Decrease of concentration and colloidal fraction of organic carbon and trace elements in response to the anomalously hot summer 2010 in a humic boreal lake

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HIGHLIGHTS
- Anomalous hot summer 2010 changed boreal lake biogeochemistry
- Carbon and trace element concentration in the epilimnion decreased by a factor of 1.3 to 6.
- Colloidal fractions of carbon and metals decreased by a factor of 1.5 to 3.
- Climate warming in boreal lakes may increase the metal and carbon bioavailability.

GRAPHICAL ABSTRACT
During anomalously hot summer (August 2010), significant decrease of the proportion of colloidal organic carbon occurred in a humic boreal lake.

ABSTRACT
The colloidal distribution and size fractionation of organic carbon (OC), major elements and trace elements (TE) were studied in a seasonally stratified, organic-rich boreal lake, Lake Svyatoe, located in the European subarctic zone (NW Russia, Arkhangelsk region). This study took place over the course of 4 years in both winter and summer periods using an in situ dialysis technique (1 kDa, 10 kDa and 50 kDa) and traditional frontal filtration and ultrafiltration (5, 0.22 and 0.025 μm). We observed a systematic difference in dissolved elements and colloidal fractions between summer and winter periods with the highest proportion of organic and organo-ferric colloids (1 kDa–0.22 μm) observed during winter periods. The anomalously hot summer of 2010 in European Russia produced surface water temperatures of approximately 30 °C, which were 10° above the usual summer temperatures and brought about crucial changes in element speciation and size fractionation. In August 2010, the concentration of dissolved organic carbon (DOC) decreased by more than 30% compared to normal period, while the relative proportion of organic colloids decreased from 70–80% to only 20–30% over the full depth of the water column. Similarly, the proportion of colloidal Fe decreased from 90–98% in most summers and winters to approximately 60–70% in August 2010. During this hot summer, measurable and significant (>30% compared to other periods) decreases in the colloidal fractions of Ca, Mg, Sr, Ba, Al, Ti, Ni, As, V, Co, Y, all rare earth elements (REEs), Zr, Hf, Th and U were also observed. In addition, dissolved (<0.22 μm) TE concentrations decreased by a factor of 2 to 6 compared to previously investigated
periods. The three processes most likely responsible for such a crucial change in element biogeochemistry with elevated water temperature are 1) massive phytoplankton bloom, 2) enhanced mineralization (respiration) of allochthonous dissolved organic matter by heterotrophic aerobic bacterioplankton and 3) photo-degradation of DOM and photo-chemical liberation of organic-bound TE. While the first process may have caused significant decreases in the total dissolved concentration of micronutrients (a factor of 2 to 5 for Cr, Mn, Fe, Ni, Cu, Zn and Cd and a factor of >100 for Co), the second and third factors could have brought about the decrease of allochthonous DOM concentration as well as the concentration and proportion of organic and organo-mineral colloidal forms of non-essential low-soluble trace elements present in the form of organic colloids (Al, Y, Ti, Zr, Hf, Th, Pb, all REEs). It can be hypothesized that climate warming in high latitudes capable of significantly raising surface water temperatures will produce a decrease in the colloidal fraction of most trace elements and, as a result, an increase in the most labile low molecular weight LMW. 1 kDa fraction.

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1. Introduction

The response of carbon biogeochemistry in high latitude aquatic ecosystems to increasing ground and water temperatures is an important issue in light of on-going environmental changes. However, there is a lack of knowledge concerning how aquatic ecosystems generally respond to the primary effect of climate warming, the rise of surface water temperatures. This lack of knowledge significantly hampers prediction of their chemical responses. A well-known example of the effect of increasing temperatures on the aquatic environment is the migration of dissolved organic carbon (DOC) in watersheds and surface waters. DOC removal has increased in non-permafrost regions of Western Europe and Canada (Kang et al., 2001; Hongve et al., 2004; Hejzlar et al., 2003; Freeman et al., 2001, 2004; Vuorenmaa et al., 2006; Worrall et al., 2004) for various reasons (see Porcal et al., 2009 for a review). From the other hand, increasing bacterial heterotrophic respiration of dissolved organic matter (DOM) under rising temperatures should decrease DOM concentration in the water column. Another process responsible for organic matter mineralization is photo-degradation especially pronounced under high latitudes and it is likely to accelerate with high water temperatures (Leifer, 1988; Likens, 2010).

As a working hypothesis, it can be assumed that, in the case of surface water warming at high latitudes, organic carbon production and removal will increase for a short period of time but will eventually decrease due to biological mineralization and photo-degradation processes. The same processes are likely to modify the distribution of dissolved major and trace elements linked to organic matter, but the absence of quantitative modeling of other than carbon element fluxes in boreal aquatic environments does not allow prediction of possible changes. For example, although it is known from temperate settings that the photo-degradation of DOC releases bound metals (Kopaček et al., 2005, 2006; Shiller et al., 2006; Brooks et al., 2007; Kelton et al., 2007), thus increasing their bioavailability, it is unknown the degree to which the photo-degradation of colloidal metal will respond to rising water temperatures in boreal aquatic environments.

It is likely that on-going warming may bring about more frequent phytoplankton blooms (cf., Carey et al., 2012; Kosten et al., 2012; Paerl and Paul, 2011; Sinha et al., 2012) caused by the summertime increase in surface water temperature. The opportunity to study these unusual (at present) conditions, apart from artificially manipulating a lake (e.g., Kasprzak et al., 1988; Kasprzak, 1993; Strecker et al., 2004; Graham and Vinebrooke, 2009), can be found during extreme local weather perturbations (Jankowski et al., 2006). The anomalously hot summer of 2010 in the European part of Russia (10° above the average that lasted for almost two summer months) offered the possibility of investigating a pristine water body that had been subjected to a temperature nearly 10° higher than normal. This strong local warming caused a massive bloom of cyanobacteria that lasted several weeks, so variations in major and trace element concentrations in the epilimnion could be monitored during a diurnal photosynthesis cycle under stable weather conditions (Pokrovsky and Shirokova, 2013). The primary objective of this study was to observe changes in key lake biogeochemical parameters, i.e., the concentration and speciation of both carbon and trace element (TE) species, over the course of several years with high seasonal resolution aided by anomalous climate conditions, observations that had not been achieved before.

