Concentration Levels and Features of the Distribution of Trace Elements in the Sapropel Deposits of Small Lakes (South of Western Siberia)

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Abstract: The processes of the migration and concentration of trace elements during sedimentation in small continental lakes in various landscape zones of the south of Western Siberia have been studied. We provide a quantitative assessment of the concentration levels and changes in the regional geochemical background of Cd, Hg, Sb, Zn, and Pb in sapropel deposits over the past 200 years. It was shown that complex natural processes determined by a combination of azonal factors play a fundamental role in the formation of the geochemical and mineral compositions of the bottom sediments of small lakes in various landscape zones in the south of Western Siberia. These consist of: the formation of sedimentary material in the lake catchment depending on the relief, geology, soil, and vegetation cover, as well as anthropogenic influences; the formation of authigenic organic and mineral matter as a result of biological, biochemical, and physicochemical processes; and the deposition of a complex mixture of allochthonous and autochthonous matter at the bottom of a lake, which flows under conditions of prolonged ice formation (anaerobic conditions).

Keywords: small lakes; south of Western Siberia; sapropel deposits; geochemistry; Siberia

1. Introduction

Western Siberia hosts numerous small lakes, the study of which provides invaluable information about the past natural and climatic conditions of the regional and planetary level with a resolution from one year to centuries and the opportunity to assess their ecological state in the conditions of developing human economic activity both in the catchment and in the lakes themselves. The meridional length and gentle relief of the West Siberian plain from north to south determines the successive change of climatic conditions, the formation of latitudinal zonation, and landscape zones. In the southern part of Western Siberia, climate change is gradually carried out from the humid type (subtaiga, Vasyugan plain), through the temperate (forest-steppe, Baraba lowland), to the arid type (Kulunda plain, steppe and subzone of ribbon forests). The intracontinental lakes located in the Baraba lowland, Kulunda, and Vasyugan plains have significant variability in their hydrochemical parameters even within a small territory. This is manifested within a single lake system (a system of compactly located lakes in the same landscape–climatic and geological–geochemical conditions) [1]. These lakes are sensitive to climate change and anthropogenic impacts, which allow us to study the role of these factors in the formation of the geochemical composition of sapropel deposits [2–5]. Sapropel is the bottom sediment of reservoirs formed under anaerobic conditions because of biochemical, microbiological, and
mechanical processes and consisting of the remains of dying plant and animal organisms and organic and mineral impurities introduced into the reservoirs [6–8]. This is especially true for small shallow lakes since they belong to systems with properties that change rapidly over time.

Numerous paleogeographic works have shown that the limnological landscapes of the Baraba lowland and the Kulunda plain are extremely dynamic [4,5,9,10]. This is due to the combined impact of a large complex of both global and regional factors that provide and regulate the production of all parts of the aquatic ecosystem. At the same time, factors can change both in parallel with each other, and completely independently, creating new combinations and changing degrees of their impact on one or another component of the lake system.

The formation of lacustrine bottom sediments involves a substance coming from different sources: on the one hand, there is a mixture of autochthonous and allochthonous sources (averaging of the chemical composition); on the other hand, the differentiation of elements occurs due to their presence in different forms in surface waters.

For the lakes of Siberia, the accumulation of dispersed sedimentary matter by ice during a long period of ice formation (more than 6–7 months a year) and the dramatic arrival of this material to the lake during the snowmelt period are important. This is due to the specific relief of alternating hills and hollows, which is widely developed on the territory of the Baraba lowland, and consisting of lake-alluvial and cover subaerial loess-like deposits of mainly aleuropelite granulometric compositions with varying degrees of salinity of late Pleistocene age, genetically associated with suffusion–deflation processes. Because of such a surface arrangement, there is a local redistribution of moisture and easily soluble salts: their flow from the hill to the inter-hill spaces.

The biogeochemistry of bottom sediments from lake to lake in lake systems in such depressions differs significantly, and thus sapropels of different chemical compositions can form in a single lake system [11]. An important aspect of studying these lakes is that these small, closed reservoirs are subjected to significant (or complete) freezing in winter. During this period, the concentration of dissolved compounds in the waters of lakes can create a very high supersaturation. Thus, it is suitable, for example, for the deposition of carbonates with a high Mg content and those of some trace elements, or contributes to the deposition of usually unstable low-temperature amorphous aqueous phases of Na, Ca, and Mg minerals and the processes of anaerobic bacteria activity. This is important in the context of quantifying the reserve of trace elements and water in saprolip deposits of lakes. The material compositions of sapropels can exhibit substantial differences depending on its origin. The organic part of sapropel is significantly variable in its composition due to the ratio of the biological contribution of various organisms to the formation of bottom sediments, and largely depends on the balance of opposite processes—the production and destruction of organic matter [12,13]. The mineral part is determined by the source of the suspension.

Studies of the global emission of trace elements into the atmosphere carried out by various scientists have shown that almost all industrial production leads to the anthropogenic dispersion of elements in the environment [14–16]. Of particular concern is the enrichment of the biosphere with elements such as mercury, cadmium, and lead, due to their special toxicity and rapid influx in the 20th century [14,15]. Studies of Arctic ice have shown that Cd, Hg, and Pb in aerosols and fine particles can be transported over long distances, falling at considerable distances from sources of pollution and creating increased contents in regions remote from industrial centers [17–19]. Due to anthropogenic emissions, on a local, regional, and global scale, the intake of Hg by the environment has increased from two to 20 times over the past century. Mercury forms stable complexes with organic ligands, especially with sulfur (amino acids, oxycarboxylic acids, etc.), and high-molecular organic substances such as fulvic and humic acids. A significant part of Hg occurs in the suspended particles and in the form of methylated Hg; the latter can be formed both chemically and microbiologically [20]. Cadmium falls into the natural environment (soil,
water, air) due to its wide application in various branches of economic activity. The use of phosphate fertilizers has led to widespread Cd pollution of the environment on a global scale [21,22]. The global supply of Pb to the environment in the 20th century increased by more than ten times [23]. Largely, Pb forms stable forms with organic ligands containing sulfur, phosphorus, and nitrogen. The adoption of several international agreements to reduce the intake of these elements into the environment has led to a decrease in the emissions of Cd and Pb over the past 15 years.

Considering the diversity of lakes, it is relevant to study the factors determining the geochemical composition of the formed sapropels, based on extensive factual material for different lake systems from different landscape zones in the Vasyugan plain, the Baraba lowland, and the Kulunda plain using modern methods of analysis, processing, and interpretation of data. A stratified study of bottom sediments and a comparison of the upper layers (subaqual layers 0–20 cm) with deeper sediment horizons allows us to identify changes in the intake of elements, taking into account their redistribution occurring at the initial stage of diagenesis. We have previously conducted complex lithological studies with the establishment of the material composition features of sapropel lake systems and the identification of geochemical and mineral composition patterns depending on the hydrochemical, hydrobiological, geological, and hydrological conditions of sapropel formation. Based on the resulting database of analytical data, sapropels were classified according to types, depending on their ash contents and classes according to their Si/Ca ratio, as well as the dominant primary products, i.e., planktonic, macrophytic, and mixed [2,3,24,25]. The major element composition of the sapropels of the studied lakes is dominated by silicon (SiO$_2$ 59–5%), aluminium (Al$_2$O$_3$ 14–1%), and calcium (CaO 20–1%). These elements are present in the minerals of both terrigenous and biochemogenic genesis. Since the bottom sediments of lakes are the main carriers of complete information about the most important processes that occurred throughout the history of the lake, it is possible to identify the main factors determining the concentration of trace elements during sedimentation in small lakes based on the available material.

This work aims to identify the features of the regional distribution of trace elements (especially Cd, Hg, Pb, and Sb) during sedimentation in small continental lakes in various landscape zones in the south of Western Siberia and to assess the main factors determining the formation of their geochemical background in sapropel deposits over the past 200 years.

