Partition of Cd, Cu, Pb and Zn among mineral particles during their sorption in soils

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18   **Abstract**

19   *Purpose.* Heterogeneity of soil mineral particles may lead to the misinterpretation of bulk sorption data on their

20   role in metal sorption, which may be resolved through the direct observation of metal distribution among the soil

21   particles after the sorption.

22   *Materials and methods.* Analytical transmission electron microscopy was used to study metal (Cd, Cu, Pb, Zn)

23   sorption characteristics of clay minerals, Fe-oxyhydroxides and their natural assemblages in soils with contrasting

24   pH under single element and competitive situations.

25   *Results and discussion.* Iron-oxyhydroxides sorbed higher metal amounts than clay mineral particles mostly, and

26   the sorption capacity of the latter phases were more affected by competition. Iron-oxyhydroxide particles acted as

27   effective metal sorbents in soils not only as individual particles but also as coatings on other mineral particles, and

28   the structural Fe in clay minerals may also resulted in higher metal sorption in some cases. Besides the direct

29   observation of metal sorption onto soil mineral particles, metal precipitates could be identified directly, and the

30   role of organic surfaces in metal sorption could be inferred indirectly in certain cases.

31   *Conclusions.* Comparison of metal affinity sequences and their partition characteristics between the bulk soil and

32   different mineral particles were found to be an effective tool to specify the most active mineral components in

33   metal sorption at given soil and sorption condition.

34

35   **Keywords** Ferrihydrite • Metal • Smectite • Soil • Sorption

36

1 Introduction

Metal ion sorption in natural soil systems is generally proceeded through surface reactions with organic compounds, metal-(oxy)hydroxides and clay minerals. The sorption characteristics of metals on these individual compounds are known well; however, their exact role played in the soil during the metal sorption process has been established using bulk sorption data primarily. Surface chemistry of soil particles exhibits large inhomogeneity at the sub-micron level, which can be related to the natural structural irregularities of the mineral particles, and to the result of associations of several phases as coating, aggregates etc. (Serrano et al. 2009). This heterogeneity may lead to the misinterpretation of the bulk sorption data with respect to the role of the individual soil components, and it may even hinder the direct identification of the most active components in the metal sorption process (Nachtegaal and Sparks 2004). Pedogenic processes often produce complex particle assemblages, like that of metal-(oxy)hydroxides and phyllosilicates. Both laboratory experiments and field observations have demonstrated that surface modifiers in form of organic and/or metal-oxyhydroxide armoring agents, rather than bulk mineralogical composition by itself, control the surface chemistry of reactive phases in soils. Bertsch and Seaman (1999) found that Fe-oxyhydroxide surface modifiers increased the point of zero net charge of their assemblages with clay minerals, resulting in surface reactivity that is controlled by the development of positive surface charge arising from the oxyhydroxide phase. One of the reasons for their affinity to associate is that smectites have a marked influence on the hydrolysis of Fe(III), which reacts with the clay phase to form hydroxyl-Fe-montmorillonite complexes (Ferreiro et al. 1995).

Previous studies on clay mineral and metal-oxyhydroxide interaction aimed at the studying of their influence on soil aggregation and other physical properties. However, such particle assemblages are also expected to have a significant effect on ion adsorption processes in the soil. Little is known on the effect of such coatings on the intrinsic sorption mechanisms of trace metals to clay mineral surfaces, although in the most extreme scenarios, these coatings could dictate metal sorption instead of the underlying clay mineral (Nachtegaal and Sparks 2004). Up to date, only a few laboratory studies focused on the sorption properties of such particle assemblages. For example, Borgnino et al. (2009) showed that coating and/or aggregation of montmorillonite by ferrihydrite increased the specific surface area, and hereby the sorption capacity of the clay mineral phase. Additionally, Wu et al. (2009) found that Fe-montmorillonite can be characterized by larger interlayer spacing than Ca-montmorillonite, which could be also related to the higher Cd sorption capacity for the former. On the contrary, coating may also result in the lowering of the metal sorption capacity of the soil through blocking the specific binding sites on Fe-oxyhydroxides and clay minerals (Rafaey et al. 2014). Direct observations from natural systems

67   are even less frequent. Using analytical transmission electron microscopy (ATEM), Hochella et al. (2005) showed

68   that several metals were preferentially associated to hydrous Fe and Mn oxides among mineral phases in river

69   sediments affected by mining and smelting activities. Further studies of soil mineral-metal interaction

70   demonstrated that the association of Fe-oxyhydroxides and clay minerals makes a decisive contribution to the

71   retention of metals in soils (Sipos et al. 2009), sometimes even more than the individual components themselves

72   (Cerqueira et al. 2015). As expected, these studies found that metal sorption on the Fe-oxyhydroxide and clay

73   mineral assemblages is a highly selective process, which was affected by soil pH primarily. Using surface

74   complexation model calculations, Akafia et al. (2011) found that the low pH portion of the adsorption edge is

75   predominantly due to adsorption on the permanent charge site of the montmorillonite, while the adsorption at

76   higher pH represents the sum of adsorption on both the permanent charge sites and the variable charge surface

77   hydroxyl sites for several metals.

78   Development of surface complexation models for a heterogeneous system like the soil also needs support from the

79   direct analyses of the sorption characteristics of soil mineral particles. Model calculations by Serrano et al. (2009)

80   suggested the preferential role of >FeOH sites in metal sorption in mineral soils. They have also found that metals

81   selectivity and the exact immobilization processes showed also high variation with soil pH conditions. According

82   to the multi-surface soil speciation model of Gu et al. (2014), cation exchange sites and soil organic matter are the

83   main soil components for metal sorption at acidic and neutral conditions in mineral soils with relatively high clay

84   fractions and low organic matter content. On the contrary, specific sorption to iron oxyhydroxides and the edge

85   site of clay minerals are the most important surface reactions for metal adsorption in such soils at alkaline

86   conditions. The results of such model calculations are mostly compared to those of X-Ray absorption spectroscopy

87   analyses, although they do not provide any information about the exact mineralogy, and about the relationship of

88   the particles within their associations, in contrast to the results obtained by transmission electron microscopy

89   analyses (Elsass et al. 2008). Although the latest generation synchrotron light sources are already able to produce

90   micro-focused beams for μ-XANES, μ-XRD, and μ-XRF, data analysis approaches are far from standardized

91   (Gräfe et al. 2014). Additionally, the resolution of such mapping techniques used to relate trace metals to their host

92   phases is significantly lower than that of ATEM (Kopittke et al. 2017). The better understanding of metal partition

93   at particle level may have consequences also from the viewpoint of modelling of contaminant transport. Minor

94   changes in solute chemistry can induce charge reversal, which may lead to the dispersion of these mineral

95   assemblages and to the transport of colloidal mineral phases (Bertsch and Seaman 1999). Direct observations at

96   particle level are of decisive role, as utilization of bulk mineralogical data to represent predominant reactive phases

97   in complex natural systems often has failed to predict solute and contaminant behavior reliably.

98   Up to now, there are very low number of studies aiming at the direct study of the role of the individual soil particles

99   in the metal sorption process. These studies lack the systematic character generally; their most important result is

100   rather the demonstration of the usefulness of certain analytical methods in studying the individual soil particles,

101   like analytical transmission electron microscopy (Sipos et al., 2009), time of flight secondary ion mass

102   spectrometry (Cerqueira et al. 2011) and field emission scanning electron microscopy (Cerqueira et al. 2015).

103   Owing to this fact, the effect of basic factors, like competition or soil pH on the metal sorption by individual soil

104   particles has not been studied yet using direct methods, although they are expected to promote the identification

105   of the most active soil mineral components in the metal sorption. In this study, the role of Fe-oxyhydroxides, clay

106   minerals and their associations in the sorption of Cd, Cu, Pb and Zn was studied using direct mineralogical and

107   geochemical analysis by ATEM. Our aims were (1) to relate the sorption capacities of mineral particles to that of

108   the bulk soil, (2) to compare the metal affinities to different mineral species, and (3) to study the effect of mineral

109   assemblages on metals sorption under varying soil pH and under the influence of presence of competing metals.

