Hydrobiologia (2023) 850:1669–1698
https://doi.org/10.1007/s10750-023-05177-8

PRIMARY RESEARCH PAPER

Sediment records of lake eutrophication and oligotrophication under the influence of human activity and climate warming in the Urals metallurgical region (Russia)

Anna Maslennikova · Valery Udachin · Vladimir Deryagin · Dmitry Artemyev · Ksenya Filippova · Vasiliy Gulakov · Nikolai Udachin · Pavel Aminov

Received: 24 May 2022 / Revised: 9 February 2023 / Accepted: 15 February 2023 / Published online: 4 March 2023

Abstract The lakes of mining and metallurgical regions are modified not only by climate warming, but also by diverse human impacts. The primary hypothesis of this study was that the response of lakes in the Ural metallurgical region to global warming and human land use was mediated by loading of potentially toxic elements (PTEs) and acidification. To test this hypothesis, we carried out a diatom and geochemical analysis of sediments accumulated through the past 800–1200 years and a hydrochemical analysis of four lakes. All lakes were characterized by shifts in diatom assemblages and changes in diatom indices and planktonic diatoms in the nineteenth and the twentieth centuries. Despite contamination by PTEs, lakes Turgoyak, Tavatui, and Syrytkul experienced an increase in trophic state and in planktonic diatoms. Oligotrophication was inferred only in the record of Lake Ufimskoe which was most contaminated by PTEs, but marked by the least other human impact. We conclude that diatom assemblages in the Middle and Southern Urals lakes primarily reflect the influence of local human activity, rather than the global warming. Industry-related acidification and higher PTEs altered lake development only under the condition of weak influence of other human activities.

Keywords Lake sediments · Eutrophication · Diatoms · Potentially toxic elements · Paleolimnological reconstruction · Urals

Introduction

Lakes are an important part of water resources in the forest zone of the Eastern Slope of the Urals. They are a source of drinking and technical water to cities and are actively used for industrial enterprises, fisheries, and recreation. According to a number of studies, Southern and Middle Ural lakes are rapidly degrading, possibly due to climate change and human impacts (Gavrilkina et al., 1998; Rogozin, 1998; Bayanov, 2012; Isakova et al., 2015).

Climate warming has been observed in the studied region since the middle of the nineteenth century. The most pronounced increase in average

Handling editor: Jasmine Saros

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s10750-023-05177-8.

A. Maslennikova (✉) · V. Udachin · D. Artemyev · K. Filippova · V. Gulakov · N. Udachin · P. Aminov
South Urals Federal Research Center of Mineralogy and Geoecology of the Ural Branch of the Russian Academy of Sciences, Miass, Chelyabinsk Region, Russia
e-mail: adenophora@inbox.ru

V. Udachin
South Ural State University, Chelyabinsk, Russia

V. Deryagin
South Ural State Humanitarian Pedagogical University, Chelyabinsk, Russia

annual temperature began in the twentieth century (Pogoda i klimat, 2022, http://www.pogodaiklimat.ru/history/28440.htm). Climate warming can cause alteration of lake stratification patterns, extension of the growing season and open water period, changes in light and nutrient availability, and habitat alterations that lead to biotic composition shifts (Magnuson et al., 2000; Smol et al., 2005; Winder & Sommer, 2012; O'Reilly et al., 2015; Rühland et al., 2015; Reavie et al., 2017). Both direct and indirect climate impacts may be superimposed on the influence of local human activities. For instance, changes in hydrological lake conditions, wastewater discharge, deforestation, and active recreation due to population growth and urbanization contribute to the rapid eutrophication of lake ecosystems (Rogozin, 1998; Bayanov, 2012; Isakova et al., 2015). In addition, the Ural region has long been the most important mining and metallurgical region in Russia. For the last three centuries, more than 300 metallurgical plants have been built there (Alekseev, 2001). Industrial construction and related population growth reached a maximum in the twentieth century. Industrial emissions may cause lake acidification and an increase in potentially toxic elements (PTEs) in water and lake sediments. These factors result in changes in the phytoplankton structure, emergence of species tolerant to pollution (Ruggiu et al., 1998; Cattaneo et al., 2004; Salonen et al., 2006; Tuovinen et al., 2012; Morin et al., 2014; Snit'ko & Snit'ko, 2015, 2019; Sivarajah et al., 2019), reduction in planktonic species (Salonen et al., 2006; Tuovinen et al., 2012; Thienpont et al., 2016), and changes in lake trophic state (Denisov et al., 2020). It is necessary to specify the lake ecosystem response to human and natural impacts to provide effective management and forecasting of lake development in the metallurgical region under the global warming. Diatoms are important bioindicators characterized by a significant sensitivity to changes in hydrochemical parameters, particularly to nutrients, PTEs, and water pH. The study of diatom assemblages corresponding to different lake developmental periods makes it possible to assess lake ecosystem changes under the influence of different human and natural factors.

Paleolimnological studies are very limited in the Ural region. Sedimentary diatom assemblages from several Northern Ural lakes show distinct changes involving planktonic diatoms in the twentieth century, likely due to a temperature increase in June and September that extended the duration of the ice-free season (Solovieva et al., 2008). Paleolimnological reconstructions based on diatom analysis of sediment cores from the Polar Urals revealed changes in lakes over the past 100–150 years that were related to climate warming (Palagushkina et al., 2019). Changes in diatom assemblages of Lake Bol'shoe Miassovo (Southern Urals) were interpreted as responses to global climate warming (Rogozin et al., 2017). The study of Holocene sediments of small lakes in the Southern Urals (Maslennikova & Udachin, 2017) showed changes in diatom assemblages likely related to dam construction and acidification related to the Karabash copper smelter. However, the limited number of analyzed samples for the period prior to these human impacts prevented assessment of the possible role of natural factors in the lakes' changes. In the study of Holocene sediments from the larger and deeper Lake Tavatui (Middle Urals), Maslennikova (2022) concluded that, since the mid-nineteenth century, lake water phosphorus content changed in accordance with the main trend of increasing annual temperature. Meanwhile, the impact of changes in concentrations of PTEs, as well as the possible acidification of Lake Tavatui, located in the Middle Urals mining and metallurgical region, was not assessed. In a previous study of Lake Turgoyak, which is one of the deepest lakes of the Southern Urals, diatom analysis of several samples from sedimentary horizons accumulated over the last 12 cal ka BP revealed that the lake ecosystem repeatedly changed over this time (Maslennikova et al., 2018). The upper part of the sediment during the Anthropocene has not been studied yet.

We hypothesize that the response of shallow and deep lakes of the Ural metallurgical region to climate warming and local human activities is substantially changed by industry-related acidification and contamination by PTEs. To test this hypothesis, we used the following approach: (1) assess and compare the ecosystem state and water quality in present-day lakes subject to different degree and type of human impacts; (2) assess the ecosystem changes of Ural metallurgical region lakes over the past 1000 years; and (3) identify the main factors that caused changes in the Ural lake ecosystems.

Regional setting

We studied four lakes (Ufimskoe, Syrytkul, Tavatui, and Turgoyak) in the Ural mountain-forest zone, differing in morphometric (Table 1) and hydrochemical parameters (Table 2), human impact type and degree (Fig. 1).

The Urals became a mining and metallurgy center in the eighteenth century. In the first half of the eighteenth century, the Middle Urals was an object of intensive mining development. In the second half of the eighteenth century, the Southern Urals turned into one of the leading mining industry centers in Russia. The Middle Urals was an area of concentration of ferrous metallurgy plants. The Southern Urals mainly specialized in the production of copper. In the eighteenth century, copper smelting plants of the region produced more than 80 kt of copper which accounted for 67.5% of the copper smelting industry of Russia (Kulbahtin, 2008). Many plants were closed after 1861 AD. A new period of industrial activity beginning in the twentieth century was interrupted by the October Revolution in 1917 AD. Many plants started working again after 1925 AD. The largest industrial growth in the Urals occurred following industrialization (1928–1941 AD) and World War II (1939–1945). A reduction in industry was observed in the 1990s. The new growth of industry began only at the beginning of the twenty-first century. At present, many ferrous and non-ferrous metallurgy plants are located in the Middle Urals. The Sredneuralsk and Kirovgrad plants founded in 1931 AD and 1914 AD are the closest copper smelters to Lake Tavatui (30 km). The Karabash copper smelter, which exerted the greatest impact on natural ecosystems of the Southern Urals, has been operated since 1910 AD (Udachin et al., 2014). After a brief hiatus (1918–1925 AD), the copper smelter continued to increase the smelting of copper ore and coarse copper until 1989 AD. In the period between 1989 AD and AD 1998, the smelter was stopped due to substantial ecological problems (Alekseev, 2001). At the beginning of the twenty-first century, production modernization made it possible to reduce sulfur dioxide and PTEs emissions. Lakes Ufimskoe, Syrytkul, and Turgoyak are located 7, 12, and 36 km from the Karabash copper smelter, respectively.

Population data covering a significant period of time is available only for large cities of the Southern and Middle Urals. Since 1723 AD, the population of Yekaterinburg (Middle Urals) increased from four thousand to 1493 thousand people. Since 1739 AD, the population of Chelyabinsk (Southern Urals) increased from one thousand to 1200 thousands of people. The fastest population growth was observed since the 1930s. The decline in the population in the 1990s was reversed by a steady increase since the twenty-first century (Kolotova et al., 2009).

Table 1 Location and morphometry of studied Urals lakes

Parameter	Ufimskoe	Tavatui	Syrytkul	Turgoyak
Core latitude and longitude	55°31′20.61″N, 60°07′08.50″E	57°13′05.85″N, 60°17′98.89″E	55°19′733″N, 60°15′233″E	55°16′817″N, 60°05′481″E
Altitude, m a.s.l	472	259	358	320
Surface area, km^2	0.87	21.2	0.6	26.4
Maximum water depth, m	3	9	6.5	32.5
Average water depth, m	1.1	5	3.7	19
Water volume, mln m^3	1	124	2.2	507
Water depth at core site, m	3	7.5	5.2	19
Catchment area, km^2	4.9	104	2.9	76
Catchment area/Lacustrine surface area	5.6	4.9	4.8	2.9
Lacustrine surface area/Water volume	0.9	0.2	0.3	0.1
Dates of hydrological regulation	–	1762 AD, 1914 AD	Since 1871–1919 AD	1960–2007 AD

Table 2 Hydrochemical parameters of studied lakes

Parameter	Code	Unit	Ufimskoe		Tavatui		Syrytkul		Turgoyak	
			Mean	STDEV	Mean	STDEV	Mean	STDEV	Mean	STDEV
pH			7.0	0.1	7.5	0.3	7.2	0.1	7.6	0.4
Electrical conductivity	EC	µS cm^{-1}	65.6	7.3	124.9	21.8	172.0	8.7	125.5	5.9
Total water hardness	TWH	mmol L^{-1}	0.6	0.1	1.4	0.4	1.9	0.2	1.4	0.0
Alkalinity	Alk	mmol L^{-1}	0.21	0.02	1.08	0.35	1.56	0.02	0.88	0.08
Color of water	Color	Cr-Co scale	28.8	6.4	20.9	5.0	29.1	2.5	8.8	0.3
Permanganate value	Pv	mgO L^{-1}	5.8	0.4	7.1	0.6	9.2	0.8	2.7	0.0
Salinity	Salinity	mg L^{-1}	53	6	133	27	165	4	127	3
Bicarbonate	HCO_3^-	µ eq L^{-1}	212	20	1080	354	1558	16	880	80
Chloride	Cl^-	µ eq L^{-1}	58	11	216	61	112	19	161	14
Sulfate	SO_4^{2-}	µ eq L^{-1}	468	142	531	64	452	19	729	177
Calcium	Ca^{2+}	µ eq L^{-1}	404	7	918	235	1277	58	1035	25
Magnesium	Mg^{2+}	µ eq L^{-1}	211	36	516	116	689	2	415	25
Potassium	K^+	µ eq L^{-1}	42	8	81	33	77	4	54	0.1
Sodium	Na^+	µ eq L^{-1}	145	26	250	47	281	15	219	18
Phosphate phosphorus	PO_4-P	µg L^{-1}	3	2	2	1	19	31	1	1
Total phosphorus	TP	µg L^{-1}	15	4	35	6	50	4	10	6
Nitrite nitrogen	NO_2-N	µg L^{-1}	2	0.2	5	6	3	0.02	2	0.08
Nitrate nitrogen	NO_3-N	µg L^{-1}	23	12	36	28	77	30	16	0.0
Ammonia nitrogen	NH_4-N	µg L^{-1}	125	96	44	2	91	84	43	0
Total nitrogen	TN	µg L^{-1}	503	116	617	161	1520	–	327	49
Total carbon	TC	µg L^{-1}	9643	1613	20,660	6037	43,730	–	13,993	1539
Total organic carbon	TOC	µg L^{-1}	7883	1438	11,050	1578	25,160	–	5693	994
Secchi disk	SD	m	2.6	0.06	2	0.7	1.9	0.5	10	0
TN/TP			33	11	18	6	30	10	33	11

Mean is an average value based on three water samples collected in spring, summer, and autumn

STDEV is a standard deviation

Lakes Turgoyak and Tavatui are under a significant recreation pressure and are partially used for water supply to the cities. Lake Syrytkul is located within the Ilmensky State Reserve. All lakes, except for Ufimskoe, have been subject to flow regulation activities. The level of Lake Tavatui rose by 2–3 m, with an increase in surface area, after dam construction on the Neiva River in 1762. Then in 1914–1915, an artificial passage was made to the east of the old channel, connecting Lake Tavatui with Verkh-Neivinsky pond (Lozhkin, 1971). The dam construction in Lake Syrytkul limited its flow and substantially changed its parameters (Deryagin et al., 2011). According to old maps (Strel'bickij, 1871; 1919) the dam was constructed in the period between 1871 and 1919 AD.). Since the mid-twentieth century, Lake Turgoyak water was actively withdrawn to supply Miass, and its flow was regulated from 1960 to 2007 (Gavrilkina et al., 1998).

Materials and methods

Field methods

The sediment cores were collected with a Molchanov's bathometer (for lakes Ufimskoe, Syrytkul, and Tavatui) and a Stratometer C1 (for Lake Turgoyak) from mean or maximum lake water depths (Table 1). The core sections were extruded

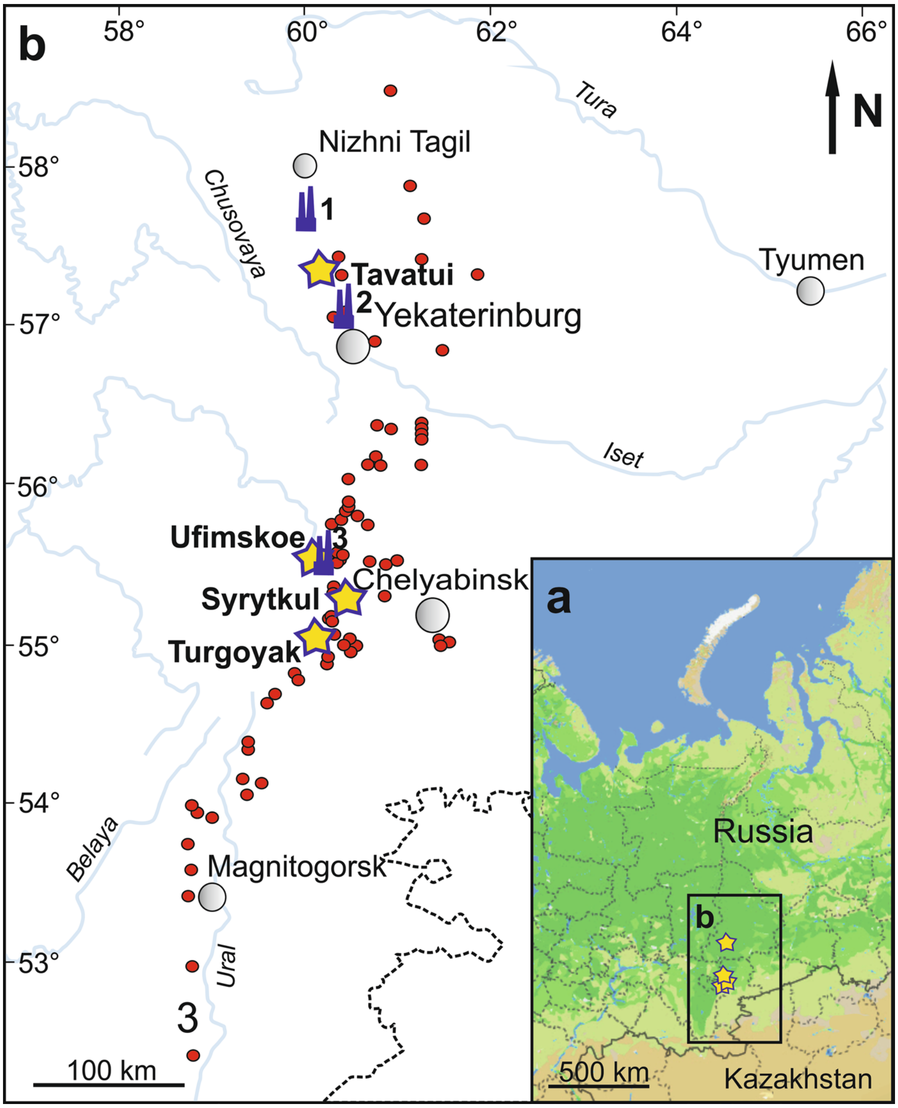

Fig. 1 Location of the study area in Russia (a), Urals lakes calibration dataset sampling sites (red circles), lake cores (yellow stars) and copper smelters of Kirovgrad (1), Sredneuralsk (2), and Karabash (3) (color figure online)

and sliced in the field. All samples were stored in plastic bags at 4 °C in the dark. Water samples were collected by hand below the surface (0.3–0.5 m depth) no less than three times during the period from May to September.

