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Benthic dissolved organic carbon fluxes and distribution in Lake Baikal sediments

Pogodaeva T.V.*, Lopatina I.N., Bashenkhaeva N.V., Shubenkova O.V., Zemskaya T.I., Khodzher T.V.

Limnological Institute, Siberian Branch of the Russian Academy of Sciences, Ulan-Batorskaya Str., 3, Irkutsk, 664033, Russia

ABSTRACT. Dissolved organic matter (DOM) simultaneously with dissolved inorganic carbon (DIC), dissolved total carbon (TC) and cations (Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{2+} and Mn^{2+}) in sediment pore waters from Lake Baikal was investigated. That is the first detailed study of a relatively highly resolved DOC profile in benthic pore water profile from the Lake Baikal. We quantified DOC fluxes under different redox conditions in surface bottom sediment, which changed direction twice at the redox boundaries. Shown, that mobilization of DOC in oxygen-free sediments closely links to reductive dissolution of ferric minerals. Oxidized surface sediments are an efficient DOC trap where DOC is bound to ferric minerals. Redox conditions appears to be the primary regulator of the DOC exchange, resulting in sedimentary uptake of DOC (83 µmol $m^{-2}d^{-1}$) under oxic conditions, and Lake Baikal sediment is a sink of DOC. The results of this study offer significant insight into the nature and properties of DOM in freshwater ecosystems.

Keywords: dissolved organic carbon, distribution, oxic and anoxic sediments, pore waters, chemical composition, absorption, Lake Baikal.

1. Introduction

Climate changes promote levels of dissolved organic carbon (DOC) have been increasing in many surface waters in the worldwide that significantly affects aquatic ecosystems (Dadi et al., 2016). To understand DOC concentration dynamics in the lake, detailed understanding of the lake internal DOC cycling processes and interactions is important. It well known the sedimentation of particulate organic matter is a one way process directed from the water toward the sediment. The flux of DOC is a two way process accomplished by diffusion, advection and sediment resuspension. Thus the sediment can be either a source or a sink of DOC. Microbial degradation of particulate organic matter typically results in elevated DOC concentrations in the sediment pore water. Though, according the recent studies, the concentration of DOC in the presence of mineral particles is not only influenced by metabolic processes, but also by interaction with mineral surfaces. Lakes sediments recent studies have been shown that the flux of DOC linked by adsorption processes which were controlled by iron redox state (Lalonde et al., 2012; Barber et al., 2014; Yang et al., 2014; Peter et al., 2016; 2017). Thus aim of our research to gain an understanding of DOC processes and interactions at the water-bottom interface of Lake Baikal.

2. Materials and methods

Bottom sediments were sampled from the pelagic zones of Southern (depth of 1480 m) and Northern (depth of 940 m) basins of Lake Baikal, during expeditions 2018 and 2020 with using benthic corer (BC) (100 mm in diameter, 1 m long). Pore waters were extracted onboard the ship by centrifuging the sediments for 20 min at 8000 rpm, then 10 min, 14000 rpm. Pore waters cations (Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{2+} and Mn^{2+}) were determined using the atomic absorption and flame emissivity methods (relative error 2–3%). Pore waters dissolved organic carbon (DOC), dissolved inorganic carbon (DIC) and dissolved total carbon (TC) concentrations were measured using the Vario TOC cube high-temperature carbon analyzer with an IR detector (Elementar Analysensysteme GmbH, Germany). Standard deviation did not exceed 0.01. Potassium hydrogen phthalate was used as the standard. The redox potential (Eh) and pH were determined into wet sediments using pH meter (ProfLine pH 3310, Germany).

3. Results and discussion

The sediments sampled from deepwater sites in Southern and Northern Baikal were gray, biogenic–

*Corresponding author.
E-mail address: tatyana@lin.irk.ru (T.V. Pogodaeva)

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terrigenous diatomaceous silts. The uppermost layer of cores was oxidized and of a reddish-yellow-brown color (3 cm Southern and 19 cm Northern Baikal (Fig.)). Fe-Mn crusts were found on the boundary between the upper oxidized and lower reduced sediments.

