

METAL SPECIATION IN RIVER BED SEDIMENTS WITHIN
THE POLISH PART OF MUSKAU ARCH GEOPARK

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Abstract: The object of the investigation was metal contamination of bottom sediments of the Skroda and Chwaliszówka rivers, which are the right tributaries of the Lusatian Neisse river, draining the territory of the so called "anthropogenic lake district". The district came into existence as a result of mining activities in the border of Silesia and Lusatia, which date from the half of 19th century to 1974. The district includes about 100 reservoirs, of the total area of over 150 ha, which are from about 30 to 100 years old.

The rocks accompanying the Miocene coal-bearing formations were deposited on waste dumps. The dumps form embankments of the aquifers arising as a result of post-exploitation mining subsidence. The streams dewatering waste dumps inflow directly or indirectly to the Chwaliszówka and Skroda rivers. The pyrite is the mineral present in mine waste material. The pyrite weathering products inflow into surface waters and affect adversely the water quality. In the last stage of migration the pollutants are accumulated in the bottom sediments of rivers and lakes. The samples of bottom sediments of the two rivers were analysed by means of a five-step sequential extraction procedure performed for the partitioning of selected trace metals (Fe, Mn, As, Cr and Al). It was determined that the bottom sediments of the two analysed rivers contain significant concentrations of aluminium and iron. The concentrations of other metals (Mn, Cr and As) are in the range of geochemical background of water sediments in Poland. Concentrations of arsenium, chromium and manganese, which are bound to easy-available fractions (I – exchangeable and II – bound to carbonates) are not significant, so it could be assumed that they are not expected to be released and they do not threaten the river ecological system. There is, however, the possibility of the aluminium and iron re-mobilisation, taking into account the high concentrations of easy-available fractions of these metals in the sediment. Fe and Al are potential source of water contamination, and re-mobilisation of these metals will produce the aggravation of quality parameters of river waters.

INTRODUCTION

The Skroda and Chwaliszówka rivers flow throughout the Muskau Arch region (known also as Muskauer Faltenbgen), where the exploitation of lignite was performed until 1974. The rocks accompanying the Miocene coal-bearing formations were deposited on waste dumps. The dumps form embankments of the aquifers arising as a result of post-exploitation mining subsidence. The streams dewatering waste dumps inflow directly or indirectly to the Chwaliszówka and Skroda rivers. The pyrite is the mineral present in mine waste material. The pyrite weathering products inflow into surface waters and affect adversely the water quality. In the last stage of migration the pollutants are accumulated in bottom sediments of rivers and lakes.

The purpose of the undertaken investigation is the determination of pollution extent of the Chwaliszówka and Skroda bottom deposits. The analysis of Fe, Mn, Al, As, and Cr content, as well as the assessment of their real threat to the water environment were performed.

STUDY AREA

The composition of river bottom sediments reflects the natural and anthropogenic environmental conditions. The increased metal concentration in the deposits is of various origin, e.g. in the upper course of the river metals could originate from natural sources, whereas in the lower course from industrial pollution [3, 11].

The Skroda and Chwaliszówka rivers, being the right tributaries of the Lusatian Neisse river (Nysa Łużycka), drain the territory of the so called "anthropogenic lake district" in the east part of Muskau Arch (Fig. 1). The investigated area, situated within the „Muskau Arch Geopark”, is under legal protection, because of the special natural and landscape values. The Skroda river spring is situated near Boruszyn and its average flow is rather low, i.e. 1.15 m³/s. Its tributary area is 219.2 km². The Skroda is recharged by two main tributaries: the Skródka and the Skrodzica. The Chwaliszówka river is about 6.4 km long, and the river has its spring to the NE from Chwaliszowice. The tributaries are: one right side inflowing stream of over 2 km length, and two left side inflowing streams (their lengths are 750 m and 1200 m respectively), as well as the waters from one of the anthropogenic lakes [1, 7].

The moraine forms of Muskau Arch and Żarki Hills are Tertiary formations shaped by glacial-tectonic disturbances [13]. The Oligocene and Miocene deposits contain lignite deposits; moreover, in the Miocene formation there are glass-sands and clay deposits. Clay minerals occur also in Pliocene formation [5, 15].

