

CHEMOSTRATIGRAPHIC CORRELATION OF SEDIMENTS CONTAINING EXPANDABLE CLAY MINERALS BASED ON ION EXCHANGE WITH Cu(II) TRIETHYLENETETRAMINE

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Abstract—Copper(II) triethylenetetramine [Cu(trien)]²⁺ is an agent suitable for the 1-step determination of the cation exchange capacity (CEC) of many geomaterials using a procedure much less laborious than other, commonly used methods. It is also suitable for the determination of the composition of original exchangeable cations. In contrast to other common ions used for CEC analysis, the Cu(II) complex with triethylenetetramine, [Cu(trien)]²⁺, is specific for expandable clay minerals. The robustness of [Cu(trien)]²⁺ analysis was verified using reference clays, ion-exchanged reference clays, sediments, and soils. The [Cu(trien)]²⁺-based CEC of expandable clay minerals is not influenced significantly by ferrihydrite, goethite, manganite, birnessite, calcite, and gypsum. Birnessite, calcite, and gypsum admixtures affect the composition of the evolved cations. [Cu(trien)]²⁺ does not recover the entire CEC of soils (but rather that of the clay minerals only) which contain components other than clays which contribute to the CEC, e.g. soil organic matter. In a series of loess with buried paleosols and recent soils the [Cu(trien)]²⁺-based CEC ranged from 30 to 110% of total CEC obtained by traditional BaCl₂ methods. The relative ratio of Ca to Mg, the prevailing exchangeable cations in soils and sediments in exogenic environments, are similar after [Cu(trien)]²⁺ and conventional BaCl₂ treatments. The Ca/Mg ratio in the exchangeable fraction was used successfully for chemostratigraphic correlation of paleolacustrine sediments from a large lake in the Upper Carboniferous basins of eastern equatorial Pangaea and a series of recent flood plain sediments of the meandering Morava River in the Czech Republic. The Ca/Mg ratio obtained by [Cu(trien)]²⁺ analysis is proposed as a novel tool for the chemostratigraphic correlation of sediment series containing expandable clay minerals.

Key Words—Chemostratigraphy, Expandable Clay Minerals, Flood Sediments, Lacustrine Sediments, Smectite.

INTRODUCTION

The total CEC of geomaterials is evaluated using numerous procedures. The CEC can be obtained by saturating the material to be analyzed with excess ions, e.g. NH₄⁺ (referred to as the index cation), that are subsequently replaced by further cations, e.g. Na⁺ from NaOH (Borden and Giese, 2001), K⁺ (e.g. Beldin *et al.*, 2007), or Mg²⁺ (e.g. Dohrmann, 2006a). In other methods, CEC is considered to be equal to the sum of alkaline and alkaline earth metal cations, Al³⁺, and H⁺ evolved by interaction with an excess of suitable cations, such as Ba²⁺ (Hendershot and Duquette, 1986) or K⁺ (e.g. Turpault *et al.*, 1996). A method based on X-ray fluorescence elemental analysis of Ba-exchanged clay specimens for the CEC determination was also tested (Battaglia *et al.*, 2006). In clay mineral analysis, complex cations are

currently preferred, such as a Ag-thiourea complex (Dohrmann, 2006b, 2006c) and a [Cu(trien)]²⁺ complex (Bergaya and Vayer, 1997; Ammann *et al.*, 2005; Czimerová *et al.*, 2006); one of the series of Cu-polyen (polyen refers to: ethylenediamine, triethylenetetramine, or tetraethylenepentamine complexes easily intercalated into expandable clay minerals (ECMs) (Schoonheydt *et al.*, 1979; Bergaya and Vayer, 1997; Meier and Kahr, 1999). [Cu(trien)]²⁺ is the abbreviated term for the Cu complex with triethylenetetramine [Cu(NH₂(CH₂CH₂NH)₂CH₂CH₂NH₃)]²⁺. The introduction of the [Cu(trien)]²⁺ technique was part of a systematic effort to simplify CEC analysis with respect to older, more traditional procedures. The improvements are intended to allow quick, routine work with large series of samples (Meier and Kahr, 1999; Borden and Giese, 2001; Battaglia *et al.*, 2006).

In soils, several different components contribute to the CEC *via* different mechanisms: highly stable cation exchangers, such as ECMs; less stable, but nonetheless important, soil organic compounds; to a lesser extent also, charged surface defects of all minerals; charged

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hydrated surfaces of all particles at potentials above their point of zero charge; and, in some procedures, minerals dissolving in the extracting solution. In soils, the prevalence of the contribution of one of the two major CEC components, *i.e.* soil organic matter and clay minerals, depends on their relative concentrations (Turpault *et al.*, 1996; Beldin *et al.*, 2007). Soil organic matter has a specific CEC which is about an order of magnitude larger than that of clay minerals (Beldin *et al.*, 2007), but is usually present in much smaller concentrations than clays. Recently, [Cu(trien)]²⁺ was used to estimate the CEC of soils (Hernández-Soriano *et al.*, 2007; Haslinger *et al.*, 2007; Stanjek and Marchel, 2008) irrespective of the fact that the methodology has not been developed for soils but for ECM specimens, and its interaction with non-ECM components of the cation-exchange complex of soils has not been studied.

Cu[trien]²⁺, a stable, planar, chelate complex, is intercalated into ECMs in a very specific manner, combining the electrostatic interaction of the central ion and van der Waals interactions of the ligand with ECM structural layers. The ternary complex of [Cu(trien)]²⁺ and ECMs has been studied extensively and its nature is well established (*e.g.* Choy *et al.*, 1997). The [Cu(trien)]²⁺ method has been validated for CEC analysis of ECM samples (Bergaya and Vayer, 1997; Ammann *et al.*, 2005; Czímerová *et al.*, 2006) used in the analysis of bentonites (Ammann *et al.*, 2005), sediments (Grygar *et al.*, 2005, 2007; Lojka *et al.*, in prep.), and soils (Hernández-Soriano *et al.*, 2007; Kadlec *et al.*, in prep.). One of the most remarkable features of Cu-polyen analysis is its simplicity and speed, making it very suitable for routine analyses of large series of samples (Meier and Kahr, 1999). An additional advantage of the [Cu(trien)]²⁺ method is that a single solution, where both Cu consumed for ion exchange and cations evolved, can be analyzed (Bergaya and Vayer, 1997). No side redox reactions of this complex with sediments or soils have been reported. Additional information obtained in some procedures by CEC analysis is the composition of the ion-exchangeable or water-soluble cations. Recently, we have successfully used the Ca/Mg ratio obtained by [Cu(trien)]²⁺ analysis for chemostratigraphic correlation of sediments containing ECMs (Kadlec *et al.*, in prep.; Lojka *et al.*, in prep.). In soils it is a possible tracer of soil parent material and pedogenesis (Saif *et al.*, 1997; Shaw *et al.*, 2001). In geochemistry, the Ca to Mg ratio in autochthonous carbonates is used to evaluate lacustrine and continental sediments because they mirror the Ca to Mg ratio in the parent paleoenvironment (Kelts and Talbot, 1990; Crausbay *et al.*, 2006) and can serve as a tool for distinguishing lacustrine-deltaic facies (Dill *et al.*, 2005). While carbonates are common in many lacustrine and marine sediments, ECMs are practically omnipresent in sediments and soils and they can also record the Ca and Mg relative activity in the parent environment. The ECMs are more stable over larger timescales than other

components of soil or sediment CEC, such as organic matter. A very specific method with [Cu(trien)]²⁺ could hence be a useful tool for the analysis and chemostratigraphic of almost all sediments.

The aims of this research were to test the [Cu(trien)]²⁺ ion-exchange reaction for the chemostratigraphic correlation of sedimentary series via variations of CEC and the ratio of ion-exchangeable metal cations. First, the robustness of that reaction was tested with pure ECMs, then with ECMs mixed with the mineral admixtures most likely to interfere with the CEC estimate, and then with sediments and soils. The correctness of the method for pure ECMs has already been verified (Bergaya and Vayer, 1997; Ammann *et al.*, 2005; Czímerová *et al.*, 2006) so the present study focused only on minimizing factors that could cause irreproducibility or mass-dependence of the laboratory results. The [Cu(trien)]²⁺ analysis of recent soils and paleosols were compared with the results of the standard BaCl₂ method for CEC analysis in soil science (Hendershot and Duquette, 1986; ICP Forest, 2006). The [Cu(trien)]²⁺ analysis is proposed as a novel tool for chemostratigraphic correlation using examples of two recently solved problems (Kadlec *et al.*, in prep.; Lojka *et al.*, in prep.).

