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Seasonal and spatial variation in hydrochemical parameters of Lake Onego (Russia): insights from 2016 field monitoring

Tatyana A. Efremova [a], Albina V. Sabylina [a], Petr A. Lozovik [a], Vera I. Slaveykova [b], Mariya V. Zobkova [a] and Natacha Pasche [c,d]

[a]Northern Water Problems Institute, Karelian Research Center, Russian Academy of Sciences, Petrozavodsk, Russia; [b]Environmental Biogeochemistry and Ecotoxicology, Department F.-A. Forel for Environmental and Aquatic Sciences, Earth and Environmental Sciences, Faculty of Sciences, University of Geneva, Geneva, Switzerland; [c]Limnology Center, Lausanne, Switzerland; [d]Physics of Aquatic Systems Laboratory, Margaretha Kamprad Chair, Lausanne, Switzerland

ABSTRACT

This study describes seasonal water quality parameters measured in Petrozavodsk Bay, Lake Onego, Russia. Petrozavodsk Bay (PB) lies in the north of Lake Onego and adjacent to the city of Petrozavodsk. PB water quality is controlled by anthropogenic input, inflow of the Shuya River, and water exchange with open areas of the greater Lake Onego. We measured ion composition, organic matter, nutrients, gas composition, trace elements, and mercury throughout 2016, to evaluate PB water quality. Elevated humic content and organic matter, including total organic carbon ($TOC = 17.0\ mg\ L^{-1}$), total phosphorus ($TP = 36\ \mu g\ L^{-1}$), and water color ($134\ mg\ Pt\ L^{-1}$), demonstrated the eutrophic character of Shuya River input. Low humic and organic matter content ($TOC = 6.5\ mg\ L^{-1}$, $TP = 7\ \mu g\ L^{-1}$, water color $= 26\ mg\ Pt\ L^{-1}$) indicated the oligotrophic character of open lake waters. During winter, the PB hydrochemical regime was primarily controlled by Shuya River inflow because water exchange between the bay and open lake was restricted during its ice-covered period. As a result, PB chemical indices varied considerably. TOC varied from 7.6 to $17.8\ mg\ L^{-1}$, TP from 7 to $55\ \mu g\ L^{-1}$, and O_2 from 69% to 87% saturation during this period. Total filterable mercury concentrations (THg = inorganic mercury plus methylmercury) at all measurement sites remained low. Overall, these results help constrain understanding of lake dynamics, anthropogenic influence, and river input to the lake during ice-covered periods.

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Introduction

Lake Onego, located in the northwest of the Russian Federation, is the second largest freshwater lake in Europe. Lake Onego's hydrochemistry arises from a complex interplay among hydrologic, biogenic, and anthropogenic influences (Sabylina 2007, Rukhovets and Filatov 2010, Filatov 2015, Sabylina and Ryzhakov 2018). Lake Onego represents an important freshwater resource used to supply cities, residential areas, and large industrial centers, but it suffers from industrial, urban, and agricultural pollution. The lake accesses the White Sea through the White Sea–Baltic canal and accesses the Caspian and Black seas through the Volga–Baltic waterway and Volga River and thus represents a major transportation route. Eutrophication and chemical pollution from point sources (Lozovik et al. 2019) are the primary factors responsible for the deterioration of Lake Onego water quality. With its many embayments, the northern part of Onego Lake offers an example of complex interactions between waters of the lake proper and the >1000 rivers that flow into it.

Comprehensive hydrophysical, hydrobiological, and hydrochemical studies of Lake Onego were conducted as part of the international “Lake Ladoga: life under ice” project. As part of that project, this study provides baseline information about Lake Onego and the Shuya River water quality as measured during 2016 field campaigns.

This investigation focused on Petrozavodsk Bay (PB) hydrochemistry, which results from mixing of tributary (runoff and infiltration) and lake water. The city of Petrozavodsk, located along the shores of PB, makes major anthropogenic contributions to the bay, which affects its hydrochemical regime (Filatov 2015). Despite numerous previous studies, current, detailed understanding of seasonal and spatial variation in PB hydrochemical characteristics is lacking. This study sought to fill that gap by measuring seasonal and spatial water quality indices

CONTACT Tatyana A. Efremova ✉ efremova.nwpi@mail.ru

from PB and interpreting them relative to corresponding values for the greater Lake Onego and the Shuya River.

Study area

Lake Onego is located between 59°54′N and 61°47′N and has a surface area of 9720 km^2, a mean depth of 30 m, and a water volume of 291 km^3 (Filatov 2010). The lake's large volume leads to a 15.6-year water exchange period and a lacustrine ecosystem conservative of inputs. Geologically, Lake Onego rests on the crystalline basement of the Baltic Shield–Russian Platform conjugation zone. The glaciotectonic origin of the Lake Onego basin creates a rugged shoreline, with numerous bays and cliffs to the north and a more gentle depositional shoreline to the south.

Morphometric differences in Lake Onego limnic zones are responsible for differences in their thermal regimes as well as the beginning, end, and overall length of hydrological seasons. The central part of Lake Onego is totally covered by ice only during its severe winters. Water surface temperature in August reaches 24 °C in the south, 18–20 °C in the center, and 4 °C near the lake bottom. Temperatures are 0–2 °C under the ice in winter. Ice cover in PB usually forms in December and reaches the central part of the lake by January, but not every year. The ice break-up begins first in the bays in early May. A spring frontal zone (thermobar) forms in May–June.

PB occupies an area of 87 km^2 and contains a water volume of 1.55 km^3, representing <1% of the area and water volume of Lake Onego. With a mean annual runoff of 3.12 km^3 yr^{-1}, the Shuya River represents a major tributary to PB and Lake Onego. Smaller rivers such as the Neglinka (0.01 km^3 yr^{-1}) and the Lososinka (0.02 km^3 yr^{-1}) also flow into the bay. PB receives an estimated 0.04 km^3 yr^{-1}precipitation and 0.002 km^3 yr^{-1} ground water infiltration. The volume of stormwater and other runoff supplied to the bay from the city of Petrozavodsk reaches 0.05 km^3 yr^{-1}. The total volume of tributary flow into the bay is 3.35 km^3 yr^{-1}, 93% of which comes from the Shuya River.

Lozovik et al. (2019) found that water exchange in the bay varies significantly on a seasonal basis. The longest exchange period occurred in winter (2.9 months) while the shortest occurred in autumn (0.8 month). The mean annual PB water exchange period is 1.6 months.

Materials and methods

Sampling sites

The 2016 hydrochemical study of Lake Onego focused on its different limnological regions, which are herein referred to as the central part, Big Onego, and PB (Table 1, Fig. 1). The study was carried out at different monitoring stations in PB (St.1 through St.4) and at the mouth of the Shuya River (CO2) in March 2016, a time frame interpreted as the winter season. Monitoring of the central part of Lake Onego (C-3), PB (P-3), and the Shuya River mouth (CO2) in June 2016 was interpreted as the spring season. Monitoring of the central part of Lake Onego (C-1), Big Onego (B-1, B-2), and PB (P-2) conducted in October 2016 was interpreted as the autumn season. Monitoring consisted of water sample collection from the surface, mid-, and near-bottom depths at each station.

Table 1. List of the sampling locations and their coordinates.