The thickness of quaternary deposits is from 0 up to 163 m. They are represented by Pleistocene formation (three glaciation episodes), as well as Holocene formation. The youngest deposits of the last glacial period and Holocene period are present along the rivers and in areas with no run-off. In the Cenozoic formation the chronology of the sediments is disturbed by glacial tectonics. The most intense folding belt comprises rock complex at least 150 m thick. The extreme deformations are located near Łęknica, Żarki Wielkie and Chwaliszowice [2].

The Muskau Arch is a tongue-shaped ice thrust ridge with deep soft sediment deformations. It is an Elsterian push moraine deformed by the activity of Saalian Stage glaciation (Warthe stadium). As a result of glaciotectionic deformation the Tertiary deposits were folded severely. The present morphology is caused by deep erosion. The Oligocene and Miocene sediments contain lignite layers, which were originally laid on the depth of about 100–200 meters. The sediments were compressed and pushed up, what made possible the brown coal exploitation in open pits [8].

The resource-based industry in the region, especially brown coal mining activities, caused a severe flora damage, geomorphological changes as well as water conditions disturbance. As a result of underground and open pit mining activities the elongated collapse sink holes were formed [1, 7]. The valleys were being gradually filled with water, and, as a consequence, the largest artificial lakes district in Poland came into existence. The chemical composition of waters is influenced by pyrite (FeS₂) weathering products. Pyrite



Fig. 1. The morphology of Muskau Arch in German-Polish border (after [13])

is a sulfide mineral, common in Miocene coal formations. The contamination of waters with pyrite weathering products makes them ferruginous, with high level of acidity and elevated concentration of sulfates.

The Skroda river drains the south part of the “anthropogenic lake district”, whereas the Chwaliszówka drains the central part of it, by means of streams and dewatering ditches system.

Bottom sediments of both rivers were classified to the group of clay and they have mineral character. The content of mineral substance varies from 91.2 to 97.2%, while organic carbon ranges from 0.87 to 1.37%. Sediments contain slight concentrations of total nitrogen (from 0.005 to 0.63% of dry matter), total phosphorus (from 0.01% to 0.014% of dry matter), calcium (from 0.01 to 0.11% of dry matter) and potassium (from 0.02 to 0.06 % of dry matter). The concentrations of heavy metals amount to: for zinc – from 2.9 to 25 ppm; for cooper – from 4.3 to 67 ppm; for lead – from 0.8 to 46 ppm; for cadmium – from 0.19 to 2.7 ppm and for nickel – from 3.8 do 19 ppm [6].

METHODS

The investigated material was fluvial bottom sediments sampled from the Chwaliszówka and Skroda rivers in 2008 (Fig. 2). The sampling instrument was Kajak sediment core sampler.

The Chwaliszówka and side streams deposits were taken in 5 points:

- A – in riverhead part,
- B – in the river, lower down the ditch dewatering one of the anthropogenic lakes,
- C – situated on the longest right side stream,
- D – on the left side stream,
- E – in the river mouth part, where the Chwaliszówka flows in the Lusatian Neisse.

The Skroda bottom deposits were sampled in 3 points:

- 1 – 30 m from the Skroda flow into the Lusatian Neisse,
- 2 – situated 200 m from point 1,
- 3 – in the central part of the river; near the bridge of Łęknica-Przewóz road.

