Metal pollution of sediments in small water reservoirs in the Kielce Highland (South Eastern Poland)

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Abstract: The aim of the study was to evaluate the degree of pollution of bottom sediments from small water reservoirs with heavy metals on the basis of geochemical criteria: the enrichment factor and the geo-accumulation index. The investigations concerned sediment from eight small water reservoirs located in the Kielce Highland. Selected heavy metals, including cadmium, chromium, copper, lead and zinc, were determined using inductively coupled plasma-*atomic emission spectrometry* method. Additionally, particle size distribution and the content of organic matter expressed as loss of ignition were designated. The concentration of heavy metals in sediments was characterized by a great variety. The sediments of Morawica and Rejów show very high and extremely high enrichment in Cr, Zn, Pb and Cd. The values of EF>20 indicate also an extremely high enrichment in Cd of sediments in Mostki. In addition, over 50% of the samples of sediment from Suchedniów, Kaniów, Mostki and Jaśle reservoirs (the value of EF for Cr exceeded 5) indicate a moderately high enrichment of this element. Results of the analysis of the I_{geo} values indicate that the tested sediments are characterized by moderately high ($2<I_{geo}<3$) or high ($3<I_{geo}<4$) pollution. The differences in individual enrichment factor and geoaccumulation index values may result in the nature of heavy metals, their pollution loads, as well as speciation forms of trace elements occurrence in sediment-water complex. These findings indicate that the integration of geochemical methods is necessary for an appropriate ecological risk assessment of heavy metals in bottom sediments.

Introduction

The natural environment is affected by many factors, including the growth and distribution of population, the use of different chemical compounds, and also forms of land use. Sediment quality has been recognized as an important indicator of water pollution since sediments are the main sink for various pollutants, including metals discharged into the environment (Ibragimow et al. 2013, Nasr et al. 2006, Nocoń et al. 2013, Nriagu 1989, Tam and Wong 2000). Bottom sediments play a major role in determining the pollution pattern of aquatic systems, in the remobilization of contaminants under favourable conditions, and in interactions between water and sediment. They also act as both carriers and sinks for contaminants, thus reflecting the history of pollution (Ghrefat et al. 2011, Smal et al. 2015). Sediment is a matrix of materials comprising inorganic and organic particles, which is relatively heterogeneous in terms of its physical, chemical and biological characteristics (Charlesworth et al. 2003). The results of the bottom sediment study can provide important information about the current state of the environment and to trace – where sedimentation periods are documented – a change in concentration of pollutants over time.

Metals are a group of pollutants of high ecological significance. Pollution associated with metals is a serious problem due to their toxicity and their ability to accumulate in the biota. One of the most crucial properties of metals is that they are not biodegradable in the environment (Karbassi et al. 2008, Nuremberg 1984, Schuurmann and Market 1998, Wu et al. 2012). They are not removed from water by natural attenuation, but accumulate in suspended particulates and sediment, and then enter the food web via passing to higher consumer. Sources of metals in aquatic sediments are both natural and anthropogenic. The main natural sources are the weathering of soils and rocks and atmospheric deposition. Agricultural, municipal, residential or industrial waste products discharged into water bodies are anthropogenic sources. In the sediments, metals accumulate through complex physical and chemical adsorption/absorption mechanisms, depending on the nature of the sediment matrix and the properties of the adsorbed compounds (Anderson and Kravitz 2010, Zabetoglou et al. 2002, Zahra et al. 2014). Intense sedimentation within estuarine and marine environments traps heavy metals within fine grained particles and organic matter. This intense sedimentation concentrates heavy metals and helps to limit their environmental impact. However, sequestration can be

of concern due to the long residence times which increase the possibility of re-suspension and re-entry to the biosphere.

The main objectives of the current study were as follows: (i) to find out if concentrations of heavy metals (Cr, Zn, Cu, Pb, Cd) that occur in the studied water reservoirs are high enough to be considered toxic to the aquatic environment, (ii) to assess the degree of pollution with metals, and the origin of those metals, using the enrichment factor, the geoaccumulation index, (iii) to determine the factors which affect the spatial differences in the concentration of investigated elements between individual water bodies in the region.

Materials and methods

Study area
The investigations concerned eight small water reservoirs located in the Kielce Highland (Fig. 1). Those differ in age, capacity, and also the catchment size and land use. The volume of examined reservoirs is from 28000 m³ to over 1165000 m³, while submersion area is from 1.7 ha to 30 ha. The catchment basins of the reservoirs are varied both in terms of area (2.7–222 km²) and land use. In the area of seven catchments dominates the forest economy – forests occupy from 52.4% to over 84% – while in the catchment area of the Morawica reservoir agricultural areas make up over 57% of the total catchment area. Areas occupied by construction, transportation infrastructure and industry in the catchment areas of the surveyed areas account for up to 5% of their total area.

The basic parameters of the reservoirs and their catchments are presented in Table 1. More information on some analyzed reservoirs can be found in the references (Bąk 2017).

Sample collection and preparation
Samples of bottom sediments from the studied water bodies were collected in the years 2012–2015 using the Becker-type sampler. The kit allows for collecting sediment samples at the quasi-undisturbed state, i.e. with their structure and layer thickness preserved, into transparent cylinders. The physico-chemical investigations were conducted on the top layer of sediment deposits, 10 cm in thickness, which was placed, immediately after collection, into sterile polyethylene containers, in compliance with international standards. Containers with samples were tightly sealed and transported to

the laboratory for physico-chemical analyses. In the laboratory, bottom sediment samples were naturally dried to obtain air-dry condition. Dried sediments were sieved (2 mm mesh) to remove the gravel fraction and plant debris, and finally crushed. Sediment samples prepared in this way were stored in pre-washed glass containers at room temperature.

The sediment sampling sites (a single sample of sediments was collected at a given location), shown in Figure 1, were positioned using differential GPS receiver.

