

Size Fractionation of Trace Elements in a Seasonally Stratified Boreal Lake: Control of Organic Matter and Iron Colloids

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Abstract The colloidal distribution and size fractionation of organic carbon and trace elements were studied in a seasonally stratified, organic-rich boreal lake, Lake Maselga, located in the European subarctic zone (NW Russia, Arkhangelsk region). This study took place over the course of 5 years in winter (glacial) and summer periods and during the spring and autumn overturn. A newly developed in situ dialysis technique (1, 10, and 50 kDa) and traditional frontal filtration and ultrafiltration (20, 10, 5, 0.22, and 0.025 μm) were used to assess element concentrations at different depths. No significant changes in element concentrations occurred during filtration through sub-colloidal pore-size membranes (20–0.22 μm), suggesting a negligible amount of particulate Fe, OC, and associated trace metals. Large colloids (0.025–0.22 μm) were found to be the main carriers of poorly soluble elements (Fe, Al, Ti, Zr, REEs, Th, and U) during the summer and winter stratification. There was also a clear change in the vertical pattern of the percentage of colloidal Al, Ti, V, Cr, Fe, and Ni during different seasons, and the greatest proportion of colloidal forms was observed during the spring and autumn overturn. This pattern is most likely linked to the dominance of soil (allochthonous) organic carbon, which complexes with trace metals during these periods. During the summer seasons, autochthonous production of small exometabolites or photodegradation increases the concentration of the low-molecular weight fractions (<1 kDa) that dominate the speciation of divalent heavy metals

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in surface horizons. The colloidal status of As (30–60%), which was documented in different seasons along the full depth of the water column, is most likely linked to the presence of organic complexes. The overall results of this study suggest that changes in the colloidal speciation of trace elements with depth in different seasons depend on changes in the redox conditions, the input of soil OM, the biodegradation of plankton biomass releasing dissolved organic matter in the bottom horizons, and in upward diffusion from the sediments.

Keywords Trace element · Carbon · Lake · Boreal · Speciation · Colloids

1 Introduction

Lakes in boreal zones regulate the fate of dissolved carbon, nutrients, and trace metals during their transport from the watershed to the ocean. However, knowledge of the seasonal variations in the concentration, size fractionation, and speciation of trace elements (TEs) in stratified boreal lakes remains rather limited. This lack is particularly true for the Baltic and White Sea basin, which possesses high lake coverage. Small lakes (<1–10 km²), which are very abundant in this territory, are especially important in the biogeochemical cycle of carbon and related elements.

Until now, detailed biogeochemical studies of TEs in seasonally stratified lakes were restricted to temperate zones with rather limited numbers of TEs, such as Al, Fe, Mn, Cu, Zn, Co, Ni, Cr, Mo, Ti, Pb, and Ba (Hamilton-Taylor et al. 1996, 2005; Achterberg et al. 1997), whereas significant efforts have been devoted to the biogeochemistry of organic carbon (OC), nutrients, and some TEs in Scandinavian (Tranvik et al. 2009; Kortelainen et al. 2006) and Canadian (Johannesson and Lyons 1995; Alfaro-De la Torre et al. 2000; Gibson et al. 2002; Laurion et al. 2010) lakes. In contrast to the fairly detailed studies of TE speciation and migration in rivers and soil solutions in the NW Russian boreal zone (Pokrovsky and Schott 2002; Pokrovsky et al. 2005, 2006, 2010; Vasyukova et al. 2010), the lakes in this zone have received much less attention, and only occasional, explorative studies of total dissolved TE concentrations in surface horizons are currently available (e.g., Moiseenko and Gashkina 2007).

To gain a better understanding of the biogeochemical mechanisms that control the distribution of dissolved, particulate, and colloidal OC and TEs in surface boreal waters, we studied one seasonally stratified lake in the Arkhangelsk region (NW Russia, White Sea basin) from 2007 to 2011. For these studies, we used a dialysis technique that allows for the in situ sampling of dissolved, low-molecular weight (LMW) organic matter (OM), and TEs over the entire water column. Dialysis probes have occasionally been used before, notably for porewater sampling (e.g., Kepkay 1985; Burdige and Kepkay 1983; Carignan et al. 1985), under estuarine conditions (Hamilton-Taylor et al. 2002), in the anoxic zone of a meromictic lake (Albéric et al. 2000), and in an acid bog lake (Koenings 1976). Dialysis was also used in comparison with other techniques for trace metal speciation in organic-poor lakes (Gimpel et al. 2003) and for thermodynamic modeling (Lead et al. 1998; Lofts et al. 2008). In this work, in situ dialysis allowed for high-resolution TE sampling along the water column in a typical boreal organic-rich lake during different seasons.

Our systematic, multi-annual study of the total dissolved and colloidal concentrations OC and TEs as a function of water column depth addressed the following specific questions to help improve our knowledge of OC and TE biogeochemistry in small stratified boreal lakes: (1) How variable is the vertical profile of dissolved (<0.22 μm) TEs during

different seasons over several years? (2) What is the size distribution of OC, Fe, and TEs from 20 μm to 1 kDa over the entire depth of the column? (3) Can we distinguish between the control exerted by Fe-rich and OM-rich particles and the control by colloids on TE behavior? And (4) Does the proportion of colloidal fractions of different elements and the chemical nature of colloids vary among different seasons (summer and winter stagnation and spring/autumn overturn)? We anticipate that answering these questions should provide the first-order features of TE concentration and size fractionation in the still poorly studied boreal lakes of NW Russia. This information, in turn, should create a solid experimental basis for the quantitative modeling of element distribution and transport fluxes between the water column and sediments and should aid in understanding the changes of element speciation and bioavailability in the context of redox stratification in summer and winter.

2 Materials and Methods

2.1 Site Description

Lake Maselga, located in the southern part of NW Russia (Arkhangelsk region, pristine zone of Kenezersky National Park), has a surface area of 3.44 km^2 , an average depth of 2.9 m, a maximum depth of 20.5 m, and a volume of 0.01 km^3 (Fig. 1). The lake is situated in a granitic moraine lithologic environment over Permian limestone in a southern taiga zone. The taiga zone has an average annual temperature of 1°C and average annual precipitation of 700–750 mm. The chemical composition of the lake water is dominated by $\text{Ca}(\text{HCO}_3)_2$, with typical mineralizations of 50–80 mg/L and with 1.5–2.0 mg/L of sulfate, 0.4–0.5 mg/L of chloride, 7–15 mg/L of dissolved organic carbon, and a pH ranging from 7 to 7.5 in the epilimnion to 6–6.5 in the hypolimnion. The lake is mesotrophic with typical values of primary productions in the photic zone ranging from 7 to 40 $\text{mg C m}^{-3} \text{d}^{-1}$; the organic matter aerobic mineralization rate ranges from 10 to 300 $\text{mg C m}^{-3} \text{d}^{-1}$ (Shirokova et al. 2009b).

At the deepest monitoring point, the lake exhibits distinct seasonal and chemical stratification of temperature and oxygen depth profiles, as illustrated in Fig. 2a and b, respectively. In comparison with other temperate or subarctic lakes, Lake Maselga exhibits two main periods of pronounced stratification (December to April and June to October) and two periods of lake overturn (November and May). The typical ice thickness at the end of winter based on our 5-year period of observation is 70 ± 30 cm. The maximum winter stratification is achieved in March, and the highest water temperature typically occurs in July.

2.2 Sampling, Size Fractionation Procedure, and Analysis

The sampling, filtration, dialysis, and chemical analysis techniques used in this study are similar to those reported in our previous studies (Vasyukova et al. 2010; Pokrovsky et al. 2011). Ultraclean sampling and handling procedures were used throughout all work in the field (Shirokova et al. 2010). Water samples were taken from a PVC boat (summertime) or from the ice cover (wintertime) in the deepest part of the lake using a precleaned, polycarbonate horizontal water sampler (Aquatic Research Co). The hypolimnion samples at the 20 m depth were collected using submersible sediment column sampler (Aquatic Research Co) that was deployed from the lake surface allowing to retrieve an undisturbed sediment column with ~ 20 cm overlaying water. The water samples were then

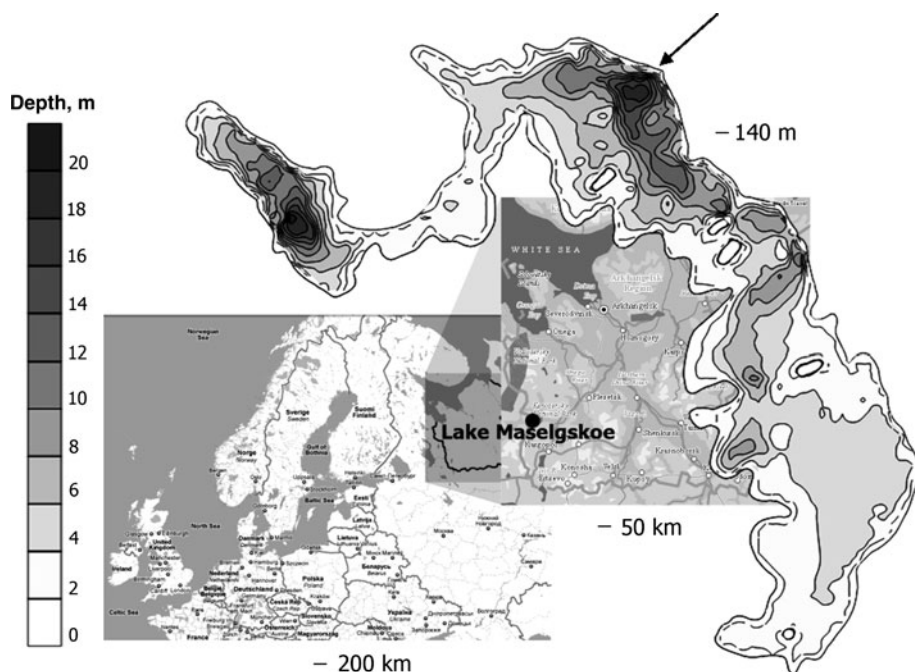


Fig. 1 Schematic map of the studied area and bathymetric map of the Lake Maselga. The deepest (monitoring) station is marked by *arrow*

immediately filtered in parallel through sterile, single-use Minisart[®] filter units (Sartorius, acetate cellulose filter) with pore sizes of 20, 10, 5, 0.22 (or 0.45), and 0.025 μm . The amount of dissolved oxygen and the temperature was measured in situ using a WTW oximeter Oxi 197i with a Cellox 325 submersible sensor ($\pm 5\%$ and $\pm 0.2^\circ\text{C}$ uncertainty, respectively).