MATERIALS AND METHODS

Expandable clay minerals and soil samples

Montmorillonite samples SAz-1, SWy-2, and STx-1, and interstratified illite-smectite sample ISCz-1 were obtained from the Source Clays Repository (of The Clay Minerals Society, Chantilly, VA, USA); the mineral purity of the specimens was described by Chipera and Bish (2001). All clay minerals were used in their equilibrium hydration state at 50% relative humidity. Two reference soil materials were used, acid soils NCS DC85105 and NCS DC85106 with certified values of CEC and evolved cations obtained by the ammonium acetate method (China National Analysis Centre for Iron and Steel, Beijing, China, 2004).

Buried paleosol and loess samples were obtained in Litovel, Czech Republic, 234 km southeast of Prague, from a 7.4 m long section of loess, paleosols, and pedosediments deposited between the Holstein interglacial and the present (Žigová and Št'astný, 2006). Non-buried paleosols, *terra fuscae*, formed by means of clay illuviation, were obtained at Doutnác (denoted D#) and Újezdce (denoted Ú#) in Bohemian Karst, Czech Republic, 35 km southwest of Prague. These soils were developed on limestone. The CaCO₃ contents of *terra fuscae*, paleosol, and loess samples were determined by a volumetric method (ISO 10693); the CEC and evolved Ca²⁺ and Mg²⁺ were determined by BaCl₂ solution buffered to pH 8.1 (ISO 13536). The analyses were performed at the Research Institute for Soil and Water Conservation, Prague, Czech Republic.

Recent soils denoted 1.2 and 1.6 are from West Bohemia, Czech Republic: the parent material was gneiss and the soil, developed in a spruce forest, was classified as Dystric Cambisol. Soils 7.2 and 7.6 are from West Bohemia: the parent material was leucogranite, and the soil, developed in a spruce forest, was classified as Dystric Cambisol. Soils 1.1 and 2.5 are from the Bohemian Karst, Czech Republic: the parent material was limestone, and soil was developed in an oak-hornbeam forest. The samples denoted ORG were from an organic horizon (0–20 cm, non-decomposed litter was removed) and MIN were from mineral horizons (55–60 cm) (Hofmeister, 2002). These samples were subjected to several methods of CEC analysis (Nekutová, 2005). The CEC and expandable cations were measured using the BaCl_2 exchange methods adapted from Hendershot and Duquette (1986), namely in the modification recommended for analysis of forest soils (ICP Forest, 2006).

Sediment profiles to Ca/Mg chemostratigraphic correlation

Paleolacustrine sediments were obtained in two drill cores from Mšec Horizon, lacustrine sediments of Stephanian B age (~301 My BP) (Holub *et al.*, 1975; Skoček, 1994; Pešek *et al.*, 2001; Lojka *et al.*, in prep.). The cores covered the entire Mšec Horizon, fine clayey to silty sediments of a large paleolake that existed for $\sim 10^4$ y (Skoček, 1994). The 42 m long core, Tr-1, was obtained close to Slaný (~30 km northwest of Prague) in former deep-water facies; and the 63 m long core, DV-1, was obtained close to Plzeň (~80 km southwest of Prague), in a near-shore lake part closer to river deltas. The Mšec horizon is traceable over the area of ~ 5000 km² in several basins in west, central, and northeast Bohemia, Czech Republic (Holub *et al.*, 1975; Skoček, 1994; Pešek *et al.*, 2001). The sediments originated in surrounding mountains and hills continuously denuded by intensive tropical chemical weathering. The Mšec lake sediments contain mainly kaolinite, quartz, minor expandable clay minerals, and autochthonous carbonates, mainly siderites and less calcite (Skoček, 1994; Lojka *et al.*, in prep.). The carbonates in Tr-1 and DV-1 were identified by powder X-ray diffraction (XRD) (D5005, Bruker, Germany), and their contents and elemental compositions were determined by 5 min extraction of samples powdered to analytical fineness (<0.05 mm) with boiling in 6 M HCl and analysis of the filtrates by atomic absorption (AAS) (Mg, Fe) and emission spectroscopy (AES) (Ca) (AAS 3, Zeiss, Germany).

Recent flood-plain sediments of the Morava River were obtained from Strážnické Pomoraví, South Moravia, Czech Republic (Vrbová-Dvorská *et al.*, 2005; Kadlec *et al.*, in prep.). Up to 5 m thick sediment series were deposited in the flood-plain in the study area. The sediments from the sections studied contained

varying proportions of clay, silt, and very fine sand as is usual for muddy flood sediments (loam) of such rivers (Bridge, 2003). The sediments at some depths were preserved as buried soils such as Gleysols and Fluvisols (Havlíček and Smolíková, 1994). The samples were taken from the erosional river banks after removing ~ 0.5 m of material. The samples were air dried under ambient laboratory conditions and ground to analytical fineness (<0.05 mm). The sections were dated by ¹⁴C according to the procedure of benzene synthesis (Gupta and Polach, 1985). The benzene obtained was measured using a Quantulus 1220, low-background liquid scintillation counter. The resulting conventional radiocarbon age and its uncertainty were converted to an interval of calibrated age utilizing IntCal04 (Reimer *et al.*, 2004).

[Cu(trien)]²⁺ analysis and testing its robustness

The $[\text{Cu}(\text{trien})]^{2+}$ solution was obtained by mixing an aqueous solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (Penta, Czech Republic) with an aqueous solution of triethylenetetraamine (1,4,7,10-tetraazadecane, Sigma-Aldrich), to a final concentration of 0.01 M. The reproducibility of the ratio of ligand to metal in $[\text{Cu}(\text{trien})]^{2+}$ solution was confirmed by potentiometric measurement during addition of the trien to Cu^{2+} solution with the use of Cu-metal and saturated calomel reference electrodes. Ligand was added to the CuSO_4 solution when the potential of the Cu working electrode reached -100 mV relative to the SCE. The following procedure for $[\text{Cu}(\text{trien})]^{2+}$ ion exchange was used in this work as well as in our previous studies (Grygar *et al.*, 2005, 2007). A dry powder of analytical fineness (<0.05 mm) placed in a 50 mL beaker, wetted, and suspended in 5 mL of distilled water by stirring. Then 5 mL of 0.01 M $[\text{Cu}(\text{trien})]^{2+}$ solution was added. The sample was stirred for 5 min using a magnetic stirrer and the suspension was filtered into a 50 mL flask. The resulting filter cake containing all of the solids was then filter washed several times with distilled water. The total volume of the filtrate was adjusted to 50 mL. The 'calibration' and blank solutions were prepared from 2, 3, and 5 mL of $[\text{Cu}(\text{trien})]^{2+}$ solution added to 50 mL flasks and the volume adjusted to 50 mL. The 'calibration' solutions served to adjust the sample weight as described below. The solutions were analyzed by AAS (Cu and Mg) and AES (Ca and Na and possible further cations that could be evolved into the solution on exchange of $[\text{Cu}(\text{trien})]^{2+}$). The sample weight was re-adjusted depending on its actual CEC; usually 30–70 mg of pure montmorillonite, ~ 100 –150 mg of soils or sediments with medium and up to 500 mg of soils and sediments with low CEC were used; the details of which are given below. The results of the analyses were expressed either in mmol(+)/g or mmol(+)/100 g, *i.e.* in units equivalent to conventional meq/g and meq/100 g, respectively.

The influence of selected mineral phases suspected to interfere with the $[\text{Cu}(\text{trien})]^{2+}$ ion exchange and which

are common in many sediments and soils was examined. Ferrihydrite (2-line) was prepared by fast hydrolysis of a Fe(NO₃)₃·9H₂O solution by NaOH solution up to an OH:Fe ratio of 3:1. Goethite was obtained by precipitation from Fe(NO₃)₃·9H₂O by addition of NaOH and aging the suspension at 60°C for 70 h following the procedure given by Schwertmann and Cornell (2000). Birnessite (K_xMnO₂) was synthesized by mixing 50 mL of 1.4 M glucose solution (Czech Pharmacopoeia, purity of 4) and 50 mL of solution with 3 g of KMnO₄ (Lachema, Czech Republic), heating the gel at 130°C on a hot plate, decanting, heating again for 2 h at 400°C, and washing out the excess K⁺ ions using water, according to procedure described by Ching *et al.* (1997). Manganite (MnOOH) was formed by neutralization of 3000 mL of a 0.06 M solution of MnSO₄·5H₂O with 900 mL of a 0.2 M NH₃ solution followed by addition of 61.2 mL of 30% H₂O₂, according to Giovanoli and Leuenberger (1969). The identity of all synthetic solids was determined by powder XRD (Siemens D5005, Bruker).