110   The studied metals are among the most frequent metal pollutants of the soil affecting industrial, agricultural and

111   even urban areas (Soylak et al, 2001; Turkoglu et al, 2003). Cadmium and Pb are known of their toxic effects on

112   soil biota primarily, but Cu and Zn may often show deficiency in certain soil types, which need artificial

113   fertilization to be prevented (Alloway, 2013). Moreover, the studied metals possess significantly different sorption

114   characteristics in soils, as some of them (like Cu) are retained on soil components through inner-sphere complexes,

115   whereas others (like Zn) are bound through outer-sphere complexes predominantly (Rafaey et al, 2017).

116

117   **2 Materials and methods**

118   2.1 Studied samples and their preparation for the analyses

119   Two soil samples were selected for this study. They exhibit contrasting pH, but very similar further

120   physicochemical and mineralogical properties (Table 1). The acidic sample was collected from the B_t horizon of

121   a Luvisol profile (AL), whereas the alkaline one was sampled from the C_k horizon of a Pheaozem profile (CP).

122   The air-dried samples were passed through a 2 mm sieve. They were gently crushed in an agate mortar for the

123   analysis of their major physicochemical properties and bulk mineralogy, as well as for the sorption experiments.

124   For the chemical analyses, samples were further grounded to fine powder (<10 μm). Clay fraction (<2 μm) of the

125   samples was separated from the <2 mm fraction by aqueous sedimentation. Ethylene glycol solvation at 60°C,

126   Mg-saturation followed by glycerol solvation at 95°C, K-saturation, and heating at 350 and 550°C were used to

127   identify the clay mineral species. For the ATEM analyses, the samples were slightly grounded under ethanol to

128   form a suspension, and they were dropped onto an Au-grid.

129   The soil samples were spiked with metal ions by performing single element and competitive batch sorption

130   experiment (see details in Sipos et al. 2018). In the present study, only the samples spiked with the highest initial

131   metal concentrations were studied by ATEM. The samples were shaken with solutions containing 10 mmol/L Cd,

132   Cu, Pb and Zn (in form of nitrate) both separately and jointly for 24 hours at 22°C using a soil: solution ratio of

133   1:30. A background electrolyte of 0.01 M $Ca(NO_3)_2$ and initial pH of 5.25 ± 0.10 was used in each cases. The soil

134   and the solution were separated by centrifugation at 4000 rpm for 20 minutes and the supernatant was filtered. The

135   sediment was washed out by distilled water (at 1:30 solid:water ratio) for 30 minutes and separated by centrifuging.

136

137   2.3 Analytical techniques

138   Soil pH was studied in 0.1M $CaCl_2$ solution with a soil:solution ratio of 1:2.5. The TOC content of the samples

139   was measured with a TOC analyzer (Tekmar-Dohrmann Apollo 9000N). The BET surface area of the samples was

140   determined using gas sorption with N_2 gas (Quantochrome Autosorb-1-MPV). Particle size distribution of the

141   samples was studied with laser diffraction (Fritsch Analysette Microtech A22). Cation exchange capacity of the

142   studied soils was studied on the bases of the ISO 23470:007 (2007) method with $[Co(NH_3)_6]Cl_3$ solution, and

143   atomic absorption spectrometry (AAS) was used to measure the Co concentrations in the solutions (Perkin Elmer

144   AAnalyst 300). Bulk mineralogical analysis was carried out by powder X-Ray diffraction (Rigaku Miniflex 600).

145   Total Fe and metal concentrations were analyzed by inductively coupled plasma optical emission spectrometry

146   (ICP-OES) (Spectro Arcos). Samples were dissolved by 4-acid digestion using the mixture of HNO_3-$HClO_4$-HF

147   and after HCl. Dithionite extractable Fe content of the samples was studied by dithionite-citrate-bicarbonate

148   extraction after Mehra and Jackson (1960), and Fe concentrations were analysed by AAS. This latter method was

149   used to analyse the metal concentrations in the solutions of the sorption experiments, as well.

150   Both the initial and the metal-spiked samples were analysed by analytical transmission electron microscopy

151   (ATEM) (Philips CM20 equipped with Noran energy dispersive spectrometer (EDS)). The microscope was

152   operated at 200 kV with LaB_6 filament. Selected area electron diffraction (SAED) was used to identify the mineral

153   structure of the particles. Their chemical composition was analysed with 5 nm beam parameter and 100 sec of

154   counting time. Both the diffraction pattern and the chemical composition data were used for the mineralogical

155   identification of the particles, and the latter one was also used to study the sorbed metal amounts on the studied

156   particles.

157

158   **3 Results**

159   3.1 Characteristics of the bulk soils

160   Both of the studied samples have a low TOC content, as well as a medium surface area, cation exchange capacity

161   and clay content. Slight accumulation of Fe could be observed in both of them, and that of calcite in the CP sample.

162   They exhibit similar total Fe content of which significant ratio was extractable by dithionite (Table 1).

163   The clay mineralogy of the bulk samples can be characterized by the dominance of smectite and illite, with higher

164   illite ratios in the AL sample (Figure S1). The presence of Fe-oxyhydroxides could not be detected in the samples

165   by XRD. As shown by the ATEM analyses, Fe-oxyhydroxide (primarily ferrihydrite but also goethite) flakes with

166   the size of 20-100 nm are often placed on the surface of larger (generally 100-500 nm, and sometimes up to 1000

167   nm) clay lamellae in both samples. These particles appear also individually both as single particles and aggregates,

168   and they show high variability in their crystallinity. In the CP sample, the clay-oxyhydroxide phase associations

169   may be attached also to calcite particles with the size of 50-500 nm (Figure 1).

170   The samples contain the studied metals at average concentrations with no indication of any contamination. The

171   adsorbed metal amounts were higher by several orders of magnitude when compared to the natural ones, and they

172   showed high variation depending on the sorption conditions as well as on soil pH (Table 2). The sequences of the

173   sorbed metal amounts on the bulk soils are shown in Table 3. Generally, Pb showed the highest sorption among

174   the studied metals. The only exception is the CP soil at single element situation, where higher Cu than Pb amount

175   was sorbed. Copper mostly followed Pb in these sequences, except in the AL sample at single element situation,

176   where it showed similar sorbed amounts to that of Cd. The lowest sorbed metal amounts were generally found for

177   Zn, except in the CP sample at single element situation, where Cd exhibited the lowest sorption among the studied

178   metals. As expected, higher metal sorption was found in the alkaline CP soil than in the acidic AL sample, and

179   this difference was more pronounced in the single element situation. Similarly, competition by other metals

180   resulted in lower metal sorption in each case, and this effect was found to be higher in the CP than in the AL soil.

181   The more detailed characterization of the sorption of the studied metals in the bulk samples can be found elsewhere

182   (Sipos et al. 2018).

183

184   3.2. Sorption characteristics of the individual particles

185 Our ATEM analyses were primarily focused on particles which are expected to exhibit significant sorption capacity

186 (i.e. clay minerals and Fe-oxyhydroxides), but phases with lower expected sorption (calcite and other silicates),

187 and those formed during the sorption process (precipitates) were also studied. Sorting of particles was done

188 according to their chemistry, as our data showed that the Fe content of the particles and particle associations had

189 primary influence on the sorbed metal amounts in accordance with the results of others (Nachtegal and Sarks 2004,

190 Cerqueira et al. 2015). Hence, the following particle categories will be used in the followings: 1) clay particles; 2)

191 Fe-rich clay particles (with $Fe_2O_3 > 10$wt% and the absence of Fe-oxyhydroxide flakes on their surface); 3) Fe-

192 oxyhydroxide-clay mineral assemblages (clay particles with Fe-oxyhydroxide flakes on their surface); and 4) Fe-

193 oxyhydroxides. Distribution of clay mineral species among the studied particles was 55% illite/smectite, 32%

194 smectite and 13% illite in both samples. This did not correspond exactly to the natural distribution of the clay

195 particles in the studied soils, as we rather tend to compare similar particle types and assemblages in the studied

196 samples. Additionally, 90% of the studied Fe-oxyhydroxide particles were ferrihydrite with highly varying

197 crystallinity, and the rest was identified as goethite.

