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ASSESSMENT OF HEAVY METAL POLLUTION IN BOTTOM SEDIMENTS OF SMALL WATER RESERVOIRS WITH DIFFERENT CATCHEMENT MANAGEMENT

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Abstract

The main purpose of this work was to determine the degree of negative impact of heavy metals accumulated in the water sediments to aquatic organisms. Samples of sediments were collected in winter 2013, from 4 layers of sediment (0-5, 5-10, 10-20 and 20-30 cm) at three points along the water reservoir. Sediments were prepared for analysis in accordance with the procedures applied in soil science. The analysis was carried out for the fraction with a particle diameter less than 1 mm. The total content of such elements as Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn, was determined by atomic absorption spectrometry (using the Thermo Scientific iCE 3000 series spectrometer) after digestion in a mixture (5:1) of concentrated acid HNO_3 (65 %) and $HClO_4$ (60%). The total Hg content was obtained by using the AMA 254 analyzer. Only the lead content in the analyzed samples of bottom sediments exceeded the contamination value given by polish law (the Regulation of the Minister of Environment). According to the classification of PGI samples of sediments are classified mainly as medium polluted sediments (Class II), with the exception of zinc and lead concentrations (Class III). Due to the value of the indicator of sediments ecological risk (Er) for cadmium, the examined sediments from small water reservoirs no. 1 and 2 should be classified as deposits with a higher rate of environmental contamination risk. The sediments from small water reservoirs no. 3 and 4 belong to the class of a much higher index of contamination risk. On the basis of the PER indicator (a degree of potential environmental risk) the sediments from small water reservoirs located within the area of organic farming can be classified as contaminated by heavy metals to a moderate degree. On the other hand, the analyzed sediments of small water reservoirs no. 3 and 4 were classified as deposits with a severe degree of heavy metal contamination. On the basis of the LAW classification one can say that the bottom sediments of examined ponds were classified into different classes depending on the analyzed chemical element.

Key words: agriculture, ecology, heavy metals, sediments, ponds, classification

INTRODUCTION

Sediments constitute integral part of the aquatic environment. They create a specific natural geosorbent accumulating all substances introduced to the aquatic environment. Therefore, a specific balance is established between the water and the sediment, which can be disturbed as a result of natural and anthropogenic processes causing the release of the accumulated substances into the water column. Such phenomenon may limit or disable the use of waters in agriculture, municipal management and industry (Baran and Tarnawski 2013; Szydłowski and Podlasińska 2015). Sediments accumulating the substances introduced to waters constitute an important source of information on the human pressure on the aquatic environment (Pietrzak *et al.* 2013; Haziak *et al.*, 2013; Brysiewicz *et al.* 2013; Baran and Tarnawski 2013; Szydłowski and Podlasińska 2016). The heavy metal content in sediments may also serve as a significant indicator of the geochemical situation of water body catchment (Szafran 2003). Heavy metals are especially dangerous in the aquatic environment due to their toxicity, durability and bioaccumulation. Many authors (Fu *et al.*, 2013; Bai *et al.* 2011; Caeiro *et al.* 2005; Suresh *et al.* 2012) indicate that sediments are a very sensitive indicator of pollution and that they are a good sorbent for pollutants found in the aquatic environment. Considerable amount of pollutants is deposited in bottom sediments due to adsorption, hydrolysis, co-precipitation (Gaur *et al.* 2005; Hau *et al.* 2013). The conduct of chemical analyses in bottom sediments enables determination of the level of anthropogenic pollution only, without providing any information on the biological effects caused by the pollution. To this end, the study utilized different methods for evaluation of negative impact of heavy metals accumulated in bottom sediments on the ecosystem and aquatic organisms (Zhang *et al.* 2011; Su *et al.* 2012; Macdonald *et al.* 2000; Niu *et al.* 2009; Håkanson 1980; Müller 1969).

The study aimed at the determination of the level of negative impact of heavy metals accumulated in aquatic sediment on aquatic organisms.

