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ORIGINAL PAPERS

LEAD CONCENTRATION AND THE CONTENT OF SELECTED MACROELEMENTS IN LAKE SEDIMENTS IN POLAND

Izabela Bojakowska[1], Joanna Krasuska[1], Jacek Retka[1], Bogusław Wiłkomirski[2]

[1]Polish Geological Institute - National Research Institute
[2]Department of Environmental Protection and Management
The Jan Kochanowski University, Kielce

Abstract

Lead has been used extensively for thousands of years. Once introduced into the environment, like any other heavy metal, lead accumulates in soil and sediments. High lead concentrations in river and lake sediments can be harmful to aquatic organisms. At present, uncontaminated water sediments in the northern and central parts of Poland contain below 9 mg of lead per kg. The lakes located within the following lake districts: Greater Poland, Pomeranian and Masurian, provided 409 samples of surface sediments from deep spots (the profundal zone). All the samples were tested for the content of Pb and other selected macroelements. The content of Ca, Mg, Fe, K, Mn, Na, P, Pb and S was determined by ICP-OES and the total organic carbon (TOC) was evaluated by the coulometric titration method. The observed range of lead concentration was from below 3 to 222 mg kg^{-1}. The average content was 37 mg kg^{-1}, the geometric mean 30 mg kg^{-1}, and the median 33 mg kg^{-1}. In the majority of samples, the lead concentration was higher than the geochemical background. Only in 5.77% of the samples, the lead content was lower than 10 mg kg^{-1}. The lead concentration in the sediments was relatively well correlated with the total organic carbon (r = 0.59), aluminium (r = 0.45) and sulphur (r = 0.47), moderately correlated with iron (r = 0.26) and potassium (r = 0.28), very weakly correlated with phosphorus (r = 0.12) and negatively correlated with the calcium concentration (r = -0.28). No correlation was observed for manganese (r = -0.05), magnesium (r = 0.07) and sodium (r = -0.07). Factor analysis revealed the presence of two factors that together accounted for nearly 45% of variation. The first factor included aluminium, potassium and magnesium, and the second one - sul-

prof. dr hab. Izabela Bojakowska, Polish Geological Institute - National Research Institute, 4 Rakowiecka Street, 00-975 Warsaw, Poland, e-mail: izabela.bojakowska@pgi.gov.pl

phur and organic carbon. The lead share was low in the first factor (0.343), but very high in the second factor (0.757). Based on the results of the factor analysis, it can be assumed that lead in the organic matter-rich sediments of the profundal zone is deposited mainly in the form of sulphides. Lead concentration varied among the sediments obtained from various lake districts; it was lower in the lakes located within the Pomeranian Lake District than in those from Greater Poland and Masurian Lakes.

Key words: lake sediments, lead, macroelements.

