



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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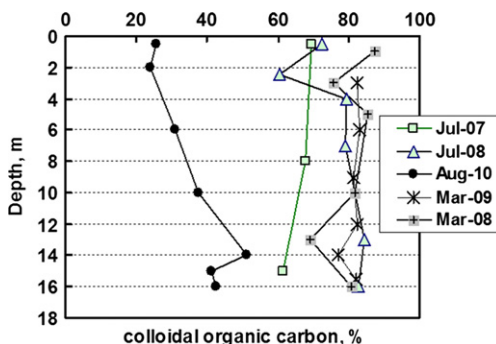
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HIGHLIGHTS

- 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 bio-availability.

GRAPHICAL ABSTRACT

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



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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 Svyatoye, 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

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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 DOC 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 DOC 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 (Kopáček 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 (Ingri 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 Hassellöv, 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 Svyatoye. 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 Ca²⁺ and HCO₃⁻, 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

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