A second major issue that was addressed in this study was the evolution of the element colloidal status during climate warming. High concentrations of allochthonous DOM are responsible for the colloidal form of most trace elements (TE) in the boreal subarctic zone (Ingrī et al., 2000; Pokrovsky and Schott, 2002; Pokrovsky et al., 2006). In addition to organic colloids, organo-ferric (FeOOH) large size entities bound significant fraction of a number of insoluble TE (cf. Stolpe et al., 2010; Stolpe and Hasselöv, 2007). The bioavailability of humic and fulvic colloids for autotrophic phytoplankton is rather low (Xue and Sigg, 1998). By contrast, heterotrophic bacterioplankton is capable of efficiently mineralizing allochthonous DOM in boreal organic-rich lakes (Tranvik, 1988; Tranvik and Jorgensen, 1995; Kritzberg et al., 2004; Jansson et al., 2000, 2007; Ask et al., 2008). The majority of trace elements and non-negligible fractions of major elements such as alkali-earth metals are complexed with DOM of soil origin in the surface runoff that delivers these components to the lake. Thus, respiration of DOM by heterotrophs, presumably enhanced by rising temperature (Roiha et al., 2012), may 1) liberate or consume associated trace metals and 2) modify the speciation and size fractionation of TE in the water column of a lake. To gain a better understanding of the biogeochemical mechanisms that control the distribution of dissolved, particulate and colloidal OC and TE in surface boreal waters in response to climate warming and water temperature rise, we studied one seasonally stratified lake in the Arkhangelsk region (NW Russia, White Sea basin) over 4 years, from 2007 to 2010. We aimed to address the following specific questions of OC and TE biogeochemistry in this typical small boreal lake: 1) Are there systematic differences in organic carbon and major element and trace element concentrations in the epilimnion during ‘normal’ periods and an anomalously hot summer? 2) What are the quantitative impacts of an elevated water temperature that persisted for two months in a boreal lake on the size distribution of OC, Fe and TEs from 5 μm to 1 kDa over the entire depth of the column? 3) Can the effects of phytoplankton uptake of metal micronutrients and trace elements, heterotrophic bacterioplankton mineralization and photo-degradation of organic and organo-mineral colloids controlling TE speciation be distinguished from each other? We anticipate that answering these questions should provide a first-order evaluation of TE concentration and size fractionation evolution in boreal aquatic environments under an on-going climate warming scenario.

2. Materials and methods

2.1. Site description

We studied the typically humic Lake Svyatoe. The lake is located in the Arkhangelsk region (Northern Europe) within the watershed of the Onega River (White Sea basin, see map and site description in the ESM-1.1). The chemical composition of the lake water is dominated by Ca$^{2+}$ and HCO$_3^-$, with typical total dissolved solids of 100–200 mg/L and with 1.8–2.5 mg/L sulfate, 0.2–0.6 mg/L chloride, 15–20 mg/L
DOC and a pH ranging from 7.9 in the epilimnion to 6.6 in the hypolimnion. The lake is mesotrophic with typical primary production in the photic zone ranging from 0.02 to 0.2 mg C m\(^{-3}\) d\(^{-1}\); the organic matter aerobic mineralization rate ranges from 0.05 to 0.2 mg C m\(^{-3}\) d\(^{-1}\) (Shirokova et al., 2009).

At the deepest monitoring point, the lake exhibits distinct seasonal and chemical stratification in the temperature and oxygen depth profiles, as illustrated in Fig. 1A and B, respectively. The typical ice thickness at the end of winter during our 5-year period of observation is 45 ± 10 cm. The maximum winter stratification is achieved in March, and the highest water temperature typically occurs at the end of July or the beginning of August.

2.2. Sampling and in-situ measurements

Sampling at various lake water depths at the deepest monitoring station was performed in July 2007, 2008, 2009, March 2008, 2009, 2010 and August 2010 at essentially anticyclone conditions with in-situ measurements of pH, temperature and dissolved oxygen. The most complete data on depth profile and colloidal fractions were collected in July 2008, 2009, March 2009 and August 2010. Over the 4 days of August 5th–8th of 2010, observations were made concerning bloom conditions linked to high concentrations of cyanobacteria in the surface layer (10–50 mg POC L\(^{-1}\)). The typical cyanobacteria responsible for summer blooms in Lake Svyatoe are Anabaena flos-aquae, Gloeocapsa turgida, and Microcystis pulvnea (Shirokova et al., 2007; Pokrovsky and Shirokova, 2013).

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, 2012a; Shirokova et al., 2010, 2013). The clean trace-metal technique was employed throughout sample collection, filtration, dialysis and analysis as presented in the Electronic Supplementary Material 1.2.

3. Results

3.1. Thermal and redox stratification and variation of element concentrations in the epilimnion

Full compilation of lake chemical composition at different depths and during different seasons is given in the Electronic Supporting Information 2 (Table ESM-2). As shown in Fig. 1A, the lake exhibited clear seasonal stratification, with the bottom temperature ranging from 3 to 12 °C (below 12 m). The surface water temperature was quite variable in the summer, ranging from 18 °C in July 2009 to 28–30 °C in August 2010, an anomalously hot summer in NW Russia. During the summer and winter, the lake water was oxygen-saturated within the first 4 m of the surface, but the water contained 1–2 mg O\(_2\) L\(^{-1}\) below a depth of 14 m. The decrease in oxygen concentration from the surface to the bottom is rather smooth; the oxycline is not strongly pronounced, unlike in that typical stratified temperate lakes.