Object	Station name	Latitude N	Longitude E
Petrozavodsk Bay	P-2	61°48.269′	034°26.066′
	P-3	61°46.133′	034°31.883′
	St.1	61°49.601′	034°22.206′
	St.2	61°49.029′	034°23.364′
	St.3	61°46.708′	034°31.797′
	St.4	61°48.028′	034°28.070′
Central part of Onego Lake	C-1	61°38.113′	035°28.201′
	C-3	61°41.901′	034°59.066′
Big Onego	B-1	62°04.186′	034°51.604′
	B-2	61°55.609′	034°50.077′
Shuya River	CO2	61°50.788′	034°21.438′

Water sampling and sample preservation

Samples were analyzed for major anion and cation composition, dissolved organic matter, nutrients, trace elements, and mercury (Hg). Some components were analyzed on site while others were preserved using standard techniques (Lozovik and Efremenko 2017; Table 2) and transported to the laboratory. Chemical analyses were performed at the Laboratory of Hydrochemistry and Hydrogeology, Northern Water Problems Institute, Karelian Research Center, Russian Academy of Sciences (NWPI KarRC RAS). Reliability of the methods and quality of analyses underwent annual control according to the international cooperative programme on assessment and monitoring effects of air pollution on rivers and lakes (ICP 2016).

For Hg analyses, all collection materials were precleaned following procedures detailed in Dranguet et al. (2017). Briefly, collection tools were soaked in 2 successive baths of 10% nitric acid (HNO_3, pro-analysis, Merck, Darmstad, Germany) for 1 week each and a 10% HCl (pro-analysis, Merck, Darmstad, Germany) bath for another week. Tools were then thoroughly rinsed with milliQ water (resistivity = 18.2 MΩ cm, total organic carbon < 5 ppb; Millipore Direct Q-8, Merck, Schaffhausen, Switzerland), dried under a laminar flow hood, and double-bagged for transport to the study sites. Sterivex filters were rinsed prior water sampling by filtering 10% HNO_3 (Suprapur, Merck, Darmstadt, Germany), 10% HCl

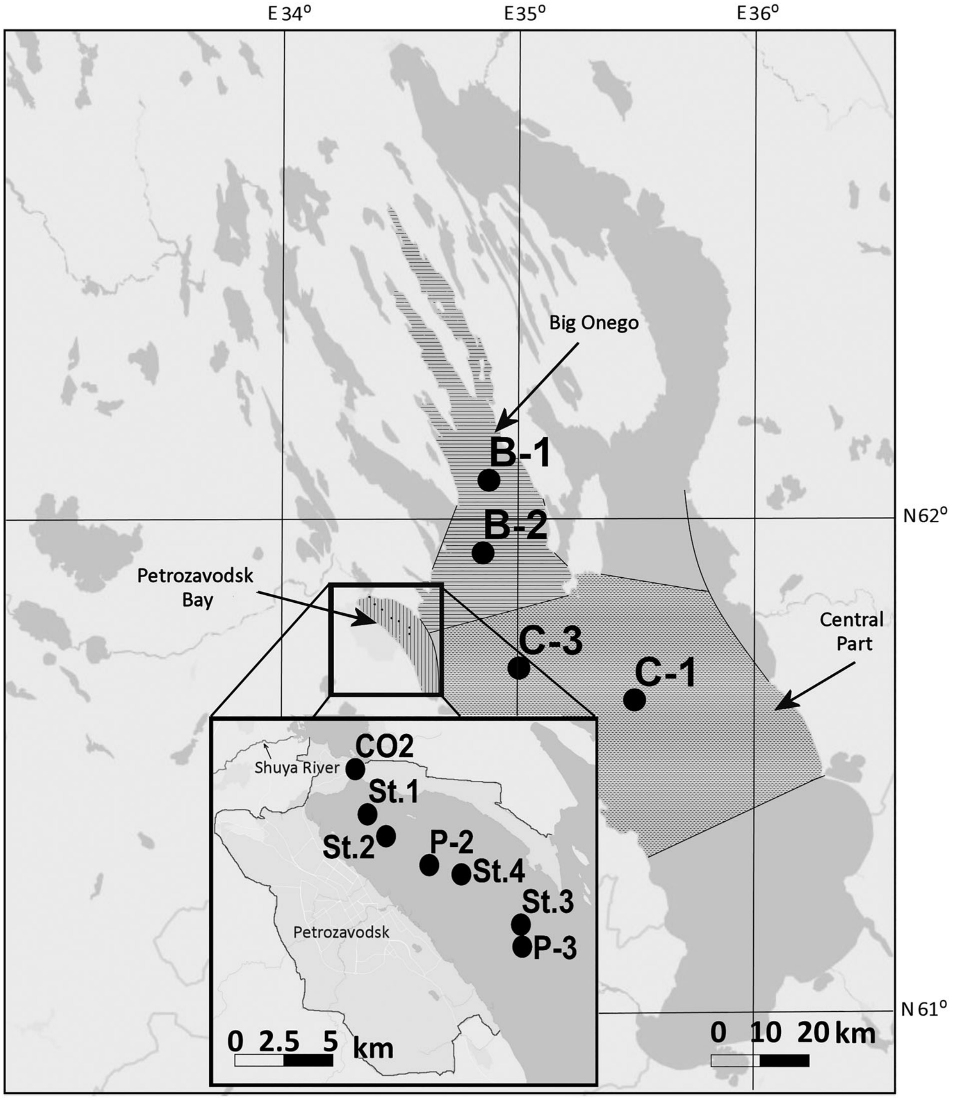

Figure 1. Water sampling locations in Petrozavodsk Bay and Lake Onego. Station names are listed in Table 1.

(Ultrex), ultrapure water and sampling site water. For mercury analyses, field blanks were performed regularly by filtration of ultrapure water in the field throughout the sampling period. Samples of lake or river water (100 mL) were filtered through 0.45 µm Sterivex filters, acidified to 1% (v/v final concentration) with HCl (Ultrex, J.T. Baker, VWR, Nyon, Switzerland), and stored at 4 °C in the dark until further analysis.

Chemical analyses

Major ion (calcium [Ca^{2+}], magnesium [Mg^{2+}], sodium [Na^{+}], potassium [K^{+}], bicarbonate [HCO_3^-], sulfate [SO_4^{2-}], and chloride [Cl^-]) concentrations and alkalinity of waters sampled at each site and depth were measured following standard analytical procedures (Table 2). Organic matter was characterized from water color and using permanganate and bichromate chemical oxygen demand (COD_{Mn} and COD_{Cr}, respectively), total organic carbon (TOC), and organic nitrogen (N_{org}) measurements (Table 2). TOC was quantified by standard UV/peroxodisulphate methods (ISO 1999) using an experimental setup described in Zobkov and Zobkova (2015). Nutrients were characterized from mineral phosphorus (P_{min}), total phosphorus (TP), ammonium nitrogen (NH_4-N), nitrate nitrogen (NO_3-N), nitrite nitrogen (NO_2-N), and total nitrogen (TN) concentrations using various techniques (Table 2). Trace element concentrations (total iron [Fe_{tot}] and manganese [Mn]) were analyzed by atomic absorption spectrometry. Water samples were also analyzed for oxygen (O_2) and carbon dioxide (CO_2) concentrations, pH, temperature, conductivity, and suspended particulate matter (Table 2).

