Achievements in the Life Sciences 9 (2015) 32–36

Contents lists available at ScienceDirect

Achievements in the Life Sciences

journal homepage: www.elsevier.com/locate/als

Organic Matter in the Small Lakes of the Sikhote-Alin Biosphere Reserve

T.N. Lutsenko *, E.N. Chernova, E.V. Lysenko, D.S. Ryzhakov

Vladivostok, Pacific Institute of Geography of FEBRAS, Russian Federation

ARTICLE INFO

Available online 3 July 2015

Keywords:
Small lakes
Sikhote-Alin Biosphere Reserve
Organic matter
Dissolved organic matter
Particulate organic matter
$SUVA_{254}$
Fluorescence

ABSTRACT

The carbon concentration and distribution in dissolved organic matter (DOM) and particulate organic matter (POM) in the lagoon lakes Blagodaty and Golubichnoe located in the Sikhote-Alin Nature Reserve and Lake Vaskovskoye of the Dalnegorsk urban district of Primorsky Krai were analysed using data collected in July–August of 2011–2014. The content of DOM carbon ranged from 1.9 to 8.6 mg/l, representing 68–90% of the total organic carbon. Reductions in the POM carbon concentration and organic carbon percentage of the particulate matter in the sequence of the lakes Blagodaty–Golubichnoe–Vaskovskoye were determined. Analysis of the $SUVA_{254}$ dynamics and the fluorescence intensity revealed a trend of simplification of the molecular structure of DOM from the surface to a depth of 1 to 1.5 m in lakes Golubichnoe and Vaskovskoye as well as at the northern station in the brackish Blagodaty Lake.

Introduction

The natural waters of the Sikhote-Alin Nature Reserve are insufficiently studied compared to its flora and fauna. Hydrochemical studies of small lakes of the reserve began in 2004 and 2008 (Sikhote-Alin Nature Reserve, 2009). In recent years, lakes Blagodaty and Golubichnoe were studied by scientists from the geochemistry laboratory of PGI FEB RAS (Chernova et al., 2014). The data obtained describe the content and spatial–temporal dynamics of the macro- and microelements, the patterns of distribution of the microelements in particulate matter and the plankton. A distinctive feature of Lakes Blagodaty and Golubichnoe is the high bogginess of their catchments, as a result of which bog waters with a high content of organic matter (OM) enter the lakes. Flows of allochthonous organic matter of soil and plant origin fall into the lakes from the catchment area. The main sources of intrabasin organic matter are phytoplankton, submerged aquatic vegetation, zooplankton and zoobenthos. The study of the organic forms of carbon present helps to shed light on the biogeochemical details of how lake ecosystems function.

The aims of this work were to evaluate the content of carbon in dissolved organic matter (DOM) and particulate organic matter (POM), identify the organic carbon in the suspended matter and characterise the optical properties of DOM in the lagoon lakes Blagodaty and Golubichnoe of the Sikhote-Alin Nature Reserve. For comparison, a small lake of tectonic origin Vaskovskoe, located in the Dalnegorsk urban district of Primorsky Krai, was included in the study.

* Corresponding author.
E-mail addresses: luts@tig.dvo.ru, lutsenko53@bk.ru (T.N. Lutsenko).
Peer review under responsibility of Far Eastern Federal University.

http://dx.doi.org/10.1016/j.als.2015.05.005
2078-1520/

Table 1
Morphometric characteristics of the lakes studied.

Lake	Area of water surface, km^2	Catchment area, km^2	Per unit catchment	Bog area, km^2	Bogginess of the catchment, %
Blagodati	2.04	26.2	12.8	5.54	21.1
Golubichnoe	0.45	6.1	13.6	3.67	60.2
Vaskovskoe	0.36	15.8	43.9	0.53	3.4

Materials and Methods

The small lakes Blagodaty (44°66′N, 135°32′E) and Golubichnoe (44°55′N, 136°31′E) are located in the Terney region of Primorsky Krai, and their depths are less than 4 m (Sikhote-Alin Nature Reserve, 2009). Other morphometric characteristics of the lakes are presented in Table 1. These lagoon lakes were formed during the late Holocene, approximately 2.2 thousand years ago (Korotkiy et al., 1988). Water enters the lakes by precipitation, groundwater and surface runoff (Sikhote-Alin Nature Reserve, 2009).

