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CONTENT OF HEAVY METAL COMPOUNDS IN BOTTOM SEDIMENTS OF THE SUCHEDNIOW WATER RESERVOIR

ZAWARTOŚĆ ZWIĄZKÓW METALI CIĘŻKICH W OSADACH DENNYCH ZBIORNIKA SUCHEDNIÓW

Abstract: Water reservoirs become silted at various intensity levels. Within the reservoir bowls, both allochtonic (built up outside the sedimentation area) and autochtonic (built up in the sedimentation area) matter is accumulated. As a result, reservoirs need desilting after a while. Then a problem arises how to manage the sludge removed from the reservoir bottom. The chemical properties of the bottom sludge, and particularly the content of heavy metals, decide whether it will be possible to use the sludge, and in what way. The chemical properties of the bottom sludge depend, to a far extent, on the character of the reservoir basin, the level of its urbanisation, and also on the climatic conditions. The paper presents the results of investigations into the content of heavy metals in the bottom sediments in the Suchedniow water reservoir. This water body is characterised by small mean depth of 1.05 m and mean annual flow across the dam profile of 0.63 $m^3 \cdot s^{-1}$. Forests dominate in the reservoir basin covering 45 % of its area, arable land constitutes 18 %, and the percentage of built-up area does not exceed 5 %. In recent years (2009–2011), the water reservoir has become much silted because of storing large soil masses near the local watercourses during the construction of S7 expressway. The amount of stored soil is estimated at 7.8 thousand m^3. For investigations, nine bottom sediments samples were collected, in which the content of the following heavy metals: Pb, Cr, Cd, Cu, Ni, Zn, Fe, and Mn was determined. Quasi-undisturbed sludge was taken into transparent cylinders with Eijkelkamp sampler, which made it possible to conduct analysis in sediment layers 20 cm in height. In order to evaluate the sediment pollution with heavy metals, the geoaccumulation index, the pollution coefficient and level were calculated. On the basis of admissible soil chemical pollution tables, the possibility of the sludge use in agriculture after extracting it from the reservoir bowl was assessed.

Keywords: reservoir, reservoir basin, bottom sediments, heavy metals

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Mineral, organic material and chemical pollutants transported by water are accumulated in water reservoirs. The amount of sediment deposits delivered and permanently retained in the reservoir, and also amount and type of pollution are determined by many factors. Those include: the hydrological regime of the basin, erosion processes, soil types, management and use of the basin area, and anthropogenic activity. Heavy metals, transported by river waters, are accumulated mainly in the bottom deposits due to sedimentation and sorption processes [1]. Heavy metals can penetrate to the aquatic environment with industrial and municipal sewage, and also with precipitation wastewater – as runoff from fields and meadows (containing chemical fertilisers, plant protection chemicals), transportation infrastructure, or the products of dust emission into the atmosphere [2, 3]. Precipitation wastewater contains zinc and lead, which occur in highest concentrations, copper and chromium, which have slightly lower concentrations, and trace amounts of cadmium and nickel. Transportation routes are the main source of pollution with heavy metals [4–7]. Uncontrolled introduction of heavy metals into the aquatic environment poses a particular hazard, even if they are delivered periodically and in small amounts. The threat results from their stability (they do not undergo biodegradation) and ability to accumulate in sediments and living organisms (plants, animals) [8]. Conducting tests on the content of heavy metals in bottom sediments is especially important for small water reservoirs, which are usually not covered by the State Environmental Monitoring, and in which the rate of silting is high enough to cause problems related to the management of removed silt.

One of the first studies on the chemical composition of bottom sediments was presented by Pasternak and Glinski [9]. Basing on the tests carried out on samples from twelve largest dammed reservoirs in southern Poland, the authors found out that the Turawa Reservoir on the river Mala Panew was the most polluted water body. The content of vanadium and zinc in its bottom sediments was 371 ppm and 135 ppm, respectively. Investigations into bottom sediments in one of Poland's largest reservoirs (Wloclawek Reservoir) indicate that the bottom material is strongly polluted with heavy metals (Table 1). Cadmium, chromium, copper, lead, nickel contents exceed geochemical background values many times. The calculations made by Bojakowska et al [10] show that the reservoir fine grained sediments contain approx. 190 Mg of cadmium, 7.600 Mg of chromium, 4.200 Mg of copper and 2.200 Mg of lead. The presence of caesium, uranium and radium is also detected in the sediments [11, 12].

