Final report

Project title: Complex environmental geochemical study of the sorption of heavy metals by soil mineral constituents
Project number: OTKA K105009

Introduction

Metal sorption properties of bulk soils and individual soil components are fairly well known. So the relationship between the major physicochemical properties of soils and their metal sorption capacity have been described thoroughly. As a result, we are able to tell which soil can (or can not) be expected to be an effective sorbent of metals. However, bulk sorption data may often obscure metal affinities to specific soil components present in the soil under study. Moreover, (mineralogical) changes in the solid after the metal sorption have been characterized mostly in single component systems but rarely in the bulk soils. This is partly because bulk mineralogical methods are generally of low sensitivity to specify such changes in individual components within the soil. On the other hand, soil components can be characterized by largely heterogeneous surface properties, which affect their sorption characteristics significantly. This is further complicated by that pedogenic processes often produce particles associations (like coatings or aggregates) which result in significantly different surface properties (and so sorption characteristics) for soil particles in the soil. This heterogeneity can lead to misinterpretation on the role of soil components in the sorption process, and it even may hinder the direct identification of the most active soil components. To overcome these limitations, combination of several analytical and methodological approaches have to be used for such studies. For example, the combination of batch sorption experiments with selective dissolution techniques and with the study of metal sorption capacity of individual soil mineral particles was proven to be an effective tool by our earlier studies to investigate the rate of the contribution of soil mineral components to the metal sorption capacity of the soil. In this project, this approach was applied to study the effect of pH, competition and mineral particle assemblages on the sorption properties of soil mineral components. Additionally, metal sorption characteristics of the soil mineral particles have been compared to the sorption properties of the bulk soils as well.

Materials

The soil sampling focused on profiles characterized by simultaneous clay mineral and Fe-oxyhydroxide accumulation in the same horizon. These soils are expected to provide appropriate samples to study the associations of these phases, which are the most important mineral components affecting the sorption characteristics of soils. To fulfil this requirement, we have sampled forest soil (Luvisols), alluvial soil (Fluvisols) and meadow soil profiles (Phaeozems). Each genetic soil horizons (or distinguishable soil layers) of eight profiles were sampled providing 43 soil samples in total (Table 1). After the basic physico-chemical and mineralogical characterization of the collected samples, six samples were chosen out of them for the adsorption experiments. On one hand, this was carried out according to the OECD guideline No. 106 (2000), which support a guidance for selection of soil samples for adsorption studies based on their major physicochemical soil properties. On the other hand, we primarily intended to study soils containing smectites as dominant clay species, as they were shown to have a marked influence on the hydrolysis of Fe(III) promoting the formation of clay mineral-Fe-oxyhydroxide assemblages in soils. As a result, the six selected samples showed high variation in their pH, total organic carbon and clay content, as well as in their texture (Table 2). Their common mineralogical feature is that their dominant clay mineral species are smectite and illite-smectite phases.

Table 1. The sampled soil profiles.

WRB soil type	**Soil description**	**Sampled horizons/layers**	**Location**
Luvisol	forest soil with clay illuviation	A1, A2, B1, B2, C	Sopron
Luvisol	forest soil with clay illuviation	A1, A2, B, C1, C2	Kisbárkány
Luvisol	forest soil with clay illuviation	A1, A2, B1, B2, C	Karancslapujtő
Pseudogley	pseudogley	A1, A2, B1, B2, C	Sopron
Fluvisol	alluvial soil	A, L2, L3, L4, L5, L6, L7, L8	Vízvár
Fluvisol	alluvial soil	A, L2, L3, L4, L5, L6, L7, L8	Ipolyszög
Phaeozem	meadow soil	A, C1, C2	Ceglédbercel
Gleysol	peaty meadow soil	A1, A2, A3, AC	Ceglédbercel

Table 2. The major physicochemical properties of the samples selected for the adsorption experiments.

Sample	**Soil type**	**Horizon**	**pH**	**TOC**	**BET-surface**	**CEC**	**Fe_t**	**Fe_d**	**Clay**
			($CaCl_2$)	(%)	(m^2/g)	(cmol/kg)	(%)	(%)	(%)
S1	Luvisol	A1	4.61	4.99	10	14.6	3.03	1.14	9.0
S2	Luvisol	B1	4.28	0.54	33	14.0	4.03	1.54	19.2
S3	Luvisol	A1	3.31	3.74	3.0	4.8	0.91	0.34	5.5
C1	Phaeozem	A2	7.65	3.69	27	20.9	4.52	2.84	37.3
C2	Phaeozem	A	8.10	2.72	13	15.8	1.21	0.23	14.9
C3	Phaeozem	C2	7.93	0.34	29	12.3	4.45	2.69	18.1

Methods

Basic characterization of the soil samples involved the analysis of their pH (in 0.1 M $CaCl_2$), total organic carbon content (Tekmar-Dohrmann Apollo 9000N TOC analyzer), particle size distribution (Fritsch Analysette Microtech A22 laser diffractometer), mineralogy of bulk samples and their clay fraction after several diagnostic treatments (Philips PW1729 and Rigaku Miniflex 200 X-ray diffractometer), and chemical composition (after a 4-acid digestion by Perkin Elmer Elan 9000 ICP-MS for total content of 35 chemical elements). Samples selected for the adsorption experiments were also analyzed for their BET-surface area (Quantochrome Autosorb-1-MPV) and cation exchange capacity (after ISO 23470:2007 method using Perkin Elmer AAnalyst 300 AAS).

Single element and competitive batch sorption experiments were carried out in the initial concentration range between 0.1 and 10 mmol/L of Cd, Cu, Pb and Zn at six different concentration level. Metal concentration in the solutions were analyzed by a Perkin Elmer AAnalyst 300 AAS. pH-stat experiments were carried out using DKK TOA 701 automatic titration instrument on two selected samples (S2 and C3) between pH 3 and 8 at 1 mmol/L metal concentrations. Experiments were carried out in duplicates in each case.

The adsorption experiments resulted in 222 solid samples treated with different type and amount of metals. The potential mineralogical changes in the mineralogy of the bulk soils due to metal sorption were analyzed by XRD (Philips PW1729, Rigaku Miniflex 200) and ATR-FTIR (Bruker Vertex 70) analyses. Samples treated with the highest concentration of metals (e.g. 10 mmol/L at 1:30 solid solution ratio) in the batch experiments and those used for the pH-stat experiments were analyzed by TEM-EDS (Philips CM20 equipped with Noran EDS) to study the sorption capacities of soil mineral particles and their associations (42 soil samples).

To study the effect of Fe-oxyhydroxide removal on the sorption properties of soils and their mineral particles, Fe-oxyhydroxide extractions were carried out on selected soil samples after the method by Mehra and Jackson (1960). On the Fe-oxyhydroxide-extracted samples sorption experiments were also carried out, and the resulted bulk samples and their particles were analyzed by XRD, FTIR and TEM through the same way as described above.

Results

1. Sorption characteristics of metals in the bulk soils

1.1. Relationship between metal sorption and soil properties

After the first year of the project, a summary about the behavior of Cu and Pb in soils was carried out based on the results of earlier projects and on some samples of this project, as well. During this work, total metal concentration data, results of single and sequential extraction studies and that of sorption experiments were evaluated together, in which total metal and sorption data of samples from several soil profiles of the recent project were also incorporated. Our results (Sipos et al. 2014a) showed that in soils with background metal concentrations, both Cu and Pb showed higher amounts in the acidic Luvisols than in alkaline non-Luvisols, although a higher rate of leaching could be expected in the former. Distribution of these elements within the profiles could be related to the major pedogenic processes characteristic of these soil types. Luvisols characterized by clay and iron oxide accumulation showed a slight Cu accumulation in their mineral horizons. Alkaline non-Luvisols characterized by organic matter accumulation, however, enriched both Cu and Pb in their organic horizons. This was also found for Pb in Luvisols, suggesting its accumulation in organic-rich horizons independent of soil type and characteristics. Although high variance for the easily-soluble metal fractions was found for both metals in the studied soils, sorption analyses provided detailed information on the behavior of these metals in these fractions. In alkaline conditions, which was characteristic mostly of the non-Luvisols in our case, precipitation could be the primary immobilization process for both metals. Generally, Pb showed higher sorption than Cu, which is in agreement with the observation that the former metal showed lower leaching from the topsoil of the acid Luvisol profiles than the latter one. Both metals showed the highest affinity and sorption in the sample richest in organic matter, which could be related to the fact that they are able to form stable chelate complexes. Samples characterized by clay mineral accumulation showed also high metal retention but the affinities of the studied metals for different kind of clay mineral species were highly dependent on soil pH. Moreover, it can be stated that joint accumulation of clay minerals and iron oxides significantly influence the sorption properties of samples with such characteristics.

The above results (and many others) showed that the evaluation of the effect of soil properties on metals' sorption in soils is a highly complicated task due to the large heterogeneity of factors affecting this process. To lower this heterogeneity with respect to soil clay mineralogy, we have chosen smectitic soils in this project, and their sorption capacities were related to their major physicochemical properties of the soils (Sipos et al. 2018). Higher sorption of Pb and Cu than Cd and Zn was found also in smectitic soils, and this difference was increased by competition. In acidic soils, organic matter and smectites provided the sorption sites for Pb and Cu primarily, whereas precipitation of Pb as carbonate and sorption of Cu on soil organic matter was characteristic at alkaline conditions. Contrarily, Cd and Zn showed the highest affinity to smectites primarily if they are accumulated together with iron-oxyhydroxides. Our results showed that Cd and Zn may pose a higher risk to the environment than Pb and Cu in case of their release to the soil. However, accumulation of smectites together with iron may significantly decrease this risk. Elimination of one single variable was not enough to get a much deeper insight into soil-metal interaction, although several advantageous characteristics of smectites could be confirmed regarding metal sorption in soils.

