



Ecological risk assessment of metals and metalloid in bottom sediments of water reservoir located in the key anthropogenic “hot spot” area (Poland)

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Abstract

Study was aimed to assess the potential ecological risk of nine metals (Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) and one metalloid (As) in bottom sediments of the Dzierżno Duże Reservoir located in the key anthropogenic “hot spot” area—Upper Silesian Industrial Region (Poland). Sediments were collected in seven sampling sites, along the main axis of a reservoir. Statistical analysis revealed a significant correlation ($p < 0.05$) between the potentially toxic elements, which indicated that they plausibly originate from the same source of contamination or have a similar accumulation behavior. Several indices were used to assess ecological risk associated with examined elements, i.e., Enrichment Factor, Geoaccumulation Index, Contamination Factor, Potential Ecological Risk Factor, Probable Effect Concentration, Threshold Effect Concentration, Degree of Contamination and Risk Index. The values of analyzed indices indicate that sediments are highly to extremely highly contaminated, especially by Cd, Pb, Zn, and As, which simultaneously pose the highest ecological risk. The results of Cluster Analysis (CA) and Principal Component Analysis (PCA) indicate that Cd, Cr, Fe, Ni, Pb, Zn, and As in the bottom sediments are most likely of anthropogenic origin, while Mn rather from natural sources. The obtained results confirm the usefulness of different indices in assessing the ecological condition of water bodies and prove that the problem of toxic elements contamination in bottom sediments of the Dzierżno Duże Reservoir poses a serious environmental threat.

Keywords Metals and metalloids · Bottom sediments · Ecological risk · Contamination level · Upper Silesian Industrial Region · Dzierżno Duże Reservoir

Introduction

Metals and metalloids (potentially toxic elements) present in the environment pose a serious threat to human health and living organisms, due to their toxicity, environmental stability, and ease of entry into food chain (Milošković et al. 2013; Baran et al. 2016). The chemical composition of bottom sediments, which are an integral part of aquatic environment, is conditioned by many natural and anthropogenic factors. It results from the geological structure of the catchment,

land geomorphology, climate conditions, the way of management and use of catchment area, as well as the amount of contaminants reaching surface waters (Smal et al. 2015). The natural sources of metals and metalloids in water bodies are atmospheric inputs, as well as geological weathering of rocks and soil (Ghaleno et al. 2015; Wardhani et al. 2017), but the majority of these toxic elements are of anthropogenic origin (mining, disposal of wastewaters, metal chelates from different industries, use of fertilizers, atmospheric deposition, etc.) (Siebielec et al. 2015; Szydłowski et al. 2017). It should be emphasized that only a small pool of free metal or metalloid ions remains dissolved in water, while a large quantity of them are accumulated in the bottom sediments (as a result of adsorption, hydrolysis and co-precipitation processes) (Wardhani et al. 2017). Sediments act both as a sink and source of potentially toxic elements in aquatic ecosystems (Saleem et al. 2015; Devanesan et al. 2017), which may be re-suspended and cause secondary contamination to the water bodies (Wardhani et al. 2017). Moreover, these

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potentially toxic elements may accumulate in the tissues of aquatic organisms and cause various negative effects, associated with limiting of growth, metabolic processes, etc. (Milošković et al. 2013). There are some studies focused on the bioaccumulation of toxic elements in aquatic organisms. For example, Rzymiski et al. (2014) indicate a high bioaccumulation of Cd, Cr, and Cu in different bivalve species, as well as high concentrations of Cd and Pb in leaves of selected macrophyte, living in the artificial water body (Malta Reservoir, Poland). Moreover, positive correlations were found between Pb concentration in sediments and tissues of all examined bivalve species. While, Wu et al. (2014) show the moderate to very high ecological risk to humans from fish, because of elevated levels of Hg and Cd concentration in selected water reservoirs (Hongfeng and Baihua Reservoirs, China).

Therefore, the assessment of metals and metalloids concentration in the sediments of different water bodies may be useful in assessing human impact on the aquatic environment and its ecological state (biota), especially in case of reservoirs located in areas of high industrialization and urbanization. Moreover, to fully assess the level of contamination and ecological risk posed by potentially toxic elements in water bodies, it is necessary to take into account also the ecotoxicological criteria based on the relation between measured concentrations of these elements and observed biological effects.

The Dzierżno Duże Reservoir is located in the Silesian Region (Upper Silesian Industrial Region; GOP), which is one of the most urbanized areas of Poland (Central Europe). This part of country is characterized by great intensity of industrialization, particularly coal mining, metallurgy, energy, heavy industry and transportation, which cause high environmental contamination by metals and metalloids, including those toxic one. Therefore, the chemical composition of bottom sediments in this area depends mainly on the degree of human impact (Baran et al. 2016). The reservoir is supplied with waters of the Kłodnica River, which is one of the most contaminated rivers in Poland. Within Kłodnica catchment, hard coal mines, industrial plants and wastewater treatment plants, etc., are located (Barbusiński and Nocoń 2011). It is important to note that properties of toxic elements, i.e., their concentrations, non-biodegradability and toxicity are the major reason for their monitoring in an aquatic environment (Smal et al. 2015). Strong attention should be, therefore, put to ecological state of contaminated water bodies located in Silesian Region, which makes this issue one of the most current research topic in Poland.

Previous studies indicate that bottom sediments from the rivers and artificial reservoirs located in Silesian Region are characterized by potentially higher concentration of toxic elements, compared to other places in Poland and abroad. For example, sediments of the Malta Reservoir, which is

located in the northwestern part of Poland (Wielkopolska Region) are characterized by lower concentrations of Cd, Cr, Cu, Fe, Ni, Pb, and Zn, compared to sediments of the Dzierżno Duże Reservoir (Rzymiski et al. 2014; Rzętała 2016). Similar dependence was observed in reservoirs located in other countries, such as in Italy (Pertusillo Reservoir) or Spain (Castilseras Reservoir), where sediments showed lower levels of selected elements, i.e., Al, As, Cd, Cu, Fe, Pb, and Zn (Colella and D'Orsogna 2014; García-Ordiales et al. 2016), compared to those analyzed in this work.

Therefore, taking into account the above facts, it can be assumed that there is a possibility of existence of high contamination degree and potential ecological risk, associated with the presence of potentially toxic elements in bottom sediments of the Dzierżno Duże Reservoir, which encourage us to comprehensive analysis of these issues. Presented approach may lead to gain more knowledge about the potentially toxic elements, which occurred in the studied bottom sediments, as well as in other water bodies located in the key anthropogenic “hot spot” areas, such as Silesian Region. Due to the fact, that bottom sediments are habitat for many aquatic organisms and also taking into account the possibility of their use in agricultural (as a fertilizer) or as material for ground reclamation, to avoid secondary contamination of the environment, it is very important to know their chemical composition (Bartoszek et al. 2015).

To assess the contamination level and ecological risk of selected toxic elements in sediments of the Dzierżno Duże Reservoir, different indices were used, i.e., related to a single element or to a group of elements. The first group includes: Enrichment Factor (EF), Geoaccumulation Index (I_{geo}), Contamination Factor (CF), Potential Ecological Risk Factor (ER), Probable Effect Concentration (PEC), Threshold Effect Concentration (TEC). Whereas, the second one: Degree of Contamination (DC) and Risk Index (RI). Several previous research have shown the usefulness of different groups of indices in the assessment of the sediments contamination level and ecological risk posed by metals and metalloids (Zhao et al. 2012; Ghaleño et al. 2015; Saleem et al. 2015; Baran et al. 2016; Sivakumar et al. 2016). Study on the relationship between different indices allows a more reliable assessment of the risks associated with the presence of potentially toxic elements in aquatic environment, which makes this approach comprehensive. This is particularly important in case of reclamation of water reservoirs, e.g., by removing the backlog of sediments through dredging of reservoir, which may cause a migration of potentially toxic elements accumulated in sediments into the water (Bartoszek et al. 2015).

The aims of this study were (1) to investigate the total concentrations of nine metals (Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn) and one metalloid (As) in bottom sediments of the

Dzierżno Duże Reservoir, which are the most commonly analyzed toxic elements in the considered study area, (2) to evaluate the level of sediments contamination, (3) to carry out a comprehensive analysis of the ecological risk connected with the presence of metals and metalloid in bottom sediments, and (4) to demonstrate the usefulness of diverse indices to estimate the real contamination level and ecological risk.

Materials and methods

Study area

Dzierżno Duże Reservoir is located in the middle part of the Kłodnica River valley (right-hand tributary of the Odra River), in Silesian Region, Southern Poland (50°22'24"N; 18°33' 25"E). It lies in the upland area. Moreover, together with the Dzierżno Małe and Pławniowcie Reservoirs, as well as Gliwicki Canal creates the West Water Junction Node (also called the Kłodnica River hydrotechnical system). It plays an important role in water management and in the processes of shaping water quality (Kostecki and Suschka 2013). The map of study area is presented in Fig. 1.