To assess the element concentration response in the epilimnion to the surface water temperature rise during the anomalous summer of 2010, we calculated the ratio (R) of the average TE concentration in the epilimnion measured in July 2007, 2008, 2009, and March 2008, 2009 (n = 14) to that measured in August 2010 (n = 3). Three groups of elements could be distinguished:

1. Elements indifferent to the biota that are present in ionic, non-colloidal forms with R = 1.0 ± 0.2 (Li, B, Na, Mg, K, Ca, Ga, As, Rb, Sr, Sb, Cs, Ba, W and U). Several biogenic elements present as organic-free, ionic or neutral species such as Si, Ge, V, and Mo also belong to this group;
2. Essential metal micronutrients, present in organic colloids with 2 ≤ R ≤ 6 (Cr, Mn, Fe, Ni, Cu, Zn and Cd). A complete removal of P and Co from the surface layers in August 2010 was observed (R > 100);
3. Non-essential, soluble trace elements present as organic and organo-mineral colloids with 2 ≤ R ≤ 8 (Al, Sc, Ti, Y, Zr, Nb, all REEs, Hf, Pb, Th).

It should be noted that this classification does not change significantly when the March data are not included for calculating average concentrations.

3.2. Dissolved organic carbon (DOC)

The concentration of DOC in Lake Svyatoe ranged between 15 and 20 mg/L and exhibited a steady concentration decrease (ca. 20 to 30%) from the surface to the bottom during wintertime and a rather constant vertical distribution during the summertime (Fig. 2). The DIC concentration steadily increased from 18 ± 2 mg/L at the surface
to 30 ± 2 mg/L at the bottom. The R values for DOC and DIC are equal to 1.33 and 1.05, respectively.

Examples of organic carbon (OC) concentrations in different dialysates and filtrates during all investigated seasons are plotted in Fig. 2A–D. It can be seen that there was no significant change in the OC concentration after filtration through 5 μm filters down to the 0.22 and 0.025 μm filters. Some organic matter (OM) particles (0.22–5 μm) became detectable below 4 m depth in March 2009 (Fig 3C) but disappeared in summer (Fig 3D). The proportion of OM colloids (1 kDa–0.22 μm) ranged between 60 and 80% during the summers of 2007–2008 and between 80 and 90% during the winters of 2008–2009 (Fig. 3). In contrast to other summer periods, in August 2010, there was only 25–50% of colloidal OC. Analyses of available data on dissolved organic nitrogen in March 2009 (see Table ESM-2 and Moreva, 2010) demonstrated a systematic change in the C/N ratio of DOM, decreasing from 62 at the surface to 12 at the bottom. Other investigated seasons demonstrated similar ranges of the C/N ratio (from 20 to 33 in July and March 2008).

3.3. Trace element size fractionation as a function of depth during different seasons

Concentrations of filtered, ultrafiltered and dialyzed components of the lake water at various depths during all sampled seasons are listed in Table ESM-2 of the Electronic Supporting Information 2. The in situ dialysis technique employed in the present study allowed new insights into the evolution of major elements and TEs in the colloidal and LMW fractions along the water column. Those fractions can be assessed with the help of a series of diagrams presented in Figs. 4–7 and ESM 2.1–2.18. For this analysis, we selected 1) major and trace alkali-earth cations (Ca, Sr and Ba); 2) typically insoluble low-mobility elements (Al, Ti, Y, Zr, REEs, and Th); 3) redox-sensitive Fe and Mn; 4) Metal micronutrients present in the form of divalent cations (Ni, Cu, Co) and oxyanions (V, Mo); 5) As and Sb, which can be present in the form of neutral molecules or anions; and 6) U, which is known to occur in both inorganic uranyl–carbonate complexes and organo-colloidal forms. The efficiency of in situ dialysis procedures can be assessed from the plot of Si concentration. Si is known present exclusively in inorganic non-colloidal forms in boreal waters (Pokrovsky and Schott, 2002; Pokrovsky et al., 2010, 2012a). It can be observed from Fig. ESM-2.1 of the Electronic Supporting Information 2 that there are very similar concentrations of Si in each fraction during all studied seasons, suggesting a true equilibrium distribution of solutes under the experimental conditions chosen for this study.

Similar to boreal rivers of NW Russia, alkali earth metals exhibited non-negligible proportions of colloidal forms, with the size of these
colloids between 10 kDa and 0.025 μm (Figs. ESM-2.2 to 2.4). The minimal proportion of Ca and other alkali-earth elements in colloids was observed in August 2010. The Mn concentration remained virtually the same after filtration through 0.025 μm and after dialysis through 1–10 kDa at surface depths ≤4 m, but in deeper layers, up to 50% of the Mn was present as large and small-size colloids that were especially pronounced during the winter period (Fig. 4C) and disappeared during summer (Fig. 4D). The minimal fraction of colloidal Mn was measured during August 2010.

Aluminum and iron demonstrated the dominance of small colloidal forms (1 kDa–0.025 μm) below a depth of 4 m during all seasons and over the full depth of the water column in winter. In summer, at most surface depths, the speciation of these elements included a non-negligible amount of the LMW (≤1 kDa) forms (Figs. 5 and ESM-2.5 for Fe and Al, respectively) that were most likely microbial exudates or the products of the photo-degradation of Fe(III) and Al(III) as organic complexes as discussed in Sections 4.1–4.2 below. The vertical distribution of Ti size fractions demonstrated a rich spectrum of colloidal forms with HMW particles and colloids (0.025 μm–5 μm) present during winter and a LMW (<1–50 kDa) fraction accounting for up to 50% of the total filterable Ti in summer (Fig. ESM-2.6). Other insoluble trivalent and tetravalent elements (Y, REEs, Zr, Hf, Th) closely followed the pattern of Fe with the maximum proportion of HMW (50 kDa–0.025/0.22 μm) colloids in the winter and the highest contribution of LMW <1 kDa at a 0–4 m depth in August 2010 (Figs. ESM 2.7, 2.8, 2.9, 2.10 and 2.11 for Y, La, Zr, Hf and Th, respectively).