ZALEŻNOŚĆ MIĘDZY ZAWARTOŚCIĄ OŁOWIU A ZAWARTOŚCIĄ WYBRANYCH PIERWIASTKÓW GŁÓWNYCH W OSADACH JEZIOR POLSKI

Abstrakt

Ołów jest wykorzystywany powszechnie od tysięcy lat. Uruchomiony do środowiska, podobnie jak inne metale ciężkie, podlega akumulacji w glebach i osadach wodnych. W osadach rzecznych i jeziornych duża zawartość Pb może szkodliwie oddziaływać na organizmy wodne. We współczesnych niezanieczyszczonych osadach wodnych na obszarze północnej i środkowej części Polski zawartość ołowiu wynosi poniżej 9 mg kg^{-1}. Z jezior Pojezierzy: Wielkopolskiego, Pomorskiego i Mazurskiego pobrano 409 próbek powierzchniowych osadów z głęboczków jezior (strefa profundalna). We wszystkich próbkach określono zawartość Pb oraz wybranych pierwiastków głównych. Zawartość Ca, Mg, Fe, K, Mn, Na, P, Pb i S określono metodą ICP-OES, a zawartość węgla organicznego (TOC) – metodą kulometrycznego miareczkowania. Stężenie ołowiu wynosiło od <3 do 222 mg kg^{-1}, średnia zawartość – 37 mg kg^{-1}, średnia geometryczna – 30 mg kg^{-1}, a mediana – 33 mg kg^{-1}. W większości zbadanych próbek zawartość ołowiu była podwyższona w stosunku do wartości tła geochemicznego. Jedynie w 5,77% próbek zawartość ołowiu była niższa niż 10 mg kg^{-1}. Stężenie ołowiu w osadach wykazuje stosunkowo wysoką korelację z zawartością węgla organicznego (r = 0,59), glinu (r = 0,45) i siarki (r = 0,47), słabą – ze stężeniem żelaza (r = 0,26) i potasu (r = 0,28), bardzo słabą – ze stężeniem fosforu (r = 0,12), ujemną – z zawartością wapnia (r = -0,28) oraz brak korelacji ze stężeniem manganu (r = -0,05), magnezu (r = 0,07) i sodu (r = -0,07). Analiza czynnikowa wykazała obecność 2 czynników, które łącznie wyjaśniają blisko 45% zmienności. Pierwszy czynnik grupuje glin, potas i magnez, drugi – siarkę i węgiel organiczny. Udział ołowiu w czynniku pierwszym jest niski (0,343), a w drugim – bardzo wysoki – 0,757. Na podstawie wyników analizy czynnikowej można przyjąć, że w bogatych w materię organiczną osadach strefy profundalnej jezior ołów występuje przede wszystkim w formie siarczków. Zaobserwowano zróżnicowanie w zawartości ołowiu w osadach różnych pojezierzy; osady jezior Pojezierza Pomorskiego zawierają mniej Pb niż osady jezior Pojezierzy Wielkopolskiego i Mazurskiego.

Słowa kluczowe: osady jeziorne, ołów, pierwiastki główne.

INTRODUCTION

Having been introduced into the environment, lead - similarly to other heavy metals - accumulates in soils and water sediments. Lead mobility in hypergenic environment is controlled through sorption of clay minerals, organic matter, secondary compounds of aluminium, iron and manganese and poorly soluble lead compounds such as galena – PbS, anglesite ($PbSO_4$), cerussit ($PbCO_3$) and pyromorphite ($Pb_5[Cl/(PO_4)_3]$). Lead is released into the environment from many natural and anthropogenic sources. Its natural

content in soils depends on the content in the bedrock, and its concentration in contemporary river and lake sediments is conditioned by the catchment area's lithology. Lead is a chalcophylic element and can be found in several minerals, the most important of which are galena, cerussite and anglesite. As a trace element, lead is distributed in other minerals, especially in orthoclase, plagioclases, micas, zircon and magnetite. The average lead abundance in the Earth's crust is 15 mg kg^{-1}; it is low in ultramafic rocks (1 mg kg^{-1}) and much higher in acidic rocks, i.e., granites (15-19 mg kg^{-1}). The lead concentration in sedimentary rocks is determined by the presence of detrital minerals - feldspars, micas and sulphides, and is controlled by clay minerals and organic matter. Limestone contains approximately 5 mg kg^{-1} of lead, sandstone about 10 mg kg^{-1}, loess about 13 mg kg^{-1}, and shales 23 mg kg^{-1}. The lead concentration in the oldest, pre-industrial lake sediments was 2-5 mg kg^{-1} (Pearson et al. 2010). In contemporary, uncontaminated stream sediments in the northern and central part of Poland, the lead content is below 9 mg kg^{-1}, which is due to the presence of quaternary deposits, characterized by a relatively low content of this element (de Vos et al. 2006). The average content of lead in sediments of the littoral zone calculated for 993 lakes was estimated at 7 mg kg^{-1} (Lis, Pasieczna 1995). A significantly higher lead content was recorded in lacustrine deposits of the profundal zone. Geometric means of the concentrations of lead in lake sediments in the area of the Regional Water Management Authority in Gdańsk, Poznań, Szczecin and Warsaw range from 27 to 33 mg kg^{-1} (Bojakowska et al. 2,006). The lead concentration in lake sediments depends significantly on the lithology of the lake catchment. Lakes formed in areas of till occurrence are characterized by a higher content of Pb than sediments of lakes located in areas of sand occurrence (Bojakowska, Gliwicz 2009). Previous studies of lake deposits in Poland showed the presence of a very high content of lead in sediments of some lakes such as Czarnówek (292 mg kg^{-1}), Moczydło (189 mg kg^{-1}), Arkońskie (141.7 mg kg^{-1}), Piaseczno Małe (136.7 mg kg^{-1}) (Bojakowska et al. 2006, Cieślewicz, Różański 2010) An extremely high lead content, such as 469 mg kg^{-1}, was recorded in the sediments of Lake Wigry in the estuary of the Czarna Hańcza River (Alexander-Kwaterczak, Kostka 2011).

