR and IL remain the best extractants for the anomalous detection of Au, since they were not  
488 quantified with ICP-MS after  $\text{CaCl}_2$  and  $\text{HNO}_3$  extractions due to their comparatively high LOQs.  
489 Consequently, analytical methods with lower LOQs, such as electrochemical stripping techniques,  
490 could improve the detection of element anomalies when detecting these environmentally friendly  
491 reactants.

492

493

494 **Conclusions**

495 Field soil extractions using CaCl<sub>2</sub> and HNO<sub>3</sub> performed on fresh soil samples gave similar results to  
496 those from the standard protocol used in the laboratory, except for Fe and Zn. Both methods are thus  
497 promising for on-site extraction of most mobile and reactive REEs and trace elements. Elements such  
498 as Au, Sn and W, which are too strongly adsorbed on mineral soil particles, and/or occur at too low  
499 concentrations, were not quantifiable by these methods. To solve this limitation, optimization must  
500 be performed to lower the LOQ of ICP-MS analyses for both methods, or to use voltammetric  
501 techniques that have a very low detection limit (ng.l<sup>-1</sup>). Within the context of deep penetrating  
502 geochemistry, the detection of pathfinder elements for Au mineralization, such as Co, could be  
503 achieved with CaCl<sub>2</sub> and HNO<sub>3</sub> extractants. Both CaCl<sub>2</sub> and HNO<sub>3</sub> were also effective for the detection  
504 of REEs (especially Ce and La in this study) and trace elements, including Cd, Mn and Ni by CaCl<sub>2</sub> and  
505 Cd, Co, Pb and U by HNO<sub>3</sub>. Using these two types of extractants with electrochemical stripping  
506 techniques could offer a promising perspective for direct on-site trace element and REE  
507 quantification for the detection of concealed mineralization.

508

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517

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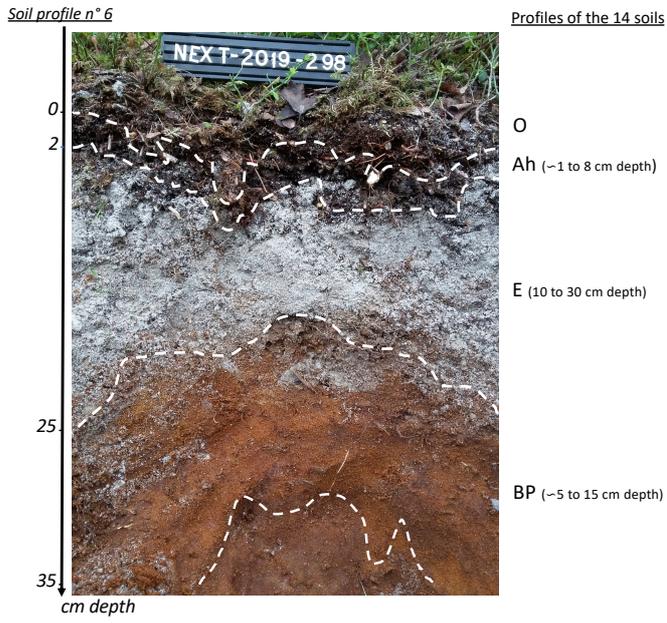
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697 **Supplementary data**

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699 **Supp. Data 1.** Typical soil profile at the study site



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**Supp. Data 2.** List of elements analysed with ICP-MS after CaCl<sub>2</sub>, HNO<sub>3</sub>, aqua regia (AR) and ionic leaches (IL). Green and red indicate the elements that are and are not quantified by ICP/MS, respectively. The numbers are related to the limits of detection for AR and IL and the limits of quantification for CaCl<sub>2</sub> and HNO<sub>3</sub>

	AR	IL	HNO <sub>3</sub> FIELD	CaCl <sub>2</sub> FIELD	HNO <sub>3</sub> LAB	CaCl <sub>2</sub> LAB
	ALS CANADA		ALS Praha			
	mg.kg <sup>-1</sup>	µg.kg <sup>-1</sup>	µg.l <sup>-1</sup>	µg.l <sup>-1</sup>	µg.l <sup>-1</sup>	µg.l <sup>-1</sup>
Ag	0.001	0.1	100	20	100	20
Al	10		200	40	200	40
As	0.01	0.5	20	4	20	4
Au	0.0002	0.02	10	2	10	2
Ba	0.5	10	20	4	20	4
Be	0.01	0.2	20	4	20	4
Bi	0.0005	0.3	100	20	100	20
Ca	10	200			200	40
Cd	0.001	0.2	2	0.4	2	0.4
Ce	0.003	0.1	10	2	10	2
Co	0.001	0.3	5	1	5	1
Cr	0.1	1	20	4	20	4
Cs	0.005	0.1	10	2	10	2
Cu	0.01	1	100	20	100	20
Dy		0.1	5	1	5	1
Er		0.1	5	1	5	1
Eu		0.1	5	1	5	1
Fe	1	100	200	40	200	40
Ga	0.004	0.5	100	20	100	20
Gd		0.1	5	1	5	1
Ge	0.005	0.1	100	20		
Hf	0.002	0.05	100	20	100	20
Hg	0.004	0.1				
Ho		0.1	5	1	5	1
In	0.005	0.1	100	20		
Ir			50	10	50	10
K	10	10				
La	0.002	0.1	50	10	50	10
Li	0.1	0.2	100	20	100	20
Lu		0.1	50	10	50	10
Mg	10	10			200	40
Mn	0.1	10	10	2	10	2
Mo	0.01	0.5	100	20	100	20
Na	1	1				
Nb	0.002	0.1	100	20	100	20
Nd		0.1	50	10	50	10
Ni	0.004	1	20	4	20	4
P	1	1				
Pb	0.005	0.1	5	1	5	1
Pd	0.001	0.05	50	10	50	10
Pr		0.1	50	10	50	10
Pt	0.002	0.1	50	10	50	10
Rb	0.005	0.1	50	10	50	10
Re	0.0002	0.01	100	20		
Rh			50	10	50	10
Ru			50	10	50	10
S	10	10				
Sb	0.005	0.5	5	1	5	1
Sc	0.005	1	100	20	100	20
Se	0.003	2	20	4	20	4
Sm		0.1	50	10	50	10
Sn	0.01	0.2	100	20	100	20
Sr	0.01	1	50	10	50	10
Ta	0.005	0.05	100	20	100	20
Tb		0.1	50	10	50	10
Te	0.003	0.5	50	10	50	10
Th	0.002	0.02	10	2	10	2
Ti	1	0.05	100	20	100	20
Tl	0.001		50	10	50	10
Tm		0.1	50	10	50	10
U	0.005	0.05	10	2	10	2
V	0.1	0.2	5	1	5	1
W	0.001	0.1	100	20	100	20
Y	0.003	0.1	50	10	50	10
Yb		0.1	50	10	50	10
Zn	0.01	10	200	40	200	40
Zr	0.01	0.1	100	20	100	20

