Pol. J. Environ. Stud. Vol. 23, No. 4 (2014), 1317-1321

Short Communication

Concentrations of Metals in Water of Unmonitored Lakes Near a Landscape Park

Krzysztof Gwoździński[1]*, Janusz Mazur[2], Anna Pieniążek[3]

[1]Department of Molecular Biophysics,
[2]Laboratory of Computer and Analytical Techniques,
[3]Department of Thermobiology,
University of Łódź, 90-236 Łódź, Poland

Received: 4 November 2013
Accepted: 4 May 2014

Abstract

The concentrations of metals in water of unmonitored lakes in Bory Tucholskie near the southwestern border of Wdzydzki Landscape Park were evaluated using atomic absorption spectroscopy. Twelve elements were divided into two groups: alkaline metals (Na, K, Ca, Mg) and heavy metals (Zn, Mn, Fe, Cu, Cr, Ni, Pb, Cd). Concentrations of these metals were determined in water of the following lakes: Brzeźno, Młosino Wielkie, Raduń, and Młosino Małe. The highest concentration of heavy metals was noted in Młosino Małe, but in other lakes it was lower and declined in the following order: Raduń, Brzeźno, and Młosino Wielkie. These lakes differ in trophy conditions and water purity.

Keywords: monitoring of lakes, alkaline metals, heavy metals, Bory Tucholskie

Introduction

Metals enter lake and river water from a variety of natural and anthropogenic sources such as rainfall, geologic weathering, agriculture, municipal, and industrial waste products. Generally, in natural, uncontaminated environments the concentrations of most of metals is very low. They can enter water from atmospheric deposition during rainfall because global atmospheric pollution increases [1]. They can be transported by air for long distances in the form of dusts and powders. For example, fuel and gasoline combustion is one of the important sources of heavy metals [2]. During rain, surface water with soil, mud, and humus enters lakes, rivers, and other water reservoirs.

Heavy metal concentrations in water depends on physicochemical parameters of water, such as pH, oxygen concentration, the presence of chelators, anions, like sulphates, phosphates, humic acids, and more [3]. Most heavy metals are immobilized and accumulate in sediments. Heavy metals such as iron, copper, and zinc, are essential for life at trace levels. These metals are essential components of many proteins and enzymes in living organisms. On the other hand, at higher concentrations they become a serious threat to people and ecosystems [4].

Pollution of aquatic environments by heavy metals has an important influence on survival of aquatic organisms, plants, and animals, including fish. Their accumulation can damage function of enzymes and proteins and induce damage of cells, tissues, and organs [5-7]. Heavy metals are potential catalysts in many chemical reactions and biochemical processes.

Bory Tucholskie is one of the largest pine forests in Poland, situated in a postglacial area crossed by numerous streams, rivers, and lakes. In 2010 it became a biosphere reserve. It spreads over 3,000 km^2. This area consists of a national park, four landscape parks, and a Natura 2000 area. Nearly 60% of the surface of this area is covered by pine forest. Due to an increase in the number of tourists and development of urbanization with local sources of pollution this area should be intensively monitored. However, lakes

*e-mail: kgwozdz@biol.uni.lodz.pl

Table 1. Morphometrical characteristics of the monitored lakes.

Name of lake	Area [ha]	Volume [×1000 m³]	Max. Depth [m]		Max. Length [m]	Max. Width [m]
Brzeźno	71.6	3146.9	9.7	8.0*	2405	560
Młosino Wielkie	66.0	4784.3	22.4	21*	1780	575
Raduń	29.5	1268.5	12.7	12*	850	450
Młosino Małe	15.2	325.7	10.7	9.0*	815	375

*results measured in this study

Brzeźno, Młosino Wielkie, Raduń, and Młosino Małe are not frequently monitored.

The aim of this study was to determine the content of alkaline and heavy metals in the water of four selected lakes located near the southwestern border of Wdzydzki Landscape Park in comparison to other previously investigated basic physicochemical parameters of waters.

Experimental Procedure

Description of the Study Area

The selected lakes (Brzeźno, Młosino Wielkie, Raduń, and Młosino Małe) in Bory Tucholskie are situated near the southwestern border of Wdzydzki Landscape Park. The natural postglacial origin is covered mainly by forest and meadows. Lakes Brzeźno, Młosino Małe, and Młosino Wielkie are situated on the trail of Młosina river. Lake Raduń is connected with Młosino Wielkie lake by a small stream. All studying lakes are located in Chojnicki district and have different size, depth, and trophy of water. All lakes are situated in the northwestern subglacial channel. Locations of the investigated lakes are shown below (Fig. 1).

