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Allochthonous and autochthonous carbon in deep, organic-rich and organic-poor lakes of the European Russian subarctic

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To reveal the degree of allochthonous *vs*. autochthonous control on carbon dynamics in deep, boreal lakes, we studied two (one organic-rich and one organic-poor) small (~0.1 km^2) and deep (~40 m), seasonally stratified lakes located in the European subarctic zone (NW Russia, Arkhangelsk region) during a 2.5-year period. The dissolved organic and inorganic carbon (DOC and DIC, respectively) concentrations were 15–30 mg l^{-1} and 0.5–1.9 mg l^{-1} in the humic lake and 0.8–4.3 mg l^{-1} and 18–52 mg l^{-1} in the organic-poor lake, respectively. The DOC profile in the organic-poor lake was sensitive to phytoplankton blooms in July–August and snowmelt in May, whereas the organic-rich lake was a highly stable system throughout the year in both the epilimnion and hypolimnion, with significant (ca. 40%) increase in DOC concentration in the hypolimnion relative to the epilimnion. The ratio of dissolved organic carbon to organic nitrogen (C_{org}/N_{org}) was significantly lower in the organic-poor lake, reflecting a strong impact of autochthonous N_{org} production and N diffusion from the sediment to the water column. There was a clear difference in the vertical pattern of the proportion of the low molecular weight ($LMW_{< 1 kDa}$) organic carbon (OC) between the humic and the organic-poor lakes. Regardless of season, the organic-poor lake's $LMW_{< 1 kDa}$ was 40%–90%, whereas that of the organic-rich lake 20%–30%. This difference was most likely linked to the dominance of peat soil and bog providing allochthonous OC to the organic-rich lake throughout the year, and possible production of LMW autochthonous organic ligands by phytoplankton and photodegradation in the organic-poor lake. The important role of allochthonous organic matter (OM) in the color properties of the lake water was confirmed by the light absorbance in the visual range and specific ultraviolet absorption measurements. Overall, deep humic (organic-rich) lakes are expected to be less sensitive to external impacts and possible climate change. The evaluation of both number and depth of humic lakes in the boreal zone is crucial for assessing their CO_2 emission and carbon storage potential.

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Introduction

In the European boreal zone, numerous lakes regulate the fate of dissolved carbon, nutrients and trace metals during their transport from the watershed to the ocean (Kothawala *et al.* 2014) and the exchange of CO_2 with the atmosphere (Denfeld *et al.* 2015, Lundin *et al.* 2015). However, knowledge regarding seasonal variation in concentration and size fractionation of organic carbon (OC) in deep, stratified, boreal lakes remains rather limited. This is particularly true for the Arkhangelsk Region (area of 590 000 km^2) which extensively covered by lakes and bogs (3% and 12%, respectively) (Fig. 1). The majority of the lakes in the Arkhangelsk Region were formed after last glaciers retreated, but some lakes have tectonic origin (Zhil and Alushkinskaya 1972, Morgunova *et al.* 1976). Small lakes (< 0.1–1 km^2), abundant in the Region, are especially important from the viewpoint of a carbon and related element biogeochemical balance.

Despite a considerable number of studies on a detailed characterization of dissolved organic matter (DOM) in large, shallow lakes in the boreal zone (Smith *et al.* 2004, Hiriart-Baer *et al.* 2008, Wang *et al.* 2009, Laurion *et al.* 2010, Bouillon *et al.* 2012, Catalan *et al.* 2013, Manasypov *et al.* 2014), small, deep and seasonally stratified lakes in the European subarctic remain outside the mainstream of scientific research, with most studies devoted to deep, clear-water lakes, dominating the arctic and subarctic aquatic settings (Forström *et al.* 2007 and references therein). In particular, thermal regime of small (< 0.1 km^2) lakes is sensitive to variation of dissolved OC (DOC) concentration (Read and Rose 2013). In accord with previous studies from Canada Snucins and Gunn (2000) and Read and Rose (2013) reported that lakes low in DOC should be more sensitive to climate variability, suggesting that DOC may act as a buffer against warming.

One may expect that poorly studied lakes of the Arkhangelsk Region (NW Russia) will have distinct patterns of carbon biogeochemistry depending on the content of DOC in the water column. Those lakes, remote from major industrial centers, are especially interesting for the assessment of climate change effects as they are minimally under the influence of acid rain and local human activity.

Clear water lakes are expected to have a dynamic seasonal DOC pattern, controlled by autochthonous processes in the water column, such as phytoplankton productivity and heterotrophic bacterioplankton respiration, strongly linked to solar radiation (Fortune *et al.* 2008, Ruiz-Gonzalez *et al.* 2013). In contrast, humic lakes should be more sustainable ecosystems, as their DOC is largely controlled by allochthonous OM input from adjacent forests and bogs. To test these hypotheses in the previously unstudied region, we selected two small (~0.1 km^2), boreal lakes with highly contrasting DOC levels but similar depths (~40 m) and degree of thermal stratification to investigate the concentration and size fractionation of DOC in the water column throughout the main hydrological seasons. Specific questions were: (i) How does water column DOC vary seasonally in organic-poor *vs.* organic-rich lakes? (ii) To what extent does the degree of thermal and redox stratification affect the DOC concentration and DOC/DIC ratio in the water column? (iii) Can the proportion of low molecular weight (< 1 kDa) OC fractions, the optical properties of the DOM and organic carbon to nitrogen ratio (C_{org}/N_{org}) in the water column be linked to the concentration of DOC and degree of stratification? Answering these questions should help to understand, which parameters of the lake's watershed and surrounding landscape determine the concentration, nature and seasonal dynamics of DOC in humic (organic-rich) and organic-poor lakes thus contributing to our knowledge of carbon cycling in small and deep lakes of a poorly studied subarctic region.

Material and methods

Site description

The two study lakes (Fig. 1 and Table 1) are located in the northern part of the boreal zone in European Russian, within boreal taiga, 80–100 km NNE of the town of Arkhangelsk and are not under any direct anthropogenic influence. According to local population, neither of