Blagodaty is a meromictic lake separated from the Udobnaya Sea bay by a narrow neck. The lake is connected with the sea during periods of high water content. The northwestern part of the lake is swampy. The peat deposits of the catchment are 0.1–1.0 m thick (Voropaeva, 2012). The eastern part of the littoral is a strip of aquatic and swamp vegetation.

Golubichnoe is a freshwater lake, with yellow-coloured water. The lake is surrounded by forest (Mongolian oak, alder, birch, etc.). A stream flows out of the lake into a swampy meadow located 25 m from the lake (Sikhote-Alin Biosphere Reserve, 2009). A number of rare and relict species of aquatic flora grow in Golubichnoe Lake (Nesterova and Pimenova, 2012).

Vaskovskoe Lake (44°21′N, 135°49′E) is located in the Dalnegorsk region of Primorsky Krai. Its maximum depth is approximately 9 m. The water-withdrawal point for the drinking water supply of the Rudnaya Pristan settlement is located in the western part of the lake. Smychka Village and a science research station of PGI FEB RAS are located on the northern shore. The Vaskovskiy stream, which drains the boggy landscape, flows into the southern part of the lake. The bottom of the lake's littoral is sand with plant residue.

The samples were collected in July, 2011, 2012 and 2014, and in August and October, 2013. Samples from the following watercourses were studied: one of the streams flowing into Lake Golubichnoe, water from the Golubichnaya River, and water from the Vaskovskiy Stream. In 2011–2014, water samples were collected from the rubber boat from the subsurface level, at stations 1.0–1.5 m deep, in the northern and eastern areas of the lakes of the Sikhote–Alin Nature Reserve, and in the northern part of Vaskovskoe Lake at levels found in the central part of the lake.

The study area belongs to the East Sikhote-Alin mountain–coastal province. The climate of the study area is moderately cool and excessively wet, and the average annual rainfall is 700–800 mm. The main component in the structure of the soil cover of the catchment of the lakes is mountain–forest brown skeletal soil (Ivanov, 1976). It is formed on dissected low hills on shallow rock–gravel–loam eluvium and on scree rudaceous talus with massive rock. The vegetation is represented by poor oak forests (Mongolian oak). The main soil-forming processes are humus formation and argillization area. Soddy gley soils on loamy eluvium–deluvium are formed under meadow scrubs on smooth slopes bordering on the lakes of the Sikhote-Alin Nature Reserve. These soils are characterised by hindered water exchange that influences the forming of gley. Meadow gley, peaty and peaty-gley soils on the alluvial and marine sediments under sedge and reed coenoses are formed on coastal plains in the estuary areas of the brooks (Soil map of Primorsky Krai, 1983).

On the sampling day, the samples were vacuum filtered through a 0.45-micron filter (Durapore). The filtered samples was analysed for its carbon content in DOM with a thermocatalytic oxidation method using IR registration (TOC-VCPN analyser, Shimadzu) in the geochemistry laboratory of the PGI FEB RAS. The variation coefficient of the analysis of the samples and standards did not exceed 3%. Samples of brackish water from Blagodati Lake were diluted with bidistilled water to salinity no greater than 3%.

To determine the content of carbon in the POM water samples were filtered through Whatman GF/F filters that were previously calcined at 450 °C for 2 h. The carbon concentration in the POM was determined by a TOC-analyser using the SSM-5000A module.

The electronic absorption spectra of the filtrates were recorded in the wavelength range of 200 to 600 nm using a Shimadzu UV-2450 PC spectrophotometer and a quartz cuvette of 1-cm thickness in reference to bidistilled water. The standard spectral coefficient $SUVA_{254}$ was calculated as the ratio of the absorption at 254 nm to the concentration of dissolved carbon (Weishaar et al., 2003).

Fluorescent emission spectra were obtained using an RF-5301 PC spectrofluorimeter (Shimadzu) in a quartz cuvette of 1 cm at a constant excitation wavelength of 355 nm. The samples were diluted with doubly distilled water 20 times to suppress the internal filter effect. Fluorescence emission spectra were recorded in the range 380–700 nm. The value of the maximum fluorescence intensity was normalised by the concentration of dissolved carbon.