Laboratory analyses of water and sediments

Trace element concentrations in the lake sediments were determined by inductively coupled plasma-source mass spectrometry (ICP–MS) using Perkin Elmer ELAN 6000 in the Ural Electrochemical Integrated Plant (for Lake Tavatui sediments) and Agilent 7700 (for lakes Ufimskoe and Syrytkul). Trace elements for Lake Turgoyak were analyzed by laser ablation mass spectrometry using Agilent 7700×ICP-MS coupled to a New Wave Research UP-213 nm laser ablation system owned by South Urals Federal Research Center of Mineralogy and Geoecology of the Ural Branch of the Russian Academy of Sciences. The methods were described in detail by Maslennikova et al. (2020).

Chemical analysis of water was carried out in the Laboratory of the South Urals Research Center of Mineralogy and Geoecology in accordance with standard hydrochemical analysis methods also listed and briefly described in Maslennikova (2020). Total nitrogen, total carbon and total inorganic carbon were determined using a Topaz NC analyser. The operation principle of Topaz NC is based on high-temperature thermal catalytic oxidation of nitrogen and carbon compounds contained in a water sample, followed by detection of element oxides and calculation of the initial content of all forms of nitrogen and carbon compounds in the sample. Trace elements concentrations in the lake water were determined by ICP-MS using Agilent 7700 in South Urals Federal Research Center of Mineralogy and Geoecology of the Ural Branch of the Russian Academy of Sciences.

Chronology

Age-depth models were developed based on ^{210}Pb, ^{137}Cs and AMS^{14}C measurements. AMS ^{14}C measurements of the considered Urals lakes were presented in previous publications (Maslennikova et al., 2016, 2020, 2022). Additionally, two samples of organic carbon-rich bulk sediments collected from the Turgoyak and Tavatui cores were dated by AMS ^{14}C at the Center for Collective Use "Laboratory of Radiocarbon Dating and Electron Microscopy," Institute of Geography, Russian Academy of Sciences, and at the Centre for Applied Isotope Studies, University of Georgia, USA. All radiocarbon dates were calibrated using the IntCal20 calibration curve (Reimer et al., 2020). Activities of ^{210}Pb for lakes Syrytkul, Turgoyak, and Tavatui were measured with application of Ortec alpha spectrometry system. Activity of ^{226}Ra used to establish supported ^{210}Pb activity, as well as activity of ^{210}Pb for Lake Ufimskoe was determined by gamma spectrometry with application of hyper-pure planar germanium detector. Activity of ^{137}Cs was estimated for lakes Ufimskoe and Syrytkul. Unsupported ^{210}Pb activity was determined by subtracting supported activity from the total activity, with supported ^{210}Pb estimated from the asymptotic activity at depth (for Lake Turgoyak) or ^{226}Ra activity (for lakes Syrytkul, Turgoyak, and Tavatui). Sediment age/depth relationships for upper sediments were calculated using the constant rate of supply (CRS) and constant initial concentration (CIC) model (Appleby & Oldfield, 1978). The chronological information obtained based on ^{210}Pb, ^{137}Cs and AMS ^{14}C measurements was integrated and modeled using Bacon (version 2.2) (Blaauw & Christen, 2011) (Supplementary Table S1, Fig. S1). Results of ^{210}Pb, ^{137}Cs, and AMS ^{14}C measurements applied to age-depth models are reported in the supplementary material (Tables S2, S3).

Diatom analysis

For diatom analysis, samples were treated with nitric and perchloric acids to remove organic matter. Slides were mounted using an Elyashev's mountant ($n = 1.67–1.68$) (Proshkina-Lavrenko, 1974). A Mikmed 6 var. 7 microscope using bright-field oil immersion optics at 1000 × magnification was used counting. Measurements for taxonomic identification were made using ToupView 3.7 software, and photomicrographs were obtained with a ToupCAM UCMOS14000KPA digital camera. At least 500 valves were counted per sample (diatom total) to determine the relative abundances (percentage) of individual taxa in the assemblages. Diatom identification was based on Krammer & Lange-Bertalot (1986, 1988, 1991a, b), Kulikovskiy et al. (2016), Lange-Bertalot et al. (2017), and Reichardt (2018). The diatom nomenclature was updated using the online Algaebase catalogue (Guiry and Guiry, 2022).

Modern lake trophic state and nutrients enrichment assessment

The trophic state index (TSI) was used to assess the current trophic state of lakes based on the hydrochemical data. Average concentrations of total phosphorus (TP), total nitrogen (TN), and total organic carbon (TOC) as well as Secchi disk depth (SD) were used as trophic state indicators. A value of $TSI < 40$ indicates oligotrophic conditions, with mesotrophic from 40 to 50, eutrophic from 50 to 70, and hypertrophic > 70. TSI values were calculated by the formulae of Carlson (1977), Kratzer & Brezonic (1981), and Dunalska (2011).

Evaluation of lake water contamination in potential toxic elements

Water pollution by PTEs was assessed based on Criterion Cumulative Unit (CCU) (Clements et al., 2000), which is defined as:

$$CCU = Concentration\ of\ pollutant / Criterion\ value\ for\ pollutant$$

.

The criterion values for pollutants represent the statutory fisheries water quality standards in force in the Russian Federation (Normativy kachestva, 2016 with changes in 2018, 2020). RUC (Rebasamiento del Umbral de Contaminación or Pollution Threshold Overshoot) was applied to unify the combined effect of all pollutants in one metric (Fernández et al., 2018). RUC was calculated from CCU through the following mathematical expression: $RUC = \log 2\left(\sum CCU\right)$.

For the correct calculation of RUC, CCU values from 0 to 0.75 were set equal to 0. Unpolluted sites have RUC = 0, whereas sites that are polluted or at high risk of being polluted with one or more PTEs have RUC > 0 (Fernández et al., 2018).

Evaluation of lake sediment contamination by potentially toxic elements

The enrichment factor (EF) was utilized for assessment of PTE contamination levels in lake sediments. EF values were calculated for both pre-industrial and industrial lake sediments using the following formula: $EF = (Xs/Es)/(Xr/Er)$, where (Xs/Es) is the ratio of the element of interest (X) to the reference element (E) for the studied samples, and (Xr/Er) is the ratio of the element of interest to the reference element for the reference sediments. We used lithium as the reference element (Loring, 1991). For reference sediments, we used sediments of the same type, but accumulated in the pre-industrial time in the same lake (Chassiot et al., 2019). We did not use several samples between industrial and pre-industrial period for calculation of industrial and reference values due to possible diagenetic migration of PTEs. Five categories were used for assessment based on EF: none-to-slight enrichment (<2), moderate (2–5), severe (5–20), very severe (20–40), extremely severe (>40) (Sutherland, 2000). The enrichment index (EI) was calculated by analogy with the pollution load index (PLI) (Tomlinson et al., 1980) to compare the degree of PTE enrichment in sediments of different lakes.

$PLI = \sqrt[n]{CF1 \times CF2 \ldots \times CFn}$, where CF is the contamination factor obtained by calculating each potentially toxic element concentration and its background value and n is the quantity of PTEs. However, instead of the contamination factor, we used the enrichment factor in the formula to consider terrigenous dilution of sediments:

$$EI = \sqrt[n]{EF1 \times EF2 \ldots \times EFn}$$

Reconstructions of lake ecosystem changes

Reconstructions are based on the analysis of diatom flora shifts and changes in diatom ecological groups.

To understand the general trends of diatom flora shifts, a principal component analysis (PCA) was applied to the full diatom data of the four study lakes. Indicator species with known ecological preferences were used for qualitative reconstructions. Saprobity and trophic state were also evaluated based on the ecological groups of Van Dam et al. (1994).

Paleolimnological reconstructions based on diatom indices of water quality

Diatom indices of water quality were used to evaluate the history of organic pollution and eutrophication over the last 800–1200 years. The diatom analysis raw counts were entered into Omnidia version 6.1.4 for ecological analysis and calculation of 23 water quality diatom indices (Lecointe et al., 1993). Several pH indices were also calculated in Omnidia based on the models of Andrén & Jarlman (2009), Renberg & Hellberg (1982), Huttunen & Turkia (1990), and Håkansson (1992). Firstly, we determined which of diatom indices presented in Omnidia software met the condition of the availability of ecological information for at least 60% of the assemblage species and that these species comprised 60% of the assemblage in each studied lake. Then, we tested remaining diatom-based indices to determine the most reliable ones for reconstruction of pH, water quality, and trophic status for Urals lakes. Specifically, we used a modern lake database with diatom and hydrochemical data to evaluate how well each index was correlated to hydrochemical variables. The applied lake database contains the data on hydrochemical parameters and diatoms of 73 lakes of the Urals (Maslennikova, 2020). We performed correlation analysis between individual diatom indices and hydrochemical variables with application of Statistica v. 10.0 software. Hydrochemical parameters (except for pH) were log-transformed before the correlation analysis. Pearson correlation coefficients (r) as well as references for diatom indices are presented in the supplementary material (Table S4). Reconstructions of nutrient status were carried out using only the indices with a moderate or strong correlation ($r > 0.5$) with nutrient variables (TP, TN, TOC, Pv, Color, N-NO3, P-PO4, N-NH4). To facilitate comparison between indices, all water quality indices presented in Omnidia version 6.1.4 were transformed to the scale from 1 to 20. A decrease in index value indicates eutrophication and degradation in water quality. We also used original index values, if needed, with an appropriate explanation in the text. The pH indices based on the models of Andrén & Jarlman (2009), Renberg & Hellberg (1982), Huttunen & Turkia (1990), and Håkansson (1992) were used only if their values had moderate or strong correlation with measured pH of the 73 Urals lakes.

Diatom-based inference models for electrical conductivity (EC) and total phosphorus reconstructions

For electrical conductivity reconstructions, a transfer function developed using a 72-lake regional diatom dataset was applied (Maslennikova, 2020). For total phosphorus reconstructions, two TP diatom datasets were applied: a combined TP diatom dataset from the European Diatom Database Initiative (EDDI) (Lotter, 1989; Bennion, 1994; Wunsam & Schmidt, 1995; Bennion et al., 1996a, b; Rioual, 2000) and a regional Urals lakes dataset (Maslennikova, 2020). Diatom-based inference models were developed by simple weighted averaging (WA) and weighted averaging partial least squares (WA–PLS) methods using log-transformed species relative abundance data (ter Braak & Juggins, 1993; Birks, 1998). The performance of all transfer functions was evaluated by mean square error of prediction, as estimated by bootstrapping ($\mathrm{RMSEP_{boot}}$) and associated model statistics such as average bias, maximum bias, and coefficient of determination (r^2_{boot}) between predicted and observed values (Birks et al., 1990). Transfer functions and reconstructions of EC and TP were developed using C2 software (Juggins, 2007).

Assessment of reliability of EC, TP and diatom indices reconstructions

For assessment of reliability of EC and TP reconstructions, the modern analogue technique (MAT) (Laird et al., 1998; Birks, 1998), which evaluates the similarity of modern diatom assemblages to core assemblages, was used. The analysis of ecological groups and the calculation of indices for paleolimnological reconstructions were carried out only if the ecological information was available for at least 60% of the assemblage species, and these species comprised at least 60% of the assemblage.

The extent to which EC, TP, or diatom indices tracked the main directions of variation in the fossil diatom assemblages was assessed a) by calculation of correlation between DI–EC, DI–TP, pH indices values in the core to the PCA axis– 1 and – 2 scores of the fossil diatom assemblage; b) by calculation of the λ_R/λ_P ratio where λ_R is the eigenvalue of the first axis of a redundancy analysis (RDA) of the fossil diatom assemblage constrained to the diatom-inferred parameter, and λ_P is the eigenvalue of the first axis of a principal component analysis of the same down-core diatom assemblage (Juggins, 2013; Cumming et al., 2015).

Detection of lake ecosystem shift drivers

To detect influence of different factors on lakes ecosystems, we used the historical data on industry development and local land use activity. In addition, RDAs with PTEs concentrations, enrichment factors, enrichment index, climatic parameters (annual mean temperature (AMT), annual precipitation (AP)), and population as explanatory variables were applied for detection of the relationship between diatom assemblages and underlying driving forces. Climatic parameters were obtained from meteorological archives containing data for the Middle Urals since 1832 AD (http://www.pogodaiklimat.ru/history/28440.htm) and the Southern Urals since 1837 AD (http://www.pogodaiklimat.ru/history/28630.htm). Population data were obtained for the biggest city of the Southern Urals (Chelyabinsk) since 1739 AD and for the biggest city of the Middle Urals (Yekaterinburg) since 1732 AD (Kolotova et al., 2009). To assess whether the variable of interest explained a unique and significant fraction of variance in the diatom species assemblages, an RDA was run for each variable individually and with other significant variables as conditional covariables. All ordinations were implemented in CANOCO 4.5. (ter Braak & Smilauer, 2002).

Results

Chronology

The Lake Tavatui core covered approximately 1200 years of sediment accumulation (Supplementary Table S1). Lake Tavatui ^{210}Pb ages calculated using the CRS and CIC models were in good agreement with each other until the depth of 14 cm. This could be associated with sediment compaction with depth, which did not take into account in CIC model. Sediment accumulation rate (SAR) for upper 18 cm calculated using CRS model varied between 0.15 and 0.33 cm/year. Mean sediment accumulation rate assessed with application of CIC model was 0.26 ± 0.04 cm/year (Supplementary Table S2). The sedimentation rate at the bottom of the core was ten times less (0.03 cm/year).

The Lake Turgoyak sediment core spanned more than the past millennia. For Lake Turgoyak, sedimentary ^{210}Pb unsupported activity reached background concentrations (supported ^{210}Pb) after the top 6 cm of the sediment core (Supplementary Table S2). Background concentration calculated based on ^{210}Pb activity from 6 to 24 cm (67 Bq/kg) was in accordance with the results for another core taken in 2021 AD (68 Bq/kg) and ^{226} Ra activity determined for Lake Turgoyak sediment core taken in 2014 AD (55–72 Bq/kg) (unpublished data of V.N. Udachin). SAR estimated by CRS model was 0.051 ± 0.014 cm/year and by CIC model was 0.058 ± 0.017 cm/year. For the bottom of the core sedimentation rate was 0.03 cm/year.

The Lake Syrytkul sediment core spanned more than the last 800 years. ^{210}Pb CRS and CIC ages were in good agreement with each other until the depth of 18 cm. Then CRS model showed older age. SAR estimated by CRS model varied between 0.2 and 0.26 cm/year. SAR calculated with application of CIC model was 0.24 ± 0.03 cm/year. These values were in good agreement with SAR determined by ^{137}Cs method (0.25–0.26 cm/year). Increase in ^{137}Cs from 98 Bq/kg to 294 Bq/kg most likely associated with the beginning of nuclear tests in the USSR (1949 AD). ^{137}Cs peak (341 Bq/kg) at 10–12 cm indicated the date of 1963 AD when global ^{137}Cs fallout deposition was maximum. This date corresponds well with the date of that level derived from the ^{210}Pb CIC and CRS models (Supplementary Table S2). Accumulation rate of the core bottom sediments was 0.06 cm/year (Supplementary Table S1).

The Lake Ufimskoe sediment core spanned approximately 800 years. Sedimentation rate was 0.05 cm/year at the bottom of the core. Since ^{210}Pb did not reached balance with ^{226}Ra, for SAR and age determination we applied only CIC model. Mean sediment accumulation rate for upper 12 cm was 0.25 ± 0.06 cm/year. Increase in ^{137}Cs from 87 Bq/kg to 201 Bq/kg was associated with 1949 AD. Peak of ^{137}Cs (214 Bq/kg) 6–8 cm indicated the date of 1963 AD. These dates are within error of CIC age determinations. Although SAR estimated based on ^{137}Cs was lower (0.17–0.2 cm/year), it was within error of mean sediment accumulation rate determined using CIC model (Supplementary Table S2). In addition, SAR for Lake Ufimskoe sediments core taken in 2009 (unpublished data of Udachin V.N.) in 50 m from the studied core was close to obtained value (0.19 cm/year).

Since SAR calculated by CIC model had substantial error, for the age-depth models of lakes Tavatui, Turgoyak and Syrytkul we included dates determined with application of ^{210}Pb CRS model. For Lake Ufimskoe we used dates obtained with application of ^{137}Cs method (Supplementary Fig S1).