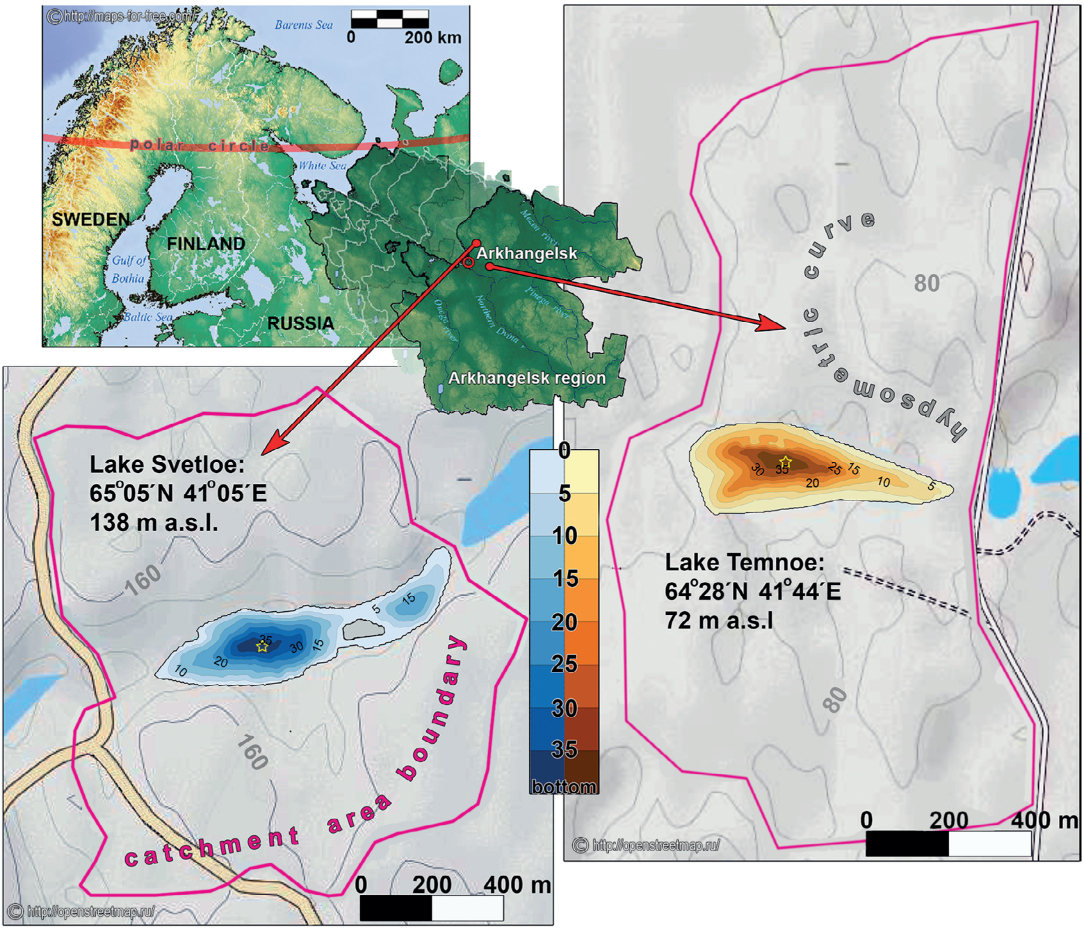

Fig. 1. Map of the study area (top left) and the bathymetric maps of Temnoe (humic, oranic-rich lake) and Svetloe (clear, organic-poor lake). The vertical color scale is for lake depth (m). The monitoring stations (stars) are above the deepest point of each lake.

the lakes was affected by human activity in the past 50 years. Thus, only long-range atmospheric transport of pollutants can affect the lakes' hydrochemistry. The proportion of bogs in the watershed was equal to 0.44% and 31.4% for organic-poor and organic-rich lakes, respectively, as quantified from the topographical maps (1:100 000). The water residence time in the lakes was estimated based on the watershed area, annual precipitation/evaporation of the region and the discharge through the lake outlets . The latter was measured in the field on the selected transect of the outlet channel from the water velocity and depth profile (Rozhdestvensky 2004, 2007). Note that possible underground input/output of the lakes could not be evaluated.

The information on lithology and soil coverage of the lake watersheds was obtained from the geological, landscape, Q deposits and soil maps of the Arkhangelsk Region (Morgunova *et al*. 1976). The watersheds of both lakes are on the glacial moraine over later Carboniferous (C_3) limestones in the northern taiga zone, which has an average annual temperature of 0 °C and average annual precipitation of 700 ± 50 mm. The soils of the watershed of organic-poor Svetloe are podzols and carbonate podzols on carbonate moraine deposits, whereas gley-peat-podzols over carbonate-free glacial till developed on the watershed of organic-rich Temnoe.

Similar to other boreal and subarctic lakes, the studied lakes exhibit two main periods of

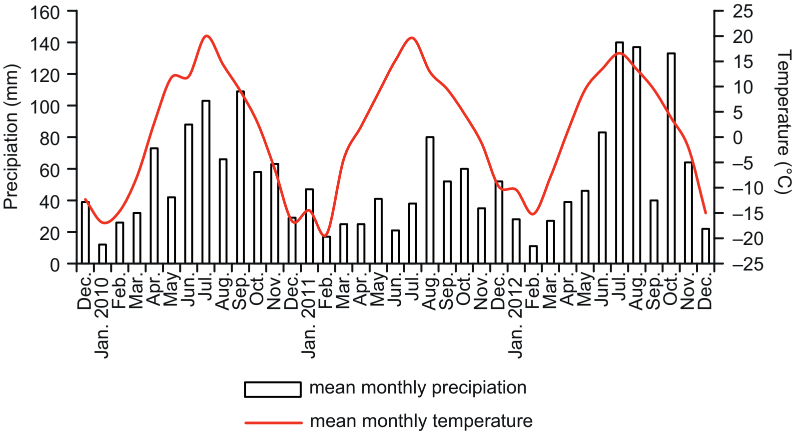

Fig. 2. Monthly mean temperature and precipitation in the vicinity of the lakes during the period of this study.

pronounced stratification (November to April and June to September) and two periods of lake overturn (October and May). The typical ice thickness at the end of winter is 50 ± 10 cm. Winter stratification maximum is in March, and the highest water temperature typically occurs in July. The length of the ice-cover period for the lakes of the region is between 195 and 201 days; the average freeze over date is 25–30 October and the average ice out date is 12–14 May (Morgunova *et al*. 1976). The study years were similar in the mean temperature but differed in the amount of precipitation, which was ca. 30% higher in 2011 compared with that in 2010 and 2012 (Fig. 2).

Table 1. Basic morphological characteristics of organic-poor (OP) and organic-rich (OR) lakes. CA:LA = the ratio of catchment area to lake area.

	Svetloe (OP)	Temnoe (OR)
Watershed area (km^2)	1.450	3.41
Lake surface (without islands) (km^2)	0.149	0.0939
Maximal depth (m)	39	37
CA:LA	9.7	36.3
Bog (%)	0.44	31.4
Secchi depth (m)	11 ± 1	3.5 ± 0.5
Water residence time (days)	321	394
Rock lithilogy	Carbonate moraine	Silicate loamy moraine
Soil	Podzol	Peat, podzol, gley
Average slope of the watershed slopes (m km^{-1})	33	3.06

Sampling

Both lakes were sampled ca. once a month or once per two months during a 2.5-year period (December 2009 to June 2012). The sampling was carried out in the entire water column from the surface to the bottom. The total number of sampling campaigns was 20 and 13 for Svetloe and Temnoe, respectively. The limited sampling and the existence of some gaps between October and May were due to limited access to these remote lakes. The water samples were taken at the deepest point of the lake (*see* Fig. 1) from a PVC boat between May and October, and through a hole in ice in winter (from November to April) using a pre-cleaned polycarbonate horizontal water sampler (Aquatic Research Co, ID, USA). The samples were immediately filtered through sterile, single use Minisart® filter units (Sartorius, acetate cellulose filter) with a pore sizes of 0.45 μm. Filtration was performed *in situ*. Dissolved O_2 level and temperature were measured *in situ* with the Oxi 197i oximeter (WTW, Germany) with a Cellox 325 submersible sensor (WTW, Germany; ± 0.5% and ± 0.2 °C uncertainty, respectively). The Winkler titration method was used for O_2 determination during two Temnoe samplings in 2010. The conductivity and pH were measured on site using a Hanna HI991300 conductivity meter and a WTW portable pH meter with combined electrode, respectively. Filtered water samples for nutrient analyses were frozen (–20 °C) within 1–3 h after collection and analysed within 1 week after sampling. Epilimnion was defined based on thermal and chemical stratification, namely oxygen and specific conductivity profiles: in Svetloe it was between 0 and 20 m, and in Temnoe between 0 and 25 m. Hypolimnion was below 20 and 25 m in Svetloe and Temnoe, respectively.

