

## ADSORPTION OF COPPER ON THE ILLUVIATION AND ACCUMULATION HORIZONS OF A LUVISOL

Tibor NÉMETH<sup>1</sup>, Péter SIPOS<sup>1</sup>, Réka BALÁZS<sup>2</sup>, Zoltán SZALAI<sup>3</sup>, Erzsébet MÉSZÁROS<sup>3</sup>  
& Mária DI GLÉRIA<sup>3</sup>

<sup>1</sup>*Institute for Geochemical Research, Hungarian Academy of Sciences, Budaörsi út 45, 1112 Budapest, Hungary  
e-mail: ntibi@geochem.hu*

<sup>2</sup>*Eötvös Loránd University, Pázmány Péter sétány 2/a, 1117 Budapest, Hungary*

<sup>3</sup>*Geographical Research Institute, Hungarian Academy of Sciences, Budaörsi út 45, 1112 Budapest, Hungary*

**Abstract:** Copper adsorption capacity of the illuviation (E) and accumulation (B) horizons of a Luvisol profile was studied in high ionic strength NaCl solution and at pH 4-5. The maximum copper adsorption calculated by Langmuir equation was 0.052 mol/kg Cu (3 304 mg/kg Cu) for the E horizon, and 0.071 mol/kg (4 512 mg/kg) Cu for the B horizon. The differences arise from the different mineral composition of the distinct horizons. Hydrous iron oxides and swelling chlorite/vermiculite in the accumulation layer increase Cu adsorption capacity, while hydroxy-interlayering in vermiculite, and absence of iron oxides decrease Cu uptake of the eluviated horizon. Based on XRD studies, measurable fraction of Cu was sorbed in the interlayer space of vermiculite by ion exchange mechanism. This adsorbed Cu caused the loss of expansion capacity of the vermiculite.

**Keywords:** copper adsorption, illuviation, accumulation, vermiculite, brown forest soil

### 1. INTRODUCTION

The nutrient supply of the pedosphere affect plant growth, but the essential macro- and micro elements have to be in available form. Nevertheless, the essential elements may be present in toxic concentration for the organisms due to anthropogenic activities. Therefore, investigation of natural distribution and immobilization forms, processes of nutrient metals (Cu, Zn, Fe) in soil is an important issue from environmental point of view.

Copper is one of those elements which are essential in small amount for vital functions, but toxic in high concentrations. The metal accumulation in soils may involve various mechanisms, such as chemisorption, ion exchange, or surface precipitation. Copper can be bound in calcareous soils by precipitation of metal carbonates (Sipos et al., 2008). Swelling clay minerals are excellent metal sorbents due to their high specific surface area and cation exchange capacity. Iron minerals in soils and hydrous iron oxide coatings on mineral surfaces play important role in copper adsorption (Komárek et al., 2008).

Different soil types and different horizons within a soil profile have different ability to immobilize heavy metal contaminations due to their mineral, physical and chemical features. Soils characterized by high amount of organic matter, swelling clay mineral accumulation horizon and calcareous subsoil were found suitable medium to immobilize metal pollution (Sipos et al., 2005).

Several authors have investigated the heavy metal distribution and immobilization in disturbed topsoil layers (Arias et al., 2006), in different horizons of agricultural soils (Vega et al., 2010), in urban soils of polluted areas (Damian et al., 2008) and in unpolluted forest soil profiles (Sipos et al., 2009; Németh et al., 2008).

In this study copper immobilization ability in high ionic strength NaCl solution and at acidic pH is examined by comparing the sorption properties of two distinct soil horizons within one profile. The adsorption experiments were carried out on the well distinguishable illuviation and accumulation horizons of a brown forest soil, one of the dominating soil types in Hungary.

## 2. METHODS AND EXPERIMENTS

The clay fraction ( $<2\ \mu\text{m}$ ) of soil samples was separated by sedimentation. X-ray diffraction (XRD) measurements were carried out using a Philips PW 1710 diffractometer with  $\text{CuK}\alpha$  radiation at 45 kV and 35 mA. The semi-quantitative mineral composition of the bulk soil was determined on random-powdered samples. Clay minerals corresponding to each horizon were identified by XRD diagrams obtained from parallel-oriented specimens sedimented on glass slide. The following diagnostic treatments were carried out for all of the samples: ethylene glycol solvation at  $60^\circ\text{C}$  overnight, Mg-saturation followed by glycerol solvation at  $95^\circ\text{C}$  overnight, K saturation, and heating at 350 and  $550^\circ\text{C}$  for 2 hours. The Cu-adsorbed samples (200 and 1000 mg/l Cu) was washed three times in distilled water and the clay fraction was also separated. Then the specimens sedimented on glass slides were air-dried and stored under conditions of controlled humidity ( $\text{RH} = 25\text{--}30\%$ ) in a desiccator before XRD analysis.