More details of the above results can be found in the following papers:

Sipos P, Németh T, Choi C, Szalai Z, Balázs R (2014a) Distribution, geochemical fractionation and sorption of Cu and Pb in soils characteristic of Hungary. Central European Geology 57: 265-285. http://real.mtak.hu/21486/

Sipos P, Balázs R, Németh T (2018) Sorption properties of Cd, Cu, Pb and Zn in soils with smectitic clay mineralogy. Carpathian Journal of Earth and Environmental Sciences 13/1: 175-186. http://real.mtak.hu/60224/

1.2. Fitting of sorption curve equations to the experimental data

The evaluation of sorption curves of metals in soils is generally restricted to the fitting of Langmuir and/or Freundlich equations to the experimental data. However, there are several other equations providing more parameters and much better fit to the experimental data. Moreover, these equations may provide a much correct estimation of sorption capacities of soils, which is the most important parameter when sorption properties of metals in soils are studied. That is why we carried out the evaluation of the sorption curves using twelve more equations in addition to Langmuir and Freundlich equations, namely: Jovanovich, Sips, Langmuir-Freundlich, Tóth, Redlich-Peterson, Fritz-Schundler, Temkin, Radke-Prausnitz, Brunauer-Emerett-Teller, MacMillan-Teller, Dubinin-Radushkievich and Halsey equations. When it was applicable, fitting of both linear and non-linear equations were compared. The goodness of fit were studied using six different error functions (R^2 (coefficient of determination), ERRSQ (sum of the error squared), HYBRID (hybrid fractional error function), MPSD (Marquardt’s percent standard deviation), ARE (average relative error), EABS (sum of the absolute errors)). The fitting of our data set of 180 data by the above equations and error functions resulted in 570 calculations and 195 parameters for each sample describing the sorption of metals.

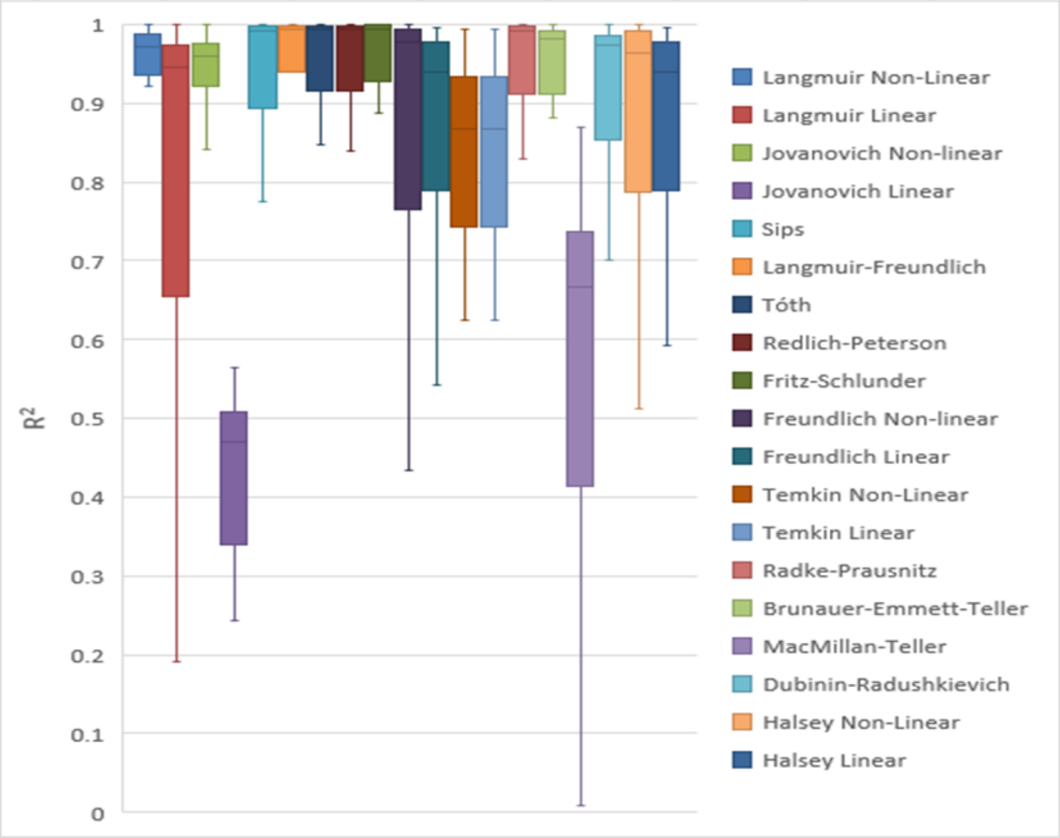

Figure 1. *Presentation of the results of fitting of fourteen equations on the experimental data as shown by the resulted coefficient of determination (R^2) values.*

We found that the linear variants of the equations provide generally significantly lower fit to the experimental data so their use is not preferred over the non-linear equations, although linear equations are still the mostly used ones in sorption studies. For example, the median of the coefficient of determination values of the most often used equations, like Langmuir and Freundlich were 0.97 and 0.95, as well as 0.98 and 0.94 for non-linear and linear fitting, respectively, whereas much larger differences were found for the non-linear and linear variant of the Jovanovich equation (Figure 1). Generally, better fit was found for the acidic samples than for the alkaline ones, which could be related to the fact that metals' precipitation in the alkaline samples resulted in worsening of the goodness of fit. However, if the contribution of the precipitation to the complete immobilization of a given metal is not dominant (which may occur also in alkaline soils), sorption curve evaluation by these equations can be still used. We found that Temkin and MacMillan-Teller equations never showed a good fit (although acceptable ones). The median values of the former were generally between 0.7 and 0.8 R^2, whereas slightly lower values were found for the latter, so they are not advised to be used to describe soil-metal interaction. On the contrary, there are several equations, which generally showed very good fit both for acidic and alkaline soils and for each studied metals. These are the Sips, Langmuir-Freundlich, Tóth, Redlich-Peterson, Fritz-Schundler and Radke-Prausnitz equations of which the median of the coefficient of determination was 0.99. They are all three-parameter models so their generally better fit (when compared to that of two-parameter models) was expected. However, there are only three models allow to calculate maximum sorption capacities, those derived from the Langmuir equation (Langmuir-Freundlich, Fritz-Schundler and Radke-Prausnitz). Taken into account that the shape of the sorption curves shows generally both Freundlich and Langmuir characteristics, we suggest the use of Langmuir-Freundlich equation to fit the experimental data. Moreover, this equation allows us to calculate parameters related to the sorption capacity of the sorbent (both Langmuir monolayer coverage and Freundlich capacity) and those related to the adsorption intensity or affinity (Langmuir *b* and Freundlich *n*). Among the two-parameter models, the most often used ones, the Freundlich and Langmuir showed the best fit with median values of the coefficient of determination of 0.98 and 0.97, respectively.

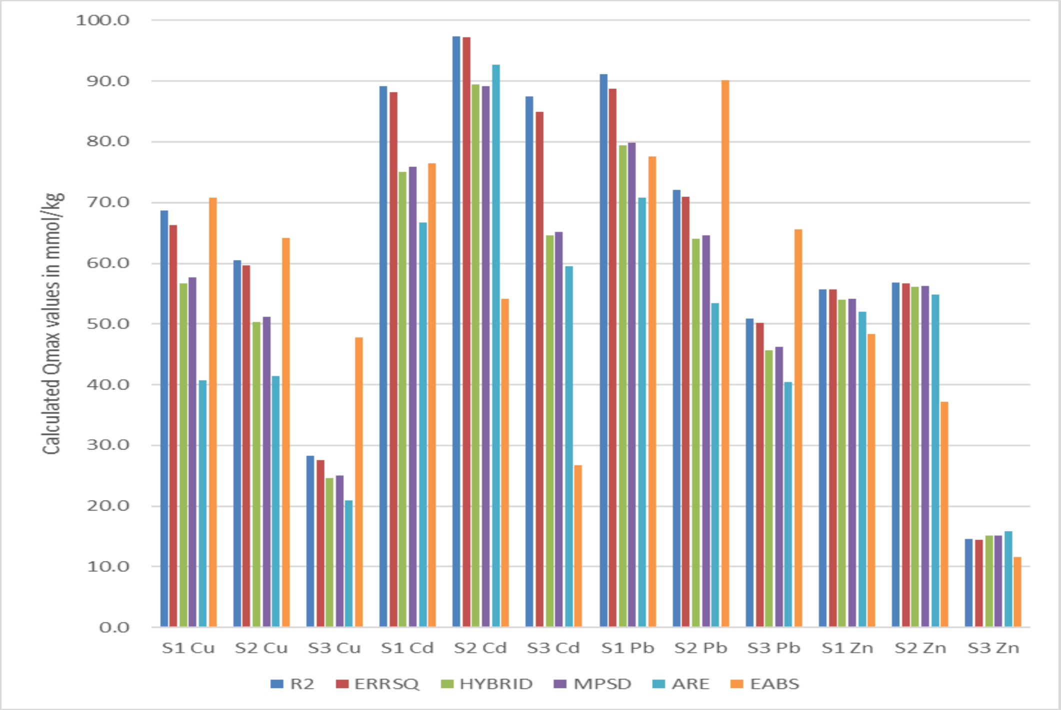

***Figure 2**: Comparison of the calculated Q_{max} values using different error functions.*

When the six error functions used are compared, we found that R^2 and ERRSQ, as well as HYBRID and MPSD resulted generally similar Q_{max} values to each other, and the latter ones resulted in slightly lower values (by 9 %). ARE and EABS functions showed no systematic characteristics, but generally resulted very different Q_{max} values when compared to those produced by the previous four functions (Figure 2). Based on our data, the use of R^2 and ERRSQ functions can be suggested when sorption equations are fitted to experimental data as these two functions resulted the best fit generally besides the EABS function. Consequently, care must be taken when Q_{max} values resulted by fitting with different error functions are compared.

