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METAL POLLUTION OF SURFACE WATER FROM WIELKOPOLSKA REGION

ZANIECZYSZCZENIE METALAMI WÓD POWIERZCHNIOWYCH WIELKOPOLSKI

Abstract: Polish water resources in comparison to other European countries are small. It is one of the factors leading to increased interest in monitoring tests for their quality. Heavy metals are major water pollutants in Poland. The aim of this study was to determine seasonal variability in concentrations of cadmium, lead, zinc and copper in various reservoirs and water courses in the Wielkopolska region. Water samples were collected from lakes, large and small rivers and drainage ditches. These water bodies differ in land use in the surrounding. These were mostly rural. The study was conducted during the growing season from May to December 2012. Quantitative analysis of heavy metals was performed on the AA spectrometer Agilent 280Z. The results showed high seasonal variation in heavy metal contents in different water bodies. The concentrations of cadmium and zinc mainly depend on the date of discharge to water. Lead concentrations were caused by emissions and depended mainly on cultivation measures in fields. The highest concentration of copper was observed in the lakes, which could be due to the use of compounds that eliminate algal blooms. Under Polish law, all water bodies are classified into water quality classes I or II intended for drinking. Living conditions for cyprinids and salmonids were satisfactory in all the locations.

Keywords: heavy metals, surface waters, Wielkopolska

Introduction

The hydrosphere is struggling with surface water pollution with different undesirable substances. As a result municipal and industrial waste waters have to be treated before they may discharged into rivers and various water bodies. The main sources of water pollution include: industrial waste water discharge, discharge of cooling water from the power industry, mine water discharge, surface runoff from agricultural areas, runoff from landfills and industrial areas and pollution from precipitation [1, 2].

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Heavy metals are elements which have a specific gravity greater than 4.5 grams per cubic centimeter [3]. In various chemical reactions they tend to donate electrons to form cations. They are characterized by good electrical and thermal conductivity, have high boiling and melting points and exhibit reducing properties. They are toxic to living organisms and some of them have radioactive properties. Pollution of these elements is a worldwide problem, as they are irreducible and their accumulation at a particular place can be toxic to living organisms [4–6]. Their circulation and migration in the environment is caused by processes such as weathering of rocks, steaming oceans, volcanic eruptions or forest fires. Inorganic metal compounds are most dangerous to living organisms as they easily break down and permeate through the mucous membranes, and thus get into the internal organs. Heavy metals usually accumulate in the kidneys, liver, lungs, even in the hair and on the skin. They may cause hypertension, cancer, renal failure, brain and liver diseases, and also lead to a variety of mental disorders [7–11].

Metals in the form of cations have the ability to connect to proteins and biological tissues leading to their bioaccumulation. Each metal has a specific selectivity to connect to different tissues, for example, such as lead and radon accumulate in the bone tissue, while mercury and cadmium in the kidneys [8, 12, 13]. Metal ions bind readily with amino acids, enzymes and -SH groups. These are the active sites, causing disturbances in the functioning of many important enzymes in the body [14]. Surface waters are among the elements of the environment contaminated with heavy metals. Contamination with these elements is generally caused by anthropogenic factors. Rivers in the Upper Silesia region contain more metals than those in the northern part of the country. The Wielkopolska region is exposed to factors that increase heavy metal levels in surface waters, such as agriculture, mainly due to the chemicals used and waste discharge. Increased levels can be caused by the use of compounds to eliminate algae blooms. The presence of certain heavy metals may be caused by emissions from agricultural machines. Water reservoirs due to their location in the lowest point of the catchment area are receivers of pollutants from the whole catchment [15].

The natural content of zinc in river waters is about 10 micrograms per liter. Most inland waters are characterized by a significant content of this element, the Wistula has an average of about 20 to 180 $\mu g \cdot dm^{-3}$ [16]. Zinc toxicity in water is not high and depends on its ionic form. The concentration at 300 $\mu g \cdot dm^{-3}$ can be harmful to a variety of aquatic organisms [17].

Lead naturally occurring primarily in the form of lead (II) sulphide and it is susceptible to treatment. Its properties, however, make it toxic in situations where it is absorbed in large amounts by humans and animals. It is characterized by similar properties to calcium, which is why it is accumulated in the bones of humans and animals [18]. The lead content in unpolluted rivers amounts to micrograms per liter. In polluted waters this value can go up to tens of micrograms.