Table 2
Types of organic carbon in lake waters in July, 2011, 2012, and 2014 and August, 2013. (The range is in the numerator, and the average value is in the denominator).

Lakes	C_{DOM}, mg/l	C_{DOM}, %	C_{POM}, mg/l	C_{POM}, %	PM, mg/l	C_{PM}, %
Blagodati	3.0–8.4/6.3	68.9–76.9/74.1	0.9–3.8/2.2	25.9–31.1/25.9	4.1–14.2/7.4	15.4–45.9/26.6
Golubichnoe	5.2–8.2/6.7	82.0–89.7/83.8	0.6–1.8/1.3	10.3–18.0/16.3	2.8–3.6/2.9	19.6–29.6/24.6
Vaskovskoe	2.3–5.1/4.0	88.5–89.5/88.9	0.3–0.8/0.5	11.5–14.0/11.1	2.0–10.7/5.2	5.1–25.6/13.6

Results and Discussion

In 2011–2014, the hydrological situation in the area was quite dynamic (Weather report RP5). The spring and summer of 2012 followed the dry winter of 2011. However, there was abundant rainfall in Primorye in the autumn of 2012, and the soils were humid in the first half of 2013. Therefore, when a cyclone brought more than 670 mm of rain in many areas of the southern Far East in July, 2013, catastrophic floods followed. According to our estimates, the rise of the water level in Vaskovskoe Lake was approximately 2 m. Flooding was caused in part because large amounts of water were dropped during this time from the Dalnegorsk reservoirs into the Rudnaya River, where a creek flows from the lake.

The concentration of total organic carbon varied between 2 and 12.2 mg/l. The highest content was found in the Blagodati and Golubichnoe Lakes due to the inflow of organic matter related to bog creation, and the lowest content was in the water of Vaskovskoe Lake (Table 2). The carbon content in DOM was 2.3–8.4 mg/l (average of 5.2 mg/l), and so 68–90% of the total carbon was found in the dissolved organic matter of the lakes.

In the year-to-year dynamics, higher concentrations of carbon in the DOM were observed in Blagodati and Golubichnoe Lakes in 2011–2012 (7.5–8.4 mg/l). The concentrations were lower due to their dilution in the high-water year 2013, and the lowest concentrations (4.5 mg/l) were observed in the dry year 2014, apparently due to a large-scale removal of terrigenous DOM reserves during floods in 2013.

The concentration of particulate matter (PM) in the small lakes varied from 1 to 14 mg/l. The lowest content of particulate matter was found in Golubichnoe Lake, 2–4 mg/l, and it reached as high as 11 mg/l in Vaskovskoe Lake. The content of particulate matter increased in all lakes in the bottom layers due to its subsidence. In Vaskovskoe Lake, which is the deepest lake, the smallest content of particulate matter was recorded in the middle of vertical profile (3 m). The quantity of particulate matter depends on the hydrological regime, the type of the drained soil, rock composition and geomorphology of the catchment. Apparently, the contribution of the latter was the most significant factor for Vaskovskoe Lake: during the extreme high water conditions in 2013, the content of suspended matter in the water doubled (compared to the average) thanks to the steep ridges limiting its catchment from the west and east.

The contribution of the POM in the overall pool of organic carbon did not exceed 10–30%. The largest share (25–30%) of carbon in the POM was found in Blagodati Lake. Particulate matter is mainly represented by plankton and detritus, making Blagodati Lake likely the most productive one. During the sampling in July, 2014, the water in Blagodati Lake was turbid, and flakes of foam were present on the water surface and on the shore, which apparently evidenced ongoing, intense production/destruction processes. According to Agatova et al. (2004) the main component of particulate organic matter is protein, and its presence is associated with bacterial activity.

The content of carbon in particulate matter varies greatly, with average values ranging from 5 to 46% of the particulate matter mass. The water of Blagodati Lake mainly contains particulate matter enriched with organic carbon (up to 42–46%) from diatom phytoplankton (Medvedeva, 2001). Even visually, the particulate matter from the lake placed onto filters has a notable bright-greenish colour associated with the presence of large amounts of phytoplankton. The particulate matter of Golubichnoe Lake is enriched in organic carbon at 20–29%. Vaskovskoe Lake mainly contains less organic particulate matter: the concentration of organic carbon is approximately 14% on average (Table 1).

