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Metals in Lake Sediments as Indicators of Human Activities in Prehistory: Case Study of the Southeastern Baltic, Kamyshovoe Lake

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Abstract: This paper presents the results of geochemical research on the Kamyshovoe Lake sediments (Kaliningrad oblast, Russian Federation). The study of Pb, Ni, Zn, As, Co and Cu concentration and enrichment factors (EF) combined with the results of the lithological, geochronological, magnetic susceptibility and microcharcoal studies revealed possible anthropogenic sources of metals in southeastern Baltic lake sediments from the Neolithic to the Medieval period. Increasing Co EF value and peaks of the Pb EF in Kamyshovoe Lake sediments, starting from ~6000 cal yr BP in the Neolithic, probably show the growing role and usage of metals as dyes and fixatives. Since ~3100 cal yr BP, in the end of the Bronze Age, a simultaneous increase in the content of indicators of metallurgical production Pb, Ni, Zn and As, coinciding with growth of the microcharcoal curve, can show a growing demand for metal objects in the southeastern Baltic region and the input of the local or regional ancient metallurgy into the metal pollution of the lake sediments.

Keywords: metals; lake sediments; prehistory; ancient dyes and fixatives; ancient metallurgy; pollution history; lead; geochemistry; archaeology; southeastern Baltic

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1. Introduction

Presence of metals in human life dates back to Palaeolithic times, when metals were used for ritual purposes and as mineral colourants. And since then, up until modern times, metals have been present in human life in the form of dyes and fixatives (Cu, Fe, Pb, Co, As) and metal objects, etc. [1,2]. The appearance of metallurgy in the Neolithic–Bronze Age period brought crucial changes in prehistoric life. Simultaneously, ancient metallurgy as a new essential activity started to play a role in transforming the landscapes, causing metal pollution due to mining, smelting and working, and deforestation due to demand for wood and charcoal [3].

While studies seem to focus on the objects made of metal, their aesthetics and social function, the level of knowledge about the environmental impact of ancient metal mining and metalworking is very limited [3]. The palaeoecological aspects about pre-metallurgical use of metals seems to be unknown, though from the early days of extensive metal smelting onwards, evidence of the impact of metallurgy on atmospheric chemistry is present, as it is reflected in the Greenland ice cores, European lake sediments and in peatbogs [4,5]. Despite that, the scale and directions of the atmospheric metal dispersal remain disputable as does the impact of ancient metallurgy on surface runoff and groundwater [3,6].

Numerous studies testify that lake sediments are very sensitive indicators of the geochemical processes occurring in the lake and in the catchment area [3,7–10]. Of particular value are lake deposits, which have a continuous succession throughout the Holocene and allow for tracing possible anthropogenic influence on the landscapes at all stages of society development. One of such lakes is Kamyshovoe Lake considered in this study. To date, lake sediment research has provided numerous and diverse data that are shedding light on the various aspects of environmental dynamics, including the ancient anthropogenic impact. The previous research of Kamyshovoe Lake revealed both environmental and anthropogenic processes that affected the geochemical composition of the sediment sequence [8–10]. The study showed an increase in the concentration of heavy metals (Zn, V, Cr, Pb) from depths corresponding to the end of the Neolithic [9]. The simultaneous increase in the microcharcoal value and rate of erosion reflected the intensification of human activities surrounding the lake [9]. The aim of the present paper is to consider the elevated values of heavy metals in the Kamyshovoe Lake sediments in the context of possible regional and local anthropogenic activities, which could be sources of the metal input in the lake during the Neolithic–Medieval period.

2. Methods

2.1. Fieldwork and Sampling, Geographical Background

Kamyshovoe Lake (N 54°22′; E 22°42′) occupies an area of 0.32 km^2, is 850 m long and 570 m wide, and is shallow with a maximum depth of 4.5 m. It is located on the terminal moraine ridge formed during the retreat of the ice-sheet associated with the Baltija stage of Weichselian (Vistulian) glaciation. The Quaternary deposits forming the relief are mosaic, with a thickness of around 200 m: glaciofluvial sand, gravel interlayers, boulder loam (till).

At the present time, the area surrounding the lake is forested and not used for agricultural purposes. Archaeological data, however, provides evidence that the landscapes surrounding the lake were settled and exploited by humans during all historical periods (Figure 1), starting from the late Palaeolithic, while the anthropogenic impact on the environment reflected in the lake sediments becomes visible from the end of Mesolithic [9].