The exchange of Ca and Mg in the reference clay minerals was performed in order to examine the possible influence of a type of expandable clay mineral on the Ca/Mg ratio. The exchange was performed by stirring the suspension for several hours with 0.5–20 mM Ca²⁺ and Mg²⁺ in varying proportions of CaSO₄·2H₂O, MgSO₄·7H₂O, Ca(NO₃)₂·4H₂O, or Mg(NO₃)₂·6H₂O (analytical grade, Penta, Czech Republic). Residual Ca²⁺ and Mg²⁺ in filtrates were analyzed by flame AAS (Mg) or AES (AAS 3, Zeiss Germany).

RESULTS AND DISCUSSION

Critical parameters of [Cu(trien)]²⁺ analysis of expandable clay minerals

The stability of the results under varying experimental conditions and sample matrix effects (robustness) is the most important feature of any analytical method.

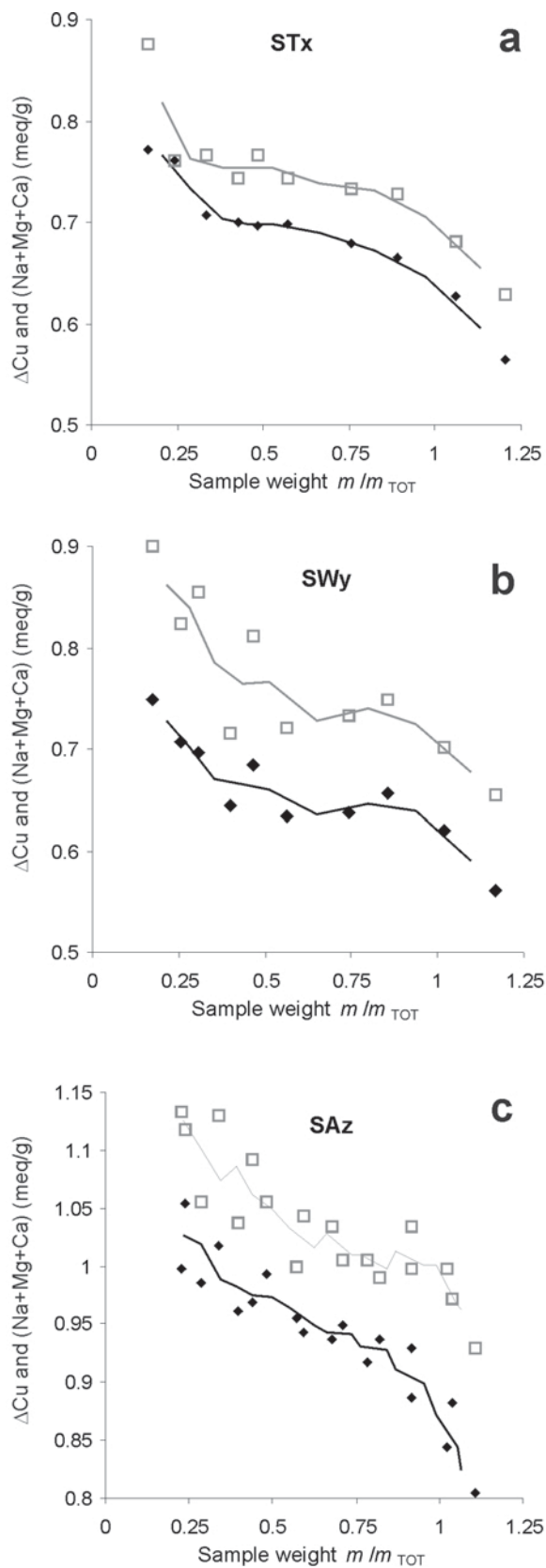
The influences of varying experimental conditions in the analysis of montmorillonite specimens SAz-1, STx-1, and SWy-2 are summarized in Table 1 and shown in Figures 1 and 2. The values obtained are smaller than 120, 84.4, and 76.4 meq/100 g, respectively, reported by Van Olphen and Fripiat (1979), but the specimens were not pre-treated with respect to size fractionation and admixture removal, nor were the results corrected for water content in the present study.

The most important variable which requires careful control in routine laboratory analysis is the sample weight (Figure 1). The sample should consume about half of the [Cu(trien)]²⁺ used for ion exchange in order to obtain results which are least dependent on sample weight. The sample weight can be roughly re-adjusted even without instrumental analysis of Cu in solution after the exchange by visual comparison with Cu 'calibration' solutions. The shade of the resulting solution should be between that of a 'calibration' solution and a solution with 2–3 mL of Cu[trien]²⁺, if 5 mL of [Cu(trien)]²⁺ solution is used in the cation exchange. As is obvious from Figure 1, the resulting CEC values depend only slightly on sample mass if the [Cu(trien)]²⁺ consumption to ion exchange is ~40–70%. This conclusion is close to the original conclusion by Bergaya and Vayer (1997) that 50–100% of the Cu-bis(ethylene diamine) complex guarantees quantitative replacement of the original interlayer ions. The adjustment of the sample weight according to its actual CEC was also recommended by Bergaya and Vayer (1997), Ammann *et al.* (2005), and Haslinger *et al.* (2007).

Another important variable in [Cu(trien)]²⁺ ion exchange is the stoichiometry of the [Cu(trien)]²⁺ solution (Figure 2). Non-stoichiometry could affect the actual speciation of Cu²⁺ and the pH of the solution, both of which could subsequently affect the ion exchange. Ferric oxides are known to adsorb Cu²⁺ cations in aqueous solution so sufficient ligand concentration is desired for real samples where ferric oxides are

Table 1. Parameters affecting the results obtained using the proposed procedure for [Cu(trien)]²⁺ exchange. The term "significant" means significant at >95% probability level, "observable" means poorly reproducible but definite variations (significant at 90% probability level), and "insignificant" means variation due to changing parameters which are less than the usual variation of repeated results under constant conditions.

Variable	Variation in ΔCu and cation release	How to minimize the effect
[Cu(trien)] ²⁺ solution stoichiometry	Observable decrease of ΔCu and evolved Mg ²⁺ , observable variations in Ca/Mg ratio	Potentiometric control of ligand-to-metal ratio (Cu working electrode)
Mass of sample	Significant	Sample weight is re-adjusted depending on its actual CEC. Least variation on sample weight close to 50% [Cu(trien)] ²⁺ consumption to exchange.
Stirring time (5–25 min)	Insignificant	
Water addition to suspend sample (0–15 mL)	Insignificant	



abundant, because they would adsorb free (uncomplexed) Cu^{2+} cations. The present results indicate that actual $[\text{Cu}(\text{trien})]^{2+}$ consumption and concentration of evolved ions depends on the actual stoichiometry of the $[\text{Cu}(\text{trien})]^{2+}$ solution (Figure 2), although the dependences were close to statistical significance (Table 1). Therefore the actual Cu/trien ratio in the $[\text{Cu}(\text{trien})]^{2+}$ solution should be controlled carefully, *e.g.* by potentiometric monitoring. This seems to be the easiest way to handle varying content of water of crystallization in Cu sulfates and moisture in trien. A titration curve of CuSO_4 solution by ligand solution is shown in Figure 3, where the actual ligand-to-metal ratio recommended in this work is indicated; the potential of a working Cu electrode of -100 mV relative to the SCE was reached at $\sim 1.4\%$ overstoichiometry of ligand. A slight excess of ligand was also recommended by Bergaya and Vayer (1997).

