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Fe–Al–organic Colloids Control of Trace Elements in Peat Soil Solutions: Results of Ultrafiltration and Dialysis

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Abstract. Size fractionation of ~40 major and trace elements (TE) in peat soil solutions from the Tverskaya region (Russia) has been studied using frontal filtration and ultrafiltration through a progressively decreasing pore size (5, 2.5, 0.22 μm, 100, 10, 5, and 1 kD) and *in situ* dialysis through 6–8 and 1 kD membranes with subsequent analysis by ICP-MS. In (ultra) filter-passed permeates and dialysates of soil solutions, Fe, Al, and organic carbon (OC) are well correlated, indicating the presence of mixed organo-mineral colloids. All major anions and silica are present in "dissolved" forms passed through 1 kD membrane. According to their behavior during filtration and dialysis and association with mineral or organic components, three groups of elements can be distinguished: (i) species that are weakly affected by size separation operations and largely (> 50–80%) present in the form of dissolved inorganic species (Ca, Mg, Li, Na, K, Sr, Ba, Rb, Cs, As, Mn) with some proportion of small (1–10 kD) organic complexes (Ca, Mg, Sr, Ba), (ii) biologically essential elements (Co, Ni, Zn, Cu, Cd) mainly present in the fraction smaller than 1 kD and known to form strong organic complexes with fulvic acids, and, (iii) elements strongly associated with aluminum, iron and OC in all ultrafiltrates and dialysates with 30–50% being concentrated in large (>10 kD) colloids (Ga, Y, REEs, Pb, Cd, V, Nb, Sn, Ti, Zr, Hf, Th, U). For most trace metals, the proportion in the colloidal fraction correlates with their first hydrolysis constant. This implies a strong control of negatively charged oxygen donors present in inorganic/organic colloids on TE distribution between aqueous solution and colloid particles. It is suggested that these colloids are formed during plant uptake of Al, Fe, and TE from mineral matrix of deep soil horizons and their subsequent release in surface horizons after litter degradation and oxygenation on redox or acid/base fronts. Dissolved organic matter stabilizes Al/Fe colloids and thus enhances trace elements transport in soil solutions.

Key words: peat, soil, solution, colloids, ultrafiltration, dialysis, trace elements, speciation

1. Introduction

It has been known for decades that the chemistry of soil solutions provides invaluable information on the biogeochemical cycles of major and trace

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elements because the composition of soils solutions is the consequence of all the processes that control the partitioning of trace elements between the rocks, soils and plants. Use of this approach requires characterization of organo-mineral colloids that are likely to control the transport of many elements in soil solutions. Ultrafiltration and dialysis are two major techniques implemented for this purpose and, in particular, for quantifying colloid size distributions. While many studies have been devoted to colloid characterization in surficial aquatic environments such as rivers, lakes and seawater (see Buffle et al., 1992; Tanizaki et al., 1992; Benoit et al., 1994; Buesseler et al., 1996; Guo and Santschi, 1996; Wen et al., 1996; Lead et al., 1997; Pham and Garnier, 1998; Eyrolle and Benaim, 1999; Dupré et al., 1999; Ross and Sherrell, 1999; Olivié-Lauquet et al., 1999, 2000; Ingri et al., 2000; Hoffmann et al., 2000; Sigg et al., 2000; Vesely et al., 2001; Lyvén et al., 2003), soil solutions have received much less attention (Berggren, 1989; Menzies et al., 1991; Gasser et al., 1994; Gooddy et al., 1995; Huber and Denaix, 2000; Riise et al., 2000; Van Hees and Lundstrom, 2000; Van Hees et al., 2000).

The first step in the rigorous characterization of aquatic colloids is the approximation of their size using various separation procedures. In contrast to thorough applications of ultrafiltration techniques to separate colloids in natural waters, only few authors used dialysis as an *in situ* technique of colloid characterization (Benes and Steiness, 1974; Borg and Andersson, 1984; Berggren, 1989; Gimpel et al., 2003; Nolan et al., 2003). This paper is aimed at bridging this gap by presenting a detailed study of major and trace element behavior during dialysis and ultrafiltration of soils solutions extracted from three different boreal soil environments. Boreal soils such as podzols and peatlands are believed to play a crucial role in the control of the CO_2 cycle in the biosphere by storing organic matter in thick humus horizons (Thurman, 1985). As a result, temperate (Shotyk, 1988, 1997) and tropical (Weiss et al., 2002) peatlands have been extensively studied from the viewpoint of elements concentration in soil profile, biological accumulation mechanisms and solution chemistry of major elements (Gorham et al., 1985; Shotyk, 1993, 1997). In such organic-rich environments, aluminum and iron are always associated to humic and fulvic acids (Beck et al., 1974; Tipping et al., 1995, 2002; Olivié-Lauquet et al., 1999, 2000; Schäfer et al., 2003a, 2003b). As a result, most of chemical elements released by weathering, notably trace metals, are transported as mixed Fe–Al–organic colloids. Neither the molecular size of these colloids nor their true chemical nature are well known. In addition, except for several detailed studies of Fe, Al, and OC in various fractions of podzol soil solutions (Keller and Domergue, 1996; Riise et al., 2000), the data on trace elements concentration in peat soils are quite scarce.

In this paper we present results of in-field size separation experiments coupled with ICP-MS analyses of trace elements in the filter-passing permeates. We conducted in-series cascade filtrations through 5, 2.5, 0.2 μm, 100, 10, 5, and 1 kD pore size membranes combined with *in situ* dialysis experiments using 6–8 and 1 kD membranes.

The goal of this study is to address the following issues: (i) to quantitatively compare two different colloid separation procedures (filtration and dialysis), (ii) to characterize the major thermodynamic constraints (solubility of solid hydroxides and complexation with dissolved organic matter) on TE concentration level and speciation in various molecular weight fractions of soil solution; and (iii) to quantify the distribution coefficients of TE between solution and colloids, characterize the affinity of TE to various size colloids and discuss the mechanisms of colloids formation. We hope that results of this study will provide new insights on the speciation, transport and bioavailability of trace elements in organic-rich boreal soil solutions and help to better understand the chemical processes operating in boreal peatlands.

2. Materials and Methods

2.1. SAMPLING

Three peat soils under coniferous forest of Scots pine and Norway spruce (No. 1a, 1b, and 2), a podzol soil under grass vegetation (No. 3) and soil solutions from the surface horizon of a swamp zone (peatland) (No. 4) were sampled during September 2001. Depths of sampling and dominant vegetation for each sample are given in Table I. The studied area is situated at 150 m above mean sea level (MSL) in the Tverskaya region, 120 km NW from Moscow, Russia. Quaternary deposits primarily consisting of coarse-grained and sandy till or glacio-fluvial deposits of granito-gneissic moraines dominate the bedrock composition. In this region, thick peat soils are very abundant. This area is influenced by some industrial and agricultural activities; as a result, the chemistry of soil solution samples contain an anthropogenic signature.

Table I. Description of soil samples studied in the present work

Sample No.	Type of soil	Vegetation	Sampling depth (cm)
1a	Peat	*Pinus sylvestris* and *Picea abies*	30–40
1b	Peat	*Pinus sylvestris* and *Picea abies*	10
2	Peat	*Pinus sylvestris*	30–40
3	Podzol	Grass	30–40
4	Swamp zone (peat)	*Betula pubescens*	30–40

Samples for ultrafiltration were collected after a short intense rainy period (2–3 days) without special extraction procedure as soils were sufficiently saturated to provide free gravitational water in sampling pit. Samples were collected in 1-L high-density polyethylene (HDPE) containers. Plastic gloves were used during all sampling handling.

2.2. FILTRATION AND DIALYSIS

In this work, we use the terms "filtrate" and "dialysate" for ultrafilter-passing solution (permeate) and the portion of solution retained inside the dialysis bag after the end of dialysis procedure, respectively. The term "frontal ultrafiltration" procedure indicates that separation occurs in the same direction as solution flow, in contrast to more usual tangential or cross-flow filtration processes. The filtration procedure was performed in "cascade" mode, corresponding to in-series filtration of the same initial stock solution through a progressively decreasing pore size.

Collected waters were immediately filtered through sterilized, pre-washed, single-use filter units Minisart® (Sartorius, acetate cellulose filter) having a diameter of 25 mm and a pore size of 5 μm. First, 150–200 mL of filtrate were discarded. Filtration through 2.5 and 0.2 μm membranes was performed using a Sartorius polycarbonate filter holder and nitrate cellulose Sartorius single-used filters having a diameter of 47 mm. Filtrations were carried out using a MITYVAC® manual vacuum pump within 1 h after solution sampling. The first 300–400 mL of the filtrate were systematically discarded. Frontal ultrafiltrations (UF) were performed using a 50-mL polycarbonate cell (Amicon 8050) equipped with a suspended magnet stirring bar located above the filter to prevent its clogging during filtration. Filtration was performed as specified by the manufacturer with 100, 10, and 1 kD membranes (Diaflo YM Amicon, regenerated cellulose, 200 μm thick and 44.5 mm diameter) which are routinely used for molecular size fractionation of soil organics (i.e., Suominen et al., 2003) and metal speciation (Van Hees et al., 1999, 2001, 2002). Before each filtration step, the system was cleaned by flushing MilliQ water, then ~1 M ultrapure HNO_3 and, finally, MilliQ water through the system. During filtration, the first 30–50 mL of solution were discarded thus allowing the saturation of the filter surface prior filtrate collection. Each filter was washed in MQ water before the experiment and used only once. This greatly decreased the probability of cross-contamination during sample filtration, improved the OC blank, provided unique conditions of filtration for all samples and allowed high recovery of colloidal particles. The typical filtered masses for each filter size were between 250 mL (0.22 μm, 100 kD) and 100 mL (10, 1 kD). The concentrations of TE in filter-passed (permeate) fraction were independent of the volume filtered. The mass balance calculations performed in each sample as the difference between ultrafilter-passing (permeate) and ultrafilter retained (retentate) concentrations was always better than 90%, except in several cases for Cu, Cd, and Pb when a clear contamination was detected (see Appendix).

Details of experimental procedure, discussion on adsorption of TE on filter materials and other possible artifacts of this technique are provided elsewhere (Pokrovsky and Schott, 2002). Ultrafiltration at 5 kD pore size was made by passing a 0.22 μm filtered solution through pre-washed Ultrafree Biomax 5 kD NMWL disposable vials (Millipore®) while centrifuging at 2200 g during 15 min.

