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COPPER AND OTHER TRACE ELEMENTS IN SEDIMENTS OF LAKES NEAR KONIN (POLAND)*

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Abstract

High concentrations heavy metals accumulate in sediments of some lakes, possibly excerting adverse effects on lake-dwelling organisms. Sediment samples were collected from the surface layer of the profundal zone in 14 lakes located near Konin, in the southern part of the Gniezno Lake District, in order to determine the content of Ag, As, Ba, Cd, Co, Cr, Cu, Hg, Ni, Pb, Sr, V, Zn, Ca, Fe, Mg, Mn, P, S and TOC. Significant differences in the content of trace elements in sediments of the lakes were observed. A very high copper content was found in sediment of the lakes included in the cooling system of the Konin-Pątnów power plant, esepecially in comparison with its content in sediments of the lakes outside that system. The lake sediment samples from lakes within the power plant cooling system are also characterized by higher levels of barium, mercury, manganese, strontium and zinc, but lower concentrations of lead, sulfur and organic matter. In the sediments of lakes within the power plant cooling system, the geometric means of the content of elements were as follows: 385 mg kg^{-1} Cu, 309 mg kg^{-1} Ba, 20 mg kg^{-1} Pb, 613 mg kg^{-1} Sr, 129 mg kg^{-1} Zn and 0.152 mg kg^{-1} Hg; and in sediments of the lakes whose water was not used by the power plant cooling system: 14 mg kg^{-1} Cu, 93 mg kg^{-1} Ba, 33 mg kg^{-1} Pb, 193 mg kg^{-1} Sr and 63 mg kg^{-1} Zn. The copper pollution of sediments of the lakes Licheńskie, Gosławskie, Pątnowskie, Wąsowsko-Mikorzyńskie and Ślesińskie is most likely created by passing the lake water through the Konin-Pątnów power plant cooling system. Copper brought to the lakes in water discharged from the cooling system probably originates from corroded heat exchangers made of copper or copper alloys.

Keywords: lake sediments, trace elements, corrosion, power plant cooling water.

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MIEDŹ I INNE PIERWIASTKI ŚLADOWE W OSADACH JEZIOR W REJONIE KONINA (POLSKA)

Abstrakt

Wysokie stężenia metali ciężkich akumulowanych w osadach niektórych jezior mogą szkodliwe oddziaływać na organizmy bytujące w tych jeziorach. Ze strefy profundalnej 14 jezior położonych w rejonie Konina, w południowej części Pojezierza Gnieźnieńskiego, pobrano próbki 5 cm powierzchniowej warstwy osadów. W próbkach określono zawartość Ag, As, Ba, Cd, Co, Cr, Cu, Hg, Ni, Pb, Sr, V i Zn oraz Ca, Fe, Mg, Mn, P, S i TOC. Zaobserwowano duże zróżnicowanie w zawartości pierwiastków śladowych w osadach jeziornych. W osadach jezior, których wody wykorzystywane są w systemie chłodzącym elektrowni Konin-Pątnów, stwierdzono bardzo wysoką zawartość miedzi w porównaniu z jej zawartością w osadach jezior, których wody nie są wykorzystywane przez elektrownię. W osadach jezior, których wody włączono w system chłodzący, zawierają również więcej baru, rtęci, manganu, strontu i cynku, a jednocześnie mniej ołowiu, siarki i materii organicznej. W osadach jezior antropogenicznie zmienionych średnie geometryczne zawartości wynosiły: 385 mg kg^{-1} Cu, 309 mg kg^{-1} Ba, 20 mg kg^{-1} Pb, 613 mg kg^{-1} Sr, 129 mg kg^{-1} Zn i 0,152 mg kg^{-1} Hg, a w osadach jezior antropogenicznie niezmienionych: 14 mg kg^{-1} Cu, 93 mg kg^{-1} Ba, 33 mg kg^{-1} Pb, 193 mg kg^{-1} Sr, 63 mg kg^{-1} Zn i 0,084 mg kg^{-1} Hg. Na zanieczyszczenie miedzią osadów jezior Licheńskiego, Gosławskiego, Pątnowskiego, Wąsowsko-Mikorzyńskiego oraz Ślesińskiego ma najprawdopodobniej wpływ wykorzystywanie wody jezior w systemie chłodzącym elektrowni Konin-Pątnów. Miedź wnoszona do jezior przez wody wykorzystane w obiegu chłodzącym elektrowni najprawdopodobniej pochodzi z korozji wymienników ciepła wykonanych z miedzi lub jej stopów.