A manuscript presenting these results has been submitted to an international journal, but it was rejected. The manuscript is under revision and will be re-submitted to an other international journal soon.

1.3. Effect of pH on metal sorption in soils

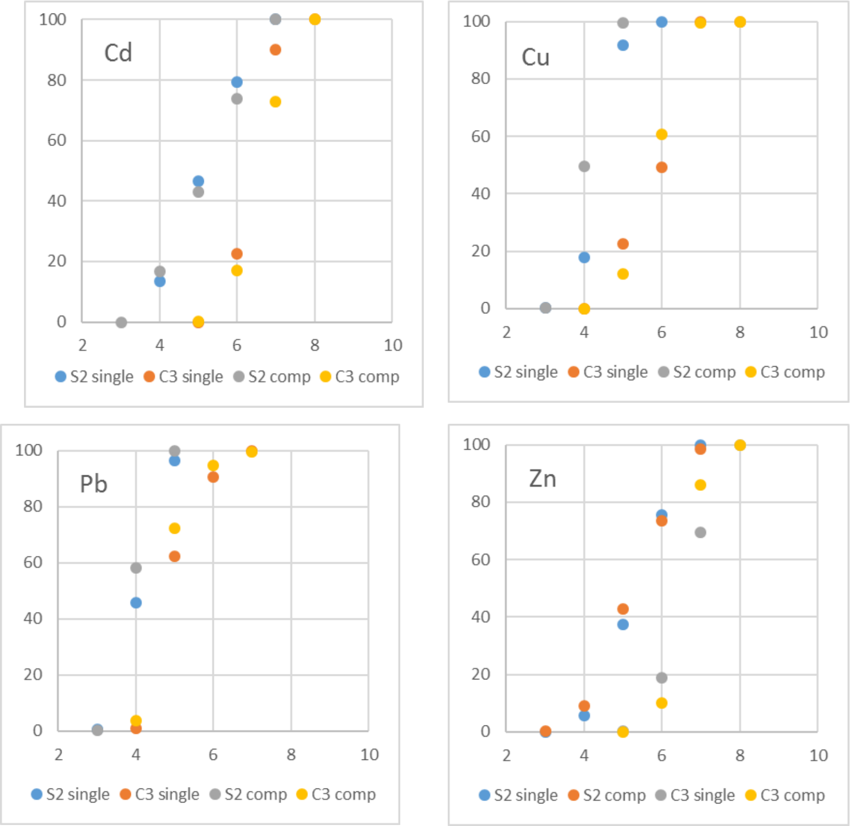

Figure 3. *Results of pH-stat experiments in an acidic (S2) and an alkaline (C3) sample.*

The effect of pH was studied by processing the adsorption edges of the studied metals established as the result of the pH-stat experiments. No significant differences between single element and competitive situations were found (Figure 3). This suggested that the same types of processes take place during the single element and competitive sorption of the studied metals at given pH, only the number of metal ion competing for the same number of available sorption sites show differences. Cadmium and Zn sorption edges were found between pH 3 and 7, and between pH 5 and 8 for the acidic and alkaline samples, respectively. For Cu and Pb, these values were between pH 3 and 5, and between pH 4 and 7 for the acidic and alkaline samples, respectively. Hence, sorption edges covered narrower range for Cu and Pb than for Cd and Zn at both soil conditions. This shows that complete sorption of Cu and Pb proceeded much faster than that of Cd and Zn when soil pH increases, e.g. latter metals pose a higher risk to the environment when they are released. Differences were also found in the characteristics of the sorption edges of the metals between the acidic and alkaline soil, as the

sorption edges were observed at lower pH in acidic soils by 1-2 units than in the alkaline ones. In harmony with our earlier results, this demonstrates that different sorption processes takes place in acidic and alkaline soils, which could be related to the significant role of the precipitation in the alkaline soil. Moreover, metal sorption could be also affected by higher the Ca mobilization in the alkaline soil, as acidification by metal sorption may have promoted calcite dissolution.
Results of pH-stat experiments have not published yet. They are planned to be published together with the results of direct TEM analyses of soil mineral particles of samples used in these experiments. As producing the TEM data is still in progress, their publication will be possible only after the closing of the project.

1.4 Mineralogical changes in bulk soil mineralogy after metal sorption

Bulk mineralogical methods are often used to characterize mono-mineral materials after metal sorption. For example, XRD was used to support the ion exchange of metals with interlayer cations of clay minerals, whereas FTIR was used to demonstrate the interaction of metals with the surface functional groups of such phases successfully. Unfortunately, these methods are very rarely used to characterize soils after sorption, primarily due to the large heterogeneity of this material. Additionally, precipitation of metals during the sorption experiments has been often found, but precipitates may have of low amounts, low crystallinity and small particle size resulting in low efficiency to be identified with bulk methods. That is why we have combined the above two methods with the use of TEM to study the changes in soil mineral components due to metal sorption in the soil.

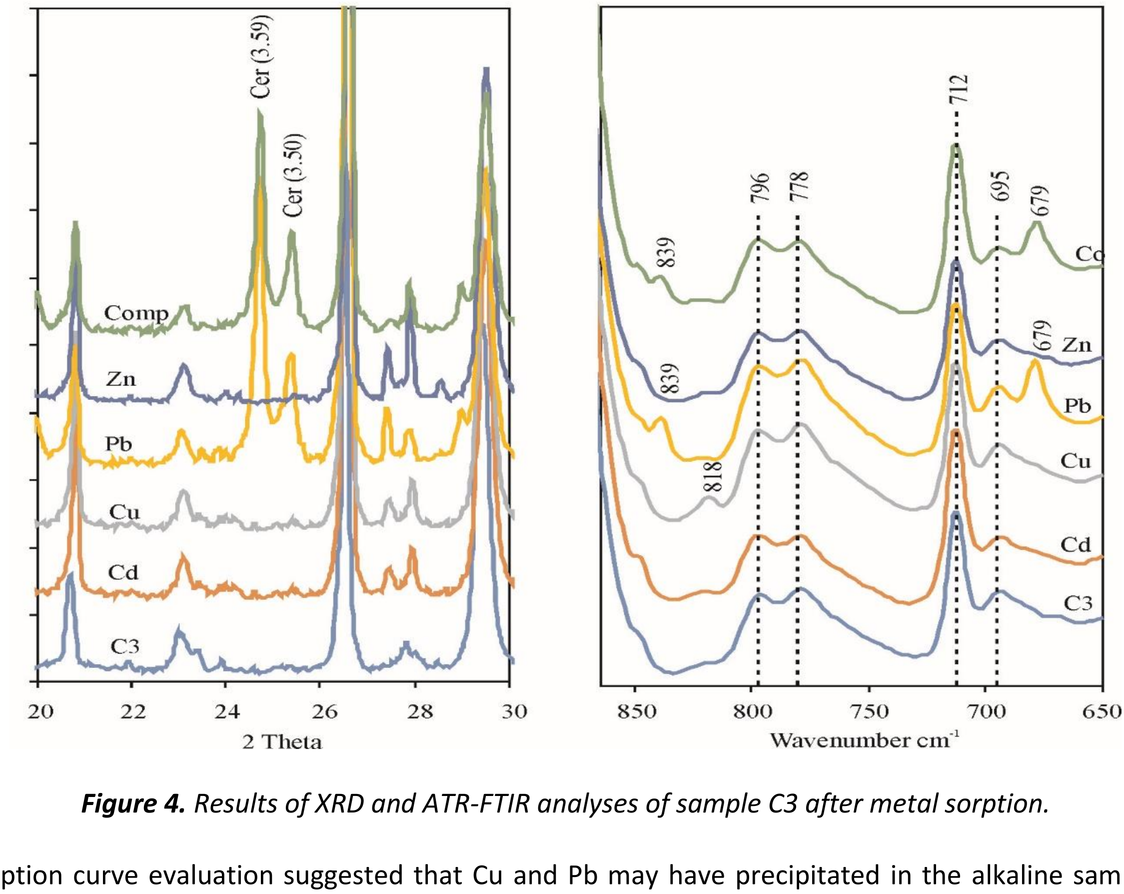

Figure 4. *Results of XRD and ATR-FTIR analyses of sample C3 after metal sorption.*