Filtered and dialyzed samples were kept at 4–5°C in the dark before analysis. Concentrations of DOC, Cl, SO_4 , cations and TEs, and alkalinity were measured using routine methods in our laboratory for the analysis of boreal water samples (Vasyukova et al. 2010; Pokrovsky et al. 2010, 2011). Dissolved inorganic carbon (DIC) concentrations were obtained from alkalinity following a standard HCl titration procedure using an automatic Schott TitroLine alpha TA10^{plus} titrator with an uncertainty of $\pm 2\%$ and a detection limit of 5×10^{-5} M. DOC was measured using a Shimadzu TOC 6000 with an uncertainty of 5%. TEs were measured using inductively coupled plasma-mass spectrometry (ICP-MS, Agilent 7500) with indium and rhenium as internal standards and a precision better than $\pm 5\%$. 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 each analysis. A good agreement was obtained between our replicated measurements of SLRS-4 and the certified values (relative difference $< 10\%$).

Dissolved divalent iron was measured spectrophotometrically after sample acidification with HCl using phenanthroline. The detection limit was 10 $\mu\text{g/L}$, and the uncertainty was 5%. A number of samples were also analyzed for Fe^{2+} using ferrozine (Viollier et al. 2000); the agreement between the two methods was better than 15%.

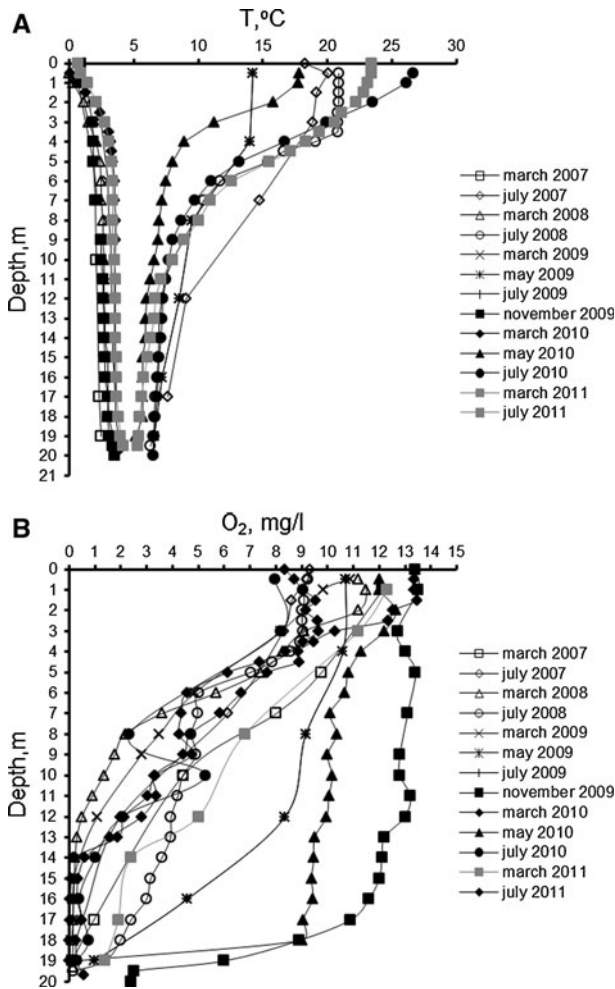


Fig. 2 Temperature (A) and oxygen concentration (B) profiles in Lake Maselga during different seasons

In situ dialysis experiments were performed using 20–50 ml precleaned dialysis bags that were placed directly in the lake water in March 2008 and 2009, July 2008 and 2009, and in May and November of 2009. The duration of this dialysis procedure was between 72 and 96 h. The exposure time was selected based on kinetic experiments on the dialysis equilibrium attainment for DOC, Si, and trace metals (Pokrovsky et al. 2011). The scheme of the dialysis experiment is shown in Fig. 3 with an insert of the kinetics of equilibrium distribution achievement. For the dialysis experiments, EDTA-cleaned, trace-metal pure SpectraPor 7[®] dialysis membranes made of regenerated cellulose and having pore sizes of 50, 10, and 1 kDa were thoroughly washed in 0.1 M double-distilled HNO₃. The membranes were then washed with ultrapure water, filled with ultrapure MilliQ deionized water, and then placed into natural water. The efficiency of the dialysis procedure was evaluated by comparing major anion and cation concentrations (e.g., Cl⁻, SO₄²⁻, Na⁺, K⁺, and Rb⁺) or neutral species (H₄SiO₄⁰) not associated with colloids between the dialysis bag and the external solution. Within ±10% variation, these concentrations were always

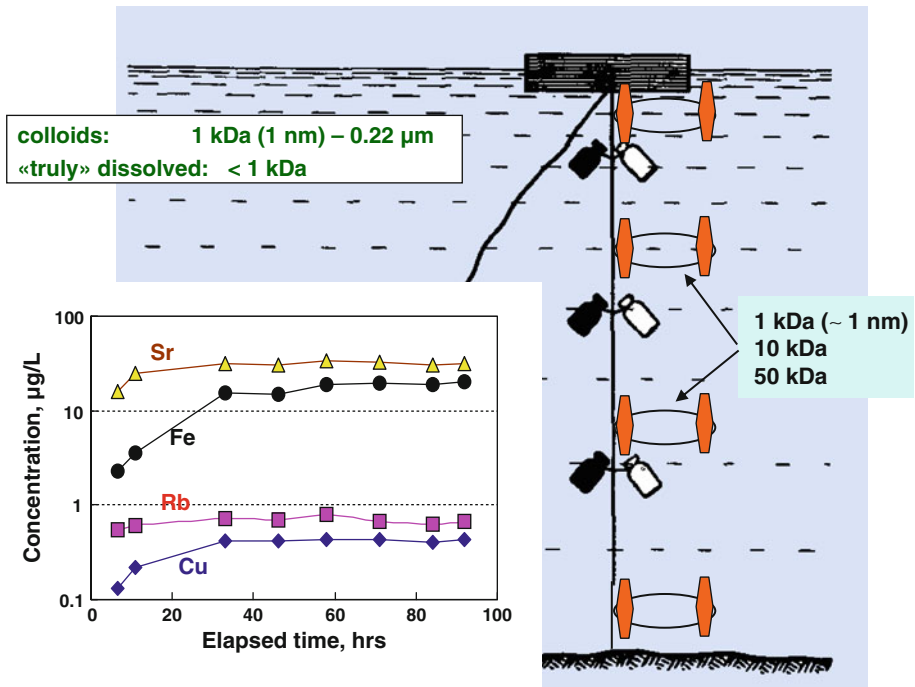
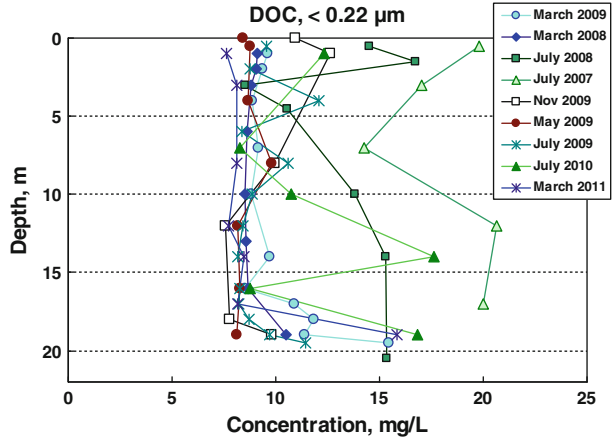


Fig. 3 Conceptual scheme of experimental in situ dialysis and kinetic plots of element concentrations (*log scale*) that have passed through a 1-kDa dialysis membrane as a function of time. In this experimental setup, the dialysis probes can be used together with dark/light bottles for measuring primary productivity/respiration

identical, suggesting an equilibrium distribution of dissolved components. The crucial requirements for successful dialysis separation are (i) a high external solution/dialysate ratio and (ii) constant concentration of dissolved and colloidal components in the external solution over the entire dialysis procedure. The first condition was fully met during the in situ dialysis procedure since the ratio of the internal compartment to the external reservoir is infinity. The second condition was met for most experiments described here, as corroborated by the analysis of OC, major, and trace elements in $<0.45 \mu\text{m}$ filtrate of the lake water from a given depth before and after dialysis. The concentrations remained constant to within $\pm 10\%$ for OC and major elements including Fe and $\pm 10\text{--}20\%$ for trace metals.