Sources of cadmium include discarded batteries, industrial and household sewage, fertilizers and plastic waste. The content of cadmium in water depends mainly on anthropogenic factors. The natural content is around $0.02~\mu g \cdot dm^{-3}$ of water. Currently this value is exceeded in most rivers. In the Odra catchment the concentration of this

element is around 1 μ g · dm⁻³ [19]. As a toxic element, it usually causes pathological changes in the kidneys and lungs [7, 8, 20].

Copper is strongly bound by organic matter and clay minerals – it is precipitated as sulphides, sulphates, carbonates, etc. Copper content in the river water is about $1-2 \, \mu g \cdot dm^{-3}$. Rivers in Poland exceed this concentration, even several times. At higher concentrations this element poses a serious risk to aquatic organisms. A high concentration of copper can be detected in the vicinity of copper mines [21].

The aim of this study was to determine seasonal variability in concentrations of selected heavy metals (cadmium, lead, zinc and copper) in various reservoirs and water courses in the Wielkopolska region.

Material and methods

The experimental material consisted of water samples collected on a monthly basis from ten sites around selected ditches and ponds, which were characterized by a diversity of land uses. One of the objectives was to illustrate migration of heavy metals, mainly from agricultural areas to areas not necessarily related to agriculture. Sampling took place in the middle of each month from May to December during the growing season in 2012. Samples (about 2 dm³) were collected using a bucket immersed to a depth of about 20 cm below the water table, which were then transported and stored in sterile canisters (refrigerated conditions) until analysis. Water samples were filtered through Filtrak no. 389 filter paper (Filtrak, Germany) and GF/B filter glass microfiber filters (Whatman, England). Quantitative analysis of copper, zinc, lead and cadmium were performed using 280Z AA spectrometer, which is designed for the determination of trace metals in the environment. Standard solutions of these heavy metals were used at a concentration of 1000 μ g·g⁻¹.

For this purpose, electrothermal atomization is run in a graphite furnace with a zone of constant temperature (GTA module 120). An automatic dosing system makes it possible to adjust the sample volume of a given analyte, down to low concentrations (5–70 mm³). The apparatus is equipped with 8 lamps and is completely automated. This is a big advantage because it allows the spectrometer to perform fast and accurate measurements.

Results and discussion

Water quality assessment indicates whether there is seasonal variability in water components and how natural land features and human activity affect those conditions. Water quality is defined in terms of its physical, chemical and biological parameters [22].

Analyses provided concentrations of selected metals in different water bodies in the Wielkopolska region.

Seasonal variation of cadmium content was observed in selected streams and reservoirs (Table 1). The highest cadmium content was observed in the Miloslawka River amounting to $-0.368 \, \mu \text{g} \cdot \text{dm}^{-3}$ in October while the lowest was detected in

Table 1

Seasonal variation of cadmium in water samples (three replicates for each sample) during growing season in 2012

Location	>	VI	ΙΙΛ	VIII	XI	×	IX	IIX	Seasonal	Standard deviation*
					. gn]	[µg · dm ⁻³]				
Jeziory Male Lake	0.001	0.130	0.164	0.257	0.174	0.199	0.135	0.123	0.148	0.074
Raczynskie Lake	0.018	0.042	0.135	0.145	0.154	0.214	0.168	0.164	0.130	0.066
Miloslawka	0.001	0.017	0.150	0.167	0.125	0.368	0.232	0.200	0.158	0.118
Maskawa	0.005	0.064	0.182	0.239	0.214	0.166	0.209	0.187	0.158	0.081
Struga Sredzka	0.008	0.133	0.208	0.275	0.261	0.205	0.115	0.176	0.173	0.087
Sredzkie Lake	0.002	0.107	0.166	0.223	0.225	0.179	0.166	0.146	0.152	0.072
Drainage ditch Lorenka	0.031	0.162	0.163	0.164	0.149	0.115	0.084	0.078	0.118	0.050
Warta the bridge of Queen Jadwiga	N	0.053	0.150	0.185	0.244	0.168	0.163	0.142	0.158	0.057
Warta near Cytadela	N	0.031	0.186	0.158	0.279	0.085	0.079	990.0	0.126	0.086
Bogdanka	NT	0.175	0.213	0.151	0.237	0.168	0.176	0.154	0.182	0.032

* Calculated standard deviation from the average seasonal aimed to show the seasonal variability of concentrations of heavy metals in each water sample; NT - not tested.