Total mercury concentration (THg = inorganic mercury plus methylmercury) in 0.45 µm filtered water was measured by cold vapor atomic fluorescence

Table 2. Chemical methods used to analyze water samples (Lozovik and Efremenko 2017).

Characteristic	Analytical method
pH	Potentiometric determination by glass electrode
Temperature and conductivity	Determination by temperature meter and conductivity meter of water
Na^+, K^+	Flame photometric determination
Ca^{2+}, Mg^{2+}	Atomic-adsorption spectrometric determination
Alkalinity	Titrimetric determination
Cl^-	Spectrophotometric determination with mercury thiocyanate and iron (III) nitrate
SO_4^{2-}	Spectrophotometric determination with barium chloride and sulfonazo III
Fe_{tot}, Mn_{tot}	Total iron, total manganese atomic-adsorption spectrometric determination
SiO_2-Si	Spectrophotometric determination to form a yellow silicomolybdenum heteropolyacid
NH_4-N	Spectrophotometric indophenol method with phenol and hypochlorite, $\lambda = 630$ nm
NO_2-N	Spectrophotometric method with sulfanilamide and N-(1-Naphthyl)-ethylenediamine-dihydrochloride, $\lambda = 543$ nm
NO_3-N	Reduction to NO_2^- with a Cd-reduction column and determination as NO_2^-
N_{org}	As the difference between TN and sum NH_4-N + NO_3-N + NO_2-N
TN	Spectrometric method with potassium persulfate following mineralization in a thermostat to NO_3^- $\lambda = 207$ nm
P_{min}	Spectrophotometric method with ammonium molybdate and ascorbic acid reduction to phosphatomolybdic heteropolyacid, $\lambda = 882$ nm
TP	Oxidation of organic matter by $K_2S_2O_8$ in acidic media and determine P_{min}
COD_{Mn}	Titrimetric determination in acidic media (Kubel method)
TOC	Photochemical oxidation with ammonium persulfate in a persistent gas flow
COD_{Cr}	Dichromate sulfuric acid oxidation of organic matter and titrimetric determination with ferroin
Color	Photometric determination
O_2	Titrimetric determination (Winkler method)
BOD	Determination by light-and-dark-bottle method using O_2
SPM	Gravimetric determination
Total mercury	Cold vapor atomic fluorescence spectrometry with the MERX Automated Analytical System

spectrometry with the MERX Automated Analytical System (Brooks Rand Instruments, Seattle, WA, USA), following procedures detailed in Dranguet et al. (2017). Operations followed manufacturer's instructions and used EPA method 1631 (US EPA 2002). The certified reference material ORMS-5 (National Research Council Canada) was used as an analytical standard. Analyses of THg were performed at the University of Geneva, Switzerland. Differences in Hg concentrations from different sampling sites were determined from multivariate analysis of variance (ANOVA) with Tukey's post hoc test in SigmaStat ($p < 0.05$).

Results and discussion

Major physicochemical characteristics

Waters from all sampling stations were well oxygenated throughout 2016, evident from O_2 saturation values of 79–97%. A low O_2 event was recorded, however, in winter at PB St.3 (69%). A vertical temperature profile from St.3 also included a bottom layer temperature 0.5 °C higher than that of other nearby stations (Fig. 2). The bay bottom has a consistent slope beginning from the River Shuya inlet down to the exit from PB with a hollow in the middle, where station 3 is situated. The low O_2

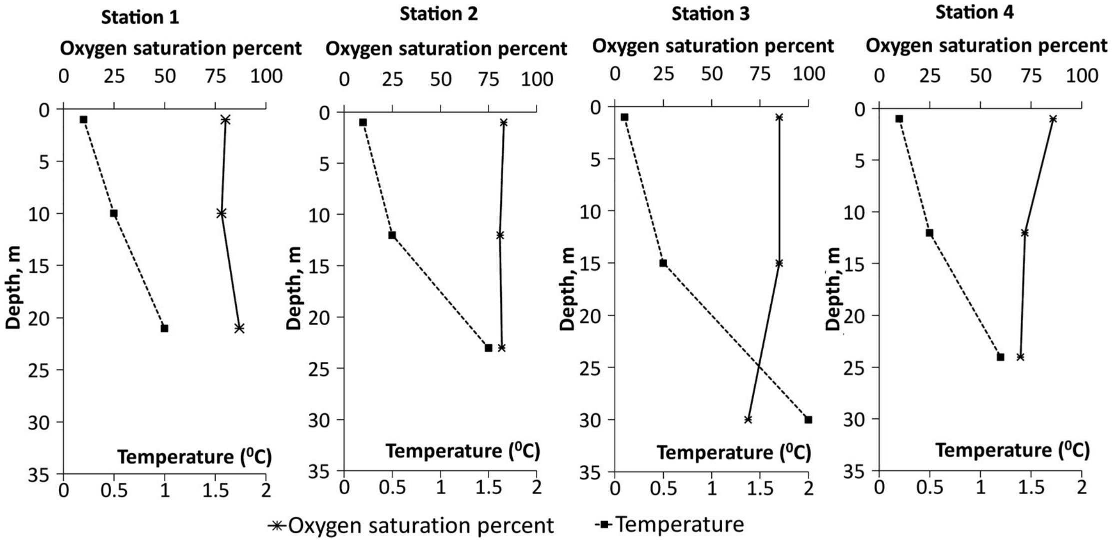

Figure 2. Vertical distribution of the water temperature and oxygen saturation in Petrozavodsk Bay in winter 2016.

Table 3. Gas composition, suspended particulate matter (SPM), and water pH of study sites (mean values and variation ranges) in 2016.

Waterbody	O_2		CO_2, mg L^{-1}	Suspended particular matter, mg L^{-1}	pH
	mg L^{-1}	%			
			Winter		
R. Shuya	11.6	79	7.4	2.0	6.3
Petrozavodsk Bay	10.4 – 12.5 12.0	69 – 87 78	2.2 – 6.8 3.8	0.2 – 0.8 0.4	6.1 – 6.9 6.6
			Spring		
R. Shuya	7.8	77	3.2	7.8	6.4
Petrozavodsk Bay	8.9 – 10.3 9.8	79 – 94 85	2.2 – 4.7 4.2	0.3 – 2.2 1.8	6.5 – 6.9 6.6
Central part of Onego Lake	12.0 – 12.0 12.0	91 – 97 94	2.2 – 2.6 2.4	0.5 – 1.0 0.8	7.0 – 7.0 7.0
			Autumn		
Petrozavodsk Bay	8.9 – 9.7 9.3	79 – 87 83	3.1 – 4.4 3.8	1.0 – 2.4 1.7	6.4 – 6.7 6.5
Central part of Onego Lake	9.9 – 10.4 10.2	82 – 90 86	2.4 – 3.9 3.2	0.2 – 0.4 0.3	6.6 – 6.8 6.7

value likely reflects input from nearby wastewater treatment plants (Filatov 1999).