The Dzierżno Duże Reservoir was created in 1964 by introducing waters of the contaminated Kłodnica River into

the mine, where previously the backfilling sand was excavated. Currently it is the largest reservoir of this type in Poland. It covers an area of over 6 km² and has a capacity of 94.0 hm³. The average water flow rate is 6.6 m³/s. The catchment area of the reservoir covers about 545 km² and is partially owned by the Upper Silesian Industrial Region. The length of the major axis of the reservoir is 5.9 km, maximum width of 1.5 km, and the maximum depth less than 20 m (average depth of about 15 m). The minimum, normal and maximum water levels are 194.5 m a.s.l., 202.5 m a.s.l. and 203.5 m a.s.l., respectively. Moreover, there is an underwater dyke in the reservoir, which divides it into two separate basins, slow down the water flow, and in consequence influence the way of sediments accumulation. The average retention time of water in the reservoir is about 200 days. A complete exchange of water takes 1 month, if so-called high water situation occur ("Program for the reclamation of dam reservoirs in the catchment area of Kłodnica River" 2016).

The main functions of the Dzierżno Duże Reservoir are ensuring the invasive flow of the Kłodnica River, reducing its flood wave, supplying water for the Gliwice Canal (to improving its navigability), protecting biodiversity, supplying the inviolable flow of the lower section of the river (minimum flow that should be maintained), and purifying waters of heavily contaminated river by acting as a "natural" clarifier.

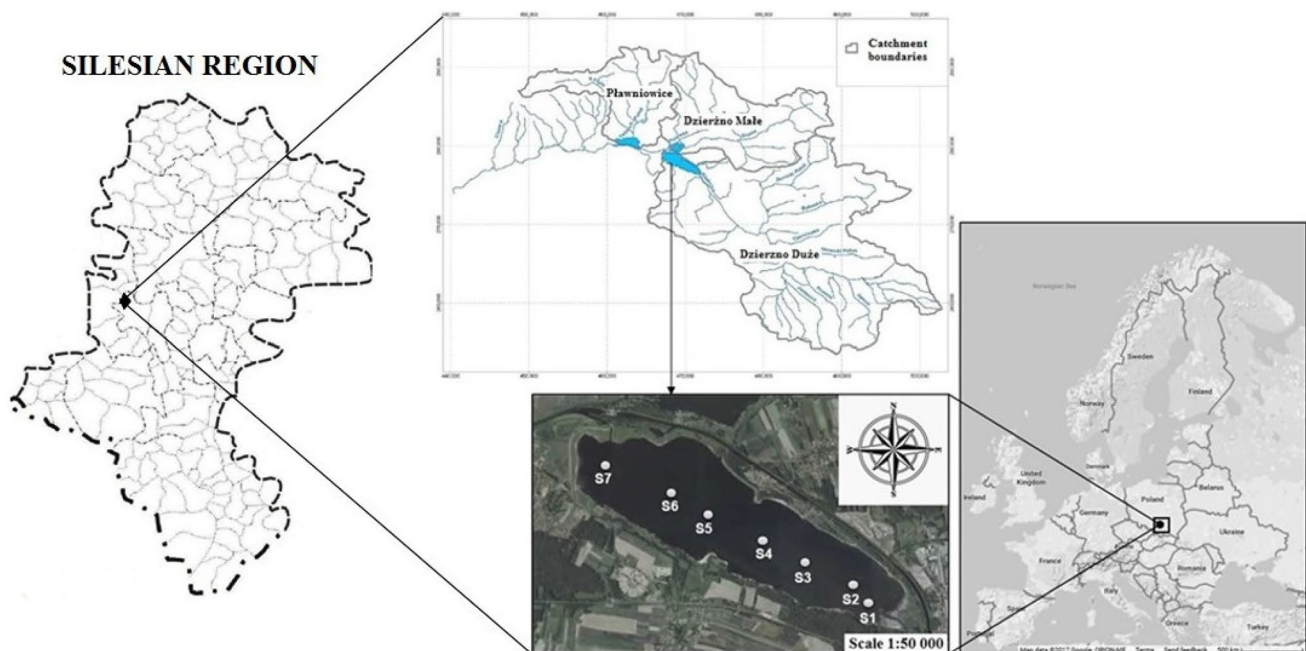


Fig. 1 Location of study area. The map on the left presents the borders of Silesian Region (Southern Poland, Central Europe). The map at the bottom presents the sampling sites at the Dzierżno Duże Reservoir (<https://www.google.com/maps>). The map on the top presents the catchment area of Dzierżno Duże Reservoir ("Program for the reclamation of dam reservoirs in the catchment area of Kłodnica River"

2016). The map was created using ArcGIS on the basis of Raster Hydrographical Map of Poland (<http://www.kzgw.gov.pl/index.php/pl/>; map after modification). The map on the right shows the Europe with borders of Poland (the original source file from: <https://www.google.pl/maps/@56.5060646,29.3968922,4z/data=!5m1!1e4?hl=en>)

The urban as well as industrial nature of the Dzierżno Duże Reservoir catchment is reflected by the main forms of land use, where the industrial areas cover—32%, industrial wasteland areas with agricultural land—43%, whereas forests—23% (Rzętała 2016) (Fig. 2). The rapid growth of urbanization and industrial development in the Upper Silesian Industrial Region has resulted in increasing metals and metalloids contamination in the waters and sediments of the Kłodnica River, which had a significant impact on the ecological state of Dzierżno Duże Reservoir. In the study area, the following types of industrial activity can be distinguished: energy sector, production and processing of metals, mineral industry, chemical industry, waste and wastewater management, paper and wood production and processing, intensive livestock production and aquaculture, animal and vegetable products from the food and beverage sector, etc. Different anthropogenic sources in the catchment area of Dzierżno Duże Reservoir enhance potentially toxic elements

contamination in sediments. The localization of the main sectors of industrial activity in the Upper Silesian Industrial Region is presented in Fig. 3.

Sampling

Samples were collected at seven sampling sites (S1–S7) from the surface layer of the sediments (to a depth of 5 cm) with the usage of Birge-Ekman sampler. All samples were collected during summer period (August 2016). The sampling sites were located 0.2 km, 1 km, 2 km, 3 km, 4 km, 5 km, and 6 km from the shoreline (S1–S4—before the underwater dike, S5–S7—after dike). Due to the asymmetry related to variable reservoir depth, sediments were collected along its main axis from the depth of 0.4 m–18 m (Fig. 1). At each site, three samples were collected, and then well mixed to obtain a representative one. All sediment samples were kept in polyethylene

