Article

Ecological State of Lake Gusinoe—A Cooling Pond of the Gusinoozersk GRES

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Abstract: The study of the transformation of substances in the basin of the Selenga River—the main tributary of Lake Baikal—under anthropogenic pressure and in the context of global climate change, is especially important for the lake, a globally important source of drinking water. The ecosystem of Lake Gusinoe is one of the key objects in the Selenga River basin that is exposed to significant anthropogenic pressure. This study presents the results of an analysis of water level changes and physicochemical parameters of the water mass of Lake Gusinoe; literature data from 1951 to 2017 and own data from 2017 to 2021. The water level in the lake had depended on natural factors before the Gusinoozersk GRES was launched; however, since the plant has begun using the lake as a cooling pond, its level has actually been regulated by the economic entity. Over the years, there has been a significant increase in mineralization, sulfate, sodium, fluoride and organic matter fractions resistant to oxidation. Seasonal increases in iron and manganese concentrations in water were detected. Increased concentrations of nutrients and organic matter fractions resistant to oxidation were registered at the wastewater discharge sites. Heavy metals in the bottom sediments of Lake Gusinoe accumulate mainly in the silt of the deep zone of the lake. Plants growing in the zones of influence of the Gusinoozersk GRES and Gusinoozersk wastewater discharge accumulate the largest amount of metals.

Keywords: Lake Gusinoe; Selenga River basin; cooling pond; water quality; anthropogenic activity; bottom sediments

1. Introduction

Drinking water scarcity, worsened by industrial pollution of surface water, has been a global problem since the twentieth century [1–4]. Climate change, melting glaciers, an increase in average water temperatures and in the frequency of droughts and floods exacerbate these problems [5,6].

Climate change and anthropogenic pressure make it important to study the ecological condition of water bodies located in the basin of the Selenga River, the main tributary of Lake Baikal. The river's runoff accounts for 50% of the total water inflow and more than 50% of the chemical inflow into the lake. This is notable, given that Baikal is a World Natural Heritage site and a source of drinking water of global importance [7–9].

Lake Gusinoe is one of the key water bodies in the Selenga basin. The amount of precipitation and volume of water coming with river runoff and groundwater are the main natural factors that determine the ecological condition of the lake [10,11]. The lake is

used intensively for water and fishery purposes, and it is the only source of domestic and drinking water for the town of Gusinoozersk and the adjacent settlements with a population of about 30 thousand people. The industrial hub of Gusinoozersk—one of the largest in Buryatia—has formed near the lake. It includes power generating, processing and transport enterprises, most of which are located near the town of Gusinoozersk on the northern and northeastern shores of the lake. On the southwestern part of the lake is the village of Gusinoe Ozero with a railway station and locomotive depot. The 1190 MW Gusinoozersk GRES (GRES stands for 'state-owned regional electricity-generating station') makes 85.1% of the total surface water consumption in Buryatia. As it is located on the lake shore, it is the largest source of pollution. Historic records show that GRES wastewater discharges have increased along with an intensified withdrawal of water for power generation [12].

Huge amounts of the GRES emissions into the atmosphere (79 thousand tons/year) [13] are largely deposited on the surface of the lake, worsening its ecological condition. Since the beginning of underground coal mining in the Gusinoozersk coal basin in 1940, over 40 million m^3 of untreated mine waters have been discharged into the lake. In 1961, the development of the Kholboldzhinsky coal mine began on the eastern shore of the lake, the pit waters of which were also discharged into the lake. Currently, the negative impact is caused by the unreclaimed overburden rocks of the coal mine, located along the entire eastern coast. There is a potential threat to Baikal's ecosystem due to the above-mentioned pollution sources, since the only river flowing out of Lake Gusinoe, the Bain-gol, flows into the Selenga River, the main tributary of Baikal, after 14 km [14–16].

The Buryat Center for Hydrometeorology and Environmental Monitoring (CHEM) has regularly surveyed the hydrochemical condition of the lake since 1951 at a water gauge near the village of Gusinoe Ozero, but its location near the confluence of the Tsagan-gol River characterizes the mixing zone of river and lake waters. Obozhin and Klikunova [17] data on the hydrochemical condition of Lake Gusinoe in 1958 and 1974 can be considered background, as they were obtained before the opening of the Kholboldzhinsky coal mine in 1961 and the launch of the GRES in 1976. Hydrochemical studies by Samarina and Khudyakova [18], conducted in 1965–1967, and by Domysheva et al. [19] in 1991–1992 confirmed chemical changes in the lake waters due to pollution by sewage from coal mines and the GRES, respectively [14]. A recent study by Lukyanova et al. [20] of the hydrological structure of the lake has shown that intensive water exchange between water layers plays a significant role in the lake regime. In addition to hydrologic and hydrochemical studies, it is important to characterize the current climatic and anthropogenic impact on the entire ecosystem of Lake Gusinoe: on the chemical composition of the water, on BS and biota.

The aim of this study is to analyze the current ecological condition of the ecosystem of Lake Gusinoe, in view of the spatial and temporal changes in the water regime and the chemical composition of the lake waters for a long-term period (1951–2021). With this objective in mind, the following tasks were defined: (i) to analyze spatio-temporal changes in the lake level; (ii) to evaluate the influence of the dynamics of precipitation and river flow on the lake level; (iii) to identify spatio-temporal changes in physicochemical characteristics, concentrations of major ions, biogenic elements and trace elements in the water; and (iv) to evaluate distribution and accumulation of HMs in BSs and aquatic vegetation.

2. Materials and Methods

2.1. Study Area

Lake Gusinoe is the largest freshwater body in Transbaikalia with a catchment area of 924 km^2, water surface area of 163 km^2, a length of 24.8 km, an average width of 8 km, a maximum depth—26 m and average depth—15 m. The volume of water is estimated at 2.4 km^3, the level of the coastline is 551 m a.s.l. [14]. The lake is located in the Gusinoozerskaya depression, a graben-synclinal basin located between two crystalline uplifts—the Khambinsky Ridge in the northwest and the Monostoisky Ridge in the southeast. From the hydrogeological point of view, the lake occupies a significant part of the subaquatic artesian basin of the Transbaikalian type, which was formed during the Jurassic-Cretaceous pe-

riod [15]. The littoral part (<2 m depth) of the lake is only 6.3% of the total surface area [17]. The coastline has a length of 65 km, is slightly dissected, in some places precipitous, but mostly low and sandy. The bottom is predominantly muddy. The lake belongs to low-flow reservoirs (with the relative water exchange rate of 0.0125). The sum of the flow of all tributaries is only 4 m^3/s in the closing alignment, which is low-flow. Most tributaries often freeze over in winter, and in summer they often do not reach the lake, getting lost in loose sediments at a distance of 300–500 m from the lake shore. The hydrographic network is represented by 72 watercourses with a total length of 312 km. The largest tributary in terms of water content is the Tsagan-gol River, which flows from the Temnik River and flows into the lake in the south-western part. The Zagustai River, the longest river (44 km) with the largest catchment area (382 km^2), flows into the lake in its northern part, cutting through the Khambinsky Ridge. Only one river—the Bain-gol—flows out of the lake in its southeastern part and after 14 km flows into the Selenga River [14].

The climate is sharply continental with large annual and daily temperature fluctuations and a small amount of precipitation during the year. The average annual temperature is 1.6 °C. The average monthly air temperature in July is 20.3 °C and is 25.1 °C in January. The average annual precipitation (250 mm) and the average monthly precipitation (2–64 mm) fluctuates greatly (Figure 1), resulting in frequent spring droughts [21].

The lake is covered with ice by the end of October or beginning of November. Ice melting begins in late March or early April and ends in late April or early May. Due to the discharge of heated water from the GRES, the lake does not freeze completely. Near the discharge channel, an open hollow of 0.4–0.5 km^2, which is about 0.25% of the water area, remains open every winter (Figure 2) [22]. According to the thermal survey data of 26 March 2017, an ice-hole of 3 × 3 km^2 in size with a surface water temperature of 14 °C at the discharge site was formed as a result of heated water discharge from the GRES. To validate the temperature fields retrieved from Landsat-8 TIRS data, autonomous temperature loggers (Onset HOBO ± 0.5 °C accuracy) were installed [23].

For the period of 1970–2020, the average monthly water temperature in the lake in May, July and September is 6.5 °C, 20.1 °C and 6.3 °C, respectively (gauging station at Gusinoe Ozero) [24].