2. Objects and Research Methods
2.1. The Objects

The objects of the study were natural small continental lakes (91 lakes) located in different landscape zones in the south of Western Siberia (Figure 1; Table A1). In the presented work, only lakes with an area of less than 4 km$^2$ were studied. In small lakes, there is no fractionation of particles as they move away from the shore, with a depth, a temperature wedge, the entire water column falls into the wind mixing zone, then the composition of bottom sediments reflects the geochemical processes occurring in the water column of lakes and in their catchment areas. Lakes have a depth of up to 3 m. These lakes are drainless, with low sloping shores, and as a rule, overgrown with reeds, cattails. The water balance of lakes periodically experiences strong fluctuations: intra-annual (winter, summer); intra-century—a period of 30 years [4]. Climate and relief are the leading factors of the natural environment, which have a primary influence on the nature and number of lakes in a particular landscape zone, and the mineralization of lake waters is the most unstable parameter that depends on them. The studied lakes are located in various zones of surface water mineralization and landscape zones; for the convenience of comparing the reservoirs with one another, we have combined them into groups for landscape zones: the subtaiga of the Vasyugan plain (11 lakes), the forest-steppe zone of the Baraba lowland (32 lakes), the steppe zone of the Baraba lowland (18 lakes), the dry-steppe zone of the Kulunda plain (16 lakes), and the subzone of ribbon forests located in the Kulunda plain (14 lakes). When choosing lakes for the study, the authors paid attention to the fact that
the sample included lakes in which man-made extraction of any natural resources was not carried out. The exception is three lakes (Kulunda Plain) in which either NaCl or NaCO$_3$ were mined more than 50 years ago. Another three lakes are now actively used in tourism activities, but it is not comparable with the load on lakes in the European part of Russia. The issue of anthropogenic influence on the biogeochemistry of sediments in the presence of settlements in the direct catchment of the lake is considered in a series of papers [2,3,25–27]. Differences in the biogeochemistry of sediments were revealed in a sharp increase in nitrogen in the system of lakes on the shores of which there are settlements. The material about of Corg, N and P in sediment of particular lakes have been shown in several articles [2,3,24–28].

![Figure 1](image-url). The layout of the studied small lakes in the south of Western Siberia [24] with additions.

The importance of using the landscape approach in studying the processes of human relations with the geographical environment and the allocation of landscape macroregions has been discussed in the works of many authors. Here, we have applied a new methodological principle of a detailed study of a single lake in close relationship with the entire system of compactly located lakes (lake system) in the same landscape–climatic and geological–geochemical conditions, providing an idea of the general features of the mineral–geochemical composition both within the landscape zones and lake systems, and each individual lake, in particular.
2.2. Methods

The concept of continuous sampling of stratified bottom sediment core was applied in this research, which had a significant advantage in the study of lake sediments in obtaining more reliable and detailed information about the past changes in the natural environment. Moreover, the idea of complexity was applied in the processing of bottom sediment samples, that is, the involvement of the maximum possible number of various methods and analyses. In the field, water samples for all analyses were taken according to standard methods. For a sampling of bottom sediments, the sampling site was chosen away from settlements or at a maximum distance from them, if they were located in the coastal zone of the reservoir, from areas of bottom sediments that excluded mixing as a result of anthropogenic activity. A core of bottom sediments was sampled using a cylindrical sampler with a vacuum shutter designed by Scientific and Production Association Typhoon, Russia (diameter 82 mm, length 120 cm). The core of the bottom sediments was sampled in layers with a step of 3 or 5 cm, depending on the sediment density to a depth of 50 to 250 cm. The sediment was weighed after sampling and then dried to an air-dry state under laboratory conditions. Soil sampling was carried out to the depth of the entire soil section along the genetic horizons.

The sample preparation of various components of 96 lakes was carried out under laboratory conditions: 119 samples of surface lake water, 47 soil profiles (an average of eight samples in the section), 111 cores of bottom sediments (an average of 20 samples in the core), 104 samples of hydrobionts, and rocks from the lakebed (84 samples).

Analytical studies of the lake components were conducted in the Analytical Centre for Multi-elemental and Isotope Research SB RAS, Novosibirsk and in the Laboratory of Geochemistry of Noble and Rare elements of the Institute of Geology and Mineralogy SB RAS, Novosibirsk. The major (Ca, Na, K, Al, Fe, Mg, Mn) and trace (Sb, Sr, Ba, Be, Cd, Co, Ni, Cr, etc.) elements were determined via atomic absorption using a Solar M6 instrument equipped with a Zeeman and deuterium background corrector (Thermo Electron, Waltham, MA, USA). Two versions of atomic absorption were used: flame atomization (acetylene–air and nitrous oxide–acetylene) to quantify the content of a wide range of chemical elements, the content of which in the samples was >0.0001 mass %, and electrothermal atomization for the quantitative determination of elements present in lower concentrations (less than 0.000001 mass %). The major element composition was also determined by X-ray fluorescence analysis (ARL-9900-XP, Applied Research Laboratories, Austin, TX, USA). The sample morphology, and phase and elemental compositions were determined using a scanning electron microscope (SEM) MIRA 3 TESCAN (Tescan, Brno-Kohoutovice, Czech Republic).

The current modification of the equipment used a Si (Li) energetic detector (Oxford, Oxford Instruments, Abingdon, UK). The method allowed quantitative chemical analyses to be carried out on micro volumes. The INCA Energy 300 program (Labspec 5) was used for quantitative chemical analysis with reference standards (2145 definitions of mineral compositions). All microphotographs presented in this work were taken using the SEM MIRA 3 TESCAN (212 samples of bottom sediments and 28 samples of biota). X-ray diffractometry (XRD) (ARLX’TRA, Thermo Fisher Scientific (Ecublens) SARL, Waltham, MA, USA) (emission CuKα) was used to determine the mineral composition of 114 samples of bottom sediments and 34 soil samples, and in all others using mineralogical methods. The anion composition of the lake waters (concentrations of nitrates, chlorides, bromides, and fluorides) was determined by highly efficient liquid chromatography with the use of a Prominence 20 LC HELC system (Shimadzu, Japan) with a conductometric detector, Star-Ion A300 column 10 × 4.6 mm (Phenomenex, Torrance, CA, USA), eluent: 1.7 mmol/L NaHCO₃/1.8 mmol/L Na₂CO₃, flow rate 1.5 mL/min. The content of bicarbonate was determined by potentiometric titration with the use of an ATP-02 automatic titrator (Akvilon, Moscow, Russia) in accordance with the procedure PND F 142.99-97. The sapropel samples were subjected to thermal analysis for C, H, O, N, and S contents on a Vario EL Cube (Elementar Analysensysteme GmbH, Langenselbold, Germany) at the Boreskov Institute of Catalysis of the SB RAS.
The bottom sediments were dated by assessing the activity of $^{137}$Cs and $^{210}$Pb. This method for estimating the rates of modern sedimentation was proposed by Krishnaswamy et al. [29] and has been used here as well as in past studies [29–31]. The analysis of $^{210}$Pb was performed using gamma-spectrometry on a planar semiconductor detector with “ultrapure-Pb,W” protection from natural radiation. Sediment accumulation rates were determined from excess $^{210}$Pb activities that decreased exponentially below a zone of uniform activity (surface mixed layer) using a constant sedimentation rate model described in [30–33]. In the equation, deep mixing is assumed to be negligible, hence the calculated sediment accumulation rate represents the upper limit to the true sediment accumulation rate. The effects of deep mixing can be evaluated, for example, by testing with another radionuclide such as $^{137}$Cs covering comparable time intervals [30]. The joint distribution patterns of $^{137}$Cs and $^{210}$Pb allow the determination of the sediment's age, provided that the following conditions are realized: (1) both the $^{210}$Pb inflow to the sediments and the sedimentation rate are constant and (2) there is no post sedimentation migration of $^{210}$Pb.

The primary production and destruction of organic matter were determined by the light-and-dark-bottle method under oxygen modification. Macrophyte production was examined by standard methods on test grounds located in phytocenoses dominating in the studied areas. The air-dry weight was converted to a net annual production with a factor of 1.2 for air–water plants, and 2.5 for submerged and floating ones. The share of carbon in the organic matter of aquatic plants was taken equal to 46.4%, nitrogen in terms of nitrogen 2.0% of the air-dry mass, and phosphorus—0.3% [34]. The ratio of the autochthonous and allochthonous matter was obtained by experiments with sediment traps [25] and with the help of further calculations of the plankton and macrophytes mortmass inflow, considering the filtration activity of zooplankton and the intensity of pellet flux formation.

