Geochemical Approach to the Reconstruction of Sedimentation Processes in Kamyshovoye Lake (SE Baltic, Russia) during the Late Glacial and Holocene

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Abstract: The article is devoted to a reconstruction of the sedimentation processes in Kamyshovoye Lake (the Kaliningrad Region, Russia) during the Late Glacial and Holocene. The results of the geochemical analysis of Kamyshovoye Lake's bottom sediments, accompanied by statistical processing and detailed radiocarbon dating, are presented. It was established that a high proportion of mineral matter dominated in the intervals between 15,000 and 11,400 and between 1400 and 600 cal y BP; enrichment with carbonates was noted between 11,400 and 5200 cal y BP and during the past 600 years; and a high percentage of organic matter was recorded between 7800 and 600 cal y BP. We conclude that the increase in mineral matter was influenced by such factors as reduced vegetation cover due to natural and anthropogenic processes, aeolian transfer, and dead-ice melting during the Late Glacial. The increase in carbonate matter was mainly associated with humidity and the reduction conditions of the lake ecosystem. Organogenic matter content was affected by the autochthonic (biological) productivity of the lake, which directly depends on more favorable climatic conditions.

Keywords: geochemistry; environmental changes; Late Glacial; Holocene; sedimentation; lacustrine sedimentation; Lake Kamyshovoye; Kaliningrad Region

1. Introduction

Under the conditions of modern climate change, paleogeographic studies are important for predicting the vectors of the development of natural conditions in the future. Lacustrine deposits are a universal material for studying paleoenvironmental changes because sediments preserve various bioindicators (i.e., pollen, diatoms, plant macrofossils, and chironomid capsules). The abiotic composition of bottom deposits can give reliable information about the surrounding catchment and physicochemical and biological processes [1]. A sufficiently large number of qualitative studies of vegetation changes during the Late Glacial and Holocene exist for the Kaliningrad Region, SE Baltic [2–5], which enabled us to carry out a comprehensive reconstruction of the natural conditions of the Kamyshovoye Lake surroundings during the Late Glacial to early Holocene transition [3,6]. This article presents the results of a geochemical analysis in combination with statistical processing, along with depth/age models for the entire core of the bottom sediments of the Kamyshovoye Lake (the Vishtynets

Upland, Kaliningrad Region, Russia). The sedimentation processes in the Kamyshovoye Lake have been intensive and continuous since its formation (~15,000–16,000 cal y BP). The thickness of the deposits, at 9.79 m, made it possible to perform a study with high resolution. This study is important for understanding sedimentation processes and the factors that influenced their changes in the Late Glacial and Holocene.

2. Study Area

Kamyshovoye Lake is located in the Vishtynets Upland (192 m a.s.l.) (Figure 1), which was formed as a result of the Baltija stage of the Late Glacial [7]. The heights of the Vishtynets Upland are about 50 m a.s.l. in the northwest and 200–300 m a.s.l. in the southeast [8]. The relief was formed by marginal glaciers, with a wide development of glacial forms such as moraine hills, kames, outwash plains (sandurs), glaciofluvial plains, kame terraces. Depressions between moraine hills are heavily swampy, and some are filled with lakes [9]. The territory is located on the border of a marine and continental type of climate. The average annual humidity is 700 mm, and the average annual temperature is from −4.5 °C (January) to +15.5 °C (July) [10]. The dominant types of soils are cambisols and luvisols, mostly formed on till, clay sands, and loam. The semihydrogenic and hydrogenic soils, such as histosols, gleysols, and fluvisols, have developed in the depressions between moraines, along rivers and lakes. The current vegetation is diverse: more than half of the forested area is composed of pines and spruces, slightly less is accounted for by small deciduous forests, and broad-leaved forests occupy about 10% of the territory [8].
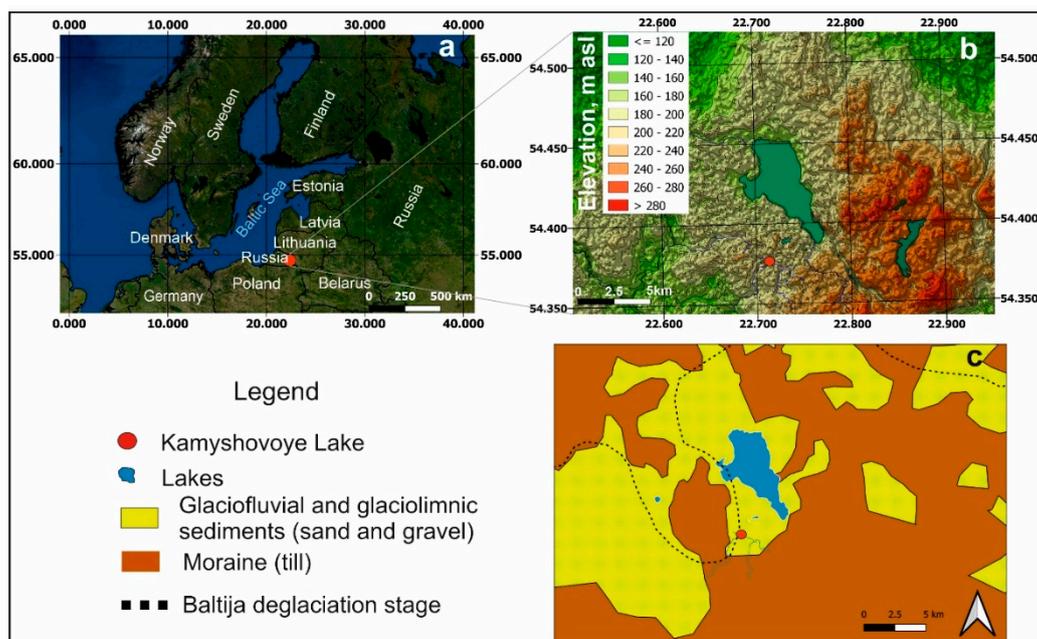

Figure 1. (**a**) Location of the Kamyshovoye Lake in the Baltic region, (**b**) relief, (**c**) quaternary geology of the surrounding area.

The Kamyshovoye Lake is located in a kettle hole, oriented from SW to NE, whose maximum length is 1200 m and width is 600 m. The total area is 0.26 km^2. The lake is shallow, with a maximum depth of 3.8 m. Two streams up to 4 m wide flow into the lake from the southeast and northeast. The southwestern part of the lake is drained by a river 8 m wide. The basin of the Kamyshovoye Lake is up to 90% filled with limnoglacial (silty clay) and lacustrine (clay gyttja and gyttja) deposits [6].