Chemical analysis of lake water

According to the hydrochemical analysis (Table 2), all studied lakes are freshwater. The electrolyte content is the lowest in Lake Ufimskoe and the highest in Lake Syrytkul. Lakes Tavatui and Syrytkul are calcium bicarbonate-dominated with sulfate as the subdominant anion and magnesium as the sub-dominant cation. The dominant anions of Lake Turgoyak are bicarbonate and sulfate, and the dominant cation is calcium. Lake Ufimskoe is calcium sulfate-dominated

Table 3 Trophic state indices (TSI) calculated based on total phosphorus (TP), Secchi depth (SD) (Carlson, 1977), total nitrogen (TN) (Kratzer & Brezonic, 1981), and total organic carbon (TOC) (Dunalska, 2011)

Lake	Ufimskoe		Tavatui		Syrytkul		Turgoyak	
	Mean	STDEV	Mean	STDEV	Mean	STDEV	Mean	STDEV
TSI(TN)	45	3.5	47	3.6	60	–	38	2.3
TSI(TOC)	53	2.9	58	2.2	71	–	48	2.7
TSI(TP)	43	5	55	2	61	2	37	12
TSI(SD)	46	0.3	50	5.7	51	2	27	0

Mean is an average value based on three water samples taken in spring, summer, and autumn

STDEV is a standard deviation

with bicarbonate as the sub-dominant anion and magnesium as the sub-dominant cation.

Based on trophic state indices calculated from average TP, TN, and SD, Lake Ufimskoe is mesotrophic, Lake Turgoyak is oligotrophic, while lakes Syrytkul and Tavatui are eutrophic (Table 3). TSI values calculated from TOC are higher than those calculated from other parameters. This pattern was observed in other Urals lakes and may be due to regionally elevated organic matter content in Southern and Middle Urals lakes that affected not only TOC values, but also permanganate values (Pv). In descending order of TSI, the studied lakes are arranged as follows: Syrytkul, Tavatui, Ufimskoe, and Turgoyak.

In all studied lakes, RUC was more than zero (Table 4). In descending order of RUC, the studied lakes are arranged as follows: Ufimskoe, Syrytkul, Turgoyak, and Tavatui. In Lake Ufimskoe, Zn and Cu exceed the criterion value for fishery reservoirs by 5 and 16 times, respectively (Normativy kachestva, 2016 with changes in 2018, 2020). Lake Syrytkul is characterized by a slight excess of threshold values not only of Cu, but also of Mo. In Turgoyak and Tavatui, Cu concentration is approximately twice as high as the threshold value.

Geochemistry of lake sediment

Enrichment by PTEs through time

Enrichment index of Lake Tavatui gradually increased from 1500 AD, then reached values of 6–7 at 1880

Table 4 Concentrations of potentially toxic elements (PTEs) in lake water

Chemical element	Criterion value	Lake	Tavatui		Turgoyak		Ufimskoe		Syrytkul	
		n	5		3		4		3	
		Unit	Mean	STDEV	Mean	STDEV	Mean	STDEV	Mean	STDEV
Cu	1	μg L^{-1}	1.7	0.7	2.0	0.7	16.6	10.4	1.1	1.2
Zn	10	μg L^{-1}	1.9	1.5	4.4	5.7	56.5	52.9	3.3	0.2
As	50	μg L^{-1}	2.0	0.4	1.9	0.2	15.5	3.7	8.8	2.8
Mo	1	μg L^{-1}	0.3	0.2	0.9	0.1	0.4	0.2	1.2	0.7
Sn	112	μg L^{-1}	0.095	0.139	0.053	0.011	0.079	0.033	0.013	0.001
Sb	5	μg L^{-1}	0.4	0.1	0.3	0.0	2.2	0.5	0.7	0.4
Tl	0.1	μg L^{-1}	0.008	0.005	0.005	0.001	0.026	0.009	0.003	0.001
Pb	6	μg L^{-1}	0.5	0.3	0.4	0.2	1.9	2.0	0.7	0.6
Bi	100	μg L^{-1}	0.013	0.004	0.008	0.006	0.024	0.023	0.004	0.001
RUC	0		0.8	0.5	1.5	0.5	4.5	0.9	1.2	1.1

Mean is an average value of chemical element concentration in water sampled in 2014–2021, *STDEV* is a standard deviation, *n* is the number of water samples. Criterion value is based on the statutory fisheries water quality standards of the Russian Federation (Normativy kachestva, 2016 with changes in 2018, 2020); *RUC* is the Rebasamiento del Umbral de Contaminación or Pollution Threshold Overshoot (Fernandez et al., 2018)

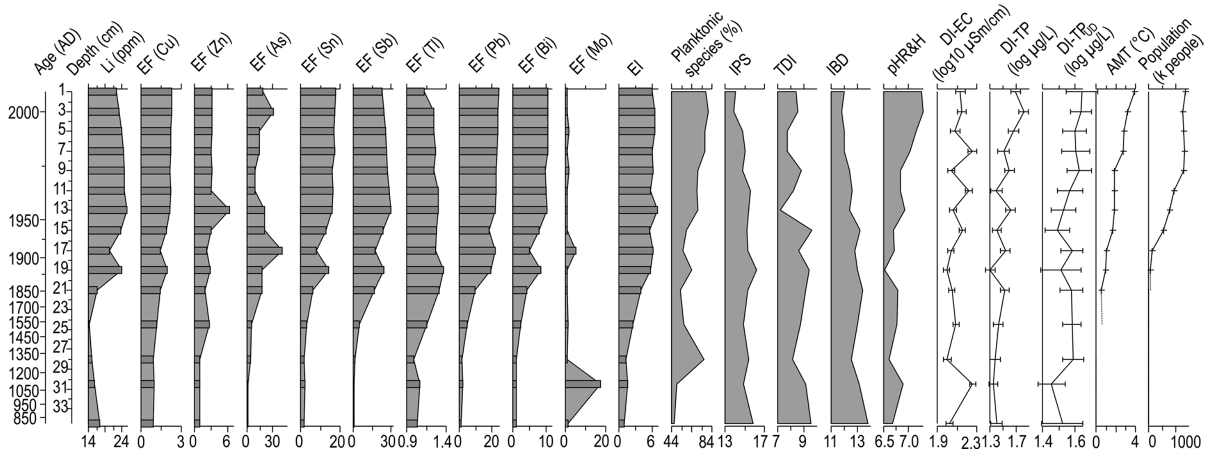

Fig. 2 Lake Tavatui sedimentary record of changes in enrichment factors of potentially toxic elements, planktonic diatom abundance, diatom indices, and diatom-inferred water parameters. Error bars on the DI–EC and DI–TP curves represent sample-specific standard errors (SEB) generated using 1000 bootstrap iterations. Data on diatom indices and diatom-inferred water parameters are provided in Table S9 (electronic supplementary material)

AD, and varied little until 2009 AD (Fig. 2 Supplementary Table S5). Enrichment factors of Cu, Sb, Sn, and Bi increased gradually from 1500 AD, decreased at 1912 AD, and then increased again. EF of Pb had similar pattern except for a decrease at 1940 AD. EFs of Zn and As increased at 1850 AD as well, but had maxima at 1912 AD and 1955 AD, respectively.

Enrichment index of Lake Turgoyak and enrichment factors of all PTEs displayed the same general pattern (Fig. 3, Supplementary Table S5). They increased slightly from 1300 AD and then showed a marked increase from 1930 AD and the maximum enrichment of surface sediments (0–1 cm).

Enrichment index of Lake Ufimskoe slightly increased from 1800 AD and substantially increased from 1955 AD (Fig. 4, Supplementary Table S5). All PTEs, with exception of Tl, Sb and As, had maximum EFs in surface samples.

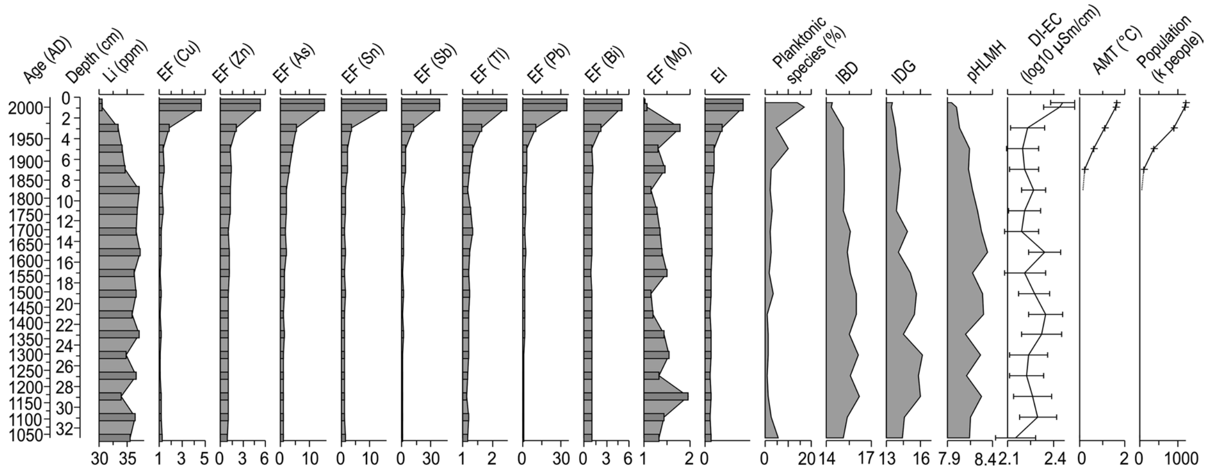

Fig. 3 Lake Turgoyak sedimentary record of changes in enrichment factors of potentially toxic elements, planktonic diatoms abundance, diatom indices, and diatom-inferred water parameters. Error bars on the DI–EC curve represent sample-specific standard errors (SEB) generated using 1000 bootstrap iterations. Data on diatom indices and diatom-inferred water parameters are provided in Table S11 (electronic supplementary material)

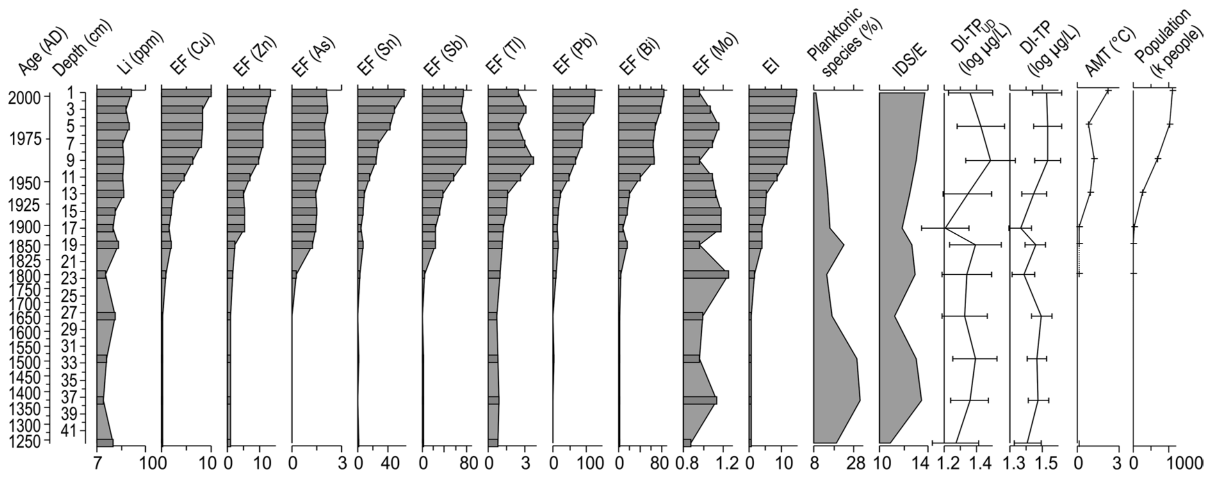

Fig. 4 Lake Ufimskoe sedimentary record of changes in enrichment factors of potentially toxic elements, planktonic diatoms abundance, diatom indices, and diatom-inferred water parameters. Error bars on DI–EC and DI–TP curves represent sample-specific standard errors (SEB) generated using 1000 bootstrap iterations. Data on diatom indices and diatom-inferred water parameters are provided in Table S13 (electronic supplementary material)

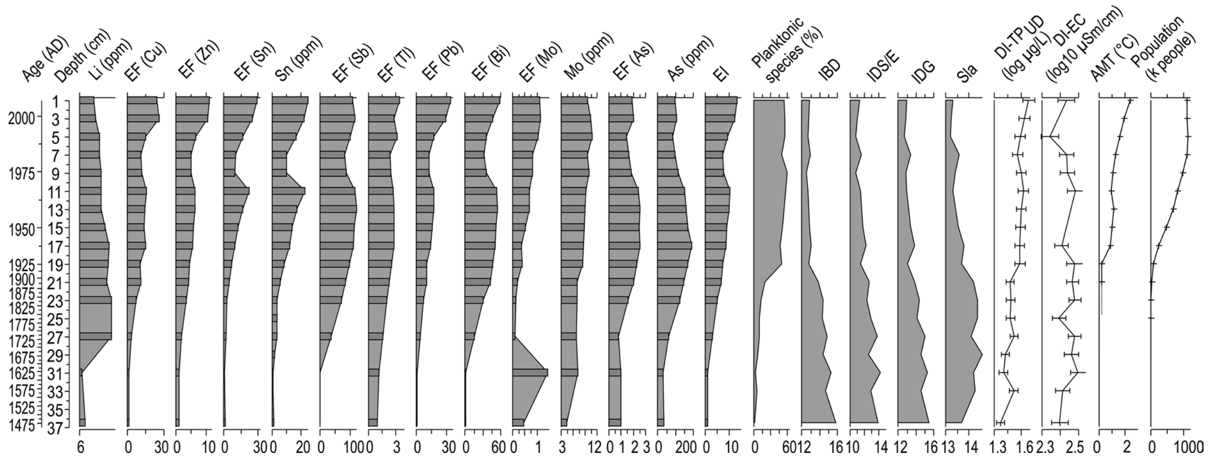

Fig. 5 Lake Syrytkul sedimentary record of changes in enrichment factors of potentially toxic elements, planktonic diatoms abundance, diatom indices, and diatom-inferred water parameters. Error bars on DI–EC and DI–TP curves represent sample-specific standard errors (SEB) generated using 1000 bootstrap iterations. Data on diatom indices and diatom-inferred water parameters are provided in Table S15 (electronic supplementary material)

Enrichment index of Lake Syrytkul and enrichment factors of Cu, Zn, Pb and Sn displayed almost the same general pattern (Fig. 5, Supplementary Table S5). They increased gradually from 1725 to 1960 AD, slightly decreased from 1960 to 1980 AD, and reached maximum in the 1998–2006 AD. EFs of Sb, Bi, and As had a similar pattern, but maximum values at 1944–1965 AD. EF of Tl increased gradually from 1725 AD to the maximum values at 1980–2011 AD.

Comparison of sediments PTE concentrations, enrichment indices and enrichment factors

According to the geochemical analysis, Lake Ufimskoe features extremely severe enrichment in Sb (73), Pb (92), and Bi (66), very severe enrichment in Sn (36), severe enrichment in Zn (11) and Cu (7.5), moderate enrichment in Tl (2.9) and As (2). Lake Ufimskoe sediments are characterized by the highest

Table 5 Enrichment factors (*very severe enrichment, **extreme enrichment), enrichment index (EI), and concentrations of PTEs in lake sediments in industrial and pre-industrial periods

Parameter	Industrial value		Reference value		Enrichment factor		Industrial value		Reference value		Enrichment factor	
	Mean	STDEV	Mean	STDEV	Mean	STDEV	Mean	STDEV	Mean	STDEV	Mean	STDEV
Lake	Tavatui						Syrytkul					
n	10		14		10		10		3		10	
Cu	182	96	64	8.5	2.1	1.6	540	132	20	1.3	15	5.3
Zn	453	209	99	14	3.3	1.3	545	130	47	1.6	6.5	2.4
As	50	28	1.9	0.6	20*	12	134	38	35	3.7	2.1	0.4
Mo	2.4	4.5	1.2	0.2	1.5	4.1	9.4	0.8	5.9	1.3	0.9	0.2
Sn	10	4.9	0.5	0.2	15	6.9	16	5.9	0.6	0.3	15	8.0
Sb	2.9	1.4	0.1	0.0	25*	12	14	2.5	0.08	0.02	102**	14
Tl	0.5	0.1	0.3	0.0	1.3	0.1	0.5	0.1	0.09	0.008	2.8	0.4
Pb	125	58	4.1	1.8	22*	10	258	78	8.3	0.4	17	7.5
Bi	1.3	0.6	0.1	0.0	9.5	4.0	2.8	0.6	0.03	0.01	46**	8.5
EI	6.2 ± 0.4						9.3 ± 2.1					
Lake	Ufimskoe						Turgoyak					
n	6		6		6		4		15		4	
Cu	1729	458	199	110	7.5	1.9	120	72	63	5.1	2.3	1.6
Zn	970	216	79	22	11	2.2	227	154	110	13	2.5	1.9
As	619	56	269	7.9	2.0	0.2	62	45	11	2.2	7.1	5.6
Mo	2.7	0.2	2.2	0.4	1.0	0.1	24	7.0	26	8.7	1.1	0.3
Sn	28	14	0.7	0.2	36*	17	8.0	8.6	1.7	0.1	5.9	6.7
Sb	20	2.6	0.2	0.1	73**	9	6.9	7.5	0.6	0.1	15	17
Tl	0.8	0.1	0.2	0.1	2.9	0.5	0.8	0.2	0.6	0.0	1.6	0.6
Pb	719	249	6.8	1.5	92**	30	183	206	18.4	1.4	13	15
Bi	6.6	1.6	0.1	0.0	66**	15	2.2	1.5	1.1	0.1	2.4	1.8

Mean is an average value, *STDEV* is a standard deviation, *n* is the number of sediment samples

EI of each lake was calculated as an average of EIs calculated for each sample of industrial period sediments

concentrations of Cu, Zn, As, Pb, Sn, Sb, Bi, and Tl and the highest mean EI (12.2) for sediments of industrial period (Table 5). Lake Syrytkul has lower EI (9.3), PTEs, and EFs than Lake Ufimskoe, except for Cu (severe enrichment; 15) and Sb (extremely severe enrichment; 102). Even lower EI (6.2) is noted for Lake Tavatui. In contrast to lakes Ufimskoe and Syrytkul, the Lake Tavatui sediments are distinguished by severe enrichment in As (20) although its average concentrations are lower. The lowest EI value (5.0) is in Lake Turgoyak. All lakes are characterized by severe or extremely severe enrichment in Sn, Sb, and Pb.