Statistical processing of analytical data included the formation of selection, the assessment of the uniformity of selection, the distribution law, the average, standard deviation, and correlation analysis. The measurement results for all dates were processed using the Statistica Base software program package for Windows. The Pearson correlation (R-type) was applied to compare the parameters. The correlation between the parameters was taken to be significant, if the significance level ($p$) was lower than a specified critical level ($p = 0.05$). The Statistica program determined the significance of the correlation coefficients. The methodology of cluster analysis is based on the ability to combine, using some criteria, into a homogeneous cluster a heterogeneous collection of objects. The nodal point is the choice of a measure of proximity (or distance) between objects, on which the final division into classes depends. The Euclidean distance is used as a measure of proximity. The matrix $m \times n$ was used for the calculation ($n$ is the samples of bottom sediments or soils; $m$ is the number of factors or variables (Hg, Cd, Pb, Cu, Zn, Ni, Co, Cr, Mn, Fe and others). The number of variables in the solutions changed in order to detect stable relationships between variables and obtain stable groups. Calculation is performed separately for R and Q factors. Q-analysis clusters samples (objects); R-analysis combines factors (chemical elements). In R-analysis, the measure is the correlation coefficient, in Q-analysis, Euclidean distance in the M-dimensional space [35].

3. Results

The total dissolved solids (TDS) value of the water varies significantly from fresh and brackish, occurring in all landscape zones, to brines in the steppe landscape. In the territories with a humid climate (subtaiga, Vasyugan plain), mainly ultra-fresh and freshwater is formed due to excess moisture and the migration of easily soluble salts and soil formation products to lower soil horizons. In the zones of the temperate and arid climate of the forest-steppe and steppe landscapes (Baraba lowland, Kulunda plain), there is a more intensive accumulation of easily soluble salts, and, in this regard, the water composition of the entire salinity spectrum is formed in these territories: from fresh to brine. As a result of the chemical composition transformation of the waters in the studied lakes, mainly bicarbonate waters with variations in the cationic composition of Ca-Na are
formed due to evaporation and wintry cryogeochemical processes. The waters are mostly alkaline, except for some lakes in the subtaiga zone (pH 5.1–6.8). The Eh indicator of the waters of all lakes is positive and quite high. The content of $O_2$ dissolved in water (in the surface layer of water) in most lakes is high and varies from 133.7% (11.47 mg/L) to 72% (6.29 mg/L), and only in some lakes it is significantly lower (<50%), which is explained by active processes of organic matter destruction occurring during the formation of sapropel. The concentrations of elements are mainly lower than in the hydrosphere in the waters of the studied lakes [36], and are at the level of the values attributed to the northern lakes of Eurasia. Lake waters are enriched with a group of elements that are usually found in the form of a suspension and/or sorbed by a suspension (Al, Fe, Mn, Cu, Zn). High values of carbon and phosphorus were also observed.

As mentioned earlier, the lakes are grouped into lake systems to identify patterns of geochemical and mineralogical compositions depending on different conditions. The ionic composition diagram of the water shows the chemical composition of sapropels formed in these lakes to assess the degree of the chemical composition dependence of bottom sediments on the composition of water. Sapropel deposits of different types, classes, and genesis occur in lakes located compactly in the same landscape and climatic conditions (in the same lake system), having a single or similar catchment area and water sources (Figure 2). All types and classes of sapropel are also found among the lacustrine sediments within a single landscape zone. Organic–mineral and mineral–organic sapropels of silicon, calcium, or mixed class of macrophytic and macrophytic–planktonic species predominate in different landscape zones (Appendix A Table A1). A comparative analysis of the data on the values of TDS in comparison with the chemical composition of sapropels that are formed from these waters showed that the influence of the TDS value on the chemical composition of sapropel was not revealed.

Let us consider the example of the lakes of the Kuibyshev and Tanatar lake systems (Table A1). The Kuibyshev lake system is located in the forest-steppe zone and the Tanatar lake system is located in the steppe and partly in the ribbon forest subzone. The contents of dissolved oxygen in both of the studied lake systems was within the ecological optimum ($8.0 \pm 2.0$ mg/L). The highest concentrations were observed in the littoral zones of the Bilgen, Zhiloye, and Mostovoye lakes overgrown with air–water vegetation: 9.5–13.0 mg/L (Kuibyshev system), and the Rublevo and Demkino lakes—7.4–7.6 mg/L (Tanatar system). The minimum values were observed in the open (not overgrown) littoral zones of the Bugristoe and Yargol lakes—5.7–6.1 mg/L (Kuibyshev system): the Jodnoe and Korostelevskoye—5.4–6.2 mg/L (Tanatar system).
The concentrations of newly formed and easily oxidized organic matter in the waters of most lakes (according to BOD$_5$) was high (3.0 ± 1.9 mgO$_2$/L) and corresponded to mesotrophic–eutrophic waters. A high concentration of organic matter was noted in lakes which are near inhabited localities and experiencing a significant anthropogenic influence (Lakes B. Kaili and Tsybovo), or during the period of mass development of cyanobacteria (Lake B. Tassor). The value of the gross primary production of phytoplankton in the studied lakes varied widely (0.02–2.21 mgO$_2$/L·hour). The highest values were noted during the period of mass development of cyanobacteria (blue-green algae) in the forest-steppe zone lakes with planktonic sapropels (Lakes Peschanoe, Mostovoe, Zhiloe, and Tsybovo). In these lakes, diatoms and cyanobacteria make the greatest contribution to the formation of planktonic bottom sediments. Diatoms concentrate Si in shells, creating amorphous silica and burying it in bottom sediments. The most favorable conditions for the development of diatoms and the formation of diatomites (diatom sapropels) exist in small oligotrophic and mesotrophic reservoirs with clear and cool water. There is a polydominant phytoplankton community with a significant contribution of diatoms among the studied lakes (the Kambala, Tsybovo, B. Kayly, and Yargol lakes). In eutrophic lakes, a decrease in the transparency of water and its heating throughout the entire thickness contributes to the intensive development of blue-green algae (cyanobacteria). The rate of destruction of organic matter in the lakes varied from 0.007 to 1.84 mgO$_2$/L·hour. In most lakes, the production processes were more intensive than the destruction ones (on average, 2.4 times). In such lakes, the processes of organic matter formation prevail over the processes of its decomposition, and organic matter accumulates in bottom sediments. The flux of autochthonous organic matter into the studied lakes ranged from 3.2% in the hypersaline Lake Malinovoe (in which the basis of the sedimentation flux consists of chemogenic halite) to 84.2% in Lake Peschanoe (a lake with an autochthonous type of matter accumulation) of the total mass of the sedimentary flux. According to the contribution of phytoplankton to the value of the sedimentation flow, all studied lakes were divided into two groups: (1) with an insignificant contribution (0.001–0.04 g/m$^2$·day)—the Sarbalyk, Kaili, and Bilgen lakes and others and (2) with an average value of the contribution (0.19–0.57 g/m$^2$·day)—the Mostovoe, Zhiloe, and Tsybovo lakes and others. The calculated values of the phytoplankton contribution to the organic carbon, nitrogen, and phosphorus supply to the bottom sediments amounted to 0.18–245.4 g$_{org}$/m$^2$·year, 0.03–43.19 gN/m$^2$·year, and 0.01–5.89 gP/m$^2$·year, respectively. In lakes with a high gross primary production of phytoplankton, its significant contribution to the sedimentation flow into bottom sediments was also observed.