Owing to its relatively wide distribution, easy extraction from ores and processing, lead has been widely used for thousands of years. Straightforward mining and extraction, as well as very good malleability contributed to a very early use of lead in the manufacture of various products (mainly dishes, ornaments and water pipes). Half of the current lead production is used for manufacturing batteries, ammunition, sailboat ballast, for lining chambers, towers and tanks for sulphuric acid production, covering cables, obtaining metal alloys and soft solders or stained glass windows. Numerous lead compounds are applied in ceramic and glass industry, in the production of paints and varnishes (PbO, PbO_2 2PbO, $PbCO_3$, $PbCrO_4$, PbNCN), primers ($Pb(N_3)_2$ - initiating material) or plastics (3PbO $PbSO_4$ H_2O - stabilizing agent). Tetraethyllead ($Pb(C_2H_5)_4$) used to be added to gasoline fuels

as an antiknock agent, and sodium arsenate was applied as an insecticide in orchards. The fact that lead has been used for thousand of years, and extensively in the last 150 years, is reflected in lake sediments (Bränvall et al. 2001, Yang, Rose 2005, Cooke et al. 2009, Pompeani et al. 2013).

High levels of lead in the sediments may be harmful for aquatic organisms (Míguez et al. 2012). Considering the potential toxicity of lead to the organisms living in the sediments, it was assumed that Pb content below 36 mg kg^{-1} (TEC – threshold effect concentration) does not affect negatively these organisms, but Pb concentration above 130 mg kg^{-1} (PEC – probable effect concentration) may produce adverse effects in aquatic organisms (MacDonald et al. 2000)

SCOPE AND METHODS

The paper is based on the results of research on water sediments in Poland carried out within the State Environmental Monitoring (SEM) program - Monitoring the quality of inland surface waters, and aims to determine the content of selected heavy metals and harmful organic compounds in the contemporary river and lake sediments in Poland. The analyses have been performed by the Polish Geological Institute - National Research Institute since 1990. The research program is supervised directly by the Monitoring Department in the Chief Inspectorate of Environmental Protection. Every year, about 130 samples of lake sediments taken from lakes in Poland are investigated. Lake sediments have been collected from the selected lakes belonging to the regional monitoring network and 23 reference lakes belonging to the national lake monitoring network. The regional network includes 1,032 lakes with a surface area greater than 50 hectares, and smaller lakes of ecological and economic importance. Analyses of sediments in the regional network lakes are carried out every few years, usually five, and the sediments from the reference lakes are scrutinized every 2 years.

In 2010-2012, the lakes from the Greater Poland, Pomeranian and Masurian Lake Districts were the sources of 409 samples of surface sediments collected from deep sites (profundal zone). All the samples were tested for the content of lead and other elements such as calcium, magnesium, iron, potassium, manganese, sodium, phosphorus, sulphur and organic carbon, contained in the phases that can retain Pb in the sediments. The content of Ca, Mg, Fe, K, Mn, Na, P, Pb and S was determined by atomic emission spectrometry with inductively coupled plasma ICP-AES (iCAP6500 Thermo Scientific) in the solutions obtained after digesting the sediments with aqua regia, and the total organic carbon (TOC) was determined by coulometric titration of a solid sample (Coulomat 702 CS/LI, Ströhlein). To assess the quality of the analyses a reference material, WQB-3 lake sediment, was tested.

RESULTS AND DISCUSSION

Lead content in the lake sediments ranged from below 3 to 222 mg kg^{-1}. The average concentration was 37 mg kg^{-1}, the geometric mean 30 mg kg^{-1}, and the median was 33 mg kg^{-1} (Table 1). The geometric mean of the lead content in the sediments of the profundal zone was much higher than an

Table 1

Statistical parameters of lead and main elements in lake sediments (n = 409)