Dialysis experiments were performed directly in sampling holes filled by soil solution. The duration of the dialysis procedure was about 72 h. Our laboratory experiments demonstrated that, for both 1 and 6–8 kD membranes, the equilibrium distribution is achieved by 6 h, in agreement with specifications given by the manufacturer. During the dialysis procedure, soil solution composition did not change by more than 10% compared to initial value as proved by analysis of 30 trace and major elements in 0.22 μm filtered sample before and after experiments. EDTA-cleaned SpectraPor 7® dialysis membranes of 6–8 and 1 kD were thoroughly washed in 0.1 M bidistilled HNO_3, ultrapure water, and filled with ultrapure MQ deionized water for dialysis experiments.

2.3. ANALYSIS

Filtered or dialyzed solutions for cations and trace element analyses were acidified ($pH = 2$) with ultrapure double-distilled HNO_3 and stored in pre-washed HDPE bottles. The preparation of bottles for sample storage was performed in a clean bench room. The samples for OC analyses were collected in pyrolyzed Pyrex glass tubes. Blanks were performed to control the level of pollution induced by sampling and filtration. The OC blanks of filtrate and ultrafiltrates never exceeded 0.1 mg/L which is quite low for the organic-rich waters sampled in this study (i.e., 10–60 mg/L OC). For all major and most trace elements, concentrations in blanks were below the detection limits. In several cases, however, clear contamination by Zn, Cu, Ni, and Pb was detected in 10 and 1 kD ultrafiltrates. These samples were not considered in the analysis of results.

pH was measured in the field using a combined Schott–Geräte electrode calibrated against NIST buffer solutions ($pH = 4.00$ and 6.86 at 25 °C). The accuracy of pH measurements was ± 0.02 pH units. Aqueous silica concentrations were determined colorimetrically (molybdate blue method) with an uncertainty of 1% using a Technicon automated analyzer. OC was analyzed using a Carbon Total Analyzer (Shimadzu TOC 5000) with an uncertainty better than 3%. Major anions (Cl, SO_4, F, NO_3) concentrations were measured by ion chromatography (HPLC, Dionex 2000i) with an uncertainty of

2%. Calcium, magnesium, sodium and potassium concentrations were determined using a flame atomic absorption Perkin Elmer 5100PC spectrometer with an uncertainty of 1%. Trace elements (TE) were measured without preconcentration by ICP-MS. For several ultrafiltrates having very low TE concentration, an automated desolvator was used which allowed increasing the detection limit by a factor of 5. Indium and rhenium were used as internal standards and corrections for oxide and hydroxide ions were made for REEs and metals (Ariés et al., 2000). The international geostandard SLRS-4 (Riverine Water Reference Material for Trace Metals certified by the National Research Council of Canada) was used to check the validity and reproducibility of the analyses. Recently, the list of certified trace elements in this standard was extended to include B, Cs, Ga, Ge, Li, P, Rb, Si, Th, Ti, W, Y, Zr, and REEs (Yeghicheyan et al., 2001). A good agreement between our replicated measurements of SLRS-4 and the certified values was obtained (relative difference $<10\%$). Interferences with Fe and Al were assessed by analyses of artificially prepared TE standard multi-element solution ($\sim$10–50 μg/L of each element), enriched by Fe and Al. No significant interferences were detected up to 3 mg/L of added metal. For several elements exhibiting interference with Fe at [Fe] $>$ 0.5 mg/L, simultaneous measurements of different isotopes (i.e., ^{52,50,53}Cr, ^{70,72,74,76}Ge) allowed precise determination of their concentrations even in complex soil solutions. Interferences with OC, especially for heavy elements, are unlikely because, in the ultrafiltration series, elements concentration often decreases 10-fold while OC changes are not more than 30–50%.

3. Results and Discussion

Measured major and trace elements concentrations in various filtrates and dialysates are reported in Appendix. In the following section, we will discuss the behavior of major and trace elements during ultrafiltration and dialysis separation experiments.

3.1. COMPARISON BETWEEN DIALYSIS AND ULTRAFILTRATION

For all soil solutions samples, most of the trace and major elements considered in this study exhibit close separation upon ultrafiltration or dialysis: 6–8 kD dialysates fall between 1 and 10 kD filtrates (see Sections 3.3–3.8 below). This means that the nominal pore size attributed to dialysis and ultrafiltration membranes is comparable and not strongly affected by artifacts due to the separation procedures.

A quantitative comparison between ultrafiltration and dialysis was performed for a sample from a coniferous peat soil (No. 2). For most elements affected by the 1 kD separation procedure, filtrates and dialysates concentrations only differ by ≤10–25%. Ten elements, however, are significantly enriched in dialysates compared to ultrafiltrates: Fe (40%), Ti (80%), Cd (30%), Sn (150%), La (200%), Ce, Pr, Nd (40–50%), Yb (60%), and Th (100%). This trend suggests that the nominal pore size for 1 kD UF membranes is lower than that of corresponding dialysis membranes.

3.2. MAJOR COMPONENTS OF SOIL SOLUTIONS

The soil waters examined are slightly acidic with pH values varying from 3.9 to 4.7. The pH values of the filtrates and ultrafiltrates was within ±0.05 pH units. The Eh value ranged from 400 to 500 mV indicating well aerated (i.e., non-gley) soil environments. All solutions exhibited high concentrations of Al, Fe, and OC (1–2, 0.5–1, and 50–70 mg/L, respectively) which is typical of peatland areas.

Al concentrations ranged between 1200 and 2000 μg/L in soil solutions (No. 1, 2, and 3) and ~700 μg/L in Fe-rich swamp waters (No. 4); this is comparable to concentrations found in podzol soils (Keller and Domergue, 1996; Riise et al., 2000) and Fe-organic rich surface streams (Pokrovsky and Schott, 2002), respectively. In the case of the peat soil solutions investigated in this study, only 20–25% of Al is in the "dissolved" form (<1 kD). Numerous studies of organic-rich peat and podzol soil solutions from the Russian plain reported high aluminum concentrations (i.e., 500–2000 μg/L, Strelkova, 1967; Ponomareva and Sotnikova, 1972; Ushakova, 1990; Motuzova and Degtyareva, 1993) with 90–100% being complexed by colloidal organic matter (Nozdrunova, 1965; Kaurichev et al., 1968). At the same time, one should not neglect the important role of low-molecular weight (LMW) organic ligands; such LMW ligands can account for up to 40% of total bound Al, as demonstrated by ultrafiltration with size exclusion chromatography for solutions from podzolized forest soils (Van Hees et al., 2001). LMW carboxylic acids, which are very abundant under coniferous vegetation, can account for up to 10% of OC in soil solutions from upper soil horizons (Strobel, 2001).

Organic carbon, aluminum, and iron are strongly affected by size separation procedures. In peat soil solutions (No. 1a, 1b, and 2), these components are mostly concentrated in 1–100 kD fractions, whereas in surface waters of swamp region under birch vegetation (No. 4), more than 50% of OC has a size less than 1 kD (Figure 1). In the course of filtration, concentrations of all three components significantly decrease for pore sizes <0.1 μm. In all filtrates and ultrafiltrates, as well as in dialyzates, OC, Fe, and Al concentrations are well correlated (Figure 2). This indicates, in agreement with studies on podzol soils (Keller and Domergue, 1996; Lundstrom et al., 2000), that soil colloids produced during cellulose degradation

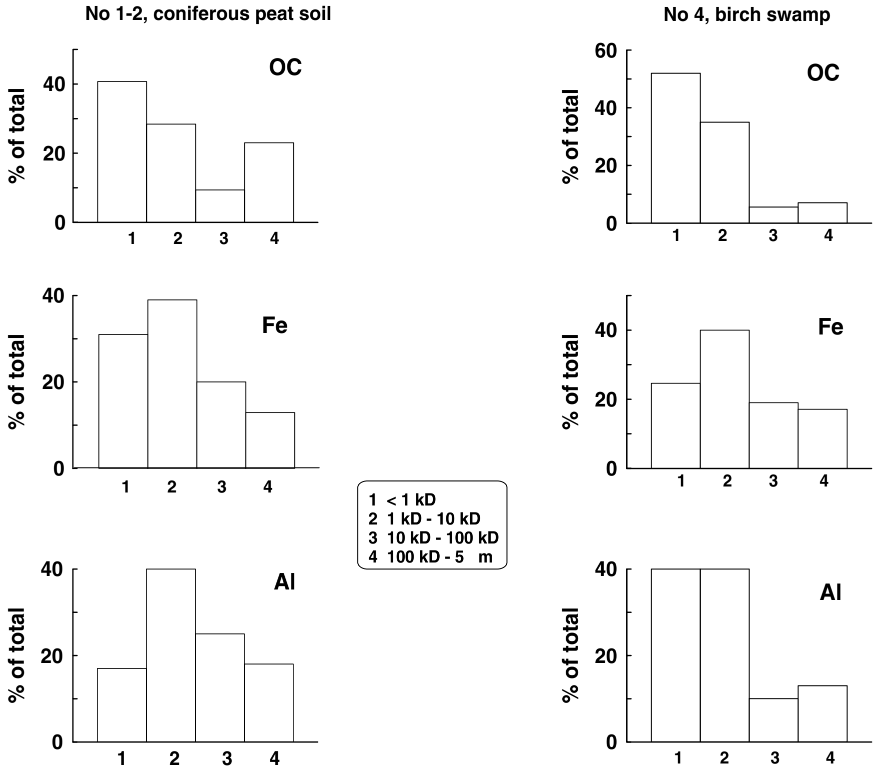

Figure 1. Distribution diagrams of Fe, Al, and organic carbon (OC) in various fractions of filtrates and ultrafiltrates for a coniferous peat soil (No. 1–2) and a birch swamp zone (No. 4). The *X*-axis represents the fractions passed through 1 kD filter (1), retained by 1 kD filter and passed through 10 kD (2), retained by 10 kD filter and passed through 100 kD (3) and retained by 100 kD membrane (4). All fractions between 100 kD and 5 μm are sum up for clarity.