2.2. Data Sources

Historical data on water levels in the lake (gauging station at Gusinoe Ozero), precipitation (Novoselenginsk weather station), average monthly air temperature and hydrologic data for the Russian part of the Selenga River basin are provided by the Buryat Center for Hydrometeorology and Environmental Monitoring, a branch of the Zabaikalsky Department for Hydrometeorology and Environmental Monitoring, and from state reports "On the state of Lake Baikal and measures for its protection".
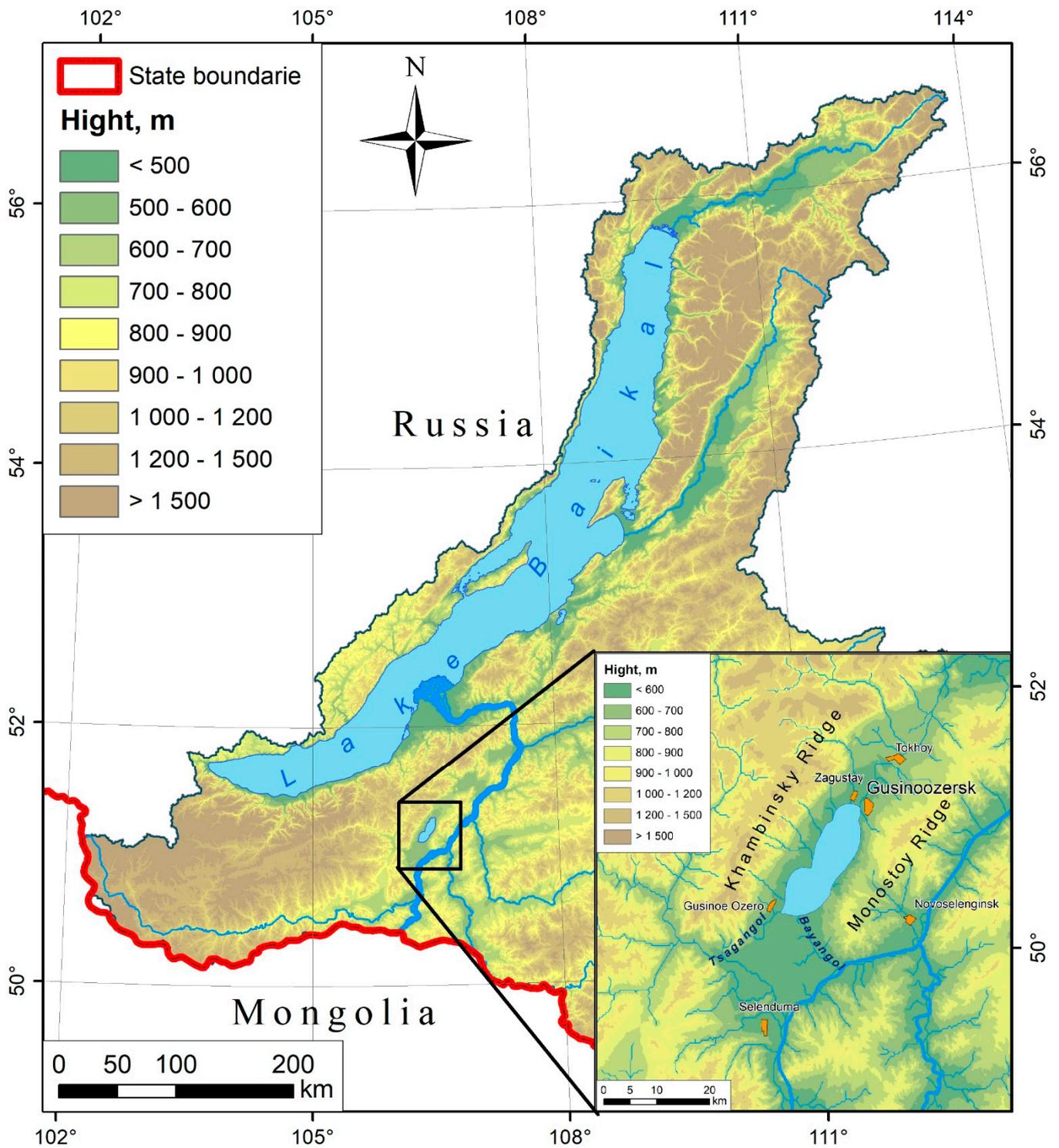
Figure 1. Russian part of the Lake Baikal basin and the Lake Gusinoe basin.

Aquatic area	Area (km²)	Area (%)	Acquisition date
	0.41	0.25	21-12-2017 without ice cover
	0.30	0.18	13 Jan 2018
	0.16	0.10	14 Feb 2018
	0.78	0.49	11 Mar 2018
	0.92	0.56	27 Mar 2018
	0.87	0.53	03 Apr 2018
	1.86	1.14	12 Apr 2018
	157.76	96.75	30 May 2018

LEGEND

Waste liquid channel
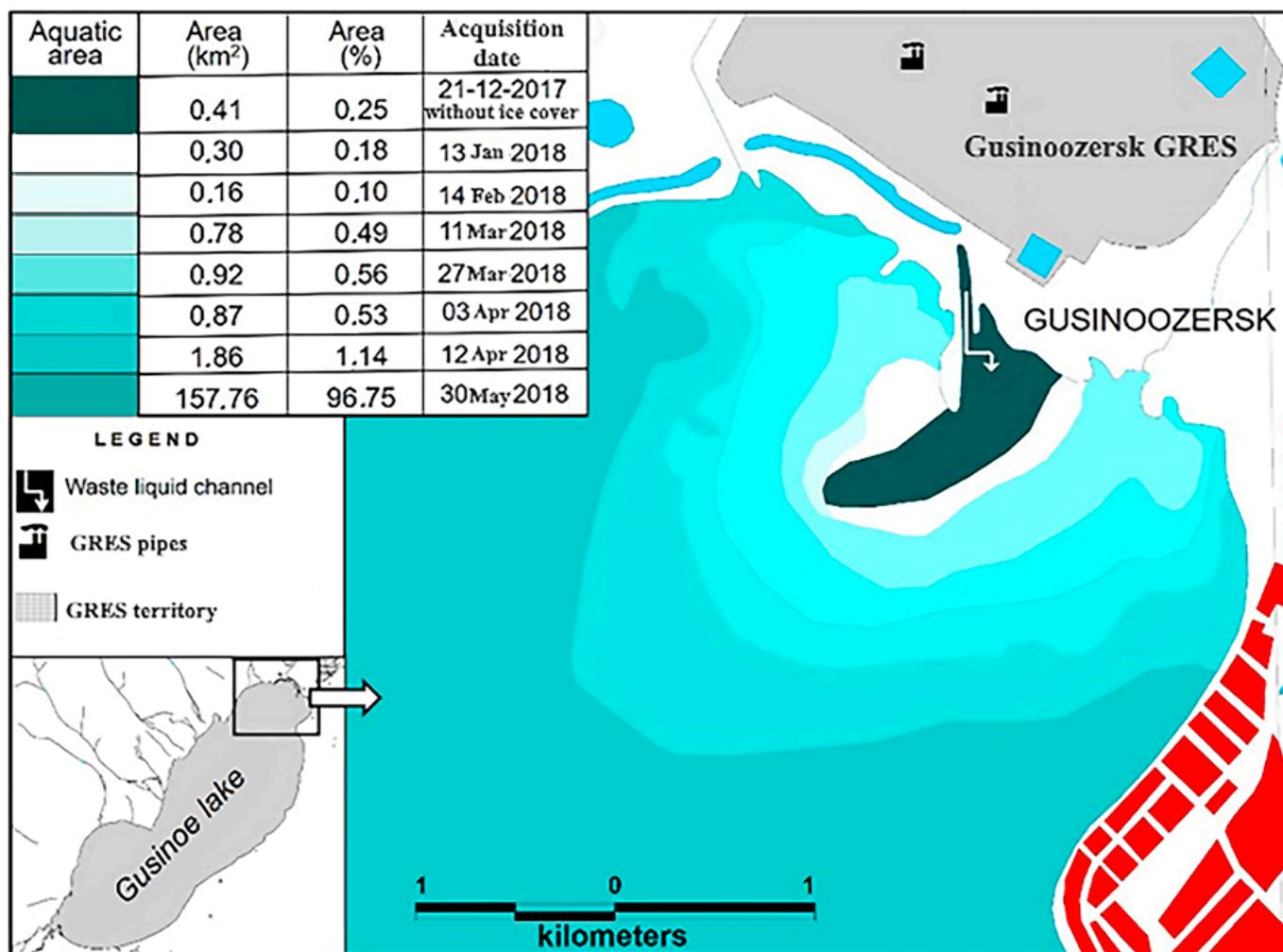
GRES pipes

GRES territory

Figure 2. Ice regime of the lake near the GRES.

2.3. Methods

2.3.1. Field Studies

To comprehensively study the ecological condition of Lake Gusinoe based on geo-chemical analyses, we conducted field work—collecting water samples, BSs and aquatic vegetation from 2017–2021 in the central and coastal parts of the lake. Sampling was carried out in the deep-water areas, as well as in the coastal zone in key areas, taking into account the sources of pollutants. A total of 27 aquatic plant samples were collected during the summer period (July–August); 92 BS samples (42 at a depth of 15–25 m, 50 at a depth of 0.5–10 m) and 176 surface (0.2–0.5 m depth) and 98 bottom (15–25 m depth) water samples during the winter–spring, spring, summer and fall periods (February–March, May, July and September–October). The number of samples in each sampling point was: in the coastal zone (points 1–12)—4–8 surface water samples and 3–5 BS samples, in the deep-water zone (points 13–21—10–12 surface and bottom water samples and 4–6 BS samples. Coastal waters of Lake Gusinoe were sampled at a distance of 3–5 m from the shore and a depth of 50 cm. In the pelagic area, water samples were taken from the surface (98 samples from 0.2–0.5 m depth) and the bottom (98 samples from 15–25 m depth) with a deep–water sampler (Figure 3). Water was taken in a pre-cleaned polypropylene bottle and immediately filtered through disposable sterile Sartorius filter elements (pore size 0.45 μm). The first 50 mL of the filtrate was discarded. The filtered solutions for cation and trace element analysis were acidified (pH = 2) with ultrapure bidistilled HNO_3 and stored in HDPE bottles prewashed with 1 M HCl and rinsed with MilliQ deionized water. Filtered water

samples for anions were not acidified and stored in HDPE bottles prewashed according to the procedure described above for cations. Some components were analyzed directly at the sampling sites; the remaining samples were fixed according to the analysis procedure and transported in a refrigerated box at 1–3 °C, within two days to the institute's laboratory.
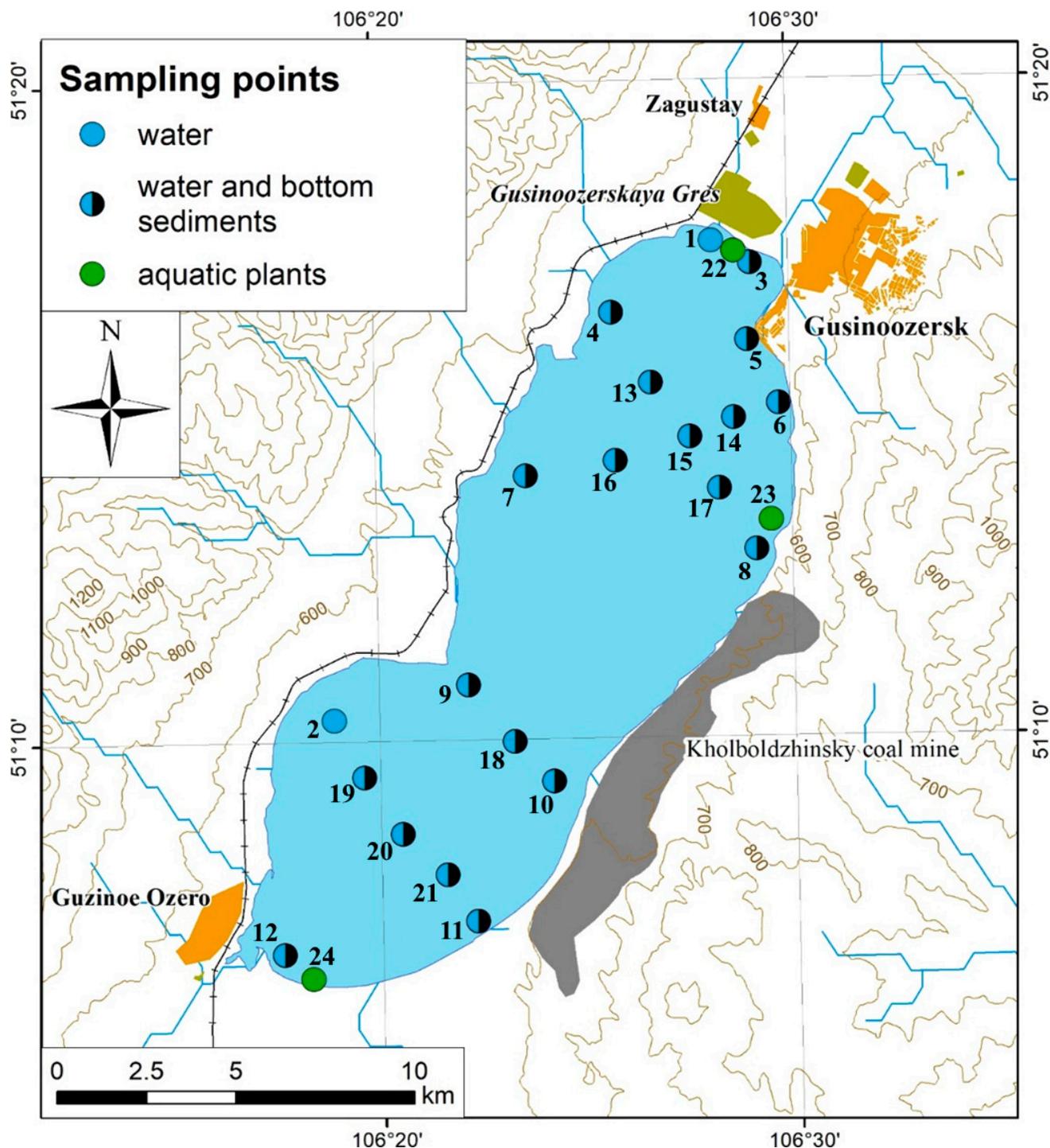

