Contribution of individual pure or mixed-phase mineral particles to metal sorption in soils

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Abstract

The contribution of individual minerals and their associations to metal sorption in soils is little known. We therefore determined the concentrations of Cd, Cu, Pb, and Zn in individual mineral particles (clay minerals, Fe-rich clay minerals, clay-Fe oxide associations, Fe-oxyhydroxides, calcite) after equilibration of an acid and an alkaline soil sample with 10 mmol/L of these metals with the help of Transmission Electron Microscopy equipped with Energy-dispersive X-Ray Spectroscopy (TEM-EDX). The results of the TEM-EDX measurements were compared with those of batch sorption experiments.

The alkaline soil showed a stronger sorption of all studied metals than the acidic soil, as expected. This was also true when the individual mineral (associations) were considered, although the clay mineral and clay mineral-rich particles in the acidic soil sorbed more Cd and Zn than those in the alkaline soil. In line with the literature, we consistently observed a stronger sorption of Cu and Pb than of Cd and Zn both in the bulk soil and on the particles with the exception of Zn that showed the highest sorption on clay particles in the acidic soil among the studied metals. Although Cu and Pb may also have precipitated in the alkaline soil, their higher sorption was found on the particles directly, as well. The Fe concentrations of the individual mineral particles correlated with the sorbed amounts of metal. It could be related to the increasing contribution of Fe-oxyhydroxides within the particle associations in the alkaline soil, and rather to the increasing Fe concentration of clay mineral particles in the acidic one. Our results emphasize the important role of Fe oxides as pure minerals or in mineral associations for the sorption of trace metals in soils depending on the soil pH conditions.

Highlights

- metal sorption preferences of soil minerals were revealed by direct observations
- metal sorption show a strong variation among mineral particles
- sorption increased with the amount of Fe-oxyhydroxides in the alkaline soil
- sorption increased with the Fe concentration of clay particles in the acidic soil

Key words: selectivity, soil mineral particles, sorption capacity, transmission electron microscopy

1. Introduction

Elucidation of the speciation of heavy metals in the environment is paramount to understand their potential mobility (McNear et al., 2005). The sorption capacity of soils is influenced by several properties, such as pH and presence of sorption sites on soil components. In a mineral soil, clay minerals and Fe- and Al-(oxy)hydroxides control metal sorption, although minor contents of carbonates and organic matter may also contribute to that (Stumm, 1992). Batch equilibrium techniques are generally used to study metal sorption, and the data are described using isotherms, providing estimates about the sorption capacity of the bulk soil. Sorption isotherms, however, do not inform about the metal partitioning on the surface of soil minerals (Cerqueira et al., 2015a). Soil surface chemistry can vary at microscopic scale considerably, which may come from natural structural irregularities of a mineral or as a result of associations of several mineral phases (Serrano et al., 2009). This heterogeneity can lead to misinterpretation of the role of soil components in the sorption process (Cerqueira et al., 2011) and it may even hinder the direct identification of the most active components (Nachtegaal and Sparks, 2004). A characteristic example of such heterogeneity is that of the intimate association of Fe-(oxy)hydroxides and clay minerals in soils. Their important role in sorption processes has been widely demonstrated (e.g. Sipos et al., 2008; Yaghi and Hartikainen, 2013). To be able to describe their role in the sorption of metals in soils, specific analytical approaches targeting the minerals directly are needed besides isotherm data evaluation.

Several analytical techniques are available which are suitable to characterize the soil phases even at particle level. For example, Cerqueira et al. (2015b) and Arenas-Lago et al. (2016) demonstrated that the combined use of Time-Of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) and Field Emission Scanning Electron Microscopy (FE-SEM) is an effective tool to identify the selectivity of soil components for metals. These techniques, however, do not provide direct information about the mineralogy of the studied particles. Another promising technique is X-Ray Absorption Spectroscopy (XAS); its results up to now, however, mostly provided bulk spectroscopic information about the local structural and chemical environment of sorbed metals, so they were only used in single phase and metal model systems (McNear et al., 2005). Although the latest generation synchrotron light sources are already able to produce micro-focused beams for μ-X-Ray Absorption Near Edge Structure (μ-XANES) imaging, which can be even combined with μ-X-Ray Diffractometric (μ-XRD) analyses, data analysis approaches are far from standardised (Gräfe et al., 2014). Among the analytical techniques available for the study of very fine particles, TEM is perfectly adapted to their characterization in soils despite their large heterogeneity. This technique provides its greatest value when coupled with chemical microanalysis (mostly Energy-dispersive X-Ray

Spectroscopy (EDX)) to associate the chemical composition and crystal structure of the soil particles (Elsass et al., 2008). This advantage was also utilized in studying soil-metal interaction in some cases (Sipos et al., 2009; Németh et al., 2011).

Studies of metal sorption in soils at particle level demonstrated that the association of Fe-oxyhydroxides and clay minerals contribute substantially to the retention of metals, even greater than the summation of the effects of the individual components themselves (Sipos et al., 2008; Cerqueira et al., 2015a). The results of these studies suggested that metal sorption on such particle associations is a strongly selective process showing high variation with soil conditions. The low number of such studies and lack of their systematic character, however, does not allow us to draw clear conclusions about their specific role in metal sorption in soils. Still little is known on the effect of metal oxide coatings on the intrinsic sorption mechanisms of metals to clay mineral surfaces, although in the most extreme scenarios, these coatings could dictate metal retention instead of the underlying clay mineral (Nachtegaal land Sparks, 2004). Additionally, development of surface complexation models based on theoretical calculations also needs support from direct analyses (Serrano et al., 2009). A challenge to improving and extending both approaches is the need for better characterization of the most important mineral phases in soils responsible for metal sorption.

In this study, the role of Fe-oxyhydroxide and clay mineral associations in the sorption of Cd, Cu, Pb and Zn was investigated through the comparison of the results of batch adsorption experiments and direct mineralogical and geochemical analyses of soil mineral particles. Our aims were (1) to compare the sorption properties of metals in the bulk soils and on the individual soil mineral particles and (2) to study the effect of the presence of Fe-oxyhydorxides on the metals’ sorption by clay minerals. To the best knowledge of our knowledge, this is the first study presenting direct data on the selectivity of a large number of metals on the surface of such particles. Metal sorption and selectivity on these soil components is expected to be specified in more details when compared to results of metal sorption in bulk soils.