Choice of diatom indices for reconstructions of a lake ecosystem changes

Only IPS (Pollution Sensitivity Index), IBD (Biological Diatom Index), IDG (Generic Diatom Index) and ACID (Andrén & Jarlman, 2009) can be applied in all lakes. In addition, IDS/E (Louis-Leclercq Diatomic Index) and Sla (Sládeček Saprobic Index) can be used for lakes Syrytkul and Ufimskoe, and TDI (Trophic Diatom Index) can be used for Tavatui. The indices pH R&H (Renberg & Hellberg, 1982) and pH Eloranta (Eloranta & Turkia, 1990) are applicable for lakes Tavatui, Turgoyak, and Ufimskoe. For lakes Turgoyak and Syrytkul we can use pH LMH (Håkansson, 1992). In the Lake Turgoyak record, TDI and IPS indices are highly dependent on the abundance of *Pseudostaurosira brevistriata* (Grunow) D.M. Williams & Round. After removing this species from the results, the IPS and TDI curves changed significantly, so these indices were not used in the interpretation. Analysis of correlation between selected diatom indices and hydrochemical parameters demonstrated that IPS, IBD, IDG, IDS/E and Sla were correlated with nutrient parameters of Urals lakes (Supplementary Table S4). IBD is focused on saline and organic pollution effects (Prygiel & Coste, 2000). IPS reflects organic pollution and inorganic nutrients effects (Cemagref, 1982). IDG is an analogue of IPS, but IDG is based on the generic composition of assemblages (Cemagref, 1982; Rumeau & Coste, 1988). TDI indicates degree of eutrophication and reflects diatom response to common nutrient enrichment (Kelly & Whitton, 1995). IDS/E is a saprobity-eutrophication index with values between 1 and 5 representing levels of degradation due to organic pollution and eutrophication (Leclercq & Lecointe, 2008). Sla is a saprobity index which corresponds to six classes of water quality and self-purification zones in water ecosystems (Sládeček, 1986) (Supplementary Table S6).

The indices pH R&H and pH LMH were characterized by moderate correlation ($r = 0.5$) with measured average pH values. ACID had weak correlation with measured values. Values of the index pH Eloranta did not correlate with measured pH (Supplementary Table S4). Thus, pH Eloranta and ACID indices were excluded from the ecological analysis.

Assessment of transfer functions and reliability of reconstructions of DI–EC, DI–TP, and diatom indices

WA with classical deshrinking ($\text{RMSEP}_{\text{boot}} = 0.2$ log10 µS cm^{-1}, bootstrap $r^2 = 0.79$, maximum bootstrap bias = 0.2 log10 µS cm^{-1}) was the best performing model for EC (Maslennikova, 2020). WA-PLS-Component 2 was the best performing model for TP based on both the combined EDDI dataset and the Urals lakes dataset. $\text{RMSEP}_{\text{boot}}$ for both models was 0.3 log10 µg L^{-1}. The bootstrap r^2 and maximum bootstrap bias for the transfer function developed based on the EDDI combined dataset was higher (0.75 and 0.6 log10 µg L^{-1}) than that for the transfer function developed using the Urals lakes dataset (0.5 and 0.5 log10 µg L^{-1}).

According to modern analogue technique, Ufimskoe, Tavatui, and Syrytkul fossil samples had good analogue samples in both the Urals lakes calibration dataset and the combined EDDI dataset. Most diatom taxa of Lake Turgoyak were well represented only in the Urals lakes calibration dataset.

The diatom-inferred TP reconstructions for Lake Tavatui correlated to PCA axis-1 scores ($r = 0.58–0.77$) (Supplementary Table S7). The diatom-based EC reconstruction correlated to PCA axis-2 scores ($r = 0.66$). DI–TP explained the greatest amount of variance in the fossil diatom assemblages (30%) and showed the highest λ_R/λ_P ratio (0.73), followed by DI–TP$_{\text{UD}}$ (18%, 0.44) and DI–EC (7%, 0.17). Diatom indices (IBD, IPS, and TDI) negatively correlated to PCA axis-1 scores ($r = -$ 0.56–0.85) captured 32%, 18%, and 17% of fossil diatom assemblages variance and had λ_R/λ_P ratios of 0.75, 0.44, and 0.2, respectively. Diatom index pH R&H positively correlated to PCA axis-1 scores ($r = 0.79$) explained 27% of variance and showed a λ_R/λ_P ratio of 0.66. Given λ_R/λ_P ratios of less than one, we supposed that other variables could influence diatom assemblages. According to the unrestricted Monte Carlo permutation test, IDG did not significantly ($P < 0.05$) explain fossil diatom assemblage variance. So, it was excluded from the interpretation.

Diatom assemblages of Lake Turgoyak were not well represented in the EDDI diatom dataset, so we used only reconstructions based on the Urals diatom dataset for this lake. DI–EC correlated to PCA axis-1 scores ($r = 0.5$) explained 13.7% of diatom variance, and showed a λ_R/λ_P ratio 0.4. DI–TP$_{\text{UD}}$ was not a significant variable (Supplementary Table S7). Diatom indices pH LMH, IBD, and IDG were highly correlated to PCA axis-1 scores ($r = -$ 0.76–0.9) and showed λ_R/λ_P ratios of 0.67, 0.85, and 0.76 (Supplementary Table S7). The indices explained a highly significant ($P < 0.005$) proportion of variance in the fossil diatom assemblages: IBD – 28%, IDG – 25%, and pH LMH – 22%.

Diatom-inferred TP based on both EDDI and Urals lakes diatom datasets correlated with PCA axis-1 ($r = 0.65$ and $r = 0.79$) explained a significant portion of the Lake Ufimskoe diatom assemblage variance (30% and 24%) and showed λ_R/λ_P ratios of 0.67 and 0.53. Among diatom indices, only IDS/E had significant explanatory power (32%, $P < 0.005$) with a λ_R/λ_P ratio of 0.71.

For Lake Syrytkul, the highest λ_R/λ_P ratio (0.77), variance (46%, $P < 0.005$) and correlation with PCA axis-1 scores ($r=0.87$) was observed for DI–TP$_{UD}$. Total phosphorus inferred using EDDI was not a significant variable ($P>0.05$) (Supplementary Table S7). DI–EC negatively correlated with PCA axis-1 scores (− 0.61) captured a significant portion of variance (24%, $P<0.005$) and showed a λ_R/λ_P ratio of 0.42. IBD, IDS/E, IDG, and Sla negatively correlated with PCA-1 axis score ($r=-$ 0.83–0.93) explained a significant proportion ($P<0.005$) of the fossil diatom assemblages variance (44–53%) and λ_R/λ_P ratios varied between 0.74 and 0.89. IPS and pH LMH did not significantly explain diatom variance.

Thus, for Lake Tavatui ecosystem changes assessment, we can use diatom-inferred total phosphorus and electrical conductivity, pH R&H, and several diatom indices reflecting nutrient status: IBD, IPS, and TDI. The Lake Turgoyak ecosystem changes can be assessed with application of DI–EC, pH LMH, IBD, and IDG. The Lake Ufimskoe ecosystem shifts can be reconstructed using diatom-inferred total phosphorus and IDS/E. Lake Syrytkul parameters can be evaluated based on reconstruction of TP and EC inferred using Urals lakes dataset and several diatom water quality indices (IBD, IDS/E, IDG, and Sla).

Determination of driving forces with application of RDA

For the Lake Tavatui full sequence, we used RDA with PTEs and population. RDA showed that population had λ_R/λ_P of 0.88, enrichment factors of Sn and Bi had λ_R/λ_P of 0.85. Only concentrations and EFs of As, Mo, and Tl were not individually significant variables. Other PTEs had λ_R/λ_P that varied from 0.41 to 0.73. All significant variables correlated with each other. RDA of the Lake Tavatui reduced sequence (1863–2009 AD) with PTEs, climate parameters (AP and AMT), and data on population demonstrated that AMT was the most significant environmental variable with the highest λ_R/λ_P (0.87). Population had λ_R/λ_P of 0.84, EFs Cu and Bi had λ_R/λ_P of 0.83. The variables correlated with each other ($r>0.8$). A unique significant variance ($P<0.05$) was observed only for EFs of Cu and Bi (10%), when using AMT and population as covariables. Spearman rank order correlation (R) demonstrated that AMT, population, EFs Cu, and Bi had strong correlation with IBD ($R=0.94$, 0.92, 0.82) and planktonic diatoms ($R=0.95$, 0.95, 0.86).

For Lake Syrytkul, RDA of the full sequence included population and PTEs. Mo concentration and enrichment factor were the most significant variables with λ_R/λ_P of 0.86 and 0.83. Population had λ_R/λ_P of 0.73. Other PTE concentrations and enrichment factors were all individually significant ($P<0.05$) variables with λ_R/λ_P of 0.41–0.81. Population, concentration of Mo, As, and Sn explained a unique significant ($P<0.05$) variance (12.6%, 14.8%, 19.6%, and 14.1%). RDA of the reduced sequence (1832–2011 AD) with AMT, population, and PTEs demonstrated that the highest λ_R/λ_P (0.7) was observed for enrichment factor of Mo. Concentration of As, Mo, and Li had λ_R/λ_P of 0.64, 0.61, and 0.54. AMT and population had λ_R/λ_P of 0.52. Annual temperature, population, concentration, and enrichment in Mo had strong Spearman rank order correlation ($R>0.9$) and correlated to PCA axis-1. All these variables positively correlated with planktonic diatoms ($R=0.74$–0.84). As and Li correlated with each other ($R>0.9$), IDS/E and PCA axis-2.

Due to a relatively low sedimentation rate of Lake Ufimskoe and especially Lake Turgoyak, less than 10 samples covered the period of meteorological observations. So, we did not include climatic parameters in a redundancy analysis. RDA of the Lake Turgoyak sequence showed that population was the most significant explanatory variable with λ_R/λ_P of 0.9. Population correlated with PTEs (with exception of Mo), which had λ_R/λ_P of 0.83–0.89. All these environmental variables correlated with IBD, IDG, pH LMH, and planktonic diatoms.

RDA of the Ufimskoe sequence demonstrated that concentrations and EFs of Cu, Pb, and Sn as well as population had λ_R/λ_P of 0.84. All other PTEs were significant explanatory variables (with exception of Mo) with λ_R/λ_P between 0.58 and 0.8. Population correlated with PTEs ($R=0.88$–0.94) (with exception of Mo) and negatively correlated to planktonic diatoms ($R=-$ 0.87). Enrichment index and enrichment factors of Cu, Zn, As, Sn, Tl, and Pb correlated with organic pollution and eutrophication index (IDS/E) ($R>0.5$).

Paleolimnological analysis based on the diatom data

Lake Tavatui

In total, 72 taxa were identified across 15 samples in the Lake Tavatui sediment core (Supplementary

Table S8). Until the beginning of the twentieth century, planktonic diatoms were represented mainly by β-mesosaprobic, eutrophic *Aulacoseira ambigua* (Grunow) Simonsen and, rarely, by β-mesosaprobic, mesotrophic *Fragilaria crotonensis* Kitton. The widespread occurrence of planktonic diatoms, dominantly *Aulacoseira ambigua,* in 1300 AD was followed by a decline and then by an increase in their abundance and diversity at the beginning of the twentieth century (Fig. 6). For instance, the early twentieth century was marked by sporadic valves of α-meso-polysaprobic, hypereutrophic *Stephanodiscus hantzschii* Grunow in Cleve & Grunow and β-mesosaprobic, meso-eutrophic *Asterionella formosa* var. *formosa* Hassall. Since the mid-twentieth century, the relative abundances of *Stephanodiscus hantzschii*, β-mesosaprobic, eutrophic *Aulacoseira granulata* (Ehrenberg) Simonsen and β-mesosaprobic, eutrophic *Lindavia radiosa* (Grunow) De Toni and Forti increased, while α-mesosaprobic, eutrophic *Cyclostephanos dubius* (Hustedt) Round appeared.

Benthic diatoms of the Lake Tavatui sediments are represented mainly by freshwater species with wide ecological ranges (*Pseudostaurosira brevistriata, Staurosira venter* (Ehrenberg) Cleve & J.D. Möller*, Staurosira construens* Ehrenberg*, Staurosirella pinnata* (Ehrenberg) D.M. Williams & Round, and *Navicula radiosa* Kützing). Diatom assemblages also include species preferring electrolyte-poor habitats *(Neidium ampliatum* (Ehrenberg) Krammer in Krammer & Lange-Bertalot*, Stauroneis phoenicenteron* (Nitzsch) Ehrenberg*, Stauroneis siberica* (Grunow) Lange-Bertalot & Krammer*, Stauroforma exiguiformis* (Lange-Bertalot) R.J. Flower, V.J. Jones & Round*, Tabellaria flocculosa* (Roth) Kützing*, Eunotia faba* Ehrenberg, and *Eunotia minor* (Kützing) Grunow) and low-pH species of oligotrophic lakes and streams *(Pinnularia subgibba* Krammer and *Pinnularia neomajor* Krammer) (Kulikovskiy et al., 2016; Lange-Bertalot et al., 2017).

The relative abundance of planktonic species varies from 46 to 76%. Planktonic diatoms decreased simultaneously with an increase in PTEs (Fig. 2). However, since the beginning of the twentieth century, planktonic diatoms have positively correlated with Bi and Sn sediment enrichment. Since the mid-twentieth century, planktonic diatoms consistently increased, oligosaprobes decreased, β-mesosaprobes increased, α-meso-polysaprobes appeared, and diatom-inferred TP increased (Supplementary Table S9). While mesotrophic species decreased, diatoms preferring eutrophic and hypereutrophic habitats increased.

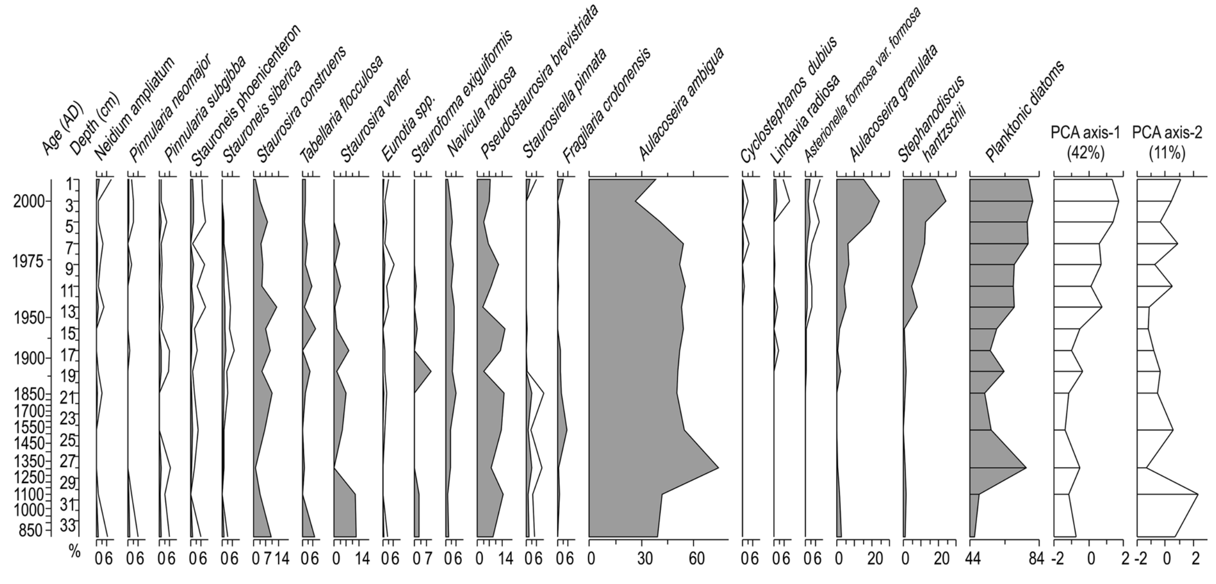

Fig. 6 Diatom stratigraphy of the Lake Tavatui. The % below PCA axes refers to the variance explained by each axis. Diatom abundances (%) are provided in Table S8 (electronic supplementary material)

Trophic state index calculated based on values of DI–TP and DI–TP$_{UD}$ showed that Lake Tavatui remained eutrophic throughout the considered period (Supplementary Table S9). However, since the beginning and especially in the second half of the twentieth century, total phosphorus increased. This process was accompanied by a pH R&H increase. According to DI–EC, the lake remained freshwater during the whole studied period.