The massive development of macrophytes in the littoral zone of lakes determines the organic carbon budget for plankton and regulates nitrogen compounds in water and bottom sediments. According to the degree of overgrowth with macrophytes and the size of its primary production, all the studied lakes could be divided into four types: (1) with a border type of overgrowth, which occurs in some lakes of Kuibyshev and prevails in the Tanatar lake system (Lakes Bilgen, Kambala, Korostylevskoe, B. Tassor). In such lakes, rigid air-water vegetation bordering the lake prevails. The area of overgrowth is about 5–10% of the total lake area and the annual production of phytocenoses is from 138.1 to 1377.7 g/m$^2$·year of organic matter; (2) with a massive-overgrown type (Lakes Tsybovo, Zhiloe, Sarbalyk), characteristic of most lakes within the Kuibyshev lake system. Rigid air-water vegetation dominates along the shores of those lakes, represented by communities of Phragmites australis (Cav.) Trin. ex Steud., and Typha angustifolia L. In the water-covered area—soft submerged plants with a dominance of Ceratophyllum demersum L. and Stratiotes aloides L. prevail. The overgrown area covers up to 70% of the total and the annual production of macrophytes is from 418.7 to 1945.8 g/m$^2$·year of organic matter; (3) with the floating type (Lakes Mostovoye and Demkino), which is dominated by air-water vegetation, formed by floating islands, the annual production of phytocenoses is up to 2261 g/m$^2$·year of organic matter; (4) with the overgrowth type, representing the last stage of overgrowth of the reed.
during their growth season, macrophytes produce from 86.4 to 4193.6 g/m$^2$ of organic matter, from 76.2 to 764.2 gC$_{org}$/m$^2$, from 3.8 to 35.2 gN/m$^2$, and from 0.5 to 4.4 gP/m$^2$. The maximum productivity of macrophytes was observed in lakes of the forest-steppe zone with floating and massive-overgrown types of overgrowth. Equally, the highest contents of C$_{org}$ and N$_{org}$ was noted in the bottom sediments of these lakes. After dying off, a part of the macrophytes already decomposes in the coastal zone, and most of them are carried away into the lake, undergoing further changes there. In sapropel bottom sediments, the bulk of plant residues undergoes anaerobic decay. One of the main intermediate products of this anaerobic decomposition are fatty acids, which break down very quickly to form methane and carbon dioxide. The fibers and carbohydrates of plant residues, in addition to fatty acids, also release carbon dioxide and hydrogen, which, with the participation of bacteria, are converted into methane, which makes up a significant part of a lake gasses. However, a significant part of organic matter is buried in bottom sediments.

The organic matter formed by primary producers determines the biomass and production of consumers belonging to different trophic levels. The development of large filtering Cladocera promotes phosphorus deposition because Cladocera pellets contain many undigested cells of diatoms and blue-green algae, which actively concentrate phosphorus, converting it into poorly soluble phosphates [37,38]. The high production of Copepoda (both predatory forms and detritivores) leads to an increased percentage of organic nitrogen (N$_{org}$) and organic carbon (C$_{org}$) in the bottom sediments since Copepoda enriches the pellet material with ammonium nitrogen and C$_{org}$ during metabolism. The shell pellets of Copepoda do not allow material to dissipate and it slows down bacterial processing. Our calculations show that due to the withering away of zooplankton, 47.4–1625.1 gC$_{org}$/m$^2$, 5.09–127.5 gN/m$^2$, and 0.701–19.039 gP/m$^2$ entered the bottom sediments of the studied lakes every year. Additionally, zooplankton excreted up to 21 gP/m$^2$, 138 gN$_{org}$/m$^2$, and 1648 gC$_{org}$/m$^2$ per year. At the shallow depths of the studied lakes, almost the entire flow of matter which formed during the day in the upper layers of the lake managed to reach the bottom without being subjected to mineralization in the water column. Further transformation of biological material occurred at the bottom as a result of the vital activity of bacteria and benthic organisms [2]. The sharp enrichment of bottom sediments with pyrite indicates that sulphate reduction occurred, which indicates the active development of the mineralization of organic matter under anaerobic conditions at the bottom of lakes. Framboidal pyrite or its single crystals of various habitus (cube, octahedron, pentagonal dodecahedron) are unevenly distributed throughout the bottom sediment core. Sometimes they form thin layers, nest-like separations, or they are uniformly interspersed among other minerals of the bottom sediments throughout several centimeters.

Analytical data on the major and trace element compositions of lacustrine bottom sediments and the soils of their catchment area were averaged over various landscape zones, depending on the type and class of sapropel. The primary analytical data on the contents of major and trace element compositions in bottom sediments for interpretation were grouped according to various factors: landscape zones, ash contents of the bottom sediments, the mineral composition of the inorganic part, and the group composition of the organic part, and others. The average analytical data on the major and trace element compositions of the lakes’ bottom sediments for various types and classes of sapropel are given in the tables (Tables 1 and 2). For the silicon and mixed classes, these values are comparable with the data for the upper continental crust [39] and siltstone-sandstone rocks of the Russian Plate [40]; for the calcium class, the values are comparable to the carbonate rocks of the Russian Plate [40] for elements such as Mg, Ca, K, Sr, Pb, Zn, Co, Cr, Fe, Th, V, and Li, but not for Mn, Ba, Na, Cu, or Sb.
According to the microscopic study and the X-ray spectral analysis of the lakes' bottom sediments, it was found that the mineral composition of the terrigenous fraction was similar: quartz and feldspar (albite, oligoclase, potassium feldspar) play a leading role with a subordinate amount of mica (muscovite, less often biotite), chlorite (Fe ~ Mg), and illite (Fe ~ Mg). Different types and classes of sapropel deposits from lakes in the same landscape zones differ not only in their major element compositions but also in their contents of several trace elements. We have previously shown that these values for soils of the catchment are comparable with the data for soils of Western Siberia [3,24] and the average values for the soil of the continents [36] for elements such as Mg, Ca, K, Sr, Ba, Pb, Cu, Zn, Co, and Be. The average values of trace element contents in soils are close to the average for soil-forming rocks [2,3,24,41]. After comparing the contents of elements in

Table 1. Average content of major (%) and trace elements (mg/kg) in sapropels of lakes of various types and classes in the south of Western Siberia (arithmetic mean ± standard deviation).

| Sapropel Class | Mg | Ca | K | Na | Fe | Al | Mn | Sr | Ba |
|----------------|----|----|---|----|----|----|----|----|----|
| Organic-mineral with ash content of 30–50% |    |    |   |    |    |    |    |    |    |
| Silicon (Si >> Ca) | 0.5 ± 0.1 | 1.3 ± 0.6 | 0.6 ± 0.2 | 0.4 ± 0.2 | 1.0 ± 0.9 | 2.2 ± 1.9 | 339 ± 240 | 171 ± 90 | 163 ± 112 |
| Calcium (Ca >> Si) | 0.7 ± 0.5 | 9.5 ± 6.6 | 0.4 ± 0.4 | 0.5 ± 0.4 | 1.1 ± 0.8 | 1.3 ± 0.8 | 664 ± 401 | 698 ± 215 | 167 ± 156 |
| Mixed (Si ~ Ca) | 0.7 ± 0.5 | 3.5 ± 1.8 | 1.1 ± 0.7 | 0.7 ± 0.6 | 1.7 ± 0.8 | 3.2 ± 2.8 | 435 ± 256 | 193 ± 95 | 150 ± 102 |
| Mineral-organic with ash content of 50–70% |    |    |   |    |    |    |    |    |    |
| Silicon (Si >> Ca) | 0.8 ± 0.3 | 1.7 ± 0.4 | 1.2 ± 0.4 | 0.6 ± 0.2 | 1.9 ± 0.4 | 3.9 ± 1.9 | 485 ± 230 | 203 ± 148 | 212 ± 112 |
| Calcium (Ca >> Si) | 1.5 ± 0.4 | 4.6 ± 2.7 | 0.2 ± 0.1 | 0.2 ± 0.1 | 0.7 ± 0.2 | 0.5 ± 0.3 | 1066 ± 530 | 1120 ± 915 | 388 ± 234 |
| Mixed (Si ~ Ca) | 2.3 ± 0.8 | 23.6 ± 8.5 | 1.2 ± 0.6 | 1.5 ± 0.5 | 1.7 ± 0.7 | 3.6 ± 1.8 | 644 ± 313 | 668 ± 395 | 279 ± 156 |
| Mineralized with ash content of 70–85% |    |    |   |    |    |    |    |    |    |
| Silicon (Si >> Ca) | 1.1 ± 0.1 | 1.4 ± 0.3 | 2.2 ± 0.9 | 1.2 ± 0.4 | 3.1 ± 1.5 | 6.9 ± 1.9 | 225 ± 130 | 108 ± 48 | 231 ± 98 |
| Calcium (Ca >> Si) | 4.8 ± 1.4 | 27 ± 8 | 0.1 ± 0.1 | 6.0 ± 2.1 | 0.4 ± 0.1 | 0.3 ± 0.1 | 1966 ± 444 | 1134 ± 887 | 445 ± 111 |
| Mixed (Si ~ Ca) | 0.3 ± 0.2 | 9.6 ± 3.9 | 0.9 ± 0.2 | 0.7 ± 0.2 | 1.1 ± 0.5 | 2.6 ± 1.8 | 571 ± 301 | 785 ± 509 | 240 ± 98 |