For small dammed reservoirs located in the basins where forests and arable land take up a substantial part of the area (*eg* Krempna-2, Niedzwiadek, Cierpisz reservoirs) generally lower levels of trace elements are observed in the bottom material than it is the case with large water bodies (Table 1). Small reservoirs located in urban areas, in contrast, can be characterised by elevated content of some heavy metals. That is caused by pollutants that come from roads, residential areas, tourist facilities and are discharged with the surface runoff. The Kielce Reservoir, in whose vicinity busy transportation routes are located, is an example of such category. Bottom deposits of this reservoir show a high content of lead and cadmium (lead – 151.9 mg $\cdot$ kg^{-1}, cadmium – 14.5 mg $\cdot$ kg^{-1}), the source of which definitely lies in transportation. A high

Table 1

Content of heavy metals in bottom sediments in for selected dammed reservoirs

Sample collection site	Pb	Cr	Cu	Mn	Ni	Zn	Cd
	[mg · kg^{-1}]						
Mlyny Reservoir [13]	18.2	—	32.1	—	7.0	90.7	—
Kielce Reservoir [14]	151.9	34.9	14.4	—		41.1	14.5
Krempna-2 Reservoir [15]	1.7	10.4	50.8	—	52.9	76.5	0.3
Cierpisz Reservoir [15]	5.4	17.3	1.9	—	7.4	64.6	0.9
Maziarnia Reservoir [15]	9.5	11.5	5.2	—	9.3	24.6	0.3
Niedzwiadek Reservoir [15]	23.8	29.9	27.6	—	23.7	157.8	1.3
Besko Reservoir [16]	41.6	55.2	30.6	0.6	49.7	116.2	0.8
Psurow Reservoir [1]	18.2	—	32.1	—	7.0	90.7	—
Dzierzno Male Reservoir [17]	106.6	—	27.1	—	22.9	560.0	—
Wloclawek Reservoir [18]	5.5–50.1	—	—	114–3024	—	—	—
Reservoirs in Saxony, Germany [19]	130.0	—	75.0	—	57.0	490.0	—
Flumendosa Lake, Sardinia [20]	202.6	—	136.8	—	—	—	4.8
Guan-Ting Reservoir, China [21]	129.7	—	42.4	—	—	117.8	2.5

content of zinc (560.0 mg · kg^{-1}) and lead (106.6 mg · kg^{-1}) is noticeable in the sediments of the Dzierzno Male Reservoir (Table 1). That can be caused by discharge of industrial sewage from plants located in the basin area, which has continued for many years [17].

In the case of the Suchedniow reservoir, anthropogenic pollution sources include mainly domestic sewage carried from unsewered areas, and also agricultural runoffs. In the years 2009–2010, works related to the construction of S7 expressway were conducted in the Kamionka river catchment. During construction works, a significant increase in the volume of silt deposited in the reservoir bowl (7828 m^3 in total) and water quality deterioration (high content of mineral suspension) were observed [22]. The investigations aim to determine the content of heavy metals in the bottom sediments and to map their spatial distribution in the Suchedniow reservoir bowl.

Material and methods

Object description

The Suchedniow reservoir is located in the Suchedniow commune, Skarzysko county, Świętokrzyskie province. It was constructed in the years 1965–1974 by damming the river Kamionka (right-bank tributary of the river Kamienna) with earth-filled structures km 7 + 754. The reservoir has not been de-silted since when it was put in service. The thickness of sediments deposited in the reservoir ranges from 0.15 m (near the reservoir discharge system) to 1.2 m in the upper part of the reservoir. This water body is characterised by small mean depth of 1.05 m and mean annual flow across the dam profile of 0.63 m^3 · s^{-1}. At the normal water damming level of 258.0 m above sea level, the surface area of the water table is 21.40 ha, and the volume – 226000 m^3 [23].

