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CONCENTRATION OF ZINC IN WATER AND BOTTOM SEDIMENTS IN SMALL WATER RESERVOIRS LOCATED IN RURAL AREAS

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Abstract

Depending on its concentration in the environment, zinc can be either an important bio-element for development of living organisms, or a toxic heavy metal. Small water reservoirs are especially sensitive to contamination, as because of their location in the lowest point of the catchment they tend to receive contaminants from its whole area. The purpose of this work was to assess changes in concentration of zinc in surface, supra-bottom and interstitial water, and in the upper layer of sediment, in five small water reservoirs located in rural areas. The reservoirs G1 and G2 were located in a golf course, water body SW was in a village, very close to farmyards, water body P1 was in the middle of a crop field, and water body P2 was on fallow land. For this research, samples were collected once a month, during three vegetation seasons. The water reservoirs contained an elevated average concentration of zinc in water from 0.026 to 0.063 mg dm^{-3}). The average concentration of zinc in the sediments (from 25.8 to 118.2 mg kg^{-1}) classified the examined reservoirs into the geochemical purity class 1. The highest content of zinc was in the village pond. Highly significant correlations were determined between the content of organic matter and zinc in the bottom sediment in the investigated reservoirs. At the same organic matter content, the zinc concentration in the bottom sediments of the rural pond was find-fold higher than in the other reservoirs. The concentration of zinc in water and the factor of its accumulation in the sediment showed a clear seasonal character of changes. In the spring season, concentration of zinc in interstitial water was lower than in the water depth, whereas in the vegetation season, the zinc concentration was observed to rise in all layers, up to over ten-fold in the interstitial water. In the sediment, the zinc accumulation factor changed in a reverse manner, i.e. it reached thee highest values during spring but fell the lowest in autumn.

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Key words: zinc, interstitial and surface water, bottom sediment, small water reservoirs.

ZAWARTOŚĆ CYNKU W WODZIE I OSADACH DENNYCH MAŁYCH ZBIORNIKÓW WODNYCH ZLOKALIZOWANYCH NA OBSZARACH WIEJSKICH

Abstrakt

Cynk, w zależności od jego zawartości w składnikach ekosystemów, może być ważnym w rozwoju organizmów żywych biopierwiastkiem lub toksycznym metalem ciężkim. Szczególnie wrażliwe na zanieczyszczenia są małe zbiorniki wodne, które ze względu na swoje położenie w najniższym miejscu zlewni odbierają zanieczyszczenia z całego jej obszaru. Celem pracy była ocena zmian zawartości cynku w wodzie: powierzchniowej, przydennej i międzyosadowej oraz w powierzchniowej warstwie osadu w pięciu małych zbiornikach wodnych zlokalizowanych na terenach wiejskich. Zbiorniki G1, G2 były umiejscowione na terenie pola golfowego, zbiornik SW w centrum wsi, zbiornik P1 na polu uprawnym, a zlewnię zbiornika P2 stanowił zadarniony odłóg. Próby do badań pobrano 1 raz w miesiącu w ciągu trzech sezonów wegetacyjnych. W badanych zbiornikach stwierdzono podwyższoną koncentrację cynku w wodzie (od 0,026 do 0,063 mg dm^{-3}). Średnia zawartość cynku w osadach (od 25,8 do 118,2 mg kg^{-1}) klasyfikowała badane zbiorniki do I geochemicznej klasy czystości. Największą zawartość cynku stwierdzono w stawie wiejskim. Obliczono wysoce istotne korelacje między zawartością materii organicznej i cynku w osadzie dennym. Przy tej samej zawartości substancji organicznej, zawartość cynku w osadzie dennym stawu wiejskiego była pięciokrotnie większa niż w pozostałych zbiornikach wodnych. Stężenie cynku w wodzie oraz współczynnik jego kumulacji w osadzie wykazywały wyraźną sezonowość zmian. W sezonie wiosennym stężenie cynku w wodzie międzyosadowej było mniejsze niż w toni wodnej, natomiast w trakcie sezonu wegetacyjnego stwierdzono wzrost jego stężenia we wszystkich warstwach wody, w wodzie międzyosadowej nawet o kilkanaście razy. Odwrotnie zmieniał się współczynnik kumulacji cynku w osadzie, przyjmując największe wartości w sezonie wiosennym, a najmniejsze w sezonie jesiennym.