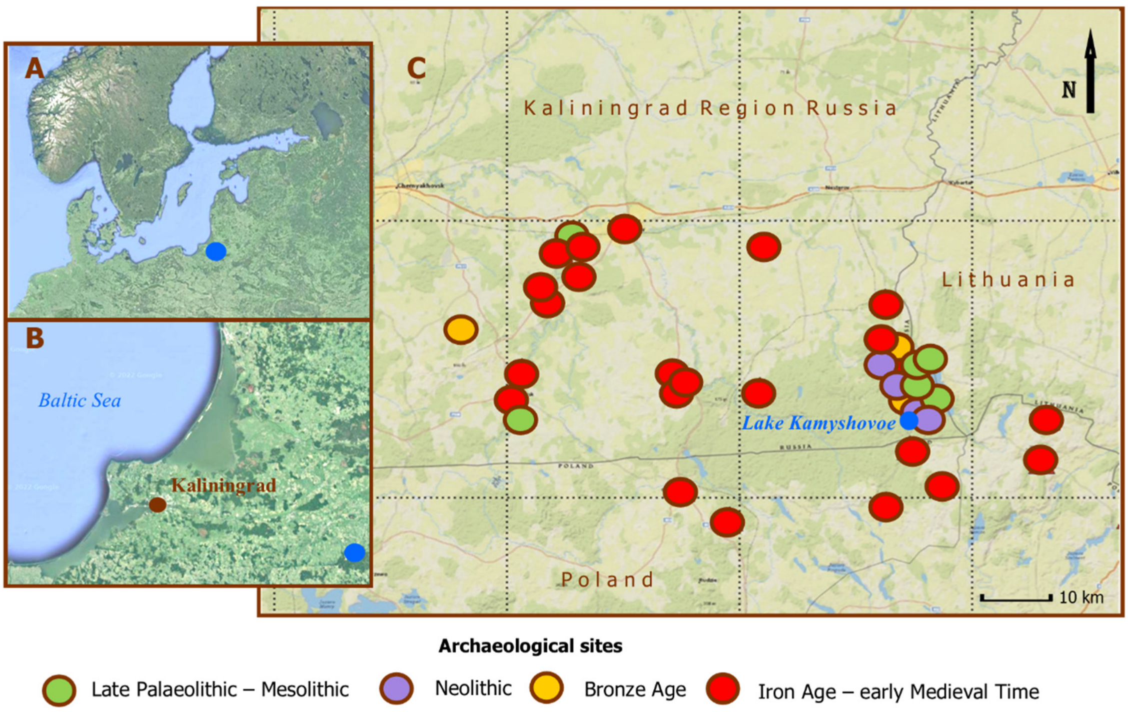


Figure 1. (**A**)—Location of the studied site on the map of Europe. (**B**)—Location of Kamyshovoe Lake in the Kaliningrad region. (**C**)—Archaeological sites of different periods in the vicinity of the lake.

A 9.8 m long core of bottom sediments was obtained from the ice surface using a Russian peat corer (100 cm long chamber; diameter 7 cm). Detailed results for the entire sediment section (1199–230 cm) and its palaeoenvironmental and possible anthropogenic impact interpretation were presented in [8,9]. The recent study is limited to the interval

730–245 cm, coinciding with Neolithic–Medieval period, the time when human activities related to use of metals would be expected to have intensified.

2.2. Geochronological and Lithological Analysis

Sediments were described based on the visual and physical description of the composition and colour of bottom sediments [10]. Thirteen radiocarbon analyses were performed for bulk gyttja for the section analysed in this paper (730–245 cm). From the data obtained, an age–depth relationship using linear interpolation was calculated. Using radioactive carbon (^{14}C), the absolute age of the sediments was determined at the Laboratory of Geochronology, St. Petersburg State University, Russia (laboratory index LU). OxCal v 4.2.4 was used for calibrating the dates [11].

2.3. XRF Geochemical Analysis, Magnetic Susceptibility (MS) Measurements and Microcharcoal Concentration

The geochemical analysis was performed for 1 cm intervals. The samples were dried at 105 °C until the moisture evaporated completely and were then powdered in a mortar. Tablets for geochemical analysis were prepared using boric acid as a base and a laboratory press (pressure 110 bar). A SPECTROSCAN MAKC-GV X-ray fluorescence spectrometer at Herzen State Pedagogical University of Russia, St. Petersburg, was used to perform the analysis. Accuracy of the spectrometer was tested by analysing over 50 certified international standard reference samples (CRMs). 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 % [10]. In the recent study, only the data on Cu, Ni, Pb, Zn, Co, As and TiO_2 were used for interpretation. TiO_2/Al_2O_3 and MnO/Fe_2O_3, as indicative of the mafic rocks and redox conditions, were also considered in the present study. The total number of samples used for the XRF geochemical analysis was 250: n = 250, Medieval period n = 26, Iron Age n = 44, Bronze Age n = 77, Neolithic n = 87, Mesolithic n = 16.

Magnetic susceptibility analysis was applied for 2 cm intervals. The analysis was performed at the Palaeomagnetic Laboratory, Nature Research Centre, Vilnius, Lithuania, using the standard MFK1-B kappa bridge (AGICO) static specimen method with a manual holder. The data obtained were analysed using SAFYR software (Safyr Metadata Discovery Software for Enterprise Application Packages. Silwood Technology Ltd., Ascot Berkshire, UK), and MS values were expressed in SI units (10^{-9} m^3 kg^{-1}) [8]. The number of samples used for the MS analysis totalled 83: Medieval period n = 8, Iron Age n = 15, Bronze Age n = 26, Neolithic n = 28, Mesolithic n = 6.

Microscopic charred particles with a longer axis of 10–25 µm [12] were counted on the prepared slides in during pollen analysis [9]. The percentage of charred particles was calculated in relation to the total pollen sum (ΣSUM = ΣP + ΣC). Microscopic charcoal particles were counted within a 230–700 cm sediment range. The total number of samples used for the microcharcoal concentration analysis was 137: Medieval period n = 9, Iron Age n = 22, Bronze Age n = 51, Neolithic n = 53, Mesolithic n = 2.

2.4. Enrichment Factors (EF)

Element concentrations can be influenced by the amount and intensity of mineral matter transported from the catchment into the lake. This is clearly observed in the late Pleistocene part of the Kamyshovoe sediment sequence. Here, the concentrations of all metals are generally higher due to more intensive weathering and erosion processes in the vicinity of the lake with unstabilised soils [8] and due to lower organic matter (either allochthonous or autochthonous) concentrations.

