MIDDLE POMERANIAN SCIENTIFIC SOCIETY OF THE ENVIRONMENT PROTECTION
ŚRODKOWO-POMORSKIE TOWARZYSTWO NAUKOWE OCHRONY ŚRODOWISKA
Annual Set The Environment Protection
Rocznik Ochrona Środowiska
Volume/Tom 18. Year/Rok 2016 ISSN 1506-218X 667-680

Analysis of Heavy Metals in Selected Particular Granulometric Fractions of Bottom Sediments

Małgorzata Wojtkowska, Magdalena Matula
Warsaw University of Technology

1. Introduction

The nature of bottom sediments in watercourse depends on many factors including natural and anthropogenic factors (Report 2013, Wojtkowska 2011). The natural factors are: bottom and geochemical structure of soil, climatic condition, the dynamics of mixing and physico-chemical composition of water. The anthropogenic factors include: land use planning in areas adjacent to the water, their development and water inflow. Heavy metals are widespread in the environment from natural and anthropogenic sources. They get to all components of biosphere and are deposited there in various forms (Wojtkowska 2011, 2013). One of the major problems that cause the heavy metals with respect to their effects on aquatic organisms is that they are non-biodegraded and toxic (Tokalioglu et al. 2002, Yuan et al. 2004). Therefore, they are among the most frequently monitored micropollutants, and reliable techniques have been established for their extraction. Studies of aquatic environment of rivers are essential due to the high probability of heavy metals getting to the rivers (Milenkovic 2005). There is a dynamic interchange in water stream between dissolved forms and bottom sediments. Heavy metals are capable to deposit in bottom sediments as well as become mobile and move along with water. This process depends on the nature of environmental conditions. Therefore, sudden change of the water ingredients concentration can cause release of heavy metals and their rapid transportation for long distance from their origin.

The important and frequently studied factor is the size of grains of bottom sediments due to interdependence of the surface of grains and their ability to temporarily immobilize. The kind of immobilization on surface of grains and sorption ability can be evaluated from the size of the grains (Frankowski et al. 2008, Ying et al. 2006). Therefore, many researchers suggest that the grains of smaller size contain more heavy metals then thicker ones. It can be justified by bigger surface relative to the volume (Salomons 1984, Martincic 1990). Other researches did not confirm this theory, e.g. in Singh (2006) report it was proved that bigger grains of bottom sediments contain similar or even higher amount of heavy metals.

Grain size analysis of bottom sediment can expand knowledge about accumulation of heavy metals relative to the size of grains. Various analytical procedures are used in research, making it impossible to compare results of heavy metal content in relation to grain size. Polish procedure (ISO 11466) assumes the analysis of heavy metals in fraction 0.15 mm from dry sieving method (Bojakowska et al. 2006). In Germany legislation LAWA it is assumed that heavy metal should be measured in grains of 0.02 mm in size by means of wet sieving method (Irmer 1997). Takalioglu et al. (2000) Singh et al. (2006) and Cuong and Obbard (2006) measured heavy metals in fraction < 0.063 mm. In research of Adamiec and Helios-Rybicka (2002) and Helios Rybicka et al. (2005) wet analysis of fraction < 0.02 mm was used.

The main purposes of this the paper was measuring of the amount of heavy metals in bottom sediment in Utrata river and defining the relationship between selected the grain size fractions and accumulation of heavy metals in bottom sediment.

2. Materials and Methods

The research concerned bottom sediment from Utrata river located in Masovian Voivodeship (Poland). The part of the river which is under consideration is situated in Pruszków town, the part of Warsaw agglomeration. The river Utrata is 78.2 km long and its source is located on north slope of Wysoczyzna Rawska south to towns Kaleń and Źelachów with estuary in Sochaczew (Public Information Bulletin, District Pruszków). Utrata river is right tributary of the river Bzura. Nearby Utrata river the areas are used mainly for forestry and agriculture (Wojtkowska

2013). The localization of the places from where samples were taken is shown in figure 1.

