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Diurnal variations of dissolved and colloidal organic carbon and trace metals in a boreal lake during summer bloom

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ABSTRACT

This work describes variation of element concentration in surface water of a subarctic organic-rich lake during the diurnal cycle of photosynthesis. An unusually hot summer 2010 in European part of subarctic Russia produced elevated surface water temperature (28–30 °C) and caused massive cyanobacterial bloom. Diurnal variation of ~40 dissolved macro and trace elements and organic carbon were recorded in the humic Lake Svyatoe in the White Sea drainage basin. Two days continuous measurements with 3 h sampling steps at the surface (0.5 m) allowed tracing cyanobacterial activity via pH and O_2 measurement and revealed constant concentrations (within ±20–30%) of all major elements (Na, Mg, Cl, SO_4, K, Ca), organic and inorganic carbon and most trace elements (Li, B, Sc, Ti, Ni, Cu, Ga, As, Rb, Sr, Y, Zr, Mo, Sb, medium and heavy REEs, Hf, Pb, Th, U). The concentration of Mn demonstrated a factor of 3 decrease during the day following Mn adsorption onto cyanobacterial cells due to ~1 pH unit raise during the photosynthesis and Mn release during the night due to desorption from the cell surface. The role of Mn(II) photo-oxidation by reactive oxygen species could be also pronounced, although its contribution to Mn diurnal variation was much smaller than the adsorption at the cell surfaces. Similar pattern, but with much lesser variations (c.a., 10–20%), was recorded for Ba and Fe. On-site ultrafiltration technique allowed to distinguish between low molecular weight (LMW) complexes (<1 kDa) and high molecular weight (HMW) colloids (1 kDa–0.22 μm) and to assess their diurnal pattern. Colloidal Al and Fe were the highest during the night, when the contribution of HMW allochthonous colloids was maximal. Typical insoluble trivalent and tetravalent elements exhibited constant complexation (>80–90%) with HMW allochthonous organics, independent on the diel photosynthetic cycle. Finally, biologically-relevant metals (Cu, Co, Cr, V, and Ni) demonstrated significant variations of colloidal fractions (from 10 to 60%) not directly related to the photosynthesis. The majority of possible metal nutrients, being strongly associated with organic and organo-mineral colloids do not exhibit any measurable concentration variation during photosynthesis. The two types of element behavior during cyanobacterial bloom in the water column – constant concentration and sinusoidal variations – likely depend on element speciation in solution and their relative affinity to surfaces of aquatic microorganisms and complexation with authochthonous and allochthonous organic matter.

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1. Introduction

The increasing importance of arctic and subarctic aquatic ecosystems stem from their potential role in carbon cycle regulation in high latitudes (Tranvik et al., 2009), their fast response to climate warming, and their fragility to the local and dispersed (atmospheric) pollution (Roederer, 1991; de Caritat et al., 1996). A major issue of lake biogeochemistry is the variation of dissolved components concentration in response to diurnal photosynthesis/respiration cycle of phyto- and bacterioplankton. In contrast to detailed knowledge of the diel behavior of biological components (e.g., Tilzer, 1973; Staehr et al., 2010; Guasch et al., 1998), the majority of available data on trace metals and to a lesser degree, of organic carbon, represent results of punctual or seasonal sampling without sufficient diurnal resolution (e.g., Hamilton-Taylor et al., 1996, 2005; Viollier et al., 1997; Albéric et al., 2000). Whereas the diel variations of solutes are thoroughly characterized in rivers (Brick and Moore, 1996; Neal et al., 2002; Jones et al., 2004; Gammons et al., 2005a,b; Nimick et al., 2005; Parker et al., 2005, 2007a,b; Lourino-Cabana et al., 2010, 2011; Nimick et al., 2011; Balistrieri et al., 2012) and in marine and coastal systems (Luengen et al., 2007), subarctic organic-rich lakes remained very poorly investigated.

It is likely that on-going warming may bring about more frequent phytoplankton blooms in the high latitude lakes and will certainly cause the increase of surface water temperature in summer. There are an emerging number of evidences that climate warming will favor cyanobacteria over other phytoplankton (Carey et al., 2012; Kosten et al., 2012; Paerl and Paul, 2011; Sinha et al., 2012). The opportunity of studying these unusual (at present) conditions, apart from artificial lake manipulation, may be created during local weather perturbation. An unusually hot summer 2010 in European part of Russia (10° above the average that lasted almost two summer months) offered the possibility to investigate the pristine water objects having almost 10-degree higher surface water temperatures than the normal value. This strong local warming caused massive cyanobacterial bloom that lasted several weeks and allowed monitoring major and trace element composition variation in the diurnal cycle of photosynthesis.