2. Materials and methods

2.1. Characteristics of the studied samples

Two soil samples with contrasting pH and with high similarity for their further physicochemical and mineralogical characteristics were selected for this study (Table 1). Sample S2 was collected from a Luvisol B horizon, whereas sample C3 from a Phaeozem C horizon. The former had an acidic pH and the latter one had an alkaline pH. Both samples contained low concentration of organic carbon and had a medium clay content and significant ratio of dithionite extractable Fe. They could be characterized by medium cation exchange capacity (CEC) value. The clay mineralogy of both samples were dominated by smectites and illite/smectite mixed layer phases. Tiny (20-100 nm) Fe-oxyhydroxide flakes were found to be placed on the surface of larger (100-500 nm) smectite and illite-smectite lamella in the acidic soil (Figure 1). Occasionally, these clay particles could be as large as 1 μm, and individual aggregates of Fe-oxyhydroxides were also found up to 500 nm of size. The mineralogy of Fe-oxyhydroxides could be characterized mostly by ferrihydrite with highly varying crystallinity but goethtite flakes were also frequent. Very similar phase associations were observed in the alkaline soil, but these associations were also attached to calcite particles of 50-500 nm (Figure 1). Additionally, much larger (up to 1-2 μm) calcite grains also surrounded these associations. Transmission Electron Microscopy analyses with EDX (TEM-EDX) were primarily focused on the mineralogy and chemistry of the compounds of Fe-oxyhydroxide-clay mineral-(calcite) associations.

Table 1. Major physico-chemical properties of the studied soils.

	pH	TOC	BET	CEC	Fe	Fed	Clay	Cu	Pb	Zn	Cd
	($CaCl_2$)	(g/kg)	(m^2/g)	(mmol/kg)	(g/kg)			(mg/kg)			
S2	4.28	5.4	33	140	40.3	1.54	19.2	28	28	91	<0.4
C3	7.93	3.4	29	123	44.5	2.69	18.1	3	<5	5	<0.4

TOC = total organic carbon, BET = BET-surface area, CEC = cation exchange capacity Fed = dithionite extractable Fe

Soil pH was measured in 0.1 M $CaCl_2$ solution using 1:2.5 solid:solution. Total organic carbon content (TOC) was analysed with a Tekmar-Dohrmann Apollo 9000N TOC instrument. The BET surface area was determined using Quantochrome Autosorb-1-MPV automated gas sorption system using N_2 gas. The CEC of the samples was determined using the hexamine-cobalt-trichloride solution standard method (ISO 23470:2007 standard method). Particle size distribution of the samples was analysed with a Fritsch Analysette Microtech A22 laser diffraction instrument.

Bulk clay mineralogy of the samples was analysed by X-Ray Diffractometry (XRD) (Philips PW 1729) using the clay fractions of the samples. Their separation was carried out by sedimentation in aqueous suspension. Several diagnostic treatments were carried out to distinguish the clay mineral species in the samples (ethylene glycol solvation at 60 °C, Mg-saturation followed by glycerol solvation at 95 °C, K-saturation, heating at 350 and 550 °C) (Harris and White, 2008).

An acid digestion was used to analyse the total metal and Fe content of the soils. A 0.25-g of soil was heated in HNO_3-$HClO_4$-HF to fuming and taken to dryness and then the residue was dissolved in HCl. Metal concentrations in the solutions were analysed by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) (Spectro Arcos). To check the accuracy of our measurements, we also analysed the standard reference material OREAS45E. The analysed and expected concentrations were found to be 4.63 ± 0.13 and 4.45 ± 0.05 % for Fe, <0.4 and 0.20 ± 0.01mg/kg for Cd, 52 ± 7.1 and 43 ± 2.1 mg/kg for Cu, 18 ± 2.8 and 22 ± 1.7 mg/kg for Pb, 47 ± 3.2 and 44 ± 1.1 mg/kg for Zn, respectively. Pedogenic or free Fe-oxyhydroxide content of the samples was determined by dithionite-citrate-bicarbonate extraction (Mehra and Jackson, 1960), and Fe concentrations were analyses with Atomic Absorption Spectrometry (AAS) (Perkin Elmer AAnalyst 300).

2.2. Sorption experiments

The sorption characteristics of Cd, Cu, Pb and Zn in the bulk soil samples were studied in single element batch sorption experiments. The experiments were carried out in duplicates, soil:solution ratio was 1:30, metal concentrations were set to 0.1, 0.2, 0.5, 1, 2, 5 and 10 mmol/L, and 0.01 M $Ca(NO_3)_2$ was used as a background electrolyte. The pH of the initial solution was set to 5.5 to avoid metal hydroxide precipitation in the initial solution (Vidal et al., 2009). Soil samples were equilibrated with the solutions by shaking them for 24 hours at 22°C. After that, they were centrifuged at 4000 rpm for 20 minutes and the supernatant was filtered and analysed for the metals' concentrations. Metal concentrations in the equilibrated solution were analysed by AAS method. The relative standard deviations of duplicate analyses are less than 5 % for each metal at equilibrium concentrations above 100 mg/L and never reached 10 % at lower concentrations.

The Langmuir isotherm equation (1) was used to describe the adsorption of the studied metals from the solution:

$$Qe = \frac{Qmax \cdot b \cdot Ce}{1 + b \cdot Ce} \text{ (1),}$$

where Q_{max} is the sorption capacity of the solid (mmol/kg) and b represents the Langmuir bonding term related to the adsorption energy (L/kg). Isotherm model parameters were obtained using non-linear regression analysis. The coefficient of determination (R^2) was used to evaluate the applicability of the Langmuir isotherm to the experimental data by a trial-and-error procedure with the Solver add-in function of Microsoft Excel. Sorption curve evaluation was performed after Giles et al. (1974).

TEM-EDX analyses were carried out to characterize the soil mineral particles before and after metal sorption (Philips CM20 with Noran energy dispersice spectrometer). In the latter case, samples treated with the solution with the highest initial metal concentrations were studied. The samples were slightly ground under ethanol and the resulted suspensions were dropped on an Au grid for analyses. The TEM-EDX instrument was operated at 200 kV with a LaB6 filament. For chemical analyses, 5 nm beam parameter and counting times of 100 s were used. The chemical composition was calculated on the basis of 100 nm sample thickness and 2.5 g/cm^3 density, except in case of large Fe-oxyhydroxide aggregates where the density and thickness was set to 4.5 g/cm^3 and up to 500 nm, respectively. The relative standard deviations of the EDX analyses were below 5 % at >10 at% of metal concentration, below 15 % at 1-10 at%, and below 30 % at <1 at%. Joint evaluation of diffraction pattern and chemical composition of the particles were used for their identification. Linear correlation between the Fe and metal concentrations of the studied particles were carried out using MS Excel, the presented correlation coefficients are significant at the level of $P < 0.05$.

