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1       **INTERACTIONS OF ACIDIC SOIL NEAR COPPER MINING AND SMELTING**  
2                   **COMPLEX AND WASTE-DERIVED ALKALINE ADDITIVES**

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15  
16  
17       **Abstract**

18       Liming is a common practice in the treatment of acidic and metal contaminated soils, aiming  
19       at pH regulation, enhancing of the nutrient availability and attenuation of trace metals  
20       mobility. Replacement of natural limestone with alternative soil alkalizers found among  
21       waste materials represents a step towards sustainable resource management and reduced  
22       waste storage. In this study, waste seashells (SW) and red mud (RM) were applied in  
23       different doses to the soil sampled in the vicinity of mining and smelting complex. The soil  
24       was characterized by acidic reaction (pH 4.93), increased Cu concentration (219.2 mg/kg)  
25       and a very low level of P-supply (3.61 mg P<sub>2</sub>O<sub>5</sub>/100g). The study aimed to quantify and  
26       compare additive-induced effects onto soil physicochemical properties, the status of

27 macronutrients and distribution of trace metals. Targeted effect on soil pH was achieved with  
28 SW dose of 0.3% and RM dose of 2%. RM was found to be a source of available P and gave  
29 rise to the available P concentrations in the soil. Medium level of P-supply (15.60 mg  
30 P<sub>2</sub>O<sub>5</sub>/100g) was achieved with RM dose of 5%, however, the increase in soil salinity and total  
31 trace elements concentrations have become significant adverse effects at such dose. The  
32 decrease in the ion-exchangeable content of Cu and other trace metals was in correlation with  
33 the increase in soil pH after the treatments. Redistribution of metal cations was mainly  
34 directed to carbonate/acid soluble and Fe, Mn-oxide bonded fraction after SW addition. Even  
35 though trace metals concentration has increased in the soil after application of the RM, they  
36 were principally found in the residual fraction. The results emphasize low amounts of  
37 contained trace elements and lower doses for achieving targeted effects on pH and metal  
38 mobility as the main benefits of SW treatments. On the other hand, moderate and controlled  
39 use of RM may represent multiple benefits in terms of simultaneous pH regulation, P-supply,  
40 and reduced trace metals mobility.

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43 **Keywords:** Acidic soil; Remediation; Waste recycling; Red mud; Seashell waste

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## 52 **1. Introduction**

53 In addition to the content of organic matter, pH is designated as the most frequently  
54 used soil quality indicator with direct and indirect effects onto chemical and biological  
55 processes associated with soil fertility (Bünemann et al., 2018). Factors including parent  
56 material, climate, vegetation, soil management, and human activities, determine whether the  
57 soil has a neutral, acidic, or alkaline reaction. Most favorable pH values for individual plant  
58 nutrient elements fluctuate in the ranges: 6-8 for N, 6.5-7.5 for P, >6 for K and S, 7-8.5 for  
59 Ca and Mg, <6 for Fe, 5-6.5 for Mn, and 5-7 for Cu and Zn (Goulding, 2016). As a result,  
60 acidic soils exhibit limited availability of P, deficiency of basic essential cations (Ca and  
61 Mg), increased solubility and toxicity of most harmful elements (Pb, Cd, etc.), and reduced  
62 activity of soil organisms (Bolan et al., 2003).

63 Liming is universal management practice aiming at pH regulation, reducing solubility  
64 and phytotoxicity of Al and Mn, increasing the solubilization of soil P as well as enhancing  
65 the rate of organic matter decomposition and the resulting release of associated nutrients  
66 (Adriano, 2001). Simultaneously, liming provides conditions for improved natural attenuation  
67 of toxic metals availability and leaching, by increasing the negative surface charge of soil  
68 constituents with amphoteric surface groups, by the formation of strongly-bound hydroxy  
69 metal species, and by the precipitation of metals as hydroxides (Bolan et al., 2003).

70 Alternative materials are increasingly considered to reduce the exploitation of natural  
71 limestone reserves. In that sense, the utilization of alkaline waste materials and by-products  
72 represents a step forward towards sustainable resource management and contributes to  
73 reduced waste storage and associated issues.

74 The seashell material attracts attention due to high calcium-carbonate content, low-  
75 cost, and availability provided by the fast developing seafood industry (Barros et al., 2009).  
76 Application of mussel shells to acidic soil increased pH and content of exchangeable Ca,

77 decreased exchangeable Al, and had a positive effect on dry matter yield and concentration of  
78 Ca in the plant (Álvarez et al., 2012). Addition of seashell waste was found effective in  
79 reducing Cu concentrations available to plants in Cu-polluted vineyard soil (Fernández-  
80 Calviño et al., 2017), and decreasing bioavailability of Pb in an army firing range soil  
81 (Ahmad et al., 2014).

82 Furthermore, a range of industrial by-products such as fly ash, mining residues,  
83 incinerator waste, and metallurgical slag are investigated as potential soil additives due to the  
84 alkaline reaction and favorable mineralogical composition (O'Day and Vlassopoulos, 2010).  
85 Notably, research into the possibility of using red mud (bauxite processing residue) as an  
86 alkaline additive to soil has been intensified after accident in Ajka alumina plant (Hungary) in  
87 2010 (Ruyters et al., 2011) caused by collapsing of the dam of the red mud reservoir and  
88 spilling of the accumulated red mud/water mixture (pH~12). The results of worldwide  
89 conducted laboratory and field studies on the red mud application to soil were recently  
90 reviewed (Hua et al., 2017). Overall, the red mud application contributed to lowering the  
91 availability of potentially toxic elements in contaminated soil, which was linked to high pH  
92 of the waste, as well as with Fe and Al oxide/oxyhydroxide content involved in  
93 metals/metalloids immobilization.

94 Results on waste materials applicability in soil management strongly point to the need  
95 of detailed site-specific testing and risk assessment, in particular, the risks associated with the  
96 potential leaching of waste material sourced hazardous constituent (Cornelis et al., 2008), and  
97 should be designed to encompass the effects on overall soil properties.

98 In the present study, waste-derived alkaline materials were investigated as additives  
99 for improving the quality of acidic soil. In central Serbia, acidic soils dominate over 60% of  
100 the total arable land, due to the composition of the parent substrate, climate, vegetation and  
101 anthropogenic impacts (Ličina et al., 2011). Adverse human impact on the ecosystem as a

102 whole, including the quality of the soil, is predominantly evidenced near mining and  
103 metallurgical complex located in the town of Bor (SEPA, 2017). The economy of the region  
104 is based on mining and ore processing activities, and to the present day, water, air, and soil  
105 around the mining and smelting complex are exposed to pollution by toxic metals and acid  
106 oxides of sulfur. Toxic metals reach the soil through the discharge of wastewater,  
107 precipitation of aerosol particles, and depletion from the tailings. The soil near the flotation  
108 pool was found to be heavily contaminated with Cu, Fe and As, with an average content of  
109 1585.6, 29462.5 and 171.7 mg/kg, respectively (Antonijević et al., 2012). Furthermore, the  
110 elevated concentrations of toxic metals, especially Cu, were determined in the soil samples  
111 collected in the broader area of the mining and metallurgical complex (SEPA, 2017).

112 Although Cu is a part of enzymes involved in metabolic processes and represents an  
113 essential element in the human diet, continuous exposure to Cu in food causes gastrointestinal  
114 distress, compromise the immune and neurological systems as well as the reproductive ability  
115 (ATSDR, 2004). At the European level, Cu accumulation in the soil is mainly attributed to  
116 the anthropogenic origin (mining and industrial activities and agricultural use of products  
117 containing Cu), with agricultural land most affected in France, Italy, Portugal and Romania  
118 (Tóth et al., 2016). Consequently, the measures to improve soil and crop quality are needed.

119 The principal aims of the study were to assess and compare the performance of waste  
120 materials in the amelioration of the acidic and contaminated soil near copper mining and  
121 smelting complex. Seashell waste and red mud were selected as alkaline materials with  
122 substantially different chemical and mineralogical composition. The soil and the additives  
123 were properly characterized, mixtures with varying proportions of additives were prepared  
124 and the changes in soil physicochemical properties, the total concentration of potentially  
125 toxic elements and distribution of metals, were analyzed after an aging period of two months.

126 Both favorable and adverse effects onto soil characteristics were identified, and the prospects  
127 of practical use of additives were discussed.

128

## 129 **2. Materials and methods**

### 130 ***2.1. Collection and preparation of soil additives***

131 The material denoted SW was a composite sample of seashell waste collected at the  
132 North Greek Aegean Sea coast (Egerić et al., 2018). Free of flesh shells were washed with  
133 hot water to remove soluble impurities as well as the sand particles, dried at 50°C, ground in  
134 a laboratory ball mill and sieved to a particle size fraction <0.2 mm. Both the X-ray  
135 diffraction (XRD) and the Fourier transform infrared (FT-IR) spectroscopy have confirmed  
136 that calcium-carbonate in the form of aragonite polymorph was the single mineralogical  
137 constituent of SW (Egerić et al., 2018).

138 The red mud (RM) collected from Zvornik Alumina Refinery (Republic of Srpska,  
139 BiH) was thoroughly washed with tap water, to eliminate free alkalinity and sodium content  
140 coming from bauxite ore processing reagent (NaOH). The washing was conducted by adding  
141 fresh portions of water to red mud, mixing, settling, and decanting. The process was stopped  
142 when the pH of the supernatant became steady at ~9, and the RM was left to dry at room  
143 temperature. The investigated sample was composed mainly of Fe<sub>2</sub>O<sub>3</sub> (44%), Al<sub>2</sub>O<sub>3</sub> (18%),  
144 SiO<sub>2</sub> (12%), Na<sub>2</sub>O (8%), TiO<sub>2</sub> (4.70%) and CaO (3%), while hematite, gibbsite, bayerite,  
145 sodalite, rutile, anatase, quartz, and calcite were identified by XRD analysis as the main  
146 crystalline phases (Smiljanić et al., 2010).

147

### 148 ***2.2. Characteristics of the sampling site, soil sampling, and preparation***

149 The sample of the agricultural soil (denoted S) was taken in October 2016 near the  
150 town of Bor and the village of Slatina (44° 01' 31.2" N, 22° 11' 00.2" E). A sample of about

151 30 kg was taken from the surface to a depth of 20 cm and transported in plastic containers.  
152 Remnants of plant material and fine stones were removed from the sample, and the soil was  
153 dried on the filter paper sheets at room temperature for two weeks. The soil was crushed in a  
154 mortar, homogenized and passed through a sieve with apertures of 2 mm.

155

### 156 **2.3. Preparation of soil/additive mixtures**

157 The influence of the type and the quantity (% w/w) of added waste material on soil  
158 properties was examined by mixing the powdered additives with previously dried and  
159 homogenized soil. Considering the chemical composition of SW and the recommended doses  
160 for agricultural limestone application in clay loam soils ([Benton Jones, 2012](#)), the effect of  
161 SW has been tested at the dose of 6 t/ha or 0.15% (sample SW0.15). Generally, 3–6 t/ha was  
162 found to be the effectiveness threshold of liming rate, regardless of environmental and  
163 experimental conditions ([Li et al., 2019](#)). Additionally, given that the investigated soil was  
164 non-carbonate and that recommended quantities of CaCO<sub>3</sub> imply a periodic repetition of the  
165 treatment, higher doses of 0.3%, 2%, and 5% were also considered (samples SW0.3, SW2,  
166 and SW5) to determine the effects of larger quantities added at once. As there are no  
167 recommended doses for the application of industrial sludge in the soil, red mud was tested at  
168 doses of 0.3%, 2%, and 5% (samples RM0.3, RM2, and RM5). Precisely weighed masses of  
169 soil and sorbents were dry mixed and homogenized on a rotary shaker for 2 hours to achieve  
170 uniform distribution and subsequently transferred to the pots. The experiments have been  
171 carried out in triplicates. Only distilled water was periodically added to the pots to maintain  
172 approximately 60% of the soil water-holding capacity. The two-months incubation time was  
173 selected as adequate for the evaluation of the performance of both waste materials, based on  
174 previous studies that showed most prominent pH changes in respect to the control soil within  
175 35-70 days after application of calcitic additive ([Jones and Mallarino, 2018](#)), and shorter time



176 (e.g. 10 days) in which soil pH becomes steady after the addition of the red mud (Friesl et al.,  
177 2004).

178

#### 179 ***2.4. Characterization of the soil, additives and their mixtures***

180 For the physicochemical characterization, the soil, the additives, and their mixtures  
181 were dried in air. The pH(H<sub>2</sub>O) was determined in deionized water by InoLab WTW pH  
182 meter, according to the US EPA 9045D method (US EPA, 2004) for soil and waste pH  
183 measurement (solid-to-solution ratio of 1:2). Furthermore, the electrical conductivity of clear  
184 supernatants (EC1:2) was measured using the conductivity meter InoLab Cond 7110.  
185 Ammonium acetate method was applied for the determination of the soil cation exchange  
186 capacity (CEC) (Sumner and Miller, 1996). Available amounts of P and K were determined  
187 by ammonium acetate lactate (AL) method (Enger and Riehm, 1958). The contents of total  
188 carbon, nitrogen, and sulfur were determined using a CHNOS elemental analyzer (Vario EL  
189 III - Elementar Analysensysteme GmbH, Hanau, Germany), following dry burning of the  
190 samples at 1150°C (Nelson and Sommers, 1996). The Scheibler calcimeter method was used  
191 for the determination of CaCO<sub>3</sub> content, while the organic carbon content (C<sub>organic</sub>) was  
192 obtained as a difference between the total and the inorganic carbon. The particle size  
193 distribution was determined with a combined method of sieving and a pipette method -  
194 modified International “B” method (Gee and Or, 2002), and the texture of the soil was  
195 evaluated according to the United States Department of Agriculture (USDA) Textural  
196 Classification (NRCS Soils, 2018).