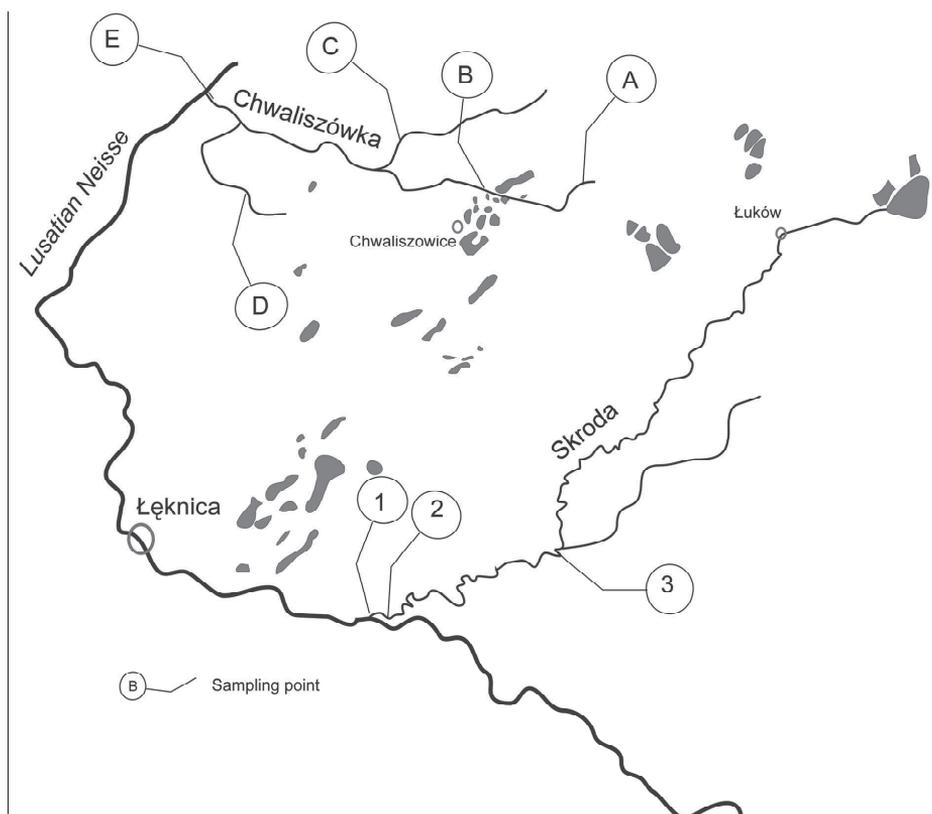


Fig. 2. Sampling points on Chwaliszówka and Skroda rivers

Samples of bottom sediments underwent a five-step sequential extraction procedure by Tessier [14]. This analytical procedure was performed for the partitioning of selected trace metals (Fe, Mn, As, Cr and Al) into five fractions: exchangeable, bound to carbonates, bound to iron and manganese oxides, and bound to organic matter and residual. The particular steps of the sequential extraction procedure are presented in Table 1. The metal concentrations were determined by atomic emission spectrometry (spectrometer ICP-AES Jobin-Yvon 2000). Sequential extraction was carried out in three repetitions. The average values of obtained results were compiled in Table 2.

Table 1. Sequential extraction procedure methods

Fraction	Chemical forms of metals	Analytical method (sample mass 1.0 g)
I	Exchangeable	20 cm ³ 1M CH ₃ COONH ₄ , pH = 7, shaking time 1h, room temperature
II	Bound to carbonates	40 cm ³ 1M CH ₃ COONH ₄ , pH = 5, shaking time 5h, room temperature
III	Bound to Fe-Mn oxides	40 cm ³ 0,04M NH ₂ OH w 25% CH ₃ COOH, shaking time 5h, temperature 95°C
IV	Bound to organic matter	1) 10 cm ³ 0,02M HNO ₃ +10cm ³ 30% H ₂ O ₂ , pH = 2, shaking time 2h, temperature 85°C 2) 10 cm ³ 30% H ₂ O ₂ , pH = 2, shaking time 2h, temperature 85°C 3) 20 cm ³ 3,2M CH ₃ COONH ₄ w 20% HNO ₃ , shaking time 0,5h, room temperature
V	Residual	microwave mineralizer „Plazmotronika”

The five-step sequential extraction procedure by Tessiere is one of the speciation analysis methods. It enables determination of specific geochemical phases of metals associated with suspended matter or bottom sediments in which they may exist [12]. The Tessiere model distinguishes 5 groups of metals, which are fractions likely to be affected by various environmental conditions.

The most harmful, in terms of their bio-availability, are metals exchangeable adsorbed on solid matter (fraction I) and metals bound to carbonates (fraction II), because even slight changes of water pH or red-ox conditions are likely to affect sorption-desorption processes.

Metals bound to iron and manganese oxides (reducible fraction III) show some mobility, but their releasing is rather hard and demands a significant pH drop. Fraction IV (oxidizable) is bound to organic matter. In this case soluble trace metals could be released under oxidizing conditions, when organic matter is degraded. The residual fraction (V) is bound to residual solid containing minerals, which may hold trace metals within their crystal structure. These metals are not expected to be released, so they are not threatening for water contamination of for living organisms.