198 We have found large variance among the studied metals with respect to their sorbed amounts in the function of

199 soil particle types, soil pH and sorption conditions. Distribution of the sorbed metal amounts on the studied mineral

200 particle types are shown in Figure 2. Despite the sorbed metal amounts could be characterized by high deviation

201 within each particle types, we have found that Fe-oxyhydroxide particles showed the highest metal sorption

202 generally, whereas clay mineral particles the lowest one. Moreover, an increase in the metal sorption with the Fe

203 content of the particles was found mostly. These phenomena were the most expressed at single element situation.

204 Exceptions are the sorption of Zn in the AL sample and that of Pb in the CP sample. The sorption capacity of the

205 particles with clay component showed very similar metal sorption capacities at competitive situation, and only the

206 Fe-oxyhydroxide particles could be characterized by higher metal sorption. The only exception is the sorption of

207 Zn in the Al sample where each particle types showed similar sorbed metal amounts. The distinguished role of the

208 Fe-oxyhydroxides in metal sorption was also shown by the observation that metal sorption capacity of the clay-

209 Fe-oxyhydroxide assemblages increased with their Fe (e.g. Fe-oxyhydroxide) content. The correlation study

210 between the Fe and sorbed metal concentrations of these particles showed close relationship for Cd ($r = 0.87$ at P

211 < 0.05), Cu ($r = 0.69$) and Pb ($r = 0.86$) in the AP soil, and for Cu ($r = 0.62$) and Pb ($r = 0.67$) in the CP sample at

212 single element situation. At competitive situation, this relationship was found for Cd ($r = 0.50$) and Pb ($r = 0.52$)

213 in the AL sample, and for Cu ($r = 0.50$), Pb ($r = 0.85$) and Zn ($r = 0.77$) in the CP sample. In some cases, like that

214 of the sorption of Cu in the AL sample and Zn in the CP sample, the sorption of these metals ($r = 0.71$ and $r = 0.93$

215 at P < 0.05, respectively) increased with the Fe content of the clay mineral particles at single element situation.

216 Additionally, sorption of Pb and Zn increased with the Fe content of the Fe-rich clay mineral particles in the AL

217 sample at both situations (with r = 0.97 and 0.74 for Pb and with r = 0.55 and r = 0.70 for Zn at P < 0.05). The

218 significant role of Fe-oxyhydroxide coatings in metal sorption was also shown by the case of calcite particles in

219 the CP sample. In this case, metal sorption also increased with the increasing Fe content of these particles at both

220 situations (with r-values above 0.75 at P < 0.05). Metal amounts on the studied calcite particles decreased in the

221 order of Pb (0.91 ± 1.27 at%), Cu (0.64 ± 0.36 at%), Cd (0.63 ± 0.34 at%) and Zn (0.14 ± 0.12 at%).

222 Similarly to the sorption characteristics observed in the bulk soils, higher metal sorption was found on the studied

223 mineral particles in the CP than in the AL sample. Also, competition resulted in lower sorbed metal amounts on

224 the particles in both soils, and it affected the sorption of Cd and Zn at higher rate than that of Pb and Cu (Figure

225 2). Based on the sequences of the sorbed metal amounts (Table 3), Pb showed the highest sorption in the AL

226 sample at single element situation, and it is followed by Cu. However, their sorbed amounts showed very similar

227 concentration values for the clay mineral and Fe-oxyhydroxide particles. Cadmium exhibited higher sorbed

228 amounts than Zn in most of the particles, except in clay particles, where sorbed Zn amounts were higher than that

229 of Cd. These latter two metals showed very similar sorbed amounts in each particle types. In the AL sample at

230 competitive situation, Pb and Cu exhibited very similar sorbed amounts, which were always higher than those for

231 Cd and Zn. Zinc showed slightly higher sorbed concentration values on the studied particles than Cd in this case,

232 but still very similar values were observed also for these tow metals. Quite different features were observed in the

233 CP sample at single element situation. Lead exhibited the highest sorption on the clay particles, followed by Cu

234 and Zn with similar values and at least by Cd with the lowest ones. All other particle types sorbed very similar

235 amounts for Cu, Zn and Pb, which were much higher than those for Cd. In the CP sample at the competitive

236 situation, the same characteristics were observed for each particle types. That was the highest sorption for Cu

237 followed by Pb with similar sorbed amounts for the Fe-oxyhydroxide particles. These two metals exhibited

238 significantly higher sorbed amounts than Zn and Cd in this case. Zinc showed slightly higher sorbed metal amounts

239 than Cd for each particle types, which was the most expressed for the clay and Fe-oxyhydroxide particles.

240 The ATEM analyses also showed the formation of Cu and Pb precipitates in the CP sample during the sorption

241 process. Although this process may have also occurred on the surface of the calcite particles, presence of individual

242 precipitates was observed, as well (Figure 3). Lead precipitated in form of a carbonate phase with aragonite-type

243 structure as shown by the characteristic indexes of 110, $1\bar{1}1$ and $\bar{1}3\bar{2}$ from the crystallographic direction of [$\bar{1}12$

244] (Figure 3a). The well-crystalline cerussite (PbCO$_3$) particles are relatively large (up to 200 nm), and their tabular

245 shape can be suspected. Besides Pb, they may contain small amount of Ca (1.5-3.8 at%). In contrast to Pb, Cu

246 precipitated not only in form of carbonate but also as hydroxide (Figure 3b). This latter phase appears as large (2-

247 400 nm) xenomorphic aggregates. It shows low crystallinity with structural characteristics similar to ferrihydrite

248 as shown by the diffraction rings at 1.25, 1.5, 2.4 and 2.8Å. They may also contain Ca and Fe up to 5 at%. In the

249 case of Cu, formation of a hydroxy-carbonate phase, the mineral malachite ($Cu_2[(OH)_2 \cdot CO_3]$) was also observed.

250 Its identification is based on the observation of 111 indexes from the [$\bar{1}10$] crystallographic orientation (Figure

251 3c). It is present as smaller (up to 100 nm), well-crystalline particles with lath-shaped habit extended along the c-

252 axis. They may contain small amount of Ca (<1.2 at%) and Fe (0.3-2.2 at%), as well. The presence of metal

253 carbonates were also detected but only for Pb by XRD analyses in the bulk soils. The appearance of the peaks at

254 3.59Å and 3.50Å on the XRD pattern of the CP sample after the single element Pb and competitive experiments

255 showed the presence of cerussite in these samples (Figure S2).

256

257 **4. Discussion**

258 4.1 Comparison of metal sorption in the bulk soil and on their mineral particles

259 Sequences of the sorbed metal amounts in the different particle types showed some differences when compared to

260 those established for the bulk soils (Table 3). Lead showed considerably higher sorbed concentrations than the

261 other metals for the bulk acidic soil. On the particles, however, Cu showed also similarly high sorption, which

262 suggests that the contribution of organic substances to Pb sorption could be supposed in the acidic sample, whereas

263 Cu was rather sorbed by the soil mineral components in this case. Antoniadis et al. (2015) showed that soil organic

264 compounds are capable of affecting Cu retention only when their amount is higher than a threshold. This was also

265 found by synchrotron-based microscopic studies of Yang et al. (2014), who found that Cu is associated with Fe-

266 oxides in mine soils with low concentrations of organic matter. Rafaey et al (2014) also found the dominant role

267 of the mineral phase in Cu bonding. Based on laboratory experiments, they observed the decreased affinity of Cu

268 for soils rich in Fe-oxyhydroxide and smectite after their enrichment with organic matter. In our case, the low TOC

269 content of the samples supported low amount of organic surface sites for the high load of both metals, so their

270 contribution to the metal sorption could be only expected for the one with higher affinity towards the organic

271 surfaces. Zinc also showed similar sorbed concentrations to Pb and Cu on the clay particles at single element

272 situation in the acidic sample. According to Proust et al. (2013), Zn is the only one that is able to be adsorbed by

273 specific chemical bonding to the hydroxyl edge sites of the phyllosilicates at acidic conditions, whereas the other

274 ones form rather outer-sphere complexes. EXAFS studies of Fan et al. (2016) also showed the high affinity of Zn

towards layer silicates in spiked soils. These observations supports our finding on the relatively high sorption of

Zn onto the clay mineral particles at single element and acidic soil conditions.