3. Methods

The bottom sediments of the Kamyshovoye Lake were drilled from ice in March 2012 using a Russian corer (100 cm long chamber with a 5 cm diameter). At 2.3 m lake depth, 9.8 m deposits were recovered intact and subsampled for micropaleontological, loss-on-ignition (LOI), geochemical, and radiocarbon analyses.

3.1. Lithology

Sediments were described according to Subetto 2009 [1]. The method is based on a visual and physical description of the composition and color of bottom sediments. Classification was applied to determine the genesis of bottom sediments. Three types of deposits were identified: terrigenous (less than 10% carbonate and less than 10% organic matter)—silty clay; chemogenic sediments (more than 10% of carbonates)—clay gyttja and gyttja; and organic-matter-containing sediments (>10% organic matter)—gyttja [11].

3.2. Radiocarbon Analysis and Sedimentation Rate

The absolute age of sediments was determined by radioactive carbon (^{14}C) at the Laboratory of Geochronology, Saint-Petersburg State University, Russia; a total of 22 samples were taken for this analysis. AMS ^{14}C dating of three samples from the lower part of the section was conducted at the Radiocarbon Dating Laboratory, Poznan, Poland. For the calibration and modeling of dates, OxCal v. 4.2.4 with an IntCal 13 calibration curve [12] was used. The calibrated years were expressed in cal y BP, given at the 2-sigma confidence level (68.2%). Previously described by Druzhinina et al. [3,6], biostratigraphic dates were also used for the model. Samples with obvious inversions, such as LU-6927, LU-6931, and POZ-60941, and dates with questionable results, such as POZ-60943 and POZ-60940, were not used for the age–depth model preparation. The sedimentation rate was calculated between adjacent dates by the median values.

3.3. Geochemical Analysis

3.3.1. Loss-on-Ignition (LOI)

To evaluate the conditions of sedimentation in Kamyshovoye Lake, the LOI method was applied. LOI was conducted at the Laboratory of Geochronology, St. Petersburg State University, following standard procedures [13,14]; sediments covering 10 cm intervals were dried at 105 °C for 24 h and combusted at 550 °C for 4 h. This allowed us to determine the organic matter (LOI) in 97 sediment samples.

3.3.2. Elementary Analysis

The selected portion of the sedimentary column (depth: 1199–220 cm) was divided into 1 cm samples. Geochemical analysis was performed using a SPECTROSCAN MAKC-GV X-ray fluorescence spectrometer at the Herzen State Pedagogical University of Russia, Saint-Petersburg. The instrument was calibrated on 20 soil and sea-bottom deposit reference samples analyzed by WD-XRF on Spectron equipment ("Spectron", Ltd., Saint-Petersburg, Russia) [15]. Accuracy was tested by analyzing over 50 certified international standard reference samples (CRMs) and by repeated exchange of samples with other laboratories. The maximum deviations for major elements in CRMs are mostly below 5%, and below 10% for sodium and trace elements. Before the analysis, the samples were dried at 105 °C until the moisture evaporated completely, then ground to a powder in a mortar. Tablets for geochemical analysis were prepared using boric acid as a base, and a laboratory press (pressure ~110 bar). The mass fractions of chemical elements and oxides, such as Ba, La, Rb, Nb, Zr, Cr, Sr, As, Pb, Zn, Cu, Ni, Co, V, TiO_2, MnO, Fe_2O_3, CaO, Al_2O_3, SiO_2, P_2O_5, K_2O, MgO, and Na_2O, were measured and expressed in ppm or %. The analytical error is presented in Table 1. Due to the low detection limits, Ba

and La were not included in the analytical error table. In total, 483 samples were studied as part of this work. The MnO/Fe_2O_3 ratio can be an indicator of both alkaline and reducing conditions of the lake ecosystem. When the value of Mn correlates positively with the values of Zn and Pb elements, the MnO/Fe_2O_3 ratio is an indicator of alkaline conditions [16]. According to the PCA analysis, SiO_2 and Al_2O are antagonists, which allows us to consider the SiO_2/Al_2O ratio as a biogenic indicator [17] associated with an increase in diatoms in the reservoir. P_2O_5 was used as an indirect indicator of the human impact [18].

Table 1. The analytical error for geochemical elements.

Geochemical Elements	Standard Error	Geochemical Elements	Standard Error
TiO_2	0.05%	MnO	50 ppm
MgO	0.1%	Fe_2O_3	0.5%
Al_2O_3	1.5%	Co	5 ppm
SiO_2	10%	Ni	5 ppm
P_2O_5	0.02%	Cu	10 ppm
K_2O	0.4%	Zn	10–80 ppm
CaO	0.07%	As	10 ppm
V	5 ppm	Sr	25 ppm
Cr	40 ppm	Pb	12 ppm

3.4. Statistical Processing

To unveil the depth-dependent concentration variation pattern of certain elements, the data obtained were processed using correlation and factor analysis methods in StatSoft Statistica 8.0. (Dell corporation, Austin, TX, USA).

3.4.1. Correlation Analysis

In discussing the palaeoenvironmental evolution of the basin, several groups of chemical elements associated with different mineral fractions were distinguished. For this, Pearson correlation coefficients were calculated for all cases and elements. Elements whose correlation coefficients were positive and higher than 0.73 were grouped into three groups.

3.4.2. PCA

PCA was used to study the relationships between the values of elementary variables for the whole sediment core and deposits core [19].

4. Results and Interpretation

4.1. Lithology

The lowermost part of the Kamyshovoye Lake sediment sequence is represented by silty clay (older than 12,800 cal y BP [3]), clay gyttja (formed ca. 12,800–9800 cal y BP), and organic gyttja (younger than 9800 cal y BP). The sediment descriptions are presented in Table 2.

4.2. Radiocarbon Analysis, Age–Depth Model, and Sedimentation Rate

The Kamyshovoye core chronology was reconstructed, based on ^{14}C and biostratigraphical data (Table 3). The age–depth model, lithology, and sedimentation rate are presented in Figure 2. The highest sedimentation rate (more than 1 mm/y) was noted in 10,400–9500 and 4000–2500 cal y BP, and the lowest rate (less than 0.2 mm/y) was seen in 9500–8600 cal y BP.

Table 2. Sediment description of lithostratigraphical units.