RESULTS

Iron concentration

The results of speciation analysis are presented in Table 2 and in Figure 3. In the bottom deposits of the Chwaliszówka river the iron concentration is in the range from 908.35 ppm

Table 2. Speciation analysis results of bottom sediments of rivers Skroda and Chwaliszówka

Sampling point No	Metal	Fraction I exchangeable [ppm]	share %	Fraction II carbonate [ppm]	share %	Fraction III reducible [ppm]	share %	Fraction IV oxidable [ppm]	share %	Fraction V residual [ppm]	share %	Total [ppm]
A	Fe	8.33	0.84	6.68	0.67	73.33	7.41	9.81	0.99	891.2	90.08	989.34
	Mn	0.004	0.01	0.055	0.08	0.91	1.37	0.024	0.04	65.3	98.5	66.29
	Al	6.32	3.21	5.6	2.85	29.82	15.15	0.23	0.12	154.82	78.67	196.79
	As	0.002	0.16	BDL	-	0.005	0.42	0.003	0.26	1.29	99.16	1.300
	Cr	BDL	-	BDL	-	BDL	-	BDL	-	BDL	-	-
B	Fe	12.36	0.47	14.55	0.55	105.67	3.98	9.81	0.37	2513	94.63	2655.39
	Mn	0.09	0.09	0.09	0.09	1.15	1.09	0.02	0.02	104.1	98.71	105.45
	Al	12.78	1.29	19.04	1.92	185.9	18.73	8.55	0.86	766.29	77.2	992.56
	As	0.005	0.19	0.007	0.27	0.003	0.14	0.003	0.14	2.47	99.26	2.488
	Cr	BDL	-	BDL	-	BDL	-	BDL	-	BDL	-	-
C	Fe	22.6	2.49	5.65	0.62	89.65	9.87	1.22	0.13	789.23	86.89	908.35
	Mn	0.001	<0.01	0.23	0.29	0.98	1.22	0.11	0.14	78.69	98.35	80.01
	Al	7.69	3.02	11	4.33	32.63	12.84	2.53	1	200.31	78.81	254.16
	As	0.053	1.26	0.016	0.38	1.35	32.06	0.002	0.05	2.79	66.25	4.211
	Cr	BDL	-	BDL	-	BDL	-	BDL	-	BDL	-	-
D	Fe	11.5	1.12	8.69	0.85	89.3	8.69	4.56	0.44	913.55	88.9	1027.6
	Mn	0.03	0.07	0.01	0.02	0.67	1.45	0.006	0.01	45.5	98.45	46.22
	Al	8.98	1.61	11.22	2.01	100.25	17.96	3.52	0.63	434.26	77.79	558.23
	As	0.003	0.06	0.023	0.46	1.5	29.81	0.005	0.1	3.5	69.57	5.031
	Cr	BDL	-	BDL	-	BDL	-	BDL	-	BDL	-	-
E	Fe	11.89	0.96	4.23	0.34	95.26	7.73	2.23	0.18	1120	90.79	1233.61
	Mn	0.011	0.02	0.43	0.64	1.23	1.84	0.003	<0.01	65.23	97.50	66.904
	Al	10.6	3.28	7.74	2.39	19.14	5.92	6.65	2.06	279.13	86.35	323.26
	As	0.044	1.11	0.011	0.28	1.05	24.15	0.001	0.02	3.24	74.53	4.347
	Cr	BDL	-	BDL	-	BDL	-	BDL	-	BDL	-	-

1	Fe	0.845	0.1	2.23	0.3	40.16	5.9	1.72	0.3	640.29	93.4	685.24
	Mn	0.018	0.3	0.048	0.8	0.31	5	0.017	0.3	5.807	93.7	6.20
	Al	6.18	2.4	7.53	2.9	57.0	22	7.40	2.9	181.34	69.9	259.45
	As	0.00401	0.2	0.00491	0.3	BDL	-	0.00403	0.2	1.67705	99.2	1.69
	Cr	BDL	-	BDL	-	BDL	-	BDL	-	BDL	-	-
2	Fe	0.843	0.3	2.45	0.7	75.2	22.6	1.54	0.5	253.17	76.0	333.20
	Mn	BDL	-	0.064	1.1	0.75	12.7	0.010	0.2	5.066	86.0	5.89
	Al	6.12	2.5	7.74	3.2	57.7	24	8.07	3.4	160.55	66.8	240.18
	As	0.00408	0.3	BDL	-	0.00504	0.3	0.00427	0.3	1.58661	99.2	1.60
	Cr	BDL	-	BDL	-	BDL	-	BDL	-	4.32	100	4.32
3	Fe	0.879	0.2	4.76	1.0	34	7.0	1.8	0.4	444.80	91.5	486.24
	Mn	0.183	1.6	0.158	1.4	0.56	5.0	0.018	0.2	10.321	91.8	11.24
	Al	6.19	2.3	7.68	2.9	55.7	20.9	8.07	3.0	188.51	70.8	266.15
	As	0.00185	0.1	0.00448	0.3	BDL	-	0.00427	0.3	1.5694	99.3	1.58
	Cr	BDL	-	BDL	-	BDL	-	BDL	-	1.40	100	1.40