On the contrary, Zn showed similar sorbed concentrations on the soil particles to Cu and Pb in the alkaline sample

and at single element situation, although Zn could be characterized by significantly lower sorption in the bulk

sample as compared to Pb and Cu. The only exceptions are the clay particles, which preferentially sorbed Pb in

this case and much lower Cu and Zn amounts. According to the complexation model carried out by Gu et al.

(2010), adsorption of metals occurred on the variably charged edge sites of montmorillonite through the formation

of inner-sphere surface complexes. At such conditions, they found the following affinity sequence towards the

edge sites of smectite: Pb > Cu > Zn > Cd, which is in accordance with our direct observations. The higher bulk

sorption of Pb and Cu could be primarily related to their immobilization by non-mineral surfaces or by other

retention processes, like precipitation (see below), which was also characteristic also at competitive situation. This

is in accordance with the results of Abat et al. (2012), who found that Ca displaces Zn rather than Cu at wide pH

range, and this latter metal is more strongly held by the SOM than Zn.

4.2 Relationship between the metal sorption and Fe content of the mineral particles

An increase in the metal sorption with the Fe content of the studied particles was found in many cases. This could

be only partly related to the fact that Fe-oxyhydroxides exhibited the highest metal sorption in general. Although

this phenomenon is the most expressed in the alkaline sample, it can not be related to the surface charge properties

of the Fe-oxyhydroxides solely, which exhibit net negative surface charge only at alkaline conditions (Wang et al.

2016). This is because these phases are the most efficient sorbents for each metal also in the acidic soil. Covelo et

al. (2007) studied the correlation between the metal sorption capacities of bulk soils and their Fe-oxide content,

and they found close relationship for certain metals only. According to Antoniadis et al. (2015) this relationship

showed high variation among samples with varying pH, as well. In line with the above, clay particles with low Fe

content sorbed the lowest metal amounts, although some exceptions were found, like the sorption of Zn in the

acidic sample and that of Pb in the alkaline one at single element situation. Data of Akafia et al. (2011) from

potentiometric titration and adsorption curves suggested that metals were mainly bond through the formation of

outer sphere complexes on the permanently charged basal surface sites of smectites at acidic conditions, so their

adsorption was strongly affected by ionic strength. On the contrary, adsorption occurred mainly on the variably

charged edge sites through the formation of inner-sphere surface complexes in the higher pH range. A strong

tendency of Zn to sorb on smectite in soils was found also by Rafaey et al. (2014). This can be explained by the

305   findings of Glatstein and Fransisca (2015), who showed that the threshold pH value at which metal concentrations

306   start to drop sharply in the metal-montmorillonite systems is the lowest for Zn when compared to Cd, Cu and Pb.

307   Their results showed that Zn can be adsorbed on this clay mineral still above pH 5 by ion exchange mechanisms.

308   On the contrary, hydrolization ability of Pb at relatively low pH promote its highest sorption through surface

309   complexation when pH increases (as it is common during cation adsorption) (Liu et al. 2016). In competitive

310   situation, however, particles with clay component showed very similar metal sorption for each metal, and only Fe-

311   oxyhydroxide particles could be characterized by considerably higher metal sorption. Although Fe-oxyhydroxides

312   bear pH-dependent surface charge that is negative only at alkaline conditions, they could be effective sorbents of

313   metals even in acidic soils, which is related to their low crystallinity resulting in not evenly-distributed charge

314   properties (Sahroui et al. 2015). Additionally, because Fe-oxyhydroxides do not have large permanent negative

315   charge like smectites, electrostatic interactions will have been much smaller on their surfaces (Rafaey et al. 2014),

316   primarily at the equilibrium pH values observed in our experiments. The primary role of Fe-oxyhydroxides in

317   metal sorption is also supported by the metal sorption trends observed in the clay-Fe-oxyhydroxide assemblages.

318   Moreover, increasing metal sorption with the increasing Fe content of the calcite particles shows that not metal

319   precipitation but metal sorption by Fe-oxyhydroxide coatings can be expected on the surface of the calcite particles

320   in alkaline soil. Study on the sorption properties of limestone by Sdiri and Higashi (2012) showed that samples

321   with high impurities containing Si and Fe exhibited higher sorption for metals, suggesting that clay and Fe-

322   oxyhydroxide coatings promoted metal sorption onto the surface of calcite particles. Iron may also play a different

323   role in metal sorption in soils as the Fe content of clay mineral particles could be also related to their Pb sorption

324   capacity in single element situation. According to Wu et al. (2009) Fe-montmorillonite synthesized in laboratory

325   exhibited higher interlayer spacing indicating higher affinity for metal cations as compared to its parent Ca-

326   montmorillonite. The adsorption capacity of the Fe-rich variant was higher than that of the Ca-montmorillonite at

327   a wide pH range (from 2 to 9), and as long as the latter one removed metals from the solution by ion exchange, the

328   former one by surface complexation and surface precipitation.

329

330   4.3 Effect of soil pH on metal partition among mineral particles

331   Higher metal amounts were sorbed in the alkaline sample than in the acidic soil, and this phenomenon was also

332   observed on their studied particles. It could be expected, as soil pH directly controls the surface charge properties

333   of soil components, the solubility of metal precipitates and organic matter, and the metal hydrolysis, all resulting

334   in increase of the adsorption of cationic elements with pH (Young 2013). We have calculated the ratios (e.g. the

335   differences) of the sorbed metal amounts between the alkaline and acidic bulk soils, as well as between their

336   respective particle types. At single element situation (Figure 4a), the highest difference between the sorbed metal

337   amounts by the bulk alkaline and acidic soils was found for Cu, followed by Zn, Pb and Cd. Contrarily, Zn showed

338   the highest difference on the particles in this case, primarily on those with high Fe content (e.g. Fe-rich clay

339   minerals, clay-Fe-oxyhydroxide assemblages and Fe-oxyhydroxides). The very similar ratios between the bulk

340   soils and the Fe-rich particle types suggests that the higher Zn sorption in the alkaline soil could be primarily

341   attributed to its sorption onto Fe-rich clay minerals, clay-Fe-oxyhydroxide assemblages and Fe-oxyhydroxides.

342   For similar reasons, the higher Cd sorption in the alkaline soil could be attributed to Fe-oxyhydroxides. The

343   primary role of these latter phases in metal sorption by soil was already discussed in the previous section. In

344   contrast to Zn and Cd, the differences between the sorbed Cu and Pb amounts in the alkaline and acidic samples

345   were significantly higher for the bulk soil than for their particles, primarily for Cu. Moreover, the differences were

346   found to be very similar for the studied particle types. Consequently, we could not have specify any particle type(s)

347   for Cu and Pb, which is responsible to higher degree for their higher sorption at alkaline conditions. This suggests

348   again the contribution of non-mineral surfaces or that of the precipitation in this case. These observations

349   supplement the major findings of recent surface complexation models. For example, Gu et al. (2014) found that at

350   acidic and neutral conditions, cation exchange sites and SOM are the main soil components for metal sorption,

351   whereas at alkaline conditions, specific sorption to Fe-oxyhydoxides and the edge site of clays are the most

352   important surface reactions for metal adsorption in soils. Only clay mineral particles showed slightly higher

353   contribution to the Pb sorption by the alkaline soil. Liu et al. (2016) found that metal sorption occurs by

354   complexation with hydroxyl edge sites on clay minerals at pH above 6.0. As Pb hydrolyzes at the lowest pH among

355   the studied metals, and the equilibrium pH values in the alkaline samples were higher than 6.0, interaction of Pb

356   with the edge hydroxyl sites is more likely than for the other studied metals in the alkaline sample.

