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# DEPENDENCE BETWEEN THE CONTENT OF COPPER AND THE CONTENT OF MAJOR ELEMENTS IN SEDIMENTS OF POLISH LAKES

## ZALEŻNOŚĆ MIĘDZY ZAWARTOŚCIĄ MIEDZI A ZAWARTOŚCIĄ PIERWIASTKÓW GŁÓWNYCH W OSADACH JEZIOR POLSKI

**Abstract:** In 416 sediment samples taken from the deepest waters of 260 lakes located within the following Lake Districts: Greater Poland, Pomeranian and Masurian, the content of Cu, Ca, Mg, Fe, Mn, K, Na, P and S was determined by the ICP-OES method and the content of the Total Organic Carbon (TOC) was determined by the coulometric titration method. The analyses revealed that in the majority of tested samples, the Cu content did not exceed 50 mg/kg and that the geometric mean of the copper content is 13 mg/kg, and thus it is much higher than the geochemical background for aquatic sediments in Poland. The high dependence determined between the Cu content in sediments and the concentration of Al, K, Mg, S and TOC and a weaker correlation between the Cu concentration and the content of P and Fe indicate that copper in sediments is primarily related to the organic matter and clay minerals and, to a lesser extent, to phosphates and iron compounds. The variation in the copper content in sediments of different Lake Districts and also the variation in the present correlations were observed.

**Keywords:** copper, lakes, correlations, clay minerals, organic matter, iron compounds, phosphates

## Introduction

Copper is considered to be one of the most toxic metals in the water environment [1, 2]. At the same time, it is an essential element for the life of many organisms. It participates in the carbohydrate metabolism and plays a role in the action of several dozen enzymes. However, excessive concentrations of copper may be toxic. Algae are

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particularly vulnerable to copper. And the fish exposed to its too high concentrations suffer from gill damage and malfunction in the transport and excretion of sodium and potassium chlorides as well as from inhibition of Na+/K+-ATPase [3–8]. Heavy metals, including copper, present in lake sediments may accumulate in a food chain to the level which is toxic for organisms, especially the ones of predators, and may also pose a risk to humans [9, 10].

Natural content of copper in lake sediments, like of other minor elements, mostly depends on the chemical composition of geological formations present within the catchment area of a given lake. In natural conditions, sediments that accumulate at the bottom of the lake are formed as a result of the accumulation of a material derived from erosion of soil, *ia* from quartz grains, feldspars, carbonate minerals, clay minerals, and of a material formed in the place of sedimentation – remains of dead plant and animal organisms and also substances that precipitate from the water, *ia* carbonates, phosphates, sulphides, hydrated iron and aluminium hydroxides [11]. The concentration of elements in lake sediments is also affected by the size of the lake catchment area, lake surface area and depth, shape of the lake basin. The speciation of copper in the water environment, and consequently its availability to aquatic organisms, is strongly affected by the alkalinity, water hardness and pH [12]. Copper in the environment is mobile under oxidative conditions, especially in the acid environment. However, it is easily bound by sediment components, mainly by the organic matter, sulphides, and also by hydrated iron oxides and phosphates [13, 14]. On the territory of Poland, the average Cu content in sediments is 7 mg/kg [15]. In view of harmful effects of copper on aquatic organisms, its permissible content in sediments was determined as 149 mg/kg [16].

An increase in the concentration of heavy metals observed nowadays in lake sediments in non-industrialised areas is often a result of their deposition from the atmosphere and of rain and thaw water runoff from urban and rural areas [17–23]. In developed areas, sediments are also contaminated by heavy metals contained in effluents discharged sometimes to surface waters. Copper, known to man for almost 6,000 years, is widely used in industry (electrical wiring, water supply, heating, electromagnets, roof covering), in alloys (tools, brake discs, heat exchangers, jewellery), and it is also used as an ingredient of algaecides, fungicides and molluscacides. It is released to the environment from many sources: *ia* as a result of coal combustion, copper ore processing, copper smelting, transport, agriculture (micro-fertiliser, plant protection products, additive in animal feed), fish culture (growth control of algae and pathogens in fish ponds), and also as a result of deterioration of buildings by atmospheric factors and use of transport means.