The area of the Kamionka river basin, closed with the Suchedniow dam, is 83 km^2. Forests dominate in the reservoir basin covering 45 % of its area and arable land constitutes 18 %. Although the percentage of built-up area is small and does not exceed 5 %, because of a very elementary sewerage level, domestic sewage constitutes a potential source of pollution for the river Kamionka. Low-fertility soils within the basin are represented by: brown soils of light and medium boulder clays, podzolic soils of sands and loose gravels, poorly clayey and clayey soils of aquagenic loams [23]. The annual mean precipitation in the basin is 750 mm [24].

Investigation methodology

Samples of bottom sediments from the Suchedniow reservoir were collected in June 2012, in the thirty-eighth year of its service. With the use of boats, the samples were collected into the transparent cylinders with Ejkelkamp sampler, which allows silt sampling at quasi-undisturbed state. The samples to be studied were extracted from the following sites: dam-adjacent reservoir part (sample No. 1), along the mainstream running to the right of the island (samples No. 2, 6, 7), a tributary (sample No. 8), and from the south-western part of the bowl (samples No. 3–5, 9), where marina for water sports equipment and a beach are situated. Fig. 1 shows the location of sites, at which sediment samples were collected. After transporting the cylinders to the laboratory, the collected material was divided into layers 20 cm in thickness, from which identical sediment volumes were taken in order to average them. For each averaged sediment sample, the total content of selected heavy metals (Pb, Cr, Cd, Cu, Ni, Zn, Fe, Mn) was determined.

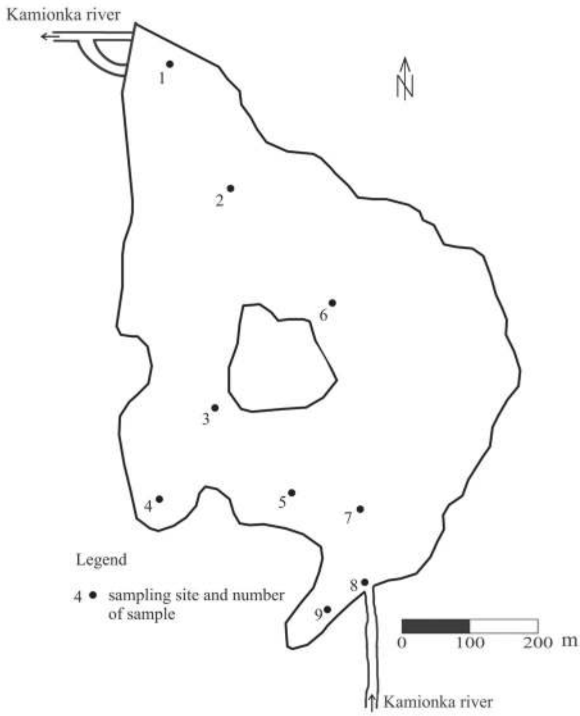

Fig. 1. Location of sites of bottom sediment sample collection

The samples thus prepared were dried to constant mass at 60 ^{o}C to prevent the growth of mould and microorganisms, which leads to the redistribution of chemical components and changes in isotopic composition. Dried samples were ground using an automatic mill until < 0.063 mm size fraction was obtained. Then they were subjected to microwave-assisted total mineralisation, using multi-stand Multiwave 3000 microwave mineraliser. The content of trace elements, depending on the concentration levels and the matrix obtained, was determined with AAS techniques with the use of SavantAA Sigma and SavantAA Zeeman atomic absorption spectrometers.

In accordance with the adopted geochemical method [25], the following indicators were employed: geoaccumulation index (I_{geo}), pollution coefficient (C^i_f) and pollution level (C_{deg}) to assess the pollution of the bottom sediments with heavy metals. The geoaccumulation index (I_{geo}) makes it possible to evaluate pollution by comparing current amounts of heavy metals in bottom sediments with the so-called pre-industrial concentrations [26]:

$$I_{geo} = \log_{10}\left(\frac{C_n}{1.5B_n}\right) \quad (1)$$

The following contents of trace elements in sediments were assumed to constitute the geochemical background: lead – 15 mg · kg^{-1}, chromium – 6 mg · kg^{-1}, cadmium – 0.5 mg · kg^{-1}, copper – 7 mg · kg^{-1}, nickel – 5 mg · kg^{-1}, zinc – 73 mg · kg^{-1}.