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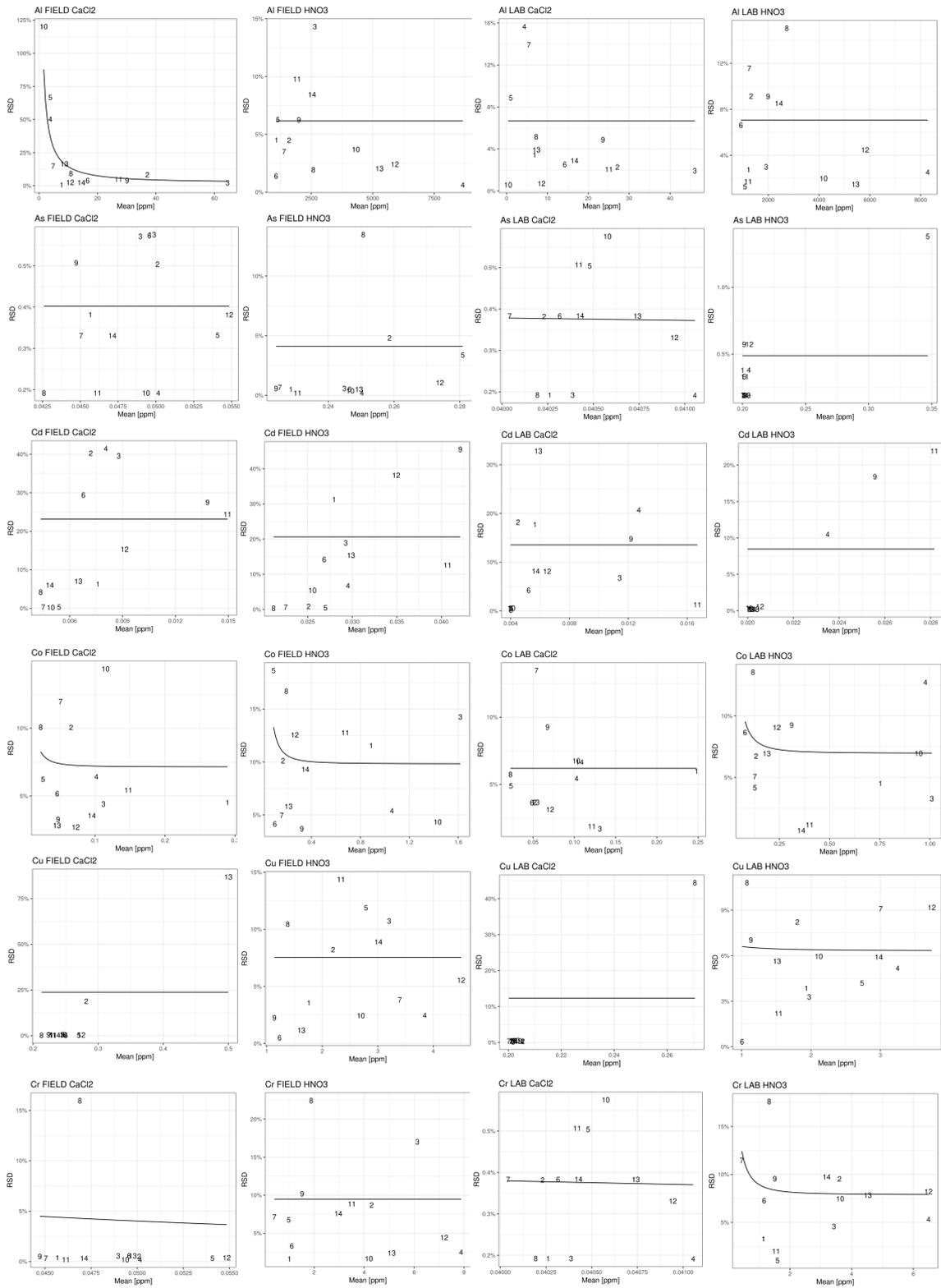
**Supp. Data 3.** Table of element concentration data after CaCl<sub>2</sub> and HNO<sub>3</sub> extractions in the field and in the laboratory  
<https://doi.org/10.24396/ORDAR-138>