Sorption curve evaluation suggested that Cu and Pb may have precipitated in the alkaline samples during the sorption experiments. Our XRD analyses showed that Pb precipitated in the form of well-crystalline cerussite ($PbCO_3$) in these samples both in single element and competitive situations, as shown by the appearance of the sharp peaks at 3.59 and 3.50 Å (Figure 4). The Rietveld analysis of the XRD patterns by the Siroquant software showed that between 4 and 6% of cerussite has been formed during the experiments in the alkaline samples treated with solutions containing 10 mM Pb. This showed that between 50 and 75% of the total available Pb have precipitated in these samples, and only the rest of the initial amount of Pb interacted with the surface of the soil particles through sorption processes (as almost complete retention was found). The ATR-FTIR analyses of the same samples also showed the precipitation of cerussite both in the single element and in competitive situations shown by the appearance of the bands at 839 and 679 cm^{-1} (Figure 4). These bands correspond to the out-of-plane and in-plane bending vibrations characteristic of Pb-carbonate, respectively. In addition, a small band at 820 cm^{-1} also appeared in the sample treated with Cu solutions. This could be related to the precipitation of this metal as hydroxy-carbonate as this band is corresponding to the out-of-plane bending vibration of malachite. TEM analyses also showed the presence of these (and also that of other type of) precipitations. Cerussite and malachite were identified based on their SAED patterns (Figure 5). Pb-carbonate single crystal was tilted in zone axis orientation. The measured interplanar spacing in this orientations agree well with d(1-11) and d(110) of cerussite, implying [-112] zone axis pattern. The splitting reflecions indicate {110} twinning which is common in aragonite type carbonates. The thickness of individual twin lamellae is on the few tens of nanometre scale. In case of Cu-carbonate, a lath-like morphology was observed. The zone axis SAED pattern of the crystal proved malachite structure with interplanar spacing corresponding to d(001) and d(110), implying [-110] orientation. In the Cu-treated sample, large and sometimes thick, 200-500 nm sized aggregates with hairy contrast were also observed. SAED patterns indicated a poorly organized random nanocrystalline structure with diffraction rings at 2.4, 1.5 and 1.25 Å, and some diffraction spots at 2.8 Å. Based on morphological and structural similarities with ferrihydrite, these high Cu containing particles were identified as Cu-oxyhxyroxides (“cuprihydrite”). Solubility calculations by the MINTEQA software also supported that the above metal phases may have precipitated at the experimental conditions as CO_3^{2-} mobilization to the solution from the alkaline samples could be expected during the experiments. Our calculations showed that the following phases were oversaturated at the initial conditions of the single element 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 competitive 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 $Pb(OH)_2$s at CO_3^{2-} > 2.76 mM.

FTIR analysis of the interaction of metals with the clay minerals (primarily smectites) provided no evidence for this process. Spectral differences between the clay minerals and metal sorbed clay minerals refer to two wave number ranges generally: between 3800 and 3000 cm^{-1} corresponding to the bands originating from OH group stretching vibrations, and between 1200 and 600 cm^{-1} corresponding to bands assigned to asymmetric Si-O-Si vibrations. As long as the latter range could not be evaluated generally due to the co-absorbance of several silicate phases in soils, a slight shift in the former one has been often observed, which is generally attributed to the different tendencies of metal ions to form aqua-complexes and to hydrate in an aqueous environment. In our case, however, no evidence was observed in the studied samples, as OH group stretching vibrations at 3697 and 3620 cm^{-1} in the acidic samples and those at 3617 and 3549 cm^{-1} in the alkaline ones showed the same characteristics before and after metal sorption. On the contrary, XRD analyses provided evidence for the ion exchange processes between the studied metals and soil smectites (Figure 6). A shift in the basal (001) reflection of smectites is often found after metal sorption both in mono-mineral materials. In the acidic soils, the basal reflection of soil smectites shifted from 14.6 to 14.3 Å after Cu sorption. The sharp shape of the peak suggest homoionic interlayer for this metal. For Pb, however, the basal reflexion shifted towards 14.2 Å and exhibited diffuse shape which is characteristic of Pb-smectites. This latter characteristic was observed in these samples after the competitive metal sorption showing the preferential interaction of Pb with smectites among the studied metals. No effect after Cd and Zn sorption was found in the acidic samples. On the contrary, basal reflection of smectite showed some shift after the sorption of each studied metal in the alkaline samples. The same effect was found after Cd and Zn sorption, e.g. shifting from 14.7 to 14.3 Å and slightly diffuse peaks. After Cu sorption, the peak moved to 14.8 Å, but the shape of the peak have not changed. Largest effect was found again after Pb sorption as shown by the basal reflection shifting to 13.9 and the very diffuse peaks. The same effect was found in the samples after competitive metal sorption. The results showed that the same interaction takes place for Cu and Pb in each samples characterized by highly contrasting physicochemical properties and pH. On the contrary, Cd and Zn showed ion exchange on the smectites only in the alkaline samples.