The pollution of the bottom sediments was assessed using such parameters as: pollution coefficient (C^i_f) and pollution level (C_{deg}) [27], which were calculated from the following dependence:

$$C^i_f = \frac{C^i_{0-1}}{B_n} \quad (2)$$

The pollution level (C_{deg}) of a site/area is expressed as the sum of individual coefficients C^i_f. Also, the possibility of the sediment use for farming, following its extraction from the reservoir bowl, was examined on the basis of tables of permissible level of soil pollution with chemicals.

As all the series of results concerning the content of the studied metals in sediments did not have normal distribution, the assessment of the strength of statistical relations between examined variables (averaged values of pollution indicators) was made on the basis of Spearman rank correlation.

Results and discussion

Results of investigations into the content of selected trace elements in averaged samples of bottom sediments collected from the Suchedniow reservoir are presented in Table 2.

Table 2

Heavy metal content in the Suchedniow reservoir bottom sediments collected in June 2012

No.	Pb	Cr	Cd	Cu	Mn	Ni	Zn	Fe
	[mg · kg^{-1}]							
1	75.68	63.92	10.75	42.97	621.80	29.38	216.94	20835
2	101.23	58.39	6.47	28.95	606.30	31.41	203.35	10911
3	86.92	37.36	8.24	26.39	499.76	31.38	196.38	19827
4	59.39	39.01	8.41	29.03	522.96	29.11	184.35	14298
5	72.22	40.02	9.28	33.25	674.23	29.01	195.29	11004
6	110.02	38.41	5.24	36.07	696.34	27.34	177.49	18005
7	96.23	49.35	5.02	29.11	557.27	29.34	196.35	21948
8	105.49	48.02	8.14	29.57	535.91	30.06	204.42	17324
9	104.24	45.11	10.47	32.95	698.45	31.21	209.56	17907

The analysis of the amounts of heavy metals in averaged samples indicates that the lowest variation of the obtained results is observed for nickel. The content of this element in the sediments did not exceed 32.00 mg · kg^{-1}. For chromium and copper, the values ranged 26.39–63.92 mg · kg^{-1}. Lead content ranged 59.38–110.02 mg · kg^{-1}, and that of zinc and manganese – 177.49–698.45 mg · kg^{-1}. The highest variation in the studied metals was observed for cadmium and iron. The content of these elements ranged substantially – from 5.02 to 10.75 mg · kg^{-1} for cadmium and 10911–21948 mg · kg^{-1} for iron.

As regards the content of heavy metals under consideration, the bottom sediments in the Suchedniow reservoir are characterised by high spatial differentiation (Fig. 2 and 3). The largest amounts of chromium, zinc, copper and cadmium were found in sample No. 1, collected at the front of the reservoir dam. The highest content of iron was revealed in samples No. 1 and 7 (the lower and the upper part of the reservoir, respectively), of nickel – in sample No. 3, and those of manganese and lead – in sample No. 6 (middle part of the reservoir). The lowest values of chromium, manganese and copper were found in sample No. 3, of zinc and nickel – in sample No. 6, of lead at stand No. 4, and those of cadmium and iron in samples No. 7 and 2, respectively.

