Holocene hydrological variability of Lake Ladoga, northwest Russia, as inferred from diatom oxygen isotopes

SVETLANA S. KOSTROVA (iD), HANNO MEYER (iD), HANNAH L. BAILEY, ANNA V. LUDIKOVA (iD), RAPHAEL GROMIG (iD), GERHARD KUHN (iD), YURI A. SHIBAEV, ANNA V. KOZACHEK, ALEXEY A. EKAYKIN AND BERNHARD CHAPLIGIN

BOREAS

This article presents a new comprehensive assessment of the Holocene hydrological variability of Lake Ladoga, northwest Russia. The reconstruction is based on oxygen isotopes of lacustrine diatom silica ($\delta^{18}O_{diatom}$) preserved in sediment core Co 1309, and is complemented by a diatom assemblage analysis and a survey of modern isotope hydrology. The data indicate that Lake Ladoga has existed as a freshwater reservoir since at least 10.8 cal. ka BP. The $\delta^{18}O_{diatom}$ values range from +29.8 to +35.0‰, and relatively higher $\delta^{18}O_{diatom}$ values around +34.7‰ between *c.* 7.1 and 5.7 cal. ka BP are considered to reflect the Holocene Thermal Maximum. A continuous depletion in $\delta^{18}O_{diatom}$ since *c.* 6.1 cal. ka BP accelerates after *c.* 4 cal. ka BP, indicating Middle to Late Holocene cooling that culminates during the interval 0.8–0.2 cal. ka BP, corresponding to the Little Ice Age. Lake-level rises result in lower $\delta^{18}O_{diatom}$ values, whereas lower lake levels cause higher $\delta^{18}O_{diatom}$ values. The diatom isotope record gives an indication for a rather early opening of the Neva River outflow at *c.* 4.4–4.0 cal. ka BP. Generally, overall high $\delta^{18}O_{diatom}$ values around +33.5‰ characterize a persistent evaporative lake system throughout the Holocene. As the Lake Ladoga $\delta^{18}O_{diatom}$ record is roughly in line with the 60°N summer insolation, a linkage to broader-scale climate change is likely.

Svetlana S. Kostrova (Svetlana.Kostrova@awi.de), Alfred Wegener Institute Helmholtz Centre for Polar and Marine Research, Research Unit Potsdam, Telegrafenberg A45, Potsdam 14473, Germany, and Vinogradov Institute of Geochemistry, Siberian Branch of Russian Academy of Sciences, Favorsky str. 1a, Irkutsk 664033, Russia; Hanno Meyer and Bernhard Chapligin, Alfred Wegener Institute Helmholtz Centre for Polar and Marine Research, Research Unit Potsdam, Telegrafenberg A45, 14473 Potsdam, Germany; Hannah L. Bailey, Department of Ecology and Genetics, University of Oulu, Oulu 90014, Finland, and Alfred Wegener Institute Helmholtz Centre for Polar and Marine Research, Research Unit Potsdam, Telegrafenberg A45, 14473 Potsdam, Germany; Anna V. Ludikova, Institute of Limnology, Russian Academy of Sciences, Sevastyanova str. 9, St. Petersburg 196105, Russia; Raphael Gromig, Institute of Geology and Mineralogy, University of Cologne, Zuelpicher Str. 49a, Cologne 50674, Germany; Gerhard Kuhn, Alfred Wegener Institute Helmholtz Centre for Polar and Marine Research, Am Alten Hafen 26, Bremerhaven 27568, Germany; Yuri A. Shibaev and Anna V. Kozachek, Arctic and Antarctic Research Institute, Bering str. 38, St. Petersburg 199397, Russia; Alexey A. Ekaykin, Arctic and Antarctic Research Institute, Bering str. 38, St. Petersburg 199397, Russia, and Institute of Earth Sciences, St. Petersburg State University, Universitetskaya nab., 7–9, St. Petersburg 199034, Russia; received 30th October 2018, accepted 17th January 2019.

Lake Ladoga in northwest Russia is the largest freshwater body in Europe (Fig. 1). Long-term studies of the lake and its catchment are mostly based on lithology (Subetto *et al.* 1998; Aleksandrovskii *et al.* 2009), pollen (Arslanov *et al.* 2001; Wohlfarth *et al.* 2007), diatoms (Davydova *et al.* 1996; Saarnisto & Grönlund 1996; Dolukhanov *et al.* 2009), organic carbon and mineral magnetic parameters (Subetto *et al.* 2002) of lake and mire deposits (Subetto 2009; Shelekhova & Lavrova 2011; Subetto *et al.* 2017). These studies have revealed that the Holocene climate and environment around the lake and its ecosystem underwent significant changes, mainly caused by long- and short-term variations in air temperature and atmospheric precipitation patterns, as well as by glacio-isostatic movements of the Earth's crust.

Additionally, these studies have disclosed several stages of the lake's development from the Ladoga being a gulf of the palaeo-Baltic basin to an independent lacustrine reservoir (e.g. Subetto 2009). The formation of the current lake water system began after deglaciation around 14 cal. ka BP (calibrated calendar ages are used consistently in this study; Björck 2008; Gorlach *et al.* 2017; Gromig *et al.* in press). At about 10.7–10.3 cal. ka BP (Björck 2008), the Ancylus transgression led to the rise of the Lake Ladoga water level, the flooding of the northern part of the Karelian Isthmus and Lake Ladoga turned into an eastern deep-water bay of the former Lake Ancylus. The regression of the Baltic Sea at *c.* 10.2 cal. ka BP (e.g. Björck 2008) was accompanied by a decrease in the Lake Ladoga water level and from *c.* 10–9 cal. ka BP (Björck 2008; Saarnisto 2012) Lake Ladoga began to exist as independent freshwater reservoir draining to the northwest via the Hejnjoki threshold into the Baltic Sea through the palaeo-Vuoksi River (Timofeev *et al.* 2005; Dolukhanov *et al.* 2009; Saarnisto 2012). As a result of a continuous glacio-isostatic uplift and a change in the flow direction (change of the outflow of the Lake Saimaa system in Finland to the southeast), at *c.* 5.7 cal. ka BP water started entering Lake Ladoga from the northwest via River Vuoksi (Saarnisto & Grönlund 1996; Dolukhanov *et al.* 2009; Subetto 2009; Saarnisto 2012). The water level in Lake Ladoga further increased and reached the
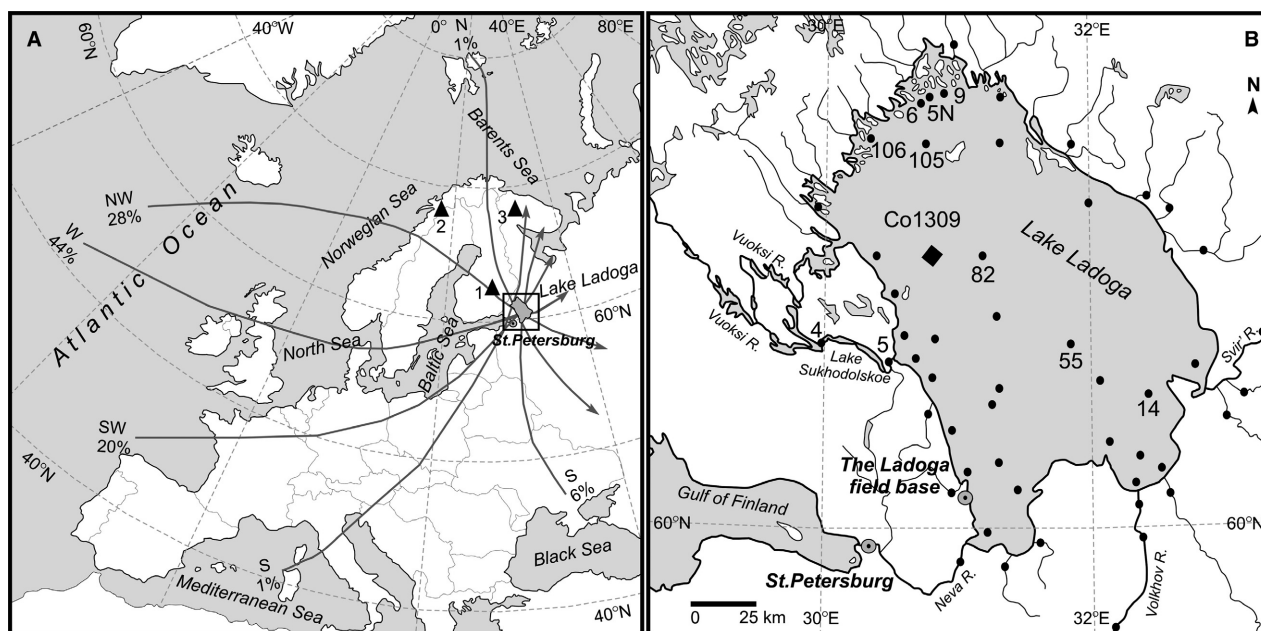
Fig. 1. A. Schematic maps showing the Lake Ladoga region with typical trajectories for cyclones modified from Shver *et al.* (1982) and Mätlik & Post (2008). Locations of Lake Saarikko (southeast Finland), Lake 850 (Swedish Lapland), Lake Chuna (Kola Peninsula, northwest Russia) mentioned in the text are given (black triangles 1, 2 and 3, respectively). B. Location of Lake Ladoga (59°54′–61°47′N; 29°47′–32°58′E, 5 m a.s.l.) with the position of the Co 1309 sediment core (black diamond) and the water sampling sites (black circles, numbers indicate positions mentioned in the text); as well as location of the Losevskaya channel and modern River Burnaya (numbers 4 and 5, respectively).

maximum level at *c.* 3.35 cal. ka BP (Saarnisto 2012; Kulkova *et al.* 2014; Virtasalo *et al.* 2014), resulting in the formation of the Neva River outlet in the southern part of the lake (Saarnisto & Grönlund 1996; Subetto *et al.* 1998, 2002; Dolukhanov *et al.* 2009). Despite the fundamental synthesis, the question of the hydrological development of Lake Ladoga and its basin remains under discussion until now, especially regarding Holocene lake-level fluctuations and the formation of major outlet rivers (e.g. Subetto 2009).

To address this knowledge gap and provide fresh insight into the hydrological development of Lake Ladoga, we use the oxygen isotope composition of diatoms ($\delta^{18}O_{diatom}$). Diatoms, photosynthetic microalgae with an external frustule composed of biogenic silica (opal, $SiO_2 \cdot nH_2O$), are abundant in most aquatic systems and typically well preserved in lacustrine sediments (Round *et al.* 1990). Diatom oxygen isotopes in combination with data of taxonomy analysis have become one of the most reliable sources of information about past ecological, hydrological, environmental and climate changes especially for northern regions where ice archives are unavailable and/ or biogenic carbonates limited (Shemesh *et al.* 2001; Jones *et al.* 2004; Swann *et al.* 2010; Chaplgin *et al.* 2012b, 2016; Narancic *et al.* 2016). Lacustrine $\delta^{18}O_{diatom}$ reflects the oxygen isotope composition of the lake water ($\delta^{18}O_{lake}$) and lake temperature (T_{lake}) (Leng & Barker 2006). Existing $\delta^{18}O_{diatom}$ records have been interpreted to evaluate past changes in air temperature (Chaplgin *et al.* 2012b), precipitation amounts and/or air-mass sources (Barker *et al.*

2001; Shemesh *et al.* 2001; Jones *et al.* 2004; Rosqvist *et al.* 2004; Kostrova *et al.* 2013; Meyer *et al.* 2015; Bailey *et al.* 2018), the precipitation/evaporation balance (Rioual *et al.* 2001; Kostrova *et al.* 2014) and palaeo-hydrological variability (Mackay *et al.* 2008, 2011, 2013; Chaplgin *et al.* 2016; Narancic *et al.* 2016).

Here, we use $\delta^{18}O_{diatom}$ as an independent environmental and/or climatic proxy to trace Holocene hydrological changes in Lake Ladoga region. Our inferences are accompanied by a diatom assemblage analysis of the same sedimentary succession, as well as a comprehensive survey of the modern hydrological system. These data are further explored in the context of existing palaeo-environmental studies (Saarnisto & Grönlund 1996; Subetto *et al.* 1998, 2002; Timofeev *et al.* 2005; Dolukhanov *et al.* 2009; Subetto 2009; Saarnisto 2012; Ludikova 2015) to assess if and how Holocene environmental changes at Lake Ladoga have responded to local, regional and/or global (i.e. internal/external) drivers.

Regional setting

Lake Ladoga (latitude 59°54′–61°47′N, longitude 29°47′–32°58′E, altitude 5 m a.s.l.) is a dimictic, freshwater lake located in northwest Russia, ~40 km east of St. Petersburg (Fig. 1A). The lake surface area is 18 329 km², with a mean and maximum water depth of 48.3 and 235.0 m, respectively (Rumyantsev 2015). The lake occupies an ancient tectonic and glacially sculpted depression orientated north-northwest to south-southeast (Fig. 1B). The

basin comprises metasediments with effusive and sedimentary rocks of Archean to Cambrian age, overlain by thick Quaternary deposits (Subetto *et al.* 1998; Shabalina *et al.* 2004; Subetto 2009; Rumyantsev *et al.* 2015). Lake bathymetry is broadly defined by a deep northern sector (70–235 m) that gradually shallows to the south (3–13 m) (Rumyantsev 2015). Numerous fjords and islands characterize the northern region of the lake, while large and shallow open bays occupy the southern shores.