Supp. Data 4

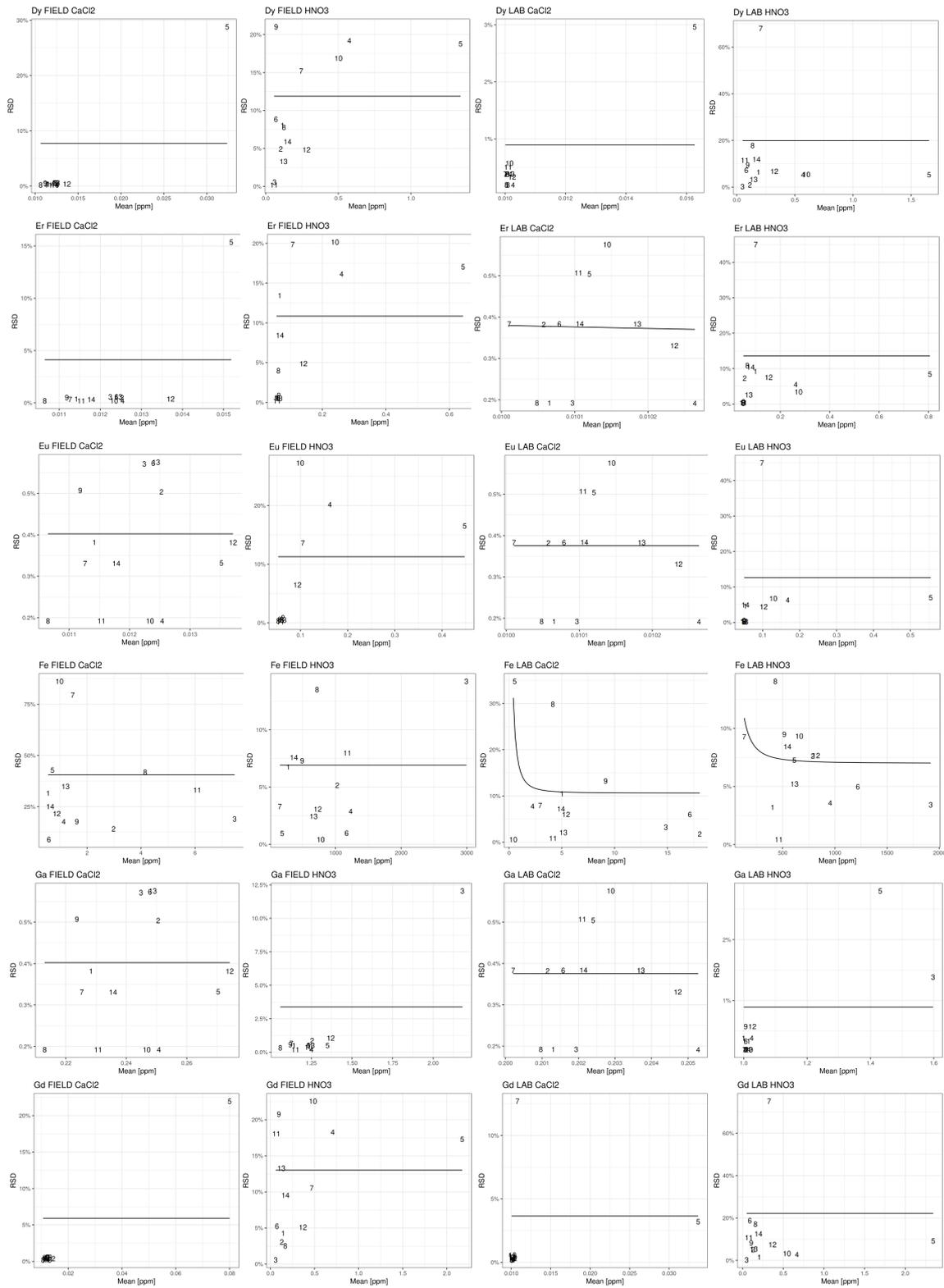
Treatment Site	Al	Fe	Ti	As	Cd	Co	Cr	Cu	Ga	Mn	Ni	Pb	Rb	Th	U	V	Zn	Ce	Dy	Er	Eu	Gd	Ho	La	Nd	Pr	Sm	Y	Yb	Ca	Mg	Sb	Sc		
																																		LAB	
FIELD	1	3.68	5.52	6.28	0.41	25.54	9.44	1.33	2.91	0.41	8.19	14.25	5.29	0.41	0.41	6.79	0.41	3.98	6.58	10.98	0.41	3.50	0.41	3.46	3.42	0.41	0.41	0.41	2.70	12.58	0.31	0.31			
	2	3.65	4.21	4.56	3.93	0.72	8.27	7.11	6.72	0.72	16.13	47.72	7.17	0.72	0.72	5.68	15.08	0.51	4.02	0.72	0.72	2.50	0.72	2.19	0.66	0.72	0.72	0.72	0.47	0.47	0.47	0.47			
	3	11.69	11.61	11.84	0.47	15.47	11.64	13.89	8.76	9.84	8.63	1.60	8.07	12.72	0.47	0.47	12.60	6.53	0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.47			
	4	0.50	2.35	1.40	0.16	0.16	5.53	4.41	2.06	2.02	0.16	6.07	6.07	0.16	4.20	6.66	2.06	1.72	13.55	15.67	13.19	16.47	14.93	13.04	14.70	10.24	15.32	15.26	18.48	0.47	0.47	0.47	0.47		
	5	1.12	0.79	6.32	2.77	0.41	15.22	5.53	9.71	0.41	14.77	36.76	6.04	0.41	0.41	1.77	10.15	36.62	18.13	15.35	13.93	13.50	14.13	13.89	13.73	16.53	16.60	13.93	18.26	0.47	0.47	0.47	0.47		
	6	5.13	0.80	9.25	0.41	11.60	3.99	2.73	0.41	0.41	1.19	2.26	0.77	0.41	0.41	0.41	4.36	10.42	7.85	7.23	0.41	4.28	0.41	0.41	0.41	0.41	0.41	0.41	0.41	0.41	0.41	0.41	0.41		
	7	2.87	2.70	4.80	0.54	0.54	4.05	5.84	3.13	0.54	38.86	11.90	8.11	0.54	0.54	0.54	1.14	0.54	7.56	12.42	16.22	11.12	8.61	0.54	10.91	7.18	7.86	0.54	16.19	0.47	0.47	0.47	0.47		
	8	1.57	11.03	13.08	11.00	0.27	13.63	18.31	8.54	0.27	10.66	29.29	8.80	10.88	0.27	0.27	9.69	79.04	4.16	6.36	3.26	0.27	2.06	0.27	2.06	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27		
	9	5.10	5.96	7.04	0.47	37.14	3.01	8.24	1.84	0.47	7.71	19.38	3.65	0.47	0.47	0.47	6.56	54.02	16.77	17.16	0.47	16.96	0.47	5.56	0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.47	
	10	3.02	0.34	2.61	0.31	4.46	3.54	1.37	2.00	0.31	18.82	8.55	1.88	0.31	3.45	2.65	2.65	20.70	15.99	13.79	16.46	22.24	18.42	14.28	17.19	14.43	0.31	0.31	11.20	0.47	0.47	0.47	0.47		
	11	7.98	6.51	2.57	0.16	10.29	10.42	7.24	11.73	0.16	10.65	17.52	9.22	3.53	0.16	0.16	8.76	29.53	4.93	0.16	0.16	0.16	14.76	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16		
	12	1.96	2.50	5.38	0.87	31.17	10.26	3.64	4.53	0.87	2.13	8.00	4.89	0.87	0.87	4.13	2.40	6.77	4.06	3.95	3.98	5.29	4.16	0.87	4.09	5.44	0.87	0.87	7.58	0.47	0.47	0.47	0.47		
	13	1.66	2.00	2.88	0.41	12.59	4.75	1.98	0.96	0.41	4.52	5.31	1.22	0.41	0.41	1.20	26.22	4.75	2.69	0.41	0.41	10.84	0.41	0.41	0.41	0.41	0.41	0.41	0.41	0.41	0.41	0.41	0.41		
	14	6.89	6.19	7.58	0.00	0.00	7.61	6.21	7.27	0.00	7.61	7.12	3.10	0.00	0.00	0.00	7.12	25.44	10.26	4.81	6.88	0.00	7.80	0.00	11.09	8.64	0.00	0.00	2.41	0.41	0.41	0.41	0.41		
FIELD	1	0.51	25.84	0.31	0.31	5.16	3.69	0.31	0.31	14.40	2.74	0.31	0.31	0.31	0.31	0.31	0.31	4.10	0.31	0.31	0.31	0.31	0.31	0.31	0.31	0.31	0.31	0.31	0.31	0.31	0.31	0.31			
	2	6.78	11.57	0.41	0.41	32.86	8.22	0.41	15.38	0.41	6.89	11.10	0.41	0.41	0.41	0.41	0.41	7.92	0.41	0.41	0.41	0.41	0.41	0.41	0.41	0.41	0.41	0.41	0.41	0.41	0.41	0.41	0.41		
	3	1.77	15.48	0.47	0.47	32.29	3.61	0.47	0.47	0.47	7.16	3.27	2.18	1.51	0.47	0.47	0.47	3.64	0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.47		
	4	41.03	14.47	0.16	0.16	33.84	5.25	0.16	0.16	0.16	9.55	4.43	0.16	0.16	0.16	0.16	21.04	13.77	10.85	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16		