The content of lead, chromium, cadmium, nickel and zinc in the bottom sediments of the Suchedniow Reservoir is much higher than the content of those metals in a majority of small storage reservoirs (Cierpisz, Maziarnia, Niedzwiadek, Mlyny), at the same time it is comparable with the values recorded for the Kielce Reservoir (Table 1). Such concentration values may indicate an occurrence of additional pollution sources in the basin, resulting in elevated heavy metal content. Municipal sewage discharged into the river Kamionka or rain wastewater from the street drainage of the town of Suchedniow may be such a source. During the site inspection, in a number of locations, the authors revealed illegal municipal sewage discharge into the river Kamionka upstream the reservoir. However, it proved impossible to collect samples for the analysis of heavy metal content. Both Kielce and Suchedniow water bodies share some characteristics, they lie in urban areas, busy transportation routes, residential areas and recreational facilities are situated nearby, which can explain the congruence of the data obtained for both reservoirs. Only in comparison with large reservoirs, namely Flumendosa, Guan-Ting and Saxony, the sediments under consideration show better results as regards Pb, Cu and Ni. The content of manganese rarely becomes a subject of investigations, therefore it is difficult to draw any satisfactory conclusions concerning the pollution with this element. An average content of manganese in Suchedniow bottom sediments equals 601 mg · kg^{-1} (Table 2) and is comparable with the mean value (780 mg · kg^{-1}) obtained based on 15 samples collected in the years 2008–2009 from the Wloclawek Reservoir [18] and 1000 times higher than the manganese content in the Besko Reservoir sediments [16] – Table 1.

During the 32-year service time, 78000 m^3 of sediments were deposited in the reservoir bowl [22]. On the basis of the assumptions on average heavy metal content in sediments (Table 2), calculations were made for individual elements. The results (in Mg) amount to: iron – 1.529, chromium – 4.2, zinc – 17.9, nickel – 2.7, copper – 54.4, lead – 2.9, and cadmium – 0.7.