Based on structural studies of DOM and humic substances of various origins, it has been demonstrated that spectroscopic characteristics can be used for a relative assessment of the degree of aromaticity of the structure and molecular weight (MW) of water DOM (Peuravuori and Pihlaia, 1997; Weishaar et al., 2003). A higher $SUVA_{254}$ value indicates a higher contribution of allochthonous humic substances with a higher proportion of condensed carbon and a higher molecular weight.

The $SUVA_{254}$ value varied from 1.60 to 4.96 l/mol·m in the lake water. The highest $SUVA_{254}$ values were usually characteristic of influent streams and the Golubichnaya River. The year-to-year spatial and temporal dynamics of the $SUVA_{254}$ values follow the hydrological conditions (Fig. 1) because precipitation removes DOM from the humus layers of the soil.

The minimum contributions of humic substances ($SUVA_{254}$ values of 2.5 and 2.7 for lakes Golubichnoe and Blagodati) were registered in July of the dry year 2012. The most significant inflow of humic substances and highest $SUVA_{254}$ values (4.19–4.45), comparable to the river values, were recorded after the flood in July, 2013.

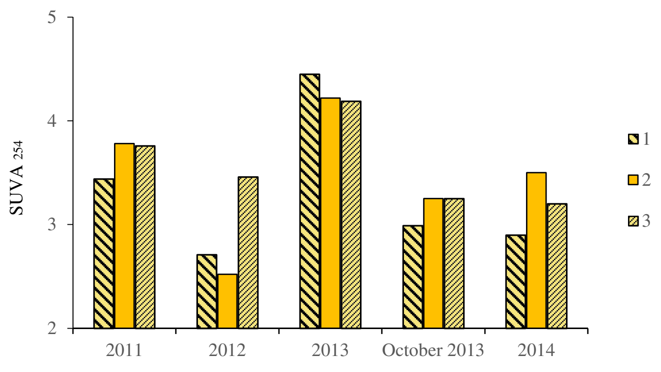

Fig. 1. Year-to-year dynamics of the spectral coefficient $SUVA_{254}$ in the water of the northeastern Primorye lakes (1—Lake Blagodati, 2—Lake Golubichnoe, and 3—Lake Vaskovskoe).

In October, 2013, when the dry season settled in Primorye, the $SUVA_{254}$ values decreased to 3 (to 4 in streams), i.e., the contribution of chromophores in the lake DOM decreased almost by half compared to that in August of the same year (Fig. 1).

The range of variation in the $SUVA_{254}$ values was significantly more pronounced in the lakes of the Sikhote-Alin Nature Reserve (27 and 23% for the Blagodati and Golubichnoe lakes, respectively); in contrast, in the waters of Vaskovskoe Lake, the coefficient of variation did not exceed 13%. Apparently, this reflects the differences in the sources, the nature of the inflow and the degradation of terrigenous DOM.

In 2013–2014, the characterisation of the optical properties of DOM was expanded using fluorescence spectroscopy. The intensity and wavelength of the fluorescence of DOM depends on the degree of macromolecule humification and the type and number of substituents in the aromatic nucleus. The indicator of allochthonous humic substance fluorescence is the quenching of the signal by the most mature macromolecules, which have a high degree of carbon condensation, electron-accepting substituents and high molecular weights (Chen et al., 2003; Senesi et al., 1991). On the contrary, more aliphatic and lower-molecular-weight humic substances are able to produce intense fluorescence.

Under 355-nm excitation, the fluorescence maxima of water were observed in the range 446–452 nm. The fluorescence intensity varied from 108 to 489 (rel. units). In August, 2013, when flooding brought large amount of allochthonous DOM into the lake, the fluorescence intensity of the samples was relatively low at 145–225 (rel. units) and generally similar to that of the streams and the Golubichnaya River.