(in sediments of right side stream – the sampling point C) to 2655.39 ppm in the river sediments lower down the ditch inflow (the sampling point B). The most part of iron is immobilised in the residual fraction (V), and amounts to 86.89% in sample C, and 94.63% in sample B. A significant is also share of reducible fraction (III). The concentration of metal in this fraction reaches 105.67 ppm in a sample from point B. The bio-availability of iron in this form is small. There were also recorded elevated concentrations of iron bound to oxidable fraction (IV) of 9.81 ppm. The fact concerns samples taken in points B and E, but the mobility of this form of iron is not significant.

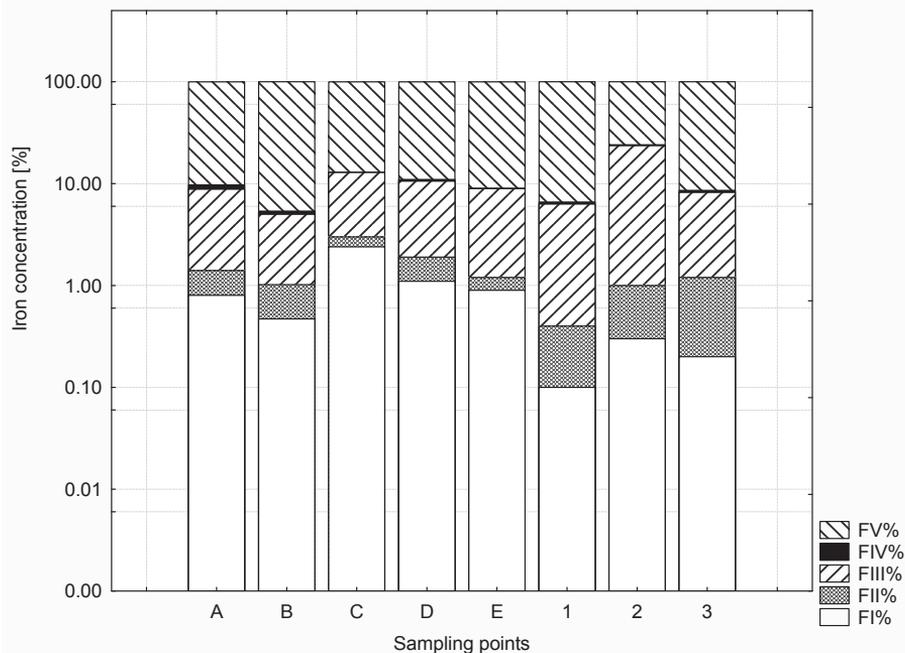


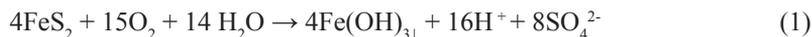
Fig. 3. Percentage share of iron's fractions in bottom sediments of Chwaliszówka and Skroda rivers (A, B, 1 – sampling points; FI – FV – fractions)

Total concentrations of iron bound to available fractions, exchangeable (I) and carbonate (II), are significant and range between 15.01 ppm in deposits from riverhead part (the sampling point A) and 28.25 ppm in deposits of the sampling point B. These are the amounts of iron which could be easily released into the water environment.

In bottom deposits of the Skroda river the concentrations of iron are significantly lower than in the Chwaliszówka river. The iron content is from 333.2 ppm in sediment from the sampling point 2 to 685.24 ppm in sediment from the sampling point 1. The dominant part is fraction IV – residual, the percentage of which is from 76% (sampling point 2) to 93.4% (the sampling point 1). Also there is a significant share of reducible fraction (III) – from 5.9 % in point 1 to 22.6 % in a sample from point 2; which corresponds to the amount of 75.2 ppm. In all sampling points the concentration of iron of oxidable fraction (IV) does not exceed 2 ppm. The total values of iron concentration

bound to easy-available fractions, exchangeable (I) and carbonate (II), reach 5.64 ppm in sediments taken from the sampling point 3 [9].

