

Impact of mine water disposal on concentration of barium and strontium in waters and sediments of the Odra River

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The effect of mine water disposal on the occurrence of barium, strontium, calcium and magnesium was investigated in waters and alluvia of the Odra River and its tributaries with their heads in the Upper Silesia. Barium concentration in alluvium of the Odra reaches a very high level of 2435 ppm; at the same time, its concentration in sediments of the Upper and Middle Odra courses is scores of times higher than its geochemical background. Sediments deposited in the Lower Odra course, downstream from the confluence with the Warta River, contain barium in amount close to geochemical background of this element in aqueous sediments in Poland. Barium concentrations in alluvium of the Odra tributaries occurred to be as high as 1700 ppm; maximum concentration is typical for sediments of the Olza River. The effect of saline water disposal on the occurrence of strontium in aqueous sediments of the Odra is much lower; however, higher concentrations than those in sediments of the Lower Odra are observed in alluvium of the Upper and Middle Odra. Similar range of strontium concentrations appears in alluvium of the Odra tributaries. A considerable increase of content of barium and strontium in relation to calcium in sediments is a consequence of a discharge of saline mine waters to the Odra catchment area; in particular, this deals with barium. Considerably elevated content of barium and strontium is a characteristic feature of the Odra waters; particularly affected is the Upper Odra course where waters from hard coal mines are discharged. 39 to 188 ppb is a common range of barium concentration in the Odra waters while 13 to 150 ppb is the range for the Odra tributaries. A discharge of mine waters of excessive salinity to the river has more important bearing on strontium than on barium. Its presence in the Odra waters was recorded at 267 to 901 ppb; maximum concentration was noted in the upper and middle river courses. As concerns tributaries, strontium was recorded in the range of 103 to 1888 ppb. A considerable increase in strontium in relation to calcium was also noted.

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INTRODUCTION

It is a very common situation that extraction of mineral raw materials from underground mines (particularly those at considerable depths) is associated with a pumpage of huge amount of formation waters flowing to underground workings. Both quality and quantity of such waters depend on local hydrogeological conditions, overburden properties and depth of workings. Mineralization of water increases with actual depth of mining. Waters pumped out from extracting levels at depth below 400 m are highly mineralized; they are waters of excessive salinity (total mineralization between 3 and 70 g/l) as well as brines (total mineralization. When discharged to

rivers, saline mine waters cause their excessive salinity and consequently, exert harmful influence on biocenosis and make economic utilization of river waters in possible. Apart from huge amount of chloride and sulphate ions as well as sodium and magnesium, they also supply surface waters with other constituents (such as barium and strontium) that are present in saline waters.

Catchment of the Odra River is a receiver of saline mine waters disposed from the Upper Silesian hard coal mines and Legnica–Głogów copper mines. Salinity of the Odra water is expected to have been caused in 72% by hard coal industry, 12% — copper industry, 10% — chemical plants, and 5.5% — agriculture and municipal waste management (J. Dobrzański, 1995). A total amount of saline waters disposed every year to surface waters reaches almost 50 mln m³, with



Fig. 1. Content of barium in sediments of the Odra in ppm (mg/kg) Zawartość baru w aluwiach Odry w ppm (mg/kg)

its load of salt equal to 450 000 t (J. Dulewski, M. Chaber, 1995). Mine waters are discharged to the Szotówka, Olza, Ruda, Bierawka, Bytomka and Kłodawka Rivers (A. Jeżewski, I. Węgrzynowska, 1995). Saline formation waters from copper mines, in total 28 mln m^3/a , containing 380 000 t of salt, are discharged to the Żelazny Most tailing reservoir and from there to the Odra at Głogów (S. Downorowicz, M. Kalisz, 1995).

