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ACCUMULATION OF SELECTED METALS IN THE BOTTOM SEDIMENTS OF THE POND IN SZCZYTNICKI PARK IN WROCLAW

KUMULACJA WYBRANYCH METALI W OSADACH DENNYCH STAWU W PARKU SZCZYTNICKIM WE WROCŁAWIU

Abstract: The study was designed to establish the pollution of the water and bottom sediments as well as the accumulation rates of selected metals (lead, cadmium, zinc, copper, nickel) in the bottom sediments of the pond in Szczytnicki Park in Wroclaw, Poland. Samples for the study were taken from eight locations on four occasions during a 12-month period: in spring (24 April 2008), summer (19 July 2008), autumn (18 November 2008), winter (10 February 2009). The following were determined for the water: temperature, reaction, total hardness and selected metals (Zn, Cu, Cd, Pb, Ni). For the bottom sediments the content and accumulation of the above metals were established. The accumulation rates of the studied metals in the bottom sediments were found to be arranged as follows: Ni > Cu > Zn > Pb > Cd, whereas metal concentrations in the bottom sediments were: Zn > Cu > Ni > Pb > Cd. Lead and cadmium had the lowest accumulation rates and contents in the bottom sediments. The water and bottom sediments covered by the study were found not to be polluted with metals.

Keywords: lead, cadmium, zinc, copper, nickel, bottom sediments, accumulation, the Szczytnicki pond

The pond in the Szczytnicki Park in Wroclaw forms part of the Odra old river-bed. It may be supplied with water from the Odra indirectly, via the Japanese Garden pond. Most pollutants carried by water are deposited in bottom sediments. Knowledge of the phenomena and processes occurring between water and bottom sediments, which are in constant contact with each other, is of extreme importance. Sediments act as a regulator of the physicochemical properties of water. The chemical composition of sediments is affected by many factors, the most important of which is the geological structure of soil [1, 2]. The composition is also influenced by chemical compounds present in the water that accumulate in the sediments. Water often acts as a receptor of particles of organic matter from plants growing nearby. The pond covered by the study is located in a park

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and surrounded by deciduous trees, which periodically feed organic matter into the reservoir, which sometimes leads to blooming [3].

Both the water and the sediments retain and accumulate biogens, suspensions and highly toxic substances, such as metals, which seriously deteriorate the water environment [4–6]. Whether accumulation poses a threat may be assessed by calculating the accumulation rate and the amounts of metals accumulated.

The study in question was to determine metal accumulation in the bottom sediments of the pond in the Szczytnicki Park in Wroclaw.

Material and methods

The study material consisted of the water and bottom sediments from the pond, which has an area of 0.18 ha and the average depth of 1 m, and is located from 51°06′ north and 17°04′ east to 51°06′ north and 17°04′ east. Analytic material was collected in four seasons between 2008 and 2009 on eight different sites:

– Site 1 – 51°06′49.61″ N 17°04′58.70″ E
– Site 2 – 51°06′47.33″ N 17°04′58.48″ E
– Site 3 – 51°06′47.83″ N 17°04′56.55″ E
– Site 4 – 51°06′45.09″ N 17°04′51.88″ E
– Site 5 – 51°06′42.82″ N 17°04′48.52″ E
– Site 6 – 51°06′43.77″ N 17°04′47.45″ E
– Site 7 – 51°06′43.77″ N 17°04′47.45″ E
– Site 8 – 51°06′38.79″ N 17°04′46.58″ E.

The following parameters were measured directly on the sites:

– temperature using a Slandi TC 204 electronic thermometer;
– electrolytic conductivity using electrometer [7];
– reaction using electrometric method [8];
– dissolved actual oxygen using Hanna Instruments 9143 oxygen probe [9].

The other parameters were measured under laboratory conditions:

– total hardness [10];
– Zn, Cu, Cd, Pb, Ni [11].