(Guggenberger et al., 1998a, 1998b) are mainly composed of organic molecules associated with oxy(hydr)oxides of Al and Fe. Soil solutions under coniferous vegetation (No. 1 and 2) are enriched in Al compared to Fe whereas colloids from soil surface waters under birch trees (No. 4) are Fe-dominant. This is in agreement with previous studies of organic-rich podzols of NW Russia: for the same bedrock, soil solutions from surface horizons of coniferous forest contain in average 2 and 0.4 mg/L of Al and Fe, respectively, while under birch/grass vegetation, concentration of Al and Fe is 0.8 and 3 mg/L, respectively, as reported by Shilova and Strelkova (1974), based on 4 years of lysimetric observations. This result can be explained by lower Fe/Al ratio in litter of Scots pines (0.23) than in birch trees (1.7–2.9), according to Hongve et al. (2000) and Reimann et al. (2001). Degradation of forest floor litter serves as an important source of these elements in upper soil horizons and, consequently, in soil solutions.

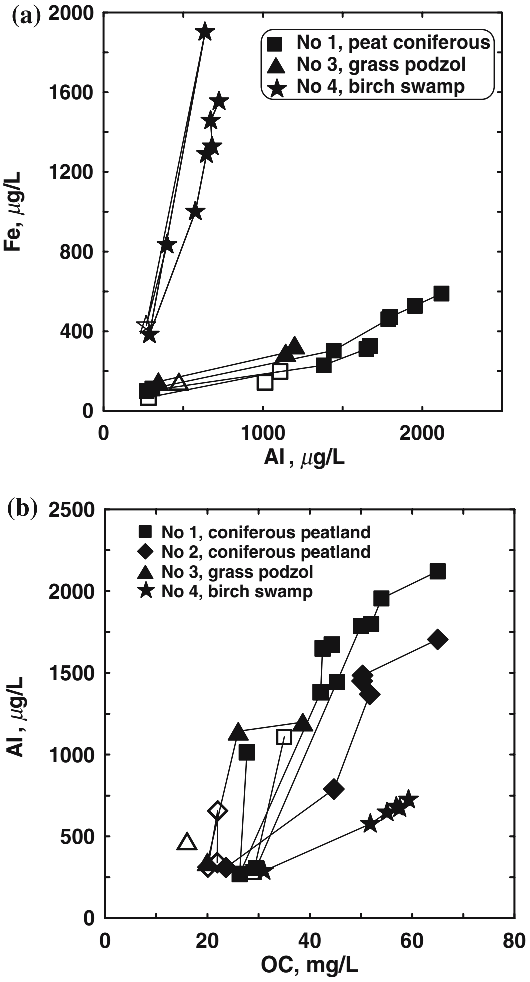

Figure 2. Correlation between Fe and Al (a) and Al and OC (b) in all filtrated and ultrafiltrated (solid symbols) samples and dialysates (open symbols).

OC concentrations in peat soil solutions and surface waters varies from 50 to 70 mg/L, which is comparable with OC concentration in upper horizons of podzol soils (i.e., 30–50 mg/L, Keller and Domergue, 1996; Guggenberger et al., 1998a, 1998b). In lysimetric soil solutions from peatlands, OC concentrations of 50–150 mg/L have been often observed (Skrynnikova, 1948, 1961; Sotnikova, 1970). It is important to note that a significant part of organic matter in our samples (i.e., >40–50%) has a molecular weight of <1 kD, whereas for Al and Fe, the proportion of <1 kD fraction is only 20–30%. Therefore, one can suggest that organic rather than inorganic compounds dominate the "dissolved" fraction of soil solutions. This observation is consistent with results of Riise et al. (2000) who reported 60% of

OC in the <1 kD fraction of soil solutions of Scandinavian podzols. Previous Russian studies on boreal and temperate streams draining podzol and peat soils indicate that LMW fulvic acids (FA) constitute at least 50% of DOC in river waters (Varshal, 1973).

Among major elements, dissolved silica is the least affected by ultrafiltration: for peat soil and surface waters, only 4 and 7% of Si is in the <1 kD colloidal fraction, respectively. If silica is almost entirely concentrated in the dissolved fraction, it cannot be precluded that a small proportion (i.e., ~5%) is associated with aluminum or iron colloids; such associations are known from studies of soils solutions from E horizon of Scandinavian podzols (Riise et al., 2000) and laboratory experiments on Al/Fe-silica interactions (Pokrovski et al., 1996, 2003; Pokrovski and Schott, 1998). Concentrations of anions such as chloride and fluoride do not change in the course of ultrafiltration and dialysis. In podzol soils and surface waters from peat swamps, sulfate concentrations decrease by less than 5% upon filtration to 1 kD.

3.3. ALKALI AND ALKALINE-EARTH METALS

Na, Mg, Ca, K, Li, Rb, and Sr are mostly present in the dissolved pool (>70% passes through 1 kD membrane). However, in organic-rich peat soils and surface swamp waters (No. 1a, 1b, 2, and 4), Ba and Cs concentration decreases by 40–50% upon filtration from 5 μm to 1 kD pore size. Positive correlations between [Ca], ([Mg]), and [OC] in (ultra) filter-passed fractions and dialysates suggest an important role of organic colloids in speciation of these elements in peat soils. Van Hees et al. (2000) estimated that about 13–14% of Ca and Mg can be bound to LMW organic ligands in O horizon of podzol soil solutions. Colloidal forms of alkaline-earth elements were also detected by ultrafiltration and potentiometry in organic-rich boreal rivers (Pokrovsky and Schott, 2002; Dahlqvist and Ingri, 2002, respectively), and by dialysis in soil solutions of serpentinic soils (Gasser et al., 1994).

3.4. DIVALENT METALS: Mn, Co, Ni, Cu, Zn, Cd, Pb

The Mn concentrations in the soil solutions evaluated varied between 50 and 100 μg/L for coniferous peat soil and 800 and 900 μg/L in birch swamp zone. In these slightly acidic solutions ($3.9 \leq pH \leq 4.7$), Mn is mainly present as Mn^{2+} and is unlikely to be controlled by the solubility of Mn oxides or oxy(hydr)oxides (see Section 3.8.1). Ultrafiltration experiments give evidence of only a slight decrease (≤25%) of Mn concentrations during filtration from 1 to 10 kD. This is consistent with Mn^{2+} high mobility reported in humus profile of podzol and peat soils (Riise et al., 2000; Vinogradov, 1957, respectively) and in organic-rich boreal rivers (Laxen et al., 1984; Ponter et al., 1992). Extremely high Mn concentrations, up to 15 and even 100 mg/L, were reported in organic-rich peat swamp and peat-gley soil solutions of pH ~4 (Malinina and Motuzova, 1994). Between 50 and 60% of Co and Ni is in the form of LMW (<1 kD) organic complexes as illustrated by clear positive correlation between these elements and OC in peat soil samples (Figure 3).

Concentrations of Cu and Zn in soil solutions investigated in this study (2–4 and 30–40 μg/L, respectively) are within the range measured in podzol (Keller and Domergue, 1996) and peat (Arzhanova and Elpatievskii, 1979; Malinina, 1993; Malinina and Motuzova, 1994) soil solutions. Zinc concentrations only slightly decreases upon filtration from 5 μm to 1 kD. "Truly" soluble forms of Zn have been shown to control its speciation in organic-rich soil solutions of mountain regions (Arzhanova and Elpatievskii, 1979) and in brown soil solutions (Cancès et al., 2003). Up to 60% of Cu is present in the form of <1 kD complexes (Figure 3), in agreement with previous speciation studies of A_0 horizon soil solutions (Arzhanova and Elpatievskii, 1979). Strong complexation of Cu by LMW ligands in organic-bearing surface waters and soil solutions was also demonstrated by electrochemical (Florence, 1977; Sanders, 1982) and ion exchange (Fujii et al., 1982) measurements and thermodynamic modeling (Benedetti et al., 1996).

High concentrations of Cd and Pb in organic-rich soil solutions (0.1 and 1 μg/L, respectively) likely result from the colloidal status of these metal ions as demonstrated by their concentration decrease during ultrafiltration and dialysis experiments (Figure 4a and b). About 30 ± 15% of Pb and 56 ± 10% of Cd in peat soil environments (samples 1 and 2) is concentrated

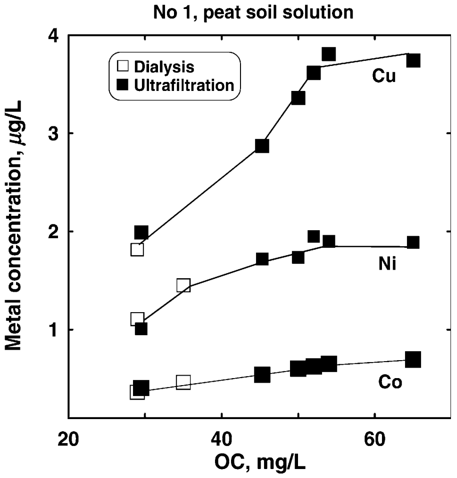

Figure 3. Correlation between Cu, Ni, and Co concentrations and that of OC for filtrates (closed symbols) and dialysates (open symbols) of soil solution from the coniferous peatland.

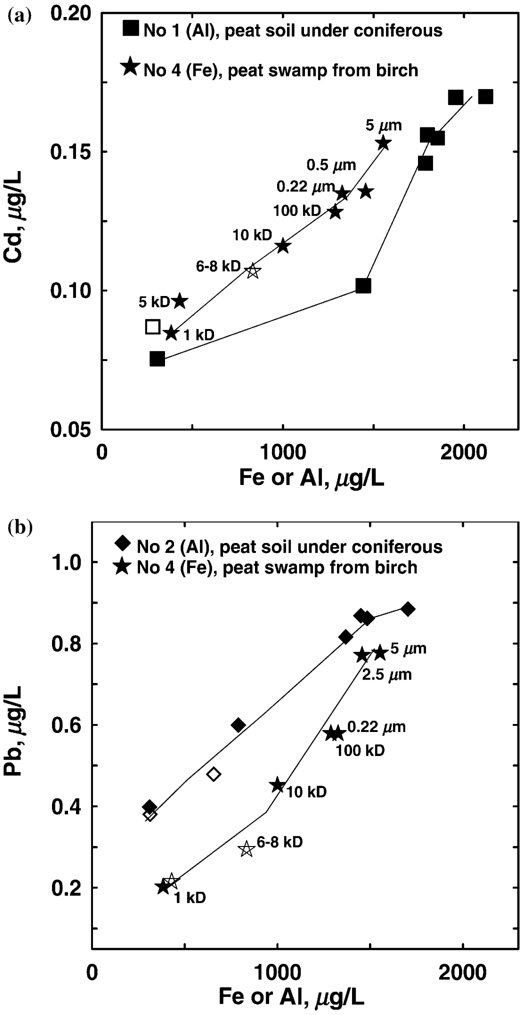

Figure 4. Cadmium (a) and lead (b) concentrations in filtrates and dialysates as a function of the concentration of the dominant element in the peat coniferous soil (Al) and the birch swamp (Fe).

in the fraction <1 kD. The last value is in agreement with Cd speciation in humic soil solutions as deduced from dialysis (Berggren, 1989) and thermodynamic modeling (Benedetti et al., 1996). Another dialysis/ultrafiltration study of Cd in soil extracts containing 245 mg/L of OC demonstrated that a high proportion (70–80%) of >10 kD metal–organic associations (Benes and Mizera, 1998). At the same time, according to our results in podzol soil solutions containing less amount of OC (No. 3), about 90% of Cd and 70% of Pb are in the form of LMW colloids (<1–10 kD).