The lake is a hydrologically open system with a water residence time of *c.* 11 years and a catchment area of 258 600 km^2 (Kimstach *et al.* 1998; Subetto 2009; Rumyantsev 2015; Rumyantsev *et al.* 2015). Lake Ladoga receives water from numerous rivers including three main inflows: (i) the Svir' (34%) entering the lake from the east, (ii) the Vuoksi (27%) from the west; and (iii) the Volkhov (23%) from the south (Subetto *et al.* 1998; Rumyantsev 2015). The River Neva outflows from the southwest of the lake into the Gulf of Finland (Fig. 1B). The lake water balance has been shown to predominantly reflect the inflow from rivers and streams (~85%), as well as direct input from precipitation (~10%). Groundwater inputs are insignificant (Kimstach *et al.* 1998; Shabalina *et al.* 2004; Rumyantsev & Kondratyev 2013). Mean lake water temperature is persistently low, *c.* +6 °C. Mean surface water (0–10 m depth) temperature can reach +16 °C in August (Rumyantsev 2015). The lake is typically ice-covered for more than half the year from early November to ice-out in late May (Karetnikov & Naumenko 2008). However, occasionally incomplete freezing of Lake Ladoga may occur with areas of open water remaining in the northern part throughout the winter (Karetnikov *et al.* 2016).

The regional climate is transitional between maritime and continental, although westerly Atlantic air masses prevail year round (Rumyantsev *et al.* 2015). Average annual air temperature in the Lake Ladoga region is +3.2 °C, ranging from −8.8 °C (February) to +16.3 °C (July) (Rumyantsev & Kondratyev 2013; Rumyantsev 2015). Annual precipitation varies spatially from 380 to 490 mm in the northwest region of the lake, to 500–630 mm in the south. The driest months are February and March (24 mm) and the wettest is September (58 mm) (Rumyantsev & Kondratyev 2013; Rumyantsev 2015; Rumyantsev *et al.* 2015).

Climate in this region reflects the trajectories of the prevailing air masses. Typically, marine cyclones moving from the west, southwest or northwest (Fig. 1A; Shver *et al.* 1982) bring cloudy, windy weather and precipitation, and cause abrupt warming in winter and cooling in summer. Conversely, dry continental air masses from the east, south or southeast induce relatively hot summers and cold winters. Incursions of dry Arctic air masses from the north (e.g. Barents Sea) and northeast (e.g. Kara Sea) are accompanied by clear weather, reduced precipitation and a sharp drop in air temperatures (Lydolph 1977; Shver *et al.* 1982; Rumyantsev *et al.* 2015).

Material and methods

Sediment and water recovery

A 22.7-m-long sediment core (Co 1309) was retrieved from Lake Ladoga (60°59′N, 30°41′E; water depth: 111 m; Fig. 1B) in September 2013, using gravity and percussion piston-corers operated from a floating platform (UWITEC Ltd., Austria). The core was split, described and subsampled for sedimentological, biological and geochemical analyses at the University of Cologne.

Lake water samples were collected at semi-regular intervals in the water column between the surface and bottom (*n* = 190), at different spatial locations across the lake (Fig. 1B). Water was sampled directly from inflow and outflow rivers connected to the lake (*n* = 61), and event-based precipitation samples (*n* = 57) were collected at the Ladoga field base of the Arctic and Antarctic Research Institute (AARI, St. Petersburg, Russia). All water samples were stored cool in airtight bottles prior to stable isotope analyses.

Core lithology and chronology

This study focuses on the upper 202 cm of the core Co 1309 from Lake Ladoga sediments for diatom oxygen isotope investigation. A recent lithological study on core Co 1309 (Gromig *et al.* in press) reported that the selected part of the core (Fig. 2A), consisting of predominantly massive silty clay (160–202 cm) and laminated clayey silt with minor occurrence of fine sand (0–160 cm), was deposited during the last *c.* 11.2 cal. ka BP, i.e. it covers the whole Holocene. For the entire postglacial succession, the age-depth model for the core Co 1309 was established on the basis of two radiocarbon dates (7559±70 and 2547±171 cal. a BP; Fig. 2A) and an independent varve chronology, further confirmed by an OSL age of 7000±300 cal. a BP at a depth of 130 cm. The complete age-depth model for the sediment core is presented in Gromig *et al.* (in press). The Holocene onset is supported by the results of pollen analyses (Savelieva *et al.* 2019).

Biogenic silica and diatom analyses

Biogenic silica (BSi) analysis was performed on 0.45 g of dry sediment sampled from Co 1309 at 16-cm intervals down core (*n* = 14). Samples were ground and analysed for BSi using the automated sequential leaching method (Müller & Schneider 1993) at the Alfred Wegener Institute Helmholtz Centre for Polar and Marine Research (AWI Bremerhaven, Germany). Biogenic opal was calculated from BSi assuming a 10% water content within the frustule (Mortlock & Froelich 1989; Müller & Schneider 1993).

These 14 samples were also processed for diatom taxonomy analysis using sediment disintegration in
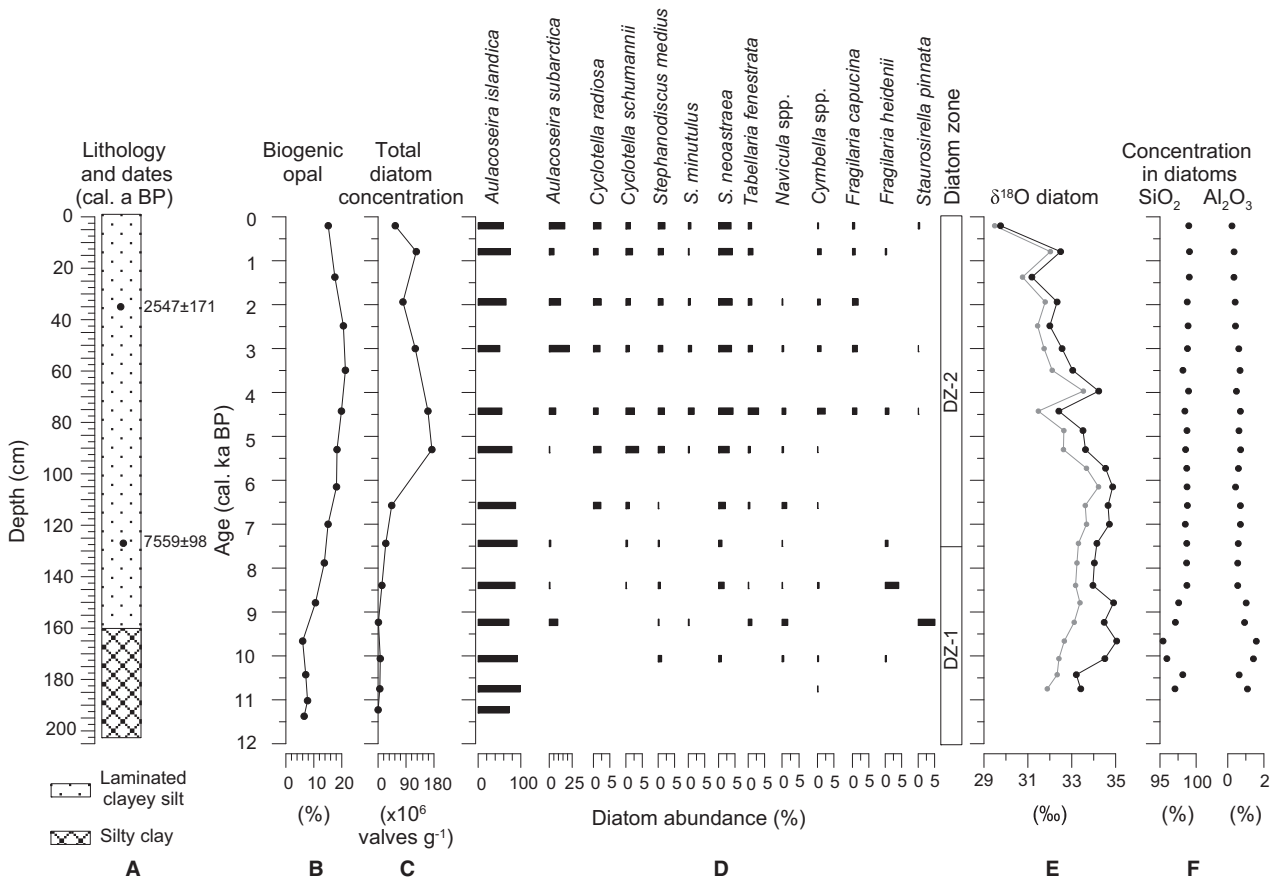
Fig. 2. Summary data from Lake Ladoga Co 1309 core. A. Sediment lithology and radiocarbon dates (Gromig *et al.* in press). B. Biogenic opal. C. Total diatom concentration. D. A simplified diatom taxonomy diagram. E. Measured $\delta^{18}O_{meas}$ (grey line), contamination-corrected $\delta^{18}O_{corr}$ values of diatoms (bold black line). F. SiO_2 and Al_2O_3 concentrations of the purified diatom samples analysed by EDS and measured for $\delta^{18}O$.

sodium pyrophosphate ($Na_4P_2O_7·10H_2O$) and subsequent fraction separation in heavy liquid (specific density 2.6 g cm^{-3}) (e.g. Gleser *et al.* 1974). Species abundance data were converted to percentages and diatom concentrations ($\times10^6$ valves g^{-1} of dry sediment) were calculated according to the method outlined by Davydova (1985). Taxonomic identification followed Krammer & Lange-Bertalot (1986, 1991).

Diatom preparation and purity estimation

Twenty-four sediment samples with an initial biogenic opal content (Fig. 2B) above 6% taken at 8-cm intervals and yielding an average temporal resolution of about 440 years throughout the past *c.* 10.8 ka were processed for $\delta^{18}O_{diatom}$ analysis. Diatom purification involved a multi-step procedure based on Morley *et al.* (2004). In summary, sediment samples were treated with 35% H_2O_2 on a heating plate at 50 °C for 3 days, before using 10% HCl at 50 °C to eliminate carbonates. Samples were then centrifuged in sodium polytungstate (SPT; $3Na_2WO_49·WO_3·H_2O$) heavy liquid (2.50–2.05 g cm^{-3}) at 2500 rpm for 30 min to separate diatoms from the detrital contam-

inants with higher density. This detritus was retained for a contamination assessment and $\delta^{18}O_{diatom}$ correction. Purified diatoms were then washed in ultra-pure water using a 3 μm filter. Finally, samples were wet sieved using a nylon mesh and sonication system, resulting in two diatom size fractions (3–10 and >10 μm). Only the 3–10 μm fraction yielded sufficient material (>1.5 mg) to be used for $\delta^{18}O_{diatom}$ analysis.

To assess sample purity, the chemical composition of all diatom samples, as well as of three samples of heavy liquid-separated detrital material, was measured using energy-dispersive X-ray spectroscopy (EDS; Chapl‐gin *et al.* 2012a). Measurements were performed with a ZEISS ULTRA 55 Plus Schottky-type field emission scanning electron microscope (SEM) equipped with a silicon drift detector (UltraDry SDD). The analysis was carried out using the standardless procedure (three repetitions, an acceleration voltage of 20 kV; excited area size of 100–200 μm, measuring time of 0.5 min; Chap‐ligin *et al.* 2012a, b) at the German Research Centre for Geosciences (GFZ), Potsdam. The EDS data (Table 1; Fig. 2F) indicate 19 of the 24 prepared diatom samples were exceptionally pure, comprising between 98.2 and

Table 1. Main geochemical characteristics of diatoms from Lake Ladoga based on EDS data. Measured $\delta^{18}O$ values ($\delta^{18}O_{meas}$), calculated contamination (c_{cont}) and $\delta^{18}O$ values corrected for contamination ($\delta^{18}O_{corr}$) are given.

Core	Sample depth (cm)	Age (cal. ka BP)	SiO_2 (%)	Al_2O_3 (%)	Na_2O (%)	MgO (%)	K_2O (%)	CaO (%)	MnO (%)	FeO (%)	Total	$\delta^{18}O_{meas}$ (‰)	c_{cont} (%)	$\delta^{18}O_{corr}$ (‰)
Co1309-14-III	3	0.203	98.98	0.23	0.55	0.10	0.02	0.06	0.01	0.05	100.00	29.49	1.6	29.76
Co1309-14-III	11	0.793	99.08	0.35	0.33	0.04	0.03	0.04	0.04	0.10	100.00	32.03	2.4	32.49
Co1309-14-III	19	1.373	99.05	0.34	0.30	0.04	0.03	0.10	0.03	0.11	100.00	30.76	2.3	31.18
Co1309-14-III	27	1.939	98.77	0.41	0.37	0.08	0.06	0.08	0.03	0.19	100.00	31.79	2.8	32.33
Co1309-14-III	35	2.483	98.89	0.43	0.32	0.07	0.06	0.03	0.04	0.16	100.00	31.44	2.9	32.00
Co1309-14-III	43	3.001	98.80	0.61	0.19	0.07	0.09	0.06	0.03	0.16	100.00	31.74	4.1	32.56
Co1309-14-III	51	3.495	98.17	0.68	0.58	0.13	0.10	0.07	0.04	0.23	100.01	32.11	4.6	33.04
Co1309-14-III	59	3.969	98.95	0.48	0.21	0.07	0.01	0.09	0.06	0.14	100.00	33.53	3.3	34.23
Co1309-14-III	67	4.425	98.44	0.70	0.25	0.10	0.06	0.11	0.07	0.27	100.00	31.48	4.7	32.41
Co1309-14-II	75	4.868	98.73	0.62	0.21	0.09	0.10	0.08	0.03	0.16	100.01	32.64	4.2	33.51
Co1309-14-II	83	5.301	98.54	0.71	0.23	0.10	0.03	0.11	0.06	0.22	100.00	32.62	4.8	33.62
Co1309-14-II	91	5.727	98.70	0.59	0.34	0.06	0.04	0.08	0.05	0.15	100.00	33.67	4.0	34.54
Co1309-14-II	99	6.150	98.74	0.43	0.46	0.08	0.06	0.04	0.04	0.16	100.00	34.22	2.9	34.86
Co1309-14-II	107	6.574	98.79	0.70	0.13	0.07	0.02	0.05	0.03	0.21	100.00	33.62	4.7	34.65
Co1309-14-II	115	7.001	98.50	0.70	0.40	0.10	0.06	0.07	0.04	0.15	100.01	33.67	4.7	34.71
Co1309-14-II	123	7.437	98.70	0.58	0.25	0.10	0.03	0.08	0.02	0.23	100.00	33.31	3.9	34.15
Co1309-14-II	131	7.883	98.68	0.55	0.35	0.11	0.03	0.06	0.03	0.19	100.00	33.24	3.7	34.03
Co1309-14-I	140	8.394	98.72	0.55	0.22	0.13	0.06	0.11	0.01	0.21	100.01	33.18	3.7	33.97
Co1309-14-I	147	8.790	97.58	1.02	0.28	0.27	0.11	0.16	0.02	0.57	100.00	33.38	6.9	34.91
Co1309-14-I	155	9.235	97.13	0.93	0.85	0.27	0.13	0.13	0.07	0.50	100.00	33.11	6.3	34.48
Co1309-14-I	163	9.662	95.42	1.58	0.80	0.69	0.28	0.07	0.02	1.14	100.00	32.66	10.7	35.05
Co1309-14-I	171	10.062	95.95	1.42	0.65	0.64	0.26	0.12	0.01	0.95	100.00	32.42	9.6	34.51
Co1309-3-II	179	10.428	98.15	0.63	0.58	0.14	0.10	0.12	0.05	0.24	100.00	32.34	4.3	33.21
Co1309-3-II	187	10.750	97.07	1.09	0.57	0.38	0.15	0.11	0.03	0.61	100.01	31.89	7.4	33.41