Uranium accumulated in the hypolimnion in winter both as a LMW <1 kDa fraction and 0.025 μm–1 kDa colloids but remained rather constant over the water column in summer, with clear enrichment of the surface depths (<6–8 m) by the LMW <1 kDa fraction (Fig. ESM 2.12). Similar to other insoluble and low-mobility elements, this fraction dominated the surface waters in August 2010.

Divalent transition metals (Ni, Co, V) exhibited a significant contribution of LMW species (1–10 kDa in July 2008; 1–50 kDa in July 2009). “Traditional” colloidal forms (1 kDa–0.22 μm) of Ni, Co, Cu, V and Cr were especially visible during winter stagnation when they constituted between 40 and 80% of the total dissolved elements (Fig. 6, and Figs. ESM-2.13, 2.14, 2.15, and 2.16, respectively). Colloidal forms of Ni and V almost completely disappeared in August 2010 over the full depth of the water column (Figs. 6D and ESM-2.15D, respectively) whereas Cr preserved an approximately 50% colloidal fraction, notably in the hypolimnion during August 2010 (Fig. ESM 2.16D) and Cu increased the fraction of LMW colloids (1–50 kDa) almost 2 times compared to the ‘usual’ summer 2009 (Fig. ESM 2.14).

Anionic metal micronutrients such as Mo demonstrate the dominance of truly soluble (<1 kDa) forms during summer periods and ≤20% of 1 kDa–0.025 μm colloids in winter (March 2009 and 2008), as illustrated in Fig. ESM 2.17. The presence of a significant (up to 50%) proportion of colloidal (1 kDa–0.025 μm) as was noted at all lake depths of the lake water, particularly in winter (Fig. 7). Sb is less prone to colloidal forms, with a 1 kDa–0.025 μm fraction detectable only in winter, similar to Mo (Fig. ESM-2.18C).
Fig. 5. Plot of Fe concentrations as 5 μm, 0.22 μm and in situ dialysis through 1, 10 and 50 kDa membranes during four typical seasons.

Fig. 6. Plot of Ni concentrations as 5 μm, 0.22 μm and in situ dialysis through 1, 10 and 50 kDa membranes during four typical seasons.
3.4. Proportion of colloidal (1 kDa–0.22 μm) forms of TEs during different seasons over the full depth profile

Assessing size fractionation using both conventional filtration (0.22 μm) and in situ 1 kDa dialysis as a function of depth allowed for the characterization of the seasonal distribution of TE colloidal fractions as described below. Iron was essentially present in colloidal state during both summer 2007–2009 and winter 2008–2009 stagnation, while in August 2010, there was an approximately 20–30% decrease in the colloidal fraction of Fe (Fig. 8A). The divalent Fe exerted a very small effect on the total Fe speciation in the water column because even during winter stagnation in the hypolimnion, iron was present as >80–90% Fe(III), as follows from on-site spectrophotometric measurements of dissolved Fe with phenanthroline and ferrozine. Al and Ti also exhibited the smallest fraction in a colloidal form in August 2010 and the highest proportion of colloids in winter (Fig. 8B, C). Other insoluble trivalent elements such as Y and REEs and insoluble tetravalent elements (Zr, Hf, Th) demonstrated clear and statistically significant decreases of colloidal forms in August 2010 compared to July 2008, July 2009 and winter periods (Fig. ESM-2.19). Sr and Ba usually had 10–20% in colloidal forms but also demonstrated a decrease in the relative proportion of colloids during August 2010 compared to other seasons (Fig. ESM-2.20). Among divalent metal nutrients, only Cu and Ni colloidal forms could be quantitatively resolved with sufficient precision. In August 2010, there was a decrease in the Ni colloidal fraction over the full depth of the water column compared to other seasons from 40–70% to 20–40%, respectively (Fig. 9A). Among oxyanions, V and As demonstrated the highest proportion of colloidal fractions in March 2009 (~60%) and the lowest proportion in August 2010 (~5–20%, Fig. 10A, B). Copper was the only element demonstrating an increase in colloidal forms during August 2010. Indeed, the LMW (< 1 kDa) fraction of Cu was approx. 20% more abundant during summer 2010 compared to 2008 and 2009 (Fig. 9B).

Uranium exhibited a complex vertical profile of colloidal fraction distribution. In July 2008 and 2009, there was an increase of colloids from 30–50% at the surface to ~80% in the hypolimnion, while in March 2008 and 2009, the U colloidal fraction decreased from 70% in the epilimnion to 30–50% in the hypolimnion. Similar to other elements affected by organic and/or organo-ferric colloids, the relative contribution of the 1 kDa–0.22 μm fraction was minimal in August 2010 compared to all other investigated seasons (Fig. ESM-2.21).

4. Discussion

4.1. Stratification of carbon and trace elements and the role of colloids

The typical feature of the Lake Svyatoe is the existence of significant temperature and redox condition stratification, especially during winter stagnation (see Fig. 1). This stratification is much less severe for nutrients such as N and P (Table ESM-2) and only Si became depleted at the 0–4 m depth compared to the bottom layers (Fig. ESM-2.1). The DIC increased from the surface to the bottom (cf. Table ESM-2), which could be linked to the anaerobic mineralization of OC and sulfate reduction (Kokryatskaya et al., 2012). Intensive mineralization of dissolved organic matter is further supported by low δ13CDIC values (Shirokova et al., 2009) that ranged from −12.9‰ at the surface to −12.4‰ at the bottom in March 2009. This result suggested i) a clear disequilibrium with the atmosphere and ii) the 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‰ on average, Striegl et al., 2001). In August 2010, δ13CDIC exhibited some diurnal variations with daytime values (c.a., −10.5 to −9.8‰) being less negative than the night time values (c.a., −11.4 to −10.6‰, Pokrovsky and Shirokova, 2013).