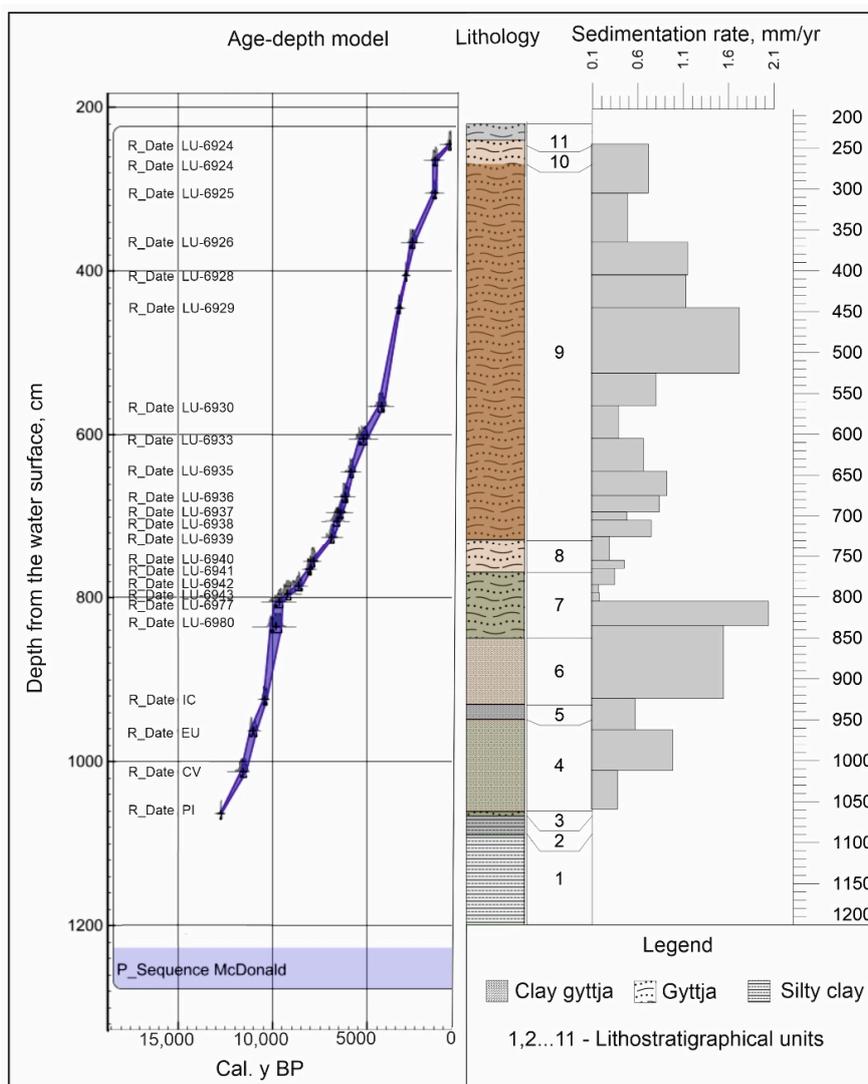| Lithostratigraphic Units	Depth from the Water Surface, cm	Sediment Description
11	230–247	Gray gyttja
10	247–270	Light brown gyttja
9	270–730	Dark brown gyttja
8	730–770	Light brown gyttja
7	770–850	Greenish-brown gyttja
6	850–932	Greyish-brown clay gyttja
5	932–950	Gray clay gyttja
4	950–1061	Greenish-grey clay gyttja
3	1061–1067	Greenish-brown gyttja
2	1067–1089	Dark grey silty clay
1	1089–1199	Grey silty clay

Figure 2. Age–depth model for the sediment sequence of Kamyshovoye Lake.

Table 3. AMS, radiocarbon, and biostratigraphic data and calibrated age ranges for Kamyshovoye Lake.

Sample ID	Dating Material	Depth from the Water Surface, cm	Lithostratigraphical Units, No.	^{14}C y BP	Age Ranges (cal y BP) 68.2% conf. Intervals
			^{14}C data		
LU-6924	Bulk gyttja	240–250	11	650 ± 100	675–549
LU-6925	Bulk gyttja	260–270	10	1490 ± 100	1520–1303
LU-6926	Bulk gyttja	300–310	9	1520 ± 90	1522–1342
LU-6927 *	Bulk gyttja	320–330	9	1480 ± 120	1522–1295
LU-6928	Bulk gyttja	360–370	9	2530 ± 90	2748–2490
LU-6929	Bulk gyttja	400–410	9	2850 ± 90	2996–2926
LU-6930	Bulk gyttja	440–450	9	3100 ± 40	3369–3250
LU-6931 *	Bulk gyttja	480–490	9	3700 ± 40	4090–3980
LU-6932	Bulk gyttja	520–530	9	3510 ± 80	3889–3650
LU-6933	Bulk gyttja	560–570	9	3850 ± 100	4415–4102
LU-6934	Bulk gyttja	600–610	9	4560 ± 120	5450–5040
LU-6935	Bulk gyttja	640–650	9	5100 ± 90	5932–5735
LU-6936	Bulk gyttja	670–680	9	5390 ± 90	6287–6021
LU-6937	Bulk gyttja	690–700	9	5590 ± 110	6493–6285
LU-6938	Bulk gyttja	700–710	9	5790 ± 120	6730–6453
LU-6939	Bulk gyttja	720–730	9	6010 ± 90	6967–6739
LU-6940	Bulk gyttja	750–760	8	7010 ± 90	7937–7757
LU-6941	Bulk gyttja	760–770	8	7220 ± 80	8157–7965
LU-6942	Bulk gyttja	780–790	7	7830 ± 90	8773–8463
LU-6943	Bulk gyttja	790–800	7	8220 ± 100	9300–9030
LU-6977	Bulk gyttja	800–810	7	8630 ± 130	9885–9486
LU-6980	Bulk gyttja	830–840	7	8740 ± 160	10,117–9545
POZ-60941 *	Plant remain	962–964	4	10,310 ± 50	12,375–11,992
POZ-60943 *	Plant remain	1011–1012	4	11,810 ± 60	13,720–13,577
POZ-60940 *	Bulk gyttja	1062–1063	3	11,600 ± 60	13,483–13,351
			Biostratigraphic Data [6]		
Event		Depth from the Water Surface, cm	Lithostratigraphical Units, No.		Age, cal y BP
Immigration of Corylus (IC)		924	6		10,400
Establishment of Ulmus (EU)		962	4		11,050
Closing of Vegetation (CV)		1012	4		11,550
Maximum of Pinus (PI)		1059	4		12,750

* Inversion data, not included in the age–depth model.