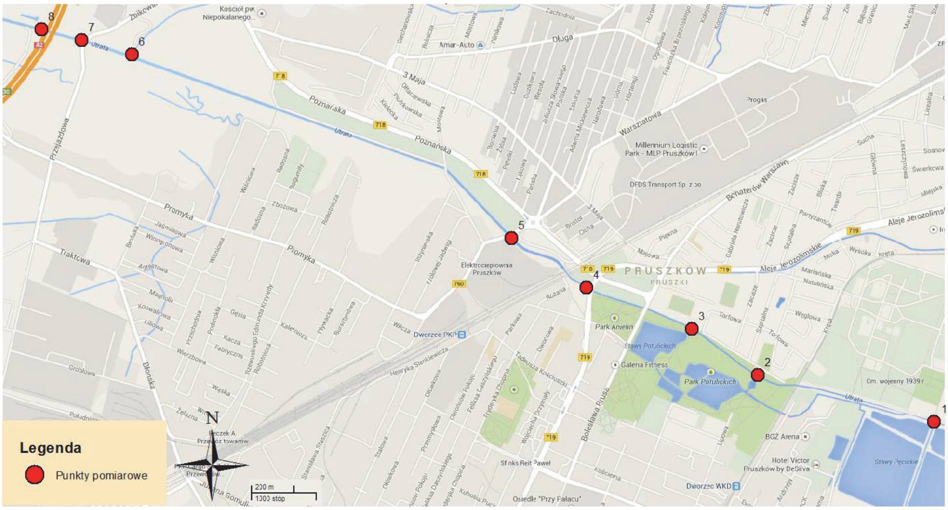

Fig. 1. Location of sampling points on Utrata river
Rys. 1. Lokalizacja punktów pomiarowych rzeki Utraty

The places were chosen due to potentially influential objects which are located nearby the river. The bottom sediments were collected to plastic containers from the surface layer from 0 to 5 cm by the sampler Kajak KC Denmark Research Equipment (Denmark). Then the samples were taken to laboratory and dried in 20°C. The grain size distribution was measured in air-dry samples. Analysis were made using the dry sieving method ([Dı´az-Zorita et al. 2007) with nine sieves of mesh sizes: 1; 0.71; 0.5; 0.355; 0.25; 0.18; 0.125; 0.09 and 0.063 mm. Each fraction was weighed and specified according to its share in the total sample.

Six grain size fractions for measuring content of heavy metals were chosen: 0.5, 0.25, 0.125, 0.09, 0.063 and < 0.063 mm. In these six fractions the content of heavy metals: zinc, copper, lead, nickel and cadmium were measured. From each of the selected fractions 1 g air-dry sediment to extraction with a water solution of an concentrated nitric acid and hydrochloric acid (3 HNO_3 65% :1 $HClO_4$ 60%) was weighed. After extraction, samples were filtered into volumetric flasks. In prepared samples heavy metals were analyzed using atomic absorption spectrometry with flame atomization (F-AAS). Curves set for a series of pre-prepared standard solutions were used. The burner 100 mm wide was used, powered with a mixture of air and medical acetylene. The temperature of flame was from 2100 to 2300°C. The hollow cathode lamps manufactured by Philips was used as the source of the radiation. The spectrophotometer was operated by program – Unicam Atomic Absorption- Data Station ver. 1.7 by Unicam. The detection limits for individual metals (calculated for the dry weight of the sediments) were: cadmium – 0.005 mg Cd/g, copper – 0.03 mg Cu /g, lead – 0.005 mg Pb/g, zinc – 0.01 mg Zn/g, nickel – 0,005 mg Ni/g. The Measurement accuracy was determined by reference sediments S-Mess3. The level of recovery of each of metals from reference sediments fluctuated between 92-111%.

3. Results and discussion

In this study the grain size distribution in samples collected from 8 locations selected from Utrata river (Fig. 1) was defined. The results can be useful in determining the composition of the bottom sediments and therefore their properties. 10 fractions were selected from the collected samples, including: mesh over fraction (skeleton), of the diameter greater than 1 mm and mesh under fraction, of the diameter smaller then 0.063 mm.