The decrease of the C/N ratio in DOM from 62 at the surface to 12 at the bottom depth in March 2009 suggests a systematic transformation...
of the OM source throughout the water column. C/N values of approximately 20 are typical for aquatic phytoplankton and macrophytes and their humification products (Wolfe et al., 2002), whereas a C/N value close to 100 would be similar to the biomass of coniferous trees and ligno-cellulose complex of pine and birch litter, similar to other peat bog soil waters (Guggenberger et al., 1994; See and Bronk, 2005; Tremblay and Benner, 2006). As such, high C/N values in the surface layers of Lake Svyatoe support both allochthonous and autochthonous sources of DOM during the studied periods. Intensive mineralization of sunken planktonic biomass occurred in the bottom layers, notably in winter.

Although Fe is often stratified in temperate and boreal humic lakes (Hamilton-Taylor et al., 1996, 2005; Achterberg et al., 1997), this stratification is rather small in Lake Svyatoe, achieving only a factor of 2 between the epilimnion and the hypolimnion in July 2009 and August 2010. The lack of a significant increase of the Fe concentration at bottom depths may be due to strong Fe(III) complexation with allochthonous large-size organic ligands preventing Fe(III) reduction, in contrast to other organic-poor seasonally stratified lakes. A pronounced decrease (×2) in the Fe concentration in the photic layer in August 2010 compared to a depth >8 m may be partially linked to Fe uptake by phytoplankton due to bloom events. Indeed, a recent bloom in this lake was characterized by net productivity of 2 mg C L$^{-1}$ day$^{-1}$, capable to drawdown up to 2–4 μg Fe L$^{-1}$ day$^{-1}$ taking into account a typical Fe concentration in the phytoplankton of 500–1000 ppm (Savenko, 1988; Shaked et al., 2004; Sunda and Huntsman, 1998; Finkel et al., 2006). Over 2–4 weeks of stable bloom, this would bring about the removal of 25–100 μg L$^{-1}$ of dissolved Fe in the photic layer, comparable to what is observed in August 2010 (Fig. 5D).

The results of filtration and in situ dialysis, together with previous observations in lakes and rivers in this region, allow us to hypothesize the existence of two colloidal pools: small-size OM-rich colloids (1 kDa–0.025 μm) and large-size Fe-rich colloids (0.025 μm–0.22 μm).
These pools can be visualized via the plot of Fe vs. DOC shown in Fig. 11. It can be seen that the slope of the dependency of [Fe] on [DOC] changes after filtration through a 0.025 μm filter in March but remains almost constant in August 2010. Small-size (0.025–0.45 μm) Fe-poor, C-rich colloids and LMW–1 kDa organic compounds are especially important during the hot summer 2010 period, as observed from Fig. 11.

In the latter case, small-size organic colloids dominate both in the surface layers and at the bottom; however, the concentration of colloidal Fe is a factor of 5 lower during summer compared to that in winter. The existence of two types of 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)—is consistent with observations in other natural waters (Leah et al., 1997; Lyvén et al., 2003; Allard et al., 2004; Baalousha and Lead, 2007; Stolpe and Hassellöv, 2010; Stolpe et al., 2010).

Typically insoluble elements (Al, Ti, Ga, Y, all REEs, Zr, Hf and Th) and U exhibited slight increases in the <0.22 μm concentration with depth in the summer, and these elements were strongly associated with both large-size organo-ferric colloids (0.22–0.025 μm) in the lower depths and with small size OM-rich colloids (0.025 μm–1 kDa) in the surface depths. Judging from the shape of the element concentration profile during different seasons, organic colloids are the most important forms for these insoluble elements in winter. There is a similarity in the TE and OC profiles in March 2008 and March 2009, namely, a pronounced concentration decrease below the 4 m depth, most likely linked to mineralization of DOM by heterotrophic bacterioplankton and release/coagulation of related trace elements. Similar coupling of organic carbon and TE behavior was reported in shallow thermokarst lakes in W Siberia (Pokrovsky et al., 2011; Audry et al., 2011; Shirikova et al., 2013).

None of the micronutrients (Cu, Zn, Ni, Cr, V and Mo) exhibited significant stratification in the water column except Mn and Co. This coupling between Mn and Co may be linked to the well-known scavenging of Co with Mn oxy(hydr)oxides via oxidation of Mn(II)– or Mn(IV)–oxide particles (Murray, 1975) of biological origin (Lienemann et al., 1997), followed by release of both elements during bacterial dissolution at the chemocline (Taillefert et al., 2002). Note that the limitation of both Mn and Co for phytoplankton production in the photic layer and/or uptake by heterotrophic bacterioplankton may be responsible for significant uptake of Co over the full depth of the water column in August 2010 (i.e., Pokrovsky and Shirikova, 2013), leading to Co concentrations below 0.001 ppb in this period. The absence of stratification for other oligoelements may be due to their strong complexation with allochthonous DOM and/or lack of biological uptake.

A distinct difference in the U colloidal fraction distribution between summer and winter 2008–2009 (see Figs. ESM-2.12, 2.21) is most likely linked to the change in the relative proportion of uranyl–carbonate complexes versus U organic and organo-mineral colloids. In summer 2008–2009, a decrease in the colloidal fraction in the photic layer compared to the hypolimnion may be due to the increase of pH during cyanobacteria blooms at otherwise similar DIC concentrations along the water column. In winter, a significant build up of DIC in the hypolimnion increased the proportion of uranyl–carbonate complexes compared to U organic colloids, a feature that is well established for large rivers in this boreal region (Pokrovsky et al., 2010) and, recently, for another boreal lake (Pokrovsky et al., 2012a).