Sample analysis

Dissolved carbon

DOC and DIC concentrations were measured using methods routinely used in the Geosciences and Environment Toulouse (GET) laboratory to analyze boreal water samples (Pokrovsky *et al*. 2012a, Shirokova *et al*. 2013a). Pyrolyzed (2.5 h at 550 °C) glassware was used for sample collection and storage. DIC concentration was obtained from alkalinity following a standard HCl titration procedure using an automatic Titro-Line alpha TA10^{plus} titrator (Schott, Germany) with an uncertainty of ±2% and a detection limit of 5×10^{-5} M. In organic-rich waters of Temnoe, DIC was also measured by means of total infrared analysis with Shimadzu TOC-V$_{CSN}$ (acid addition without combustion), with a detection limit of 0.01 mM and uncertainty of 5%. The agreement between the two methods of DIC analysis was within 10%. The internationally certified water samples (ION-915, MISSISSIPPI-03, RAIN-97, Pérade-20) were used to check the validity and reproducibility of the DIC analysis. DOC was measured using Shimadzu TOC-V$_{CSN}$ with an uncertainty of 5% and a detection limit of 0.1 mg l^{-1}. Good agreement between our replicated measurements and the certified values was obtained (relative difference < 10%).

Size fractionation of organic carbon

A study of size fractionation using conventional filtration and *in situ* 1 kDa dialysis performed as a function of depth during the main hydrological seasons allowed for characterization of two compositional features, specifically colloidal and the truly dissolved, low molecular weight (LMW$_{< 1\ kDa}$), fraction of organic carbon. *In situ* 1 kDa (~1.4 nm) dialysis experiments were performed using 20–50 ml pre-cleaned Spectra Por 7® dialysis bags filled with MilliQ water and placed at various depths during different seasons as described in Pokrovsky *et al*. (2012a) and Shirokova *et al*. (2013b). The typical duration of the dialysis was 5 days, sufficient for establishing the equilibrium between the interior compartment and the lake water. The OC blank in the dialysis membrane was typically between 0.1 and 0.05 mg l^{-1}, as assessed by a systematic study of DOC blanks inside the dialysis membranes performed both in the field (5 samples) and in a class 10 000 clean room (10 samples).

Spectrophotometry of DOM and nutrient analysis

The values of the optical wavelength ratio a_{365}/a_{470}, a_{470}/a_{665} and specific UV-absorbency (SUVA$_{254}$, 1 mg^{-1} m^{-1}) can be used as proxies for aromatic C, molecular weight and source of DOM (Uyguner and Bekbolet, 2005, Weishaar *et al*. 2003, Ilina *et al*. 2014 and references therein). In particular, SUVA$_{254}$ describes the nature of DOM in terms of hydrophobicity and hydrophilicity; a value > 4 indicates mainly hydrophobic and especially aromatic material, whilst a value < 3 corresponds to the presence of mainly hydrophilic material (Edzwald and Tobiason, 1999, Minor and Stephens, 2008, Matilainen *et al*. 2011). The absorption spectra of the 0.45 μm filtrates in the range 200–700 nm with 1 nm resolution were measured in the laboratory using 1 cm quartz cuvette in a CARY-50 UV-VIS spectrophotometer (Bruker, UK). The UV-absorbency was measured at 245 nm and normalized to the DOC concentration in the sample.

The nutrient analyses were based on colorimetric assays (Koroleff 1983a, 1983b). Total dissolved organic nitrogen (DON) was evaluated from the difference between the total dissolved nitrogen (persulfate oxidation) and the total dissolved inorganic nitrogen (DIN, or the sum of NH_4^+, NO_2^- and NO_3^-). Uncertainties of DON and DIN analyses were between 10% and 20%, and detections limits were between 10 and 50 μg l^{-1}. Si concentration was measured by spectrophotometry with molybdate blue with an uncertainty of ±5% and a detection limit of 2 μg l^{-1}. Major anion concentrations (Cl and SO_4) were measured by ion chromatography (HPLC, Dionex ICS 2000) with an uncertainty of 2%. Ca, Mg, Na, K were determined with an uncertainty of 1%–2% using a Perkin-Elmer 5100 PC atomic absorption spectrometer (AAS). Chl *a* determination included filtration of 1–1.5 l of lake water onto a regenerated cellulose filter (0.45 μm) and extraction with acetone followed by spectrophotometric analysis at 664, 647, 750 nm wavelength. The calculation of the chlorphyll *a* (Chl *a*) concentration was performed using the Jeffrey-Humphrey equation adjusted for the presence of pheophytin.

Statistical analyses

Each sample set (component concentration as a function of depth) was checked for normality using Shapiro-Wilk's test (*W*-test, $p = 0.05$). This criterion is most powerful for small samples. Altogether we analyzed 278 data sets including the concentration of LMW fraction of OC and optical parameters of DOC. We found that > 40% of samples were not normally distributed. Therefore we used median value with 1st and 3rd quartiles as indicators of the dispersity. The non-parametric statistics was used to test the data applying quartile coefficient of dispersion as a non-parametric analogue of the coefficient of variation. To assess significance of difference between lakes or depths for a given component, we used a Mann-Whitney *U*-test. To plot the vertical distribution of optical parameters ($SUVA_{245}$, $a_{365/470}$, $a_{470/665}$) we used a method of locally weighed linear regression with a LOWESS algorithm. All calculations were performed in STATISTICA ver. 10 (StatSoft Inc., Tulsa) at $p = 0.05$.

Results

Thermal and chemical stratification

Both lakes exhibited clear seasonal thermal stratification, with rather small variation in temperatures in the bottom layers (below 18 and 12 m in Svetloe and Temnoe, respectively; *see* Table 2 and Fig. 3A). The inter-annual variation in temperature profile was also small in both lakes. The redox stratification was clearly pronounced, with the minimal O_2 concentration during all seasons below 20 and 24 m for Svetloe and Temnoe, respectively (Table 2 and Fig. 3B). Although both lakes turned anoxic below 20–25 m in June–July, the O_2 depth profile in Svetloe and Temnoe was never homogeneous, with the presence of anoxic waters even in October, when thermal stratification ins the smallest (temperature variation of 1.8 and 0.7 °C in Svetloe and Temnoe, respectively). This strongly suggest existance of the permanent anoxic zones below 20 and 25 m in Svetloe and Temnoe, respectively. pH of both lakes remained fairly constant throughout the depth profile, with ca. 1–1.5 units more acidic in humic (organic-rich) Temnoe than in clear-water (organic-poor) Svetloe (Table 2 and Fig. 3C). Specific conductivity (SC) differed the most between epilimnion and hypolimnion in Svetloe. Seasonal variation in SC was most pronounced in humic (organic-rich) Temnoe, especially in the hypolimnion. The median values of the quartile coefficient of dispersion for the 5-m layer of the epilimnion were 0.06 and 0.07 for Svetloe and Temnoe, respectively. Respective values for the hypolimnion were 0.06 and 0.13, (Fig. 3D).