Published data

Upper continental crust [39] | 1.3 | 3.0 | 2.8 | 2.6 | 3.1 | 7.7 | 527 | 316 | 668 |
RPSC (clay + siltstone) [40] | 1.0 | 2.4 | 2.15 | 0.56 | 2.75 | 4.94 | 500 | 170 | 566 |
RPSC (carbonate) [40] | 4.99 | 27.9 | 0.41 | 1.0 | 0.87 | 0.78 | 300 | 566 | 84 |

Table 2. Average content of trace elements (mg/kg) in sapropels of lakes of various types and classes in the south of Western Siberia (arithmetic mean ± standard deviation).

| Sapropel Class | Cd | Pb | Cu | Zn | Ni | Co | Hg | Sb | Cr | V | Li |
|----------------|----|----|----|----|----|----|----|----|----|---|----|
| Organic-mineral with ash content of 30–50% |    |    |   |    |    |    |    |    |    |   |    |
| Silicon (Si >> Ca) | 0.43 ± 0.32 | 14 ± 12 | 20 ± 16 | 110 ± 90 | 23 ± 10 | 7 ± 2 | 0.08 ± 0.05 | 0.85 ± 0.33 | 44 ± 20 | 32 ± 19 | 10 ± 7 |
| Calcium (Ca >> Si) | 0.14 ± 0.11 | 18 ± 11 | 12 ± 9 | 39 ± 15 | 14 ± 4 | 4 ± 1 | 0.04 ± 0.02 | 1.5 ± 0.6 | 38 ± 27 | 17 ± 11 | 7 ± 5 |
| Mixed (Si ~ Ca) | 0.27 ± 0.15 | 10 ± 8 | 20 ± 11 | 70 ± 55 | 23 ± 6 | 7 ± 2 | 0.05 ± 0.02 | 1.4 ± 0.4 | 69 ± 38 | 49 ± 29 | 12 ± 8 |
| Mineral-organic with ash content of 50–70% |    |    |   |    |    |    |    |    |    |   |    |
| Silicon (Si >> Ca) | 0.29 ± 0.22 | 14 ± 11 | 26 ± 20 | 77 ± 40 | 30 ± 12 | 9 ± 3 | 0.05 ± 0.01 | 1.95 ± 0.63 | 88 ± 60 | 63 ± 49 | 18 ± 11 |
| Calcium (Ca >> Si) | 0.04 ± 0.04 | 4 ± 5 | 4 ± 5 | 23 ± 10 | 6 ± 2 | 3 ± 1 | 0.02 ± 0.01 | 0.72 ± 0.32 | 16 ± 9 | 18 ± 11 | 9 ± 5 |
| Mixed (Si ~ Ca) | 0.18 ± 0.11 | 12 ± 8 | 21 ± 16 | 61 ± 35 | 25 ± 5 | 7 ± 2 | 0.04 ± 0.02 | 0.72 ± 0.21 | 51 ± 38 | 59 ± 41 | 25 ± 18 |
| Mineralized with ash content of 70–85% |    |    |   |    |    |    |    |    |    |   |    |
| Silicon (Si >> Ca) | 0.20 ± 0.12 | 14 ± 10 | 27 ± 19 | 71 ± 27 | 33 ± 12 | 9 ± 2 | 0.05 ± 0.02 | 0.39 ± 0.13 | 57 ± 35 | 75 ± 456 | 26 ± 17 |
| Calcium (Ca >> Si) | 0.27 ± 0.19 | 9 ± 11 | 43 ± 29 | 21 ± 12 | 6 ± 1 | 6 ± 1 | 0.07 ± 0.03 | 0.65 ± 0.12 | 5 ± 3 | 12 ± 5 | 31 ± 25 |
| Mixed (Si ~ Ca) | 0.03 ± 0.05 | 10 ± 8 | 4 ± 6 | 33 ± 10 | 23 ± 9 | 5 ± 2 | 0.03 ± 0.01 | 0.67 ± 0.24 | 32 ± 23 | 46 ± 27 | 5 ± 1 |

Published data

Upper continental crust [39] | 0.10 | 17 | 14.3 | 52 | 18.6 | 11.6 | 0.056 | 0.3 | 35 | 53 | 22 |
RPSC (clay + siltstone) [40] | 0.09 | 12 | 26 | 52 | 29 | 9.1 | - | 0.9 | 43 | 61 | 27 |
RPSC (carbonate) [40] | 0.22 | 7 | 9 | 17 | 7.8 | 2.2 | - | 0.3 | 17 | 22 | 13 |
soil samples from different landscape zones, it can be argued that, except for calcium, the variation of the contents of all studied elements did not exceed the arithmetic mean ± 3σ (three standard deviations).

When comparing the contents of elements in the lacustrine bottom sediments of various landscapes in the south of Western Siberia with the composition of the upper continental crust, an excessive accumulation of Ca, Cr, Ni, Cu, Cd, and Sb and a significant depletion of Be, K, Al, Si, Ti, Th, and Ba, as well as Fe and Co during modern sedimentation was established (Figure 3). The gradual enrichment of Ca, Sr, Mg, Na, Li, and U in the bottom sediments from north to south and the meridional zoning of depletion of Cu, Zn, Cd, and Sb (i.e., the reverse) in bottom sediments were revealed.

![Figure 3](image-url)

**Figure 3.** The multi-element spectrum of the average values of the studied elements for bottom sediments of lake systems in the different type of landscape of South of Western Siberia (according to our data) normalized to the values of the upper continental crust (UCC) contents according to [39].

A comparison of the data on the average values of the studied elements in the bottom sediments of Siberian lakes and their catchment area soils shows that higher contents of Sb, as well as Ca, Mg, Sr (the steppe landscape), and Cd (Baraba forest-steppe landscapes) were recorded in the bottom sediments of all landscape zones (Figure 4). The contents of the other elements are at the same level as the content of these metals in the soils of the catchment areas.

![Figure 4](image-url)

**Figure 4.** The multi-element spectrum of the average values of the studied elements for bottom sediments of lake systems in the different type of landscape of South of Western Siberia normalized to the values of the soils of the catchment area of the lakes (according to our data).

Authors [3,24] have analyzed the vertical distribution of elements in individual lakes and lake systems. The sediments of 56 lakes from all landscape zones were dated by estimating the activity of 137Cs and 210Pb [24]. Earlier, the authors found that the vertical distribution of the studied trace elements in the soil profiles of the catchment areas of lakes is characterized by uniformity with a general tendency of chaotic changes in values within less than one standard deviation. At the same time, their contents in the upper horizons do
not exceed the values for the lower intervals. Cd and Hg are elements with a pronounced character of increasing contents from the lower to the upper soil horizons in all landscape zones of Siberia [24].

The analysis of the vertical distribution of Cd, Hg, and Pb reveals differences in their distribution in comparison with other major and trace elements in the generalized columns of the studied lakes by types and classes of sapropel of various genesis, various landscape zones of the south of Western Siberia, and lakes of individual lake systems. For most of the studied elements, the vertical distribution is not characterized by any trend: the upper and lower horizons of bottom sediments practically do not differ in contents (Cu, Cr, Ni, Co, Mg, Be, Sb, V, Li, and others). Examples of such a distribution of elements in sediments include a huge number of lakes, near which there are no settlements or industrial production. In Figure 5, this distribution is demonstrated by the example of the distribution of the averaged contents of Al, Ca, Mg, Na, Cu, Ni, and Zn in sapropels of the organomineral type of various classes (silicon, calcium, mixed). In all sections of sapropel deposits the contents of Cd and Hg, and in certain classes and types, Pb, Mn, and V, increase to the geochemical barrier “water-bottom sediments” (Figures 6 and 7).

Figure 5. Vertical distribution of the averaged contents of Al (%), Ca (%), Na (%), Mg (%), Ni (mg/kg), Cu (mg/kg), Zn (mg/kg) and ash content (%) in sapropel sediments of organic–mineral type in the various classes (Silicon, Calcium, Si/Ca (mixed)) along cores (according to our data).
Figure 6. Vertical distribution of the averaged contents of Cd (mg/kg); Hg (mg/kg)×10 and Pb (mg/kg)×10^{-2} in sapropel sediments of various types (organic–mineral; mineral–organic; mineralized) and class (Silicon; Calcium, Si/Ca (mixed)) along cores (according to our data).

