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Forms of the Occurence of Elements-Toxicants in the Waste of Baritopolymetallic Ores and Natural Waters (Salair City, Kemerovo Region)

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Abstract

The state of surface waters, which are polluted with the waste of the lead-zinc enriching factory in Salair city (Kemerovo Region), is described. The total salt composition, total content of elements and their distribution in surface water downstream the river, in suspension and bottom sediments, and also the amount and fractions of mobile forms are studied. It is noted that Zn, Cd migrate in water generally in the truly dissolved form, Ba, Fe, Pb in the sorbed one, Cu, As are distributed approximately equally between these forms. It is shown that the elements are accumulated and fixed in bottom sediments, but they can become a cause of secondary pollution with the acidification of the medium. For the given region, the metals Ba, Zn, Cu, Cd are the most dangerous ones in the ecological aspect.

INTRODUCTION

The main feature of the modern stage of biosphere evolution is a permanent increase in the role of anthropogenic factor in the formation of migratory fluxes of elements. Until 1960 the majority of the mining industry waste was stored directly in the river channels. There are many such tailing dumps in Russia and abroad: Coeur d'Alene (USA), El Salado (Chile), the Illinois river (USA), stream flow of Montana State (USA), Restronget-Creek (Great Britain), Mokry Berikul' (Russia), Talmovskiye Peski (Russia), *etc*. The beginning of active study of metals' and other toxic compounds' migration is referred to the end of 70ies of the previous century [1, 2]. The gravity of arisen problem and the first obtained results are reflected in the generalized monograph of German researchers [3], where hydrogeochemical and biochemical aspects of interaction of sulphide waste with the water medium components are considered. Due to intensive development of analytical techniques, a huge contribution to the studies of the processes of toxic element distribution is made by the works on direct determination of different forms of the element occurence and migration in solutions and in solid phases [4, 5]. Many works consider migration, redistribution, mobility rows of heavy metals in fresh surface water [6–8, *etc*.]. The study of bottom sediments in the regions with man-caused pollution regions is directed to revealing migration regularities of toxic components, their sedimentation in natural reservoirs and rivers [9–12, *etc*.]. The effect of tailing dumps on the environment is studied in different aspects, but there are still a lot of obscure problems, *i.e.*, about migration forms of heavy metals, and especially about mobile forms (the most dangerous ones for a man) in man-caused and natural fluxes, and also about the destiny of elements buried in bottom river sediments and their danger for biota, hence, for trophic chains.

The objects of our study are the M. Talmovaya and Talmovaya rivers (Salair city, Kemerovo Region). The waste of the lead-zinc enriching factory was stored in the channel of the M. Talmovaya as a narrow band with the length of 7 km during the period from 1932 to 1946.

The goal of the study is the determination of occurence forms of the elements (Zn, Cd, Pb, Cu, Fe, As, Ba) in solutions of different origin, in the matter of stored waste and in river bottom sediments, and estimation of their ecological danger. The selection of the elements under investigation is caused by mineral composition of the Salair baritopolymetallic ores in which the sulphide component is represented by pyrite (FeS_2), sphalerite (ZnS), galenite (PbS), chalcopyrite (CuFeS), gray ores $(Cu,Ag)_{10}(Fe,Zn)_2(As,Sb)_6S_{13}$. As and Cd are present in sulphides as extrinsic elements in the noticeable amount. Among the tasks of the study there was the determination of the element content (Zn, Cd, Pb, Cu, Fe, As, Ba) and their occurence forms in surface water, suspension and bottom sediments of the M. Talmovaya, B. Talmovaya, Talmovaya rivers, and estimation of the elements' ecological danger for the region.

INVESTIGATION TECHNIQUES

Field testing of the river network was carried out in summer, 2001. Water and bottom sediments were sampled in the same sites (Fig. 1). A testing scheme was made in such a way that actual data characterized the river from the background site (essentially upper the stream, without the influence of any man-caused factors) till the sites with the maximal effect of the tailing dump and then – after its merge with the relatively pure B. Talmovaya river.