Organic matter and total bound nitrogen was determined by Tekmar Dohrmann Apollo 9000N NDIR and chemiluminescent spectrometer.

The adsorption experiment was performed by mixing 400 mg of soil sample from the E and B1 horizons with 40 ml of Cu-sulfate solution containing various concentrations of copper. The initial metal concentrations were set to 20, 40, 50, 80, 100, 150, 200, 500, 1000 and 1500 mg/l. The ionic strength was controlled by 0.1 M NaCl. The initial pH of the solutions was set to 4.5–5.0 by adding some drops of dilute  $\text{H}_2\text{SO}_4$  to retain the measured potential acidity of the soil samples. Two replicates of 200 and 1000 mg/l Cu experiments were performed. The relative error of the determination of the copper adsorption is 5%. The samples were shaken for 48 hours at room temperature and then centrifuged at 3000 rpm. The equilibrium concentrations of Cu in the supernatant solutions were measured by atomic absorption spectrometry (AAS) (Perkin Elmer AAnalyst 300). The amounts of adsorbed metals were calculated from the difference between concentration of the initial and equilibrium solutions.

## 3. DESCRIPTION OF THE PROFILE

The studied forest soil profile is situated in the Karancs Mountains (Inner Western Carpathian volcanic range) in the north part of Hungary at 430 m. The area has a temperate subcontinental climate, with a mean annual temperature of  $8.9^\circ\text{C}$ , a mean

annual precipitation of 650 mm. The profile developed on slope topography in a Quercus petraea-Carpinetum forest on Oligocene carbonaceous siltstone bedrock, dominated by chloritic clay mineralogy (*Szécsényi Schlier Formation*).

The whole profile is quite shallow due to the steep topography. The thin organic material rich A level is followed by the 20 cm thick, pale colored illuvation horizon (E), and the accumulation horizon, which can be divided into two parts: a 20 cm thick reddish B1 and a thin gray B2. The main physical, mineral and chemical features of the genetic soil horizons are summarized in Table 1.

The E horizon is remarkably leached of clay minerals, Fe and Al. Consequently, B horizon is enriched in these minerals and elements. The C horizon and the siltstone parent rock contain high amount of calcite. Above the C horizon calcite is absent, and the potential acidity increases significantly. The sum of quartz and feldspars, as residual, inert, inherited minerals decreases downward. Clay mineral content reaches its maximum in the B2 horizon, but the parent rock itself is also rich in primer phyllosilicates, such as micas and chlorite.

## 4. RESULTS

### 4.1 Clay mineralogy

Figures 1A and B show the X-ray diffractograms after the different diagnostic treatments of the clay fractions from the E and B horizon, respectively. The dominant peaks at 14, 10 and  $7\ \text{\AA}$  refer to vermiculite and/or chlorite, illite, and chlorite, respectively. The greatest peak at  $14.3\ \text{\AA}$  shifted to  $15.3\ \text{\AA}$  upon ethylene-glycol solvation in the B horizon, while there is no significant expansion in the E horizon. For Mg-saturated and glycerol solvated samples, the basal peak remained in all cases at  $14.5\ \text{\AA}$ , indicating the vermiculitic character of the swelling clay mineral. The peak appearing after heating at  $550^\circ\text{C}$  near  $12\ \text{\AA}$  may indicate 1) mixed layer chlorite-vermiculite and/or 2) hydroxy-interlayered vermiculite. It is noteworthy, that no structural collapse has been occurred due to K saturation, suggesting also OH-interlayering in both E and B1 horizons. The  $10\ \text{\AA}$  reflection belongs to a minor amount of illite in the two samples. Based on the XRD features above, the clay mineral characteristics of B1 and E horizons differ from each other: B1 contains partly swelling vermiculitic clay, most probably mixed layer chlorite-vermiculite, which mineral has been found in a similar and close soil profile in the Cserhát