The nutrient pattern in the lakes

Concentrations of DIN, phosphate and Si were 10, 100 and 6, respectively, times higher in the hypolimnion of organic-poor Svetloe than in the same layer of Temnoe (e.g., for DIN *U*-test: $U = 1894$, $p < 0.05$, $n_1 = 74$, $n_2 = 61$; Fig. 4A–C and Table 2), whereas in the epilimnion of the lakes, the concentrations of these nutrients were rather similar. Accumulation of DIN, phosphate and Si in the hypolimnion of organic-rich Temnoe relative to its epilimnion was much weaker than that in Svetloe, achieving only a factor of 4, 10 and 1.5, respectively. The chlorophyll *a* (Chl *a*) concentration in the photic zone of both lakes varied within a similar range (1–2 μg l^{-1} and < 1 μg l^{-1} during open water and ice cover periods, respec-

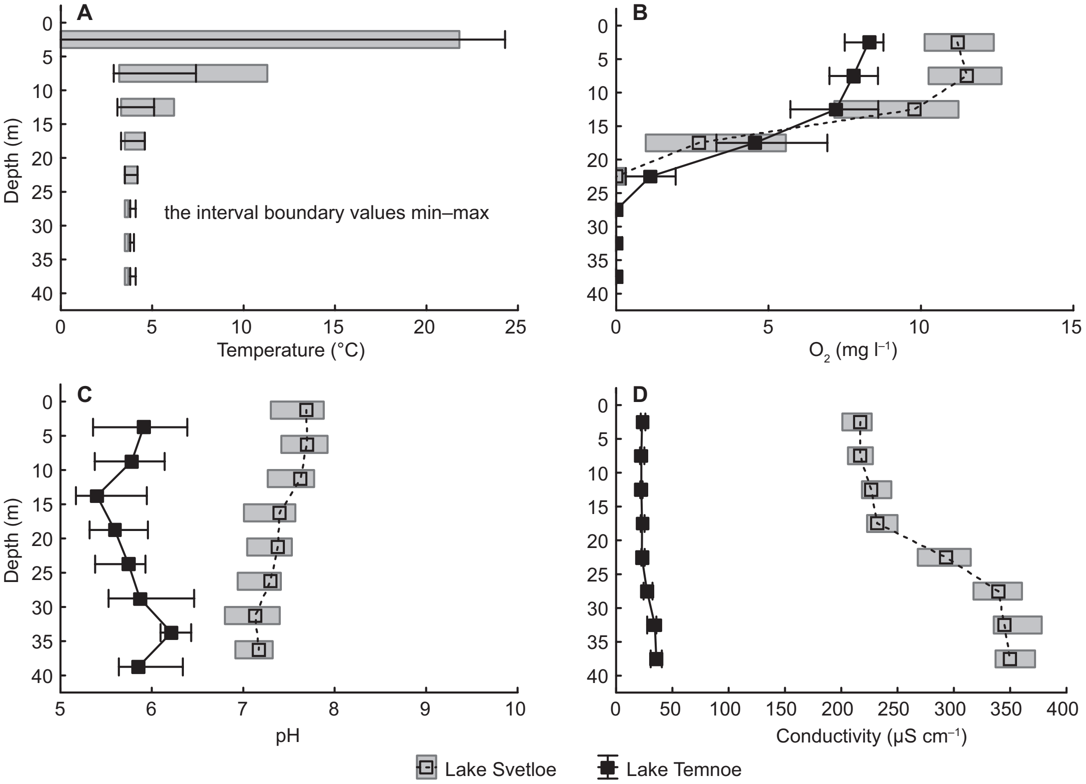

Fig. 3. (**A**) Temperature, (**B**) oxygen concentration, (**C**) pH and (**D**) specific conductivity in Svetloe (open squares, dashed connecting line) and Temnoe (solid squares, black line). The Whiskers are for interquartile range of Temnoe and the grey rectangles are for interquartile range of Svetloe.

tively, Fig. 4D). There was a clearly pronounced maximum of Chl *a* between 20 and 25 m depth in Svetloe, persistent during all seasons.

DOC, DIC and C_{org}/N_{org} patterns

The DOC concentration in Svetloe ranged between 1 and 3.5 mg l^{-1} and exhibited a convex-like profile at a minimum depth of ca. 15–20 m and an elevated concentration in the surface (1–3 m) and bottom (> 25 m) layers (Fig. 5A). During the study period, maximal DOC was found in March–April in the hypolimnion and the minimal concentration was encountered during the autumn overturn in October and, episodically, in the surface layer in July (not shown). DOC concentration in the surface layer during different months could differ by a factor of 1.5–4.0. DOC in deep and humic Temnoe, was stratified, with non-systematic variation between 15 and 24 mg l^{-1} in the epilimnion and an increase from ca. 22 to ca. 30 mg l^{-1} in the hypolimnion (Fig. 5A). This distribution was extremely stable in all seasons during 2.5 years of observation. The variation in [DOC] did not exceed 20% and 15% in the epilimnion and hypolimnion, respectively.

The DIC concentration varied significantly (for lake Svetloe *U*-test: $U = 9$, $p < 0.05$, $n_1 = 70$, $n_2 = 60$; for lake Temnoe *U*-test: $U = 16.5$, $p < 0.05$, $n_1 = 52$, $n_2 = 20$) with depth in both lakes, with a 1.5–2 time increase in the hypolimnion relative to the epilimnion (Fig. 5B). This accumulation of DIC was mostly pronounced in organic-poor Svetloe, anoxic below 20 m (Fig. 3B). Despite the relatively similar shape of the DIC–depth dependence for the two deep stratified lakes, DIC was 40 to 50 times greater in organic-poor Svetloe than in organic-rich Temnoe (Fig. 5B). DIC/DOC ratio (Fig. 5C) in the 15–20-m layer in Svetloe differed the most

Table 2. Median values with 1st and 3rd quartiles of hydro-chemical characteristics of lake water for 5-m layers. The unit of concentration is mg l^{-1} except for DIN (mg N l^{-1}), P-PO_4^{3-} (mg l^{-1}) and Chl *a* (µg l^{-1}); the unit for specific conductivity (SC) is µS cm^{-1}.