4.3. Statistical Processing

4.3.1. Correlation Analysis

In the course of the correlation analysis, three groups of major elements with a positive correlation index were identified. We undertook a statistical analysis, taking into account that: (1) Group 1 includes elements associated with the terrigenous supply into the reservoir as a result of physical weathering of bedrock, glacial, and glaciofluvial deposits—SiO_2, Al_2O_3, K_2O, clay minerals, silicates (feldspars), Fe_2O_3, MgO (hornblende), Zr, TiO_2 (zircon), and titanomagnetite; (2) Group 2 consists of chemical elements that are part of the alkaline–carbonate components of Na_2O and CaO, formed as a result of chemical weathering of bedrock and deposition; and (3) Group 3 comprises elements that form part of the organomineral complexes and are associated with the formation of organic detritus comprising Zn, Pb, Co, P_2O_5, and MnO. These groups of elements are accumulated under different sedimentation conditions, as indicated by a factor analysis.

4.3.2. PCA

The first factor (F1) of PCA shows the antagonism between the elements of the carbonate component (CaO, Na$_2$O) and the components of the clastic, terrigenous component (SiO$_2$, Al$_2$O$_3$, TiO$_2$, and Zr). The positive values of F1 are associated with climate warming, increasing humidity, and the formation of alkaline conditions. The second factor (F2) is characterized by the formula (Zn, Co, Pb, Fe$_2$O$_3$, SiO$_2$, P$_2$O$_5$/CaO, Na$_2$O, MnO, Al$_2$O$_3$). The factor reflects the antagonism of chemical components (Zn, Co, Pb, Fe$_2$O$_3$, SiO$_2$, and P$_2$O$_5$) that characterize the reduction conditions of the lake's ecosystem and elements (CaO, Na$_2$O, MnO, and Al$_2$O$_3$), whose compounds are characteristic of more oxidizing conditions. The relationships between the values of elementary variables and the dynamic of both factors are presented in Figure 3.
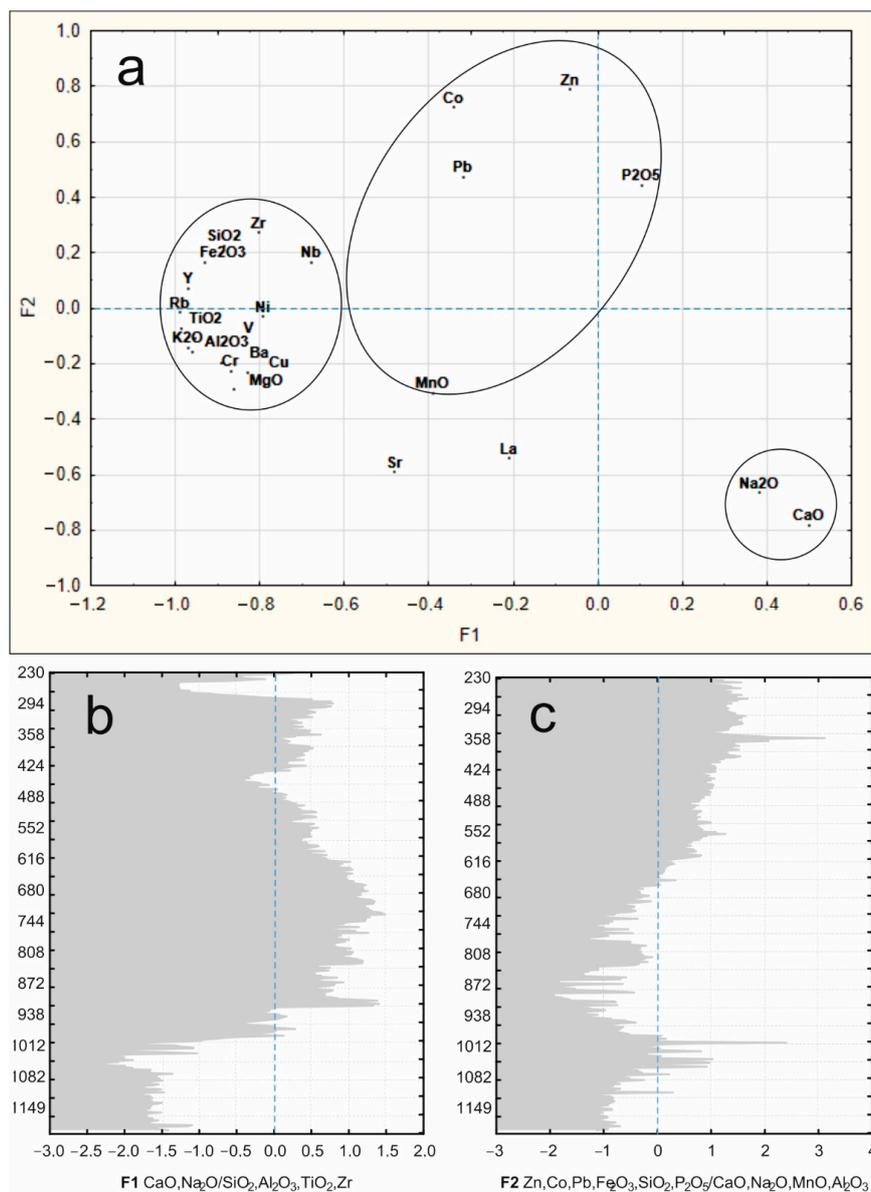

Figure 3. Results of PCA: (**a**) biplot, (**b**) dynamics of the first factor, (**c**) dynamics of the second factor.

4.4. Geochemistry

Following the geochemical analysis, the percentages of 15 elements and 10 oxides of each of 483 samples were estimated (Figure 4). Eleven geochemical zones (Chez 1–11) with differing geochemical