Element	Parameter					
	mean	geometric mean	median	minimum	maximum	standard deviation
Al (%)	0.50	0.37	0.39	0.04	2.23	0.40
Ca (%)	13.50	8.91	13.75	0.05	30.63	8.62
Fe (%)	1.55	1.26	1.39	0.10	10.91	1.01
K (%)	0.112	0.081	0.086	0.005	0.510	0.091
Mg (%)	0.32	0.26	0.27	0.01	1.25	0.19
Mn (mg kg^{-1})	901	644	713	32	11770	962
Na (%)	0.026	0.020	0.019	0.006	0.536	0.043
P (%)	0.108	0.087	0.088	0.005	1.925	0.118
Pb (mg kg^{-1})	37	30	33	<3	222	24
S (%)	1.045	0.825	0.933	0.023	4.629	0.687
TOC (%)	7.15	5.93	6.11	0.19	22.90	4.12

average Pb content in sediments from the littoral zone, which was established as 7 mg kg^{-1} (Lis, Pasieczna 1995). In the majority of the examined samples, the lead concentration was higher than the geochemical background. Only in 5.77% of the samples it was lower than 10 mg kg^{-1}. The lead level below the TEC value (36 mg kg^{-1}) was found in 51.68% of the analyzed samples. Only in 2.88% of cases, the Pb content exceeded 91 mg kg^{-1} (PEL – probable effect level), and the Pb concentration higher than 130 mg kg^{-1} (PEC value) was found only in the sediments from Karczemne Lake. Seven lakes in the analyzed group had a sediment lead level above 100 mg kg^{-1} and these were: Karczemne (222 mg kg^{-1}), Człuchowskie (120 mg kg^{-1}) and Bobięcińskie Wielkie (112 mg kg^{-1}) in the Pomeranian Province, Trześniowskie (119 mg kg^{-1}) and Malcz (103 mg kg^{-1}) in the Lubuskie Province and Nicemino (119 mg kg^{-1}) and Trzesiecko (111 mg kg^{-1}) in the West-Pomeranian Province. Karczemne Lake is located in the vicinity of Kartuzy, Człuchowskie Lake is on the outskirts of Człuchów, Trzesiecko Lake on the outskirts of Szczecinek; there is a village called Łagów on Trześniowskie Lake and Bobięcin on Bobięcińskie Wielkie Lake. Moreover, there is an early medieval settlement from the 9th-12th century on an island on Bobięcińskie Wielkie Lake, and Malcz Lake is

located within a military training ground. These lakes were excluded from the analysis of correlations between the content of lead and other selected macroelements in the sediments (scatter graphs, correlation coefficients, factor analysis), and were not considered in the calculation of statistical parameters for sediments from different lakelands.

Lake sediments from the Pomeranian, Greater Poland and Masurian Lake Districts were characterized by a variable lead content. The sediments from the Pomeranian Lake District contained on average 33 mg kg^{-1} Pb (geometric mean 25 mg kg^{-1}, median 27 mg kg^{-1}), from the Greater Poland Lakes 38 mg kg^{-1}, (geometric mean 31 mg kg^{-1}, median 33 mg kg^{-1}), and an average Pb content in the lakes from the Masurian Lakes was 38 mg kg^{-1} (geometric mean 31 mg kg^{-1}, median 38 mg kg^{-1}). This diversity is also visible in the histograms, illustrating the number of samples in different Pb concentration ranges (Figure 1). The largest share of sediments from the Pomeranian Lake District contained 10-40 mg Pb kg^{-1}, in the Masurian Lake District the majority of lake sediments fell into 10-50 mg Pb kg^{-1} range, and in the lakes from Greater Poland the most common range of Pb content was 10 to 60 mg Pb kg^{-1}.