Physical and chemical analysis of bottom sediments
For heavy metal determination, the sediment samples were oven-dried at 80ºC on glass dishes until constant weight. Each of the weighed samples (approximately 0.5 g) was transferred into a Teflon vessel, and then digested with 8 ml HNO_3 in the microwave oven (Multiwave 3000, Anton Paar). The digestates were left to cool at room temperature and then filtered through a 0.45 μm nitrocellulose membrane filter. The filtered digestates were diluted with distilled and deionised water to 100 ml in a volumetric flask. The total concentrations of lead, chromium, cadmium, copper, zinc and iron were determined using inductively coupled plasma-*atomic emission spectrometry* ICP-AES (Perkin Elmer Optima 8000) with certified multi element standards. Analytical blanks and standard reference material were run in the same way as the samples, and heavy metal concentrations were determined using standard solutions prepared in the same acid matrix. Total heavy metal concentrations were determined in accordance with the PN-EN ISO 11885:2009.

Organic matter (OM) was determined by the loss of ignition test (LOI). Bottom sediment water content, bulk density, organic matter and carbonate content may be estimated by weight loss measurements in core sub-samples subjected to sequential heating. Weight losses associated with water and carbon dioxide evolutions are easily quantified by recording sample weights before and after controlled heating (ignition at 550ºC) and, in turn, may be correlated to water content, and also organic matter and carbonate content (PN-EN 12880:2004, Santisteban et al. 2004).

Particle size distribution in sediment sample was determined using the Casagrande method modified by Pruszyński, which is a variant of the hydrometer method (PN-R-04032:1998). Particle density was determined pictometrically and bulk

Table 1. Selected parameters of the reservoirs and their catchments

| Reservoir | Catchment area | water surface are | Initial capacity | Year of construction | Land use in the catchment | | | |
| | | | | | agricultural land | grassland | forests | others |
	km²	ha	thou. m³		[%]			
Jaśle	16.2	3.7	65.8	2004	2.2	37.7	59.5	0.6
Kaniów	7.4	1.7	28.0	1986	13.4	6.2	80.3	0.1
Krasna	78.0	7.2	153.0	2004	9.8	15.2	70.1	4.9
Morawica	222.0	6.6	120.0	2011	57.7	11.4	27.6	3.3
Mostki	49.1	7.8	110.0	1900	4.8	9.2	84.1	1.9
Nieskurzów	2.7	4.3	70.0	2012	36.5	8.5	52.4	2.6
Rejów	103.0	30.0	1 165.0	1939	31.2	4.8	59.0	5.0
Suchedniów	87.9	21.4	303.0	1978	31.7	3.9	60.2	4.2
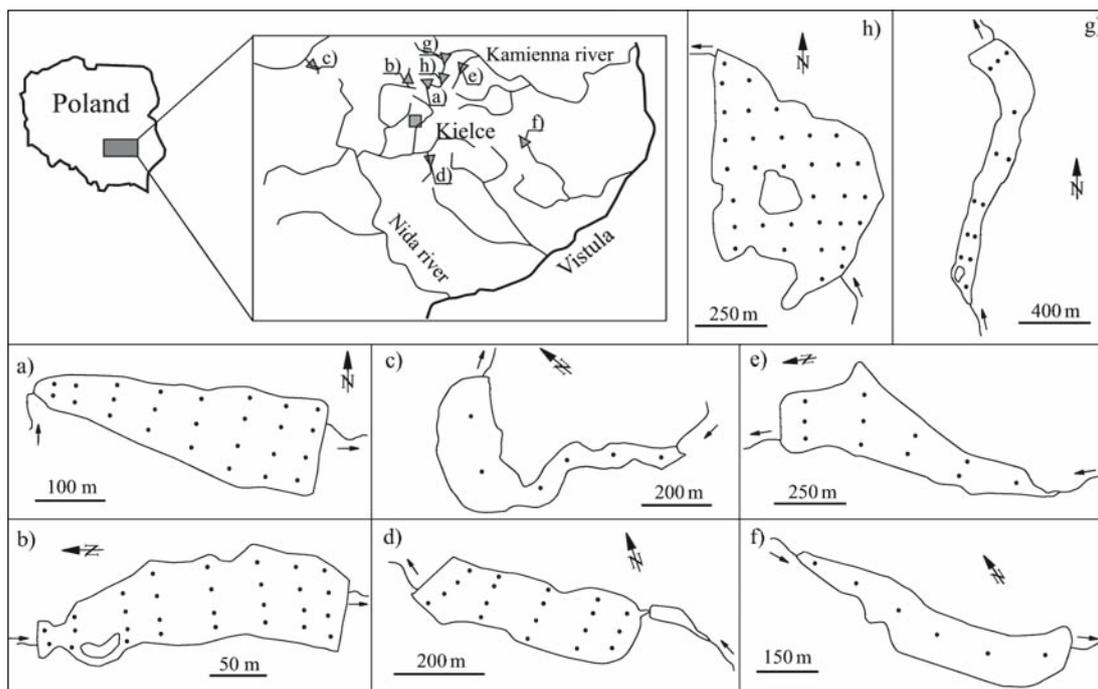
Fig. 1. Investigated water reservoirs: a – Jaśle; b – Kaniów; c – Krasna; d – Morawica; e – Mostki; f – Nieskurzów; g – Rejów; h – Suchedniów: ● – sediment sampling sites (25 – Jaśle reservoir, 29 – Kaniów reservoir, 6 – Krasna reservoir, 19 – Morawica reservoir, 11 – Mostki reservoir, 6 – Nieskurzów reservoir, 13 – Rejów reservoir and 33 – Suchedniów reservoir)

density was calculated as the ratio of the mass of the sediments sample to its total volume.