Diatom indices (IBD, IPS, and TDI) were significant explanatory variables for Lake Tavatui diatom assemblage variances (Supplementary Table S7). Based on IBD, Lake Tavatui had good to medium water quality. The degree of pollution and eutrophication varied between moderate eutrophication to moderate pollution or heavy eutrophication (Supplementary Table S6). Based on IPS, Lake Tavatui was characterized by moderate eutrophication and good water quality. A decrease in IBD was observed since the beginning of the twentieth century with minimum values since 1980–1990 AD. IPS decreased in the second half of the twentieth century. According to TDI, in the second half of the twentieth century, Lake Tavatui trophic state shifted from mesotrophic to eutrophic (Supplementary Table S8, S9).

Lake Turgoyak

The sedimentary diatom assemblages of Lake Turgoyak are characterized by 96 taxa across 18 samples (Supplementary Table S10). The number of diatom taxa in sediments increased from 24 to 31 since the eighteenth century and reached a maximum (41) in the upper samples. Until the mid-twentieth century, diatom assemblages of the Lake Turgoyak sediments comprised mostly benthic species with a wide trophic tolerance ranging from oligo- to eutrophic environments (*Staurosira venter, S. construens, Staurosirella lapponica* (Grunow) D.M. Williams & Round, and *Pseudostaurosira brevistriata)* and species occurring in oligotrophic and oligo-mesotrophic habitats with low to medium electrolyte content (*Ellerbeckia arenaria* (G. Moore ex Ralfs) R.M. Crawford 1988, *Cavinula jaernefeltii* (Hustedt) D.G. Mann & A.J. Stickle, *Gliwiczia calcar* (Cleve) M. Kulikovskiy, Lange-Bertalot & A. Witkowski, *Staurosira oldenburgioides* (Lange-Bertalot) Kulikovskiy, Lange-Bertalot & Witkowski, *Staurosira grigorszkyi* (W. Smith) Leuduger-Fortmorel, and *Karayevia suchlandtii* (Hustedt) Buktiyarova) (Fig. 7). Planktonic diatoms increased significantly only at the beginning of the twentieth century. In contrast to Lake Tavatui, planktonic diatoms did not correlate with PTEs (Fig. 3). Until the mid-twentieth century, planktonic

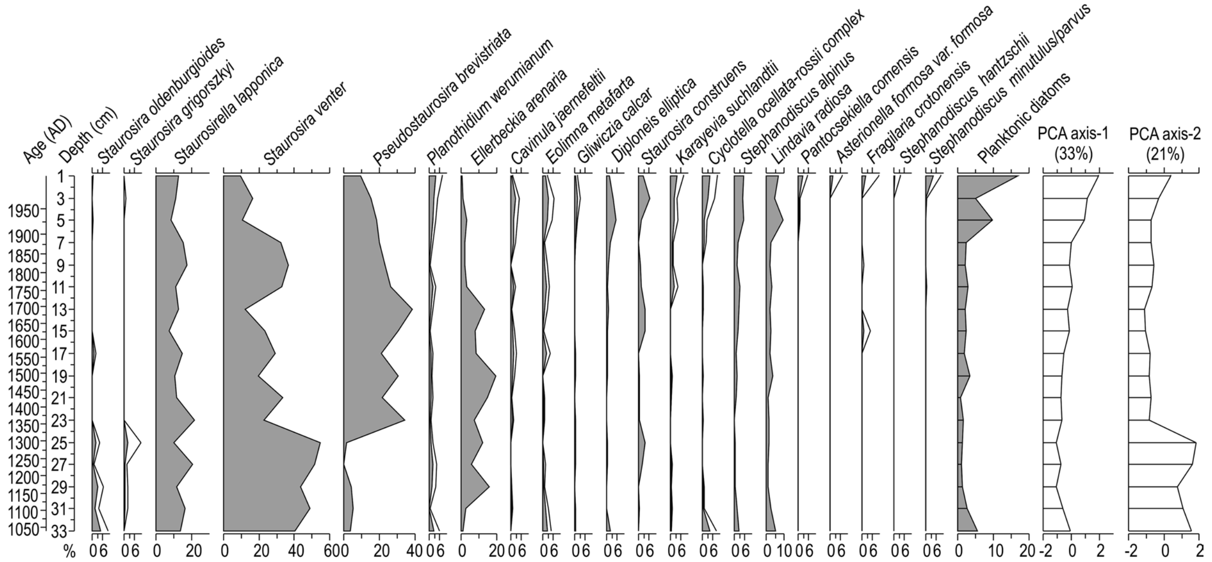

Fig. 7 Diatom stratigraphy of the Lake Turgoyak sediment core. The % below PCA axes refers to the variance explained by each axis. Diatom abundance data are provided in Table S10 (electronic supplementary material)

diatoms were represented by *Stephanodiscus alpinus* Hustedt in Huber-Pestalozzi and *Pantocsekiella comensis* (Grunow) K.T. Kiss & E. Ács, which were found in the Urals only in oligotrophic and oligo-mesotrophic mountain lakes, as well as by *Lindavia radiosa*, which is marked by a wide trophic tolerance. The second half of the twentieth century was characterized by an appearance of diatoms usually abundant in mesotrophic and eutrophic lakes (*Stephanodiscus hantzschii, Stephanodiscus parvus* Stoermer & Håkansson*, Stephanodiscus minutulus* (Kützing) Cleve & Möller*, Asterionella formosa var. formosa,* and *Fragilaria crotonensis*).

Diatom indices IBD and IDG were significant in explanation of Lake Turgoyak diatom assemblage variances. IBD and IDG correlated with each other (Fig. 3, Supplementary Table S11). Both indices showed good water quality and moderate eutrophication for the considered period. Indices fluctuated in the pre-industrial period and a steady decline began long before the beginning of the twentieth century. Minimum values since the second half of the twentieth century are likely a response to both an increase in EC and higher nutrient concentrations. The pH LMH gradually decreased long before the beginning of industrial period without relation to PTE sediment enrichment (Fig. 3).

Lake Ufimskoe

The diatom assemblages of Lake Ufimskoe are represented by 71 taxa across 11 samples (Supplementary Table S12). The number of taxa per sample varied without a clear regularity. Benthic taxa, which dominated the assemblages, were characterized by species preferring oligotrophic freshwater habitats with a low electrolyte content (*Stauroforma exiguiformis, Pinnularia neomajor,* and *Tabellaria flocculosa*), as well as by species with a wide ecological amplitude (*Staurosira binodis* (Ehrenberg) Lange-Bertalot in Hofmann, Werum & Lange-Bertalot, *S. construens, S. venter,* and *Staurosirella pinnata*) (Fig. 8). Relative abundances of *Achnanthidium minutissimum* (Kützing) Czarnecki, which is tolerant of heavy metal pollution (Cattaneo et al., 2004), varied over this period of Lake Ufimskoe development unrelated to industrial impact.

Planktonic species found in Lake Ufimskoe sediments are represented by *Aulacoseira ambigua, A. granulata, Lindavia radiosa* and, rarely, *Discostella stelligera* (Cleve & Grunow) Houk & Klee. The abundance of planktonic species varies from 20 to 46% during the period under consideration (Supplementary Table S13). Planktonic diatoms, which began to decrease before the twentieth century, reached their minimum abundance in the second

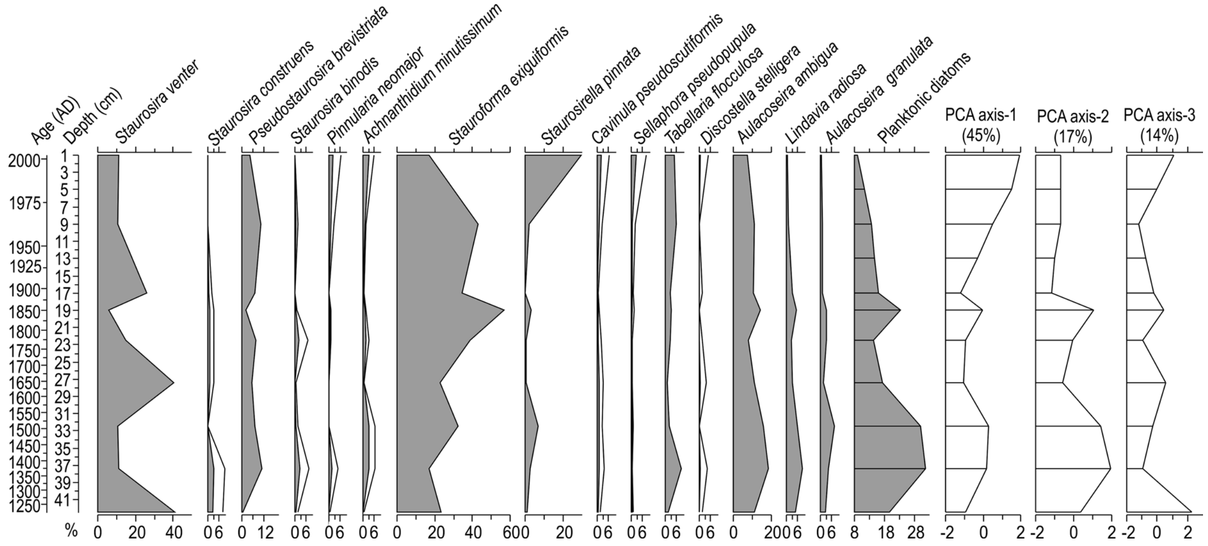

Fig. 8 Diatom stratigraphy of the Lake Ufimskoe sediment core. The % below PCA axes refers to the variance explained by each axis. Diatom abundance data are provided in Table S12 (electronic supplementary material)

half of the twentieth century as sediment enrichment by PTEs increased (Fig. 4). In relation to saprobity, β-mesosaprobes and oligosaprobes comprise the largest proportion in Lake Ufimskoe sediments, and in terms of trophic state, species preferring oligotrophic and meso-eutrophic conditions are most abundant. Oligosaprobes and species of oligotrophic habitats became more abundant in accordance with an increase in PTEs.

According to trophic state index calculated based on DI–TP and DI–TP$_{UD}$, Lake Ufimskoe was eutrophic or mesotrophic throughout the considered period. In contrast to DI–TP$_{UD}$, total phosphorus inferred using the EDDI diatom dataset overestimated the real values (Table 2, Supplementary Table S13). So, we supposed that the lake was mesotrophic. Since the beginning of the twentieth century, total phosphorus began to increase with maximum values of 31 μg/L (DI–TP$_{UD}$) and 34 μg/L (DI–TP).

Among diatom indices, only IDS/E was significant in explanation of Lake Ufimskoe diatom assemblage variance. It varied between 3.1 and 3.7, corresponding to moderate and low degradation level (Supplementary Tables S69 and S13).IDS/ also showed non-existent (< 10%) organic pollution throughout the considered period and shifted from moderate to low eutrophication since the end of the nineteenth century. Increase in IDS/E was in accordance with sediment enrichment by PTEs (Fig. 4).

Lake Syrytkul

In total, 75 diatom species were identified in Lake Syrytkul sediments across 19 samples (Supplementary Table S14). Until the beginning of the twentieth century, the diatom assemblages of Lake Syrytkul were mainly represented by benthic species with wide ecological amplitude (*Staurosirella pinnata, S. lapponica, Staurosira construens, S. venter,* and *Pseudostaurosira brevistriata*) (Fig. 9). *Gyrosigma attenuatum* (Kützing) Rabenhorst and *Gogorewia exilis* (Kützing) Kulikovskiy & Kociolek, species of alkali freshwater habitats that are sensitive to organic pollution above the β-α mesosaprobic level, were also present but in low percentages (Lange-Bertalot et al., 2017). Planktonic diatoms are represented by β-mesosaprobic *Aulacoseira ambigua* and *Aulacoseira granulata* and single valves of α-mesosaprobic *Cyclostephanos dubius*.

In general, until the end of the nineteenth century, diatom assemblages were predominantly characterized by β-mesosaprobes and oligosaprobes. In relation to trophic state, the largest number of species preferred meso-eutrophic conditions (Supplementary Table S15). Since the end of the nineteenth century,

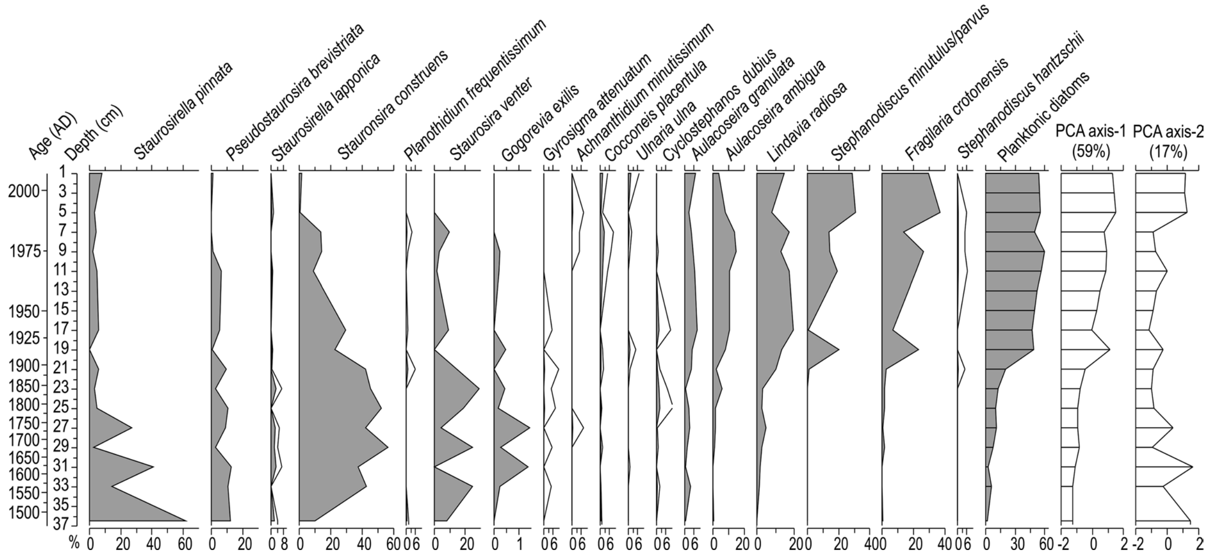

Fig. 9 Diatom stratigraphy of the Lake Syrytkul sediment core. The % below PCA axes refers to the variance explained by each axis. Diatom abundance data are provided in Table S14 (electronic supplementary material)

α-mesosaprobes and α-meso-polysaprobes became more important. Species preferring eutrophic and hypereutrophic conditions also became more abundant. Diversity and relative abundance of planktonic diatoms increased mostly due to *Lindavia radiosa*, *Stephanodiscus minutulus, Stephanodiscus parvus*, and *Fragilaria crotonensis*.

Based on trophic state index calculated from DI–TP_{UD}, Lake Syrytkul was eutrophic throughout the considered period. DI–TP_{UD} has increased consistently since the nineteenth century (Fig. 5, Supplementary Table S15).

The diatom water quality indices (IBD, IDG, Sla, and IDS/E) were significant in explanation of the Lake Syrytkul diatom assemblage variance. All indices were correlated with each other and changed since the beginning of the twentieth century. IBD and IDG values demonstrated a shift from moderate eutrophication and good water quality to moderate pollution or heavy eutrophication and medium water quality (12.5–13.5) (Supplementary Table S6, S15). IDS/E indicates a shift from low degradation without pollution with low to moderate eutrophication to moderate degradation with low eutrophication and moderate pollution. Sla remained in oligosaprobic self-purification zone with good water quality but decreased from 1.1–1.3 to 1.3–1.4 since the beginning of the twentieth century. Sla overestimated water quality due to absence of *Stephanodiscus minutulus* and *Stephanodiscus parvus* in index dataset presented in Omnidia 6.1.4.

Discussion

Water quality and sediment contamination assessment

According to water and sediment analysis, Lake Ufimskoe is the most polluted by PTEs. It is located 7 km from the Karabash copper smelter and features maximum concentrations of Cu, Zn, As, Pb, Sb, and Bi in water and sediments and the highest RUC and EI (Tables 4 & 5). Lake Syrytkul located 12 km from the Karabash copper smelter ranks the second in terms of concentration of PTEs in water and sediments. Lake Tavatui located in the Middle Ural center of mining and metallurgy has higher EI value than Lake Turgoyak due to great differences in the toxic element supply during the industrial and pre-industrial periods. Based on these results, the lakes should be ranked as follows in terms of heavy metal loading due to mining and metallurgical plant activities: Ufimskoe, Syrytkul, Tavatui, and Turgoyak. The higher RUC value, as well as higher reference and industrial concentrations of As, Mo, Sb, Tl, Pb, and Bi in the Lake Turgoyak sediments compared to Lake Tavatui are likely related to the differences in catchment rock composition. The high Mo concentration in Lake Syrytkul water is explained by the predominance of alkali rocks with Mo mineralization in the lake's catchment (Petrov et al., 2015).