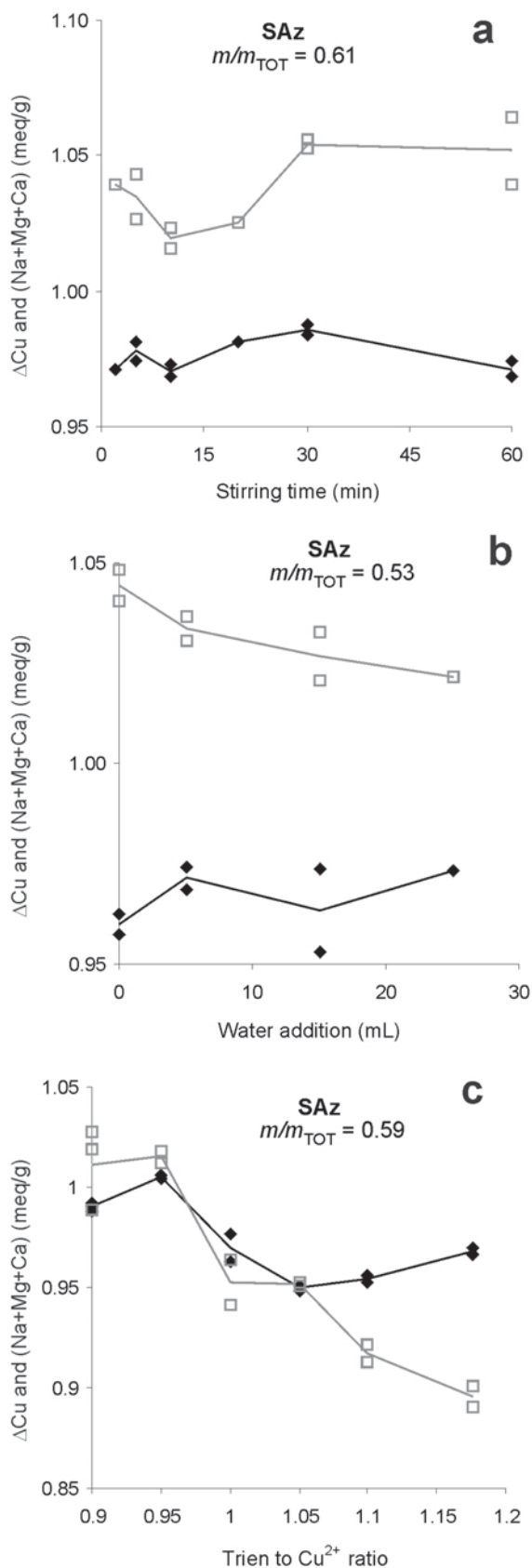
Changes of stirring time and water addition within the ranges specified in Table 1 do not have a statistically significant influence. In previous reports on Cu-polyen complexes, stirring times of 3 min (Meier and Kahr, 1999), 5 min (Czímerová *et al.*, 2006), or 30 min (Bergaya and Vayer, 1997; Amman *et al.* 2005) were recommended, and the actual concentration of the Cu-polyen complex, which corresponds to water addition in the procedure proposed in this work, was equally liberal.

The influence of selected mineral phases on the $[\text{Cu}(\text{trien})]^{2+}$ ion exchange is summarized in Table 2. The pure Fe and Mn oxides tested adsorbed statistically insignificant amounts of $[\text{Cu}(\text{trien})]^{2+}$. If the amount present in the mixture with smectite SAz-1 or SWy-2 was $<30\%$, they did not systematically affect the consumption of $[\text{Cu}(\text{trien})]^{2+}$. The most relevant effect of these admixtures was re-sorption of Ca cations evolved from montmorillonite by birnessite that is known to be a cation exchanger for alkaline and alkaline earth metal cations.

CEC of soils: difference between $[\text{Cu}(\text{trien})]^{2+}$ and conventional analyses

The paleosol/loess profile from Litovel included autochthonous and reworked loess intercalated with soils and pedosediments (Žigová and Št'astný, 2006). The materials contain only a few % of the sand fraction. The clay fraction consists mostly of quartz, illite, smectite, and kaolinite, and the soils and loess in the upper part of the profile contained X-ray amorphous CaCO_3 and calcite (Žigová and Št'astný, 2006). The

Figure 1. Dependence of ΔCu , $[\text{Cu}(\text{trien})]^{2+}$ consumed ($-\blacklozenge-$) and sum of cations evolved ($-\square-$) on the sample weight for three montmorillonite reference specimens. The weights are expressed as m/m_{TOT} , where m is the sample weight and m_{TOT} is the hypothetical sample weight corresponding to the total consumption of $[\text{Cu}(\text{trien})]^{2+}$. The lines (running averages) were plotted for clarity.



mean [Cu(trien)]²⁺ consumption of the samples was ~67% of the total CEC values obtained by the conventional BaCl₂ method (Table 3). The amounts of exchangeable Mg²⁺ determined by the two methods was very similar (Figure 4a). Also, the Ca/Mg ratios in exchangeable fractions, determined by these methods was correlated (Figure 4b). A substantial part of the Ca²⁺ evolved during the ion-exchange reactions originated from dissolution of Ca minerals. This is obvious from the fact that CaCO₃ produced excess evolved cations as shown in Figure 4c.

Twenty samples of recent soils, non-buried paleosols, and reference soil samples were also tested to compare the results of [Cu(trien)]²⁺ and BaCl₂ ion exchange (Table 4). Because the samples were obtained from various localities, they produced more scattered ratios of [Cu(trien)]²⁺ consumption and conventional total CEC by BaCl₂, the latter having been in the range 30–110% with respect to total CEC (Table 4). This scatter is consistent with the naturally varying, relative contribution of ECMs to the total CEC of soils. The use of [Cu(trien)]²⁺ in the CEC determination of soils (Hernández-Soriano *et al.*, 2007; Haslinger *et al.*, 2007; Stanjek and Marchel, 2008) can hence give misleading outputs, because the [Cu(trien)]²⁺ method produces estimates of the ECM contribution to the total CEC rather than total CEC as it is defined in soil science. The description of the [Cu(trien)]²⁺ consumption as CEC in the case of soils should hence be avoided or it should only be given with a description of the method used.

Two main reasons why [Cu(trien)]²⁺ recovers 30–110% of the total CEC of soils are: the lower specificity of [Cu(trien)]²⁺ to non-clay components of the cation exchange complex and the single-step extraction. The majority of other ion-exchange procedures involves two or three successive steps with fresh portions of ion-exchange solution, be it the KCl (*e.g.* Turpault *et al.*, 1996), BaCl₂ (*e.g.* Ciesielski and Sterckeman, 1997; ICP Forest, 2006), or ammonium acetate method (*e.g.* Ciesielski and Sterckeman, 1997).

Stoichiometry of ion exchange

One of the benefits of using a one-step cation-exchange reaction is that the amount of the [Cu(trien)]²⁺ consumed by the interaction can easily be compared to the cations evolved into solution. The stoichiometry of the ion exchange can be evaluated by the difference $\Delta Cu - \Sigma M^{n+}$, where ΔCu is the [Cu(trien)]²⁺ consumption and ΣM^{n+} is the sum of evolved cations; in the case of the reference expandable clay minerals, ΣM^{n+} was the

Figure 2. Influence of stirring time (a), water addition in extraction (b), and stoichiometry of extracting solution (c) on the results of [Cu(trien)]²⁺ ion exchange in SAZ-1 montmorillonite. The lines (running averages) were plotted for clarity.

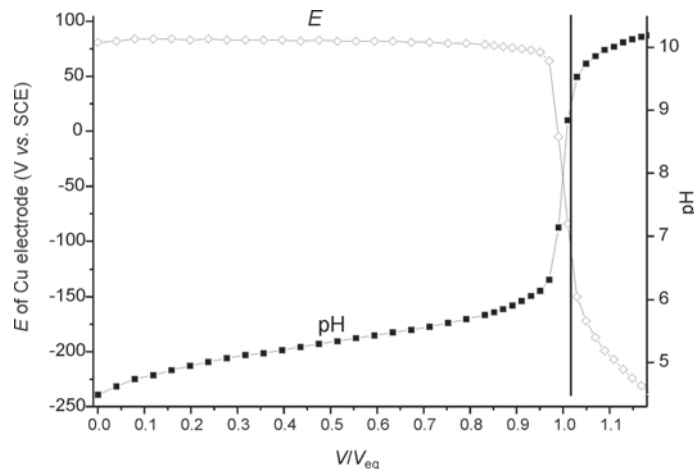


Figure 3. Potential of Cu-electrode and pH change during titration of 100 mL of 0.01 M CuSO_4 solution by 0.2 M trien solution. V/V_{eq} is the added volume of ligand normalized to the volume at the equivalence point. The solid vertical line denotes the solution recommended in this work (1.4% excess of ligand, $E_{\text{Cu}} = -100$ mV vs. SCE).

sum of Ca, Mg, and Na. Calcite and gypsum are known to be extracted partly and completely, respectively, during the determination of CEC (Dohrmann, 2006a). Calcite and gypsum, either pure or mixed with smectites, did not consume a statistically significant amount of $[\text{Cu}(\text{trien})]^{2+}$ (Table 2). Calcite causes an overstoichiometry of Ca^{2+} evolution, as is also demonstrated by the comparison of $[\text{Cu}(\text{trien})]^{2+}$ analysis and CaCO_3 content in the paleosol sequence from Litovel section (Figure 4c).

