IMPACT OF MINING DUMP ON THE ACCUMULATION AND MOBILITY OF METALS IN THE BYTOMKA RIVER SEDIMENTS

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Abstract: The research aim was to determine the long-term impact of the mine waste stored at the coal waste dump *Hałda Ruda* on the content of heavy metals in the bottom sediments of the Bytomka River. It is a watercourse flowing along this coal waste dump and has been under its influence for over fifty years. The research also attempted to determine the seasonality of changes (2 years) and mobility of selected elements.

The article presents total contents of Cr, Mn, Ni, Cu, Zn, As, Cd and Pb in the bottom sediments collected from the Bytomka River. It also focuses on the distribution of these elements in particular geochemical fractions determined with the Tessier's sequential chemical extraction procedure. Total element contents were determined with an EDPXRF (*Energy Dispersive X-ray Fluorescence*) technique. The extractants of particular Tessier's fractions were determined quantitatively with an ICP-MS (*Inductively Coupled Plasma Mass Spectrometry*) spectrometer. The research results show that the stored waste significantly influences the contents of heavy metals in the Bytomka River bottom sediments. The lowest concentration of heavy metals was observed at the B1 spot (above the dump), while the highest one was measured at the B3 spot (below the dump).

Sequential chemical extraction of the bottom sediments indicates that the Zn content in the ion-exchange and carbonate fractions diminished within a year. Nevertheless, Zn bound to Fe and Mn oxides acted in the opposite way. Mn, Zn and Pb are the most dangerous elements from the viewpoint of environmental hazards, as their total concentrations were high. Moreover, their high contents were observed in the most mobile (ion-exchange and carbonate) fractions. Extremely toxic Cd was bound to the oxide fraction to the largest extent. Cu was mainly bound to the organic fraction while environmentally hazardous Cr was bound to the residual fraction.

INTRODUCTION

Areas that have been under the influence of industrial activity causing degradation still make a large part of the Upper Silesian Industrial Region (*Górnośląski Okręg Przemysłowy*). Coal waste dumps are the effect of human activity in the region of

bituminous coal exploitation. They are an inseparable element of the Upper Silesia (*Górny Śląsk*) landscape. They began to appear simultaneously with the coal mining development. They traditionally formed near coal mines and were raised with barren rock and post-mining waste. Housing estates for miners and their families were often located nearby. With time, it turned out that coal waste dumps could be both troublesome for the environment and harmful to the inhabitants' health [12, 48, 49, 56].

Coal waste dumps constitute a source of heavy metal pollution (both in the close and distant dump surroundings), which mainly results from weathering processes, oxidation of Fe sulfides and a decrease in pH that causes an increase in their leaching. If surface watercourses flow close to such polluted areas, they make up a secondary source of heavy metals accumulated most often in the bottom sediments and vegetation.

River bed sediments are now considered an environmental matrix to be controlled, and many countries have included sediment samplings in their monitoring of river quality [15, 27, 28, 35, 53]. Examinations of the post-mining areas that consisted in determining concentrations and influence of heavy metals (Zn, Cu, As, Pb, Sb, Mn, Ni, Cr, Cd, Hg, Ag) on watercourses existing close to the former copper mine were performed in German Mansfeld-Sudharz region. An increased concentration of harmful substances was observed as far as 20 km from the pollution source [61].

At present, one of the best methods used in the qualitative and quantitative analyses of heavy metals is EDXRF (*Energy Dispersive X-Ray Fluorescence*). It enables examining concentrations of main and trace amounts of elements present in the soil [11, 18, 19, 31, 63], bottom sediments [1, 3, 9, 26, 29], ashes [50] or minerals [13, 17, 34]. EDXRF is relatively simple and inexpensive when compared to other methods for qualitative and quantitative analyses of heavy metals.

Heavy metals influence living organisms in various ways. They can be divided into three main categories, i.e. mechanisms responsible for blocking important functional groups in biomolecules (e.g. proteins and enzymes), those accountable for displacing important metal ions from biomolecules and finally the ones altering active conformation of biomolecules. They can block enzyme networks and thus lead to physiological changes that can bring about cell and tissue necrosis in extreme cases. The results of toxicological tests show that (in many cases) it is not the total content of a given element but its various forms that have a decisive impact on the living organisms. Knowing easily-leached forms and *ipso facto* bioavailable metals is especially important when determining the waste storage impact on the natural environment.

The occurrence of different physical and chemical forms of a given element in the specific examined material is called *speciation*, whereas their identification and quantitative determination is the concern of *speciation analytics* [10]. Determining a physical and chemical form in which a given element occurs helps to define its properties such as toxicity, bioavailability, migration possibility, accumulation or biomagnification.