Water samples as well as river bed sediment samples were collected from the Odra and its tributaries with their heads in the Upper Silesia. Sampling of the Odra was arranged in 1995, from 153 sites 5 km apart from each other, while samples from the tributaries (18) were collected at their confluences to the Odra. Samples of active alluvia were collected from banks of river beds, at places where transported material was deposited. Water samples were collected at the same places; sampled water was filtered trough 0.45 μ m membrane filters. An emission spectrometer ICP (Inductively Coupled Plasma) was employed to determine barium, strontium, calcium and magnesium concentrations in samples. Fraction of sediment < 0.2 mm was taken in analytical study; it was treated with



Fig. 2. Content of barium in waters of the Odra in ppb (μg/kg) Zawartość baru w wodach Odry w ppb (μg/kg)

aqua regia. All water and sediment samples were prepared and analysed by the Central Chemical Laboratory of the Polish Geological Institute in Warsaw.

BARIUM

Alluvium. Barium in bed sediment is first of all present in feldspar minerals, micas and barite; it is also connected with hydrated oxides of Fe and Mn, clay minerals, and organic matter. Mobilised from aluminosilicates by weathering, it fastly precipitates as sulphates and carbonates is bound by clay minerals, iron and manganese hydroxides as well as phosphates. Barium content in aqueous sediments treated with hydrochloric acid (1:4) usually does not exceed 50 ppm (J. Lis, A. Pasieczna, 1995). Naturally increased content of this element occurs in alluvia in the Sudetes and their foreland. Such situation is caused by mineralization of barite in this area. Higher Ba concentration is also typical for rich in

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Table 1

Element	River	Number of samples	Minimum content	Maximum content	Arithmetic mean	Geometric mean	Median
Ba [ppm]	Odra Upper and Middle Odra Lower Odra tributaries	153 116 37 18	10 33 10 48	2435 2435 276 1701	576 790 78 434	335 660 57 312	513 742 62 302
Sr [ppm]	Odra Upper and Middle Lower Odra tributaries	153 116 37 18	4 12 4 17	173 173 66 172	51 64 20 54	40 53 16 44	47 60 18 45
Ca [%]	Odra Upper and Middle Odra Lower Odra tributaries	153 116 37 18	0.06 0.12 0.06 0.07	1.84 1.84 1.84 1.42	0.52 0.56 0.51 0.60	0.43 0.44 0.40 0.49	0.44 0.47 0.40 0.49

Statistical parameters of Ba, Sr, Ca and Mg in sediments of the Odra River

organic matter lacustrine sediments as well as alluvia of rivers in peaty areas (I. Bojakowska, G. Sokołowska, 1996).

Very high concentrations (up to 2435 ppm) are a characteristic feature of barium in the examined alluvia of the Odra River. Barium concentration > 200 ppm is usually considered as anomalous; it has been noted in all the samples, collected in the Upper and Middle Odra courses from a state border at Chałupki to the confluence with the Warta River (Fig. 1). Considerably lower Ba concentrations are characteristic for the Lower Odra course; their values near geochemical background are most common (J. Lis, A. Pasieczna, 1995; Table 1). Ba content in sediments of the Upper and Middle Odra, expressed as geometric mean (660 ppm), is over 10 times higher than in sediments of the Lower Odra (57 ppm). Alluvia of rivers that flow out the Upper Silesia contain barium of 48 to 1700 ppm. Sediments of many of these rivers contain barium in excess of 200 ppm (Table 2). Very high Ba concentrations have been noted in sediments of the Olza.

Disposal of saline mine waters to the Odra is the factor which also contributes to relative enrichment of sediments with barium in relation to calcium and magnesium. Mean value of the ratio Ba/Ca in 340 sediment samples collected from rivers in Poland (data base for geochemical monitoring of aqueous sediments in Poland) is equal to 7×10^{-3} ; the ratio is twenty times greater in case of sediments of the Upper and Middle Odra, and three times in sediments of the Lower Odra (Table 3). Similarly, if a mean ratio Ba/Mg for river alluvia in Poland is equal to 49×10^{-3} , then it is six times greater in sediments of the Upper and Middle Odra, and 2.5 times greater in sediments of the Lower Odra.