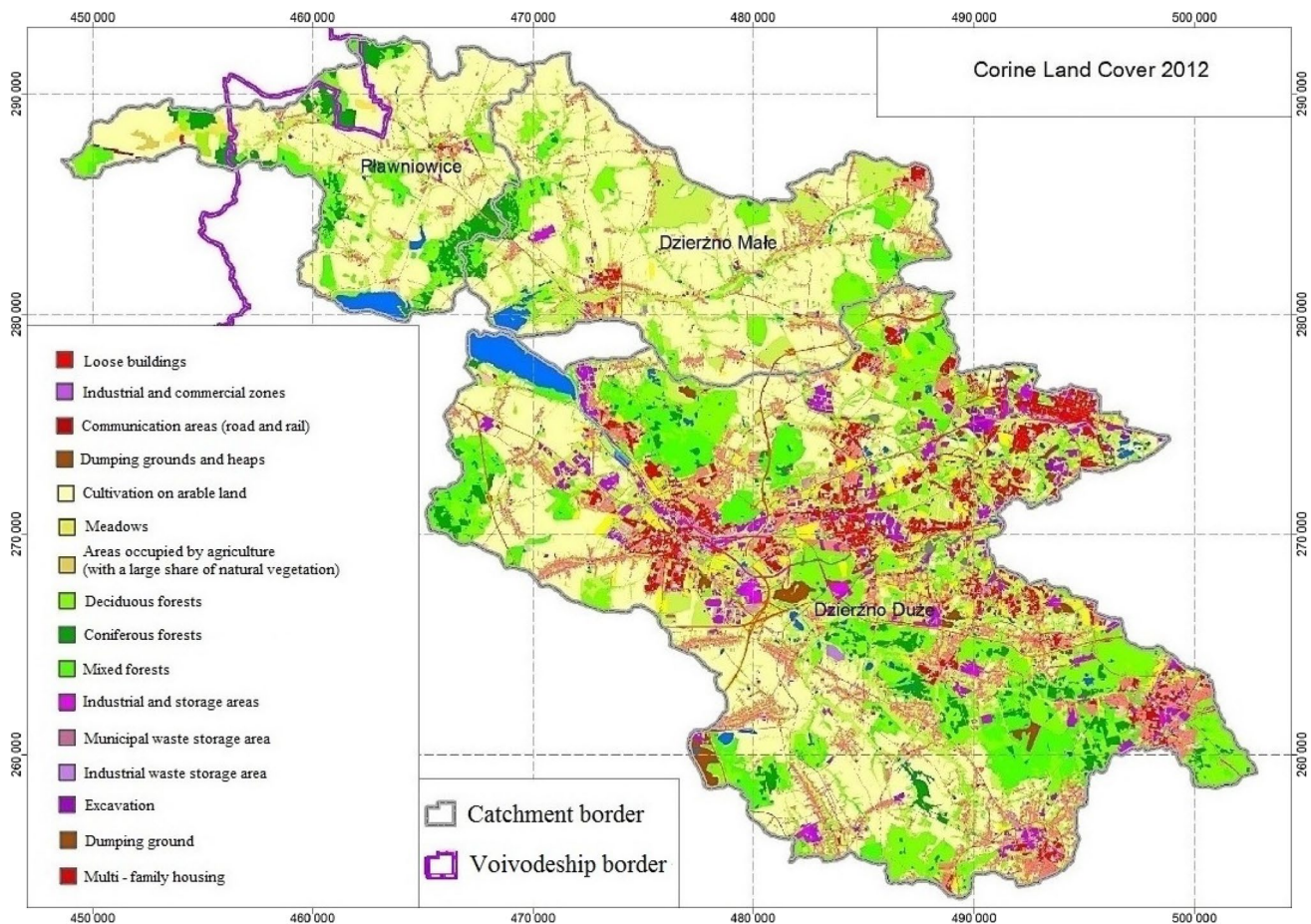


Fig. 2 Land covers in the catchment area of the Kłodnica River—including the catchment of the Dzierżno Duże Reservoir (“Program for the reclamation of dam reservoirs in the catchment area of Kłodnica River” 2016). The map was prepared using database created as part of the project Corine Land Cover 2012 (Corine Land Cover

2012 project in Poland was implemented by the Institute of Geodesy and Cartography and financed by the European Union). The results of the project were obtained from the website of the Chief Inspectorate for Environmental Protection (clc.gios.gov.pl). The legend on the map was modified

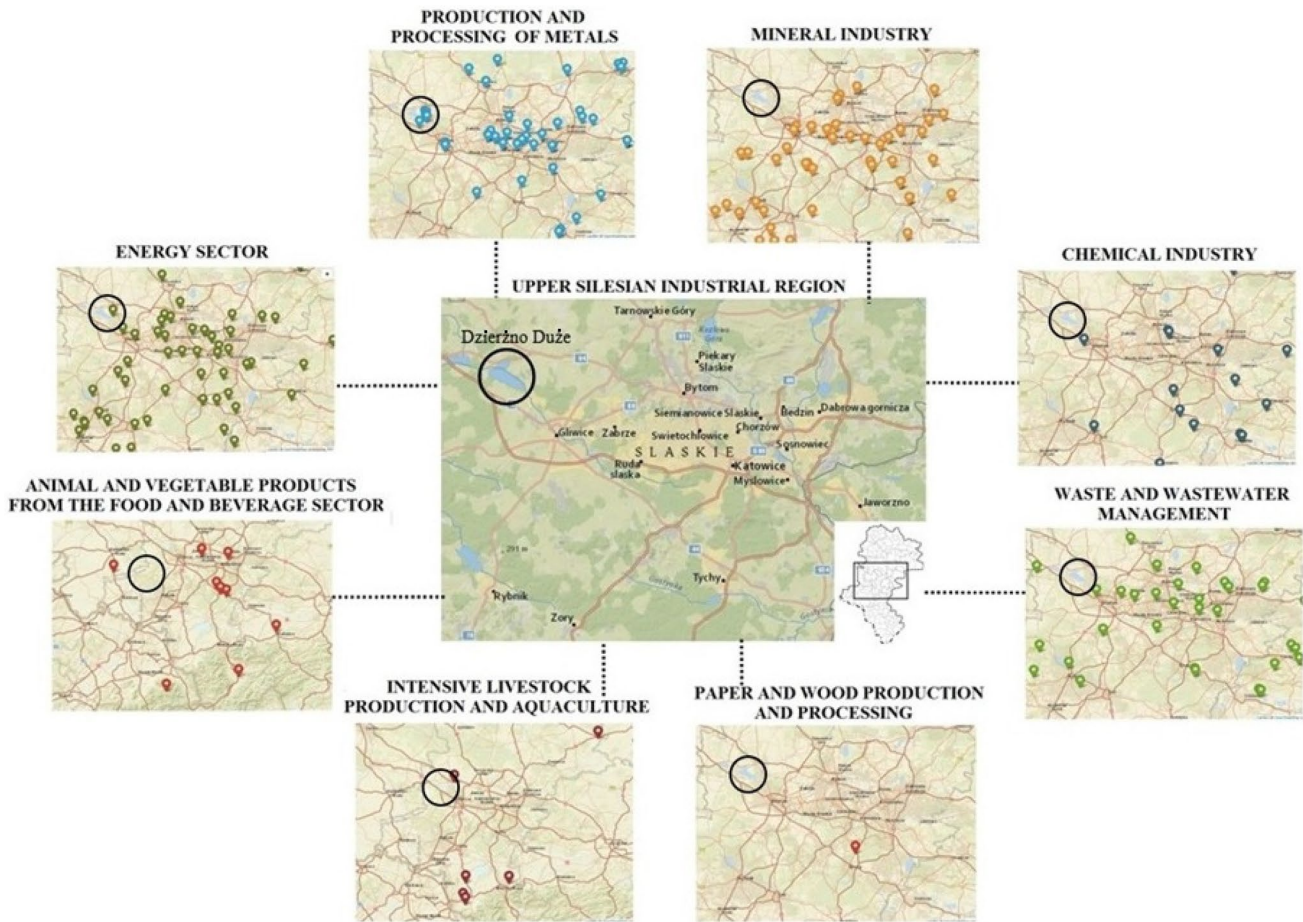


Fig. 3 Industrial activity in the Upper Silesian Industrial Region. The original source files from: <http://prtr.ec.europa.eu/#/industrialactivity> (European Environment Agency, EEA) and <http://www.arcgis.com/home/webmap/viewer.html>

Table 1 Geographical location of the sampling sites

Sampling sites	Latitude	Longitude	Depth (m)
S1	50°354'N	18°601'E	0.4
S2	50°357'N	18°597'E	0.8
S3	50°362'N	18°584'E	1.1
S4	50°365'N	18°574'E	8.0
S5	50°368'N	18°564'E	13.0
S6	50°370'N	18°558'E	17.0
S7	50°373'N	18°543'E	18.0

(HDPE) containers and stored in refrigerator at 4 °C, until the analysis. The sediments were collected once, at the peak of summer stagnation, when the most unfavorable oxygen–thermal conditions prevailed in the reservoir (the possibility of occurrence of conditions, favoring metals release from sediments into the water). Geographical locations and depth of the sampling sites are shown in Table 1.

Analytical procedures

Potential redox (Eh) and pH of the sediment samples were measured using Multifunctional Meter CX-401 (Elmetron) and electrodes as in order: ERPt-111 (Hydromet), ERH-111 (Hydromet). dry matter (DM) and organic matter (OM) content were determined in accordance with PN-ISO 11465 (1999) “Soil Quality—Determination of dry matter content of soil and water in soil on the basis of dry matter—Weight method”. Selected metals and metalloid concentrations in sediments were analyzed by spectrometric methods. The concentrations were presented in mg/kg_{DM}.

Sample pretreatment

The sediment samples were air-dried through exposure to ambient air for 48 h. After that, stones, sticks, etc., were manually removed. The air-dried sediments were milled in a mortar grinder and sieved through a 0.2 mm sieve. In next step, 0.5 g of sediment sample was digested with HNO₃ and HCl in Teflon flask. To control the digestion process, blank

reagent sample with the same amount of acids but without the sediments was used. Obtained solutions were filtered through the fine filters (0.45 μm) and diluted with 5% HNO_3 to volume of 50 ml. The digestion process was conducted in accordance with PN-EN 13657 (2006) “Characterization of waste. Digestion for subsequent determination of aqua regia soluble portion of elements”.

Determination of metals and metalloid concentrations

Concentrations of the Al and Fe in the obtained digests were determined by means of Inductively Coupled Plasma Mass Spectrometry (ICP-MS 6100 DRC-E, PerkinElmer Inc.) in accordance with Institute of Environmental Engineering (Polish Academy of Sciences in Zabrze) own procedure—“The application of inductively coupled plasma mass spectrometry in water quality studies” and PN-EN ISO 17294:2007 “Water quality. Application of inductively coupled plasma mass spectrometry (ICP-MS). Part 1: General guidelines”. While, concentrations of As, Cd, Cr, Cu, Mn, Ni, Pb, and Zn were determined using Inductively Coupled Plasma Optical Spectrometry (ICP-OES Optima 2000 DV, PerkinElmer Inc.) in accordance with PN-EN ISO 11885 (2009) “Water quality—Determination of selected elements by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)”. All standards were prepared on the day of analysis. The measurements were made in triplicate. The evaluation of uncertainty and precision of the analytical methods were not confirmed by the certified reference materials.