Waters from all study sites exhibited elevated CO_2 concentrations. CO_2 concentrations in the central part of Lake Onego were ~2.2–3.9 mg L^{-1} while those in PB were 2.2–6.8 mg L^{-1} (Table 3). Water samples from the Shuya River exhibited the highest CO_2 concentrations (up to 7.4 mg L^{-1}), values that accorded with its slightly acidic pH of 6.3–6.4. The pH values for PB samples exceeded those measured from the Shuya River while Lake Onego water samples exhibited near-neutral pH values.

All water samples except those from the Shuya River yielded low suspended particulate matter (SPM) values with average concentrations of 0.2–2.4 mg L^{-1}. The highest SPM value recorded from the Shuya River (7.8 mg L^{-1}) occurred in spring 2016, consistent with increased runoff from the watershed during spring flooding.

Mineralization and ionic composition

Lake Onego waters exhibited low mineralization (total dissolved solids [TDS] < 100 mg L^{-1}) of hydrocarbonate-calcium type (Table 4). The central part of the lake (C-1, C-3) is characterized by homogeneous ion composition (with depth) and low a low interannual variability (average annual TDS = 35.5 mg L^{-1}). These observations are consistent with Lake Onego being one of the world's largest, most poorly mineralized lakes. Its TDS values are 1.5, 3, and 4–5 times lower than those of Lakes Ladoga and Baikal (Russia) and the Great Lakes (USA), respectively (Filatov 1999).

Interestingly, during winter 2016, water TDS in samples at 0–12 m depth for PB St.1 and St.2 were 27.4–27.9 mg L^{-1}, values significantly lower than those measured from below 12 m depth (TDS = 36.7 mg L^{-1}). During this period, the Shuya River was ice-free, and its warmer water occupied the 0–12 m surface water layer of PB while lake water masses occupied depths below 12 m.

At the bay edge, St.4 data indicate that river water occupies middle depths (TDS = 27.0 mg L^{-1}; color = 132 mg Pt L^{-1}). Total ion content of the surface and near-bottom water layers measured at St.4 were 28.5 and 37.2 mg L^{-1}, respectively, and Ca^{2+} concentrations were 1.5 times higher than those of Mg^{2+} in the winter period and slightly lower in the open lake. These findings indicate that the Shuya River exerts a primary influence on the chemical composition of the PB water column during winter.

The low TDS of the Shuya River during the spring flood (19.4 mg L^{-1}) also contributes to low TDS in PB. TDS increased along the Shuya River–open lake gradient from 27.3–31.5 mg L^{-1} at the head of the bay (St.1) to 29.5–33.3 mg L^{-1} at P-3, where the bay opens into the lake proper. Amounts of HCO_3^- equivalent followed similar trends as those of TDS, which increased from 57%-eq. to 61%-eq. The average sulfate ion content (13%-eq.) in the bay water slightly exceeded that of chloride (10%-eq.). The Ca^{2+} content of bay water was more or less uniform at all depths throughout the lake with an average value of 4.5 mg L^{-1} (47%-eq.), which exceeded Mg^{2+} content by a factor of 2.6. Weathering and geological conditions of the watershed contribute Ca^{2+} and Mg^{2+} to the bay. The average concentration of organic acid (A_{org}) anions (33%-eq.) measured at bay sites was 4 times higher than corresponding concentrations measured at the open-lake station.

In autumn, ion compositions also displayed distinctive patterns at different stations (Table 4). During autumn homothermy, TDS values remain uniform throughout the entire central part of Lake Onego (C-1, B-2, B-1), averaging 33.4 mg L^{-1}. HCO_3^- equivalent

Table 4. Concentrations of cations, anions, and total dissolved solids in Lake Onego samples.

Station	Depth, m	Ca^{2+}, mg L^{-1}	Mg^{2+}, mg L^{-1}	K^{+}, mg L^{-1}	Na^{+}, mg L^{-1}	NH$_4$-N, mg L^{-1}	HCO$_3^-$, mg L^{-1}	SO$_4^{2-}$, mg L^{-1}	Cl$^-$, mg L^{-1}	NO$_2$-N, mg L^{-1}	NO$_3$-N, mg L^{-1}	TDS, mg L^{-1}
Winter												
Petrozavodsk Bay (St.1)	1.0	4.1	1.6	2.1	0.5	0.02	14.0	3.2	1.7	<0.001	0.14	27.4
	10.0	4.0	1.6	2.1	0.5	0.01	14.8	2.9	1.5	<0.001	0.10	27.5
	21.0	5.0	1.9	2.4	0.6	0.01	21.0	3.9	1.7	<0.001	0.17	36.7
Petrozavodsk Bay (St.2)	1.0	4.1	1.6	2.1	0.5	0.02	14.0	3.2	1.7	<0.001	0.12	27.9
	10.0	4.0	1.6	2.1	0.5	0.02	14.8	2.9	1.5	<0.001	0.13	27.7
	21.0	5.0	1.9	2.4	0.6	0.01	21.0	3.9	1.7	<0.001	0.16	36.7
Petrozavodsk Bay (St.3)	1.0	4.7	1.9	2.5	0.6	0.01	14.0	3.2	1.7	<0.001	0.14	28.8
	10.0	5.2	2.0	2.4	0.6	0.01	14.8	2.9	1.5	<0.001	0.17	29.6
	21.0	5.7	2.1	3.2	0.7	0.06	21.0	3.9	1.7	0.001	0.29	38.6
Petrozavodsk Bay (St.4)	1.0	4.6	1.8	2.4	0.6	0.02	14.0	3.2	1.7	<0.001	0.14	28.5
	10.0	3.8	1.5	2.3	0.6	0.01	14.8	2.9	1.5	<0.001	0.09	27.5
	21.0	5.1	2.0	2.4	0.9	0.01	21.0	3.9	1.7	<0.001	0.18	37.2
R.Shuya	surface	3.9	1.6	2.9	0.6	0.03	12.9	2.5	2.4	<0.001	0.14	27.0
Spring												
Petrozavodsk Bay (P-3)	1.0	4.3	1.6	2.1	0.5	0.06	16.8	2.6	1.5	<0.001	0.06	29.5
	15.0	4.4	1.7	2.4	0.6	0.02	17.0	2.9	1.7	<0.001	0.20	30.9
	29.0	4.7	1.9	2.5	0.5	0.01	18.5	3.3	1.7	<0.001	0.18	33.3
Petrozavodsk Bay (St.1)	1.0	4.0	1.5	2.2	0.5	0.02	14.8	2.7	1.5	<0.001	0.09	27.3
	11.0	4.4	1.7	2.2	0.5	0.03	16.0	2.7	1.6	0.001	0.19	29.3
	21.0	4.5	1.7	2.4	0.5	0.02	17.4	3.2	1.6	0.001	0.18	31.5
Petrozavodsk Bay (St.4)	1.0	4.4	1.6	2.3	0.5	0.03	16.5	2.7	1.6	0.001	0.12	29.7
	12.0	4.6	1.8	2.2	0.5	0.02	16.3	2.7	1.6	0.001	0.15	29.9
	24.0	4.9	1.8	2.2	0.5	0.02	19.4	2.9	1.6	0.001	0.17	33.5
Central part of Onego (C-3)	1.0	5.2	2.0	2.6	0.6	0.02	21.9	3.5	2.6	<0.001	0.16	38.6
	23.0	5.3	2.0	2.4	0.6	0.02	22.2	3.3	1.6	<0.001	0.19	37.6
	46.0	5.3	2.0	2.4	0.5	0.02	21.2	3.5	1.6	<0.001	0.18	36.7
River Shuya	surface	3.0	1.2	1.9	0.5	0.04	9.7	1.7	1.3	<0.001	0.03	19.4
Autumn												
Central part of Onego (C-1)	1.0	5.3	2.1	0.6	1.9	0.020	18.6	4.7	1.6	<0.001	0.18	35.0
	30.0	5.2	2.1	0.6	1.9	0.010	17.4	3.4	1.6	<0.001	0.20	32.4
	56.0	5.2	2.0	0.6	1.9	0.030	17.7	3.5	1.6	<0.001	0.23	32.8
Petrozavodsk Bay (P-2)	1.0	4.9	1.9	0.6	2.1	0.004	11.3	3.3	1.6	<0.001	0.12	25.8
	25.0	4.3	1.7	0.6	1.9	0.010	15.4	2.9	1.5	<0.001	0.13	28.4
Big Onego (B-2)	1.0	5.3	2.1	0.6	1.9	0.010	19.4	3.6	1.6	<0.001	0.18	34.6
	22.0	5.3	2.0	0.6	1.9	0.020	16.7	3.6	1.5	<0.001	0.20	31.8
	44.0	5.3	2.0	0.6	2.2	0.010	17.4	3.6	1.6	<0.001	0.23	32.9
Big Onego (B-1)	1.0	5.3	2.0	0.6	1.9	0.010	18.6	3.4	1.5	<0.001	0.19	33.5
	37.0	5.2	2.0	0.6	2.0	0.003	17.7	3.3	1.6	<0.001	0.21	32.5
	72.0	5.3	2.1	0.6	2.0	0.004	17.9	3.6	1.5	<0.001	0.24	33.2