Fractionation is a method enabling differentiation of metal forms occurrence, while the sequential extraction procedure allows to separate trace metals into chemical forms that can be released into the solution under different environmental conditions. One of the most frequently used types of sequential extraction is the extraction scheme suggested by Tessier et al. [54] Procedure of Tessier et al. was the first complete concept of the sequential extraction of metals and has become a commonly applied approach

in environmental geochemistry. The procedure described is not intended to identify all chemical individuals, but it only describes their types depending on the mode of binding and it is defined by the type of chemical operations being carried out. Due to its vital importance, fractionation of heavy metals in bottom sediments has attracted numerous researchers from many countries [2, 8, 20, 21, 25, 36, 43–45, 47, 55, 60].

The following paper presents the findings concerning bottom sediment samples collected from the Bytomka River, which flows close to the coal waste dump *Hałda Ruda* in Zabrze, Poland. The aim of the research was to determine the long-term impact of the dump on the content of heavy metals in the Bytomka River bottom sediments and the seasonality of those changes. It also attempted to define mobility and bioavailability resulting from fractionation of metals from bottom sediments.

The coal waste dump *Hałda Ruda*, which belongs to the former coal mine *Zabrze--Bielszowice*, is situated on the southern bank of the Bytomka River. It is located in the western part of the Upper Silesian Conurbation placed on the Silesian Uplands (*Wyżyna Śląska*). Their geological foundation is constituted by carboniferous rocks. The coal exploitation brought about the establishment of highly urbanized and industrialized area called the Upper Silesian Industrial Region (*Gornośląski Okręg Przemysłowy*). The area in which the research took place (the upper part of the Bytomka River) entails not only hard coal deposits but also dolomites containing zinc-lead ore deposits that were exploited for several hundred years [30].

The dump exploitation began in 1957 and finished in 1997. Its eastern part was covered with trees, while the western one was reclaimed and turfed, and bushes were planted there using fly ashes and humus. What remained are the very steep slopes on the western part of the dump. They are subjected to water and wind erosion. The exposure intensifies as the slopes are not covered with plants. Moreover, this part of the dump has become thermally active, which is a threat not only to the vegetation but also (and more importantly) to the local inhabitants and animals.

The Bytomka River, which is a tributary of the Kłodnica River, flows along the northeast part of the coal waste dump. Its watercourse does not have natural sources. It begins at the Karbowski Ditch (*Row Karbowski*), which drains municipal and industrial sewage. Then it flows through the cities of Ruda Śląska, Zabrze and Gliwice, where it finally flows into the Kłodnica River (Sośnica district). The whole river course is situated in a highly urbanized area. The Bytomka River is supplied chiefly with mine wastewater, industrial wastewater discharges, municipal wastewater and rainwater. The content of heavy metals in its bottom sediments is higher than that in the sediments of those Polish rivers that are not subjected to the intense anthropogenic impact on the environment [38].

EXPERIMENTAL

Sampling and analytical methods

Samples of the Bytomka River bottom sediments were collected monthly (in the years 2009–2011) from the 5 cm sediment surface layer at three sampling sites, i.e. upstream from the dump, at the dumpsite cross-section, downstream from the discussed coal waste dump (Fig. 1). Sampling took place in the littoral zone, where the sedimentation of the suspended material was possible (e.g. counter currents, current slowdown). pH, Eh and

conductivity were measured immediately after the sampling and transportation of the samples into the laboratory. Sample preparation for the determination of metal contents involved drying to obtain dry-air condition, sieving through a nylon sieve with a 2 mm mesh and drying at the temperature of 45°C to obtain constant mass. In order to determine total contents of metals and metalloids in the bottom sediment samples, they were ground in a tungsten-carbide grinder (grain size below 100 μm), pressed with binder and then measured with the Epsilon 5 EDPXRF spectrometer (Panalytical). Due to the application of polarized Cartesian geometry and various secondary targets, the spectrometer allowed obtaining low limits of detection.

Fig. 1. Satellite photo of the Bytomka River and Hałda Ruda dump with the marked sampling sites and direction of groundwater runoff

54 certified reference materials were used to calibrate the apparatus. 52 standards were employed to create calibration curves. 2 standards (NCSDC 73310, NCSDC 73309) were put into use for the subsequent verification of the calibration and establishing coefficients such as the repeatability, intermediate precision or recovery. Repeated analyses of the certified reference materials indicated appropriate precision and recoveries for the examined elements ranged between 85% and 105%. Table 1 shows limits of detection, limits of quantification, relative repeatability and reproducibility, and recovery.