The contamination degree and ecological risk assessment

The contamination level and potential ecological risk of selected toxic elements in bottom sediments of Dzierżno Duże Reservoir were calculated by the equations shown in Table 2. Due to a varied toxicity of elements depending on the level of their valence state, while assessing the ecological risk, the authors reported the valences of specific elements, i.e., Al^{3+} , $\text{As}^{(\text{TOT})}$, Cd^{2+} , $\text{Cr}^{(\text{TOT})}$, Cu^{2+} , $\text{Fe}^{(\text{TOT})}$, Mn^{2+} , Ni^{2+} , Pb^{2+} , Zn^{2+} . In the case of arsenic, chromium and iron, the valence state is given as TOT (Total), as most probable species of these elements are $\text{As}^{3+/5+}$, $\text{Cr}^{3+/5+}$, $\text{Fe}^{2+/3+}$ (no speciation analysis was carried out).

Statistical analysis

All calculations and figures were performed using Statistica 12.0 and Excel 2013. Pearson’s correlation coefficients (r) were calculated to determine relationships among different toxic elements in the bottom sediments (the analyzed data

had a Gaussian distribution). Cluster Analysis (CA) was used to group elements into meaningful groups (clusters) based on their concentrations at each sampling site (the method by Ward was used for data agglomeration). The Principal Component Analysis (PCA) was carried out to obtain more reliable information about the relationships between the elements in sediments. Data analysis also included mean (\bar{x}), coefficient of variation (CV), and standard deviation (SD).

Results and discussion

Physicochemical characteristics of bottom sediments

Table 3 presents the statistical summary of pH, Eh, DM, OM, as well as metals and metalloid in bottom sediments of the Dzierżno Duże Reservoir, at various sampling sites (S1–S7). The pH and Eh values ranged from 7.1 to 7.9 and -349.3 to -294.1 mV, respectively. Both parameters did not show any significant fluctuations depending on the sampling site (pH; CV 4.4%, Eh; CV 6.4%). Whereas, DM and OM ranged from 16.0 to 48.9% and 4.6 to 20.0%, respectively, and characterized by high variability (DM; CV 53.5%, OM; CV 58.2%).

The highest overall metals and metalloid concentrations in studied sediments were observed at the sampling site S6 (after the underwater dike), while the lowest at S2 (before the underwater dike). Fe, Al, and Zn were found to be the dominant metals. The mean concentrations of potentially toxic elements in the bottom sediments were as follow: $\text{Fe} > \text{Al} > \text{Zn} > \text{Mn} > \text{Pb} > \text{Cu} > \text{Cr} > \text{Ni} > \text{As} > \text{Cd}$, in except of S5 and S7, where the contents of Cu and Pb were in the reverse order. The obtained results indicate that bottom sediments accumulated elements similarly, depending on the location of sampling sites. Moreover, among the considered metals, Mn was characterized by the greatest variability (CV 43.3%), while Cr by the lowest one (CV = 14.7%).

The highest concentrations of metals and metalloid in sediments (except of Al and Cu) were observed at two sampling sites, i.e., S4 (at 8 m depth) and S6 (at 17 m depth). First one was located near to Kłodnica River (before the underwater dike), where waters are rich in these elements (Barbusiński and Nocoń 2011). Whereas, the second one 5 km from the reservoir shoreline (after the underwater dike). Higher accumulation of toxic elements in this part of reservoir is probably associated with a reduction in flow velocity and sedimentation of suspended solids (SS), which resulted in an increased sorption capacity of these elements. Furthermore, the amount of metals or metalloids in sediments may also increase because of the self-purification processes of the surface waters. As a result of these processes potentially toxic elements migrates from water into

Table 2 The criteria of contamination level and potential ecological risk of toxic elements in bottom sediments

Indices	Equation with description	Category	Category with description and abbreviations
Enrichment Factor (EF) index of single-element (Sakan et al. 2009)	$EF_x = \frac{(C_x/C_{ref})_{\text{sediment}}}{(C_x/C_{ref})_{\text{crust}}}$ C_x and C_{ref} —concentrations of the element x and the reference element in the Earth's crust (Kabata-Pendias 2011); C_x are related to the concentration C_{Al} of Al as a reference element for the Earth's crust (Wedepohl 1995)	EF < 1	No enrichment (NE)
		EF 1–3	Minor enrichment (ME)
		EF 3–5	Moderate enrichment (MDE)
		EF 5–10	Moderately severe enrichment (MSE)
		EF 10–25	Severe enrichment (SE)
		EF 25–50	Very severe enrichment (VE)
Geoaccumulation Index (I_{geo}) index of single-element (Müller 1969)	$I_{geo} = \log_2 \left(\frac{C_n}{1.5B_n} \right)$ C_n —measured concentration of element in the sediment sample, B_n —geochemical background value in the Earth's crust (Kabata-Pendias 2011)	$I_{geo} \leq 0$	Practically uncontaminated (PUC)
		$0 < I_{geo} \leq 1$	Uncontaminated to moderately contaminated (U-MC)
		$1 < I_{geo} \leq 2$	Moderately contaminated (MC)
		$2 < I_{geo} \leq 3$	Moderately to Heavily contaminated (M-HC)
		$3 < I_{geo} \leq 4$	Heavily contaminated (HC)
		$4 < I_{geo} \leq 5$	Heavily to Extremely contaminated (H-EC)
Contamination Factor (CF) index of single-element (Hakanson 1980)	$CF = \frac{C_{0-1}^i}{C_n^i}$ C_{0-1}^i —mean content of elements from at list five sampling sites, C_n^i —concentration of elements in the Earth's crust	CF < 1	Low contamination (LC)
		$1 < CF < 3$	Moderate contamination (MC)
		$3 < CF < 6$	Considerable contamination (CC)
		CF > 6	Very high contamination (VHC)
Potential Ecological Risk Factor (ER) index of single-element (Hakanson 1980)	$ER = T_f^i CF$ T_f^i —toxic response factor of element; CF—Contamination Factor	ER < 40	Low risk (LR)
		$40 < ER \leq 80$	Moderate risk (MR)
		$80 < ER \leq 160$	Considerable risk (CR)
		$160 < ER \leq 320$	High risk (HR)
		ER > 320	Very high risk (VHR)
Probable Effect Concentration (PEC) Threshold Effect Concentration (TEC) index of single-element (Macdonald et al. 2000)	Ecotoxicological criteria	$C_n < TEC$	Non-polluted (NP)
		$TEC < C_n < PEC$	Neither polluted nor non-polluted (P-NP)
		$C_n > PEC$	Polluted (P)
Degree of Contamination (DC) index of multi-element (Hakanson 1980)	$DC = \sum CF$ CF—Contamination Factor	CD < 6	Low degree of contamination (LD)
		$6 < CD \leq 12$	Moderate degree of contamination (MD)
		$12 < CD \leq 24$	Considerable degree of contamination (CD)
		CD > 24	Very high degree of contamination (VHD)
Risk Index (RI) index of multi-element (Hakanson 1980)	$RI = \sum ER$ ER—Potential Ecological Risk Factor	RI < 150	Low risk (LR)
		$150 < RI < 300$	Moderate risk (MR)
		$300 < RI < 600$	Considerable risk (CR)
		RI > 600	High risk (HR)

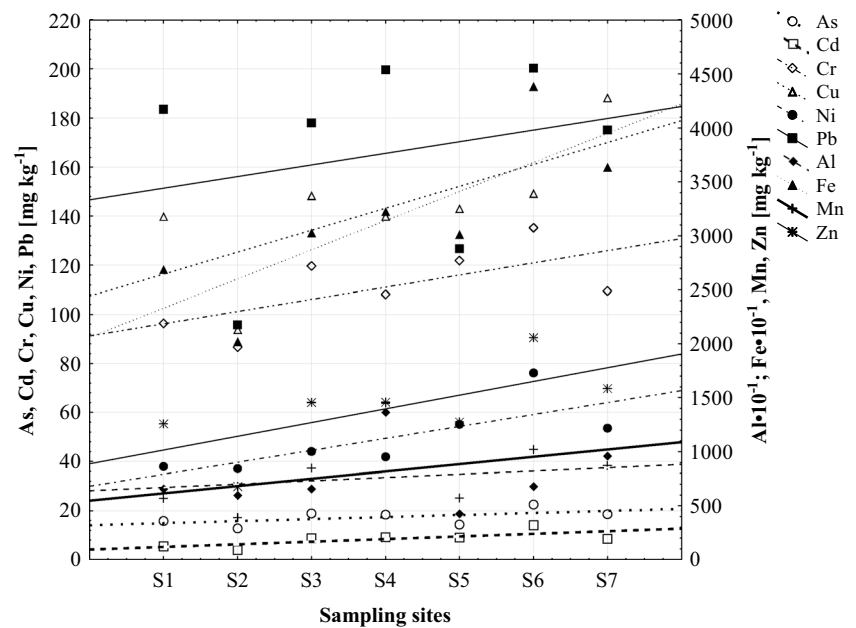
sediments (Barbusiński and Nocoń 2011). However, it was observed, that concentrations of metals and metalloid in studied sediments generally increased with the depth of reservoir (refers to sampling sites) (Fig. 4), but only for Fe and Ni this relationship was significant ($R^2 > 0.6$). Moreover, the analyzed elements were not correlated with other parameters, except of Cd, Cr, Fe, Zn, in case of DM (Table 4). However, there is no certainty that potential release of potentially

toxic elements from sediments into water, will not appear. It may occur due to the lowering values of pH or Eh, resulted from uncontrolled discharges of wastewater, surface runoff, etc. Moreover, to determine the potential mobility, bioavailability and toxicity of examined elements, more extensive studies including the analysis of their chemical forms of occurrence, as well as the temporal variability in sediments characteristics, are necessary.