Materials and methods

Characteristics of study objects

The study objects are located in the West Pomeranian Voivodeship, Barlinek municipality near the Mostkowo township. The small water reservoirs selected for this study are within the areas where an organic farming is applied – reservoirs no. 1 and 2 (52°59'54.24"N15° 3'17.95"E and 53° 0'4.52"N15° 3'39.96"E respectively) and within the area where farming with rational mineral fertilization (NPK) is carried – reservoirs no. 3 and 4 (52°59'32.97"N15° 2'59.87"E and 52°59'26.76"N15° 2'45.66"E respectively). The surface waters of examined small water bodies in 2013 years was about: 0.27; 1.59; 0.06 and 0.05 ha, respectively for objects no. 1, 2, 3 and 4. At the time of study (2013 year) within the catchment of the no. 1 and 2 small water reservoir was cultivated wheat, whereas on the area adjacent to no. 3 and 4 water bodies rapeseed was grown.

Characteristics of sediment sample collection and chemical analysis

Sediment samples (48 ones) were collected in winter 2013. Sampling sites were located at three points along the water body from the layers: 0-5, 5-10, 10–20 and 20-30 cm. Sediments were treated as soil material and were prepared for further analyzes following the procedures used in soil science. The analyzes were conducted for the particle fraction below 1 mm. Sediments samples (0.5 g) were mineralized in a mixture (5:1) of concentrated acids HNO_3 (65%) and $HClO_4$ (60%). The total element content, i.e.: Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn were determined using the Thermo Scientific iCE 3000 series atomic absorption spectrophotometer. The Hg content was determined using the AMA 254 analyzer. All statistic calculations were provided by using the Statistica 12.0 software. The Shapiro-Wilk test of normality was applied ($p \leq 0.05$), which confirmed the normality of the result distributions.

Detailed obtained results are presented by Szydłowski and Podlasińska (2017).

For the assessment of sediment contamination from small water reservoirs the following methods were used with maximum concentration values:

- aquatic sediment quality classification used by the Polish Geological Institute (Bojakowska and Sokołowska 1998; Bojakowska 2001),
- Regulation of the Minister of Environment of April 16 2002 on the types and concentrations of substances contaminating the excavated material,
- Em geoaccumulation index (Igeo) (Müller 1981),
- LAW sediment classification (based on Nocoń 2009).

The above methods for assessment of sediment contamination differ in the number of levels, classes as well as factors influencing the threshold values of the mentioned classes.

The influence of contamination on aquatic organisms was determined using three different methods, including the sediment quality guidelines (SQGs), potential ecological risk index of individual element (E_r) and potential ecological risk (PER), which constitutes the sum of all ecological potential indicators (Håkson 1980).

RESULTS

Using the maximum values of heavy metal concentrations in the analyzed samples, an assessment of small water reservoirs sediment contamination was performed (Table 1). The eventual assigning a class to the examined sediment is determined by the highest class of the analyzed heavy metals. For the evaluation, geochemical background provided by the Polish Geological Institute was used (Bojakowska and Sokołowska 1998).

Following the Igeo classification, the analyzed sediments remain between the uncontaminated class (0) and extremely contaminated class. In both small water body reservoir types (located in catchments with organic and intensive farming) the lowest Igeo values characterizes cadmium and mercury. On the other hand, considering concentrations of the remaining heavy metals in the examined sediments samples, these sediments must be classified as heavily and extremely contaminated (Table 1).

Out of all guidelines provided in all the methods, the Regulation of Polish Ministry of Environment (2002) contains the least restrictive assessments for sediment quality. Concentrations of the analyzed heavy metals, with the exception for lead, whose concentration exceeded the value determining contamination of the obtained sediment, were below the threshold values for contaminated sediments (Table 1).

Following the Polish Geological Institute classification (Bojakowska 2001), the sediment samples obtained from the examined small water reservoirs are classified primarily as medium polluted (Class II), with the exception for the content of nickel, zinc and lead (Table 1). Class II indicates that the sediment in question contains such amounts of the contaminant that its harmful effect for aquatic organisms is frequently observed. Class III sediments possess the highest content of harmful components. Those sediments (class III) can be placed in selected areas in the water (relocated), whereas on the land they can be stored to a limited extent, since concentrations of certain harmful components may restrict their usage only for industrial cultivation or, in certain cases, exclude their agricultural usage entirely.