	Lake Svetloe								Lake Temnoe							
Layer (m)	0–5	5–10	10–15	15–20	20–25	25–30	30–35	35–bott.	0–5	5–10	10–15	15–20	20–25	25–30	30–35	35–bott.
O_2	11.2	11.5	9.8	2.7	0	0	0	0	8.3	7.8	7.2	4.6	1.1	0	0	0
25%	10.1	10.3	7.2	1.0	0	0	0	0	7.5	7.0	5.7	3.3	0.3	0	0	0
75%	12.4	12.7	11.2	5.6	0.3	0	0	0	8.8	8.6	8.6	6.9	2.0	0	0	0
pH	7.69	7.70	7.62	7.40	7.38	7.30	7.13	7.17	5.91	5.78	5.40	5.59	5.75	5.87	6.22	5.85
25%	7.30	7.42	7.27	7.00	7.04	6.94	6.80	6.92	5.36	5.38	5.17	5.32	5.38	5.53	6.10	5.64
75%	7.88	7.92	7.78	7.57	7.53	7.41	7.40	7.32	6.39	6.14	5.95	5.96	5.93	6.46	6.43	6.34
SC	217	217	227	232	293	340	345	350	23.1	22.5	22.4	23.1	22.9	27.5	34.5	35.8
25%	201	206	219	223	268	318	336	337	22.0	21.3	21.5	22.0	22.5	24.5	27.7	30.8
75%	227	228	245	250	315	361	378	372	26.0	25.2	23.6	25.4	25.2	32.3	35.9	40.7
Ca	26.2	27.4	29.4	30.5	44.5	49.0	47.8	50.6	1.99	2.00	2.04	2.17	2.23	2.49	2.67	2.69
25%	25.3	26.4	28.8	28.7	35.0	42.6	32.1	49.3	1.95	1.94	1.98	2.03	2.09	2.47	2.61	2.67
75%	29.6	29.8	30.3	32.6	46.7	50.9	53.3	51.8	2.13	2.05	2.12	2.19	2.33	2.58	2.77	2.70
Mg	13.3	13.7	13.9	14.5	14.5	14.4	14.4	14.5	1.06	1.02	1.05	1.07	1.13	1.19	1.22	1.24
25%	12.1	12.8	13.4	13.7	14.1	14.1	13.5	13.7	0.99	0.99	1.03	1.01	1.10	1.15	1.20	1.21
75%	13.8	14.1	14.3	15.1	15.0	14.6	15.3	14.8	1.13	1.07	1.09	1.11	1.17	1.24	1.26	1.28
Na	1.32	1.36	1.43	1.42	1.38	1.41	1.32	1.38	1.06	1.01	1.04	1.05	1.10	1.11	1.16	1.19
25%	1.27	1.31	1.37	1.36	1.35	1.37	1.29	1.34	1.02	1.01	1.02	1.02	1.04	1.08	1.14	1.16
75%	1.42	1.41	1.49	1.46	1.43	1.43	1.44	1.40	1.08	1.05	1.05	1.09	1.13	1.13	1.18	1.19
Cl^-	1.38	1.37	1.38	1.41	1.43	1.46	1.52	1.47	0.67	0.66	0.69	0.72	0.75	0.76	0.77	0.77
25%	1.33	1.35	1.37	1.40	1.41	1.44	1.46	1.45	0.65	0.65	0.68	0.71	0.73	0.75	0.75	0.76
75%	1.43	1.38	1.40	1.45	1.48	1.53	1.65	1.51	0.73	0.70	0.71	0.74	0.76	0.78	0.77	0.80
SO_4^{2-}	4.40	4.51	4.63	4.71	0.88	0.08	0.08	0.05	1.75	1.64	1.66	1.68	1.69	1.56	1.16	1.16
25%	4.26	4.42	4.56	4.60	0.54	0.06	0.05	0.05	1.64	1.46	1.43	1.48	1.61	1.30	1.00	0.90
75%	4.65	4.63	4.71	4.89	1.59	0.12	0.10	0.07	1.81	1.77	1.86	1.76	1.77	1.61	1.31	1.37
DIN	0.10	0.07	0.085	0.09	0.89	2.25	2.15	2.34	0.10	0.10	0.11	0.13	0.14	0.29	0.35	0.42
25%	0.08	0.06	0.075	0.08	0.17	1.97	1.49	1.70	0.05	0.07	0.07	0.09	0.11	0.19	0.32	0.37
75%	0.18	0.11	0.095	0.12	1.40	2.33	2.55	2.66	0.14	0.15	0.12	0.15	0.16	0.31	0.39	0.48
P-PO_4^{3-}	0.005	0.006	0.008	0.009	0.698	1.58	2.17	1.50	0.008	0.011	0.015	0.019	0.023	0.148	0.191	0.238
25%	0.002	0.003	0.006	0.006	0.098	1.31	1.36	1.06	0.005	0.007	0.009	0.015	0.018	0.088	0.135	0.221
75%	0.007	0.009	0.015	0.016	1.007	2.41	2.86	2.60	0.013	0.014	0.027	0.027	0.034	0.183	0.227	0.310
Si	2.28	2.42	2.85	4.22	8.16	12.6	12.7	12.9	1.92	2.01	2.08	2.30	2.58	3.08	3.25	3.46
25%	1.99	2.34	2.74	3.83	6.50	11.0	11.5	11.7	1.69	1.94	2.03	2.19	2.37	2.97	3.05	3.32
75%	2.47	2.59	2.91	4.53	10.03	13.8	13.6	14.9	2.04	2.06	2.16	2.35	2.65	3.15	3.30	3.54

DOC	1.8	1.7	1.4	1.2	2.2	1.8	2.7	2.3	16.9	17.8	17.9	18.8	18.8	24.9	26.0	28.7
25%	1.5	1.4	1.3	1.0	1.7	1.6	2.1	1.8	16.1	16.9	17.0	17.6	18.6	23.0	24.8	26.4
75%	2.3	1.9	1.9	1.5	2.7	2.7	3.1	2.6	19.0	18.2	18.8	20.2	19.7	25.4	27.6	29.2
DIC	29.3	29.5	31.3	32.0	42.7	47.4	46.7	49.1	0.67	0.60	0.67	0.75	0.80	1.05	1.25	1.37
25%	27.7	28.0	30.0	30.3	37.3	45.5	45.5	46.5	0.59	0.56	0.56	0.67	0.71	0.96	1.20	1.19
75%	30.8	30.7	31.8	32.6	45.4	48.5	47.5	51.0	0.74	0.66	0.71	0.82	0.92	1.18	1.48	1.52
DIC/DOC	15.7	17.5	22.2	29.5	21.4	28.2	19.3	21.7	0.039	0.035	0.037	0.040	0.044	0.044	0.049	0.048
25%	13.2	14.3	15.6	22.2	17.7	21.1	15.6	19.9	0.033	0.030	0.032	0.035	0.038	0.043	0.045	0.042
75%	18.9	23.3	26.9	32.7	25.6	32.3	21.9	28.8	0.043	0.036	0.040	0.043	0.046	0.046	0.051	0.053
Chl-a	0.57	0.58	0.54	0.78	11.0	3.81	3.93	3.32	0.69	0.11	0.01	0.01	0.15	0.31	0.62	0.65
25%	0.26	0.19	0.20	0.12	3.5	1.95	3.08	2.81	0.01	0.01	0.01	0.01	0.01	0.27	0.01	0.55
75%	0.89	0.98	1.25	2.55	13.6	5.28	4.78	3.70	1.39	0.24	0.20	0.15	0.48	0.69	1.22	0.69
C_{org}/N_{org}	17.8	18.0	20.7	17.4	2.8	2.0	2.1	1.6	66.5	68.8	62.8	69.7	65.5	76.9	65.6	90.9
25%	10.4	11.6	14.5	9.6	2.3	1.5	1.4	1.2	52.3	51.8	50.9	59.2	61.1	71.1	63.5	81.7
75%	27.4	20.4	24.9	20.8	6.7	3.4	3.8	1.9	72.5	73.9	99.9	81.7	68.4	86.7	82.1	96.0

from the ratios in 15–20 m and 20–25 m layers (*U*-test: $U = 79$, $p < 0.05$, $n_1 = 15$, $n_2 = 15$ for 10–15 m *vs*. 15–20 m; and $U = 99$, $p < 0.05$, $n_1 = 19$, $n_2 = 17$, for 15–20 m *vs*. 20–25 m). DIC/DOC rations in other layers of in both lakes did not differ. DIC/DOC rose in 0–10 m layer from summer (June to September) to autumn (October) in both lakes (*U*-test: $U = 0$, $p < 0.05$, $n_1 = 10$, $n_2 = 2$, for Svetloe; and $U = 6$, $p < 0.05$, $n_1 = 13$, $n_2 = 4$, for Temnoe).

In organic-poor Svetloe, the molar ratio C_{org}/N_{org} decreased by an order of magnitude from the epilimnion to the hypolimnion (Fig. 5D). In contrast, in Temnoe, only a slight increase in C_{org}/N_{org} (ca. by a factor of 1.25) from the epilimnion to the hypolimnion was observed between October and May.

In the epilimnion of both lakes, C_{org}/N_{org} was higher by a factor of 3 in July and August than during other months of observation. Overall, the highest C_{org}/N_{org} values were found in samples with the highest DOC (Fig. 5A and D).

Size fractionation and optical properties of DOM

The $LMW_{< 1\ kDa}$ fraction constituted 40%–95% of $[DOC]_{< 0.45\ \mu m}$ in Svetloe. During all sampling periods, this fraction did not increase or decrease with the depth (Fig. 6A). In Temnoe, the $LMW_{< 1\ kDa}$ OC concentration was stable throughout the depth profile, with minimal variation during the different seasons. With respect to Svetloe, the proportion of the $LMW_{< 1\ kDa}$ fraction remained constant at ca. 20% ± 3% in the epilimnion, with somewhat greater variation in the hypolimnion (20% ± 5%). Overall, the relative contribution of the LMW fraction to the total DOC was smaller by a factor of 2–3 in humic Temnoe than in organic-poor Svetloe. Therefore, the proportion of colloidal (0.45 μm–1 kDa) organic fraction in Temnoe was significantly higher than in Svetloe.