Table 3 Concentrations of toxic elements in bottom sediments of the Dzierżno Duże Reservoir

Sampling sites	Al	As	Cd	Cr	Cu	Fe ($\text{mg kg}^{-1}_{\text{DM}} \pm \text{SD}$)	Mn	Ni	Pb	Zn	pH	Eh mV	DM %	OM %
S1	6555 ± 1640	15.8 ± 4.6	5.4 ± 0.54	96.3 ± 16.4	139.9 ± 15.4	26,852 ± 5649	569 ± 108.1	38.0 ± 5.31	183.5 ± 31.3	1258.9 ± 390	7.3	-294.1	48.9	20.0
S2	5952 ± 1490	12.8 ± 3.7	4.0 ± 0.04	86.7 ± 14.7	93.9 ± 10.3	20,199 ± 4240	390 ± 74.0	37.1 ± 5.2	95.8 ± 16.3	679.4 ± 210	7.1	-315.8	48.7	19.4
S3	6566 ± 1640	18.9 ± 5.5	8.8 ± 0.88	119.7 ± 20.0	148.4 ± 16.0	30,272 ± 6360	849 ± 161.0	44.1 ± 6.2	178.1 ± 30.0	1455.8 ± 453	7.1	-345.8	21.6	8.3
S4	13,659 ± 3430	18.4 ± 5.3	9.2 ± 0.92	108.1 ± 18.0	140.0 ± 15.0	32,242 ± 6760	1450 ± 276.0	41.9 ± 5.9	199.7 ± 34.0	1459.4 ± 453	7.2	-342.0	18.0	5.9
S5	4268 ± 1070	14.4 ± 4.2	9.1 ± 0.91	121.9 ± 21.0	143.1 ± 16.0	30,112 ± 6320	571 ± 108.0	55.1 ± 7.7	126.8 ± 22.0	1276.7 ± 397	7.5	-317.5	22.8	8.3
S6	6781 ± 1700	22.5 ± 6.5	14.1 ± 0.14	135.3 ± 23.0	149.3 ± 16.0	43,827 ± 9200	1020 ± 194.0	76.2 ± 10.7	200.3 ± 34.0	2059.2 ± 639	7.7	-346.4	16.7	6.0
S7	9602 ± 2400	18.6 ± 5.4	8.5 ± 0.85	109.5 ± 19.0	188.2 ± 21.0	36,360 ± 7644	872 ± 166	53.6 ± 7.5	175.2 ± 30.0	1586.1 ± 493	7.9	-349.3	16.0	4.6
Mean	7626	17.3	8.4	111.1	143.3	31,409	817.3	49.4	165.6	1353.6	7.4	-330.1	27.5	10.4
Minimum	4268	12.8	4.0	86.7	93.9	20,199	390.0	37.1	95.8	679.4	7.1	-349.3	16.0	4.6
Maximum	13,659	22.5	14.1	135.3	188.2	43,827	1450.0	76.2	200.3	2059.2	7.9	-294.1	48.9	20.0
SD	3092	3.3	3.2	16.3	27.5	7403	353.6	13.7	39.4	414.3	0.3	21.1	14.7	6.0
CV (%)	40.5	18.7	38.1	14.7	19.2	23.6	43.3	27.8	23.8	29.7	4.4	6.4	53.5	58.2
Detection limit ($\text{mg kg}^{-1}_{\text{DM}}$)	12.5	0.58	1.0	0.08	0.38	12.5	0.2	0.14	0.21	2.5	-	-	-	-
Measurement uncertainty (%)	25	29	10	17	11	21	19	14	17	31	-	-	-	-

Fig. 4 Metals and metalloid concentrations versus reservoir depth (sampling sites S1–S7)



The mean concentrations of toxic elements in studied bottom sediments were compared with the reported studies from Poland and other countries around the world, as presented in Table 5. These data indicate that sediments of the Dzierżno Duże Reservoir are characterized by higher levels of selected elements concentrations compared to other water bodies. Thus, it can be stated, that studied sediments are loaded by potentially toxic elements, which may cause ecological risk.

Assessment of contamination level and potential ecological risk

The obtained results indicate that, mean concentration of toxic elements in sediment samples exceeded the geochemical background levels. Geochemical quality classification (GQC), includes four classes of sediments, i.e., class I (non-contaminated), class II (moderately contaminated), class III (contaminated), class IV (highly contaminated) (Bojakowska 2001; Siebielec et al. 2015). It was found that Cd, Cr, Cu, Ni, Pb, and Zn were in the III and IV class (in except of: Cr and Ni in S1, as well as Cr, Cu, Ni and Pb in S2), while As represents the II class. Thus, it can be concluded that according to the above classification, sediments of Dzierżno Duże Reservoir are highly contaminated by examined metals and metalloid, which was also confirmed by other scientists (Rzętała 2016).

The evaluation of contamination level and ecological risk of selected metals and metalloid in studied bottom sediments were carried out using different indices. The obtained results are shown in Table 6. First group of considered indices is “single-element indices”, in which we can

distinguish, i.e., the Enrichment Factor. This index indicates the anthropogenic impact on sediments, using normalization element to alleviate the variations produced by heterogeneous sediments (Sakan et al. 2009; Saleem et al. 2015). In this study, aluminum was selected as a reference element for the Earth’s crust (consequently, $EFAI = 1$) (Wedepohl 1995). The obtained results showed that studied sediments were moderately to extremely severe enrichment with Cd (520.4–1651.1), Zn (118.2–335.9), Pb (75.5–153.4) and As (58.0–145.2), regardless of the sampling site. The EF of elements order in the following sequence: $Cd > Zn > Pb > As > Cu > Ni > Cr > Fe > Mn$. In comparison, Baran et al. (2016) indicate, that in sediments from other reservoir situated in the research area (Rybnik Reservoir, Southern Poland), Cd and Cu demonstrated extremely severe enrichment. The above results partly confirm our observations. Whereas, other scientists found that sediments from reservoir located in a different region of Poland (Besko Reservoir, Podkarpackie Voivodeship, Southeastern Poland) showed a minor to moderate enrichment for Cd, Zn, Cu, Ni, and Cr (Piwińska et al. 2018). Therefore, the above observations revealed different anthropogenic impact on the sediments contamination, depending on the location of reservoir. The second one of considered indices is Geoaccumulation Index computed by comparing the current and pre-industrial concentrations of elements in the Earth’s crust (Müller 1969). The values of I_{geo} revealed that studied sediments were heavily to extremely contaminated by Cd (4.7–6.6), Zn (2.7–4.8), Pb (2.1–3.1) and As (2.2–3.1). Moreover, the I_{geo} of examined elements were found in the sequence: $Cd > Zn > Pb > As > Ni > Cu > Cr > Mn > Fe > Al$. The above results were partly confirmed by Zemełka and

Table 4 Pearson's correlation coefficients between toxic elements and parameters of bottom sediments

	Al	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn	pH	Eh	DM	OM
Al	1.0000													
As	0.3647	1.0000												
Cd	0.1342	0.8532	1.0000											
Cr	-0.1003	0.7371	0.9449	1.0000										
Cu	0.2848	0.6003	0.4999	0.5119	1.0000									
Fe	0.2441	0.9083	0.6052	0.8367	0.7020	1.0000								
Mn	0.8427	0.7078	0.6052	0.4221	0.4069	0.6061	1.0000							
Ni	-0.1581	0.6863	0.8942	0.4786	0.4373	0.8775	0.2548	1.0000						
Pb	0.5611	0.8462	0.6011	0.4786	0.6129	0.7108	0.7712	0.3328	1.0000					
Zn	0.2447	0.9451	0.9193	0.8442	0.7091	0.9766	0.6330	0.8039	0.8162	1.0000				
pH	0.0207	0.4486	0.5280	0.4711	0.7506	0.7288	0.1220	0.7261	0.2710	0.6212	1.0000			
Eh	-0.4694	-0.7344	-0.6681	-0.5831	-0.5250	-0.6711	-0.6807	-0.4944	-0.4391	-0.6248	-0.3557	1.0000		
DM	-0.3936	-0.7121	- 0.8196	- 0.7949	-0.6971	- 0.7952	-0.7118	-0.6304	-0.5154	- 0.7595	-0.5180	0.8653	1.0000	
OM	-0.5801	-0.5621	-0.0948	0.1164	-0.1678	-0.2605	-0.4749	0.0400	-0.5528	-0.3004	0.0163	0.4671	0.0912	1.0000