Figure 3. Sampling points for water, BS and aquatic plants at Lake Gusinoe.

Samples of BSs were taken from the surface layer with a Petersen dredger with a grab area of 250 cm^2 and stored in polyethylene bags. Submerged macrophytes: higher plants—*Potamogeton* L., *Myriophyllum* L., *Fontinalis antipyretica* Hedw., *Elodea canadensis* Michx and algae—*Chara* spp. algae, Green filamentous (*Chlorophyta*) were collected at a

constant depth of 50 ± 20 cm; each sample consisted of a group of 5–7 plants of each species, which were thoroughly washed in situ with lake water before being placed in polyethylene bags. In the laboratory, they were rinsed again with distilled water to remove all material adhering to the surface [25–27].

2.3.2. Laboratory Analyses

We performed chemical analyses at the Laboratory of Nature Systems Chemistry (Baikal Institute of Nature Management SB RAS) using Russian National standard methods (GOST). The concentrations of some elements in water samples were determined in the field chemical laboratory on the day of sampling taking into account the requirements of GOST [28–32]. Temperature, turbidity, pH value, dissolved oxygen (DO), total dissolved solids (TDS), the content of hydrocarbonates, phosphates, ammonium, nitrites, nitrates and chemical oxygen demand (COD) in water were measured in a field laboratory using additional equipment (pH-tester, Hanna portable instruments (HI 991300, HI 98703), photoelectric colorimeter (PE-5400 UV, Ecroskhim, Russia) on the day of sampling. Water pH was measured by the potentiometric method, DO content by the Winkler test with an error 0.3%, hydrocarbonates were measured by the titrimetric method, mass concentration of nitrites—by photometric detection using Griss reagent. Nitrate concentration was determined by the photometric method using salicylic acid, the concentration of ammonium ion by photometric detection using Nessler reagent, and phosphate concentration by photometric detection through ascorbic acid deoxidation. Nutrients were analyzed using a photocolorimeter (2–5% error). COD was determined based on oxidation of organic substances by excess potassium dichromate in sulfuric acid solution in the presence of a catalyst (silver sulfate) and subsequent photometric detection (2–5% error) [33]. Concentrations of F^- and major anions (Cl^-, SO_4^{2-}), cations (K^+, Na^+, Ca^{2+} and Mg^{2+}) were analyzed by ion chromatography (Dionex 1600), 2–5% error. The reliability of the obtained results was controlled using ionic balance error evaluation and comparison of the calculated and measured specific conductivity [34].

The BSs samples were divided into two parts after transportation to the laboratory. The first part of the sediment was dried at 21 °C. Subsequently, the total organic matter (TOM) content was determined. TOM was measured by the Tyurin method with wet oxidation, followed by ferrous ammonium sulphate titration [35]. Granulometric composition of sediment samples was analyzed by laser diffraction on a laser particle analyzer Analysette 22 MicroTec Plus (Fritsch, Germany).

The second part of the sediment samples was dried in an oven for 48 h at 60 ± 2 °C, grinded in an agate mortar, till the whole sample then passed through an 80 μm acrylic mesh before bulk elemental analysis. The sediment was digested according to EPA method 3052 [36]. Briefly, approximately 0.5 g (dry weight) of sediment was placed in a nitric acid-washed XP-1500 Teflon digestion vessel with a mixed acid (9 mL of HNO_3, 3 mL of HF and 2 mL of HCl), then the sealed vessels was placed in the microwave system MARS 6 (CEM Corporation, Matthews, NC 28106, USA), connected to temperature and pressure sensors. The temperature of each sample was raised to 180 ± 5 °C for 15 min and maintained at 180 ± 5 °C for 10 min. At the end of the microwave program, the vessels were cooled to almost room temperature. The samples were then transferred to an acid-cleaned volumetric flask and diluted with ultrapure water to 50 mL. If the digested sample contained particulates, the sample was filtered.

The aquatic plants were digested according to EPA method 3052 with minor modifications. Briefly, approximately 0.5 g (dry weight) of dried plants were placed in a nitric acid-washed XP-1500 Teflon decomposition vessel with 10 mL of HNO_3. Further operations were the same as in the case of precipitation decomposition. The diluted solution was stored at 4 °C for HM analysis.

Then concentrations of HMs (Fe, Mn, Zn, Ni, Cd, Cr, Cu and Pb) were determined using an atomic absorption spectrometer (Solaar M6, Thermo Electron Corporation, San Diego, CA 92121, USA) coupled with a graphite furnace and flame atomizer, error 5–10%. The

content of mercury in BSs and aquatic plants was determined by the cold vapor method using a VP-100 generator with a Solaar M6 atomic-absorption spectrophotometer. The detection limits for mineral elements determination in bottom sedimens and water plants by spectrophotometric analysis: Ni (0.5 mg/kg), Pb, Cr (0.2 mg/kg), Fe (4 mg/kg), Cd (0.01 mg/kg), Mn, Cu and Zn (0.1 mg/kg) [28].

Quality assurance and quality control were evaluated using blank reagents and Certified Reference Materials (Sediment from Lake Baikal BIL-2 (GSO 7176-95); Elodea canadensis EK-1 (GSO 8921-2007, SO KOOMET 0065-2008-RU) with each sample batch (1 blank and 1 standard sample for every 10 samples). The recovery rates with the addition of standards ranged from 91 to 103% (Table 1). The precision of the method was evaluated by measuring a sample of BIL-2 (n=5). The measured precision (% RSD) was: Fe (1.2%), Mn (1.5%), Zn (0.9%), Cu (1.4%), Ni (4.7%), Cr (3.4%) and Pb (6.7%). Blanks were prepared using the same protocol (rea-gents only), and its values were distracted from sample measurements results. The blank values for BS/water plants were (mg/L): Fe—0.249/0.046 , Mn—0.037/0.025, Zn—0.020/0.003, Cu—0.020/0.010, Ni—0.004/0.001, Cr—0.004/0.001, Pb—0.001/0.001. The reagents used were analytically pure, and the water was purified to a resistivity of 18.2 MΩ·cm (at 25 °C) using a Direct-Q UV3 Ultrapure Water Systems apparatus (Millipore, France). During the atomic absorption determinations, a multi-standard STD IV-STOCK-8 solution (in 5% (*v/v*) HNO$_3$) (Inorganic Ventures, Christiansburg, VA, USA) was used.

Table 1. Results of analysis of (mg/kg) of standard reference materials. (mean ± standard deviation).

Element	Determining Threshold	BIL-2			EK-1		
		Certified	Measured	Recovery%	Certified	Measured	Recovery%
Fe *	4	37,700	33,800	92	2600	2580	99.2
Mn *	0.1	929	892	96	520	534	101.9
Zn	0.1	64	66	103	20.6	19.66	95.4
Cu	0.1	18	17	94	11.2	10.83	96.7
Ni	0.5	31	24.3	97	3.7	3.77	101.9
Cr	0.2	158	160	101	5.1	5	98
Pb	0.2	14	13	93	-	-	-

* g/kg.

We used the method of comparison of received concentrations of heavy metals in BSs with Clarke's value for sedimentary rocks (Cclarke) calculated by Vinogradov. We calculated the contamination factor (CF) for the BSs. CF value was defined as CF = Cmetal/Cclarke. CF values were interpreted as suggested by Hakanson [37]: CF < 1 indicates low contamination, 1 < CF < 3 is moderate contamination, 3 < CF < 6 is considerable contamination, and CF > 6—very high contamination.