Overall, divalent metals are associated with organo-mineral colloids (>1 kD molecular size) in the following order: Mn ~Zn < Cu ≤ Ni ≤ Co < Cd < Pb; this order most likely reflects their affinity with organic matter and peat (Irwing and Williams, 1948; Ringqvist and Oborn, 2002). Similar rankings of Me^{2+} association with soil humic acids (Kerndorff and Scnitzer, 1980) and solid-solution partitioning coefficients for 60 organic horizon samples of forest soils (Sauvé et al., 2003) have been reported. For three biologically important elements (Mn, Zn, Cu), whose concentration in coniferous needles, lichen, mosses and peat are in the range of 300–600, 20–40, and 3–10 mg/kg, respectively (Zhulidov et al., 1997; Cebernus and Steinnes, 2000; Chiarenzelli et al., 2001), degradation of plants litter and release of small organic complexes may serve as an important source in soil solutions. However, the chemical nature of organic complexes and organo-mineral colloids bearing these elements cannot be assessed solely from UF and dialysis procedures used in the present study and complementary voltammetric (Smith, 1976; Eyrolle et al., 1996; Benedetti et al., 2002) and spectroscopic (Olivié-Lauquet et al., 1999, 2000; Plaschke et al., 2002; Schäfer et al., 2003a, 2003b) techniques would be essential to characterize the status of divalent elements in these soil solutions.

3.5. TRIVALENT ELEMENTS: Ga, Y, REE

These elements are largely present in the colloidal pool with only 15–40% being concentrated in <1 kD fraction. In ultrafiltrates, gallium closely follows aluminum, as illustrated in Figure 5. Yttrium and REE's are strongly affected by filtration: their concentration decreases ~4 times upon

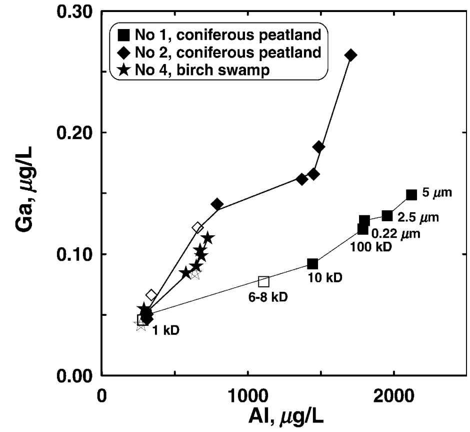

Figure 5. Gallium concentration as a function of aluminum concentration in successive filtrates and dialysates of studied peat soil solutions.

filtration from 0.8–5 μm to 1 kD. An example of Ce concentration decreases in peat soil and swamp waters is shown in Figure 6. For all samples we observe an enrichment of the "dissolved" fraction (<1 kD) by heavy REE. This is in agreement with REE speciation schemes identified in temperate (Sholkovitz, 1992, 1995) and boreal rivers (Pokrovsky and Schott, 2002): the shale-normalized REE pattern (Taylor and McLennan, 1985) exhibits an enrichment of heavy REE in the <1 kD fraction (Figure 7) reflecting complexation of these elements with small size organic compounds whereas light REE adsorb/coprecipitate on/with large (>10–100 kD) Fe–Al–organic colloids.

3.6. TETRAVALENT ELEMENTS: Ti, Zr, Hf, Th

Titanium concentration in peat soil solutions under coniferous vegetation reach 46 μg/L. Ti concentrations in acid solutions of peat swamp and peat gley soils of temperate region may attain 10–200 μg/L which is likely to originate from its colloidal status (Malinina and Motuzova, 1994). Results of our ultrafiltration and dialysis experiments demonstrate the dominant role of colloids in Ti speciation: a positive correlation is observed between [Ti] and [Al] (taken as an index of colloid abundance) in fractions of all studied soil solutions (Figure 8). Dissolved Zr, Hf, and Th concentrations range from 0.6 to 0.9, 0.02 to 0.06, and 0.06 to 0.1 μg/L, respectively. These elements are likely to be present in large-size colloids with only ~20% having molecular size of <1 kD. During filtration and dialysis, concentration of these elements decreases almost linearly with that of Al (Figure 9).

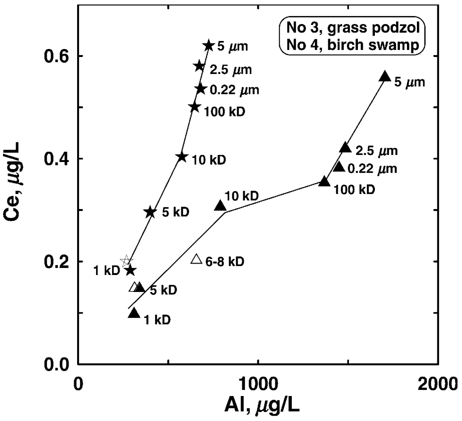

Figure 6. Cerium concentration as a function of aluminum concentration in successive filtrates and dialysates of studied peat soil solutions.

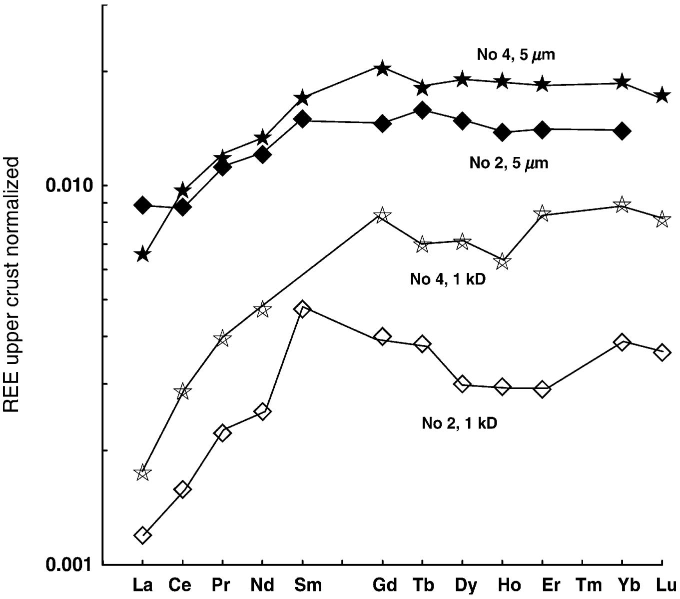

Figure 7. Upper crust normalized REE pattern of filtrates and ultrafiltrates of peat soil solutions.

Tetravalent elements are generally known to be immobile during weathering, accumulating in weathering products (Vinogradov et al., 1957; Gaillardet et al., 2003). However, the presence of organo-mineral colloids in soil solutions greatly increases their concentrations in solution. For titanium, the role of organic matter in affecting the behavior of Ti is as important as are Fe/Al oxyhydroxides. Indeed, it has been known for some time that the concentration of Ti in world soils is inversely correlated with that of organic matter (Vinogradov, 1957). High mobility of Ti in tropical soil solutions from Cameroon and Amazonia induced by organic or mineral colloids has been recently reported by Viers et al. (1997) and Cornu et al. (1999), respectively.

3.7. OTHER TRACE ELEMENTS (V, As, Sb, Sn, Nb, U)

The ranges of V, Cr, and As concentrations (2–6, 0.7–1.5, and 1–4 μg/L, respectively) are similar to those reported for boreal rivers (Pokrovsky and Schott, 2002) and podzol and peat soil solutions (Malinina and Motuzova, 1994; Tyler and Olsson, 2001) whereas concentrations of Sb, Sn and Nb are about 10 times higher than corresponding values for surface streams. Among these elements, As and Sb are weakly affected by ultrafiltration, as they are primarily present in the truly-dissolved pool

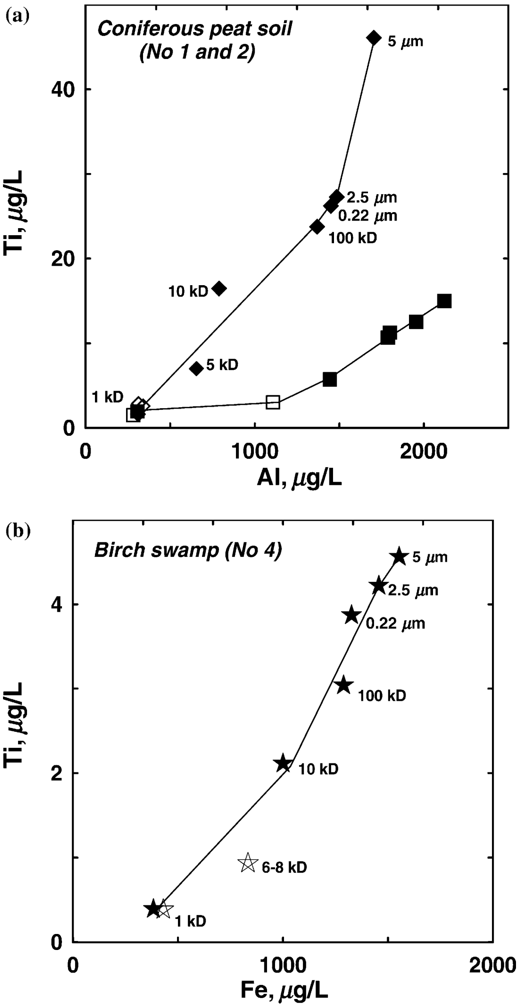

Figure 8. Titanium concentration as a function of aluminum concentration in filtrates and dialysates of peat coniferous soil (a) and birch swamp (b).