Bold—significant correlations at $p < 0.05$

Szalińska (2017), who indicated that Dzierżno Duże Reservoir is heavily to extremely contaminated with Cd, as well as moderately to heavily with Pb and Zn. Unfortunately, the above work includes only five of eight examined metals (Cd, Cr, Cu, Pb, Zn). Moreover, also values of the Contamination Factor (Hakanson 1980) confirmed that studied sediments were very highly contaminated with Cd, Zn, Pb, and As ($CF > 6$). The CF of elements formed the following series in descending order: $Cd > Zn > Pb > As > Cu > Ni > Cr > Fe > Mn > Al$. The above observations are in good agreement with the results obtained by Rzętała (2016) who indicate, that studied sediments are very highly to moderately contaminated with $Cd > Cu > Zn > As > Cr$. In contradiction to our study, the same scientist has shown that in the case of sediments from other reservoir located in short distance from Silesian Region (Otmuchów Reservoir, Opolskie Voivodeship, Southern Poland), the main source of contamination was arsenic. Furthermore, it was also found that according to Potential Ecological Risk Factor calculated by Hakanson (1980); Cd, As (except of S2 and S5) and Pb (except of S2 and S7) posed the highest, considerable and moderate potential ecological risk, respectively, whereas other elements posed low risk ($ER < 40$). The ER for examined elements was found in the following order: $Cd > As > Pb > Zn > Cu > Ni > Cr > Mn$ (classification does not include concentration of Al and Fe). In contradiction to our observations, other scientists such as Baran et al. (2016) or Szedłowski et al. (2017) indicated moderately to low risk posed by $Cd > Cu > Pb > Cr > Zn$ (Rybnik Reservoir, Southern Poland) and $Ni > Cd > Pb > Cu > Cr > Zn$ (Stare Czarnowo, Zachodniopomorskie Voivodeship, Northwestern Poland), respectively. The above results confirmed that sediments of the Dzierżno Duże Reservoir cause higher ecological risk than sediments from other water bodies in the country. Moreover, risk assessment was also carried out using the ecotoxicological criteria, i.e., Probable Effect Concentration and Threshold Effect Concentration (Macdonald et al. 2000; Baran and Tarnawski 2015). This approach is based on the relation between measured concentrations of elements and observed biological effects (classification does not include Al concentration). We found that depending on the sampling site, mean concentrations of Cd, Pb, Zn, Mn, Ni, Cr, Cu, and Fe exceeded PEC limit values, which confirmed high contamination of studied sediments with these elements. This means, that they cause an adverse effect on aquatic organisms. Whereas, the concentrations of remaining elements were higher than the TEC but lower than PEC values, which means that they do not pose a threat to the living organisms. In comparison to our experiment, Dąbrowska (2011) indicated that concentrations of Cd, Zn, and Pb in sediments of the Kozłowa Góra Reservoir located close to the Dzierżno Duże Reservoir (Silesian Region, Southern Poland) exceeded PEC values. Whereas, Baran and

Table 5 Mean concentrations of toxic elements in bottom sediments of the Dzierżno Duże Reservoir in comparison with other studies

Location	Al (mg/kg ⁻¹ _{DM})	As (mg/kg ⁻¹ _{DM})	Cd (mg/kg ⁻¹ _{DM})	Cr (mg/kg ⁻¹ _{DM})	Cu (mg/kg ⁻¹ _{DM})	Fe (mg/kg ⁻¹ _{DM})	Mn (mg/kg ⁻¹ _{DM})	Ni (mg/kg ⁻¹ _{DM})	Pb (mg/kg ⁻¹ _{DM})	Zn (mg/kg ⁻¹ _{DM})	References
Dzierżno Duże Reservoir, Poland	6555.0	15.8	5.4	96.3	139.9	26852.0	569.0	38.0	183.5	1258.9	This study
Rybnik Reservoir, Poland	–	–	25.8	129.8	451.7	38782.3	2018.7	71.1	118.6	1583.4	Loska and Wiechula (2003)
Dzierżno Małe Reservoir, Poland	–	12.3	2.4	66.1	21.5	–	–	23.8	69.6	342.6	Jaguś et al. (2013)
Malta Reservoir, Poland	–	–	0.09	7.8	11.0	4460.0	693.0	4.2	2.7	72.0	Rzyski et al. (2014)
Brody Iłzeckie Reservoir, Poland	–	–	2.5	41.4	16.6	–	549.0	14.3	69.2	345.0	Smal et al. (2015)
Poraj Reservoir, Poland	4840.0	–	–	–	–	12170.0	–	–	–	–	Rozpondek et al. (2017)
Jose Antonio Alzate Reservoir, Mexico	–	–	2.5	85.0	35.0	37203.0	–	33.0	26.0	145.0	Avila-Péres et al. (1999)
Pertusillo Reservoir, Italy	6149.9	1.7	0.7	7.9	9.5	5924.1	131.2	8.6	4.8	32.0	Colella and D'Orsogna (2014)
Asejire Reservoir, Nigeria	–	–	–	0.03	43.7	39978.8	1.5	0.1	72.0	20.9	Godwin et al. (2015)
Castilseras Reservoir, Spain	14.2	11.3	–	64.4	14.6	4.3	539.1	43.4	40.7	103.6	García-Ordiales et al. (2016)
Hoedong Reservoir, Korea	–	–	1.6	28.7	57.6	–	–	17.2	60.5	247.8	Lee et al. (2017)

Table 6 Contamination and ecological risk of toxic elements

	Metal	EF		I_{geo}	CF	ER	PEC/TEC	DC	RI		
S1	Al	1.0	–	–4.1	PUC	0.1	LC	–	–	100.0 VHD	1811.7 HR
	As	103.7	EE	2.5	M-HC	8.8	VHC	87.8	CR	P-NP	
	Cd	637.9	EE	5.2	EC	54.0	VHC	1620.0	VHR	P	
	Cr	11.4	SE	–0.6	PUC	1.0	MC	1.9	LR	P-NP	
	Cu	30.1	VE	0.8	U-MC	2.5	MC	12.7	LR	P-NP	
	Fe	10.3	SE	–0.8	PUC	0.9	LC	–	–	P-NP	
	Mn	7.5	MSE	–1.2	PUC	0.6	LC	0.6	LR	P-NP	
	Ni	22.4	SE	0.3	U-MC	1.9	MC	9.5	LR	P-NP	
	Pb	144.5	EE	3.1	HC	12.2	VHC	61.2	MR	P	
	Zn	212.5	EE	3.6	HC	18.0	VHC	18.0	LR	P	
S2	Al	1.0	–	–4.3	PUC	0.1	LC	–	–	68.8 VHD	1332.9 HR
	As	92.5	EE	2.2	MC	7.1	VHC	71.1	MR	P-NP	
	Cd	520.4	EE	4.7	H-EC	40.0	VHC	1200.0	VHR	P	
	Cr	11.3	SE	–0.8	PUC	0.9	LC	1.7	LR	P-NP	
	Cu	22.2	SE	0.2	U-MC	1.7	MC	8.5	LR	P-NP	
	Fe	8.5	MSE	–1.2	PUC	0.7	LC	–	–	P-NP	
	Mn	5.6	MSE	–1.8	PUC	0.4	LC	0.4	LR	P-NP	
	Ni	24.7	SE	0.3	U-MC	1.9	MC	9.5	LR	P-NP	
	Pb	83.1	EE	2.1	MC	6.4	VHC	31.9	LR	P-NP	
	Zn	126.2	EE	2.7	MC	9.7	VHC	9.7	LR	P	
S3	Al	1.0	–	–4.1	PUC	0.1	LC	–	–	139.3 VHD	2853.0 HR
	As	123.8	EE	2.8	MC	10.5	VHC	105.0	CR	P-NP	
	Cd	1037.9	EE	5.9	EC	88.0	VHC	2640.0	VHR	P	
	Cr	14.1	SE	–0.3	PUC	1.2	MC	2.4	LR	P	
	Cu	31.8	VE	0.8	U-MC	2.7	MC	13.5	LR	P-NP	
	Fe	11.6	SE	–4.1	PUC	1.0	MC	–	–	P-NP	
	Mn	11.1	SE	–0.7	PUC	0.9	LC	0.9	LR	P-NP	
	Ni	26.0	VE	0.6	U-MC	2.2	MC	11.0	LR	P-NP	
	Pb	140.0	EE	3.1	HC	11.9	VHC	59.4	MR	P	
	Zn	245.3	EE	3.8	HC	20.8	VHC	20.8	LR	P	
S4	Al	1.0	–	–3.1	PUC	0.2	LC	–	–	144.9 VHD	2976.6 HR
	As	58.0	EE	2.8	M-HC	10.2	VHC	102.2	CR	P-NP	
	Cd	521.6	EE	5.9	EC	92.0	VHC	2760.0	VHR	P	
	Cr	6.1	MSE	–0.5	PUC	1.1	MC	2.2	LR	P-NP	
	Cu	14.4	SE	0.8	U-MC	2.5	MC	12.7	LR	P-NP	
	Fe	5.9	MSE	–0.5	PUC	1.0	MC	–	–	P-NP	
	Mn	9.1	MSE	0.1	U-MC	1.6	LC	1.6	LR	P	
	Ni	11.9	SE	0.5	U-MC	2.1	MC	10.5	LR	P-NP	
	Pb	75.5	EE	3.1	HC	13.3	VHC	66.6	MR	P	
	Zn	118.2	EE	3.8	HC	20.8	VHC	20.8	LR	P	
S5	Al	1.0	–	–4.8	PUC	0.1	LC	–	–	133.9 VHD	2900.4 HR
	As	145.2	EE	2.4	M-HC	8.0	VHC	80.0	MR	P-NP	
	Cd	1651.1	EE	5.9	EC	91.0	VHC	2730.0	VHR	P-NP	
	Cr	22.1	SE	–0.3	PUC	1.2	MC	2.4	LR	P-NP	
	Cu	47.2	VE	0.8	U-MC	2.6	MC	13.0	LR	P-NP	
	Fe	17.7	SE	–0.6	PUC	1.0	LC	–	–	P-NP	
	Mn	11.5	SE	–1.2	PUC	0.6	LC	0.6	LR	P	
	Ni	50.0	VE	0.9	U-MC	2.8	MC	13.8	LR	P	
	Pb	153.4	EE	2.5	M-HC	8.5	VHC	42.3	MR	P-NP	
	Zn	330.9	EE	3.6	HC	18.2	VHC	18.2	LR	P	