Water. Due to poor solubility of its salts and sorption in river bed sediments, barium appears in relatively poor concentrations in inland surface water. Whereas its geometric mean in surface waters in Poland is 55 ppb, then its content in the Odra water is between 39 and 189 ppb, and its geometric mean is equal to 79 ppb (Table 4). Markedly elevated content of this element in the Odra water is noted the Upper Odra, particularly at mouths of its tributaries, containing formation waters from hard coal mines (Fig. 2). Waters of tributaries contain barium concentration between 13 and 150 ppb. Barium concentration > 100 ppb was recorded in the Olza, Ruda and Łącka Woda Rivers and some unnamed streams (Table 5). Relative load of barium in waters appeared significantly increased, if compared to calcium and magnesium (Table 6).

Table 2

Content of Ba, Sr, Ca and Mg in the sediments of the Odra tributaries

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River	Ba [ppm]	Sr [ppm]	Ca [%]	Mg [%]
Olza	1700	172	0.80	0.27
Łęgoń I	392	85	0.57	0.27
Plęśnica	497	55	0.79	0.33
Łęgoń II	418	49	0.41	0.25
Ruda	232	39	0.22	0.20
Pogonica	471	23	0.20	0.16
BN	302	30	0.29	0.26
Bierawka	96	17	0.07	0.04
BN	857	58	0.48	0.27
BN	174	23	0.30	0.25
Kłodnica	48	21	0.72	0.12
Gliwice Canal	278	96	1.39	0.23
Łącka Woda	147	33	0.49	0.09
BN	208	69	1.42	0.21
BN	296	40	1.01	0.25
BN	952	64	0.81	0.32
Czarnka	565	71	0.63	0.23
Mała Panew	109	37	0.41	0.09

BN --- unnamed rivers





Fig. 3. Content of strontium in sediments of the Odra in ppm (mg/kg) Zawartość strontu w aluwiach Odry w ppm (mg/kg)

Fig. 4. Content of strontium in waters of the Odra in ppb (μg/kg) Zawartość strontu w wodach Odry w ppb (μg/kg)

STRONTIUM

Alluvium. In general, concentration of strontium in sediments of unpolluted rivers does not exceed 40 ppm. In Poland, greater Sr concentrations in alluvia are observed in areas with exposed gypsum (as in the Nida Trough), deposits of native sulphur (region of Tarnobrzeg) and Cretaceous carbonatemarly rocks (area of Roztocze). Dominant strontium in alluvia is bound with feldspars and calcium carbonates. At pH > 5.5, strontium precipitates as of carbonates; it can be also bound by clay minerals, organic matter as well as organisms with carbonate skeletons.

Studies of aqueous sediment from the Odra River revealed strontium concentration of 4 to 173 ppm. Its arithmetic mean is 51 ppm while geometric mean 40 ppm; moreover, there is greater Sr concentration in sediments in the Upper and Middle Odra in comparison with alluvia of the Lower Odra (Fig. 3).

Sediments of rivers flowing into the Odra contain strontium in concentrations from 21 to 172 ppm. High strontium content has been recorded in alluvia of the Olza and Łęgoń Rivers as well as the Gliwice Canal (Table 2), with greatest concentrations in sediments of the Olza.

As the geochemical properties of strontium and calcium are very close to each another, there is common circulation of both elements in natural environment. The ratio Sr/Ca for alluvia in Poland does not exceed 5 x 10^{-3} and its mean value is 3 x 10^{-5} (Table 3). The ratio is higher (12×10^{-3} ; Table 3) in sediments of the Upper and Middle Odra. For sediments in many tributaries the ratio is much higher: it is equal to 21×10^{-3} in the Olza, 15×10^{-3} — the Łęgoń I, 18×10^{-3} — the Ruda and 24×10^{-3} — the Bierawka. Compared to alluvial sediments in Poland, the Odra alluvium is characterized by slightly less strontium content in relation to magnesium.