To assess the mass balance during the dialysis procedure, concentrations of major elements, TEs, and OC were measured in the external solution and the internal compartments and compared using $<0.45 \mu\text{m}$ filtrates. In all cases, a recovery of 95% or more was achieved for major elements, OC, Al, and Fe, and a recovery of 90% was achieved for selected TEs (Ti, Sr, As, Y, Ba, and Zr), indicating that the adsorption of colloids and associated TEs onto the thin Spectra Por 7 membrane was negligible. Systematic studies of element blanks inside the dialysis membranes were performed both in the field (5 samples) and in a 10,000 class clean room (10 samples) and revealed negligible ($<1\%$ of measured concentration) contamination for 45 major and trace elements, with the exception of Cu and Fe, which had contamination of up to 1% of the measured concentrations. The blank of OC in the dialysis membrane was typically below 0.2–0.3 mg/L. A contamination in Zn was detected in <1 kDa dialysates. Necessary corrections were taken into account for Fe,

Fig. 4 Dissolved (<0.22 μm) organic carbon (DOC) concentrations in the water column during different seasons



Cu, and OC evaluations, whereas the evaluation of [Zn] in <1 kDa fractions was not possible. Similar quality control for ultrafiltration through carefully pre-treated 0.025 μm membrane performed according to previously developed rigorous experimental protocol (see Vasyukova et al. (2010) for details) demonstrated negligible adsorption of most TE on the membrane (i.e., <10%) and negligible blank contamination for OC and all TE including Zn.

3 Results

3.1 Thermal and Redox Stratification

As shown in Fig. 2a, the lake exhibits clear seasonal stratification with a small variation of temperature ($6 \pm 3^\circ\text{C}$) at the bottom layers (below 14 m). The surface water temperature was quite variable in the summer, ranging from 14°C in July 2009 to 27°C in July 2010, which was an anomalously hot summer in NW Russia. The measurements of water temperature during lake overturn in May and November of 2009 did not reveal a truly homogenous profile, as some stratification was still present below 12–14 m. This result is in contrast with the oxygen concentration profiles taken during the spring and autumn, which showed a constant distribution down to a depth of 18 m (Fig. 2b), thus confirming full mixing and oxygenation of the water column. During the summer and winter, the lake water was oxygen-saturated within the first 4 m of the surface, and the water become almost anoxic below a depth of 14 m.

3.2 Dissolved Organic and Inorganic Carbon

The concentration of DOC in Maselga Lake ranged between 8 and 20 mg/L and exhibited a homogeneous vertical distribution during wintertime [9 ± 2 mg/L with some accumulation in the bottom layers (18–20 m)] and significant variations, from 9 to 20 mg/L, in the summertime (Fig. 4). The DIC concentration remained quite constant (5 ± 1 mg/L) over the full depth of the lake in summer and during lake overturn. Contrarily, in winter, there was an increase in the DIC concentration by a factor of 3–4 at depths below 14 m, which is most likely linked to the anaerobic mineralization of OC and sulfate reduction

(Kokryatskaya et al. 2012). Intensive mineralization of dissolved organic matter is further supported by the $\delta^{13}\text{C}_{\text{DIC}}$ values (Shirokova et al. 2009b) that ranged from -9‰ at the surface to -14‰ at the bottom in March 2009 suggesting (i) clear disequilibrium with the atmosphere and (ii) importance of benthic respiration and DOM mineralization by heterotrophic bacteria in the water column. These values are similar to those of other boreal lakes (-13.8‰ in average, Striegl et al. 2001).

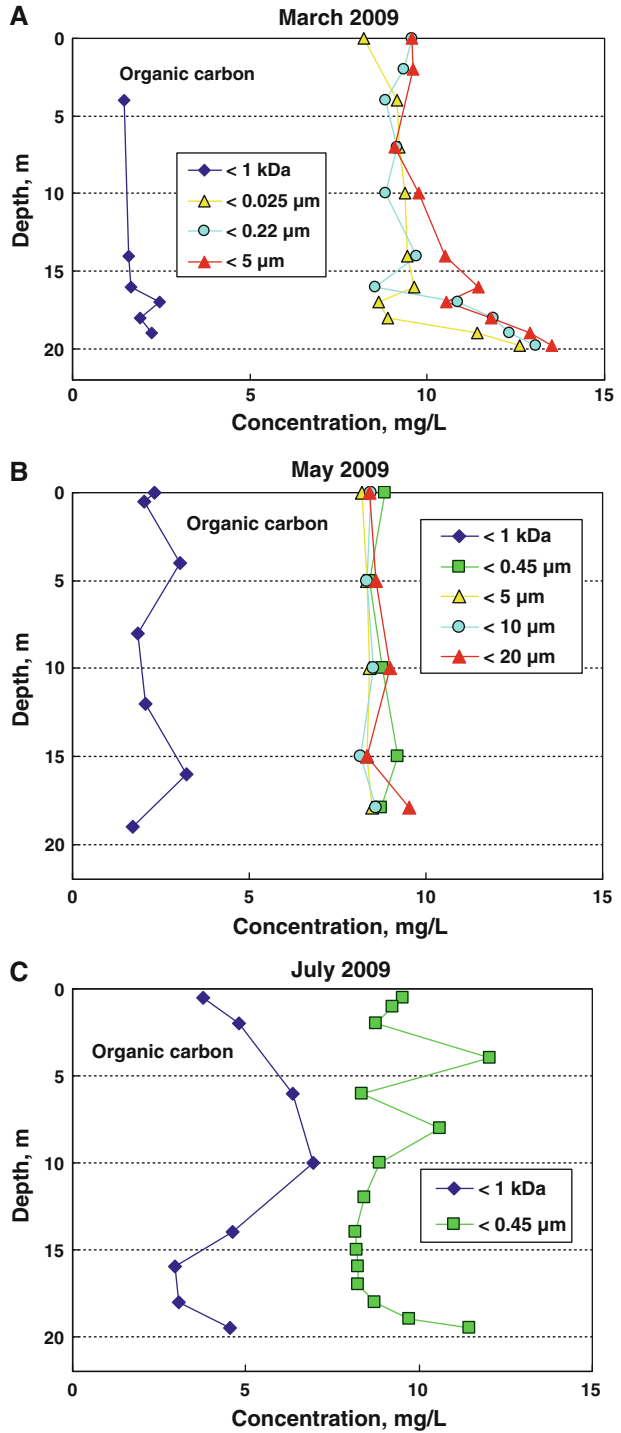
Examples of OC concentrations in different dialysates and filtrates in March, May, and July of 2009 are plotted in Fig. 5a, b, and c, respectively. It can be seen that there is no significant change in the OC concentration after filtration through 20 or 5 μm filters down to the 0.45 and 0.025 μm filters. The largest decrease in OC concentration occurred after dialysis through a 1-kDa membrane, most notably during the winter stagnation and the spring overturn (Fig. 5a and b). This result indicates that the LMW form of DOC (<1 kDa) constituted between 20 and 30% of the total filtered concentrations in March and May, while the role of the particulate form and coarse colloids (0.025–20 μm) was negligible. The proportion of OM colloids (1 kDa–0.45 μm) decreased by a factor of 2 to 3 during the summer (Fig. 5c, July 2009), while the LMW (<1 kDa) constituents comprised up to 80% of the DOC in the water column. Analyses of available data on dissolved organic nitrogen in March 2008 (see Electronic Annex EA-1 and Moreva 2010) demonstrated systematic evolution of C/N ratio in DOM, ranging from 20 to 27 in the water column and decreasing to 13 at the depth of 19 m. Other investigated seasons demonstrated similar range of C/N ratio (from 20 to 35). Such low values unequivocally support the dominantly autochthonous origin of DOM during these periods with even more intensive mineralization of sunken planktonic biomass occurring in the bottom layers.

3.3 Vertical Profiles of Trace Element Concentration

Concentrations of filtered, ultrafiltered, and dialyzed components of the lake water at each depth during all 4 seasons are listed in Electronic Annex 1. The specific redox conditions and elevated DOC concentrations of the lake water determine the spatial pattern of Fe and Mn, which both exhibit a very strong stratification (Fig. 6a, b). In fact, concentrations of these metals at the bottom layers ranged between 1 and 10 mg/L, which is comparable or higher than that of the major cations (Ca, Mg, and Na). Normally, such high concentrations of Fe and Mn are typical for organic-rich (10–20 mg/L DOC), acidic ($\text{pH} < 5$), temperate lakes (Urban et al. 1990). Cobalt followed the pattern of manganese (Fig. 6c), whereas barium exhibited a somewhat lower stratification with a concentration increase in the bottom horizons (below 15 m) by a factor of 3–5 as compared to the rest of the water column (Fig. 6d). Divalent trace metals, such as Ni, Cu, Zn, Cd, and Pb, demonstrate the absence of significant stratification and concentration increases in the bottom layers as compared to the rest of the water column. However, they do exhibit significant inter-annual and inter-seasonal variability that fluctuates up to factor of 5 (illustrated for Ni, Cu, and Zn in Fig. 6e, f and g, respectively), which is most likely linked to the variable biological uptake and release of metals in the water column (Zn, Ni, Cu, and Cd) or atmospheric precipitation (Pb). Finally, uranium exhibits very uniform distributions over the first 15 m during all seasons, with a significant accumulation (factor of 2 to 3) in the 2–3 m of the bottom horizons during winter stagnation (Fig. 6h).