357   At competitive situation (Figure 4b), the highest ratio between the sorbed metal amounts by the alkaline and the

358   acidic bulk samples was found for Pb, followed by Cu, Cd and Zn. On the contrary, these ratios were found to be

359   very similar on the different particle types for most metals, suggesting that each studied particle type contributed

360   at similar degree to the higher metal sorption at alkaline conditions. This similarity, however, might be rather the

361   effect of competition (see section 4.4) and not that of differences in soil pH. The only exception is Zn in this case,

362   which exhibited (slightly) higher differences on the clay mineral (and Fe-oxyhydroxide) particles than on the other

363   ones. According to Ford and Sparks (2000) Zn can be incorporated very effectively into neo-formed precipitates

364   developed on the surface of phyllosilicates at higher pH, which can be related to the higher contribution of clay

13

365 surfaces to Zn sorption in the CP sample at competitive situation. For Zn and Cd, the studied ratios are very similar

366 for the bulk soils and for the different particle types. This suggests that their higher sorption in the alkaline soil

367 can be due to that of on the surface of the studied mineral particles. Contrarily, additional retention process(es)

368 and/or non-mineral surfaces could be also contributed to the higher sorption of Cu and Pb also at competitive

369 situation. This is again suggested by the differences between the sorbed Cu and Pb amounts by the CP and AL

370 samples, which were significantly higher for the bulk soil than for their particles, but primarily for Pb in this case.

371 Although the studied soils contained low amounts of organic matter, its contribution to the sorption of these metals

372 could not be neglected. Several studies have found that soil organic matter is able to adsorb Cu (and Pb) even at

373 low pH with high preference over the other studied metals (Vidal et al. 2009). Additionally, we have observed the

374 precipitation of Cu and Pb in the alkaline sample at both situations (see Figure 3). The direct effect of carbonates

375 on the metal retention in soils is often related to the formation of alkalinity-derived insoluble species (Orucoglu et

376 al. 2018). Additionally, carbonates may play a major role even in the adsorption of metals in alkaline soils (Halmos

377 et al. 2015). Solubility calculations of Hale et al. (2012) showed that cerussite precipitate at pH above 4.5 in soils

378 treated with alkaline materials. This pH value is 5.4 for the hydroxy-carbonates of Cu, whereas carbonates of Zn

379 and Cd are expected to precipitate only at higher pH values (above 5.8 and 6.0, respectively). These additional

380 processes were primarily characteristic for Cu at single element situation and for Pb at competitive one. As the

381 precipitation of Cu was probably preceded by that of Pb at competitive situation, sorption of Cu by soil organic

382 matter may have also contributed to the higher sorption of Cu besides precipitation in the alkaline sample.

383

384 4.4 Effect of competition on metal partition among mineral particles

385 Similarly to those found in the bulk samples, competition resulted in a decrease of metal sorption also on the

386 mineral particles. The ratios between the sorbed metal amounts in single element and competitive situations were

387 calculated for the respective bulk samples and for their particles. Competition affected the sorption to the highest

388 degree for Zn, followed by Cd, Cu and Pb in the bulk soils. This sequence showed slightly different features in the

389 case of the studied mineral particles, as the effect of competition decreased as follows in the acidic and alkaline

390 soils, respectively, Cd ≥ Zn > Pb ≥ Cu, and Zn > Cd > Pb ≥ Cu. The higher effect of competition on the sorption

391 of Cd and Zn is a well-known phenomenon in soils, as these metals are mainly immobilized by non-specific

392 adsorption, while Pb and Cu by specific sorption as shown by the metal leaching study of Sanguimskan and

393 Punrattanas (2014). Vega et al. (2010) also found that competition of Cd and Zn with Cu and Pb is particularly

394 unfavorable for the binding of the former metals to soil under acidic soil conditions (between pH 4 and 6). This

14

395　can be also related to the lower pH dependency of Cu sorption than that of Zn on the clay fraction of soils

396　(Fernandez et al. 2015), as well as on individual soil components (Glatstein and Fransisca, 2015). The latter authors

397　found that the simultaneous presence of metals affect the sorption of Cu on bentonite the least, while having a

398　higher effect on Pb, and a strong influence on Zn and Cd removal at a wide pH range (between 3 and 9).

399　In the acidic sample, decrease of sorption by competition in the bulk soil could be explained by the decrease of

400　metal sorption on the soil mineral particles quite well, as similar ratios were found for the bulk soils and their

401　particles between the sorbed amounts in single element and competitive situations (Figure 5a). Additionally, only

402　slight differences were found among these ratios calculated for the studied particle types, which showed that

403　competition resulted in lower sorption on each particle types near equally. Sorption of Cu decreased at lower rate

404　on the mineral particles than in the bulk soil suggesting that the competition probably affected its immobilization

405　also on non-mineral surfaces. Copper and Pb show generally higher affinities for the available organic and mineral

406　surfaces in soils than Zn and Cd (Covelo et al. 2007). However, partition of available surfaces among soil

407　components may affect the selectivity of metals. For example, Perelomov et al. (2011) showed that Pb inhibits Cu

408　sorption in soils strongly, but this effect decreases with increasing ratio of available organic surfaces. In the alkaline

409　soil, however, competition resulted in significant differences among the ratios between the sorbed amounts in

410　single element and competitive situations calculated for the studied particle types (Figure 5b). Very high decrease

411　due to competition was found for Cd in Fe-oxyhydroxides, for Pb in clay particles and for Zn in Fe-rich particles.

412　Rafaey et al (2017) also found that Cu is the most strongly sorbed and the strongest competitor for soil constituents

413　(like smectite, oxyhydroxides and OM), so its presence may significantly affect the sorption behavior of other

414　metals. This can be also related to the different behavior of Cu, which showed similar features to that found in the

415　acidic sample from this point of view, suggesting similar decrease due to competition on each particle type.

416　Additionally, the ratios calculated for the mineral particles were significantly lower than that found for the bulk

417　soil, suggesting that Cu sorption decreased on non-mineral surfaces, or its precipitation was inhibited due to

418　competition in this sample. This can be explained by the effect of pH on the formation of the carbonates and

419　hydroxy-carbonates of Cu and Pb as above. Similar feature was found also for Zn. This can be related to the low

420　selectivity of Zn to the available soil surfaces (like organic matter, ferrihydrite) in competition with other metals

421　(like Cu), which is generally found by others (Capasso et al. 2004). Although no evidence for Zn precipitation was

422　found in the alkaline sample, this process could be also supposed in our case.

423　The selective characteristics of competition has been shown by several studies in soils, which is affected not only

424　by other metals present in solution but also by the presence of phases supporting sorption sites with different

15

affinities. For example, Antoniadis et al. (2017) found that amorphous oxides were found to become a lot more important in influencing Zn sorption when another adsorptive surface has been extracted. This behavior can be also affected by the phenomenon that metals probably come in contact with a sorbent sequentially in soils (Violante et al. 2010). Our direct observations on the variation of metal partition among soil particle types also supported these observations.

5 Conclusions

A strong selectivity of metals was found for mineral surfaces in the function of particle type, soil pH and metals' competition. Iron-oxyhydroxides played the most important role in metal sorption in soils for each metal and soil condition. These phases contributed to the sorption of metals not only as single particles, but significantly enhanced the sorption capacities of clay, or even calcite particles through coating, primarily at single element condition for Cu and Pb. In some cases, like that of Pb at single element condition, Fe increased the sorption capacity of clay particles as the constituent of the mineral structure. Smectites played a less important part in the sorption of metals, but in certain cases, like that of Zn in acidic soil and of Pb in alkaline one, they also preferentially sorbed these metals.

Comparison of the sorbed metal amounts on bulk soils and on their particles found to be useful in identification the most active soil components in the sorption process at given conditions. Higher Zn sorption in the alkaline soil than in the acidic one could be primarily attributed to its increased sorption onto Fe-rich clay minerals, clay-Fe-oxyhydroxide assemblages and Fe-oxyhydroxides, and that of Cd to Fe-oxyhydroxides at single element situation. Under competition, however, each studied particle type contributed to their higher sorption at similar degree, and this was the case of Pb and Cu at both situation. Additionally, non-mineral surfaces and precipitation played also an important role in the higher sorption by the alkaline soil for the latter metals, but with higher degree for Cu at single element and for Pb at competitive situation.