concentration in the central part of Lake Onego during autumn was 55%-eq., 10% lower than that observed during the spring (65%-eq.). With an average value of 5.1 mg L^{-1} (49%-eq.), autumn Ca^{2+} concentrations exceeded spring Ca^{2+} concentrations. Autumn values for organic acid (A$_{org}$) anion concentrations for Lake Onego were particularly high relative to those observed during other seasons. The central part of the lake had values 2.2 times higher than those observed during the spring season. The A$_{org}$ concentration in PB water (32%-eq.) likely reflects humic input from the Shuya River, which spreads throughout the surface layer (A$_{org}$ = 42%-eq.) and also affects water color (82 mg Pt L^{-1}).

Organic matter characteristics

Organic matter (OM) concentrations varied considerably among different samples. The limnic heterogeneity of Lake Onego and its bay contributes to the observed variation. Shuya River input strongly influenced winter and spring water color in PB (Fig. 3). In March 2016, ice on the Shuya River thawed early, creating a warm water mass (4–7 °C) within the surface layer at 0–15 m. The area adjacent to PB was ice-bound. OM indices for 0–12 m depths in the bay resembled those of Shuya River water with high humic loads (Table 5). The OM concentration (TOC), color, and COD$_{Mn}$ (as O$_2$) of near-bottom water layers were 7.6–8.5 mg L^{-1}, 32–45 mg Pt L^{-1}, and 7.5–8.3 mg L^{-1}, respectively (Fig. 3, Table 5). The OM composition for PB during ice-free periods depends largely on annual precipitation and hydrometeorological conditions, which control the intensity of water exchange with the bay. Given high precipitation during spring 2016, Shuya River input to the bay displayed elevated water color values (130 mg Pt L^{-1}) and COD$_{Mn}$ (as O$_2$ content, 19.7 mg L^{-1}) and COD$_{Cr}$ (42.4 mg L^{-1}). TOC content of the water was 16.2 mg L^{-1}. This warmer water (16.1 °C) occupied the upper 0–15 m of the bay but remained near

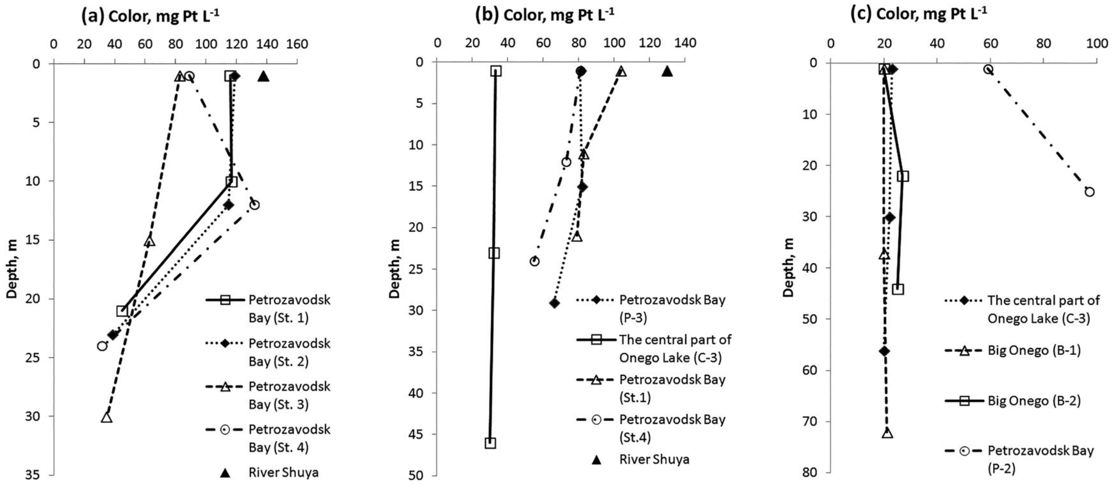

Figure 3. Vertical distribution of Petrozavodsk Bay and Lake Onego water color indices in (a) winter, (b) spring, and (c) autumn 2016.

Table 5. Variation in color, TOC, and permanganate and bichromate oxidation of Lake Onego waters in winter, spring, and autumn 2016.

Stations (levels)	Color, mg Pt L^{-1}	TOC, mg L^{-1}	C/N	COD$_{Cr}$, mg L^{-1}	COD$_{Mn}$, mg L^{-1}
			Winter		
R. Shuya	138	18.0	21	51.3	21.5
Petrozavodsk Bay, St. 1,2 (1.0–12 m)	115–119	16.7–17.8	51–54	41.1–46.1	18.2–19.1
Petrozavodsk Bay, St. 3,4 (1.0–15.0 m)	63–132	9.8–17.3	36–64	26.1–39.4	10.1–14.4
Petrozavodsk Bay, St. 1–4 (near bottom)	32–45	7.6–8.5	31–42	20.4–23.5	7.5–8.3
			Spring		
R. Shuya	130	16.2	36	42.4	19.7
Petrozavodsk Bay, P-3 (1.0;15.0;29.0)	66–81	11.0–12.4	39–44	26.8–33.2	12.2–14.7
Petrozavodsk Bay, St.1 (1.0;11.0;21.0)	79–104	11.5–14.0	34–40	28.0–36.0	13.5–16.5
Petrozavodsk Bay, St.4 (1.0;12.0; 24.0)	55–81	8.7–11.7	31–43	24.0–32.4	10.2–14.2
Lake Onego, C-3 (1.0;23.0;46.0)	30–33	6.3–6.7	28–54	15.6–16.4	6.0–6.9
			Autumn		
Lake Onego, C-1 (1.0;30.0;56.0)	20–23	6.2–6.6	34–35	16.2–17.2	6.5–7.5
Lake Onego, B-2 (1.0;22.0;44.0); B-1(1.0;37.0; 72.0)	20–27	6.14–6.6	40–44	15.8–17.4	6.5–7.2
Petrozavodsk Bay, P-2 (1.0; 25.0)	59–97	10.9–15.2	30–31	27.8–37.2	13.6–17.9

Petrozavodsk shorelines. The water in this warmer layer contained more humic substances.