## Material and methods

In this paper, results of tests on aquatic sediments in Poland were used. The results were obtained from the implementation of the task of the State Environmental Monitoring – Monitoring of the quality of inland surface waters, which include the determination of the content of heavy metals and selected harmful organic compounds in sediments formed nowadays in rivers and lakes within the country. Over the period of

2010 to 2012, 416 sediment samples were taken from the deepest waters of 260 lakes (from the lakes with their surface area up to 250 ha – one sample was taken; from the lakes with their surface area from 250 to 500 ha – two samples; from the lakes with their surface area from 500 to 1,000 ha – three samples; from the lakes with their surface area from 1,000 to 5,000 ha – four samples; from the lakes with their surface area over 5,000 ha – five samples). A 5 cm thick sediment layer is taken for tests from the profundal zone of the lakes.

The content of copper and elements – calcium, magnesium, iron, potassium, manganese, sodium, phosphorus, sulphur and TOC, being part of phases (organic matter, clay minerals, carbonates, phosphates and sulphides), which may retain copper in sediments, was determined in all the samples. The content of Ca, Cu, Fe, K, Mg, Mn, Na, P and S was determined by the ICP-OES method, *ie* by the Inductively Coupled Plasma Optical Emission Spectrometry (iCAP6500 manufactured by Thermo Scientific), from the solutions obtained after digestion of sediment samples with aqua regia; the content of the Total Organic Carbon (TOC) was determined by the coulometric titration method from the solid sample (Coulomat 702 CS/LI manufactured by Strohlein). To assess the quality of made tests, a reference material (WQB-3 lake sediment) was also analysed.

## Results and discussion

Copper in sediments was found to be from 2 to 537 mg/kg. In ten out the tested samples, the copper content exceeded 50 mg/kg and in the histogram, the Cu content created a separate anomalous population of sediments contaminated with this element. These were the sediments of the Karczemne Lake, at which the town of Kartuzy is located; of the Elk Lake, at which the town of Elk is located; of the Czluchow Lake, which is located in the area of the town of Czluchow; of the Trzesiecko Lake, which is located in the area of the town of Szczecinek; of the Wasowsko-Mikorzynskie Lake and of the Patnowskie Lake, of which waters are used in the cooling cycle of the Konin Power Plant. The analysis of dependence of the copper concentration in sediments on the content of major elements does not include the results of determining elements in sediments of these lakes. In the population of sediments, taken into consideration, the copper content was found to be from 2 to 49 mg/kg, its average content was 15 mg/kg, and its geometric mean and median – 13 mg/kg. The average copper content determined in tested sediments of the profundal zone of the lakes is much higher than the average content in sediments of the littoral zone of the lakes in Poland, amounting to 3 mg/kg [15]. The variation in the copper content in sediments of different Lake Districts was observed. The geometric mean of the copper content in sediments of the Pomeranian Lake District – 11 mg/kg is slightly lower than the value calculated for sediments of the Greater Poland and Masurian Lake Districts, amounting to 13 mg/kg (Table 1).

This variation is also seen on histograms that illustrate the number of samples in different concentration classes (Fig. 1). Among the tested sediments of the lakes of the Pomeranian Lake District, the largest share has the samples containing copper within the range from 5 to 10 mg/kg; whereas among the samples taken from the lakes of the