	5	54.47	35.02	0.27	0.27	5.10	0.27	5.10	0.27	0.27	15.53	0.27	0.27	0.27	0.27	0.27	10.34	57.82	23.53	23.52	12.55	0.27	17.95	0.27	27.17	18.20	19.30	0.27	25.20	0.47	0.47	0.47	0.47		
	6	3.23	7.29	0.47	0.47	24.00	4.23	0.47	0.47	0.47	2.03	8.80	0.47	0.47	0.47	0.47	5.00	51.97	0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.47		
	7	12.16	64.92	0.27	0.27	0.27	9.78	0.27	0.27	0.27	22.73	8.11	0.27	0.27	0.27	0.27	0.27	1.10	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27		
	8	7.52	34.21	0.16	0.16	3.42	8.24	13.04	0.16	0.16	18.06	8.11	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16		
	9	3.23	14.48	0.41	0.41	22.46	2.67	0.41	0.41	0.41	2.40	8.05	0.41	0.41	0.41	0.41	0.41	2.72	4.36	0.41	0.41	0.41	0.41	0.41	0.41	0.41	0.41	0.41	0.41	0.41	0.41	0.41	0.41	0.41	
	10	38.07	70.34	0.16	0.16	0.16	11.74	0.16	0.16	0.16	0.16	21.35	24.41	0.16	0.16	0.16	5.24	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16		
	11	4.02	27.08	0.16	0.16	19.92	4.45	0.16	0.16	0.16	6.49	5.70	0.16	0.16	0.16	0.16	18.20	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16		
	12	2.05	17.62	0.31	0.31	12.51	2.20	0.31	0.31	0.31	0.31	28.49	2.49	0.31	0.31	0.31	0.31	26.27	7.26	0.31	0.31	0.31	0.31	0.31	0.31	0.31	0.31	0.31	0.31	0.31	0.31	0.31	0.31		
	13	13.51	28.48	0.47	0.47	5.74	2.31	0.47	0.47	0.47	70.94	0.47	11.31	56.87	0.47	0.47	0.47	2.68	0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.47		
	14	1.97	20.45	0.27	0.27	4.90	2.91	0.27	0.27	0.27	23.27	2.78	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27		
LAB	1	2.26	2.62	6.79	0.31	0.31	3.70	2.69	0.31	0.31	7.11	2.78	2.23	0.31	0.31	0.31	0.31	0.31	0.31	0.31	0.31	0.31	0.31	0.31	0.31	0.31	0.31	0.31	0.31	0.31	0.31	0.31			
	2	7.47	6.23	7.21	0.16	0.16	5.50	7.78	6.71	0.16	8.80	6.04	6.66	0.16	0.16	0.16	1.10	1.53	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16			
	3	2.45	2.80	3.04	0.16	0.16	2.68	3.74	2.69	1.13	1.16	2.47	1.26	0.16	0.16	0.16	2.82	5.95	15.49	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16		
	4	2.07	2.93	3.99	0.31	0.31	8.58	10.39	4.36	4.23	0.31	15.32	33.05	4.69	0.31	0.31	3.28	2.68	10.36	4.81	4.33	4.48	5.16	2.31	5.83	5.26	2.85	4.50	4.20	3.44	0.31	0.31			
	5	1.05	5.94	4.23	1.13	0.00	3.42	0.84	3.43	2.29	5.26	0.00	6.26	0.00	5.34	3.37	2.60	10.67	7.30	4.39	6.89	5.76	7.52	6.33	7.10	6.85	6.52	7.77	6.35	5.45	13.48	1.49	6.73	0.00	
	6	5.41	4.07	3.77	0.27	0.27	7.08	5.94	0.27	0.27	2.88	17.32	5.68	0.27	0.27	0.27	5.73	8.08	12.16	5.92	0.27	0.27	12.74	10.97	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	
	7	9.45	7.59	6.91	0.16	0.16	4.15	9.36	7.43	0.16	7.50	7.28	2.17	0.16	0.16	0.16	8.98	18.92	70.75	55.51	36.75	36.69	61.31	3.99	62.65	58.84	31.04	11.84	38.52	0.16	3.56	8.64	1.13	0.16	
	8	12.29	11.47	10.72	0.16	0.16	11.06	14.37	8.82	0.16	13.61	15.10	16.20	0.16	0.16	0.16	10.99	69.65	9.38	14.56	8.89	0.16	13.99	0.16	8.78	15.09	0.16	0.16	12.69	0.16	14.27	12.83	0.16	0.16	
	9	7.45	7.76	8.30	0.47	15.05	7.55	7.80	5.74	0.47	7.89	6.00	6.13	0.47	0.47	0.47	11.27	33.32	7.73	7.73	0.49	0.47	6.75	0.47	1.47	0.28	0.47	0.47	0.47	0.47	0.47	0.47	0.47		
	10	1.62	7.63	6.62	0.16	0.16	5.68	6.11	4.86	0.16	12.52	7.33	4.89	0.16	0.16	0.16	6.22	7.61	23.51	2.42	4.45	2.80	5.53	2.65	2.86	1.87	2.71	0.16	0.16	1.47	0.16	10.44	2.70	0.16	0.16
	11	1.41	0.36	1.54	0.27	17.92	0.96	1.63	1.80	0.27																									