In repeated experiments performed with reference clay mineral specimens, departures from stoichiometry were observed, namely a certain deficiency of ΔCu , *i.e.* $\Delta\text{Cu} - \Sigma M^{n+} < 0$, even in the absence of calcite admixtures. The experimentally obtained ratio of $(\Delta\text{Cu} - \Sigma M^{n+})/\Delta\text{Cu}$ varied between -7 and -15% in the case of SWy-2 and between $+3$ and -7% in the case of SAz-1 under the optimal experimental conditions of the proposed procedure. Chipera and Bish (2001) gave gypsum among the trace admixtures of SWy-2 and no soluble Ca-admixtures in SAz-1 thus explaining the larger non-stoichiometry of the ion exchange of the former specimen. Approximately 1% of gypsum in SWy-2 'as shipped' should produce $\sim 15\%$ excess of

Ca^{2+} over the $[\text{Cu}(\text{trien})]^{2+}$ consumption. The residual variability of the $(\Delta\text{Cu} - \Sigma M^{n+})/\Delta\text{Cu}$ values, almost 10% in terms of non-stoichiometry, may be attributed to unidentified variations of experimental conditions and the common inaccuracy of chemical analyses. Czimerová *et al.* (2006) found no systematic non-stoichiometry of $[\text{Cu}(\text{trien})]^{2+}$ ion exchange in a set of ten specimens, but observed that some of the reference ECMs (including SWy-1) produced inter-laboratory variations of CEC on the order of 8–15%. This result shows the limits of accuracy expected in practical analyses.

Ammann *et al.* (2005) listed many reasons why the cation exchange could not be exactly stoichiometric. Among them, two specific reasons for overstoichiometry of the evolved cations over consumed $[\text{Cu}(\text{trien})]^{2+}$ were: (1) possible $M^{\text{II}}(\text{OH})^{1+}$ ionic pairs instead of M^{2+} in the interlayer of the original ECM; and (2) partial $[\text{Cu}(\text{trien})]^{2+}$ complex replacement by H^+ during washing the $[\text{Cu}(\text{trien})]^{2+}$ -exchanged ECM with water. In the present procedure, washing with distilled water is used, which can contribute to partial desorption of some $[\text{Cu}(\text{trien})]^{2+}$ into solution. On the other hand, in the previous systematic analysis of Lake Baikal sediments,

Table 2. The effect of common admixtures to montmorillonite SAz-1 on the ΔCu and evolved cations recalculated to pure SAz-1 weight. The maximum weight of tested admixtures was 30% in mixtures with the montmorillonite.

Admixture	Variation in ΔCu	Variation in cation release (Ca^{2+} , Mg^{2+})
CaCO_3	Insignificant	Excess Ca^{2+} due to partial calcite dissolution
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (gypsum)	Insignificant	Excess Ca^{2+} due to complete gypsum dissolution
Ferrihydrite	Insignificant	
Goethite	Insignificant	
Birnessite	Insignificant	Resorption of Mg^{2+}
Manganite	Insignificant	

Table 3. Comparison of the ion-exchange analysis of buried loess/paleosol samples from Litovel, Czech Republic, performed by the Cu(trien)²⁺ and BaCl₂ methods. The percentage of ΔCu by the former method with respect to conventional CEC is given in the last column.

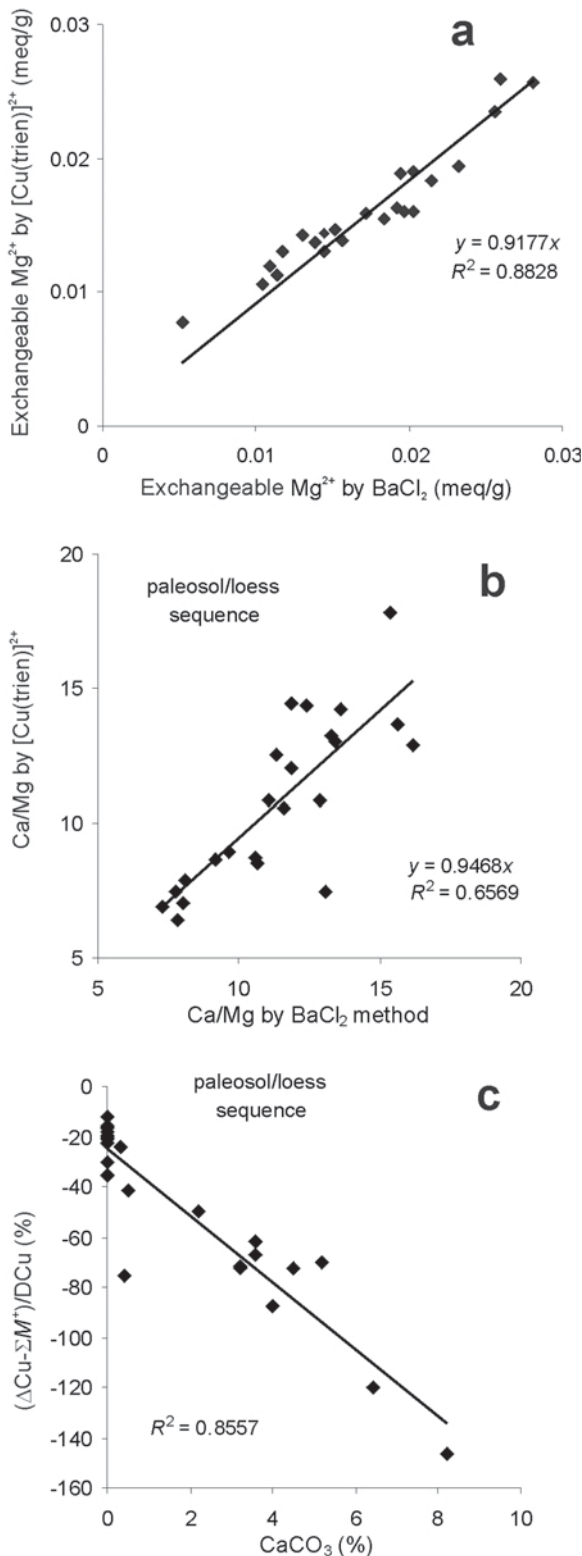
Depth (cm)	Cu(trien) ²⁺ method (mmol+/g)			— BaCl ₂ method (mmol+/g) —			ΔCu/CEC (%)
	ΔCu	Ca ²⁺	Mg ²⁺	CEC	Ca ²⁺	Mg ²⁺	
0–43	0.115	0.187	0.0144	0.190	0.195	0.0145	61
43–75	0.102	0.163	0.0120	0.141	0.171	0.0109	72
75–303	0.085	0.195	0.0137	0.136	0.189	0.0139	63
303–309	0.119	0.177	0.0163	0.261	0.248	0.0192	46
309–326	0.107	0.168	0.0130	0.182	0.189	0.0117	59
326–361	0.090	0.188	0.0105	0.141	0.160	0.0104	64
361–384	0.121	0.167	0.0139	0.178	0.185	0.0156	68
384–392	0.107	0.187	0.0130	0.152	0.172	0.0145	70
392–412	0.130	0.158	0.0155	0.200	0.204	0.0184	65
412–439	0.143	0.229	0.0160	0.224	0.252	0.0203	64
439–464	0.129	0.200	0.0160	0.195	0.223	0.0197	66
464–469	0.122	0.195	0.0147	0.174	0.202	0.0152	70
469–477	0.181	0.206	0.0195	0.278	0.269	0.0232	65
477–500	0.148	0.158	0.0183	0.214	0.197	0.0215	69
500–529	0.152	0.166	0.0189	0.212	0.206	0.0195	72
529–547	0.145	0.170	0.0190	0.214	0.195	0.0203	68
547–557	0.100	0.121	0.0142	0.156	0.140	0.0131	64
557–585	0.056	0.058	0.0078	0.080	0.068	0.0052	70
585–602	0.115	0.125	0.0159	0.163	0.140	0.0172	71
602–638	0.171	0.174	0.0235	0.236	0.199	0.0256	72
638–641	0.185	0.182	0.0259	0.245	0.208	0.026	76
661–695	0.174	0.177	0.0257	0.239	0.204	0.0281	73
695–740	0.069	0.072	0.0112	0.095	0.089	0.0114	73

Table 4. Parameters obtained by ion exchange using [Cu(trien)]²⁺ and BaCl₂ methods. The results are expressed as mmol(+)/100 g except for the relative ratio of ΔCu by [Cu(trien)]²⁺ and CEC by BaCl₂, in the last column.