Water samples were taken into chemically pure plastic vessels with the preliminary three-multiple rinsing in the sampling site. At the place, pH was measured with the ion-selective electrode by means of the "Anion-210" device graduation with standard buffer solutions. The following scheme was used for experimental determination of the mobile forms of the elements in surface water: water sample was separated into suspended (includes sorbed forms) and dissolved (truly dissolved forms) parts by filtration through a 0.45 μm membrane filter. The fist part of the filtrate intended for the determination of the element content was preserved by ultra pure concentrated HNO_3. The second one was kept for the analysis of the basic ion composition. The filters were dried up at room temperature. Bottom sediments were sampled into polyethylene bags, dried up under field conditions, then kept carefully packed till the laboratory study.

All the laboratory studies were carried out in the Analytical Centre of the United Institute of Geology, Geophysics and Mineralogy, SB RAS (Novosibirsk). Complete decomposition of solid samples was made according to the standard procedure. The elements were determined in the obtained solutions of the samples by means of atomic absorption spectroscopy with flame and electrothermal atomization. Mobile forms of the elements from the solid samples of bottom sediments were determined employing double-step leaching: 1. Water leaching was carried out according to the standard procedure [13] to determine the content of water-soluble forms Me [W]. For the realization of this experiment, a weighed portion of 8 g was placed into a flask, and 40 ml of twice-distilled water was added. Then (in every 15 min) the flask contents were stirred by circular motions for 2 h and filtered through a White tape paper filter. 2. Weakly acidic leaching was carried out according to the standard procedure [14] to determine the content of exchange forms Me [S] using AAB (ammonium acetate buffer pH 4.5–4.7). The 4 g sample portion was placed into a flask, with the addition of 40 ml of AAB. The rest was made as in water leaching.

RESULTS AND DISCUSSION

The content of Zn, Cd and Pb in the solid matter of Talmovskiye Peski (Table 1) exceeds the background values by two orders of mag-