Table 6 (continued)

	Metal	EF		I_{geo}	CF	ER		PEC/TEC	DC	RI		
S6	Al	1.0	–	–4.1	PUC	0.1	LC	–	–	206.8 VHD	4487.6 HR	
	As	142.8	EE	3.1	HC	12.5	VHC	125.0	CR	P-NP		
	Cd	1610.2	EE	6.6	EC	141.0	VHC	4230.0	VHR	P		
	Cr	15.5	SE	–0.1	PUC	1.4	MC	2.7	LR	P		
	Cu	31.0	VE	0.9	U-MC	2.7	MC	13.6	LR	P-NP		
	Fe	16.2	SE	–0.1	PUC	1.4	MC	–	–	P		
	Mn	12.9	SE	–0.4	PUC	1.1	LC	1.1	LR	P		
	Ni	43.5	VE	1.3	MC	3.8	CC	19.1	LR	P		
	Pb	152.5	EE	3.2	HC	13.4	VHC	66.8	MR	P		
	Zn	335.9	EE	4.3	H-EC	29.4	VHC	29.4	LR	P		
	S7	Al	1.0	–	–3.6	PUC	0.1	LC	–	–	139.1 VHD	2768.0 HR
		As	83.3	EE	2.8	M-HC	10.3	VHC	103.3	CR	P-NP	
		Cd	685.3	EE	5.8	EC	85.0	VHC	2550.0	VHR	P	
Cr		8.8	MSE	–0.5	PUC	1.1	MC	2.2	LR	P-NP		
Cu		27.6	VE	1.2	MC	3.4	CC	17.1	LR	P		
Fe		9.5	MSE	–0.3	PUC	1.2	MC	–	–	P-NP		
Mn		7.8	MSE	–0.6	PUC	1.0	LC	1.0	LR	P-NP		
Ni		21.6	SE	0.8	U-MC	2.7	MC	13.4	LR	P		
Pb		94.1	EE	3.0	HC	11.7	VHC	58.3	MR	P		
Zn	182.7	EE	3.9	HC	22.7	VHC	22.7	LR	P			

Bold indicates the highest levels

Tarnawski (2015) made a similar observations in relate to Zn, Cd, Cr, and Cu (Rybnik Reservoir, Southern Poland). Thus, it can be concluded, that the above results are in good agreement with those presented here.

The contamination level and ecological risk of examined metals and metalloid in sediments of the Dzierżno Duże Reservoir were also assessing using multi-element indices, i.e., Degree of Contamination and Risk Index (Hakanson 1980). The above indices were used to estimate the overall level of contamination and ecological risk at a given sampling site. The obtained results indicate, that the highest contamination of bottom sediments occurred at sampling site S6 (depth = 17 m), while the lowest at S2 (depth = 0.8 m). The values of DC were extremely high and ranged from 68.8 to 206.8. The above observations were also confirmed by RI values, which was in the range of 1332.0 (S2)–4487.6 (S6). The obtained results indicate that bottom sediments at each sampling sites were found to be highly contaminated with potentially toxic elements, which may cause a high risk to aquatic ecosystem and living organisms. It was revealed that Cd, As, Zn, and Pb pose the greatest threat to the environment, which was consistent with the results obtained using single-element indices. Moreover, high contamination and risk levels suggest that toxic elements in sediments of the Dzierżno Duże Reservoir are most probably of anthropogenic sources. It is most likely related to the location of the reservoir. The middle part of the Kłodnica River valley is

one of the most polluted rivers in Silesian Region. However, in this case a more detailed statistical analysis is needed. The similar experiment was made by Baran et al. (2016) who found that bottom sediments from other anthropogenic reservoir (Rybnik Reservoir, Southern Poland) were considerably to highly contaminated by Zn, Cd, Pb, Ni, Cu, Cr, and Hg (DC; 14.2–358.0). Whereas, in contradiction to our results, Szydłowski et al. (2017) showed that: Cd, Co, Cr, Cu, Ni, Pb, Zn, and Hg in sediments of the Żeliszewiec Reservoir (Zachodniopomorskie Voivodeship, Northwestern Poland), cause only moderate risk to the aquatic ecosystem (RI 164.1). However, it must be emphasized, that the above reservoir is situated in a totally different geographical region of Poland, than the studied one, and characterized with low degree of urbanization and industrialization.

In conclusion, in can be assumed that the contamination level and ecological risk of metals and metalloids in water reservoirs depend on several factors, i.e., sediments characteristics (origin), reservoir location (sources of contamination) and data used as background values (for individual elements).

The source of metals and metalloid contamination

The high content of metals and metalloids most often occurs in sediments of water reservoirs, to which wastewater from mining and processing of metal ores, as well as large urban

and industrial centers are discharged (like in the studied area) Trace elements are also introduced to the water bodies as a result of destruction of building materials by atmospheric agents (Cu, Cr, Pb, Zn), corrosion of the water supply and sewage systems (Cd, Zn) (Szydłowski et al. 2017). A considerable amount of potentially toxic elements accumulated in the sediments are introduced to water bodies with wastewater (municipal, industrial, post-mining waters) and with surface runoffs from, i.a., agricultural areas (As, Cd, Ni, Pb, Zn, Cu), urbanized areas or routes communication (Pb, Zn, Cd) (Siebielec et al. 2015; Ghaleno et al. 2015; Szydłowski et al. 2017). Another sources of metals and metalloids, such as: As, Cd, Fe, Pb and Zn are low emission (home furnaces), as well as dust and gas emissions (thermal power plants, mines, steelworks) (García-Ordiales et al. 2016; Szydłowski et al. 2017). Moreover, hard coal mining has an impact on the Mn and Fe concentrations due to the discharge of mine wastewater (Barbusiński and Nocoń 2011). The production processes in the food and paper industry also increase the pollution of environment with toxic elements (Szydłowski et al. 2017). It can be concluded that the concentrations of metals and metalloids in bottom sediments of the Dzierżno Duże Reservoir should be combined primarily with the anthropopressure of the surrounding area.

An indication of metals and metalloids sources in the sediments of water reservoirs, constitute a very important aspect of their monitoring and quality control. The traditional statistical approaches such as Pearson's correlation, Cluster Analysis, and Principal Component Analysis are the effective tools for uncovering the contamination sources and have been used by many researchers in studies regarding

reservoirs contamination (Loska and Wiechuła 2003; Widziewicz and Loska 2012; Baran et al. 2016). Moreover, as it was mentioned, in this study aluminum has been selected as a normalizing element for the calculation of the sediments EF, which implies that it is of natural origin. For this reason, it was not included in the CA and PCA analysis.