Water. In general, there is poor concentration of strontium in surface waters due to poor solubility of strontium sulphates and carbonates (similarly to barium). Geometric mean for strontium content in surface waters of Poland is equal to 263 ppb.

Table 3

Ratio	River	Number of samples	Minimum value	Maximum value	Arithmetic mean	Geometric mean	Median
Ba/Ca x1000	Odra Upper and Middle Odra Lower Odra tributaries	153 116 37 18	1 13 1 7	738 738 314 236	125 167 45 90	78 140 24 64	113 149 24 90
Sr/Ca x1000	Odra Upper and Middle Odra Lower Odra tributaries	153 116 37 18	3 3 1 3	32 32 21 24	11 13 6 11	10 12 5 9	11 12 5 10
Ba/Mg x1000	Odra Upper and Middle Odra Lower Odra tributaries	153 116 37 18	9 53 9 40	974 974 601 630	294 357 172 193	239 320 135 161	296 349 134 151
Sr/Mg x1000	Odra Upper and Middle Odra Lower Odra tributaries	153 116 37 18	1 3 1 3	32 32 17 24	11 13 6 11	9 12 5 9	11 12 5 10

Statistical parameters of quantitative relations between Ba, Sr, Ca and Mg in sediments of the Odra River

Strontium in the Odra water was detected in concentrations from 267 to 801 ppb, and with geometric mean of 478 ppb (Table 4). High strontium concentrations have been traced in the Upper and Middle Odra while it is significantly smaller in the lower course of the river, downstream from the confluence with the Warta (Fig. 4). Concentration of strontium in relation to calcium is twice as high as most in inland water bodies (3 x 10^{-3}); difference in relation to magnesium is insignificant.

Concentration of strontium in waters of the Odra tributaries is equal to 103-1888 ppb. Considerably greater Sr concentrations were found in waters of the Łęgoń (1652 ppb), Bierawka (1888 ppb) and Kłodnica (1258 ppb) Rivers, and the Gliwice Canal (1558 ppb).

RECAPITULATION

In the Odra drainage basin a disposal of excessively saline mine waters from mines and mineral raw materials dressing and processing plants, especially from the Upper Silesian hard

Table 4

Element	River	Number of samples	Minimum content	Maximum content	Arithmetic mean	Geometric mean	Median
	Odra	153	39	188	83	80	81
Ba [ppm]	Lower Odra	37	. 65 . 39	93	60	92 59	90 58
2007 11	tributaries	18	13	150	82	75	77
	Odra	153	267	801	495	478	488
Sr	Upper and Middle Odra	116	272	801	564	555	567
[ppm]	Lower Odra	37	267	422	353	351	354
	tributaries	18	103	1888	694	505	401
	Odra	153	53.0	96.7	72.0	72.0	73.0
Ca	Upper and Middle Odra	116	53.0	96.7	71.2	70.9	71.4
[%]	Lower Odra	37	65.8	83.4	74.1	74.0	75.3
	tributaries	18	21.6	138.4	84.0	74.6	83.1
	Odra	153	9.8	22.0	15.3	15.1	15.8
Mg	Upper and Middle Odra	116	11.4	22.0	16.9	16.8	16.8
[%]	Lower Odra	37	9.8	13.9	12.1	12.1	12.2
	tributaries	18	4.1	74.9	24.1	17.9	17.8

Statistical parameters of Ba, Sr, Ca and Mg in the Odra waters

Table 5

Content of Ba, Sr, Ca and Mg in the waters of the Odra tributaries

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River	Ba [ppb]	Sr [ppb]	Ca [ppm]	Mg [ppm]
Olza	121	831	69.0	16.6
Łęgoń I	75	1652	116.2	40.6
Plęśnica	79	339	67.6	14.6
Łęgoń II	65	290	53.5	9.3
Ruda	124	787	69.0	19.1
Pogonica	73	103	21.6	4.1
BN	71	205	30.1	6.2
Bierawka	89	1888	103.5	74.9
BN	65	226	46.3	8.4
BN	13	301	53.3	12.2
Kłodnica	55	1258	123.0	51.6
Gliwice Canal	53	1558	130.3	56.8
Łącka Woda	113	408	110.7	13.1
BN	102	1158	132.4	28.5
BN	150	394	138.4	26.8
Czarnka	61	510	103.0	18.9
Mała Panew	92	314	47.2	8.5