All insoluble trivalent and tetravalent elements exhibited effectively constant concentrations as a function of depth, with slight (factor of 2–3) increases below 16–19 m, as illustrated for Al, Ti, La, and Th in Figure EA-2-1 A, B, C, and D, respectively (Electronic Annex EA-2). The elevated concentration of Ti (0.2–0.5 $\mu\text{g/L}$), which is usually an

Fig. 5 Organic carbon concentrations in different dialysate and filtrate fractions as a function of depth in March 2009 (A), May 2009 (B), and July 2009 (C)



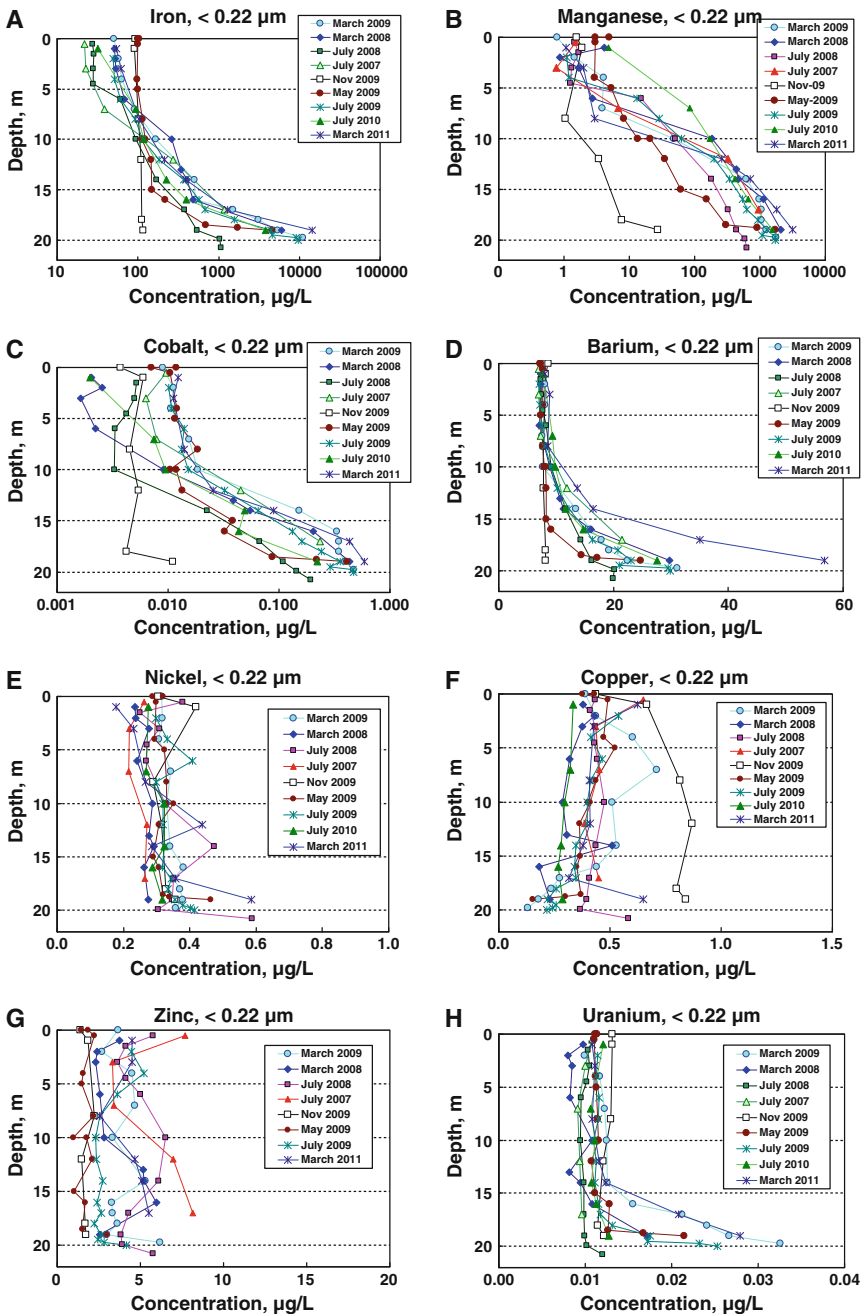


Fig. 6 Total dissolved (<math>< 0.22 \mu\text{m}</math>) Fe (A), Mn (B), Co (C), Ba (D), Ni (E), Cu (F), Zn (G), and U (H) concentrations as a function of depth during the 4 studied seasons in 2007–2011. Note the logarithmic scale for Fe, Mn, and Co

extremely immobile element in lakes (e.g., Ingri et al. 2011), is notable in these data. Oxyanions, such as Cr and V, and soluble TEs, present in the form of anions and neutral molecules (such as As and Mo), all demonstrate very uniform concentration distributions as a function of depth with only insignificant variations among different seasons over the 5 years of observation (Fig. EA-2-1 E, F, G, and H, respectively of the Electronic Annex 2).

3.4 Particulate and Colloidal Size Fractionation as a Function of Depth During the Winter and Summer Stagnation and Spring Overturn

A size fractionation scheme is illustrated in the form of a histogram for the Fe, Cu, Al, Ti, Ce, and U concentrations in filtrates and dialysates of five particulate and colloidal fractions for surface and bottom horizons sampled in May 2009: $<20\ \mu\text{m}$, $<10\ \mu\text{m}$, $<5\ \mu\text{m}$, $<0.45\ \mu\text{m}$, and $<1\ \text{kDa}$ (Fig. EA-2-2 of the Electronic Annex 2). It can be seen that for all selected elements, large particles and coarse colloids (between 20 and $0.45\ \mu\text{m}$) play insignificant roles in the overall size distribution of these six contrasting elements. For insoluble trivalent and tetravalent elements and uranyl, the main concentration changes occurred between $0.45\ \mu\text{m}$ and $1\ \text{kDa}$, thus confirming the dominant role of colloids in the speciation of these elements. In contrast, copper is chiefly present in LMW forms ($<1\ \text{kDa}$).

Further insights into the evolution of TEs in the colloidal and LMW fractions along the water column can be assessed with the help of Fig. 7, which presents the concentration-depth profiles of Fe, Mn, As, several trivalent and tetravalent elements, and uranium in $0.22\ \mu\text{m}$, 50, 10, and $1\ \text{kDa}$ dialysis fractions as assessed in July 2008 during the summer stagnation. For this analysis, we selected typical insoluble elements (Al, Ti, Zr, and REE), redox-sensitive Fe and Mn and As, which can be present in the form of neutral molecules or anions. The efficiency of in situ dialysis procedures can be assessed from the plot of Si concentration in various dialysates as a function of depth (Fig. EA-2-3 of Electronic Annex 2). This analysis shows that there are very similar concentrations of Si in each fraction, thus confirming the well-established absence of colloidal fractions of silica in boreal waters (Pokrovsky and Schott 2002). It can be seen from Fig. 7a that the Mn concentration remains virtually the same after filtration and dialysis over the full depth of the water column with up to 50% present as colloids only in the bottom layers. Iron and aluminum demonstrate the dominance of large colloidal forms ($50\ \text{kDa}$ – $0.22\ \mu\text{m}$) below a depth of 4 m, whereas in most surface horizons, the speciation of these elements is controlled by the LMW ($\leq 1\ \text{kDa}$) forms (Fig. 7b, c), most likely microbial exudates or the products of the photodegradation of Fe(III) and Al(III) complexes with allochthonous fulvic compounds (see below). The vertical distribution of Ti size fractions demonstrates that this element is less affected by colloids (Fig. 7d) than is Zr, which is present mainly in the form of $50\ \text{kDa}$ – $0.22\ \mu\text{m}$ (Fig. 8e). All REEs are strongly complexed with large colloidal fractions with only a negligible amount of 1 – $50\ \text{kDa}$ and LMW forms, as illustrated for La in Fig. 7f. Finally, uranium is almost entirely complexed with large organo-mineral colloids of $>50\ \text{kDa}$ molecular weight (Fig. 7g). A novel and unexpected finding was the presence of a significant (i.e., 30–50%) proportion of colloidal As in all of the depth profiles of the lake water (Fig. 7h). This finding is in contrast to the distribution of other anions and neutral molecules, such as Mo and Sb, that do not exhibit any significant differences in the concentration of different dialysates (Table EA-1 and illustrated for Mo in Fig. EA-2-4 of the Electronic Annex 2).