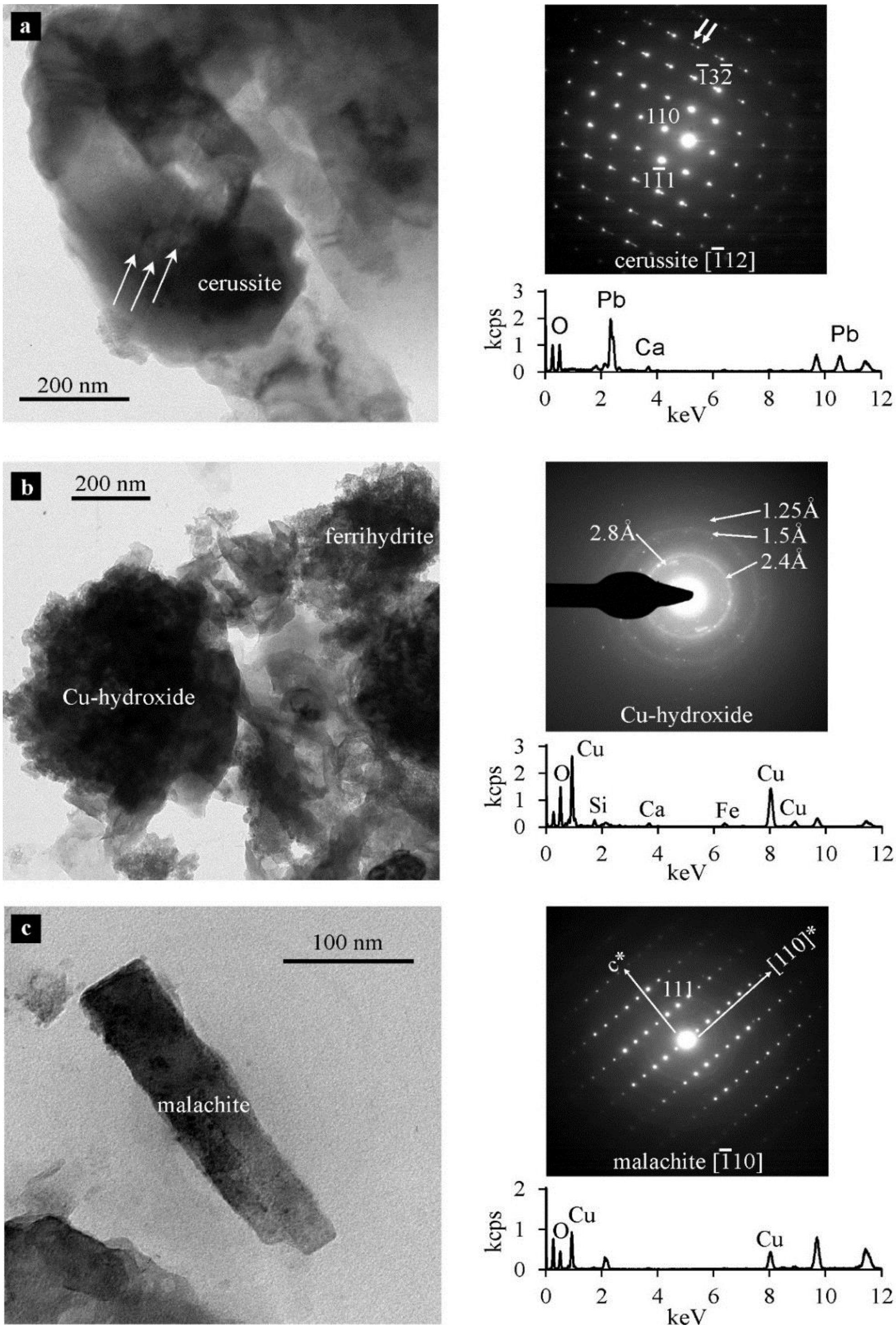

Figure 5. *Metal precipitates in the sample C3 as observed by TEM analyses.*

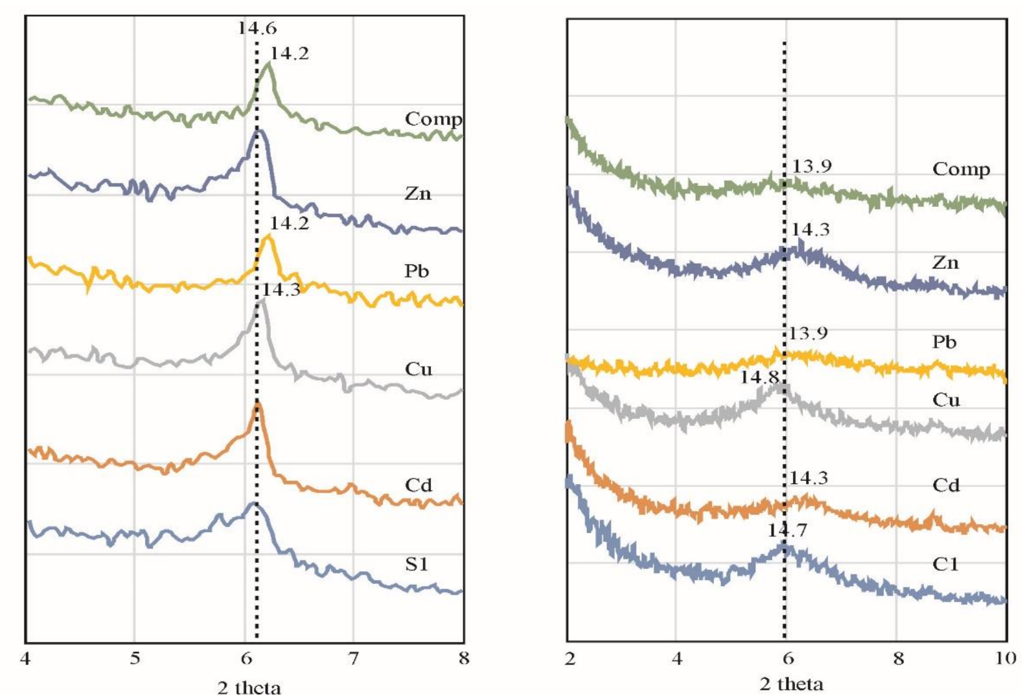

Figure 6. *Results of XRD analyses after metal sorption in selected soils samples (S1 – acidic, C1 – alkaline).*

The above results have been published only at conferences yet (e.g. Goldschmidt 2015, SEGH Conference 2015). A manuscript about the mineralogical changes in soils after metal sorption has been prepared and submitted to an international journal recently.

1.5. Effect of Fe-oxyhydroxide removal on metal sorption in bulk soils

Extraction of Fe-oxyhydroxides are widely used in soils primarily for genetic studies. The most widely used extraction method is that of Mehra and Jackson (1960) which use a mixture of citrate, dithionite and bicarbonate (CDB method) to extract these phases. Its advantage is thought to be that acids are not used for the extraction so it can be used also in alkaline soils without attacking carbonates. That is why we also used this method to extract Fe-oxyhydroxides from our soil samples. However, XRD study of the extracted samples showed that concentration of smectite, chlorite and calcite decreased significantly, even by 20-30%, as shown by the Rietveld analysis of the XRD patterns. In addition, TEM analyses of the particles showed corrosion of clay mineral and calcite particles, and also the presence of tiny Fe-oxyhydroxide particles even after the extraction (Figure 7). Repetition of the CDB extraction on selected samples resulted in further dissolution of silicate and carbonate particles and survival of certain Fe-oxyhydroxide particles. Due to these unexpected mineralogical changes, we started a new set of experiments to study the effect of temperature and citrate concentration on the mineralogy of soils and the Fe-oxyhydroxide extraction. Besides the original extraction method (0.3 M citrate at 80°C for 1 h), we carried out the extraction at different citrate-concentration (0.57 M citrate at 21°C for 16h after Jeanroy (1991)) and at different temperatures (0.3 M citrate at 45 and 21°C for 1 h) on an acidic (S2) and an alkaline (C3) sample. We found that the method of Jeanroy (1991) resulted lower Fe extraction (by 25-33%), but similar changes in the mineralogy of the samples (decrease in the amount of smectite, chlorite and calcite). Lowering the temperature in the method by Mehra and Jackson (1960) to 45°C resulted in slightly lower extracted Fe concentrations, and also very similar changes in mineralogy to those found at 80°C. Further lowering the temperature to 21°C, however, resulted significantly lower extracted Fe concentrations (by 60%), and the mineralogical changes were rather characteristic to calcite which showed still significant decrease in its concentration. Consequently, we have not found the “ideal” method for Fe-oxyhydroxide extraction, e.g. (almost) complete removal of Fe-oxyhydroxides together with negligible changes in soil mineralogy can not be fulfilled. Carrying out further experiments to find a better method was beyond the scope and capacity of this project. The experiments aiming at the study of the effect of Fe-oxyhydroxide removal on metal sorption were carried out on the samples extracted by the original method of Mehra and Jackson (1960), as this was the most effective one to extract Fe-oxyhydroxides. However, the changes in the mineralogical composition of soils due to Fe-oxyhydroxide extraction have to be taken into account when sorption characteristics of samples before and after the extraction are compared.

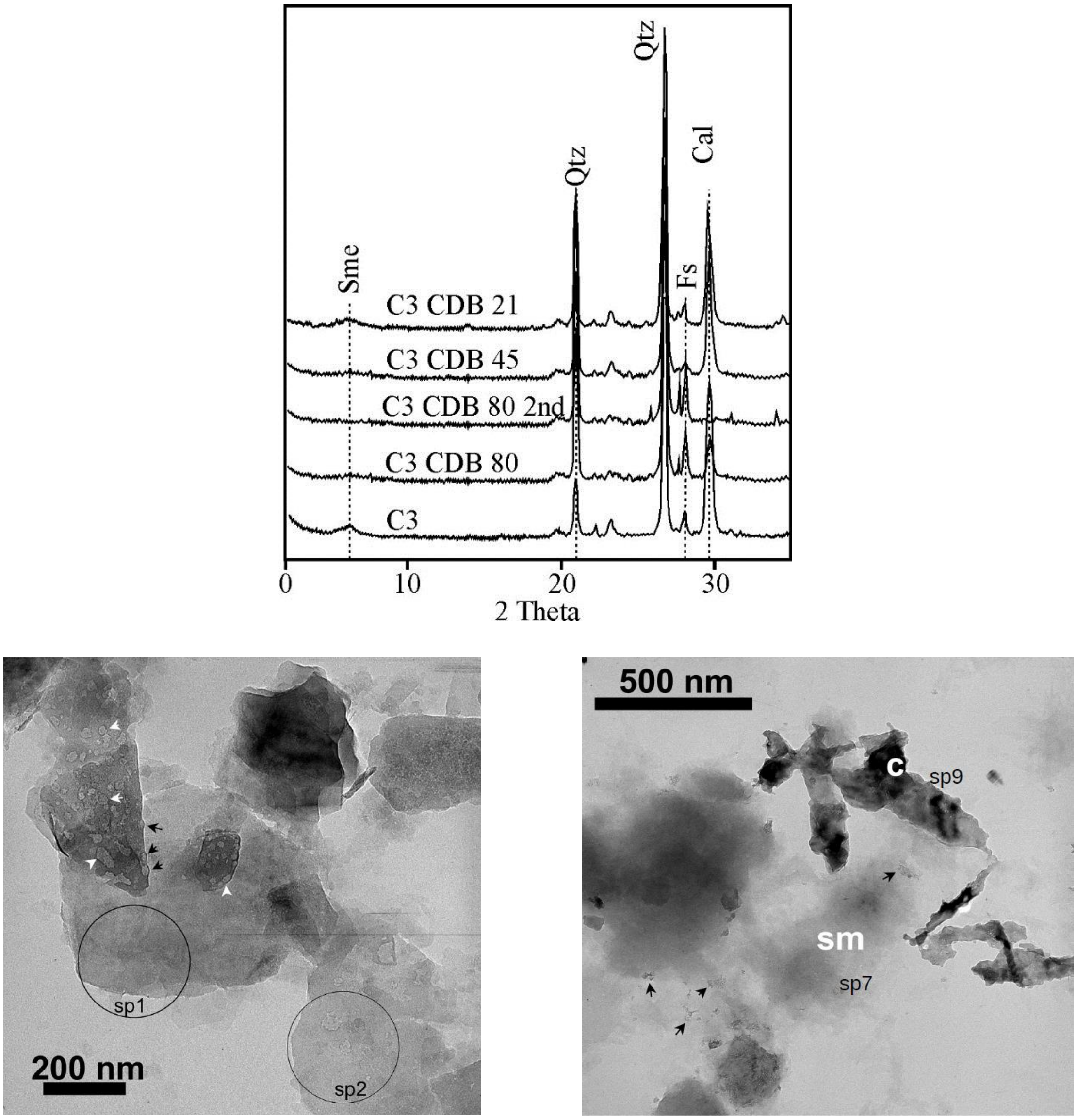

Figure 7. *Unexpected effect of Fe-oxyhydroxide extraction on the mineralogy of the studied samples as shown by decrease of smectite (Sme) and calcite (Cal) and increase of quartz (Qtz) and feldspar (Fs) peaks in the XRD patterns (upper picture) at different extraction temperatures, and corrosion of smectite (lower left picture) and calcite (lower right picture) particles, and the remains of Fe-oxyhydroxides (black arrows lower right picture) after the CDB extraction as observed by TEM.*

Extraction of Fe-oxyhydroxides resulted in significant decrease of the sorption of Cd, Cu and Zn in the studied soils. This decrease was much higher in the alkaline than in the acidic soils for Cd and Cu, the maximum sorption capacities of these two metals were lower by 50% in the former and by 20% in the latter soils. For Zn, however, these values were around 40% in both alkaline and acidic soils. The decrease could be related to the loss of sorption sites after removal of Fe-oxyhydroxides. As this was found also in the acidic soils (where Fe-oxyhydroxides possess positive surface charge), the sorption of these metals could not be related to the cation exchange capacity of the soils (as it is done generally), but rather to the amount of available surface sites. Interestingly, sorption of Pb increased after Fe-oxyhydroxide extraction in the acidic soils. This could be related to the liberation of sorption sites on the surface of un-extracted minerals (like clay particles), which were coated by Fe-oxyhydroxides before the extraction. At these conditions, Pb was able to compete for the lower number of sorption sites more effectively than the other studied metals, that is why higher sorption was found for this metal after the extraction (Figure 8).