Preparation of standards for the analysis consisted in mixing the precisely weighed amount of a given standard (7.2 g) with the binder (0.8 g), which was a 10% addition of the synthetic wax (STW wax batch 64). The mixture was then pressed with a manual hydraulic press (under the approx. 20-tonne pressure) within a 2-minute period of time. Real samples of the bottom sediments were prepared in a similar way. Excitation conditions for particular elements in bottom sediment samples were presented in [24].

Table 1. Limits of detection, limits of quantification, relative repeatability and reproducibility, and recovery in EDPXRF method

Analyte	VR [%]	Vr [%]	LOD [mg/kg]	LOQ [mg/kg]	Recovery NCS DC 73387 [%]
V	**5.6**	**3.4**	6.01	18.02	92.06
Cr	**7.2**	**2.7**	0.41	1.22	101.06
Mn	**4.6**	**2.0**	5.31	15.94	102.91
Fe_2O_3	**8.6**	**0.5**	4.63	13.90	100.25
Ni	**9.9**	**3.5**	2.53	7.58	109.21
Cu	**7.6**	**4.6**	0.71	2.14	95.88
Zn	**6.1**	**0.5**	0.97	2.92	101.98
As	**8.5**	**3.8**	1.02	3.06	93.54
Mo	**7.2**	3.8	0.55	1.64	101.28
Cd	**9.1**	**7.5**	0.80	2.40	104.18
Sb	**4.9**	**3.5**	0.76	2.29	99.93
Ba	**3.5**	**0.3**	0.96	2.87	92.97
Pb	**6.4**	**1.9**	0.60	1.80	100.47
Sn	**9.9**	**4.3**	1.02	3.07	101.93

LOD – Limit of detection; LOQ – Limit of quantification, V_R – Relative standard deviation of reproducibility, V_r – Relative standard deviation of repeatability

In order to categorize the quality of the Bytomka River bottom sediments in terms of heavy metal contents, the LAWA classification was applied [42]. The LAWA system accepts 7 purity classes which depend on heavy metal contents. It is thought that the content of metals in the dry sediment matter for the I and I–II classes is at the level of the geochemical background, whereas classes between II and IV indicate an increasing anthropogenic impact on the river sediment pollution and the whole aquatic ecosystem.

Selected bottom sediments collected from three sampling sites during each season went through the sequential chemical extraction. Despite their well-known limitations, sequential extraction methods are a useful tool serving to evaluate bioavailability, potential mobility of metals as well as the origin of metals (in some cases). The sequential extraction method described by Tessier et al. in 1979 [54] was used to determine the distribution of metals in the bottom sediment fractions.

Fraction 1 (ion-exchange fraction), fraction 2 (metals bound to carbonates), fraction 3 (metals bound to Fe and Mn oxides), fraction 4 (metals bound to the organic compounds and sulfides) and fraction 5 (metals bound to the aluminosilicate matrix) were determined in accordance with this method. The method was modified with the introduction of fraction 0 (metals solved in water). The applied analytical and chemical reagents as well as the conditions for the sequential extraction procedure are given in Table 2.

Table 2. Chemical reagents and analytical conditions for the sequential extraction procedures carried out on the samples of the Bytomka River [26]

Fraction	Extraction solution	Bound to
F0: Water-soluble metal fraction	H_2O, shaken for 1 h, solid/solution ratio 1:8, room temperature	metals in porous solution
F1: Exchangeable	1M CH_3COONa, pH 8,2, shaken for 1 h, solid/solution ratio 1:8, room temperature	sediments as loosely adsorbed cations and anions
F2: Acido-soluble	1M CH_3COONa/CH_3COOH, pH=5, shaken for 5 h, solid/solution ratio 1:8, room temperature	carbonates and very reactive oxyhydroxides
F3: Reducible	0,04 M $NH_2OH \cdot HCl$ dissolved in CH_3COOH 25%, shaken for 6 h, solid/solution ratio 1:20, Temperature 96±2°C	manganese and iron oxyhydroxides (mainly amorphous and poorly crystallized)
F4: Oxidisable	a) 0,2 M HNO_3, H_2O_2 30%, pH=2, shaken for 5 h, solid/solution ratio 1:8, temperature 85±2°C b) 3,2 M CH_3COONH_4 dissolved in 20% HNO_3, shaken for 0,5 h, room temperature	organic matter and sulfides
F5: Residual	HF (10 ml), $HClO_4$ (2 ml) solid/solution ratio 1:12, evaporate almost to dryness HF (10 ml), $HClO_4$ (1 ml) solid/solution ratio 1:12, evaporation almost to dryness $HClO_4$ (1ml) evaporation to white fumes	The crystal lattice of primary and secondary minerals

The quantitative analysis of metals in solutions obtained at the consecutive stages of the sequential extraction was carried out with an ICP-MS spectrometer (Elan DRC-e 6100 model, Perkin-Elmer). The apparatus was equipped with a standard ICP quartz torch, crossflow nebulizer, nickel cones as well as samples and standards handed with a peristaltic pump.