Table 1

Statistic parameters of elements in lake sediments

| Element | Mean | Geometric mean | Median | Minimum | Maximum |
|---|---|---|---|---|---|
| Lakes, overall total (n = 406) | | | | | |
| Copper [mg/kg] | 15 | 13 | 13 | 2 | 49 |
| Phosphorus [%] | 0.104 | 0.086 | 0.087 | 0.005 | 0.595 |
| Aluminium [%] | 0.50 | 0.37 | 0.39 | 0.04 | 2.23 |
| Magnesium [%] | 0.32 | 0.26 | 0.27 | 0.01 | 1.25 |
| Manganese [mg/kg] | 901 | 640 | 712 | 32 | 11,770 |
| Potassium [%] | 0.112 | 0.080 | 0.086 | 0.005 | 0.510 |
| Sulphur [%] | 1.040 | 0.819 | 0.932 | 0.023 | 4.629 |
| Sodium [%] | 0.025 | 0.020 | 0.019 | 0.006 | 0.536 |
| Calcium [%] | 13.40 | 8.80 | 13.57 | 0.05 | 30.63 |
| TOC [%] | 7.14 | 5.91 | 6.11 | 0.19 | 22.90 |
| Iron [%] | 1.55 | 1.26 | 1.41 | 0.10 | 10.91 |
| Pomeranian Lake District (n = 86) | | | | | |
| Copper [mg/kg] | 14 | 11 | 10 | 2 | 38 |
| Phosphorus [%] | 0.095 | 0.075 | 0.077 | 0.011 | 0.510 |
| Aluminium [%] | 0.50 | 0.36 | 0.35 | 0.05 | 2.23 |
| Magnesium [%] | 0.26 | 0.22 | 0.24 | 0.01 | 0.69 |
| Manganese [mg/kg] | 748 | 542 | 668 | 33 | 4,999 |
| Potassium [%] | 0.108 | 0.080 | 0.086 | 0.005 | 0.330 |
| Sulphur [%] | 1.037 | 0.790 | 0.924 | 0.031 | 3.757 |
| Sodium [%] | 0.046 | 0.025 | 0.021 | 0.009 | 0.536 |
| Calcium [%] | 11.57 | 6.38 | 10.87 | 0.09 | 29.41 |
| TOC [%] | 6.43 | 4.95 | 6.08 | 0.19 | 21.00 |
| Iron [%] | 1.43 | 1.14 | 1.39 | 0.10 | 4.96 |
| Masurian Lake District (n = 210) | | | | | |
| Copper [mg/kg] | 15 | 13 | 13 | 2 | 45 |
| Phosphorus [%] | 0.115 | 0.097 | 0.094 | 0.015 | 0.60 |
| Aluminium [%] | 0.55 | 0.40 | 0.43 | 0.06 | 1.97 |
| Magnesium [%] | 0.38 | 0.32 | 0.32 | 0.023 | 1.25 |
| Manganese [mg/kg] | 997 | 698 | 726 | 73 | 11.770 |
| Potassium [%] | 0.129 | 0.091 | 0.102 | 0.011 | 0.510 |
| Sulphur [%] | 0.963 | 0.794 | 0.913 | 0.049 | 4.23 |
| Sodium [%] | 0.019 | 0.018 | 0.018 | 0.007 | 0.05 |
| Calcium [%] | 13.29 | 9.19 | 14.20 | 0.15 | 30.63 |
| TOC [%] | 7.64 | 6.58 | 6.31 | 0.48 | 21.40 |
| Iron [%] | 1.68 | 1.43 | 1.52 | 0.22 | 10.91 |

Table 1 contd.

| Element | Mean | Geometric mean | Median | Minimum | Maximum |
|---|---|---|---|---|---|
| Greater Poland Lake District (n = 102) | | | | | |
| Copper [mg/kg] | 15 | 13 | 14 | 2 | 49 |
| Phosphorus [%] | 0.086 | 0.074 | 0.076 | 0.005 | 0.437 |
| Aluminium [%] | 0.40 | 0.31 | 0.35 | 0.04 | 1.45 |
| Magnesium [%] | 0.24 | 0.20 | 0.23 | 0.01 | 0.59 |
| Manganese [mg/kg] | 843 | 627 | 706 | 32 | 4.193 |
| Potassium [%] | 0.077 | 0.060 | 0.064 | 0.005 | 0.302 |
| Sulphur [%] | 1.200 | 0.888 | 0.947 | 0.023 | 4.629 |
| Sodium [%] | 0.022 | 0.021 | 0.021 | 0.006 | 0.079 |
| Calcium [%] | 15.42 | 10.73 | 16.98 | 0.05 | 30.27 |
| TOC [%] | 6.47 | 5.33 | 5.96 | 0.19 | 15.50 |
| Iron [%] | 1.40 | 1.08 | 1.11 | 0.10 | 6.43 |

Greater Poland Lake District, the range of the most frequently observed concentrations is much wider – from 5 to 20 mg/kg; and in sediments of the Masurian Lake District, this range is from 5 to 15 mg/kg.