99.1% SiO_2, and 0.2–0.7% Al_2O_3; and five samples were less pure with 95.4–97.1% SiO_2, and 0.9–1.4% Al_2O_3. In general, all samples contained <2.5% Al_2O_3 (Chapligin *et al.* 2012a) and hence, were analysed for $\delta^{18}O_{diatom}$.

Diatom isotope analysis and $\delta^{18}O_{diatom}$ correction

Purified diatom samples ($n = 24$) and the detrital contaminant subsamples ($n = 3$) were analysed for $\delta^{18}O$ at AWI Potsdam. Samples were placed inside an inert gas flow dehydration (iGFD) chamber and heated to 1100 °C under argon gas to remove exchangeable oxygen (Chapligin *et al.* 2010). Dehydrated samples were then fully reacted using laser fluorination with a BrF_5 reagent to liberate O_2 (Clayton & Mayeda 1963) and directly measured against an oxygen reference sample of known isotopic composition with a PDZ Europa 2020 mass spectrometer. Replicate analyses of the calibrated working standard BFC (Chapligin *et al.* 2011) yielded $\delta^{18}O = +28.73\pm0.18$‰ ($n = 31$) indicating an accuracy and analytical reproducibility within the method's long-term analytical reproducibility (1σ) of ±0.25‰ (Chapligin *et al.* 2010).

All measured diatom $\delta^{18}O$ values were contamination corrected using the geochemical mass-balance approach (Swann & Leng 2009; Chapligin *et al.* 2012a, b):

$$\delta^{18}O_{corr} = (\delta^{18}O_{meas} - \delta^{18}O_{cont} \cdot c_{cont}/100)/(c_{diatom}/100) \qquad (1)$$

where $\delta^{18}O_{meas}$ is the original measured $\delta^{18}O$ value of the sample. $\delta^{18}O_{corr}$ is the measured $\delta^{18}O$ value corrected for contamination, with $\delta^{18}O_{cont} = +12.8\pm0.6$‰ ($n = 3$), which represents the average $\delta^{18}O$ of the heavy detrital fractions after the first heavy liquid separation. The percentages of contamination (c_{cont}) and diatom material (c_{diatom}) within the analysed sample are calculated using the EDS-measured Al_2O_3 content of the individual sample divided by the average Al_2O_3 content of the contamination (14.8 ± 0.9% in heavy fractions, $n = 3$) and as ($100\% - c_{cont}$), respectively.

Stable water isotope analysis

Water samples were measured for oxygen ($\delta^{18}O$) and hydrogen (δD) isotopes at the AARI using a Picarro L2120-i ($n = 281$) and at AWI Potsdam with a Finnigan MAT Delta-S mass spectrometer ($n = 7$). At the AARI, sequences of measurements included the injection of five samples, followed by the injection of an internal laboratory standard with an isotopic composition close to that of the samples. Replicate measurements on 10% of all samples indicate an analytical precision of 0.30‰ for δD and 0.06‰ for $\delta^{18}O$. AWI measurements were performed using equilibration techniques and yield an analytical uncertainty (1σ) of ±0.8‰ for δD and ±0.1‰ for $\delta^{18}O$ (Meyer *et al.* 2000). The secondary parameter deuterium excess is calculated as $d = \delta D - 8 \cdot \delta^{18}O$ (Dansgaard 1964), and all values are reported in per mil

(‰) difference relative to Vienna Standard Mean Ocean Water (VSMOW).

Results

Holocene diatom flora

Diatom frustules in core Co 1309 are well preserved down core and 118 different lacustrine taxa were identified in the Holocene. No marine or brackish taxa were observed in the upper 201 cm (11.18 cal. ka BP). An exception is the lowermost part, where negligible amounts of reworked Eemian marine diatoms are present. However, these samples did not contain sufficient biogenic opal for purification and diatom isotope analyses.

Two main diatom zones (DZs) are defined in the record based on species diversity and diatom concentration (Fig. 2C, D).

DZ-1 (202–125 cm; *c.* 11.2–7.5 cal. ka BP) is dominated by planktonic *Aulacoseira islandica* (O. Müll.) Sim. (85–95%). The abundances of other planktonic *Aulacoseira subarctica* (O. Müll.) E.Y. Haw., *Stephanodiscus* spp., *Tabellaria fenestrata* (Lyngb.) Kütz. and benthic *Cymbella* spp., *Fragilaria* spp. sensu lato, *Navicula* spp. do not exceed 1–2% (Fig. 2D). An exception is the interval from 145 to 165 cm (*c.* 8.7–9.8 cal. ka BP), where the relative abundance of *A. islandica* decreases to 72%, while planktonic *A. subarctica* and epiphytic *Staurosirella pinnata* (Ehr.) Will. & Round and *Fragilaria heidenii* (Østr.) abundances increase to 9, 5 and 4%, respectively. Negligible amounts of *Chaetoceros* spp. (resting spores) and more sporadically *Coscinodiscus* spp. and *Thalassiosira gravida* Cl. reworked from marine Eemian sediments are observed at 202 cm (*c.* 11.2 cal. ka BP). Diatom concentration in this zone is low, reaching a maximum of 24.8×10^6 valves g^{-1} at 125 cm (Fig. 2C).

DZ-2 (125–0 cm; *c.* 7.5–0 cal. ka BP) is further dominated by *A. islandica* (51–91%). *A. subarctica* is another dominant taxon at some levels with abundances between 0.6 and 22% (Fig. 2D). The abundances of planktonic *Cyclotella radiosa* (Grun.) Lemm., *C. schumannii* (Grun.) Håk., *Stephanodiscus medius* Håk., *S. minutulus* (Kütz.) Round, *S. neoastraea* Håk. & Hick., and *T. fenestrata* range between 1 and 4%. In the interval 45–70 cm (3.1–4.6 cal. ka BP), the relative abundances of *A. islandica* decrease to its minimum of 51% whereas *A. subarctica* reaches its maximum of 22%. A sharp increase up to 14% in the abundance of the benthic taxa, e.g. *Cymbella* spp., *F. capucina* Desm. et vars., *F. heidenii*, *Navicula* spp., occurs at 67 cm (4.4 cal. ka BP). Over the past *c.* 3.1 cal. ka BP, the relative abundance of *A. islandica* increases to 75% at 11 cm (*c.* 0.8 cal. ka BP) and then decreases to 59% at 3 cm (*c.* 0.2 cal. ka BP) (Fig. 2D). Total diatom concentration in DZ-2 is considerably higher than in DZ-1, peaking at 83 cm (*c.* 5.3 cal. ka BP) with 173×10^6 valves g^{-1}, before decreasing to 55×10^6 valves g^{-1} in the uppermost sample (Fig. 2C).

Holocene oxygen isotope record

Holocene $\delta^{18}O_{corr}$ values in Lake Ladoga range between +29.8 and +35.0‰ (mean: +33.5‰) (Fig. 2E; Table 1). Diatom $\delta^{18}O_{corr}$ values (further referred to as $\delta^{18}O_{diatom}$) exhibit the same trend as $\delta^{18}O_{meas}$ values, but due to the contamination correction are, on average, about 0.8‰ higher in the upper part of the core (younger than 8.8 cal. ka BP) and approximately 1.8‰ higher for the lower part (older than 8.8 cal. ka BP).

Between *c.* 10.7 and 10.4 cal. ka BP, $\delta^{18}O_{diatom}$ are relatively low, around +33.2‰. After 10.2 cal. ka BP values steadily increase, attaining a Holocene $\delta^{18}O_{diatom}$ maximum at 9.6 cal. ka BP (+35.0‰). After 9.6 cal. ka BP $\delta^{18}O_{diatom}$ values slightly decrease to +34.0‰, before increasing to a second maximum of +34.9‰ at *c.* 6.1 cal. ka BP. A sharp drop to +32.4‰ at *c.* 4.4 cal. ka BP and subsequent rise to +34.2‰ at *c.* 4.0 cal. ka BP in $\delta^{18}O_{diatom}$ are observed. The Late Holocene interval between *c.* 4.0 and 0.2 cal. ka BP exhibits a continuous decrease of 4.4‰ in $\delta^{18}O_{diatom}$ values, reaching the Holocene minimum of +29.8 ‰ at *c.* 0.2 cal. ka BP. However, there are two local maxima with +32.3 and +32.5‰ at *c.* 1.9 and 0.8 cal. ka BP, respectively. Overall, the record exhibits a continuous gradual $\delta^{18}O_{diatom}$ depletion of ~0.55‰ per 1000 years from the Early Holocene to the sediment surface with an accelerated depletion of ~1.1‰ per 1000 years after *c.* 4.0 cal. ka BP (Fig. 2E).

Water isotopes

Stable water isotope data ($\delta^{18}O$, δD and *d* excess) are presented in Fig. 3 and summarized in Table 2.

The modern Lake Ladoga water isotope composition varies between −10.3 and −9.2‰ (mean: −9.8‰) for $\delta^{18}O_{lake}$ and from −78.2 to −71.8‰ (mean: −75.5‰) for δD_{lake}. *d* excess values range from +1.5 to +5.5‰ (mean: +3.1‰). In the northern part of the lake, $\delta^{18}O_{lake}$ values range between −10.2 and −9.7‰ (mean: −9.9‰) and δD_{lake} from −76.7 to −74.9‰ (mean: −75.8‰). *d* excess ranges from +2.2 to +5.5‰ (mean: +3.3‰). The southern basin has similar isotopic composition that ranges between −10.3 and −9.2‰ (mean: −9.8‰) for $\delta^{18}O_{lake}$ and from −78.1 to −71.8‰ (mean: −75.1‰) for δD_{lake}. *d* excess ranges from +1.8 to +4.6‰ (mean: +3.0‰). Water column $\delta^{18}O$ profiles reveal no substantial changes with depth, with a maximum range of ±0.4‰ (Fig. 4). Similarly, the inflow rivers exhibit mean values of −9.8, −74.8 and +3.8‰ for $\delta^{18}O$, δD and *d* excess, respectively (*n* = 39). The outflow (Neva River) displays slightly higher mean values of −9.6‰ for $\delta^{18}O$, and −74.2‰ for δD (*d* excess: +2.7‰).
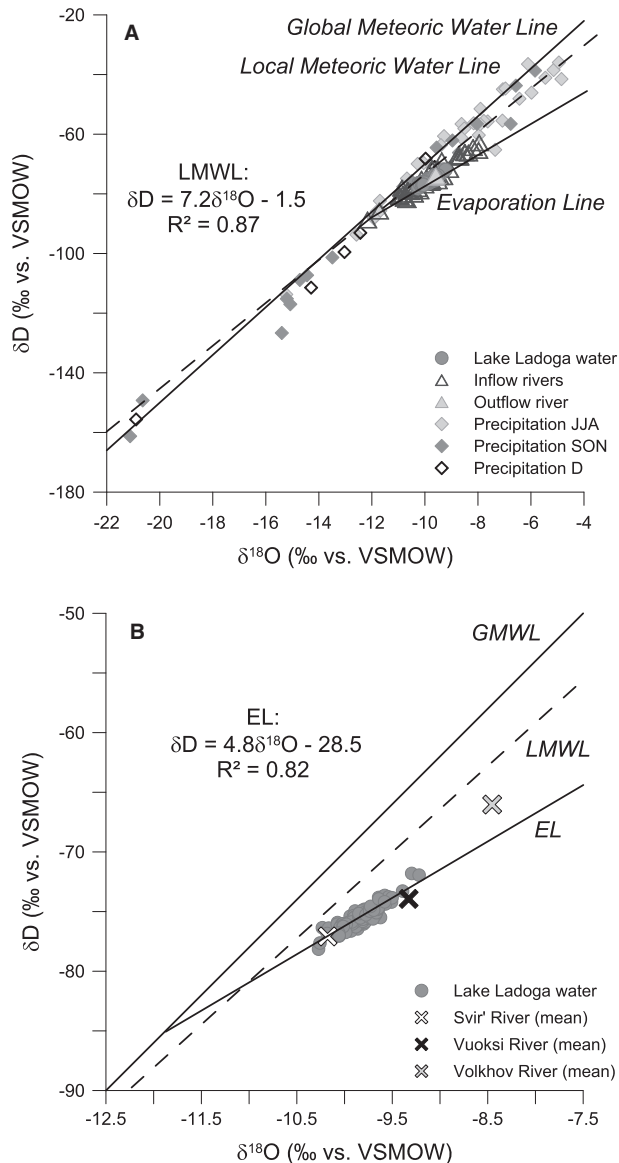
Fig. 3. $\delta^{18}O$–δD diagram for water samples. A. Lake Ladoga and rivers connected to the lake as well as precipitation (compare with Table 2). B. Lake Ladoga hydrology. Additionally, the Global Meteoric Water Line (GMWL; $\delta D = 8 \cdot \delta^{18}O + 10$; Craig 1961; Rozanski *et al.* 1993) and Local Meteoric Water Line (LMWL) based on GNIP data (IAEA/WMO 2018) as well as an evaporation line (EL) for Lake Ladoga waters are given.