BN - rivers unnamed

coal mines, has an important impact on geochemistry of barium and strontium in waters and sediments of the Odra River, particularly in its upper and middle courses.

Concentration of barium in alluvia of the Upper and Middle Odra are tens times as great as its geochemical background in stream sediments in Poland. Sediments in the Lower Odra (downstream from the confluence with the Warta) contain barium near its geochemical background. Influence of saline water disposal on occurrence of strontium in the Odra sediments is markedly smaller. However, concentrations of strontium in alluvia of the Upper and Middle Odra are much greater than in the Lower Odra. Alluvia of many tributaries from the Upper Silesia contain high concentration of barium and strontium. Particularly high concentrations of these two elements have been found in sediments of the Olza River.

The waters of Odra are characterized by distinctly higher concentrations of barium and strontium. This particularly deals with the Upper Odra, being supplied by tributaries that are carrying formation waters from the hard coal mines. A discharge of excessively saline waters affects more a concentration of strontium than of barium. Increased strontium concentration has been detected in waters of the tributaries such as the Łęgoń, Bierawka and Kłodnica Rivers as well as the Gliwice Canal. Increased content of barium appears in waters of the Olza, Ruda and Łącka Woda Rivers, and some smaller unnamed streams.

A considerable increase in concentrations of barium and strontium in aqueous sediments (in relation to calcium) is the effect of a disposal of saline waters from mines; this particularly deals with barium. As concerns waters, a distinct increase in strontium in relation to calcium was observed.

Translated by Zdzisław Siwek

Table 6

Ratio	River	Number of samples	Minimum value	Maximum value	Arithmetic mean	Geometric mean	Median
Ba/Ca x1000	Odra Upper and Middle Odra Lower Odra tributaries	153 116 37 18	0.5 0.7 0.5 0.2	2.8 2.8 1.4 3.4	1.2 1.3 0.8 1.2	1.1 1.3 0.8 1.0	1.1 1.2 0.8 1.1
Sr/Ca x1000	Odra Upper and Middle Odra Lower Odra tributaries	153 116 37 18	3.3 4.5 3.3 2.8	10.6 10.6 6.0 18.2	6.9 7.9 4.8 7.8	6.7 7.8 4.7 6.8	6.8 8.0 4.6 6.2
Ba/Mg x1000	Odra Upper and Middle Odra Lower Odra tributaries	153 116 37 18	3.3 3.3 4.0 0.9	12.6 12.6 7.2 17.8	5.4 5.7 4.9 5.8	5.3 5.5 4.9 4.2	5.1 5.2 4.8 5.5
Sr/Mg x1000	Odra Upper and Middle Odra Lower Odra tributaries	153 116 37 18	21.0 21.1 27.2 11.7	43.6 43.7 30.7 50.1	31.9 33.2 29.0 29.7	31.7 33.0 29.0 28.1	30.8 33.1 28.9 27.2

Statistical parameters of quantitative relations between Ba, Sr, Ca and Mg in the Odra waters

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WPŁYW WÓD KOPALNIANYCH NA STĘŻENIE BARU I STRONTU W WODACH I ALUWIACH ODRY