3. Results

3.1. Analysis of Water Level

For the period of 1970–2020 (according to the Buryat CHEM data), the long-term average annual water level in Lake Gusinoe was 141 cm above the zero mark on the water gauge (the zero mark—549.55 m in Baltic system, (b.s.)). Its maximum level was 160 cm (551.15 m b.s.) and minimum—125 m (550.80 m b.s.) for the entire survey period. A noticeable increase in the level occurred in 1982 as a result of the damming of the only outflowing the Bain-gol River, and in 2006—after dredging the Temnik River to increase the flow of water into the lake. The maximum water level was recorded in August 1995 (196 cm), the minimum—in April 2006 (49 cm). The highest intra-annual amplitude was recorded in 2012 (79 cm), the lowest—in 2003 (5 cm). Thus, the water level in Lake Gusinoe varies within a large range, both within a year and over a multi-year period (Figures 4 and 5).
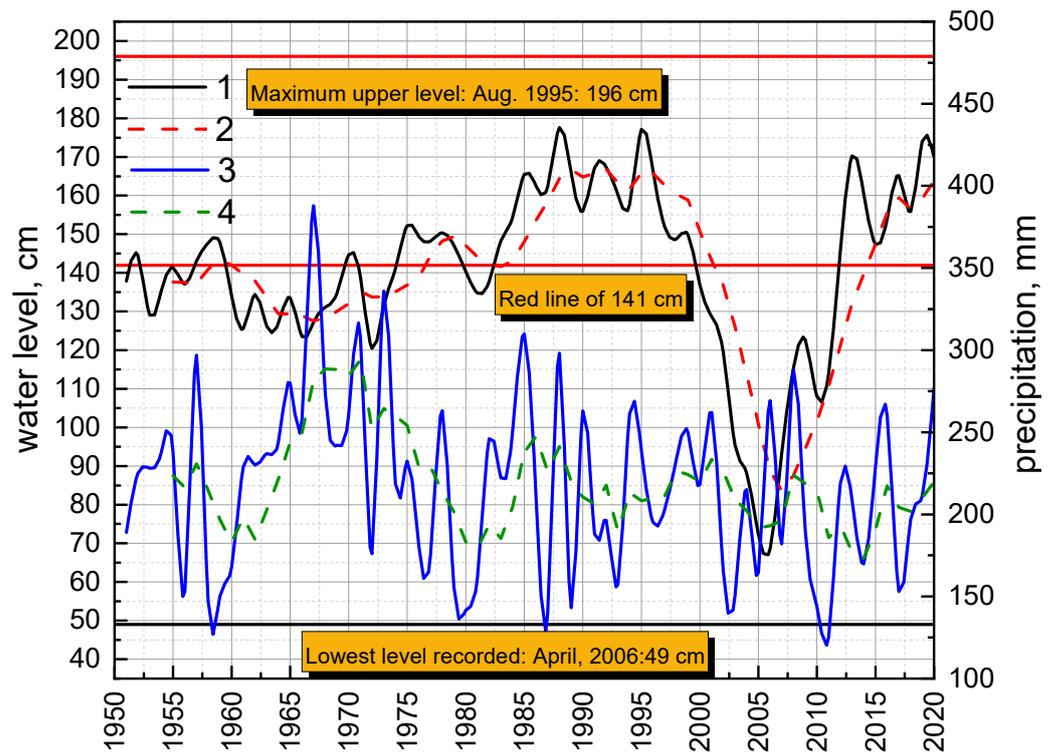
Figure 4. Meteorological data on Lake Gusinoe: (**1**) average annual water level in the lake (gauging station at Gusinoe Ozero); (**3**) annual average precipitation (Novoselenginsk weather station); five-year running averages of water (**2**) level and precipitation (**4**).
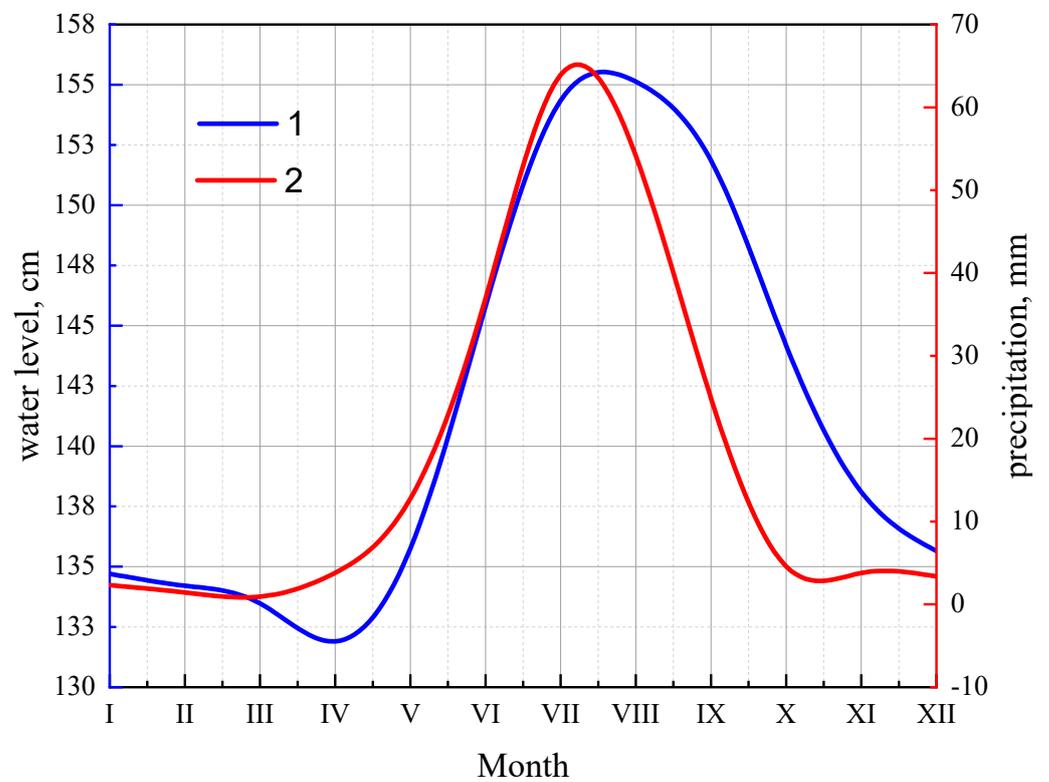

Figure 5. Monthly averages of the water level (**1**) in Lake Gusinoe and precipitation (**2**) during the period of 1970–2020.

The variations of the water level in the lake before the launch of the GRES in 1976 were determined by the natural variability of water content in the lake catchment area, as well as in the whole Selenga basin, when high-water and low-water cycles alternated in the Baikal region (the maximum intra-annual amplitude of water level fluctuations before 1977 was 29 cm). However, in the following decades, the GRES operation has had a strong impact on both the quantity and quality of water in the lake.

3.2. Analysis of Physicochemical Conditions, Major Ions, Nutrients and Heavy Metals

As a rule, the physicochemical indicators and chemical composition of water change significantly upon alteration of the water level in a water body. The use of lakes as cooling ponds for thermal power plants usually leads to changes in the gas regime [38]. The oxygen content in the water of Lake Gusinoe in the survey period of 2017–2021 was quite high even in the subglacial period (10.9–15.6 mg/L), due to the higher aquatic vegetation enriching the bottom layers of water with oxygen. In winter period water saturation with oxygen reached 107%. During the open water period, dissolved oxygen content was within the favorable for hydrobionts range of 7.8–13.1 mg/L. At the site of the heated water discharge of the GRES, the oxygen content was slightly lower than in the water body, due to a decrease in oxygen solubility with increasing temperature. Lake waters are slightly alkaline and alkaline: pH varies within 8.12–9.03. The water has a low turbidity of 0.41–5.5 NTU with minimal values in the subglacial period (Table 2).

Table 2. The maximum, minimum and average content of chemical components in the surface and bottom waters of Lake Gusinoe [1].

Parameters	Surface Water			Bottom Water			WHO Standard, 2004 [39]	Russian National Standard (MAC) [40] [2]	% of Samples Exceeding MAC
	Max	Min	Avg	Max	Min	Avg			
t	23.8	0.1	10.74	20.6	1	8.35	–	–	–
pH	9.03	8.12	8.50	8.40	8.03	8.23	6.5–8.5	6.5–8.5	12
Turbidity	5.5	0.41	2.28	3.66	0.80	1.62	5	–	–
DO	15.59	6.28	11.55	13.6	7.55	9.45	5.0	4–6	0
TDS	444	336	384	380	295	320	600	1000	0
NO_2^-	0.049	0.000	0.005	0.009	0.001	0.004		0.08	0
NO_3^-	0.938	0.005	0.224	0.181	0.001	056	50	40	0
NH_4^+	0.072	0.001	0.015	0.045	0.003	0.023	1.5	0.5	0
PO_4^{3-}	0.025	0.000	0.007	0.033	0.004	013	–	0.05	0
COD	73.38	8.10	33.35	71.07	17.66	35.44		30.0	58
F^-	3.80	0.65	2.13	3.57	0.68	18	1.5	0.75	96
Cl^-	9.46	6.96	7.20	7.06	6.75	64	200	300	0
SO_4^{2-}	68.47	48.01	52.44	57.24	55.79	56.66	200	100	0
HCO_3^-	248.57	189.10	197.95	219.60	210.45	216.31	350		0
Na^+	59.08	45.96	47.61	52.25	51.01	51.59	200	120	0
K^+	4.67	2.30	3.31	4.28	2.78	3.53	20	10	0
Mg^{2+}	16.68	2.24	7.33	3.28	3.00	3.19	30	40	0
Ca^{2+}	36.90	13.26	19.91	15.33	14.75	15.04	75	180	0
Fe	0.146	0.018	0.012	0.019	0.001	0.008	0.3	0.1	5
Mn	0.012	0.001	0.003	0.004	0.000	0.002	0.1	0.01	3
Zn	0.048	0.000	0.006	0.032	0.000	0.004	4	0.01	17
Cu	0.009	0.001	0.003	0.003	0.000	0.001	2	0.001	62
Pb	0.009	0.000	0.002	0.007	0.000	0.003	0.01	0.006	2
Cd	0.003	0.000	0.001	0.001	0.000	0.001	0.003	0.005	0
Ni	0.009	0.000	0.001	0.002	0.000	0.001	0.07	0.01	0
Cr	0.009	0.000	0.002	0.006	0.000	0.002	0.05	0.02	0

[1] TDS, Major anions, cations and dissolved oxygen in mg/L; element concentration in ppm, t in °C, turbidity in NTU. [2] Maximum allowable concentration.

3.2.1. Mineralization and Major Ions

The analysis of the ionic composition of surface and near-bottom waters, sampled in Lake Gusinoe in 2017–2021, revealed (Figure 6) the interval of water salinity in the subglacial period 377–444 mg/L, with higher values near the surface due to desalination from the ice, and lower in the bottom layer. During the open water period, an intensive wind mixing of water provided uniform mineralization throughout the lake basins (336–376 mg/L), and no significant differences were observed for surface and bottom water layers. Low salinity was registered in the southern part of the lake (near the village of Gusinoe Ozero), which is caused by low mineralized waters of the Tsagan-gol River (52–77 mg/L). Seasonal dynamics of major ions is characterized by maximum values in the subglacial period and minimum during spring and rainfall floods. Concentrations of ions, dominating in the macrocomponent composition of waters of the lake, varied within the range: hydrocarbonate (189–248 mg/L), sulfate (48–68 mg/L), sodium (46–59 mg/L) and calcium (13–37 mg/L).