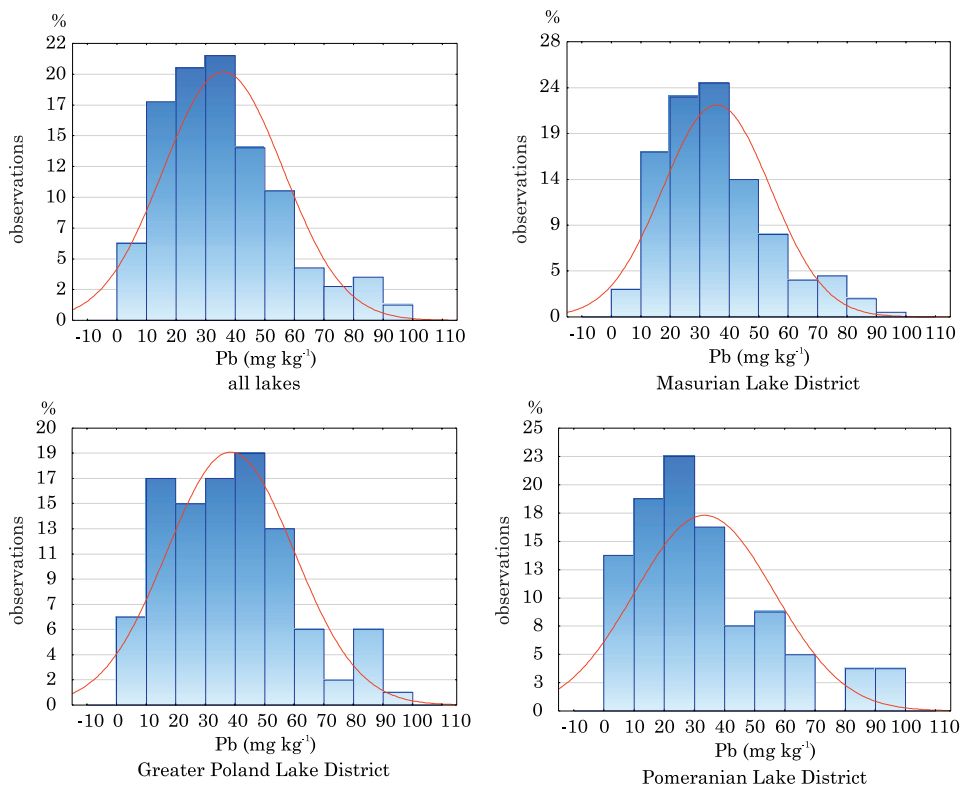

Fig. 1. Histograms presenting lead content in lake sediments

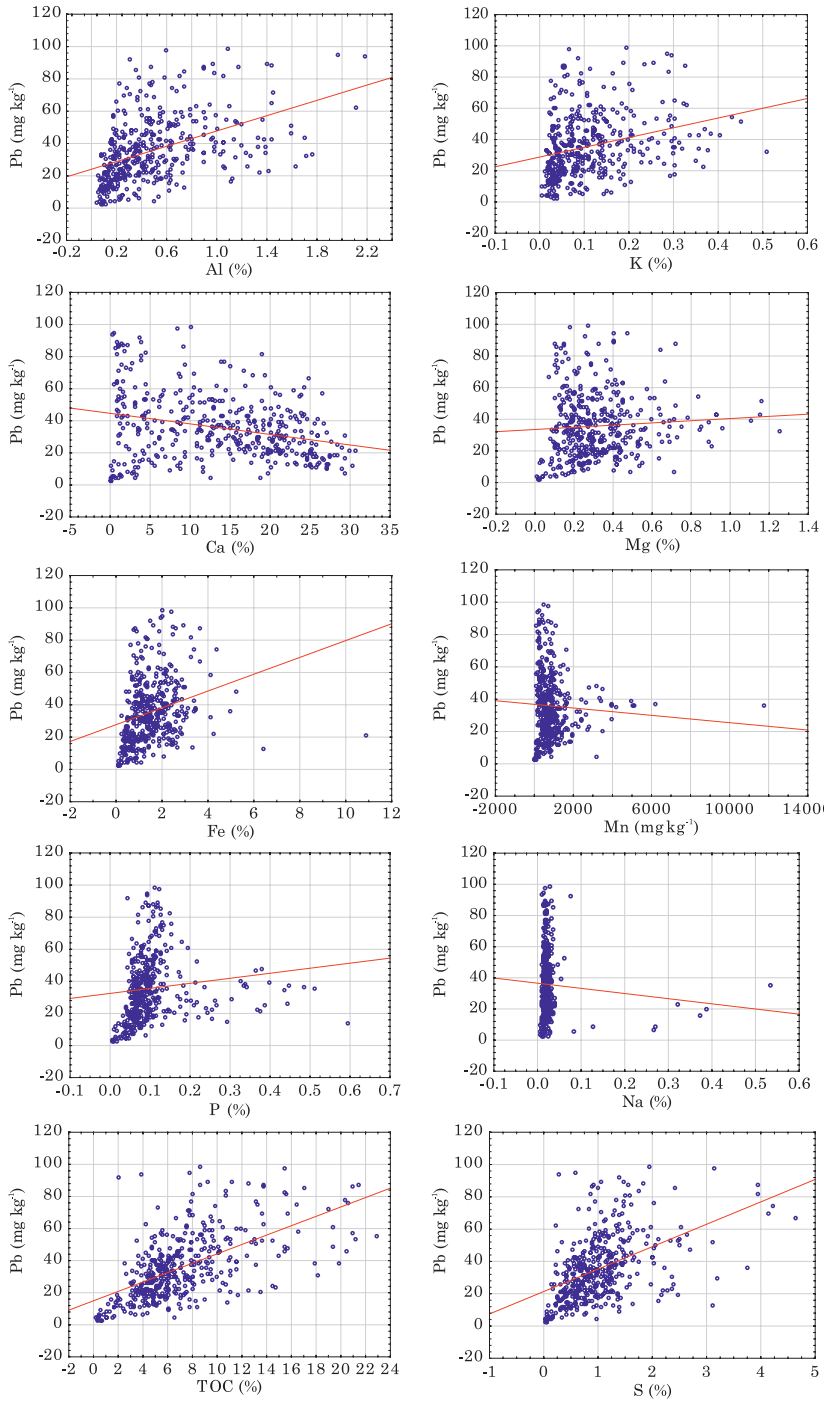

Fig. 2. Scatter graphs displaying the content of Pb and other macroelements

Table 2

Results of factor analysis of the concentration of lead and main elements in lake sediments

Element	Factor 1	Factor 2
Al	0.952	0.145
Ca	-0.629	-0.256
Fe	0.446	0.318
K	0.961	-0.022
Mg	0.780	-0.266
Mn	-0.060	-0.044
Na	0.028	0.191
P	0.128	0.308
Pb	0.343	0.757
S	-0.060	0.722
TOC	0.062	0.734
Baseline	6.966	5.081
Share	0.249	0.181

Lead concentration in the sediments was relatively well correlated with the total organic carbon (r = 0.59), aluminium (r = 0.45) and sulphur (r = 0.47), moderately correlated with iron (r = 0.26) and potassium (r = 0.28), very weakly correlated with phosphorus (r = 0.12), and negatively correlated with calcium concentration (r = -0.28). No correlation was observed for manganese (r = -0.05), magnesium (r = 0.07) and sodium (r = -0.07). Scatter graphs showed a clear relationship between the content of lead and organic carbon, sulphur, aluminium, potassium and iron, a negative correlation with calcium content, a very weak correlation with phosphorus level and lack of any correlation with the presence of manganese, sodium, and magnesium (Figure 2). Strong correlation between the Pb content and the level of organic carbon and sulphur indicates that the lead present in organic matter-rich sediments in deep sits is mostly deposited in the form of sulphides, most likely as PbS or in iron sulphides. The role of iron sulphides in retaining heavy metals in sediments has been described in a number of publications. For example, mercury immobilization in contaminated sediments is facilitated by iron sulphide nanoparticles, and this discovery was the basis for patent applications (Jeong 2007, Xiong et al. 2009). A good correlation between the content of lead and aluminium and potassium suggests that a