Table 1. Main physical, chemical and mineral properties of the soil profile

	Depth (cm)	Colour	Moisture (%)	pH (H <sub>2</sub> O)	pH KCl	OM (%)	TN <sub>B</sub> (mg/kg)	CaCO <sub>3</sub> (%)	Fe <sub>2</sub> O <sub>3</sub> (%)	Al <sub>2</sub> O <sub>3</sub> (%)	CM (%)	Qtz + Fs
A	0-5	10YR; 3/3	2.48	7.31	4.72	8.26	2167	0	3.78	11.32	13	87
E	5-25	10YR; 5/4	1.27	7.30	4.51	1.03	517	0	3.66	10.95	16	84
B1	25-45	7.5YR; 4/6	2.10	7.11	4.23	0.52	390	0	5.29	15.61	21	79
B2	45-50	10YR; 4/3	2.13	7.24	4.69	0.40	386	0	5.92	12.82	28	72
C	50-	2.5Y; 4/2	0.88	7.83	7.33	0.29	364	18.8	3.74	9.64	27	58
pr		2.5Y; 3/2	0.78	7.91	7.40	0.26	430	14.5	3.87	11.25	26	55

OM: organic matter, TN<sub>B</sub>: total bound nitrogen, CM: clay minerals, Qtz+Fs: quartz and feldspars, pr: parent rock