To address to which extent the element concentration and speciation will be affected by diel variation of photosynthetic activity/heterotrophic respiration in organic-rich lake, we monitored organic carbon, major and trace element concentration in conventionally dissolved (<0.22 μm) and $LMW_{<1\ kDa}$ form in the surface layer of a humic lake in the subarctic zone of the White Sea basin. We show that both concentration and speciation of very limited amount of metal nutrients are influenced by diurnal pH change caused by photosynthesis cycle, whereas the majority of trace metals are not subjected to diurnal variations. We also attempted to quantify the change in colloidal proportion in the course of photosynthesis in order to link it with the bioavailability of trace metals and identify potentially limiting metal micronutrients. It is anticipated that addressing these objectives will improve our knowledge of factors controlling the biogeochemical cycles of trace elements and biologically important heavy metals migration in lake systems of high latitudes subjected to frequent phytoplankton bloom due to climate warming.

2. Materials and methods

We studied a typical humic Lake Svyatoe located in the Arkhangelsk region (Northern Eurasia) within the watershed of the Onega River (White Sea basin) at the Rotkovetz Scientific Monitoring Station (60°51′ N; 39°32′ E, Fig. 1). The studied area can be considered as weakly influenced by local agricultural activity. The concentration level of most major and trace elements is within the range of other pristine lakes of the region (e.g., Shirokova et al., 2010). The watershed lithology is represented by glacial moraine (products of granite–gneisses erosion) and carbonate rocks. The lake surface area is 2.11 km^2, its volume is 0.00749 km^3, the maximal depth is equal to 16 m and the average depth is 3.6 m. There are several inlets in this lake and one outlet river Svyataya. Sampling was performed in August 2010 at essentially anticyclone conditions with *in-situ* measurements of pH, temperature and dissolved oxygen. The observations were performed during 50 h at stable bloom conditions linked to high concentrations of cyanobacteria in the surface layer (500 ± 100 mg POC L^{-1} corresponding to ~1000 mg biomass L^{-1} compared to usual 10–50 mg POC L^{-1} at no-bloom conditions in the lake). The typical cyanobacteria responsible for summer bloom in

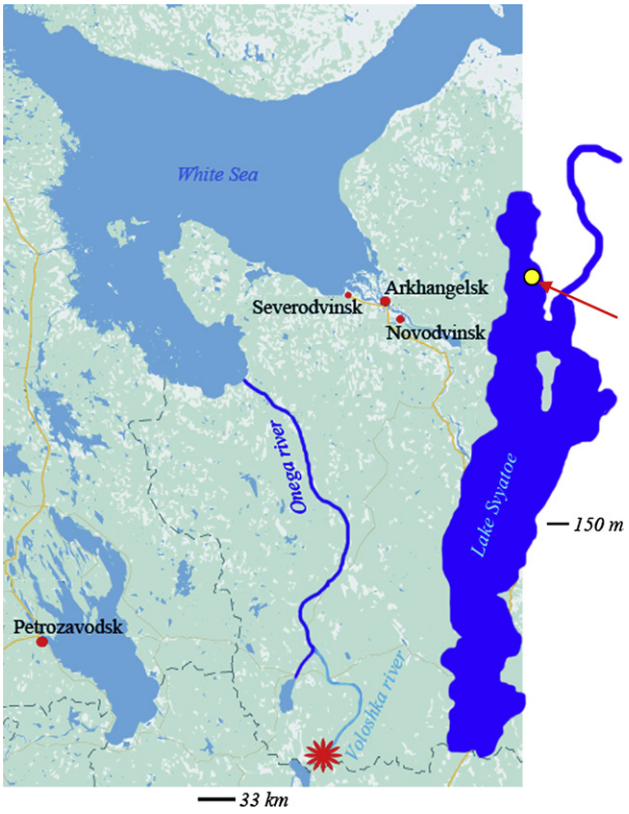

Fig. 1 – Schematic map of the region and Svyatoe Lake. The asterisk represents the location of the lake and the sampling point is shown by an arrow.