To minimise a possible influence of erosional input, metal concentrations were normalised to Ti, which is a conservative element and a good tracer of minerogenic inputs in lakes [13]. Counting was done according to the formula proposed by [13]:

$$XEF = (X/Ti)sample/(X/Ti)bkg$$

where X is element, EF—enrichment factor and bkg—mean relative background values calculated for the depth of 730 cm. This depth is chosen considering lithology: while downwards in the sequence we observe the alternation of sediment types formed by terrigenous and, to a lesser extent, chemogenic processes, here starts the deposition of organogenic gyttja comprising the upper 5 m of the core, nearly to the top, formed in more stable environmental conditions of the Middle and Late Holocene. The depth of 730 cm also coincides with the end of the Mesolithic, a period when the anthropogenic impact related to metal pollution is still expected to be minimal, while it can be increasing upwards in the sediment sequence during the later historical periods.

2.5. Statistical Analysis

Spearman rank R correlation coefficients between the content of trace metal, TiO_2/Al_2O_3 and MnO/Fe_2O_3, MS and microcharcoal were calculated by Statistica software (StatSoft. Inc., Hamburg, Germany (2007). STATISTICA (Data Analysis Software System), version 8.0.). Calculation was done for the entire section using 250 samples (valid n) for all elements and 25 samples (valid n) for microcharcoal data. Significance levels (*p*-values) for the correlations were calculated as well. Significant ($p < 0.05$) Spearman correlation coefficients are marked.

3. Results

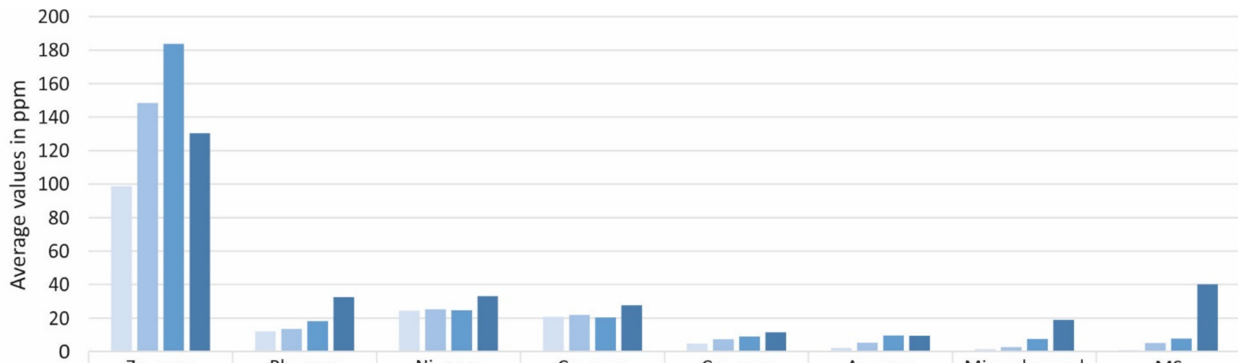
3.1. Lithology and Geochronology

Analysis of lithological composition and geochronological modelling revealed the following lithological units: dark brown gyttja (730–270 cm), light brown gyttja (270–247 cm), and gray gyttja (247–240 cm). The analysed interval comprised four historical periods from the Neolithic to the Medieval period.

3.2. Geochemistry, Magnetic Susceptibility and Microcharcoal Concentration

In this study, the focus was on a selected group of elements (Cu, Pb, Zn, Co, As, Ni), which could be tracers of various human activities related to metal use in daily life or tracers of ancient metal smelting. Meanwhile, the detailed description of the full geochemical composition and its palaeoenvironmental and possible anthropogenic impact interpretation was presented in previous articles [8–10].

The average and maximum values of Cu, Zn, Pb, As, Co and Ni in ppm, compared with average values of MS and microcharcoal percentage against the historical periods, are presented in Figures 2 and 3 (Table S1).



	Zn, ppm	Pb, ppm	Ni, ppm	Cu, ppm	Co, ppm	As, ppm	Microcharcoal	MS
Av Neolithic	98.69 (n = 87)	12.085 (n = 87)	24.46 (n = 87)	20.76 (n = 87)	4.86 (n = 87)	2.19 (n = 87)	1.5 (n = 53)	0.91 (n = 28)
Av Bronze age	148.55 (n = 77)	13.63 (n = 77)	25.18 (n = 77)	21.97 (n = 77)	7.48 (n = 77)	5.31 (n = 77)	2.6 (n = 51)	5.11 (n = 26)
Av Iron age	183.76 (n = 44)	18.22 (n = 44)	24.68 (n = 44)	20.49 (n = 44)	9.14 (n = 44)	9.59 (n = 44)	7.6 (n = 22)	7.71 (n = 15)
Av Medieval	130.43 (n = 26)	32.46 (n = 26)	33.13 (n = 26)	27.78 (n = 26)	11.63 (n = 26)	9.39 (n = 26)	18.98 (n = 9)	40.25 (n = 8)

Figure 2. The average values of element concentrations in the Kamyshovoe Lake sediments according to historical period.

	Zn, ppm	Pb, ppm	Ni, ppm	Cu, ppm	Co, ppm	As, ppm	Microcharcoal	MS
Max Neolithic	203.23 (n = 87)	23.18 (n = 87)	30.80 (n = 87)	26.46 (n = 87)	10.48 (n = 87)	9.88 (n = 87)	3.1 (n = 53)	3.08 (n = 28)
Max Bronze age	229.11 (n = 77)	25.78 (n = 77)	46.22 (n = 77)	55.57 (n = 77)	15.51 (n = 77)	15.31 (n = 77)	5 (n = 51)	9.95 (n = 26)
Max Iron age	259.52 (n = 44)	29.94 (n = 44)	39.2 (n = 44)	31.96 (n = 44)	15.3 (n = 44)	16.7 (n = 44)	19.2 (n = 22)	21.78 (n = 15)
Max Medieval	157.16 (n = 26)	44.84 (n = 26)	42.06 (n = 26)	36.23 (n = 26)	19.38 (n = 26)	14.76 (n = 26)	23.2 (n = 9)	58.24 (n = 8)

Figure 3. The maximum values of element concentrations in the Kamyshovoe Lake sediments according to historical period.