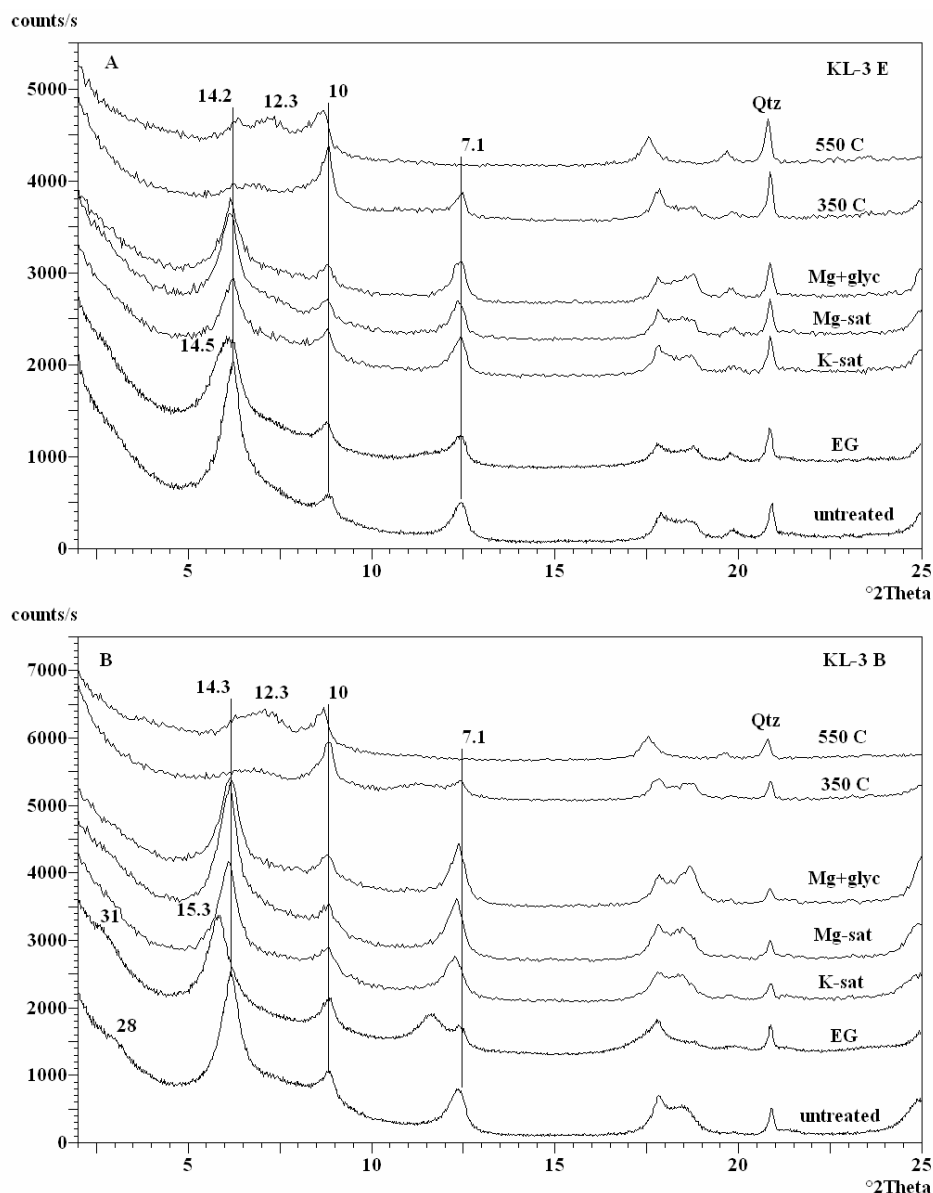


Figure 1. X-ray diffractograms of the clay fraction of E (A) and B1 horizons (B) after the diagnostic treatments. EG: ethylene-glycol solvated; K-, Mg-sat: K-, Mg-saturated; Mg+glyc: Mg-saturated and glycerol solvated.

Mountains (Németh & Sipos, 2006); and E contains non-swelling, but partly heat instable chloritic clay minerals, which can be a hydroxy-interlayered vermiculite. The relevant difference

between the active and potential acidity may arise from this interlayer Al.

A very diffuse reflection at 28 Å, which shifted to 31 Å upon glycolation suggests the

presence of small amount of regularly interstratified chlorite/vermiculite (corrensite). This peak characteristic of corrensite occurs only in the B horizon within the profile, indicating its pedogenic origin. To the authors' knowledge, this could be the first occurrence of corrensite in Hungarian soils. Few occurrence of pedogenic corrensite interpreted as the weathering product of chlorite was found in podzolic, acidic forest soils (Bain and Griffen, 2002).

## 4.2 Copper adsorption

The copper adsorption isotherms for the E and B horizons are plotted in Figure 2. Langmuir equation fitted satisfactorily ( $R^2 = 0.991$  and  $0.982$ ) to both adsorption isotherms. The maximum copper adsorption calculated based on the linearized Langmuir equation is  $0.052 \text{ mol/kg}$  ( $3\,304 \text{ mg/kg Cu}$ ) and  $0.071 \text{ mol/kg}$  ( $4\,512 \text{ mg/kg Cu}$ ) on the bulk soil in the E and B1 horizons, respectively. The shape of the adsorption curves is L-type for both samples, as they have convex shape and their slopes remain constant. This suggests high affinity for copper and progressive saturation of the soil. The curve reaches strict plateau, which means that complete saturation is achieved. The isotherm shapes also suggest the higher affinity of Cu to the sample of B horizon, since higher Cu sorption was found at lower concentrations and the plateau can be found at higher adsorbed Cu concentrations. The

Langmuir bonding term related to the adsorption energy  $K_L$  is  $0.54 \text{ L/}\mu\text{mol}$  for the E, and  $K_L$  is  $3.83 \text{ L/}\mu\text{mol}$  for the B1 horizon. The equilibrium pH of the adsorption processes varies from 4.4 to 4.10 for the E horizon, and from 5.0 to 4.1 for the B1 horizon with the increase of the initial copper concentration. Figure 3A and 3B show the X-ray diffractograms of the separated clay fraction of the soil samples adsorbed by 200 and 1000 mg/l Cu-solutions compared to the original non-adsorbed soil, and their ethylene-glycol solvated forms. The intensity ratio of the 14 and 7 Å reflections decreases markedly from 4.4 (E) and from 2.8 (B1) to 1.5 (in both samples) during the Cu adsorption. A well defined shoulder and then a peak remained at 14.2 (E horizon) and 14.4 Å (B1 horizon) besides the 14.5 (E) and 15.2 Å (B1) reflections after the ethylene-glycol solvation in the case of the Cu adsorbed samples. This loss of expansion capacity is more conspicuously reflected in the intensity decrease of the second order reflection at 7.6 Å for the Cu adsorbed ethylene-glycol solvated samples.

## 5. DISCUSSIONS

The illuviation (E) and accumulation (B1) horizons of the studied soil profile differ from each other in their mineral composition and clay mineral characteristics. The clay mineral content of B1 horizon is 30% higher than that of E horizon.