The above results have been published only at conferences yet (e.g. MECC 2016, BIOGEOMON 2017, ICC 2017). They will be published together with the results of direct TEM analyses of soil mineral particles of samples used in these experiments. Although TEM data have been already collected, some data should be revised and certain samples should be re-analyzed due to the unexpected mineralogical changes and to the experiments carried out to find the most convenient method for Fe-oxyhydroxide extraction. As these activities are still in progress, the publication of these results will be possible only after the closing of the project.

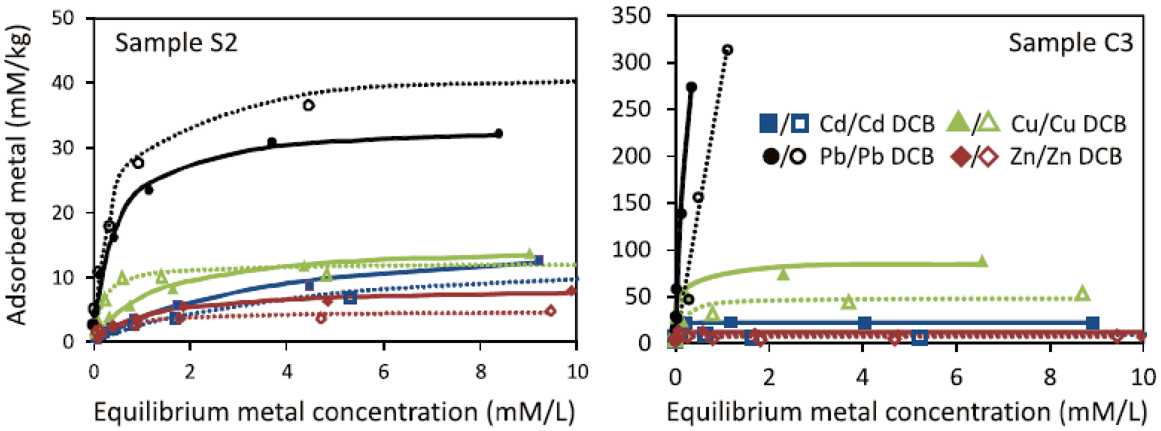

Figure 8. *Sorption curves of metals in an acidic (S2) and an alkaline (C3) soil before and after Fe-oxyhydroxide extraction in competitive situation.*

2. Sorption characteristics of metals on soil mineral particles

2.1. Metal partition at particle level in single element and competitive situations

As it was expected, mineral particles of the alkaline soils adsorbed higher metal amounts than those in the acidic ones in both single element and competitive situations. However, the ratios of metal sorption in the alkaline and acidic bulk soils and those in their particles showed large differences (Figure 9). In single element situation, Zn showed the largest difference in its sorption on particles between the alkaline and acidic sample. This could be primarily attributed to the higher sorption of Zn onto Fe-rich particles at alkaline conditions. Iron-oxyhydroxides were also found to show the largest contribution to the higher sorption of Cd (and Cu) in the alkaline soil. No single particle type responsible for the higher metal sorption could be specified for Cu and Pb at alkaline condition. However, clay mineral particles showed slightly higher contribution to the Pb sorption by the alkaline soil. In competitive situation, however, no single particle type could be specified which might have primarily contributed to the sorption for most of the studied metals at alkaline conditions. This, however, might be rather the effect of competition. The only exception is Zn in our case, of which sorption increased on the clay mineral and Fe-oxyhydroxide particles at the most under competition in the alkaline soil.

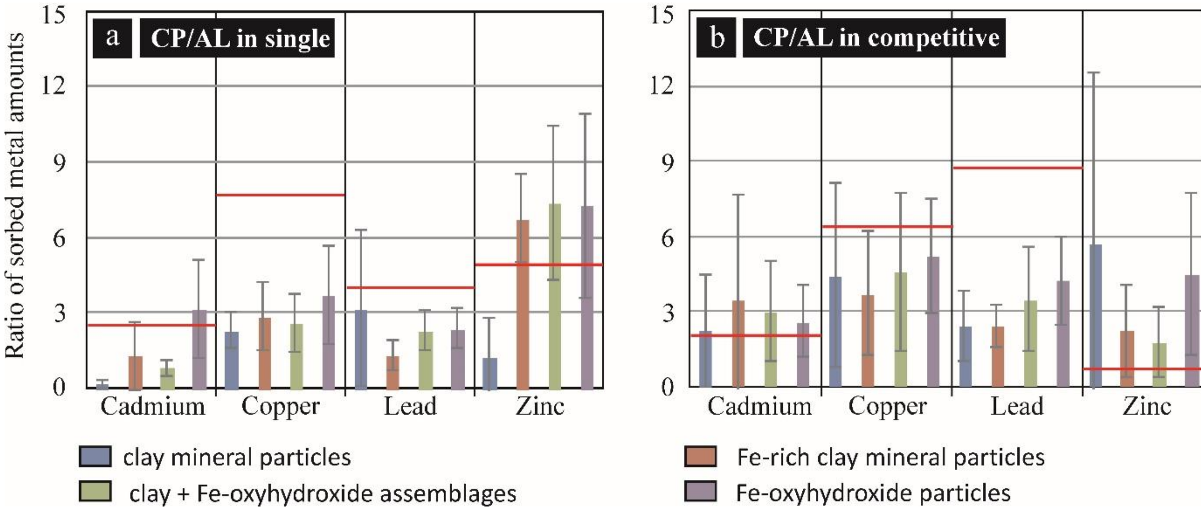

Figure 9. *Ratios of average sorbed metal amounts on different particle types from the alkaline (CP) and the acidic (AL) samples. Red lines show the same ratios for the bulk soil samples.*

Additional retention process(es) and/or non-mineral surfaces could be also contributed to the higher sorption of Cu and Pb in both single element and competitive situation (and also of Cd in single element one), as their sorption on the bulk samples increased at much higher rate than on mineral particles in the alkaline soil. Although the studied soils contained low amounts of organic matter, its contribution to the sorption of these metals could not be neglected. Additionally, precipitation of Cu and Pb in the alkaline sample was also observed directly by TEM and bulk mineralogical methods.

Another similar feature between the metal sorption on the bulk samples and their mineral particles is the decrease of metal sorption due to competition (Figure 10). This decrease, however, showed large variation among the studied particle types. This selectivity was also supported by our observation that differences among the metal sorption capacities of the studied particle types could be even vanished due to competition; e.g. competition resulted almost equal sorption capacity for these particles. This effect was characteristic mostly of particles with clay mineral component in our case, and it is stronger in the acidic than in the alkaline soils, and it is characteristic for the metals with lower sorption (Cd, Zn). Competition affected the metal sorption on the soil mineral particles for Cd the most and for Cu the least in our case. In the acidic samples, decrease of sorption in the bulk samples due to the competition could be explained by the decrease of sorption of Cd and Pb on the soil mineral particles at similar rate. Zinc sorption showed the largest decrease in the clay mineral particles, whereas this phenomenon could not be related solely to the decrease of sorption on the soil mineral particles for Cu, e.g. slight contribution of other surfaces like those on soil organic matter could have also contributed to this process. Differences among the contribution of soil mineral types to the decrease of metal sorption due to competition were more expressed in the alkaline soils. Our data showed that this decrease could be primarily due to the decreasing role of clay mineral particles for Pb and that of the Fe-oxyhydroxides for Cd. For Cu, however, only low differences were found between the sorption on mineral particles in single and competitive situation in the alkaline soils, suggesting the contribution of precipitation to the higher difference found between the bulk samples. Similar feature was found for Zn, e.g. contribution of non-mineral surfaces could be suspected to the decrease in its sorption due to competition, although sorption on particles with high Fe content showed also very large decrease. Consequently, precipitation of Zn in the alkaline sample under competition could be also supposed, although the presence of Zn-precipitates was not found by our analyses.

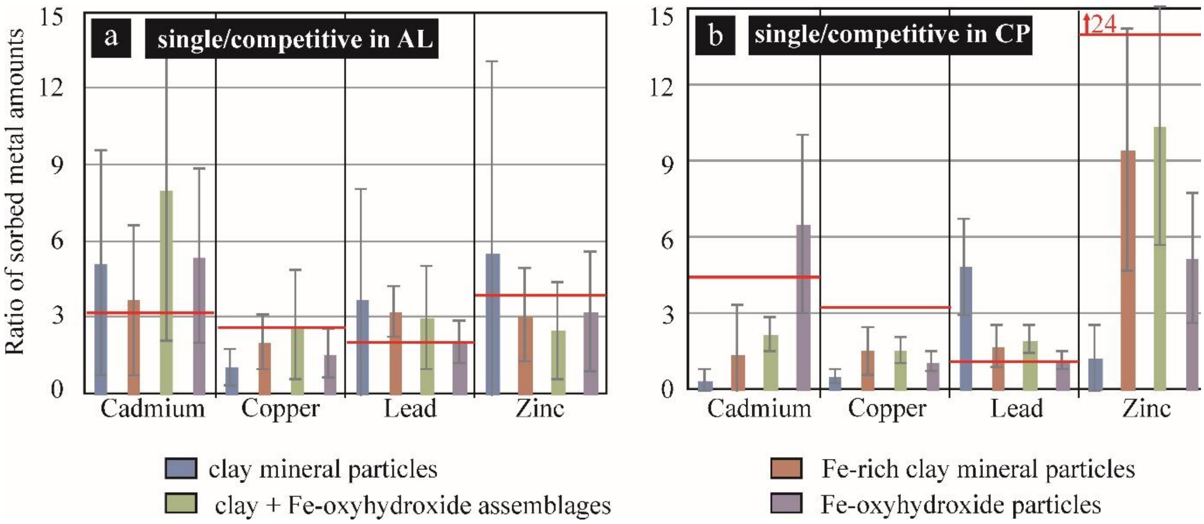

Figure 10. *Ratios of average sorbed metal amounts on different particle types in the single element and competitive situations in the acidic (AL) and the alkaline (CP) samples. Red lines show the same ratios for the bulk soil samples.*

The above results have been published only at conferences yet (e.g. ICC 2017, CBW 2017). A manuscript about the comparison of metal sorption on particles in single element and competitive conditions is under review in an international journal now.