The spectrometer was optimized daily with a 10 µg/L solution (Mg, Cu, Rh, Cd, In, Ba, Ce, Pb, U) in 1-% HNO_3 Elan 6100 Setup/Stab./Masscal. Solution manufactured by Perkin-Elmer. The spectrometer was optimized to provide maximal intensity for ^{24}Mg, ^{115}In, ^{238}U, and minimal values for CeO/Ce (below 3%) and Ba^{2+}/Ba (below 3%). All reagents used for titration were analytically pure. High-purity double-distilled and deionized water for dilution and all titration reagents preparation were obtained with Millipore's Milli-Q System. All solutions of multi-elemental (Merck, Germany) and monoelemental ICP-MS standards were prepared daily by the dissolution of the reference materials in water obtained from Milli-Q System and used for the calibration. Standards, blanks and samples were measured with ^{103}Rh as the internal standard (10 µg/L, Merck, Germany). 10 µg/L Rh solution was introduced into all solutions on-line, with the second tubing on the peristaltic pump. Table 3 shows limits of detection, limits of quantification, relative repeatability and reproducibility, and recovery.

A special application was prepared, which enabled [52]Cr isotopes measurement in the DRC mode and [75]As, [55]Mn, [60]Ni, [65]Cu, [66]Zn, [114]Cd, [75]As, [208]Pb measurements in the standard mode. Methodology for the determination of metals/metaloids using ICP-MS spectrometer was presented in [24].

Table 3. Limits of detection, limits of quantification, relative repeatability and reproducibility, and recovery in ICP-MS method

Analyte	V_R[%]	V_r [%]	LOD [ug/l]	LOQ [ug/l]	Recovery NIST 1643-e [%]
V	3,8	3,2	0,09	0,27	**101,14**
Mn	10,4	6,3	0,033	0,098	**108,08**
Co	4,6	4,6	0,002	0,007	**109,63**
Ni	4,6	3,9	0,024	0,072	**106,95**
Cu	5,8	3,5	0,064	0,191	**96,07**
Zn	11,4	7,6	0,181	0,543	**80,27**
As	5	4,8	0,096	0,289	**87,99**
Rb	3,1	3,9	0,003	0,008	**104,62**
Sr	5,1	5,9	0,008	0,025	**107,31**
Ag	6,9	3,2	0,002	0,007	**95,39**
Cd	5,3	13,9	0,04	0,12	**96,81**
Ba	8,2	6,5	0,01	0,03	**103,25**
Tl	7,1	3,9	0,002	0,006	**107,02**
Pb	13,9	11,3	0,036	0,107	**105,67**
Cr	5,5	5,9	0,013	0,039	**106,43**

LOD – Limit of detection; LOQ – Limit of quantification, V_R – Relative standard deviation of reproducibility, V_r – Relative standard deviation of repeatability

RESULTS AND DISCUSSION

Seasonality of changes in the total metal concentrations in sediments
Table 4 presents total metal and metalloid contents in the bottom sediment samples determined with the EDPXRF spectrometer.

The obtained results show that the waste stored at the coal waste dump *Hałda Ruda* has a significant influence on the increase of heavy metal contents in the Bytomka River bottom sediments. In each case the lowest concentration was observed at the B1 spot, (upstream from the dump), whereas the highest one was noted at the B3 spot (downstream from the dump). The Bytomka River itself is a highly polluted watercourse and for this reason considerable contents of heavy metals were observed at the B1 spot. It was

Table 4. Heavy metals concentration in bottom sediments of the Bytomka River in three points: B1 – upstream
from the dump, B2 – at the dumpsite cross-section, B3 – downstream from the dump

Analyte	–	B1 [mg/kg]	B2 [mg/kg]	B3 [mg/kg]
Cr	Min	50,50	57,68	92,12
	Max	488,03	567,96	952,59
	Median	126,21	175,33	283,80
Mn	Min	99,96	132,90	136,35
	Max	685,02	909,61	1177,51
	Median	376,39	437,71	552,63
Ni	Min	5,39	6,40	8,61
	Max	29,90	38,28	49,09
	Median	14,56	17,46	23,94
Cu	Min	20,58	39,18	72,29
	Max	158,13	226,47	353,98
	Median	90,26	113,26	176,46
Zn	Min	211,37	443,58	563,12
	Max	2056,89	2933,60	4410,60
	Median	1003,81	1392,71	2055,10
As	Min	0,97	1,91	3,74
	Max	5,43	8,31	11,97
	Median	3,16	4,11	6,24
Cd	Min	0,77	1,36	2,12
	Max	5,11	8,61	10,68
	Median	2,54	3,21	7,00
Pb	Min	22,78	45,45	61,67
	Max	116,07	213,29	351,75
	Median	69,12	104,92	176,74

perceived that when thaw took place in spring and the water level in the river rose, the river current moved away the surface sediment layer. Consequently, the contents of heavy metals in the sediments were depleted, which is presented in Figures 2 and 3. On the other hand, drought periods causing decrease in the water level and the flow rate reduction led to higher sedimentation level.