Our TEM analyses were focused on the mineral phases and their associations affecting metal sorption in soil, like clay mineral and Fe-oxyhydroxide particles. The analysed particles were sorted into the following groups based on their mineralogy and metal sorption characteristics: (1) clay particles (mostly smectite and illite-smectite particles with varying proportion of the interlayered compounds for the latter, as well as illite and chlorite subordinately); (2) Fe-rich clay particles without individual Fe-oxyhydroxide particles on their surface (same as the previous one but with Fe_2O_3>10wt%); (3) Fe-oxyhydroxide and clay mineral associations (refers mostly to Fe-oxyhydroxide flakes attached to the surface of clay particles or more rarely their aggregates); (4) Fe-oxyhydroxides (ferrihydrite and goethite with varying crystallinity). Based on our data, further particle types within each group could not be distinguished based on their metal sorption capacity.

The evolution of the saturation indexes of metal-(hydroxy)carbonates as a function of CO_3^{2-} concentration under the initial and equilibrium experimental conditions was calculated by using the chemical equilibrium model Visual MINTEQ 3.0 (Gustaffson, 2012). Complex chemical analysis of the equilibrium solutions was not carried out (only equilibrium pH and metal concentrations were analysed), so the primary role of these calculations was just to check whether the studied metals could be precipitated during the sorption experiments.

3. Results and Discussion

Metal sorption on bulk soil

Based on their sorption curves, strongly different behaviour of the studied metals was found in the two soils (Figure 2). In the acidic soil, lack of saturation was suggested by the L1 type isotherms, except for Pb, where the saturation was reached as shown by the L2 type curve. In the alkaline samples, however, each metal curve was shown to be of the H1 type curve, suggesting such high affinity of the solute that in dilute solutions they were completely adsorbed (Giles et al. 1974). Moreover, Cu and Pb showed almost complete retention in the whole initial concentration range. Consequently, much higher sorption of metals for the alkaline than for acidic soil was shown. The fit of the Langmuir curves to the experimental data were generally excellent with $R^2>0.95$. For curves showing complete retention (Pb and Cu in the alkaline sample) the goodness of fit was slightly lower with R^2 values of 0.71 and 0.76, respectively. This can be due to the small fluctuations in the experimental data affecting the goodness of fit of the practically vertical sorption curve strongly. Based on the sorption capacities (Q_{max}) calculated from the Langmuir isotherms (see Figure 2), differences were found between the sorption sequences of the metals in the acidic and alkaline soils. The sequence was Pb>Cd>Cu>Zn in the former, whereas Cu>Pb>>Zn>Cd in the latter case. As all major physico-chemical parameters of the soils were similar with exception of pH, differences between their sorption capacities can be related to this property primarily. Evidently, the higher pH is favourable for the sorption of cationic elements due to the increase in negative charge and subordinately to the decrease in competition with H^+ (Young, 2013). The almost complete retention of Pb and Cu in the alkaline soil can be due to their precipitation, probably as (hydroxy)carbonates. Lead may be precipitated in form of carbonate in soils at pH 6-10 when free carbonate is available (Cao et al., 2003). Additionally, precipitation of Cu as carbonate can be also expected at this pH range (Pozinovsky et al., 2007), but this process may be strongly inhibited by the presence of soil organic matter

(Rutkowska et al., 2013). As no strong influence of the organic matter can be expected in our alkaline sample because of its low TOC content, carbonate precipitation of both metals could be expected. This was also supported by the calculated saturation indexes of metal-(hydroxy)carbonates using the software MINTEQA. These data showed that the following phases are oversaturated at the initial conditions of the experiments: malachite at CO_3^{2-} > 0.04 mM, azurite at CO_3^{2-} > 0.19 mM, $CuCO_3$ at CO_3^{2-} > 2.49 mM, cerussite at CO_3^{2-} > 0.09 mM, and hydrocerussite at CO_3^{2-} > 0.08 mM solution concentration. The concentration values were as follows at the equilibrium conditions of the experiments: malachite between 0.18 and 4.19 mM CO_3^{2-}, cerussite at CO_3^{2-} > 0.10 mM, hydrocerussite at CO_3^{2-} > 0.03 mM, and $Pb(OH)_2s$ at CO_3^{2-} > 2.76 mM. The higher sorption of Cu and Pb than Cd and Zn in the alkaline soil, however, can not only be explained by the Cu and Pb precipitation. The results of the metal leaching study by Sanguimskan and Punrattanasin (2014) showed that Cd and Zn were mainly immobilized by non-specific adsorption while Pb and Cu were mainly immobilized by specific sorption in soils. This behaviour of metals can be related to their certain electrochemical properties (such as hydrolysis constant, electronegativity, ionic radius etc.) (Zhang et al., 2012). In the acidic soil, retention of Pb was the strongest among the studied metals. This is supported by the surface complex model calculations of Serrano et al. (2009) who found that Pb was able to bind to hydroxyl groups at lower pH than Cd. These authors related this behaviour of metals to the ability of Pb to form chemical bonding at pH where Cd only interacts with exchange sites. This could result in the strong sorption of Pb at equilibrium pH of 4.0-4.3, where other metals showed only low sorption in the studied soil. According to Vytoplilova et al. (2015), soil organic matter could adsorb Cu also at low pH. However, this is not the case in the acidic soil, supporting its relatively low Cu sorption. The low number of preferred sorption sites, and the decreasing ability to form hydroxy complexes with decreasing pH may also resulted in lower sorption for Cd and Zn in the acidic sample, as also suggested by the data of Vidal et al. (2009). Nevertheless, Cd showed as high sorption as Cu at the highest initial metal concentrations (and at lowest equilibrium pH) suggesting that the retention of Cd was still significant by ion exchange processes at such a low pH. Meanwhile, sorption of Cu was strongly inhibited due to the low amount of available sites on organic compounds, as shown also by the results of Covelo et al. (2007).