(75–85% is in <1 kD fraction). In contrast, V, Sn and Nb concentrations are strongly affected by ultrafiltration: between 50 and 60% of V and 20–30% of Sn and Nb are present in the <1 kD fraction. They are also well correlated with Al in ultrafiltrates and dialysates (Figure 10 for Sn and Nb); this demonstrates the important role of colloidal carriers in the transport of these elements.

Transport of U in peat and podzol soil solutions by organic colloids is similar that found in organic- and Fe-rich boreal rivers (Porcelli et al., 1997; Pokrovsky and Schott, 2002). This conclusion is confirmed by results of our ultrafiltration/dialysis experiments which show that U and Al concentrations

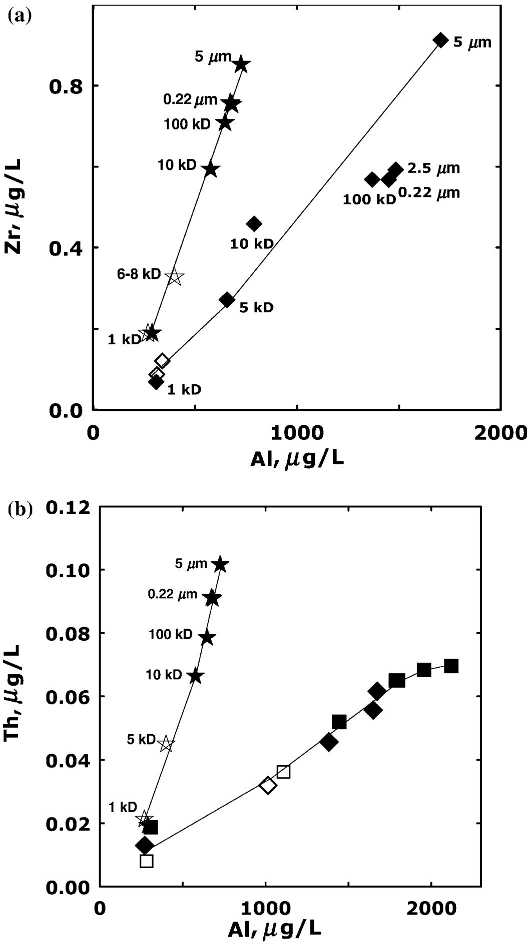

Figure 9. Zirconium concentrations as a function of aluminum concentration in successive filtrates and dialysates of coniferous peat soil solutions and birch swamp surface horizons.

are almost proportional (Figure 11). Percentage of U-bearing colloids (>1 kD) varies from ~80% in peatland (No. 1, 2, and 4) to ~70% in podzol soil solutions (No. 3).

3.8. THERMODYNAMIC ANALYSIS

3.8.1. Complexation with organic matter

Soil solutions sampled in this study exhibit relatively simple inorganic compositions: low pH values (i.e., 4–4.5), Cl and SO_4 concentration and negligible phosphate content (i.e., <1 µM) suggesting that most of dissolved TE are present either in the form of free ions or organic complexes. There is a

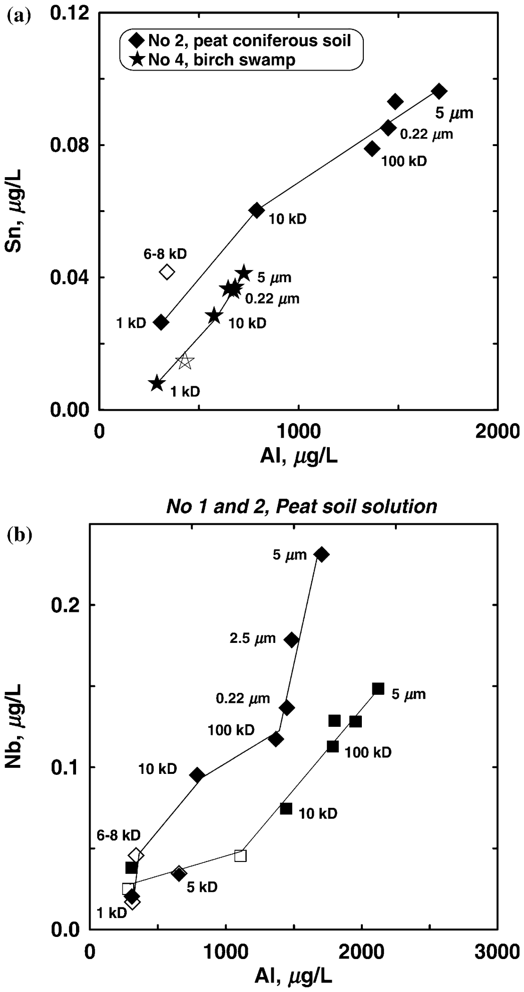

Figure 10. Tin (a) and niobium (b) concentrations as a function of aluminum concentration in successive filtrates and dialysates of coniferous peat soil solutions (Sn and Nb) and birch swamp surface horizons (Sn).

large number of thermodynamic models describing the interactions of Al^{3+}, Fe^{3+} and divalent transition metals with dissolved organic matter (i.e., NICA, Benedetti et al., 1995; MODELm, Huber et al., 2002; WHAM, Tipping, 1994, 1998). To use these models, an extensive set of both protons and metal binding parameters is required. Normally, high-resolution potentiometric titrations and electrochemical complexation measurements are necessary to assess the main thermodynamic information for such modeling (total concentration of each complexant, stoichiometry of metal-ligand species being studied and the stability constant for each species (Buffle et al., 1990; Cancés et al., 2003)). This information is not available for the

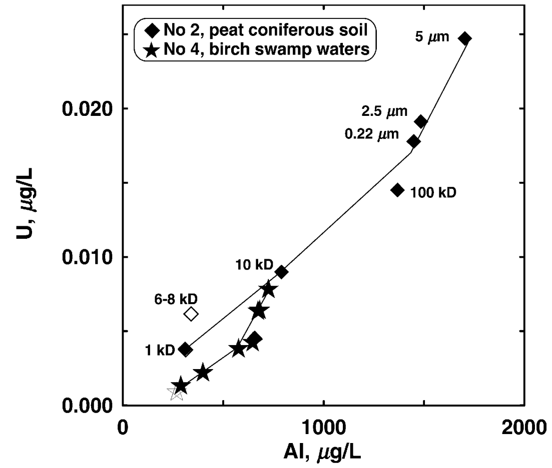

Figure 11. Uranium concentration in successive filtrates and dialysates of coniferous peat soil solution sand the birch peat swamp zone as a function of aluminum concentration.

humic and fulvic acids evaluated in this study. Therefore, we tried to approximate these elements speciation using the MINTEQA2 computer code (Allison et al., 1991) in conjunction with a database for binding of metals to discrete carboxylic sites (Allison and Perdue, 1994). This calculation has been performed assuming a constant content of 10 μeq COO^- per mg DOC (Oliver et al., 1983). Results of MINTEQA2 speciation calculations for Al, Fe, Ca, Mg, Cu, Zn, Ni, Cd, and Pb for three samples at pH of 3.9–4.75 are represented in Figure 12. The proportion of organic complexes increases in the order Mg $<$ Ca $\leq$ Ni $<$ Cd $\leq$ Zn $<$ Cu $\leq$ Pb $\leq$ Fe $\leq$ Al. This order is not compatible with the distribution of these elements as a function of colloid size between 1 kD and 0.22 μm, as inferred from our ultrafiltration/dialysis experiments. Moreover, the calculated proportion of organic complexes for 5 μm and 1 kD fractions of surface swamp horizon (No. 4) remains essentially the same (Figure 12b). This strongly suggests that thermodynamic modeling of TE complexation with carboxylic groups of OM, while possibly capable of predicting speciation in the <1 kD fraction, cannot alone describe TE distribution between different colloidal fractions. The impact of dissolved humic and fulvic acids on other trivalent and tetravalent elements is hard to assess because of the lack of data on stability constants. Results of the present study do not allow to rigorously distinguish between two possible colloidal pools, i.e., LMW organic colloids (<1–10 kD) and OM-stabilized Fe–Al hydroxides. Because the sorptive affinity of soil colloids for heavy metals is not the simple sum of those for single soil constituents (Cruz-Guzman et al., 2003), the use of polyphasic sorbent models is preferable.

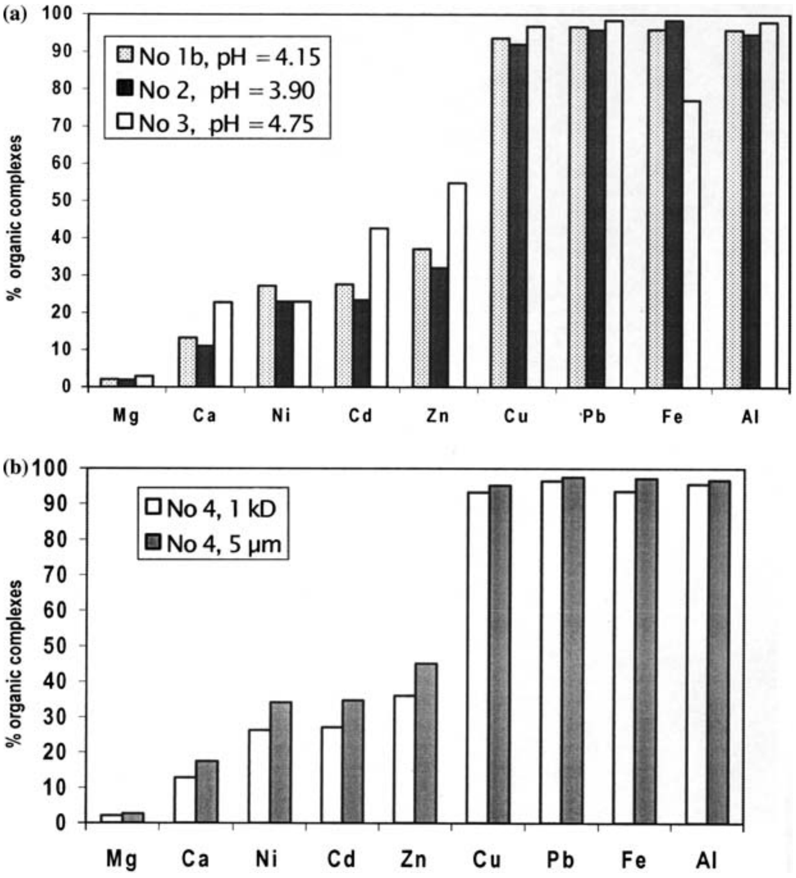

Figure 12. The calculated proportion of organic complexes for Al, Fe, Ca, Mg, Cu, Zn, Ni, Cd, and Pb for three samples in <0.22 μm fraction (a) and for 5 μm and 1 kD filter-passed fractions of surface swamp horizons (No. 4) (b).