According to Polish standard (PN-EN ISO 14668-2 2006) the bottom sediments were classified as sand. Each of the samples had similar gain size composition. Middle sand dominated in most of the samples. The most pronounced differences were found between the contents of the thickest and the thinner fraction in samples. Their percentage was strongly varied and did not present any specified trend.

Analysis of separated fractions showed that the strongest relationship concerns samples 1, 2 and 5, 6. Medium sand was dominating in these samples. Grain size distribution in sample 3 was significantly different from the others. The skeleton fraction was the 43% share of the sample number 3. According to mechanical composition of soil and sediment (PN-EN ISO 14688-1 2006) stones, gravel, coarse, gravel medium, fine gravel and coarse sand belong to this fraction.

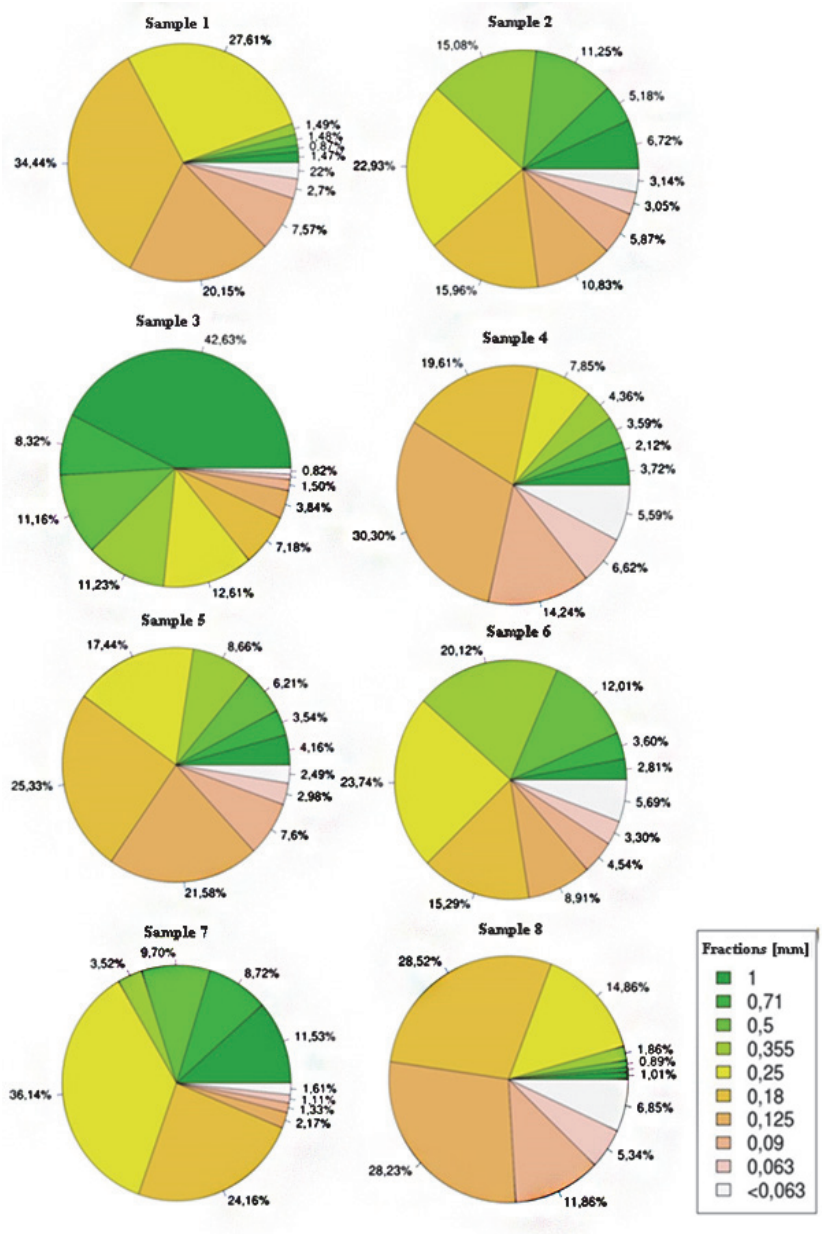

Fig. 2. Percentage distribution of granulometric fractions in samples 1 to 8
Rys. 2. Rozkład procentowy frakcji granulometrycznych w próbkach 1-8