4.2. Processes in the water column controlling the concentration and colloidal pattern of trace elements.

The processes controlling trace element migration and speciation in a lake include the following: 1) scavenging by phytoplankton, 2) mineralization of organic colloids by heterotrophic bacterioplankton, 3) photo-degradation of DOM in surface layers, 4) dissolution of sinking particles at the oxycline and transformation of redox-sensitive elements, and 5) diffusion of elements from sediment porewaters to the lake bottom.

Compared to other boreal stratified lakes, the reduction of Fe in the anoxic hypolimnion of Lake Svyatoe was very weak, as the proportion of colloidal Fe remained constant over the full depth of the water column during the two main hydrological seasons. Therefore, the lack of significant Fe enrichment in the hypolimnion in the form of <1 kDa (presumably ionic Fe$^{2+}$) species (Fig. 5) suggests that there is no reduction of Fe (III) by either the water-column colloids or sinking particles. A possible reason for weak reduction of Fe(III) in the hypolimnion of Lake Svyatoe compared to other boreal lakes (cf., Maselga Lake, Pokrovsky et al., 2012a) is the presence of significant, 2 to 5 mg L$^{-1}$, O$_2$ concentration. Moreover, the concave shape of the concentration profiles typical for the influx of metal from sediments (e.g., Audry et al., 2011 and references therein) is not clearly seen for Lake Svyatoe. As such, the main process controlling Fe distribution over the full depth of the lake is the input of surface soil/bog water from adjacent bog zones containing high concentrations of allochthonous DOM (Shirokova et al., 2007; Pokrovsky and Shirikova, 2013). This pool is subjected to heterotrophic mineralization and photo-degradation of organo-ferric colloids, leading to sedimentation of Fe-rich particles to the bottom layers. The latter is especially visible from the increase of the [Fe]$^{-5}$ μm fraction in the hypolimnion (>10 m) during March 2009 (Fig. 5C). The large size (0.22–5 μm) subcolloidal particles are also formed during the summer period; their production in the photic layer was most pronounced in August 2010 (Fig. 5D).

An important and poorly understood process of the Fe cycle in lakes is the mixing of anoxic hypolimnetic waters with the epilimnion, which occurs during the spring and autumn overturns. Upon mixing and aeration of the water column, Fe(II) is oxidized and forms Fe(III)–DOC colloids (Maloney et al., 2005). This process has been seen in another boreal lake, Lake Maselga, which contains a lower concentration of DOC and receives a much smaller allochthonous input of Fe(III) and DOC from adjacent bogs compared to Lake Svyatoe (Pokrovsky et al., 2012a). The relative contribution of hypolimnetic Fe(II) oxidation compared to the significant input of soil- and bog-derived Fe(III) should be
much smaller in Lake Svyatoe, although we do not have observations during the overturn process.

Among all studied major and micro nutrients and trace elements, Mn exhibited by far the largest gradient in concentration from the surface to the bottom layers. The convex-shaped Mn profile in the water column, which is fairly well established for other temperate and boreal lakes, is most likely linked to in situ dissolution of falling particles (Davison et al., 1982; Balistrieri et al., 1992). The first plausible explanation is that Mn is being more readily reduced than Fe thus exhibiting greater diffusion from the sediments. However, one cannot exclude the possibility of Mn being a limiting micronutrient for phytoplankton production in the photic zone of the lake. This is supported by i) a factor of 500- to 3000-fold Mn concentration depletion at the surface relative to the bottom, which is significantly higher than that of such limiting nutrients as PO\textsubscript{4} (a factor of 3 to 30, see Table ESM-2); ii) the essentially dissolved bioavailable status of Mn\textsuperscript{2+} in the photic layer as follows from dialysis experiments in this study (cf. Fig. 4) in contrast to other studies of temperate organic-rich waters (i.e., Graham et al., 2012); iii) a systematic response of the Mn concentration to the diurnal photosynthesis cycle in boreal lakes during summer bloom (Shirokova et al., 2010; Pokrovsky and Shirokova, 2013); and iv) a significant uptake of dissolved Mn during incubation of lake water (Shirokova et al., 2007 and our unpublished results). Therefore, a decrease of Mn concentration from the bottom to the surface, mostly pronounced during hot summer 2010, may be linked to Mn binding inside and at the surface of photosynthesizing phytoplankton cells of the lake photic layer, down to 3–6 m. A mass balance calculation similar to that of Fe (see Section 4.1) yields the possibility of ~10 μg L\textsuperscript{−1} decrease in the photic layer over 1 month of summer bloom, consistent with the concentration profile shown in Fig. 4D.

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 (\textlessthan 1kDa) ligands originated from phytoplankton exometabolites, aquatic plant exudates and leaching and heterotrophic mineralization products, another process responsible for the production of LMW organic ligands in the surface layers may be the photo-oxidation of DOM (e.g., Amin and Benner, 1996; Moran and Zepp, 1997; Jonsson et al., 2001; Anesio and Granéli, 2004; Bertilsson and Tranvik, 2000). In a humic boreal lake, photo-oxidation is responsible for at least 10% of the total OM degradation (Pers et al., 2001), although the relative importance of this process for the production of LMW complexes of TEs in Lake Svyatoe cannot be evaluated. It can be hypothesized, however, that elevated surface water temperatures during the hot subarctic summer of 2010 could enhance the magnitude of photo-oxidation and production of LMW (\textlessthan 1kDa) organic ligands as it is known that photochemical mineralization of DOC in the Arctic surface waters may be as high as 30% of bacterial mineralization of DOC (Cory et al., 2007). These photochemically-produced organic ligands may complex some TE, thus increasing the relative contribution of LMW forms. In summertime, the photoreaction of Fe(III) under visible light and UV is known to produce labile (<100 Da) Fe, as shown in experiments on boreal stream waters (Kelton et al., 2007). This photo-reduction, which exhibits a diurnal pattern (Emmenegger et al., 2001), may partially explain the decrease of colloidal forms at the expense of LMW forms of Fe in the photic zone (first 3–4 m) of Lake Svyatoe that was observed in August (Fig. 8A).