Sample	Description	[Cu(trien)] ²⁺ method			— BaCl ₂ method —			ΔCu/CEC (%)
		ΔCu	Ca	Mg	CEC	Ca	Mg	
1.2	ORG, recent soils	8.52	1.36	0.73	8.87	2.63	0.78	96
1.6	MIN, recent soils	1.01	0.24	0.32	3.28	0.58	0.06	31
7.2	ORG, recent soils	9.33	0.79	0.54	9.65	1.95	0.62	97
7.6	MIN, recent soils	2.31	0.25	0.22	4.39	0.68	0.07	53
1.1	ORG, non-buried paleosol	27.9	31.9	2.41	86.2	80.5	4.01	32
1.1	MIN, non-buried paleosol	24.3	25.4	1.39	45.4	43.2	1.51	54
2.5	ORG, non-buried paleosol	29.1	32.3	3.18	75.8	69.1	4.19	38
2.5	MIN, non-buried paleosol	24.9	27.3	1.81	50.4	47.3	1.84	49
NCS DC85105	reference material	4.51	3.57	1.13	7.02	4.75	1.1	64
NCS DC85106	reference material	2.06	1.76	0.24	3.69	2.47	0.23	56
D 0–3 cm	Ah	10.0	10.2	1.11	26.3	20.4	1.57	38
D 3–17 cm	AhEv	7.79	7.63	0.72	26.1	11.2	1.03	30
D 17–40 cm	Ev	5.98	3.48	0.38	14.5	3.39	0.26	42
D 40–62 cm	Brt ₁	15.0	14.6	1.03	25.3	16.2	1.11	59
D 62–82 cm	Brt ₂	24.1	25.1	1.44	21.6	25.0	0.84	111
D 82–115 cm	Brt ₂ Crk	18.9	28.3	0.72	17.3	23.2	0.46	110
Ú 0–5	Ah	19.2	20.4	1.54	60.1	53.5	2.55	32
Ú 5–15 cm	Ev	14.8	14.4	0.89	29.8	16.4	0.93	50
Ú 15–39 cm	Brt	19.8	21.4	0.69	33.2	30.9	0.88	60
U 39–59 cm	BrtCrk	16.1	22.2	0.43	26.3	28	0.61	61

ORG: organic horizon; MIN: mineral horizon; A, B, E, C soil horizons (surface, subsurface, elluvial, and substrate, respectively); v, r, t, and k more detailed specifications of horizons (cambic, rubified, luvic, calcic); Ah: surface mineral horizon with humified organic matter.

the cation non-stoichiometry was much less under the same procedure: the mean $(\Delta\text{Cu}-\Sigma M^{n+})/\Delta\text{Cu}$ of 166 analyses reported by Grygar *et al.* (2005) was -0.5%



and the mean $(\Delta\text{Cu}-\Sigma M^{n+})/\Delta\text{Cu}$ of a further 332 analyses reported by Grygar *et al.* (2007) was -3.4% . This smaller non-stoichiometry was obtained with apparently more complex, polymineral mixtures if compared to the reference mineral SAz-1. Worth mentioning, however, is that the Baikal sediments were deposited from fresh water and their sedimentation was very slow, so the clay minerals in the sediments have been perfectly equilibrated with water. This comparison of the ion exchange stoichiometry of individual types of samples indicates that the actual results should be evaluated individually. For example, in real samples of the Litovel paleosol/loess section (Figure 4c), the non-stoichiometries of CaCO_3 -free samples (-20%) are larger in absolute terms than could be expected from the experimental accuracy, and the further growth of the excess $\text{Ca}+\text{Mg}$ is unequivocally attributable to the soluble Ca compounds. The non-stoichiometry of the ion exchange can serve as another proxy of chemical variations in the sediment series analyzed by $[\text{Cu}(\text{trien})]^{2+}$.

Ca/Mg ratio in exchangeable ions: measurement and interpretation

The most common exchangeable cations in soils and sediments evolved to neutral solutions are Ca^{2+} and Mg^{2+} . In the present study, a series of experiments with equilibration of ECM species using solutions with varying Ca^{2+} and Mg^{2+} ratios was performed to check whether individual ECMs have similar affinities for these cations. The results, shown in Figure 5, do not depend on the nature of anions in the mother solution, either SO_4^{2-} or NO_3^- . The record of Ca/Mg ratio from the solution to the expandable clay minerals is non-linear, with the preference for Ca most pronounced at low Ca/Mg ratios and less at greater Ca/Mg ratios in solution. The larger affinity of Ca^{2+} than Mg^{2+} for smectites was also found by Wada and Seki (1994), Rytwo *et al.* (1996), and Curtin *et al.* (1998). The actual behavior of two smectites and one illite-smectite interstratified mineral with different charge densities are similar in this respect and hence the actual Ca/Mg ratio should not depend on the actual 'recording' mineral. In the simplest case, *i.e.* when ECMs were exposed to a solution with a certain defined Ca/Mg ratio, they should be able to record this ratio in an unequivocal manner. This phenomenon could allow reconstruction of changes in Ca^{2+} and Mg^{2+} ratios in lake water from pelagic sediments even in weakly mineralized lake water.

Figure 4. Comparison of several parameters of cation exchange in paleosol/loess sequence obtained by the $[\text{Cu}(\text{trien})]^{2+}$ and BaCl_2 methods and by chemical analysis of carbonates. (a) Exchangeable Mg^{2+} by the $[\text{Cu}(\text{trien})]^{2+}$ method plotted vs. Mg^{2+} obtained by the BaCl_2 method. (b) Ca/Mg ratios in exchangeable fractions obtained by $[\text{Cu}(\text{trien})]^{2+}$ plotted vs. the BaCl_2 method. (c) Non-stoichiometry of ion exchange by $[\text{Cu}(\text{trien})]^{2+}$ plotted vs. CaCO_3 content obtained by chemical analysis.

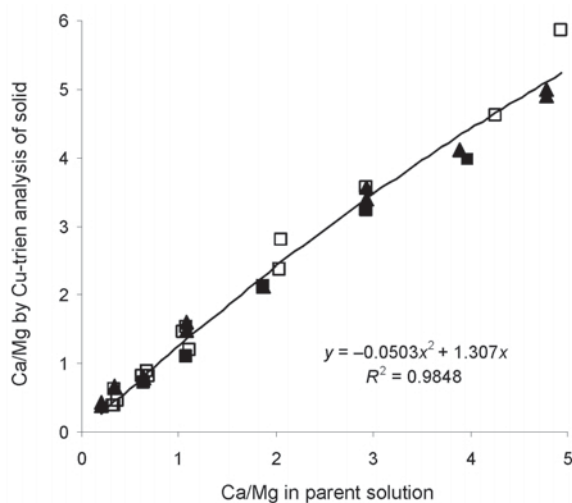


Figure 5. Ca/Mg molar ratios in expandable clay minerals after equilibration with solutions with varying Ca/Mg ratio. Points: smectites (□ SAz-1, ▲ SWy-2) and illite-smectite (■ ISCz-1); line: 2nd order polynomial regression of all points.

However, because of the low affinity of ECMs for Na (Wada and Seki, 1994; Rytwo *et al.*, 1996) little possibility exists for reconstructing a complete paleosalinity from exchangeable cations in expandable clay minerals.

Before stating that the Ca/Mg ratio in exchangeable cations can be used for any kind of sediment or soil analysis, evaluation of its variability is necessary if various ion-exchange procedures are used. The Ca/Mg ratio in the exchangeable fractions in soils obtained by [Cu(trien)]²⁺ follows the same trends as the Ca/Mg ratio obtained by BaCl₂ methods but the slope of the regression was only 0.95 in the Litovel paleosol/loess sequence (Figure 4) and 0.82 in the set of recent soils (Figure 6). The soil organic matter has a larger preference for Ca²⁺ than Mg²⁺, which selectivity is also greater than clay minerals (Curtin *et al.*, 1998; Jiang *et al.*, 2005), so a complete ion exchange of soils containing organic matter should produce a larger Ca/Mg ratio than the soil clay minerals. Additionally, the actual Ca/Mg values of soils depend on the sample weight-to-volume ratio during the extraction, probably due to the dissolution of CaCO₃ admixture. The larger the volume-to-mass ratio during the ion exchange, the larger the relative dissolution of calcite and consequently the larger the Ca/Mg ratio to be expected. If the Ca/Mg ratio in the exchangeable fraction is to be evaluated in sediments or soils, the volume-to-mass ratio should not be varied and the same ion-exchange technique must be used for the entire section.