records were identified based on the statistical evaluation of samples. Interpretation of the geochemistry data allowed us to make a reconstruction of the sedimentation changes during the Late Glacial and Holocene in the Vishtynets Upland (Figure 5).
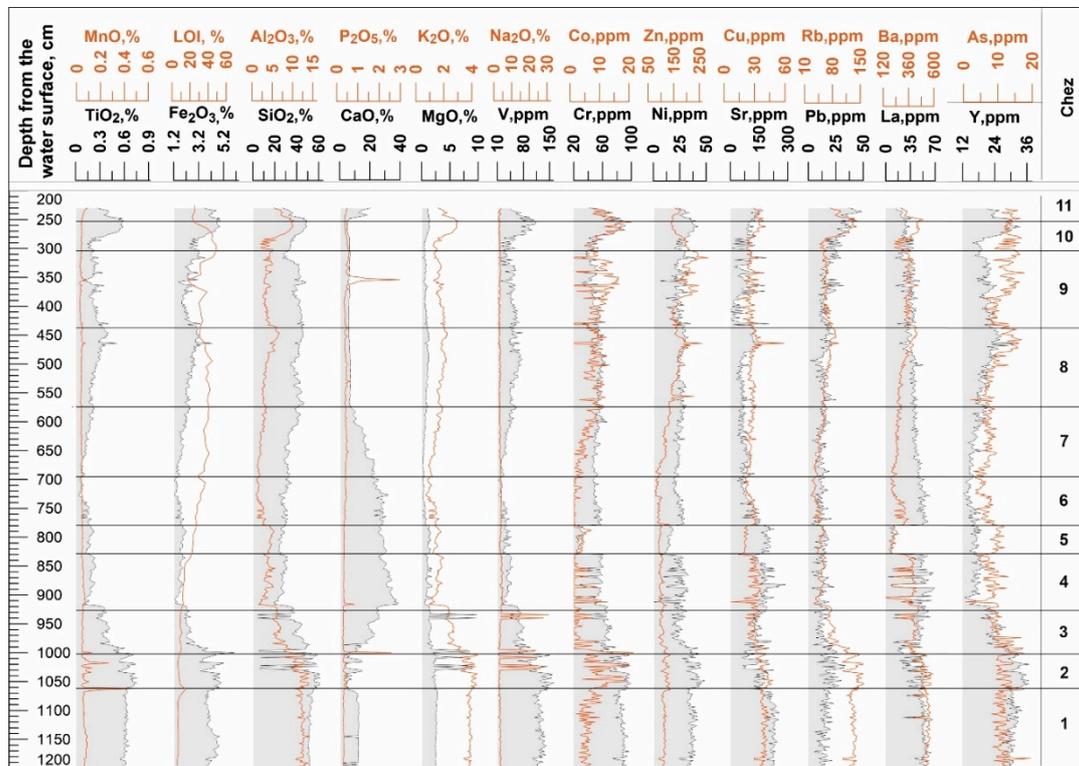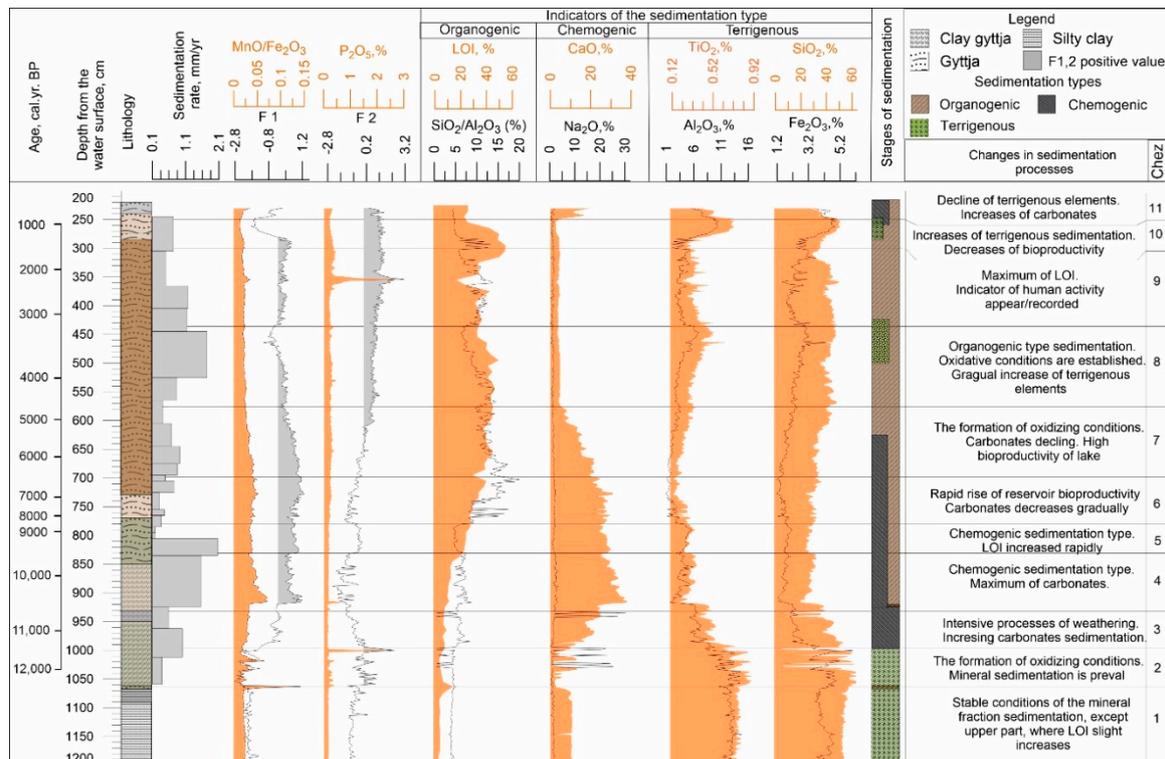

Figure 4. Results of the geochemical analysis.

Figure 5. The reconstruction of sedimentation changes.

The lowermost zone, Chez 1 (1199–1061 cm, 14,900–12,800 cal y BP [6]), exhibited fairly stable concentrations for most of the elements and oxides analyzed. Terrigenous and the so-called weathering elements in this zone, including SiO_2 (49–53%), Al_2O_3 (12.7–14.3%), K_2O (2.8–3.2%), and TiO_2 (0.7–0.8%), clearly predominated. The lowest part of the column of Chez 1 (1199–1061 cm) was represented by grey silty clay, while in the upper part of the zone, there was a thin layer of greenish-brown gyttja (1067–1061 cm). This interval was dominated by terrigenous-type sediments, which was confirmed by the LOI and F1 (Figure 3) of PCA. The lowest content of LOI (up to 4%) and SiO_2/Al_2O (up to 4%) indicate almost complete lack of productivity in the reservoir; diatoms were also not found in this part of the column [3,6]. However, some increase in productivity in the greenish-brown gyttja horizon occurred (1067–1061 cm), where the LOI reached 15%. The negative values of F2 indicate the predominance of oxic conditions. According to the age–depth model, the sedimentation in this interval took place during the Bølling–Allerød period, just after 15,000 cal y BP [6]. During this period, natural conditions were most likely uniform, contributing to a stable inflow of mineral fractions into the Kamyshovoye lake basin.