Precipitation sampled at Lake Ladoga between July and December is characterized by mean values of $-7.6‰$ for $\delta^{18}O$ and $-55.7‰$ for δD (*d* excess $+5.3‰$). Precipitation samples were not collected during the rest of the year.

Discussion

Modern water isotope hydrology

The $\delta^{18}O_{lake}$ is affected by precipitation and additional hydrological parameters (i.e. evaporation and inflow/outflow ratio), and hence, assumed to be one of the main controls on the lacustrine $\delta^{18}O_{diatom}$ (Leng & Barker 2006). Therefore, the modern isotope hydrology of Lake Ladoga has been comprehensively assessed and compared to regional precipitation (own samples (Table 2) and Global Network of Isotopes in Precipitation (GNIP), St. Petersburg) as background information for the $\delta^{18}O_{diatom}$ interpretation.

Stable isotope data for precipitation collected on the western shore of Lake Ladoga (field base; Fig. 1B) display clear seasonal variations with higher mean $\delta^{18}O_{prec}$, δD_{prec} and *d* excess values of -8.8, -62.8 and $+7.3‰$, respectively, in summer (June–August) and lower mean values of -13.4, -99.8 and $+4.8‰$, respectively, in December (Table 2). The $\delta^{18}O$–δD relationship for collected precipitation is characterized by a slope of 7.7 and intercept of $+4.3$ ($R^2 = 0.98$; Table 2), slightly higher than the respective values for the Local Meteoric Water Line (LMWL; Fig. 3; $\delta D = 7.2 \cdot \delta^{18}O - 1.5$; $R^2 = 0.87$; GNIP database; IAEA/WMO 2018).

In contrast, the isotopic composition of the Lake Ladoga water varies in a relatively narrow range around average values of $-9.8‰$ for $\delta^{18}O_{lake}$, $-75.5‰$ for δD_{lake} and a mean *d* excess of $+3.1‰$ (Table 2). These values are in good agreement with those of the rivers (mean $\delta^{18}O = -9.8‰$; $\delta D = -74.8‰$ and *d* excess $= +3.8‰$; Table 2; $n = 39$) draining into the lake. Lake Ladoga water isotope samples are situated below the GMWL (Fig. 3A), and follow a linear dependence with a slope of 4.8 and an intercept of -28.5 ($R^2 = 0.82$), suggesting that the lake water is substantially influenced by evaporative enrichment. The intersection point of this evaporation line (EL) and the GMWL is at about $-12.0‰$ for $\delta^{18}O$ and at $-86.0‰$ for δD and, hence, quite similar to the weighted mean annual isotope composition of precipitation in St. Petersburg of -11.4 and $-87.2‰$ for $\delta^{18}O_{prec}$ and δD_{prec}, respectively (1980–1990, IAEA/WMO 2018). This is slightly lower than the mean isotopic composition of the inflow rivers (Table 2), suggesting that Lake Ladoga is predominantly fed by meteoric waters, i.e. precipitation with an important riverine contribution. The share of river water and precipitation in the water balance of the lake is about 85 and 10%, respectively (Rumyantsev 2015). Evaporation may comprise about 8% of the annual output from Lake Ladoga (Rumyantsev & Kondratyev 2013) and is likely to be seasonally related to the lake ice cover.

Lake Ladoga receives water from numerous rivers (Subetto *et al.* 1998; Rumyantsev 2015). The $\delta^{18}O_{lake}$ and δD_{lake} values for Lake Ladoga in the inflow area of River Svir' are -10.3 and $-77.9‰$, respectively, and, thus this area has an isotope composition similar to that of River Svir' (Table 2). River Vuoksi flows into Lake Ladoga by a northern and a southern tributary (through Losevskaya channel, Lake Sukhodolskoe and modern River Burnaya; Fig. 1B; Rumyantsev & Kondratyev 2013). The average isotope composition of the lake water in

Table 2. Summary of stable isotope data (δ^{18}O, δD and *d* excess), including minimum, mean and maximum values, standard deviations (SD) as well as slopes and intercepts from the δ^{18}O–δD diagram for the analysed samples of Lake Ladoga water (collected in August 2015, June and September 2016), water from rivers connected to Lake Ladoga (collected in August and October 2015, June 2016) and precipitation water (collected in July–December 2015; June–August 2016).

Sample type	No. total	δ^{18}O (‰) min.	δ^{18}O (‰) mean	δ^{18}O (‰) max.	δ^{18}O (‰) SD	δD (‰) min.	δD (‰) mean	δD (‰) max.	δD (‰) SD	*d* (‰) min.	*d* (‰) mean	*d* (‰) max.	*d* (‰) SD	Slope	Intercept	R^2
Water, Lake Ladoga	190	−10.3	−9.8	−9.2	0.2	−78.2	−75.5	−71.8	0.8	1.5	3.1	5.5	0.6	4.8	−28.5	0.82
Inflow rivers, Lake Ladoga	39	−12.2	−9.8	−8.0	1	−88.7	−74.8	−62.8	6.2	−1.6	3.8	8.9	2.6	5.9	−16.6	0.94
Svir' (inflow river)	6	−10.7	−10.2	−9.7	0.4	−79.0	−77.1	−73.1	2.2	2.2	4.3	6.5	1.8	4.8	−28.3	0.63
Vuoksi (inflow river)	2	−9.4	−9.3	−9.1	0.3	−74.2	−73	−71.8	1.7	0.8	1.1	1.3	0.4	6.6	−12.1	1
Vuoksi-Burnaya (inflow river)	4	−9.5	−9.3	−9.1	0.2	−75.6	−73.9	−71.8	1.6	0.2	0.7	1.3	0.5	7.9	−0.7	0.9
Volkhov (inflow river)	8	−8.8	−8.5	−8.0	0.3	−67.6	−66.0	−62.8	1.7	0.6	1.6	2.8	0.7	5.8	−17.3	0.94
Outflow (Neva river)	2	−9.6	−9.6	−9.6	0	−74.4	−74.2	−74.0	0.3	2.6	2.7	2.7	0.1	11.9	40.3	1
Precipitation (summary)	57	−21.1	−7.6	−4.8	3.8	−161.3	−55.7	−36.0	30	−6.4	5.3	15.9	4.4	7.7	4.3	0.98
Precipitation (JJA)	34	−15.2	−8.8	−4.8	2.5	−113.7	−62.8	−36.0	18.5	−6.4	7.3	13.6	4.6	7.2	0.39	0.95
Precipitation (SON)	17	−21.1	−12.1	−5.8	4.6	−161.3	−90.1	−38.7	36.6	−3.5	6.9	15.9	4.6	7.8	4.7	0.98
Precipitation (D)	6	−20.9	−13.4	−9.6	4.1	−155.6	−99.8	−68.2	32	2.9	7.2	11.6	3.6	7.8	4.1	0.99

both areas influenced by rivers Vuoksi and Burnaya is −9.8‰ for δ^{18}O and −75.4‰ for δD (*d* excess of +2.8‰) and close to the isotope composition of the connected riverine inflows (Table 2). Average values for rivers Vuoksi and Svir' fall into the field of isotope composition of the lake water (Fig. 3B). Notably heavier isotope compositions of about 1‰ for δ^{18}O and about 8‰ for δD are observed for River Volkhov as well as for lake water near the Volkhov inflow probably because of River Volkhov draining the southern part of the Ladoga catchment. Despite this, the average lake isotope composition in the area of the River Volkhov mouth is −9.6‰ for δ^{18}O and −74.1‰ for δD (*d* excess = +2.9‰), and in general comparable with the mean values for Lake Ladoga (Table 2), indicating that Volkhov River has a negligible influence on the overall water isotope balance of the lake. Rumyantsev & Kondratyev (2013) also observe significant differences in the ion content of Lake Ladoga and River Volkhov waters, supporting this assumption.

Consequently, δ^{18}O$_{lake}$ and δD$_{lake}$ can, theoretically, be fully explained by water input of rivers Vuoksi and Svir', with a smaller contribution from Volkhov. However, as both river and lake water samples are situated below the LMWL (Fig. 3B), evaporative effects are very likely both in the catchment and in the lake itself. As compared to the most important inflow Svir', the western Vuoksi river displays a distinctly more evaporative isotope signature, probably due to its drainage through several shallow waterbodies (Rumyantsev & Kondratyev 2013). The calculated share of losses through evaporation from the Ladoga catchment in summer is substantial, and has been estimated at 23% (Rumyantsev *et al.* 2017). The river waters draining into Lake Ladoga are distributed all over the lake due to efficient mixing processes. Nonetheless, the river input cannot significantly change the average isotope composition of the lake water within a single year. The total river discharge into the lake of about 71 km^3 a^{-1} (Holopainen & Letanskaya 1999) is 10 times lower compared to the whole volume of Lake Ladoga of ~848 km^3 (Rumyantsev *et al.* 2015). Additionally, no large offsets between the lake and river water samples entering the lake (slope and intercept are 5.9 and −16.6, respectively; Table 2) are notable (Fig. 3B).

Lake Ladoga δ^{18}O-depth profiles exhibit a narrow range of ±0.2‰ (Fig. 4A), thereby indicating a well-mixed water column with no isotopic stratification. An intensive full vertical mixing of water-masses usually occurs twice a year during intensive spring warming and autumn cooling (Tikhomirov 1982; Malm & Jönsson 1994; Rumyantsev 2015). However, there are minor dissimilarities of 0.1–0.2‰ in δ^{18}O values of the lake water depending on the sampling period. Late summer lake water of 2015 (Fig. 4A) displays a slightly lower isotope composition with average values of −9.9‰ for δ^{18}O, −75.6‰ for δD and a slightly higher mean *d* excess of +3.3‰ as compared to early summer lake water of
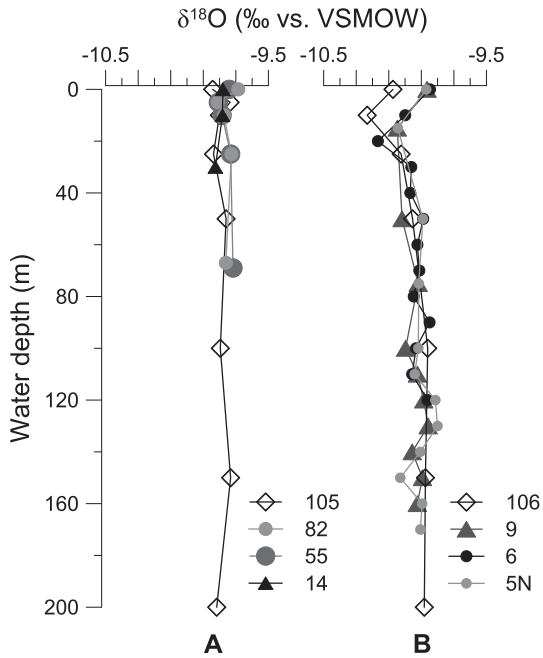
Fig. 4. Water isotope depth profiles at different locations in the lake. A. In the northern (105), central (55; 82) and southern (14) parts (sampled in June 2016). B. In the northern deeper part (106; 9; 6; 5N sampled in August 2015).

2016 (Fig. 4B) with −9.7, −74.8 and +2.7‰ for $\delta^{18}O$, δD and d excess, respectively. The spatial variability in the isotope signature of Lake Ladoga is also low (±0.1‰), ranging from −9.9±0.1‰ ($\delta^{18}O_{lake}$; $n = 77$) and −75.8± 0.4‰ (δD_{lake}) in the northern basin, to −9.8±0.2‰ ($\delta^{18}O_{lake}$; $n = 52$) and −75.1±1.2‰ (δD_{lake}) in the southern part.

In summary, Lake Ladoga shows a well-mixed and temporally and spatially rather uniform isotope signature that reflects local precipitation and riverine inflow, and both river and lake water underwent notable evaporative enrichment.

Ecological and species effects

Despite a few reworked Eemian marine diatoms, which were only found at the very beginning of the Holocene at *c.* 11.2 cal. ka BP, diatom analysis revealed the complete absence of brackish and marine diatom species in the analysed Holocene part of the Co 1309 core. This means that Lake Ladoga (at the coring position) existed as a freshwater reservoir at least for the last *c.* 10 800 years, an interpretation that is further substantiated by diatom isotope analyses.