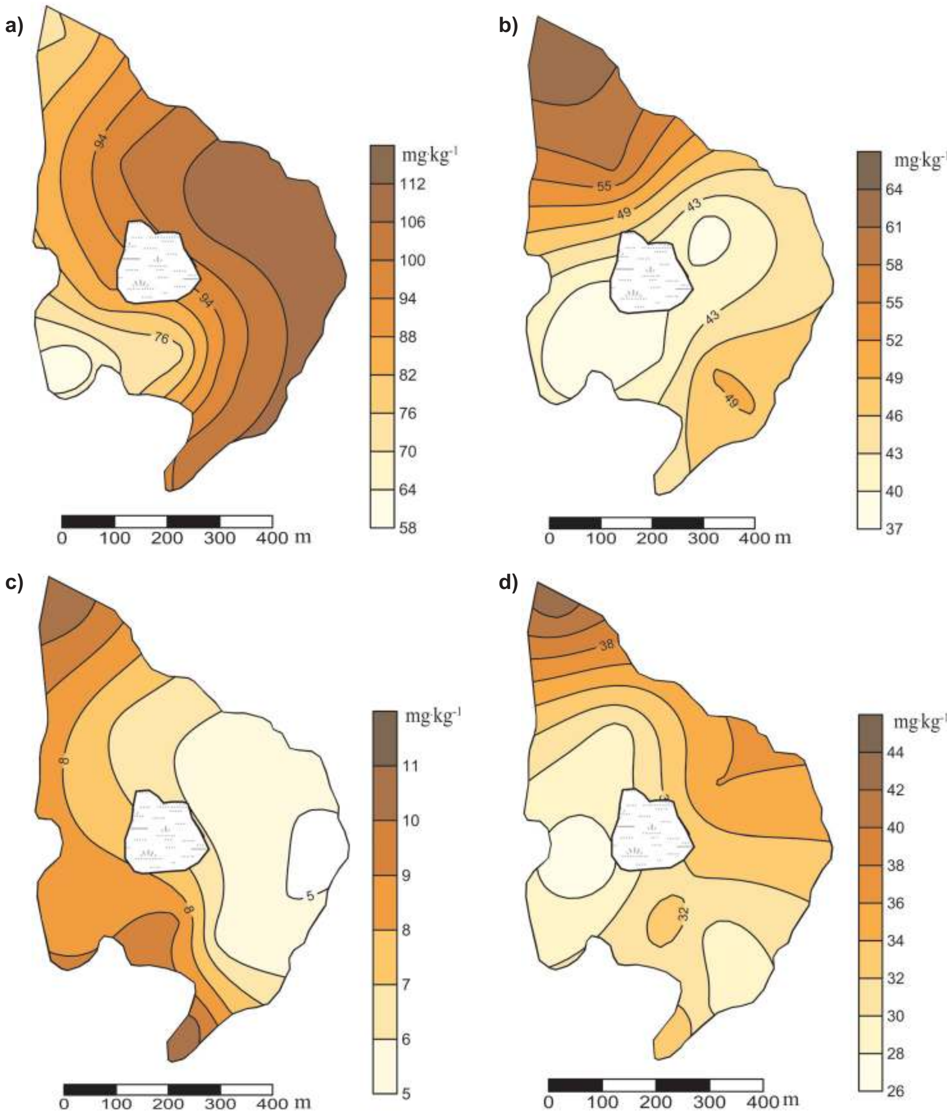

Fig. 2. Spatial distribution of heavy metal content in averaged samples of the Suchedniow reservoir bottom sediments: a) Pb, b) Cr, c) Cd, d) Cu

For all metals, except for zinc-nickel and manganese-copper pairs, no strong or very strong statistically significant relation at the level of p = 0.05 was found between results at individual points. For Zn-Ni and Mn-Cu pairs of metals, high correlation (r = 0.68–0.73) statistically significant at the level of p = 0.05 was observed.

The geoaccumulation index for studied metals, except for cadmium, ranged 0–1, which indicates low pollution of bottom sediments with those metals. As regards

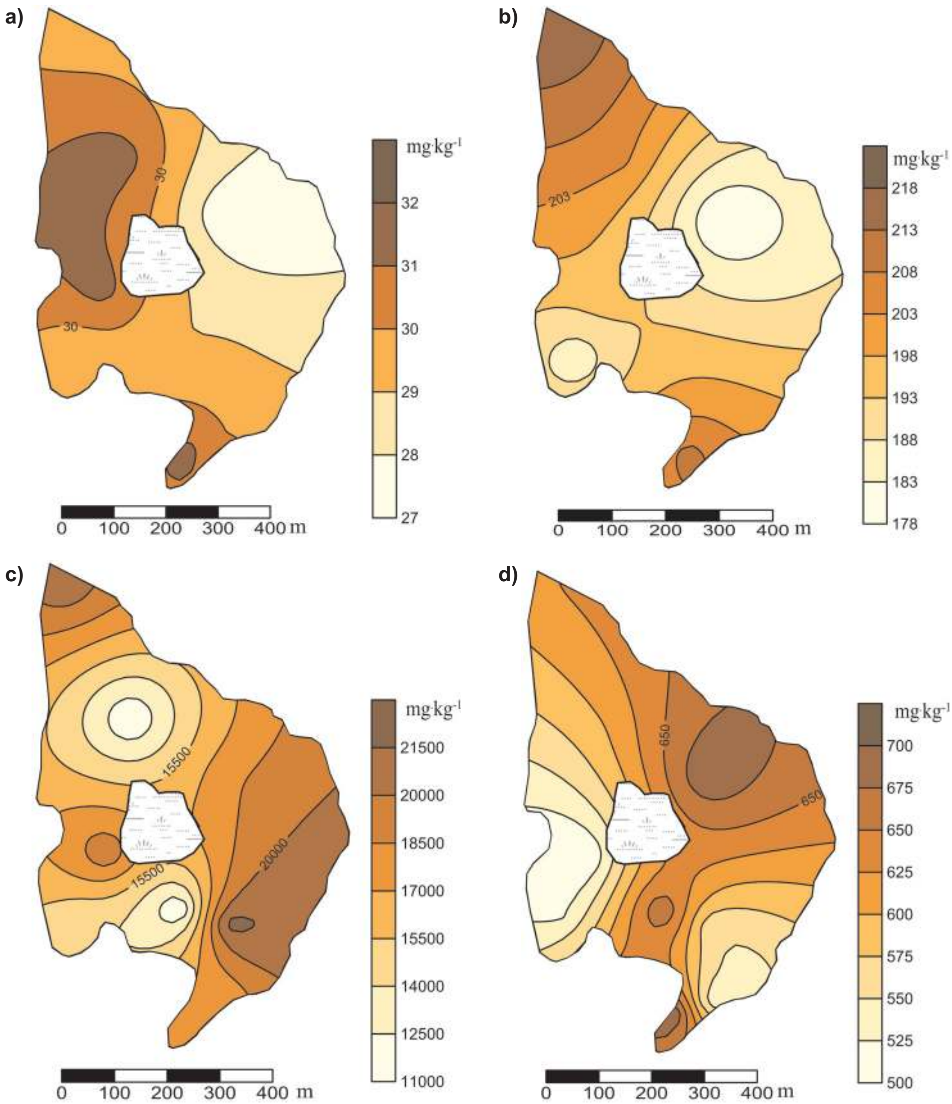

Fig. 3. Spatial distribution of heavy metal content in averaged samples of the Suchedniow reservoir bottom sediments: a) Ni, b) Zn, c) Fe, d) Mn