Between upper and external zones, the color index of the water varied from 104 to 79 mg Pt L^{-1}, COD$_{Mn}$ varied from 16.5 to 13.5 mg L^{-1}, and COD$_{Cr}$ varied from 36.0 to 28.0 mg L^{-1}. Near-bottom layers gave much lower values for these indices (Fig. 3). Winter OM concentrations varied with depth in PB but not in the open lake. The highest OM concentrations occurred at middle depths in the PB water column while lower OM concentrations occurred in near-bottom layers (Fig. 3). The darker (humic-rich) Shuya River water occupied middle layers to cause this pattern.

Following Lozovik and Efremenko (2017), the fraction of dissolved autochthonous OM (ρ_{aut}) was calculated according to the formula:

$$\rho_{aut} = \frac{COD_{Cr(adsorption)}}{COD_{Cr(centrifugation)}}, \tag{1}$$

where COD$_{Cr(adsorption)}$ was the COD$_{Cr}$ of water after adsorption of diethylaminoethyl celluloset, and the fraction of dissolved allochthonous OM (ρall) was given by:

$$\rho_{all} = 1 - \rho_{aut}. \tag{2}$$

In spring, dissolved OM in PB waters was largely of allochthonous origin (percentage content allochthonous OM, $\rho_{all} = 77\%$).

Spring OM indices measured from the central part of the lake were homogeneous with depth. Organic carbon concentration varied from 6.3 to 6.7 mg L^{-1}, the water color varied from 30 to 33 mg Pt L^{-1}, COD$_{Mn}$ varied from 6.0 to 6.9 mg L^{-1}, and COD$_{Cr}$ varied from 15.6 to 16.4 mg L^{-1}. With the onset of homothermy in autumn, OM concentration indices in the central part of the lake and at Big Onego became uniform with depth. For example, average TOC concentration was 6.5 mg L^{-1}, water color was 22 mg Pt L^{-1}, COD$_{Mn}$ was 6.7 mg L^{-1}, and COD$_{Cr}$ was 16.9 mg L^{-1}. During this period, OM concentration indices in PB varied considerably with depth (Table 5). The difference in water color index values

Table 6. Molecular OM composition and the caloricity (Q) of the waterbodies studied (mean values).

Object	Seasons	Chemical formula	OM, mg L^{-1}	Q, cal g^{-1}
R. Shuya	Winter, spring	$C_{34.2}\ (H_2O)_{16.3}O_{4.1}\ NH_3$	31.0	155
Petrozavodsk Bay, (St.1,2)	Winter	$C_{28.6}\ (H_2O)_{13.4}O_{2.5}\ NH_3$	23.7	144
Petrozavodsk Bay (P-2, P-3)	Winter, spring, autumn	$C_{45.5}\ (H_2O)_{21.6}O_{4.4}\ NH_3$	20.4	93
The central part of Onego Lake (C-3)	Spring, autumn	$C_{43.9}\ (H_2O)_{20.7}O_{3.1}\ NH_3$	11.8	54

and TOC between the surface and near-bottom water layers was 38 mg Pt L^{-1} and 4.3 mg L^{-1}, respectively. In autumn, cold Shuya River water rich in humic substances occupied near-bottom water layers of the bay basin. Based on the humic and Fe content of the water, PB is classified as a mesohumic waterbody, the Shuya River is also mesopolyhumic, and the central part of Lake Onego is oligomesohumic.

Element composition of OM and its gross formula and caloricity were determined following methods described in Bikbulatov (2009). A large stratified lake typically significantly transforms OM. The average C:N mass ratio in the central part of Lake Onego was 35 while caloricity was only 54 cal g^{-1} (Table 6). In winter and spring, OM caloricity in PB surface water (93–144 kcal g^{-1}) was higher than that of the central part of Lake Onego. Caloricity in the Shuya River during winter 2016 reached 155 kcal g^{-1}.

Nutrients

Nutrient concentrations varied with different sampling stations and different seasons (Fig. 4, Table 7). The highest TP (55 µg L^{-1}) and P_{min} (46 µg L^{-1}) concentrations occurred during the winter in the near-bottom layer at PB St.3, which could reflect wastewater treatment plant (WWTP) releases and P diffusion from sediment. Discharge from the Petrozavodsk WWTP could explain warmer and denser waters occupying the near bottom layer during winter months, as previously suggested by Filatov (2010). P release from lake sediment could also arise because of limited oxygen conditions (O_2 saturation was 69%) during the ice-covered period. These 2 factors could intermingle to cause P enrichment in sediments (Belkina 2015).

Both Shuya River and PB waters showed elevated TP concentrations (mean values 36 and 22 µg L^{-1}, respectively). The central part of Lake Onego exhibited low TP concentrations (mean 7 µg L^{-1}). Observations indicate that the TP content of Lake Onego does not vary significantly with time and space. Because it acts as the major limiting nutrient in the surface waters of humid climate regions, we used TP to differentiate water column trophic conditions. According to classification parameters detailed in Lozovik (2013), the central part of Lake Onego is oligotrophic, PB is mesotrophic, and the Shuya River is eutrophic. These designations are consistent with the European classification of trophic conditions (Nürnberg 1996).

The distribution of N in Lake Onego exhibited a distinctive pattern (Table 7). Concentration of NO_3-N resembled that of N_{org} (~ 0.2 mg L^{-1}), NH_2-N concentration was low (<0.06 mg L^{-1}), and NO_2-N was below

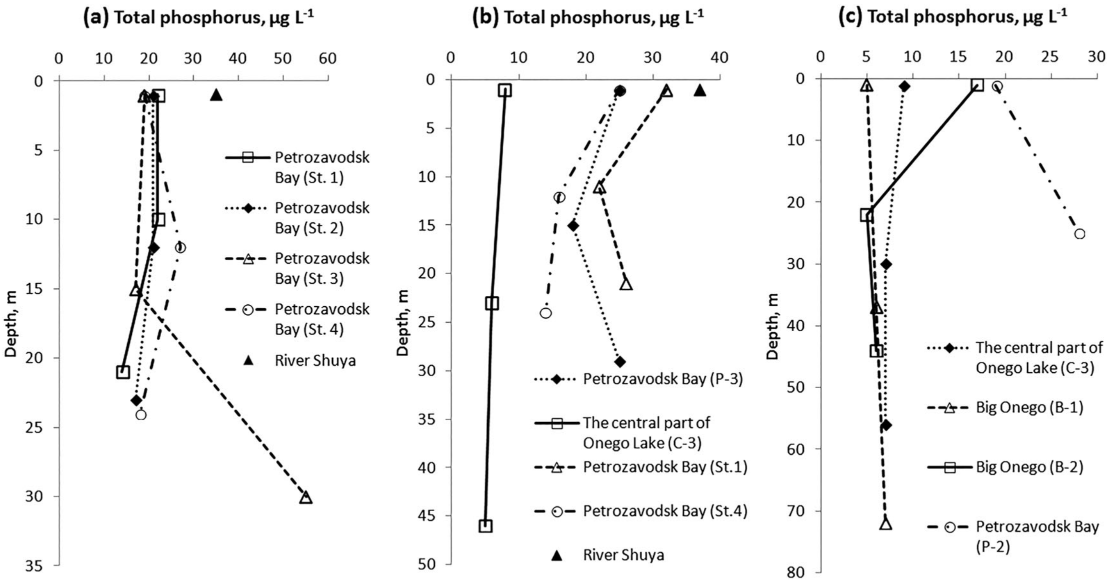

Figure 4. Total phosphorus depth distribution in Lake Onego in (a) winter, (b) spring, and (c) autumn 2016.