At the beginning of the zone Chez 2 (1061–1000 cm; 12,800–11,550 cal y BP), the geochemical record indicates a considerable variation in the content of almost all elements, and the culmination of most elements or oxides related to erosional processes and terrigenous material transportation. SiO_2 values increase by up to 61.5%, Al_2O_3 by up to 15.2%, K_2O by up to 3.5%, TiO_2 by up to 0.89%, and P_2O_5 by up to almost 0.4%. The rapidly decreased MnO/Fe_2O_3 ratio displays considerable variation throughout the zone, with a peak at the bottom of the interval, while the SiO_2/Al_2O_3 ratio remains similar to that of Chez 1. The sediments of Chez 2 are represented by silt and clay, enriched with terrigenous and clastic components (SiO_2, Al_2O_3, TiO_2, and Zr). The internal conditions of the lake at the end of the zone changed to a reducing environment, which led to an increase in elements such as Zn, Co, Pb, and Fe_2O_3, as well as a decreased MnO/Fe_2O_3 ratio and an increase in F2. Despite the minimal content of carbonates in this zone (i.e., the average values do not exceed 5%), short-term increases in the proportion of carbonates of up to 13% were observed at depths of 1036–1030 cm (12,160–12,000 cal y BP) and 1012–1017 cm (11,600–11,730 cal y BP). The age–depth model showed that this sedimentation could have occurred during Younger Dryas cold and dry conditions.

CaO concentrations decreased to 1.4% at the beginning of zone Chez-3 (1000–930 cm, 11,550–10,400 cal y BP). This chemical element is increased in the upper part of the zone by up to 26%. The other elements also demonstrated a continuous instability of the sedimentation regime. The amounts of TiO_2, SiO_2, Al_2O_3, and K_2O tended to decrease, while the contents of MgO, Zr, Rb, and Ba showed remarkable fluctuations. Fe_2O_3 started to decrease after a peak value of 5.6% at the very beginning of the zone; the LOI slightly increased and fluctuated between 7% and 10%, while the SiO_2/Al_2O_3 ratio increased more significantly. The age–depth scale and the contributing elements, as well as increasing F1 and decreasing F2, lead to the conclusion that the transition from the Late Glacial to the Holocene was characterized by a change in the type of sedimentation from terrigenous to chemogenic. This phenomenon has already been described in the region [2]. Nevertheless, this stage is characterized by the higher productivity of the reservoir and increased humidity of the climate compared with the previous period. However, the conditions are still not favorable for vegetation, and apparently, intensified humidity leads to more intensive denudation processes of the surrounding deposits (especially carbonate enriched moraines), which were dissolved and accumulated in lake sediments, forming carbonate gyttja.

At the onset of the Chez 4 zone (930–830 cm, 10,400–9700 cal y BP), a rapid drop in the so-called weathering-related elements and oxides occurred. After a noticeable decrease at the beginning of the zone, the amounts of Al_2O_3, SiO_2, K_2O, Zr, TiO_2, and Rb remained stable or demonstrated a slight increase as one moves upwards in the zone (930–830 cm), while MgO, Sr, Ba, As, Pb, Cu, and Na_2O still showed considerable fluctuations. CaO displayed the highest values from this zone. At the same time, a rapid increase was seen in the MnO/Fe_2O_3 ratio, LOI curve, F1, and SiO_2/Al_2O_3 ratio. The amount of P_2O_5 in the sediments stabilized and started to increase, though insignificantly. During this time, the sedimentation rate reached 1.5 mm/y, which is three times higher than in the

previous zone. During this time, there was an accumulation of carbonate greyish-brown clay gyttja and carbonate greenish-brown gyttja. The abovementioned sediment composition characterized the alkaline conditions in the lake, which persisted during their deposition and may have contributed to the formation of the carbonate-enriched gyttja.

Chez 5 (830–780 cm, 9700–8500 cal y BP) was characterized by the stabilization at a low level of terrigenous elements. The sharp reduction in Ni, Cu, Cr, Co, and Ba was also noteworthy. These changes were probably associated with a reduction of the reservoir oxic conditions. Deposits were characterized by a higher proportion of carbonates (up to 30%) and a slight increase in organic matter (up to 30%); however, the share of SiO_2/Al_2O_3 was reduced. At the depth of ~800 cm (9700–9500 cal y BP), the sedimentation rate reached its highest value (up to 2 mm/y); however, it dropped afterward.

In the uppermost part of the geochemical record, Chez 6 (780–695 cm, 8500–6400 cal y BP) displays a gradual decline in the Al_2O_3, TiO_2, Fe_2O_3, and MgO curves, while the levels of Cu and Ba recovered within this interval. The Ba curve at the beginning of the stage was high but later diminished. This zone was characterized by the high values of LOI (up to 45%) and SiO_2/Al_2O_3. Nevertheless, the carbonate content decreased from 28% at the beginning of the zone to 16% at the end of the zone; F2 also had a gradually increasing trend, which points to further reduction of the oxidizing conditions. Probably due to an increase of bioproduction, the elements associated with the mineral fraction were reduced to a minimum. This stage corresponds to the Atlantic period. Increasing temperatures contributed to the active growth of bioproductivity, resulting in a reduction in the oxygen in the water.

Chez 7 (695–575 cm, 6400–4500 cal y BP) was characterized by gradually increasing concentrations of terrigenous elements such as Al_2O_3, TiO_2, SiO_2, MgO, and K_2O, as well as increasing Co, Ba, Rb, and Pb. A rapid decline in CaO (from 20% to 5%) was observed. Gradually decreasing F1 confirmed that clastic and terrigenous components were increasing in comparison with carbonate components. The sedimentation in the middle of the zone increased, and the uniformly high proportion of organogenic parameters was distinguished by a decrease in chemogenic parameters.

In Chez 8 (575–437 cm, 4500–3200 cal y BP), the CaO concentration decreased by 4% and stayed stable, while LOI rose to 50% and MnO/Fe_2O_3 decreased to a minimum. A gradual increase in terrigenous elements such as Al_2O_3, TiO_2, SiO_2, MgO, and K_2O was observed. From about 3600 cal y BP, F1 reached negative values, which indicates a decrease in the degree of chemical weathering. Along with this process, there was an increase in the values of F2 and three groups of elements associated with a higher plant and detritus component, which is an indicator of the eutrophication of the reservoir. The productivity of the reservoir during this sedimentation stage was still high, but much lower in comparison with the previous one. The timing of this stage corresponds to the Subboreal period.

In Chez 9 (437–298 cm, 3200–1500 cal y BP), on average, the concentrations of Al_2O_3, TiO_2, SiO_2, K_2O, and MgO remained stable or demonstrated a slight decline throughout the rest of the zone, while Sr, Co, Ba, As, and Pb showed considerable fluctuations. In the middle of the zone (at about 2650 cal y BP, 361–364 cm), a remarkable peak of P_2O_5 occurred. Alongside that, a reduction in TiO_2, Fe_2O_3, and LOI and an increase in SiO_2, Zr, and Co were detected. An increase in the proportion of carbonate versus terrigenous matter (F1) and an increase in F2, even if the sedimentation rate is gradually decreasing, could be good indicators of intensified, humid climatic conditions.