cadmium, the index exceeds the value 1 for samples No. 1, 3–5, 8, 9 (Table 3). That points to moderate sediment pollution with this element.

The pollution coefficient makes it possible to categorise sediments into groups depending on how many times the actual values are greater than those characteristic of the geochemical background. In accordance with the criterion established by Hakanson [27], the studied silts demonstrate a low pollution coefficient for Cr, Ni, Zn, and a moderate one for Pb, Cu. As regards Cd, the coefficient value is substantial, and very high in the case of sample No. 1. The pollution level ranges 6–12 (Table 3), which following the HÍkanson classification [27], indicates a moderate level of pollution with heavy metals.

Table 3

Geoaccumulation index, pollution coefficient and pollution level for individual trace elements in averaged samples of the Suchedniow reservoir bottom sediments

No.	Pb	Cr	Cd	Cu	Ni	Zn	Pb	Cr	Cd	Cu	Ni	Zn	C_{deg}
	I_{geo}						C_f^i						
1	0.53	0.85	1.16	0.61	0.59	0.30	1.76	0.34	6.57	1.22	0.61	0.77	11.27
2	0.65	0.81	0.94	0.44	0.62	0.27	1.77	0.18	5.98	1.69	0.59	0.33	10.55
3	0.59	0.62	1.04	0.40	0.62	0.25	1.35	0.17	2.08	2.18	0.20	0.46	6.44
4	0.42	0.64	1.05	0.44	0.59	0.23	1.22	0.16	3.16	1.04	0.21	0.53	6.32
5	0.51	0.65	1.09	0.50	0.59	0.25	1.20	0.19	3.45	1.29	0.39	0.64	7.16
6	0.69	0.63	0.84	0.54	0.56	0.21	1.29	0.23	3.25	1.25	0.30	0.86	7.18
7	0.63	0.74	0.83	0.44	0.59	0.25	1.41	0.16	4.02	1.20	0.19	0.61	7.60
8	0.67	0.73	1.04	0.45	0.60	0.27	1.89	0.17	5.68	2.12	0.21	0.66	10.73
9	0.67	0.70	1.14	0.50	0.62	0.28	2.42	0.21	5.38	2.23	0.34	0.92	11.50

In accordance with water sediment classification developed by the Polish Geological Institute (PIG) [28], bottom sediments of the Suchedniow reservoir were categorised as belonging to Class II (slightly polluted sediments) due to the content of Cr, Cu, Ni, Zn, to Class III (polluted sediments) because of the amount of Pb, and to Class IV (heavily polluted sediments) as a result of the content of Cd.

Analysing the quality of the bottom sediments in the Suchedniow reservoir with respect to the Regulation of the Minister of Environment of 16th April 2002 [29], it can be stated that in samples No. 1, 3, 4, 5, 8, 9, cadmium content exceeded the limit value. Consequently, the sediment should be treated as polluted. In accordance with the requirements set in the Regulation of the Minister of Environment of 9th Sept 2002 [30], however, it can be claimed the sediments, depending on the content of studied heavy metals, comply with the quality standards for A or B group soils. As a result, they are deemed to pose no threat to the soil environment, and therefore may be used for farming land, forest land and wastes.

Conclusions

1. The sediments in the Suchedniow reservoir are polluted with heavy metals, the content of which shows high spatial differentiation. In sediments collected near the dam front, the highest values were found for: Cr, Zn, Cu, Cd and Fe, whereas in the upper parts of the reservoir – for Pb, Cd, Ni and Fe.