In order of decreasing TSI and nutrient-related variables (TN, TOC, TP, Pv, and TON) and increasing SD, the studied lakes are arranged as follows: Syrytkul, Tavatui, Ufimskoe, and Turgoyak (Tables 2 & 3). Hence, Lake Ufimskoe is currently the most contaminated by potentially toxic elements and is mesotrophic. Lake Syrytkul is less polluted by PTEs, but characterized by eutrophic conditions. Lakes Tavatui and Turgoyak are characterized by even less contamination by PTEs. In terms of TSI (TN, TP, and SD), Lake Turgoyak is oligotrophic, while Lake Tavatui is eutrophic. Sediment accumulation rates of the studied lakes varied in accordance with their trophic state. The highest SAR was observed for eutrophic lakes Tavatui and Syrytkul, and the lowest SAR, for oligotrophic Lake Turgoyak. Although lakes Turgoyak and Tavatui are both characterized by substantial human impact (flow regulation, recreational pressure, catchment alteration, and nutrient loading), their trophic state is different, possibly due to morphometric parameters. Lake Turgoyak is characterized by a weak water exchange and a low specific catchment/surface area, and the lake processes may be relatively independent of the catchment (Andreeva, 1973). The combination of greater depth and minimum surface area/water volume ratio produces a negligible lake eutrophication trend (Table 1). Lake Tavatui is characterized by a higher ratio of catchment to surface area, so it is more influenced by nutrient loading from its human-modified catchment. The lake's shallower depths and higher surface area/water volume ratio possibly contribute to enhanced rates of natural and anthropogenic eutrophication due to nutrient recycling at the water–sediment interface

(Wetzel, 2001; Scheffer, 2004). Lake Ufimskoe is the shallowest of the lakes under consideration, and its ratios of surface area to water volume and catchment area to surface area are the highest. These morphometric parameters could contribute to natural eutrophy. However, Lake Ufimskoe is mesotrophic, while Lake Syrytkul is eutrophic, despite lower ratios of catchment area to surface area and surface area to water volume. This fact could be due to differences in human impact, with higher acid and PTE loading in Lake Ufimskoe and flow regulation in Lake Syrytkul.

Enrichment in PTEs over the past period of lakes history

A discrepancy between proposed history of anthropogenic PTE deposition and changes in concentration and enrichment in PTEs can be explained by uncertainties in age-depth models. In addition, it may be associated with natural factors. Since we use EF, influence of clastic material enriched in PTEs transported to the sediments due to increase in catchment erosion can be excluded. Other most likely natural factors are a supply of soil organic matter rich in PTEs and migration of chemical elements after burial (Boyle, 2001). The surface sediment PTE enrichment, especially expressed in Lake Turgoyak, can be explained by cycling processes in the water column or upward diffusion when trace elements are released by mineralization (Morfett et al., 1988; Boyle, 2001). Thus, to determine PTEs influence on diatoms, we did not only compare the diatom record with the PTE sediment profiles, but tried to identify thechanges in the diatom record according to the proposed history of anthropogenic PTE deposition.

Factors affecting the development of lake ecosystems in the Southern and Middle Urals

Climate warming

We consider the known climate warming effects on lake ecosystems in order to understand the extent the changes in the Ural lakes are explained by climate warming, and to what extent, by human impacts.

Climate warming could provide more stable and longer periods of stratification, triggering compositional shifts within the phytoplankton communities to the benefit of mobile, small-sized or colony-forming species (Winder et al., 2009; Michelutti et al., 2015; Rühland et al., 2015). Due to changes in thermal structure and timing of stratification, nutrients released from the sediment are largely restricted to the hypolimnion, and phytoplankton production is supported mainly by the external load (Radbourne et al., 2019). At the same time, increases in water temperature of shallow lakes could stimulate mineralization mediated by microorganisms, which could liberate organic-bound P and release it into water column (Wang et al., 2019). Climate warming can increase the input of nutrients due to faster weathering or intensification of microbiological processes in soils (Jeppesen et al., 1998; Cardoso et al., 2007; Fritz & Anderson, 2013). Climate warming can affect the trophic state due to changes in aquatic vegetation (Canfield & Jones, 1984; Tichá et al., 2019).

As for Lake Turgoyak, despite an increasing abundance of planktonic diatoms since the beginning of the twentieth century, small-sized (*Lindavia comensis, Stephanodiscus parvus*) or colony-forming species (*Asterionella formosa, Fragilaria crotonensis*), which usually are favored in the stratification period, increased only in the second half of the twentieth century after dam construction. In lakes Syrytkul and Tavatui, a wide distribution of small-sized or colony-forming species is also coincident with an increase in large-celled planktonic *Aulacoseira* taxa favored during the stronger vertical mixing periods. *Discostella stelligera*, which was the only small-sized planktonic species identified in Lake Ufimskoe, did not increase during the warming period. Therefore, we conclude that lengthening or strengthening of stratification due to warming was not a main factor influencing changes in the number of small, planktonic cyclotelloid diatoms (*Stephanodiscus parvus, Stephanodiscus minutulus, Lindavia comensis,* and *Discostella stelligera*) and colony-forming pennate species (*Asterionella formosa* and *Fragilaria crotonensis*).

Diatom indices that reflect nutrient status decreased in the upper sediments of all studied lakes with the exception of Lake Ufimskoe. These changes were a response to lakes eutrophication. Based on the analysis of Lake Tavatui diatom assemblages, quantitative hydrochemical reconstructions, and diatom indices, we conclude that nutrient concentrations and lake trophic state increased since the beginning of the twentieth century. The eutrophication process was noticeably enhanced since the second half of the twentieth century. According to RDA, AMT was strongly correlated with diatom indices and was the most significant variable in explanation of the Lake Tavatui assemblage variability. So, despite a possible increasing of stratification, which could lead to low nutrients in surface water, we can conclude that the climate warming plays substantial role in Lake Tavatui eutrophication possibly due to an increase in the nutrient loading from the catchment. This process could also be human-induced. The relatively high ratio of catchment area to lacustrine area suggests a strong influence of catchment on lake processes and confirms a possible main role of external loading in the lake eutrophication.

An increase in the abundance of planktonic diatoms in Lake Turgoyak was clearly recorded since the beginning of the twentieth century, and an evident expansion of eutrophic and hypereutrophic species was noted since the second half of the twentieth century. Reliable quantitative reconstructions of TP are unavailable for Lake Turgoyak, while variations in IBD and IDG showed an increase in nutrients long before the beginning of the twentieth century and in the second half of the twentieth century. An increase in thermal stratification and decrease in nutrient availability due to restriction in hypolimnion suggest a decrease in phytoplankton, especially in species that require high nutrient content as a result of climate warming. The low ratio of catchment area to lacustrine area does not suggest substantial compensation by a warming-induced increase in external nutrient loading. So, the evident increase in the nutrient status of Lake Turgoyak in the second half of the twentieth century suggests it is caused by another factor.

According to PCA, the largest changes in the Lake Syrytkul diatom assemblages occurred at the beginning of the twentieth century. The lake ecosystem was characterized by growing proportion of planktonic species, increase in total phosphorus, drop in Sla, IDS/E, IBD, and IDG, as well as the appearance of α-mesosaprobes and α-meso-polysaprobes. These features are likely a response to the lake eutrophication. In contrast to Lake Tavatui, the relatively low value of λ_R/λ_P of AMT suggests the greater impact of other driving forces to explain the diatom assemblage shifts.

Lake Ufimskoe is the shallowest of the studied lakes with the highest expected impact of the catchment. These parameters could contribute to natural and anthropogenic eutrophication. Climate warming could contribute to natural eutrophication not only due to increase in nutrient external load, but also by intensification of nutrient cycling and remobilization of phosphorus from sediments due to water warming. Due to the lake's shallowness, an increase in stratification does not likely influence nutrient availability. However, despite the climate warming, higher percentage of oligosaprobes and species of oligotrophic habitats, and an increase in IDS/E since the nineteenth century indicated a decrease in organic pollution and eutrophication. Natural oligotrophication could be caused by changes in the vegetation in the catchment area. For example, expansion of the coniferous forests could decrease microbiological mineralization rate (Sorokina & Sorokin, 2007), which would reduce nutrient flux into the lake. However, according to palynological analysis (Maslennikova, 2020), the role of coniferous forests continued to decrease, while the role of birch grew in the twentieth century. In addition, oligotrophication could be caused by lower nutrient availability due to more abundant aquatic macrophytes developed under the warming climate (Tichá et al., 2019). However, the palynological data do not indicate an increase in aquatic vegetation. In addition, the aquatic vegetation of recent Lake Ufimskoe is not diverse and is represented by rare *Potamogeton perfoliatus* Linnaeus, which does not form a continuous carpet, in contrast to the aquatic vegetation of many other shallow lakes in the Southern Urals. Planktonic diatoms became a minor component of the diatom assemblage as early as the eighteenth century. Warming since the middle of the nineteenth century did not contribute to a widespread occurrence of planktonic diatoms, as in the Northern Urals (Palagushkina et al., 2019). These facts imply other factors have influenced Lake Ufimskoe oligotrophication.

Human impacts

Human impacts in this territory include drivers that have antagonistic effects on lake ecosystems. Mining and metallurgy activity lead to increases in PTEs and decreases in pH, which reduce productivity and plankton abundance and decrease lake trophic state (Salonen et al., 2006; Tuovinen et al., 2012; Thienpont et al., 2016; Denisov et al., 2020). While recreation, wastewater discharge, dam construction, and water intake lead to eutrophication.

Changes in Lake Tavatui since the beginning of the twentieth century could be related to eutrophication not only due to ongoing climate warming but also the creation of an artificial passage to the east of the old channel, connecting the Lake Tavatui with the Verkh-Neivinsky water reservoir (Lozhkin, 1971). Since the mid-twentieth century, eutrophication processes and organic pollution could be influenced by the climate warming, as well as a rapid population growth in the Sverdlovsk region, which peaked in the 1990s, expansion of recreation activity, and exploitation of the coastline for the construction of recreation centers and cottage settlements. Based on the historical data, an increase in the abundance of planktonic diatoms and decreasing values of diatom indices due to eutrophication should have occurred as early as 1762 AD, as the level of Lake Tavatui rose by 2–3 m with an increase in surface area due to the dam construction on the Neiva River (Lozhkin, 1971). However, this event was not reflected in the lake sediment record. The lake ecosystem response to this human-induced impact could have been modified due to climate cooling (the Little Ice Age). In addition, this discrepancy could be related to the Middle Urals becoming a mining and metallurgy center in the first quarter of the eighteenth century (Gorshkov, 1957). The entry of toxic elements into the lake could reduce the eutrophication rate and the number of planktonic diatoms, as was observed in lakes of the Murmansk region (Denisov et al., 2020), lakes of SW Finland (Salonen et al., 2006; Tuovinen et al., 2012), and the subarctic lake of Canada (Thienpont et al., 2016). Positive correlation between planktonic diatoms, Cu and Bi, could be spurious (Fig. 2). The increase in planktonic diatoms is also correlated with AMT, population, DI–TP, and IBD and more likely explained by increase in external nutrient loading.

Changes in the Lake Turgoyak ecosystem recorded in diatom assemblages since the beginning of the twentieth century could be related to both the ongoing warming in the Southern Urals and more active land use that resulted in deforestation near the lake and a higher recreation load (Sementovskiy, 1913). Changes in the lake ecosystem since the second half of the twentieth century most likely reflect its eutrophication due to a growing complex human-induced impact. 1955 AD was marked by initiation of a few events: construction of the Mashgorodok microdistrict, rapid growth of the population of the city of Miass and the Chelyabinsk region, intensive water intake for water supply to Miass (since 1952 AD) followed by lake flow regulation (1960 AD) (Gavrilkina et al., 1998), and active construction of cottages and recreation centers on the lake shore. The maximum number of planktonic diatoms and the minimum values of IBD and IDG were observed in the period when the highest heavy metal concentrations accumulated (Fig. 3). These results suggest that the lake ecosystem did not react clearly to the industrial impact. The increased supply of potentially toxic elements reflected in the geochemical record did not slow down the eutrophication process likely because of relatively low concentrations of PTEs and the substantial human-induced eutrophication.

The eutrophication of the Lake Syrytkul ecosystem in the twentieth century that is reflected in the diatom record could be explained by dam construction that increased lake water depth, productivity, and organic matter content. Lake flow rate was reduced and external nutrient load increased due to coastal erosion. This suggestion is confirmed not only by a low value of λ_R/λ_P for annual mean temperature, but also abrupt changes in the diatom record. The extensive supply of toxic elements into the lake as a result of industrial activities did not have a noticeable effect on the lake eutrophication process or diatom composition. Higher concentrations of hardness-causing cations (e.g., Ca^{2+} and Mg^{2+}), in comparison with Lake Ufimskoe, could mitigate the toxicity of metals (Yim et al., 2006; Pociecha et al., 2020). An increase in *Stephanodiscus parvus* was coincident with increasing concentrations of PTEs in the Lake Syrytkul sediments, which is similar to Lake Lamba in the Murmansk region (Slukovskii et al., 2018). However, change in the abundance of *S. parvus* was more likely related to increasing total phosphorus (Fig. 5). The abundance of planktonic diatoms in Lake Syrytkul sediments is positively correlated with PTEs (especially Bi and Sb). Planktonic diatoms are also correlated to diatom-inferred TP and diatom indices (IBD, IDS/E, IDG, and Sla). So, the correlation between PTEs and planktonic diatoms could be spurious, as was the case in Lake Tavatui. At first sight, relatively high ratios λ_R/λ_P of Mo, As, and Li point to direct influence of these trace elements on diatoms. However, it also can be explained by one factor that influenced both the diatom assemblage and geochemistry of these chemical elements. A rise in lake level and eutrophication could lead not only to a diatom assemblage shift, but also to change in migration of As and Mo, and decrease in Li due to dilution of sediments by organic matter.

The decrease in organic pollution and eutrophication of Lake Ufimskoe since the twentieth century, which we could not explain by natural forces, most likely was associated with an increase in heavy metal concentrations and a decrease in pH due to industrial impact. An increase in IDS/E since the twentieth century indicated a decrease in eutrophication and organic pollution. However, after decreasing in the end of the nineteenth century, DI–TP increased (Fig. 4). Such inconsistency can be explained as follows: an increase in TP may be due to pH decrease associated with industrial activity. Phosphorus is more mobile in acidic water. Despite higher TP, lake productivity and therefore organic matter in water decreased due to lowering of pH and high PTEs. So, the value of IDS/E increased which indicates oligotrophication. Lower abundance of planktonic diatoms could also be related to higher concentrations of heavy metals and other potentially toxic elements (Salonen et al., 2006; Tuovinen et al., 2012; Thienpont et al., 2016). No shift toward domination of known metal-resistant species (Cattaneo et al., 2004; Tuovinen et al., 2012; Sivarajah et al., 2019) was noted. The declining importance of *Aulacoseira granulata*, which tolerates metal pollution and copper sulfate (Morin et al., 2008), since the beginning of the industrial period could be related to lake oligotrophication.

Comparison with other Ural lakes

The most pronounced change in diatom water quality indices in the studied lakes occurred at the nineteenth and twentieth century. Diatom indices decreased, and planktonic diatom abundances increased in the lakes subjected to intensive land use and greater human-induced nutrient loads. In Lake Ufimskoe, without this factor, but with high loads of PTEs, the indices increased and the abundance of planktonic diatoms was reduced, despite the climate warming. For comparison, the number of planktonic species does not generally decrease in Lake Serebry, which is located only 4 km from the Karabash copper smelter and is even more contaminated by PTEs than Lake Ufimskoe. This phenomenon is likely related to the impact of artificial changes in the hydrological regime (dam construction) of Lake Serebry (Maslennikova, 2019).

In contrast to the studied lakes of the Northern Urals (Solovieva et al., 2005, 2008), which were not affected by local pollution and with low atmospheric pollution sources, changes in the lakes of the Southern and Middle Urals do not reflect the impact of climate warming independent of the human impact. As with lakes of the Polar Urals (Palagushkina et al., 2019), a substantial shift in diatom assemblages and an increase in planktonic species were observed in the studied lakes of the Southern and Middle Urals from the nineteenth century to the twentieth century. However, the increases in planktonic species, including small cyclotelloid and colonial diatoms, as well as variations in the diatom quality indices in the studied Ural lakes, are primarily related to the human land use activity with warming playing a secondary role. This conclusion is supported by the fact that, during the period under consideration, covering not only the Little Ice Age, but also the Medieval Warming, there were no changes in diatom assemblages similar to those observed in the beginning and in the second half of the twentieth century. Our conclusions about the dominant influence of human land use on lake ecosystems contradict those of Rogozin et al. (2017), who argued that changes in diatom assemblages over the past 40 years in Lake Bol'shoe Miassovo (Southern Urals) were related to climate warming. However, during the same period as the observed changes, the lake was a reservoir with a regulated flow connected with the pond system of a fish farm in the Upper Karasi Settlement (Rogozin & Tkachev, 2000). This factor, rather than the climate warming since the 1970s, could explain the main changes in the lake ecosystem, which resulted in a greater abundance of species such as *Fragilaria crotonensis* and *Stephanodiscus hantzschii* recorded in the sediments (Rogozin et al., 2017).