Table 7. Nutrient distribution (ranges/mean values) for Lake Onego waters in 2016.

Stations	P_{min}, µg L^{-1}	TP, µg L^{-1}	NH_4-N, mg L^{-1}	NO_2-N, µg L^{-1}	NO_3-N, mg L^{-1}	N_{org}, mg L^{-1}	TN, mg L^{-1}
			Winter 2016				
R. Shuya	16	35	0.03	1	0.14	0.87	1.04
Petrozavodsk Bay (St. 1, 2, 3,4)	7 – 46 9	7 – 55 20	0.01 – 0.06 0.02	≺ 1 – 1 ≺ 1	0.12 – 0.29 0.15	0.19 – 0.38 0.27	0.37 – 0.57 0.44
			Spring 2016				
R. Shuya	10	37	0.04	<1	0.03	0.45	0.52
Petrozavodsk Bay (St. 1, 4; P-3)	2 – 7 4	14 – 32 23	0.01 – 0.06 0.03	≺ 1 – 1 1	0.06 – 0.20 0.15	0.28 – 0.45 0.32	0.42 – 0.54 0.51
Central part of Onego Lake (C-3)	1 – 1 1	5 – 8 6	0.01 – 0.02 0.02	≺ 1 – 1 ≺ 1	0.16 – 0.19 0.18	0.12 – 0.24 0.17	0.32 – 0.42 0.37
			Autumn 2016				
Petrozavodsk Bay (P-2)	4 – 8 6	19 – 28 24	0.004 – 0.01 0.01	≺ 1 – 1 ≺ 1	0.12 – 0.13 0.13	0.35 – 0.47 0.40	0.48 – 0.60 0.54
Central part of Onego Lake (C-3)	1 – 1 1	7 – 9 8	0.01 – 0.03 0.02	≺ 1 – 1 ≺ 1	0.18 – 0.23 0.20	0.17 – 0.20 0.20	0.36 – 0.46 0.40
Big Onego (B-2, B-1)	1 – 1 1	5 – 17 8	0.004 – 0.02 0.01	≺ 1 – 1 ≺ 1	0.18 – 0.24 0.21	0.14 – 0.18 0.16	0.36 – 0.40 0.38

detection limits (<1 µg L^{-1}). The distribution of N in open Lake Onego has peculiarities similar to other large and deep northern lakes (Filatov 2015). Consistent with observations from surface waters in humid climate regions, N_{org} predominated PB and the Shuya River samples.

N species can assume 3 different regimes. In a type 1 regime, N_{org} predominates over other forms (Shuya River). Humic-rich surface waters in Karelia exhibited this pattern (Lozovik et al. 2017). In a type 2 regime, NO_3-N content resembles N_{org} content (central part of Lake Onego). In a type 3 regime, N_{org} content exceeds NO_3-N content (Petrozavodsk Bay in all seasons). All the waters analyzed here exhibited low NH_4-N content (0.01–0.03 mg L^{-1}) and almost no NO_2-N (<0.001 mg L^{-1}). In large stratified lakes like Lake Onego, NO_3-N forms from N_{org} transformation (N_{org}→NH_4-N→NO_2-N →NO_3-N). Provided the water column remains oxygenated, dark and cold water column conditions make NO_3-N a conservative constituent in these reactions..

Monitoring data spanning back to 1992 indicate that the distribution of N species in Lake Onego has not varied significantly over the years. By contrast, the Great Lakes (USA) exhibit nitrate declines over the last 2 decades (Mida et al. 2010, Evans et. al. 2011).

Trace elements

Trace element distributions resembled those of OM (Fig. 5). The highest Fe (0.99–1.23 mg L^{-1}), Mn (0.047–0.088 mg L^{-1}), and SiO_2-Si (1.8–2.2 mg L^{-1}) concentrations occurred in Shuya River samples. PB exhibited lower Fe, Mn, and SiO_2-Si concentrations (0.45, 0.028, and 1.3 mg L^{-1}, respectively) while the central part of Lake Onego exhibited the lowest concentrations (0.06, 0.01, and 0.3 mg L^{-1}, respectively) during all seasons. The spatial trends in trace element concentrations are consistent with the findings of Sabylina (2007) that Fe, Mn, and particularly SiO_2-Si, are primarily controlled by river input to PB.

Total filterable mercury

During winter (March, Fig. 6a), THg concentrations in PB surface waters (St.1, St.2, and St.3) increased to twice the values measured during the spring season (June, Fig. 6b). Samples collected in March from the Shuya River or other intermediate stations did not show corresponding changes or gradients in THg concentrations (Fig. 6).

Changes in THg concentrations during the winter period may arise from convective mixing, vertical stratification, and the influence of river input into the bay (Bouffard et al. 2016). Similar to other hydrochemical variables, winter Hg concentrations apparently reflect Shuya River input that spreads into and occupies the 0–12 m depth horizon in the bay. In spring, THg concentrations from open-lake sampling sites were much lower than those measured from PB sampling sites (Fig. 6b). This Hg distribution pattern indicates Shuya River Hg input is processed by the bay's internal hydrodynamic processes, which in turn depend on the intensity of the bay–lake water mass exchange. Lower THg values coincide with higher SPM content, a pattern not consistent with findings by Diaz et al. (2009) that particles adsorb Hg to remove it from the water column through sedimentation. Further research is needed to understand whether or not this mechanism operates in the Shuya River–PB–Lake Onego system.