Słowa kluczowe: cynk, woda interstycjalna i powierzchniowa, osad denny, małe zbiorniki wodne.

INTRODUCTION

Zinc is a heavy metal and, like some other heavy metals e.g. iron, copper, nickel, and chrome, it is essential for proper functioning of living organisms and only after exceeding a certain level it becomes harmful. Although zinc is one of the least toxic heavy metals, concentration of this element has an effect on the quality of water in a reservoir. Zinc levels above 5 mg dm^{-3} give water a bitter and metallic taste and in an alkaline environment they cause turbidity of water. Zinc does not bio-accumulate in organisms very well, which limits its migration in the trophic chain (BROOKS, MAHNKEN 2003, DEAN et al. 2006). Concentrations of zinc in water substantially affect biotic processes occurring in it. Zinc is incorporated into enzymes and takes part in the bio-synthesis of nucleic acids and polypeptides. This influence is most frequently observed in biocenoses that overgrow underwater subgrades (Paulsson et al. 2000, 2001, Zhou et al. 2007). Based on micro-system laboratory tests, Paulsson et al. (2001) stated that as the concentration of mobile zinc in water increases, the amount of phosphorus in the peryphiton and the biomass of organisms decrease, while the activity of phosphohydrolytic enzymes increases. Growing activity of these enzymes on the residue surface associated with a rise in the amount of zinc in interstitial water was also recorded by Zhou et al. (2007). A high concentration of zinc results in its accumulation in the radicular system, leading to some disturbance of photosynthesis, chlorosis and metabolism disorders. If the concentration of zinc exceeds 0.100 mg dm^{-3}, ions of this metal slow down the process of water self-purification.

The thin line between zinc deficit and toxicity is very easy to cross. Among the contributing factors are: increasing use of chemicals in agriculture, industrialization and using some waste materials for agricultural purposes. Small water reservoirs are especially pollution sensitive, as their location is a bio-geo-chemical barrier for metals, where they are captured mainly in bottom sediments (Szyperek 2005, Senze et al. 2010). Like all other heavy metals, zinc has a distinct ability to accumulate in various elements of aquatic environments, especially in bottom sediments. Thus, bottom sediments constitute an element of the water environment which acts as a moderator, influencing chemical qualities of the water which remains in contact with these sediments. This is particularly true about heavy metals that are arrested in bottom sediments by precipitation, sedimentation or sorption, but in the course of chemical and bio-chemical decomposition, dissolution and desorption, they can pollute the water environment again.

The content of zinc is usually tested in reservoir waters and bottom sediments in drainage basins which have been polluted by industrial sewage (Nocoń 2006). There are no comprehensive studies on the content of zinc in reservoirs located in agricultural areas. The aim of this research is to evaluate the seasonal character of fluctuations in the content of zinc during a plant growing season in small water reservoirs located in agricultural areas. Changes in the zinc content were tested in the upper, benthic and interstitial waters and in the top layer of bottom sediments.

MATERIAL AND METHODS

The research involved five, small, drainless, pond-like water reservoirs with the permanent water table, located in Szczecin Landscape Park. These reservoirs are characterized by differently developed direct drainage basins. Two (G1, G2) are located within the premises of a golf club in Binowo. Their drainage basins are dominated by brown ground soils (mainly fawn), produced from light clay, sanded on top (*Soil-agricultural map* 1973). Two other reservoirs are located on fields in the village Kolowo. During the study, the drainage basin of reservoir P1 was a farm field and the one of reservoir P2 was turfed fallow land. The fifth reservoir (SW) is a typical rural pond, located in the nearest vicinity of the farmyards in Kolowo. The drainage basin of this reservoir covers areas of brown, leached soil, formed from light clay sand that transforms into light clay at the depth of 50-100 cm, and of typical brown soil made from light clay. (*Soil-agricultural map* 1973).