Table 2

Seasonal variation of zinc in water samples (three replicates for each sample) during growing season in 2012

Location	>	VI	IIA	VIII	XI	×	IX	IIX	Seasonal	Standard deviation*
					[µg·dm ⁻³]	dm ⁻³]				
Jeziory Male Lake	0.907	0.121	0.088	0.195	0.155	0.455	0.421	0.332	0.334	0.269
Raczynskie Lake	0.907	0.098	0.156	0.023	0.155	0.451	0.425	0.156	0.296	0.289
Miloslawka	0.913	0.013	0.059	0.065	0.047	0.401	0.387	0.210	0.262	0.305
Maskawa	0.940	0.077	0.172	0.031	0.154	0.423	0.401	0.316	0.314	0.291
Struga Sredzka	0.933	0.005	0.157	0.036	0.095	0.444	0.409	0.303	0.298	0.305
Sredzkie Lake	0.843	0.204	0.083	0.124	0.067	0.415	0.408	0.392	0.317	0.258
Drainage ditch Lorenka	0.783	0.060	0.124	0.012	0.033	0.401	0.386	0.274	0.259	0.262
Warta the bridge of Queen Jadwiga	NT	0.069	0.047	0.039	0.113	0.365	0.323	0.313	0.181	0.145
Warta near Cytadela	NT	0.064	0.043	0.021	0.089	0.395	0.375	0.218	0.172	0.159
Bogdanka	NT	0.082	0.035	0.019	0.099	0.417	0.410	0.402	0.209	0.190

* Calculated standard deviation from the average seasonal aimed to show the seasonal variability of concentrations of heavy metals in each water sample; NT – not tested.

Table 3

Seasonal variation of lead in water samples (three replicates for each sample) during growing season in 2012

	>	IV	IIA	VIII	XI	×	IX	XII	Seasonal	Standard
Location				. gn]	[µg·dm ⁻³]				mean	deviation*
Jeziory Male Lake	0.210	0.581	1.085	2.797	1.172	30.626	12.584	12.084	7.643	10.596
Raczynskie Lake	0.180	0.765	1.633	0.344	0.833	32.182	6.882	5.138	5.995	10.863
Miloslawka	0.323	0.794	1.708	1.395	1.823	8.119	0.198	0.086	1.806	2.640
Maskawa	996.0	2.032	1.661	0.964	2.012	36.769	36.472	32.528	14.176	17.507
Struga Sredzka	0.430	0.893	1.526	0.835	1.568	51.470	27.077	22.158	13.245	18.809
Sredzkie Lake	0.380	1.325	1.034	0.797	2.325	31.272	20.777	18.853	9.596	12.174
Drainage ditch Lorenka	0.206	1.366	1.052	0.828	6.024	000.89	32.130	28.951	17.320	24.304
Warta the bridge of Queen Jadwiga	ZN	968.0	1.087	0.848	26.326	33.076	14.603	10.112	12.421	13.072
Warta near Cytadela	N	0.894	1.246	0.786	30.769	33.747	22.073	18.742	15.466	14.450
Bogdanka	NT	1.269	1.307	0.755	10.258	12.547	25.934	20.185	10.322	10.006

* Calculated standard deviation from the average seasonal aimed to show the seasonal variability of concentrations of heavy metals in each water sample; NT - not

Table 4

Seasonal variation of copper in water samples (three replicates for each sample) during growing season in 2012

Location	>	VI	IIA	VIII	XI	×	IX	IIX	Seasonal	Standard deviation*
					$[\mu g \cdot dm^{-3}]$	dm ⁻³]				
Jeziory Male Lake	4.096	19.523	31.630	29.960	26.346	5.846	0.490	0.444	14.792	13.492
Raczynskie Lake	6.073	17.646	30.980	26.135	25.103	24.198	3.788	3.025	17.119	11.250
Miloslawka	9:056	11.603	15.493	14.322	7.530	5.029	3.021	2.873	8.616	4.889
Maskawa	5.936	15.433	15.746	13.750	7.766	2.903	4.135	4.012	8.711	5.417
Struga Sredzka	4.700	12.846	14.616	13.893	7.851	2.560	999.0	0.602	7.217	5.930
Sredzkie Lake	4.820	50.080	22.117	18.473	11.560	4.405	0.681	0.557	14.087	16.596
Drainage ditch Lorenka	1.483	6.326	13.936	11.330	10.826	3.481	0.309	0.223	5.990	5.442
Warta the bridge of Queen Jadwiga	NT	16.783	17.670	18.816	16.643	0.646	0.423	0.409	10.199	9.107
Warta near Cytadela	NT	19.086	18.190	15.960	10.315	1.708	0.108	0.994	9.480	8.476
Bogdanka	NT	11.656	29.996	27.180	18.753	6.028	1.515	1.054	13.741	11.862