Słowa kluczowe: osady jeziorne, pierwiastki śladowe, korozja, elektrowniane wody chłodnicze

INTRODUCTION

Under natural conditions, lake benthic sediments build up by accumulation of material derived from erosion and weathering of rocks in the catchment area (including grains of quartz, feldspars, carbonate minerals and clay minerals) and through on-site sedimentation (remains of dead plants and animals as well as substances that precipitate from lake water, such as carbonates, phosphates, sulfides, hydrous iron and aluminum hydroxides). Concentrations of trace elements in sediments mainly depend on properties of geological formations occurring in the catchment area of a lake. The content of elements in lake sediments is also affected by morphological properties, such as the size of the catchment area, the surface area and depth of a given lake and the shape of the lake basin. In industrial, urbanized and agricultural areas, lake sediments are contaminated by heavy metals contained in wastewater which is sometimes discharged to surface waters. An increase in the concentration of heavy metals in lake sediments is often caused by their deposition from the atmosphere as well as from rain and snowmelt runoff from urbanized and agricultural areas (BIRCH et al. 2001, LINDSTROM, 2001, MECRAY et al. 2001, ROCHER et al. 2004, REISS et al. 2004, WILDI et al. 2004). Heavy metals and other hazardous substances found in lake sediments may accumulate in the trophic chain up to a level which is toxic to organisms, especially predators. Such elements and compounds may also be harmful to humans (Šmejkalová et al. 2003, Vink 2009). Moreover, sediments with high amounts of hazdrous constituents are a potential source of environmental contamination.

Copper is an essential element in many organisms because of its involvement in the carbohydrate metabolism and in functions of several enzymes. However, excessive concentrations of copper can be toxic. Besides, copper is one of the most toxic metals in an aquatic environment (Beaumont et al. 2000, Dethloff et al. 2001), with algae being particularly sensitive to this metal. Regarding fish, high copper concentrations cause gill damage and disturbances in the transport and excretion of sodium and potassium chlorides as well as Na+/K+-ATPase inhibition (Cerqueira, Fernandes 2002, Grosell et al. 2002, 2004, Takasusuki et al. 2004, De Boeck et al. 2007, Sorour, Harbey 2012). Copper, known to man for over 6000 years, is widely used in different industries, e.g. its alloys can be found in many tools, brake discs, heat exchangers, jewellery, electrical systems; copper is also a component of algaecides, fungicides and molluscicides. It is released to the environment from many sources, including coal combustion, copper ore processing, copper processing in metallurgy, transport, agriculture (microfertilizer, pesticides, feed additive, control of algae and pathogens in fish breeding ponds). Due to the harmful effects of copper to aquatic organisms, its permissible level in sediments has been set at 149 mg kg^{-1} (MacDonald et al. 2000. Alkalinity, hardness and pH of water strongly influence the speciation of copper in sediments and consequently its availability to aquatic organisms (Carvalho, Fernandes 2006). In the hypergene zone, copper is mobile under aerobic conditions, especially in an acidic environment. However, it is readily captured by sediment components, mainly organic matter and hydrated iron oxides.

MATERIAL AND METHODS

The Gniezno Lake District is located in the eastern part of the Great Poland Lake District, between the Warta River valley and Gopło Lake. Its relief was shaped by the Vistulian Glaciation. Among the lakes, N-S and NE-SW-oriented ribbon lakes are dominant. All Pleistocene and Holocene deposits (tills and ice-dammed lake sediments, clays, sands, muds, peats and gyttjas) in this area are characterized by a low content of potentially harmful metals and metalloids. Sediment samples were collected from the 5-cm thick surface layer of the profundal zone in 14 lakes (Brdowskie, Budzisławskie, Godowskie, Gosławskie, Licheńskie, Lubstowskie Mąkolno, Pątnowskie, Powidzkie, Powidzkie Małe, Suszewskie, Ślesińskie, Wąsosko-Mikorzyńskie and Wilczyńskie) located in the south of the Gniezno Lake District near Konin (Figure 1, Table 1). Each sediment sample was averaged from two or three independent samplings taken from a single deeper place of the lake.