The high iron concentration in river deposits is caused by infiltration of pyrite weathering products, which are present in mine waste material from the aquifers embankments. The weathering process proceeds according to the reaction:



Manganese concentration

The concentration of manganese in the Chwaliszówka river deposits ranges from 46.22 ppm in deposits sampled from left side stream (point D) to 105.45 ppm in sediments taken from the sampling point B. The most significant is residual fraction (V): from 97.5 % in samples from point E (mouth part of the river) to 98.71% in sediments from point B. The concentration of manganese bound to the other fractions are very small, and do not exceed 1.5 ppm.

The concentrations of manganese in Skroda river sediments are not significant, and much lower than in Chwaliszówka river. The amounts of manganese comprise in range of 5.89 ppm in sample from point 2, to 11.24 ppm in sample from point 3. The most significant part makes residual fraction; from 86% in the sampling point 2, to 93.7% in the sampling point 1. The manganese concentration bound to other fractions are negligible and reach 0.75 ppm at the outside.

Both in Chwaliszówka and Skroda river sediments, the concentrations of manganese are rather low in comparison to geochemical background of water sediments in Poland, which is extremely 770 ppm [10]. The insignificant amounts of manganese bound to easy-available fractions means that manganese is not dangerous for water environment of two examined rivers.

Aluminium concentrations

In Chwaliszówka river the aluminium concentrations range from 196.79 ppm in sample from riverhead part (sampling point A) to 992.56 ppm in sample from point B (Fig. 4). The most part of the aluminium concentration is bound to residual fraction (V), which share is from 77.2% in sample B, to 86.3% in sample E. There is significant share of reducible fraction (III), and it ranges from 5.92% in sample from point E, to 18.75 % in sample from point B (what corresponds to value of 185.9 ppm). The aluminium concentration bound to oxidable fraction (IV) oscillates from 0.23 ppm in sediment from the sampling point A, to 8.55 ppm from the sampling point B. In the case of aluminium, there is visible significant amount of easy-available fractions: exchangeable (I) and carbonate bound (II). Total aluminium concentrations bound to these fractions are quite high, and range from 11.92 ppm (sampling point A) to 31.82 ppm (sampling point B).

In Skroda river the aluminium concentrations in all of the sampling points are comparable, and comprise in range of 240.18 ppm (sampling point 2) to 266.15 ppm (sampling point 3). The dominant is residual fraction (V), but the amounts of aluminium in this fraction is lower than the other metals. It oscillates from 66.8% (in the sampling point 2), to 70.8% (in the sampling point 3). Significant shares of reducible fraction (III) touching 24% in the sample from point 2, which corresponds to the amount of 57.7 ppm, were also noted.

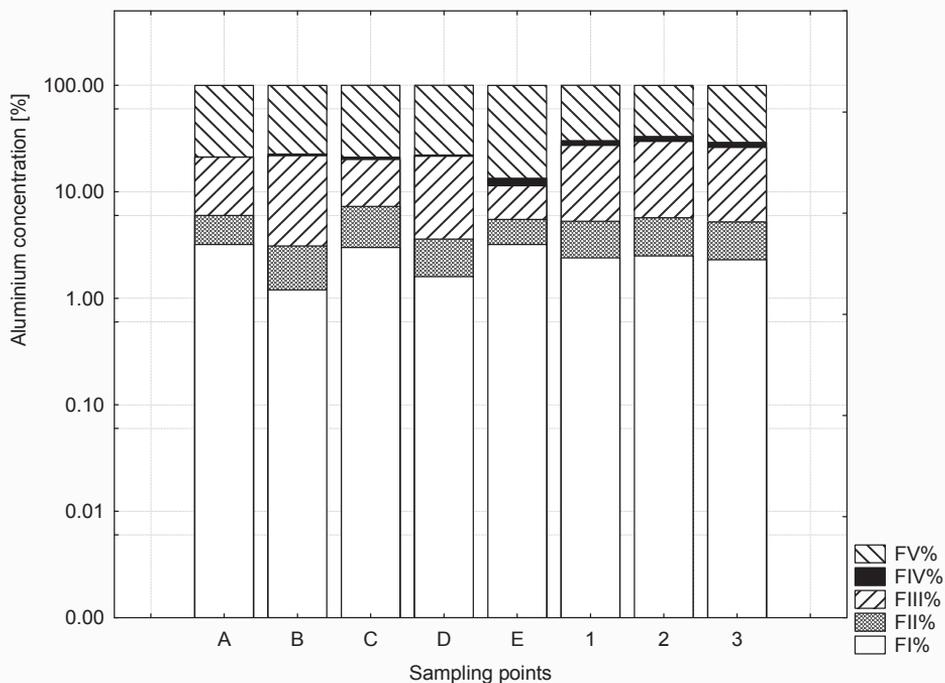
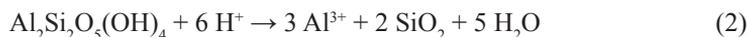