The transformation of DOM in lakes is associated with the activities of the biotic community (Agatova et al., 2004; Zhang et al., 2009). The change in the $SUVA_{254}$ coefficients and the fluorescence intensity in the vertical profiles of the lakes in July, 2014 illustrates this (Fig. 2). At the central station (the surface) of Blagodati Lake, the $SUVA_{254}$ values were lower than in the surface layer at the northernmost station, due to a smaller percentage of the chromophore allochthonous DOM fractions at a distance from the shore. The contribution of these fractions decreased with the depth at both stations due to the coagulation of the high-molecular-weight fractions (Fig. 2A and B). However, strong fluorescence (310 rel. units), decreasing threefold at a depth of 1.5 m, indicates the appearance of substances of marine origin that quench the fluorescence. At this station, the chloride ion concentration varies sharply between 13.6 g/l on the surface and 27.0 g/l at a depth of 1.5 m. Thus the dynamics of the optical properties primarily associated with the distribution of seawater.

In the freshwater Golubichnoe Lake, the carbon concentration in the DOM is the highest (5.2 mg/l), which is related to the large additional supply of allochthonous DOM. Macromolecules of DOM are the most humified ($SUVA_{254}$ of 3.5), but both indices do not change due to the good mixing of the water (Fig. 2C). However, the increase in the more sensitive fluorescent signal indicates a simplification of the molecular structure of allochthonous DOM with depth. A similar trend can be seen in Vaskovskoe Lake up to a

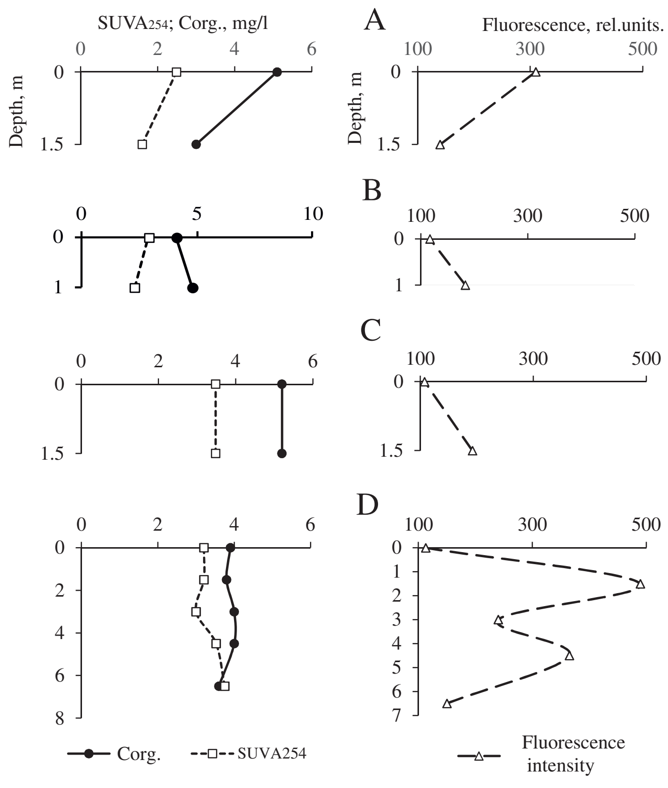

Fig. 2. Vertical distribution of carbon in the DOM, $SUVA_{254}$ values and fluorescence intensity in samples of lake water in July, 2014 (A—Lake Blagodati, centre, B—Lake Blagodati, north; C—Lake Golubichnoe, and D—Lake Vaskovskoe, centre).

depth of 1.5 m (Fig. 2D). Water in the deeper layers of Vaskovskoe Lake showed a bimodal distribution of fluorescence. These dynamics, as well as the high relative fluorescence intensity of the water require further study. Based on the conclusion of Agatova et al. (2004) that lake ecosystems actively transform and assimilate allochthonous organic matter, one can assume that the optical characteristics of the water indicate certain stages of these processes.

At the northern station of Blagodati Lake, the chloride ion distribution was more uniform than in the centre, 10.5 and 11.5 g/l, respectively; i.e., the water was freshened almost by half. The situation was different at the station in the centre of Blagodati Lake: here, the vertical change in the fluorescence corresponded to that of the freshwater lakes Golubichnoe and Vaskovskoe, probably due to a larger contribution from allochthonous DOM.