Diatom species changes may have the potential to affect $\delta^{18}O_{diatom}$ because of (i) differences in habitats and/or blooming periods of taxa and (ii) species-specific fractionation effects (e.g. Chaplin *et al.* 2012a). The freshwater planktonic *Aulacoseira islandica* is the main primary producer in both modern (Holopainen & Letan-

skaya 1999; Letanskaya & Protopopova 2012) and palaeo-Lake Ladoga (Fig. 2D). During May–June, this taxon forms a biomass of up to 4.4 g m^{-3} in the photic zone when turbulence is high and the water temperature range is 5–8 °C (Letanskaya & Protopopova 2012). A secondary bloom with *A. islandica* typically occurs in autumn, but the produced biomass does not exceed 1 g m^{-3} (Letanskaya & Protopopova 2012). In summer, when T_{lake} can reach 16 °C (Rumyantsev & Kondratyev 2013; Rumyantsev 2015), diatoms are scarce and mainly occur in areas influenced by rivers (Holopainen & Letanskaya 1999).

As diatom production mainly occurs in the late spring–early summer, $\delta^{18}O_{diatom}$ should reflect early season $\delta^{18}O_{lake}$, possibly influenced by isotopically depleted snow-melt. In contrast, summer–autumn $\delta^{18}O_{lake}$ would be dominated by the composition of summer precipitation and evaporative enrichment. However, as seasonal variations in the isotope composition of Lake Ladoga water are relatively low (Fig. 4), any possible effects of $\delta^{18}O_{lake}$ seasonality on $\delta^{18}O_{diatom}$ are also assumed to be low.

There is no notable relationship between $\delta^{18}O_{diatom}$ and species assemblage trends during the Holocene (Fig. 2D, E). Hence, considering the Holocene sediment succession is dominated by *A. islandica* (up to 98%), we assume that species effects have negligible impact on the isotopic signal at Lake Ladoga. This assumption is valid considering that existing studies have demonstrated no visible species composition effects on lacustrine $\delta^{18}O_{diatom}$ (Chaplin *et al.* 2012a; Bailey *et al.* 2014). Therefore, we conclude that the obtained Holocene $\delta^{18}O_{diatom}$ values mainly reflect conditions during the *A. islandica* bloom, which typically occurs in late spring/early summer.

Isotope fractionation and controls on $\delta^{18}O_{diatom}$

Lake water temperature (T_{lake}) and $\delta^{18}O_{lake}$ are the main controls affecting $\delta^{18}O_{diatom}$ (Labeyrie 1974; Juillet-Leclerc & Labeyrie 1987; Brandriss *et al.* 1998; Leng & Barker 2006; Dodd & Sharp 2010).

Using the isotope fractionation between fossil diatom silica and water introduced by Juillet-Leclerc & Labeyrie (1987):

$$1000 \cdot \ln \alpha_{(silica-water)} = 3.26 \cdot 10^6 / T^2 + 0.45 \quad (2)$$

where the fractionation coefficient $\alpha_{(silica-water)} = (1000 + \delta^{18}O_{diatom})/(1000 + \delta^{18}O_{lake})$, we calculated the expected $\delta^{18}O_{diatom}$ for recent Lake Ladoga conditions. Taking (i) the mean $\delta^{18}O_{lake}$ of −9.8‰ and (ii) the lake temperature range between 5 and 16 °C (Letanskaya & Protopopova 2012; Rumyantsev & Kondratyev 2013; Rumyantsev 2015), expected recent $\delta^{18}O_{diatom}$ values (Fig. 5A) range between +30.0 and +33.3‰ (mean $\delta^{18}O_{diatom}$ = +31.6‰). As the main diatom bloom dominated by *A. islandica* occurs at T_{lake} of 5–8 °C (Letanskaya & Protopopova

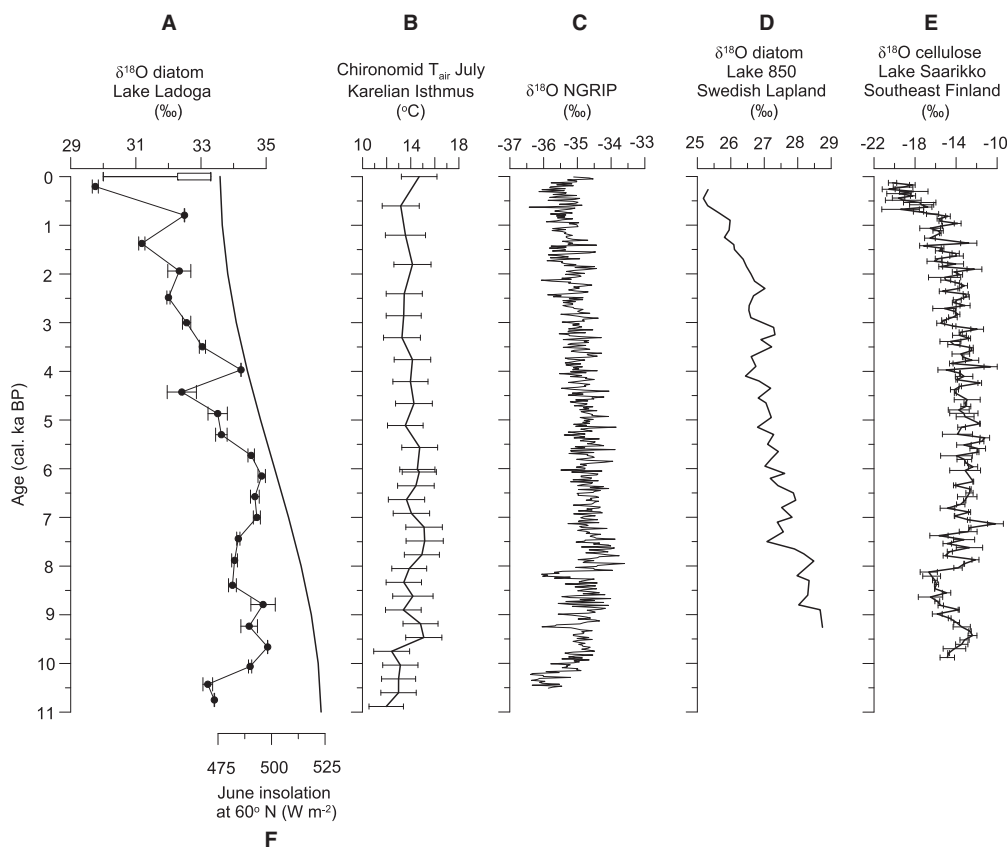*Fig. 5.* Holocene palaeoenvironmental comparison. A. Contamination-corrected δ[18]O_{diatom} record from Lake Ladoga (this study) and expected range of recent δ[18]O_{diatom} values calculated for T_{lake} between 5 and 16 °C using the correlation of Juillet-Leclerc & Labeyrie (1987); the open rectangle represents the expected δ[18]O_{diatom} for the *Aulacoseira islandica* blooming period at T_{lake} of 5–8 °C. B. July air temperatures reconstructed from chironomids in Karelian Isthmus (Nazarova *et al.* 2018). C. NGRIP δ^{18}O record from Greenland (Svensson *et al.* 2008) as an indicator of the Northern Hemisphere air temperatures. D. δ[18]O_{diatom} record from Lake 850, Swedish Lapland (Shemesh *et al.* 2001). E. δ[18]O_{cellulose} record from Lake Saarikko, southeast Finland (Heikkilä *et al.* 2010). F. Northern Hemisphere summer insolation at 60°N (Berger & Loutre 1991).

2012), the expected recent δ[18]O_{diatom} values can be further constricted to values between +32.3 and +33.3‰ (Fig. 5A). As this range generally matches the range of the Holocene δ[18]O_{diatom} values at Lake Ladoga, we assume that our δ[18]O_{diatom} data are in the right order of magnitude.

When considering a temperature coefficient of −0.2‰ per °C (Swann & Leng 2009; Dodd & Sharp 2010), the overall ~4‰ Holocene decrease in δ[18]O_{diatom} (Fig. 2E) would result in an unrealistic late spring/summer T_{lake} change of ~20 °C (which would yield negative T_{lake} in the Early Holocene). Hence, T_{lake} alone cannot be the primary controlling factor on Lake Ladoga δ[18]O_{diatom}. Instead, we propose that changes in δ[18]O_{lake} are the primary control on δ[18]O_{diatom} in Lake Ladoga, as observed in similar studies elsewhere (e.g. Kostrova *et al.* 2013; Meyer *et al.* 2015; Bailey *et al.* 2018). These changes in δ[18]O_{lake} originate either from isotopic variations in precipitation (δ[18]O_{prec}) and/or from changes in the hydrological conditions.

Both air temperature (T_{air}) and the pathways of atmospheric moisture are major impact factors on δ[18]O_{prec} (Dansgaard 1964; Clark & Fritz 1997). The relationship between monthly mean δ[18]O_{prec} and T_{air} for St. Petersburg has been determined as $\delta^{18}O_{prec} = 0.18 \cdot T_{air} - 12.3\,(R^2 = 0.81)$ (IAEA/WMO 2018). This isotope–temperature relationship of 0.18‰ per °C for the Lake Ladoga region coincides well with the gradient of 0.17‰ per °C calculated for marine stations (Rozanski *et al.* 1993; Clark & Fritz 1997) and indicates the prevalence of maritime air masses from the Atlantic to the region's water balance. Consequently, this relatively low positive T_{air}–δ[18]O_{prec} gradient would be largely counterbalanced by the negative T_{lake}–δ[18]O_{prec} relationship. Taking into account that T_{air} at Lake Ladoga (monthly means from −8 to +16 °C) varies by a factor of *c.* 2 more than T_{lake} (5–16 °C), T_{air} will be always more effective than T_{lake}. Hence, we conclude that (i) lake temperatures will fully be counterbalanced by air temperature changes; (ii) T_{air} changes probably have little effect on δ[18]O_{lake}, and hence

(iii) the dominant parameter affecting $\delta^{18}O_{lake}$ and accordingly $\delta^{18}O_{diatom}$ is $\delta^{18}O_{prec}$.

Presently, Atlantic air masses supply moisture to the Lake Ladoga region year-round, whereas continental and Arctic air masses deliver comparably less moisture (Shver *et al.* 1982; Rumyantsev *et al.* 2015). As different air masses carry distinct isotopic signals (e.g. Clark & Fritz 1997), changes in the prevailing atmospheric circulation pattern can subsequently change $\delta^{18}O_{prec}$ and $\delta^{18}O_{lake}$. Lake Ladoga precipitation originating from Atlantic maritime air masses should theoretically be characterized by higher $\delta^{18}O_{prec}$ compared to precipitation derived from Arctic/continental air masses. Changes in the relative contribution of these air masses to the local precipitation should, hence, impact on $\delta^{18}O_{lake}$ and $\delta^{18}O_{diatom}$.

Moreover, prevalent summer precipitation in the region and enhanced evaporation would enrich $\delta^{18}O_{lake}$ and shift $\delta^{18}O_{diatom}$ towards higher values. In contrast, higher amounts of winter precipitation and a more persistent and enduring lake ice cover in colder climate conditions would reduce evaporation effects and lead to lower $\delta^{18}O_{diatom}$.

Hence, we suggest that the changes in Lake Ladoga $\delta^{18}O_{lake}$ are mainly driven by changes in $\delta^{18}O_{prec}$ signal, varying input sources and rates and by evaporative effects, but less by T_{air} changes. However, as evaporative effects, enhanced summer precipitation and T_{air} increase all lead to more enriched $\delta^{18}O_{lake}$, the diatom isotope record should show 'apparent' T_{air} changes (containing a combined information on T_{air}, evaporation and precipitation seasonality).

Temporal changes in $\delta^{18}O_{diatom}$, diatom taxonomy and lake hydrology

Pollen-based reconstructions from Lake Ladoga demonstrate a shift to Holocene interglacial conditions starting at *c.* 11.2 cal. ka BP (Savelieva *et al.* 2019) when winter and summer temperatures increased by 4–5 °C (Wohlfarth *et al.* 2007). Despite the general warming since the Lateglacial, regional climate during the Early Holocene remained relatively cold and dry (Arslanov *et al.* 2001; Heikkilä *et al.* 2010; Shelekhova & Lavrova 2011; Subetto *et al.* 2017). Climate conditions became slightly more humid and warmer around *c.* 10 cal. ka BP (Subetto *et al.* 2002). In general, lower than present temperatures (by 1–2 °C in July and by 2–2.5 °C in January) and lower annual precipitation (by 25–30 mm) in the region during the Early Holocene have been reconstructed (Arslanov *et al.* 2001).

The earliest Holocene is characterized by rather lower $\delta^{18}O_{diatom}$ values of about +33.3‰ at 10.8–10.4 cal. ka BP (Fig. 5A). This interval coincides with an increase in local air temperatures (Fig. 5B; Nazarova *et al.* 2018) and probably reflects the influx of isotopically light meltwater due to widespread thaw of glacier ice in the Lake Ladoga catchment (e.g. Subetto 2009).

Additionally, noticeable changes occurred in the Lake Ladoga hydrological system at *c.* 10.7 cal. ka BP when the lake formed an eastern deep-water bay of the Ancylus Lake (Davydova *et al.* 1996; Saarnisto & Grönlund 1996; Subetto 2007, 2009; Björck 2008). The retreating Scandinavian Ice Sheet still contributed significant amounts of meltwater to the freshwater Ancylus Lake, particularly in the northern and eastern parts of the basin (Heikkilä *et al.* 2010). This process was accompanied by a sharp increase in the lake water level (Subetto 2007; Dolukhanov *et al.* 2009).