Metal sorption on mineral particles

Our data showed (Figure 3) that higher metal amounts were adsorbed by the particles in the alkaline than by those in acidic soil generally. Similarly to the bulk soils, cationic elements can be characterized by higher sorption at alkaline conditions (Young, 2013). Additionally, Fe-oxyhydroxides exhibit point of zero charge between pH 7.8 and 9.0 (Kosmulski, 2009), so they compensation potential on the negative charge of the clay minerals decreases with increasing pH, and they can even contribute to the net negative charge of soils above these pH values. However, some exceptions could be also observed. Higher Cd amounts were detected on the clay mineral, Fe-rich clay mineral and Fe-oxyhydroxide and clay mineral associations in the acidic soil than in the alkaline one on average; although maximum concentrations were still higher on the particles form the alkaline soil. Moreover, both higher average and maximum values were found for Zn in clay mineral particles in the acidic soil when compared to the alkaline one. Although calcite dissolution rate is independent of the concentration of H^+ ions in the pH range of 5-10 (Dolgaleva et al., 2005), increase of H^+ ions in the solution due to metal sorption may have even contributed to the basically high Ca concentration in the solution. This may have generated competition (even in our single element scenarios) between the metals and Ca for the available surfaces of clay particles in the alkaline sample. Several studies presented the higher effect of competition on the sorption of Cd and Zn as compared to Pb and Cu (Lu and Xu, 2009).

Sorption sequences of the studied metals on different particle types showed high variation (Table 2). These sequences show which metal sorbed at the highest added metal concentration on the studied particles types on average. Based on these data, Pb generally showed the highest sorption on the mineral particles in both soil samples, and it is mostly followed by Cu. Cadmium could be characterized, however, by the lowest sorbed amounts on each particle type, and those of Zn were only slightly higher. Exceptions were the strongest sorption of Zn onto clay mineral particles in the acidic soil, and the relatively high sorption of Zn onto Fe-oxyhydroxide-clay mineral associations in the alkaline soil. Consequently, observed sorbed metal amounts on the soil particles showed only partly agreement with those found for bulk soils. The high ability of Zn to be adsorbed on montmorillonite is a well-known phenomenon in soils (Proust et al., 2013). In acidic environment, Zn partitioning to phyllosilicate surfaces mainly occurs by electrostatic interactions and by specific chemical binding to hydroxyl edge sites. At higher pH, Zn can be incorporated into neo-formed precipitates developed on the surface of phyllosilicates (Ford and Sparks, 2000). The other studied metals, however, forms outer-sphere complexes with clay minerals at acidic conditions (Strawn and Sparks, 1999), and they rather prefer sorption on Fe-oxyhydroxides (Pb and Cd) and organic matter even in mineral soils (Cu) (Vidal et al., 2009). Association of Fe-oxyhydroxides and clay minerals strongly affected the sorption of Zn in the alkaline sample. According to Saidy et al. (2013), surface coating of montmorillonite by Fe-oxyhydroxides may compensate the negative charge of the clay mineral by their positive surface charge in acidic conditions. At near-neutral and slightly alkaline conditions, however, some Fe-oxyhydroxides might possess negative surface charge, which may promoted the sorption of Zn.

Table 2. Sorption sequences of the studied metals on different particle types.

	acidic sample S2	alkaline sample C3
Calcite	not present	Cu > Cd > Pb > Zn
Clay minerals	Zn > Pb > Cu > Cd	Pb > Cu > Cd > Zn
Fe-rich clay minerals	Pb > Cu > Zn > Cd	Pb > Cu > Zn > Cd
Fe-oxyhydroxide and clay mineral associations	Pb > Cu > Cd > Zn	Pb > Zn > Cu > Cd
Fe-oxyhydroxides	Pb > Cu > Cd > Zn	Cu > Pb > Zn > Cd

Generally, the sorption capacity of the studied particles increased with their Fe content (Figures 4 and 5). This was most expressed for Cu both in acid and alkaline soils. The same applied for Cd and Pb, although higher Pb amounts were sorbed on low-Fe clay minerals than on other particles with clay minerals in the alkaline soil. The observation is characteristic for Zn only for the particles from the alkaline soil. An opposite trend was found for clay particles in the acidic soil, although Fe-oxyhdyroxides showed higher Zn sorption than their associations with clay minerals in this sample. The increase of metal sorption with the Fe concentration of particles does not necessarily be the result of higher sorption of metals on Fe-oxyhydroxides. Fe-SEM observations of Cerqueira et al. (2015b) showed that metals were often retained by micro/nano-aggregates rather than individual particles. These aggregates composed of varying proportion of clay minerals, Fe-oxyhydroxides and organic compounds, and they sorbed metals selectively. For example, mapping of soil particles after sorption by TOF-SIMS showed that both Cu and Pb showed the same spatial distribution and they exhibited good concordance with that of Fe and Mn, whereas their relationship with elements forming silicates were slightly poorer (Cerqueira et al., 2011). We found a strong variation of the relationship between the sorbed metal and the Fe content within the different particle types.

In the acidic sample, only Cd and Cu concentrations showed linear correlations with the Fe content of the particles (r = 0.51 and 0.76, respectively). However, if particle types are studied separately, this relationship could be applied only for the clay mineral-Fe-oxyhydroxide assemblages for Cd, and clay mineral, clay-Fe-oxyhydroxide assemblages and Fe-oxyhydroxide particles for Cu. For Pb, particles with high Fe content adsorbed more Pb than those with low Fe. However, a linear correlation was only found for the Fe and Pb content of the clay mineral particles, whereas this was also found for the Fe and Zn content of the Fe-rich clay mineral particles (Figure 4). In contrast, sorption of all metals increased with the Fe content of particles in the alkaline soil (with r values of 0.54 for Cd, 0.67 for Cu, 0.57 for Pb and 0.85 for Zn). Iron content of clay particles showed linear relationship with the amount of sorbed Cd. Such a relationship was also found for Cu, Pb and Zn in the case of the iron-rich clay mineral particles. Sorption of Pb also increased with increasing Fe content of the clay-Fe-oxyhydroxide associations and concentration of Zn also increased with increasing Fe content of Fe-oxyhydroxides. We also found a strong linear correlation between the Fe content of calcite particles and their metal content (Figure 5). Although calcite is expected to affect metal sorption strongly, results of Sdiri and Higashi (2012) showed that Pb and Cu was removed from the solution rather by precipitation when reacted with limestones, whereas Cd and Zn by non-specific adsorption. They also found that limestone with high impurities (Si, Fe) exhibited stronger sorption for the latter metals suggesting that the calcite surface is not the primary target of metal sorption. Accordingly, metal sorption on calcite particles could be rather related to the presence of Fe-oxyhydrixodes on their surface in our case, The Fe content detected on calcite particles could be as high as 10 at%, which could be rather attributed to the presence of Fe-oxyhydroxide coatings. Results of correlation analyses also support the surface complexation and ion exchange model calculations of Serrano et al. (2009). These authors suggested that adsorption of Pb and Cd was mainly associated with >FeOH sites in soils. Their results confirmed the greater tendency of Cd to be retained on exchange sites compared to Pb, which had a higher affinity for specific adsorption on >FeOH sites. Sorption on >SOH functional groups increased with increasing pH but was small compared to >FeOH sites. Several studies showed that Fe-oxyhydroxide coating may positively and also negatively affect the metal sorption onto clay minerals. Lothenbach et al. (1997) found that coating of montmorillonite resulted in enhanced sorption of heavy metals only at pH>6, whereas sorption dominated on untreated montmorillonite in acidic conditions. Nachtegaal and Sparks (2004) showed that Zn initially was bound to >FeOH groups of the goethite coating on kaolinite first. With aging, inclusion of Zn into a mixed Zn-Al layered double hydroxide took over as dominant sorption mechanism suggesting that formation of a precipitate phase at the kaolinite surface is favoured over adsorption to goethite. This process, however, is primarily characteristic at high Zn concentrations, which rarely occur in natural soils. In case of low Zn concentrations, the preference of Zn sorption on Fe-oxyhydroxides over clay minerals can be expected within such particle associations. Literature data also show that coating of clay particles with Fe-oxyhydroxides may result in higher metal sorption due to increase in CEC, reinforcing the negative charge in the surface and formation of further sorption sites (Park et al., 2012). However, this applies only for metals, which show a high ability to be sorbed onto Fe-oxyhydroxides and not for those showing it to clay minerals, because coating may also cover sorption sites on clay surfaces.