Table 1. Classification of small water reservoirs sediments contamination according to selected methods of assessment.

Type of catchment management	Element	Maximum value [mg · kg^{-1}]	According to PGI*	$I_{geo/class}$**	According to the Regulation****
Small water reservoirs no. 1 and 2	Cd	1.13	II	1.41/0	BELOW
	Co	11.52	-	3.94/IV	-
	Cr	54.45	II	7.50/VI	BELOW
	Cu	57.31	II	7.84/VI	BELOW
	Fe	32769	-	-	-
	Mn	491.76	-	-	-
	Ni	33.45	II	6.80VI	BELOW
	Pb	30.57	III	7.67/VI	BELOW
	Zn	304.45	III	13.25/VI	BELOW
	Hg	0.18	I	-7.35/0	BELOW
Small water reservoirs no. 3 and 4	Cd	1.99	II	-0.56/0	BELOW
	Co	13.72	II	4.19/V	-
	Cr	94.90	II	8.31/VI	BELOW
	Cu	75.92	II	8.25/VI	BELOW
	Fe	34022	-	-	-
	Mn	389.30	-	-	-
	Ni	40.62	III	7.08/VI	BELOW
	Pb	339.81	IV	11.15/VI	ABOVE
	Zn	369.01	III	13.53/VI	BELOW
	Hg	0.33	II	-6.51/0	BELOW

Source: * (Bojakowska 2001); ** (Müller 1981); *** (Regulation2002)

The calculated values of the potential ecological risk index of individual element (E_r) in the test period for the risk of metal contamination can be arranged in two decreasing series. For the small water reservoirs adjacent to organic farming the series is as follows: Cd>Cu>Ni>Cr>Pb>Zn, whereas for the remaining tested objects: Pb>Cd>Cu>Ni>Cr>Zn (Table 2). Due to the highest value for cadmium for reservoirs no. 1 and 2, which influenced the ecological index for sediment contamination risk (E_r), the tested sediments were classified as having an elevated ecological index of contamination risk. Sediments from reservoirs no. 3 and 4 had a higher ecological index for sediment contamination due to the cobalt content (Table 2). Based on the level of potential ecological risk (PER) for the reservoirs no. 1 and 2 (located within the organic farming areas) their sediments can be classified as sediments with medium level of contamination with the analyzed heavy metals. On the other hand, the tested sediments of reservoirs no. 3 and 4 were classified as sediments with severe contamination with the analyzed heavy metals (Tables 2 and 3).

A separate classification for sediments is the LAW classification (Tables 4 and 5). Contrary to the national classifications, this method concerns sediment contamination with heavy metals and divides sediments into seven classes in terms of increasing contamination concentration. The I-II class reflects the natural contents of given elements (geochemical background) in sediments, whereas the remaining classes from II to IV demonstrate an increasing influx of pollutants to aquatic ecosystems (based on Nocoń 2009).

By comparing the study results with the LAW classification it can be stated that the sediments from small water reservoirs were assigned to different classes depending on the given chemical compound (Tables 4 and 5). Classifications were conducted on the basis of the highest concentrations.

Table 2. Ecological risk index values and the ratio of ecological potential index for heavy metal content in the tested types of small water reservoirs

Class	Elements					
	Cd	Cr	Cu	Ni	Pb	Zn
Small water reservoirs no. 1 and 2 (Organic farming catchment management)						
E_r	67.67	21.78	47.76	40.15	15.28	6.34
PER	198.98					
Small water reservoirs no. 3 and 4 (Sustainable farming catchment management)						
E_r	119.69	37.96	63.27	48.74	169.90	7.69
PER	447.25					

Table 3. Standards for Er and PER classes

The potential ecological risk index of individual element [E_r]	Ecological risk index	Index of potential ecological risk (PER)	Degrees of potential ecological risk
<40 40 – 80 80 – 160 160 – 320 >320	Low Moderate Higher Much higher Serious	< 150 150 – 300 300 – 600 >600	Low quality Moderate Heavy Serious

Table 4. The limits [mg·kg^{-1}] of the LAW classification of the small water reservoirs bottom sediments (according to Nocoń 2009)