significant portion of Pb binds to clay minerals, probably those of illite-smectite type, fairly common in the quaternary deposits. Moraine clays contain also montmorillonite and kaolinite (Kenig 2009). The possibility of lead adsorption by clay minerals has been widely discussed (Etci et al. 2012 , Hizal, Apak 2012). The correlation between lead and phosphorus was found to be relatively

poor. Although numerous works have proved the usefulness of apatites for the immobilization of heavy metals in the contaminated sediments (Arey 2001, Corami et al. 2008), it was reported that the formation of pyromorphite (lead phosphate) was inhibited under reducing conditions (Scheckel et al. 2010).

The factor analysis revealed the presence of two factors that together accounted for nearly 45% of variation (Table 2). The first factor included aluminium, potassium and magnesium, and the second sulphur and organic carbon. The lead share was low in the first factor (0.343), but very high in the second factor (0.757). Based on the results of the factor analysis, it can be assumed that lead deposited in the profundal zone sediments is mainly stored in the form of sulphides.

CONCLUSIONS

1. In most of the analyzed lake sediments, the lead content was greater than the geochemical background in Poland, but only in a few lakes its concentration was high enough to pose a possible threat to aquatic organisms dwelling in the sediments.

2. It was confirmed that the lead content in the sediments was significantly correlated with the content of organic carbon and sulphur, and to a lesser extent with the concentration of aluminium, iron and potassium. A negative correlation was observed for calcium content.

3. Lead concentrations varied among the sediments from various lakelands, being lower in the lakes located within the Pomeranian Lake District than in those from Greater Poland and Masurian Lake Districts.

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