4. Conclusions

Direct observation of the sorption characteristics of soil mineral particles helped to determine metal sorption preferences exactly which could be obscured by the bulk sorption data otherwise. Metal sorption preferences showed high variation among the studied mineral particle types within a given soil.

Although Fe-oxyhydroxide particles played the primary role among the studied particle types in the metal sorption at both soil conditions, association of Fe with clay mineral particles affected the metal sorption capacity of the given particle decisively. In the acidic soil, metal sorption increased with the Fe concentration of clay mineral particles suggesting the preferential sorption of metals by the FeOH functional groups of the clay minerals, except for Zn that sorbed on low-Fe clay minerals primarily. In the alkaline soil, however, the increasing proportion of Fe-oxyhydroxides in the particle associations resulted in a stronger metal sorption.

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Figure captions

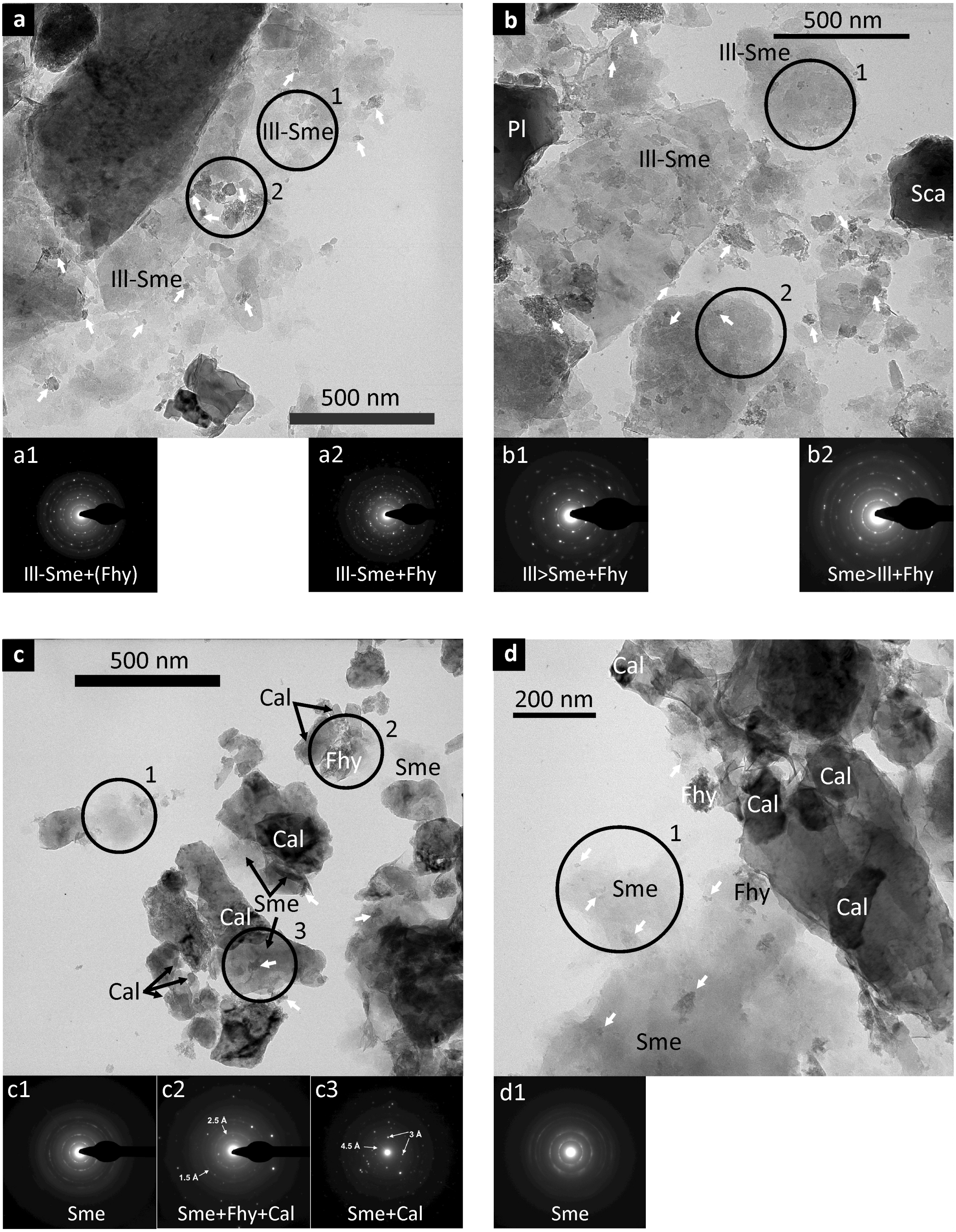
Figure 1. TEM micrographs showing the particle associations characteristic of the studied samples. a) aggregates of illite-smectite with low (a1) and high (a2) amounts of Fe-oxyhydroxide flakes attached to their surface from sample S2; b) aggregates of illite-smectite and Fe-oxyhydroxides with low (b1) and high (b2) fraction of smectite within the mixed layer particle from sample S2. c) Fe-rich smectite particle with no Fe-oxyhydroxide flakes on its surface (c1), agglomerate of smectite, ferrihydrite and calcite (c2), and agglomerate of smectite and calcite (c3) from sample C3; d) turbostratic smectite (d1) with Fe-oxyhydroxide flakes on its surface and surrounded by individual calcite and ferrihyrdite particles from sample C3. Further Fe-oxyhydroxide flakes are shown by white arrows on all micrographs. Ill = illite, Sme = smectite, Fhy = ferrihydrite, Cal = calcite, Pl = plagioclase, Sca = silica (α-SiOx).