Conclusion

Studies have shown that the lagoon lakes Blagodati and Golubichnoe, located in the Sikhote-Alin Nature Reserve, and the tectonic lake Vaskovskoe, also located in the northeast of the Primorsky Krai, contain different carbon contents in their DOM and POM. These lake are also distinguished in the enrichment of the particulate matter with organic carbon and in the structural dynamics of the optically active components of the DOM. These differences are conditioned by the entire geological history of the formation of these lakes, which has determined the landscape features of the lake catchment areas and the conditions for the functioning of the lake ecosystems. The characteristics studied for the organic matter have shown that a more intense transformation occurs in the small lakes than in the streams, and that this fact is closely related to the hydrological conditions because it is most pronounced in dry years.

References

Agatova, A.I., Lapina, N.M., Torgunova, N.I., Sapozhnikov, V.V., Milovskaya, L.V., 2004. Organic matter and its rate of transformation in spawning and feeding lakes of Kamchatka. Water Resour. 31 (6), 691–701 (in Russian).

Chen, I., LeBoef, E., Dai, S., Gu, B., 2003. Fluorescence spectroscopic studies of natural organic matter fractions. Chemosphere 50, 639–647.

Chernova, E.N., Shulkin, V.M., Lysenko, E.V., Lutsenko, T.N., Boldeskul, A.G., 2014. Hydrochemical and Biogeochemical Characteristics of Fresh and Brackish Lakes of East Sikhote-Alin//Izvestiya TINRO vol. 178 pp. 157–172 (in Russian).

Ivanov, G.I., 1976. Soil Formation in the South of Far East. M.: Nauka (198 pp. [in Russian]).

Korotkiy, A.M., Pletnev, S.P., Pushkar, V.S., 1988. The Development of Natural Environment of the South of Far East (Late Pleistocene–Holocene). M.: Nauka (240 pp. [in Russian]).

Medvedeva, L.A., 2001. Biodiversity of aquatic algal communities in the Sikhote-Alin Nature Reserve (Russia). Cryptogam. Algol. 22 (1), 65–100.

Nesterova, I.A., Pimenova, E.A., 2012. The results of the study of rare aquatic plants in Sikhote-Alin Reserve. Sikhote-Alin Biosphere Area: The State of Ecosystems and Their Components: Collection of Scientific Papers for the 75th Anniversary of Sikhote-Alin Reserve. Dalnauka, Vladivostok, pp. 130–146 (in Russian).

Peuravuori, J., Pihlaia, K., 1997. Molecular size distribution and spectroscopic properties of aquatic humic substances. Anal. Chim. Acta 337, 133–149.

Senesi, N., Miano, T.M., Provenzano, M.R., Brunetti, G., 1991. Characterization, differentiation, and classification of humic substances by fluorescence spectroscopy. Soil Sci. 152 (4), 259–271.

Sikhote-Alin Nature Reserve, 2009. Research report for 2009. Topic 2: Monitoring of Aquatic Ecosystems. Subsection 2.1.2. Studies of Chemical and Hydrological Conditions of Macrobenthic Habitat in the Western and Eastern Streams of the Reserve and its Transit Zonepp. 18–30 (Ternei, in Russian).

Soil map of Primorsky Krai. Scale: 500000/edited by Ph.D. G.I. Ivanov, 1983. State department of geodesy and cartography, 9 sheets. [in Russian]

Voropaeva, I.S., 2012. Structure and history of the development of bog complexes of eastern Sikhote-Alin. Sikhote-Alin Biosphere Area: The State of Ecosystems and Their Components: Collection of Scientific Papers for the 75th Anniversary of Sikhote-Alin Reserve. Dalnauka, Vladivostok, pp. 100–129 (in Russian).

Weather Report RP5 Source. www.rp5.ru.

Weishaar, J., Aiken, G., Bergamaschi, B., Fram, M., Fugii, R., Mopper, K., 2003. Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. Environ. Sci. Technol. 37, 4702–4708.

Zhang, Y.L., van Dijk, M.A., Liu, M.L., et al., 2009. The contribution of phytoplankton degradation to chromophoric dissolved organic matter (CDOM) in eutrophic shallow lakes: field and experimental evidence. Water Res. 43 (18), 4685–4697.