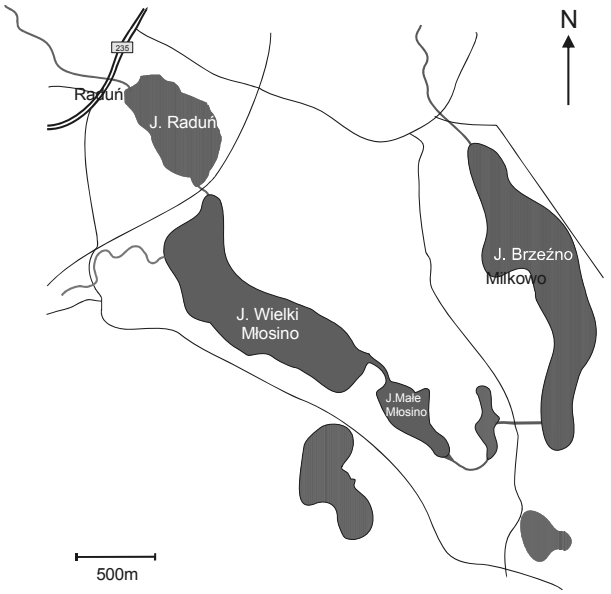

Fig. 1. Map of the selected lakes.

Collection and Treatment of Samples

Samples of water were taken in the deepest part of each lake twice a year, during the spring mixing time and summer thermal stratification 1 m under the surface and 1 m over the bottom. The deepest point of the lake was determined by a sonic sounder. The samples were taken using a Patalas sampler and were filtered using medium paper filter. To each 50 ml sample 0.5 ml of conc. nitric acid was added immediately after collection and filtration. The samples were stored for 24 hours at 4ºC before measurements.

The concentration of metals in the samples of water was measured using an atomic absorption spectrometer Varian Spectra A300/400 in the acetylene-air or nitrous oxide flame or in electric atomizer (GTA 96) in a graphite cuvette (for heavy metals). The concentrations of metals are expressed in $mg \cdot dm^{-3}$ or $\mu g \cdot dm^{-3}$. Basic parameters of water were determined strictly according to the current Polish standards and recommendations used in monitoring of lake water [8-11]. The results are presented as metal concentrations from spring and summer.

Results

Morphometric and bathymetric data of lakes were taken from Choiński [12] and Jańczak [13] and are given in Table 1.

Characteristics of Physicochemical Parameters of Waters of the Selected Lakes

Basic physicochemical parameters of waters of studied lakes were presented in an earlier study [14].

Brzeźno lake was the biggest in the group of studied lakes. In turn, Młosino Wielkie lake was the deepest (22.4 m) in this area. During the summer stagnation lakes Młosino Wielkie and Raduń were characterized by stratification of waters. Thickness of epilimnion was between 7 m and 4 m, respectively. Oxygen concentration was very low and near the bottom was approx. 0.33 $mg \cdot dm^3$ [14]. The range of basic physicochemical parameters is shown in Table 2.

The range of all physicochemical factors is broad. The pH value of water is an important indicator of its quality and it depends on the carbon dioxide and bicarbonate-carbonate equilibrium. The pH value of water was between

Table 2. Selected physicochemical factors (the range of values from spring and summer sampling dates) of investigated lakes.

Parameters	Mesotrophic lakes
Transparency [m]	0.95-2.4
pH	7.4-7.7
Specific electrolytic conductivity [mS·cm^{-1}]	271-371
Phosphate concentration [mg P·dm^{3}]	0.84-1.37
Nitrate concentration [mg N·dm^{3}]	4.22-12.91

7.4-7.7 in the studied lakes. For Lake Młosino Wielkie the best transparency of water was observed. In other lakes transparency was much lower (Table 2). Electrolytic conductivity was elevated in Raduń, but in other lakes it was lower. Bigger differences were found in concentrations of phosphate, nitrate, chloride, and sulphate ions.

Metal Concentrations in Lakes

Concentrations of alkaline and heavy metals in lake water are expressed in mg·dm^{-3} or μg·dm^{-3}, respectively. The concentrations of alkaline metals such as sodium, potassium, magnesium, and calcium in the lakes are given in Table 3.