Table 4 presents the results of the Pearson's correlation analysis for toxic elements in bottom sediments of the Dzierżno Duże Reservoir. The obtained results indicate the presence of strong positive correlations between selected elements: As and Cd, Fe, Pb, Zn; Cd and As, Cr, Fe, Ni, Zn; Cr and Fe, Ni, Pb, Zn; Fe and As, Cd, Cr, Ni, Zn; Mn and Al, Pb; Ni and Cd, Cr, Fe, Zn; Pb and As, Mn, Zn; Zn; As, Cd, Fe, Ni, Pb and Al and Mn. Only in the case of Cu, weak but positive correlation with Fe, Pb and Zn, was observed. It can be assumed that significant correlations among the above elements may indicate that they possibly have a similar accumulation behavior or originate from the same contaminant sources. Considering the location of the Dzierżno Duże Reservoir, metals and metalloid in bottom sediments are likely of anthropogenic origin. The only exception may constitute Mn, which correlates with Al. Similar observations to the presented one were made by Baran et al. (2016) who found a strong positive correlation between concentrations of Cd, Cu, Cr, Hg, Ni, Pb and Zn in the sediments of reservoir located a short distance from the studied area (Rybnik Reservoir, Southern Poland). It is important to emphasize that both reservoirs are under a strong anthropogenic influence.

Figure 5 presents the results of Cluster Analysis according to which two main groups of potentially toxic elements can be distinguished. First group contains As, Cd, Cr, Cu,

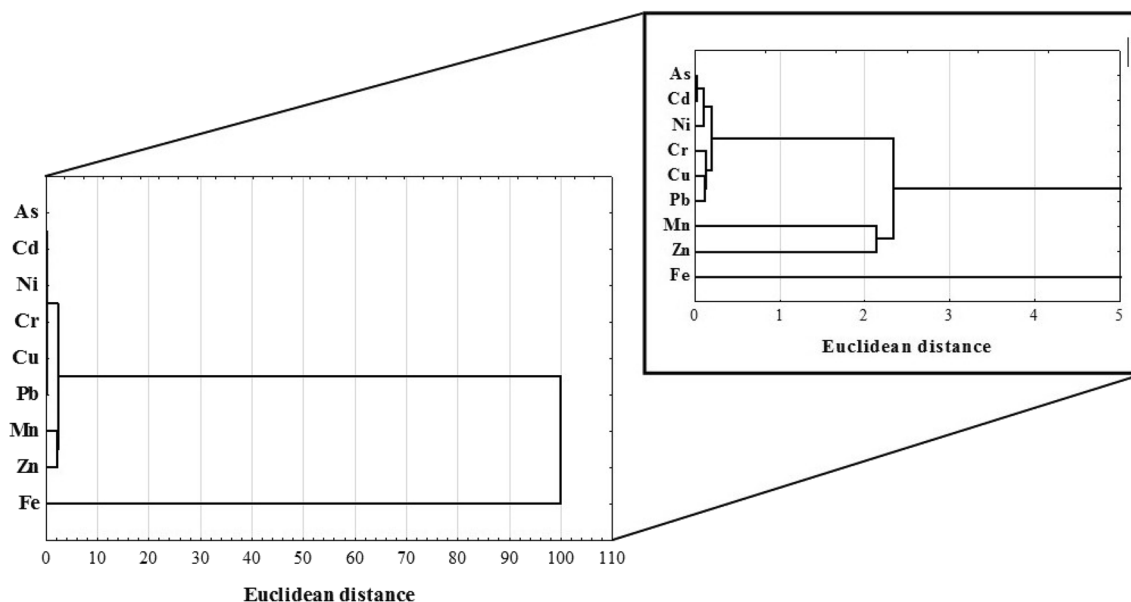


Fig. 5 Cluster analysis (CA) by Ward for Dzierżno Duże Reservoir

Ni and Pb, while the second one: Mn, Zn and Fe. Despite the similarities in the occurrence of toxic elements and changes in their concentrations reflected by the dendrogram, these two groups are strict different in term of Euclidean distances. Smaller distance was recorded for the elements from the first group, which means that they are probably strongly correlated. Moreover, to find similarities between measured parameters (potentially toxic elements), to determine the source of their origin, PCA analysis was carried out (Fig. 6). The obtained results indicated that examined elements could be grouped into a two principal components (PCs), which explained approx. 87.90% of total original data variance. The variance indicates the amount of total information presented by each element. The PC1 accounted for 74.70% of the total variance and was characterized by large fractions of As, Cd, Cr, Fe, Ni, Pb, and Zn, suggesting of similar origin for these potentially toxic elements. While the second principal component (PC2) accounted for 13.20% of the total variance and included large fraction of Mn. Each parameter is represented by a vector. The direction and length of these vectors determine to which extent particular parameters affect the main components. Close position of two parameters indicates a strong correlation between them, for example: Cr and Ni, whereas vectors perpendicular to each other indicate a lack of correlation, like in the case of Mn and Ni. These results coincide with the conclusions resulting from the correlation analysis. Strong relationships between As, Cd, Cr, Cu, Ni, and Pb, as well as small Euclidean distances and large fractions of these elements in PC1, indicate that they may originate from same contamination sources, probably anthropogenic. Moreover, PC1 includes a large fraction of Fe and Zn, which occurrence may be closely related to overall emission of industrial pollutants in the studied area, discharged from: mine wastewater, municipal, industrial and post-mining waters, etc. Furthermore, the correlation matrix and PCA analysis confirm a strong relationship between Fe and other examined elements, despite of the results of CA analysis. Whereas, in case of Mn, neither Pearson's correlation matrix nor PCA analysis, not confirm the strong relationship between Mn and Zn concentrations, even despite of a small Euclidean distance between these two elements. In addition, the content of Mn does not correlate with any of examined elements, except Al. Therefore, we can assume that manganese is probably of natural origin.

In conclusion, taking into account the level of industrialization of the studied area, it is very difficult to identify a single source for selected toxic elements in the bottom sediments of the Dzierżno Duże Reservoir. Moreover, the contamination and ecological risk levels, as well as the results of statistical analysis indicate that the major contaminants in the analyzed sediments, which pose the greatest threat to the environment, are Cd, Pb, Zn, and As. The conducted research indicates the necessity of combining chemical

analyses of sediments and ecological risk posed by toxic elements with in-depth statistical analysis, which will allow to determine a probable source of their origin.

Conclusion

In this study, different groups of indices were successfully used to assess the levels of contamination and ecological risk of nine metals (Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) and one metalloid (As) in bottom sediments of the Dzierżno Duże Reservoir located in the key anthropogenic "hot spot" area. In general, the level of contamination and ecological risk associated with the presence of toxic elements in studied sediments, were very high. The highest risk poses Cd, As, Zn, and Pb. Taking into account high industrialization and urbanization of the research area, it can be assumed that toxic elements are probably of anthropogenic origin (except Mn). With reference to the above findings, it must be emphasized that comprehensive analysis of the contamination level and ecological risk of toxic elements in the bottom sediments constitute the basis in assessing the ecological state of water bodies. This is particularly important in case of reservoirs located in the key anthropogenic "hot spot" areas such as Upper Silesia, where all water bodies are of anthropogenic origin. It should be note that water bodies are an integral part of ecological networks in urban and industrial areas and they have important economic, environmental and landscape role. Therefore, for proper assessment of the contamination and ecological risk levels posed by metals

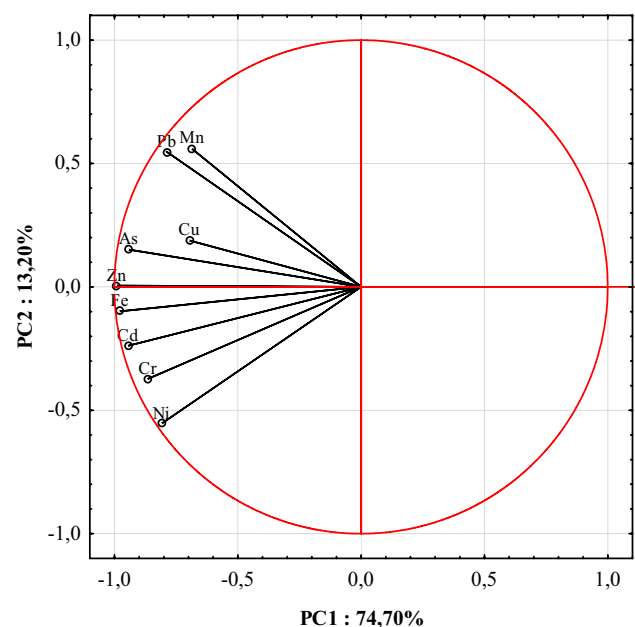


Fig. 6 Results of PCA analysis for Dzierżno Duże Reservoir

and metalloids, determination of their potential source of origin is necessary. In this case, detailed statistical analysis is required. The combination of the abovementioned components, allows an accurate assessment of the ecological status of water bodies.

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