2. The content of lead, chromium, cadmium, nickel and zinc in bottom sediments of the Suchedniow Reservoir is higher than in other Poland's small reservoirs with the Dzierzno Male Reservoir being the only exception, and comparable with that in the Kielce Reservoir. That indicates the presence of additional (municipal) source of pollution in the Kamionka River basin, which is largely agricultural in character.

3. The assessment of the bottom sediment pollution using the geoaccumulation index, pollution coefficient, pollution level, and the classification developed by the Polish Geological Institute and stated in the Regulation of the Minister of Environment demonstrate that with respect to the content of studied trace elements, the sediments are polluted to a different extent. Depending on the adopted criteria, bottom sediments can be classified as moderately to strongly polluted. Comparing the content of studied metals with adopted geochemical background it can be noted that Cr, Cu, Ni, Zn values do not exceed those of the background. Only Pb and Cd values are higher than those of the background. The share of the latter in the total pollution of the bottom sediments is the highest.

4. Only for Zn-Ni and Mn-Cu pairs of metals, the occurrence of strong or very strong correlation was found, which was statistically significant at the level of $p = 0.05$.

Nomenclature

I_{geo}	geoaccumulation index [-]
C_n	content of a given metal in the bottom sediment [$mg \cdot kg^{-1}$]
$1.5B_n$	geochemical background (B_n) and natural fluctuations in the content of a given metal in the environment, with small anthropogenic impact (1.5) [$mg \cdot kg^{-1}$]
C^i_f	pollution coefficient [-]
C^i_{0-1}	metal content in the bottom sediment [$mg \cdot kg^{-1}$]
C_{deg}	pollution level [-]

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ZAWARTOŚĆ ZWIĄZKÓW METALI CIĘŻKICH W OSADACH DENNYCH ZBIORNIKA SUCHEDNIÓW

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Abstrakt: Zbiorniki wodne ulegają zamuleniu z różną intensywnością. W obrębie ich czasz akumulowany jest materiał alochtoniczny (powstały poza obszarem sedymentacji) jak również autochtoniczny (utworzony w miejscu sedymentacji). W związku z powyższym po pewnym czasie wymagają one odmulenia. Powstaje wówczas problem zagospodarowania osadów wydobytych z dna zbiornika. Możliwość i sposób wykorzystania osadów dennych zależy od ich cech chemicznych, a zwłaszcza od zawartości metali ciężkich. Właściwości chemiczne osadów zależą w dużej mierze od charakteru zlewni zbiornika, stopnia jej zurbanizowania, jak również warunków klimatycznych. W pracy przedstawiono wyniki badań zawartości metali ciężkich w osadach dennych zbiornika Suchedniów. Akwen ten charakteryzuje się niewielką głębokością średnią, wynoszącą 1,05 m oraz średnim rocznym przepływem w profilu zapory równym 0,63 $m^3 \cdot s^{-1}$. Na obszarze zlewni dominują lasy – 45 % powierzchni zlewni, pola orne – 18 %, a udział terenów zabudowanych nie przekracza 5 %. W ostatnim okresie (2009–2011), na skutek składowania w pobliżu lokalnych cieków mas ziemnych, powstałych podczas budowy trasy ekspresowej S-7, doszło do jego intensywnego zamulenia, a ilość odłożonego materiału oszacowano na około 7,8 tys. m^3. Do badań pobrano 9 próbek osadów, w których oznaczono zawartość następujących metali ciężkich: Pb, Cr, Cd, Cu, Ni, Zn, Fe, Mn. Osad pobrano w stanie quasi-nienaruszonym, do przezroczystych cylindrów, za pomocą próbopobieraka „Eijkelkamp”, co umożliwiło wykonanie analiz w warstewkach osadu o wysokości 20 cm. W celu oceny stanu zanieczyszczeń osadów metalami ciężkimi obliczono indeks geoakumulacji, współczynnik oraz stopień ich zanieczyszczenia. Określono także (na podstawie tabel dopuszczalnego, chemicznego zanieczyszczenia gleb) możliwość rolniczego wykorzystania osadów po ich wydobyciu z misy zbiornika.

Słowa kluczowe: zbiornik, zlewnia, osady denne, metale ciężkie