In summer the decrease in the levels of alkaline metals in comparison to spring was observed for all lakes except calcium ions (Table 3). The small differences between their concentrations under the surface and over the bottom as an average in spring and summer were observed.

For comparison of metals concentrations in all studied lakes, the average values from the surface and bottom of each of them were estimated for spring and summer. Concentrations of sodium in lake waters varied from 2.6 mg·dm^{-3} in lake Brzeźno to 4.7 mg·dm^{-3} in Młosino Małe lake. The level of potassium was approx. 2 times higher in Brzeźno than that found in Młosino Małe. Concentrations of magnesium were the lowest in Brzeźno (1.8 mg·dm^{-3}) and the highest in Raduń (4.6 mg·dm^{-3}). In turn, concentrations of calcium were in the range 17.5 mg·dm^{-3} in Brzeźno to 36.2 mg·dm^{-3} in Młosino Małe.

Larger changes in the range of concentrations were observed in the case of heavy metals. Table 4 shows the levels of these metals in the studied lakes.

The highest concentrations of manganese (171.4 μg·dm^{-3}) were found in Raduń, the lowest in Brzeźno (55.6 μg·dm^{-3}). Maximal concentration of iron was found in Młosino Małe (103.3 μg·dm^{-3}) and minimal in Młosino Wielkie (16.5 μg·dm^{-3}).

The lowest concentration of copper, 2.4 μg·dm^{-3}, was found in Młosino Wielkie and the highest in Raduń and Młosino Małe (4.0 μg·dm^{-3}).

In turn, the lowest concentration of zinc was found in Młosino Wielkie (5.4 μg·dm^{-3}) and the highest in Brzeźno and Młosino Małe (14.2 μg·dm^{-3} and 14.3 μg·dm^{-3}, respectively). Cadmium and lead appeared at the highest concentrations in the water of all lakes in the narrow range 1.5-1.8 μg·dm^{-3} and 13.0-16.7 μg·dm^{-3}, respectively. The range of nickel concentrations was also narrow in all the studied lakes: 1.5-2.1 μg·dm^{-3}. Chromium concentrations were low in all lakes below 1 μg·dm^{-3}.

Discussion of Results

All studied lakes are of natural origin, situated in pine forests (77%) and meadows.

The concentrations of metals in water depend mainly on the geological structure of the catchment and intensity of material transport into water of lakes [14]. Although the lakes are connected and are situated on the route of the Młosina River, they are characterized by different values of pH, transparency of water, and anion content, as well as alkaline and heavy metals. In this area any apparent signs of anthropopressure are rather lacking. There is no significant source of human impact in this region. However, on

Table 3. Concentration of alkaline metals (mg·dm^{-3}) in water of chosen lakes.

Name of Lake		Na		K		Mg		Ca	
		spring	summer	spring	summer	spring	summer	spring	summer
Brzeźno	S	3.6	1.6	3.7	0.4	3.1	0.5	31.7	2.3
	B	3.6	1.6	4	0.4	3.1	0.5	33.6	2.4
Młosino Wielkie	S	4.0	3.5	1.0	0.8	3.9	4	24.2	28.7
	B	4.1	3.6	1.6	0.9	3.7	4.2	34.8	30.2
Raduń	S	5.3	3.4	1.9	0.8	5.5	3.7	14.5	31.4
	B	5.3	3.3	1.8	1	5.6	3.7	43.2	32.9
Młosino Małe	S	3.6	4.3	1.2	1.1	2.0	5.1	28.2	35
	B	-	4.7	-	1.8	-	6.1	-	45.26

S – 1 meter below the surface of the water
B – 1 meter above the bottom

Table 4. Concentrations of heavy metals (μg·dm^{-3}) in water of chosen lakes.