197 The total content of selected elements in the samples was extracted by microwave-  
198 assisted acid digestion method US EPA 3051A (US EPA, 2007). Association of the elements  
199 with various fractions in the soil and the effect of additives on their mobility was monitored  
200 by sequential extraction. Modified Tessier extraction protocol (Tessier et al., 1979) was

201 applied as a tool for assessment of the metal distribution. Namely, the first four fractions  
202 were extracted according to the original procedure (F1 – exchangeable, 8 mL of 1 mol/L  
203 MgCl<sub>2</sub>, pH=7, for 1 h; F2 – carbonate/acid soluble, 8 mL of 1 mol/L  
204 CH<sub>3</sub>COOH/CH<sub>3</sub>COONa, pH=5, for 5 h; F3 – bound to iron and manganese oxides/reducible  
205 phase, 20 mL of 0.04 mol/L NH<sub>2</sub>OH•HCl in 25% CH<sub>3</sub>COOH at 96±3°C for 6 h; F4 - bound  
206 to organic matter, 3 mL 0.02 mol/L HNO<sub>3</sub> and 5 mL 30% H<sub>2</sub>O<sub>2</sub> at 85°C for 2 h, addition of 3  
207 mL 30% H<sub>2</sub>O<sub>2</sub> at 85°C for 2 h, and finally 5 mL 3.2 mol/L CH<sub>3</sub>COONH<sub>4</sub> in 2% HNO<sub>3</sub>,  
208 dilution to 20 mL, 30 min), while the fifth fraction was separated from the F4 – step residue  
209 in the same way as the total content (F5 – residual fraction, 9 mL concentrated HNO<sub>3</sub> and 3  
210 mL concentrated HCl, microwave assisted acid digestion method USEPA 3051A ([US EPA,](#)  
211 [2007](#)).

212 Extractions were followed by phase separation using Thermo Scientific Heraeus  
213 Megafuge 16 (9000 rpm for 15 minutes) and membrane filters (0.45 µm). Clear supernatants  
214 were acidified if necessary and analyzed for metal concentrations using Inductively Coupled  
215 Plasma Optical Emission Spectrometry (ICP-OES). Thermo Scientific iCAP 6500 Duo ICP  
216 (Thermo Fisher Scientific, Cambridge, United Kingdom) spectrometer was equipped with  
217 RACID86 Charge Injector Device (CID) detector and iTEVA software. The radial view was  
218 chosen because of its high matrix tolerance. The Multi-Element Plasma Standard Solution 4,  
219 Specpure®, 1000 µg/ml (Alfa Aesar GmbH & Co KG, Germany) and SS-Low Level  
220 Elements ICV Stock (VHG Labs, Inc- Part of LGC Standards, Manchester, NH 03103 USA)  
221 were used to prepare calibration solutions for ICP-OES measurement. Quality control was  
222 carried out using blank samples, matrix-matched calibration solutions, and triplicate  
223 measurements (n=3) for each sample. The reliability of measurements was approved by  
224 relative standard deviation lower than 0.5%. The analytical process quality control performed  
225 by the use of the certified reference material EPA Method 200.7 LPC Solution (ULTRA

226 Scientific, USA) indicated that the resulting concentrations were within 97-104%. The  
227 concentrations of all investigated elements are presented on a dry matter basis.

228

## 229 **2.5. Statistical analysis**

230 The relationships between different physicochemical properties of the control and  
231 amended soil samples, as well as between the essential properties of soil samples and metal  
232 distribution patterns, were established using correlation analysis (CA). The Pearson's  
233 coefficients ( $r$ ) were calculated, and the data obtained at the level of significance  $\alpha=95\%$   
234 ( $p<0.05$ ) were discussed. Statistical analysis was performed using statistical software  
235 (MINITAB). Means of three replicates were subjected to one-way ANOVA, and the Fisher's  
236 least significant difference (LSD) test was chosen to identify the differences between  
237 properties of differently treated samples. The chosen confidence level was 95%.

238

## 239 **3. Results and discussion**

### 240 **3.1. Physicochemical properties of investigated soil and additives**

241 The physicochemical properties of the soil, additives, and their mixtures are  
242 summarized in [Table 1](#), [Table 2](#), and [Table 3](#).

243 The relative content of particles of various sizes in soil S ([Table 1](#)) indicates a clay  
244 loam texture. The soil was non-carbonate and exhibited an acidic reaction with water (pH  
245 4.93). The capacity of the cationic exchange (CEC) of 11.5  $\text{cmol}_c/\text{kg}$  was low concerning  
246 CEC values typical for clay loam soil (29-40  $\text{cmol}_c/\text{kg}$ ) ([Jones, 2001](#)), which could be due to  
247 the clay composition and soil acidity. Furthermore, the soil was non-saline, with electrical  
248 conductivity (EC) of 0.378 dS/m. The content of available phosphorus in the soil of 3.61 mg  
249  $\text{P}_2\text{O}_5/100\text{g}$  fits into the range of very low levels (0-6 mg/100g) ([Džamić and Stevanović,](#)  
250 [2000](#)), in agreement with the survey of the content of available P in central Serbia ([SEPA,](#)

251 2017). In the acidic soils, the amount of available phosphorus decreases due to its binding to  
 252 free  $Al^{3+}$  and  $Fe^{3+}$  ions or the positively charged surfaces of Al, Fe, and Mn hydroxides  
 253 (Bolan et al., 2003).

254

255 **Table 1.** The granulometric composition of the control and amended soil samples.

Sample	Granulometric composition (%)				Texture
	Coarse sand >0.2 mm	Fine sand 0.2-0.02 mm	Silt 0.02-0.002 mm	Clay <0.002 mm	
S	9.8±0.5 <sup>A</sup>	30.8±1.3 <sup>BC</sup>	25.6±0.9 <sup>B</sup>	33.8±2.2 <sup>AB</sup>	Clay loam
SW0.15	7.8±0.3 <sup>C</sup>	29.0±0.9 <sup>CDE</sup>	26.4±1.1 <sup>AB</sup>	36.8±2.8 <sup>A</sup>	Clay loam
SW0.3	9.0±0.5 <sup>AB</sup>	29.8±1.0 <sup>CDE</sup>	26.1±1.0 <sup>AB</sup>	35.1±2.3 <sup>AB</sup>	Clay loam
SW2	9.1±0.6 <sup>AB</sup>	32.5±1.2 <sup>AB</sup>	26.0±1.0 <sup>AB</sup>	32.4±1.8 <sup>B</sup>	Clay loam
SW5	7.9±0.4 <sup>C</sup>	33.0±1.4 <sup>A</sup>	25.7±0.7 <sup>B</sup>	33.4±2.5 <sup>AB</sup>	Clay loam
RM 0.3	9.5±0.7 <sup>AB</sup>	30.6±1.2 <sup>CD</sup>	26.0±0.9 <sup>AB</sup>	33.9±2.0 <sup>AB</sup>	Clay loam
RM2	9.1±0.5 <sup>AB</sup>	28.2±1.0 <sup>E</sup>	27.1±1.0 <sup>AB</sup>	35.6±2.6 <sup>AB</sup>	Clay loam
RM5	8.9±0.4 <sup>B</sup>	28.9±1.1 <sup>DE</sup>	27.6±1.2 <sup>A</sup>	34.6±2.1 <sup>AB</sup>	Clay loam

256 Data presented are mean of three replicates ± standard deviation (SD); Means that do not share a letter  
 257 are significantly different; Values with different letters in the same column indicate a significant  
 258 difference at  $p < 0.05$ .

259

260 In contrast, the availability of potassium in soil S (41.1 mg  $K_2O/100g$ ) was in the  
 261 range of very high levels, most probably as the result of intensive fertilization observed in a  
 262 large number of other soil samples under vegetable and fruit cultivation in central Serbia  
 263 (SEPA, 2017). Nitrogen amount in the soil was at the moderate level, the content of organic  
 264 carbon was medium (Džamić and Stevanović, 2000), and of sulfur was in the usual range  
 265 (Maynard, 1998). In overall, the acidic reaction of the soil and the unbalanced content of  
 266 macronutrients point to the poor soil management and the need for introducing corrective  
 267 measures.

268 **Table 2.** Chemical properties of the control soil and amended soil samples.

Sample	CaCO <sub>3</sub> (%)	CEC (cmol <sub>c</sub> /kg)	N (%)	C <sub>organic</sub> (%)	S (%)	P <sub>2</sub> O <sub>5</sub> (mg/100g)	K <sub>2</sub> O (mg/100g)	pH <sub>H2O</sub> 1:2	EC <sub>1:2</sub> dS/m
S	/ <sup>D</sup>	11.5±0.5 <sup>A</sup>	0.170±0.015 <sup>AB</sup>	1.48±0.06 <sup>E</sup>	0.059±0.002 <sup>E</sup>	3.61±0.09 <sup>F</sup>	41.1±1.5 <sup>B</sup>	4.93±0.07 <sup>F</sup>	0.378±0.011 <sup>G</sup>
SW0.15	0.42±0.02 <sup>C</sup>	11.9±0.8 <sup>A</sup>	0.176±0.009 <sup>A</sup>	1.61±0.07 <sup>CD</sup>	0.075±0.004 <sup>BC</sup>	2.88±0.08 <sup>G</sup>	42.1±1.2 <sup>AB</sup>	6.03±0.12 <sup>D</sup>	0.474±0.015 <sup>F</sup>
SW0.3	0.42±0.03 <sup>C</sup>	11.4±0.7 <sup>A</sup>	0.177±0.007 <sup>A</sup>	1.65±0.09 <sup>C</sup>	0.095±0.005 <sup>A</sup>	3.86±0.11 <sup>E</sup>	42.2±1.0 <sup>AB</sup>	6.35±0.15 <sup>C</sup>	0.547±0.046 <sup>E</sup>
SW2	2.52±0.11 <sup>B</sup>	11.6±0.4 <sup>A</sup>	0.173±0.010 <sup>AB</sup>	1.82±0.05 <sup>B</sup>	0.065±0.002 <sup>DE</sup>	5.30±0.13 <sup>D</sup>	42.6±0.9 <sup>AB</sup>	7.45±0.08 <sup>B</sup>	1.12±0.07 <sup>B</sup>
SW5	6.09±0.26 <sup>A</sup>	11.6±0.7 <sup>A</sup>	0.168±0.003 <sup>AB</sup>	2.28±0.11 <sup>A</sup>	0.089±0.003 <sup>A</sup>	5.40±0.19 <sup>D</sup>	43.1±1.4 <sup>A</sup>	7.65±0.14 <sup>A</sup>	0.901±0.030 <sup>C</sup>
RM0.3	/ <sup>D</sup>	12.2±0.6 <sup>A</sup>	0.175±0.010 <sup>AB</sup>	1.53±0.06 <sup>CDE</sup>	0.071±0.004 <sup>CD</sup>	5.91±0.22 <sup>C</sup>	43.4±0.8 <sup>A</sup>	5.16±0.10 <sup>E</sup>	0.477±0.05 <sup>EF</sup>
RM2	/ <sup>D</sup>	12.2±0.7 <sup>A</sup>	0.167±0.008 <sup>AB</sup>	1.52±0.08 <sup>DE</sup>	0.074±0.002 <sup>BC</sup>	7.15±0.30 <sup>B</sup>	42.4±1.3 <sup>AB</sup>	6.48±0.13 <sup>C</sup>	0.651±0.008 <sup>D</sup>
RM5	/ <sup>D</sup>	12.2±0.6 <sup>A</sup>	0.164±0.002 <sup>B</sup>	1.46±0.05 <sup>E</sup>	0.081±0.005 <sup>B</sup>	15.6±0.5 <sup>A</sup>	42.8±1.7 <sup>AB</sup>	7.50±0.14 <sup>AB</sup>	1.24±0.053 <sup>A</sup>

269 Data presented are mean of three replicates ± standard deviation (SD); Means that do not share a letter are significantly different; Values with different letters  
 270 in the same column indicate a significant difference at p<0.05.

271

272 **Table 3.** Chemical properties of the additives.

Additive properties	Soil additive	
	SW	RM
CaCO <sub>3</sub> (%)	95.8±1.2	3.78±0.16
CEC (cmol <sub>c</sub> /kg)	2.45±0.11	11.2±0.4 B
N (%)	0.045±0.008	0.004±0.000
C <sub>organic</sub> (%)	2.34±0.10	0.530±0.023
S (%)	0.058±0.002	0.161±0.008
P <sub>2</sub> O <sub>5</sub> (mg/100g)	7.46±0.15	74.1±1.2
K <sub>2</sub> O (mg/100g)	5.96±0.06	46.3±2.1
pH <sub>H2O</sub>	9.30±0.18	10.0±0.3
EC <sub>1:2</sub>	1.20±0.05	0.942±0.045

273 Data presented are mean of three replicates ± standard deviation (SD).

274

275 The properties of the additives differed between themselves and in comparison to the  
 276 examined soil (Table 3). The reaction of SW and RM with water was alkaline (pH 9.30 and  
 277 10.0, respectively). Carbonate content in RM was 3.78%, and even 95.8% in SW. The CEC  
 278 of RM was almost identical to the CEC of the soil (11.2 cmol<sub>c</sub>/kg), while SW exhibited  
 279 smaller CEC (2.45 cmol<sub>c</sub>/kg). The content of nitrogen in both SW and RM was lower  
 280 comparing to the soil content. The availability of K in RM (46.3 mg K<sub>2</sub>O/100g) was similar  
 281 to that in the soil and much higher concerning the value characteristic for SW. A relatively  
 282 high percentage of C<sub>organic</sub> was found in the SW (2.34%) in line with its biological origin,  
 283 while RM contained almost three times lower amount of organic C in relation to the soil. On  
 284 the other hand, RM had approximately three times more S than the soil, while variation in S  
 285 content was small when S and SW were compared. Both additives exhibited higher amounts  
 286 of available phosphorus in respect to the control soil, i.e., 7.46 mg P<sub>2</sub>O<sub>5</sub>/100g in SW and even  
 287 74.1 mg P<sub>2</sub>O<sub>5</sub>/100g in RM. Although the phosphate retention by red mud was studied  
 288 intensively (Liu et al., 2011), considerably less attention was paid onto content and

289 availability of phosphates in red mud itself. [Kolencsik-Tóth et al. \(2014\)](#) have found 0.55%  
290 of total  $P_2O_5$  in a sample collected from abandoned disposal site in Hungary.  
291 Correspondingly, 0.6% and 0.3% of  $P_2O_5$  was reported for the fine and coarse fraction of the  
292 samples supplied by Rusal Aughinish Alumina (Ireland) and 0.5% for Alteo Gardanne  
293 (France) residue ([Cusack et al., 2018](#)).