Another point that must be taken into account in the analysis of the Ca/Mg ratio in exchangeable cations is the pH dependence of calcite solubility that is known to substantially affect the Ca²⁺ mobilization (larger in acid solution of unbuffered ammonium acetate) (Ciesielski

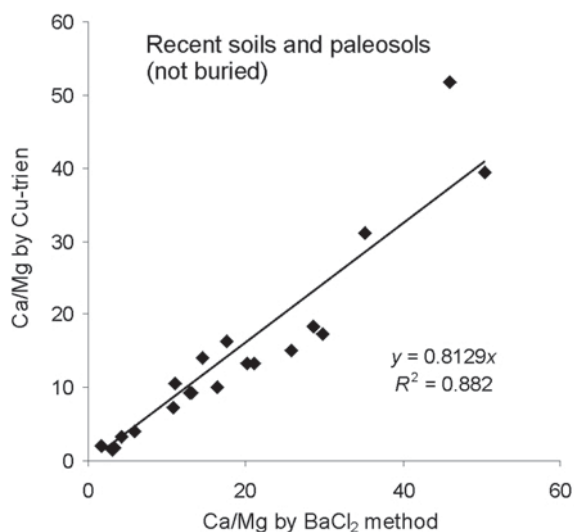


Figure 6. Ca/Mg ratio in exchangeable fractions obtained by [Cu(trien)]²⁺ and BaCl₂ methods. The figure includes the soils listed in Table 4.

and Sterckeman, 1997). The pH change close to the point of exact stoichiometry during addition of trien to Cu²⁺ solution (Figure 3) is one more reason to control carefully the exact stoichiometry of [Cu(trien)]²⁺ solution in an analysis of a series of samples.

Ca/Mg chemostratigraphic correlation of Mšec Lake sediments

Mšec Lake was studied using a set of experimental techniques to reconstruct the lake and watershed environment from drill core Tr-1 (Lojka *et al.*, in prep.). A second core, DV-1, was retrieved to confirm the general conclusions. Correlating results from two sediment cores, obtained from sites 71 km apart, using a simple lithologic correlation is difficult because the Tr-1 site represents off-shore (pelagic) lacustrine facies and DV-1 represents facies closer to river deltas. The different environments were chosen intentionally. The facies boundaries in the two cores were not identical to the isochrones of their deposition. Lithologic correlation would only be accessible by sequence stratigraphy based on extensive geophysical measurements or by coring between the two sites. The correlation of the two cores was instead performed using the Ca/Mg ratio in the ion-exchangeable clay minerals combined with chemical identification of autochthonous lacustrine carbonates. The analysis of exchangeable cations by [Cu(trien)]²⁺ revealed a smooth, wavelike change in Ca/Mg ratio within both cores (Figure 7). The change was not clearly related to sediment lithology, but a certain link between Ca/Mg values in exchangeable cations and autochthonous carbonates was observed (Table 5). Siderite containing ~20 mol.% Mg and ~7 mol.% Ca was almost omnipresent in the lake sediments except for the upper part of the DV-1 core, while low-Mg calcite was much less common

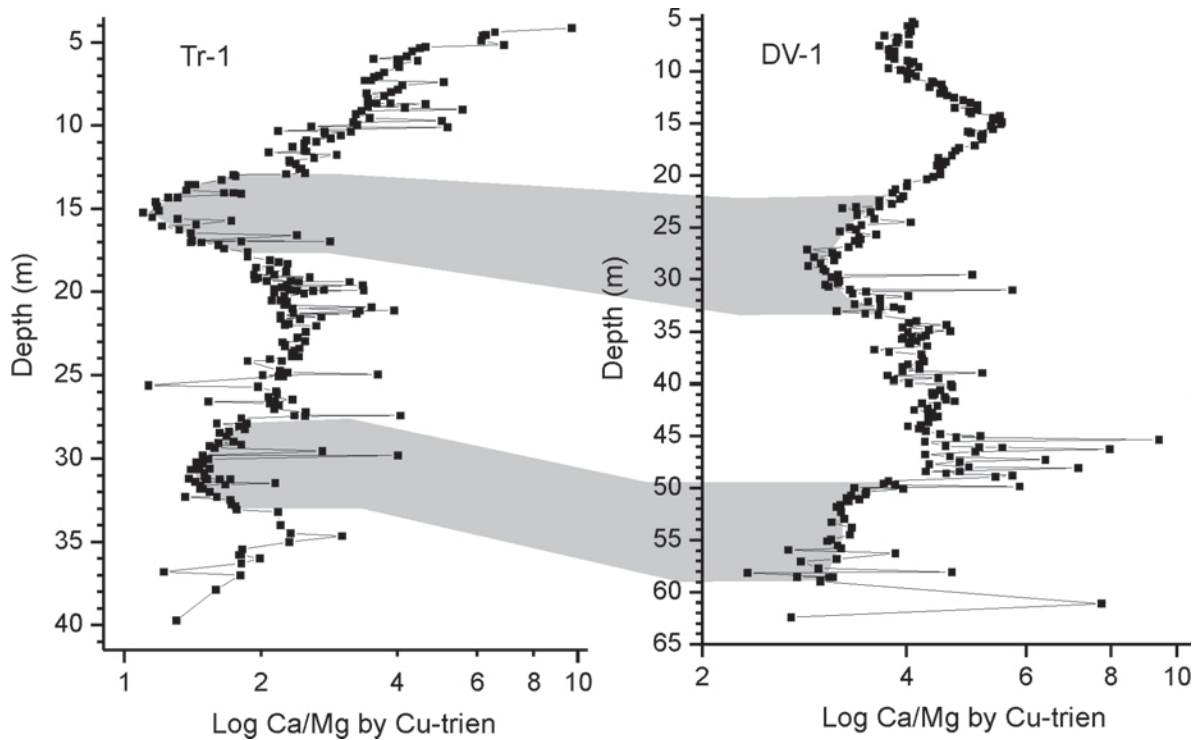


Figure 7. Ca/Mg chemostratigraphic correlation of cores Tr-1 and DV-1 using $[\text{Cu}(\text{trien})]^{2+}$ ion exchange. Massive calcite layers ($>30\% \text{CaCO}_3$) were excluded from the plots. The gray areas connect units with small Ca/Mg ratios.

and occurred in only a few very distinct layers. The analytical results indicate that siderite is not dissolved during cation exchange. The analysis with $[\text{Cu}(\text{trien})]^{2+}$ is

hence more specific than any elemental analysis that could possibly be performed by X-ray fluorescence or chemical analysis after total-sample dissolution.

Table 5. Description of the cores of Mšec Lake with a brief lithologic description, an outline of the Lake stages, and the results of the chemostratigraphic correlations.

Core, and brief lithological description		Lake stage	Chemostratigraphic correlation	
DV-1: near-shore facies (close to river inflow)	Tr-1: off-shore facies (pelagic environment)		Ca/Mg ratio by $[\text{Cu}(\text{trien})]^{2+}$	Carbonates
56.5–49 m (organic-rich, clayey, indistinct rhythms, massive siderite)	33–28 m (organic-rich, clayey, initially indistinct rhythms, tuff and massive siderite)	Initial highstand	Low	Mainly siderite
49–35 m (initially silty – sandy rhythms, distinct sandy laminae, later organic-poor, clayey, frequent siderite)	28–18 m (gradually silty rhythms, later organic-poor with distinct fining-up sandy turbidites at the top)	Regression	High	Zone starts with a few calcite layers, then mainly siderite
35–21 m (initially coarsening-up sandy rhythms, gradually fining-up sandy turbidites) – prodelta facies	18–13 m (initially organic-rich clayey-silty rhythms, gradually silty with distinct sandy turbidites at the top)	Partial recovery	Low	DV-1: calcite Tr-1: siderite, occasionally calcite
<21 m (oxic, initially silty later sandy, ripple-cross laminated) – shore-face facies	<13 m (oxic, initially silty – sandy rhythms, later sandy, laminated)	Final conversion to deltaic oxic environment	High	No carbonates

The following assumptions were made to perform the Ca/Mg chemostratigraphic correlation of the two cores: the clay minerals in the lake sediments were allochthonous, were transported in suspended form by rivers to the lake and by currents within the lake, and finally settled several tens of kilometers away from the shoreline after a time sufficiently long to allow equilibration with lacustrine water. The actual concentration of Ca²⁺ and Mg²⁺ in the lake was controlled by varying the influx of Ca²⁺ and Mg²⁺ from the watershed and/or varying the production of the lacustrine carbonates. The signs of variations of the Ca/Mg ratio in the lake water should affect the entire lake, although the absolute values of the Ca/Mg ratio within the entire lake were not necessarily homogeneous through the entire lake volume, because carbonate production was not homogeneous at such a scale.