2.2. Role of clay and Fe-oxyhydorxide particles and their assemblages

Metal affinity sequences showed large differences between bulk samples and their particles (Table 3). In the acidic soils, single element sorption on the particles was significantly higher not only for Pb but also for Cu if their sorption onto mineral particles is studied. As this is the case in the bulk soil only for Pb, the high contribution of organic substances to its sorption can be supposed, whereas Cu is rather sorbed by the soil mineral components in this case. The same feature for these metals was found in competitive situation at acidic soil conditions. Additionally, in single element situation, Zn was only able to be sorbed on the clay particles at similar rate to Cu and Pb. In the alkaline samples and in single element situation, however, both Cu and Zn showed similar sorbed amounts on the mineral particles to Pb, although only this latter metal could be characterized by extraordinarily high sorption in the bulk sample. Consequently, the higher bulk sorption of Pb can be related to its sorption on organic surfaces and/or to its precipitation. As it was shown earlier, both processes are primarily preferred by Pb in this case. Contrarily to the acidic samples, Zn was not sorbed on the clay particles at such a high rate primarily when compared to Pb. In competitive situation, differences in sorbed amounts are much higher between the metals showing high (Pb, Cu) and low (Cd, Zn) sorption than in the acidic samples. Consequently, the higher sorption of Cu and Pb can not be solely due to their precipitation, but also to their higher sorption onto soil mineral particles.

Table 3. *Comparison of metal affinities to bulk soil samples and to their mineral particles.*

		Acid (AL) sample	Alkaline (CP) sample
Single	Bulk	Pb >> Cd ≥ Cu > Zn	Cu > Pb >> Zn > Cd
	Particles	Pb > Cu > Cd = Zn	Pb ≥ Cu ≥Zn >> Cd
Competitive	Bulk	Pb >> Cu > Cd > Zn	Pb > Cu > Cd > Zn
	Particles	Cu ≥ Pb >> Zn ≥ Cd	Cu ≥ Pb >> Zn > Cd

Generally, the sorption capacity of the studied particles increased with their Fe content. This was the most expressed for Cu both in acid and alkaline soils. The same was observed 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 soils. The observation is characteristic for Zn only for the particles from the alkaline soils. An opposite trend was found for clay particles in the acidic soils, although Fe-oxyhdyroxides showed higher Zn sorption than their associations with clay minerals in these samples. The increase of metal sorption with the Fe content of particles does not necessarily the result of higher sorption of metals on Fe-oxyhydroxides. We found the high variation of the relationship between the sorbed metal and the Fe content within the different particle types.

In the acidic samples, only Cd and Cu concentrations showed linear correlation with the Fe content of the particles (r = 0.51 and 0.76, respectively), generally. However, if particle types are studied separately, this relationship could be found only for the clay mineral-Fe-oxyhydroxide assemblages for Cd (r = 0.76), and clay mineral (r = 0.78), clay-Fe-oxyhydroxide assemblages (r = 0.67) and Fe-oxyhydroxide (r = 0.87) particles for Cu. For Pb, particles with high Fe content adsorbed more Pb than those with low Fe. However, linear relationship was found only for the Fe and Pb content of the clay mineral particles (r = 0.63), whereas this was also found for the Fe and Zn content of the Fe-rich clay mineral particles (r = 0.83). In contrast, sorption of all metals increased with the Fe content of particles in the alkaline soils (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 Cd sorbed (r = 0.75). Iron-rich clay mineral particles could be characterized by such relationship for Cu (r = 0.60), Pb (r = 0.67) and Zn (r = 0.77). Sorption of Pb also increased with increasing Fe content of the clay-Fe-oxyhydroxide associations (r = 0.60) and concentration of Zn also increased with increasing Fe content of Fe-oxyhydroxides (r = 0.88). We also found strong linear correlation between the Fe content of calcite particles and their metal content (with r values between 0.61 and 0.93). Accordingly, metal sorption on calcite particles could be rather related to the presence of Fe-oxyhydrixodes on their surface in our case.

The above results have been published only at conferences yet (e.g. SEGH 2015, Goldschmidt 2015, EGU 2016 and 2017). A manuscript presenting these results has been submitted to the journal Geoderma, and it was accepted with moderate revision. The revised manuscript is under review now.

2.3. Effect of Fe-oxyhydorxide removal on sorption capacity of soil clay mineral particles

Our TEM analyses of the sorption capacity of soil mineral particles showed that Fe plays a decisive role in the metal sorption of particles through the close association of clays and Fe-oxyhydroxide phases or through the presence of Fe in the crystal structure of clay minerals. Therefore we studied the sorption capacity of clay mineral particles (primarily that of smectites) before and after Fe-oxyhydroxixe removal from the soils (using the CDB method). Although metal concentrations values showed very high variance, significant increase of metal sorption onto smectite particles was found in the acidic soil after the extraction (Figure 11). The increase was the highest for Pb (with 2.5-times higher concentration values after Fe-oxyhydroxide removal), followed by Cd (2-times higher values), Zn (nearly 2-times higher values) and Cu at least (1.3-times higher values). Our data showed that Pb showed very high affinity to smectite surfaces after Fe-oxyhydroxide extraction, similarly to Cd and Zn which were found to have higher affinity to smectites than to Fe-oxyhydroxides by our TEM analyses on untreated soil samples. The lower preference of Cu to be adsorbed on smectites suggest that this metal is adsorbed rather by other available surface sites (like those on soil organic matter). Our results suggested that smectites are able to play similar role to Fe-oxyhydroxides in the sorption process for most metals in acidic soil conditions after the CDB extraction. On the contrary, only Pb showed an increase in the sorption onto smectite particles after Fe-oxyhydroxide extraction in the alkaline soil (Figure 11). In this case, 3-times higher Pb concentrations were detected on average on the smectite particles after the CDB extraction. This showed that Pb show very high affinity to smectites both in acidic and alkaline conditions if Fe-oxyhydroxides are not present in the soil. The other studied metals, however, showed lower adsorption on the smectite particles after the Fe-oxyhydroxide removal in the alkaline sample. For Cu and Cd, half of the metal concentrations were detected after CDB extraction, whereas this ratio was 80% for Zn. This showed that smectites were not the primary adsorbents for Cd, Cu and Zn in the alkaline soil after Fe-oxyhydroxide removal, e.g. other immobilization processes (like precipitation) or adsorption by other available surfaces (like those on soil organic matter) played more significant role in their retention. These data supported our findings based on not-extracted samples, e.g. association of Fe-oxyhydroxide and clay mineral particles play a decisive role in the metal sorption at alkaline soil condition, whereas rather structural Fe in clay minerals affects metal sorption in acidic soils (which is not extracted by the CDB method theoretically).

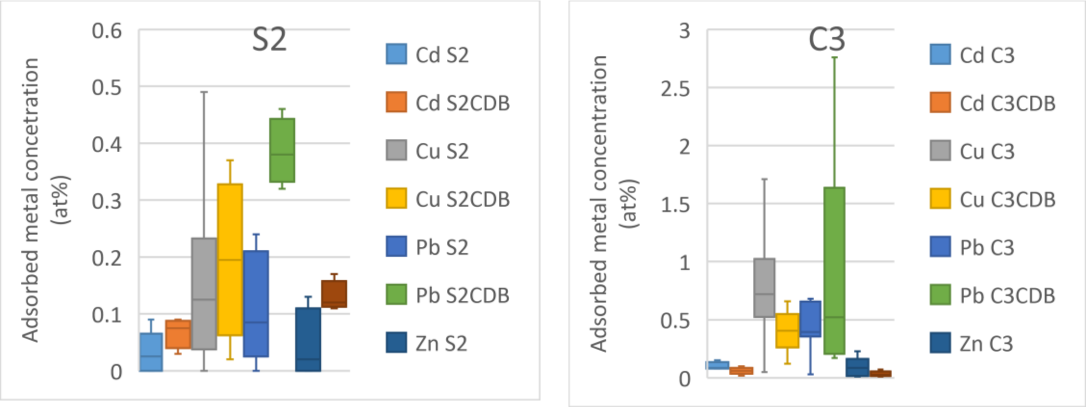

Figure 11. *Comparison of the metal sorption capacities of the smectite particles in the acidic (S2) and alkaline (C3) soils.*

The above results have been published only at conferences yet (e.g. MECC 2016, BIOGEOMON 2017, ICC 2017). Although some part of the TEM data have been already collected, part of them should be revised and certain samples should be re-analyzed due to the unexpected artefacts of the Fe-oxyhydroxide extraction methods. As these activities are still in progress, the publication of these results will be possible only after the closing of the project.