Name of Lake		Mn		Fe		Cu		Zn		Cd		Pb		Ni		Cr	
		spring	summer	spring	summer	spring	summer	spring	summer	spring	summer	spring	summer	spring	summer	spring	summer
Brzeźno	S	92.9	44.1	35.3	119	5.1	2.8	8.2	16.7	< 1	1.3	3.31	17.3	1.5	1.5	< 1	< 1
	B	44.4	41	23	146	3.9	3.4	5.3	26.6	2.7	1.3	19.3	12.2	1.3	1.7	< 1	< 1
Młosino Wielkie	S	7.2	41.1	15.7	13	0.6	2.2	0	7.9	< 1	2	0.2	26.1	0.8	1.7	< 1	< 1
	B	100	90	20.8	16.5	4.3	2.4	6	7.7	1.2	1.4	8.5	31.8	1.6	1.8	< 1	< 1
Raduń	S	200	44.4	16.4	18.3	5.3	3.2	2.6	10.5	< 1	1.3	2.4	30.6	1.3	2.8	< 1	< 1
	B	209	232	15.5	16.6	4.7	2.9	3.8	11.4	< 1	2.2	5	16.1	1.2	2.2	< 1	< 1
Młosino Małe	S	80.1	22.2	73.9	18.9	3.7	4.2	17.8	11.3	2.4	< 1	15	9.1	1.2	2.5	< 1	< 1
	B		262	-	217	-	4.1	-	13.9	-	1	-	25	-	2.7		< 1

S – 1 meter below the surface of the water
B – 1 meter above the bottom

the shores of Brzeźno the village and recreation and sport centre are situated, which affects the quality of the lake water. For example, in 1997 Brzeźno lake was in the first class of water purity but in 2010 was in the second class, near the third class [15].

The concentration of alkaline metals in the studied lakes was compared with lakes Kosobudno, Dybrzk, and Łąckie in Zaborski Landscape Park (ZPK), characterized by similar trophy and class of water purity [16]. Only the concentration of calcium, which stayed at the medium range, was lower in the studied lakes than in the water of lakes in ZLP. Low levels of calcium and magnesium classified these lakes as soft-water lakes. On the other hand, the lowest concentrations of alkaline and heavy metals were found in lakes situated in Bory Tucholskie National Park [17].

Higher differences were noted in the case of heavy metals. For example, manganese concentrations were similar in both groups of lakes except Raduń, where the highest concentration was determined. The highest concentration of manganese in Raduń may be caused by inflow of a stream from the agricultural area in the northern part of the lake and/or the effect of geological conditions. A similar situation occurs in the case of Brzeźno, where the highest cadmium concentration was found.

The levels of iron and copper were similar. Concentration of zinc in lakes in ZLP was 3-4 fold higher than in the studied lakes (except Młosino Małe). However, concentrations of lead and cadmium were more than 2-times lower than in the group of studied lakes. For example, a higher concentration of heavy metals in comparison to studied lakes was found in water from the agricultural area [18]. An interesting tendency in the content of heavy metals was observed in Goczałkowickie Lake. The increase of manganese and iron concentrations and a decrease of the copper and lead levels from 1994 to 2007 was found [19].

After comparison with current official standards we can conclude that the quality of waters in the studied lakes was in good condition with some exceptions. In terms of concentrations of alkaline metals, all studied lakes were in the first class of water purity. In the case of heavy metal concentrations they did not exceed the concentration of metals such as iron, copper, zinc, nickel, and chromium adopted for I class of water purity. However, higher concentrations of manganese were observed in the waters of all the studied lakes. Lakes Brzeźno and Młosino Wielkie could be classified to class II, while lakes Raduń and Młosino Małe to the grade III of purity water. We also observed exceeding of standards for class III for cadmium concentrations in all the studied lakes. We also detected high concentrations of lead in all lakes, in class III of water purity.

Conclusions

The present study reveals that most water samples of lakes were found less polluted by heavy metals, except cadmium and lead, and show a trend in seasonal variation.

The occurrence of heavy metals in the studied ecosystems might come from materials derived from geological sources, and from air as dusts and powders, as well as anthropogenic sources.

The highest concentrations of heavy metals were determined in Młosino Małe, while in other lakes a decrease of these metal levels was observed in the following order: Raduń, Brzeźno, and Młosino Wielkie.

We conclude that the concentrations of heavy metals in water of the studied lakes were lower in comparison to other lakes [17, 18]. However, these lakes are situated generally in uncontaminated areas in forests, far from towns and potential sources of pollution.