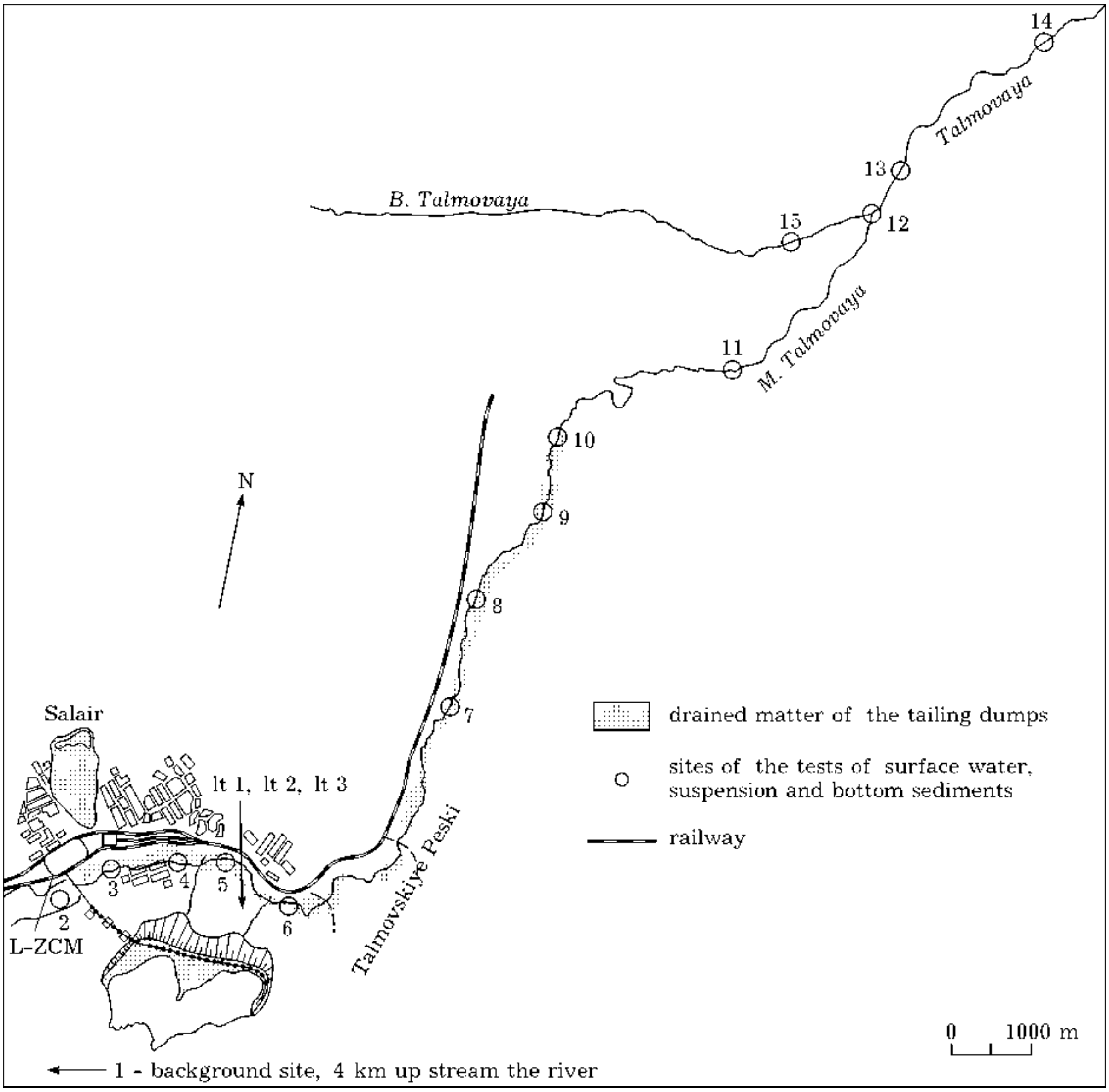

Fig. 1. Chart-scheme of the tests of the Talmovskiye Peski tailing dump and the rivers.

nitude; Cu, As by a factor of 35 and 60, respectively. At the same time, the fractions of water-soluble forms of zinc, copper and cadmium on average do not exceed several per cent of their total content, achieving 24, 35 and 56 %, respectively (Table 2). Lead is rather inert under such conditions; the fraction of its water-soluble forms does not exceed 0.9 %.

High total content of the elements in combination with the large fraction of easily mobile forms result in their active washing out from the waste matter, which results in the formation of acidic mineralized solutions in landlocked pools along the river banks (see Fig. 1 and Table 3).

Waters of the M. Talmovayay and Talmovaya rivers, the most affected by the tailing dump, refer to the sulphate-carbonaceous calcium-magnesium type on the basic ion composition, in difference with the carbonate-calcium magnesium type of water of the B. Talmovaya (Kurlov's formula [15]):

River	Formula
M. Talmovaya	$M_{0.5}\dfrac{HCO_3^- 46SO_4^{2-} 44Cl^- 7.0NO_3^- 3.0}{Ca^{2+} 76Mg^{2+} 12Na^+ 10K^+ 2.0}pH\,7.3$

TABLE 1

Mass concentrations of the elements in solid matter of the Talmovskiye Peski tailing dump, % mass

Value	Zn	Cd	Pb	Cu	As	Fe	Ba
Mean	1.07	0.0050	0.21	0.081	0.044	3.5	14
Minimal	0.058	0.00013	0.004	0.004	0.0015	1.9	1.4
Maximal	2.68	0.024	0.79	0.34	0.097	7.6	22
Standard deviation	0.55	0.0039	0.18	0.06	0.029	1.4	5.1
Exceeding above background	180	100	110	35	60	1.4	–
n*	76	76	76	76	49	20	20
Background	0.006	0.00005	0.0019	0.0022	0.00075	2.5	Not found

Note. Crossed out section means the absence of data.
*Here and in Table 2, 6: n is the number of samples.

TABLE 2

Mass concentrations of water-soluble forms of the metals in solid matter of the Talmovskiye Peski tailing dump, % mass

Value	Zn	Cd	Pb	Cu
Mean (n = 43)	1.5	4.1	0.06	3.3
Minimal	0.004	0.014	0.0009	0.005
Maximal	24	56	0.9	35
Standard deviation	4.4	11	0.1	9.1

TABLE 3

Content of the elements in stagnant water of the M. Talmovaya river, μg/l

Sample	pH	Zn	Cd	Pb	Cu	Fe	As	Ba
LT1	5.6	$3.9 \cdot 10^5$	1100	230	850	$9.3 \cdot 10^4$	<0.3	220
LT2	4.8	$2.0 \cdot 10^5$	800	1400	6400	$1.8 \cdot 10^5$	4.1	240
LT3	4.5	$5.8 \cdot 10^5$	1900	1300	8100	$1.8 \cdot 10^4$	3.5	160

Talmovaya $M_{0.32}\frac{HCO_3^- 58SO_4^{2-} 36Cl^- 6.0}{Ca^{2+} 68Mg^{2+} 10Na^+ 11K^+ 1.0}$ pH 7.4