Samples of water and sediments for specific tests were taken twice during the spring (March-May), summer (June-August) and autumn (September-November) in three consecutive years: 2005-2007. The samples were collected from the central parts of the water reservoirs. Firstly, surface layer water was sampled with a scoop from the depth of 30 cm. Secondly, samples of benthic water and of ceiling sediment with an undisturbed structure were taken with the use of a sediment core sampler (produced by KC- Denmark). A 10-centimeter layer of benthic water was probed by the means of a sampling pipe with a semi-automatic pipette Swiftpet. From the remaining sample, a 4-centimeter surface layer was extracted and separated with a special set consisting of a piston and a tray for samples. Each time, extraction of samples was repeated four times. When delivered to the laboratory, the samples were centrifuged in a lab centrifuge for ten minutes at 3000 rpm. Water collected above the centrifuged sediment was decanted and treated as inter-sedimentary. After each sampling of water and sediment, averaged aggregated samples from the surface layer of the sediment and from each layer of water (surface, benthic and interstitial) were analyzed chemically.

In the examined samples of water and sediment, after wet mineralization of the sedeiments in concentrated nitric acid in a microwave oven, total content of zinc was determined with atomic absorption spectrometry, where zinc detectability limit was 2.5 mg kg^{-1}. Determination of zinc was conducted in a spectrometer Solaar S by ThermoElemental. Additionally, in the centrifuged sediments, organic carbon was determined with Orlow and Grindel's method. The determinations were conducted in a double-beam spectrophotometer UV/VIS 8500 by Techcomp. The content of organic carbon was converted into an organic substance quantity by multiplying it by the modulus 1.724.

RESULTS AND DISCUSSION

Our comparison of the concentrations of zinc in the examined reservoirs to the threshold boundary values, given in the guidelines for classification of surface waters (*Regulation*... 2008), showed that all the examined water reservoirs were in good ecological condition as far as the content of zinc was concerned. In the surface stratum, the mean concentration of that element calculated for the whole vegetative season remained in the range of 0.026 mg dm^{-3} in reservoir G2 at the golf club and 0.063 in reservoir P2, whose drainage basin was a fallow field (Table 1). In each reservoir, the mean concentration of zinc in water tended to increase towards the bottom, with the difference between zinc levels in interstitial water and those in the water column being relatively small. It was only in reservoir G1 that the concentration of zinc in interstitial water was three-fold higher than in the benthic layer, while in the other reservoirs it was only 30% higher.

The mean content of zinc in the sediments of the examined water reservoirs was within 25.8 mg kg^{-1} (in reservoir G2 at the golf club) and

Table 1

Concentration of zinc in water and sediment, n=18

Examined layer	Reservoir	Statistical parameter					
		average	min.	max.	geometric mean	median	SD
Surface water (mg dm^{-3})	G1	0.057	0.010	0.493	0.060	0.046	0.044
	G2	0.026	0.006	0.034	0.018	0.021	0.029
	SW	0.032	0.006	0.178	0.021	0.026	0.048
	P1	0.046	0.004	0.165	0.041	0.044	0.047
	P2	0.063	0.004	0.268	0.039	0.037	0.076
Bottom water (mg dm^{-3})	G1	0.028	0.010	0.100	0.027	0.027	0.020
	G2	0.077	0.001	0.619	0.020	0.022	0.173
	SW	0.079	0.007	0.502	0.031	0.030	0.145
	P1	0.053	0.010	0.183	0.041	0.038	0.051
	P2	0.063	0.018	0.165	0.057	0.059	0.048
Interstitial water (mg dm^{-3})	G1	0.087	0.001	0.443	0.046	0.100	0.131
	G2	0.103	0.005	0.253	0.050	0.060	0.111
	SW	0.089	0.004	0.719	0.038	0.071	0.197
	P1	0.078	0.002	0.303	0.051	0.072	0.091
	P2	0.078	0.015	0.357	0.060	0.037	0.116
Sediment (mg kg^{-1} d.m.)	G1	111.1	20.8	195.9	101.5	118.7	30.2
	G2	25.8	17.7	151.1	28.8	24.7	7.9
	SW	118.2	28.9	167.3	105.2	117.8	45.0
	P1	34.4	21.1	48.1	28.5	26.0	11.4
	P2	40.4	15.9	51.6	36.5	38.7	26.8