Figure 7. Vertical distribution of the averaged contents of Mn (mg/kg)×10^{-1}; V (mg/kg) and Fe (mg/kg)×10^{-3} in sapropel sediments of various types (organic–mineral; mineral–organic; mineralized) and class (Silicon; Calcium, Si/Ca (mixed)) along cores (according to our data).
4. Discussion

The contribution of various biotic components of the ecosystem to the formation of bottom sediments in different lakes can vary significantly, affecting the final chemical and mechanical composition of their bottom sediments. As shown above, in several lakes, good heating of water throughout the entire thickness and a high concentration of organic matter contribute to the intensive development of blue-green algae (cyanobacteria) and macrophytes. The massive development of small-cell colonial cyanobacteria, capable of depositing calcium carbonate inside or on the surface of the mucous membrane surrounding the cell or multicellular colony, and the high production of macrophytes (reed, *Chara* sp., *Ceratophyllum* sp., and *Potamogeton* sp.) accumulating in the leaves and stems of oxalates and calcium carbonates, contribute to the formation organo-carbonate sapropels. Zooplankton and benthic organisms also contribute to the utilization of calcium from the water and its active precipitation. In such lakes, the carbonate system becomes the main controlling factor of the geochemical regime, while a significant part of calcium, magnesium, and carbon binds to the authigenic carbonates of the calcite–dolomite series, forming classes of calcium and mixed sapropel deposits. The high production of diatoms, equisetum, *Stratiotes aloides*, *Nuphar lutea* (L.), *Lemna trisulca* L., *Najas* sp., and some other plants assimilating silicon leads to the deposition of a significant amount of biogenic silica. According to Nelson D.M [42], diatoms building their cells from silica annually dehydrate and remove 1010 tons of dissolved silicic acid from the ocean. The shells of diatoms are resistant to high temperatures, rotting, and the effects of alkalies and acids, so their transformation in the sediment during diagenesis and catagenesis occurs over a significant time interval. That is, in modern silts, the shells of diatoms are not transformed, and, consequently, the unique properties of diatoms as natural sorbents are preserved in the bottom sediments.

An increase or decrease in production indicators not just of one or another taxonomic group of aquatic organisms, but even of one or another species within the group, leads to a significant change in the biochemical composition of the autochthonous substance. It has been established that variations in the chemical composition of sapropels in lakes with similar values of total water mineralization within the same landscape zone can be as significant as between fresh and salt waters, or between lakes of different landscape zones. This is clearly shown by the example of lakes grouped into lake systems, for example, the Kuibyshev lake system of the forest-steppe zone of the Baraba lowland (18 lakes). According to the obtained analytical data on their basic ionic composition and physicochemical parameters, the lake waters are mainly bicarbonate–magnesium–sodium or bicarbonate-sodium, and alkaline. Due to mineralization, the lake waters are fresh (0.2–0.6 g/L), salty, and slightly salty (1.3–4.2 g/L). In more mineralized waters, the cationic composition practically does not change, and in the anionic part, a chlorine ion is added to the bicarbonate ion, except for Lake Tsybovo (sulphate ion). All types and classes of sapropel of macrophytic and planktonic–macrophytic genesis were identified in these lakes. At the same time, the bottom sediments of lakes differ markedly in their chemical and mineralogical composition, and these differences are comparable to those of lakes of different landscape zones.

Based on the statistical processing of data on the distribution of 28 chemical elements in the bottom sediments of 91 lakes, R-type cluster analysis revealed (with a probability of 95%) correlations between major and trace elements with their groupings, resulting mainly in three clusters with high positive correlation coefficients within groups (Figure 8).
Figure 8. The dendrogram of the R-type cluster analysis, where analytical data on the contents of major (Si, Ca, Na, K, Al, Mg, Fe) and trace elements (Ti, P, Mn, Sr, Ba, Pb, Cd, V, Cu, Zn, Co, Ni, Cr, Hg, U, Th) in different types of sapropel sediments are used: organic–mineral; mineral–organic; mineralized. An oval is a group of organophilic elements; a rectangle is a group of carbonatophiles.

In all three types and classes of sapropel deposits, there is a correlation of Al–K with iron, chromium, nickel, cobalt, copper, thorium, and others. In all sapropel deposits of the lakes, components of this group are mainly part of feldspar, muscovite, biotite, actinolite, hornblende, as well as a few accessory minerals (terrigenous mineral fraction). It is important to note that iron is concentrated in the silicates and aluminosilicates of the detrital fraction and, therefore, will not reduce the quality of sapropel raw materials due to the inertia of these mineral phases. The Na content is controlled not only by the plagioclase grains of the terrigenous fraction but also by the presence of buried crystals of easily soluble salts (trona, halite, soda, etc.). In the mineralized type of bottom sediments, the main sources of silica are quartz and feldspar, despite the presence of silica biota, contributes to the separation of Si from the elements of the terrigenous fraction. With a more fractional cluster analysis, considering the class of sapropel deposits (Si and Ca ratio), the dominant type of production (planktonic, macrophytic, planktonic–macrophytic), and the study of their phase compositions using scanning electron microscopy and IR-spectroscopy, it was found that the bonds between the elements of individual groups reflect their joint occurrence in mineral phases. Thus, in the organic–mineral and mineral–organic types of Si and mixed classes, the contents of silica are controlled by the presence of a significant amount of biogenic silica in the sapropel deposit. Biogenic silica is usually composed of the shells of siliceous organisms (mSiO$_2$·nH$_2$O) and the remains of macrophytes (Figure 9).

The carbonatophilic group Ca-Mn with variations in different classes (Mg, Sr, Sb) is clearly distinguished in all diagrams. The elements of the group (Ca, Mn ± Sr, Mg, Ba,) are part of the authigenic carbonates of the calcite–dolomite series or form minerals that are in paragenetic association with them (barite, gypsum).

The group comprising Cd, Hg ± Zn, Pb, and U occupies a separate position on all diagrams. A direct correlation between the contents of these elements and the amounts of organic matter in the bottom sediments was revealed. The contents of a group of elements (Cd, Hg ± Zn, Pb, U), which occupies a separate position on the dendrogram of cluster analysis, directly correlate with the amounts of organic matter in bottom sediments. It is known that these elements have a high ability to bioaccumulate and humic substances increase their absorption/co-deposition. The analysis of the obtained information allowed us to conduct a comparative analysis of the vertical distribution of trace elements in the bottom sediments of lakes, considering the influence of the composition of rock-forming elements (sapropel class, the genesis of its organic part, mineral composition, and hydrochemical characteristics of waters).
For the main rock-forming elements that depend on the predominance of the terrigenous fraction in their composition (Al, Ba, Th, and to a lesser extent Si and K, are determined by the amounts of feldspar, clastic silicates); the distributions of newly formed authigenic carbonates (Ca, Sr, Mn) change in opposite directions, and the total trend naturally changes depending on the amount of organic matter (the inverse amount of the ash content). It is important to note that the ratio of biochemogenic carbonates and minerals of the terrigenous fraction in the bottom sediments of a particular lake does not strongly depend on landscape conditions but is determined by the development of certain types of biota in a particular lake.