In single element situation, metal sorption capacities of the studied particles could be distinguished well, but particles with clay component showed very similar sorption capacities under competition. In the acid soil, decrease of sorption on mineral particles due to competition explained the decrease of the sorption in the bulk soil quite well. In the alkaline soil, however, certain soil mineral types could be specified which were primarily affected by competition, like Fe-oxyhydroxides for Cd and Zn and smectites for Pb.

Besides the direct observation of the sorption onto soil mineral particles, metal precipitates could be identified directly in the alkaline soil. Additionally, the role of organic surfaces in metal sorption could be inferred indirectly

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455 in certain cases, like that of Pb in the acidic soil. Direct observation of metal sorption on soil particles not only

456 supports surface complexation models, but they complete these models effectively about the specification of the

457 role of soil components in soils at given conditions.

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597 **Table 1.** Major physicochemical properties of the studied samples. Fe_t and Fe_d refer to the total and dithionite

598 extractable Fe content of the samples.

Sample	pH (CaCl$_2$)	TOC (%)	BET (m^2/g)	CEC (cmol/kg)	Fe$_t$ (%)	Fe$_d$ (%)	Clay (%)
AL	4.28 ± 0.01	0.54 ± 0.07	33 ± 1.1	14.02 ± 0.46	4.03 ± 0.20	1.54 ± 0.01	19.2 ± 1.65
CP	7.93 ± 0.01	0.34 ± 0.09	29 ± 0.5	12.35 ± 0.22	4.45 ± 0.14	2.69 ± 0.03	18.1 ± 2.10

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Table 2. Metal concentrations (mmol/kg) in the studied samples before (i) and after the single element (ss) and

competitive (sc) sorption experiments.

Sample	Cd_i	Cd_{ss}	Cd_{sc}	Cu_i	Cu_{ss}	Cu_{sc}	Pb_i	Pb_{ss}	Pb_{sc}	Zn_i	Zn_{ss}	Zn_{sc}	pH_{eq}
AL	<0.001	40 ± 0.54	13 ± 0.32	0.44 ± 0.02	39 ± 1.5	14 ± 0.25	0.14 ± 0.02	63 ± 1.3	32 ± 0.44	1.4 ± 0.11	33 ± 1.5	8.3 ± 0.34	4.02 ± 0.25
CP	<0.001	101 ± 0.68	22 ± 0.25	0.05 ± 0.01	289 ± 2.9	88 ± 0.42	<0.005	247 ± 0.95	274 ± 1.6	1.6 ± 0.08	155 ± 0.98	6.4 ± 0.2	6.15 ± 0.25

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607 **Table 3.** Sequences of average sorbed metal amounts on the bulk soil samples and on their mineral particles.

		Acid (AL) sample	Alkaline (CP) sample
Single	Bulk soil	Pb >> Cd ≥ Cu > Zn	Cu > Pb >> Zn > Cd
	Clay mineral particles	Pb ≥ Cu ≥ Zn > Cd	Pb > Cu ≥ Zn > Cd
	Fe-rich clay mineral particles	Pb > Cu > Cd ≥ Zn	Cu ≥ Zn ≥ Pb > Cd
	Clay-Fe-oxyhydroxide assemblages	Pb > Cu > Cd ≥ Zn	Pb ≥ Zn ≥ Cu > Cd
	Fe-oxyhydroxide particles	Pb ≥ Cu ≥ Cd > Zn	Cu ≥ Pb ≥ Zn > Cd
Competitive	Bulk soil	Pb >> Cu > Cd > Zn	Pb >> Cu > Cd > Zn
	Clay mineral particles	Cu ≥ Pb > Zn > Cd	Cu > Pb > Zn > Cd
	Fe-rich clay mineral particles	Pb ≥ Cu > Zn > Cd	Cu > Pb > Zn ≥ Cd
	Clay-Fe-oxyhydroxide assemblages	Pb ≥ Cu > Zn ≥ Cd	Cu > Pb > Zn ≥ Cd
	Fe-oxyhydroxide particles	Cu ≥ Pb > Zn ≥ Cd	Cu ≥ Pb >> Zn ≥ Cd

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Figure captions

Figure 1. Characteristic mineral particle associations observed by ATEM in the studied samples. a) Small ferrihydrite flakes on large illite/smectite lamellae with changing ratio of the clay components within the mixed layer phases (illite and smectite dominance are shown on SAED 1 and 2, respectively) in the acidic sample (AL). b) Agglomerate of calcite and smetcite without (1) and with Fe-oxyhydorxide flakes (2), and that of smectite, ferrihydrite and calcite (3) in the alkaline sample (CP). Thick black arrows indicate Fe-oxyhydroxide flakes when other phase is not indicated. Pl = plagioclase, Sca = silica.

Figure 2. Metal concentrations (at%) of the studied soil mineral particle types in the acidic (AL) and alkaline (CP) samples after single element (a and b, respectively) and competitive (c and d, respectively) sorption of the studied metals. Concentration data were produced by TEM-EDS analyses of individual soil mineral particles or their associations, and one single box and whisker plot represents the direct analysis of between 8 and 17 single particles.

Figure 3. Transmission electron microscopy micrographs, selected area electron diffractions patterns and energy dispersive X-ray spectra (EDS) of the mineral phases formed through the precipitation of Pb and Cu in the alkaline CP sample as cerussite (a), Cu-hydroxide (b) and malachite (c). Unmarked peaks on the EDS spectra belong to Au composing the sample holder.

Figure 4. Ratios of the sorbed metal amounts on different particle types (bars) and on the bulk soils (red lines) between the alkaline (CP) and the acidic (AL) samples at single element (a) and competitive (b) situations. The ratio values were calculated by dividing the sorbed metal amounts in the alkaline soil with those amounts in the acidic soil, as the metal concentrations were always higher in the alkaline sample than in the acidic one.