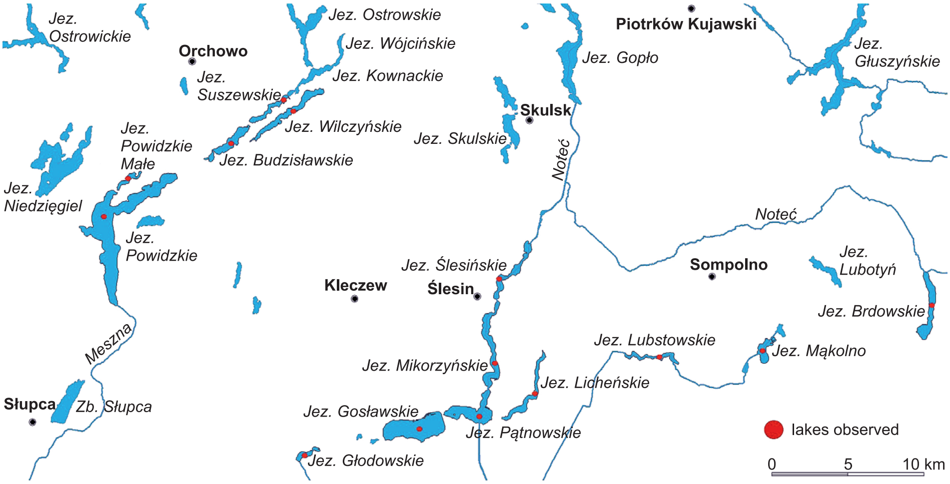

Fig. 1. Geographic location of sampled lakes

Table 1

The characteristics of sampled lakes

No	Lake	Area (ha)	Maximum depth (m)	Average depth (m)	Volume (thousand m^3)
Lakes outside in the power plant cooling system					
1	Brdowskie	194.7	4.9	2.5	4 796.2
2	Budzisławskie	140.8	35.2	10.8	15 240.8
3	Głodowskie	93.9	8.2	4.5	2 600.3
4	Lubstowskie	85.3	5.9	2.5	2 142.7
5	Mąkolno	82.5	6.7	3.2	2 636.8
6	Powidzkie	1 035.9	45.4	12.7	131 279.2
7	Powidzkie Małe	52	7.5	3.5	1 820
8	Suszewskie	81.7	21.8	6.5	5 325.7
9	Wilczyńskie	173.8	23.2	7.3	12 615.4
Lakes within the power plant cooling system					
10	Gosławskie	454.5	5.3	3.9	13 485.3
11	Licheńskie	147.6	12.6	4.5	67 12.3
12	Pątnowskie	282.6	5.5	2.6	7 255.4
13	Ślesińskie	152.3	24.5	7.6	11 5500
14	Wąsosko-Mikorzyńskie	251.8	36.5	11.5	29 050.1

The sediment samples were dried at room temperature and sieved through 0.2-mm mesh nylon sieves to obtain a grain fraction finer than 0.2 mm, which was used for analytical studies. The sediment fraction with grains less than 0.2 mm faithfully reflects the concentration of trace elements in rocks of the catchment area of a lake or river, and therefore this grain fraction is most commonly used in geochemical mapping and monitoring studies. Concentrations of copper as well as Ag, As, Ba, Cd, Co, Cr, Cu, Ni, Pb, Sr, Ti, V, Zn and elements included in the phases whose compounds can retain pollutants in aquatic sediments (Ca, Mg, Fe, Mn, P and S) were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) from solutions obtained after digestion in *aqua regia*. The detection limits for the elements were as follows: Ag and Cd – 0.5 mg kg^{-1}, Co, Cr, Cu, Mn, Ni, Sr and Zn – 1 mg kg^{-1}, As – 3 mg kg^{-1}, Pb – 2 mg kg^{-1}, P and S – 0.005%, Ca, Fe, Mg – 0.01%. The mercury concentration was determined on a solid sample using the absorption spectrometry method with pre-concentration on a gold amalgamator trap with the detection limit of 0.005 mg kg^{-1}. Total organic carbon (TOC) was determined by coulometric titration of a solid sample, after removal of carbonate carbon by hydrochloric acid, with the determination limit of 0.01%.

The results were subjected to statistical analysis. Statistical parameters such as a mean, geometric mean, median, minimum, maximum, standard deviation and correlation matrix were determined using the Statistica software. While computing averages, geometric means, medians, standard deviation and correlation matrix, whenever the determined content of an element was below the detection limit set for a given analytical method, half of the detection limit value was taken for calculations.