Bottom sediment samples were collected at the same sites by means of an Ekman grab. Hydrated sediments were dried in room temperature, sieved through a 1-mm mesh sieve and pounded in a porcelain mortar. The sediments were then subjected to wet mineralization with a mixture of acids in a MARS-5 oven. Metal contents (Ni, Cd, Pb, Zn, Cu) in the mineralizate were determined using an atomic absorption spectrophotometry unit AAS-1N (Zeiss Jena) [12]. Obtained results were statistically analysed using Statistica 8.0 programme.

Results and discussion

Water temperature in the pond was ranging between 1.7 °C and 20.5 °C which is a standard temperature for Polish waters. The surface water temperature depends on the season (in summer 20 °C and more while in winter 0 °C) [13].

Water reaction of the Szczytnicki pond was ranged between 7.4 and 7.6. The average water hardness of the Szczytnicki pond was between 178.5–196.3 mg · $CaCO_3$ · dm^{-3}.

The average zinc content in water of the Szczytnicki Park pond was 0.0176 mg · dm^{-3} (Table 1), which is ten times less than that determined for south-west Poland in the 1980s by Szulkowska-Wojaczek et al [14].

Table 1

The metals concentration in water of the Szczytnicki pond

Metal	Season	Average	Min	Max	Standard deviation
Zn	spring	0.0175	0.0058	0.0367	0.0114
	summer	0.0085	0.0012	0.0235	0.0070
	autumn	0.0158	0.0012	0.0387	0.0114
	winter	0.0288	0.0161	0.0487	0.0120
Cu	spring	0.0076	0.0062	0.0117	0.0017
	summer	0.0026	0.0014	0.0037	0.0008
	autumn	0.0036	0.0018	0.0070	0.0017
	winter	0.0074	0.0038	0.0112	0.0027
Cd	spring	0.0004	0.0000	0.0011	0.0004
	summer	0.0002	0.0000	0.0004	0.0001
	autumn	0.0007	0.0000	0.0010	0.0004
	winter	0.0019	0.0013	0.0032	0.0007
Pb	spring	0.0026	0.0000	0.0126	0.0047
	summer	0.0004	0.0000	0.0015	0.0006
	autumn	0.0038	0.0012	0.0075	0.0020
	winter	0.0092	0.0060	0.0136	0.0029
Ni	spring	0.0007	0.0000	0.0012	0.0004
	summer	0.0011	0.0001	0.0023	0.0007
	autumn	0.0042	0.0032	0.0048	0.0005
	winter	0.0045	0.0025	0.0065	0.0015

In 2000 Karczewska et al [15] conducted a study regarding the presence of heavy metals in the soils in the Szczytnicki Park in Wroclaw. Individual metal concentrations in 2000 were as follows: 60–435 mgPb · kg^{-1}, 170–720 mgZn · kg^{-1}, 0.05–4.5 mgCd · kg^{-1}, and 40–570 mgCu · kg^{-1}. The values found for individual metals did not meet the criteria set by the State Environmental Inspection (PIOS) as permissible for public or recreational areas [15–17].

Zinc is necessary for organisms to grow, but its excess is harmful, also to fish. According to Liebmann [18] zinc is toxic to fish at concentrations of 0.1–2.0 mg · dm^{-3}, while at a concentration of 0.1 mg · dm^{-3} it hinders self-purification [18]. At the concentration discovered in the pond, zinc is not a threat to fish. The average zinc concentration in the water was the highest out of all the metals examined.

Tests done by PIOS in 2007 showed that the arithmetic mean zinc concentration in 125 lakes amounted to 92 mgZn · kg^{-1}. During the study in question the measured concentration at eight sites was four times smaller, at nearly 25 mgZn · kg^{-1} (Table 2).