The Zn content in the Bytomka River bottom sediments varied between 200 and nearly 4,500 mg/kg DM. The Pb concentration ranged between 20 and nearly 352 mg/kg DM, whereas As content extended between 0.97 and 11.97 mg/kg DM. The contents of Cd and Cr ranged from 0.77 mg/kg to 10.68 mg/kg DM and 50.50 mg/kg DM to nearly 1,000 mg/kg DM, respectively. The Cu content fluctuated between 20.58 and almost 354 mg/kg DM, while the Ni concentration ranged between 5.39 and 49.09 mg/kg DM.

Finally, Mn concentrations varied between 100 and nearly 1,200 mg/kg DM. Interestingly, the sediment samples collected at the B3 spot indicated higher contents of elements.

The quality evaluation of the Bytomka River bottom sediments was conducted in compliance with the LAWA classification [32]. The comparison of the results and the LAWA classification shows that the Bytomka River bottom sediments are heavily polluted. Sediments containing Cr, Cu and Pb belong to the purity class III (heavily polluted sediments), while the ones comprising Zn are given the purity class IV (very heavily polluted). The increased levels of the determined elements are related to the presence of the previously exploited lead-zinc ore deposits together with the co-existing Cd in the river catchment area as well as the location of the examined coal waste dump.

It turns out that even old (more than fifty years) coal waste dumps constitute a threat as they influence contents of heavy metals which accumulate in the water-soil environment surrounding the dump. Figures 2 and 3 present total contents of heavy metals obtained at sampling fixed dates. The results helped to observe changes in the metal concentrations in time.

Bioavailability and mobility of elements with the application of the sequential extraction

The main threat to the environment is posed by metals bound to the ion-exchange and carbonate fractions as they can easily migrate into the solution. As a result, they become more assimilable and potentially toxic. On the other hand, metals bound to the organic and aluminosilicate fractions are thought to be hardly bioavailable because the risk of their release into the solution is low.
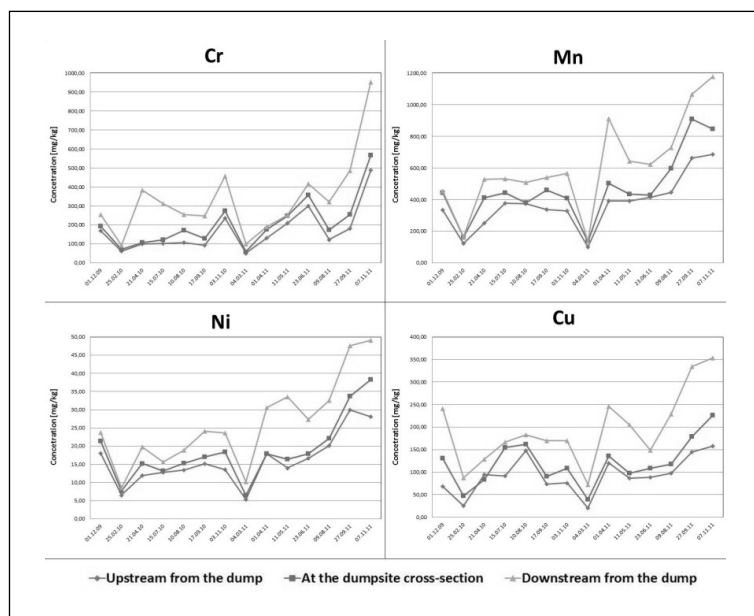