The results showed that the geochemical elements under consideration do not follow a uniform trend from the Neolithic to the early Medieval period, though the concentrations of almost all the elements show increased values towards the upper part of the core. The average values of most of the elements together with microcharcoal and MS reached a maximum during the Medieval period. The exception was Zn, which had a clear peak during the Iron Age, and As with nearly the same concentration during the Iron Age and the Middle Ages. The values of such elements as Pb, Co and As in the Iron Age and the Medieval period became 2–3 times higher than in Neolithic, while concentration of Cu and Ni grew smoothly.

Regarding the highest concentrations throughout the historical periods, the pattern was slightly different. While maximum value trends of Pb, Zn, Co and As coincided with those of average values, Ni and Cu reached the maximum concentration not in the Medieval period but during the Bronze Age.

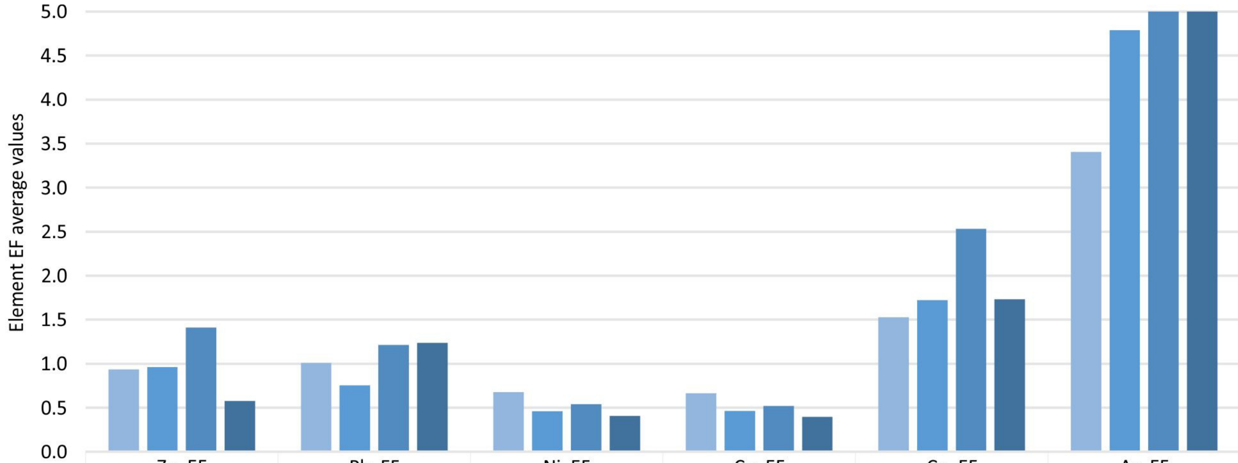
TiO_2/Al_2O_3 ratio reflected the mild intensity of weathering during the period studied (Figure S1). Compared to the lower part of the sediment profile [9,10], increased TiO_2/Al_2O_3 ratio showed that weathering indicated at the depth 730–245 cm was minimal; however, it increased a few times at about 3640–3150 cal yr BP and from 1950 cal yr BP with short, less intensive weathering events at the end of the Iron Age and beginning of the Medieval period. TiO_2/Al_2O_3 value varied between about 0.06 (more intense weathering) and 0.1 (minimal weathering).

The recorded low MnO/Fe_2O_3 ratio allows speculation about anoxic conditions throughout the interval. The decreased MnO/Fe_2O_3 ratio point to the hypothesis that the internal conditions of the lake, especially at the end of sedimentation, gradually changed to a reducing environment, which most probably led to increased precipitation of some trace metal such as Co and Pb and, especially, As [10]. MnO/Fe_2O_3 ratio varied between about 0.01 to 0.05 (Figure S1).

The highest MS and microcharcoal concentrations were observed during the Medieval period and had several high peaks during the Iron Age. On average, it increased almost 12 times for microcharcoal and almost 40 times for MS in comparison to the values observed in the Neolithic and Medieval period.

3.3. EF and Background Values

The results demonstrated different trends of average EF values for elements under consideration (Figures 4 and 5; Tables S2 and S3). Co, As and Zn showed the tendency to increase from the Neolithic (1.53, 3.40 and 0.93) to the Iron Age, when they reached their highest values (2.53, 10.93 and 1.41, respectively). Cu and Ni demonstrated a similar fluctuating trend: their values decreased from the Neolithic to the Bronze Age (from 0.67 and 0.68 to 0.46 for both elements) with some rise during the Iron Age (0.52 and 0.54). The average EF of Pb generally increased from the Neolithic to the Medieval period (from 1.01 to 1.24) with some drop during the Bronze Age (0.75). Average EF of all elements except Pb decreased during the Medieval period.



	Zn, EF	Pb, EF	Ni, EF	Cu, EF	Co, EF	As, EF
Av Neolithic	0.93 (n = 87)	1.01 (n = 87)	0.68 (n = 87)	0.67 (n = 87)	1.53 (n = 87)	3.40 (n = 87)
Av Bronze age	0.96 (n = 77)	0.75 (n = 77)	0.46 (n = 77)	0.46 (n = 77)	1.72 (n = 77)	4.79 (n = 77)
Av Iron Age	1.41 (n = 44)	1.21 (n = 44)	0.54 (n = 44)	0.52 (n = 44)	2.53 (n = 44)	10.93 (n = 44)
Av Medieval	0.58 (n = 26)	1.24 (n = 26)	0.41 (n = 26)	0.40 (n = 26)	1.73 (n = 26)	6.17 (n = 26)

Figure 4. The average values of element enrichment factors (EF) in the Kamyshovoe Lake sediments according to historical period.