Table 2

The metal concentration in bottom sediments of the Szczytnicki pond

Metal	Season	Average	Min	Max	Standard deviation	Bottom sediments concentration
Zn	spring	17.88	6.56	29.69	8.44	BBC
	summer	25.44	5.89	49.04	14.98	BBC
	autumn	28.61	8.13	54.33	16.74	BBC
	winter	25.88	7.53	70.90	21.08	BBC
Cu	spring	6.40	3.48	10.86	2.80	0
	summer	7.89	3.47	12.74	3.41	0
	autumn	13.20	2.74	49.67	16.32	+
	winter	4.76	1.88	8.04	2.61	0
Cd	spring	0.56	0.50	0.63	0.04	0
	summer	0.60	0.45	0.72	0.08	0
	autumn	0.16	0.00	0.27	0.11	BBC
	winter	0.21	0.15	0.32	0.07	BBC
Pb	spring	3.66	1.35	6.30	1.76	BBC
	summer	5.64	2.49	10.26	2.72	BBC
	autumn	6.06	1.39	11.22	3.63	BBC
	winter	5.88	0.00	25.52	8.31	0
Ni	spring	8.26	3.20	12.90	3.75	0
	summer	12.23	5.65	17.33	3.79	+
	autumn	5.03	1.18	9.79	2.93	0
	winter	3.87	1.43	6.99	2.30	0

BBC – below background concentration; (0) – unpolluted sediments; (+) – little polluted sediments; (++) – polluted sediments; (+++) – heavy polluted sediments.

The presence of metals in soils in the Szczytnicki Park in Wroclaw is also of importance to surface and underground water, to bottom sediments and plants. In 2000 Karczewska et al [15] showed that zinc concentration in the soil ranged between 170 and 720 mgZn · kg^{-1}. In a 2005 study by Licznar the metal content in the humus oscillated between 46 and 750 mgZn · kg^{-1} [16, 17]. The concentration of the element in the bottom sediment samples collected for the study was lower than that in the soil. This may be caused by its poor permeation from the soil into the park plants and so by bigger amounts of it than of other metals being carried into the water, and by poor leaching by the water over the sediments. According to the bottom sediments classification based on geochemical criteria, in terms of zinc content the sediments in question belong to purity class I, because at none of the sampling sites did the concentration exceed 200 mgZn · kg^{-1} [19] and was almost like in bottom sediment from Dubai creek [20] lower then in bottom sediments of Black Sea [21] or in the Selenga River sediments [22], mostly lower then in bottom sediments from estuary in Argentina [23].

The average annual rate of Zn accumulation in bottom sediments was calculated at $1.4 \cdot 10^{-3}$.

The research done in the 1980s by Szulkowska-Wojaczek et al [14] showed that waters in south-west Poland had an average Cu concentration of 0.011 mgCu · dm^{-3}, which is approximately the same as that found in the Szczytnicki pond in question in 2008/2009.

Only sometimes the Cu content values recorded throughout the year only slightly exceeded 0.01 mgCu · dm^{-3} (Table 1) and were about five times lower than the threshold set for surface waters [24].

Copper is a biogenic element and in water reservoirs is to be found in the form assimilable by organisms. It is necessary for plants to grow. At a concentration higher than 0.1 mg · dm^{-3} it hinders growth of aquatic plants, which is not a problem in the pond under study. The element is also very toxic to fish [18, 25]. The most harmful Cu compounds include Cu salt solutions and copper(II) hydroxide $Cu(OH)_2$, which forms an insoluble deposit. It may accumulate on fish gills and may cause fish to die [26]. Its toxicity largely depends on water hardness and pH. Copper toxicity is diminished by complexing substances [27]. Copper excess in water is highly toxic to biological activity, which in turn adversely affects self-purification [28]. According to Liebmann [18], copper is toxic to fish at concentrations of 80–800 μg · dm^{-3} and hinders self-purification at a concentration as low as 10 μgCu · dm^{-3}. The average content of the element found in the water was 0.0053 mgCu · dm^{-3} (Table 1) and as such does not pose any threat to aquatic organisms [18].

The copper concentration in the Park soil in 2000, as given by Karczewska et al [15], was 40–570 mgCu · kg^{-1}. The figures determined by the study in question were lower (Table 2) and almost like in the Selenga River sediments [22] mostly lower then in bottom sediments from estuary in Argentina [23].