Figure 5. Ratios of the sorbed metal amounts on different particle types (bars) and on the bulk soils (red lines) between the single element and competitive situations in the acidic sample (AL) (a) and in the alkaline one (CP) (b). The ratio values were calculated by dividing the sorbed metal amounts found at the single element condition with those amounts found at the competitive situation, as the metal concentrations were always higher at single element conditions than at the competitive one.
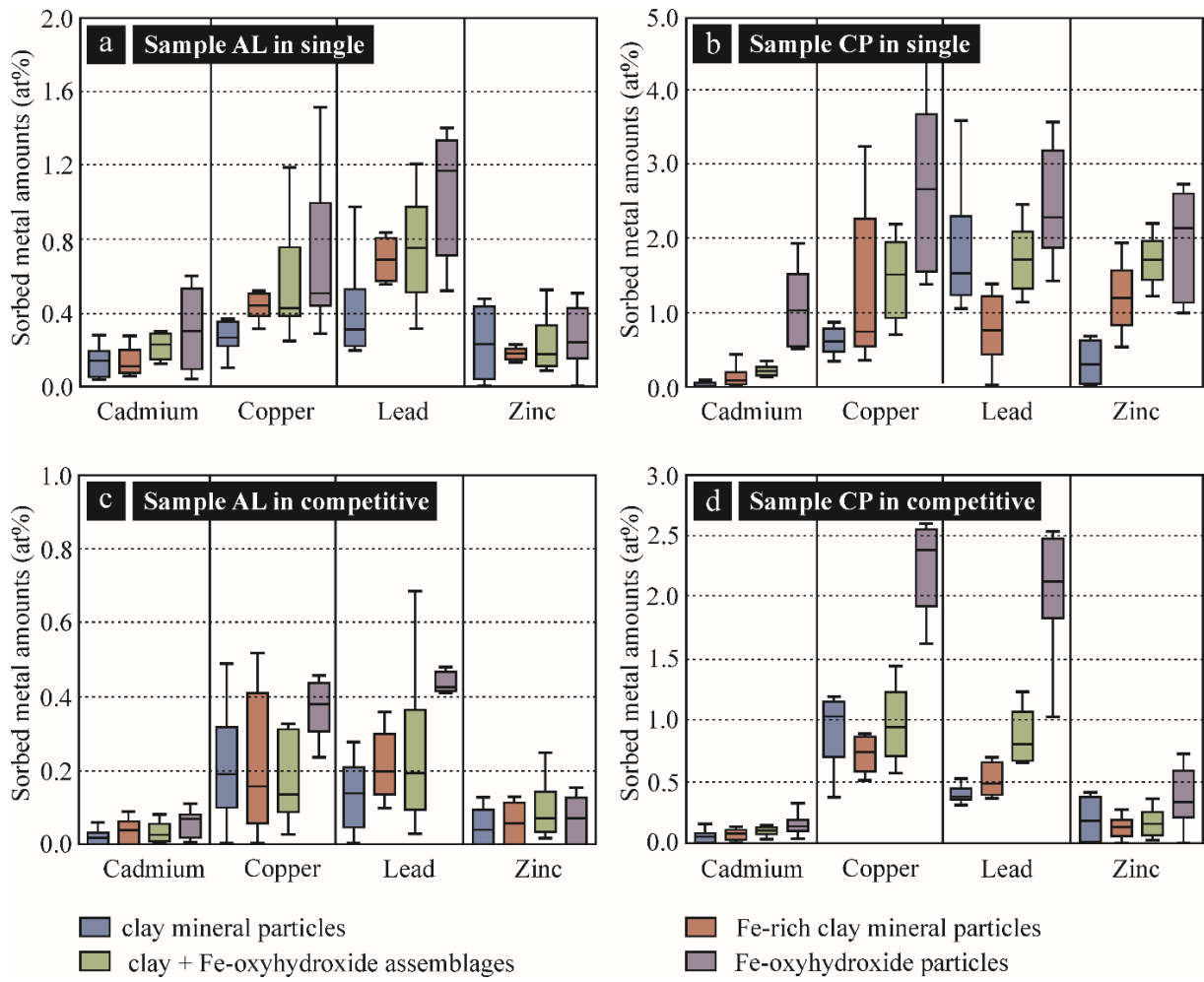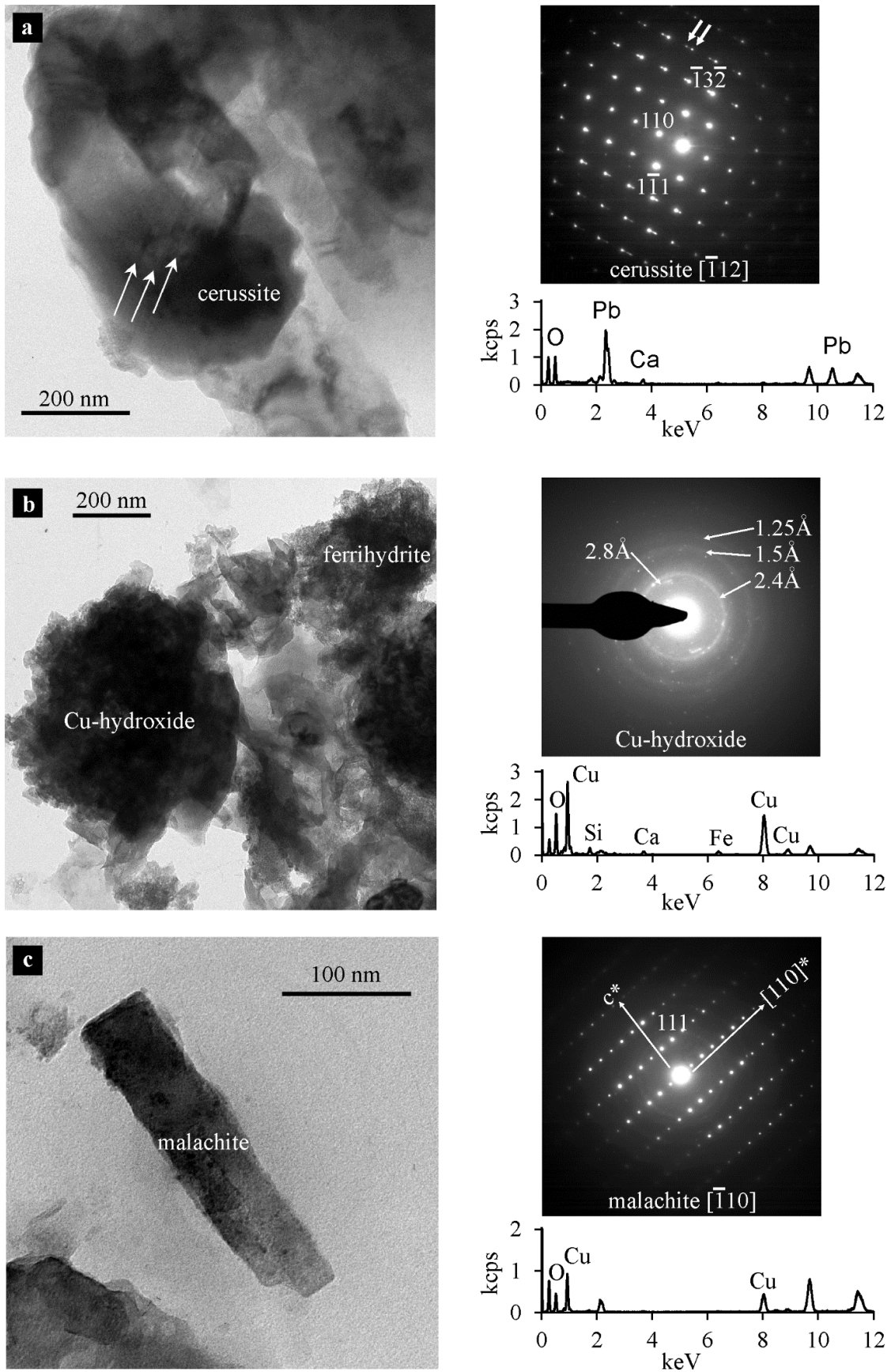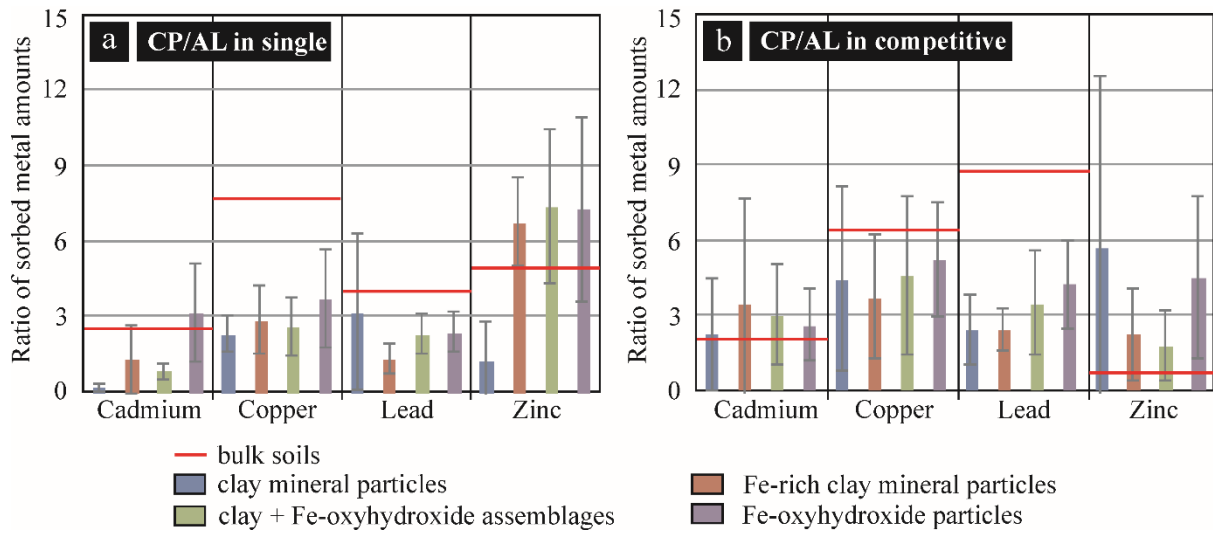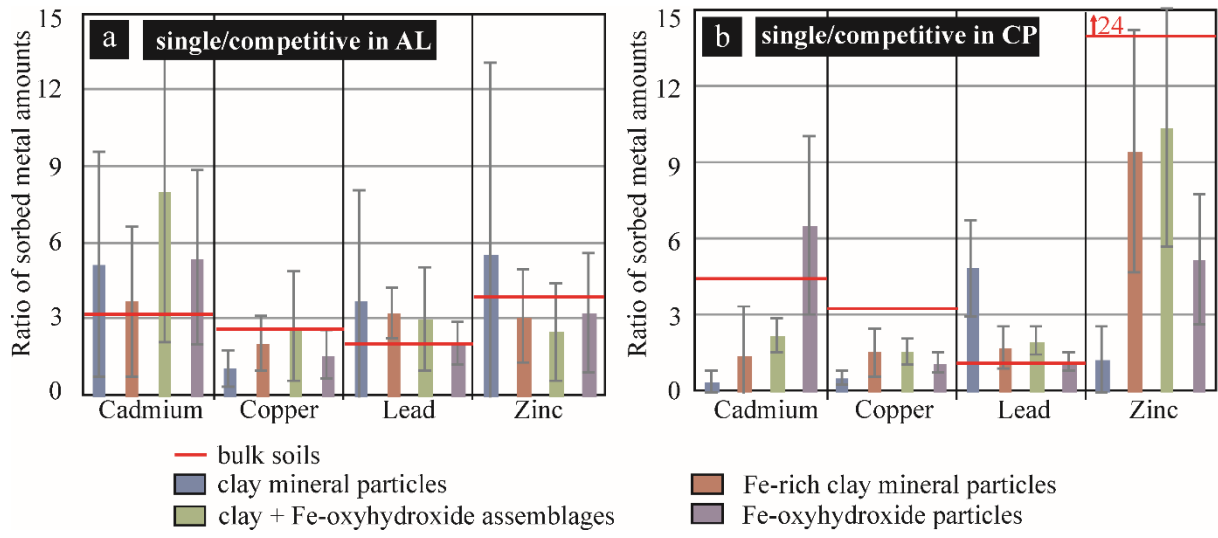
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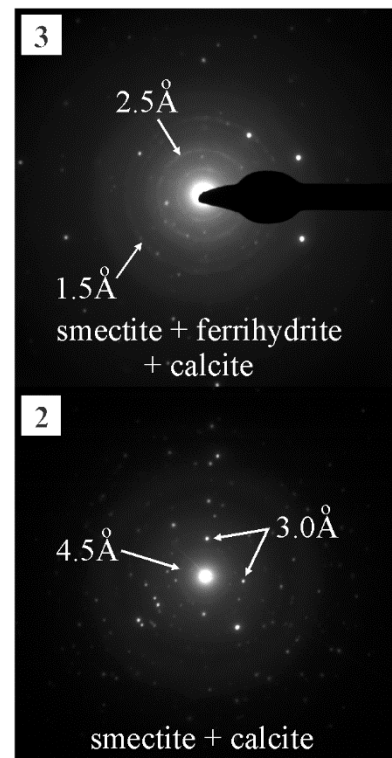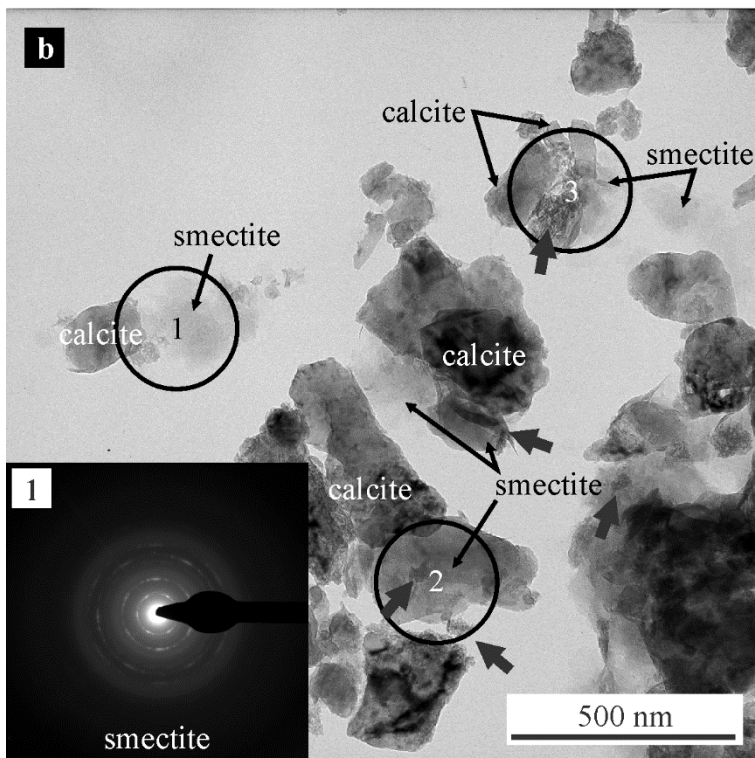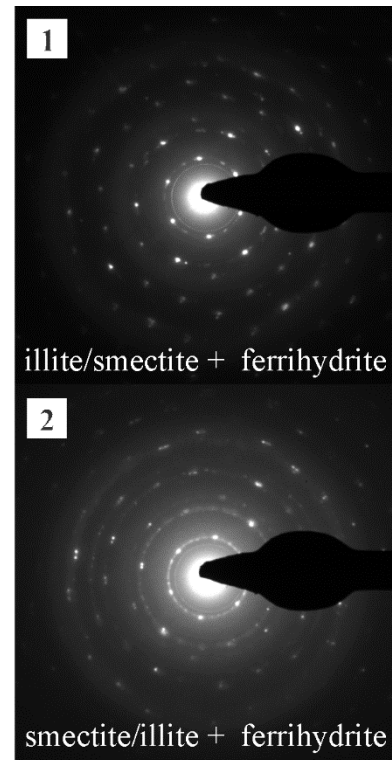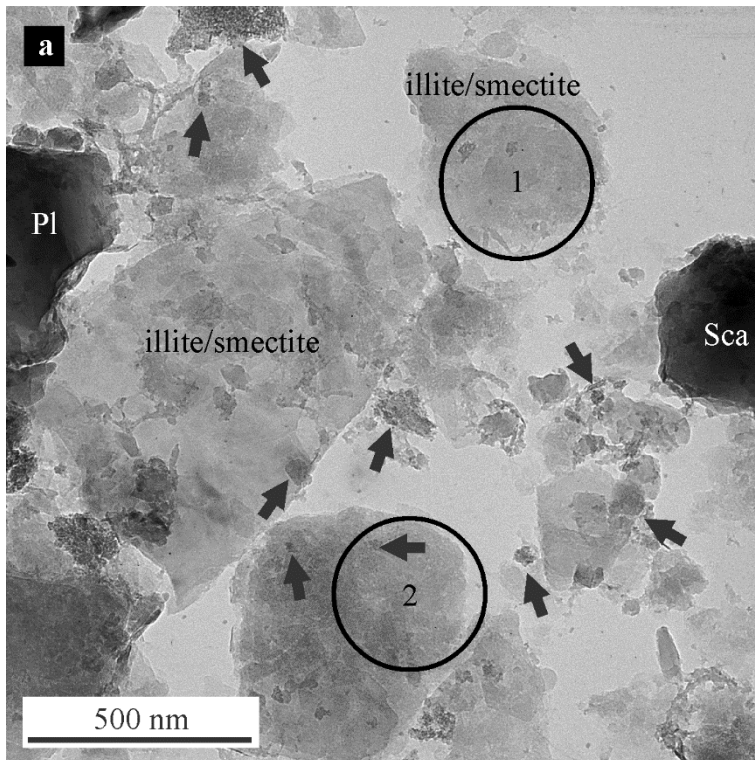
Figure 2

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