Quantitative assessment of bottom sediment pollution

Enrichment factor (EF)

Standardised enrichment factor is used to identify the origin of heavy metals and to distinguish between anthropogenic sources and those resulting from natural processes. The additional standardization procedure eliminates the effect of natural variation in sediment granulometry or mineralogical composition on the results obtained. The content of aluminium, iron, manganese, titanium, scandium, lithium or caesium (Zhang and Shan 2008) acts as a normalizing element. In clay minerals, those elements are characterised by a relatively constant content, which is usually independent of anthropogenic activities. To determine the impact of anthropogenic pollutants on the content of trace elements in bottom sediments, the values of the enrichment factor (EF) for sediments were calculated using iron concentration as a standardising factor (formula 1). The values given by Taylor and McLennan (1985) were assumed to be the geochemical background. The factor values EF≤1.0 indicate the lithogenic origin of a given metal, whereas the values of EF>1.0 signal the anthropogenic enrichment of bottom sediments with heavy metals (Chen et al. 2007) (Table 2).

$$EF = \left(\frac{C_n}{C_{Fe}}\right)_{sample} \Big/ \left(\frac{C_n}{C_{Fe}}\right)_{shale} \qquad (1)$$

where:

C_n and C_{Fe} – content of individual metals and of iron in the bottom sediment samples and in the geochemical background.

Geo-accumulation index

The geo-accumulation index (I_{geo}), developed by Müller (1979), makes it possible to assess pollution by comparing the amount of heavy metals in bottom sediments with the so--called pre-industrial levels of concentrations (formula 2). The obtained I_{geo} values were interpreted by comparison with the reference values listed in Table 2.

$$I_{geo} = \log_2\left(\frac{C_n}{1.5B_n}\right) \qquad (2)$$

where:

C_n – concentration of a given metal in bottom sediments,
B_n – geochemical background for a given metal (Taylor and McLennan 1985),
1.5 – natural fluctuations in the content of a given metal in the environment with low anthropogenic impact.

Data analyses

To compare the obtained mean values of indicators of sediment pollution in the reservoirs of concern, the analysis of variance (ANOVA) was performed. The analysis was preceded by the check of *homogeneity of variance* using the *Brown-Forsythe test*. For the ANOVA results that were statistically significant, the Tukey multiple comparison test was applied, which is most frequently used in the aquatic environment investigations (Czaplicka-Kotas et al. 2010). When the assumption of *homogeneity of variance was not satisfied*, the Kruskal-Wallis nonparametric test was employed. Analyses of variance were preceded by the tests on the normality of distribution of the variables of concern (Lilliefors version of the Kolmogorov--Smirnov test and the Shapiro-Wilk test). When the distribution of a given feature was not compliant with the normal distribution,

logarithmic transformation of variables in accordance with the log $(C_n + 1)$ function was performed (Elliott 1977).

To evaluate the strength and direction of statistical relationships between variables (values of pollution indicators), the Pearson's correlation coefficient (r) was calculated.

Results and discussion

Sediment characteristics

Bottom sediments in all studied reservoirs were characterised by high spatial differentiation in grain size. In the upper part of reservoirs, the material deposited had a high share of the sand fraction, the content of this fraction in the total sample weight was above 85%. As the distance from the dam became shorter, the share of the sand fraction in sediments decreased, and in the proximity of the dam structure, it did not exceed 0.5% in the Nieskurzów reservoir sediments, and 15% in the sediments collected from the Kaniów reservoir (Fig. 2). In all reservoirs, sediment samples collected at the dam wall showed a considerable share of the silt fraction grains, which exceeded 80%, whereas the share of the clay fraction grains did not exceed 20% by weight.

The bulk density of the examined sediments ranged from 0.24 Mg·m^{-3} to 1.53 Mg·m^{-3}. The lowest density was found in the sediments collected in the lower parts of the reservoirs, and the highest density was noted for the sediments with a high share of the sand fraction, collected near river inlets into the reservoirs. The specific density of the sediment deposits collected from the examined water bodies ranged 2.50–2.70 Mg·m^{-3}.

Sediments with dominating sand fraction were characterized by organic matter content below 2%. With the increase in the proportion of silt and clay fraction in sediment,

increase of organic matter content was also observed. In samples of sediment collected near the dam and shallow areas within reservoirs, the organic matter ranged from 6% to 12% and in a few cases exceeded 25% of the sample weight.

Metal concentrations in sediments

The content of selected heavy metals in the bottom sediment samples collected from studied reservoirs is presented in Figure 3. Results presented in Fig. 3 include the results of previous studies on the chemical status of small water reservoirs of the Kielce Upland, which can be found in references of Bąk et al. (2013, 2017). From the analysis of box plots, the concentration of metals in sediments was characterized by a great variety of comparison between individual reservoirs with each other as well as samples of sediment from a given reservoir. In addition, the distribution of the analyzed metals within the reservoirs, in a large number of cases, was asymmetric (left or right-sided).

Iron (Fe) is not considered as pollutant, however, because the oxides of this metal are excellent sorbents of other contaminants, its designation is important from the point of view of environmental analysis (Barbusiński and Nocoń 2011). The content of Fe in the sediment samples ranged from 13.5 to over 38000 mg·kg^{-1}. The highest values of iron were observed in sediments of Suchedniów, Nieskurzów and Krasna reservoirs (>25000 mg·kg^{-1}), while the lowest in sediments of Mostki, Morawica and Rejów reservoirs (<1270 mg·kg^{-1}).