Chez 10 (298–251 cm, 1500–800 cal y BP) was characterized by a rapid increase in mineral matter; however, the organic matter was reduced. A rapid increase in Al_2O_3, TiO_2, SiO_2, K_2O, MgO, Co, Cr, Pb, and Zn, LOI curves, and the decline in P_2O_5 indicate that minerogenic-type sedimentation had begun. This type of sedimentation was also confirmed by the F1 decrease.

Chez 11 (251–230 cm, 800 cal y BP to present) was characterized by a decline in Al_2O_3, TiO_2, SiO_2, K_2O, MgO, Co, and Cr. Together with the rapid increase in CaO, P_2O_5, and Pb curves, MnO/Fe_2O_3 was also observed. These changes suggest that this stage is characterized by quite sharp changes in the trophic conditions: LOI is reduced due to the higher oxygen concentration in the water, and the rate of sedimentation is decreased from 0.4 to 0.02 mm/year. Because of the quicker mineralization processes, minerogenic-type sedimentation was initiated. This stage corresponds to the Subatlantic period.

5. Discussion

5.1. Reconstruction of Sedimentation Processes

The geochemical analysis conducted, with statistical processing of the results obtained, alongside a detailed chronology, allowed us to determine the main stages of sedimentation and identify the natural conditions that caused them. Established genesis isolated basic types of sedimentation: terrigenous, chemogenic sediments, and organic-matter-containing sediments. Each of these types corresponds to certain environmental conditions that directly or indirectly affect the process of sedimentation. In the discussion, each of these types are considered separately, determining the time of predominance of each type; moreover, based on geochemical data and Late Glacial and Holocene history, a reconstruction of sedimentation processes is performed.

5.1.1. Terrigenous Deposits

We refer to mineral deposits as sediments represented by clay and silt, consisting of so-called terrigenous elements (SiO_2, Al_2O_3, K_2O, Fe_2O_3, Zr, and TiO_2), with a total content of organic matter and carbonates of no more than 10%. According to the data presented in the results, the terrigenous type of sedimentation was dominant in the Kamyshovoe Lake basin at depths of 1199–996 cm, from the moment of lake formation at ~15,000 up to 11,400 cal y BP. The sedimentation process in the lake began immediately after the retreat of the Last Scandinavian glacier. As a result of erosion processes, the terrigenous material deposited in the basin of the lake is clearly visible in the geochemical analysis data. Similar processes were also observed regionally in southern Lithuania [20] and northeastern Poland [21]. In addition, the mineral fraction in the lake increased during erosion of the slope as a result of the melting of dead ice [22,23]. There is also evidence of the development of aeolian processes during this period [24–26], but additional analyses are needed to determine whether aeolian processes are involved in the sedimentation of the Kamyshovoye Lake.

Local peaks of terrigenous elements (along with a high content of organic matter) were also observed in the Subboreal (500–425 cm; 3800–3100 cal y BP) and Subatlantic (285–245 cm; 1400–600 cal y BP) periods. The enrichment with mineral matter during these periods is associated with erosion and possibly aeolian processes, the driver of which was intensified human activity (see Section 5.2.).

5.1.2. Chemogenic Deposits

Chemogenic deposits prevailed during the period between 11,400 and 5200 cal y BP (996–607 cm). They are associated with an increase in the proportion of carbonates and a gradual increase in organic matter, along with a reduction in mineral (terrigenous) matter. An increase in the content of carbonates and their preservation in sediments might be connected with overall climate warming, increasing humidity, and the formation of alkaline conditions. An increase in the content of carbonates in bottom sediments in the Early Holocene was recorded in many parts of the Baltic region [2,27,28]. With the appearance of coniferous vegetation in the region, there was more intensive sedimentation of carbonates: the enhanced mobility of carbonates due to an acidic pH of the soils has been analyzed previously by Apolinarska et al. [29] and in north Lithuania by Gedminienė et al. [30]. Such geochemical condition changes affected the sedimentation rate: during this time, at about 9800 cal y BP, the sedimentation rate reached 1.5 mm/y.

In the upper part of the column (at about 252 cm, 850 cal y BP), there was another peak of carbonates where the concentration of CaO changed from 3% to 20%. Similar changes were also observed in the region during the Subatlantic period [28,31]. Such a sharp increase in carbonates may also be associated with the spread of coniferous species in the region [2] as a result of the more humid climate [31].

5.1.3. Increase in Organic Matter

A short-term increase in organic matter of up to 15% was observed in the greenish-brown gyttja (unit 3) horizon deposited between minerogenic sediments in the 1061–1067 cm sediment interval, during the final stage of the Allerød interstadial at about 13,200–12,750 cal y BP [6]. A similar horizon was found in the region [32–34] and beyond [1]. At the same time, some of the studied objects of the corresponding age did not have this horizon [20]. A distinctive feature of unit 3 is the increased content of organic matter, the alkaline condition (high MnO/Fe_2O_3 ratio), and the reduction in mineral matter. Similar changes in the elementary composition of bottom sediments were also observed in a geochemical analysis of Lieporiai palaeolake deposits [30]. Most likely, these changes can be associated with the increased bioproductivity in the lake as a result of warming (in the case of a shallow lake), as well as with the intensified organic matter intake from the catchment area.

The next stage of increasing the content of organic matter begins above 10,300 cal y BP. This clear trend coincides with the increase in the SiO_2/Al_2O_3 ratio, along with a reduction in the proportion of carbonates (from 40% to 9%). Climate warming and humidity contributed to the active increase in bioproductivity, resulting in a reduction in the proportion of oxygen in the water. From 5300 cal y BP, F2 showed a gradually increasing trend, which points to a further reduction in the oxidizing conditions in the lake. Higher values of phosphates indicate an increase in bioproductivity in the region's lakes [28]. It is noteworthy that, along with a high concentration of organic matter, the share of terrigenous elements had a gradually decreasing trend up to about 7000 cal y BP. A high proportion of organic matter leads to a decrease of the sedimentation rate of 0.2–0.3 mm/year 8900–7000 cal y BP. Similar changes were also observed in Poland [22] and Lithuania [30]. The maximum values of the organic matter content (50–60%) are marked in the upper part of the column 315–265 cm (1650–1300 cal y BP). The maximum values of organic matter during the Subatlantic period are also marked in the region [35].