The Ca/Mg ratio in the exchangeable fraction of sediments from the initial lake highstand was large in both cores (the lower gray area in Figure 7). The siderite precipitation tended to increase the Ca/Mg ratio in the lake, because the Ca:Mg ratio in the siderite is ~1:3 in Tr-1, and preferential precipitation of Mg²⁺ probably produced the first Ca/Mg maximum (Figure 7, Table 5, lake regression stage). The Ca/Mg growth was temporarily stopped, probably by the first calcite precipitation (in DV-1 at ~49 m and in Tr-1 at 27.4 m). The decline in the intensity of chemical weathering may have caused the decrease in the concentration of Mg²⁺ in the lake water and Mg was retained in basic minerals in the lake watershed; this would keep the Ca/Mg ratio in the lake water large or growing slowly (Figure 7). Both these mechanisms, however, would affect the entire lake-water chemistry. At depths of 35–20 m in DV-1 and 20–15 m in Tr-1, several massive calcite layers were found and, at those depths, the Ca/Mg ratio returns to the small values, producing the second minimum of Ca/Mg (Table 5, lake partial recovery). A similar mechanism probably caused the second Ca/Mg growth in both cores at the final lake stage, its conversion to an open oxic system. The lacustrine carbonate layers themselves cannot be used directly for stratigraphic correlation because they are probably not continuous within the entire lake sequence. However, combined analysis of Ca and Mg in carbonates and in ECMs allowed stratigraphic correlation of the two cores as shown in Figure 7.

The chosen approach should work in any lacustrine sediments containing at least 5–10% of expandable clay minerals. The [Cu(trien)]²⁺ consumption of the sediments in Tr-1 was 0.07 to 0.10 mmol(+)/g. The typical CEC of smectites is 0.5 to 1.1 mmol(+)/g. The ECM identified in the sediments was interstratified, randomly oriented, illite-smectite. Comparison with the previous values produced an estimate that the sediment contained 6–20% of the smectite structures to yield the observed [Cu(trien)]²⁺ consumption, assuming that only ECMs are responsible for the cation exchange. Such a concentra-

tion of expandable clay minerals can be expected even in current tropical lakes with very intense hydrolysis in the watershed. For example, up to 10% of illite-smectite was present in a clay fraction of the Holocene maar lake in Cameroon (Giresse *et al.*, 1991).

Ca/Mg chemostratigraphic correlation of Morava River flood plain sediments

Correlation of Morava River flood-plain sediments was performed to temper the problem of the scarcity of ¹⁴C datable material in flood sediments. Stratigraphic correlation and dating are bottlenecks when using any alluvial archives of the environmental change in the last two millennia that are typical of uneven sedimentation rates in individual times and places. Flood-plain sediments of an aggrading river are partly sorted, depending on the actual distance of the deposition site from the active channel and their lithology also varies with respect to the position relative to levees (Bridge, 2003). In several south Moravia rivers, including the Morava River, the flood-plain sediment sequences are composed of more clayey lower units, which sometimes included buried paleosols, ¹⁴C dated to the period 3500–1000 y BP (Havlíček, 1991; Havlíček and Smolíková, 1994); these sediments are usually covered by younger, more silty sediments deposited during the last millennium (Havlíček and Smolíková, 1994; Vrbová-Dvorská *et al.*, 2005; Kadlec *et al.*, in prep.). Havlíček and Smolíková (1994) denoted the top silty layers as reworked loess. The silty upper sediment unit is distinctive by increased Ca/Mg ratio (Figure 8, Kadlec *et al.*, in prep.) which seems to confirm the increased contribution of loess-derived materials.

The loess, or soils derived from loess, was probably the parent material of the Morava River flood sediments in the study area denoted Unit L in Figure 8. Unit L is well developed in sections M15 and M9 and is characterized by Ca/Mg values between 5.5 and 6.5. The fact that this unit is missing in Section 3 is noteworthy; however, that particular section probably has not accumulated the youngest sediments to a substantial thickness (Figure 8). Radiocarbon dating showed that Unit L was deposited in the last ~500 y. The lower gray area in Figure 8 connects Unit S with Ca/Mg values between 4.5 and 5.5. According to the dating, these sediments were deposited between ~800 and 2000 y BP. The lowest parts of the sections in Figure 8 usually contained an increased amount of coarser, channel sediments, which are more permeable to water and hence the Ca/Mg values retrieved can theoretically be affected by post-sedimentation chemical changes.

The radiocarbon ages as well as the Ca/Mg chemostratigraphic correlation confirmed uneven deposition of flood-plain sediments, a situation typical of meandering rivers. Beside the three profiles shown in Figure 8, the growing gradient of Ca/Mg in the [Cu(trien)]²⁺

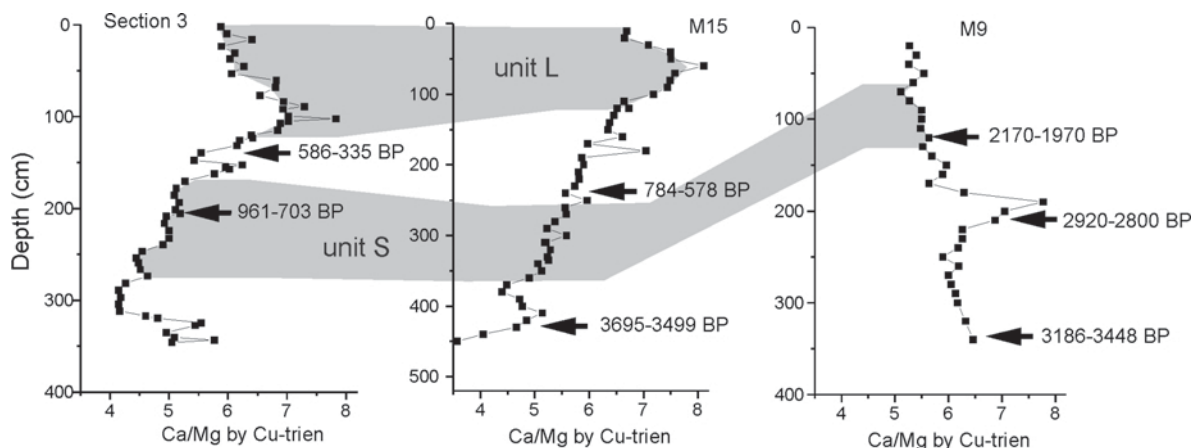


Figure 8. Ca/Mg chemostratigraphic correlation of three profiles in flood sediments exposed in erosional banks of the Morava River. The ages of wood fragments are indicated by bold arrows and numbers. Sediment units L (Ca/Mg 5.5–6.5) and S (Ca/Mg 4.5–5.5) are marked by gray areas.

exchangeable fraction has been observed in many other profiles in the study area which were deposited in the last millennium (Kadlec *et al.*, in prep.). The Ca/Mg ratio in the exchangeable fraction after $[\text{Cu}(\text{trien})]^{2+}$ exchange can, therefore, help to utilize this environmental archive assuming that at least some profiles will be radiocarbon dated at some depths.

CONCLUSIONS

$[\text{Cu}(\text{trien})]^{2+}$ analysis is a very useful laboratory tool for estimating the CEC of ECMs in geomaterials. The stability of the results under reasonable varying experimental conditions is sufficient to allow routine analyses of large series of samples. The most critical parameters are the exact stoichiometry of trien to Cu^{2+} and the re-adjustment of the actual sample weight to guarantee mass-independent results. The results of $[\text{Cu}(\text{trien})]^{2+}$ cation exchange are not simply equal to the results of other methods for the determination of the CEC of soils, e.g. BaCl_2 methods. $[\text{Cu}(\text{trien})]^{2+}$ -based CEC is equal to the conventional CEC determination for pure clay minerals only, but can be much smaller in the analysis of soils. Ion exchange with $[\text{Cu}(\text{trien})]^{2+}$ produces similar estimates of the Ca/Mg ratio in the ion exchangeable fraction as conventional methods with BaCl_2 for both pure expandable clay minerals and soils. The Ca/Mg ratio obtained can be used for chemostratigraphic correlation of sediments if the relative activities of these two cations varied in the sediment source area or in the parent aquatic environment. The actual, experimentally obtained value of Ca/Mg in the exchangeable fraction of a given sample series depends to a certain extent on the experimental procedure which must, therefore, remain constant over the analysis of each series to produce data suitable for stratigraphic correlations.

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