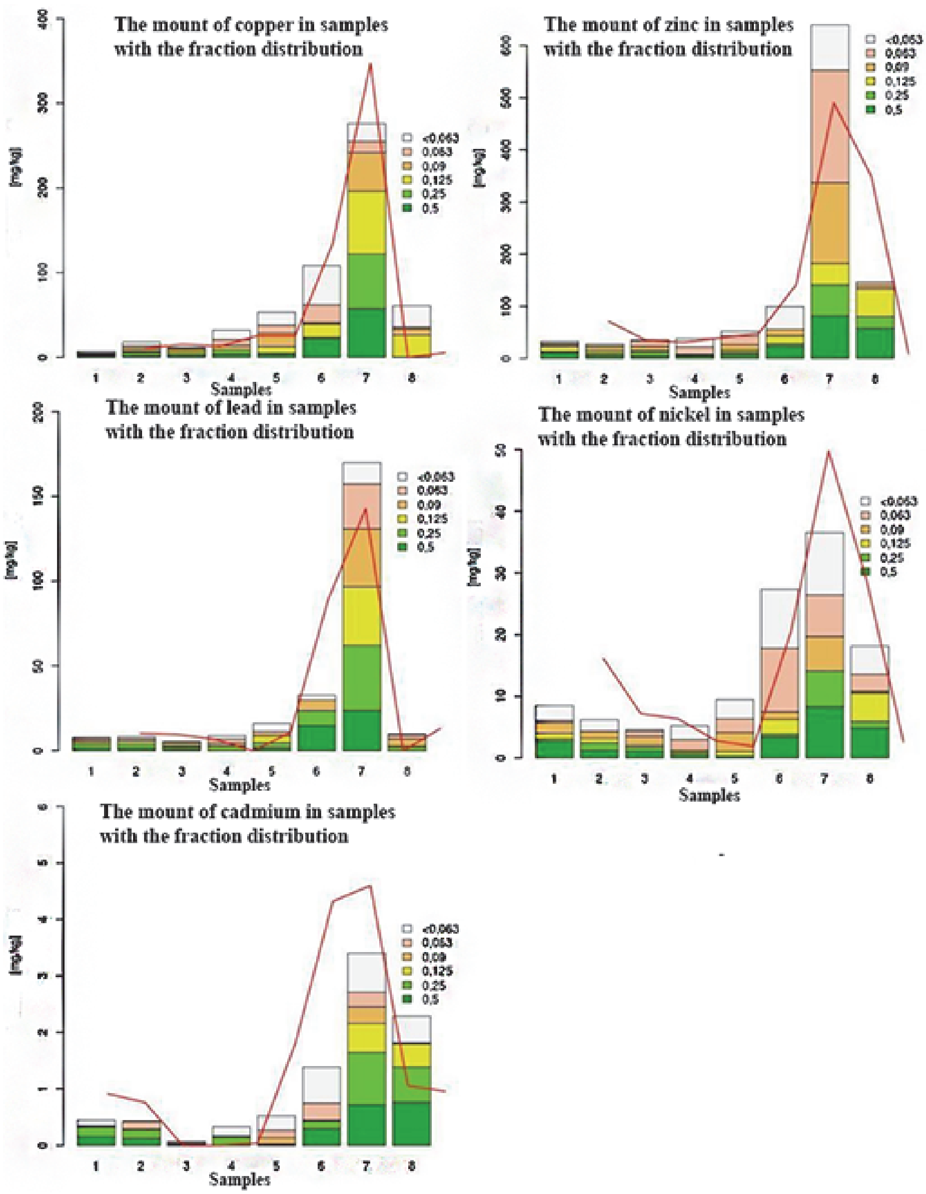

Fig. 3. The content of heavy metals in samples with fraction distribution and trend line

Rys. 3. Zawartość metali w poszczególnych próbkach z uwzględnieniem podziału na frakcje granulometryczne wraz z linią trendu

The sample number 4 was dominated by the smaller fraction including fine sand (more than half of the sample). In this sample the amount of the dust was also significant. The sample number 7 was far different from the others. The 60% of this sample consisted of fractions 0.25 mm and 0.18 mm. According to the diameter of grains, this fractions can be classified as middle sand, therefore this bottom sediment is similar to the samples number 1, 2, 5 and 6. Sample number 8 was dominated by the thinner fractions like fine sand and dust. A large amount of fractions 0.125 mm and 0.18 mm were also found in these sediments, which is similar to the fraction's distribution in sample number 7.