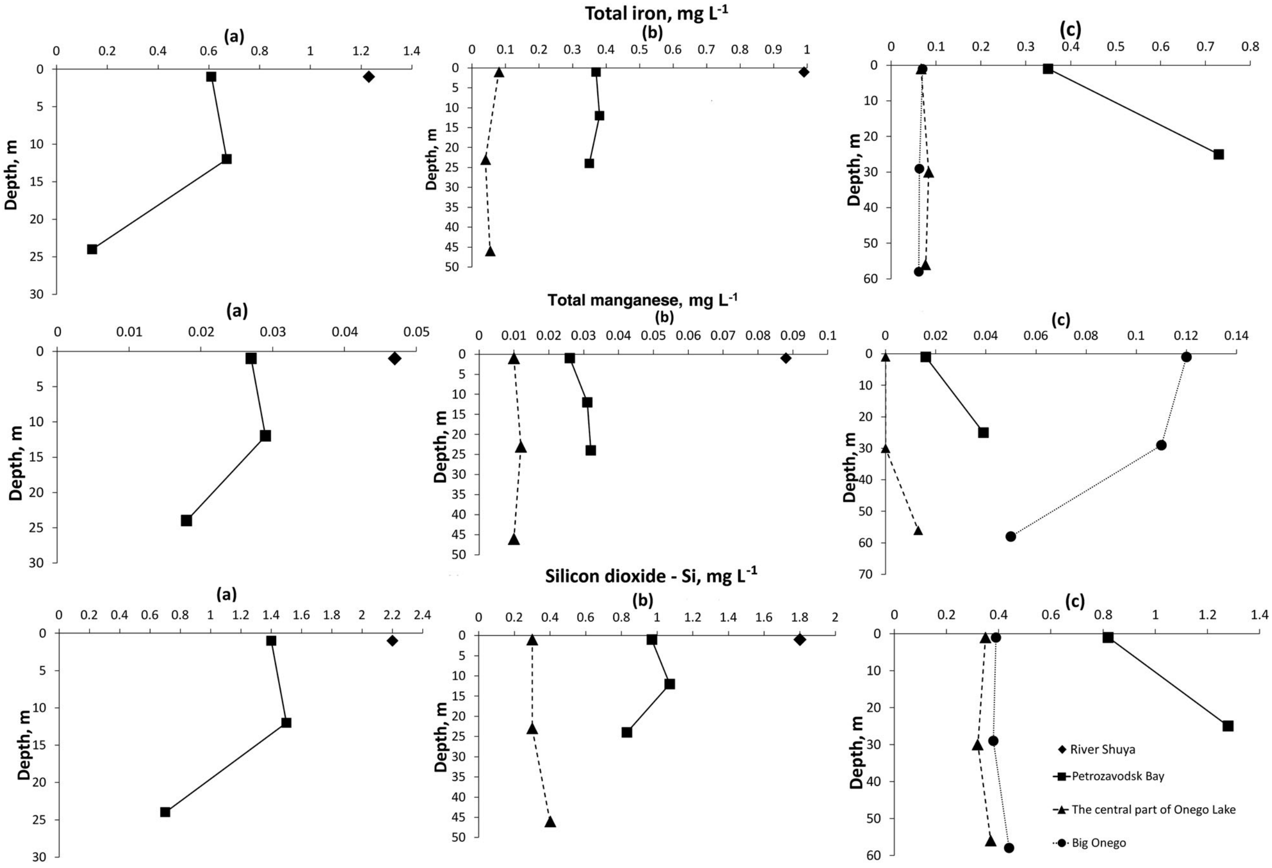

Figure 5. Total iron, total manganese, and silicon dioxide distribution in different regions of Lake Onego and River Shuya in (a) winter, (b) spring, and (c) autumn 2016.

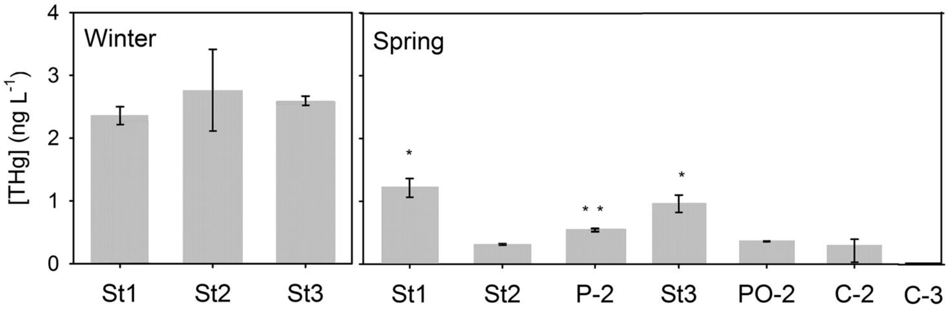

Figure 6. Total mercury concentrations (THg, filtered at <0.45 μm) in surface water from Lake Onego sampled in March and June 2016. Values represent averages from 6 measurements. * indicates significant differences between the THg concentrations of different sampling sites as revealed by ANOVA, followed by Tukey's post hoc test ($p < 0.05$). Concentrations measured at C-3 were below MERX detection limit.

Lake Onego THg concentrations exhibited the same range as those measured from other large lakes such as Listvenichenyi Bay of Lake Baikal (Ciesielski et al. 2016), Lake Geneva (Switzerland; Guédron et al. 2016), Lake Michigan (USA; Mason and Sullivan 1997), and Lake Victoria (Africa; Campbell et al. 2003). THg concentrations observed from all sampling sites and at all depths fell significantly below average annual limits of 0.05 mg L^{-1} specified by environmental quality standards for inland surface waters (EU 2008). The waterbodies studied here thus have good water quality with respect to this pollutant.

Conclusions

We conducted seasonal monitoring of water chemistry in Petrozavodsk Bay (PB), its Shuya River inlet, and in adjacent open-water areas of Lake Onego. Shuya River inflow and, to a lesser degree, sewage discharges from the city of Petrozavodsk both affect PB water quality.

The combined influence of these 2 sources depends on the intensity of the bay–lake water exchange, which in turn varies with annual precipitation and hydrometeorological conditions. In winter, PB's hydrochemical regime depends primarily on Shuya River inflow because water exchange between the bay and the open lake is restricted during its ice-covered period, demonstrated by the considerable variation in PB hydrochemistry. PB TOC varied from 7.6 to 17.8 mg L^{-1}, TP varied from 7 to 55 μg L^{-1}, and O_2 saturation varied from 69% to 87%. Sewage water exerted the strongest influence in near-bottom layers of areas adjacent to PB (St.3), where the highest TP concentration (55 μg L^{-1}) was detected. In spring and autumn, when bay water masses experience wind-induced and thermal mixing, open lake water exerts the strongest influence on PB chemical composition, evident as lower variability in TOC (from 8.7 to 14.0 mg L^{-1}), TP (from 14 to 32 μg L^{-1}), and O_2 saturation (from 79% to 94%). Seasonal monitoring indicated that sewage from the city of Petrozavodsk, which discharges into peripheral areas of PB, exerts only minor effects on bay water quality during the spring and autumn period of mixing with open waters of the greater lake. Waters analyzed from open areas of Lake Onego (central part and Big Onego) exhibited oligotrophic chemical parameters and low pollutant values. They had low water color (20–33 mg Pt L^{-1}), low TOC (6.0–6.7 mg L^{-1}), and low nutrient content, particularly TP (5–9 μg L^{-1}). Samples from all locations at different seasons showed THg concentrations indicating good water quality with respect to this major pollutant.

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Disclosure statement

No potential conflict of interest was reported by the author(s).

ORCID

Tatyana A. Efremova http://orcid.org/0000-0003-1074-1083
Petr A. Lozovik http://orcid.org/0000-0002-0062-2235
Vera I. Slaveykova http://orcid.org/0000-0002-8361-2509
Mariya V. Zobkova http://orcid.org/0000-0002-8106-3665
Natacha Pasche http://orcid.org/0000-0002-9578-9301

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