Conclusion

Based on the analysis of water and sediments, we conclude that the human-induced loading of PTEs is currently the main factor affecting PTEs in lakes of the Urals mining and metallurgical region. Rock composition in the catchment and other natural factors play a secondary role. The developmental stage of the studied lakes, in particular their trophic state and concentrations of nutrients, are related to their morphometry, type and degree of human impact. The shallow and mesotrophic Lake Ufimskoe located at 7 km from the Karabash copper smelter is established to be the most polluted by PTEs. The highest trophic state and nutrient concentrations were found in lakes Syrytkul and Tavatui, which are subjected to flow regulation and more prone, in terms of morphometric parameters, to eutrophication than Lake Turgoyak.

In contrast to the Northern and Polar Urals lakes, changes in the lakes of the Southern and Middle Urals do not reflect the impact of climate warming independent of the human impact. Increases in planktonic species, including small cyclotelloid and colonial pennate diatoms, as well as variations in the diatom indices in the studied Ural lakes, are primarily related to the human land use activity with warming playing only a secondary role.

The paleolimnological reconstructions of all lakes under consideration suggest that diatom assemblages, planktonic species abundances, and diatom indices underwent dramatic changes in the nineteenth and twentieth century. An increase in the role of planktonic diatoms and a decrease in diatom indices despite loading of PTEs were noted in the three lakes subjected to intensive human-induced nutrient loading and (or) flow regulation. Based on the results of our complex study, it is possible that in the absence of damming, intensive recreation activity, and human-induced nutrient fluxes, the industrial impact, including the supply of PTEs and acidification, can mask the lake's response to climate warming, limit natural eutrophication, and even lead to oligotrophication, as in Lake Ufimskoe. If the land use is active, then the impact of metallurgical industry on lake trophic status is moderated, even at high PTE levels in water and sediments, as in Lake Syrytkul.

Acknowledgements The authors thank Lyubov Lapshina and Lyudmila Udachina (South Urals Federal Research Center of Mineralogy and Geoecology of the Urals Branch of the Russian Academy of Sciences) for generous help with the analysis of lake water, Dmitry Pirogov (Ural Electrochemical Integrated Plant) for chemical analysis of Lake Tavatui sediments, Stephen Juggins (Newcastle University, UK) for providing the opportunity to work with the combined EDDI TP dataset, Vasiliy Grigor'ev (St. Petersburg State University) for consultation on interpretation of ^{210}Pb analysis results, and Elena Maslennikova for recommendations that improved the text. We are grateful to the reviewers of this paper for their valuable recommendations.

Funding The ecological analysis, quantitative reconstructions, Lake Turgoyak sediment analysis, and lake water analysis were supported by the Russian Science Foundation (Grant No. 21-17-00071, https://rscf.ru/project/21-17-00071/). The diatom analysis, age-depth model, and chemical analysis of the sediments of lakes Syrytkul, Tavatui, and Ufimskoe were funded by the State Contract of South Urals Federal Research Center of Mineralogy and Geoecology of the Urals Branch of the Russian Academy of Sciences.

Data availability All data generated or analyzed during this study are included in this published article and its supplementary information files. Samples and collections presented in this manuscript are kept at the South Urals Research Center of Mineralogy and Geoecology, Urals Branch, Russian Academy of Sciences (Miass, Russia) and are available on request.

Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

Alekseev, V. V. 2001. Metallurgicheskie zavody Urala [Metallugrgical factories of the Urals]. Akademkniga. Yekaterinburg. 536. (in Russian).

Andreeva, M. A. 1973. Ozera Srednego i Juzhnogo Urala [Lakes of the Middle and Southern Urals]. Southern Urals books Press. Chelyabinsk. 272. (in Russian).

Andrén, C. & A. Jarlman, 2009. Benthic diatoms as indicators of acidity in streams. Fundamental and Applied Limnology 173: 237–253. https://doi.org/10.1127/1863-9135/2008/0173-0237.

Appleby, P. G. & F. Oldfield, 1978. The calculation of lead–210 dates assuming a constant rate of supply of the unsupported lead–210 to the sediment. Catena 5: 1–8. https://doi.org/10.1016/S0341-8162(78)80002-2.

Bayanov, N. G., 2012. Troficheskij status i ekologicheskoe sostoyanie nekotoryh ozer CHelyabinskoj oblasti [Trophic status and ecological status of some lakes of the

Chelyabinsk region]. Conference proceedings: Problemy geografii Urala i sopredel'nyh territorij. https://doi.org/10.13140/2.1.5071.4569.

Bennion, H., 1994. A diatom-phosphorus transfer function for shallow, eutrophic ponds in southeast England. Hydrobiologia 275: 391–410. https://doi.org/10.1007/BF00026729.

Bennion, H., C. A. Duigan, E. Y. Haworth, T. E. H. Allott, N. J. Anderson, S. Juggins & D. T. Monteith, 1996a. The Anglesey Lakes, Wales, UK- Changes in trophic status of three standing waters as inferred from diatom transfer functions and their implications for conservation. Aquatic Conservation Marine and Freshwater Ecosystems 6: 81–92. https://doi.org/10.1002/(SICI)1099-0755(199606)6:2%3c81::AID-AQC174%3e3.0.CO;2-G.

Bennion, H., S. Juggins & N. J. Anderson, 1996b. Predicting epilimnetic phosphorus concentrations using an improved diatom-based transfer function and its application to lake eutrophication management. Environmental Science and Technology 30: 2004–2007. https://doi.org/10.1021/es9508030.

Birks, H. J. B., 1998. Numerical tools in palaeolimnology – Progress, potentialities, and problems. Journal of Paleolimnology 20: 307–332. https://doi.org/10.1023/A:1008038808690.

Birks, H. J. B., J. M. Line, S. Juggins, A. C. Stephenson & C. J. F. ter Braak, 1990. Diatoms and pH reconstruction. Philosophical Transactions of the Royal Society B Biological Sciences 327: 263–278. https://doi.org/10.1098/rstb.1990.0062.

Blaauw, M. & A. J. Christen, 2011. Flexible paleoclimate age-depth models using an autoregressive gamma process. Bayesian Analysis 6: 457–474. https://doi.org/10.1214/11-BA618.

Boyle, J. F., 2001. Geochemical methods in palaeolimnology. In Smol, J. P. & W. M. Last (eds), Tracking environmental change using lake sediments: Physical and Chemical Techniques, Vol. 2. Kluwer Academic Publishers, Dordrecht.

Canfield, D. & J. R. Jones, 1984. Assessing the trophic status of lakes with aquatic macrophytes. Lake and Reservoir Management 1: 446–451. https://doi.org/10.1080/07438148409354554.

Cardoso, A. C., A. Solimini, G. Premazzi, L. Carvalho, A. Lyche & S. Rekolainen, 2007. Phosphorus reference concentrations in European lakes. Hydrobiologia 584: 3–12. https://doi.org/10.1007/s10750-007-0584-y.

Carlson, R. E., 1977. A trophic state index for lakes. Limnology and Oceanography 22: 361–369. https://doi.org/10.4319/lo.1977.22.2.0361.

Cattaneo, A., Y. Couillard, S. Wunsam & M. Courcelles, 2004. Diatom taxonomic and morphological changes as indicators of metal pollution and recovery in Lac Dufault (Québec, Canada). Journal of Paleolimnology 32: 163–175. https://doi.org/10.1023/B:JOPL.0000029430.78278.a5.

Cemagref, 1982. Etude des méthodes biologiques d'appréciation quantitative de laqualité des eaux, Cemagref, Lyon:

Chassiot, L., P. Francus, A. De Coninck, P. Lajeunesse, D. Cloutier & T. Labarre, 2019. Dataset for the assessment of metallic pollution in the Saint-Charles River sediments (Québec City, QC, Canada). Data in Brief 26: 104256. https://doi.org/10.1016/j.dib.2019.104256.

Clements, W. H., D. M. Carlisle, J. M. Lazorchak & P. C. Johnson, 2000. Heavy metals structure benthic communities in Colorado mountain streams. Ecological Applications 10: 626–638. https://doi.org/10.1890/1051-0761(2000)010[0626:HMSBCI]2.0.CO;2.

Cumming, B. F., K. R. Laird, I. Gregory-Eaves, K. J. Simpson, M. A. Sokal, R. N. Nordin & I. R. Walker, 2015. Tracking past changes in lake-water phosphorus with a 251-lake calibration dataset in British Columbia: tool development and application in a multiproxy assessment of eutrophication and recovery in Osoyoos Lake, a transboundary lake in Western North America. Frontiers in Ecolology and Evolution 3: 1–18. https://doi.org/10.3389/fevo.2015.00084.

Denisov, D., P. Terentjev, S. Valkova & L. Kudryavtzeva, 2020. Small lakes ecosystems under the impact of non-ferrous metallurgy (Russia, Murmansk Region). Environments 7: 1–13. https://doi.org/10.3390/environments7040029.

Deryagin, V. V., A. V. Maslennikova & A. V. Deryagin, 2011. Rezhimy osadkonakopleniya v ozerah Serebry i Syrytkul (Juzhnyi Ural) [Sedimentation in lakes Serebry and Syrytkul (Southern Urals)]. Chelyabinsk State University Bulletin 5: 24–30 ((**in Russian**)).

Dunalska, J., 2011. Total organic carbon as a new index for monitoring trophic states in lakes. Journal of Oceanography and Hydrobiology 20: 112–115. https://doi.org/10.2478/S13545-011-0022-7.

de FernándezMartínCorzola Linde LópezSousa, M. R. G. A. E. G. M. M., 2018. Design and testing of a new diatom-based index for heavy metal pollution. Archives of Environmental Contamination and Toxicology. 74: 170–192. https://doi.org/10.1007/s00244-017-0409-6.

Fritz, S. C. & N. J. Anderson, 2013. The relative influences of climate and catchment processes on Holocene lake development in glaciated regions. Journal of Paleolimnology 49: 349–362. https://doi.org/10.1007/s10933-013-9684-z.

Gavrilkina, S. V., Korableva, O. E., Mityuhlyaev, D. V., Rogozin, A. G., Tanaeva, G. V., Tkachev V. A., SHimanskij L. I. 1998. Ekologiya ozera Turgoyak [Ecology of Lake Turgoyak]. IGZ UrO RAN, Miass. 154.

Gorshkov, A. A., 1957. Osnovnye etapy v razvitii Ural'skoj chernoj metallurgii za dva s polovinoj veka ee sushhestvovanija [The main stages in the development of the Ural ferrous metallurgy for two and a half centuries of its existence]. In Gorshkov, A. A. (ed), Iz istorii chernoj metallurgii Urala [From the history of ferrous metallurgy of the Urals] Ural Polytechnic Institute Press, Yekaterinburg: 7–49. **(in Russian)**.

Guiry M. D., Guiry G. M. AlgaeBase. World-wide electronic publication, National University of Ireland, Galway. http://www.algaebase.org; searched on March 1, 2022.

Håkansson, S., 1992. On numerical methods for inference of pH variations in mesotrophic and eutrophic lakes in southern Sweden. Diatom Research 7: 207–211. https://doi.org/10.1080/0269249X.1992.9705208.

Huttunen, P. & J. Turkia, 1990. Surface sediment diatom assemblages and lake acidity. In Kauppi, P., P. Anttila &

K. Kenttдmies (eds), Acidification in Finland. Springer-Verlag, Berlin/Heidelberg.

Isakova, N. A., N. B. Kuyantseva & A. G. Rogozin, 2015. Some aspects of nitrogen accumulation by tissues of submerged aquatic vegetation under conditions of anthropogenic eutrophication. Inland Water Biology 8: 25–32. https://doi.org/10.1134/S1995082915010083.

Jeppesen, E., M. Søndergaard, M. Søndergaard & K. Christoffersen, 1998. The structuring role of submerged macrophytes in lakes. In Jeppesen, E., M. Søndergaard, M. Søndergaard & K. Christoffersen (eds), Ecological studies, Vol. 131. Springer New York, New York: 427.

Juggins, S., 2007. C2 Version 1.5 User guide Software for ecological and palaeoecological data analysis and visualisation, Newcastle University, Newcastle upon Tyne:

Juggins, S., 2013. Quantitative reconstructions in paleolimnology: new paradigm or sick science? Quaternary Science Review 64: 20–32. https://doi.org/10.1016/j.quascirev.2012.12.014.

Kelly, M. G. & B. A. Whitton, 1995. The trophic Diatom Index: a new index for monitoring eutrophication in rivers. Journal of Applied Phycology 7: 433–444. https://doi.org/10.4081/10.1007/BF00003802.

Kolotova, N. S., Eliseeva, E. A., Loseva, O. A., Popov, A. I., Romanenko, L. M., Chernyshova, M. M. (Eds). 2009. Istoriya perepisej naseleniya v Rossii. Sbornik informacionnyh materialov [The history of the population census in Russia. Collection of information materials]. Chelyabinskstat, Chelyabinsk: 66.

Krammer, K. & H. Lange-Bertalot, 1986. Bacillariophyceae. In Ettl, H., J. Gerloff, H. Heynig & D. Mollenhauer (eds), Subwasserflora von Mitteleleuropa, Vol. 2. G. Fisher, Stuttgart.

Krammer, K. & H. Lange-Bertalot, 1988. Bacillariophyceae. In Ettl, H., J. Gerloff, H. Heynig & D. Mollenhauer (eds), Subwasserflora von Mitteleleuropa, Vol. 2. G. Fisher, Stuttgart.

Krammer, K., Lange-Bertalot H. 1991a. Bacillariophyceae. In: Ettl H, Gerloff J, Heynig H, Mollenhauer D (eds) Subwasserflora von Mitteleleuropa, vol 2(3). G. Fisher, Stuttgart

Krammer, K., Lange-Bertalot H. 1991b. Bacillariophyceae. In: Ettl H, Gerloff J, Heynig H, Mollenhauer D (eds) Subwasserflora von Mitteleleuropa, vol 2(4). G. Fisher, Stuttgart.

Kratzer, C. R. & P. L. Brezonik, 1981. A Carlson-type trophic state index for nitrogen in Florida Lakes. Water Resourses Bulletin 17: 713–715. https://doi.org/10.1111/j.1752-1688.1981.tb01282.x.

Kulbahtin, S.N. 2008. Medeplavil'nye zavody Simbirskih kupcov Tverdyshevyh i Myasnikovyh na Yuzhnom Urale v XVIII veke [Copper smelting plants of the Simbirsk merchants Tverdyshev and Myasnikovs in the Southern Urals in the XVIII century]. RIC BashGU, Ufa: 200.

Kulikovskiy, M. S., Glushechenko, A. M., Genkal, S. I., Kuznetsova, I. V., 2016. Opredelitel' diatomovyh vodoroslej Rossii [Identification book of diatoms from Russia]. Filigran Press, Yaroslavl (in Russian). 803.

Laird, K. R., S. C. Fritz, B. F. Cumming & E. C. Grimm, 1998. Early-holocene limnological and climatic variability in the northern great plains. The Holocene 8: 275–285. https://doi.org/10.1191/095968398673895438.

Lange-Bertalot, H., G. Hofmann, M. Werum & M. Cantonati, 2017. Freshwater benthic diatoms of Central Europe: Over 800 common species used in ecological assessment, Koeltz botanical books, Kapellenbergstr.:, 942.

Leclercq L, Lecointe C. 2008. Présentation de l'indice diatomique de saprobie-eutrophisation (IDSE) introduit dans la nouvelle version de Omnidia. 27ème Colloque de l'ADLaF Dijon 1–4 Sept. Livre des résumés. F. R. a. L. ECTOR. C23, 50.

Lecointe, C., M. Coste & J. Prygiel, 1993. Omnidia: software for taxonomy, calculation of diatom incices and inventories management. Hydrobiologia 269(270): 509–513.

Loring, D. H., 1991. Normalization of heavy-metal data from estuarine and coastal sediments. Journal of Marine Science. 48: 101–115.

Lotter, A. F., 1989. Subfossil and modern diatom plankton and the paleolimnology of Rotsee (Switzerland) since 1850. Aquatic Science 51: 338–350. https://doi.org/10.1007/BF00877176.

Lozhkin, V. A., 1971. Ozero Tavatuj [Lake Tavatui], in: A.N. Mihajlov, Chelovek i stihija Nauchno-populjarnyj gidrometeorologicheskij sbornik [Man and element. Scientific and popular hydrometeorological collection]. Press, St. Petersburg. (in Russian).

Magnuson, J. J., D. M. Robertson, B. J. Benson, R. H. Wynne, D. M. Livingstone, T. Arai, R. A. Assel, R. G. Barry, V. Card, E. Kuusisto, N. G. Granin, T. D. Prowse, K. M. Stewart & V. S. Vuglinski, 2000. Historical trends in lake and river ice cover in the Northern Hemisphere. Science 289: 1743–1746.

Maslennikova, A. V., 2020. Development and application of an electrical conductivity transfer function, using diatoms from lakes in the Urals, Russia. Journal of Paleolimnology 63: 129–146. https://doi.org/10.1007/s10933-019-00106-z.

Maslennikova, A. V., 2022. Holocene environments in the Middle Urals: Paleolimnological proxies from the Lake Tavatui (Russia). Quaternary International 622: 51–64. https://doi.org/10.1016/j.quaint.2022.02.033.