The measured amounts of heavy metals in fractions were shown in Figure 3. The greatest content of heavy metals was found in samples from locations numbered 6, 7 and 8. The results do not provide clear trend to connect metals with grain size fractions. The study shows that the contribution of copper, nickel and cadmium in the smallest fraction (dust, < 0.063 mm) was significant, which confirms the thesis presented in other studies (Zhu et al. 2006, Zou et al. 2007, Frankowski et al. 2005).

A large amount of zinc and lead was found in the thinnest fraction in sample number 7. Simultaneously, this sample was strongly contaminated with these metals. For the samples numbered from 4 to 7 the contribution of nickel and lead was observed in the smallest fraction, in contrast to sample number 8, which has lower content. Results show a substantial irregularity in contribution of heavy metals in each of grain size fraction, with the lowest content of nickel in the fraction 0.25 mm, lead in fraction 0.125 mm in samples numbered 1 and 5 and fraction < 0.063 mm in samples numbered from 6 to 8, copper in fraction 0.125 mm in samples numbered 1 and 6 and in fraction 0.063 mm in samples numbered 7 and 8, cadmium in fraction 0.09 mm in all samples. The contribution of metals in the most contaminated sample (number 7) was fairly steady for each of grain size fractions.

Obtained results show significant volatility of heavy metals association with grain size fractions (Ducaroir and Lamy 1995, Zou et al. 2007). For the analyzed metals there was found slight contribution of all fractions with the domination of one faction in samples. The dominant fractions were for four heavy metals:

- Cd – 0.063 and < 0.063,
- Cu – < 0.063,

• Ni – 0.063 and < 0.063,
• Zn – mostly smaller fractions < 0.09 mm.

From all heavy metals only nickel did not present any specific trend to accumulate in one fraction. This metal was most strongly associated with another fraction in each sample.

Figure 3 also specifies the trend line which shows arrangement of differences between the contents of heavy metals in each of the samples. The conclusion which comes from trend line is that all of heavy metals tend to have equal specifications of changes in the contents of heavy metals between samples. The lowest concentration of heavy metals occurred in the group of first few samples. For the samples numbered from 4 to 7 there can be seen the trend of increasing concentrations of metals, with a significant decrease observed in the sample number 8. The strong correlation occurred for nickel, lead and cadmium. These metals reached the lowest concentration in sample number 3.

The amounts of heavy metals in all samples were converted into percentage share in each sample due to the differences between amounts of metals in samples, especially for their high content in samples number 6, 7, 8. The content of heavy metal in each of the samples after the conversion was easy to compare and to look into for trends to accumulate metals in fraction.

The synthetic groups were created for comparison of metal's content in samples. Splitting of the fractions into the groups was based on positive correlation between adjacent granulometric fractions. Subsequently the pairs of fractions were added sequentially to each other and then the results were averaged. In the next step values were again recalculated to the percentage share. Thus three imaginary groups of fraction were created:

• Fractions 0.5 and 0.25 mm – the coarse fraction group,
• Fractions 0.125 and 0.09 mm – the middle fraction group,
• Fractions 0.063 mm and under mesh (<0.063 mm) – thin fraction group.

Obtained results are shown in figure 4. These graphs present changes between the content of heavy metals in groups. The clearly visible domination of one, specific group occurs only for cadmium and nickel. In most of the samples copper was accumulated in thin fraction group (except for samples number 3 and 7). In sample 3 the copper content was the lowest unlike in sample number 7, where the highest amount of copper was found. The highest contribution in thin fraction also concern zinc but in this case the smaller amount was found in sample 1, 2 and 8. The amount of zinc in middle fraction group was similar in each sample. For other metals there were not clear differences in the accumulation of metals in considered fractions.