3.8.2. Solubility constraints

At the pH values of soil solutions sampled in this study, the influence of aqueous and solid carbonate and hydroxycarbonates on cation solubility can be excluded; thus, metal hydroxides can potentially control the overall solubility of trace elements. In this discussion, we will consider only inorganic complexes of TE in aqueous solution.

The major constituents of inorganic colloids – Al and Fe – exhibit a <1 kD concentrations (see Appendix) much greater than the solubility of their solid phases: Al (gibbsite, 0.01–3 mg/L, Bénézeth et al., 1997), Fe (goethite, 0.06–0.6 μg/L, Baes and Mesmer, 1976). Therefore, dissolved concentrations of these elements are likely to be controlled by organic complexes. Si aqueous concentrations (1.3–2.6 mg/L) imply that this element is undersaturated with respect to quartz and clay minerals (kaolinite, montmorillonite); this is consistent with silica aqueous concentrations being independent on ultrafiltration procedure. Among trace elements, two groups can be distinguished. The first group includes those exhibiting <1 kD concentrations comparable or higher than the solubility of their solid (hydr)oxides at $4 \leq pH \leq 5$: Zr (ZrO_2, 0.001 μg/L, Baes and Mesmer, 1976), Hf (HfO_2, 0.02 μg/L, Rai et al., 2001), Th (ThO_2, 0.002 μg/L, Neck et al., 2003), Ga (α-GaOOH, 0.07 μg/L, Bénézeth et al., 1997), and Mn (MnO_2 or $MnOx \cdot nH_2O$, 0.1–0.5 mg/L, Pokrovsky and Savenko, 1995). The second group includes those elements present in concentrations of at least an order of magnitude lower than the solubilities of their (hydr)oxides: Ti (146 μg/L, Nabivanetz and Lukachina, 1964), REE (>0.1 M, Deberdt et al., 1998), Sb(III) (7.6 mg/L, Baes and Mesmer, 1976), Tl^{3+} (30 μg/L), Sn^{4+} (2000–20 μg/L), Ni, Co, Mn^{2+}, Cd, Zn, Pb, Cu, U^{6+} (>0.01 M), Cr(VI, III), V(V), As(III), Nb(V) (Baes and Mesmer, 1976). Although these element concentrations are not limited by any solid phase solubility, some of them (Ti, Y, REEs, Pb, Cd, Cu, Nb, U) are essentially controlled by large-size organo-mineral colloids while others (As, Ni, Co, Zn) are not (i.e., <30% is in >1 kD fraction). Overall, this thermodynamic analysis demonstrates the lack of direct solubility control on the colloidal status of TE.

3.8.3. TE distribution coefficients between aqueous solution and colloids

In order to distinguish between adsorption of TE on the surface of colloids and their incorporation in the bulk of these colloids (coprecipitation), we estimated the surface area of colloids in each filtrate following the method described in Pokrovsky and Schott (2002). The total surface of inorganic colloids in each (ultra) filter-passed fraction was deduced from the drop in Al (Nos 1–3) and Fe (No. 4) concentration, density of metal hydroxide ($\sim$2 g/cm^3) and the average pore size (3.7, 1.4, 0.05, 0.005, 0.002 and 0.001 μm for 2.5–5, 2.5–0.22 μm, 0.22 μm–100 kD, 100–10, 10–1 and 1 kD fractions, respectively). The overall uncertainties associated with these estimations range between 30 and 50%. Assuming that the surface sites concentration for iron or aluminum oxide is about 10 μmol/m^2 (Sverjensky and Sahai, 1996), the average concentration of available surface sites is 20 ± 10 μM among all samples studied which is more than an order of magnitude higher than the total TE concentration in soil solutions (i.e., $\sim$1 μM). This means that the overall surface area of colloids is sufficient to adsorb all trace elements. However, the number of surface sites in large-size colloids (> 10 kD) represents only 12 ± 5% of total available sites. This is not enough to accommodate all TE associated with these large-size colloids (Cd, Pb, Sn, Nb, U, Ga, REEs, Ti, Zr, Hf, Th). This demonstrates preferential incorporation of these TE in the bulk of large colloids via coprecipitation rather than their sorption on colloid surfaces.

It is known from surface coordination theory that metal–ion interaction with oxide surfaces is analogous to their complexation reactions (i.e., hydrolysis) in aqueous solution (Stumm, 1992). In Figure 13, the percentage of "dissolve" TE (present in the <1 kD fraction) is plotted as a function of the first hydrolysis constant for the TE, for two contrasting soil solutions issued from podzol and peat soils. For this correlation, five major (Na, Ca, Mg, Fe, Al) and 30 trace elements were considered. Biologically important elements (Cu, Zn) deviate from the correlation because they are unlikely to be associated with inert Fe–Al colloids but are rather present as LMW complexes of substantial strength. The generally positive correlation observed suggests that electron donors oxygen ligands ($>COO^-$, $>FeO^-$, $>AlO^-$) present on surfaces of organic and inorganic colloids, which are similar to OH^- ligands in aqueous solution, are likely to control TE distribution between aqueous and colloidal phases. This is further supported by comparison of K_d $(TE/Al)_{colloid,\ 0.22\ \mu m-1\ kD}/(TE/Al)_{dissolved,\ <1\ kD}$ values, calculated for all samples, with the first hydrolysis constant: a positive correlation ($r_{xy} = 0.7$) is observed suggesting important role of hydrolysis on TE coprecipitation with Fe–Al colloids. Analysis of K_d values for studied samples demonstrates that for trivalent and tetravalent elements most affected by colloids, the coefficient of distribution, which is equivalent to the coefficient of coprecipitation with major inorganic constituents (i.e., Al for No. 1–3 and Fe for No. 4), varies from 0.5 to 1–2. K_d values are the highest for Ti (2.3 ± 1.3), Zr and Hf (1.1 ± 0.5), Th and Nb (0.9 ± 0.4). Trivalent elements exhibit lower K_d values: 0.6 ± 0.4 for Ga and 0.38 ± 0.08 for Y.

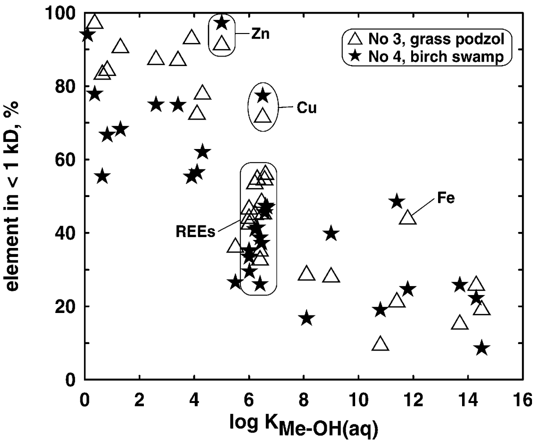

Figure 13. Correlation between the concentration of elements in the <1 kD fraction and their first hydrolysis constants taken from NIST database (Martell et al., 1997). Two contrasting solution samples, from the birch swamp zone and the grass podzol soil, are considered.

In the case of the REEs, K_d values decrease 2-fold from light to heavy elements (0.77 ± 0.15, 0.63 ± 0.12, 0.53 ± 0.10, 0.49 ± 0.08, 0.41 ± 0.08, 0.37 ± 0.08, and 0.30 ± 0.09 for La, Ce, Pr, Nd, Gd, Er, and Yb, respectively), reflecting a well-known tendency for LREE to adsorb onto and coprecipitate with metal oxides and for HREE to form stable complexes in solution. Noteworthy is the strong affinity of Pb and U (K_d equal to 0.70 ± 0.20 and 0.85 ± 0.45, respectively) for organo-mineral colloids. Overall, the range of TE coprecipitation coefficients inferred from our measurements is comparable with that reported for TE coprecipitation with $Fe(OH)_3$ during oxidation of Fe^{2+} under laboratory conditions (Savenko, 1995, 1999a, 1999b; Bau, 1999). A number of highly soluble elements (Mn, Co, Ni, Cu, Zn, Cd, As, Sb, Rb, Cs, Tl) exhibit only weak affinity to soil colloids partially because of the presence of strong LMW (<1 kD) organic complexes dominating the speciation of divalent transition metals, or due to weak interaction of neutral molecules (As, Sb) and low-charged inorganic ions with metal oxides or organic functional groups.

3.9. AFFINITY OF TE TO VARIOUS SIZE COLLOIDS AND MECHANISM OF COLLOIDS FORMATION

Most trace elements considered in the this study are associated with colloids whose major constituent elements, besides oxygen, are aluminum, iron and organic carbon. Unfortunately, conventional macroscopic size separation techniques do not allow the rigorous distinction between mineral and organic parts of colloids (1 kD–0.22 μm). Concentrations of $\sim$30 trace elements decrease upon ultrafiltration/dialysis from 5 μm to 1000 Da, being well correlated with those of Al, Fe, or OC in filtrates and ultrafiltrates. Furthermore, concentrations of many of these elements (Cd, Pb, Ga, REEs, Ti, Zr, Hf, Th, U, V, Sn, Nb) are proportional to that of Al (considered as an index of colloid abundance). In accord with Dupré et al. (1999) and Gaillardet et al. (2003), this suggests that the scavenging capacity of Fe–Al–organic colloids is independent on their size.

Only those trace elements that exhibit important biogeochemical recycling via plants, roots and soil bacteria (Mn, Zn, Cu and, to a lesser extent, Ni and Co) are not associated with large-size colloids (>10 kD). After the degradation of forest litter, these biogenic elements can percolate downwards through the soil profile in the form of soluble LMW organic complexes, specifically fulvic acid-type constituents (see Stevenson and Fitch (1986) for review). Other trace elements whose biological role is not significant or unknown (Cd, Pb, Ga, Y, REE, Ti, Zr, Hf, Th, Sn, Nb, V, U) are likely to be associated with Al and Fe oxy(hydr)oxides during their migration in organic-rich upper soil horizons. A downward leaching migration of Al-/Fe-rich organic colloids, well documented in Arctic spodosols (Ugolini et al., 1987;

Stoner and Ugolini, 1988) and recently identified in tropical rainforest ecosystems (Lorieri and Elsenbeer, 1997), is likely to enhance the transport of usually immobile trace elements considered in the present study. In many temperate and boreal rivers draining organic-rich wetlands, strong correlation between DOC, water discharge and trace element concentration is observed (Sherrell and Ross, 1999; Olivimé-Lauquet et al., 2001; Rember and Trefry, 2004). These trends support the idea that the transport of DOC and trace metals is controlled by the discharge of soil interstitial waters and shallow surface swamps reservoirs (Viers et al., 2000; Olivié-Lauquet et al., 2001; Rember and Trefry, 2004). The important Fe–Al–organic colloidal pool of trace elements present in peat soils investigated in this study is therefore likely to contribute significantly to the formation of dissolved load of peatland-draining rivers.