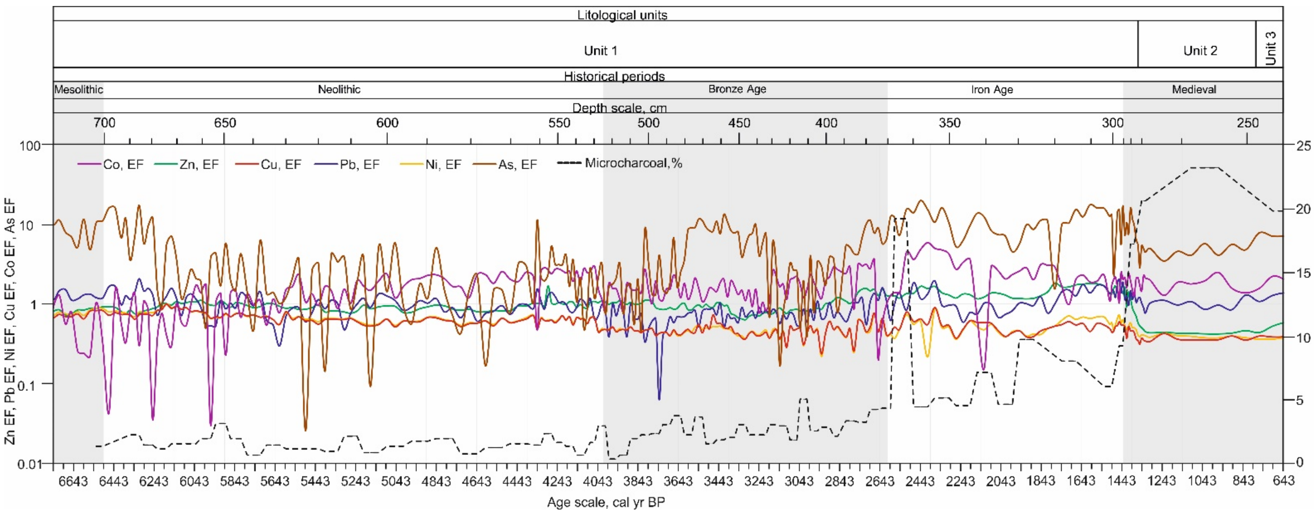


Figure 5. Co, Ni, Zn, Pb, As and Cu enrichment factors (EF) and the microcharcoal concentration in the Kamyshovoe Lake sediments. Modelled age (linear interpolation), cal yr BP.

The study showed that the EF of Co (5.88), As (19.91), Zn (1.81) and Fe (1.33) had a clearly expressed maximum during the Iron Age, while Cu, Ni and Pb did not display similar sharp fluctuations during the entire study period.

3.4. Statistical Analysis

Statistical results are presented in Table 1 and Figures S2 and S3. The highest positive correlation is seen between microcharcoal and TiO2, Co, Ni, MS; TiO_2 and Co, Ni; Co and MS; Ni and Cu; Cu and As, etc. The highest negative correlation coefficients are between Zn, MS and microcharcoal. We observe no correlation between, e.g., microcharcoal and As; Co and Pb, TiO_2 and Zn. TiO_2/Al_2O_3 ratio has the highest positive correlation with Pb (also Ni, Cu and Zn), showing that it precipitates more when weathering is less intensive; however, Co precipitation is higher when weathering is more intense. The same tendency is shown by the high negative correlation with MS, proving that the higher MS values can predict weathering intensity. MnO/Fe_2O_3 ratio has a positive correlation only with Zn and Pb. These two elements most probably precipitate in more oxic conditions and other elements, e.g., Co, Ni and As, precipitate in redox conditions.

Table 1. Spearman rank order correlations (MD pairwise deleted) of trace metal concentrations, TiO_2/Al_2O_3 and MnO/Fe_2O_3, MS and charcoal. Marked in **red** are correlations significant at $p < 0.05$.

	Microcharcoal,%	TiO_2,%	Co, ppm	Ni, ppm	Cu, ppm	Zn, ppm	Pb, ppm	As, ppm	MS, 10^{-9} m^3/kg	TiO_2/Al_2O_3	MnO/Fe_2O_3
Microcharcoal, %	1.00	0.76	0.79	0.66	0.39	−0.84	−0.53	−0.09	0.89	0.04	−0.95
TiO_2,%	0.76	1.00	0.65	0.60	0.45	−0.07	0.26	0.24	0.66	0.19	−0.6
Co, ppm	0.79	0.65	1.00	0.41	0.09	−0.28	−0.05	0.10	0.82	−0.35	−0.53
Ni, ppm	0.66	0.60	0.41	1.00	0.84	0.50	0.61	0.32	0.73	0.56	−0.18
Cu, ppm	0.39	0.45	0.09	0.84	1.00	0.56	0.53	0.60	0.56	0.67	−0.12
Zn, ppm	−0.84	−0.07	−0.28	0.50	0.56	1.00	0.84	−0.05	−0.98	0.68	0.63
Pb, ppm	−0.53	0.26	−0.05	0.61	0.53	0.84	1.00	−0.23	−0.18	0.72	0.52
As, ppm	−0.09	0.24	0.10	0.32	0.60	−0.05	−0.23	1.00	−0.20	0.23	−0.43
MS, 10^{-9} m^3/kg	0.89	0.66	0.82	0.73	0.56	−0.98	−0.18	−0.20	1.00	−0.69	−0.82