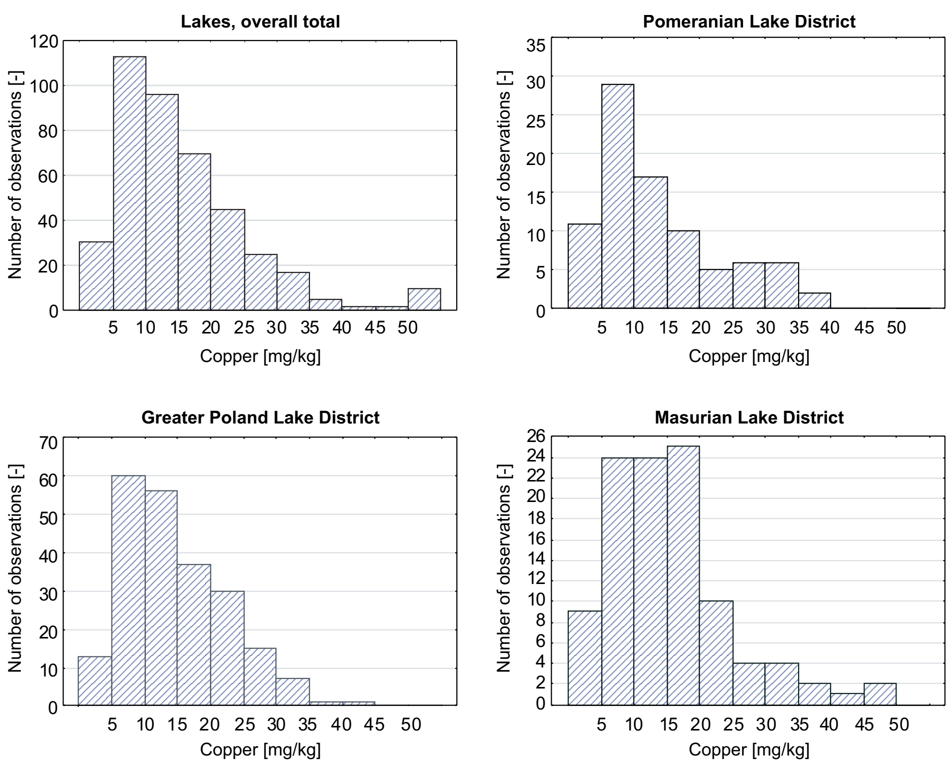


Fig. 1. Histograms of the copper content in lake sediments

The copper concentration in lake sediments shows a strong correlation with the aluminium content (r = 0.57) and with the potassium concentration (r = 0.50) (Table 2). Correlations with the concentration of iron (r = 0.34), magnesium (r = 0.33), sulphur (r = 0.34), TOC (r = 0.30) and phosphorus (r = 0.26) are weaker. The copper content does not show any correlation with the manganese content, and shows a negative correlation with the calcium concentration (r = 0.27). The variation in the correlation of copper with major elements may be observed in sediments of particular Lake Districts. For example, the copper concentration in sediments of the lakes of the Greater Poland Lake District is distinguished by the strongest correlation with the concentration of sulphur and TOC, and the Cu concentration in sediments of the lakes of the Pomeranian Lake District shows a strong correlation with the content of aluminium and iron.