294

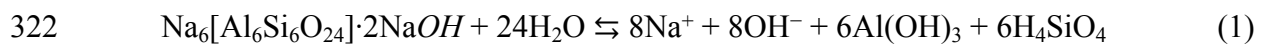
### 295 ***3.2. Physicochemical properties of amended soil samples***

296 The additives applied up to 5% w/w have provoked small fluctuations in the soil  
297 granulometric composition, without alteration of its original clay loam texture ([Table 1](#)).  
298 Given the particle size of SW used in the study, the fraction of fine sand increased with  
299 increasing doses of SW. Furthermore, as the majority of RM particles fall within the silt  
300 fraction ([Gangadhara Reddy and Hanumantha Rao, 2018](#)), the percentage of this fraction  
301 increased significantly in comparison to the control soil following the treatment with 5% of  
302 RM.

303 The relationship between the additive type, dose, and the resultant soil pH, points to  
304 their different capacities for pH regulation ([Table 2](#)). In each dose, the addition of SW was  
305 more effective. Steep pH increase up to 2% SW addition was followed by less pronounced  
306 but still significant pH change with the further rise in SW dose (pH 7.45 at 2% vs. pH 7.65 at  
307 5%). The change in carbonate content was significant after application of SW ([Table 2](#)).  
308 Addition of  $CaCO_3$  to an acidic soil leads to neutralization of free  $H^+$  ions and displacement  
309 of  $H^+$  ions attached to negatively charged mineral and organic constituents with  $Ca^{2+}$ .

310 The increase in RM amount has also provoked the significant rise in soil pH, bringing  
311 it to a favorable range after 2% and 5% addition. The lime equivalence for a variety of the red  
312 mud samples was reported to be up to 50%, at target pH 6 ([Snars et al., 2004](#)). The soil has  
313 remained non-carbonate after utilization of RM, which points to the role of other minerals

314 from RM assemblage in pH regulation. The primary buffering minerals in red mud are solids  
315 formed during the Bayer process, such as calcite, sodalite or cancrinite, containing  $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$ ,  
316  $\text{Na}^+$ ,  $\text{H}_3\text{SiO}_4^-/\text{H}_2\text{SiO}_4^{2-}$ ,  $\text{OH}^-$  and  $\text{CO}_3^{2-}$  ions (Gräfe et al., 2011). Desilication products  
317 (sodalites and cancrinites) play a particularly important role in the chemistry of bauxite  
318 residue. Considering the mineralogical composition of the RM (Smiljanić et al., 2010) and  
319 the fact that most of the free  $\text{OH}^-$  ions had been washed out during the pretreatment step,  
320 sodalite appears to be the chief pH regulator in the investigated RM, according to the reaction  
321 Eq. (1) (Gräfe et al., 2011):



323 CEC and N content in all pots have remained within the values characteristic for the  
324 control soil (Table 2). The content of S increased following all treatments, whereas the level  
325 of  $\text{C}_{\text{organic}}$  rose in the pots amended with SW. Furthermore, the increase in EC with the  
326 increasing rates of both additives was significant (Table 2). Changes in soil EC after red mud  
327 addition has been reported in different case studies, and the review of EC changes has  
328 revealed the maximum increase of over 400% after 2% red mud addition, compared with the  
329 control soil (Hua et al., 2017). In this study, the maximum increase of 330% was observed at  
330 5% RM addition. Furthermore, the effect of different red mud samples on soil EC was  
331 previously found much higher when compared to the impact of  $\text{CaCO}_3$  addition (Snars et al.,  
332 2004). Given that the increase in soil EC is generally associated with high Na content in  
333 soluble and exchangeable forms in red mud (Hua et al., 2017), the intensive washing of the  
334 RM sample turned out to be a useful pretreatment step. According to the guide to plant  
335 effects associated with different ranges of EC measured in 1:2 soil-water ratio (Dellavalle,  
336 1992), a majority of amended soil samples can be classified as very slightly saline (0.40-0.80  
337 dS/m) and moderately saline (0.81-1.20 dS/m). Nevertheless, after addition of 5% of RM, EC



338 reached the value in the range of saline soils (1.21-1.60 dS/m) and can be a factor that  
339 restricts the yield of salt-sensitive crops.

340         The observed increase in available P content was the most interesting feature, taking  
341 into account the original P-deficiency of the control soil (Table 2). Several factors that  
342 regulate the concentration of P in the soil solution may be influenced by pH increase. The  
343 proportion of readily adsorbed divalent phosphate ion ( $\text{HPO}_4^{2-}$ ) increases, but, at the same  
344 time, surface electrostatic potential becomes more negative and the anion exchange capacity  
345 of the soil decreases (Bolan et al., 2003). However, the precipitation of P as calcium  
346 phosphate may lead to increased P retention as the pH of the soil approaches 7. Available P  
347 increased from 3.61 mg  $\text{P}_2\text{O}_5/100\text{g}$  in the control sample to 5.40 mg  $\text{P}_2\text{O}_5/100\text{g}$  after  
348 application of the SW dose of 5%. The improved availability of P is in line with the previous  
349 study on Oyster-shell meal application to the acidic soil (Lee et al., 2008). Contrary, in the  
350 soil with rather high available concentrations of P (91.1 mg P/kg) the decreased availability  
351 was reported after treatments with calcined mussel shells which could be a result of calcium-  
352 phosphate precipitation (Álvarez et al., 2012). RM application improved the content of  
353 available P more efficiently than SW. The effect was proportional to the amount of RM  
354 added so that the medium level of supply (15.6 mg  $\text{P}_2\text{O}_5/100\text{g}$ ) was achieved at a dose of 5%.  
355 The effect corresponds with a high content of available P in the sample of RM. It can be  
356 assumed that available phosphate anions are associated with amorphous Fe- and Al-oxides in  
357 RM, based on the preferential association of the anions (such as arsenate) with amorphous  
358 oxide phase in the soil (Matera et al., 2003), and mineralogical composition of red mud with  
359 30% amorphous materials, on average (Gräfe et al., 2011). Al – P bonds were found to be the  
360 most labile form of P in the soil, that supplies the plants with P-nutrient (Saljnikov and  
361 Čakmak, 2011). Therefore, the existence of such bonds could explain the availability of P in  
362 RM and the enhanced availability of P in RM amended soil.

363 The correlation of essential soil physicochemical properties (Table S1), has revealed a  
364 significant ( $p < 0.05$ ) positive correlation between  $\text{CaCO}_3$  and  $\text{C}_{\text{organic}}$ . Furthermore, both  
365  $\text{CaCO}_3$  and  $\text{C}_{\text{organic}}$  were in positive correlation with the fraction of fine sand, which is an  
366 indication of their common source - SW. EC was in positive correlation with soil pH and  
367 available P. It is important to note that the association between available P and soil pH was  
368 not significant, while available P was positively correlated with the percentage of silt  
369 fraction. Such relationship points to the RM as a source of available P.

370

### 371 ***3.3. The total concentration of selected elements in the soil, the additives, and their mixtures***

372 The total concentration of different elements in the soil, the additives, and their  
373 mixtures are presented in Table 4 and Table 5.

374 Soil concentrations (Table 4) are compared with the values defined by the Finnish  
375 standard (MEF, 2007) (Table S2), considered as a good approximation of the mean values of  
376 different national systems in Europe and previously used to characterize the contamination  
377 statuses of European soils (Tóth et al., 2016). The “threshold value” is applicable for all sites  
378 and it indicates the need for further assessment of the area, whereas the so-called “guideline  
379 value” indicate a contamination level which presents ecological or health risks, if exceeded.  
380 The higher guideline values are set for industrial and transport areas, and the lower for all  
381 other land uses. In the control soil, the concentrations of As, Cd, Cr, Ni, Pb, Co, and Zn were  
382 below the threshold values. V concentration (131.1 mg/kg) exceeded the threshold; however,  
383 the lower guideline value was not reached. Furthermore, the level of V in soils around the  
384 world ranges from trace amounts to 400 mg/kg, with a mean of 150 mg/kg (Panichev et al.,  
385 2006). Finally, Cu concentration (219.2 mg/kg) exceeded even the higher guideline value,  
386 implying the significant environmental risk and disturbed soil functions which require the  
387 application of corrective measures.

**Table 4.** The total concentration of different elements in the control soil and amended soil samples.

Sample	Elements concentrations (mg/kg)							
	Al	As	Ca	Cd	Co	Cr	Cu	Fe
S	52710±2903 <sup>AB</sup>	1.073±0.043 <sup>DE</sup>	7006±378 <sup>C</sup>	0.524±0.028 <sup>CD</sup>	19.49±1.05 <sup>CD</sup>	30.03±1.70 <sup>CD</sup>	219.2±9.5 <sup>A (H)</sup>	42750±2056 <sup>D</sup>
SW0.15	52810±2903 <sup>AB</sup>	1.016±0.032 <sup>E</sup>	7157±386 <sup>C</sup>	0.598±0.032 <sup>B</sup>	19.82±0.97 <sup>C</sup>	27.26±1.18 <sup>DE</sup>	215.2±8.3 <sup>A (H)</sup>	42110±1828 <sup>D</sup>
SW0.3	51240±2822 <sup>B</sup>	1.047±0.042 <sup>E</sup>	7603±410 <sup>C</sup>	0.522±0.021 <sup>D</sup>	17.54±0.75 <sup>DE</sup>	21.60±0.94 <sup>F</sup>	213.4±10.7 <sup>A (H)</sup>	41810±1915 <sup>D</sup>
SW2	50170±2763 <sup>B</sup>	1.055±0.062 <sup>E</sup>	16046±865 <sup>B</sup>	0.546±0.028 <sup>BCD</sup>	17.49±1.21 <sup>DE</sup>	26.11±1.13 <sup>E</sup>	219.9±6.5 <sup>A (H)</sup>	42770±1357 <sup>D</sup>
SW5	51510±2837 <sup>B</sup>	1.150±0.046 <sup>D</sup>	31567±1702 <sup>A</sup>	0.528±0.018 <sup>CD</sup>	17.44±0.54 <sup>E</sup>	27.74±1.20 <sup>CDE</sup>	219.1±5.9 <sup>A (H)</sup>	41910±1119 <sup>D</sup>
RM0.3	52840±2910 <sup>AB</sup>	1.256±0.041 <sup>C</sup>	7133±385 <sup>C</sup>	0.542±0.020 <sup>CD</sup>	23.10±1.18 <sup>B (T)</sup>	30.88±1.34 <sup>C</sup>	221.3±9.6 <sup>A (H)</sup>	46560±2071 <sup>C</sup>
RM2	54310±2991 <sup>AB</sup>	1.347±0.054 <sup>B</sup>	7298±393 <sup>C</sup>	0.575±0.031 <sup>BC</sup>	24.59±1.33 <sup>B (T)</sup>	46.39±2.01 <sup>B</sup>	223.0±8.0 <sup>A (H)</sup>	51860±2251 <sup>B</sup>
RM5	56990±3139 <sup>A</sup>	1.845±0.074 <sup>A</sup>	7556±407 <sup>C</sup>	0.687±0.019 <sup>A</sup>	31.77±1.80 <sup>A (T)</sup>	88.21±3.83 <sup>A</sup>	223.0±10.8 <sup>A (H)</sup>	67290±2921 <sup>A</sup>
	K	Mg	Mn	Na	Ni	Pb	V	Zn
S	4645±202 <sup>A</sup>	6804±295 <sup>A</sup>	1070±46 <sup>BC</sup>	387.7±18.8 <sup>EF</sup>	19.80±1.06 <sup>C</sup>	27.56±1.52 <sup>C</sup>	131.1±5.7 <sup>C (T)</sup>	106.5±6.3 <sup>B</sup>
SW0.15	3367±156 <sup>C</sup>	6269±172 <sup>B</sup>	1113±58 <sup>B</sup>	317.5±11.2 <sup>F</sup>	19.77±0.68 <sup>C</sup>	25.28±1.10 <sup>D</sup>	126.9±3.5 <sup>C (T)</sup>	104.8±3.5 <sup>BC</sup>
SW0.3	3600±116 <sup>C</sup>	5961±229 <sup>BC</sup>	1027±34 <sup>C</sup>	371.9±16.1 <sup>EF</sup>	20.26±0.78 <sup>C</sup>	25.91±0.93 <sup>CD</sup>	110.5±6.8 <sup>D (T)</sup>	103.6±5.5 <sup>BCD</sup>
SW2	3501±152 <sup>C</sup>	6150±257 <sup>B</sup>	997.9±43.3 <sup>C</sup>	450.7±19.6 <sup>E</sup>	19.25±0.71 <sup>C</sup>	25.80±1.32 <sup>CD</sup>	125.2±4.4 <sup>C (T)</sup>	96.49±4.8 <sup>D</sup>
SW5	4078±147 <sup>B</sup>	6162±277 <sup>B</sup>	994.9±33.1 <sup>C</sup>	665.7±29.8 <sup>C</sup>	20.61±0.82 <sup>C</sup>	25.55±0.71 <sup>CD</sup>	130.1±5.6 <sup>C (T)</sup>	97.16±4.1 <sup>CD</sup>
RM0.3	3934±171 <sup>B</sup>	5555±211 <sup>CD</sup>	1287±56 <sup>A</sup>	555.1±22.1 <sup>D</sup>	21.30±1.02 <sup>C</sup>	26.83±1.06 <sup>CD</sup>	142.6±7.2 <sup>B (T)</sup>	102.7±5.2 <sup>BCD</sup>
RM2	3589±156 <sup>C</sup>	5484±198 <sup>D</sup>	1133±47 <sup>B</sup>	1224±75 <sup>B</sup>	42.70±1.45 <sup>B</sup>	31.32±1.66 <sup>B</sup>	126.1±6.5 <sup>C (T)</sup>	102.4±4.4 <sup>BCD</sup>
RM5	3955±201 <sup>B</sup>	5554±201 <sup>CD</sup>	1138±39 <sup>B</sup>	2975±159 <sup>A</sup>	61.31±2.26 <sup>A (T)</sup>	37.73±1.94 <sup>A</sup>	152.5±8.6 <sup>A (L)</sup>	116.1±6.0 <sup>A</sup>

389 Data presented are mean of three replicates ± standard deviation (SD); Means that do not share a letter are significantly different; Values with different letters  
390 in the same column indicate a significant difference at p<0.05; T, L, H - Concentrations that exceed threshold (T), lower (L) and higher (H) guideline values  
391 for metals in soils according to Finnish standard (MEF, 2007).