4. Discussion

The previous study shows that human activity in the Kamyshovoe Lake surroundings grew, starting from ~6500 cal BP [9]. This process is reflected not only in archaeological data, but in the simultaneous start of the microcharcoal curve, increased level of soil erosion and in the pollen record of plants-indicators of human activity [9]. The increased anthropogenic input is also confirmed by geochemical indicators. From the Neolithic onwards, the concentration of elements such as Co, Zn and As increased. The same trend can be seen in the dynamics of enrichment factors against the background of minimised contribution of erosion. As the present study shows, the EF of Co, Zn and As increase from the Neolithic and have maximum values in the Iron Age. It should be emphasised that the Iron Age is the period when all the elements in consideration have the highest values of the EF (such as Co, As and Zn) or increased values compared to the previous period (Pb, Cu and Ni). Apparently, the decrease in values observed later, in the Middle Ages, is related to local historical events that took place in the Vyshtynets Upland. After the conquest and devastation of this region by the Teutonic Order, the landscapes surrounding the lake were transformed for several centuries into 'wild lands' not involved in any economic activities.

The possible sources of the anthropogenic metal input into Kamyshovoe Lake over the last six millennia are considered further.

4.1. Use of Metals in Prehistory

Long before the mass use of metals for the production of metal objects and the emergence of 'classical' metallurgy, the use of metals in the form of minerals has its roots in the Palaeolithic, where burials accompanied with finds of mineral dyes are known. Probably just as ancient is the use of mineral dyes in 'cosmetics' for ancient rituals and ceremonies [2].

Before the emergence of metallurgy, metals could also be used by people in two other important spheres of life, such as fixatives for organic dyes in the production of textiles (and possibly as dyes themselves) and in colouring and decorating ceramics. The most commonly used dyes in prehistory were Cu, Fe, Pb, Co and As [1,2]. The data regarding the oldest regional textile production are provided by Polish archaeologists [14]. The first evidence for fibre and textile production appeared around 7450 cal yr BP (5500 BC) in southeastern Poland, and during the next two millennia the agricultural societies became well established and increasingly sophisticated. The Bronocice settlement (southern Poland) dated to 5650–4850 cal yr BP (3700–2900 BC) is an example of economically and technologically well-developed centre of fibre and cloth production, increasing in scale during the life of the settlement [14].

Archaeological data testify that new ways of settling and an economy with stationary settlements, which were also established in the Neolithic in the northern Poland [15] and Kaliningrad region [9], led to a growth of population in this part of the southeastern Baltic. It can be assumed that the gradual increase in population, accompanied by an increase in the production of daily-use items such as clothing, utensils and other household articles, could result in growing demand for metals as mineral dyes and colourants or fixatives for woodwork, leather production, textiles and pottery. Mineral dyes were certainly the subject of the oldest trade and exchange systems that already existed in prehistory [16]. In this context, it seems plausible that increasing from the Neolithic onwards Co EF and peaks of the Pb EF at about 6400–5700, 5100 and 4300–4200 cal yr BP in Kamyshovoe Lake sediments probably reflect the growing role and usage of metals in Neolithic society on local or regional scale (Figures 4 and 5).

At the same time, the idea of tracing the anthropogenic input of the most commonly and widely used mineral dyes such as Cu and Fe seems to be a challenging task. Owing to the strong affinity of Cu for complexation with organic ligands, the Cu value is strongly dependent on the influx of organic matter into the lake and autochthonous geochemical processes [13], while iron ores ($nFe_2O_3 + nH_2O$) are formed in the lakes and bogs themselves. Therefore, archaeological but not palaeolimnological data remain so far the only rigid evidence regarding usage of Cu and Fe in the life of prehistoric people. High values of As EF in the beginning of the Neolithic, before the expected growing usage of metals, shows that the dynamic of this element should be interpreted with caution as well, because As is a highly redox-sensitive element and its dynamics can also be related to autochtonic oxic/redox condition changes in the lake. However, the elevated values of As EF in later periods, when correlated with other metals, give more basis to connect it with the start of metal smelting in the region.

4.2. Metallurgy as a Source of Anthropogenic Input of Metals in the Lakes

Following the emergence of metallurgy—metal ore mining, metal smelting and production of metal objects—a new source of anthropogenic input of metals in the lakes occurred. While individual archaeological bronze artefacts found in Serbia, dating back to ~7300–6550 cal yr BP (5350–4600 BC), revealed the earliest evidence for copper smelting in Europe [17], since the late Neolithic–early Bronze Age numerous copper and polymetallic copper-bearing deposits in Europe had already been exploited [18,19]. The earliest impact of metal production on lake sediments is recorded in layers dated to 5750 cal yr BP (3800 BC) [13].

It is hypothesised that the emergence of metallurgy is closely related to the development of the production of ceramics [20,21]. The production of ceramics in the pottery kiln and usage of metals as colourants and glazes could lead to the inadvertent discovery of new qualities of metals and their melting properties. Though recent studies in the Balkans show that probably these two processes appear as related technologies and not as one being the precursor to the other [21], it is still in line with the view that people obtained their experience of metal working far before the Bronze Age. In the Eneolithic, which is interpreted by many researchers as a transitional stage from the Neolithic to the Bronze Age, metal products played an increasing role in the life of people, and a transition from a ritual meaning and an attribute of power to a more utilitarian use of objects took place [20,22].