Between *c.* 10.4 and 9.5 cal. ka BP, the Lake Ladoga $\delta^{18}O_{diatom}$ record displays higher $\delta^{18}O_{diatom}$ values (Fig. 5A) including the absolute maximum (+35.0‰) at 9.6 cal. ka BP induced by dry highly evaporative conditions. The increase in $\delta^{18}O_{diatom}$ of ~1.8‰ (Fig. 5A) is accompanied by the appearance of planktonic *A. subarctica* and of benthic *Navicula* spp. and *Fragilaria* spp. sensu lato typical for smaller basins (Saarnisto & Grönlund 1996). A simultaneous decrease in *A. islandica* abundance (Fig. 2D) also suggests a lowering of the lake level and probably enhanced evaporation. At the same time, the regression started at *c.* 10.2 cal. ka BP and Lake Ladoga changed into an isolated basin with an outflow in its northern part at *c.* 10–9 cal. ka BP (Saarnisto & Grönlund 1996; Timofeev *et al.* 2005; Saarnisto 2012; Rumyantsev & Kondratyev 2013). Lithostratigraphical investigations of numerous sediment cores from Lake Ladoga revealed lower than present lake level (Subetto *et al.* 1998; Subetto 2007, 2009). The strictly lacustrine Early Holocene diatom assemblages and the relatively low $\delta^{18}O_{diatom}$ values (around +34.3±0.8‰) indicate freshwater and not brackish or marine conditions (+40 to +45‰; Shemesh *et al.* 1992). This indicates that at the coring site, a freshwater environment has persisted at least since *c.* 10.8 cal. ka BP.

Since *c.* 8.4 cal. ka BP, a notable increase in $\delta^{18}O_{diatom}$ (Fig. 5A) is accompanied by an increase in diatom abundance (Fig. 2C) and species diversity driven by the occurrence of planktonic *Cyclotella* spp., *Stephanodiscus* spp. and *T. fenestrata* (Fig. 2D). The $\delta^{18}O_{diatom}$ values attain a second maximum of +34.7±0.1‰ between 7.1 and 5.7 cal. ka BP (Fig. 5A). At the same time, a chironomid temperature reconstruction (Fig. 5B; Nazarova *et al.* 2018) exhibits the warmest Holocene interval with a mean July T_{air} of 14.5 °C between *c.* 8.0 and 5.6 cal. BP in the Karelian Isthmus. Pollen-based reconstructions also suggest higher-than-present mean annual air temperatures (by 2–2.5 °C; Arslanov *et al.* 2001; Shelekhova & Lavrova 2011), which probably caused increased evaporation and thereby higher $\delta^{18}O_{diatom}$. However, there is no evidence of changes in the lake level from other proxies during this period. Pollen-based reconstructions suggest that from *c.* 7.5 to 5.0 cal. ka BP the climate of the Ladoga region was wet and precipitation was 100–150 mm a^{-1} higher than present (Arslanov *et al.* 2001; Shelekhova & Lavrova 2011; Borzenkova *et al.* 2015). Prevalence of summer precipitation in

the region could result in isotopic enrichment of $\delta^{18}O_{lake}$ and, hence, could contribute to high $\delta^{18}O_{diatom}$ at this time.

Between *c.* 5.7 and 4.4 cal. ka BP (Fig. 5A), $\delta^{18}O_{diatom}$ values decrease by 2‰, which could reflect lower T_{air}, reduced evaporation and subsequent lake level rise. This is confirmed by diatom taxonomy data from Lake Ladoga and surrounding lakes (Ludikova 2015), which suggest a deep freshwater basin at this time. Increases in planktonic diatoms (up to 98% in total) and a negligible concentration of benthic species (1.5–2%; Fig. 2D) further substantiate a deepening of the lake during this period. The higher lake level may relate to new inflow from the Lake Saimaa complex to Lake Ladoga via River Vuoksi as a result of the isostatic uplift and tilting of the Lake Ladoga basin (Saarnisto & Grönlund 1996; Saarnisto 2012).

The increase of $\delta^{18}O_{diatom}$ by 1.8‰ at *c.* 4.4 cal. ka BP (Fig. 5A) is accompanied by a considerable decrease in the relative abundance of *A. islandica* (to 55%) and increase of *A. subarctica* (to 7%) and benthic species (to 14% in total; Fig. 2D). The shift in $\delta^{18}O_{diatom}$ could be related to a sharp lake level drop (of 12 m; Saarnisto 2012) associated with formation of the River Neva outflow between 4.5 and 3.0 cal. ka BP (Yakovlev 1925; Koshechkin & Ekman 1993; Malakhovskiy *et al.* 1993; Saarnisto & Grönlund 1996; Dolukhanov *et al.* 2009; Subetto 2009; Saarnisto 2012), although the precise timing remains under discussion (Kulkova *et al.* 2014; Virtasalo *et al.* 2014; Ludikova 2015). Although lowering of the lake level between *c.* 4.4 and 4.0 cal. ka BP could reflect enhanced evaporation favouring higher $\delta^{18}O_{lake}$ (and consequently $\delta^{18}O_{diatom}$), the opening of the Neva outlet must have had a major impact on the local hydrology and be reflected in the $\delta^{18}O_{diatom}$ record. The lower lake level should have induced an abrupt increase of riverine influx with relatively higher $\delta^{18}O$. Thus, we interpret the peak at *c.* 4.0 cal. ka BP as a short-term reaction to this major hydrological change, which would support the hypothesis of an earlier opening of the Neva outlet.

After 4.0 cal. ka BP, $\delta^{18}O_{diatom}$ values exhibit a continuous decrease of about 4.4‰ that culminates at 0.2 cal. ka BP (Fig. 5A). This trend constitutes a twofold acceleration of the isotope decrease, to ~1‰ per 1000 years. High abundances of *A. subarctica* and visible amounts of *S. medius* and *S. minutulus* at *c.* 3.5–0.2 cal. ka BP (Fig. 2D) suggest a period of colder temperatures and a well-mixed water body. Palaeoclimate reconstructions based on regional pollen data also suggest a 1–1.5 °C cooling and increase in humidity in the region, particularly since 2.5 cal. ka BP (Arslanov *et al.* 2001; Shelekhova & Lavrova 2011). However, an overall cooling trend alone cannot be responsible for the accelerated decrease in $\delta^{18}O_{diatom}$. After the Neva breakthrough, a new hydrological situation established at a lower lake level with a smaller lake surface and a continuous outflow towards the Baltic Sea (Subetto *et al.* 1998; Saarnisto 2012). The cooling could have induced a more persistent lake ice cover and thereby reduced evapora-

tion. Furthermore, the opening of the Neva outflow could have reduced the input of isotopically heavier water draining from the southern tributaries to Ladoga Lake, and thus have favoured a decrease of $\delta^{18}O_{lake}$ in the Late Holocene.

$\delta^{18}O_{diatom}$ in the hemispheric context

A general Early to Late Holocene decrease in Lake Ladoga $\delta^{18}O_{diatom}$ values from *c.* 10.8 to 0.2 cal. ka BP (Fig. 5A) is in line with a reduced June insolation at 60°N (Fig. 5F; Berger & Loutre 1991), suggesting that the decrease in summer solar insolation is responsible for an overall cooling trend, and hence, partly directly, partly due to an overall reduction in evaporation, for the depletion trend in the $\delta^{18}O_{diatom}$ record. Furthermore, the Holocene trend of the diatom oxygen isotope record (Fig. 5A) approximately follows the Northern Hemisphere temperature as reconstructed from the Greenland ice-core (NGRIP; Fig. 5C; Svensson *et al.* 2008). Consequently, the character of the Lake Ladoga $\delta^{18}O_{diatom}$ record is consistent with many other climate reconstructions of the Northern Hemisphere (e.g. Wanner *et al.* 2008). These include other Eurasian Holocene $\delta^{18}O_{diatom}$ records such as Lake 850 in Swedish Lapland (Figs 1A, 5C; Shemesh *et al.* 2001); Lake Chuna on the Kola Peninsula (Fig. 1A; Jones *et al.* 2004); and Lake El'gygytgyn in Chukotka (Swann *et al.* 2010; Chapligin *et al.* 2012b). These records have in common an Early to Middle Holocene maximum (i.e. the Holocene Thermal Maximum; HTM) and a prominent minimum during the latest Holocene (i.e. the Little Ice Age (LIA) period), which is also visible in the Lake Ladoga $\delta^{18}O_{diatom}$ record.

The Lake Ladoga record shows a Holocene $\delta^{18}O_{diatom}$ maximum between *c.* 7.1 and 5.7 cal. ka BP (Fig. 5A), which is consistent with a summer temperature maximum inferred from other proxy sources from the Lake Ladoga region (Arslanov *et al.* 2001; Nazarova *et al.* 2018). Moreover, the Lake Ladoga record shows an accelerated $\delta^{18}O_{diatom}$ decrease starting at *c.* 4.0 cal. ka BP (Fig. 5A) towards the Holocene minimum *c.* 0.2 cal. ka BP, coinciding with the LIA cold interval (Seppä *et al.* 2009; Opel *et al.* 2013).

Pronounced cooling (accompanied by generally less evaporation and more persistent lake ice cover) is one reason for the overall depletion in all $\delta^{18}O_{diatom}$ records mentioned above. Additionally, air-mass changes are considered to be driving the Holocene trend at Lake 850 and Lake Chuna (Shemesh *et al.* 2001; Jones *et al.* 2004), whereas changes in air temperature are predominant at Lake El'gygytgyn (Swann *et al.* 2010; Chapligin *et al.* 2012b).

$\delta^{18}O_{diatom}$ in the regional context

Compared to other regional reconstructions, the $\delta^{18}O_{diatom}$ record from Lake Ladoga (Fig. 5A) is most similar to

the $\delta^{18}O_{cellulose}$ record from Lake Saarikko (Fig. 5E), southeast Finland (Fig. 1A; Heikkilä *et al.* 2010). Both reconstructions exhibit an isotopic enrichment between 10 and 9.5 cal. ka BP suggesting lower lake levels and prevailing dry conditions in Early Holocene. Despite relatively low air temperatures at this time, enhanced evaporation was probably linked with a reduced precipitation amount (Arslanov *et al.* 2001; Heikkilä *et al.* 2010) resulting in generally lower water levels of lakes in northeastern Europe (Wolfe *et al.* 2003; Heikkilä *et al.* 2010; Muschitiello *et al.* 2013). A subsequent depletion in $\delta^{18}O$ in both records from *c.* 9.5 to 8 cal. ka BP (Fig. 5A, E) could be related to a reduced evaporation and/or increase of precipitation amount (Arslanov *et al.* 2001; Subetto *et al.* 2002), especially in winter (Heikkilä *et al.* 2010). The Lake Ladoga $\delta^{18}O_{diatom}$ and the Lake Saarikko $\delta^{18}O_{cellulose}$ records display a similar HTM between 8 and 5.5 cal. ka BP. The overall increase in air temperature leads to heavier isotope composition of precipitation, and correspondingly to enrichment in lake water and diatoms (as well as in cellulose). At this time, pollen-based reconstructions show a warm and wet climate around Lake Ladoga (Arslanov *et al.* 2001), as well as in the Baltic region (Stansell *et al.* 2017) and in other regions of northwestern Russia (e.g. Nosova *et al.* 2018), probably dominated by summer precipitation, which could have additionally contributed to the Middle Holocene $\delta^{18}O_{diatom}$ maximum. Since *c.* 4 cal. ka BP, both diatom and cellulose records show an accelerated depletion in $\delta^{18}O$ (Fig. 5A, E) pointing to reduced evaporation during overall cooling (Heikkilä *et al.* 2010). The similarity of these two $\delta^{18}O$ records supports similar climatic conditions and main atmospheric patterns at both localities. Small discrepancies may reflect the different hydrological regimes (river- and precipitation-supplied Lake Ladoga vs. precipitation- and ground-water-fed Lake Saarikko) and the different temporal resolutions.

Overall decreasing Holocene $\delta^{18}O_{diatom}$ values were also found in Sweden (Fig. 5D; Shemesh *et al.* 2001) and on the Kola Peninsula (Jones *et al.* 2004). Warm enriched Atlantic air masses probably supplied precipitation to these regions between *c.* 8 and 5 cal. ka BP (Jones *et al.* 2004). Instead, colder and ^{18}O-depleted Arctic air masses dominated over Sweden and the Kola Peninsula during the past *c.* 4–5 cal. ka BP (Shemesh *et al.* 2001; Jones *et al.* 2004; Rosqvist *et al.* 2004). However, today only 1% of the trajectories arriving at Lake Ladoga derive from the north (Fig. 1A; Shver *et al.* 1982) and might have an isotopically light Arctic signature. Swedish Lapland and the Kola Peninsula are both situated much further north and closer to the sea than Lake Ladoga (Fig. 1A). We therefore assume that the gradual shift to prevalent Arctic air masses is probably only of minor importance for the Lake Ladoga region in the Late Holocene.

In general, periods of decreasing lake level of the Lake Ladoga system (e.g. Subetto 2009) are accompanied by increasing $\delta^{18}O_{diatom}$ values, whereas a depletion is observed during lake level rise. However, the reaction of the Lake Ladoga oxygen isotope signal to multiple and drastic changes in the hydrological regime of the lake system (Saarnisto & Grönlund 1996; Subetto *et al.* 1998; Subetto 2007, 2009; Björck 2008; Saarnisto 2012; Ludikova 2015) such as river inflow is downplayed and marked in the $\delta^{18}O_{diatom}$ record only by moderate changes of ~2‰ that could also be explained e.g. by evaporation changes from the surface of the lake and/or in the catchment area. Lake level changes are supposedly accompanied by evaporation changes and, at Lake Ladoga, correlated with North Atlantic oscillation patterns (Karetnikov & Naumenko 2008), at least during the past 60 years. However, the abrupt drop of the lake level after Neva breakthrough (within only *c.* 400 years; Subetto 2007, 2009) falls in a cooling period, thereby implying a more persistent ice cover and reduced evaporation despite lower lake level. In summary, evaporation effects and hydrological changes are the main drivers for $\delta^{18}O_{diatom}$ changes in the Lake Ladoga record, whereas changes in air and lake temperatures as well as the contribution of Arctic moisture are suggested to be of minor importance.