* Calculated standard deviation from the average seasonal aimed to show the seasonal variability of concentrations of heavy metals in each water sample; NT – not tested.

a drainage ditch Lorenka at 0.164 µg · dm⁻³. The highest seasonal average cadmium content was observed in the Bogdanka at 0.182 µg · dm⁻³ of water, whereas it was lowest in the drainage ditch Lorenka at 0.118 µg · dm⁻³. Seasonal variation of zinc was also observed in selected streams and reservoirs. The highest zinc content was recorded in the Maskawa at 0.940 µg · dm⁻³ in May, it was lowest in the Struga Sredzka at 0.005 μg · dm⁻³ in June. The highest seasonal average zinc content was recorded in Lake Jeziory Male at 0.334 µg · dm⁻³ of water and the lowest in the Warta River in two sampling sites, where values did not exceed 0.200 µg · dm⁻³ (Table 2). Lead concentration is also marked by seasonal variation. The highest content was observed in the drainage ditch Lorenka at 68 µg · dm⁻³ in October, the lowest in Miloslawka at 0.086 μg · dm⁻³ in December (Table 3). The highest seasonal average lead content was recorded in the drainage ditch and it amounted to 17.320 µg · dm⁻³ of water, while it was lowest in the Miloslawka at 1.806 µg · dm⁻³. Copper also showed seasonal variation. The highest copper content was detected in Lake Sredzkie at 50.080 µg · dm⁻³ in June, whereas it was lowest in the Warta River at a sampling point near Cytadela Park, amounting to 0.108 µg · dm⁻³ in November (Table 4). The highest seasonal average cadmium content was recorded in Lake Raczynskie at 17.119 µg · dm⁻³ of water, while it was lowest in the drainage ditch Lorenka amounting to 5.990 μ g · dm⁻³. Standard deviation of the seasonal means was calculated to show seasonal variability in concentrations of selected elements in the study areas.

Correlation coefficients between groups were determined in order to examine the relationship between seasonal variability in heavy metal concentrations (Table 5). For this purpose first the mean values of all intake levels were calculated for each month. In the next stage, the correlation coefficients were determined for each group of heavy metals.

Table 5

The correlation coefficients between selected heavy metals

Metals	Cd	Zn	Pb	Cu
Cd	1			
Zn	-0.714	1		
Pb	0.365	0.177	1	
Cu	0.268	-0.686	-0.654	1

High negative correlation values were found between cadmium and zinc (r = -0.714), copper and zinc (r = -0.686), and copper and lead (r = -0.654).

Contents of various heavy metals are influenced by agriculture and mining (Table 6). Different countries face the problem of high heavy metal concentrations in different water bodies inhabited by living organisms. The purpose of monitoring is to show which pollution has to be dealt with and verify the main causes of their occurrence. The following table shows examples observed worldwide that illustrate the content of heavy metals in water in the different continents.

Admissible concentrations of heavy metals are exceeded in rivers and lakes in the Wielkopolska region. Relatively high values have been shown for copper and lead,

Table 6

Concentration of hea vy metals in different water reservoirs in various countries

			Contaction of the	Constanting of Longer models [1.10 day-3]		
Locations	Country			vy metars [µg·mii]		References
LOCALIONS	Country	Zinc	Lead	Copper	Cadmium	control of the contro
Wielkopolska region	Poland	< 1.000	< 70.000	< 50.000	< 0.370	our studies
Brahmani river	India	80.100	27.000	4.700	4.000	[23]
Changijang river	China	18.750	6.400	8.400	0.300	[24]
Han river	China	LN	9.260	13.350	2.310	[25]
Ataturk Dam lake (Adiyaman)	Turkey	0.197	NT	0.220	N	[26]
Manchar lake	Pakistan	79.200	19.780	23.140	6.620	[27]
Brzezno lake	Poland	12.450	10.305	3.950	1.300	[28]
Radun lake	Poland	6.550	16.500	4.250	1.300	[28]
Mlosino Wielkie lake	Poland	3.950	13.150	1.400	2.000	[28]

NT – not tested.