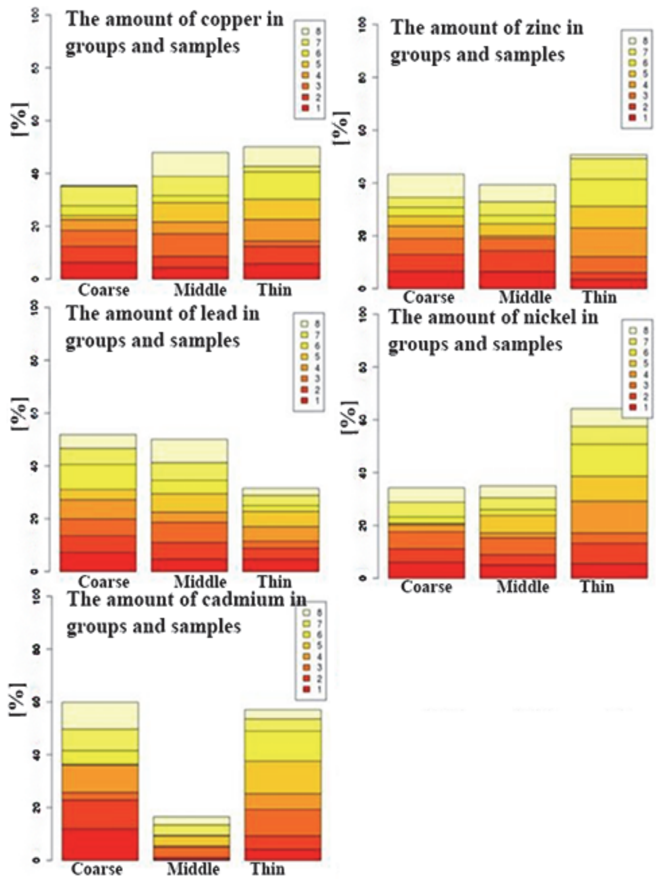

Fig. 4. The content of heavy metals in groups with samples distribution
Rys.4 Zawartość metali w poszczególnych grupach z uwzględnieniem podziału na próbki

The amount of lead was the lowest in thin fraction group and its percentage share in other groups between each of the samples was similar. In a case of nickel the opposite trend was observed – the thin fraction dominated and other two fractions showed similar percentage share of nickel in samples. The lowest accumulation was observed in middle fraction in case of cadmium. In the other two groups the amount of cadmium was similar between groups and between each of samples.

Obtained results showed relevant contamination with heavy metals of bottom sediments of the Utrata river. They also showed an increasing tendency of the raise of heavy metals contents alongside the stream of the river. These facts are associated with usage of the areas adjacent to the river. The samples from 4 to 7 were taken from the industrial areas. Nearby, where sample number 7 was taken, there is a landfill for non-industrial waste.

For the purpose of the bottom sediments monitoring in Poland the Polish Geological Institute developed the first classification of river and lake bottom sediments (Bojakowska I. & Sokołowska G 1998). The aim of this classification is to divide the bottom sediments into three contamination groups. The boundaries of group, which are describing these classes, are abnormal concentration of each of metal compared to their geochemical background.

Three classes of contamination are distinguished in the implemented classification:

I class – low polluted bottom sediments, the concentrations of heavy metals are 2 to 5 times higher than geochemical background (depending on mobility and toxicity of metal)

II class – moderately polluted bottom sediments, concentrations of heavy metals are 10 to 20 times higher than geochemical background

III class – polluted bottom sediments, concentrations of heavy metals are 20 to 100 times higher than geochemical background.

According to the proposed classification only sediments in samples 1, 2, 3 can be included in the first class. The rest of the sediments have an increased contents of heavy metals, even 20 times higher, which classifies them in the second class. The sample number 7 because of its copper contamination is classified in the third class. Tested sediments have a high content of cadmium in samples 1, 6, 7 and 8, lead in samples 6, 7 and 8 and zinc in samples 7 and 8.