The highest chromium content was observed in sediment samples collected from the Suchedniów reservoir (98 mg·kg^{-1}). In other reservoirs the maximum concentration of this metal did not exceed 45 mg·kg^{-1}. The smallest concentrations of chromium were found in the sediments of Mostki and Krasna reservoirs. The mean concentration of Cr in sediment from

Table 2. Enrichment factor (EF) and I$_{geo}$ classes in relation to sediment quality

| EF classes	Sediment quality	I$_{geo}$	I$_{geo}$ classes	Sediment quality
< 1	No enrichment	I$_{geo}$ ≤ 0	0	Unpolluted
< 3	Minor enrichment	0 < I$_{geo}$ < 1	1	Unpolluted to moderately polluted
3–5	Moderate enrichment	1 < I$_{geo}$ < 2	2	Moderately polluted
5–10	Moderately severe enrichment	2 < I$_{geo}$ < 3	3	Moderately to highly polluted
10–25	Severe enrichment	3 < I$_{geo}$ < 4	4	Highly polluted
25–50	Extremely severe enrichment	4 < I$_{geo}$ < 5	5	Highly to very highly polluted
		I$_{geo}$ > 5	6	Very highly polluted
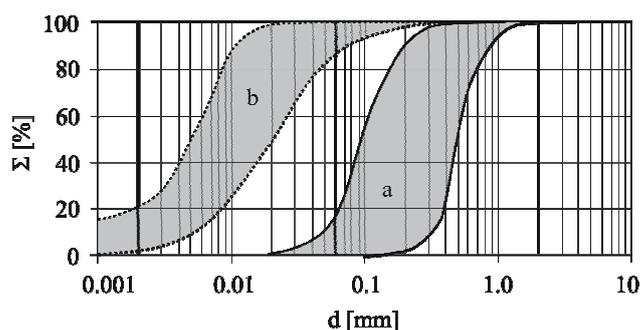
Fig. 2. Boundaries of granulometric curves of bottom sediments: a – collected from upper part of examined water bodies; b – collected from lower part of examined water bodies
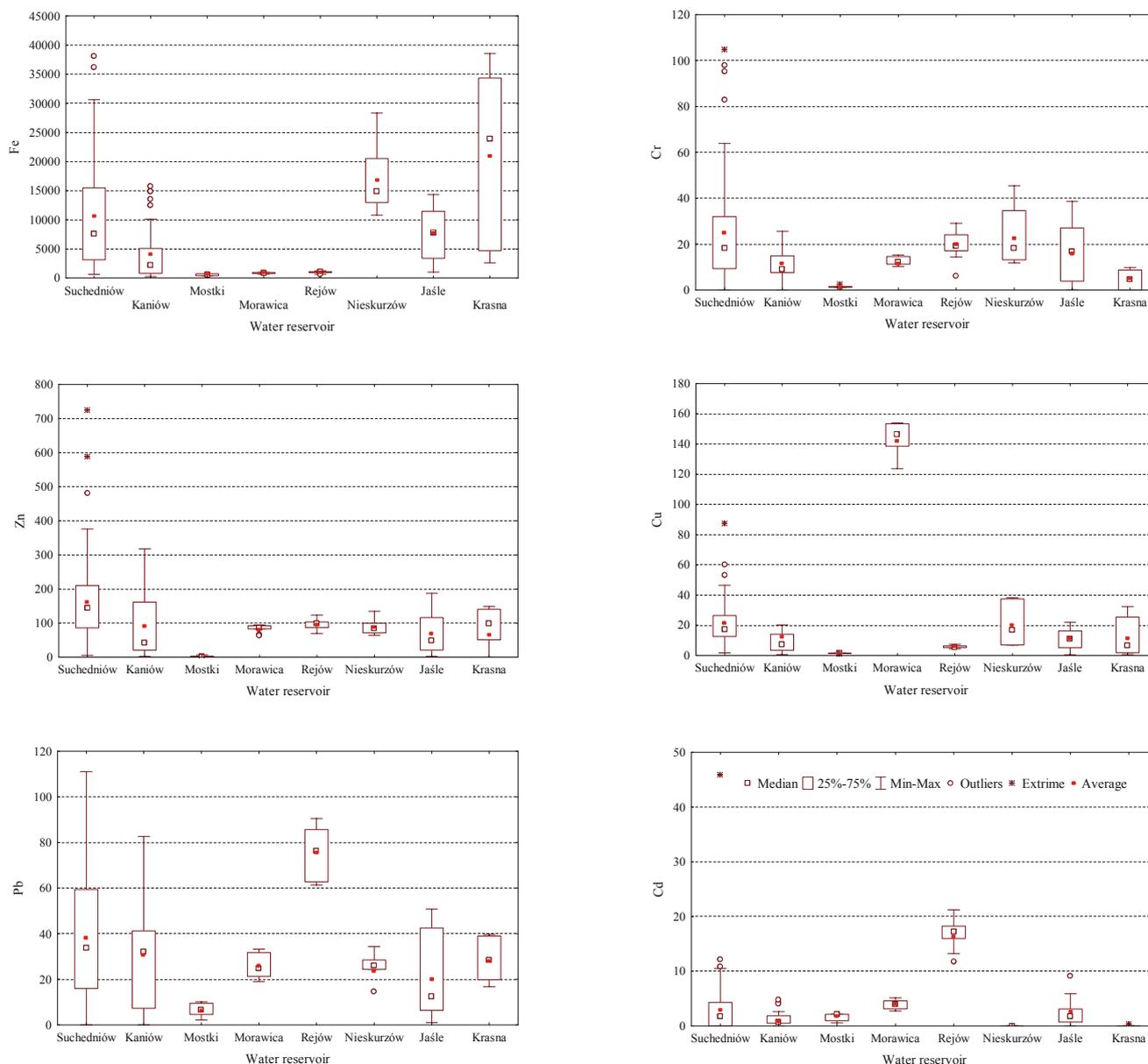
Fig. 3. Trace metal concentrations [mg·kg⁻¹] in the sediments of examined water reservoirs

these water reservoirs was 1.5 mg·kg⁻¹ (Mostki reservoir) and 4.6 mg·kg⁻¹ (Krasna reservoir), respectively.