$SUVA_{254}$ could be assessed only in Temnoe where it decreased 5-fold within the first 10 m and then increased towards the bottom horizons (Fig. 6B). The optical wavelength ratios a_{365}/a_{470} and a_{470}/a_{665} measured in June and July varied in a narrow range between 1.1 and 1.3 in

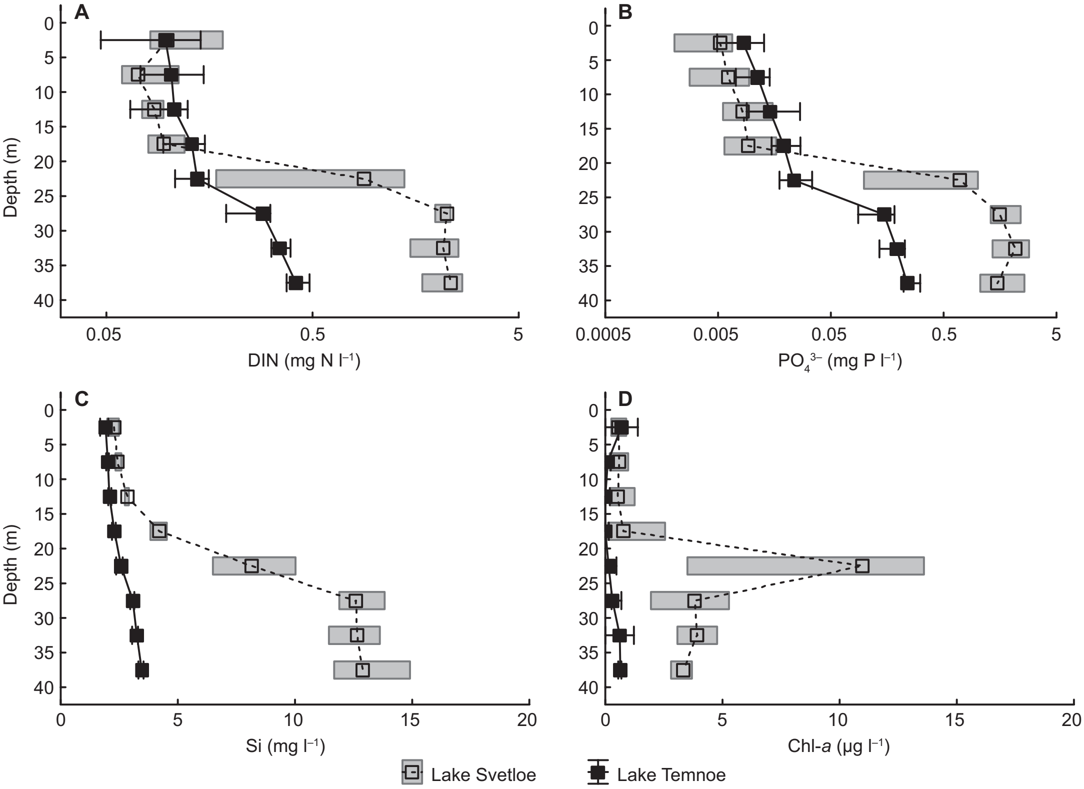

Fig. 4. (**A**) DIN, (**B**) phosphate, (**C**) Si and (**D**) Chl-*a* in Svetloe (median is shown by empty square and interquartile range is shown by grey rectangle; the dashed line is for eye guide) and Temnoe (median is shown by black square and interquartile range is shown by whiskers; the solid line is for eye guide). Note log scale for DIN and PO_4^{3-}.

organic-poor Svetloe with no clear dependence on depth. In humic Temnoe, these ratios ranged between 2.0 and 4.5 in July, decreasing by a factor of 2 to 3 from the surface horizons (0.5 m) to the hypolimnion (Fig. 6C and D).

Discussion

An important factor controlling the difference in DOC biogeochemistry between the two lakes is the proportion of bogs within the watershed, which is markedly higher for humic Temnoe than for clear-water Svetloe (31% and 0.44%, respectively). Indeed, wetlands are known to exert direct and positive effect on the DOC level in lakes and rivers (Kortelainen 1993, Gergel *et al*. 1999, Agren *et al*. 2007, Zakharova *et al*. 2007, Laudon *et al*. 2011, Umbanhowar *et al*. 2014, Rantala *et al*. 2016).

In carbonate-rich C soil horizons and rocks of organic-poor Svetloe watershed (Table 1), humus and allochthonous DOM could be retained by limestone substrate in the form of Ca humates. Such carbonate lithology-specific mechanisms are likely to operate throughout the entire boreal zone of northern Eurasia (Pokrovsky *et al*. 2012b). The processes occurring in the watershed of Svetloe contrast with those in aluminosilicate moraine and peat/gley soils of the Temnoe watershed that mobilized Fe- and Al-rich organic colloids from the soil to the surface streams and, finally, to the organic-rich lake. Thus, elevated DOC/DIC during the spring flood in May, when the mineral soil is still frozen, may be linked to considerable lateral fluxes of plant leachates mostly enriched in DOC and poor in DIC. This ratio was higher by a factor of ca. 150 in organic-rich Temnoe than in organic-poor Svetloe, primarily due to limestone substrate of the latter.

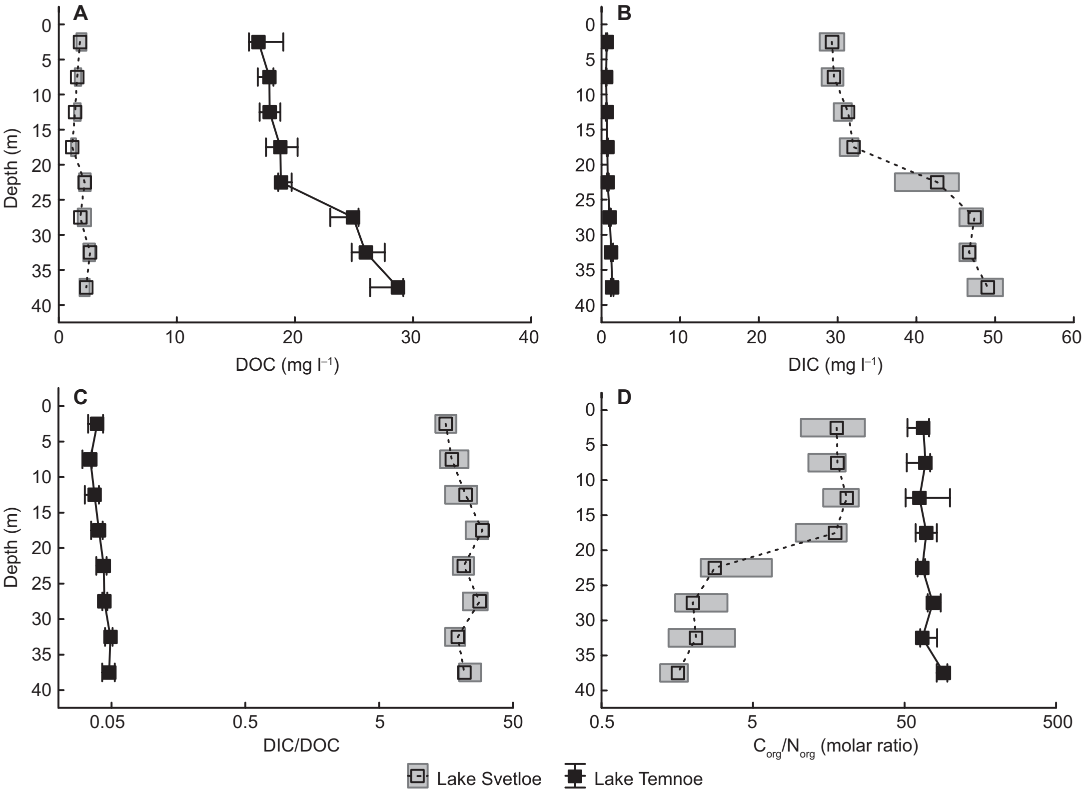

Fig. 5. Median values of (**A**) DOC, (**B**) DIC, (**C**) DIC/DOC ratio, and (**D**) C_{org}/N_{org} ratio in Svetloe (grey shaded rectangles) and Temnoe (black squares). Note log scale for C and D plots. The length of the rectangle and the Whisker represent interquartile range.