Table 2

Correlation factors of copper with major elements

| Element | Lakes | Pomeranian Lake District | Greater Poland Lake District | Masurian Lake District |
|---|---|---|---|---|
| Aluminium | 0.57 | 0.70 | 0.47 | 0.73 |
| Calcium | –0.27 | –0.20 | –0.14 | –0.49 |
| Iron | 0.34 | 0.56 | 0.33 | 0.35 |
| Potassium | 0.50 | 0.68 | 0.31 | 0.70 |
| Magnesium | 0.33 | 0.55 | 0.24 | 0.46 |
| Manganese | 0.02 | 0.12 | 0.10 | –0.05 |
| Sodium | 0.10 | 0.15 | 0.34 | 0.37 |
| Phosphorus | 0.26 | 0.37 | 0.27 | 0.22 |
| Sulphur | 0.34 | 0.44 | 0.50 | 0.16 |
| TOC | 0.30 | 0.33 | 0.54 | 0.20 |

Scatter graphs of the dependence between the copper concentration in sediments and the content of major elements, presented in Fig. 2, illustrate a great dependence between the Cu content in sediments and the concentration of Al, K, Mg, S and TOC as well as a weaker correlation between the Cu concentration and the content of P and Fe. These dependencies show that copper in sediments is primarily related to the organic matter and clay minerals and, to a lesser extent, to phosphates and iron compounds. This confirms that the organic matter plays a major role in the retention of heavy metals, also copper [24]. Such retention of heavy metals by the organic matter is primarily related to the presence of the following function groups in its structure: R-SH, R-SS-R and R-SSH. The scatter graph for Cu and Ca illustrates a negative dependence between these elements. Probably, in conditions conducive to precipitation and accumulation of calcium carbonate, the copper concentration in formed sediments becomes relatively low. The scatter graph for Mn and Cu illustrates the lack of correlation between the concentrations of these elements in sediments. Manganese is an element of which concentration variability in sediments highly depends on the redox conditions present in the sedimentation environment. The dependence between the copper content and the