The role of photo-induced transformation of other metal complexes is, at present, poorly understood. It was reported however, that photo-oxidation of river DOM decreases the concentration of organically bound Cu and Fe complexes (Brooks et al., 2007; Shiller et al., 2006) and that UV irradiation is also capable of significantly decreasing the concentration of Al and Fe bound to complexes with allochthonous OM (Kopacek et al., 2005; Kopacek et al., 2006). As such, the liberation of metal ionic forms from HMW humic and fulvic complexes under temperature-enhanced irradiation may bring about formation of new, stronger complexes with available LMW (\textlessthan 1kDa) ligands, thus decreasing the relative fraction of the colloidal form. Part of the metal pool may be subjected to coagulation in the form of oxy(hydr)oxide and sedimentation to the lake bottom (cf., Kopacek et al., 2006), thus decreasing the total dissolved metal concentration throughout the water column, as observed in Lake Svyatoe during August 2010.

Results from the present study demonstrate that not only concentrations of most TE but also their relative colloidal fractions significantly decreased through the full depth of the water column during the anomalously hot summer of 2010 compared to other periods. This decrease may be linked to 1) active uptake of micronutrients and passive uptake of other TE during the phytoplankton bloom in the photic layer; 2) heterotrophic respiration of allochthonous OM leading to coagulation and sedimentation of OM-poor, Fe-rich particles, thus scavenging associated TEs, as it is known for thermokarst lakes (Audry et al., 2011; Shirokova et al., 2013); and 3) photo-degradation of OM, photo-reduction of Fe(III) and photo-transformation of colloids/LMW complexes of other TEs. The uptake of limiting nutrients in the upper (photic) layer should be followed by sedimentation and release in the lower depths via heterotrophic mineralization of phytoplankton cells. However, the degree of element concentration increase in the hypolimnion compared to the epilimnion was rather weak and similar among all studied seasons. If metal nutrient uptake were important, it can be expected that the elements potentially limiting for phytoplankton, such as Mn, Co, Ni, P, Cu, Zn, and Mo, should be depleted. However, this is true only for Mn and Co, meaning that phytoplankton uptake can account for only a limited amount of TE transformation.

A way to test the increase of heterotrophic mineralization during the hot summer of 2010 compared to other periods could be a direct count of heterotrophic bacterioplankton. In this study, we possess only the CFU number of culturable eutrophic (nutrient-rich) and oligotrophic (nutrient-poor) aerobic bacteria obtained via agar plate counts and total microbial numbers. Statistical treatment of the available results does not demonstrate any measurable trend or systematic difference in average CFU numbers in the epilimnion and over the full depth of the water column in August 2010 compared to July 2007, 2008 and 2009. However, the heterotrophic bacteria concentration is subject to significant variations over short periods; the phytoplankton bloom occurring in August 2010 may significantly inhibit the heterotrophic bacteria number due to poisoning/protection mechanisms by cyanobacteria. It is important to note that increased concentrations of labile photo-degraded DOC have been shown to be beneficial to bacterioplankton growth (Wetzel et al., 1995; Engelhaupt et al., 2003). As such, bio- and photo-mineralization processes may be self-accelerating when water temperatures rise.

LMW carbon compounds of terrestrial origin are known to be important for bacterial growth in boreal lakes (i.e., Berggren et al., 2010), but they seem to have a minor effect in Lake Svyatoe during the hot summer of 2010 as the surface discharge during that 2-month drought period was minimal and the concentration of DOC in the main inlets to the lake remained within the usual range of summer values (authors’ unpublished data).

Taken together, enhanced photo- and bio-transformation of allochthonous DOM and production of LMW trace element binding complexes under elevated surface water temperatures seem to be the primary causes of the decreases in the DOC and TE colloidal fractions in August 2010.

4.3. Possible effect of climate warming on OC and TE concentration and speciation in boreal seasonally stratified lakes.

Differences in the OC and TE concentrations and speciation observed in the present study between the anomalously hot August 2010 and other periods may help to predict the short-term consequences of climate warming on the biogeochemistry of carbon and TE in boreal lakes. If the climate change brings about higher surface water temperatures (~3°C increase of the lake temperature in
response to a 5 °C increase of the air temperature, Hobbie et al., 1999), then the boreal humic lakes will evolve toward the following status:

1) The concentration of most TE linked to organic and organo-mineral colloids will decrease by a factor of 2 to 4 and that of DOC by more than 30%;

2) The relative proportion of colloidal Ca, Mg, Sr, Ba, V, Cr, Ni, Al, Ti, U, and all trivalent and tetravalent hydroxylates will decrease by a factor of 2 to 5.

These changes will bring about an increase in the lability of OC and TE and, most likely, their bioavailability. Indeed, LMW-1 kDa species are potentially bioavailable because the pore sizes of cell wall transport channels (10–30 Å in bacteria, 35–50 Å in plant cells (Carpita et al., 1979; Trias et al., 1992) and that of 1 kDa dialysis membranes (1–2 nm)) are comparable. This assumption may be true only for passive (diffusional) transport of metals through the biological membranes.