Variations in the distribution of trace elements in the vertical section of bottom sediments can be caused by both natural and anthropogenic factors. Of the natural causes, the main one includes differences in lithological composition, which is confirmed by the distribution of Ca and Al, and the amount of organic matter. Among the studied lakes, there are lakes where, against the normal background of the distribution of elements along the core of bottom sediments, layers sharply enriched with one or more elements (hurricane contents) are noted. In all cases of hurricane contents, samples were analyzed several times, sometimes with repeated sampling. The source of hurricane contents may be natural processes that have manifested locally. An example is the bottom sediments of Lake Porozhee (Kulunda plain). In some intervals of its precipitation, the content of Mn is so high (about 6 kg/t) that this led to the formation of iron-manganese nodules up to 6 mm in diameter. Increased contents of trace elements (Ba, U, Mo) are associated with Mn hydroxides. However, most often the probable cause of abnormal emissions of contents of elements is local man-made pollution. The highest content of Pb (3345 mg/kg) is observed in the bottom sediments of Lake Bolshye Rakity (Kulunda Plain), where pellets from a hunting cartridge were found. An interval sharply enriched with Hg (up to 2–2.3 mg/kg) was detected in Bolshoe Yarovoje Lake (Baraba lowland), on the shore of which the plant is located. The technogenic origin of Hg is proved in a series of works by the author [43]. According to the authors’ works, in the vertical distribution of elements in almost all cores of the studied lakes, anthropogenic influence on the biogeochemistry of bottom sediments in the presence of settlements in the lake catchment has not been revealed [2,3,25–27]. With the exception of N, and sometimes P, a sharp increase in their contents in the post-war period was found for these elements in the cores of the bottom sediments [44].
Significantly higher Cd, and sometimes Hg, contents in the upper part of the section of bottom sediments and the soils of their catchment areas relative to the underlying horizons can be explained by natural causes, namely their connection with the polyamides of fulvic acids of organic matter. Of all the chemical elements, Cd and Hg have the maximum ability to covalently bind to proteins. Phytoplankton and macrophytes are capable of accumulating a wide range of trace elements, transforming their soluble forms into hardly soluble ones, which, after dying off, are buried in bottom sediments. Large forms of phytoplankton, represented by blue-green algae and diatoms, accumulate Cu, Zn, and Pb in contents ranging from 11.2 to 45 mg/kg of dry weight, and in small amounts (0.40–2.40 mg/kg) Ni and Cd. Macrophytes play a significant role in the entry of heavy metals into bottom sediments. Their coastal thickets create favorable conditions for the sedimentation of suspended solids. Part of the sediments, accumulating on the surface of plants, form organomineral complexes which then also enter the bottom sediments. The level of Pb accumulation in the mortmass of macrophytes ranges from 0.92 mg/kg to 2.29 mg/kg of dry weight; that of Cd from 0.08 to 0.18 mg/kg of dry weight. Among macrophytes, the priority accumulators of heavy metals are chara and filamentous algae. The contents of Pb in individual specimens can reach 23 mg/kg, and in Cd up to 1.3 mg/kg, which is 1.2–1.5 times higher than in floating plants, and 1.7–2.4 times more than in semi-submerged plants. The root system of both hard (reed) and soft (pond) aquatic vegetation accumulates much more heavy metals than the surface and stems of plants [45].

According to experimental data [46], Zn^{2+} and Cu^{2+} are most intensively involved in migration cycles, and to a lesser extent Pb^{2+} and Cd^{2+}. The variability of the forms of Cd during migration is programmed by the ability of Cd to easily change its state under the influence of environmental factors [15,19]. Therefore, during the decomposition of organic matter, Cd and Hg fall into the pore waters and are reincorporated in the migration process. Studies of the behaviour of Cd in different components of the natural environment have shown that while the balance of natural geochemical processes is not disturbed, the geochemistry of Cd is close to natural and its affinity with Zn and Hg is manifested [15]. Consequently, with an increase in Cd contents in the cores of bottom sediments, an increase in Zn should be recorded at the water-bottom sediment boundary, which is observed in the cores of the most part of the lakes. However, in sapropels of mineralized and mineral–organic types, mixed and silicon classes, where the dominant primary production is a planktonic–macrophytic, there is a significant increase in Cd and Hg contents at the water-bottom sediment boundary, while the Zn contents of the upper and lower horizons of bottom sediments practically does not differ. According to the literature, an increase in the contents of chalcophile elements (Zn, Cu, Ni), including Cd, can also be associated with the activity of sulphate-reducing bacteria, the presence of hydrogen sulfide in the upper part of bottom sediments, and the formation of sulfides. Consequently, the likely reason for the high contents of Cd and sometimes Hg in the sections of most of the studied lakes is an increase in the intake of these elements over time, associated with an increase in the current regional level of their background contents in the biosphere of the Northern Hemisphere. According to numerous studies, the maximum levels of technogenic enrichment of the environment are characteristic of Hg and Pb, and an intensive accumulation of Pb, Hg, and Cd in the environment has been observed [15]. It was only at the beginning of the 21st century that the supply of these elements to environmental objects significantly decreased [19].

Manganese and iron hydroxides are important factors in fixing these elements. Nevertheless, there is no trend of increasing contents in the distribution of elements with variable valence (V, Mn, U, etc.) in the upper part of the sections (Figure 7), or other chalcophile elements (Cu, Ni) (Figure 5). Of course, it should be considered that the minerals of the detrital fraction determine the majority of the content of these elements. Of the elements with variable valence, only Mn is associated with authigenic, newly formed carbonates and, therefore, it is possible to attribute the distributions of its contents to diagenesis. In stratified cores of bottom sediments, the ions of soluble Mn^{2+} and Fe^{2+} usually migrate to...
the water-bottom boundary due to the lack of free O\textsubscript{2} in the bottom waters. In the studied lakes, the deficiency of free O\textsubscript{2} was confirmed by the change in Eh, which already occurs in the uppermost centimeters of the sediments, i.e., in the silt, the active development of the processes of mineralization of organic matter under anaerobic conditions at the bottom of the lakes, and the presence of frambooidal pyrite (described above). At the same time, graphs of the distribution of Mn contents with a significant increase in its concentrations at the water-bottom sediment boundary were found only in eight (out of 15) lakes of the mixed class of organic–mineral and mineral–organic sapropel type (Figure 7). In all other bottom sediments, the Mn distribution is mainly characterized by uniformity with a general tendency for chaotic changes in values within less than one standard deviation. At the same time, the contents in the upper horizons do not exceed the values for the lower intervals.

5. Conclusions

The generalization of data on the distribution of elements in the conjugate components of small lakes allowed us to identify the nature of changes in the incoming substances in their bottom sediments, the sources of the substances affecting the mineral composition of the sediments, and the main factors determining the quantitative contents of elements in them. The comparison allowed us to assert that the final chemical composition of sapropel is influenced not so much by the soil cover of the catchment, which is a source of water-soluble salts entering the waters, as by various biogeochemical processes occurring in the water column of lake ecosystems.

Summarizing the data on the distribution of the studied elements in the bottom sediments of the lakes, and considering the type, class of sapropel, and the TDS of water, it can be argued that the fundamental role in the formation of the geochemical and mineral composition of the bottom sediments of small lakes in various landscape zones of the south of Western Siberia is played by complex natural processes determined by a combination of azonal factors: the formation of sedimentary material in the lake catchment depending on the relief, geology, soil and vegetation cover, and human economic activity; the formation of authigenic organic and mineral substances as a result of biological, biochemical, and physicochemical processes; and the deposition of a complex mixture of allochthonous and autochthonous substances at the bottom of the lake, occurring under conditions of prolonged ice formation (under anaerobic conditions). Organomineral (sapropel) deposits are formed in all landscape zones in small lakes in the south of Western Siberia. The type of sapropel is determined by the ash content, which depends not only on the amount of terrigenous components but also on the biochemogenic components (amorphous silica, low-magnesium calcite, aragonite), the composition of which determines the class of sapropel. The elements of the group (Ca, Mn ± Sr, Mg, Ba,) are associated with the formation of carbonates, and the contents of Cd, Hg ± Zn, Pb, and U depend on the amount of organic matter in the bottom sediments.

The contents of trace elements, which are mainly concentrated in silicates and aluminosilicates of the detrital fraction (Co, Cr, Fe, Th, V, Li, Cu, Ni, Be, and others) in the bottom sediments of a single lake most clearly inherit their contents from soils and soil-forming rocks, and most correspond to the values of the contents of the studied elements in the upper continental crust. The revealed variations in their values from lake to lake within the same class, but different types of sapropel are comparable to the variations in the contents of elements within the same type, but different classes of sapropel. The decrease in the contents of these trace elements in the bottom sediments of lakes relative to the values in the soils of the catchment areas is associated with the dilution of sediments by biogenic silica, authigenic carbonates, or organic matter.

The analysis of the vertical distribution of major and trace elements in the generalized columns of the bottom sediments of the studied lakes in the landscape zones of the south of Western Siberia allowed us to distinguish two types of sections. In the first case, the contents of most of the studied elements (Cu, Zn, Cr, Ni, Co, Mg, Be, Sb, Mn, and others)
was characterized by uniformity with a general tendency toward chaotic changes in values within less than one standard deviation. At the same time, the contents in the upper horizons did not exceed the values for the lower intervals. Another type of distribution was noted for Cd, and sometimes Hg. In most sections, their contents increased in the upper part. The obtained data allowed us to assert that the anthropogenic load of Cd and Hg on the continental lake systems of Siberia has increased on a wide-scale over the past 70 years.

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**Data Availability Statement:** The data presented in this study are partially available on request from the corresponding author.