Conclusions

This new Holocene oxygen isotope record on fossil diatoms extracted from a Lake Ladoga sediment core is combined with the recent isotope hydrology and local diatom taxonomy data, and used to characterize the environmental, hydrological and climate variability in the Lake Ladoga region in northwest Russia. The data reveal that over the last *c.* 10.8 cal. ka the lake existed as a turbulent, well-mixed freshwater reservoir with no evidence of a Holocene brackish or marine environment. The Lake Ladoga $\delta^{18}O_{diatom}$ record is in line with the decreasing Holocene summer insolation and follows the temperature history in the region as well as the Northern Hemisphere temperature trends as described in other summer-based proxy records, i.e. Middle to Late Holocene cooling after the Holocene Thermal Maximum reaching the absolute minimum (LIA) in the Late Holocene.

Potential controls for $\delta^{18}O_{diatom}$ from Lake Ladoga comprise a combination of variations in evaporation and hydrological changes. A highly evaporative character is the likely main reason for overall high $\delta^{18}O_{diatom}$ values up to +35.0‰ during the Holocene. Changes in atmospheric circulation patterns towards an enhanced Arctic moisture supply during the Late Holocene seem unlikely for the Lake Ladoga region.

The Lake Ladoga region has undergone significant hydrological changes throughout the Holocene. The isolation of the lake basin in the Early Holocene, and the subsequent opening of the Vuoksi River inflow at *c.*

5.7 cal. ka BP and of the Neva River outflow are associated with lake level changes, notable as respective maxima and minima in the Ladoga $\delta^{18}O_{diatom}$ record. Most notably, our data provide new evidence for a rather early opening of the Neva River outflow at *c.* 4.4–4.0 cal. ka BP. After drainage of the Ladoga basin through Neva River, a continuous and accelerated decrease in $\delta^{18}O_{diatom}$ of ~4 ‰ probably reflects an overall cooling with more persistent lake ice cover and reduced evaporation.

In summary, this study highlights the complex interplay between global and regional-scale hydrological and climatological factors controlling $\delta^{18}O_{diatom}$ throughout the Holocene.

Author contributions. – S. Kostrova, H. Meyer, H. Bailey and B. Chapligin provided the diatom oxygen isotope data; A. Ludikova provided the diatom taxonomy data; R. Gromig provided the lithological data and age-depth model; G. Kuhn provided biogenic silica data; Y. Shibaev, A. Kozachek and A. Ekaykin provided the water isotope data. All co-authors contributed to the discussion and interpretation of the data and the writing of the manuscript.

Data availability statement

Data are available via the Pangaea database (www.pangaea.de).

References

Aleksandrovskii, A. L., Arslanov, Kh. A., Davydova, N. N., Doluchanov, P. M., Zaitseva, G. I., Kirpichnikov, A. N., Kuznetsov, D. D., Lavento, M., Ludikova, A. V., Nosov, E. N., Savel'eva, L. A., Sapelko, T. V. & Subetto, D. A. 2009: New data on the Ladoga transgression, the Neva River formation, and agricultural development of Northwestern Russia. *Doklady Earth Sciences 425*, 274–278.

Arslanov, K., Savelieva, L. A., Klimanov, V. A., Chernov, S. B., Maksimov, F. E., Tertychnaya, T. V. & Subetto, D. A. 2001: New data on landscape-paleoclimatic stages in northwestern Russia during the Late Glacial and Holocene. *Radiocarbon 43*, 581–594.

Bailey, H. L., Henderson, A. C. G., Sloane, H. J., Snelling, A., Leng, M. J. & Kaufman, D. S. 2014: The effect of species on lacustrine $\delta^{18}O_{diatom}$ and its implications for palaeoenvironmental reconstructions. *Journal of Quaternary Science 29*, 393–400.

Bailey, H. L., Kaufman, D. S., Sloane, H. J., Hubbard, A. L., Henderson, A. C., Leng, M. J., Meyer, H. & Welker, J. M. 2018: Holocene atmospheric circulation in the central North Pacific: a new terrestrial diatom and $\delta^{18}O$ dataset from the Aleutian Islands. *Quaternary Science Reviews 194*, 27–38.

Barker, P. A., Street-Perrott, F. A., Leng, M. J., Greenwood, P. B., Swain, D. L., Perrott, R. A., Telford, R. J. & Ficken, K. J. 2001: A 14,000-year oxygen isotope record from diatom silica in two alpine lakes on Mt. Kenya. *Science 292*, 2307–2310.

Berger, A. & Loutre, M. F. 1991: Insolation values for the climate of the last 10 million years. *Quaternary Science Reviews 10*, 297–317.

Björck, S. 2008: The late Quaternary development of the Baltic Sea basin. *In* The BACC Author Team (eds.): *Assessment of Climate Change for the Baltic Sea Basin*, 398–407. Springer-Verlag, Berlin.

Borzenkova, I., Zorita, E., Borisova, O., Kalnina, L., Kisielienė, D., Koff, T., Kuznetsov, D., Lemdahl, G., Sapelko, T., Stančikaitė, M. & Subetto, D. 2015: Climate changes during the Holocene. *In* The BACC II Author Team (eds.): *Assessment of Climate Change for the Baltic Sea Basin, Regional Climate Studies*, 25–49. Springer, Cham.

Brandriss, M. E., O'Neil, J. R., Edlund, M. B. & Stoermer, E. F. 1998: Oxygen isotope fractionation between diatomaceous silica and water. *Geochimica et Cosmochimica Acta 62*, 1119–1125.

Chapligin, B., Leng, M. J., Webb, E., Alexandre, A., Dodd, J. P., Ijiri, A., Lücke, A., Shemesh, A., Abelmann, A., Herzschuh, H., Longstaffe, F. J., Meyer, H., Moschen, R., Okazaki, Y., Rees, N. H., Sharp, Z. D., Sloane, H. J., Sonzongi, C., Swann, J. E. A., Sylvestre, F., Tyler, J. J. & Yam, R. 2011: Inter-laboratory comparison of oxygen isotope compositions from biogenic silica. *Geochimica et Cosmochimica Acta 75*, 7242–7256.

Chapligin, B., Meyer, H., Bryan, A., Snyder, J. & Kemnitz, H. 2012a: Assessment of purification and contamination correction methods for analysing the oxygen isotope composition from biogenic silica. *Chemical Geology 300–301*, 185–199.

Chapligin, B., Meyer, H., Friedrichsen, H., Marent, A., Sohns, E. & Hubberten, H.-W. 2010: A high-performance, safer and semi-automated approach for the $\delta^{18}O$ analysis of diatom silica and new methods for removing exchangeable oxygen. *Rapid Communications in Mass Spectrometry 24*, 2655–2664.

Chapligin, B., Meyer, H., Swann, G. E. A., Meyer-Jacob, C. & Hubberten, H.-W. 2012b: A 250 ka oxygen isotope record from diatoms at Lake El'gygytgyn, far east Russian Arctic. *Climate of the Past 8*, 1621–1636.

Chapligin, B., Narancic, B., Meyer, H. & Pienitz, R. 2016: Paleoenvironmental gateways in the eastern Canadian arctic – Recent isotope hydrology and diatom oxygen isotopes from Nettilling Lake, Baffin Island, Canada. *Quaternary Science Reviews 147*, 379–390.

Clark, I. & Fritz, P. 1997: *Environmental Isotopes in Hydrogeology*. 328 pp. CRC Press/Lewis Publishers, Boca Raton.

Clayton, R. & Mayeda, T. 1963: The use of bromine pentafluoride in the extraction of oxygen from oxides and silicates for isotopic analysis. *Geochimica et Cosmochimica Acta 27*, 43–52.

Craig, H. 1961: Isotopic variations in meteoric waters. *Science 133*, 1702–1703.

Dansgaard, W. 1964: Stable isotopes in precipitation. *Tellus 16*, 436–468.

Davydova, N. N. 1985: *Diatoms – Indicators of the Environmental Conditions of Water-bodies in the Holocene*. 244 pp. Publishing House Nauka, Leningrad (in Russian).

Davydova, N. N., Arslanov, K. A., Khomutova, V. I., Krasnov, I. I., Malakhovsky, D. V., Saarnisto, M., Saksa, A. I. & Subetto, D. A. 1996: Late- and postglacial history of lakes of the Karelian Isthmus. *Hydrobiologia 322*, 199–204.

Dodd, J. P. & Sharp, Z. D. 2010: A laser fluorination method for oxygen isotope analysis of biogenic silica and a new oxygen isotope calibration of modern diatoms in freshwater environments. *Geochimica et Cosmochimica Acta 74*, 1381–1390.

Dolukhanov, P. M., Subetto, D. A., Arslanov, K., Davydova, N. N., Zaitseva, G. I., Djinoridze, E. N., Kuznetsov, D. D., Ludikova, A. V., Sapelko, T. V. & Savelieva, L. A. 2009: The Baltic Sea and Ladoga Lake transgressions and early human migrations in North-western Russia. *Quaternary International 203*, 33–51.

Gleser, S. I., Jouse, A. P., Makarova, I. V., Proshkina-Lavrenko, A. I. & Sheshukova-Poretzkaja, V. S. (eds.) 1974: *The Diatoms of the USSR (Fossil and Recent). Volume 1*. 403 pp. Publishing House Nauka, Leningrad (in Russian).

Gorlach, A., Hang, T. & Kalm, V. 2017: GIS-based reconstruction of Late Weichselian proglacial lakes in northwestern Russia and Belarus. *Boreas 46*, 486–502.

Gromig, R., Wagner, B., Wennrich, V., Fedorov, G., Savelieva, L., Lebas, E., Krastel, S., Brill, D., Andreev, A., Subetto, D. & Melles, M. in

press: Deglaciation history of Lake Ladoga (north-western Russia) based on varved sediments. _Boreas._

Heikkilä, M., Edwards, T. W. D., Seppä, H. & Sonninen, E. 2010: Sediment isotope tracers from Lake Saarikko, Finland, and implications for Holocene hydroclimatology. _Quaternary Science Reviews 29_, 2146–2160.

Holopainen, A.-L. & Letanskaya, G. I. 1999: Effects of nutrient load on species composition and productivity of phytoplankton in Lake Ladoga. _Boreal Environment Research 4_, 215–227.

IAEA/WMO 2018: _Global Network of Isotopes in Precipitation._ The GNIP Database. Available at: https://nucleus.iaea.org/wiser.

Jones, V. J., Leng, M. J., Solovieva, N., Sloane, H. J. & Tarasov, P. 2004: Holocene climate of the Kola Peninsula; evidence from the oxygen isotope record of diatom silica. _Quaternary Science Reviews 23_, 833–839.

Juillet-Leclerc, A. & Labeyrie, L. 1987: Temperature dependence of the oxygen isotopic fractionation between diatom silica and water. _Earth and Planetary Science Letters 84_, 69–74.

Karetnikov, S. G. & Naumenko, M. A. 2008: Recent trends in Lake Ladoga ice cover. _Hydrobiologia 599_, 41–48.

Karetnikov, S. G., Naumenko, M. A., Guzivatyi, V. V., Shimaraev, M. N. & Kuraev, A. V. 2016: Concordance of interannual variability in ice regime of Baikal and Lake Ladoga. _Geography and Natural Resources 37_, 135–143.

Kimstach, V., Meybeck, M. & Baroudy, E. (eds.) 1998: _A Water Quality Assessment of the Former Soviet Union._ 611 pp. E&FN Spon, London.

Koshechkin, B. I. & Ekman, I. M. 1993: Holocene transgressions of Lake Ladoga. _In_ Davydova, N. N. & Koshechkin, B. I. (eds.): _Evolution of Natural Environments and the Current State of the Geosystem of Lake Ladoga_, 49–60. Publishing House of the Russian Geographical Society, St. Petersburg (in Russian).

Kostrova, S. S., Meyer, H., Chaplign, B., Kossler, A., Bezrukova, E. V. & Tarasov, P. E. 2013: Holocene oxygen isotope record of diatoms from Lake Kotokel (southern Siberia, Russia) and its palaeoclimatic implications. _Quaternary International 290–291_, 21–34.

Kostrova, S. S., Meyer, H., Chaplign, B., Tarasov, P. E. & Bezrukova, E. V. 2014: The last glacial maximum and late glacial environmental and climate dynamics in the Baikal region inferred from an oxygen isotope record of lacustrine diatom silica. _Quaternary International 348_, 25–36.

Krammer, K. & Lange-Bertalot, H. 1986: Bacillariophyceae. _In_ Ettl, H., Gerloff, J., Heying, H. & Mollenhauer, D. (eds.): _Süßwasserflora von Mitteleuropa._ Band 2/1. 876 pp. Gustav Fischer Verlag, Stuttgart.

Krammer, K. & Lange-Bertalot, H. 1991: Bacillariophyceae. _In_ Ettl, H., Gerloff, J., Heying, H. & Mollenhauer, D. (eds.): _Süßwasserflora von Mitteleuropa._ Band 2/3. 576 pp. Gustav Fischer Verlag, Jena.

Kulkova, M. A., Gusentsova, T. M., Sapelko, T. V., Nesterov, E. M., Sorokin, P. E., Ludikova, A. V., Ryabchuk, D. V. & Markova, M. A. 2014: Geoarcheological investigations on the development of the Neva River delta (Gulf of Finland) during the Holocene. _Journal of Marine Sciences 129_, 19–34.

Labeyrie, L. D. 1974: New approach to surface seawater palaeotemperatures using $^{18}O/^{16}O$ ratios in silica of diatom frustules. _Nature 248_, 40–42.

Leng, M. J. & Barker, P. A. 2006: A review of the oxygen isotope composition of lacustrine diatom silica for palaeoclimate reconstruction. _Earth-Science Reviews 75_, 5–27.

Letanskaya, G. I. & Protopopova, E. V. 2012: The current state of phytoplankton in Lake Ladoga (2005–2009). _Inland Water Biology 4_, 17–24 (in Russian).