According to the bottom sediments classification based on geochemical criteria, in terms of copper content the sediments in question belong to purity class I, because there was less than 20 mgCu · kg^{-1} of the metal in them, whereas the sediments from sites 7 and 8 in the autumn meet the requirements for purity class II (> 20 mgCu · kg^{-1}) [19].

The average annual rate of Cu accumulation in bottom sediments was calculated at $1.5 \cdot 10^{-3}$.

The water in the pond may be classified as belonging to surface water purity class I, as none of the cadmium concentrations recorded throughout the year exceeded 0.005 mgCd · dm^{-3} [18]. Most probably cadmium mainly occurs as CdS and $CdCO_3$, although in surface waters it may also be found as Cd^{2+} ion or it may form complexes $[Cd(OH)]^+$, $[CdCO_3]^0$, $[CdSO_4]^0$ and [CdCl].

According to Liebmann [18], cadmium is toxic to fish at concentrations of 3–20 mg · dm^{-3} and it hinders self-purification at 0.1 mg · dm^{-3}. In the pond examined the mean concentration of the metal amounted to 0.0008 mg · dm^{-3}, *ie* it was much lower that the threshold value quoted as harmful to fish [18].

The average cadmium concentration in the water was the lowest out of all the remaining metals covered by the study (Table 1).

Cadmium content in the bottom sediments of the pond covered by the study was much lower (Table 2) than that quoted by Dojlido [18], as 0.100 mgCd $\cdot$ kg^{-1} to over 3.000 mgCd $\cdot$ kg^{-1}.

According to the bottom sediments classification based on geochemical criteria, in terms of cadmium content the sediments in question belong to purity class I, because at none of the sampling sites did the concentration exceed 1 mgCd $\cdot$ kg^{-1}.

Tests done by PIOS in 2007 [29] covering 125 lakes showed that the arithmetic mean of the metal amounted to 0.8 mgCd $\cdot$ kg^{-1}. In a 2008–2009 study done on the pond, which had 8 sampling sites, the arithmetic mean of Cd was by 50 % lower than that calculated for the lakes [18]. The concentration of Cd in bottom sediments was lower then bottom sediment from Dubai creek 3.83–7.20 mgCd $\cdot$ kg^{-1} [20] and like in bottom sediments of Black Sea [21] mostly lower then in bottom sediments from estuary in Argentina [23]. In 2000 Karczewska et al [15] determined that cadmium concentration in soil was from 0.05 to 4.5 mgCd $\cdot$ kg^{-1}. In a 2005 study by Licznar et al [30] cadmium concentration in the humus fell within the range of 0.2–1.0 mg Cd $\cdot$ kg^{-1} [15, 16].

Gardiner claims that the cadmium accumulation rate ranges from $5 \cdot 10^3$ to $50 \cdot 10^3$ [18]. Cadmium does not remain long in water and precipitates as carbonates or is absorbed by suspensions and bottom sediments. In the study concerning the problem the accumulation annual rate amounted to nearly $0.5 \cdot 10^3$, *ie* was much lower than the figures given by Gardiner [18].

Cadmium was the metal with the lowest concentration both in water and in the bottom sediments. Its accumulation rate was also the lowest when compared with the other metals.

Lead at higher concentrations is toxic to fish. It accumulates in the food chain, in the liver and the kidneys. Toxicity to fish is acute at concentrations of 200–10 000 μg $\cdot$ dm^{-3}. According to Harrison [18], acute toxicity to fish is observed at concentrations ranging from 100 to 15 000 μg $\cdot$ dm^{-3}. Lead concentration in the pond water was below the range given above (Table 1).

The soil had much more of lead than the sediments. The low content of the element may have been caused by two factors: a significant number of trees and bushes in the park, which captured the metal very effectively and did not allow it to permeate from the nearby roads to the water, and by leaching of the metal by the water over the bottom sediments. Lead content in the park's soil in 2000 ranged from 60.0 to 435.0 mgPb $\cdot$ kg^{-1} [15]. A 2005 study by Licznar et al [28] showed that its concentration in the humus oscillated between 39.5 and 202.0 mgPb $\cdot$ kg^{-1} [15, 16].