Fig. 2. Seasonal variability of total Cr, Mn, Ni and Cu concentrations upstream from the dump, at the dumpsite cross-section, downstream from the dump
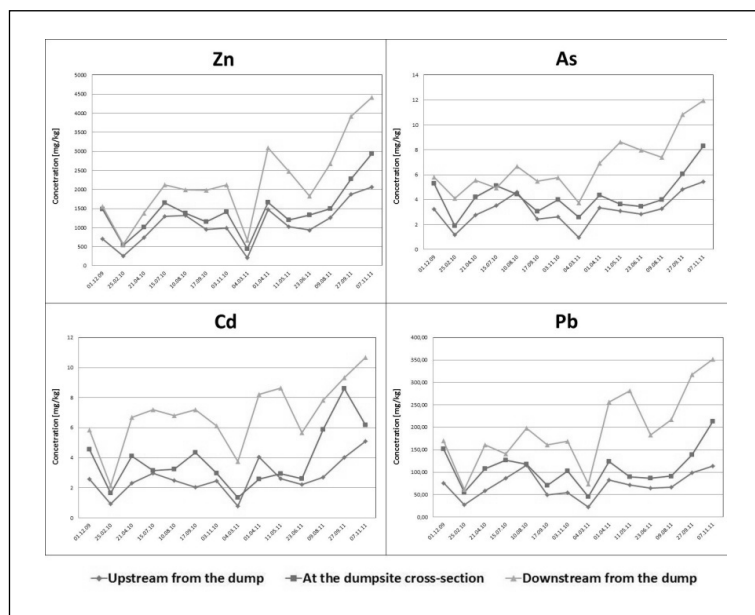
Fig. 3. Seasonal variability of total Cd, As, Cd and Pb concentrations upstream from the dump,
at the dompsite cross-section, downstream from the dump

The RAC (*Risk Assessment Code*) shown in Table 5 indicates that sediments in which metals bound to the ion-exchange and carbonate fractions make less than 1% can be regarded as safe for the environment. However, the sediments in which more than 50% of the total metal content is released from the same fractions must be acknowledged as highly dangerous because the released element can easily pass into the water food chain [40, 59].

Table 5. Values of RAC [40]

RAC	Criteria (%)	RAC for Bytomka river
No risk	< 1	–
Low risk	1–10	Cr
Medium risk	11–30	Ni, Cu, Cd, As
High risk	31–50	Pb
Very high risk	> 50	Mn, Zn

Figures 4 and 5 present the distribution of the examined elements in the individual fractions in four sample sets corresponding to respective seasons. Among those elements, Zn and Pb occur in the most mobile forms. They demonstrate the highest content in the first three fractions, which are bound to the sediments in the most unstable way. For this reason, they are the most dangerous for the environment [57].
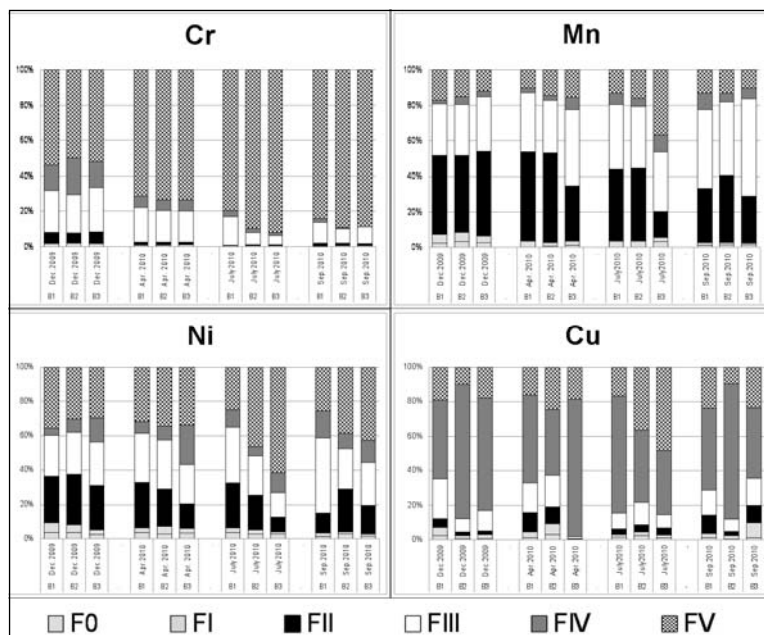
Fig. 4. Cr, Mn, Ni and Cu distribution in the different fractions in four sample sets corresponding to respective seasons
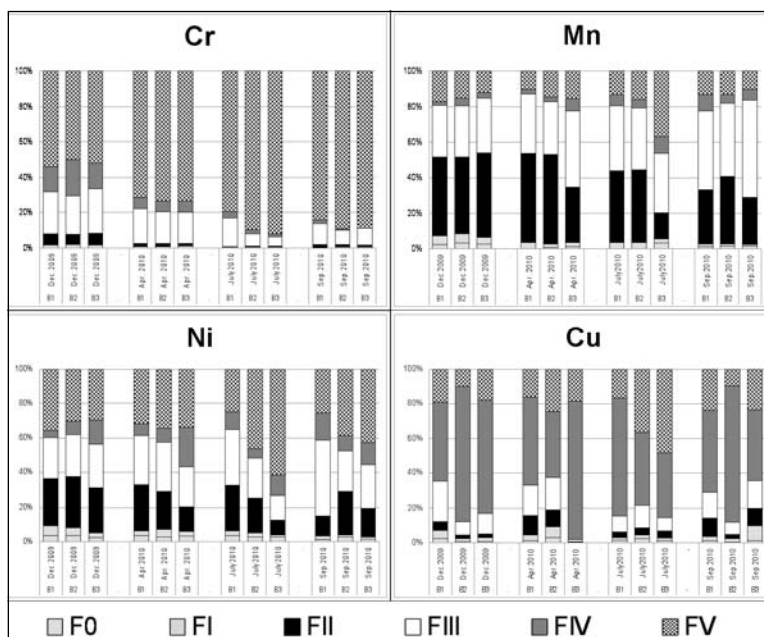