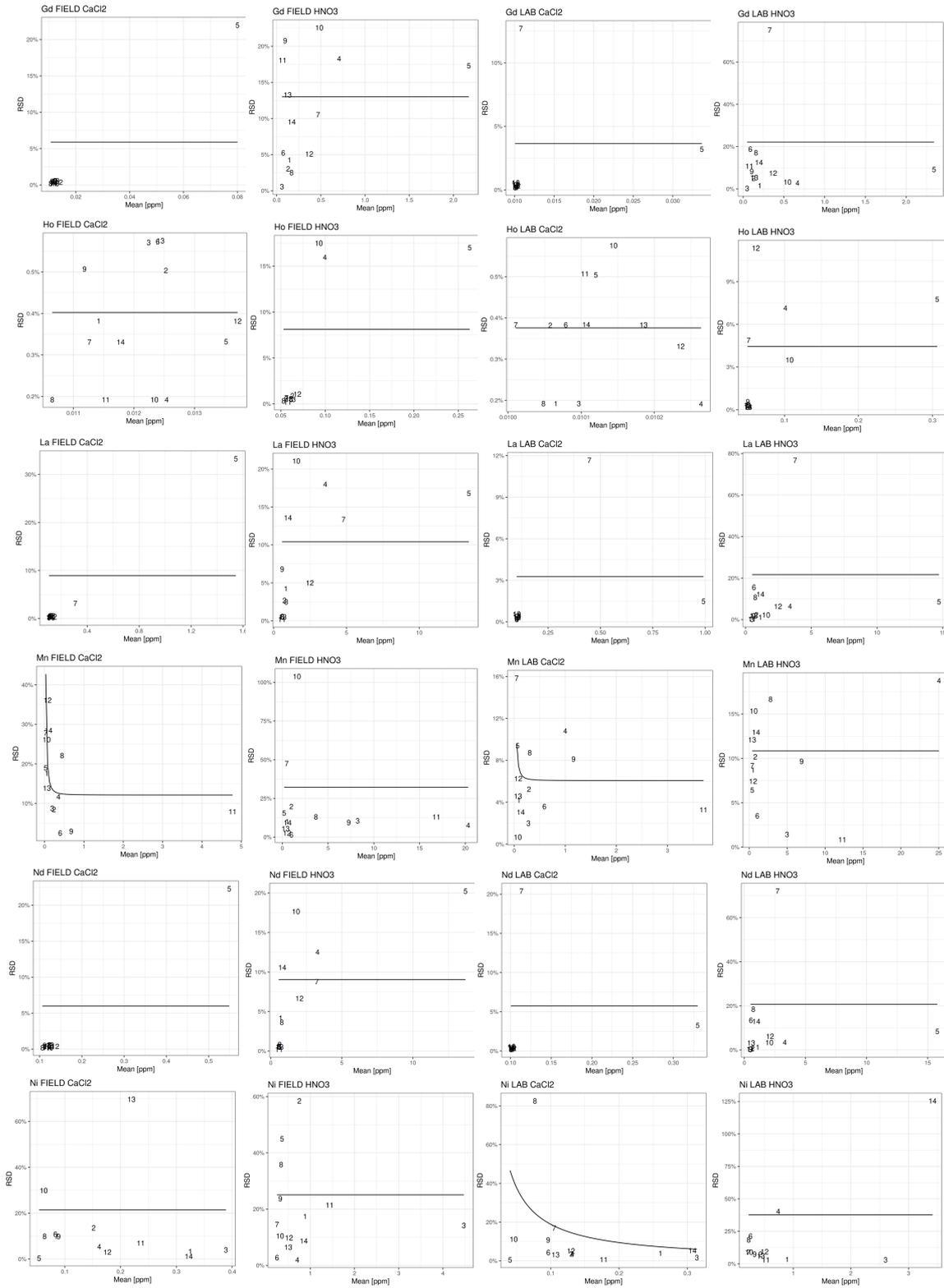
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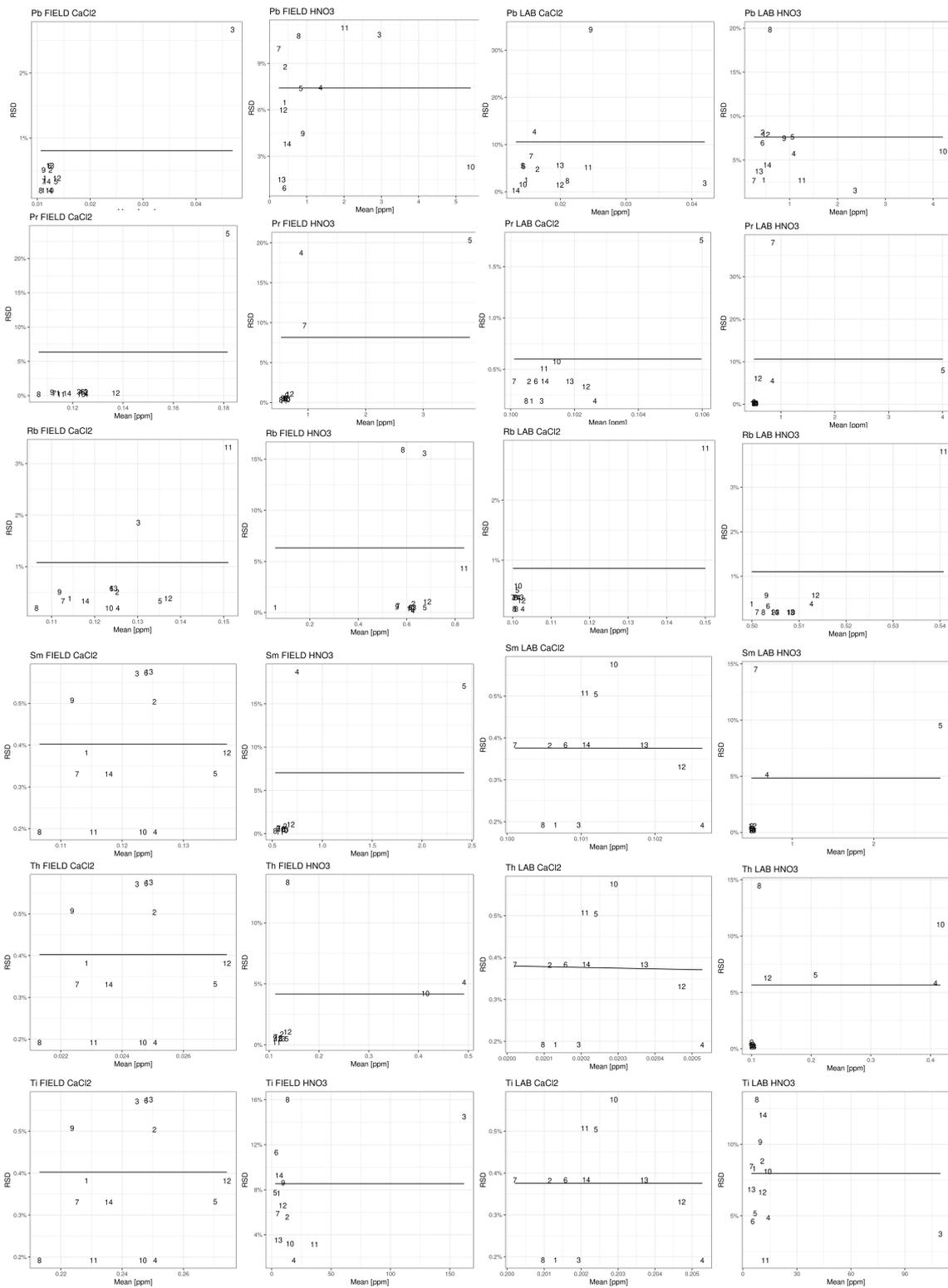
**Supp. Data 4.** Percentage of relative standard deviation (%RSD) of element concentrations after HNO<sub>3</sub> and CaCl<sub>2</sub> extractions in the field and in the laboratory.  
The estimation of the %RSD for each element had been calculated based on the EURACHEM / Guideline EURACHEM / CITAC Guide CG4 (Ellison & William, 2012)