The K^+, Mg^{2+}, and Na^+ content in the pore waters changed insignificantly throughout the entire depth of the sediment profile (Fig.). The Fe^{2+} and Mn^{2+} concentrations in the pore water were increasing and were reaching maximum concentrations 9.2 mg/l (Fe^{2+}) and 5.5 mg/l (Mn^{2+}) at 21cm, forming a peak of maximum just below the border of the oxidized and reduced sediment zones.

Significant similarity was found in the distribution of Ca^{2+} and dissolved in pore water carbon (DOC, DIC, TC), correlation coefficients consisted 0.75, 0.98, 0.92, respectively. While a high correlation between the concentrations of HCO_3^- (actually DIC) and Ca^{2+} was observed before (Pogodaeva et al., 2017). The Ca^{2+}, DOC, DIC, TC contents in the pore waters decreased rapidly from 13.2, 7.1, 13.0, 20.1 mg/l, respectively, near the water–sediment interface to 8.1, 3.2, 6.5, 9.7 mg/l, respectively, at 6 cm below the interface (Fig.). Then, the Ca^{2+}, DOC, DIC, TC concentrations increased gradually, reaching 18.3, 15.3, 19.8, 35.6 mg/l, respectively, at 21 cm (just below the oxidized-reduced sediments interface). Further down to the deeper layer of the reduced sediment, the Ca^{2+}, DOC, DIC, TC concentrations decreased rapidly up to 16.1, 11.7, 17.6, 29.3 mg/l, respectively, at 26 cm, and then insignificantly were changing throughout the entire depth of the sediment up to 45 cm.

A similar distribution of components, only with a narrowed oxidized zone, was observed in the southern basin of Lake Baikal.

The DOC concentrations in sediment pore waters are controlled by a variety of biogeochemical processes (Yang et al., 2014). The revealed Z-shaped DOC profile suggests the occurrence of different processes in the upper and deeper layers of the sediment. It is known the overlying water year-round contents a large amount of oxygen (according to our data at this station - 11.8 mg/l), which also penetrates into the bottom sediments. According to Och et al., 2012 the penetration depth of O_2 at the this station ranged 5 cm, therefore the sharp decrease in the DOC concentration in the upper layer of the sediment pore waters up to 5-6 cm may be due to the intensive aerobic decomposition of organic matter. Indeed, it was reported that in the O_2 contain sediments DOM was composed of relatively small organic compounds of low- molecular-weight (O'Loughlin and Chin, 2004; Fu et al., 2006). However, recent studies (Riedel et al., 2013; Peter et al., 2016; 2017) have shown the most important role Fe. The coagulation and sorption DOM on Fe(III) oxide-hydroxides at the oxic surface layer (faster processes) can remove from solution up to 50% of DOC, with predominantly aromatic and high molecular weight compounds. The strong association between iron and OC may inhibit microbial organic carbon degradation and enhance preservation. A pronounced influence have redox conditions. Below the O_2 depletion depth (6 cm), a decrease in Eh contributes to reductive iron Fe(III) to Fe(II) dissolution in sediments. Fe reduction consumes protons, which can introduce an increase in pH and lead to a general weakening of OC sorption and hence release sorbed DOC from solid phase (Kleber et al., 2015; Peter et al., 2017). As a result, we can observe synchronous peaks of Fe and DOC just below the oxidized-reduced sediments interface (at 21 cm). Thus, attributed increased DOC flux to the release it during Fe reduction rather than to decreased microbial DOC mineralization. Further decrease in the DOC concentration into anoxic sediments is determined by balancing the desorption processes and anaerobic degradation of OM.