Fig. 5. Zn, As, Cd and Pb distribution in the different fractions in four sample sets corresponding to respective seasons

The fact that Zn and Pb carbonates form easily can be attributed to the characteristic physical and chemical conditions of the Bytomka River. These results conform the results obtained by Nocoń and Kostecki [37], who also found high concentration of the discussed analytes in the most unstable sediment fractions at the mouth where the Bytomka River flows into the Kłodnica River. What is more, a decreasing Zn concentration was noted in the ionexchange and carbonate fractions. On the other hand, its share increased in the oxide fraction. No such interdependence was observed for Pb. The RAC values for these analytes varied between 30% and 55% and even for this reason the Bytomka River sediments can be classified as extremely dangerous for the environment.

Zn and Pb mobility also depends on the solubility of the oxide fraction as it contains large concentrations of those elements. The physical and chemical conditions of the Bytomka River help Fe and other metal co-precipitating with Fe to precipitate. That is why they become a part of the oxide fraction. The formation of Fe(III) oxide-hydroxides co-precipitated with considerable amounts of other metals, such as Zn and Pb, depends on the pH [7, 33, 41, 51, 62].

Interdependence between the increase in the pH of the bottom sediments and the location of the sampling sites was also noted. The pH of the Bytomka River bottom sediments rose in the B1<B2<B3 order. The median pH value amounted to 7.25 at the B1 spot and 8.12 at the B3 spot (within discussed period of time).

Nonetheless, Cd demonstrated the highest content in the oxide fraction. Its share reached even 70% in the summer and fall season with RAC not exceeding 10% within the same period. Cu was bound to the organic substance in the organic-sulfide fraction to the highest extent. It corroborates the fact that it easily forms complexes with the organic matter that demonstrate high stability [4, 14, 42, 52, 58]. Cr demonstrates the lowest mobility among the examined metals as it is bound to aluminosilicates. Its share exceeded 90% in the summer and fall seasons. According to Izquierdo et al. [23], elements bound to this fraction are unavailable to the ecosystem.

Nocoń et al. [39] and Nocoń [38] noted high Cr concentrations bound to the residual fraction in the bottom sediments at the place where the Bytomka River flows into the Kłodnica River. Ni demonstrated medium mobility due to the fact that its binding to the residual fraction ranged between 30 and 50%. This observation was confirmed by other researchers [36, 42]. A large Ni content was also noted in the oxide fraction. High concentrations of this metal are known to accompany Fe-Mn nodules [30]. Mn mobility can be regarded as high (similarly to Pb and Zn) because it is bound to the ion-exchange and carbonate fractions to a large extent. Close relations between Mn and carbonates were described thoroughly in the literature [22]. The Mn concentrations decreased (similarly to Zn) in the mobile fractions and increased in the oxide one in the summer and fall season. The RAC value for Mn attained the level of 50% in winter and spring.

Among all studied elements, As was (to the largest degree) bound to the ion-exchange fraction, which is the most easily available for the ecosystem. As can pass from the solid phase into water when the water ionic content changes as a result of the sorption-desorption balance shift [6, 16]. Even though As demonstrated increased mobility, its RAC value did not exceed 35%.

Similarly to Sharmin et al. [46], the obtained results make it possible to determine potential mobility of individual analytes under conditions of the researched ecosystem.

The share of specific geochemical fractions bound to the examined elements can be presented in the following way:

Cd: Fe-Mn oxide > carbonates > sulfides and organics > silicates and residual > water-soluble and exchangebles

Cu: sulfides and organics > silicates and residual > Fe-Mn oxide > carbonates > water-soluble and exchangebles

Cr: silicate and residual > Fe-Mn oxide > sulfides and organics > carbonates > water-soluble and exchangebles

Ni: silicate and residual > carbonates > Fe-Mn oxide > sulfides and organics > water-soluble and exchangebles

Mn: carbonates > Fe-Mn oxide > silicate and residual > sulfides and organics > water-soluble and exchangebles

Zn: carbonates > Fe-Mn oxide > silicate and residual > sulfides and organics > water-soluble and exchangebles

Pb: carbonates > Fe-Mn oxide > silicate and residual > sulfides and organics > water-soluble and exchangebles

As: silicate and residual > Fe-Mn oxide > carbonates > sulfides and organics > water-soluble and exchangebles

The research indicates that the potential mobility of the examined elements in the Bytomka River aquatic environment can be ordered as follows: Zn > Mn > Pb > Ni > Cd > Cu > As > Cr. It is also possible to observe interdependence between the extent of element concentrations in the residual fraction and the location of the sampling sites. It is the highest at the B3 spot and it reaches its highest value in the spring and summer seasons.