RESULTS AND DISCUSSION

Concentrations of some trace elements varied over a wide range of concentrations: for copper – 9-674 mg kg^{-1}, barium – 57-409 mg kg^{-1}, mercury – 0.058-0.366 mg kg^{-1}, nickel – 5-25 mg kg^{-1}, lead – 16-53 mg kg^{-1}, strontium – 53-758 mg kg^{-1} and for zinc – 30-184 mg kg^{-1} (Table 2). It has been found that the sediments from the lakes Gosławskie, Licheńskie, Pątnowskie, Ślesińskie and Wąsosko-Mikorzyńskie are characterized by much higher levels of copper, barium, mercury, manganese, strontium and zinc, and lower concentrations of lead, sulfur and organic matter than sediments from the other lakes, i.e. Brdowskie, Budzisławskie, Godowskie, Lubstowskie, Mąkolno, Powidzkie, Powidzkie Małe, Suszewskie and Wilczyńskie. The average concentrations of copper, nickel, lead, mercury and zinc in the sediments of the latter group of lakes are comparable with concentrations of these elements in sediments of lakes from other regions (Table 3) and are similar to the geochemical background values. They are distinguished only by a higher content of barium and strontium. The sediments from the lakes involved in the Konin-Pątnów power plant cooling system have a distinctly high concentration of copper: the geometric mean is 385 mg kg^{-1}, which is 35-fold higher than a mean copper concentration in lake sediments. In Poland, the average Cu concentration in sediments is 7 mg kg^{-1}. The average content of barium

Table 2

Statistical parameters of elements in the lake sediments

Element	Lakes within the power plant cooling system						Lakes outside the power plant cooling system					
	a	*b*	*c*	*d*	*e*	*f*	*a*	*b*	*c*	*d*	*e*	*f*
Arsenic (mg kg^{-1})	3	<3	3	<3	4	<3	6	4	6	<3	11	4
Barium (mg kg^{-1})	317	309	329	217	409	80	100	93	92	57	196	44
Chromium (mg kg^{-1})	9	8	8	7	11	2	8	7	6	4	16	4
Zinc (mg kg^{-1})	133	129	133	88	184	35	71	63	67	30	144	37
Cadmium (mg kg^{-1})	<0.5	<0.5	<0.5	<0.5	<0.5	0.0	0.8	0.7	0.7	0.5	2.0	0.6
Cobalt (mg kg^{-1})	2	2	2	1	3	1	2	2	1	1	4	1
Copper (mg kg^{-1})	415	385	412	203	679	174	14	14	13	9	24	5
Nickel (mg kg^{-1})	21	20	19	17	25	4	8	8	6	5	13	3
Lead (mg kg^{-1})	20	20	21	16	26	4	38	33	36	12	69	19
Mercury (mg kg^{-1})	0.179	0.152	0.149	0.060	0.366	0.114	0.091	0.084	0.089	0.037	0.160	0.037
Strontium (mg kg^{-1})	618	613	618	526	758	91	252	193	195	53	717	211
Vanadium (mg kg^{-1})	10	10	10	7	15	3	12	11	9	6	17	4
Phosphorus (%)	0.091	0.089	0.091	0.070	0.114	0.019	0.078	0.075	0.069	0.049	0.120	0.024
Magnesium(%)	0.41	0.41	0.41	0.37	0.43	0.03	0.30	0.29	0.27	0.22	0.45	0.07
Manganese (mg kg^{-1})	1017	935	934	587	1874	505	501	451	500	166	874	224
Sulphur (%)	0.650	0.640	0.613	0.520	0.814	0.126	0.980	0.927	0.956	0.440	1.580	0.328
Calcium (%)	22.51	22.46	21.37	21.19	24.95	1.71	17.50	15.96	19.74	4.76	24.32	6.47
Carbon org. (%)	5.37	5.32	4.99	4.68	6.81	0.85	8.53	8.22	7.29	5.43	13.82	2.57
Iron (%)	0.88	0.86	0.85	0.60	1.13	0.21	0.78	0.54	0.85	0.09	1.38	0.52

a – mean, *b* – geometric mean, *c* – median, *d* – minimum, *e* – maximum, *f* – standard deviation

in the sediments of the above lakes was three times as high as in whole Poland and the average content of nickel, mercury and zinc was double the Polish average.

The results showed that the concentrations of arsenic, cadmium, cobalt, chromium and vanadium in the sediments were low and characterized by a relatively low variability. They varied within the following intervals: for arsenic <3-11 mg kg^{-1}, cadmium – <0.5-1.3 mg kg^{-1}, cobalt – 1-4 mg kg^{-1}, chromium – 4-16 mg kg^{-1} and vanadium – 6-15 mg kg^{-1} (Table 2). These values are similar to the ones measured in sediments of lakes in the drainage basins of the Ełk and Augustów Lake District, the Włodawa and Łęczna Lake Districts and in the Suwałki Lake District (Table 3).