According to literature [17–20] and our (2017–2021) data, the ionic composition of Lake Gusinoe waters between 1951 and 2021 reflects changes after the opening of the Kholboldzhinsky coal mine (1961–1962) and the launch of the GRES (1976) (Figure 6).

Hydrochemical studies of the lake in this period show significant changes in the chemical composition of water and the concentration of major ions. As a result of anthropogenic impact, the type of water changed from calcium-hydrocarbonate to sodium-hydrocarbonate (Figure 6). After the launch of the two plants there was a significant increase in water salinity with a corresponding increase in the content of ions in the macro component composition, especially sulfate ions and alkali metals [42]. After the termination of discharges of pit waters of the Kholboldzhinsky coal mine in the 80–90 s, there was a stabilization of water levels and a cessation of accumulation of sulfates and alkali metals. However, the results of our 2017–2021 studies show that although the salt composition has remained relatively stable in recent decades, slight accumulation of sodium and sulfates continues.
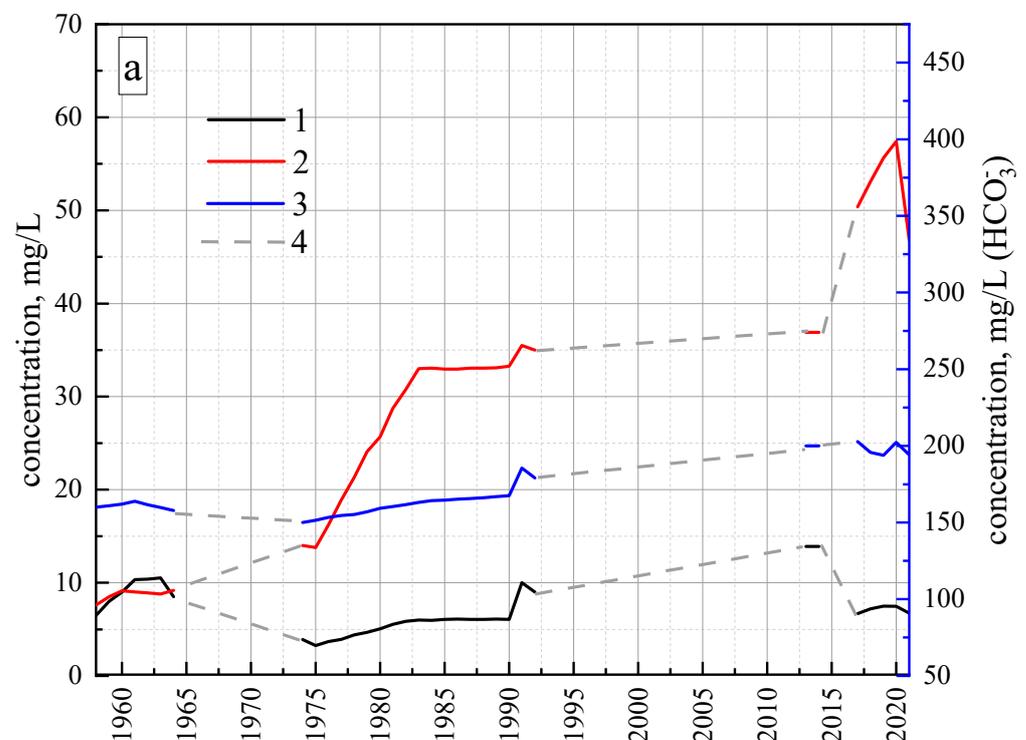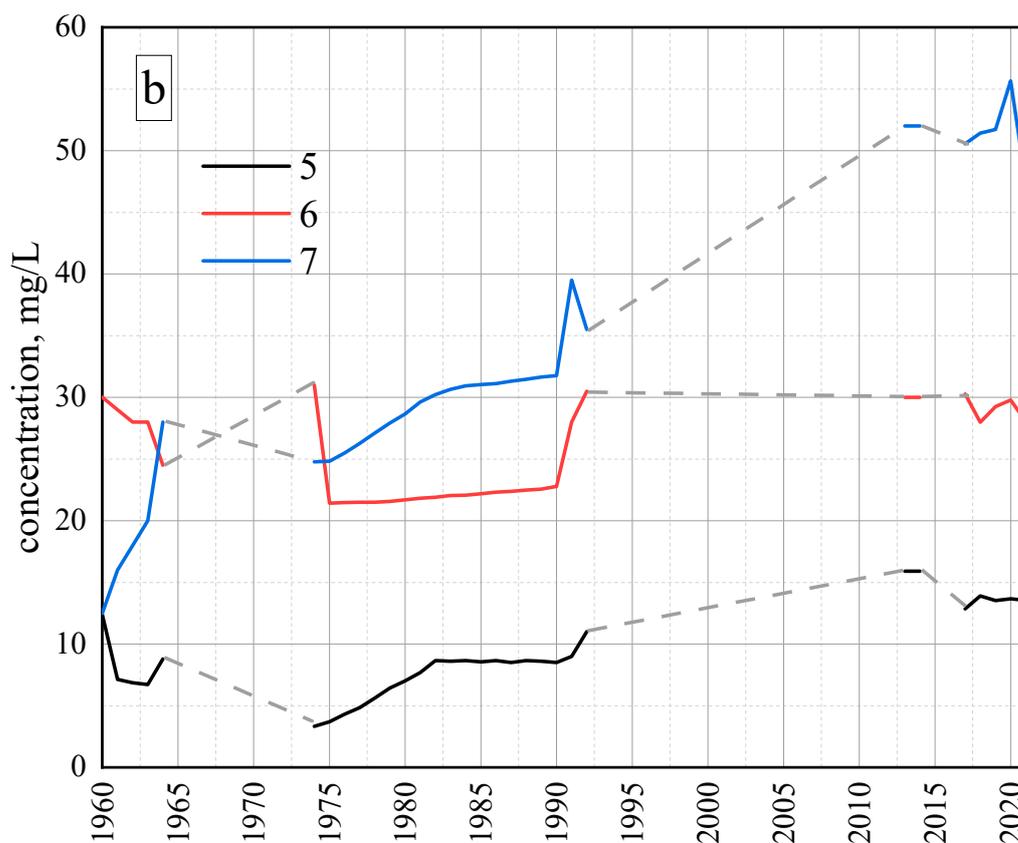

Figure 6. *Cont.*

Figure 6. Changes in the concentration of anions (**a**) and cations (**b**) in the water of Lake Gusinoe (mg/L); 1958 [17], 1974-1992 [14,18], 2013 [41], 2017–2021-author's data. 1-Cl^-; 2-SO_4^{2-}; 3-HCO_3^-; 4-no data; 5-Mg^{2+}; 6-Ca^{2+}; 7-$Na^+ + K^+$.

Fluoride ions in the lake are elevated 0.65–3.80 mg/L, although there has been some decrease in concentrations over the survey period: from 2.46–3.80 mg/L in 2017–2018 to 1.20–2.40 mg/L in 2019; 0.65–1.54 mg/L in 2020; 1.30–1.77 mg/L in 2021 (MAC is 0.75 mg/L).

3.2.2. Nutrients and Organic Matter

Nutrients drive the biological productivity of water bodies and serve as one of the indicators of water quality. With a small content of nutrients, Lake Gusinoe belongs to the oligotrophic type of water bodies. Concentrations of ammonium ions during the survey period ranged from 0.001 to 0.072 mg/L (mean 0.015/0.023 mg/L for surface/bottom waters), nitrates 0.001–0.938 mg/L (mean 0.224/0.056), nitrites 0–0.048 mg/L (mean 0.005/0.004) and phosphate concentrations 0–0.025 mg/L (mean 0.007/0.013). Seasonal and interannual dynamics of nutrients in lake waters are determined by phytoplankton development and higher aquatic vegetation, as well as the influx of pollutants from the watershed during spring and rainfall floods.

The content of OM in lake waters was evaluated by chemical oxygen demand (COD). In Lake Gusinoe, COD varied seasonally from 8.1 mg O_2/L to 73 mg O_2/L. As for interannual variations, elevated COD values were observed in 2020 when a significant amount of OM accumulated after the previous low-water period came from the watershed. There was an increase in the content of OM in the lake near Gusinoozersk and Gusinoe Ozero, the most pronounced in the subglacial period due to influx of pollutants with sewage water.

3.2.3. Heavy Metals in Water

Concentrations of trace elements in the lake water were measured. Iron content varies in a wide range—0.001–0.146 mg/L. The maximum content of manganese in the lake

water area was by an order of lower magnitude, with maximum values in the subglacial period—up to 0.012 mg/L. The highest zinc content (up to 0.048 mg/L) was also registered in the subglacial period in the southern basin. The highest copper concentrations (up to 0.009 mg/L) were measured throughout the lake water area in spring with meltwater flowing from the watershed. Average content of lead, cadmium, nickel and chromium was low—0.001–0.003 mg/L (Figure 7).
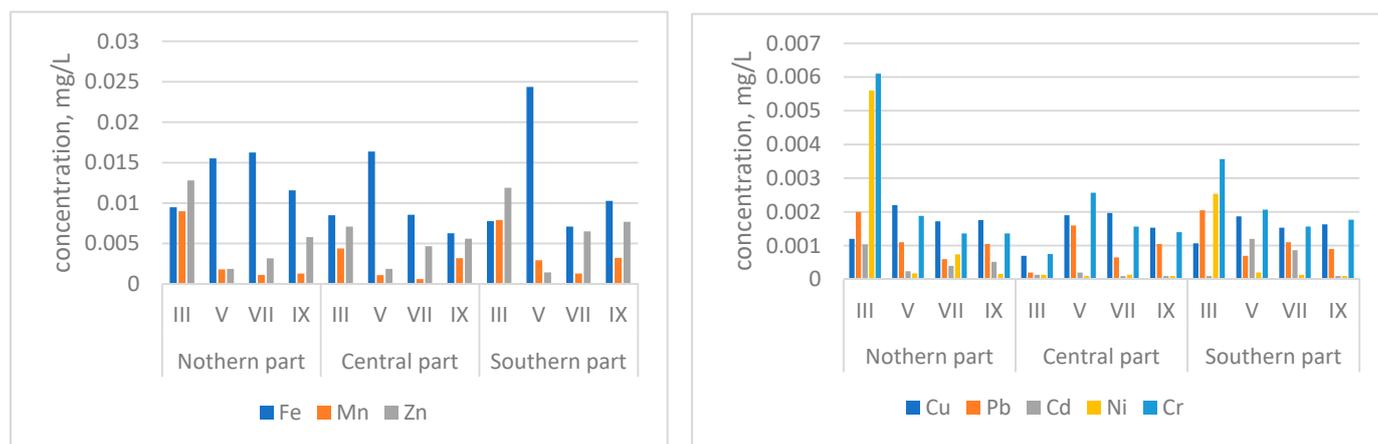

Figure 7. The seasonal variability of metals content in surface water of Lake Gusinoe. Metal concentration, mg/L.