Other features of TE size distribution are observed during the winter period of stratification in March 2009. After ultrafiltration through a $0.025\ \mu\text{m}$ filter, which provided a better representation of dissolved iron (e.g., Shaked et al. 2004), we were able to assess the

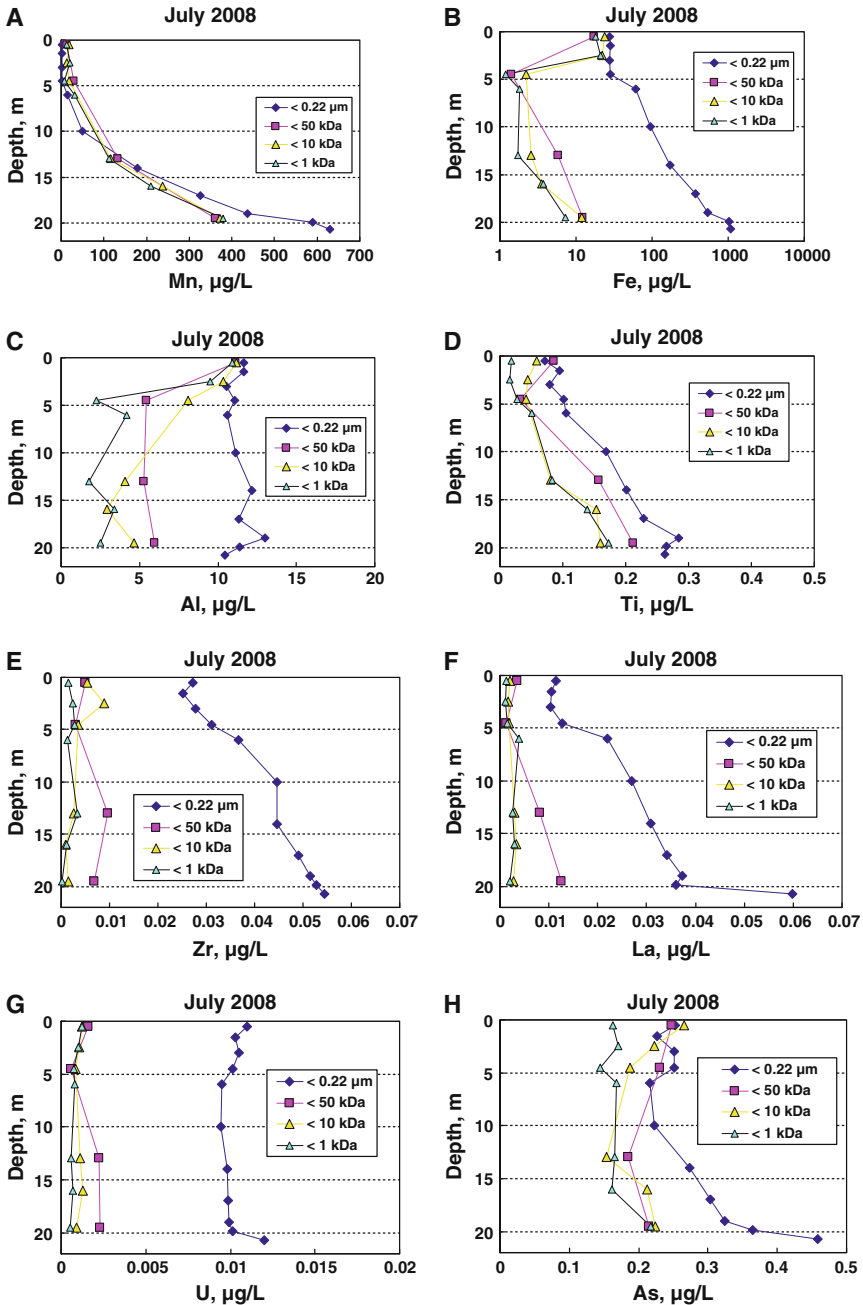


Fig. 7 Plot of Mn (A), Fe (B), Al (C), Ti (D), Zr (E), La (F), U (G), and As (H) concentrations as a function of depth for different colloidal size fractions obtained via filtration through $0.22\ \mu\text{m}$ and in situ dialysis through 1, 10, and 50 kDa membranes in July 2008

relative contribution of coarse colloids situated between 0.025 and 0.22 μm . Figure 8 shows plots of the concentration profiles of most typical insoluble elements (Fe, Al, Ti, La, Th, and U) and two divalent transition metals (Cu and Ni). Unlike in July, when the water column is more oxygenated, speciation of Fe in March, notably in the hypolimnion, is dominated by the presence of Fe^{2+} that passes through a 1-kDa membrane (Fig. 9a). A plot of Fe^{2+} and Fe_{total} in the $<0.22 \mu\text{m}$ fraction is given in Fig. EA-2-5 of the Electronic Annex 2. Aluminum is present both in particulate form (up to 50% of total Al in the bottom horizons is $<5 \mu\text{m}$) and as coarse colloids ($>50\%$ as 0.025–0.22 μm fraction, Fig. 8b). Similarly, size fractionation is observed for Ti with a significant proportion of the 0.22–5 μm fraction (Fig. 8c). Note that the particulate fraction (0.22–20 μm) of these elements was not observed in samples collected during the spring overturn in May 2009 (cf. Fig. EA-2-2). A possible reason for Al and Ti presence in 0.22–5 μm fraction could be small suspended silicate particles or, rather, the particulate Fe oxy(hydroxide) hosting these elements. Below the 10 m depth, lanthanum and other rare earth elements exhibit the presence of particulate (0.22–5 μm) forms and the dominance of large colloids (0.025–0.22 μm) (Fig. 8d). In contrast, insoluble tetravalent elements, such as Th (Fig. 8e), and Zr and Hf (not shown), are dominated by hydrolyzed species present in large Fe-rich organic colloids, and they are linked to significantly fewer particles compared to silicate-affected light elements such as Ti. Uranium is represented by the LMW ($<5 \text{ kDa}$) fraction, with a rather negligible role of large colloids and sub-colloidal particles (Fig. 8f). Divalent, biologically relevant transition metals, such as Cu and Ni, exhibit a size fractionation pattern as a function of depth, which is quite different from the pattern shown by insoluble trivalent and tetravalent elements. Cu is effectively present in the form of LMW entities, as the depth-concentration profile in the dialyzed fraction ($<1 \text{ kDa}$) largely coincides with that of the filtered ($<0.22 \mu\text{m}$) fraction (Fig. 8g). In contrast, Ni has approximately 60% of its total dissolved amount in the form of small-size colloids (1–5 kDa), with 30% being concentrated in the LMW ($<1 \text{ kDa}$) fraction (Fig. 8h). As in July, colloidal As represents between 30 and 60% of the total dissolved As seen in March, and small-size colloids (5–1 kDa) dominated the size distribution (not shown).

3.5 Proportion of Colloidal (1 kDa–0.45 μm) Forms During Different Seasons

A systematic study of size fractionation was carried out using both conventional filtration and in situ 1 kDa dialysis, which was performed as a function of depth during the four main hydrological seasons. This study allowed for the characterization of seasonal features of colloidal fractions for several typical TEs, as described below. For consistency, throughout all four studied seasons and in accord with concepts of aquatic colloids (Gustafsson and Gschwend 1997), we utilized the filtration through 0.45 μm as the upper threshold of colloid abundance. Note that there is no statistically significant difference between filtration through a 0.22 μm filter and filtration through a 0.45 μm membrane for the Lake Maselga water; the spatial and daily variations of elemental concentrations were significantly higher than the differences between these two filtrate fractions.

Iron was essentially present in colloidal status during the spring and autumn overturn when the hypolimnion is oxygenated (Fig. 9a). In contrast, during summer and winter stagnation, we observed a strong decrease in colloidal Fe_{tot} in the hypolimnion, which is certainly linked to the high concentration of Fe(II) detected in the form of inorganic complexes or free ions. During summer and winter stagnation, Al and Ti (Fig. 9b, c) demonstrated a systematic increase in colloidal forms from the surface layers (40 and 20%, respectively) toward the bottom horizons (80% and 60%, respectively). In contrast, during