Element	I	I-II	II	II-III	III-IV	IV
Zn	≤100	≤200	≤400	≤800	≤1600	>3200
Pb	≤25	≤50	≤100	≤200	≤400	>800
Cu	≤20	≤40	≤80	≤160	≤320	>640
Ni	≤30	≤60	≤120	≤240	≤480	≤960
Cr	≤80	≤160	≤320	≤640	≤1280	≤2560
Cd	≤0.3	≤0.6	≤1.2	≤2.4	≤4.8	≤9.6

Table 5. Classes of sediments contamination according to LAW classification

Class	Degree of contamination
I	Uncontaminated
I-II	Contaminated / Moderately polluted
II	Moderately polluted
II-III	Moderately polluted / Heavily contaminated
III	Heavily polluted
III-IV	Strongly / Very heavily polluted
IV	Very heavily polluted

In terms of the zinc (Zn) content in the sediments of the reservoirs located within the areas with fertilization (no. 3 and 4), as well as where fertilization is not used (no. 1 and 2), the sediment is assigned to class II (medium contamination), which indicates that these values are higher than the geochemical background for zinc (Tables 1 and 4).

Regarding the lead (Pb) content a considerable differentiation of LAW classes for both small water reservoir types was observed. The sediment of reservoirs no. 1 and 2 is classified as not contaminated or with medium contamination (Class I-II), which indicates that the lead content was at the level of the geochemical background (Tables 1, 3 and 4). The sediments of the reservoirs surrounded by NPK fertilized fields are classified as heavily/very heavily contaminated with Pb (Class III-IV) (Tables 1 and 5). On the basis of the lead content it can be concluded that the method of farming has a significant impact on the status of sediments.

The copper content in both reservoir types classified the sediments as moderately contaminated (Class II). These sediments contained elevated concentrations of copper in reference to the geochemical background.

The highest concentrations of nickel allowed for classifying the examined sediments as not contaminated or slightly contaminated (I-II class). The values ranged within the geochemical background (Tables1, 4 and 5).

The sediments of the reservoirs within the catchment of farming without fertilization (no. 1 and 2) were classified as not contaminated (I class) in terms of chromium content (Cr). The values obtained in the research are considered as concentrations similar to natural values. On the other hand, the chromium content in the sediments of reservoirs no. 3 and 4 (NPK fertilization) are classified as moderately contaminated (I-II class).

In terms of the cadmium content, the sediments of reservoirs no. 1 and 2 (no fertilization) were moderately contaminated (II class), whereas the no. 3 and 4 reservoir sediments (NPK fertilization) were classified as moderately or heavily contaminated (II-III class). These concentrations are higher than the values of geochemical background.

In summary, it can be stated that the method of land usage impacts the quality of sediments in small water bodies.

CONCLUSIONS

1. In both small water body reservoir types (located in catchments with organic and intensive farming) the lowest Igeo values characterize cadmium and mercury. On the other hand, based on the values of the remaining heavy metals in the examined samples of sediments, they should be classified as heavily or extremely contaminated.
2. In the tested samples of sediments only the lead content exceeded the value determining contamination of obtained sediment according to the guidelines of the Regulation of the Minister of Environment of April 16 2002 on the types and concentrations of substances contaminating the excavated material.
3. Following the PGI classification, the obtained samples of sediments are classified primarily as moderately contaminated (II class) with the exception for their zinc and lead content (III class).
4. Due to the ecological index for sediment contamination risk (E_r) for cadmium the examined sediments from reservoirs no. 1 and 2 were classified as sediments with an elevated ecological index of contamination risk. The sediments from reservoirs no. 3 and 4 were assigned to a considerably higher ecological index for sediment contamination risk.
5. Based on the level of potential ecological risk (PER) for the reservoirs no. 1 and 2 (located within the organic farming areas) their sediments can be classified as sediments with medium level of sediment contam-

ination with the analyzed heavy metals. On the contrary, the examined sediments from reservoirs no. 3 and 4 were classified as sediments with high level of contamination with the analyzed heavy metals.

6. Based on the performed LAW classification it can be stated that the sediments of small water reservoirs were assigned to different classes depending on the content of a given chemical element.

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