The water of organic-poor Svetloe was characterized by a quite low C_{org}/N_{org} value (between 10 and 45), typical for aquatic phytoplankton and macrophytes, as well as their humification products (ca. 20; Wolfe *et al*. 2002). During the stratified periods of the year, there was a decrease in C_{org}/N_{org} in the hypolimnion of the organic-poor, stratified Svetloe relative to the epilimnion. A likely cause was mineralization of the sediment particulate organic matter (POM) and liberation of N_{org} in the bottom part of the water column in clear-water Svetloe. This was accompanied by DIC accumulation in the hypolimnion, which is mostly linked to anaerobic mineralization of OC coupled with sulfate reduction, common in boreal lakes of the region (Kokryatskaya *et al*. 2012, Savvichev *et al*. 2017).

In humic Temnoe, small increase in C_{org}/N_{org} with depth could be caused by coagulation of DOC in the water column in light condition (von Wachenfeldt *et al*. 2008, von Wachenfeldt and Tranvik, 2008) or bacterial activity (von Wachenfeldt *et al*. 2009). The coagulation products may be subjected to dissolution in the deeper horizons as it is known to happen in humic lakes (Kortelainen *et al*. 2006). The highest C_{org}/N_{org} values in the samples with highest DOC suggest the importance of allochthonous sources such as soil and bog water and forest leachate in the organic feeding of the lakes, as it seen in Temnoe, exhibiting 31% of bog coverage and C_{org}/N_{org} values around 100 ± 50. Such high values in the humic lake may indicate leaching of chemical compounds from coniferous trees (Onstad *et al*. 2000, Twichell *et al*. 2002, Tremblay and Benner 2006). This range is also between the values reported for the soil solution of boreal taiga, ca. 100 (Ilina *et al*. 2014); 40 to 80 (Dymov *et al*. 2013, Moiseev and Alyabina, 2007) and peat, ca. 47 (Zaccone *et al*. 2014).

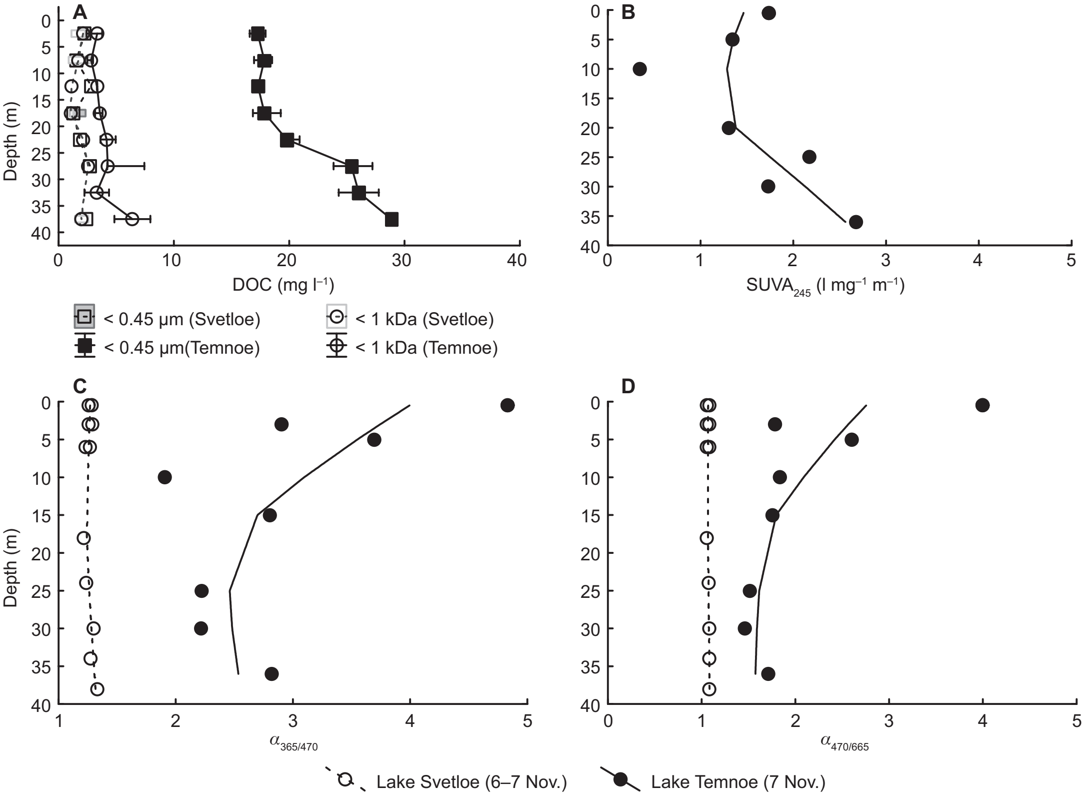

Fig. 6. (**A**) Filtered (< 0.45 μm) and dialyzed (< 1 kDa) OC concentration in Svetloe (open squares, dashed line) and Temnoe (solid squares, solid line); all seasons were combined together since the effect of individual seasons on $\mathrm{DOC}_{< 0.45\ \mu m}$ and $\mathrm{DOC}_{< 1\ \mathrm{kDa}}$ was statistically indistinguishable. (**B**) SUVA_{254} (l mg^{-1} m^{-1}, C) in < 0.45 μm fraction of Temnoe as a function of depth measured in July 2011; smooth line represents a LOWESS trend of SUVA as a function of depth. The ratios of (**C**) a_{365}/a_{470}, (**D**) and a_{470}/a_{665} in Svetloe (circles, dashed line) and Temnoe (black squares, solid line) measured in June–July 2011.

Finally, diffusive input of N from the sediments may contribute to a much lower C_{org}/N_{org} ratio in Svetloe than in Temnoe. Indeed, the N_{org} concentration in the upper 0–10 cm of the bottom water was 1–1.5 mg l^{-1} in Svetloe and 0.2–0.5 mg l^{-1} in Temnoe (Ershova *et al*. 2012). Permanent anoxic conditions below 20 m depth of organic-poor Svetloe may create favorable environments for elevated N_{org} in the deep layers. At the same time, strong depletion of nitrogen in the surface layers of both lakes suggests their significant N limitation, similar to that in other boreal lakes (i.e., Kortelainen *et al*. 2013).

Significant P depletion in surface layers suggests that this is the most important limiting nutrient in boreal lakes (*see* e.g., Arvola *et al*. 1996, Vidal *et al*. 2011). Si was limited the most in organic-poor Svetloe, presumably due to intensive uptake by diatoms (confirmed by our unpublished results from the sedimentary-trap study). Indeed, quite low concentration of Chl *a* in the studied lakes as compared with that in other boreal environments (Einola *et al*. 2011, Peltomaa and Ojala, 2012), implies strong nutrient limitation, also seen in nutrient distribution pattern, allowing to suggest a meromictic character of Svetloe. However, the lack of temperature profiles with daily to weekly resolution for the periods of lake overturn in May prevents distinguishing between pure meromictic and dimictic nature of the studied lakes.