**Conflicts of Interest:** The authors declare no conflict of interest.

### Appendix A

**Table A1.** Studied lakes (type and class of the sapropels, landscapes, and lake systems).

| Geographical Location | Landscape     | Lake System  | Lake       | Type and Class of the Sapropel |
|-----------------------|---------------|--------------|------------|--------------------------------|
| Vasyugan plain        | sub-taiga     | Samuskaya    | Yakovo     | Organic–mineral, Silicon       |
|                       |               |              | Maltcevo   | Organic–mineral, Silicon       |
|                       |               |              | Krugloe    | Mineral–organic, Silicon       |
|                       |               |              | Karbalyk   | Mineralized, Calcium           |
|                       |               |              | Urmanno     | Mineral–organic, Calcium       |
|                       |               |              | Danilovo   | Mineral–organic, Calcium       |
|                       |               |              | Linevo     | Mineral–organic, Calcium       |
|                       |               |              | Shchuchye Linevo | Mineral–organic, Calcium       |
|                       |               | Kyshtovskaya | Shchuchye Karbalyk | Mineral–organic, Silicon       |
|                       |               |              | Shchuchye Danilovo | Mineral–organic, Mixed        |
| Tom-Obskay            | forest steppe |               | Shchuchye Bazovoe | Organic–mineral, Silicon       |
|                       |               |              | Bolshoe Shchuchye | Organic–mineral, Silicon       |
|                       |               |              | Maloe Shchuchye | Mineral–organic, Silicon       |
|                       |               |              | Obskoe     | Organic, Silicon               |
|                       |               |              | Layskoe 1  | Organic–mineral, Silicon       |
|                       |               |              | Layskoe 3  | Organic–mineral, Silicon       |
| Baraba lowland        |               | Gzhatskaya   | Chulym     | Mineral–organic, Mixed         |
|                       |               |              | Barchin    | Organic–mineral, Silicon       |
|                       |               |              | Kambala    | Mineral–organic, Silicon       |
|                       |               |              | Bol. Kazatovo | Mineral–organic, Silicon       |
Table A1. Cont.

| Geographical Location | Landscape | Lake System | Lake | Type and Class of the Sapropel |
|-----------------------|-----------|-------------|------|---------------------------------|
| Bergulskaya           |           | Kajly       |      | Mineral–organic, Mixed          |
|                       |           | Bergul      |      | Mineral–organic, Mixed          |
|                       |           | Yargol      |      | Organic–mineral, Silicon        |
|                       |           | Irgol       |      | Organic–mineral, Mixed          |
| Novokievskaya         |           | Suetok      |      | Mineral–organic, Silicon        |
|                       |           | Bilgen      |      | Mineral–organic, Silicon        |
|                       |           | Bol. Kurgan |      | Organic–mineral, Silicon        |
|                       |           | Sarbalyk    |      | Organic–mineral, Silicon        |
| Ust-Tarskaya          |           | Chistoe     |      | Mineral–organic, Silicon        |
|                       |           | Tengis      |      | Mineral–organic, Silicon        |
| Mangazerskaya         |           | Tcybovo     |      | Organic–mineral, Silicon        |
|                       |           | Zhiloe-K    |      | Organic–mineral, Mixed          |
|                       |           | Mostovoe    |      | Mineral–organic, Silicon        |
|                       |           | Mangazerka  |      | Organic–mineral, Mixed          |
| Kuibyshevskaya        |           | Bol. Kajly  |      | Organic–mineral, Mixed          |
|                       |           | Pecchanoe   |      | Organic–mineral, Calcium        |
|                       |           | Chistoe     |      | Mineral–organic, Silicon        |
|                       |           | Melkoe      |      | Mineralized, mixed              |
| Barabinskaya          |           | Goldobinskoе|      | Mineral–organic, Calcium        |
|                       |           | Shubinskoе  |      | Organic–mineral, Mixed          |
|                       |           | Verhnee     |      | Mineralized, Mixed              |
|                       |           | Nizhnee     |      | Organic–mineral, Mixed          |
|                       |           | Bugristoe   |      | Mineral–organic, Silicon        |
|                       |           | Zhiloe      |      | Mineral–organic, Mixed          |
| Chulymskaya           | steppe    | Kankul      |      | Mineralized, Mixed              |
|                       |           | Kachkulnya  |      | Organic, Silicon                |
|                       |           | Itkul       |      | Mineralized, Mixed              |
|                       |           | Bolshie Toroki |   | Organic–mineral, Calcium        |
|                       |           | Malie Toroki|      | Organic–mineral, Calcium        |
|                       |           | Kankulenok  |      | Organic–mineral, Mixed          |
| Zdvinskaya            |           | Bol. Chica  |      | Mineralized, mixed              |
|                       |           | Dolgoе      |      | Mineral–organic, Silicon        |
|                       |           | Dlinoе      |      | Mineral–organic, Calcium        |
|                       |           | Novaya Opushka |   | Organic–mineral, Mixed          |
|                       |           | Zhiloe      |      | Mineral–organic, Mixed          |
| Geographical Location | Landscape       | Lake System | Lake           | Type and Class of the Sapropel |
|-----------------------|-----------------|-------------|----------------|-------------------------------|
|                       |                 |             | Kusgan         | Mineralized, mixed            |
|                       |                 |             | Krotovaya lyaga| Mineralized, Silicon          |
|                       |                 |             | Khoroshee      | Mineralized, mixed            |
|                       |                 |             | Kukley         | Organic–mineral, Mixed        |
|                       |                 |             | Chebache       | Mineral–organic, Mixed        |
| Karasukskaya          |                 |             | Krasnovishnevoe| Mineralized, mixed            |
|                       |                 |             | Nikitinskoe    | Mineral–organic, Mixed        |
|                       |                 |             | Bolshoe Yarovo| Mineral–organic, Mixed        |
|                       |                 |             | Maloe Yarovo   | Mineral–organic, Mixed        |
|                       |                 |             | Mostovo|                  | Mineral–organic, Silicon      |
| Terengulskaya         |                 |             | Milinovoe      | Mineralized, Calcium          |
|                       |                 |             | Jodnoe         | Mineral–organic, Mixed        |
|                       |                 |             | Karatan        | Mineral–organic, Mixed        |
|                       |                 |             | Krugloe        | Mineralized, Silicon          |
|                       | steppe          |             | Petukhovo (steppe) | Mineralized, Silicon    |
|                       |                 |             | Kuriche        | Mineralized, Calcium          |
|                       |                 |             | Zheltyr’       | Mineralized, Mixed            |
|                       |                 |             | Gorkoe         | Mineral–organic, Mixed        |
|                       |                 |             | Srednee        | Organic–mineral, Calcium      |
|                       |                 |             | Baevo          | Organic–mineral, Silicon      |
|                       |                 |             | Gorkoe         | Mineralized, Mixed            |
|                       |                 |             | Plotavskoe     | Mineral–organic, Mixed        |
|                       | Kulunda plain   |             | Stepnoe        | Mineral–organic, Mixed        |
|                       |                 |             | Spirino        | Organic–mineral, Silicon      |
|                       |                 |             | Travnoe        | Mineral–organic, Mixed        |
|                       |                   |             | Petukhovo (ribbon forests) | Mineralized, Silicon    |
|                       |                   |             | Tanatar-4      | Mineral–organic, Calcium      |
|                       |                   |             | Tanatar-6      | Mineralized, Mixed            |
|                       |                   |             | Rublevo        | Mineral–organic, Mixed        |
|                       |                   |             | Demkino        | Mineral–organic, Mixed        |
|                       |                   |             | Presnoe        | Organic–mineral, Silicon      |
|                       |                   |             | Gorkoe 1       | Mineralized, Calcium          |
|                       | Ribbon forests   |             | Gorko-Peresheichnoe | Mineralized, mixed         |
|                       | subzone          |             | Krivoe         | Organic–mineral, Mixed        |
|                       |                   |             | Rakiti-1       | Mineral–organic, Silicon      |
|                       |                   |             | Krugloe        | Mineral–organic, Mixed        |
|                       |                   |             | Rakiti-2       | Mineral–organic, Silicon      |
|                       |                   |             | Gorkoe 2       | Mineralized, Mixed            |
|                       |                   |             | Korostelevo-1  | Organic–mineral, Mixed        |
|                       |                   |             | Korostelevo-2  | Organic–mineral, Calcium      |
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