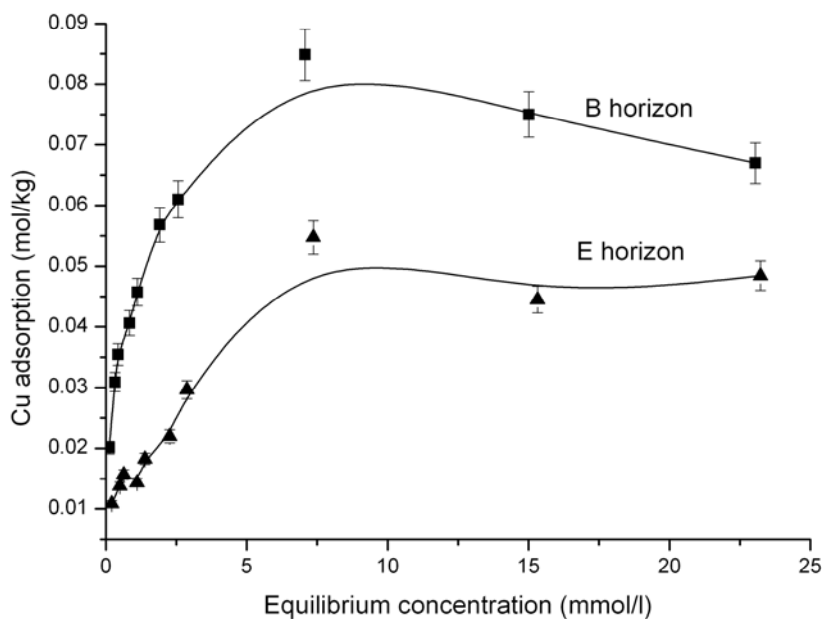


Figure 2. Copper adsorption isotherms for the E and B1 horizons of the soil profile