4. Conclusion

The anlysis grain size of sediments by dry sieving method has revealed high proportions of nine sieves of mesh sizes. This study proved that it is not possible to assess unambiguously which granulometric fractions have the strongest association with heavy metals deposited in water reservoirs. The level of heavy metals association depends on the chemical properties of each metal. The dominant fractions were for: Cd – 0,063 and < 0,063, Cu – < 0,063, Ni – 0,063 and < 0,063 and Zn mostly smaller fractions < 0,09 mm. Also, the chemical composition of bottom sediments can be responsible for the influence on level of association. Hence, in the granulometric analysis of river sediments by dry method it may be crucial to determine heavy metals not only in the finest grain-size fraction, but also in the larger fraction. For more specific description of this phenomenon further research has to be conducted, including type of minerals present in the individual fractions and their affinity with metals.

References

Adamiec, E. and Helios-Rybicka, E. (2002). Distribution of pollutants in the Odra River system, part V. Assessment of total and mobile heavy metals content in the suspended matter and sediments of the Odra River system and recommendation for river chemical monitoring. *Polish J of Environ Stud., 11(6),* 669-673.

Bojakowska I, and Sokołowska G. (1998). Geochemiczne klasy czystości osadów wodnych. *Geological Survey, 46*,1.

Bojakowska I, Gliwicz T, Małecka K. (2006). *Results of geochemical analysis of bottom sediments in Poland (2003-2005)*. The Library of Environment Monitoring. (in Polish) Warsaw: Natural Environment Protection Inspectorate.

Cuong D, and Obbard J. (2006). Metal speciation in coastal marine sediments from Singapore using a modified BCR-sequential extraction procedure. *Appl Geochem., 21*, 1335-1346. DOI: 10.1016/j.apgeochem.2006.05.001.

Dı´az-Zorita M, Grove J.H, Perfect E. (2007). Sieving duration and sieve loading impacts on dry soil fragment size distributions. *Soil & Tillage Research, 94, 15-20.*

Ducaroir, J, and Lamy, I. (1995). Evidence of trace-metal association with soil organicmatter using particle-size fractionation after physical dispersion treatment. *Analyst, 120,* 741-745.

Frankowski, M., Zioła, A., Siepak, M., Siepak, J. (2008). Analysis of Heavy Metals in Particular Granulometric Fractions of Bottom Sediments in the Mała Wełna River (Poland). *Polish J of Environ Stud., 17(3)*, 343-350.

Frankowski, M., Zioła, A., Sobczynski, T. (2005). The Effect of Grain Size Structure on the Content of Heavy Metals in Alluvial Sediments of the Odra River. *Polish J. of Environ Stud., 14*, 81-86.

Helios-Rybicka, E., Adamiec, E., Aleksander-Kwaterczak, U. (2005). Distribution of trace metals in the Odra River system: Water-suspended matter-sediments. *Limnologica, 35*, 185-198.

Irmer, U. (1997). *Bedeutung Von Hintergrundwerten für Qualitätsanforderung an Ober-flächenwässern.* IKSE-Workshop: Bewertung der Ergebnisse aus der Elbeschadstofforschung. Geesthacht.

LAWA – Länder-Arbeitsgemeinschaft Wasser. (1998). *Beurteilung der Wasserbeschaffenheit von Fließgewässern in der Bundes-Republik Deutschland – chemische Gewässergüteklassifikation, Zielvorgaben zum Schutz oberirdischer Binnengewässer*. Band 2: Berlin 10.

Martincic, D., Kwokal, Z., Branica, M. (1990). Distribution of zinc, lead, cadmium and copper between different size fractions of sediments I. The Limski Kanal (North Adriatic Sea). *Sci Total Environ., 95*, 201-215.

Milenkovic, N., Damjanovic, M., Ristic, M. (2005). Study of Heavy Metal Pollution in Sediments from the Iron Gate (Danube River), Serbia and Montenegro. *Polish J of Environ Stud., 14(6),* 781-787.

Population and Communities: Sinclair Knight Merz. Report, Characterising the relationship between water quality and water quantity, August 2013, Australian Government, Department of Sustainability, Environment, Water.