3.3. Heavy Metals in Bottom Sediments

The BSs in Lake Gusinoe are clay silt (gray and black silt), shell limestone and sand (less often) with pebbles and mixed deposits [14]. In the coastal areas of the lake, aleurite BSs sands prevail, which are replaced by fine aleuropelite as the distance from the shore increases (Table 3). Thus, the lake exhibits vertical zoning in the distribution of BSs.

Table 3. Content of predominant fractions and organic carbon in BS samples from Lake Gusinoe (% of the sum of fractions).

	Fractions						Type	According to the American System			C_{org}
	1–0.25	0.25–0.05	0.05–0.01	0.01–0.005	0.005–0.001	<0.001		Sand >0.05	Silt 0.002–0.05	Clay <0.002	
Coastal zone (0–10 m)	80.0–84.0	6.1–10.2	6.4–7.5	0.4–2.1	0.5–2.4	0.1–0.5	Unconsolidated sand	93.4–97.2	2.5–6.5	0.3–1.3	0.07–0.84
Deep zone (15–25 m)	–	9.9–29.0	43.3–49.5	10.2–15.5	14.6–21.4	2.9–3.7	Medium loam	10.1–29.0	63.5–80.0	7.5–9.9	6.01–9.58

The accumulation of HMs in BSs can potentially lead to secondary contamination of water through the reverse transfer of trace elements from BS to water. Table 4 and Figure 8 shows the concentrations of metals in the coastal and deep BSs of Lake Gusinoe in 2017–2021. The obtained values were compared with the background content of HMs in BSs typical for freshwater reservoirs [43,44]. To assess the level of pollution of the BSs, a CF was calculated.

Table 4. The maximum, minimum and average content of chemical components in the BSs of Lake Gusinoe.

Parameters µg/g	Bottom Sediments						Clarke	CF			CF		
	Deep Zone			Coastal Zone				Deep Zone			Coastal Zone		
	Max	Min	Avg	Max	Min	Avg		Max	Min	Avg	Max	Min	Avg
Fe *	58.0	27.9	43.9	12.2	4.5	8.8	43.5	1.33	0.64	1.01	0.28	0.10	0.20
Mn *	1.16	0.35	0.85	0.34	0.89	0.18	0.75	1.55	0.47	1.14	0.46	0.12	0.25
Zn	163.6	90.1	124.5	37.0	12.3	24.2	110	1.49	0.82	1.13	0.34	0.11	0.22
Cu	53.7	15.5	40.5	8.3	1.1	3.3	43	1.25	0.36	0.94	0.19	0.03	0.08
Pb	23.3	3.4	13.3	9.5	2.2	5.6	28	0.83	0.12	0.47	0.34	0.08	0.20
Cd	1.44	0.02	0.1	<0.01	<0.01	<0.01	0.35	1.23	0.00	0.25	0.00	0.00	0.00
Ni	31.5	9.8	19.2	4.3	2.1	2.8	55	0.57	0.18	0.35	0.08	0.04	0.05
Cr	61.1	27.2	42.4	15.6	2.3	6.8	96	0.64	0.28	0.44	0.16	0.02	0.07
Hg	0.57	0.05	0.37	0.14	0.01	0.07	0.3	1.9	0.17	1.23	0.47	0.03	0.23

* g/kg.

The highest metal concentrations during the survey period were registered in 2020, likely due to rising water level in Lake Gusinoe and groundwater table (2019–2020) as a result of rainfall flooding of coastal areas and influx of contaminants into tributaries and the lake. Average concentrations of iron, manganese and zinc in the deep lake silt exceeded background values for freshwater reservoirs (copper concentrations were almost equal). The content of cadmium was the highest in deep BSs in the northern part of the lake—up to 0.26–1.44 µg/g. Mercury and its compounds are substances of the first class of hazard materials, and their content in the environment is strictly limited. In 2017–2021, the content of mercury in the studied BSs was in the range of 0.05–0.57 µg/g, with the maximum values being recorded in the northern part of the lake (Table 4).

3.4. Heavy Metals in Aquatic Plants

The content of metals in the studied aquatic plants of Lake Gusinoe is shown in Figure 9. The levels are higher for algae than for higher plants collected in the same part of the lake. High contents of Fe, Cu, Zn, Mn, Pb, Cd and Cr were registered in the samples of filamentous algae (4430, 29.62, 30.59, 639.7, 6.47, 1.13 and 5.05 mg/kg, respectively) at the site of the heated water discharge of the GRES. The lowest contents were registered in aquatic plants in the area of the eastern coast of the lake.
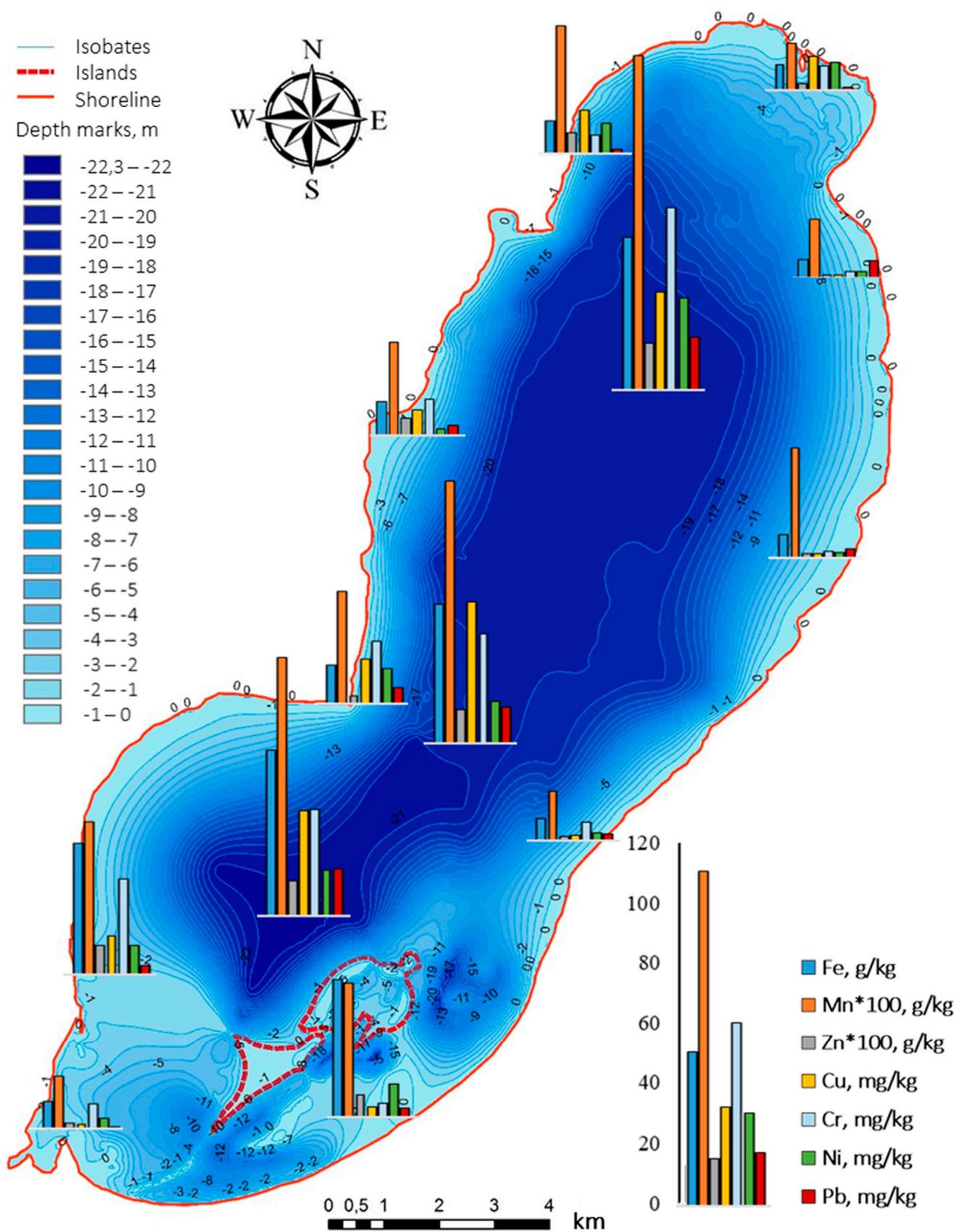
Figure 8. Content of metals in bottom sediments of Lake Gusinoe.
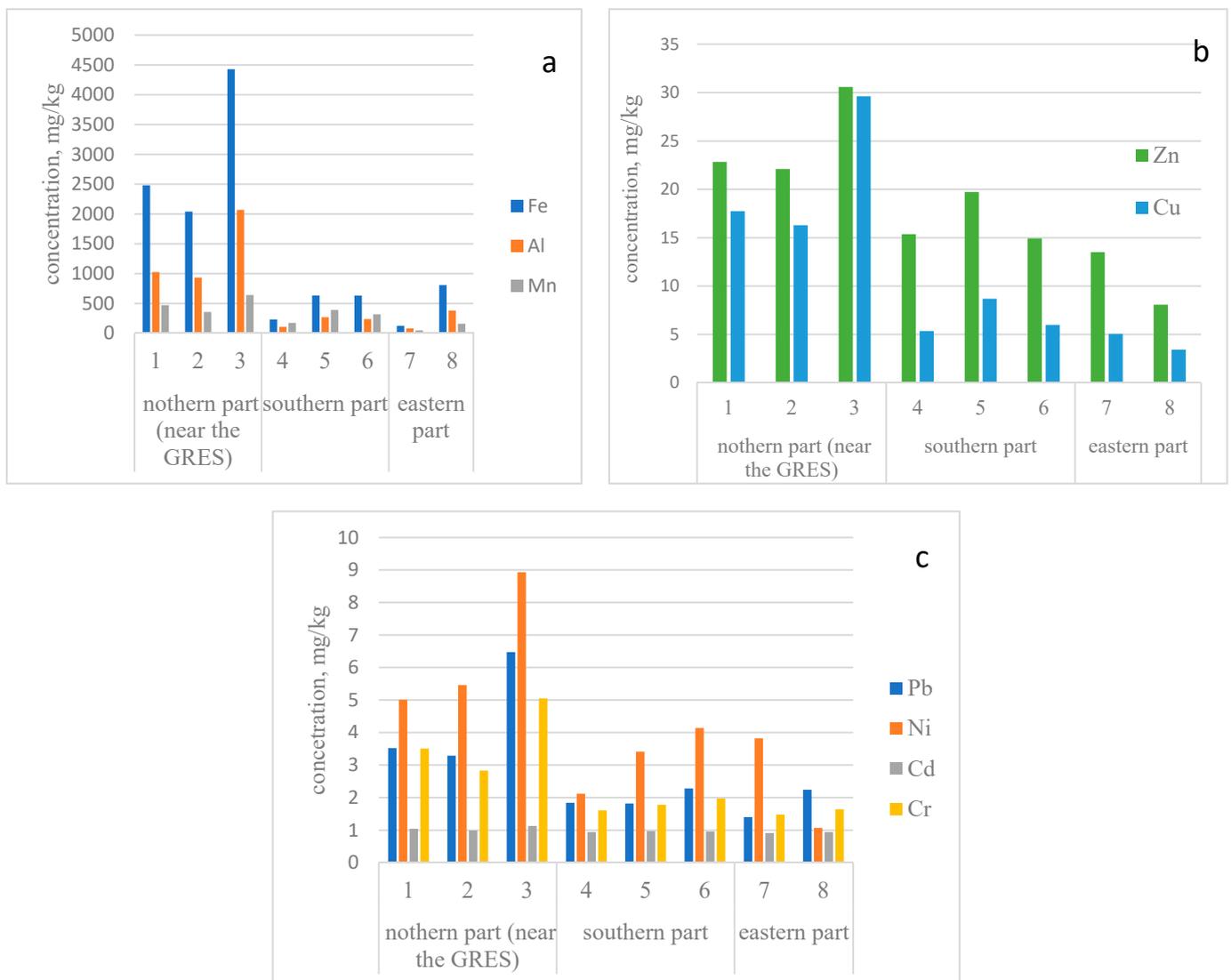
Figure 9. Content of metals in aquatic plants of Lake Gusinoe. Metal concentration, mg/kg dry weight: 1-water milfoil, *Myriophyllum* sp.; 2-waterweed, *Elodea Canadensis*; 3-filamentous green algae, Chlorophyta; 4-water milfoil, *Myriophyllum* sp.; 5-pondweed, *Potamogeton* sp.; 6-water moss, *Fontalis antipyretica*; 7-pondweed, *Potamogeton* sp.; 8-stonewort, *Chara* sp. (**a**) Fe Al Mn; (**b**) Zn Cu; (**c**) Pb Ni Cd Cr.