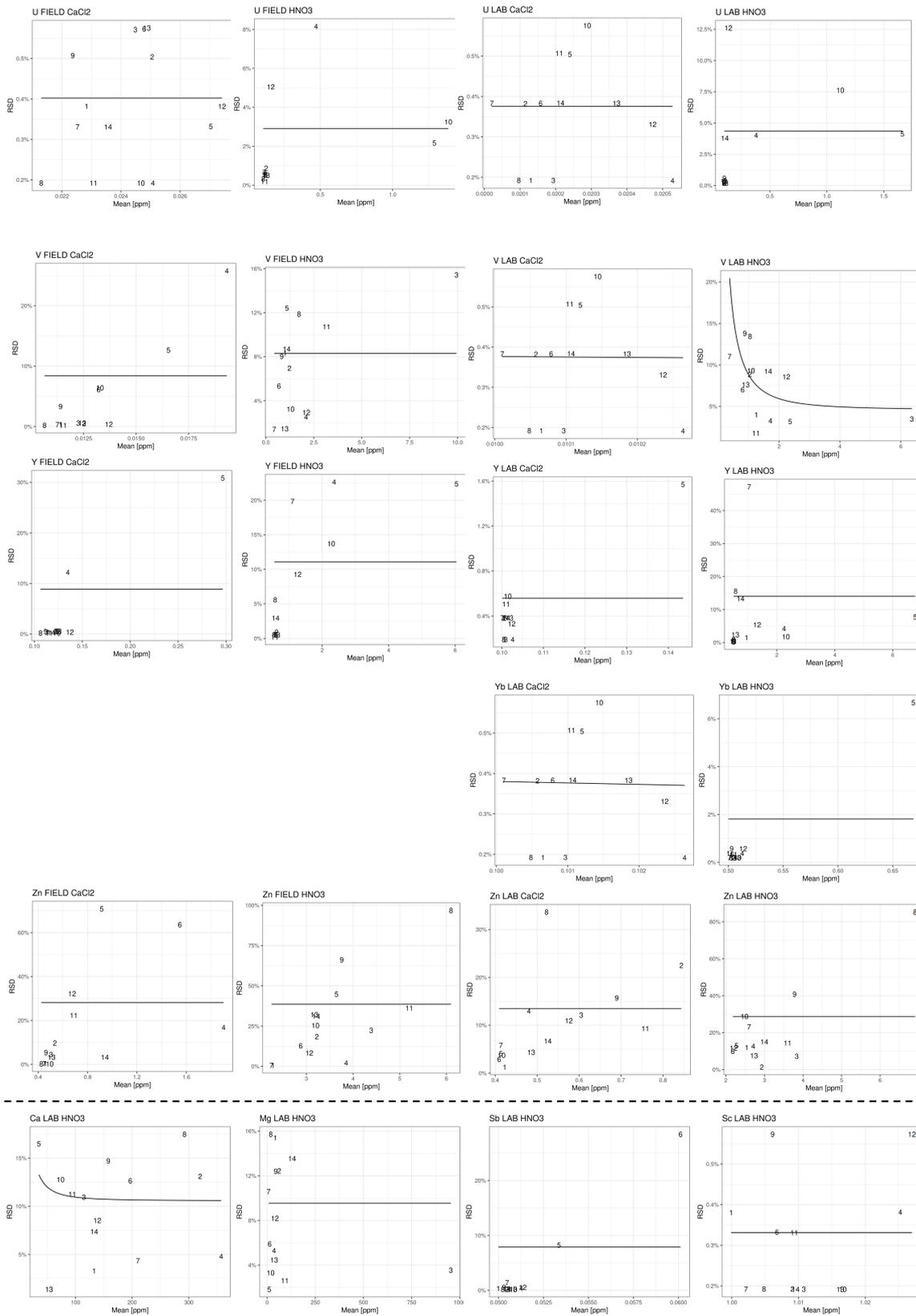


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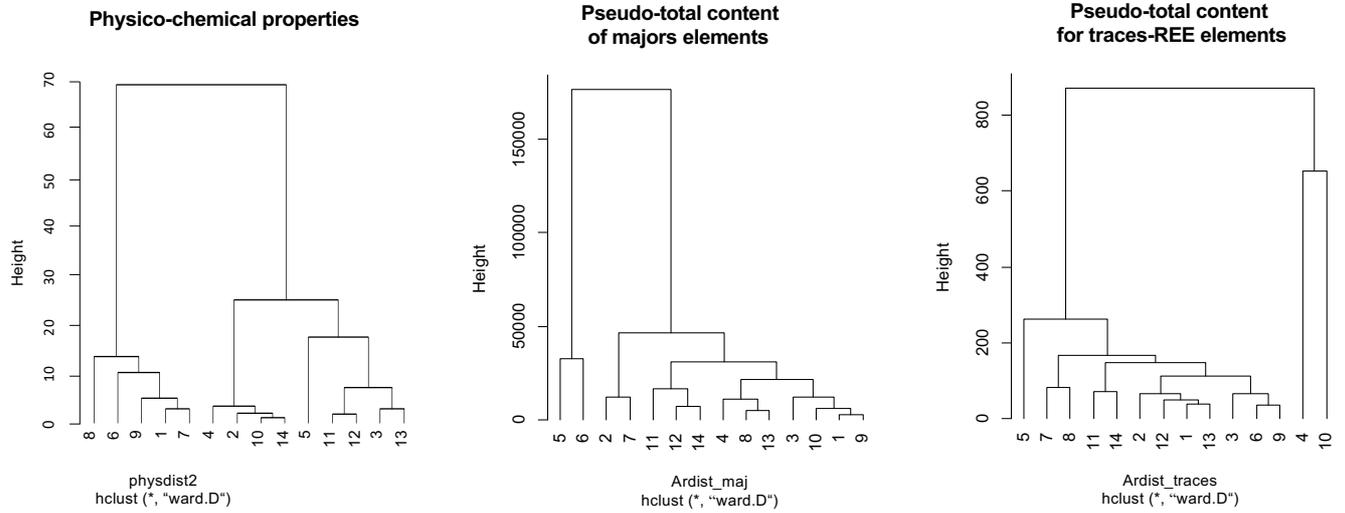


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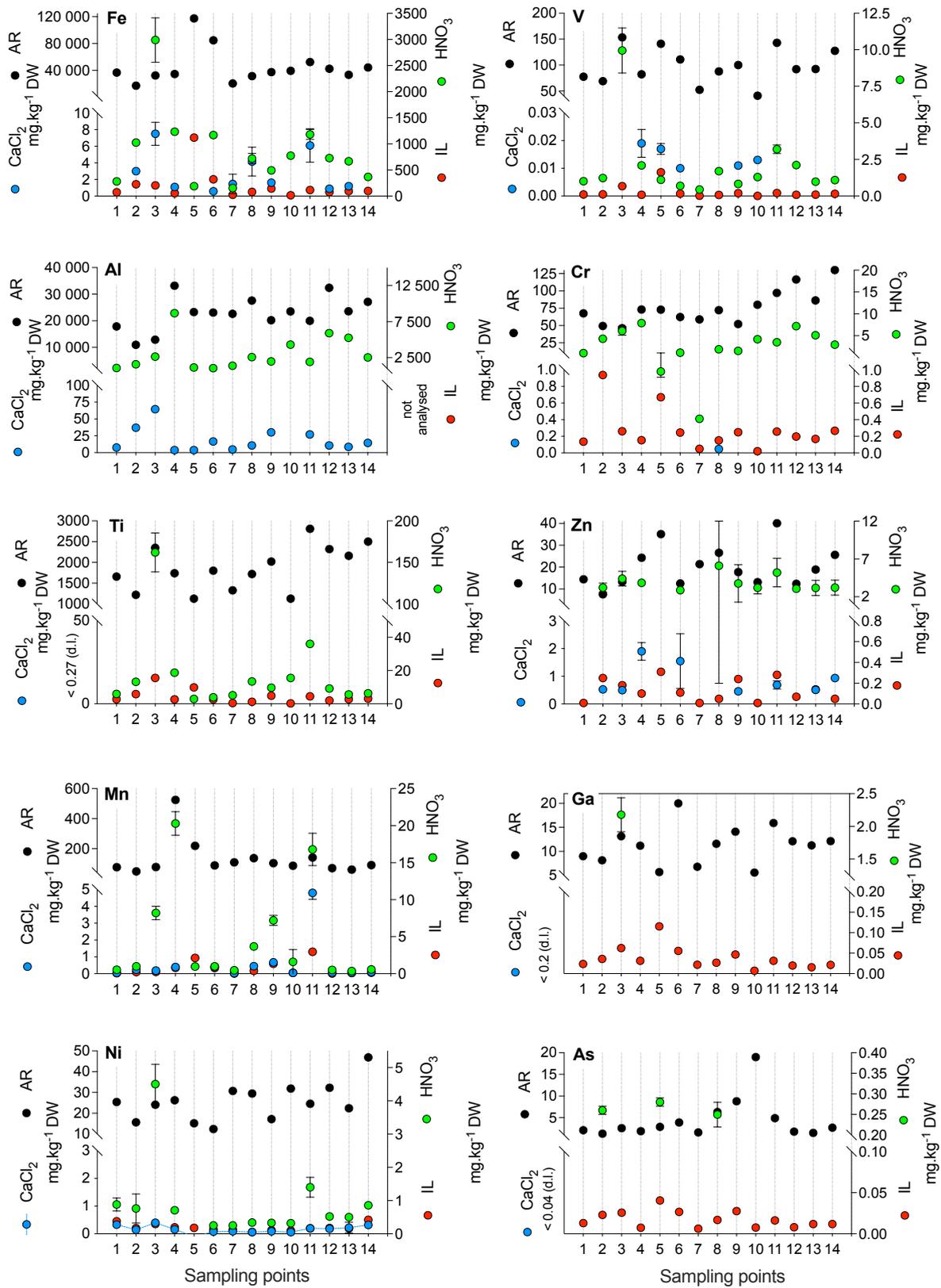
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**Supp. Data 6.** Dendrograms showing the relationships between the fourteen B-horizon soil samples and the physicochemical properties (CEC, TOC, pHw, and F<200 μm), pseudototal content (estimated using AR digestion) of the major elements (Al, Ca, Fe, Mg, Na, P, S and Ti) and trace-REE concentrations. The dendrograms were generated using the Mantel test in R-studio.