The Zn content in the analyzed sediment samples varied from 0.4 to 724 mg·kg⁻¹. The highest concentration of this metal was noted, similarly as in the case of Cr, in samples collected from the Suchedniów reservoir. The mean Zn content in the sediments of the examined reservoirs, excluding the Suchedniów and Mostki reservoir, was assumed to be within a relatively narrow range of 70–90 mg·kg⁻¹. In the case of the Suchedniów reservoir it was over 164 mg·kg⁻¹, and for Mostki reservoir was 2.5 mg·kg⁻¹.

The high content of Cu in the Morawica reservoir is remarkable in comparison with the other reservoirs. The mean concentration of this element was over 144 mg·kg⁻¹, while in the remaining reservoirs did not exceed 21 mg·kg⁻¹. This may be related to the characteristics of the reservoir basin, which accounts for over 57% of the area of agricultural land, and the source of Cu can be used in crops chemicals and fertilizers.

The highest mean concentration of lead was observed in the Rejów reservoir (75.6 mg·kg⁻¹). In the remaining water reservoir it ranged from 20.9 to 39.9 mg·kg⁻¹. This is not surprising because the catchment area of this reservoir is located in the transport industry, ceramics, and sandstone mining area.

In terms of Cd content there are two significant reservoirs: Nieskurzów and Krasna. In all sediment samples from the Nieskurzów reservoir, the Cd content was below the limit of quantification. A similar situation was observed for sediments from the Krasna reservoir, where only one marker (sediment sample collected near the dam) was found at 0.3 mg·kg⁻¹. The highest mean Cd concentration, as in the case of Pb, was observed in the sediments of the Rejów reservoir.

The ANOVA test results demonstrated that the null hypothesis on the equality of mean contents of Cr, Zn, Cu, Pb and Cd in bottom sediments of the reservoirs of concern should be rejected in favor of an alternative hypothesis

concerning the occurrence of considerable differences in the contents of elements. The results of the Tukey and the Kruskal – Wallis tests made it possible to state that bottom sediments of the Suchedniów, Morawica, Rejów and Nieskurzów reservoirs are much more chemically degraded than those of the other reservoirs. That results from significant differences in anthropogenic conditions that exist in the catchments of studied water bodies. For example, the Suchedniów reservoir is located in the urbanised area and receives stormwater from a part of the town of Suchedniów, which is a source of pollution with heavy metals including Zn, Cr, Pb, Cd and Cu (Bąk et al. 2012). Discharges of sanitary wastewater from communities and sewage treatment plants located along the Kamionka river are an additional source of pollution with heavy metals in Suchedniów and Rejów reservoirs catchment. Trace elements can also migrate into the reservoirs by means of the runoff from transportation infrastructure (vehicle tyre wear material produced by abrasion as a source of Cd, Zn, Pb, and Cr). The runoff from agricultural land can become a source of pollution with heavy metals (Pb, Zn, Cu and Cd) in the case of Morawcia and Nieskurzów reservoirs due to the use of fertilisers, both organic, and mineral ones (Gorlach and Gambuś 1997, Sady and Smoleń 2004). As regards the Kaniów, Mostki, Jasłe and Krasna reservoirs, shallow mineral deposits affected by weathering processes, atmospheric deposition, and to a lesser extent, runoff and agricultural pollutants can be the sources of sediment pollution by heavy metals.

In most of the investigated reservoirs there was no statistically significant relationship between the proportion of silt fraction and organic matter and the content of metals in the tested samples. In cases where correlation was observed, it was very weak (r <0.5). The lack of strong statistically significant relationships between trace elements and the content of organic matter and silt fraction in the sediments may result from the morphology of their bowls and hydraulic flow conditions. Most of them are shallow reservoirs with an average depth of less than 1.50 m. The bottoms and edges of these reservoirs are covered with lush vegetation being the main source of organic matter in the littoral zone. In addition, the small depth of the reservoirs is conducive to the resuspension processes and the movement of bottom sediments within their bowl during flood flows. On the basis of mutual dependencies between heavy metal content in sediments, attention should be paid to the presence of correlation relationships between iron and other trace element. The occurrence of this dependence may indicate the natural origin of a given element, while the lack of interdependence may indicate its anthropogenic origin. In the sediments of the Kaniów and Jasło reservoirs, a significant correlation was found between the iron content and the content of Cr, Zn and Cu, which confirms the natural origin of these elements. The existence of a positive relationship between Fe and Cr, Zn and Cu was also found in the sediments of the Morawica, Suchedniów and Rejów reservoirs (Fig. 4). However, due to the strong anthropopressure of the basins of these reservoirs and the
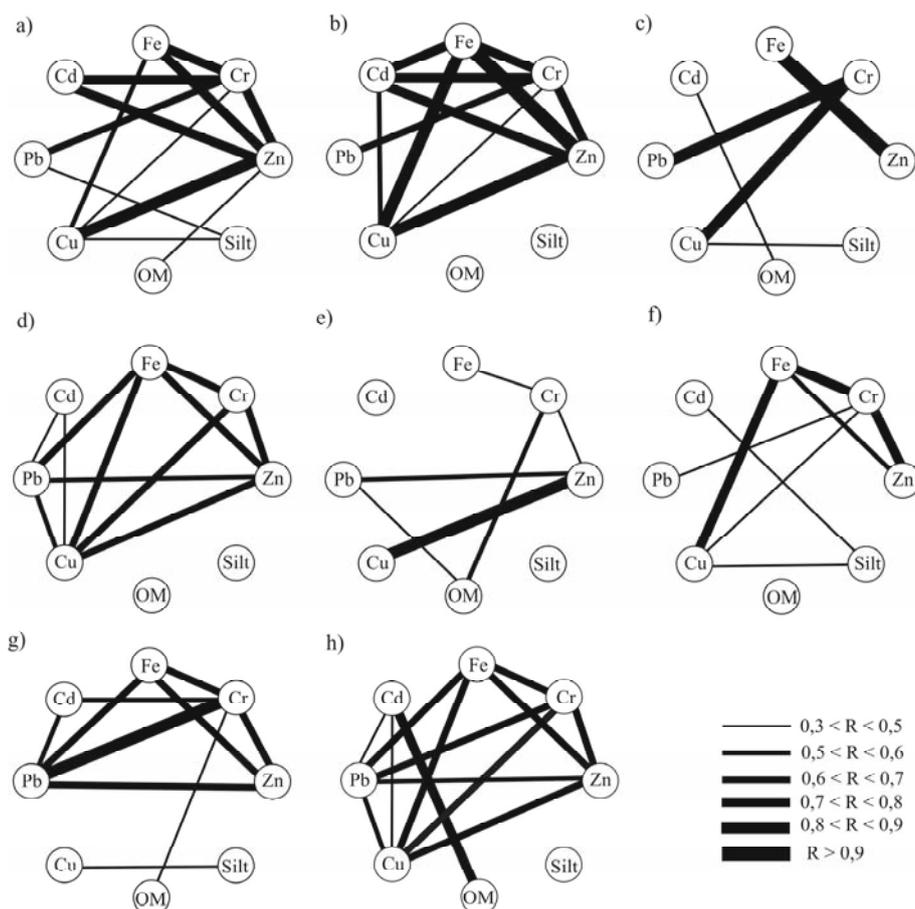