Because at none of the sampling sites did the concentration of Pb-toxic metal exceed 50 mgPb $\cdot$ kg^{-1}, according to the bottom sediments classification based on geochemical criteria, the sediments in question belong to purity class I [19]. The tests of 125 lakes done by PIOS in 2007 showed that the arithmetic mean lead concentration in them amounted to 37 mgPb $\cdot$ kg^{-1} [29]. The pond analysis conducted in 2008/2009 at 8 sampling sites showed a concentration seven times smaller than that in the lakes (Table 2). The concentration of lead was lower then in bottom sediment from Dubai creek 35.75–53.50 mgPb · kg^{-1} [20] and in bottom sediments of Black Sea [21] but almost like in the Selenga River sediments [22] mostly lower then in bottom sediments from estuary in Argentina [23].

The average annual lead accumulation rate in the bottom sediments in the Szczytnicki Park pond amounted to $1.3 \cdot 10^3$, and was 1000 times smaller than that in Ontario Lake (1.4–3.0). The accumulation rate of the element oscillates between $0.1 \cdot 10^3$ and $1 \cdot 10^3$ [18], *ie* it is higher in the sediments studied, as it amounted to $1.5 \cdot 10^3$.

According to Liebmann [18], nickel at concentrations of 25–50 mgNi · dm^{-3} has a toxic effect on fish and at 0.1 mgNi · dm^{-3} it hinders self-purification. The obtained results indicated that the element posed no threat to fish [18]. Nickel concentration in water of the Szczytnicki pond (Table 1) may be affected by its leaching from soil [31].

Nickel had the highest average annual rate of accumulation in the bottom sediments, amounting to $2.8 \cdot 10^3$. The lowest nickel concentrations were measured in the autumn and winter, oscillating around 5.0 mgNi · kg^{-1} (Table 2).

In 2008/2009 the arithmetic mean nickel concentration at 8 sampling sites on the pond was over 7 mgNi · kg^{-1} dry mass, *ie* it was similar to that established in the 2007 PIOS study [29]. The concentration of lead was lower then in bottom sediment from Dubai creek [20] and in bottom sediments of Black Sea [21].

A statistically material correlation ($p < 0.05$) between the content in the sediments of Zn and Cu, Ni, Pb and between Cd and Ni was found.

Conclusions

The water and bottom sediments in Szczytnicki Park should be regarded as unpolluted with metals.

The accumulation rates of the studied metals in the sediments should be ordered as follows: Ni > Cu > Zn > Pb > Cd.

The metal concentrations in the sediments should be ordered differently: Zn > Cu > Ni > Pb > Cd

Pb and Cd had the lowest accumulation rates and concentrations in the bottom sediments. The order of the average concentrations of the studied metals in the water (except for Pb) corresponds to that of their contents in the bottom sediments.

References

[1] Szulkowska-Wojaczek E, Marek J, Dobicki W, Polechoński R. Zesz Nauk AR Wroc. Zoot XXXVII. 1992;218:7-25.
[2] Rudnicki A, Waluta J, Waluś T. Rybactwo jeziorowe. Warszawa: PWRiL; 1965.
[3] Pączka M, Zyss E, Pulikowski K. Gosp Wod. 2005;6:246-251.
[4] Maślanka K, Policht A. Rocz AR Pozn Melior Inż Środow. 2005;26(365):267-274.
[5] Orlik T, Obroślak R. Acta Agrophys. 2005;5(3):705-710.
[6] Strużyński J, Łojek J. Zesz Nauk AR Krak Inż Środow. 2002;23(393):53-59.
[7] PN-EN 27888, 1999.
[8] PN-90/c-04540.01.
[9] PN-72/c-04545.08.