The copper concentration in sediments of lakes connected to the Konin-Pątnów power plant cooling system shows a significant correlation (r > 0.9, p=0.05, n=5) with the chromium, mercury and zinc concentrations. And its content in sediments of the lakes outside

Table 3

Geometric means of the content of trace elements in lake sediments of different regions ($mg\ kg^{-1}$)

Element	Ełk and Augustów Lake District	Suwałki Lake District*	Łęczyca and Włodawa Lake District**	Konin Lake District	
				lakes outside the power plant cooling system	lakes within the power plant cooling system
Arsnic	6	7	7	4	<2
Barium	94	94	70	93	309
Cadmium	0.6	0.7	1.3	0.7	<0.5
Chromium	10	10	8	7	8
Cobalt	2	3	3	2	2
Copper	13	11	11	14	385
Lead	26	28	39	33	20
Mercury	0.098	0.083	0.146	0.084	0.152
Nickel	7	8	8	8	20
Strontium	83	66	183	193	613
Vanadium	15	15	11	11	10
Zinc	78	74	101	63	129

* BOJAKOWSKA, GLIWICZ (2009*a*)

** BOJAKOWSKA, GLIWICZ (2009*b*)

the power plant cooling system is correlated ($r \approx 0.6$-0.7, $p = 0.05$, $n = 9$) with the concentrations of arsenic, cobalt, nickel and chromium.

The water from the lakes Licheńskie, Gosławskie, Pątnowskie, Wąsowsko-Mikorzyńskie and Ślesińskie has been drawn to the Konin-Pątnów power plant cooling system from over 50 years. Consequently, the lakes have been loaded with copper from corroded heat exchangers made of copper or its alloys. This undermines the long-held opinion that cooling water from power plants is chemically pure and its discharge to surface waters causes only thermal pollution of the environment. The past and present use of copper sulfate as a compound limiting the occurrence of algal blooms, e.g. in fish ponds and power plant cooling ponds, can be an additional source of copper in lakes.

The problem of environmental pollution with copper due to the discharge of cooling water from power plants is rarely discussed. Most studies focus on biological aspects of the impact of discharging heated cooling water on the aqueous environment, like disturbances in the species composition of flora and fauna. The scope of research is only occasionally expanded onto chemical investigations of organisms in water habitats, and the risk of chemical pollution with copper is very rarely considered. A negative impact of copper on snails and copper bioaccumulation in the tissues of riverine snails were found in receiver cooling water the Clinch River, Virginia USA (REED-JUDKINS et al. 1997). Concentrations of copper in plankton due to the cooling system of a nuclear power plants in Beloyarsk were discussed by GUSEVA and CHABOTINA (2000). The accumulation of copper and other heavy metals in the tissues of *Vallisneria spiralis* (L.), *Sinanodonta woodiana* (Lea), and *Dreissena polymorpha* (Pall.) from lakes around Konin in Poland was demonstrated by KRÓLAK et al. (2007).

The current study on lakes sediments in the region of Konin has revealed their high copper concentrations (a geometric mean of 385 mg kg^{-1}), which may cause harmful effects of copper on aquatic organisms (the boundary limit is >150 mg kg^{-1}). The analyzed lake sediments are also characterized by very high levels of calcium, organic matter and iron components, which can significantly affect the bioavailability of copper. However, it is necessary to perform further tests, such as determinations of the copper content in fish tissues and histological examinations of fish gills, because these lakes are used for recreational and angling purposes on a large scale.

CONCLUSIONS

1. The sediments of the lakes Licheńskie, Gosławskie, Pątnowskie, Wąsowsko-Mikorzyńskie and Ślesińskie, whose waters are drawn into the Konin-Pątnów power plant cooling system, are characterized by higher concentrations of copper, barium, mercury, manganese, strontium and zinc, and lower levels of lead, sulfur and organic matter than uncontaminated lakes.
2. The geometric mean content of copper in the sediments of lakes included in the cooling system is 385 mg kg^{-1} and is 35-fold higher than its average content in lake sediments from other regions.
3. The content of copper, barium, mercury, lead, strontium and zinc in the analyzed lake sediments, except lakes within the power plant cooling system, was comparable to the content in lake sediments of other lake districts.
4. The content of arsenic, cadmium, cobalt, chromium and vanadium in the analyzed sediments was low and similar to the content of these elements in lake sediments of other lake districts.
5. Copper contamination of sediments of the lakes involved in the cooling system is probably due to corrosion of heat exchangers made of copper or its alloys.

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