The optical properties of DOM were consistent with the organic-poor and organic-rich lake division proposed based on the DOC and nutrient concentration analyses. The a_{470}/a_{655} ratio is known to correlate with the degree of condensation of DOM aromatic groups and with the degree of humification (Chin *et al*. 1994, Stevenson 1994, Hur *et al*. 2006) whereas $SUVA_{254}$ is used as a proxy for aromatic C and source of DOM (Chen *et al*. 1977, Uyguner and Bekbolet 2005). The lack of seasonal and spatial variation in UV/visible absorbing functional groups (a_{365}/a_{470}) and the degree of humification (a_{470}/a_{655}) of DOC-poor Svetloe suggests: (i) the absence of detectable allochthonous input of DOC in this oligotrophic lake, and (ii) high homogeneity of autochthonous production of DOM over the water column. In contrast, the elevated values of a_{470}/a_{655} and $SUVA_{254}$ in the epilimnion of Temnoe may be linked to the presence of a high concentration of allochthonous fulvic acids from adjacent bogs and peat soils. Note that the proportion of humified material in DOC-rich deep Temnoe decreases almost two fold between 0 ad 10 m depth which also coincides with the minimum of $SUVA_{254}$ observed at 10 m depth in Temnoe. Several studies have emphasised that good agreement may exist between the ability for OM removal by coagulation and a high SUVA value (Archer and Singer 2006, Bose and Reckhow 2007). Therefore, the decrease of $SUVA_{254}$ from 0 to 10 m in Temnoe may reflect the ongoing coagulation of DOM which was freshly delivered from surrounding bogs. The reason for the increase in $SUVA_{254}$ and humification (a_{470}/a_{655}) in the deepest part of the hypolimnion of Temnoe remains uncertain. It can be hypothesized that, similar to DOC, this increase is linked to diffusion from organic-rich sediments and/or to dissolution of coagulated organic particles during their sedimentation to the lake bottom, consistent with the pattern of the C_{org}/N_{org} ratio.

The high proportion of the $LMW_{< 1 \text{ kDa}}$ OC fraction in the organic-poor Svetloe (40%–90%) contrasts with the size fractionation of DOC in the humic lake, which showed only 20%–30% of the $LMW_{< 1 \text{ kDa}}$ fraction and, consequently, 70%–80% of the colloidal (1 kDa–0.45 μm) OC. Such a high proportion of colloids is typical for humic waters in NW Russia (Pokrovsky *et al*. 2012b). It reflects the contribution of high molecular weight (HMW) organic matter from bog water and plant leachate to the streams feeding the lakes (Ilina *et al*. 2014). Note that the fraction of $LMW_{< 1 \text{ kDa}}$ in humic Temnoe equaling 20% to 30% is consistent with former observations that 20%–24% of riverine DOM pass through ultrafilters with a nominal pore size cutoff of 1 kDa (Amon and Benner 1996, Meyer *et al*. 1987, Hedges *et al*. 1994). In contrast, the LMW fraction of DOC in clear-water Svetloe was extremely high. A number of mechanisms may be responsible for the $LMW_{< 1 \text{ kDa}}$ fraction enrichment in organic-poor Svetloe relative to humic Temnoe. First, microbial degradation of large allochthonous DOM in boreal lakes of the Arkhangelsk Region may produce small organic ligands (Shirokova *et al*. 2013b) and microbial degradation of terrestrial DOM in streams is known to modify the DOM pool towards lower molecular weight molecules (Kim *et al*. 2006). Second, photo-degradation of DOC in the water column may be more important in low-DOC lake due to the deep photic layer (Granéli *et al*. 1996). Photo-oxidation of refractory DOC (HMW colloids) to a LMW fraction is documented for various boreal lakes (Lindell *et al*. 1995, 1996, Roiha *et al*. 2012). Several studies have demonstrated that HMW aromatic DOM is readily degraded by bacteria and sunlight in freshwaters (Stubbins *et al*. 2010, Sleighter *et al*. 2014, Mesfioui *et al*. 2015). Recent reactivity continuum modeling revealed that the most labile DOC fraction was greater by a factor 14 in clear-water lakes than in brown-water lakes (Koehler *et al*. 2012). The third mechanism for enhanced $LMW_{< 1 \text{ kDa}}$ generation in Svetloe is the activity of phytoplankton, as confirmed by an order of magnitude higher Chl-*a* concentration in the clear-water Svetloe as compared with that in humic Temnoe. The bloom produces autochthonous LMW exo-metabolites (Sondergaard and Schierup, 1982), and the greatest production of a LMW fraction was reported in July–August in other lakes of this boreal region (Pokrovsky and Shirokova 2013, Shirokova *et al*. 2013b).

Concluding remarks

The results demonstrate significant and systematic differenecs in DOC concentration, C_{org}/N_{org} and light absorbance ratios, as well as molecular size characteristics such as the proportion of

$LMW_{< 1\ kDa}$ fraction of DOM between humic Temnoe and clear-water Svetloe, which are representative of boreal subarctic watersheds. These crucial differences in the basic DOM parameters reflect the specificity of the lake watershed lithological and landscape setting as well as the intensity of intra-lake autochthonous processes. The difference in DOC concentration and size fractionation between the two lakes reflects the complex interplay between the two main sources of DOC: allochthonous soil humic and fulvic acids from the plant litter and bog water and autochthonous exometabolites of phytoplankton and macrophytes, and two main sinks: biodegradation and photodegradation, whose extent depends on DOM residence time in a given aquatic reservoir (del Giorgio and Peters 1994, Cory *et al*. 2007, Jansson *et al*. 2007, Ask *et al*. 2012, Köhler *et al*. 2013). In this regard, humic Temnoe is expected to contribute more significantly to the loss of terrestrial organic carbon from the watershed to the atmosphere. The highest potential emission of CO_2 from the humic lakes is due to its net heterotrophy, since its DOC concentration significantly exceeded the threshold value of 8 mg l^{-1} (Sobek *et al*. 2006). The knowledge of soil type, watershed geomorphology, lithology and underground water feeding, as well as the bog coverage, combined with the information on primary productivity and photodegradation may help predicting the concentration and chemical nature of the DOM in a given lake. The present study confirms this conceptual scheme for the full depth of the water column in deep and small, previously understudied, seasonally stratified lakes. In line with the majority of studies that dealt only with the surface layer of boreal lakes and incoming springs (Weyhenmeyer and Karlsson, 2009, Larsen *et al*. 2011, Hanson *et al*. 2003, Algesten *et al*. 2003, Sobek *et al*. 2003, Jarvinen *et al*. 2002, Stets *et al*. 2010, Erlandsson *et al*. 2012, Medeiros *et al*. 2012, Forsström *et al*. 2013, Hiriart-Baer *et al*. 2013, Kellerman *et al*. 2015, Shirokova *et al*. 2016), we speculate that the chemical and biological processes affect the vertical distribution of major available DOC parameters and that there exists a distinct difference between the epilimnion and hypolimnion. The DOC in the humic Temnoe, originated from surrounding bogs and peat soils is subjected to (i) stronger transformations in the water column, and (ii) more pronounced accumulation in the anoxic hypolimnion. Further studies with sedimentary traps are necessary to reveal the nature of precipitating organic material in the water column of these lakes. The response of boreal surface water C stock to the increasing allochthonous C loading remains difficult to quantify, because the estimation of the total number and volumes of humic *vs*. clear-water lakes, and of their degree of stratification in the boreal and subarctic zones is currently lacking.

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