3. Additional results

Sampling and basic analysis of the 43 soil profiles provided opportunity to carry out studies also on Fe fractionation and precipitation in soils, although their study was not aimed in this project. As a result, two paper were published in the following topics.

3.1. Metal fractionation as affected by Fe in soils

Although this study based on the results of other projects primarily, certain data of two soil profiles sampled also in this project were incorporated, as well. In this study (Sipos et al. 2014b), sequential chemical extractions were used to study the relationship between the geochemical fractionation of Fe and trace metals (Co, Cr, Cu, Ni, Pb and Zn) in representative soils for Hungary. Our aim was to study the effect of pedogenic processes and soil parent material on trace metal association with soil iron phases. Two major soil groups, such as Luvisols and non-Luvisols could be established based on trace metal content, distribution and fractionation in the studied soils. Such differences were found to be primarily due to the differences in the pedogenic processes in the studied soils, whereas soil parent material has not affected these characteristics significantly. We found that Fe phases affect trace metal fractionation and mobilization as their host in form of both inherited and pedogenic phases. However, pedogenic processes, primarily iron and organic matter accumulation in our case, generally overwrite the effect of inherited iron phases on trace metal accumulation, distribution and fractionation. The closest relation between the fractionation of Fe and trace metals were found for Co based on sequential extractions. This metal showed strong association with iron in almost each studied fractions, primarily due to their similar geochemical behavior. Interestingly, this phenomenon was not found for the other studied siderophile element, Ni. The relatively low affinity of this metal for organic, oxide and clay surfaces may be the major reason for that when compared to Co. Ni was only found to bound

to Fe in the residual fraction, e.g. in phases formed in non-soil environment rather inherited from the soil parent material. Contrarily, Cr was also found to be of almost similarly close association with Fe as Co has. This can be explained again with the similar geochemical behavior of Cr and Fe, which play an important role both in soil mineral formation and sorption processes. The relation of Cu and Zn fractionation to that of Fe showed very similar characteristics. These two metals could be characterized by close relation to Fe in residual and oxidizable fractions suggesting their joint presence in the resistant phases and soil organic matter. The least similarity to Fe fractionation was found for Pb. This metal could be associated to iron only occasionally in the studied fractions.
More details of these results can be found in the paper:
Sipos P, Choi C, Németh T, Szalai Z, Póka T (2014b): Relationship between iron and trace metal fractionation in soils. Chemical Speciation and Bioavailability. 26: 21-30. http://real.mtak.hu/15853/

3.2. Genesis of Fe-precipitations in an alluvial soil

During this project, the alluvial soil profile from Ipolyszög was re-sampled for further analyses as various forms of ferromanganese nodules appeared in this profile as was found in one of our earlier project. Our aim was to relate their micro-fabric to the distribution of their major chemical components, and to explain it in the function of the different stages of nodule development using micro-chemical analyses. The results showed (Sipos et al. 2016) that typic and concentric nodules in the soil exhibited both similar (presence of outer coating band) and different (undifferentiated and banded interiors, respectively) characteristics in their micro-fabric. These were related to the rate of hydromorphism in the soil which was found to determinate the major processes (accretion vs. impregnation) forming the fabric of the nodules. The following stages of the nodule development were distinguished: (1) cementation, (2) formation of outer band, (3) re-arrangement and slow impregnation of nodules' interior, and (4) fast impregnation of the interior and exfoliation of outer band. We found that separation of Fe and Mn is characteristic of each stage of nodule formation. However, as long as spatial segregation occurs in the first stages, displacement of Mn by Fe is rather typical later. We found that fabric and appearance of nodules form by varying rate and dominance of accretion and impregnation relatively slowly. However, distribution pattern of Fe and Mn within the nodules may exhibit much faster changes simultaneously. Complex micro-chemical analyses support a powerful tool to follow such changes and to get a deeper insight into the genesis of ferromanganese nodules.
More details of this study can be found in the paper:
Sipos P, Balázs R, Bozsó G, Németh T (2016) Changes in micro-fabric and re-distribution of Fe and Mn with nodule formation in a floodplain soil. Journal of Soils and Sediments 16: 2105-2117. http://real.mtak.hu/44705/

Summary

1. Differences among the metals' affinity towards the bulk soils and the effect of competition on these affinities were demonstrated. Results of the bulk sorption experiments showed that associations of clay minerals and Fe-oxyhydroxides may play a significant role in the sorption of metals exhibiting higher mobility (e.g. posing higher risk to the environment).
2. We found that it is difficult to find clear relationship between the sorption properties of metals and soil physicochemical characteristics due to the heterogeneity of soils. Decrease of the effect of one single factor (clay mineralogy in our case) could not be enough to get a much deeper insight into soil-metal interaction generally, but it may contribute to the better understanding of the sorption characteristics of certain phases in soils.
3. The effect of pH on the metal sorption in soils was verified. We found that metals with different affinities exhibit adsorption edges at different pH ranges, and they also show variation with the soil conditions. These results showed good agreement with that of the bulk sorption experiments.

4. Our data showed that the Langmuir-Freundlich equation is the most useful one to describe metal sorption characteristics in soils. Its advantages are that metals sorption mostly exhibits both Langmuir and Freundlich characteristics in soils, and this equation provides more parameters relating to sorption capacity and affinity of the sorbent. The most convenient error functions were found to be the coefficient of determination and the sum of the absolute errors.
5. Combination of bulk and direct mineralogical methods were found to be an effective tool to identify the mineralogical changes in soils due to metal sorption. Certain processes were observed with varying sensitivity using the three different methods, and the resulted data are complementary and can be inserted into the sorption models. Besides the identification of metal precipitates (like cerussite, malachite and Cu-oxyhydroxide) in the alkaline soils, ion exchange processes on smectites were also observed both in the acidic soils (for Pb and Cu) and in the alkaline ones (for each metals).
6. Extraction of Fe-oxyhydroxides from the soil resulted in significant changes in the metal sorption characteristics. As it was expected, decrease in metal sorption could be related to the lower number of sorption sites after the extraction. However, evidence was also found that extraction may enhance metal sorption due the removal of Fe-oxyhydroxide coatings from clay particles (as it was the case for Pb in the alkaline soil). Among the studied metals, Pb exhibited the highest efficiency to compete for the surface sites of clay particles. Our results demonstrated that care must be taken when such results are evaluated as extraction may results significant changes in soil mineralogy.
7. The higher sorption of the studied metals in the alkaline than in the acidic soil could be mostly observed also on the soil particles directly, except that Cd and Zn showed higher sorption on the particles with clay component in the acidic soil. The higher sorption of Cu and Pb than that of Cd and Zn was also observed on the particles with the exception of Zn that showed the highest sorption on clay particles in the acidic soil among the studied metals. The inhibitory effect of competition on metal sorption was also shown at particle level.
8. Strong selectivity was observed with respect to both metals and mineral surfaces in the function of sorption conditions and soil mineralogy at particle level. Fe-oxyhydroxides sorbed higher metal amounts than clay mineral particles mostly, and the sorption capacity of the latter phases were more affected by competition. Their associations played significant role at certain cases.
9. Relationship was found between the Fe concentration and the sorbed metal amounts of the studied particles. It could be related to the increasing proportion of Fe-oxyhydroxides within the particle associations in the alkaline soil, and to the increasing Fe concentration of clay mineral particles in the acidic one. Iron plays a decisive role in the metal sorption capacity of soil mineral particles either through the structural component of clay minerals or through Fe-oxyhydroxide and clay mineral particle associations depending on the soil pH conditions.
10. Extraction of Fe-oxyhydroxides resulted in increase of metal sorption on the smectit particles at acidic soil conditions. The high efficiency of Pb for competition was demonstrated also with direct observations. In alkaline soils, only Pb showed increased sorption on smectite particles after the extraction. This supported our observations that Fe-oxyhydroxide coating on smectite particles play the primary role in metal sorption at alkaline soil conditions. If Fe-oxyhydroxes are removed from the alkaline soils, most of the metals are immobilized by non-mineral surfaces and/or by precipitation.
11. Combination of bulk adsorption experiments with direct analytical methods to study sorption capacity of the soil components may help not only the better understanding of the role of soil mineral components in metal sorption but it may provide indirect information on the role of non-mineral surfaces and additional immobilization processes in this process.

Future plans

Our results clearly demonstrated that the use of direct analytical methods, like TEM-EDS provide novel information on the interaction of soil minerals and metals. Although producing of sufficient amount of reliable data is highly time-consuming with this method, the following research activities are planned to finish, to continue or to start after the closing of the project:

- finishing the TEM analyses of samples from the pH-stat experiments to study the effect of pH directly on metal sorption onto soil mineral particles,
- finishing the TEM analyses of samples after CDB extraction to study the effect of Fe-oxyhydroxide removal on metal sorption onto soil mineral particles,
- continuing the study of the effect of Fe-oxyhydroxide extraction on the mineralogy of soils to support data evaluation,
- starting the TEM study of the effect of initial metal concentration on the metal sorption onto soil mineral particle types, and
- starting to collect literature data to review the results on the direct study of the role of soil mineral components in metal sorption.