392 **Table 5.** The total concentration of different elements in additives.

Element	Soil additive	
	SW (mg/kg)	RM (mg/kg)
Al	8.240±0.454	84930±4678
As	<LOD	9.192±0.368
Ca	411000±22158	19730±1064
Cd	<LOD	2.61±0.14
Co	<LOD	187.8±6.1
Cr	1.181±0.051	812.6±35.3
Cu	1.291±0.056	65.52±2.84
Fe	43.22±1.88	411200±17849
K	86.87±3.77	461.2±20.9
Mg	198.4±10.6	1453±73
Mn	11.16±0.68	2784±121
Na	4484±195	41976±1822
Ni	0.192±0.008	554.8±24.1
Pb	<LOD	198.6±8.6
V	<LOD	644.3±28.0
Zn	1.430±0.042	201.8±7.8

393 Data presented are mean of three replicates ± standard deviation (SD);

394 LOD - Limit of detection (0.98 µ/L As, 0.028 µ/L Cd, 0.65 µ/L Co, 0.56 µ/L Pb, 0.18 µ/L V).

395

396 The chemical analysis has confirmed high Ca and Na contents in SW, whereas the  
 397 concentrations of other investigated elements were either below the detection limit or lower  
 398 than in the soil (Table 5). Quite the opposite, except for Cu, Mg, and K, concentrations of all  
 399 investigated RM constituents were notably higher than in the soil (Table 5). Based on the  
 400 published data, the concentrations of Cr and Zn in RM were higher in respect to mean  
 401 concentrations of these elements in red mud samples all over the globe (607 mg/kg Cr (22  
 402 samples) and 122 mg/kg Zn (38 samples)) (Hua et al., 2017). Furthermore, Ni content in RM  
 403 exceeded not only the mean concentration of 101 mg/kg (18 samples), but also the maximum  
 404 concentration (361 mg/kg) reported so far. Since the concentrations of toxic elements in the  
 405 industrial by-products indented for application in the soil are not prescribed by European

406 Directives, the results are compared with the Canadian Guidelines (GBN Canada, 2014).  
407 Industrial by-products are classified into Class A (land application allowed without further  
408 permits) and Class B (restricted land application allowed) based on their concentration (Table  
409 S2). The total content of Co and Ni in RM exceed the values prescribed for Class B materials  
410 for use in farmland. Therefore, RM use in agricultural land is likely to be omitted or strictly  
411 controlled concerning the starting composition and quantities that could be applied without  
412 compromising the quality and fertility of the soil.

413 Soil amending with SW has induced significantly increased levels of Ca at the doses  
414 of 2% and 5% and increased concentration of Na following 5% addition (Table 4). After  
415 application of RM, a significant increase in concentrations of several elements in the soil was  
416 detected (Table 4). At any RM dose, the levels of soil As, Co, Fe, Mn, Na, and V have  
417 increased. The increase in Cr, Ni, and Pb levels was significant at the doses of 2% and 5%,  
418 whereas Zn concentration increased only after adding 5% RM. Following the Finnish  
419 standard (Table S2), 5% RM induced the increase of Ni concentration over the threshold  
420 value, and V over the lower guideline value. Even though EU and Canadian regulations do  
421 not set the limit concentrations of V in soil additives, V is a frequent component of red mud  
422 samples worldwide (Hua et al., 2017), which could limit the use of red mud in agricultural  
423 soil. It is important to note that the soil amending did not affect the total Cu concentration.

424 The analysis of the correlation (Table S3) between soil properties (Table 2) and  
425 concentration of various elements (Table 4) disclosed significant ( $p < 0.05$ ) positive  
426 correlation of Ca content with  $\text{CaCO}_3$ ,  $C_{\text{organic}}$ , and fine sand, in agreement with SW addition.  
427 On the other hand, the positive correlation of the total content of Fe, Al, Cd, As, Co, Cr, Na,  
428 Ni, Pb and V with available P and with the silt fraction, confirmed RM is their common  
429 source.

430

### 431 **3.4. Metal distribution in unamended and amended soil samples**

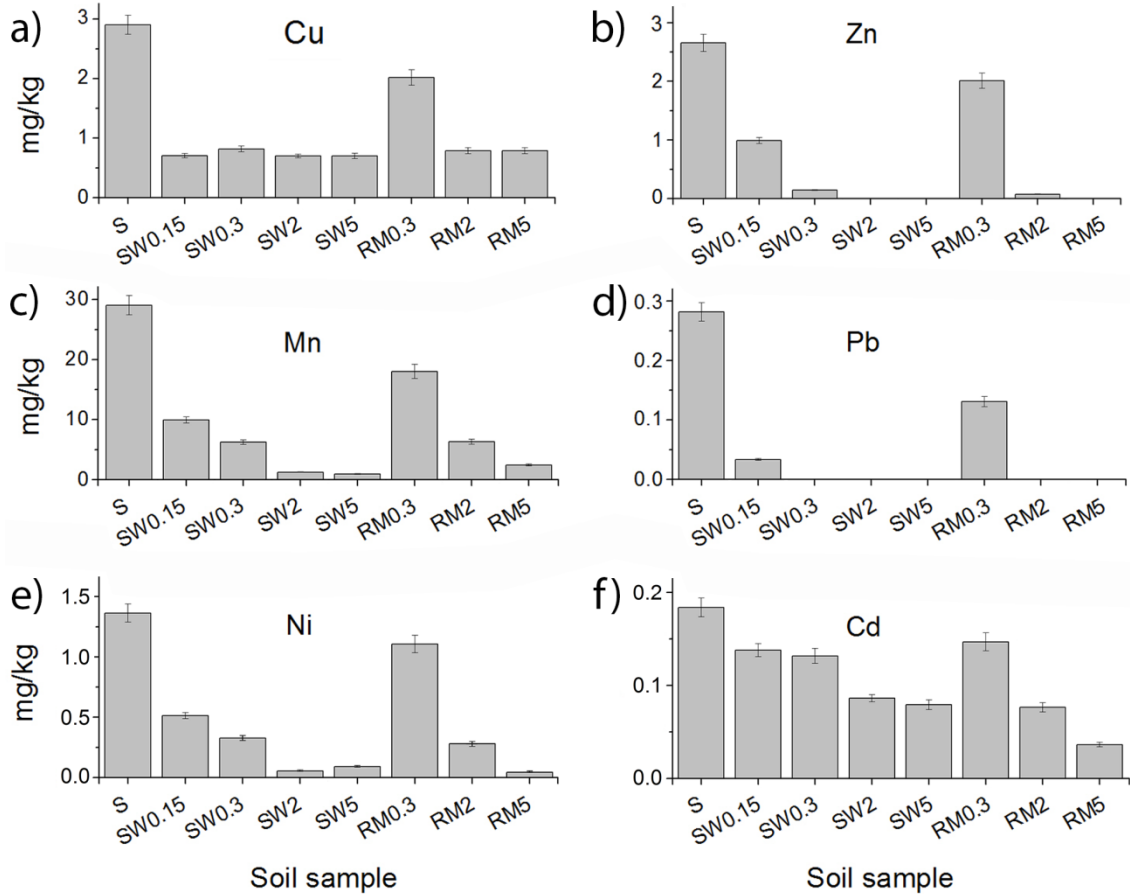
432 The environmental risks coming from trace metals in the soil does not necessarily rely  
433 on their total concentrations, but rather on their labile species or forms in both solution and  
434 solid phases (Hooda, 2010). Therefore, information obtained from the procedures which  
435 separate different chemical forms of metals is useful in terms of long-term risk assessment  
436 and for comparing the effectiveness of remediation methods. The significant differences  
437 ( $p < 0.05$ ) in metal distribution caused by treatments, are indicated in Table S4, whereas the  
438 results of correlation between soil physicochemical properties and metal distribution patterns  
439 are presented in Table S5.

440 The concentrations of metals in the exchangeable form (F1) are shown in Fig. 1. In  
441 the extract of control sample S, Mn was found in the highest concentration (29.05 mg/kg),  
442 which signifies its highest mobility. Below pH 6, the increase in Mn solubility and toxicity in  
443 plants is generally considered as one of the most significant adverse effects of soil  
444 acidification (Bolan et al., 2003). Despite the high level of Cu in the control soil (S), 2.90  
445 mg/g (1.3%) was found in the readily soluble form. The absolute concentration of other  
446 metals extracted from soil S decreased in the sequence  $Zn > Ni > Pb > Cd$ , whereas the  
447 concentrations of Fe and Co in F1 phase were below their limits of detection.

448 After all applied treatments, F1 content of Cu decreased significantly (Table S4).  
449 However, interestingly, differences between various treatments were not significant except  
450 for the sample RM0.3. On the other hand, the concentrations of Zn, Mn, Pb, Ni, and Cd were  
451 markedly reduced and commonly decreased with increasing additive doses.

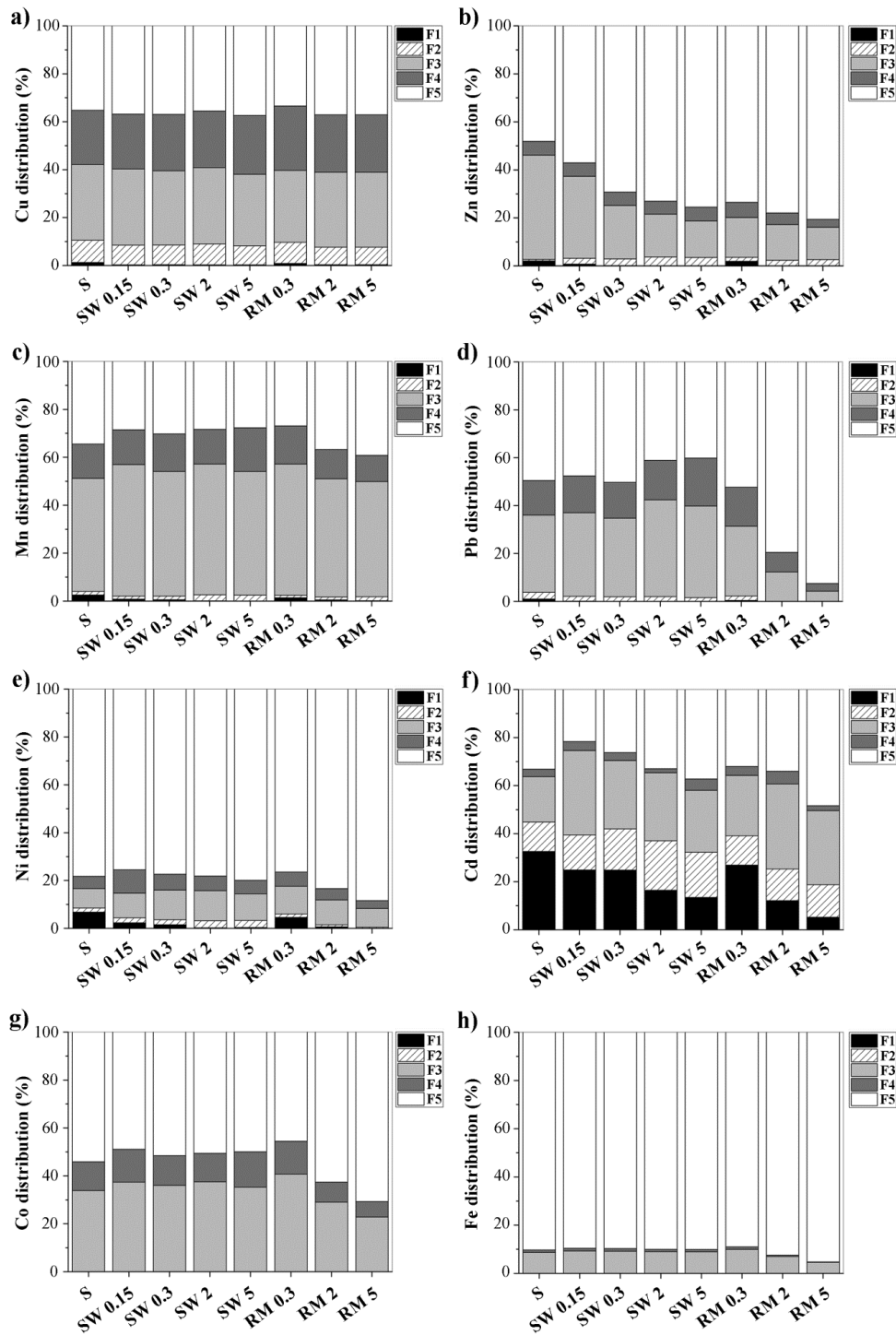
452 The significant negative correlation between F1 content and soil pH was determined  
453 for all cations, while Cd content was as well in negative correlation with available P (Table  
454 S5). The solubility of organic Cu complexes at higher pH (Bucher and Schenk, 2000) is  
455 probably the explanation as to why the exchangeable fraction of Cu was not reduced even

456 more with increasing the doses of additives. Although the availability of soluble organic Cu-  
 457 complexes to plants is not known with certainty, lower biological effectiveness is supposed  
 458 compared to free ionic species (Bucher and Schenk, 2000).