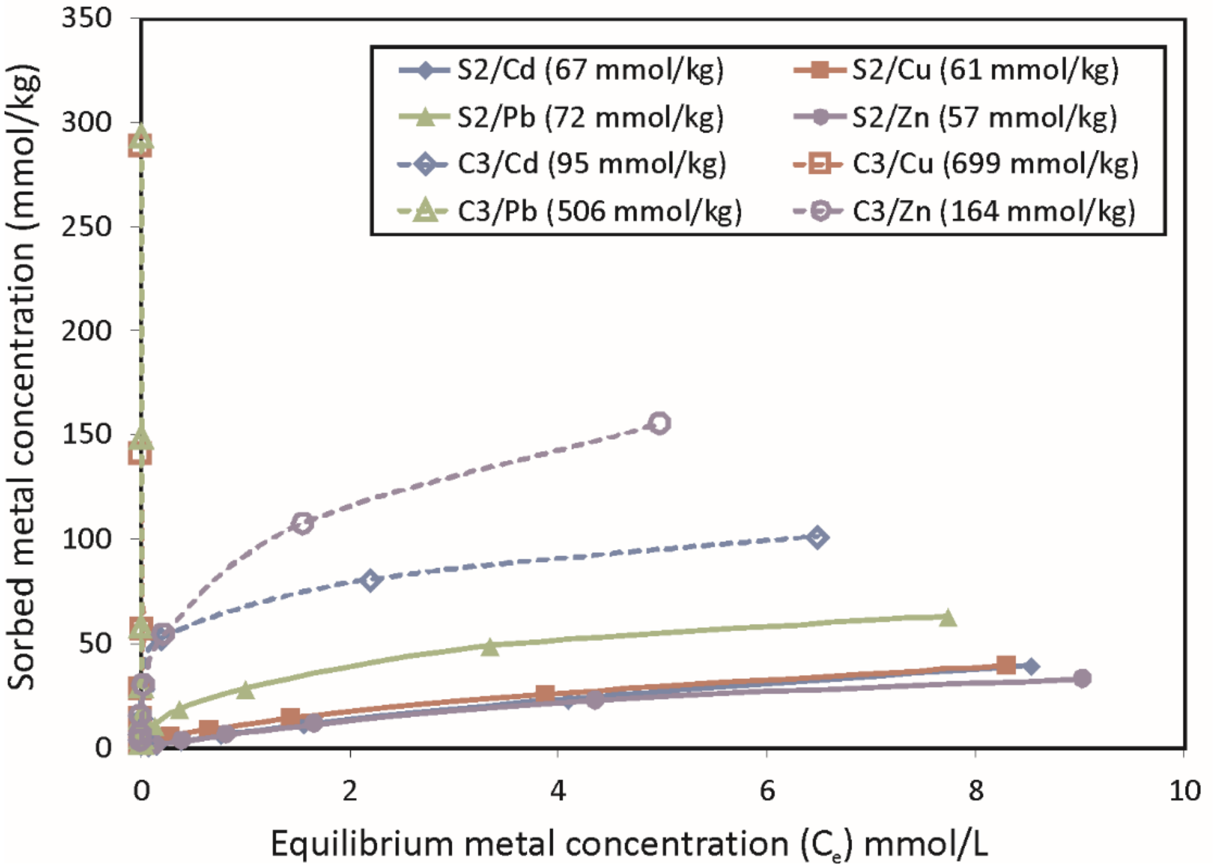
Figure 2. Langmuir isotherms fitted to the sorption curves of the studied metals. Maximum Langmuir monolayer coverage (Q_{max}) values are also shown in mmol/kg in parentheses.