[10] PN-ISO 6059, 1999.
[11] PN-ISO 8288:2002.
[12] PN-EN 13346:2002.
[13] Gomółka B, Gomółka E. Ćwiczenia laboratoryjne z chemii wody. Wrocław: Oficyna Wyd Politechniki Wrocławskiej; 1998.
[14] Szulkowska-Wojaczek E, Marek J, Dobicki W, Polechoński R. Zesz Nauk AR Wroc Zoot. XXXVII, 1992;218:7-25.
[15] Karczewska A, Kabała C, Avenarius K. Zesz Probl Post Nauk Roln. 2000;471(2):981-987.
[16] Licznar M, Licznar SE, Licznar P, Żmuda R. Acta Agrophys. 2005;5(2):345-355.
[17] Meinhardt B. Zesz Nauk AR Wroc Zoot. 1998;73(347):9-41.
[18] Dojlido JR. Chemia wód powierzchniowych. Białystok: Wyd Ekonomia i Środowisko; 1995.
[19] Bojakowska I, Sokołowska G. Przegl Geol. 1998;46(1):49-54.
[20] El-Sammak A. Dubai, United Arab Emiratem. Bull Environ Contam Toxicol. 2001;67:295-302. DOI: 10.1007/s00128-001-0124-9.
[21] Ergul HA, Topcuoglu S, Olmez E, Kýrbasxoglu C. Coastal and Shelf Science 2008;78:396-402. DOI:10.1016/j.ecss.2008.01.006
[22] Khazheeva ZI, Urbazaeva SD, Bodoev NV, Radnaeva LD, Kalinin YuO. Water Res. 2004;31(1):64-67.
[23] Ronco A, Camilion C, Manassero M. Environ Geoch and Heath. 2001;23:89-103.
[24] Rozporządzenie Ministra Środowiska z dnia 20 sierpnia 2008 w sprawie sposobu klasyfikacji stanu jednolitych części wód powierzchniowych (DzU 2008.162.1008).
[25] Kwapulinski J, Korczak K, Kmak-Kapusta D, Bondaruk J. Ekol Tech. 2007;15(6):219-224.
[26] Prost M. Choroby ryb. Lublin: Pol Tow Nauk Wet; 1994.
[27] Danielewski S. Rocz Nauk Roln. 1965;86(B):341-345.
[28] Kabata-Pendias A, Pendias H. Biogeochemia pierwiastków śladowych. Warszawa: PWN; 1999.
[29] http://www.gios.gov.pl (15.10.2009).
[30] Licznar SE, Licznar M. Roczn. Glebozn. 2005;56(1/2):113-118.
[31] Kozubek M, Marek J. Zesz Nauk AR Wroc Zoot. XLIX. 2002;447:89-99.

KUMULACJA WYBRANYCH METALI W OSADACH DENNYCH STAWU W PARKU SZCZYTNICKIM WE WROCŁAWIU

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Abstrakt: Celem pracy była ocena stopnia zanieczyszczenia wody i osadów dennych oraz ocena stopnia kumulacji wybranych metali (ołów, kadm, cynk, miedź, nikiel) w osadach dennych stawu położonego w Parku Szczytnickim. Próbki do badań pobrano z 8 stanowisk, czterokrotnie podczas roku: wiosna (24 IV 2008), lato (19 VII 2008), jesień (18 XI 2008), zima (10 II 2009). W wodzie oznaczono: temperaturę, odczyn, twardość ogólną oraz stężenie metali (Zn, Cu, Cd, Pb, Ni). W osadach dennych analizowano zawartość oraz kumulacje powyżej podanych metali. Współczynniki kumulacji badanych metali w osadach dennych uszeregowane są w sposób następujący: Ni > Cu > Zn > Pb > Cd, natomiast szereg stężeń tych metali w osadzie dennym wygląda następująco: Zn > Cu > Ni > Pb > Cd. Najniższe współczynniki kumulacji i najniższą zawartość w osadzie dennym stwierdzono dla ołowiu i kadmu. Badana woda oraz osady denne należały do niezanieczyszczonych metalami.

Słowa kluczowe: ołów, kadm, cynk, miedź, nikiel, osady denne, kumulacja, staw Szczytnicki