Streszczenie

Zlewnia Odry jest odbiornikiem zasolonych wód odprowadzanych z górnośląskich kopalni węgla kamiennego oraz legnicko-głogowskich kopalni niedzi. Ocenia się, że ładunek zasolenia wód Odry w 72% pochodzi z zakładów przemysłu węgla kamiennego (ok. 50 mln m³/a wód zawierających 450 tys. t soli), a w 12% — z zakładów przemysłu miedziowego (ok. 28 mln m³/a wód zawierających 380 tys. t soli). Wody, oprócz wielkiej ilości jonów chlorkowych i siarczanowych oraz sodu, wapnia i magnezu, wnoszą do Odry także m.in. bar i stront. Występowanie baru, strontu, wapnia i magnezu zbadano w wodach i osadach aluwialnych pobranych z Odry i tych jej dopływów, które mają obszar źródliskowy na Górnym Śląsku.

W aluwiach Odry zawartość baru dochodzi do 2435 ppm, przy czym w aluwiach górnej i środkowej Odry kilkadziesiąt razy przekracza tło geochemiczne tego pierwiastka (tab. 1). W osadach deponowanych w dolnym odcinku rzeki, poniżej ujścia Warty, stężenie baru jest zbliżone do tła geochemicznego (fig. 1). Zawartość baru w aluwiach dopływów dochodzi do 1700 ppm; najwyższą odnotowano w osadach Olzy (tab. 2).

Wpływ zasolonych wód na stężenie strontu w osadach Odry jest znacznie mniejszy niż baru, niemniej jednak zawartość tego pierwiastka w aluwiach górnej i środkowej Odry jest znacznie wyższa niż w osadach Odry dolnej (fig. 2). W osadach dopływów stront obecny był w podobnych stężeniach; najwyższą jego zawartość stwierdzono w osadach Olzy (tab. 2).

Konsekwencją odprowadzania zasolonych wód z kopalni do zlewni Odry jest znaczny wzrost w osadach względnej zawartości strontu, a zwłaszcza baru, w stosunku do wapnia (tab. 3). W osadach górnej i środkowej Odry stosunek ilościowy Ba/Ca jest dwudziestokrotnie, a w osadach dolnej Odry trzykrotnie wyższy w porównaniu do najczęściej spotykanego w osadach wodnych. W osadach górnej i środkowej Odry stosunek Sr/Ca jest dwukrotnie, a w osadach wielu dopływów trzy-pięciokrotnie wyższy (Olza, Łęgoń I, Ruda, Bierawka) w porównaniu do jego wartości w osadach rzecznych Polski.

Wody Odry charakteryzują się wyraźnie podwyższonymi zawartościami baru i strontu, zwłaszcza w górnym biegu, gdzie uchodzą dopływy, do których zrzucane są wody dołowe z kopalni węgla kamiennego (tab. 4 i 5). Zawartość baru w wodach Odry wynosi od 39 do 188 ppb, a w wodach dopływów od 13 do 150 ppb. Zawartości baru przekraczające 100 ppb występują w Olzie, Rudzie, Łąckiej Wodzie oraz w kilku niewielkich ciekach bez nazwy. Odprowadzane do rzeki nadmiernie zasolone wody wpływają bardziej na wzrost stężenia strontu niż baru. W wodach dopływów takich jak: Łęgoń, Bierawka, Kłodnica oraz Kanał Gliwicki stwierdzono znacznie podwyższone zawartości strontu, natomiast w wodach Olzy, Rudy, Łąckiej Wody oraz kilku niewielkich cieków bez nazwy --- podwyższone zawartości baru. Zawartość strontu w wodach górnego i środkowego odcinka Odry wynosi od 267 do 801 ppb, podczas gdy w dolnym odcinku, poniżej ujścia Warty, jest wyraźnie niższa (tab. 4, fig. 4). Zawartość tego pierwiastka w wodach dopływów waha się od 103 do 1888 ppb. Znacznie podwyższone zawartości strontu stwierdzono w wodach Łęgoni, Bierawki, Kłodnicy oraz Kanału Gliwickiego. W wodach zaobserwowano też wyraźny wzrost zawartości strontu w stosunku do wapnia (tab. 6).