Fig.4. Percentage share of aluminium's fractions in bottom sediments of Chwaliszówka and Skroda rivers (A, B, 1 – sampling points; FI – FV – fractions)

The aluminium concentrations bound to oxidable fraction (IV) range from 7.4 ppm in sample 1 to 8.07 ppm in samples 2 and 3. Significant aluminium concentrations are connected to exchangeable fraction (I) and carbonate bound (II). The total amount of easy-available aluminium reaches 13.87 ppm in sediment sample from the point 3. The available fractions in bottom sediments from both the Chwaliszówka and Skroda rivers are quite significant, hence the risk of release of aluminium from the deposits is high.

The high aluminium concentrations in bottom deposits could be explained by the reactions of pyrite weathering. The hydrogen ion originates from the pyrite (iron sulfide) decomposition reaction. It is responsible for acidifying the environment (reaction 1) and is conducive to aluminosilicate decomposition:



Aluminium present in the sediments could be released to the environment due to deposits acidification, but in high concentrations it could be toxic even at pH below 5 [4].

Chromium concentrations

In the sediments of the Chwaliszówka river no chromium was detected. It is possible that there is no chromium at all, or the amount of chromium is below detectable level (BDL) of emission spectrometer ICP-AES JY 2000, which is 20 ppb. In the sediments of the

Skroda river chromium is present in the two sampling points: point 2—4.32 ppm Cr concentration, and point 3—1.4 ppm Cr concentration. These values are in range of geochemical background of water sediments in Poland. The threshold value is 18 ppm [10]. All of the chromium concentration is bound to residual fraction, hence it is immobilised.

The occurrence of chromium in river deposits could be related to chromium bearing pesticides, which are used in the regions the rivers flow through [3].

Arsenium concentrations

The concentration of arsenium in the Chwaliszówka river deposits ranges from 1.3 ppm in deposits sampled from the riverhead part (the sampling point A) to 5.031 ppm in sediments taken from the left side stream (point D). The most part of arsenium is immobilised in residual fraction (V); it is from 66.25% in point C (right side stream) to 99.26% in sediments from point B. In the case of arsenium not all fractions were possible to be detected. There is no arsenium in deposits or its concentration is below detectable level (BDL), which is for emission spectrometer 70 ppb. The arsenium concentration connected to exchangeable fraction (I), fraction bound to carbonates (II), as well as oxidable fraction (IV) was insignificant, not exceeding the value of 0.05 ppm. The reducible fraction (III) share was quite high: 32.06 % in the case of a sample from the point C, but the concentration of arsenium is not significant: 1.35 ppm.

In the case of the Skroda river, in particular sampling points the concentration of arsenium were not differentiated. The values varied in the range from 1.58 ppm in the sampling point 3 to 1.69 ppm in point 1. In each sample the residual fraction (V) constitutes over 99% of total amount of arsenium. The concentration bound to the other fractions does not exceed 0.005 ppm. As in the case of the Chwaliszówka river, the determination of arsenium concentrations in reducible and carbonate fraction was not possible.

Total arsenium concentrations in the sediments of the Chwaliszówka and Skroda rivers are within the geochemical background values of water sediments in Poland. The threshold value is 5 ppm [10]. Regarding the overwhelming concentrations of the residual fraction, and neglectable share of other fractions, it could be stated that arsenium is immobilised in the sediments.

The arsenium contamination of water environment could be related to the use of phosphatic fertilizers in the examined rivers drainage area [3].

Speciation analysis results show that in the bottom sediments of the Chwaliszówka river the metals concentration (Fe, Mn) are much higher than in the Skroda river, even in the riverhead part. This situation could be explained by the position of the Chwaliszówka spring in the vicinity of anthropogenic lakes, whereas the spring of the Skroda river is situated beyond the area of the lakes influence. Moreover, metal ions migrate to the Skroda through the system of minute streams and drain ditches, while the Chwaliszówka river is additionally supplied by dewatering ditch from one of the lakes. These waters negatively affect the chemistry of Chwaliszówka water. The most significant metals concentration was just noted in a sampling point lower down the ditch dewatering the above-mentioned anthropogenic lake (point B). Going down the river the metals concentrations in bottom sediments steadily decline.