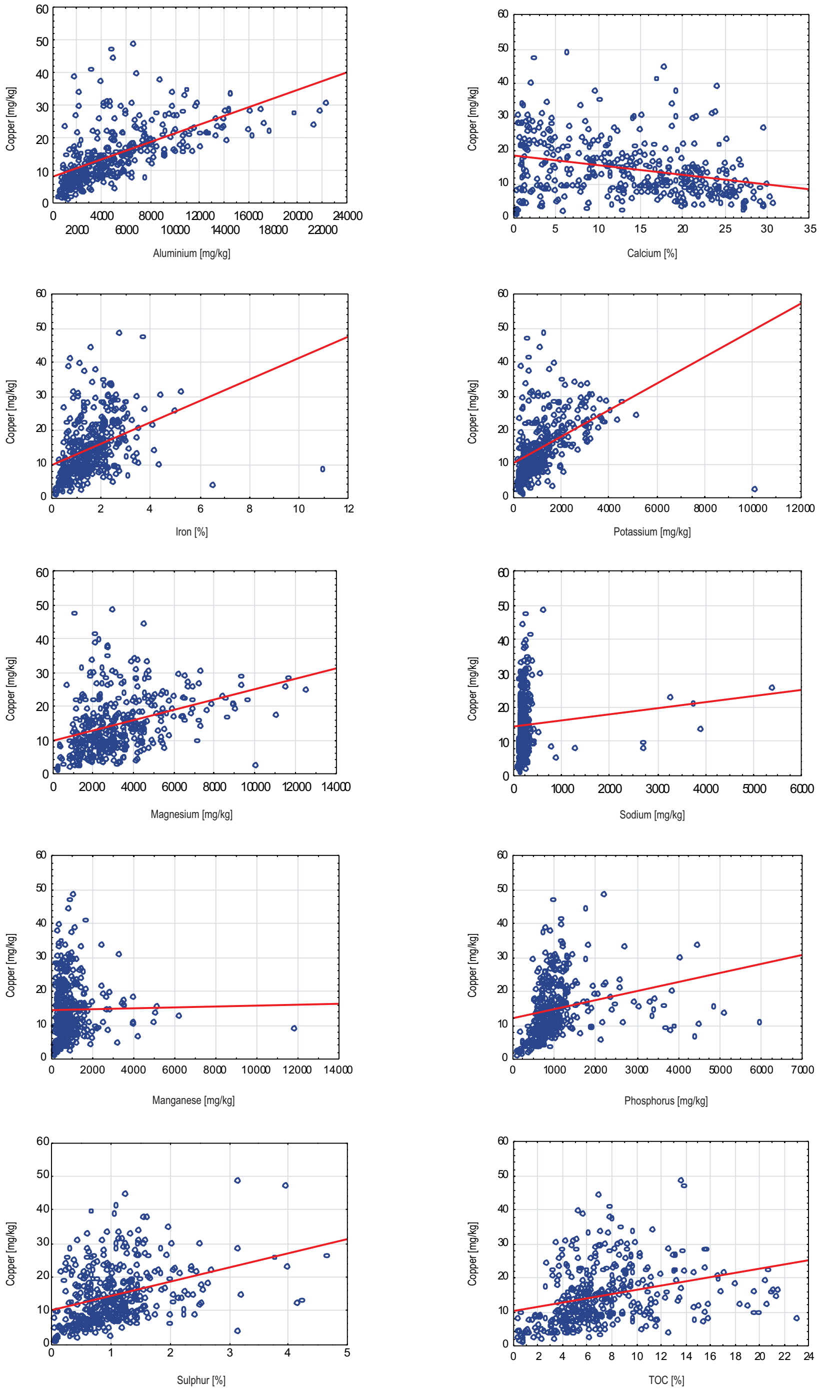


Fig. 2. Scatter graph between the copper content and the content of the major elements

phosphorus content was also observed in tested sediments. This indicates the probability of retaining this element also by phosphates. The possibility of immobilising heavy metals by apatites (calcium phosphates) is presented in many studies and such capability of apatites is used to immobilise heavy metals in contaminated environments [25, 26].

The factor analysis carried out for all the samples and for the samples of sediments taken from particular Lake Districts revealed the presence of two factors, which together explain approx. 40% of the variability (Table 3). One of them binds aluminium, potassium and magnesium (being part of minerals from the illite-smectite group) present in sediments, whereas the second factor binds sulphur and organic carbon (being part of the organic matter). Both factors have a relatively similar copper share. In sediments of the lakes of the Pomeranian Lake District, the first factor binds aluminium, potassium, copper and iron at a high share of sulphur, magnesium and TOC.

Table 3

Results of factor analysis

| Element | Overall total | | Pomeranian | | Greater Poland | | Masurian | |
|---|---|---|---|---|---|---|---|---|
| | Factor 1 | Factor 2 | Factor 1 | Factor 2 | Factor 1 | Factor 2 | Factor 1 | Factor 2 |
| Aluminium | 0.951 | 0.151 | 0.863 | –0.316 | 0.297 | 0.914 | 0.964 | 0.090 |
| Calcium | –0.650 | –0.080 | –0.470 | 0.546 | 0.133 | –0.712 | –0.654 | –0.241 |
| Copper | 0.520 | 0.640 | 0.847 | 0.169 | 0.771 | 0.272 | 0.722 | 0.544 |
| Iron | 0.419 | 0.365 | 0.741 | 0.154 | 0.513 | 0.304 | 0.457 | 0.137 |
| Potassium | 0.956 | 0.020 | 0.807 | –0.319 | 0.112 | 0.891 | 0.974 | 0.010 |
| Magnesium | 0.772 | –0.160 | 0.562 | –0.007 | 0.069 | 0.569 | 0.837 | –0.287 |
| Manganese | –0.099 | 0.137 | 0.161 | 0.675 | 0.288 | –0.210 | –0.048 | –0.057 |
| Sodium | 0.017 | 0.170 | 0.193 | 0.092 | 0.389 | –0.149 | 0.094 | 0.384 |
| Phosphorus | 0.033 | 0.387 | 0.375 | 0.599 | 0.452 | 0.015 | 0.047 | 0.263 |
| Sulphur | –0.083 | 0.710 | 0.520 | 0.334 | 0.800 | 0.044 | –0.159 | 0.638 |
| TOC | 0.053 | 0.632 | 0.496 | 0.187 | 0.728 | 0.228 | –0.062 | 0.688 |
| Output value | 7.189 | 5.910 | 10.627 | 3.860 | 8.297 | 7.068 | 8.555 | 5.859 |
| Share | 0.257 | 0.211 | 0.332 | 0.121 | 0.259 | 0.221 | 0.267 | 0.183 |

In the second factor, calcium, manganese and phosphorus have a high share. In the lakes of this Lake District, copper is primarily related to the minerals from the illite-smectite group (aluminium, potassium, magnesium) derived from glacial clays, and partly to the organic matter; whereas phosphorus compounds do not play any significant role in the binding of copper in these sediments.