Ludikova, A. V. 2015: Diatom evidences for the mid-Holocene Lake Ladoga transgression. _Izvestiya GRO 147_, 38–51 (in Russian).

Lydolph, P. E. 1977: _Climates of the Soviet Union. World Survey of Climatology. Volume 7._ 443 pp. Elsevier Scientific Publishing Company, Amsterdam.

Mackay, A. W., Karabanov, E., Leng, M. J., Sloane, H. J., Morley, D. W., Panizzo, V. N., Khursevich, G. & Williams, D. 2008: Reconstructing hydrological variability in Lake Baikal during MIS 11: an application of oxygen isotope analysis of diatom silica. _Journal of Quaternary Science 23_, 365–374.

Mackay, A. W., Swann, G. E. A., Brewer, T. S., Leng, M. J., Morley, D. W., Piotrowska, N., Rioual, P. & White, D. 2011: A reassessment of

late glacial – Holocene diatom oxygen isotope record from Lake Baikal using a geochemical mass-balance approach. _Journal of Quaternary Science 26_, 627–634.

Mackay, A. W., Swann, G. E. A., Fagel, N., Fietz, S., Leng, M. J., Morley, D., Rioual, P. & Tarasov, P. 2013: Hydrological instability during the Last Interglacial in central Asia: a new diatom oxygen isotope record from Lake Baikal. _Quaternary Science Reviews 66_, 45–54.

Malakhovskiy, D. B., Arslanov, K., Gey, N. A. & Djinoridze, R. N. 1993: New data on the history of the Neva River formation. _In_ Davydova, N. N. & Koshechkin, B. I. (eds.): _Evolution of Natural Environments and the Current State of the Geosystem of Lake Ladoga_, 49–60. Publishing House of the Russian Geographical Society, St. Petersburg (in Russian).

Malm, J. & Jönsson, L. 1994: Water surface temperature characteristics and thermal bar evolution during spring in Lake Ladoga. _Remote Sensing of Environment 48_, 332–338.

Mätlik, O. & Post, P. 2008: Synoptic weather types that have caused heavy precipitation in Estonia in the period 1961–2005. _Estonian Journal of Engineering 14_, 195–208.

Meyer, H., Chaplign, B., Hoff, U., Nazarova, L. & Diekmann, B. 2015: Oxygen isotope composition of diatoms as Late Holocene climate proxy at Two-Yurts Lake, Central Kamchatka, Russia. _Global and Planetary Change 134_, 118–128.

Meyer, H., Schönicke, L., Wand, U., Hubberten, H.-W. & Friedrichsen, H. 2000: Isotope studies of hydrogen and oxygen in ground ice–experiences with the equilibration technique. _Isotopes in Environmental and Health Studies 36_, 133–149.

Morley, D. W., Leng, M. J., Mackay, A. W., Sloane, H. J., Rioual, P. & Batterbee, R. W. 2004: Cleaning of lake sediment samples for diatom oxygen isotope analysis. _Journal of Palaeolimnology 31_, 391–401.

Mortlock, R. D. & Froelich, P. N. 1989: A simple method for the rapid determination of biogenic opal in pelagic marine sediments. _Dee -Sea Research Part A 36_, 1415–1426.

Müller, P. J. & Schneider, R. 1993: An automated leaching method for the determination of opal in sediments and particulate matter. _Deep Sea Research Part I 40_, 425–444.

Muschitiello, F., Schwark, L., Wohlfarth, B., Sturm, C. & Hammarlund, D. 2013: New evidence of Holocene atmospheric circulation dynamics based on lake sediments from southern Sweden: a link to the Siberian High. _Quaternary Science Reviews 77_, 113–124.

Narancic, B., Pienitz, R., Chaplign, B., Meyer, H., Francus, P. & Guilbault, J.-P. 2016: Postglacial environmental succession of Nettilling Lake (Baffin Island, Canadian Arctic) inferred from biogeochemical and microfossil proxies. _Quaternary Science Reviews 147_, 391–405.

Nazarova, L., Subetto, D. A., Syrykh, L. S., Grekov, I. M. & Leontev, P. A. 2018: Reconstructions of paleoecological and paleoclimatic conditions of the Late Pleistocene and Holocene according to the results of chironomid analysis of sediments from Medvedevskoe Lake (Karelian Isthmus). _Doklady Earth Sciences 480_, 710–714.

Nosova, M. B., Novenko, E. Yu., Severova, E. E. & Volkova, O. A. 2018: Vegetation and climate changes within and around the Polistovo-Lovatskaya mire system (Pskov Oblast, north-western Russia) during the past 10,500 years. _Vegetation History and Archaeobotany._ https://doi.org/10.1007/s00334-018-0693-8.

Opel, T., Fritzsche, D. & Meyer, H. 2013: Eurasian Arctic climate over the past millennium as recorded in the Akademii Nauk ice core (Severnaya Zemlya). _Climate of the Past 9_, 2379–2389.

Rioual, P., Andrieu-Ponel, V., Rietti-Shati, M., Battarbee, R. W., de Beaulieu, L.-J., Cheddadi, R., Reille, M., Svobodova, H. & Shemesh, A. 2001: High-resolution record of climate stability in France during the last interglacial period. _Nature 413_, 293–296.

Rosqvist, G., Jonsson, C., Yam, R., Karlen, W. & Shemesh, A. 2004: Diatom oxygen isotopes in pro-glacial lake sediments from northern Sweden: a 5000 year record of atmospheric circulation. _Quaternary Science Reviews 23_, 851–859.

Round, F. E., Crawford, R. M. & Mann, D. G. 1990: _The Diatoms. Biology and Morphology of the Genera._ 747 pp. Cambridge University Press, Cambridge.

Rozanski, K., Araguás-Araguás, L. & Gonfiantini, R. 1993: Isotopic patterns in modern global precipitation. _In_ Swart, P. K., Lohmann,

K. C., McKenzie, J. & Savin, S. (eds.): *Climate Change in Continental Isotope Records*, 1–36. *Geophysical Monograph 78*. American Geophysical Union, Washington.

Rumyantsev, V. A. (ed.) 2015: *Lake Ladoga and the Coastal Remarkable Sights. Atlas*. 200 pp. Nestor-History, St. Petersburg (in Russian).

Rumyantsev, V. A. & Kondratyev, C. A. (eds.) 2013: *Ladoga*. 568 pp. Publishing House of the Institute of Limnology RAS, St. Petersburg (in Russian).

Rumyantsev, V. A., Drabkova, V. G. & Izmailova, A. V. 2015: *Lakes of the European Part of Russia*. 392 pp. Lema, St. Petersburg (in Russian).

Rumyantsev, V. A., Rybakin, V. N. & Tokarev, I. V. 2017: Distribution of waters of inflows and underground waters in Lake Ladoga according to isotope indicators. *Proceedings of the Russian State Hydrometeorological University 48*, 94–109 (in Russian).

Saarnisto, M. 2012: Late Holocene land uplift/neotectonics on the island of Valamo (Valaam), Lake Ladoga, NW Russia. *Quaternary International 260*, 143–152.

Saarnisto, M. & Grönlund, T. 1996: Shoreline displacement of Lake Ladoga – new data from Kilpolansaari. *Hydrobiologia 322*, 205–215.

Savelieva, L. A., Andreev, A. A., Gromig, R., Subetto, D. A., Fedorov, G. B., Wennrich, V., Wagner, B. & Melles, M. 2019: Vegetation and climate changes during the Lateglacial and Holocene inferred from the Lake Ladoga pollen record. *Boreas*. https://doi.org/10.1111/bor.12376.

Seppä, H., Bjune, A. E., Telford, R. J., Birks, H. J. B. & Veski, S. 2009: Last nine-thousand years of temperature variability in Northern Europe. *Climate of the Past 5*, 523–535.

Shabalina, M. A., Viventsova, E. A. & Voronov, A. N. 2004: Estimation of groundwater flow to the Ladoga Lake. *Vestnik of Saint Petersburg University, Series 7. Geology, Geography 3*, 82–83.

Shelekhova, T. S. & Lavrova, N. B. 2011: Karelia's lake sediments: palaeoecological and palaeoclimatic reconstructions. Geology of Karelia from the Archaean to the present. *Proceedings of the All-Russian Conference convened to celebrate the 50th anniversary of the founding of the Institute of Geology, Karelian Research Centre, RAS*. Institute of Geology, KarRC, RAS, Petrozavodsk, 204–212 (in Russian).

Shemesh, A., Charles, C. D. & Fairbanks, R. G. 1992: Oxygen isotopes in biogenic silica: global changes in ocean temperature and isotopic composition. *Science 256*, 1434–1436.

Shemesh, A., Rosqvist, G., Rietti-Shati, M., Rubensdotter, L., Bigler, C., Yam, R. & Karlen, W. 2001: Holocene climatic change in Swedish Lapland inferred from an oxygen-isotope record of lacustrine biogenic silica. *Holocene 11*, 447–454.

Shver, T. A., Altykis, E. V. & Evteeva, L. S. (eds.) 1982: *Climate of Leningrad*. 253 pp. Gidrometeoizdat, Leningrad (in Russian).

Stansell, N. D., Klein, E. S., Finkenbinder, M. S., Fortney, C. S., Dodd, J. P., Terasmaa, J. & Nelson, D. B. 2017: A stable isotope record of Holocene precipitation dynamics in the Baltic region from Lake Nuudsaku, Estonia. *Quaternary Science Reviews 175*, 73–84.

Subetto, D. A. 2007: The history of Ladoga Lake forming and of its connection to the Baltic Sea. *Terra Humana 1*, 111–120 (in Russian).

Subetto, D. A. 2009: *Lake Sediments: Paleolimnological Reconstructions*. 343 pp. Publishing House of Herzen State Pedagogical University of Russia, Moscow (in Russian).

Subetto, D. A., Davydova, N. N. & Rybalko, A. E. 1998: Contribution to the lithostratigraphy and history of Lake Ladoga. *Palaeogeography, Palaeoclimatology, Palaeoecology 140*, 113–119.

Subetto, D. A., Nazarova, L. B., Pestryakova, L. A., Syrykh, L. S., Andronikov, A. V., Biskaborn, B., Diekmann, B., Kuznetsov, D. D., Sapelko, T. V. & Grekov, I. M. 2017: Paleolimnological studies in Russian Northern Eurasia: a review. *Contemporary Problems of Ecology 10*, 327–335.

Subetto, D. A., Wohlfarth, B., Davydova, N. N., Sapelko, T. V., Björkman, L., Solovieva, N., Wastegård, S., Possnert, G. & Khomutova, V. I. 2002: Climate and environment on the Karelian Isthmus, northwestern Russia, 13 000-9000 cal. yrs BP. *Boreas 31*, 1–19.

Svensson, A., Andersen, K. K., Bigler, M., Clausen, H. B., Dahl-Jensen, D., Davies, S. M., Johnsen, S. J., Muscheler, R., Parrenin, F., Rasmussen, S. O., Röthlisberger, R., Seierstad, I., Steffensen, J. P. & Vinther, B. M. 2008: A 60 000 year Greenland stratigraphic ice core chronology. *Climate of the Past 4*, 47–57.

Swann, G. E. A. & Leng, M. J. 2009: A review of diatom $\delta^{18}O$ in palaeoceanography. *Quaternary Science Reviews 28*, 384–398.

Swann, G. E. A., Leng, M. J., Juschus, O., Melles, M., Brigham-Grette, J. & Sloane, H. J. 2010: A combined oxygen and silicon diatom isotope record of Late Quaternary change in Lake El'gygytgyn, North East Siberia. *Quaternary Science Reviews 29*, 774–786.

Tikhomirov, A. I. 1982: *The Thermics of Large Lakes*. 232 pp. Publishing House Nauka, Leningrad (in Russian).

Timofeev, V. I., Dolukhanov, P. M., Nosov, E. N., Arslanov, K., Subetto, D. A. & Zaitseva, G. I. 2005: Evolution of the waterways and early human migrations in the northern-eastern Baltic area. *Geochronometria. 24*, 81–85.

Virtasalo, J. J., Ryabchuk, D., Kotilainena, A. T., Zhamoida, V., Grigoriev, A., Sivkov, V. & Dorokhova, E. 2014: Middle Holocene to present sedimentary environment in the easternmost Gulf of Finland (Baltic Sea) and the birth of the Neva River. *Marine Geology 350*, 84–96.

Wanner, H., Beer, J., Bütikofer, J., Crowley, T. J., Cubasch, U., Flückiger, J., Goosse, H., Grosjean, M., Joos, F., Kaplan, J. O., Küttel, M., Müller, S. A., Prentice, I. C., Solomina, O., Stocker, T. F., Tarasov, P., Wagner, M. & Widmann, M. 2008: Mid- to late Holocene climate change: an overview. *Quaternary Science Reviews 27*, 1791–1828.

Wohlfarth, B., Lacourse, T., Bennike, O., Subetto, D., Tarasov, P., Demidov, I., Filimonova, L. & Sapelko, T. 2007: Climatic and environmental changes in north-western Russia between 15,000 and 8000 cal yr BP: a review. *Quaternary Science Reviews 26*, 1871–1883.

Wolfe, B. B., Edwards, T. W. D., Jiang, H., MacDonald, G. M., Gervais, B. R. & Snyder, J. A. 2003: Effect of varying oceanicity on early- to mid-Holocene palaeohydrology, Kola Peninsula, Russia: isotopic evidence from treeline lakes. *Holocene 13*, 153–160.

Yakovlev, S. A. 1925: *Deposits and Relief of Leningrad and its Surroundings*. 476 pp. 2nd Typography Transpechat NKPS named after comrade Lokhankova, Leningrad (in Russian).