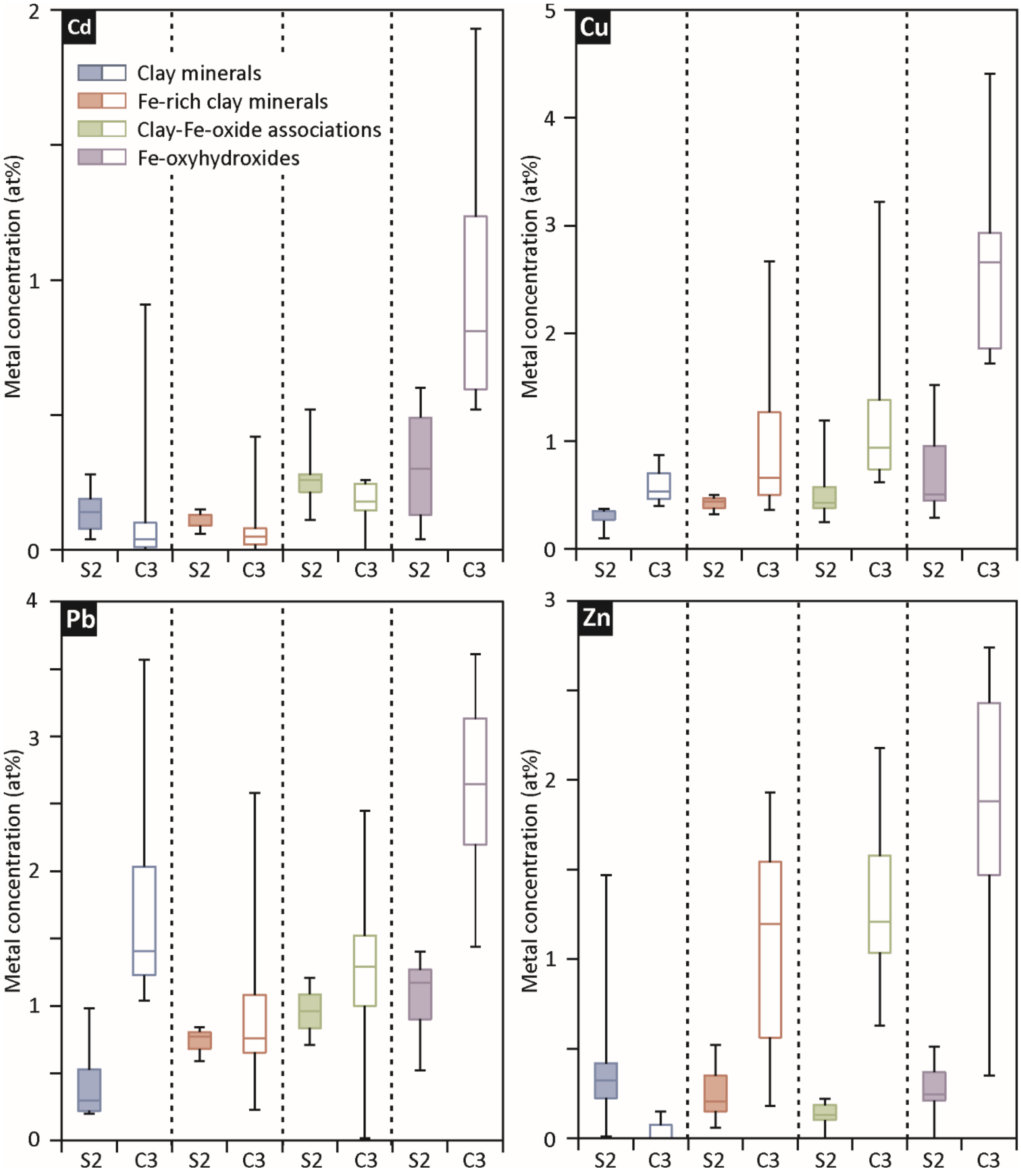
Figure 3. Amounts of metals sorbed on different mineral particle types in at% (the percentage of metal atoms relative to the total number of atoms in the particle). S2 refers to the acidic sample and C3 to the alkaline one. Distribution of the particle types analysed by TEM-EDX was as follows: 10% calcite, 20% clay mineral, 24% Fe-rich clay mineral, 24% clay mineral-Fe-oxyhydroxide assemblage, and 22% Fe-oxyhydroxide. Between 8 and 14 data were collected to produce one single box and whisker plot. Boxes show the values between the first and third quartiles, the horizontal line within the boxes gives the median of the data. Whiskers represents the lower and upper extremes.

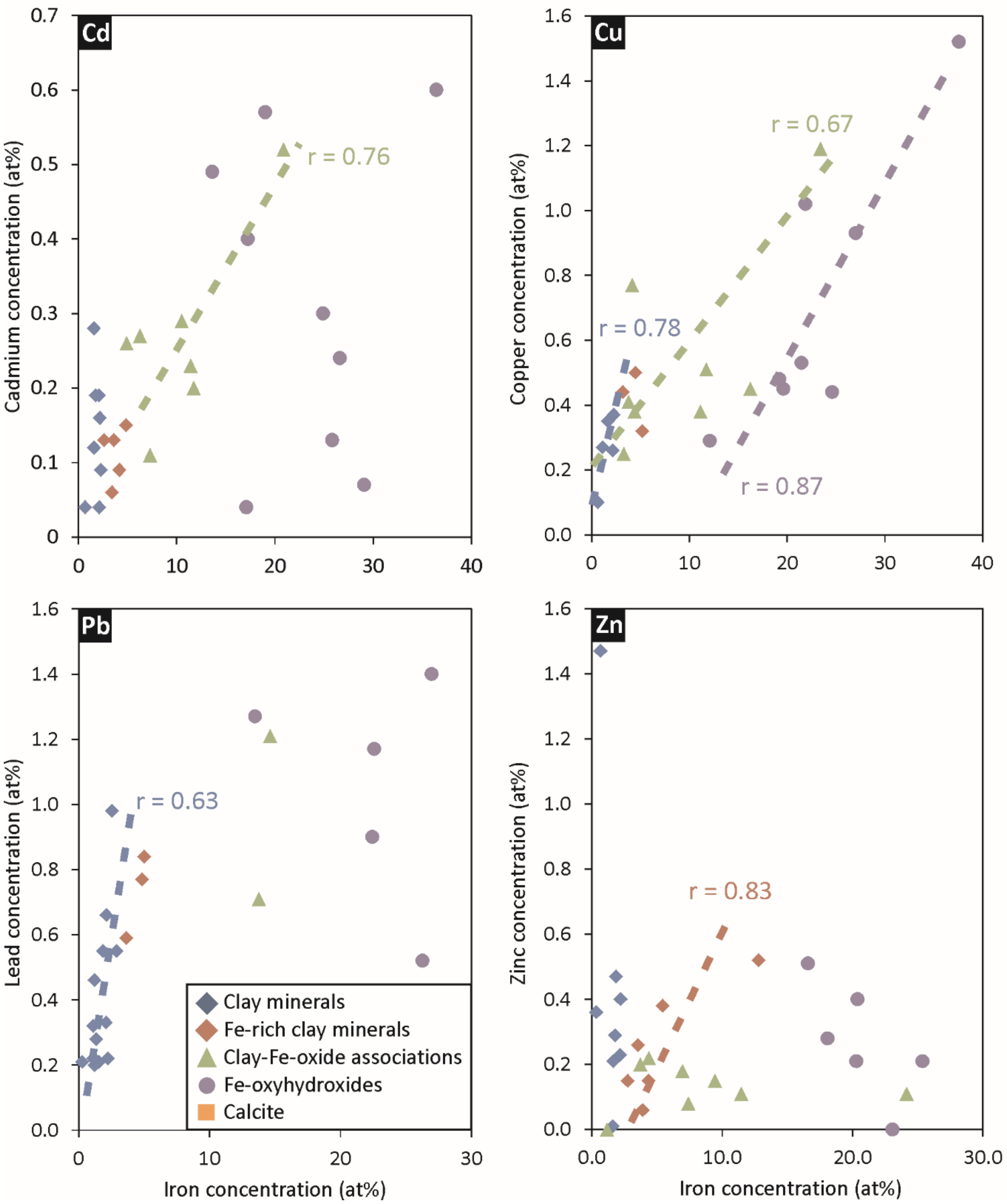
Figure 4. Correlation between the sorbed metal amounts and Fe content of the particles in the acidic sample S2. Correlation coefficients and a regression line are shown if the correlation was significant at $p < 0.05$.