References

1. DE VLEESCHOUVWER F., GERARD L., GOORMAGHTIGH C., MATIELLI N., LE ROUX G., FAGEL N., Atmospheric lead and heavy metal pollution records from a

Belgian peat bog spanning the last two millennia: Human impact on a regional to global scale. Sci. Total Environ. **377**, 282, **2007**.
2. PACYNA E., PACYNA J., FUDALA J., STRZELECKA-JASTRZAB, HILAWICZKA S., PANASIUK D., NITTER S., PREGGER T., PFEIFFER H., FRIEDRICH R. Current and future emission of selected heavy metals to the atmosphere from anthropogenic sources in Europe. Atmos Environ. **41**, 8557, **2007**.
3. ERDOGAN S., BAYSAL A., AKBA O., HAMAMCI C. Interaction of metals with humic acid isolated from oxidized coal. Pol. J. Environ. Stud. **16**, 671, **2007**.
4. JARUP L. Hazards of heavy metal contamination. Brit. Med. Bull. **68**, 167, **2003**.
5. ARAZKIEWICZ M., SKORZYNSKA-POLIT E., KRUPA Z. Effect of BSO-supplemented heavy metals on antioxidant enzymes in *Arabidopsis thaliana*. Ecotox. Environ. Safe. **73**, 1362, **2010**.
6. SAROSIEK B., PIETRUSEWICZ M., RADZIWONIUK J., GLOGOWSKI J. The effect of copper, zinc, mercury and cadmium on some sperm enzyme activities in common carp (*Cyprinus carpio*). Reprod. Biol. **9**, 295, **2009**.
7. KAMIŃSKI P., KURHALYUK N., SZADY-GRAD M.. Heavy metal-induced oxidative stress and changes in physiological process of free radicals in the blood of white stork (*Ciconia ciconia*) chicks in polluted areas. Pol. J. Environ. Stud. **16**, 555, **2007**.
8. KUDELSKA D., CYDZIK D., SOSZKA H. Guidelines for basic monitoring of lakes. State Inspectorate for Environmental Protection. Warsaw, **1994** [In Polish].
9. Regulation of the Minister of Environment: Order on the classification of the state of surface water. 20 August, **2008** [In Polish].
10. Regulation of the Minister of Environment: On the forms and methods of monitoring of surface water bodies and groundwater. 13 May **2009** [In Polish].
11. DOJLIDO J., DOŻAŃSKA W., HERMANOWICZ W., KOZIOROWSKI B., ZERZE J. Fizyczno-chemiczne badanie wody i ścieków. Arkady, Warszawa, **2010**.
12. CHOIŃSKI A., Catalogue of Polish Lakes, Wydawnictwo Naukowe UAM: Poznań. **2006** [In Polish].
13. JAŃCZAK J., Atlas of Polish Lakes. Poznań, **1997** [In Polish].
14. GWOŹDZIŃSKI K., KILAŃCZYK E., KISZAŁKIEWICZ J., OWCZAREK K., POPIEL D., SOBAŃSKA M., WEBER M. Quality of water of not monitored lakes near the western border of the Wdzydzki Landscape Park. Anthropogenic and natural transformations of lakes. Ed. W. Marszelewski, Nicolaus Copernicus University: Toruń, **5**, 57, **2011** [In Polish].
15. TYLMAN W., LYSEK K., KINDER M., PEMPKOWIAK J. Regional pattern of heavy metal content in lake sediments in northeastern Poland. Water Air Soil Poll. **216**, 217, **2011**.
16. KACZMAREK A., KISTOWSKI M., KOSTKA A. The sozological 1:50,000 scale map-sheet Karsin. Rocznik fizycznogeograficzny. University of Gdańsk. 113, **1999** [In Polish].
17. GWOŹDZIŃSKI K., MAZUR J., KILAŃCZYK E., PIENIĄŻEK A. Metals in water of selected lakes in the central and the northern part of Zaborski Landscape Park, Ecol. Chem. Eng. **11**, 1075, **2004**.
18. GWOŹDZIŃSKI K., MAZUR J. The content of heavy metals and alkaline metals in the water of the lakes in the Bory Tucholskie (Pinewoods) National Park. In. Park Narodowy Bory Tucholskie. Eds. J. Banaszak and K. Tobolski. Park Narodowy: Charzykowy, 43, **2002** [In Polish].
19. KARLIK B., SZPAKOWSKA B. Labile Organic matter and heavy metals in water of agriculture landscape. Pol. J. Environ. Stud. **10**, 85, **2001**.
20. CZAPLICKA-KOTAS A., ŚLUSARCZYK Z., ZAGAJSKA J., SZOSTAK A. Variations in the content of some heavy metals observed in lake Goczałkowickie in the time span of 1994-2007. Ochrona Środowiska. **32**, 52, **2010** [In Polish].