Fig. 4. Pearson correlation coefficient between metals, silt and organic matter (OM) for studied water reservoirs:
a – Jasłe; b – Kaniów; c – Krasna; d – Morawica; e – Mostki; f – Nieskurzów; g – Rejów; h – Suchedniów

complex nature of hydrodynamic processes within their basins, it can be assumed that geochemical relations between metals in the sediments of these reservoirs are disturbed. Additionally the complicated nature of the dependence obtained correlation between the studied metals may indicate their anthropogenic origin in those reservoirs (Zabetoglou et al. 2002).

Similar disturbances may occur in the case of other reservoirs in which there was no relationship between Fe and the examined metals, which would indicate their anthropogenic origin. However, forest management dominates in the basins of these reservoirs, and human pressure is very low. Correlations between the surveyed indicators are presented in Figure 4.

Enrichment factor (EF) and geoaccumulation index (I_{geo})

The values of the enrichment factor obtained for selected heavy metals accumulated in the sediments of studied reservoirs indicate natural and anthropogenic sources of the elements determined (Sayadi et al. 2010, Zahra et al. 2014) (Figs 4 and 5). The analysis of the results presented in Fig. 5 shows that the sediments of Morawica and Rejów contain very high and extremely high enrichment in Cr, Zn, Pb and Cd. The values of EF>20 indicate also an extremely high enrichment in Cd of the Mostki sediments. In addition, over 50% of the samples of sediment from Suchedniów, Kaniów, Mostki and Jaśle reservoirs – the value of EF for Cr exceeded 5 – indicated a moderately high enrichment of this element. A similar situation was observed in the case of Pb in the Mostki and Cd in the Jaśle and Kaniów reservoirs. The smallest enrichment in the analyzed trace elements was characterized by sediment of Krasna reservoir. In 90% of all samples analyzed for the content of Cr, Zn and Cu, the values of EF <1 were obtained – which indicates the natural origin of trace elements.

Results of the analysis of I_{geo} values are shown in Fig. 6. In the case of studied heavy metals, it can be seen that
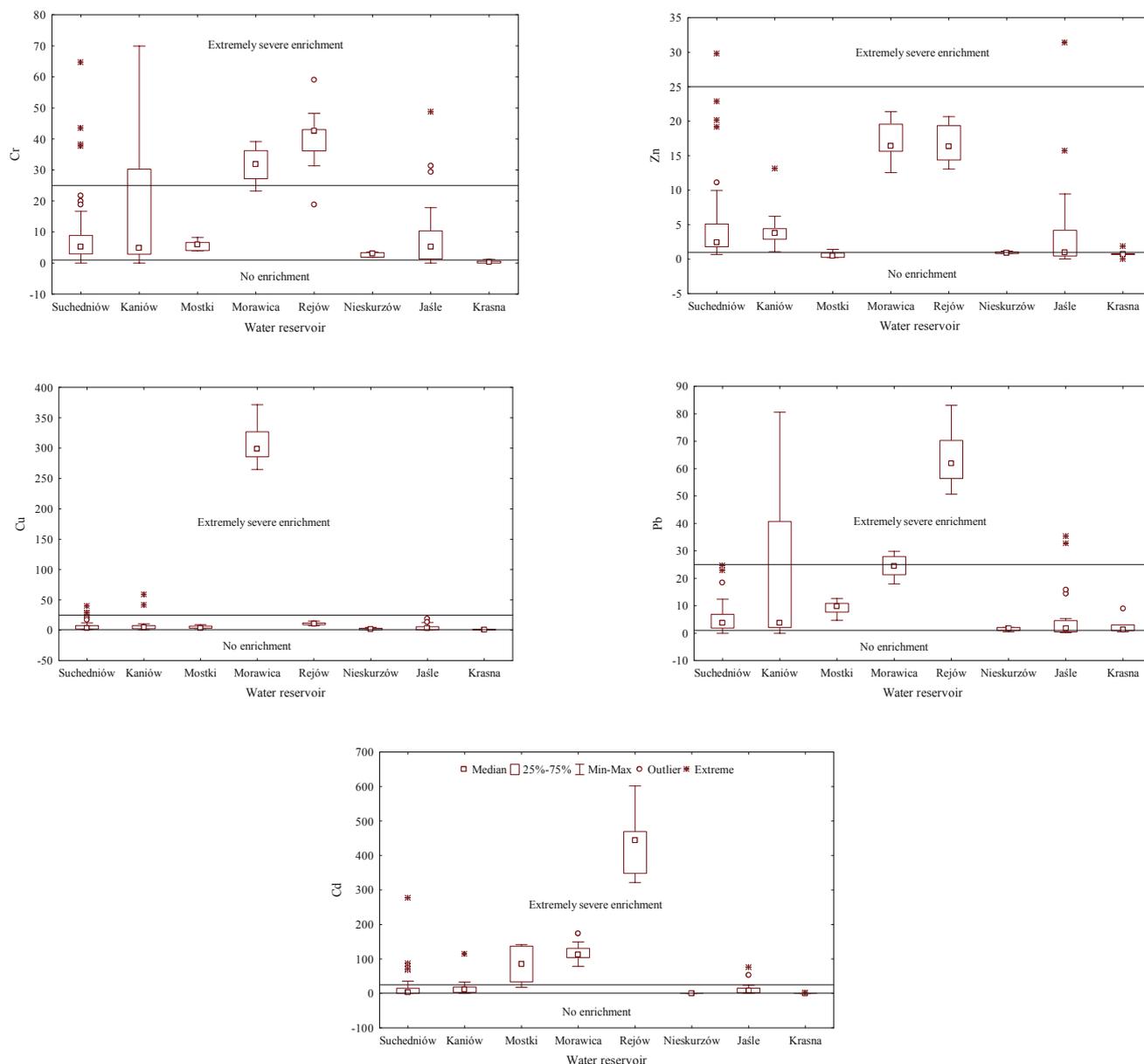

