



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.

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

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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 (Nachtgeal and 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-oxyhydroxides on the metals' sorption by clay minerals. To the best 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

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

	pH	TOC	BET	CEC	Fe	Fe _d	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 Fe_d = dithionite extractable Fe.

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 (Fig. 1). Occasionally, these clay particles could be as large as 1 μ m, 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 goethite 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 (Fig. 1). Additionally, much larger (up to 1–2 μ m) 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.

Soil pH was measured in 0.1 M CaCl₂ 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 N₂ 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 HNO₃-HClO₄-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 \pm 0.13 and 4.45 \pm 0.05% for Fe, < 0.4 and 0.20 \pm 0.01 mg/kg for Cd, 52 \pm 7.1 and 43 \pm 2.1 mg/kg for Cu, 18 \pm 2.8 and 22 \pm 1.7 mg/kg for Pb, 47 \pm 3.2 and 44 \pm 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 analysed 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

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