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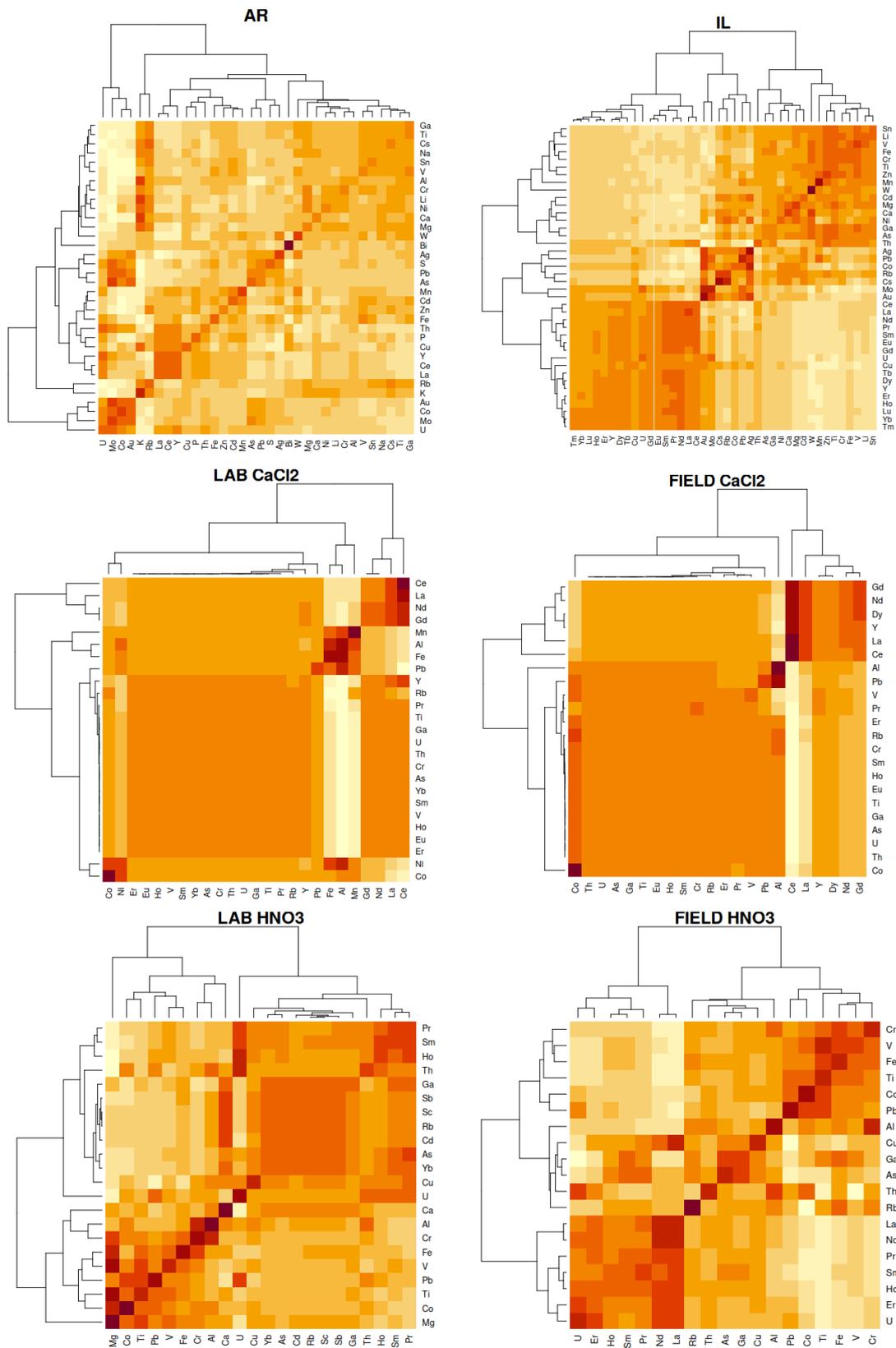
739 **Supp. Data 7.** Concentrations of major elements (Al, Fe and Ti) and trace elements (As, Cr, Ga, Mn, Ni, V  
 740 and Zn) in different Finish B-horizon soil samples measured in extractant solutions of 0.43 M HNO<sub>3</sub> (in  
 741 green), 0.01 M CaCl<sub>2</sub> (in blue), aqua regia (AR, in black), and ionic leach (IL, in red).



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**Supp. Data 8.** Relationship between elements using log-ratio variance of their concentrations after aqua regia (AR), Ionic Leach (IL), FIELD and laboratory (LAB) HNO<sub>3</sub> and CaCl<sub>2</sub> extractions.



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