459 Soil sample Soil sample  
 460 **Fig. 1.** The ion-exchangeable (F1) concentrations of a) Cu, b) Zn, c) Mn, d) Pb, e) Ni, and f)  
 461 Cd in unamended and amended soil samples.

462  
 463 The percentage distribution of elements in all five soil fractions is presented in Fig. 2.  
 464 Cu was accumulated in F5 (35%), F3 (32%) and F4 (23%) (Fig. 2a), which indicates the  
 465 establishment of chemical bonds with residual minerals, Fe- and Mn-oxides, and the organic  
 466 phase. In addition to F1, the content of Cu decreased in F2 phase after soil amending, most  
 467 significantly upon 2% and 5% RM addition, while the changes in other soil fractions were  
 468 minor (Table S4).



469

470

**Fig. 2.** Percentage distribution of selected elements in different fractions of unamended and

471

amended soil samples: a) Cu, b) Zn, c) Mn, d) Pb, e) Ni, f) Cd, g) Co, h) Fe. F1 - ion-

472

exchangeable, F2 - acid soluble (bound to carbonates, specifically sorbed), F3 - reducible

473

(bound to Fe, Mn- oxides), F4 - oxidizable (bound to organic matter), F5 - residual fraction

474

(fixed in primary and secondary minerals).



475

476 In contrast, Zn was largely re-distributed after treatments (Fig. 2b). With increasing  
477 additive doses, the significant increase in F2 fraction was observed and found to be in  
478 positive correlation with soil pH. Besides, the significant decrease in F3 fraction was  
479 accompanied by an increase in F5.

480 Mn was associated with F3 (47%) and F5 (34%) fractions in the control soil (Fig. 2c).  
481 The treatments with 2% and 5% of SW induced the most significant increase in F2 phase.  
482 The content of Mn in F2 was positively correlated with soil pH, CaCO<sub>3</sub>, and C<sub>organic</sub>.

483 In addition to the reduced concentration of exchangeable Pb, the content of Pb in F2  
484 fraction also decreased significantly following the treatments with both additives (Fig. 2d).  
485 However, the addition of SW affected the increase in Pb concentrations in F3 and F4 phases,  
486 while the drastic rise in F5 fraction was observed with the increased RM addition. The  
487 content of Pb in F2 and F3 fraction was in negative correlation with available P in the soil,  
488 whereas the positive correlation was found between F5 phase and available P.

489 Following the SW treatments, the reduction of exchangeable Ni content was followed  
490 by its simultaneous increase in F2, F3, and F4 phase (Fig. 2e). Quite the opposite, after the  
491 addition of RM, F2 content of Ni decreased while the increase in F5 was significant at 5%  
492 RM. F2 content of Ni was in negative correlation with soil CEC and in positive with C<sub>organic</sub>.  
493 Furthermore, Ni content in F4 was negatively correlated with available soil P, while the  
494 opposite was found for F5 fraction.

495 Cd was the most mobile metal cation according to distribution analyses (Fig. 2f), with  
496 33% and 12% in F1 and F2 fraction, respectively. Significant reduction in F1 content of Cd  
497 was associated with the increase in F2 and F3 fractions after SW addition, while RM addition  
498 provoked redistribution primarily to F3 and F5 phases. F2 content was positively correlated

499 with soil  $\text{CaCO}_3$  and  $\text{C}_{\text{organic}}$  content. Moreover, Cd content in F5 was positively correlated  
500 with available P in the soil.

501 Co was dominantly associated with F5 (54%) and F3 (34%) fractions of the soil S  
502 (Fig. 2g). Compared to control soil, the distribution of Co was particularly changed by RM  
503 addition in the doses of 2% and 5%, evidenced by the increase in F5 and decrease in F3  
504 phase. The available concentration of P was in negative correlation with Co content in F3  
505 phase and positive correlation with F5 fraction of Co.

506 Finally, Fe (Fig. 2h) was extracted dominantly in the scope of the F5 (90%) and F3  
507 (8.6%) fractions of the control soil. Both additives reduced the concentration in F2 phase, and  
508 the changes were in negative correlation with soil pH. Furthermore, the significant decrease  
509 in F3 and F4 content and increase in phase F5 observed after RM addition were in correlation  
510 with available P content.

511 Regarding Cu as a contaminant in the examined soil, both additives exhibited a  
512 similar effect on its exchangeable concentration as long as the dose was sufficient to increase  
513 the soil pH over pH 6. A study conducted on the heavily contaminated soil with 1245 mg/g  
514 Cu, also revealed insignificant differences in F1 phase content of Cu after application of RM  
515 and lime in the amounts (2% and 0.25%, respectively) that provided comparable soil pH (~7)  
516 (Lombi et al., 2002).

517 The stability of trace elements in RM treated soil appeared to be strong, as they were  
518 principally contained in the residual pool. The high content of Fe- oxide in red mud is  
519 primarily responsible for the containment of the majority of metals. Even though the total  
520 content of Co and Ni in RM exceed the values prescribed for Class B industrial materials for  
521 use in farmland, sequential extraction analysis indicates low environmental and health risks,  
522 in line with previous studies (Hua et al., 2017).

523

#### 524 **4. Conclusions**

525           Effects of interactions between the acidic soil and waste-derived additives (SW and  
526 RM) were evaluated and compared after two months of incubation. Addition of SW induced  
527 the increase in soil pH, EC, the content of S, CaCO<sub>3</sub>, and organic C. The favorable pH level  
528 for most crops was gained with the SW dose of 0.3%. Application of RM gave rise to the soil  
529 pH, EC, S, available P, and total concentration of trace metals. Addition of 2% RM was  
530 necessary for achieving satisfactory soil pH and doubling available P content. P-supply has  
531 reached the medium level at RM dose of 5%. Nevertheless, the EC value has increased to a  
532 level characteristic for saline soils, the threshold concentration of Ni has been exceeded while  
533 the concentration of V was close to the lower guideline value that indicates contamination  
534 risks. The reduction of the ion-exchangeable pool of the soil contaminant - Cu, and trace  
535 metals such as Zn, Mn, Pb, Ni, and Cd, was observed after application of both additives and  
536 associated with the increase in soil pH. The metal distribution analysis demonstrated high  
537 stability and a low risk of re-mobilization in soil treated with RM. Despite the increase in soil  
538 pH, application of phosphate fertilizers will still be necessary to SW amended soil with low  
539 P-content. On the other hand, reasonable use of RM could be beneficial in terms of  
540 simultaneous pH regulation, P-supply, and reduced trace metals mobility. The available  
541 content of P in RM may be a favorable feature in soils with low P-supply. Therefore,  
542 association and mobility of phosphate in red mud deserve further investigation. Furthermore,  
543 the impact of treatments on elements availability to plants and soil microbial community after  
544 the treatments needs to be assessed in the future study.

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548

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553

554 **Appendix A. Supplementary data**

555 Supplementary data to this article can be found in the file Supplementary information.

556

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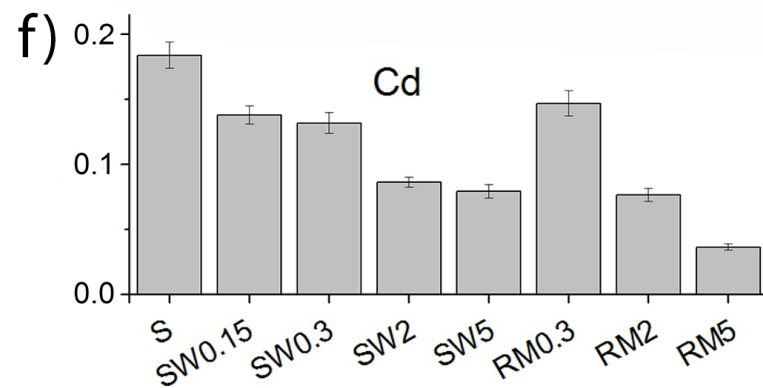
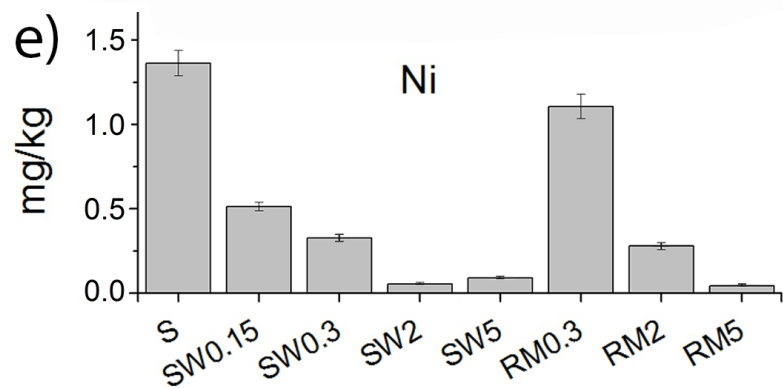
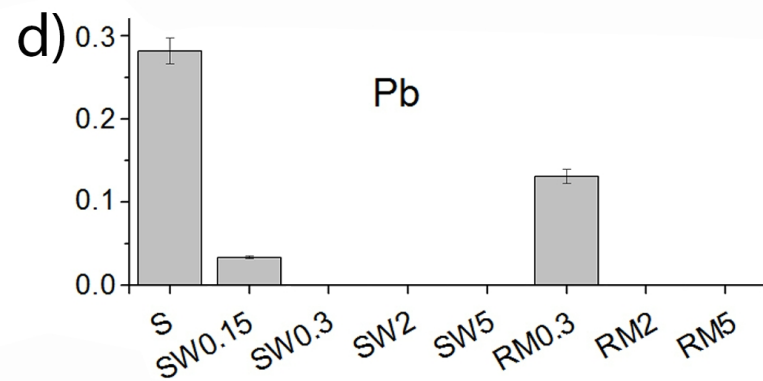
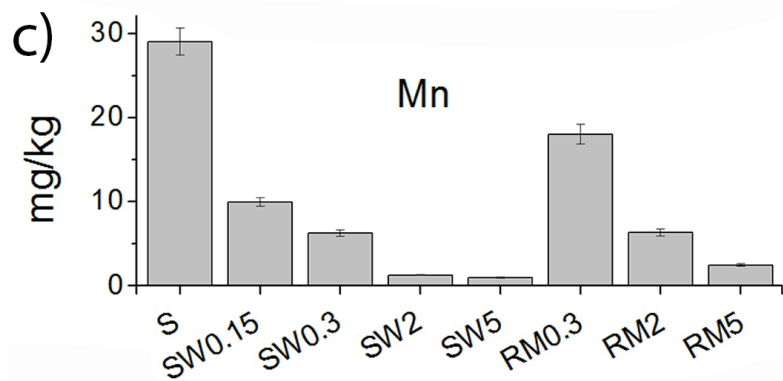
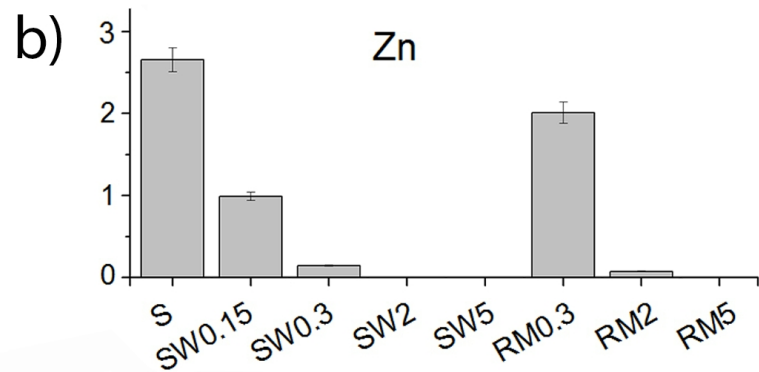
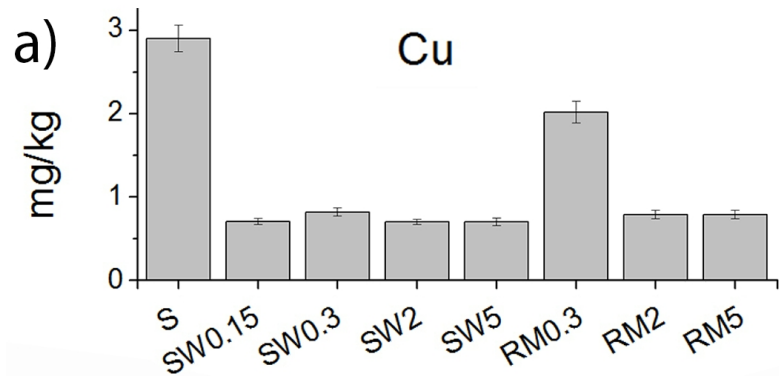
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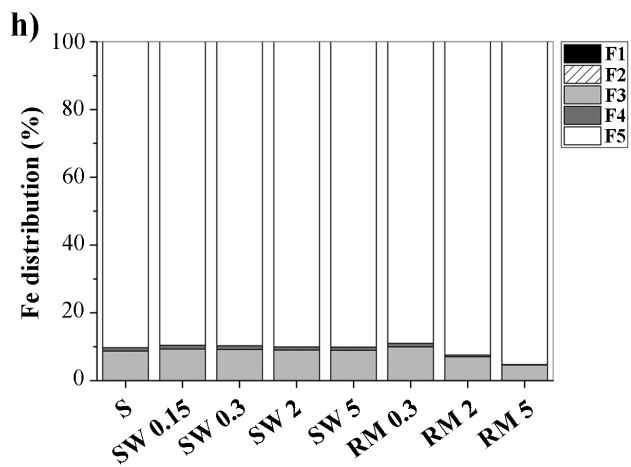
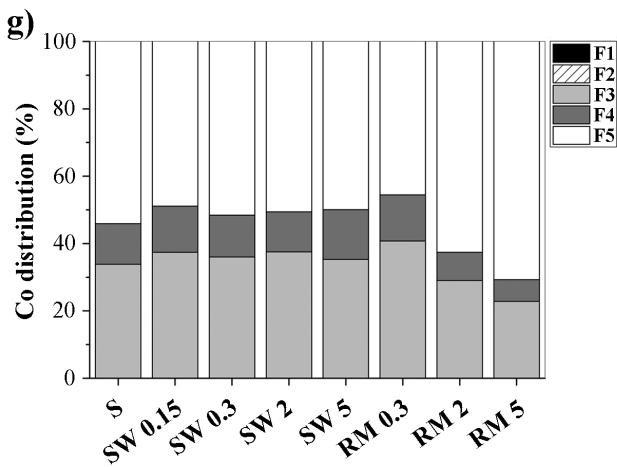
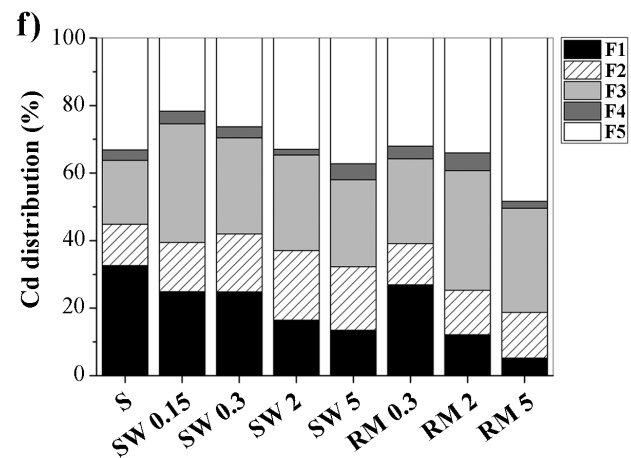
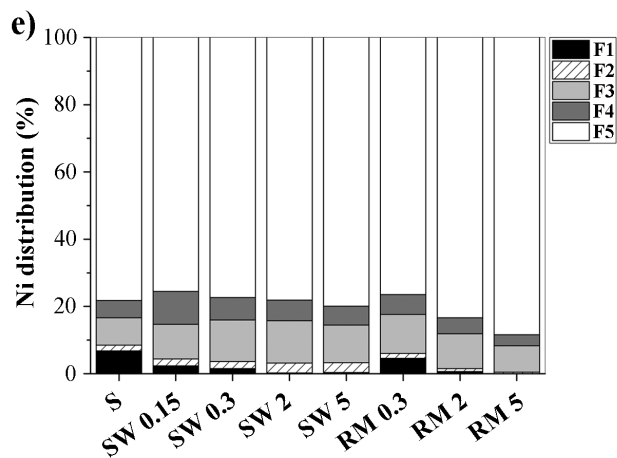
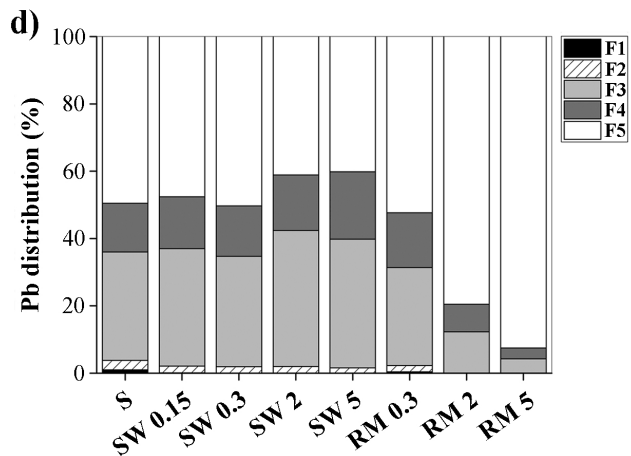
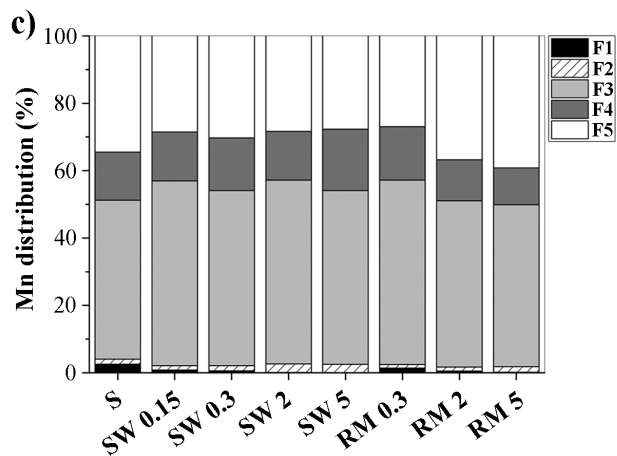
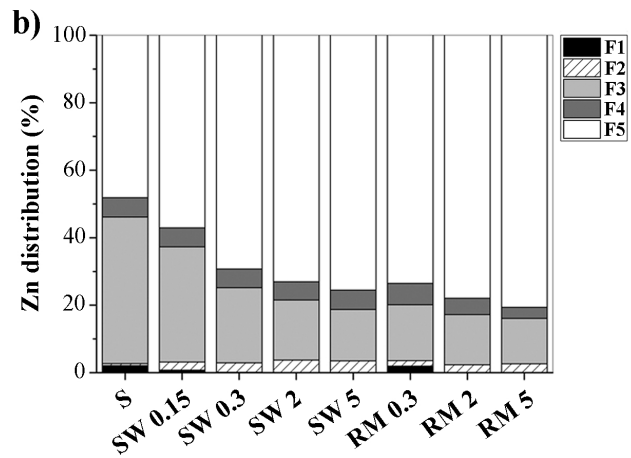
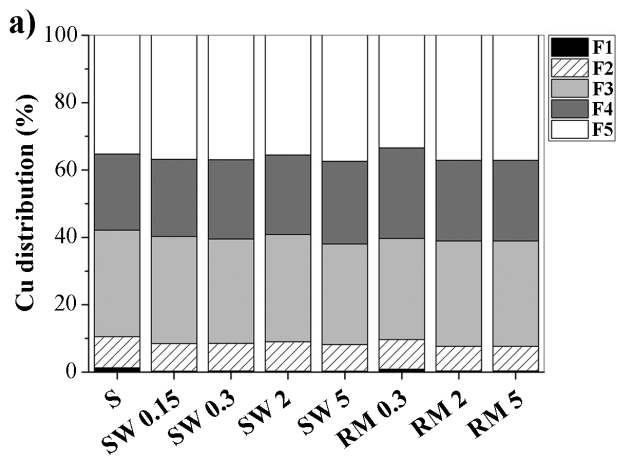
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Soil sample