Singh, K., Mohan, D., Singh, V., Malik, A. (2005). Studies on distribution and fractionation of heavy metals in Gomti river sediments – a tributary of the Ganges. *India. J of Hydrology, 312,* 14-27.

Solomons, W., Ferstner, V. (1984). *Metals in the Hydrocycle.* Berlin: Springer Verlag.

Tokalioğlu, S, Kartal, S, Elçi, L. (2000). Determination of heavy metals and their speciation in lake sediments by flame atomic absorption spectrometry after a four-stage sequential extraction procedure. *Anal Chem Acta, 413*, 33-40.

Wojtkowska, M. (2011). Content of selected heavy metals in water and riverbed sediments of the Utrata river. *Environ Prot Engin, 3(37),* 55-62.

Wojtkowska, M. (2013). Migration and Forms of Metals in Bottom Sediments of Czerniakowskie Lake. *Bull Environ Contam Toxicol., 90(2),* 165-169 doi:10.1007/s00128-012-0881-7.

Wojtkowska, M. (2013). *Rola specjacji w ocenie mobilności metali ciężkich w płynących wodach powierzchniowych*, Oficyna Wyd. Politechniki Warszawskiej.

Ying Z, Xiaodong Z, Suping F, Houquan T. (2006). The effect of grain size on the Cu, Pb, Ni, Cd speciation and distribution in sediments: a case study of Dongping Lake. China. *Environ Geol., 50*, 753-759.

Yuan, C, Shi, J, He, B, Liu, J, Liang, L, Jiang, G. (2004). *Speciation of heavy metals in marine sediments from the East Cina Sea by ICP-MS with sequential extraction.* Environ. Intern., 30, 769-783.

Zhu Y, Zou X, Feng S, Tang H. (2006). The effect of grain size on the Cu, Pb, Ni, Cd speciation and distribution in sediments: a case study of Dongping Lake, China. *Environ. Geol., 50,* 753-759.

Zou X, Yuan T, Zhu Y, Zhang X, Feng S, Shen Z, Wang W. (2007). Heterogeneous distribution of copper in different grain size and density fractions of contaminated surface sediment from Nansi Lake (China). *Environ. Geol., 51(5),* 813-820.

Analiza metali ciężkich w wybranych frakcjach granulometrycznych osadów dennych rzeki Utraty

Streszczenie

W pracy przedstawiono charakterystykę granulometryczną i stężenia metali śladowych w osadach dennych pobranych z rzeki Utraty, Polska. Próbki osadu z 8 stanowisk zebrano i analizowano na zawartości metali śladowych (Ni, Cu, Zn, Cd i Pb) i wielkość ziarna. W próbkach osadów określono 10 frakcji granulometrycznych, w tym frakcję nadsitową i podsitową. Próbki osadów charakteryzowały się podobnym składem granulometrycznym, w których dominował piasek średni. Najwieksze różnice wystąpiły dla frakcji najdrobniejszej i najgrubszej. Zmienność stężenia metali ciężkich w osadach dennych była duża. Najwięcej metali w osadach stwierdzono na stanowiskach końcowych. W uzyskanych wynikach można zaobserwować różnice w zawartości metali śladowych w analizowanych frakcjach osadów. Najniższe wartości stwierdzono dla Ni we frakcji 0,25 mm, Pb i Cu we frakcji 0,125 mm, Zn we frakcji 0,063 mm i Cd we frakcji 0,09 mm. Dla porównania zawartości metali na stanowiskach stworzono trzy grupy wynikające z dodatniej korelacji między frakcjami granulometrycznymi. Zmienność metalu w tych grupach jest wyraźna jedynie dla Cd i Ni. Zn, Cu i Pb kumulowały się głównie we frakcjach drobnych. Zgodnie z klasyfikacją osadów rzecznych (trzy klasy czystości) tylko osady z trzech pierwszych stanowisk kwalifikowały się do I klasy czystości, na pozostałych stanowiskach osady były silnie zanieczyszczone i klasyfikowały się do II i III klasy czystości.

Słowa kluczowe:
frakcje granulometryczne, metale śladowe, osady denne

Key words:
granulometric fractions, heavy metals, bottom sediments