which reached maximum values of 50 and 70 µg · dm⁻³, respectively. Different literature sources published worldwide show how industrialization affects the relevant heavy metal concentrations in surface waters. In India in the Brahmani River [23] high concentrations of zinc and cadmium (corresponding to 80 and 4 µg · dm⁻³) were reported. Content of lead and copper were lower than in the waters of the Wielkopolska region. In Chinese rivers, the Changijang and the Han [24, 25] lower concentrations of lead and copper were also reported (max. 9 and 13 µg · dm⁻³). The Han River had a higher concentration of cadmium (2.3 µg · dm⁻³), while in the Changijang it was for zinc (18.75 µg · dm⁻³). In the Turkish Ataturk Dam lake [26] in Adiyaman much lower zinc and copper concentrations were showed than it was in the Wielkopolska region (approximately 0.2 μg · dm⁻³). The Manchar lake [27] is characterized by higher concentrations of zinc and cadmium (up to 80 and 6.6 µg · dm⁻³, rerspectively). In Poland tests are also carried out to monitor the concentrations of heavy metals in surface waters. In lakes Brzezno, Radun and Mlosino Wielkie [28] lower levels of lead and copper were reported (up to 16.5 and 4.25 μ g · dm⁻³, respectively) together with higher amounts of zinc and cadmium (up to 12.45 and 2 µg · dm⁻³, respectively). In another study conducted by Antonowicz (2008) within a 24 h period daily changes in the concentrations of lead, zinc, cadmium, manganese and copper were analyzed in surface microlayers and in subsurface water of Lake Gardno. It was observed that concentrations of these metals both in surface microlayers and in subsurface water within 24 h show considerable variation, resulting from transport processes in the vertical profile of a water column [29]. Moreover, Antonowicz and Trojanowski tested the effect of salinity level on the concentration of cadmium and manganese in the surface microlayer in Lake Gardno [30]. Cadmium accumulation in microlayers of surface waters in Lake Gardno was dependent on the concentration of this metal in the deep waters and varied with water salinity, while both metal levels in analyzed surface water microlayers were higher than in the subsurface layer [30].

Conclusions

- 1. Seasonal variability of cadmium and zinc depend on the date of discharge to water, and the use of chemical fertilizers in crop fields.
- 2. The concentration of lead in water resulted from emissions and reached its peak in October (up to 60 $\mu g \cdot dm^{-3}$), due to the greater impact of crop fields during this period.
- 3. The highest copper content recorded in the lakes was probably caused by the compounds used to eliminate algae blooms.
- 4. According to the Regulation of the Minister of the Environment of 27 November 2002 on the requirements to be met by surface water used for public supply of water intended for human consumption, water samples in all the analyses, in terms of heavy metals have been classified to classes I or II.
- 5. According to the Regulation of the Minister of the Environment of 4 October 2002 on the requirements to be met by inland waters that are the habitat of fish in the wild, satisfactory living conditions for salmonids and carp were found in all tests.

6. Negative correlations were found between the content of cadmium and zinc (r = -0.714), copper and zinc (r = -0.686), as well as copper and lead (r = -0.654).

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ZANIECZYSZCZENIE METALAMI WÓD POWIERZCHNIOWYCH Z TERENU WIELKOPOLSKI

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Abstract: Zasoby wodne Polski w porównaniu do innych krajów europejskich są małe. Jest to jeden z czynników powodujących wzrost zainteresowania badaniami monitoringowymi dotyczącymi ich jakości. Jednym z istotnych zanieczyszczeń są metale ciężkie. Celem pracy było określenie sezonowej zmienności stężeń kadmu, ołowiu, cynku oraz miedzi w różnych zbiornikach i ciekach wodnych z terenu Wielkopolski. Brano pod uwagę takie źródła poboru jak jeziora, duże i małe rzeki oraz rowy melioracyjne. Miejsca poboru charakteryzowały się zróżnicowaniem użytkowania terenów występujących wokół nich. Były to głównie tereny rolnicze. Badania przeprowadzono w sezonie wegetacyjnym od maja do grudnia 2012 roku. Analizę ilościową metali ciężkich wykonano na spektrometrze 280Z AA firmy Agilent. Uzyskane wyniki wykazały dużą sezonową zmienność występowania metali ciężkich w różnych zbiornikach wodnych. Stężenie kadmu i cynku zależało głównie od terminu zrzutu ścieków do wód. Poziom stężeń ołowiu ukształtował się w wyniku emisji spalin i zależały głównie od ingerencji maszyn rolniczych na polach uprawnych. Najwyższe stężenia miedzi odnotowano w jeziorach, co mogło być spowodowane zastosowaniem związków eliminujących zakwity glonów. Zgodnie z polskim prawem, wszystkie miejsca badawcze zostały zaklasyfikowane do I lub II klasy jakości wód przeznaczonych do picia. We wszystkich miejscach były spełnione warunki do życia ryb karpiowatych i łososiowatych.

Słowa kluczowe: metale ciężkie, wody powierzchniowe, Wielkopolska