Fig. 5. Box plot of EF for the studied elements in investigated water reservoirs

a significant proportion of the tested samples (<25%) collected from urban, industrial or intensive agriculture catchments are characterized by moderately high ($2<I_{geo}<3$) or high ($3<I_{geo}<4$) pollution. To these facilities belong reservoirs of Suchedniów, Rejów and Morawica. Disturbing is the very large pollution of bottom sediments of recreational reservoirs (Morawica and Rejów) with copper, lead and cadmium. The compounds of these metals are some of the most dangerous from a health point of view.

Summary and conclusions

In the studied small water reservoirs, mainly fine-grained mineral material is trapped characterized by dominating dusty and sandy fractions. The bulk density of sediments ranged from 0.24 Mg·m^{-3} to 1.53 Mg·m^{-3} and the mean specific density was 2.50–2.70 Mg·m^{-3}. The content of OM in sediments does not exceed 25% of the sample weight.

The results show that the contents of selected heavy metals in the sediments vary greatly, which especially refers to cadmium, iron and chromium. The concentrations of metals ranged widely, from a few mg·kg^{-1} for cadmium, to several dozen thousand mg·kg^{-1} for iron. Mean concentrations of heavy metals in the bottom sediments of both reservoirs were ordered as follows: Zn>Pb>Cr>Cu>Cd. The elevated values identified for Cr, Zn, Cu and Pb (Suchedniów, Rejów, Morawica and Nieskurzów reservoirs) are the result of anthropogenic activities in the catchment area. These sources mainly include the effluent of wastewater treatment plants, treated and untreated wastewaters, and runoff from agricultural land.

The presence of a positive correlation between individual heavy metal pairs indicates their possible origin from a single source and similar behavior during transport (Suresh et al. 2012). However, the complex nature of the correlation relationships obtained between the investigated metals and lack of correlation between content of OM and duct fractions in individual
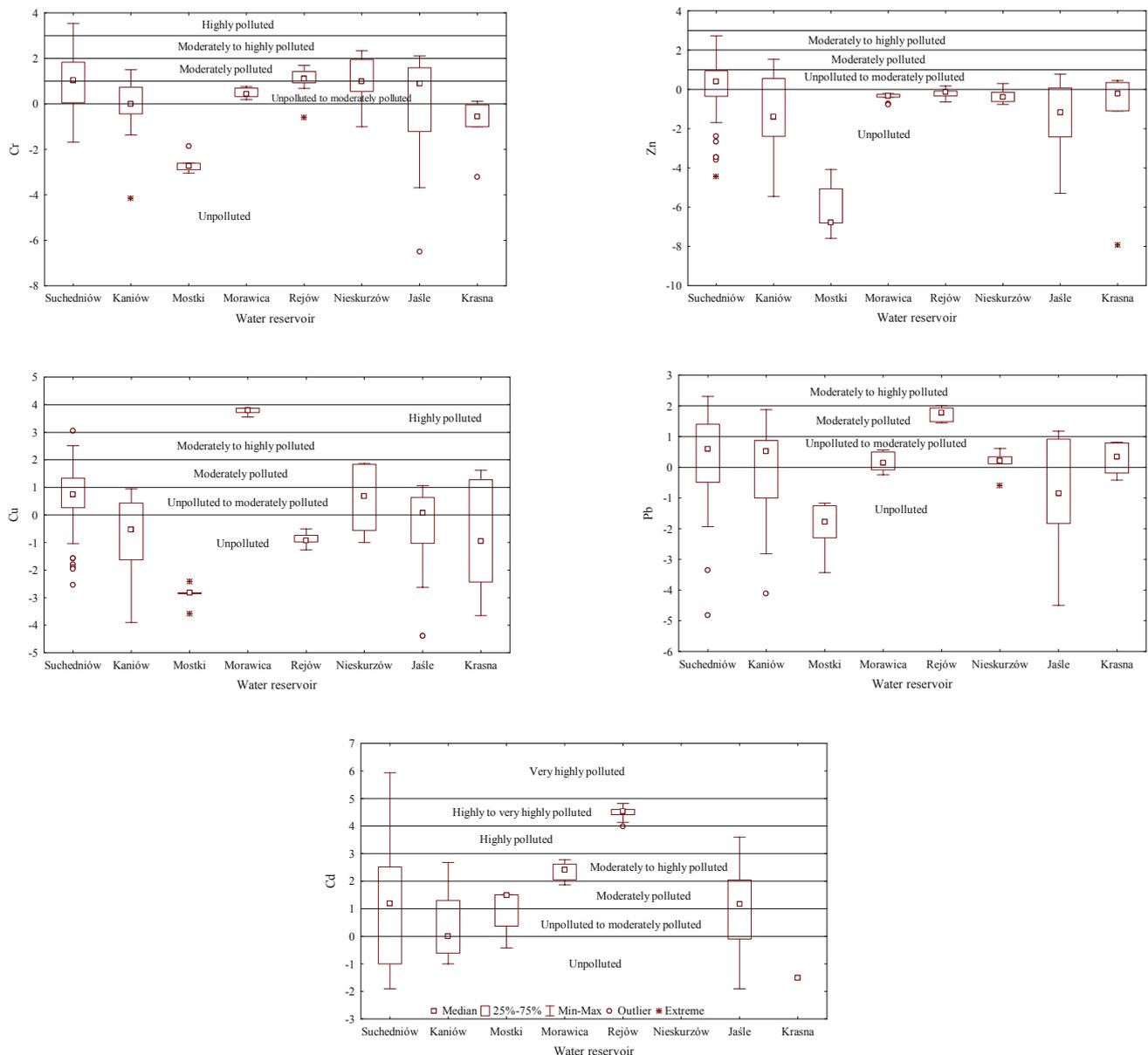