4. Discussion

Fluctuations of the lake level as the main feature of its water regime reflect the state of its ecosystem and have the main influence on the economic use of its resources. The low-water period began in this area in the mid-1990s and lasted for 20 years [45–47], creating a problem with the lake level regime—the level of the coastline reduced by tens of meters. This situation had a negative impact on the GRES water intake structure and the coolant temperature regime. To solve the problem, the management of the GRES made decisions, unauthorized by environmental and supervisory agencies, to block the source of the only river flowing from the lake—the Bayan-gol River (1982), and to increase the flow of the Tsagan-gol River (2006). Thus, during low-water years, the GRES independently set the water levels in the lake necessary for its operation.

Meanwhile, high water levels in Lake Gusinoe threaten to flood households of residents of coastal settlements. High water levels are also undesirable for the GRES. The recent high-water years (2019–2020) have forced the GRES to remove the dam at the head of

the Bayan-gol and resume water flow from the lake. In other words, the GRES management has turned Lake Gusinoe into an artificial water reservoir, the level in which is actually regulated by the economic entity.

Based on the analysis of historical data series on water levels in the lake, and the average annual amplitude of their fluctuations of 30 cm; and being guided by the necessity of the preservation of the lake ecosystem and safety of the local population as well as the needs of the economic subjects in the vicinity of Lake Gusinoe, we believe that the optimal limits of the water level fluctuation are the following: 551.15 m b.s.—maximum mark and 550.85 m b.s.—minimum mark.

To assess the impact of the Gusinoozersk GRES on the lake water level, we used the Spearman rank correlation coefficient between the Temnik River flow (as the main regulator of water level in the lake) and the water level in Gusinoe (Figure 10). The coefficients were calculated for the states of the system 'before the launch of the GRES' and 'after the launch of the GRES'.
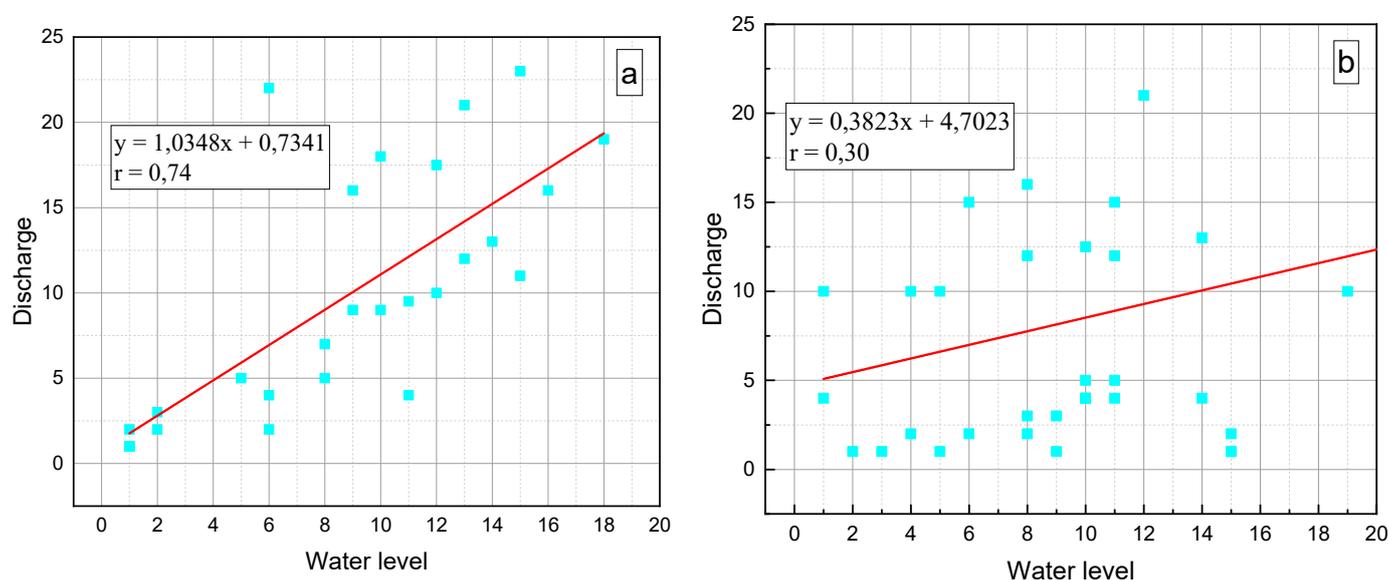

Figure 10. Spearman rank correlation coefficient between the lake water level and the Temnik runoff: (**a**)—before, and (**b**)—after launch of the Gusinoozersk GRES.

Figure 10a shows that there is a strong positive relationship between the lake level and the flow of the Temnik River before the launch of the GRES, as the Spearman's correlation coefficient is r = 0.74, and there is a weak positive relationship after the launch of the GRES (Figure 10b). This suggests that the lake water level was regulated by the water flow of the Tsagan-gol River (the Temnik River channel) into the lake before the intervention of an external factor; but after the launch of the GRES—the level is mainly regulated by the enterprise itself.

Level changes combined with long-term anthropogenic impact have affected the chemical composition of lake waters. Water salinity before the beginning of industrial activity was in the range of 219–247 [17], but after the launch of the Kholboldzhinsky coal mine and the Gusinoozersk GRES (under the influence of untreated pit waters and heated water discharges), there was an increase to 250–300 mg/L. The increase in sulfate concentrations from 12–14 mg/L [17] (1974) to 23–35 mg/L [14] (1990–1992) is particularly noticeable. Increased sulfate and sodium contents are also influenced by the ash ponds near the Tel (a channel of the Zagustai River). The dam installation at the Bain-gol River source contributed to an increase in sulfate content in water due to the rise of groundwater in the saline basin of Lake Gusinoe and its inflow into the lake.

No accumulation of sulfates and alkali metals was observed in the period 1980–1990, after the cessation of pit water discharges and stabilization of the lake water level. It

has been assumed that the content of the main ions in the lake water can remain at the level of the levels found during the 1980s and 1990s, if there is no further increase in the anthropogenic impact on the lake. During the survey period (2017–2021), lake water salinity was 336–444 mg/L, with sulfate content ranging from 48.0–62.6 mg/L and sodium—45.9–56.2 mg/L. According to our findings, the sulfate and sodium concentrations in the lake water continue to increase over the years. There was a significant increase from 2019–2020, caused by rising groundwater and the general water level in the lake due to rainfall flooding of adjacent saline areas. In 2019–2020, groundwater levels in the Gusinoozersky intermountain Artesian basin were above the long-term average values by 0.62–1.1 m [13]. Earlier in 1991, a similar phenomenon was observed when the water level in the lake rose as a result of the damming of the Bain-gol River. In 2021, there was a general decrease of salinity and especially of sulfates and sodium, caused by an artificial decrease of the lake water level and increase of flow of low-salinity tributaries (the Tel and Zagustai rivers) [13].

The increased content of fluorine in lake waters is worth noting, exceeding the MAC by up to 5 times. This may be due to the proximity of a large fluorine-bearing biogeochemical province in southeastern Transbaikalia with adjacent areas. Fluorine is contained in fluorites, fluorapatites, mica and amphiboles. These minerals are unstable and can serve as a source of fluoride ions in surface and groundwater [48,49]. As a rule, areas with an excess of chemical elements are associated with the mining of mineral deposits.

In the waters of Lake Gusinoe, the increased fluoride content can be explained by a combination of water inflows from old quarries and mines, leachate from the ash dump, and subsequent accumulation of ions in the lake due to its low flow rate.