G1, G2 – reservoirs located in a golf course
SW – a village pond
P1, P2 – reservoirs located on arable land

118.2 mg kg^{-1} of the dry sediment mass (in the village pond). It was lower than the threshold value (200.0 mg kg^{-1}), thus, in respect of this parameter, the examined reservoirs can be qualified as class 1 of geochemical purity. Reservoirs G1 and SW were an exception, because their zinc levels exceeded the geochemical background, which equals 48.0 mg kg^{-1} (Bojakowska, Sokołowska 1998). Lower or similar values of this parameter were observed in other rural water reservoirs, e.g. in Owiesno pond it was 14.9 mg kg^{-1} (Senze et al. 2010) and in Psurow pond it was 90.7 mg kg^{-1} (Gałka, Wiatkowski 2010). No significant correlations between the concentration of zinc in the examined layers of water and its content in the sediment were found. Significant positive correlations were observed between the zinc level and the content of organic matter in the sediment (Figure 1). The determination coefficient for the linear regression function for the samples collected

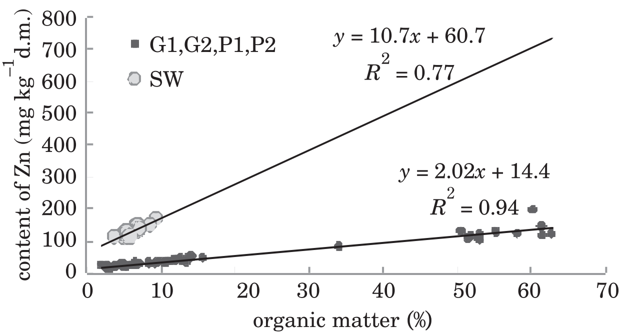

Fig. 1. Relationships between the content of organic matter and zinc in bottom sediment of the reservoirs

in the village pond was 0.77, and for the samples taken from the other reservoirs it was 0.94. With respect to this dependence, some significant correlations were also found by Basaran et al. (2009), who studied sediments in the Gulf of Gulluk, Turkey. Comparison of the regression coefficients of linear functions describing the relationship between the content of zinc and the content of organic matter in sediments in some water reservoirs indicated that, at the same content of organic matter, the level of zinc in the rural pond sediments was five-fold higher than in the other water reservoirs. This difference could be attributed to different sources of pollution, as the rural pond was mainly polluted with household sewage and run-offs from the farmyard, while the other reservoirs were fed by run-offs from their drainage basins.

Concentrations of zinc in water collected from the analyzed reservoirs underwent some distinct seasonal changes (Figure 2). In the springtime, the concentration of this element in interstitial water was lower than in the