Fig. 6. Box plot of I$_{geo}$ for the studied elements in investigated water reservoirs

reservoirs may be the result of specific hydrodynamic conditions regulating the transport and sedimentation processes within the reservoir bowl.

The values of enrichment factors calculated for selected heavy metals accumulated in the sediments of the Suchedniów and Kaniów reservoirs indicate natural and anthropogenic sources of the elements. The values of EF for sediment samples from the Suchedniów reservoir show extremely high enrichment with Cu, Cd and Pb, and also very high enrichment with Cr, and Zn at sampling collection sites located in the lover (outlet) part of the Suchedniów reservoir and upper (inlet) part of the Kaniów reservoir. In the remaining areas, EF values were < 3, which signals low enrichment with a given element, or the lack of enrichment. Quite different results were obtained for the bottom sediments of the Kaniów reservoir. In that case, the majority of determinations, as much as 64 %, showed EF<1, which means only trace amounts of the elements were found. At only a few sampling sites, very high enrichment with Cd (10<EF<25), and moderately high enrichment with at least one element were observed.

To assess the quality of bottom sediments, the geo--accumulation index I_{geo} was also applied. The analysis of the data shows a great variation in the index value, which depends on a given trace element. With respect to Mn and Cu pollution, the Kaniów reservoir sediments were categorized as belonging to Classes 0 and 1, whereas the Suchedniów reservoir sediments fell into Classes 0 (64% of determinations), 1 (32% of determinations) and 2 (4% of determinations) due to the Mn content, and even into Classes 3 (8% of determinations) and 4 (4% of determinations) because of the content of Cu. The results also indicate that cadmium is the most relevant to the chemical degradation of the Kaniów reservoir sediments. In a majority of cases, their geo-accumulation indices are responsible for the classification of the sediments as moderately or strongly polluted. The Suchedniów reservoir sediments are far more polluted. The calculated values of I_{geo} for Cr and Cd show that those sediments should be classified as belonging to Classes 3 (28%, 28% and 32% of all determinations, respectively) and 4 (8%, 12% and 16% of all determinations, respectively).

The integration of these geochemical methods is necessary for an appropriate ecological risk assessment, and it presents satisfactory results. The results of this study provide a useful aid for sustainable reservoir management in the region.

Acknowledgment

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Zanieczyszczenie metalami ciężkimi osadów dennych małych zbiorników wodnych Wyżyny Kieleckiej (Południowo-Wschodnia Polska)

Streszczenie: Celem niniejszej pracy było określenie stopnia zanieczyszczenia osadów dennych pochodzących z małych zbiorników wodnych metalami ciężkimi. Do oceny zanieczyszczenia osadów zastosowano następujące wskaźniki: współczynnik wzbogacenia (EF) oraz indeks geoakumulacji (I_{geo}). Badaniom poddano osady z ośmiu małych zbiorników zaporowych zlokalizowanych na terenie Wyżyny Kieleckiej. Zawartość wybranych metali ciężkich (kadmu, miedzi, chromu, ołowiu i cynku) określono metodą atomowej spektrometrii emisyjnej ze wzbudzeniem w plazmie indukowanej (ICP-OES). Dodatkowo określono skład granulometryczny osadów oraz zawartość materii organicznej – wyrażonej jako straty po prażeniu (LOI). Stężenie poszczególnych metali ciężkich w badanych zbiornikach było zróżnicowane. Osady zbiorników Morawica oraz Rejów charakteryzowały się bardzo dużym wzbogaceniem w chrom, cynk, ołów i kadm. Wyliczone wartości EF>20 wskazywały również na bardzo wysokie wzbogacenie w kadm osadów zbiornika Mostki. Ponadto, przeszło 50% przebadanych próbek osadów pochodzących ze zbiorników Suchedniów, Kaniów, Mostki i Jaśle odznaczało się umiarkowanie wysokim wzbogaceniem w chrom (EF>5). Natomiast wyniki analizy wartości indeksu I_{geo} wskazywały na umiarkowanie wysokie ($2<I_{geo}<3$) lub wysokie ($3<I_{geo}<4$) zanieczyszczenie osadów badanych zbiorników pierwiastkami śladowymi. Różnice w ocenie stopnia zanieczyszczenia osadów w oparciu o wyliczone wartości EF i I_{geo} mogą wynikać z samej natury pierwiastków śladowych, ładunku zanieczyszczeń wprowadzanych do środowiska wodnego jak również form specyjnych metali występujących w kompleksie woda–osad. Spostrzeżenie to implikuje konieczność integracji metod geochemicznych w ocenie ryzyka ekologicznego oraz stopnia zanieczyszczenia osadów dennych metalami ciężkimi.