Soil sample



# Supplementary data

## **INTERACTIONS OF ACIDIC SOIL NEAR COPPER MINING AND SMELTING COMPLEX AND WASTE-DERIVED ALKALINE ADDITIVES**

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**Table S1.** Pearson correlation coefficients ( $r$ ) and corresponding  $p$ -values (in parenthesis) for tests of linear association between various soil properties.

	<b>CaCO<sub>3</sub></b> (%)	<b>CEC</b> cmol <sub>c</sub> /kg	<b>N</b> (%)	<b>C<sub>organic</sub></b> (%)	<b>S</b> (%)	<b>P<sub>2</sub>O<sub>5</sub></b> (mg/100g)	<b>K<sub>2</sub>O</b> (mg/100g)	<b>pH<sub>H2O</sub></b> 1:2	<b>EC<sub>1:2</sub></b> dS/m
<b>CEC</b> cmol <sub>c</sub> /kg	-0.382 (0.350)								
<b>N</b> (%)	0.115 (-0.383)	0.786 (0.349)							
<b>C<sub>organic</sub></b> (%)	0.986 (0.000)	0.429 (0.289)	0.165 (0.696)						
<b>S</b> (%)	0.321 (0.438)	-0.124 (0.770)	-0.271 (0.517)	0.404 (0.321)					
<b>P<sub>2</sub>O<sub>5</sub></b> (mg/100g)	-0.158 (0.708)	0.586 (0.127)	-0.455 (0.257)	-0.262 (0.531)	0.145 (0.731)				
<b>K<sub>2</sub>O</b> (mg/100g)	0.379 (0.354)	0.496 (0.211)	0.049 (0.909)	0.385 (0.346)	0.378 (0.356)	0.349 (0.396)			
<b>pH<sub>H2O</sub></b> 1:2	0.610 (0.108)	-0.023 (0.956)	0.071 (0.867)	0.570 (0.141)	0.464 (0.247)	0.472 (0.238)	0.432 (0.285)		
<b>EC<sub>1:2</sub></b> dS/m	0.388 (0.342)	0.149 (0.724)	0.095 (0.824)	0.298 (0.474)	0.172 (0.684)	0.709 (0.049)	0.438 (0.277)	0.889 (0.003)	
<b>Coarse sand</b> (%)	-0.553 (0.155)	0.050 (0.906)	0.078 (0.855)	-0.594 (0.120)	-0.526 (0.181)	0.087 (0.838)	-0.257 (0.540)	-0.519 (0.187)	-0.197 (0.641)
<b>Fine sand</b> (%)	0.798 0.018	-0.540 0.167	0.445 0.270	0.774 0.024	-0.071 0.868	-0.312 0.451	0.245 0.559	0.266 0.525	0.243 0.562
<b>Silt</b> (%)	-0.433 0.283	0.695 0.056	-0.419 0.301	-0.481 0.228	0.170 0.688	0.800 0.017	0.157 0.710	0.351 0.394	0.451 0.262
<b>Clay</b> (%)	-0.494 0.213	0.297 0.476	-0.383 0.350	-0.420 0.301	0.271 0.517	-0.059 0.890	-0.254 0.543	-0.244 0.560	-0.431 0.287

**Table S2.** Threshold and guideline values for metals in soils according to Finnish standard (MEF, 2007), and Canadian Guidelines for the beneficial use of industrial by-products as soil amendments (GBN Canada, 2014).

Substance (symbol)	Prescribed concentrations in soil			Prescribed concentrations in soil additives	
	Threshold value (mg/kg)	Lower guideline value (mg/kg)	Higher guideline value (mg/kg)	Class A (mg/kg)	Class B (mg/kg)
Antimony (Sb)	2	10 (t)	50 (e)		
Arsenic (As)	5	50 (e)	100 (e)	13	75
Cadmium (Cd)	1	10 (e)	20 (e)	3	20
Cobalt (Co)	20	100 (e)	250 (e)	34	150
Chrome (Cr)	100	200 (e)	300 (e)	210	1060
Copper (Cu)	100	150 (e)	200 (e)	400	757
Lead (Pb)	60	200 (t)	750 (e)		
Nickel (Ni)	50	100 (e)	150 (e)	62	180
Zinc (Zn)	200	250 (e)	400 (e)		
Vanadium (V)	100	150 (e)	250 (e)		

Ecological risks (e); Health risks (t).

**Table S3.** Pearson correlation coefficients ( $r$ ) and corresponding  $p$ -values (in parenthesis) for tests of linear association between various soil properties and metal concentrations.

Metal concentrations (mg/kg)	CaCO <sub>3</sub> (%)	CEC cmol <sub>c</sub> /kg	N (%)	C <sub>organic</sub> (%)	S (%)	P <sub>2</sub> O <sub>5</sub> mg/100g	K <sub>2</sub> O mg/100g	pH <sub>H2O</sub> 1:2	EC <sub>1:2</sub> dS/m	Coarse sand (%)	Fine sand (%)	Silt (%)	Clay (%)
Al	-0.483 (0.225)	0.713 (0.050)	-0.743 (0.035)	-0.566 (0.143)	0.010 (0.981)	0.810 (0.015)	0.030 (0.943)	0.033 (0.938)	0.225 (0.591)	0.081 (0.849)	-0.659 (0.056)	0.836 (0.010)	0.403 (0.323)
As	-0.248 (0.554)	0.678 (0.065)	-0.579 (0.132)	-0.347 (0.400)	0.131 (0.758)	0.981 (0.000)	0.326 (0.430)	0.341 (0.408)	0.573 (0.137)	0.117 (0.783)	-0.423 (0.297)	0.824 (0.012)	0.051 (0.905)
Ca	0.996 (0.000)	-0.335 (0.417)	0.051 (0.905)	0.972 (0.000)	0.314 (0.448)	-0.101 (0.812)	0.400 (0.326)	0.611 (0.108)	0.407 (0.317)	-0.520 (0.187)	0.788 (0.020)	-0.402 (0.324)	-0.515 (0.192)
Cd	-0.331 (0.423)	0.622 (0.099)	-0.381 (0.352)	-0.407 (0.317)	0.060 (0.888)	0.828 (0.011)	0.143 (0.736)	0.359 (0.382)	0.532 (0.175)	-0.204 (0.629)	-0.568 (0.142)	0.886 (0.003)	0.364 (0.375)
Co	-0.484 (0.225)	0.794 (0.019)	-0.577 (0.134)	-0.572 (0.139)	-0.026 (0.951)	0.898 (0.002)	0.213 (0.613)	0.112 (0.792)	0.372 (0.365)	0.183 (0.665)	-0.618 (0.103)	0.867 (0.005)	0.239 (0.568)
Cr	-0.294 (0.479)	0.611 (0.108)	-0.558 (0.151)	-0.401 (0.325)	0.056 (0.895)	0.966 (0.000)	0.157 (0.711)	0.351 (0.394)	0.583 (0.129)	0.076 (0.857)	-0.477 (0.232)	0.860 (0.006)	0.121 (0.775)
Cu	-0.071 (0.868)	0.697 (0.054)	-0.336 (0.415)	-0.201 (0.633)	-0.396 (0.331)	0.668 (0.070)	0.331 (0.424)	0.168 (0.691)	0.442 (0.273)	0.358 (0.384)	-0.083 (0.845)	0.475 (0.234)	-0.319 (0.441)
Fe	-0.352 (0.392)	0.672 (0.068)	-0.526 (0.181)	-0.449 (0.265)	0.072 (0.866)	0.971 (0.000)	0.224 (0.593)	0.319 (0.441)	0.561 (0.148)	0.138 (0.745)	-0.516 (0.191)	0.884 (0.004)	0.126 (0.766)
K	0.057 (0.893)	-0.196 (0.641)	-0.469 (0.249)	-0.033 (0.938)	-0.301 (0.469)	0.085 (0.842)	-0.308 (0.458)	-0.351 (0.394)	-0.167 (0.693)	0.454 (0.259)	0.288 (0.488)	-0.339 (0.411)	-0.420 (0.300)
Mg	0.225 (0.593)	-0.784 (0.021)	0.233 (0.579)	0.233 (0.579)	-0.349 (0.396)	-0.603 (0.114)	-0.699 (0.054)	-0.270 (0.518)	-0.324 (0.433)	-0.036 (0.933)	0.443 (0.271)	-0.692 (0.057)	-0.185 (0.661)
Mn	-0.600 (0.115)	0.811 (0.014)	-0.296 (0.476)	-0.296 (0.476)	-0.241 (0.566)	0.262 (0.531)	0.329 (0.426)	-0.538 (0.169)	-0.311 (0.453)	0.324 (0.433)	-0.489 (0.219)	0.320 (0.439)	0.283 (0.498)
Na	-0.201 (0.634)	0.573 (0.137)	-0.548 (0.160)	-0.548 (0.160)	0.168 (0.690)	0.984 (0.000)	0.235 (0.575)	0.451 (0.262)	0.651 (0.080)	0.028 (0.947)	-0.418 (0.303)	0.853 (0.007)	0.076 (0.858)
Ni	-0.319 (0.442)	0.637 (0.089)	-0.578 (0.133)	-0.578 (0.133)	0.132 (0.756)	0.931 (0.001)	0.150 (0.723)	0.377 (0.357)	0.545 (0.162)	0.071 (0.867)	-0.577 (0.134)	0.928 (0.001)	0.214 (0.610)
Pb	-0.382 (0.350)	0.594 (0.120)	-0.580 (0.132)	-0.580 (0.132)	0.029 (0.945)	0.938 (0.001)	0.071 (0.867)	0.276 (0.508)	0.509 (0.198)	0.207 (0.623)	-0.543 (0.164)	0.867 (0.005)	0.133 (0.753)
V	-0.143 (0.736)	0.678 (0.065)	-0.433 (0.283)	-0.433 (0.283)	-0.264 (0.527)	0.741 (0.036)	0.364 (0.375)	0.045 (0.915)	0.379 (0.354)	0.134 (0.753)	-0.104 (0.806)	0.434 (0.283)	-0.157 (0.710)
Zn	-0.626 (0.097)	0.379 (0.355)	-0.575 (0.136)	-0.575 (0.136)	0.028 (0.948)	0.676 (0.066)	-0.226 (0.590)	-0.121 (0.774)	0.109 (0.798)	0.181 (0.668)	-0.659 (0.075)	0.659 (0.075)	0.397 (0.330)