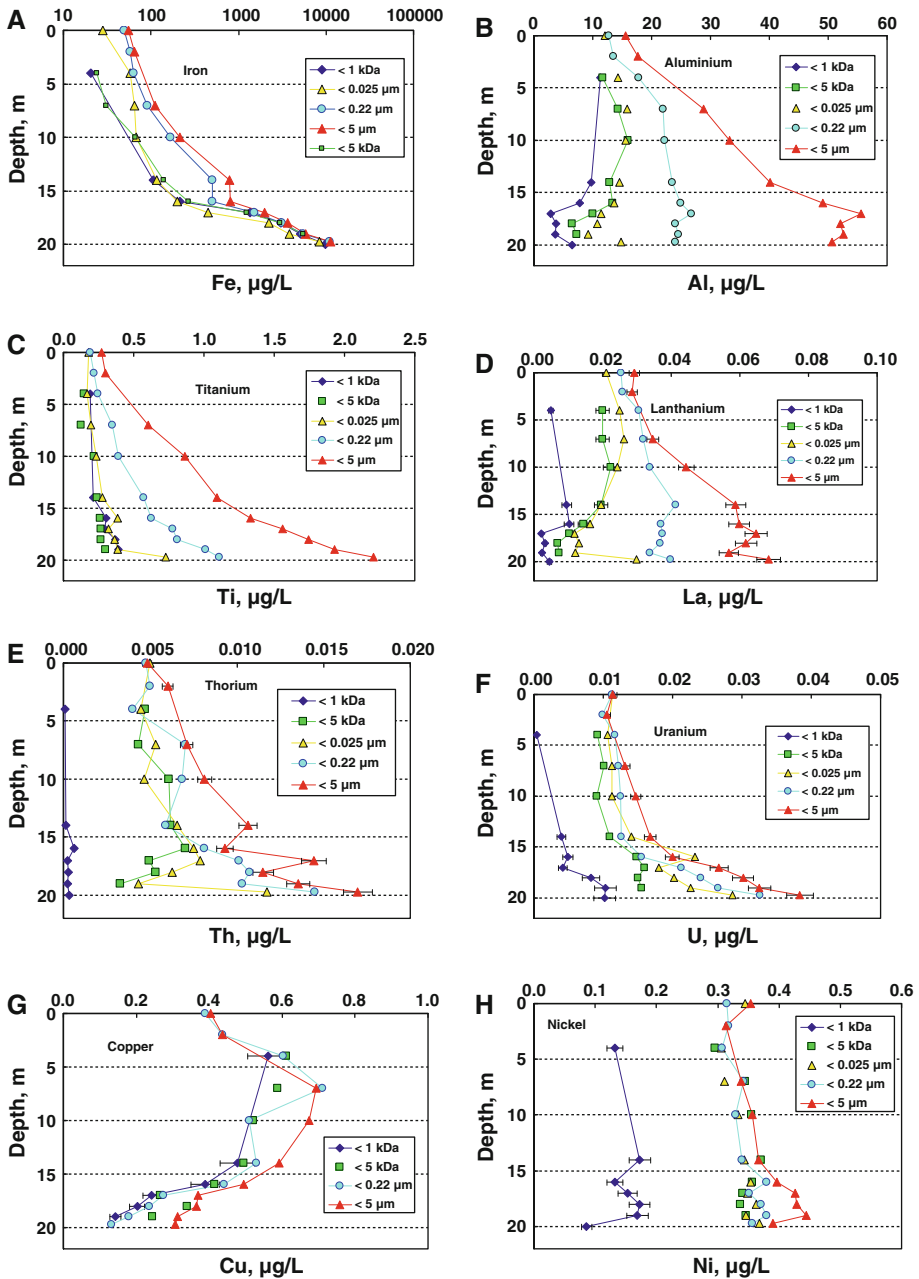


Fig. 8 Plot of Fe (A), Al (B), Ti (C), La (D), Th (E), U (F), Cu (G), and Ni (H) concentrations as a function of depth for different colloidal size fraction obtained via filtration through 5, 0.22, and 0.025 μm filters and in situ dialysis through 1 and 5 kDa membranes in March 2009

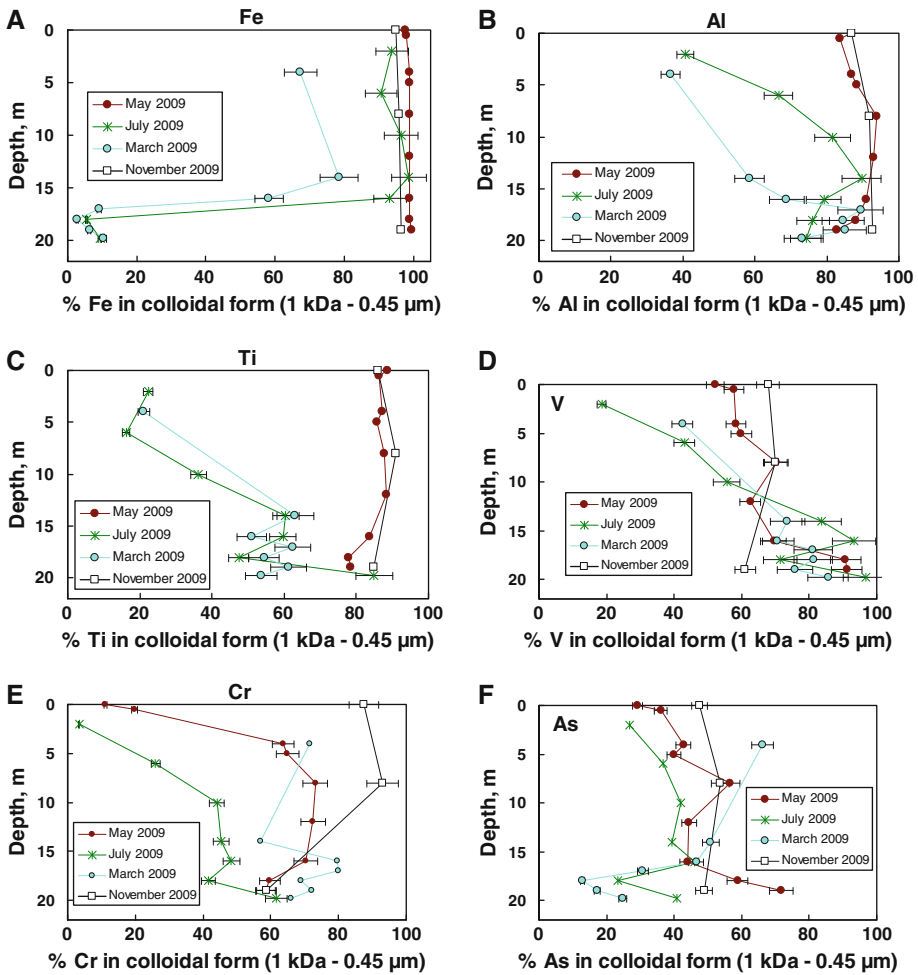


Fig. 9 Proportion of the colloidal form of Fe (A), Al (B), and Ti (C), V (D), Cr (E), As (F), Ni(G), Cu (H), and U (I) as a function of depth during the 4 hydrological seasons in 2009

the spring and autumn overturn, these insoluble elements were essentially present as colloids (80–90% of total dissolved concentration). A similar, steady increase from the surface to the bottom horizons and a much more uniform vertical distribution of colloidal fraction percentages were observed for V and Cr (Fig. 9d, e). In agreement with previously demonstrated results, we found a strong link of dissolved As with colloids (Sect. 3.4), and the proportion of colloidal As fraction did not vary significantly with depth, ranging from 20% to 60% (Fig. 9f).

Nickel exhibited a distinctly smaller proportion of colloids during summertime (20–35%) compared to the rest of the year (from 50 to 80%, Fig. 9g). In contrast, Cu typically had less than a 20% colloidal contribution during summer and winter stagnation, with a significant (up to 35%) increase in colloid proportion in November and May (Fig. 9h). Finally, the distribution of two typical colloid-controlled elements, La and U,

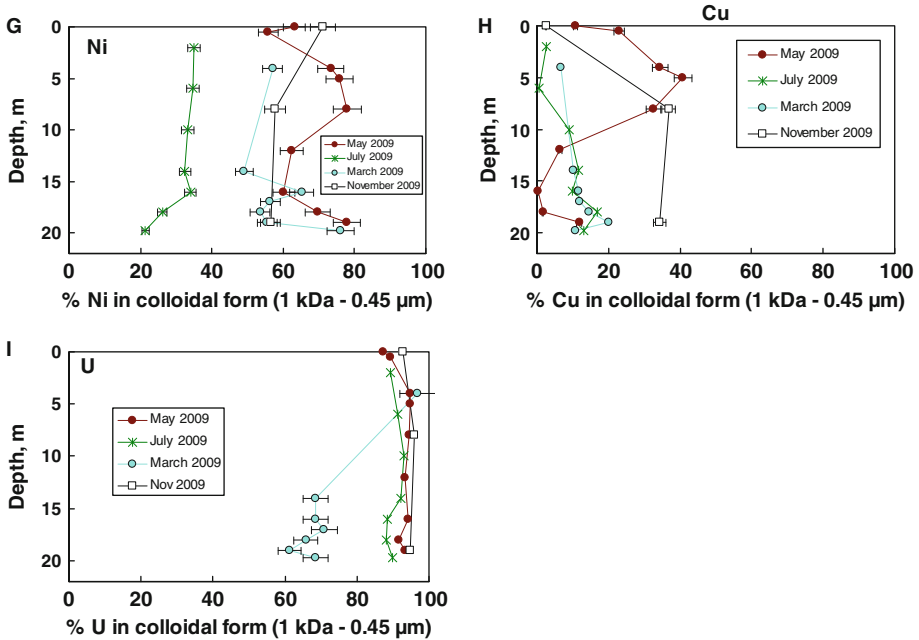


Fig. 9 continued

exhibited the dominance of colloidal forms (80–99%) all along the water column without significant variations over the four studied seasons illustrated in Fig. 9 I for uranyl. Only in March, during an almost fourfold increase in DIC in the bottom horizons, did the proportion of colloidal U decrease to 60–70%. This change was most likely at the expense of uranyl-carbonate complexes, a feature that is well established for large rivers of this boreal region (Pokrovsky et al. 2010).

4 Discussion

4.1 Stratification of Trace Elements

Several groups of elements were categorized according to their degree of stratification in the water column and their affinity to Fe- or OM-dominated colloids. Typically, insoluble elements (Al, Ti, Ga, Y, all REEs, Zr, Hf, and Th) and U exhibited slight increases in concentration with depth, and these elements were strongly associated with large-size organo-ferric colloids (0.22–0.025 μm). In this regard, the impact of both redox and of the colloidal status of iron on the distribution and speciation of trace metals encountered in lake Maselga is likely comparable to that occurring in the meromictic lakes (e.g., Hongve 1997). Typical biogenic elements (Si, P, and N) and Ba are not associated with colloids; however, they exhibit significant stratification, as they probably originated from degrading sinking plankton debris and/or reflux from the sediments to the water column. The presence of the anoxic zone below 15–18 m, which is especially notable in winter and contains up to 0.67 $\mu\text{mol/L}$ H_2S (Kokryatskaya et al. 2012), may be responsible for the increase in the bottom water concentrations of Cr, V, Mo, and As (Fig. EA-2-1, E–H). This increase is

typically observed for the anoxic layer of meromictic lakes, where these elements may dissolve or desorb from Mn- and/or Fe-oxyhydroxides below the redox interface (e.g., Balistrieri et al. 1994; Viollier et al. 1995). This increase could also originate from upward diffusive fluxes through the water–sediment interface, which has been recently shown for As in organic-rich shallow, thermokarst lakes (Audry et al. 2011).