CONCLUSIONS

The conducted research clearly showed that even old and no longer exploited coal waste dumps pose a threat to the environment. The hazard also consists in their influence on the increase in contents of heavy metals which accumulate in the soil-water environment of the adjoining areas. The research on the Bytomka River bottom sediments sheds light on their origin and character due to the application of the metal sequential extraction (which provides information on bioavailability and mobility of elements). Moreover, understanding the changeability of heavy metal contents in time (a 2-year period) and the forms of their occurrence (4 seasons) allows for complete environmental risk assessment.

The discussed bottom sediments of the Bytomka River are highly polluted with Mn, Zn and Pb. This fact and the mobility of those elements pose a significant threat for the catchment area of the Kłodnica River [5], whose tributary is the Bytomka River. Due to the high value of RAC for those elements, which exceeds 50%, the bottom sediments of the Bytomka River can be recognized as extremely dangerous for the environment.

When compared to classical analytic methods, the EDPXRF technique used in the research turned out to be a relatively simple, quick and inexpensive method serving to determine total element content. The distribution of Cr, Mn, Ni, Cu, Zn, As, Cd, Pb in particular geochemical fractions was performed in accordance with Tessier's sequential chemical extraction and with an ICP-MS technique.

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WPŁYW ZWAŁU ODPADÓW POGÓRNICZYCH NA AKUMULACJĘ I MOBILNOŚĆ METALI W OSADACH DENNYCH RZEKI BYTOMKI

Celem pracy było określenie długoterminowego wpływu odpadów pogórniczych składowanych na zwale pogórniczym Hałda Ruda na zawartość metali ciężkich w osadach dennych rzeki Bytomki płynącej wzdłuż tego zwału, na którą przez ponad pół wieku hałda wywierała wpływ, ponadto określenie sezonowości (2 lata) tych zmian oraz mobilności wybranych pierwiastków. W pracy przedstawiono zawartość całkowitą pierwiastków: Cr, Mn, Ni, Cu, Zn, As, Cd, Pb w osadach dennych pobranych z rzeki Bytomki, jak również ich dystrybucję w poszczególnych frakcjach geochemicznych z wykorzystaniem sekwencyjnej ekstrakcji chemicznej według Tessiera. Całkowitą zawartość pierwiastków określono wykorzystując technikę EDPXRF natomiast anality poszczególnych frakcji Tessiera oznaczano ilościowo za pomocą spektrometru ICP-MS. Próbki do badań pobierano comiesięcznie w okresie od grudnia 2009 do listopada 2010, w trzech punktach przed (B1), na wysokości (B2) oraz za zwałowiskiem (B3). Wyniki badań wskazują, że składowane odpady w znacznym stopniu wpływają na wzrost zawartości metali ciężkich w osadach dennych rzeki Bytomki. Najniższe stężenie metali ciężkich zaobserwowano w punkcie pobierania przed zwałem – B1, a najwyższe w punkcie pobierania za zwałem – B3. Należy również zwrócić uwagę na fakt, że wody rzeki Bytomki są bardzo zanieczyszczone, stąd już w punkcie pobierania B1 (przed zwałem) obserwuje się znaczne zawartości metali w osadzie dennym. Sekwencyjna ekstrakcja chemiczna osadów dennych pozwoliła stwierdzić, że stężenie cynku w frakcji jonowymiennej i węglanowej ulegała zmniejszeniu w ciągu roku, odwrotnie zachowywał się cynk związany z tlenkami żelaza i manganu. Z punktu widzenia zagrożenia dla środowiska najbardziej niebezpieczne są Mn, Zn, i Pb, gdyż oprócz wysokiego stężenia całkowitego, zaobserwowano wysoki ich udział w najbardziej mobilnych frakcjach: jonowymiennej i węglanowej. Silnie toksyczny kadm związany był w największym stopniu z frakcją tlenkową. Miedź związana jest głównie z frakcją organiczną, a niebezpieczny dla środowiska chrom z frakcją rezydualną. Oznaczane metale w próbkach osadów dennych w punkcie B3 (za zwałem) były w większym stopniu związane w frakcji rezydualnej, niż w przypadku punktów B1 i B2.