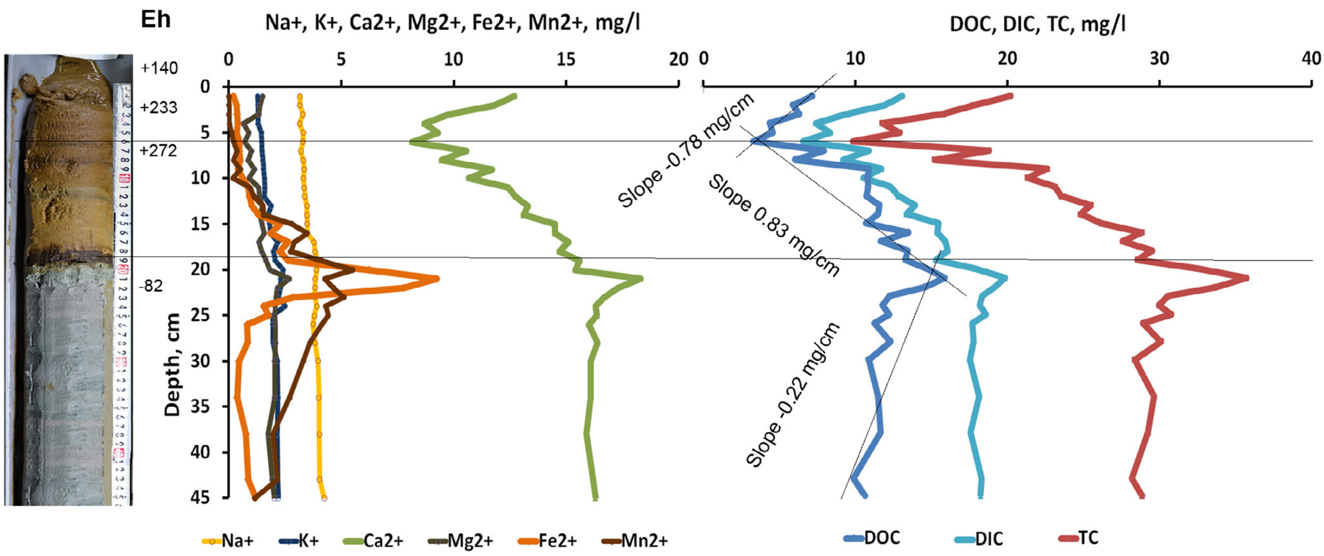

Fig. Sediment core photo, concentration profiles: of the main cations in sediment pore waters and dissolved carbon (DOC - dissolved organic carbon, DIC- dissolved inorganic carbon, TC- dissolved total carbon) from the Lake Baikal Northern basin.

The calculated according to Klump et al., 2019 the DOC fluxes in the upper and deeper layers of the surface Lake Baikal sediment changed direction twice at the redox boundaries and were 83; -90; 24 μmol C $m^{-2}d^{-1}$, respectively. A positive DOC flux was revealed near the water-bottom interface.

Given the fact that a large amount of oxygen is observed at all depths of the lake, including the bottom water, and a layer of oxidized sediment covers practically the entire lake bottom, we declare the Lake Baikal sediment is a sink of DOC. The exceptions are areas of oil and gas discharge, as well as some areas of the littoral zone, where the sediments are reduced from the surface. Future studies are required for quantifying the effects of processes on the benthic flux DOC for these areas.

4. Conclusion

The first detailed study of a relatively highly resolved DOC profile in benthic pore water profile from the Lake Baikal revealed that redox conditions are the primary regulator of the DOC exchange. Oxidized surface sediments are an efficient DOC trap where DOC sorbs on Fe(III) oxide-hydroxides. Subsequent mobilization of DOC in oxygen-free sediments closely links to reductive dissolution of ferric minerals. The calculated DOC fluxes in the upper and deeper layers of the surface Lake Baikal sediment changed direction twice at the redox boundaries and were 83; -90; 24 μmol C m – 2d – 1, respectively. The revealed positive DOC flux (83 μmol $m^{-2}d^{-1}$) near the water-bottom interface is means sedimentary uptake of DOC under oxic conditions, i.e. Lake Baikal sediment is a sink of DOC. Redox conditions are reversible, and if climate change will be to promote reducing conditions at the bottom of lakes, which might increase benthic DOC production in the future. Future studies are required for quantifying the effects of these processes on the benthic DOC flux.

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