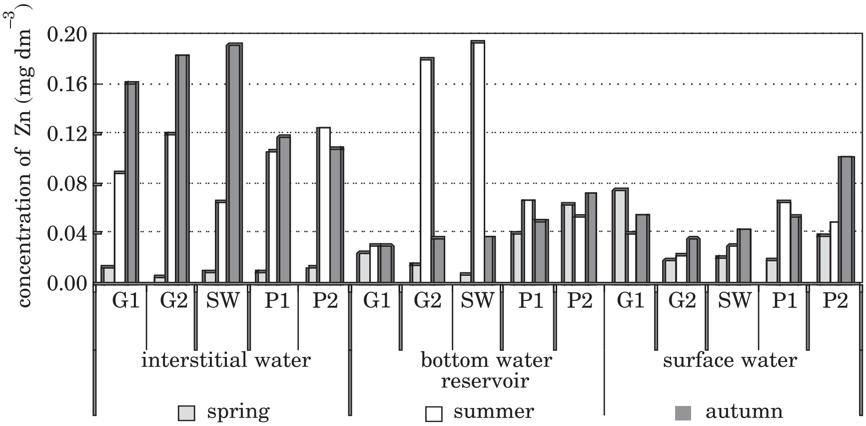

Fig. 2. Mean seasonal concentrations of zinc in investigated layers of water, *n=6*

water column, while during the vegetation season it increased even more than a dozen times. This indicates that in spring, the gradient of zinc concentration was shifted toward the water column, while during summer and autumn, it moved towards the interstitial water. In the examined reservoirs, the average concentration of zinc in summer and autumn was higher than the threshold for this element (0.0025 mg dm^{-3}), at which development of phytoplankton biomas is depressed (PAULSSON et al. 2000, 2001). The highest levels of zinc observed in the interstitial water in summer and autumn show that the seasonal variations in the concentration of zinc in the studied reservoirs might be related to some biotic processes, especially the biocenoses growing on submerged surfaces (PAULSSON et al. 2000, 2001, ZHOU et al. 2007). Seasonal fluctuations of zinc levels in the examined water reservoirs confirm that in spring zinc is permanently bound in the sediment. Then, in summer and autumn, like phosphorus and other heavy metals, it can be released in processes of organic matter mineralization and photochemical degradation, which are more intensive during the vegetation season in poly-mictic reservoirs (GÓRNIAK 1996).

Seasonal changes in concentrations of zinc in water were not reflected by a change in the zinc content in the surface layer of the sediment (Figure 3), which indicates low mobility of zinc in sediments during the vegetation season. Alkaline pH of the examined sediments may prove a potentially low risk of releasing zinc should the chemical balance in the examined reservoirs change. In the sediments, about 40% of zinc is bound to Fe-Mn oxides. This is confirmed by numerous studies, such as speciation analysis of zinc in sediments of lakes in Wielkopolski National Park (SOBCZYŃSKI, SIEPAK 2001) or in some smaller reservoirs (MADEYSKI et al. 2009). Zinc may be reinstated from this fraction into the bio-circulation if strong reducing conditions occur in the near-bottom zone.

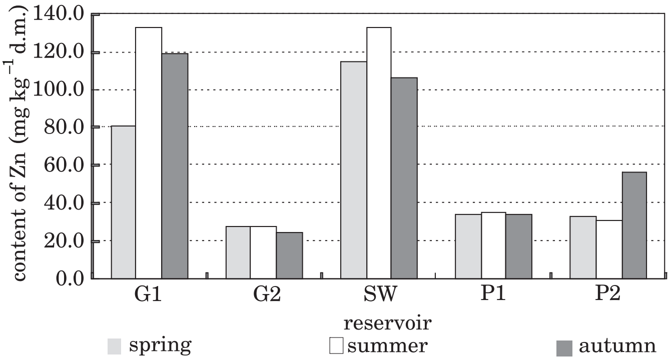

Fig. 3. Mean seasonal concentration of zinc in bottom sediments of the water reservoirs, *n=6*

CONCLUSIONS

1. With the determined concentrations of zinc, the small reservoirs examined proved to be in good ecological condition and belonged to class 1 of geochemical purity. The highest level of zinc was found in the village pond.

2. In all the reservoirs, highly significant correlations between the content of organic matter and zinc in sediments were found. At the same content of organic matter, the zinc level in the village pond sediments was fivefold higher than in the sediments of in the other reservoirs.

3. The zinc concentrations in water collected from the studied reservoirs was subject to significant seasonal changes. In spring, the gradient of concentrations of Zn ions shifted towards the water column, while during summer and autumn it moved towards interstitial water.

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