Though it frequently occurs in organic-poor meromictic lakes (e.g., Balistrieri et al. 1994), there is no significant decrease in the dissolved Cu, Ni, Pb, and Zn concentrations in the anoxic region below the sulfide maximum in Lake Maselga. This result is likely due to the strong complexation of divalent transition metals with LMW organic ligands, as discussed in the following section. In contrast to other micronutrients, cobalt exhibits very strong stratification during the winter and summer stagnation, which may be linked to well-known scavenging with Mn oxy(hydr)oxides via oxidation of Mn(III)- or Mn(IV)-oxide particles (Murray 1975) of biological origin (Lienemann et al. 1997) and by release during bacterial dissolution at the chemocline (Taillefert et al. 2002). The results of the present study do not allow us to determine the degree to which other elements associated with Fe(III) organo-mineral colloids are subjected to similar phenomena of scavenging and reductive dissolution at the chemocline.

Finally, concentrations of “inert” trace elements (Li, B, V, Rb, Sr, and Sb) did not appear to vary along the water column, despite the presence of strong redox stratification starting from 10 to 14 m and progressing down to the bottom during all seasons. Apparently, either production/mineralization processes or redox phenomena in the water column do not significantly control these elements, or the influence of these processes is not pronounced under the control of the allochthonous river water input and atmospheric precipitation.

4.2 Colloidal Speciation of Trace Elements

The dominance of small-size colloids and the LMW organic carbon fractions (see Fig. 5) contrasts with the size fractionation of total dissolved iron, which demonstrates a systematic decrease in concentration during filtration $5 \rightarrow 0.22 \rightarrow 0.025 \mu\text{m}$, as illustrated for March 2009 in Fig. 10. These observations show the possible presence of two types of

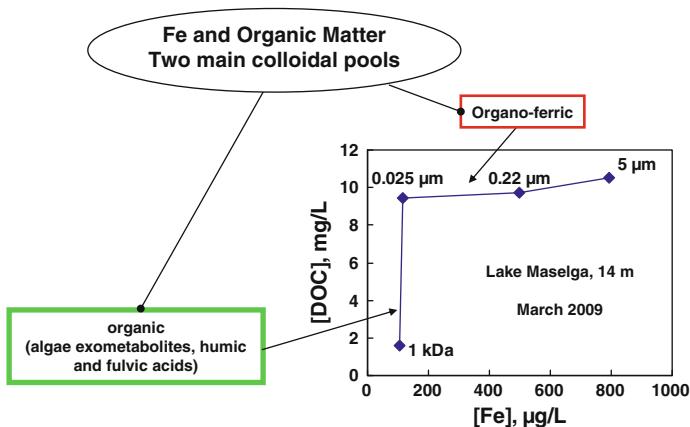


Fig. 10 Plot of organic carbon concentration as a function of Fe concentration in different filtered and dialysated fractions. The two types of colloidal/sub-colloidal fractions are organo-ferric and organic

colloidal material: Fe-rich, organic-bearing, large colloids and particles (0.025 μm –0.45/5 μm) and low-molecular weight, organic-rich, Fe-poor colloids (1 kDa–0.025 μm), consistent with numerous evidence from several types of colloidal material in natural waters (Lead et al. 1997; Lyvén et al. 2003; Allard et al. 2004; Baalousha et al. 2006). Thus, recent works on colloidal size fractionation in temperate rivers and coastal waters demonstrated the presence of small 0.5–3 nm spherical organic matter colloids and 5–40 nm sized inorganic Fe oxy(hydr)oxide colloids (e.g., Stolpe and Hassellöv 2010, Stolpe et al. 2010, 2011). The results of size fractionation in Lake Maselga are also in agreement with direct measurements of iron particle size distribution collected at the oxic–anoxic interface of a eutrophic lake that indicated that at least three-quarters of the iron particles had a size smaller than 0.13 μm , with the majority having a size of 0.1 μm (Buffle et al. 1989). Trace metals, notably trivalent and tetravalent hydrolyzed elements and UO_2^{2+} , associated with these organo-mineral colloids may be present in three main forms: (1) complexed with organic ligands of the organic part of colloids, (2) adsorbed at the surface of colloidal particles, and (3) incorporated in the bulk of Fe(Al)-rich colloids stabilized (coated) by OM, as reported in previous works (Ingri et al. 2000; Dia et al. 2000, Andersson et al. 2006; Vasyukova et al. 2010, 2011).

At the same time, the attribution of TE association in the lake water with two types of colloidal material is not straightforward and should be considered with caution. Both phases are dominated by organic matter; the proportion of Fe is much higher in HMW (colloidal, 0.22 μm to 1–5 kDa) compared to LMW (<1 kDa) pool. More importantly, the general scheme of Fe-rich and OC-rich phases as two major trace element carriers in rivers and streams (e.g., Lyvén et al. 2003; Stolpe et al. 2010) may not necessarily be true for lake waters given (i) larger proportion of autochthonous OM and exometabolites in lakes compared to rivers and (ii) the presence of high concentrations of Fe(II), Mn, phosphate, and sulfide phases in the lake hypolimnion, which are absent in the oxygenated river waters.

Copper and nickel present a size fractionation pattern that is different from insoluble, low-mobility elements. This pattern stems from the influence of (1) LMW organic ligands (<1 kDa), which most likely originate from phytoplankton exometabolites and were dominant during the summertime and constituted 20–35% and $\leq 20\%$ of Ni and Cu in colloidal form, respectively (Fig. 9g, h); (2) LMW, fulvic complexes from soil and bog water were notably present during the spring overturn when the lake is fed by running surface waters and melted snow; this result has been previously established in earlier studies of transition metal size fractionation in temperate rivers (Stolpe et al. 2010); and (3) organic colloids originated from hypolimnetic oxygenation, producing a metal release from sediments via the accelerated degradation of organic matter under less-anoxic conditions (Xue et al. 1997), which was most visible during the autumn overturn. Similar to previous studies (Balistrieri et al. 1992b; Hamilton-Taylor et al. 2005), there was no observational evidence that Cu was linked to the redox cycles of either Fe or Mn or to the colloidal status of Fe, as it was mostly complexed by LMW (<1 kDa) organic ligands. Indeed, for Cu, the stability constants of the ultrafilterable (< 3 kDa) organic ligand are reported to be significantly stronger than those of the 0.40- μm filterable fraction of freshwater (Hoffmann et al. 2007), thus confirming the high affinity of Cu to small-size organic ligands (Stolpe et al. 2010).

An unusual feature of TE size fractionation in Lake Maselga is the existence of a significant (i.e., 30–50%) proportion of colloidal As (Fig. 7 H, 9 F), which is normally present as mostly ultrafilterable (<1 kDa) fractions in boreal rivers and soil solutions (Pokrovsky and Schott 2002; Pokrovsky et al. 2011, Bagard et al. 2011). To our

knowledge, colloidal As (<20%) was observed only in the bottom anoxic waters of Lake Pavin (Albéric et al. 2000). For Lake Maselga, we tentatively link colloidal As to organic rather than organo-ferric complexes. This link was confirmed by a plot of [As] versus [DOC] in filtrates, ultrafiltrates, and dialysates, demonstrating a systematic decrease in both DOC and As (Fig. EA-2-6a), which was not observed in the comparable plot of Fe and As (Fig. EA-2-6b). The mass balance calculation demonstrates that more than fourfold decrease in colloidal Fe concentration leads to only 10% decrease in colloidal As, whereas a threefold decrease in [OC] at almost constant Fe concentration is accompanied by a twofold decrease in [As].

Given that there was significant complexation of As(III), not As(V), with DOC that was established in natural, organic-rich swamp waters (e.g., Haque et al. 2007), it is most likely that a sizeable fraction of filtered As is present in the form of As(III)-humic or fulvic complexes. Therefore, in contrast to organic-poor lakes, such as Lake Pavin, where As is strongly controlled by adsorption and coprecipitation with Fe and Mn oxy(hydr)oxides (e.g., Seyler and Martin 1989), organic colloids were dominant in the studied boreal lake. During summer stratification, the dominant size of As-organic complexes increased from 1 to 10 kDa in the epilimnion to 50 kDa–0.22 μm in the hypolimnion (Fig. 8h). This change likely reflects the transformation of dissolved organic matter from LMW phytoplankton exometabolites at the surface to high-molecular weight (HMW) refractory colloids that originated from microbial degradation in the anoxic zone, consistent with the increase in the relative proportion of HMW organic colloids (0.025 μm –1 kDa) below the 18 m depth in winter (Fig. 5a). Note that the probable contribution of thioarsenic species (as evidenced in sulfidic environments by Wilkin et al. 2003) to the observed colloidal As in the bottom water and sediment of lake Maselga could not be tested in this work, although the concentration of thiosulfate in the water column is comparable to that of sulfide (Kokryatskaya et al. 2012). However, the independence of colloidal As proportion on depth during most studied season and even its decrease in March, during the maximal anoxia in the hypolimnion (cf. Fig. 9f), may dismiss the possibility of As presence in sulfide-rich colloids.