**Table S4.** One-way ANOVA and the Fisher's least significant difference (LSD) test on the differences in metal distribution caused by the treatments.

	<b>Cu-F<sub>1</sub></b>	<b>Cu-F<sub>2</sub></b>	<b>Cu-F<sub>3</sub></b>	<b>Cu-F<sub>4</sub></b>	<b>Cu-F<sub>5</sub></b>		<b>Zn-F<sub>1</sub></b>	<b>Zn-F<sub>2</sub></b>	<b>Zn-F<sub>3</sub></b>	<b>Zn-F<sub>4</sub></b>	<b>Zn-F<sub>5</sub></b>
<b>S</b>	1.3 <sup>A</sup>	9.2 <sup>A</sup>	32 <sup>A</sup>	23 <sup>B</sup>	35 <sup>AB</sup>	<b>S</b>	2.1 <sup>A</sup>	0.6 <sup>E</sup>	43 <sup>A</sup>	5.7 <sup>B</sup>	48 <sup>E</sup>
<b>SW0.15</b>	0.31 <sup>C</sup>	8.2 <sup>BC</sup>	32 <sup>A</sup>	23 <sup>B</sup>	37 <sup>AB</sup>	<b>SW0.15</b>	0.79 <sup>C</sup>	2.4 <sup>C</sup>	34 <sup>B</sup>	5.6 <sup>B</sup>	57 <sup>D</sup>
<b>SW0.3</b>	0.35 <sup>C</sup>	8.2 <sup>BC</sup>	31 <sup>A</sup>	24 <sup>B</sup>	37 <sup>AB</sup>	<b>SW0.3</b>	0.11 <sup>D</sup>	2.8 <sup>B</sup>	22 <sup>C</sup>	5.6 <sup>B</sup>	69 <sup>C</sup>
<b>SW2</b>	0.31 <sup>C</sup>	8.7 <sup>ABC</sup>	32 <sup>A</sup>	24 <sup>B</sup>	36 <sup>AB</sup>	<b>SW2</b>	0.00 <sup>E</sup>	3.8 <sup>A</sup>	18 <sup>D</sup>	5.4 <sup>B</sup>	73 <sup>BC</sup>
<b>SW5</b>	0.30 <sup>C</sup>	7.9 <sup>CD</sup>	30 <sup>A</sup>	25 <sup>B</sup>	37 <sup>A</sup>	<b>SW5</b>	0.00 <sup>E</sup>	3.5 <sup>A</sup>	15 <sup>EF</sup>	5.7 <sup>B</sup>	76 <sup>ABC</sup>
<b>RM0.3</b>	0.89 <sup>B</sup>	8.8 <sup>AB</sup>	30 <sup>A</sup>	27 <sup>A</sup>	33 <sup>B</sup>	<b>RM0.3</b>	2.0 <sup>B</sup>	1.6 <sup>D</sup>	17 <sup>D</sup>	6.3 <sup>A</sup>	74 <sup>ABC</sup>
<b>RM2</b>	0.34 <sup>C</sup>	7.4 <sup>D</sup>	31 <sup>A</sup>	24 <sup>B</sup>	37 <sup>AB</sup>	<b>RM2</b>	0.06 <sup>D</sup>	2.3 <sup>C</sup>	15 <sup>EF</sup>	4.9 <sup>C</sup>	78 <sup>AB</sup>
<b>RM5</b>	0.34 <sup>C</sup>	7.4 <sup>D</sup>	31 <sup>A</sup>	24 <sup>B</sup>	37 <sup>AB</sup>	<b>RM5</b>	0.00 <sup>E</sup>	2.7 <sup>B</sup>	13 <sup>F</sup>	3.3 <sup>D</sup>	81 <sup>A</sup>
	<b>Fe-F<sub>1</sub></b>	<b>Fe-F<sub>2</sub></b>	<b>Fe-F<sub>3</sub></b>	<b>Fe-F<sub>4</sub></b>	<b>Fe-F<sub>5</sub></b>		<b>Mn-F<sub>1</sub></b>	<b>Mn-F<sub>2</sub></b>	<b>Mn-F<sub>3</sub></b>	<b>Mn-F<sub>4</sub></b>	<b>Mn-F<sub>5</sub></b>
<b>S</b>	0.00 <sup>A</sup>	0.04 <sup>A</sup>	8.7 <sup>B</sup>	1.0 <sup>AB</sup>	90 <sup>A</sup>	<b>S</b>	2.6 <sup>A</sup>	1.5 <sup>B</sup>	47 <sup>C</sup>	14 <sup>C</sup>	34 <sup>B</sup>
<b>SW0.15</b>	0.00 <sup>A</sup>	0.02 <sup>C</sup>	9.3 <sup>AB</sup>	1.1 <sup>A</sup>	90 <sup>A</sup>	<b>SW0.15</b>	0.84 <sup>C</sup>	1.3 <sup>C</sup>	55 <sup>A</sup>	15 <sup>C</sup>	29 <sup>CD</sup>
<b>SW0.3</b>	0.00 <sup>A</sup>	0.01 <sup>D</sup>	9.2 <sup>AB</sup>	1.1 <sup>A</sup>	90 <sup>A</sup>	<b>SW0.3</b>	0.59 <sup>D</sup>	1.5 <sup>B</sup>	52 <sup>ABC</sup>	16 <sup>B</sup>	30 <sup>C</sup>
<b>SW2</b>	0.00 <sup>A</sup>	0.01 <sup>D</sup>	9.0 <sup>B</sup>	1.0 <sup>AB</sup>	90 <sup>A</sup>	<b>SW2</b>	0.11 <sup>EF</sup>	2.6 <sup>A</sup>	55 <sup>AB</sup>	14 <sup>C</sup>	28 <sup>CD</sup>
<b>SW5</b>	0.00 <sup>A</sup>	0.01 <sup>D</sup>	9.0 <sup>B</sup>	0.93 <sup>B</sup>	90 <sup>A</sup>	<b>SW5</b>	0.08 <sup>F</sup>	2.5 <sup>A</sup>	52 <sup>ABC</sup>	18 <sup>A</sup>	28 <sup>CD</sup>
<b>RM0.3</b>	0.00 <sup>A</sup>	0.03 <sup>B</sup>	9.9 <sup>A</sup>	1.1 <sup>A</sup>	89 <sup>A</sup>	<b>RM0.3</b>	1.4 <sup>B</sup>	1.1 <sup>D</sup>	55 <sup>A</sup>	16 <sup>B</sup>	27 <sup>D</sup>
<b>RM2</b>	0.00 <sup>A</sup>	0.01 <sup>D</sup>	7.0 <sup>C</sup>	0.51 <sup>C</sup>	92 <sup>A</sup>	<b>RM2</b>	0.51 <sup>D</sup>	1.2 <sup>CD</sup>	49 <sup>BC</sup>	12 <sup>D</sup>	37 <sup>AB</sup>
<b>RM5</b>	0.00 <sup>A</sup>	0.02 <sup>C</sup>	4.5 <sup>D</sup>	0.22 <sup>D</sup>	95 <sup>A</sup>	<b>RM5</b>	0.20 <sup>E</sup>	1.6 <sup>B</sup>	48 <sup>C</sup>	11 <sup>D</sup>	39 <sup>A</sup>
	<b>Ni-F<sub>1</sub></b>	<b>Ni-F<sub>2</sub></b>	<b>Ni-F<sub>3</sub></b>	<b>Ni-F<sub>4</sub></b>	<b>Ni-F<sub>5</sub></b>		<b>Pb-F<sub>1</sub></b>	<b>Pb-F<sub>2</sub></b>	<b>Pb-F<sub>3</sub></b>	<b>Pb-F<sub>4</sub></b>	<b>Pb-F<sub>5</sub></b>
<b>S</b>	6.8 <sup>A</sup>	1.7 <sup>C</sup>	8.1 <sup>D</sup>	5.2 <sup>DE</sup>	78 <sup>B</sup>	<b>S</b>	1.0 <sup>A</sup>	2.8 <sup>A</sup>	32 <sup>B</sup>	14 <sup>C</sup>	50 <sup>C</sup>
<b>SW0.15</b>	2.4 <sup>C</sup>	2.0 <sup>B</sup>	10 <sup>C</sup>	10 <sup>A</sup>	76 <sup>B</sup>	<b>SW0.15</b>	0.12 <sup>C</sup>	2.0 <sup>B</sup>	35 <sup>B</sup>	15 <sup>BC</sup>	48 <sup>C</sup>
<b>SW0.3</b>	1.5 <sup>D</sup>	2.1 <sup>B</sup>	12 <sup>A</sup>	6.7 <sup>B</sup>	77 <sup>B</sup>	<b>SW0.3</b>	0.00 <sup>D</sup>	2.0 <sup>B</sup>	33 <sup>B</sup>	15 <sup>BC</sup>	50 <sup>C</sup>
<b>SW2</b>	0.24 <sup>FG</sup>	2.9 <sup>A</sup>	13 <sup>A</sup>	6.1 <sup>BC</sup>	78 <sup>B</sup>	<b>SW2</b>	0.00 <sup>D</sup>	2.0 <sup>B</sup>	40 <sup>A</sup>	17 <sup>B</sup>	41 <sup>D</sup>
<b>SW5</b>	0.38 <sup>EF</sup>	2.9 <sup>A</sup>	11 <sup>BC</sup>	5.7 <sup>CD</sup>	80 <sup>B</sup>	<b>SW5</b>	0.00 <sup>D</sup>	1.6 <sup>C</sup>	38 <sup>A</sup>	20 <sup>A</sup>	40 <sup>D</sup>
<b>RM0.3</b>	4.6 <sup>B</sup>	1.5 <sup>D</sup>	12 <sup>AB</sup>	5.9 <sup>C</sup>	76 <sup>B</sup>	<b>RM0.3</b>	0.44 <sup>B</sup>	1.9 <sup>B</sup>	29 <sup>C</sup>	16 <sup>B</sup>	52 <sup>C</sup>
<b>RM2</b>	0.68 <sup>E</sup>	0.89 <sup>E</sup>	10 <sup>C</sup>	4.7 <sup>E</sup>	83 <sup>AB</sup>	<b>RM2</b>	0.00 <sup>D</sup>	0.00 <sup>D</sup>	12 <sup>D</sup>	8.2 <sup>D</sup>	80 <sup>B</sup>
<b>RM5</b>	0.07 <sup>G</sup>	0.43 <sup>F</sup>	7.8 <sup>D</sup>	3.3 <sup>F</sup>	88 <sup>A</sup>	<b>RM5</b>	0.00 <sup>D</sup>	0.00 <sup>D</sup>	4.3 <sup>E</sup>	3.2 <sup>E</sup>	93 <sup>A</sup>
	<b>Co-F<sub>1</sub></b>	<b>Co-F<sub>2</sub></b>	<b>Co-F<sub>3</sub></b>	<b>Co-F<sub>4</sub></b>	<b>Co-F<sub>5</sub></b>		<b>Cd-F<sub>1</sub></b>	<b>Cd-F<sub>2</sub></b>	<b>Cd-F<sub>3</sub></b>	<b>Cd-F<sub>4</sub></b>	<b>Cd-F<sub>5</sub></b>
<b>S</b>	0.00	0.04 <sup>A</sup>	34 <sup>B</sup>	12 <sup>C</sup>	54 <sup>C</sup>	<b>S</b>	33 <sup>A</sup>	12 <sup>D</sup>	19 <sup>E</sup>	3.1 <sup>D</sup>	33 <sup>C</sup>
<b>SW0.15</b>	0.00	0.00 <sup>B</sup>	37 <sup>B</sup>	14 <sup>AB</sup>	49 <sup>DE</sup>	<b>SW0.15</b>	25 <sup>C</sup>	15 <sup>C</sup>	35 <sup>A</sup>	3.7 <sup>C</sup>	22 <sup>E</sup>
<b>SW0.3</b>	0.00	0.00 <sup>B</sup>	36 <sup>B</sup>	12 <sup>BC</sup>	52 <sup>CD</sup>	<b>SW0.3</b>	25 <sup>BC</sup>	17 <sup>B</sup>	28 <sup>B</sup>	3.2 <sup>D</sup>	26 <sup>D</sup>
<b>SW2</b>	0.00	0.00 <sup>B</sup>	38 <sup>B</sup>	12 <sup>C</sup>	51 <sup>CDE</sup>	<b>SW2</b>	16 <sup>D</sup>	21 <sup>A</sup>	28 <sup>BC</sup>	1.7 <sup>E</sup>	33 <sup>C</sup>
<b>SW5</b>	0.00	0.00 <sup>B</sup>	35 <sup>B</sup>	15 <sup>A</sup>	50 <sup>CDE</sup>	<b>SW5</b>	13 <sup>E</sup>	19 <sup>B</sup>	26 <sup>CD</sup>	4.7 <sup>B</sup>	37 <sup>B</sup>
<b>RM0.3</b>	0.00	0.00 <sup>B</sup>	41 <sup>A</sup>	14 <sup>AB</sup>	46 <sup>E</sup>	<b>RM0.3</b>	27 <sup>B</sup>	12 <sup>D</sup>	25 <sup>D</sup>	3.7 <sup>C</sup>	32 <sup>C</sup>
<b>RM2</b>	0.00	0.00 <sup>B</sup>	29 <sup>C</sup>	8.4 <sup>D</sup>	63 <sup>B</sup>	<b>RM2</b>	12 <sup>E</sup>	13 <sup>CD</sup>	35 <sup>A</sup>	5.2 <sup>A</sup>	34 <sup>BC</sup>
<b>RM5</b>	0.00	0.00 <sup>B</sup>	23 <sup>D</sup>	6.4 <sup>E</sup>	71 <sup>A</sup>	<b>RM5</b>	5.2 <sup>F</sup>	13 <sup>CD</sup>	31 <sup>B</sup>	2.1 <sup>E</sup>	48 <sup>A</sup>