An important and rather unexpected result of the long-term observations at Lake Svyatoe is > 30% decrease of the DOC concentration during a hot summer. This finding is in contrast to numerous observations in Western Europe, where on-going climate and environmental changes show increased DOC concentrations in rivers and lakes and DOC export from the watershed (Evans et al., 2005; Monteith et al., 2007; Porcal et al., 2009). It is known that the overall effect of warming on organic matter production and export in lake–watershed system may consist in increasing the OM mobilization from soils and rising the primary productivity that should bring about an increase of the concentration of allochthonous and autochthonous DOC in the water column, respectively. From the other hand, DOM mineralization rates should also increase thus decreasing DOC of the lake water. The particularity of studied boreal humic lake consists in i) significant buffering of allochthonous DOC input by adjacent bogs, ii) restricted primary productivity due to shallow photic layer in these dark, organic-rich waters, iii) high DOM respiration by aerobic heterotrophic bacterioplankton and iv) specific character of boreal (sub-arctic) allochthonous DOM comprising significant proportion of LMW-1 kDa (fulvic-like) organic acids (cf., Pokrovsky et al., 2012b). These factors may provide a first-order explanation for the difference in production and removal of organic carbon in previously studied low-DOC temperate aquatic environments and in the humic boreal lake of the present study. Another reason for such a difference may be different time scales of observation; a short-term decrease of DOC in Lake Svyatoe during the anomalously hot summer 200 may be followed by its remobilization from the sediments in the following years.

The increase in the bioavailability of trace metals linked to environmental changes may also occur due to acidification of surface waters. According to ex situ dialysis experiments, a decrease of pH by one unit (from 6 to 5) brings about a two- to three-fold increase in the proportion of non-colloidal (<1 kDa) forms of most potentially toxic metals such as Al, Cd, Co, Cu, Ni, Pb, Th, and U (Vasyukova et al., 2012), which is in agreement with available natural observations on rivers draining acid-sulfate soils (Nystrøm et al., 2012). This strongly suggests that all three mechanisms—pH decrease due to acidification (Reuss et al., 1987; Borg et al., 1989; Skjelkvåle et al., 2001; Davies et al., 2005; Neal et al., 2008), DOC decrease due to heterotrophic respiration (this study and that of Striegl et al., 2005 in Alaska) and the proportion of LMW-1 kDa increase (this study and Vasyukova et al., 2012)—will overwhelm the increase of the DOC concentration in surface waters due to climate warming that has been reported in the Nordic countries, the British Isles, and the Northern and Eastern United States (by approx. 10% over 10 years (Evans et al., 2005). Therefore, the majority of available observations suggest the increase of potential bioavailability of trace metal nutrients in lake water under a climate warming scenario.

This potential bioavailability increase will produce a positive feedback and further decrease the concentration of the <0.22 μm dissolved fraction as well as the proportion of the LMW-1 kDa pool. The main driving mechanism of these changes will be the activity of heterotrophic aerobic bacteria capable of respiring DOM of allochthonous origin (i.e., Jansson et al., 2007). At higher temperatures, metabolic rates increase considerably and bacteria are able to break down organic substrates more rapidly (Pomeroy and Wiebe, 2001) and increase secondary production (Kirchman and Rich, 1997). Therefore, temperature exerts major control on aquatic bacterial production in arctic (Adams et al., 2010) and temperate (Simon and Wunsch, 1998; Vrede, 2005) lakes. Given that DOC degradation rates are temperature-dependent (Cabani et al., 2005), DOM mineralization will be significantly enhanced by elevated water temperatures in the surface layers and will lead to production of the LMW-1 kDa organic fraction that can bind trace elements. The photo-induced degradation of DOM will be also accelerated by rising temperatures as it is known that the activation energy for DOM photolysis ranges between 10 and 30 kJ mol−1 (Likens, 2010) and a temperature rise from 0 to 25 °C may correspond to 1.5–3.0-fold photodegradation increase. Similarly, decreasing lake water pH, a common phenomenon of surface waters evolution potentially linked to climate change (Davies et al., 2005; Neal et al., 2008) should also increase the intensity of photo-induced DOM degradation (Gennings et al., 2001; Molot et al., 2005). Altogether, a decrease in [DOC]0.22 μm, [DOC]1 kDa and LMW-1 kDa TE concentrations is the most likely scenario of boreal lake chemical composition transformation under short-term water warming conditions.

5. Conclusions

Colloid origin and migration in boreal, humic Lake Svyatoe are chiefly affected by the biogeochemical cycle of carbon and iron. Two governing factors controlling the fate of these colloids are the following: (1) biological processes of phytoplankton production and heterotrophic bacterioplankton mineralization in the water column during summer and winter stagnation that lead to the appearance of organic LMW-1 kDa complexes of TE similar to other boreal and thermokarst lakes; and (2) the input of allochthonous soil and bog OM present in the form of HMW organo-mineral colloids, typical for the boreal zone of NW Russia. The role of the diffuse flux of Fe2+, other trace metals and OM from the sediment porewater to the bottom depths, is relatively small in Lake Svyatoe compared to other stratified lakes.

Increasing the surface water temperature almost 10° above normal during the anomalously hot summer of 2010 produced a measurable and significant transformation of colloids in the water column of this boreal lake. The element concentration in the epilimnion decreased compared to “normal” periods by a factor of 2 to 6, and the relative proportion of the LMW-1 kDa fraction increased by a factor of 1.5 to 3 compared to other seasons. The processes responsible for element uptake and colloid transformation include phytoplankton bloom, heterotrophic bacterioplankton mineralization and photo-degradation of DOM.

The respiration of allochthonous DOM by aerobic bacterioplankton and photo-induced OM oxidation are likely to bring about 1) the appearance of small size LMW-1 kDa organic ligands; and 2) coagulation of Fe-rich colloids in the form of >0.22 μm sub-colloidal particles. It follows that under a climate warming scenario at high latitudes, mobility and potential bioavailability of OC and TE in the colloidal fraction will increase as HMW-0.22–0.025 μm organo-ferric colloids will be replaced by organic LMW-1 kDa complexes binding TE. Regardless of the evolution of the DOC concentration in surface waters under various climate warming scenarios, three main processes controlling organic colloids in lakes—acidification, DOC mineralization by heterotrophic bacterioplankton and production of LMW organic ligands by photo-degradation—will increase the potential bioavailability of trace elements and metal micronutrients, and as such may augment both primary productivity and OM mineralization in lakes, effluent rivers, and, finally, the Arctic ocean.
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Appendix A. Supplementary data
Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2013.05.088.

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