According to studies [16,23], during the Bronze Age in Europe there was already a dynamic exchange and trade in raw metals, semifinished and finished products made from bronze and other alloys. Ling et al. [23] came to the conclusion that there were two routes for metal supply: the 'Atlantic' (western maritime route) and the continental route, 'repeating' the one for amber. During this period, the southeastern Baltic was situated at the crossroads between different centres of trade and exchange, but mainly between those located in Scandinavia and Central Europe [16].

The significance and scale of the production of bronze products during this period is evidenced by the excavation of the oldest among the currently known settlements of metallurgists in Central Europe, Szczepidło (Poland) [24]. The settlement dates back to 3300–3100 cal yr BP (1350–1150 BC). As semifinished and finished products, production waste, fragments of crucibles and casting ladles with traces of usage, and tools were found, the archaeological finds represent markers of the whole production cycle [25].

Besides metallurgy, the settlers of Szczepidło had a wide range of activities. Evidence for the production of wood for fuel and for building purposes were found, so too for pottery, clothing and agricultural practices and cattle breeding [24]. Approximately from this time, ~3100 cal yr BP, a major simultaneous increase in the content of metals—indicators of metallurgical production (Pb, Ni, Zn, As)—starts to emerge in the Kamyshovoe Lake sediments as well. This probably reflects the general picture of growing demand for metals in the southeastern Baltic. The observed trend continues during the entire Iron Age until a drop during the Migration Period.

Despite the fact that no metal production locations in the lake surroundings have been found, archaeological sites dated from the Bronze Age to the Middle Ages, as well as archaeological finds of bronze and iron items are numerous in this area and in the broader Kaliningrad region. Archaeometallurgical analysis has been applied on two of those finds, a Bronze Age hoard from the Svetly site (six items) and an early Roman neck ring from Kalinovo site.

The bronze hoard from the Svetly site was studied by means of energy dispersive X-ray fluorescence analysis. The studied samples contain significant concentrations of Ag (up to 0.61%), Ni (up to 0.74%), As (up to 1.4%), Sn (up to 15.6%) and Pb (up to 7.1%), classifying the objects as dilute fahlore copper with nickel, which is common in Central Europe in the Middle and Late Bronze Age [26].

The neck ring from the Kalinovo site, studied by electron probe microanalysis of the enamel decoration, revealed a high concentration of PbO (34.8%) and CuO (5.62%) in its chemical composition [27]. Enamel with high Cu and Pb concentration is known in Europe from ~2450 cal yr BP (500 BC), representing one more application of these metals in metalworking activities [28].

Further archaeometallurgical research of finds and expanding the database will probably help to sharpen ideas regarding the origin of the metal ores used for production of items, though this issue will remain complicated due to the long, complex and sometimes untraceable chain of transformations, which metals pass through on the way from ore to final object [29].

At the same time, the history of local and regional metallurgy—existence of metal smelting workshops, metalworking traditions and trade routes—can be reconstructed only if archaeological excavations are supplemented by targeted geochemical research on the culture-bearing layers. Geochemical analysis at archaeological sites has already demonstrated its high potential regarding the indicators of various human activities [30,31]. Another important point is the proper location, collection and analysis of metal slags, including microslags, which until now have received undeservedly much less attention from archaeologists than, for example, pottery sherds [18,32]. Microslags, if found in lake sediments, probably could be considered as a reliable indicator of local metal smelting in the surrounding of the lakes, as well as on excavation sites.

4.3. Long-Range Atmospheric Transport or Local Input?

Available regional data show that Kamyshovoe Lake displays an elevated concentration of Co (Table 2) compared to Latvian lakes [7]. The same observation applies to values of Ni in the Kamyshovoe Lake sediments (max = 46 ppm) compared to both Latvian (max = 35.7 ppm) and Polish lakes (max = 25 ppm) from the Suwalki region [7,33]. Kamyshovoe Lake shows a higher concentration of Pb than Latvian lakes but falls into range with medium values compared to Suwalkian lakes, where values of Pb in some lakes exceed 50 ppm and even 75 ppm in the sediments of Mulaczysko Lake [33].

Table 2. Concentration (ppm) of metals in the sediments of Kamyshovoe Lake (interval 730–245 cm; min and max values), Suwalki Lakeland (Preindustrial interval 52–50 cm; median value and standard deviations) and Pilvelis Lake (interval 400–0 cm; min and max values) [7,33].

Element	Kamyshovoe Lake	Suwalki Lakeland	Pilvelis Lake
Cu	16–34	16.7 ± 7.3	7.6–19.2
Ni	18–46	15.4 ± 9.1	3.1–17.8
Pb	5–45	27.6 ± 28.6	0.6–30.9
Zn	54–260	112.2 ± 60.7	46–198
Co	0.1–19	–	0.73–6.08

Concerning lead pollution identified in the lake sediments of northern Europe, it is interesting to compare the Kamyshovoe Lake Pb values during certain intervals correlating with particular historical time periods (Table 3).

Table 3. Pb concentration (ppm) in the sediments of Kamyshovoe Lake (min and max values within interval), Swedish lakes (mean value and range within different lakes) and Pilvelis Lake (Latvia) during different historical times [5,7].