In sediments of the lakes of the Greater Poland Lake District, the first factor includes copper, sulphur and TOC at a relatively high share of phosphorus and iron. The second factor binds potassium with aluminium at a high share of magnesium. In sediments of this Lake District, copper is retained primarily by the organic matter and, to a lesser extent, by phosphates, *eg* vivianite or apatites; whereas clay minerals do not play any significant role in the retaining of Cu in sediments. In sediments of the lakes of the

Masurian Lake District, the first factor groups aluminium, copper, potassium, magnesium; whereas the second factor groups sulphur and TOC. In sediments of this Lake District, copper has a relatively high share in both distinguished factors but, to a greater extent, it is retained in sediments by clay minerals, most probably from the illite-smectite group, rather than by the organic matter. This variation between the Lake Districts in the phases of sediments, which retain copper, most probably depends on the variation in the lithology of post-glacial formations related to different phases of glaciations: the Pomeranian phase (Masurian and Pomeranian Lake Districts) and the Poznan phase (Greater Poland Lake District).

## Conclusions

1. In the majority of tested samples, the copper content did not exceed the value of 50 mg/kg. Higher copper contents were found in sediments of lakes at which highly-populated towns are located or their waters are used in the cooling cycle of the power plant.
2. The geometric mean of the copper content in sediments of the profundal zone of the lakes is 13 mg/kg and is much higher than the geochemical background for aquatic sediments in Poland.
3. The high dependence determined between the Cu content in sediments and the concentration of Al, K, Mg, S and TOC and a weaker correlation between the Cu concentration and the content of P and Fe indicate that copper in sediments is primarily related to the organic matter and clay minerals and, to a lesser extent, to phosphates and iron compounds.
4. The variation in the copper content in sediments of different Lake Districts and also the variation in the present correlations, depending on the variation in the lithology of post-glacial formations related to different phases of glaciations: the Pomeranian phase (Masurian and Pomeranian Lake Districts) and the Poznan phase (Greater Poland Lake District), were observed.

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## ZALEŻNOŚĆ MIĘDZY ZAWARTOŚCIĄ MIEDZI A ZAWARTOŚCIĄ PIERWIASTKÓW GŁÓWNYCH W OSADACH JEZIOR POLSKI

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**Abstrakt:** W 416 próbkach osadów pobranych z głęboczków 260 jezior Pojezierzy: Wielkopolskiego, Pomorskiego i Mazurskiego oznaczano zawartość Cu, Ca, Mg, Fe, Mn, K, Na, P i S metodą ICP-OES oraz zawartość węgla organicznego (TOC) metodą kulometrycznego miareczkowania. Analizy wykazały, że w większości zbadanych próbek zawartość Cu nie przekraczała 50 mg/kg, a średnia geometryczna zawartość miedzi wynosi 13 m/kg i jest znacznie wyższa od tła geochemicznego dla osadów wodnych Polski. Stwierdzona wysoka zależność między zawartością Cu w osadach a stężeniem Al, K, Mg, S i węgla organicznego oraz słabsza korelacja między stężeniem Cu a zawartością P i Fe wskazuje, że miedź w osadach związana jest przede wszystkim z materią organiczną oraz minerałami ilastymi, a w mniejszym stopniu z fosforanami i związkami żelaza. Zaobserwowano zróżnicowanie w zawartości miedzi w osadach różnych pojezierzy, a także zróżnicowanie w występujących korelacjach.

**Słowa kluczowe:** miedź, jeziora, korelacje, minerały ilaste, materia organiczna, związki żelaza, fosforany