In the case of the Skroda river there was noted a decline in the concentration of most part of metal ions in sediments taken from the sampling point 2 (situated 200 m from the Skroda flow into the Lusatian Neisse) in comparison to the sampling point 3 in

the central part of the river. On the stretch of river between the sampling point 1 (30 m from the Skroda flow into the Lusatian Neisse) and the sampling point 2 the re-increase of metals content is visible. The reason is the inflow of contaminated waters from anthropogenic lake district through dewatering ditches, the mouth of which is situated between the above-mentioned sampling points.

CONCLUSIONS

The implemented method of sequential extraction enabled not only the evaluation of total metal concentration in bottom sediments but also determination of the share of specific geochemical phases of metals. The analysis of bottom sediments of the Chwaliszówka and Skroda rivers, which flow through the area of anthropogenic lake district, enables the evaluation of possible mobility of accumulated metals, and their inflow on the river environment.

Basing on the performed examinations it was stated that the bottom sediments of the two analysed rivers contain significant concentrations of aluminium and iron. The phenomenon is caused by infiltration of pyrite weathering products, present in mine waste material from the aquifers embankments. Pyrite was originally connected with Miocene beds overlying the coal-bearing formations. The concentrations of other metals (Mn, Cr and As) are in the range of geochemical background of water sediments in Poland.

The concentrations of arsenium, chromium and manganese, which are bound to easy-available fractions (I – exchangeable and II – bound to carbonates) are not significant, so it could be assumed that they are not expected to be released, and do not threaten the river ecological system. There is, however, the possibility of the aluminium and iron re-mobilisation, taking into account the high concentrations of easy-available fractions of these metals in the sediment. Fe and Al are potential source of water contamination, and the re-mobilisation of these metals will produce the aggravation of quality parameters of river water.

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FORMY WYSTĘPOWANIA METALI W RZECZNYCH OSADACH DENNYCH W POLSKIEJ CZĘŚCI GEOPARKU ŁUK MUŻAKOWA

Przedmiotem badań był stopień zanieczyszczenia metalami osadów dennych rzek Skroda i Chwaliszówka, prawobrzeżnych dopływów Nysy Łużyckiej, odwadniających obszar tzw. „pojezierza antropogenicznego”. Pojezierze to powstało na pograniczu Śląska i Łużyc wskutek działalności górniczej, obejmującej eksploatację węgla brunatnego, prowadzonej od połowy XIX w. do roku 1974. Tworzy je ok. 100 akwenów o łącznej powierzchni ponad 150 ha, o wieku od ok. 30 do powyżej 100 lat.

Skały towarzyszące mioceńskim formacjom węglonośnym, zostały zdeponowane jako odpady pogórnice na zwałowiskach, tworzących obwałowania zbiorników wodnych, które formowały się w poeksploatacyjnych nieckach zapadliskowych. Odcieki ze zwałowisk zasilają bezpośrednio i pośrednio zarówno wody tych zbiorników, jak również wody Chwaliszówki i Skrody. Produkty wietrzenia pirytu, obecnego w odpadach górniczych, przechodzą do wód i wpływają negatywnie na ich parametry jakościowe. W końcowym etapie migracji substancje te zostają zaakumulowane w osadach dennych zbiorników i rzek.

Pobrane z obu rzek osady denne poddano pięciostopniowej sekwencyjnej ekstrakcji, oznaczając zawartości metali: Fe, Mn, As, Cr oraz Al. Stwierdzono, że osady charakteryzują się znacznymi stężeniami metali: glinu i żelaza. Koncentracje pozostałych metali w osadach: manganu, chromu i arsenu mieszczą się w granicach tła hydrogeochemicznego osadów wodnych Polski. Stężenia arsenu, chromu i manganu, związanych w postaci frakcji łatwo dostępnych (wymiennej – I i węglanowej – II) są niewielkie, dlatego też można przyjąć, że są one trwale unieruchomione w osadach i nie stanowią większego zagrożenia dla ekosystemu rzek. Istnieje jednak możliwość wtórnej mobilizacji z osadów glinu i żelaza, ze względu na wysokie stężenia tych metali, związanych z frakcjami łatwo dostępnymi. Metale te stanowią potencjalne źródło zanieczyszczenia środowiska wodnego, ich ponowne uruchomienie może spowodować pogorszenie parametrów jakościowych wód rzek.