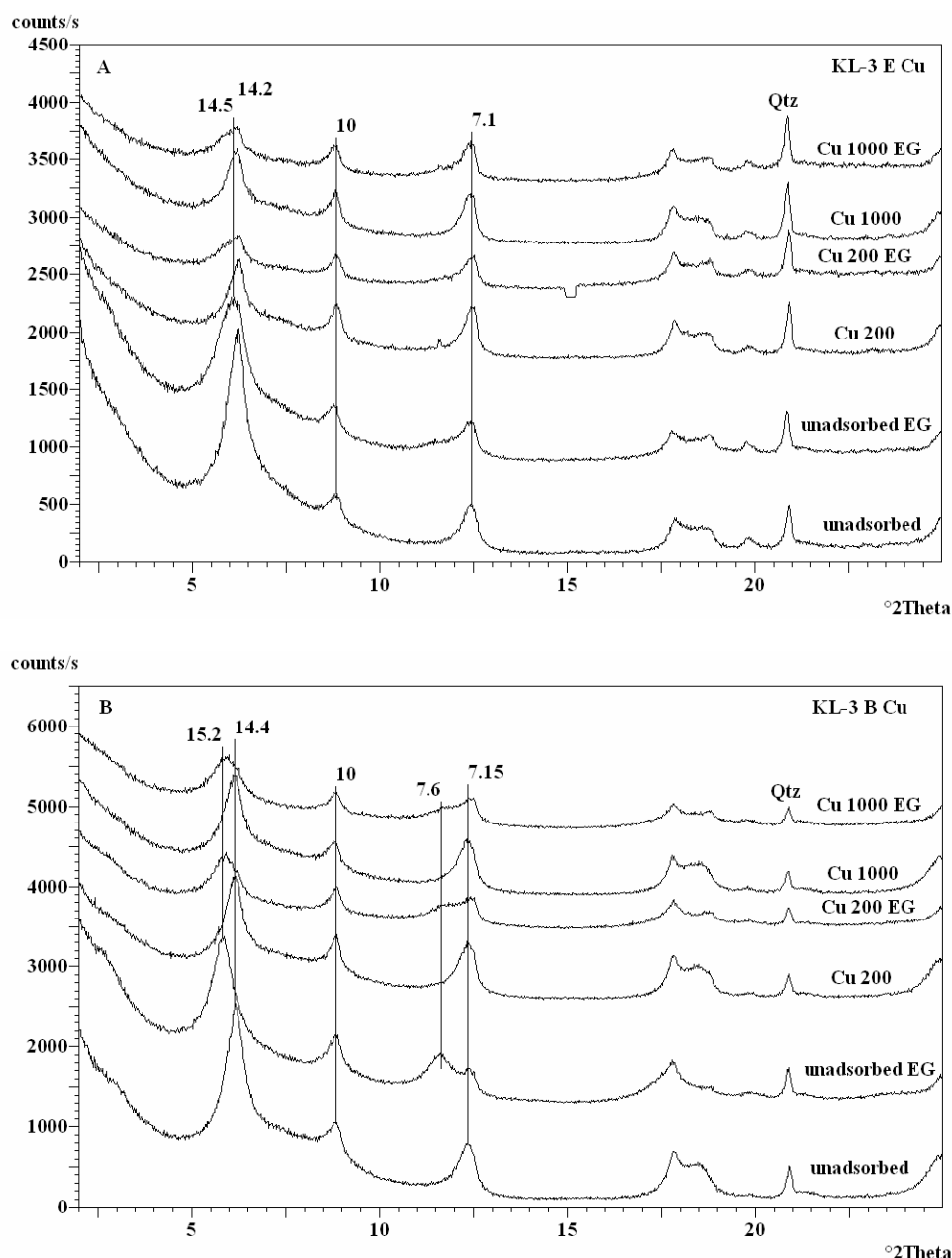


Figure 3. XRD patterns of the initial and copper adsorbed clay fractions of E (A) and B1 (B) horizons

According to the XRD studies two major clay mineral phases were distinguishable in the samples: a swelling interstratified chlorite/vermiculite in the B1 horizon, and a non-swelling, probably hydroxy-interlayered vermiculite in the E horizon. It is well known that Al-hydroxy-interlayering affects the physico-chemical properties of expandable clays, reduce the cation exchange capacity, the specific surface area and the swelling ability, consequently the metal adsorption capacity (Keren, 1986).

The remarkable (more than 40% as compared to E horizon) accumulation of iron in B1 horizon and its reddish colour denotes the formation of amorphous hydrous iron oxide in the B1 horizon. This iron phase, which is mostly present as fine

coatings on the soil constituents, takes part in the mineral surface processes and generally enhances the heavy metal adsorption. Although at the experimental acidic circumstances (pH 4–5) iron oxides are dominantly positively charged, considerable proportion (20-50%) of copper can be adsorbed on iron oxides (Jönsson et al., 2006). Hydrous iron oxide was found more efficient sorbent for Cu than clay minerals in acid mine drainage water (Andráš, 2009). These differences in the mineral composition explain why B1 horizon adsorbs by one thirds more copper than E horizon.

However, the copper uptakes – even in B1 horizon – are less than that of smectitic soil clay studied in the same area (Németh et al., 2006).

These adsorption capacities are also 15% less than that found for a Luvisol B horizon with similar chlorite/vermiculite clay mineralogy, but in that case no other cation beside  $\text{Cu}^{2+}$  was present in the adsorptive solution (Sipos et al., 2009). Accordingly,  $\text{Na}^+$  competes with  $\text{Cu}^{2+}$  for the outer-sphere adsorption sites accessible by ion exchange mechanism, i.e. interlayer space of vermiculite, mostly at low initial Cu concentrations. Nevertheless, when high amount of Cu was added, it can be adsorbed by ion exchange on vermiculite. Changes of XRD patterns of Cu adsorbed clay fractions indicate evidently that Cu adsorption – at least partly – took place in the interlayer space of vermiculite component in chlorite/vermiculite.

## 6. CONCLUSIONS

Our study of Cu adsorption on the illuviation and accumulation horizon of a brown forest soil confirmed that the different genetic layers in a soil profile can play different role in the immobilization of heavy metal contaminations. The differences arise from the various mineral composition of the distinct horizons. Hydrous iron oxides and swelling clay minerals in the accumulation layer increase Cu adsorption capacity, while their leaching from the illuviation horizon decrease the ability to immobilize Cu by the way of sorption.

However, one can put the question: whether the various metal ion adsorption abilities may arise merely from textural differences, i.e. more fine sized constituents, more adsorption? To answer – and expectedly to confute – this, similar adsorption studies on the clay fractions are planned in the future.

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