4. Conclusions

Organic-rich peatland soil solutions and surface waters from the Tverskaya region (Russia) exhibit low pH values (~4) and high concentration of dissolved Al, Fe, Mn and a number of commonly insoluble trace elements (Ti, Ga, Zr, Hf, Y, REEs, Th). These trace elements can be carried as mixed organic/Fe/Al oxy(hydr)oxides colloids. Concentrations of major cations and anions, silica and some trace elements (Mn, Zn, As, Rb) are little-affected during filtration-ultrafiltration (5 μm to 1 kD) and dialysis (1 and 6–8 kD) experiments. These elements are largely present as true dissolved species in the soil solutions described here. Speciation of other ~ 30 traces (V, Ni, Co, Sr, Ba, Cd, Pb, Sn, Nb, U, trivalent (Ga, Y, REEs) and tetravalent (Ti, Zr, Hf, Th) elements) is essentially controlled by organo-mineral colloids (>1–10 kD). The total surface sites concentration of colloids (10–20 μM) is high enough to accommodate the micromolar concentrations of available TE. However, only 10–15% of total surface sites are concentrated in the >10 kD colloids fraction which accommodates more than 50% of all dissolved trace elements. This suggests that incorporation of TE in the bulk of Fe–Al–organic humus colloids formed on redox fronts rather than surface adsorption on these colloids controls the downward transport in soil solution of TE released during degradation of forest litters in surface horizons.

Acknowledgements

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Appendix

All concentrations are in μg/L.

	No.1a							
	5 μm	2.5 μm	0.22 μm	100 kD	10 kD	5 kD	1 kD	6–8 kD
pH	ND	ND	4.66	4.66	4.68	ND	4.71	ND
Cl	ND	ND	820	ND	ND	ND	830	ND
NO_3	ND	ND	470	ND	ND	ND	450	ND
SO_4	ND	ND	4880	ND	ND	ND	4920	ND
Si	3340	3360	3320	3330	3320	3410	3330	3250
Na	645	660	636	ND	ND	686	598	ND
K	4480	4390	4410	ND	ND	4120	4020	ND
Mg	1090	1048	1030	1040	940	790	710	759
Ca	3810	3790	3660	3750	3350	2600	2430	2700
DOC	65,000	54,000	52,000	50,000	45,300	35,000	29,500	29,000
Al	2120	1955	1799	1787	1443	1108	306	281
Ti	15.0	12.5	11.2	10.7	5.72	3.01	1.94	1.49
V	6.37	6.08	6.29	6.02	5.35	4.15	3.75	ND
Cr	1.56	1.62	1.47	1.52	1.40	1.19	0.92	0.90
Mn	99	96	93	93	86	71	62	68
Fe	589	527	471	460	303	198	113	67
Co	0.694	0.651	0.624	0.604	0.541	0.462	0.405	0.362
Ni	1.89	1.90	1.95	1.73	1.72	1.45	1.01	1.11
Cu	3.74	3.81	3.62	3.36	2.87	Contam	1.99	1.81
Zn	30.1	27.4	27.6	27.4	25.6	24.1	22.9	18.6
Ga	0.15	0.13	0.13	0.12	0.09	0.08	0.05	0.055
As	3.79	3.78	3.66	3.62	3.61	3.33	3.38	3.65
Rb	9.78	9.47	9.89	9.50	9.15	8.68	8.45	8.75
Sr	16.8	16.5	16.8	15.9	13.8	10.7	11.0	11.2
Y	0.401	0.359	0.354	0.313	0.225	0.175	0.133	0.106
Zr	0.880	0.795	0.761	0.714	0.524	0.321	0.198	0.124
Nb	0.148	0.128	0.129	0.113	0.075	0.045	0.038	0.025
Cd	0.170	0.170	0.156	0.146	0.102	Contam	0.075	0.087
Sn	0.051	0.053	0.050	0.048	0.041	0.031	0.022	0.0285
Sb	0.360	0.349	0.370	0.336	0.340	0.312	0.289	0.315
Cs	0.039	0.035	0.034	0.031	0.029	0.027	0.027	0.029
Ba	23.8	21.8	21.7	20.6	16.1	14.0	10.5	12.0
La	0.453	0.399	0.370	0.327	0.194	0.159	0.088	0.100
Ce	0.991	0.864	0.821	0.739	0.448	0.352	0.213	0.216
Pr	0.122	0.110	0.099	0.092	0.056	0.046	0.029	0.029
Nd	0.477	0.433	0.410	0.374	0.251	0.202	0.126	0.118
Sm	0.101	0.086	0.089	0.074	0.056	0.042	0.025	0.022

	5 μm	2.5 μm	0.22 μm	100 kD	10 kD	5 kD	1 kD	6–8 kD
Eu	0.025	0.036	0.023	0.020	0.011	0.007	0.010	0.010
Gd	0.100	0.087	0.082	0.070	0.045	0.039	0.029	0.021
Tb	0.016	0.013	0.014	0.010	0.008	0.005	0.004	0.003
Dy	0.079	0.067	0.069	0.061	0.043	0.033	0.023	0.019
Ho	0.016	0.014	0.015	0.012	0.008	0.006	0.005	0.004
Er	0.045	0.040	0.039	0.036	0.025	0.020	0.016	0.015
Tm	0.007	0.006	0.005	0.005	0.004	0.003	0.002	0.002
Yb	0.040	0.038	0.034	0.035	0.025	0.019	0.017	0.012
Lu	0.008	0.006	0.007	0.005	0.004	0.003	0.003	0.003
Hf	0.02	0.02	0.02	0.02	0.02	0.01	0.00	0.00
Tl	0.042	0.038	0.040	0.034	0.034	0.031	0.030	0.029
Pb	1.25	1.10	0.99	0.90	0.51	Contam	0.20	0.33
Th	0.070	0.068	0.065	0.065	0.052	0.036	0.019	0.008
U	0.025	0.022	0.019	0.017	0.012	0.006	0.005	0.003

	No. 1b				
	0.22 μm	100 kD	10 kD	5 kD	1 kD
pH	4.16	ND	4.15	ND	ND
Cl	1690	ND	ND	ND	ND
SO_4	5410	ND	ND	ND	ND
Na	780	ND	ND	ND	745
K	2990	ND	ND	ND	2720
Mg	875	876	751	645	661
Ca	2950	2990	2820	2300	2110
DOC	44,300	42,500	42,100	27,700	26,300
Al	1672	1649	1381	1013	270
Si	2580	2580	2550	2600	2470
Ti	10.4	10.4	6.5	3.1	1.8
V	4.87	4.78	4.29	3.23	2.58
Cr	1.57	1.51	1.37	1.16	1.02
Mn	63	61	58	49	44
Fe	326	311	229	143	99
Co	0.485	0.477	0.459	0.368	0.344
Ni	1.25	1.20	0.99	1.06	1.02
Cu	2.96	2.61	2.76	2.14	2.21
Zn	28.3	25.1	26.3	24.5	23.3
Ga	0.124	0.126	0.095	0.070	0.050
As	2.86	2.73	2.57	2.56	2.45
Rb	8.04	8.03	7.97	7.65	7.35

	0.22 μm	100 kD	10 kD	5 kD	1 kD
Sr	13.2	13.2	12.0	9.8	9.7
Y	0.262	0.257	0.203	0.141	0.104
Zr	0.562	0.574	0.473	0.257	0.134
Nb	0.203	0.154	0.107	0.054	0.044
Cd	0.071	0.064	0.062	0.052	0.045
Sn	0.056	0.053	0.044	0.039	0.033
Sb	0.177	0.169	0.162	0.149	0.127
Cs	0.042	0.034	0.033	0.034	0.030
Ba	19.8	19.1	17.4	13.7	11.8
La	0.268	0.250	0.160	0.123	0.065
Ce	0.579	0.571	0.387	0.286	0.160
Pr	0.078	0.076	0.051	0.039	0.026
Nd	0.304	0.290	0.211	0.158	0.103
Sm	0.068	0.063	0.047	0.033	0.024
Eu	0.020	0.019	0.011	0.015	0.007
Gd	0.061	0.063	0.044	0.035	0.023
Tb	0.013	0.009	0.007	0.005	0.006
Dy	0.057	0.052	0.037	0.026	0.022
Ho	0.015	0.011	0.007	0.005	0.007
Er	0.033	0.028	0.024	0.017	0.014
Tm	0.010	0.004	0.004	0.005	0.005
Yb	0.033	0.026	0.022	0.018	0.017
Lu	0.011	0.004	0.004	0.003	0.005
Hf	0.021	0.016	0.013	0.007	0.006
Tl	0.040	0.036	0.031	0.030	0.029
Th	0.062	0.056	0.046	0.032	0.013
U	0.018	0.013	0.010	0.006	0.007

No. 2

	5 μm	2.5 μm	0.22 μm	100 kD	10 kD	5 kD	1 kD UF	6–8 kD	1 kD dialysis
pH	3.95	ND	3.90	ND	ND	ND	3.95	ND	3.92
Cl	ND	ND	1260	ND	ND	ND	ND	ND	ND
SO_4	ND	ND	6230	ND	ND	ND	ND	ND	ND
Si	2140	2100	2090	2100	2100	2120	2050	2360	ND
Na	ND	727	ND	ND	ND	ND	683	ND	ND
K	ND	1220	ND	ND	ND	ND	1125	ND	ND
Mg	698	694	700	696	703	587	520	484	419
Ca	2850	2770	2780	2800	2740	2160	1970	1880	1580
DOC	65,000	50,300	50,200	51,700	44,700	22,000	23,600	21,900	20,100