Data on nutrients in the waters of Lake Gusinoe showed that during the period of mass development of algae in the lake, the content of nitrates, as well as other nutrients, was minimal. At the same time, the lowest values were registered in the northern basin, in the warm water zone of the GRES, with the greatest amount of aquatic vegetation [44]. A significant increase in nitrate and OM concentrations in August–September 2020 was caused by a heavy rainfall flood. Nitrogen compounds usually come from the watershed with such floods, reducing algae development and increasing nitrogen concentrations in the water. In general, the increased content of all nutrients was registered at the sites of poorly treated municipal wastewater discharge: in the northern basin—near Gusinoozersk, and in the southern basin near Gusinoe Ozero. Concentrations of nutrients were not recorded as exceeding the MAC for fishery water bodies in 2017–2021. We also used COD values to measure OM fractions resistant to oxidation: in the period of 2017–2021 there was characteristic pollution (more than 50% of samples) of low (1–2-fold excess of MAC) and medium (2–3-fold excess of MAC) levels.

The trace element composition of natural waters is the most important indicator of the degree of environmental pollution. Metals play an essential role in surface waters, participating in almost all physicochemical, chemical and biological processes due to such properties as polyvalence, high reactivity and biological activity. The seasonal dynamics of trace elements in the period of 2017–2021 demonstrates the increase of iron content in water during spring and rainfall floods due to flow from adjacent areas with periodic exceeding MAC (0.1 mg/L) (Figure 7). Manganese content was elevated during the subglacial period, probably due to decomposition of aquatic vegetation and input from groundwater. An increase in the lake level and groundwater in 2019–2020 together with rainfall floods caused increased manganese and iron content in the water during this period. The maximum concentrations of other elements in water were registered in the subglacial period due to their flux with groundwater. High concentrations of copper exceeding the standards were recorded throughout the water area, and the trace elements were relatively uniformly distributed during the open water period due to wind mixing. Elevated concentrations were observed during the subglacial period near the GRES and wastewater discharges from Gusinoozersk and Gusinoe Ozero. Water pollution by copper during the survey period was characteristic (more than 50% of samples exceeding MAC) of low and medium

level (2–3-fold excess of MAC). Zinc pollution was unstable (MAC exceeding in 10–30% of samples) of low level (2–3-fold excess of MAC). Pollution of the lake waters with copper, zinc and (periodically) iron was also noted earlier according to Roshydromet [13]. For manganese, nickel and chromium, there were no exceedances of standards.

Toxic trace elements can be deposited in BS, but when the physical and chemical conditions in a reservoir change, they can move into the pore water and then into the surface water. The greatest accumulation of HMs in BSs of Lake Gusinoe occurs in silt of the deep zone of the lake with increased content of OM (6.01–9.58%) capable of binding HMs. In the coastal part of the lake sands prevail in BSs (more than 90%) with little OM (0.07–0.84%), which leads to lower content of HMs in BSs. Moderate pollution was registered for deep BSs contamination index exceeded 1 (iron, manganese, zinc, copper, cadmium and mercury). Sandy sediments in the littoral zones of the lake were characterized by much lower metal content and were classified as non-polluted. Heavy rains in the lake watershed wash out pollutants from the adjacent uncultivated dumps of the Kholboldzhinsky coal mine and the ash dumps of the GRES. We recorded the highest concentrations of HMs in BSs in 2020, after the rain flood, rising groundwater and flooding of coastal areas.

Aquatic plants actively accumulate mineral and organic substances, HM ions, radionuclides, and therefore are often used to monitor water quality, eutrophication and pollution of water bodies. The coastal part of the lake is occupied by aquatic vegetation including pondweeds, water milfoil, water moss, stonewort and green filamentous algae [50]. We found higher contents of the analyzed metals in the algae compared to the higher plants collected in the same part of the lake. Absolute maximum contents of Fe, Cu, Zn, Mn, Pb, Cd and Cr were measured in filamentous algae, which agrees with the literature data on their use for bioremediation due to their ability for high, even excessive accumulation of elements [51].

Increased concentrations of all measured metals were found in plants growing in the zone of the discharge of heated water from the GRES, unlike plants from other areas of the lake. In samples of water milfoil and moss from the southern part of the lake (near Gusinoe Ozero), absolute maximum contents of Hg (water milfoil) and Ni (water mosses) were found. Higher concentrations of Fe, Mn, Zn and Cu in *Potamogeton* sp. were found in the water area close to Gusinoe Ozero compared to samples from the northeastern part of the lake. The content of Fe, Mn, Zn and Cu in *Myriophyllum* sp. in the area of the discharge of heated water from the GRES is increased compared to plants growing in the southern part of the lake. For instance, the Fe content in water milfoil at the two sampling points differs by a factor of 10, Mn and Cu—by a factor of 2–3 (Figure 9a,b). The high gross total content of non-biophilic elements (Ni and Cr) in plants may indicate both increased metabolic processes in *Myriophyllum* plants and the accumulation of these elements in the environment with subsequent concentration (Figure 9a,c). Metals probably enter the water from Gusinoe Ozero's wastewater treatment facilities, causing elevated levels in the lake near the village. Plant samples from the northeastern part of the lake are characterized by the lowest content of the studied elements. This might be caused by sandy BSs with low content of OM, which can bind and accumulate metals.

Since there are no MACs for metals in aquatic vegetation, we can assess the pollution of the water body by comparing the measured concentrations with those for other Siberian aquatic ecosystems of the same type. The contents of Al, Cu, Zn, Ni and Cr in water milfoil and pondweeds of Lake Gusinoe were lower; contents of Fe, Zn (at the site of the heated water discharge of the GRES) and Pb—higher compared to their content in pondweeds from Bugach Reservoir (Krasnoyarsk Krai) [52]. The content of all the above elements in aquatic plants of Lake Gusinoe is higher than in pondweeds from Lake Kenon—a cooling pond of the thermal power plant (Zabaikalsky Krai) [53]. The contents of Fe, Cu, Cr, Ni, Pb, Cd and Hg in samples of *Elodea canadensis* collected at the site of heated water discharge are higher, and contents of Zn, Mn—are lower than that previously indicated for this species in Lake Gusinoe [54]. According to the same source, the content of these elements in *Elodea canadensis* (by the example of Lake Kenon) can vary widely depending on the year and

place of collection. The concentrations of iron, chromium, nickel, lead, mercury in the green algae of Lake Gusinoe are comparable with those in Lake Kenon; the content of copper is lower, and cadmium is higher than in the green algae of Lake Kenon [51,55]. Stonewort (*Chara* sp.) algae in Lake Gusinoe are characterized by lower content of iron, copper, zinc, manganese and nickel, and almost equal content of chromium, lead, cadmium and mercury compared to those of stonewort of Lake Kenon [54]. The content of extremely ecotoxic mercury in the higher aquatic vegetation can serve as an indicator of water body pollution. The lowest amount of mercury was found in pondweeds (0.01 mg/kg) from the northeastern part of the lake; its concentration is comparable with rooted plants of the Irkutsk reservoir (a background water body), whereas the concentration of mercury in other plants is comparable to the concentration of mercury in plants of the Bratsk reservoir—a water body highly contaminated with mercury [56].

5. Conclusions

A comprehensive assessment of the ecological state of Lake Gusinoe was carried out, its water level regime and the effects of long-term anthropogenic impact on the components of the lake ecosystem were characterized. The water level in the lake had depended on natural factors before the Gusinoozersk GRES was put into operation; but since the plant has begun using the lake as a cooling pond, its level has actually been regulated by the economic entity.

Level changes combined with long-term anthropogenic impact have affected the chemical composition of the waters in the lake. In a long-term period, there is a significant increase in salinity, sulfate, sodium, fluoride and OM fractions resistant to oxidation due to low flow rates of the lake, continuous discharge of pit waters from the coal mine as well as leachate from the GRES ash dump. An increase in the lake's water level due to rainfall floods leads to flooding of coastal areas and a rise in the ground water table, which in turn intensifies the flow of pollutants, including HMs from the coal mine dumps and ash dumps, from abandoned mines, and salts from the adjacent saline soils and grounds.

Chemical analysis of surface and near-bottom waters of Lake Gusinoe in 2017–2021 indicates a favorable gas regime in the lake, despite its use as a cooling pond of the GRES, and the dissolved oxygen content is high enough even in the subglacial period. Salinity of water in the lake during the subglacial period varied in the range 376–444 mg/L, with the highest values near the surface due to desalination from the ice, and lower in the bottom layer. During the open water period the distribution of the sum of ions (346–370 mg/L) over the lake water area is more uniform due to intensive wind mixing of water.

Lake Gusinoe is characterized as freshwater of sodium bicarbonate type. In terms of nutrient content, Lake Gusinoe belongs to the oligotrophic type of water bodies. Increased concentrations of nutrients and OM fractions resistant to oxidation were registered at the wastewater discharge sites: in the northern basin—near the GRES and Gusinoozersk, in the southern basin—near the village of Gusinoe Ozero. Analysis of microelement composition of water showed an increase in iron content in water during spring and rainfall floods, due to flow from adjacent areas; manganese content increased in the subglacial period, which may be due to decomposition of aquatic vegetation and input from groundwater. High concentrations of copper in water, exceeding the standards, were recorded throughout the water area. Increased concentrations of elements were observed in the subglacial period in the zones of influence of the GRES and wastewaters of Gusinoozersk and Gusinoe Ozero; during the open water period, the distribution of elements in the water area was more uniform.

Analysis of HM contents in BSs of the lake revealed higher accumulation of metals in the silt of the deep zone of the lake with an increased content of OM capable of binding HMs. For deep BSs, the index of pollution by iron, manganese, zinc, copper, cadmium and mercury reached 1.2–1.9, corresponding to moderate pollution. Sandy BS of the lake coastal zones were characterized by much lower content of metals and were classified as

non-polluted. The content of cadmium and mercury was the highest in BSs of the northern part of the lake, exposed to the highest anthropogenic pressure.

It was revealed that aquatic plants of Lake Gusinoe accumulate most of the studied metals in larger amounts than in other cooling ponds throughout Siberia. Plants growing in the zones of influence of the Gusinoozersk GRES and Gusinoozersk wastewater discharge accumulate the largest amount of metals. The data obtained show the potential of macrophytes for bioindication of the state of water bodies.

Our complex studies showed the necessity of ongoing monitoring of chemical composition of water, BSs and biota in the lake, especially during the periods of significant changes in water level. As part of this work, research on the content of heavy metals in fish, as well as persistent organic pollutants in all components of the ecosystem of Lake Gusinoe will also be carried out.

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