4.3 Processes in the Water Column Controlling the Colloidal Pattern on Trace Elements

In all samples, large colloidal forms (0.025–0.22 μm) of iron and hydrolyzed trivalent and tetravalent elements clearly dominated the size fractionation of dissolved elements. The change in speciation of TEs with depth was due to redox condition changes, the biodegradation of sinking plankton biomass that released dissolved organic matter over the entire water column and diffuse flux from the sediments to the water column in the hypolimnion. Thus, Fe^{2+} appearance at the chemocline during winter stagnation leads to a significant decrease and almost to the disappearance of colloidal forms below 17 m (Fig. 9a). The absence of colloidal Fe in the anoxic zone of meromictic lake has also been proven by dialysis through an 8-kDa membrane (Albéric et al. 2000). Given the much higher (a factor of 100 to 1000) Fe concentrations in the bottom horizons compared to the rest of the water column (Fig. 6a) and the low proportion of colloidal Fe in the bottom horizon during winter stagnation (Fig. 9a), it is unlikely that this enrichment occurs due to reduction in Fe(III) from the water column colloids or sinking particles. Rather, this enrichment should be considered to result from an influx from the sediments. This contention is supported by the concave shape of the Fe profiles, which points toward diffusive processes from the sediment rather than production processes within the water column. This result is in agreement with the large body of evidence from temperate lakes showing that the seasonal

increase in iron in the anoxic bottom waters is largely due to a release from the sediment. This phenomenon is in contrast with Mn, which was almost exclusively supplied from the in situ dissolution of sedimenting particles (Davison et al. 1982; Balistrieri et al. 1992a). The latter phenomenon is supported by the convex-shaped Mn profiles in the water column, suggesting dissolved Mn production within the water column rather than influx from the sediments.

Among all studied major and micro nutrients and trace elements, Mn exhibits by far the largest gradient in concentration from the surface to the bottom layers. Therefore, one cannot exclude the possibility of Mn being a limiting micronutrient for phytoplankton production in the photic zone of studied lake. This is supported by (i) a factor of 500–3,000 increase in Mn concentration from the surface to the bottom, which is significantly higher than that of such limiting nutrient as PO_4^{3-} (a factor of 3–30, see Electronic Annex EA-1), (ii) essentially dissolved bioavailable status of Mn^{2+} as follows from dialysis experiments of this study (Fig. 7a), (iii) systematic response of Mn concentration to diurnal photosynthesis cycle in an adjacent boreal lake (Shirokova et al. 2010), and (iv) significant dissolved Mn uptake during incubation of lake water in light bottles compared to dark control (Shirokova et al. 2007 and our unpublished results).

Judging from the depth-concentration profiles, diffusion to the water column from the porewater sediments likely dominates the vertical distribution of Ba, As, Cr, Mo, V, and U. Although constraining diffusive sediment fluxes require direct measurements of porewater chemical composition, this hypothesis follows from the abrupt increase, by a factor of 3 to 4, in dissolved element concentration in the deepest sampled horizon and at the water–sediment interface (20 m) collected using the sediment column sampler during all studied seasons. Such an upward diffusion is likely to be less pronounced for Ti and Ce and quite unlikely for Al, Th, Cu, and other divalent transition metals that are present in the form of LMW organic complexes. Indeed, trace metals, such as Ni, Cu, and Zn, known as micronutrients (Goldman 2009), are prone to form rather strong LMW organic complexes with dissolved organic matter, notably with phytoplankton exometabolites (e.g., Xue and Sigg 1993; Wu and Tanoue 2001). The high affinity of these metals to the biota leads to their uptake by phytoplankton and possible release during OM mineralization in the water column by heterotrophic bacteria. These two processes are highly seasonally and inter-annually variable and thus may be partially responsible for significant variations in the element concentration profiles (see Fig. 6f for copper). It can be seen in this figure that there is a pronounced (factor of 3–4) Cu concentration increase over the full sampled depth during the mixing period (i.e., November 2009) as compared to the summer and winter-time. This effect may be linked to hypolimnetic oxygenation that enhances the release of copper from sediments via the aerobic degradation of organic matter (Xue et al. 1997) or the regeneration of sunken organic detritus on the sediment–water interface under oxic conditions, which thus increases the hypolimnetic concentration of dissolved divalent metals (Achterberg et al. 1997).

A number of TEs (e.g., Al, Ti, V and Cr) exhibit smaller proportions of colloidal forms in the epilimnion compared to the hypolimnion. In addition to LMW (<1 kDa) phytoplankton exometabolites, another process responsible for the production of LMW organic ligands in the surface layers may be the photooxidation of DOM (e.g., Amon and Benner 1996; Jonsson et al. 2001, 2008). In a humic boreal lake, photooxidation is responsible for at least 10% of total OM degradation (Pers et al. 2001), although the relative importance of this process for the production of LMW complexes of TEs in Lake Maselga cannot be evaluated.

The photoreduction of Fe^{3+} in the surface layers (Finden et al. 1984) may additionally be important phenomena, especially in the spring and early summer after the lake overturn brings high concentrations of colloidal Fe(III) to the upper 5–7 surface layers (cf. Fig. 6a, demonstrating high Fe surface concentration in May 2009 and Fig. EA-2-2, showing the dominance of colloidal Fe (> 90%) at the lake's surface). In contrast, in summertime, the photoreaction of Fe(III) under the visible range of light and UV may produce labile (<100 Da) Fe, as shown in experiments on boreal stream waters (Kelton et al. 2007). This photoreduction, which was highly variable from 1 year to another and exhibited a diurnal pattern (Emmenegger et al. 2001), may partially explain the decrease in colloidal Fe at the expense of LMW forms of Fe in the photic zone (first 4 m) of Lake Maselga that was observed in July 2008 (Fig. 7b).

The poorly understood process that is responsible for colloidal metal production in the hypolimnion involves iron sulfide formation in the anoxic zone of sediment porewater and the adjacent water column (Hamilton-Taylor et al. 2005). These FeS nanoparticles are capable of scavenging some trace metals (Balistrieri et al. 1994, 1995). Given elevated sulfide and S^0 concentrations in the hypolimnion of Lake Maselga (from 0.15 μM at the surface to 0.45–0.67 $\mu\text{mol/L}$ at the bottom, Kokryatskaya et al. 2012), colloidal iron sulfide and elemental sulfur may be potentially important TE carriers and deserve special investigation using size fractionation techniques.

5 Concluding Remarks

To summarize, the colloid origin and migration in Lake Maselga are chiefly affected by the biogeochemical cycle of carbon and iron. Three governing factors include the following: (1) biological processes of phytoplankton production and heterotrophic bacterioplankton mineralization in the water column during summer and winter stagnation, which leads to the presence of organic LMW colloids similar to other boreal (Tranvik 1988) and thermokarst (Shirokova et al. 2009a) lakes; (2) the input of allochthonous soil and bog OM presented in the form of HMW organo-mineral colloids, which is very typical for the boreal zone of NW Russia (Pokrovsky and Schott 2002; Vasyukova et al. 2010); and (3) the diffuse flux of Fe^{2+} , other trace metals, and OM from the sediment porewater to the bottom horizons (Balistrieri et al. 1992a).

Altogether, these parallel processes create pools of autochthonous and allochthonous colloids that are dominated by OM or by OM with iron(III) oxyhydroxides. The colloidal status of insoluble trivalent and tetravalent TE may be acquired during their coprecipitation with Fe(III) oxy(hydr)oxide. In the case of a strongly stratified lake in winter, and to a lesser degree in summer, this coprecipitation occurs at the redox front (chemocline), producing large, organo-mineral colloids. Similar processes were evidenced during the underground mixing of organic-poor, Fe^{2+} -rich water with well-oxygenated, organic-rich soil leachates in small rivers and streams (Pokrovsky and Schott 2002; Vasyukova et al. 2010). Rapid oxygenation of deep water layers during the spring and autumn overturn and the input of large soil and bog water organo-ferric colloids causes changes in not only element concentration profiles but also their colloidal status. The relative proportion of these colloidal pools changes as a function of depth and season. It is therefore possible that organo-ferric colloids that control the speciation of poorly soluble elements in soil and river waters are being replaced by autochthonous organic, Fe-poor colloids in the lake system.

The quantitative modeling of biogeochemical reactions in the water column and in the sediment surface layer (e.g., Lopes et al. 2010; Moreira et al. 2010) would require

distinguishing between two main processes controlling TE transport in the lake: (1) mobilization during reduction in settling Fe(III) particles and colloids in the anoxic water column and (2) diffusion of TEs from the sediments into the overlying anoxic water. For this modeling, detailed studies of porewater chemical composition (e.g., Tessier et al. 1989; Audry et al. 2011) and analysis of sediment trap materials (e.g., Sigg 1985; Sigg et al. 1995; Viollier et al. 1997) would be necessary to constrain the mass balance and fluxes of elements within the lake body. In addition, measurements of dissolved and particulate concentrations of incoming springs and atmospheric depositions (e.g., Hamilton-Taylor and Willis 1990) should allow for the overall TE mass balance assessment at the scale of the lake and watershed of incoming rivers.

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