	5 μm	2.5 μm	0.22 μm	100 kD	10 kD	5 kD	1 kD UF	6–8 kD	1 kD dialysis
Li	1.70	1.56	1.53	1.38	1.42	1.62	1.32	1.28	ND
Al	1705	1484	1449	1368	789	656	309	339	312
Ti	46.1	27.3	26.2	23.8	16.5	7.0	1.62	2.58	2.87
V	6.07	5.45	5.29	5.08	4.20	3.75	2.23	2.84	2.45
Mn	48	48	50	51	50	46	37	33	37
Fe	545	505	490	461	453	337	213	148	291
Co	0.565	0.559	0.523	0.512	0.498	0.348	0.332	0.397	0.326
Ni	0.896	0.905	0.902	0.859	0.830	0.749	0.518	0.772	0.555
Cu	1.42	1.16	1.10	1.03	1.07	0.98	1.05	0.97	0.87
Zn	31.5	23.7	24.7	25.8	23.5	22.5	22.9	22.4	24.8
Ga	0.264	0.188	0.166	0.161	0.141	0.122	0.046	0.066	0.051
As	1.19	1.19	1.10	1.08	0.95	0.89	0.73	ND	0.79
Rb	7.62	7.28	7.18	7.15	7.09	6.87	6.31	6.47	ND
Sr	19.4	19.0	19.0	19.4	18.4	12.8	13.1	12.6	11.7
Y	0.335	0.200	0.186	0.181	0.157	0.112	0.066	0.087	0.082
Zr	0.913	0.592	0.568	0.568	0.459	0.271	0.069	0.121	0.087
Nb	0.231	0.179	0.137	0.117	0.095	0.035	0.020	0.046	0.017
Cd	0.109	0.115	0.102	0.084	0.078	ND	0.067	0.065	ND
Sn	0.096	0.093	0.085	0.079	0.060	ND	0.026	0.042	ND
Sb	0.264	0.182	0.167	0.159	0.125	ND	0.101	0.088	0.075
Cs	0.126	0.106	0.101	0.101	0.099	ND	0.082	0.079	ND
Ba	32.9	29.7	29.7	29.3	27.9	18.6	18.5	17.8	16.6
La	0.266	0.191	0.168	0.158	0.131	0.086	0.036	0.062	0.113
Ce	0.562	0.424	0.385	0.357	0.310	0.206	0.101	0.151	0.151
Pr	0.079	0.064	0.051	0.050	0.041	0.027	0.016	0.020	0.022
Nd	0.314	0.229	0.199	0.193	0.168	0.121	0.066	0.081	0.092
Sm	0.067	0.061	0.044	0.048	0.035	0.027	0.021	0.015	0.022
Eu	0.016	0.019	0.008	0.011	0.008	0.006	ND	0.007	ND
Gd	0.055	0.051	0.041	0.041	0.031	0.029	0.015	0.013	ND
Tb	0.010	0.016	0.006	0.006	0.005	0.003	0.002	0.003	ND
Dy	0.052	0.046	0.035	0.032	0.031	0.022	0.010	0.015	ND
Ho	0.011	0.016	0.007	0.007	0.005	0.004	0.002	0.003	ND
Er	0.032	0.031	0.018	0.018	0.016	0.012	0.007	0.010	ND
Yb	0.031	0.030	0.019	0.019	0.016	0.012	0.009	0.010	0.014
Lu	ND	ND	0.003	0.003	0.003	0.002	0.002	0.001	ND
Hf	0.036	0.031	0.025	0.023	0.014	0.015	0.005	0.010	0.003
Tl	0.050	0.051	0.041	0.040	0.039	0.037	0.032	ND	ND
Pb	0.885	0.862	0.868	0.816	0.600	0.479	0.398	ND	0.380
Th	0.089	0.036	0.037	0.026	0.014	0.004	<0.001	<0.001	0.008
U	0.025	0.019	0.018	0.015	0.009	0.005	0.004	0.006	0.004

	No. 3			
	0.22 μm	10 kD	1 kD	6–8 kD
pH	4.72	ND	4.75	4.76
Cl	490	ND	520	ND
SO_4	9920	ND	9550	ND
Si	1350	ND	1360	ND
Na	350	ND	ND	ND
K	1390	ND	ND	ND
Mg	971	951	853	870
Ca	3960	4050	3607	3750
DOC	38,600	26,000	20,000	23,000
Li	2.32	2.40	2.27	2.17
Al	1198	1142	343	494
Ti	7.4	5.6	1.5	3.5
V	6.73	6.60	5.56	6.07
Cr	0.71	0.67	0.36	0.44
Mn	167	169	146	157
Fe	330	291	147	172
Co	0.56	0.51	0.44	0.46
Ni	0.80	0.76	0.58	0.59
Cu	2.09	2.08	1.51	0.90
Zn	18.6	17.3	17.1	13.0
Ga	0.020	0.015	0.004	0.010
As	0.803	0.762	0.678	0.693
Rb	3.03	3.01	2.80	2.78
Sr	22.7	21.9	19.2	20.6
Y	0.311	0.298	0.172	0.203
Zr	0.806	0.753	0.213	0.321
Cd	0.034	0.032	0.032	0.024
Sn	0.009	0.007	0.003	0.003
Sb	0.313	0.308	0.315	0.303
Cs	0.006	0.005	0.005	0.005
Ba	31.0	31.2	26.0	28.8
La	0.258	0.223	0.095	0.165
Ce	0.696	0.618	0.299	0.446
Pr	0.091	0.077	0.041	0.061
Nd	0.384	0.343	0.181	0.248
Sm	0.082	0.080	0.037	0.057
Eu	0.021	0.009	0.008	0.010
Gd	0.074	0.060	0.040	0.044

	0.22 μm	10 kD	1 kD	6–8 kD
Tb	0.012	0.009	0.004	0.007
Dy	0.060	0.055	0.029	0.037
Ho	0.014	0.011	0.006	0.007
Er	0.033	0.033	0.018	0.021
Tm	0.007	0.003	0.002	0.002
Yb	0.038	0.033	0.021	0.023
Lu	0.005	0.004	0.002	0.002
Hf	0.027	0.022	0.004	0.016
Tl	0.005	0.003	0.001	0.002
Pb	0.276	0.241	0.092	0.157
Th	0.135	0.122	0.000	0.015
U	0.012	0.010	0.004	0.007

	No. 4							
	5 μm	2.5 μm	0.22 μm	100 kD	10 kD	6–8 kD	5 kD	1 kD
PH	4.14	ND	4.16	4.15	ND	ND	ND	4.20
Cl	ND	ND	3670	3850	ND	ND	ND	3720
SO_4	ND	ND	6180	6130	ND	ND	ND	5910
Si	1850	1830	1840	1840	1830	ND	1890	1730
Na	2000	1960	1960	ND	ND	ND	ND	1850
K	3190	3100	3170	ND	ND	ND	ND	2840
Mg	1390	1340	1360	1340	1300	1040	1110	1040
Ca	3840	3720	3560	3560	3440	3536	3176	2620
DOC	59,300	57,600	56,900	55,100	51,800	ND	ND	31,000
Li	2.57	2.50	2.26	2.23	2.09	1.75	2.38	2.00
Al	725	672	681	646	576	268	399	288
Ti	4.56	4.22	3.87	3.04	2.11	0.385	0.933	0.391
V	1.92	1.81	1.79	1.76	1.66	1.20	1.16	1.09
Cr	1.23	ND	ND	ND	ND	ND	ND	0.668
Mn	869	871	863	864	818	661	765	650
Fe	1554	1456	1327	1288	1000	429	833	383
Co	1.72	1.66	1.66	1.63	1.53	1.15	1.25	1.07
Ni	3.85	3.78	3.69	3.56	3.56	2.25	2.68	2.17
Cu	1.74	1.75	1.67	1.71	1.71	1.46	1.37	1.34
Zn	41.3	39.5	38.6	41.9	43.3	35.4	32.6	40.2
Ga	0.113	0.103	0.099	0.090	0.084	0.042	0.060	0.055
As	1.72	1.66	1.71	1.65	1.62	1.29	1.40	1.28
Rb	12.1	11.6	11.9	11.7	11.4	10.7	10.6	10.7

	5 μm	2.5 μm	0.22 μm	100 kD	10 kD	6–8 kD	5 kD	1 kD
Sr	22.3	21.7	20.6	20.7	19.6	15.5	17.2	14.9
Y	0.427	0.396	0.387	0.362	0.319	0.178	0.233	0.177
Zr	0.852	0.757	0.753	0.708	0.593	0.188	0.327	0.189
Cd	0.153	0.136	0.135	0.128	0.116	0.096	0.107	0.085
Sn	0.041	0.036	0.037	0.037	0.028	0.015	ND	0.008
Sb	0.135	0.124	0.135	0.133	0.118	0.091	ND	0.090
Cs	0.058	0.054	0.060	0.054	0.051	0.050	0.050	0.047
Ba	29.2	27.8	25.7	24.6	23.3	19.0	21.0	16.2
La	0.197	0.182	0.165	0.151	0.119	0.056	0.085	0.052
Ce	0.620	0.580	0.536	0.501	0.404	0.200	0.296	0.183
Pr	0.084	0.077	0.075	0.068	0.056	0.029	0.042	0.028
Nd	0.347	0.332	0.306	0.293	0.247	0.125	0.180	0.122
Sm	0.076	0.074	0.076	0.064	0.053	0.028	0.030	ND
Eu	0.016	0.015	0.019	0.021	0.016	0.009	0.013	0.017
Gd	0.077	0.070	0.072	0.064	0.054	0.032	0.037	0.032
Tb	0.012	0.010	0.015	0.009	0.008	0.004	0.005	0.004
Dy	0.067	0.059	0.064	0.056	0.050	0.025	0.037	0.025
Ho	0.015	0.013	0.018	0.013	0.010	0.006	0.007	0.005
Er	0.043	0.039	0.043	0.035	0.033	0.017	0.024	0.019
Tm	0.007	0.005	0.005	0.005	0.005	0.002	0.004	0.003
Yb	0.041	0.038	0.041	0.037	0.032	0.019	0.024	0.020
Lu	0.007	0.006	0.006	0.006	0.004	0.003	0.003	0.003
Hf	0.059	0.056	0.057	0.045	0.034	0.019	ND	0.015
Pb	0.777	0.771	0.579	0.579	0.452	0.215	0.294	0.202
Th	0.102	0.091	0.091	0.079	0.066	0.021	0.045	0.019
U	0.008	0.006	0.006	0.004	0.004	0.001	0.002	0.001

ND = non-determined; Contam = contaminated.

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