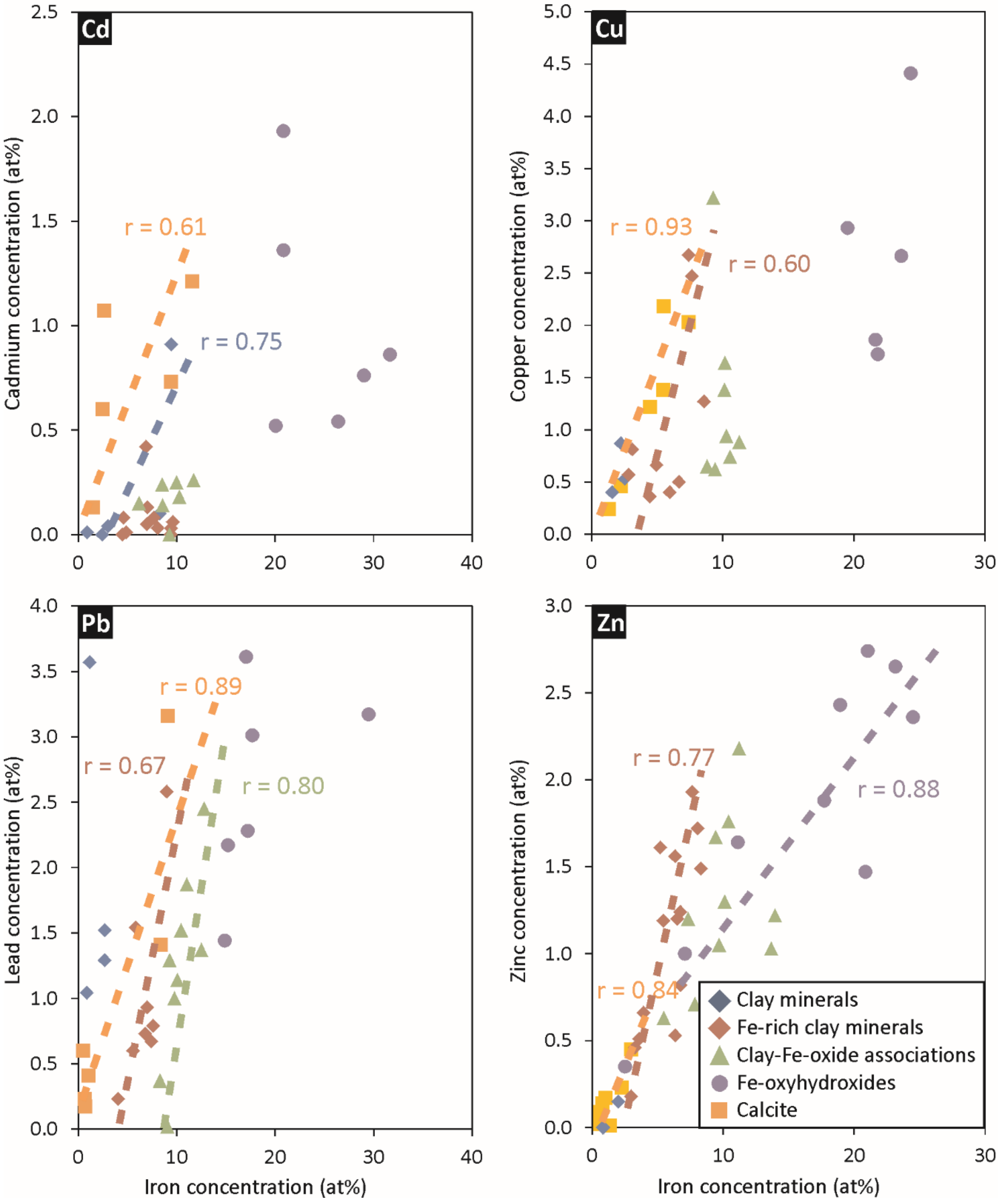
Figure 5. Correlation between the sorbed metal amounts and Fe content of the particles in the alkaline sample C3. Correlation coefficients and a regression line are shown if the correlation was significant at $p < 0.05$.


a
1
Ill-Sme
2
Ill-Sme
500 nm
a1
Ill-Sme+(Fhy)
a2
Ill-Sme+Fhy
b
500 nm
Ill-Sme
1
Pl
Ill-Sme
Sca
2
b1
Ill>Sme+Fhy
b2
Sme>Ill+Fhy
c
500 nm
Cal
2
Fhy
Sme
1
Cal
Sme
Cal
3
Cal
c1
Sme
c2
2.5 A
1.5 A
Sme+Fhy+Cal
c3
4.5 A
3 A
Sme+Cal
d
Cal
200 nm
Fhy
Cal
Cal
1
Sme
Fhy
Cal
Sme
d1
Sme


Sorbed metal concentration (mmol/kg)
Equilibrium metal concentration (C_e) mmol/L
0
50
100
150
200
250
300
350
0
2
4
6
8
10
S2/Cd (67 mmol/kg)
S2/Cu (61 mmol/kg)
S2/Pb (72 mmol/kg)
S2/Zn (57 mmol/kg)
C3/Cd (95 mmol/kg)
C3/Cu (699 mmol/kg)
C3/Pb (506 mmol/kg)
C3/Zn (164 mmol/kg)

Cd
Cu
Pb
Zn
Clay minerals
Fe-rich clay minerals
Clay-Fe-oxide associations
Fe-oxyhydroxides
Metal concentration (at%)
0
1
2
3
4
5
S2
C3


Cd
r = 0.76
Cadmium concentration (at%)
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
10
20
30
40
Cu
r = 0.67
r = 0.78
r = 0.87
Copper concentration (at%)
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
10
20
30
40
Pb
r = 0.63
Lead concentration (at%)
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
10
20
30
Iron concentration (at%)
Clay minerals
Fe-rich clay minerals
Clay-Fe-oxide associations
Fe-oxyhydroxides
Calcite
Zn
r = 0.83
Zinc concentration (at%)
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0.0
10.0
20.0
30.0
Iron concentration (at%)


Cd
r = 0.61
r = 0.75
Cadmium concentration (at%)
2.5
2.0
1.5
1.0
0.5
0.0
0
10
20
30
40
Cu
r = 0.93
r = 0.60
Copper concentration (at%)
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
10
20
30
Pb
r = 0.89
r = 0.67
r = 0.80
Lead concentration (at%)
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
10
20
30
40
Iron concentration (at%)
Zn
r = 0.77
r = 0.88
r = 0.84
Zinc concentration (at%)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
10
20
30
Iron concentration (at%)
Clay minerals
Fe-rich clay minerals
Clay-Fe-oxide associations
Fe-oxyhydroxides
Calcite