5.2. Indicators of Anthropogenic Influence Inferred from Geochemical Data

Deforestation and agricultural development can have a profound effect on lake ecosystems, altering catchment hydrology and increasing erosion and nutrient loadings. Despite the low prehistoric anthropogenic pressure on the environment, and due to primitive agricultural practices, the effect of even a slight nutrient addition to an oligotrophic forest lake could have been considerable. Therefore, this type of lake can be especially sensitive to agricultural development [36] while recording the impact of anthropogenic processes in its sediments.

The SE Baltic region is an area with historical prerequisites for the rather early temperate-zone emergence of agriculture, probably since the middle–late Neolithic [6]. In the coastal part of the SE Baltic, the earliest presence of cereal pollen, mostly wheat, is recorded in sediments dated to ~5000–4500 cal y BP [37], while archaeological evidence of crop cultivation goes back to ~4400–4200 cal y BP [38]. In the Mazurian Lakes region, occurrences of *Secale cereale* are connected to the Subboreal period [39].

Regarding the Kamyshovoye geochemical record, some indicators of anthropogenic activity in the catchment area can be observed. Among the geochemical proxies studied, Ti is a conservative lithogenic element that participates in very few biogeochemical processes. Higher Ti concentrations in the sediment point to enhanced physical weathering of aluminosilicates in the catchment, which could be due to climatic changes or to erosion from land use [40]. Starting at ~6000 cal y BP, there was an increasing trend in the TiO_2 content, with more rapid growth from ~3800 cal y BP and a clear peak at ~3500 cal y BP, coinciding with the highest sedimentation rate (0.4 mm/year) throughout the entire Middle and Late Holocene. This sign of increased erosion corresponds to the appearance of cultivated cereal (*Secale cereale*) pollen in the sediment record of Lake Chistoe (situated 1.5 km NE of Kamyshovoye) ~4700–3500 cal y BP [41], indicating Neolithic agricultural activities, which created more open, deforested areas. The second peak of the TiO_2 content is dated to ~1330–1200 cal y BP, in the late Iron Age to the early medieval period in the region, when deforestation process intensified,

as is seen from the Chistoe Lake pollen data, demonstrating the decreasing values of trees and the rise in percentage of herbs and *Isoetes* spores in the pollen spectrum [41].

The sharp increase in P_2O_5 content that occurred at about ~2650 cal y BP has very unusual leading elements. Usually, it can be connected with increased organic matter in wash into the basin and the increased bioproduction and content of nutrients in the lake. However, here LOI did not increase but actually dropped. In addition, significantly higher concentrations of terrigenous matter were observed. Nevertheless, together with these changes, the small increase in MnO/Fe_2O_3 ratios points to higher oxygen concentrations or even a lower water table during that time. Usually, oxygen changes can cause: (1) an increase in bioproduction, with a leading increase in sedimentation and/or (2) a decrease in sedimentation, when active mineralization processes are stronger than the biomass productivity. We see in our data the highest P_2O_5 content but a decrease in bioproduction. Sometimes, under certain sedimentation conditions, if there is enough phosphorus in the lake system, vivianite forms. Very calm sedimentation conditions usually lead to higher clay particle sedimentation, which covers soft sediments and preserves them for further diagenesis processes. Such diagenesis processes have previously been discussed in the context of Lake Ørn, Denmark [42]. However, this phenomenon could also be interpreted as a sign of anthropogenic activity as, in a lake catchment, detrital organic matter and nutrient inflows due to animal dung and fertilizers may produce an excessive load of nitrogen (N) and phosphorus (P) and induce an increase in lake primary productivity [36]. However, to support this conclusion, further investigation, including NPP study and in particular, identification of coprophilous fungal spores (grazing indicators [43]), is required. An extra concern about the anthropogenic origin of the high amount of P_2O_5 at a depth of 360–350 cm is related to the several signals of possible environmental change occurring at that time. Thus, the Kamyshovoe diatom data show a decreasing curve of planktonic groups and a growing number of periphytic diatoms, indicating a lowering of the water table in the lake. Species characteristic of running water almost disappeared, confirming that the lake did not have any significant water and nutrient inflow from the surroundings. The greater variety of epiphytic species (*Staurosira brevistriata*, *Achnanthes exiguum*, and *Platessa holsatica*) indicates that the lake became shallower, with water plants spread in the littoral zone [44]. The shallowing of the reservoir is also evidenced by a simultaneous decrease in K_2O. It is interesting to note that the Kamyshovoe Lake ecosystem had a simultaneous reaction to the 8.2 ka event, which was expressed in a relatively short-term shallowing of the lake, followed by peaks in the SiO_2/TiO_2 ratio, sharp variations in the Rb/Zr and CaO/Zr ratios, and an increase in P_2O_5 [45]. The changes in environmental parameters noted at depths of ~370–330 cm could be a response to a 2.8 ka climate event; further detailed study will aim to verify this conclusion.

6. Conclusions

This geochemical survey has provided an evaluation of sedimentation processes from the initial stage of the Kamyshovoye Lake formation onwards. The following outcomes were obtained.

At the beginning of sedimentation, the terrigenous component prevailed (~15,000–11,400 cal y BP), while by the end of the Alleröd (~13,200–12,750 cal y BP), the share of organic matter had increased. Geochemical indicators showed the intensity of organic matter intake from the catchment area.

During the Younger Dryas (12,750–11,750 cal y BP), minerogenic matter sedimentation dominated and oxidizing conditions prevailed. According to the geochemical indicators, cool and dry conditions, together with the opening of the vegetation and poorer soil cover, increased the mineral fractions' transport into the basin, pointing to intensified aeolian processes.

The transition from the Late Glacial to the Holocene (11,750–11,400 cal y BP) is characterized by a change in the type of sedimentation from minerogenic to chemogenic. Intensive denudation processes of surrounding deposits contributed to carbonate matter transportation to the lake, forming carbonate gyttja. This process was especially intense during the Boreal period (10,400–9800 cal y BP), characterized by increased sedimentation.

The high bioproductivity and organogenic sedimentation, typical for the period of 7900–6400 cal y BP, was probably related to the warm and wet climate conditions of the Atlantic period. Since 6400 cal y BP, a decrease in the rate of chemical weathering has been seen. Along with this process, there was an increase in detritus-associated components of organomineral complexes, which can point to eutrophication of the reservoir.

The upper part of the Kamyshovoye sediments reflected sharp changes in the proportions of organic and mineral sediment fractions. This corresponds with the timing of the Subboreal and Subatlantic periods (after 5300 cal y BP), containing geochemical indicators of ancient anthropogenic activity that are related to prehistoric agriculture in the Kamyshovoye Lake catchment and probably to the early medieval deforestation of the territory.

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