Data presented are mean of three replicates; Means that do not share a letter are significantly different; Values with different letters in the same column indicate a significant difference at  $p < 0.05$

**Table S5.** Pearson correlation coefficients ( $r$ ) and corresponding  $p$ -values (in parenthesis) for tests of linear association between soil properties and metal distribution patterns.

<b>Metal/Phase</b>	<b>CaCO<sub>3</sub> (%)</b>	<b>CEC (cmol<sub>c</sub>/kg)</b>	<b>N (%)</b>	<b>C<sub>organic</sub> (%)</b>	<b>S (%)</b>	<b>P<sub>2</sub>O<sub>5</sub> (mg/100g)</b>	<b>K<sub>2</sub>O (mg/100g)</b>	<b>pH<sub>H2O</sub> 1:2</b>	<b>EC<sub>1:2</sub> dS/m</b>
<b>Cu/F1</b>	-0.357 (0.386)	-0.110 (0.795)	-0.140 (0.741)	-0.399 (0.328)	-0.621 (0.101)	-0.238 (0.571)	-0.439 (0.277)	-0.811 (0.015)	-0.565 (0.144)
<b>Cu/F2</b>	-0.065 (0.879)	-0.494 (0.214)	0.523 (0.183)	-0.050 (0.906)	-0.571 (0.139)	-0.621 (0.100)	-0.335 (0.417)	-0.619 (0.102)	-0.473 (0.237)
<b>Cu/F3</b>	-0.452 (0.261)	-0.174 (0.679)	0.345 (0.403)	-0.475 (0.234)	-0.482 (0.226)	-0.053 (0.900)	-0.692 (0.057)	-0.048 (0.910)	0.045 (0.915)
<b>Cu/F4</b>	0.081 (0.849)	0.546 (0.162)	-0.055 (0.897)	0.092 (0.828)	0.118 (0.780)	0.180 (0.670)	0.836 (0.010)	-0.097 (0.819)	0.009 (0.983)
<b>Cu/F5</b>	0.304 (0.464)	-0.154 (0.716)	-0.359 (0.382)	0.310 (0.454)	0.607 (0.110)	0.229 (0.586)	-0.132 (0.756)	0.648 (0.083)	0.354 (0.389)
<b>Zn/F1</b>	-0.406 (0.319)	0.038 (0.930)	-0.065 (0.879)	-0.415 (0.307)	-0.595 (0.120)	-0.348 (0.398)	-0.291 (0.484)	-0.907 (0.002)	-0.696 (0.055)
<b>Zn/F2</b>	0.646 (0.083)	-0.133 (0.753)	0.384 (0.347)	0.666 (0.071)	0.511 (0.196)	0.152 (0.720)	0.529 (0.177)	0.902 (0.002)	0.711 (0.048)
<b>Zn/F3</b>	-0.296 (0.476)	-0.484 (0.224)	0.043 (0.919)	-0.284 (0.495)	-0.459 (0.253)	-0.564 (0.146)	-0.852 (0.007)	-0.656 (0.078)	-0.646 (0.083)
<b>Zn/F4</b>	0.218 (0.604)	-0.378 (0.356)	0.408 (0.315)	0.310 (0.455)	-0.147 (0.728)	-0.890 (0.003)	-0.001 (0.997)	-0.534 (0.172)	-0.683 (0.062)
<b>Zn/F5</b>	0.245 (0.559)	0.512 (0.195)	-0.105 (0.804)	0.224 (0.593)	0.460 (0.251)	0.636 (0.090)	0.805 (0.016)	0.674 (0.067)	0.677 (0.065)
<b>Fe/F1</b>	* *	* *	* *	* *	* *	* *	* *	* *	* *
<b>Fe/F2</b>	-0.608 (0.110)	0.043 (0.919)	-0.239 (0.569)	-0.651 (0.081)	-0.592 (0.122)	-0.062 (0.884)	-0.501 (0.206)	-0.832 (0.010)	-0.542 (0.165)
<b>Fe/F3</b>	0.238 (0.571)	-0.453 (0.260)	0.547 (0.160)	0.342 (0.407)	-0.095 (0.823)	-0.907 (0.002)	0.004 (0.993)	-0.444 (0.270)	-0.608 (0.110)
<b>Fe/F4</b>	0.167 (0.692)	-0.577 (0.134)	0.530 (0.177)	0.271 (0.516)	-0.090 (0.832)	-0.910 (0.002)	-0.155 (0.714)	-0.494 (0.214)	-0.639 (0.088)
<b>Fe/F5</b>	-0.225 (0.593)	0.474 (0.235)	-0.546 (0.162)	-0.329 (0.426)	0.097 (0.818)	0.911 (0.002)	0.024 (0.956)	0.457 (0.255)	0.618 (0.103)
<b>Mn/F1</b>	-0.474 (0.236)	-0.153 (0.718)	-0.145 (0.731)	-0.485 (0.223)	-0.588 (0.125)	-0.384 (0.347)	-0.606 (0.111)	-0.912 (0.002)	-0.743 (0.035)
<b>Mn/F2</b>	0.827 (0.011)	-0.508 (0.199)	0.419 (0.302)	0.781 (0.022)	0.105 (0.805)	-0.001 (0.997)	0.193 (0.646)	0.733 (0.039)	0.661 (0.074)
<b>Mn/F3</b>	0.200 (0.634)	0.013 (0.975)	0.693 (0.057)	0.295 (0.478)	0.072 (0.866)	-0.446 (0.268)	0.492 (0.215)	0.020 (0.963)	-0.086 (0.839)
<b>Mn/F4</b>	0.674 (0.067)	-0.515 (0.192)	0.242 (0.563)	0.749 (0.032)	0.288 (0.489)	-0.653 (0.079)	0.259 (0.536)	-0.061 (0.885)	-0.298 (0.473)
<b>Mn/F5</b>	-0.470 (0.240)	0.329 (0.427)	-0.600 (0.116)	-0.562 (0.147)	-0.091 (0.830)	0.680 (0.063)	-0.363 (0.377)	0.095 (0.823)	0.257 (0.539)

**Table S5.** – continued

<b>Metal/Phase</b>	<b>CaCO<sub>3</sub> (%)</b>	<b>CEC (cmol<sub>c</sub>/kg)</b>	<b>N (%)</b>	<b>C<sub>organic</sub> (%)</b>	<b>S (%)</b>	<b>P<sub>2</sub>O<sub>5</sub> (mg/100g)</b>	<b>K<sub>2</sub>O (mg/100g)</b>	<b>pH<sub>H2O</sub> 1:2</b>	<b>EC<sub>1:2</sub> dS/m</b>
<b>Ni/F1</b>	-0.411 (0.311)	-0.148 (0.726)	-0.079 (0.852)	-0.412 (0.311)	-0.558 (0.151)	-0.435 (0.282)	-0.486 (0.222)	-0.926 (0.001)	-0.760 (0.028)
<b>Ni/F2</b>	0.733 (0.039)	-0.714 (0.047)	0.649 (0.081)	0.786 (0.021)	0.086 (0.840)	-0.665 (0.072)	0.065 (0.878)	0.233 (0.579)	0.013 (0.975)
<b>Ni/F3</b>	0.358 (0.385)	-0.267 (0.523)	0.703 (0.052)	0.470 (0.240)	0.289 (0.488)	-0.513 (0.194)	0.441 (0.274)	0.162 (0.702)	-0.042 (0.922)
<b>Ni/F4</b>	0.033 (0.937)	-0.278 (0.505)	0.448 (0.266)	0.147 (0.728)	0.043 (0.919)	-0.726 (0.041)	-0.144 (0.733)	-0.247 (0.556)	-0.484 (0.224)
<b>Ni/F5</b>	-0.082 (0.847)	0.467 (0.244)	-0.580 (0.132)	-0.190 (0.653)	0.161 (0.703)	0.918 (0.001)	0.143 (0.736)	0.520 (0.186)	0.661 (0.075)
<b>Pb/F1</b>	-0.329 (0.426)	-0.187 (0.657)	-0.129 (0.761)	-0.371 (0.365)	-0.650 (0.081)	-0.307 (0.459)	-0.553 (0.156)	-0.805 (0.016)	-0.592 (0.122)
<b>Pb/F2</b>	0.132 (0.756)	-0.703 (0.052)	0.497 (0.211)	0.185 (0.661)	-0.287 (0.491)	-0.788 (0.020)	-0.371 (0.366)	-0.506 (0.200)	-0.531 (0.176)
<b>Pb/F3</b>	0.506 (0.201)	-0.709 (0.049)	0.655 (0.078)	0.576 (0.135)	-0.079 (0.853)	-0.833 (0.010)	-0.080 (0.850)	-0.125 (0.768)	-0.296 (0.477)
<b>Pb/F4</b>	0.588 (0.126)	-0.578 (0.134)	0.489 (0.219)	0.661 (0.074)	0.014 (0.975)	-0.813 (0.014)	0.096 (0.822)	-0.156 (0.713)	-0.357 (0.386)
<b>Pb/F5</b>	-0.510 (0.197)	0.685 (0.061)	-0.606 (0.112)	-0.580 (0.132)	0.077 (0.856)	0.842 (0.009)	0.057 (0.893)	0.171 (0.686)	0.341 (0.409)
<b>Co/F1</b>	*	*	*	*	*	*	*	*	*
<b>Co/F2</b>	*	*	*	*	*	*	*	*	*
<b>Co/F3</b>	0.213 (0.612)	-0.347 (0.399)	0.629 (0.095)	0.310 (0.454)	-0.135 (0.750)	-0.820 (0.013)	0.134 (0.752)	-0.405 (0.320)	-0.512 (0.195)
<b>Co/F4</b>	0.477 (0.232)	-0.491 (0.216)	0.381 (0.352)	0.562 (0.147)	0.059 (0.889)	-0.811 (0.015)	0.091 (0.831)	-0.274 (0.511)	-0.479 (0.230)
<b>Co/F5</b>	-0.308 (0.458)	0.406 (0.319)	-0.558 (0.151)	-0.404 (0.322)	0.072 (0.865)	0.836 (0.010)	0.121 (0.776)	0.370 (0.366)	0.513 (0.194)
<b>Cd/F1</b>	-0.293 (0.481)	-0.428 (0.290)	0.265 (0.525)	-0.220 (0.600)	-0.347 (0.399)	-0.773 (0.025)	-0.479 (0.230)	-0.859 (0.006)	-0.855 (0.007)
<b>Cd/F2</b>	0.734 (0.038)	-0.570 (0.141)	0.622 (0.099)	0.765 (0.027)	0.322 (0.436)	-0.221 (0.599)	0.239 (0.568)	0.695 (0.056)	0.500 (0.208)
<b>Cd/F3</b>	-0.175 (0.678)	0.485 (0.223)	-0.032 (0.939)	-0.133 (0.754)	0.301 (0.468)	0.228 (0.586)	0.211 (0.616)	0.383 (0.349)	0.215 (0.610)
<b>Cd/F4</b>	0.197 (0.641)	0.207 (0.622)	-0.496 (0.211)	0.246 (0.556)	0.255 (0.541)	-0.308 (0.457)	0.103 (0.808)	-0.172 (0.684)	-0.474 (0.235)
<b>Cd/F5</b>	0.137 (0.747)	0.363 (0.376)	-0.465 (0.245)	0.001 (0.998)	0.026 (0.951)	0.883 (0.004)	0.301 (0.469)	0.482 (0.226)	0.721 (0.044)

\* Concentrations below LOD

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