Maslennikova, A. V. & V. N. Udachin, 2017. Lakes ecosystem response to Holocene climate changes and human impact in the Southern Urals: Diatom and geochemical proxies. The Holocene 27: 847–859. https://doi.org/10.1177/0959683616675942.

Maslennikova, A. V., V. N. Udachin & P. G. Aminov, 2016. Lateglacial and Holocene environmental changes in the Southern Urals reflected in palynological, diatom, geochemical records from the Lake Syrytkul sediments. Quaternary Interantional. 420: 65–75. https://doi.org/10.1016/j.quaint.2015.08.062.

Maslennikova, A. V., V. N. Udachin, V. V. Deryagin & M. V. Shtenberg, 2018. Rekonstrukciya etapov razvitiya ozera Turgoyak (YUzhnyj Ural) v golotsene [Reconstruction of Turgoyak lake (the Southern Urals) ecosystem changes in Holocene]. Lithosphere 11: 914–927. https://doi.org/10.24930/1681-9004-2018-18-6-914-927.

Maslennikova, A. V., D. A. Artemyev, M. V. Shtenberg, K. A. Filippova & V. N. Udachin, 2020. Express multi-element determination in lake sediments by laser ablation mass-spectrometry (LA-ICP-MS). Limnology and Oceanography: Methods 18: 411–423. https://doi.org/10.1002/lom3.10372.

Maslennikova A. V. 2019. Assessment of natural and anthoropogenic transformation of Southern Urals lakes. Materialy VIII Mezhdunarodnoj nauchnoj konferencii: Problemy prirodopol'zovanija i jekologicheskaja situacija v Evropejskoj Rossii i na sopredel'nyh territorijah [Proceedings of the VIII International Scientific Conference: Problems of Nature Management and the Ecological Situation in European Russia and Adjacent Territories]. (In Russian).

Michelutti, N., C. A. Cooke, W. O. Hobbs & J. P. Smol, 2015. Climate driven changes in lakes from the Peruvian Andes. Journal of Paleolimnology 54: 153–160. https://doi.org/10.1007/s10933-015-9843-5.

Morfett, K., W. Davison & J. Hamilton-Taylor, 1988. Trace metal dynamics in a seasonally anoxic lake. Environmental Geology and Water Sciences 11: 107–114. https://doi.org/10.1007/BF02587769.

Morin, S., T. T. Duong, A. Dabrin, A. Coynel, O. Herlory, M. Baudrimont, F. Delmas, G. Durrieu, J. Schafer, P. Winterton, G. Blanc & M. Coste, 2008. Long-term survey of heavy-metal pollution, biofilm contamination and diatom community structure in the Riou Mort watershed, South-West France. Environmental Pollution 151: 532–542. https://doi.org/10.1016/j.envpol.2007.04.023.

Morin, S., N. Corcoll, B. Bonet, A. Tlili & H. Guasch, 2014. Diatom responses to zinc contamination along a Mediterranean river. Plant Ecology and Evolution 147: 325–332. https://doi.org/10.5091/plecevo.2014.986.

Normativy kachestva vody vodnyh obektov rybohozjajstvennogo znachenija, v tom chisle normativy predel'no dopustimyh koncentracij vrednyh veshhestv v vodah vodnyh objektov rybohozjajstvennogo znachenija. [Standards of water quality of water bodies of fishery significance, including standards of maximum permissible concentrations of harmful substances in the waters of water bodies of fishery significance]. Appendix to the Order of the Ministry of Agriculture of the Russian Federation No. 552 dated December 13, 2016 (as amended on October 12, 2018 and March 10, 2020). https://base.garant.ru/71586774/53f89421bbdaf741eb2d1ecc4ddb4c33/

O'Reilly, C. M., S. Sharma, D. K. Gray, S. E. Hampton, et al., 2015. Rapid and highly variable warming of lake surface waters around the globe. Geophysical Research Letters 42: 10773–10781. https://doi.org/10.1002/2015GL066235.

Palagushkina, O., L. Nazarova & L. Frolova, 2019. Trends in development of diatom flora from sub-recent lake sediments of the Lake Bolshoy Kharbey (Bolshezemelskaya tundra, Russia). Biological communications 64: 244–251. https://doi.org/10.2163/spbu03.2019.403.

Petrov, V. I., Shalaginov, A. Je., Punegov, B. N., Gorlova, L. I., Zabelkina, L. G., Grigorova, T. B., Nikol'skij, V. Ju., Shalaginova, V. I., Petrova, A. S., Sereda, V. V. 2015. Gosudarstvennaja geologicheskaja karta Rossijskoj Federacii masshtaba 1: 200 000. List N-41-VII (objasnitel'naja zapiska). Serija Juzhno-Ural'skaja. [State Geological Map of the Russian Federation scale 1: 200 000. Sheet N-41-VII (explanatory note). The South Ural series.]. MF VSEGEI, Moskow. 167. (in Russian).

Pociecha, A., A. Z. Wojtal, E. Szarek-Gwiazda, A. Cieplok, D. Ciszewski & S. Cichoń, 2020. Neo- and Paleo-limnological studies on diatom and cladoceran communities of subsidence ponds affected by mine waters (S. Poland). Water 12: 1581. https://doi.org/10.3390/w12061581.

Pogoda i klimat [Weather and climate] http://www.pogodaiklimat.ru/history/28440.htm (Accessed 30 October 2022).

Pogoda i klimat. [Weather and climate] http://www.pogodaiklimat.ru/history/28630.htm (Accessed 30 October 2022).

Proshkina-Lavrenko, A.I. (Ed.). 1974. Diatomovye vodorosli SSSR. Iskopaemye i sovremennye [Diatoms of the USSR. Fossil and modern]. V. 1, Nauka Publ., St-Petersburg. 403. (in Russian).

Prygiel, M., Coste, M. 2000. Guide méthodologique pour la mise en œuvre de l'indice biologique diatomées NF T90-354. Agences de l'Eau, MATE, Cemagref Bordeaux. 134.

Radbourne, A. D., J. A. Elliott, S. C. Maberly, D. B. Ryves & N. J. Anderson, 2019. The impacts of changing nutrient load and climate on a deep, eutrophic, monomictic lake. Freshwater Biology 64: 1–14. https://doi.org/10.1111/fwb.13293.

Reavie, E. D., G. V. Sgro, L. R. Estepp, A. J. Bramburger, V. L. Shaw Chraïbi, R. W. Pillsbury, M. Cai, C. A. Stow & A. Dove, 2017. Climate warming and changes in *Cyclotella sensu* lato in the Laurentian Great Lakes. Limnology and Oceanography. 62: 768–783. https://doi.org/10.1002/lno.10459.

Reichardt, E., 2018. Die Diatomeen im Gebiet der Stadt Treuchtlingen, V. 1–2, Selbstverlag der Bayerischen Botanischen Gesellschaft, München. 1184.

Reimer, P., W. Austin, E. Bard, A. Bayliss, P. Blackwell, C. Bronk Ramsey & S. Talamo, 2020. The IntCal20 Northern Hemisphere radiocarbon age calibration curve (0–55 cal kBP). Radiocarbon 62: 725–757. https://doi.org/10.1017/RDC.2020.41.

Renberg, I. & T. Hellberg, 1982. The pH history of lakes in southwestern Sweden, as calculated from the subfossil diatomflora of the sediments. Ambio 11: 30–33.

Rioual, P. 2000. Diatom assemblages and water chemistry of lakes in the French Massif Central: a methodology for reconstruction of past limnological and climate fluctuations during the Eemian period. Unpublished PhD thesis, University College London.

Rogozin, A. G., 1998. Sravnitel'naja saprobiologicheskaja kharakteristika ozer Turgoyak i Bol'shoe Miassovo [Comparative saprobiological characteristics of the lakes Turgoyak and Bolshoe Miassovo]. Proceedings of the Chelyabinsk Scientific Center 1: 75–81 ((**in Russian**)).

Rogozin, A.G., Tkachev, V.A. 2000. Ekologiya ozera Bol'shoe Miassovo [Ecology of Lake Bol'shoe Miassovo]. IGZ UrO RAN, Miass: 319.

Rogozin, A. G., N. A. Isakova & L. V. Snit'ko, 2017. Retrospective of diatom diversity dynamics in Thanatocenoses under climate change. Inland Water Biology 10: 153–157. https://doi.org/10.1134/S1995082917020122.

Ruggiu, D., A. Luglié, A. Cattaneo & P. Panzani, 1998. Paleoecological evidence for diatom response to metal pollution in Lake Orta (N. Italy). Journal of Paleolimnology 20: 333–345. https://doi.org/10.1023/A:1007929926526.

Rühland, K. M., A. M. Paterson & J. P. Smol, 2015. Lake diatom responses to warming: reviewing the evidence. Journal of Paleolimnology 54: 1–35. https://doi.org/10.1007/s10933-015-9837-3.

Rumeau, A. & M. Coste, 1988. Initiation à la systématique des Diatomées d'eau douce. Bulletin Francais De Pisciculture: Ichthyologie Et Hydrobiologie Appliquees 309: 69.

Salonen, V.-P., N. Tuovinen & S. Valpola, 2006. History of mine drainage impact on Lake Orijärvi algal communities, SW Finland. Journal of Paleolimnology 35: 289–303. https://doi.org/10.1007/s10933-005-0483-z.

Scheffer, M., 2004. The story of some shallow lakes. In Usher, M. B. (ed), Ecology of shallow lakes. Kluwer Academic Publishers, Dordrecht.

Sementovskiy, V. N., 1913. Zhemchuzhina Juzhnogo Urala. Ozero Turgojak [The pearl of the Southern Urals. Lake Turgoyak]. Priroda i Ljudi 15: 225–228.

Sivarajah, B., J. B. Korosi, J. M. Blais & J. P. Smol, 2019. Multiple environmental variables influence diatom assemblages across an arsenic gradient in 33 subarctic lakes near abandoned gold mines. Hydrobiologia 841: 133–151. https://doi.org/10.1007/s10750-019-04014-1.

Sládeček, V., 1986. Diatom as indicators of organic pollution. Acta Hydrochimica Et Hydrobiologica 14: 555–566.

Slukovskii, Z. I., T. S. Shelehova & E. V. Syroezhko, 2018. Otklik diatomovoj flory malogo ozera na vozdejstvie tjazhelyh metallov v uslovijah urbanizirovannoj sredy Respubliki Karelii [The response of the diatom flora of the small lake to the effects of heavy metals in the urbanized environment of the Republic of Karelia]. Vestnik SPbSU. Vestnik SPbSU. Earth Science 53: 103–123. https://doi.org/10.21638/11701/spbu07.2018.106.

Smol, J. P., A. P. Wolfe, Douglas MSV. BirksHJB, V. J. Jones, A. Korhola, R. Pienitz, K. Rühland, S. Sorvari, D. Antoniades, S. J. Brooks, M.-E. Fallu, M. Hughes, B. E. Keatley, T. R. Laing, N. Michelutti, M. Nyman, A. M. Paterson, B. Perren, R. Quinlan, M. Rautio, E. Saulnier-Talbot, S. Siitonen, N. Solovieva & J. Weckström, 2005. Climate-driven regime shifts in the biological communities of Arctic lakes. Proceedings of the National Academy of Sciences of USA 102: 4397–4402. https://doi.org/10.1073/pnas.0500245102.

Snit'ko, L. V. & V. P. Snit'ko, 2015. Many year variations of phytoplankton in the Argazinskoe reservoir (Southern Urals). Water Resources. 42: 232–240. https://doi.org/10.1134/S009780781502013X.

Snit'ko, L. V. & V. P. Snit'ko, 2019. Taxonomic structure and ecology of phytoplankton in small forest lakes in the zone of technogenesis of sulphide deposits (Southern Urals). Inland Water Biology 12: 393–400. https://doi.org/10.1134/S1995082919040151.

Solovieva, N., V. J. Jones, L. Nazarova, S. J. Brooks, H. J. B. Birks, J.-A. Grytnes, P. G. Appleby, T. Kaupila, B. Kondratenok, I. Renberg & V. Ponomarev, 2005. Palaeolimnological evidence for recent climatic change in lakes from the northern Urals, arctic Russia. Journal of Paleolimnology 33: 463–482. https://doi.org/10.1007/s10933-005-0811-3.

Solovieva, N., V. Jones, J. H. B. Birks, P. Appleby & L. Nazarova, 2008. Diatom responses to 20th century climate warming in lakes from the northern Urals, Russia. Palaeogeography Palaeoclimatology Palaeoecology 259: 96–106. https://doi.org/10.1016/j.palaeo.2007.10.001.

Sorokina, O. A. & N. D. Sorokin, 2007. The influence of pine forests of different ages on the biological activity of layland soils in the middle angara river basin. Eurasian Soil Science 40: 569–575. https://doi.org/10.1134/S1064229307050134.

Strel'bickij, I. A. 1871. Special'naja karta Evropejskoj Rossii s prilegajushhej k nej chast'ju Zapadnoj Evropy i Maloj Azii [A special map of European Russia with the adjacent part of Western Europe and Asia]. Masshtab 1:420000. Izdanie voenno-topograficheskogo otdela glavnogo shtaba, Moskow. http://retromap.ru/1418711_z12_55.326605,60.263786 (in Russian).

Strel'bickij, I. A. 1919. Special'naja karta Evropejskoj Rossii s prilegajushhej k nej chast'ju Zapadnoj Evropy i Maloj Azii [A special map of European Russia with the adjacent part of Western Europe and Asia]. Masshtab 1:420000. Izdanie voenno-topograficheskogo otdela glavnogo shtaba, Moskow. http://retromap.ru/1419197_z12_55.264837,60.233230 (in Russian).

Sutherland, R. A., 2000. Bed sediment–associated trace metals in an urban stream, Oahu. Hawaii. Environmental Geology 39: 611–627. https://doi.org/10.1007/s002540050473.

ter Braak, C. J. F. & S. Juggins, 1993. Weighted averaging partial least- squares regression (WA-PLS) – an improved method for reconstructing environmental variables from species assemblages. Hydrobiologia 269: 485–502. https://doi.org/10.1007/BF00028046.

ter Braak, C. J. F. & P. Smilauer, 2002. CANOCO reference manual and CanoDraw for windows user's guide: software for canonical community ordination (version 4.5), Microcomputer Power, Ithaca:

Thienpont, J. R., J. B. Korosi, K. E. Hargan, T. L. Williams, D. Eickmeyer, L. Kimpe, M. Palmer, J. Smol & J. Blais, 2016. Multitrophic level response to extreme metal contamination from gold mining in a subarctic lake. Proceedings Royal Society 283: 1–9. https://doi.org/10.1098/rspb.2016.1125.

Tichá, A., T. Bešta, D. Vondrák, P. Houfková & V. Jankovská, 2019. Nutrient availability affected shallow-lake ecosystem response along the Late-Glacial/Holocene transition. Hydrobiologia 846: 87–108. https://doi.org/10.1007/s10750-019-04054-7.

Tomlinson, D. L., J. G. Wilson, C. R. Harris & D. Jeffrey, 1980. Problems in the assessment of heavy-metal levels in estuaries and the formation of a pollution index. Helgolander Meeresunters 33: 566–575. https://doi.org/10.1007/BF02414780.

Tuovinen, N., K. Weckström & V.-P. Salonen, 2012. Impact of mine drainage on diatom communities of Orijarvi and Maarjarvi, lakes in SW Finland. Boreal Environment Research 17: 437–446.

Udachin, V. N., Aminov, P. G., Filippova, K. A. 2014. Geohimija gornopromyshlennogo tehnogeneza Juzhnogo Urala [Geochemistry of mining technogenesis in the Southern Urals]. Editing and publishing department UB RAS, Yekaterinburg. 252. (in Russian).

Van Dam, H., A. Mertens & J. Sinkeldam, 1994. A coded checklist and ecological indicator values of freshwater diatoms from The Netherlands. Netherlands Journal of Aquatic Ecology 28: 117–133. https://doi.org/10.1007/BF02334251.

Wang, M., X. Xu, Z. Wu, X. Zhang, P. Sun, Y. Wen & Y. Tong, 2019. Seasonal pattern of nutrient limitation in a eutrophic lake and quantitative analysis of the impacts from internal nutrient cycling. Environmental Science and Technology 53: 13675–13686. https://doi.org/10.1021/acs.est.9b04266.

Wetzel, R. G., 2001. Limnology lake and river ecosystems, 3rd ed. Academic Press, San Diego: 1006.

Winder, M. & U. Sommer, 2012. Phytoplankton response to a changing climate. Hydrobiologia 698: 5–16. https://doi.org/10.1007/s10750-012-1149-2.

Winder, M., J. E. Reuter & S. G. Schladow, 2009. Lake warming favours small-sized planktonic diatom species. Proceedings of the Royal Society b: Biological Sciences 27: 427–435. https://doi.org/10.1098/rspb.2008.1200.

Wunsam, S. & R. Schmidt, 1995. A diatom-phosphorus transfer function for Alpine and pre-alpine lakes. Memorie Dell'istituto Italiano Di Idrobiologia 53: 85–99.

Yim, J. H., K.-W. Kim & S. D. Kim, 2006. Effect of hardness on acute toxicity of metal mixtures using Daphnia magna: prediction of acid mine drainage toxicity. Journal of Hazardous Materials 138: 16–21. https://doi.org/10.1016/j.jhazmat.2005.11.107.