Historical Time	Kamyshovoe Lake	Swedish Lakes	Pilvelis Lake
Before 2000 BC	6–18	7 (range = 2–17)	0.6–7
2000–500 BC	6–30	7	0.6–7
500 BC–400 AD	10–28	11–20 (range = 2–41)	7–15
400 AD–900 AD	12–36	-	15–30.9
900 AD–1400 AD	24–45	10–50 (range = 3–110)	20

In Central and Southern Europe, increased Hg and Pb enrichment values in the lake sediments, compared with crustal values and Pb isotopes, provide evidence for the impact of human activities during the Chalcolithic (~3800 BC) [13], while studies of the northern lakes show different results. According to Brännvall et al. [5], the first traces of atmospheric lead pollution in Swedish lake sediments are recorded ~3500–3000 cal BP (1550–1050 BC) with a clearly expressed peak of pollution at around 2550 cal BP (600 BC), while Pb values of earlier periods should be considered rather as natural background. The next pollution peak in the Iron Age–Roman Times (500 BC–400 AD) is followed by a decline of pollution in Early Medieval period (400 AD–900 AD); then (from about 1000 AD), a significant and permanent increase in lead pollution starts with clear peaks at 1200 AD and 1530 AD.

The most clearly expressed difference between the Kamyshovoe Lake Pb concentrations and other lakes (Table 3) concerns the Bronze Age–beginning of the Iron Age interval (2000–500 BC). Here, pronounced elevated values of Pb (up to 30 ppm) are recorded compared to other studied lakes, where the concentrations remain at the natural background values, despite pollution revealed by isotope analyses in some Swedish lakes [5]. The results show that peaks of Pb EF in the Kamyshovoe sediments are expressed at 850–350 BC (end of the Bronze Age–first half of the Iron Age), 150–400 AD (Roman Period) and after 1050 AD.

Considering the historical metal pollution in the Kamyshovoe Lake, the following question deserves further deeper study: Does the observed phenomenon reflect only the long-range atmospheric transport associated with metal mining in the main centres of Southern Europe, or is there a contribution of a more regional or even local component to the increased content of metals?

The hypothesis, that peaks of heavy metals (Pb in particular) found in the sediments of various water bodies in Northern Europe are the result of long-range atmospheric transport from centres of active metallurgy (Iberia, the Alps, the British Isles, etc.), is based mainly on results of isotopic analysis of metals, suggesting nonlocal origin [5]. However, when attempting to explain the peaks of metals with 'nonlocal signature' in the sediments of northern Europe by long-range atmospheric transport, two points must be taken into account. First, as Elbaz-Poulichet et al. [13] point out, different metals have different residence time in the atmosphere. This, along with the windrose for a particular time period and area, must be taken into account when reconstructing long-range transport of metals. Respective residence time in the atmosphere for different metals ranges from approximately 6 months for Hg to a few days or weeks for Pb, Sb and Cu, which can result in their atmospheric dispersal. An example from the Falu mine in Sweden, provided by [5], shows that lead pollution from the copper mines can be limited to a very local scale, not ranging beyond the first tens of kilometres. Secondly, as Ling et al. [23] and Melheim et al. [16] show, the sources of raw materials for local metalworking workshops in Northern Europe during the Bronze Age were mostly nonlocal but imported from the Mediterranean, the Alps, the British Isles and other mining and smelting centres. Since processing of this imported metal took place in local smelting workshops, it is possible that the recorded elevated content of heavy metals with a 'nonlocal geochemical signature' in lakes is rather the result of regional or local atmospheric and surface runoff or groundwater transport and pollution. Probably, some difference in the metal concentration and in the timing of the major Pb elevated values revealed in Kamyshovoe Lake, compared to Polish, Latvian and Swedish lakes, correlates better with an assumption about the local or regional, rather than long-range atmospheric metal input. This version is also supported by the fact that the reason for the observed decline of elemental EF in the Middle Ages has a local origin as well. Undoubtedly, the concentration and dynamics of metals in bottom sediments largely depend on the intensity of erosion, the input of organic matter, changes in the oxygen regime, etc.; however, it should be emphasised that anthropogenic impact is precisely one of the most important factors affecting the listed natural parameters. Still, to approach further understanding of local vs. long-range metal pollution, joint palaeolimnological and archaeological studies are required, for example, the study of lake sediments in the vicinity of ancient metallurgical centres such as Szczepidło archaeological site in Poland.

5. Conclusions

The results show that Cu, Pb, Zn, Co, As and Ni do not follow a uniform trend from the Neolithic to the early Middle Ages, though the concentrations of almost all of them show an increasing trend. The values of elements such as Pb, Co and As in the Iron Age and the Medieval period become 2–3 times higher than in the Neolithic, while the concentration of Cu and Ni grows insignificantly. Probably, the increasing Co EF value and the peaks of Pb EF in the Kamyshovoe Lake sediments, starting from ~6000 cal yr BP and during the entire Neolithic, show an increasing role and use of metals as dyes and fixatives. A major simultaneous increase in content of the Pb, Ni, Zn and As indicators of metallurgical production since ~3100 cal yr BP may show a growing demand for metal objects in the southeastern Baltic area, and input of local or regional metal smelting workshop pollution into lakes. The observed trend continues during the entire Iron Age until a decrease during the Migration Period. To give greater foundation to assumptions regarding metal use in prehistoric society, further combined palaeolimnological and archaeological research is necessary, with a focus on the study of microslags and detailed geochemical investigation of the culture-bearing layers of archaeological sites.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/min12101216/s1, Table S1: Basic statistics for the entire sediment section under consideration: values of the selected elements, microcharcoal and MS; Table S2: Natural background values; Table S3: Basic statistics for the EF of selected elements on the background of historical periods; Figure S1: TiO_2/Al_2O_3 and MnO/Fe_2O_3 as indicatives of the weathering and redox conditions; Figure S2: Box and whisker plot, mean values and the 25th and 75th percentiles; Figure S3: Box and whisker plot, mean values, SE and SD.

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