B. Talmovaya $M_{0.26}\frac{HCO_3^- 90SO_4^{2-} 6.0Cl^- 4.0}{Ca^{2+} 80Mg^{2+} 10Na^+ 8.0K^+ 2.0}$ pH 8.2

The concentration of the elements in the M. Talmovaya river exceeds the background values for all the elements (Table 4): Zn – 59–130-fold, Cd – 5–24-fold, Pb – 23–190-fold, Cu – 13–30-fold, Fe – 5.5–33-fold, As – 1.6–2.5-fold, Ba – 3–13-fold; in the Talmovaya river: Zn – 24–58-fold, Cd – 1.8–8.4-fold, Pb – 30–75-fold, Cu – 7.0–14-fold, Fe – 17–30-fold, As – 2.3-fold, Ba – 4.8–6.2-fold; in the B. Talmovaya river: Zn – 5.0-fold, Pb – 7.6-fold, Cu – 5.9-fold, Fe – 3.6-fold, As – 1.5-fold, Ba – 4-fold. Water of the B. Talmovaya (see Table 4) is rather pure in comparison with water of the M. Talmovaya where the content of the elements along Talmovskiye Peski is rather high but decrease downstream, especially after the merge with the more pure B. Talmovaya. This is more likely linked with the dilution of surface water.

Mean ratios of the values of the truly dissolved form (P) to the one sorbed on suspension (C): 2 – for Zn and Cd, 0.07 – for Pb, 0.5 – for Cu, 0.08 – for Ba and Fe – are the evidence of Zn and Cd presence in water of the rivers mainly in the actually dissolved form, Ba, Fe, Pb – in the sorbed one, Cu and As – approximately equally in both forms. This trend is confirmed by the results of thermodynamic modeling (Table 5), according to which the major part of Zn (60 %) and Cd (82 %) forms

TABLE 4

Content of the elements in surface water of the rivers, μg/l

Sample number	Zn	Cd	Pb	Cu	Fe	As	Ba
1	15	0.19	0.8	2.7	20	5.6	100
2	880	1	18	34	110	5	300
3	1600	3.7	60	70	400	9.5	800
4	1500	3.6	75	47	660	4.7	1300
5	1800	4.6	65	60	400	9.1	660
6	1900	5	70	59	280	10	1000
7	1800	3.5	110	65	280	9.1	500
8	1900	4.3	150	80	400	12	580
9	1700	3.6	130	60	400	14	400
10	1300	2.9	100	35	340	7.5	970
11	1500	2.9	80	51	280	11	490
12	1300	3	90	48	280	7.7	400
13	880	1.6	60	37	600	12	620
14	360	0.36	24	19	340	13	480
15	76	0.16	6.1	16	72	8.4	400

aqua ions in solution, Cu (60 %) and Pb (95 %) makes up carbonate and hydrocarbonate complexes, Fe – hydroxide complexes, As – arsenates and hydroarsenates.

The results obtained allow constructing a mobility row of the elements under given conditions: Ba, Fe < Pb < Cu < As < Zn, Cd.

High mobility of zinc and cadmium causes their migration with water flows at long distances whereas barium, iron and lead are sorbed on suspension or go to bottom sediments as their individual compounds.

Bottom sediments mainly consist of silicate minerals (57 %). Along with aluminosilicates (clay particles, quartz, micas, *etc.*) the major part of bottom sediments is made up of the organic matter (12 %). High barium content in them is the evidence of great man-caused effect, since there is a lot of barite (15 %) in Talmovskiye Peski. Bottom sediments can well sorb heavy metals and As; this is confirmed by the high content of the elements in them (Table 6). The element contents in river bottom sediments (see table 6) exceed the background values: Zn – 20–110-fold, Cd – 25–180, Pb – 20–90, Cu – 5–15, As – 1.6–5.5, Ba – 3.5–14-fold. Downstream the M. Talmovaya the element contents increase along the whole studied interval till the merge with the B. Talmovaya, which is the evidence of mechanical drift of minerals and gradual sedimentation of suspension with the sorbed forms of the elements.

Under the conditions characteristic of the given river, the elements are strongly bound by the waste matter and practically do not invoke secondary pollution of the river water.

TABLE 5

Mass concentrations of the metal chemical forms in surface water, % mass

Metal form	Zn	Cd	Pb	Cu	Ba
Me^{2+}	60	82	3.0	5.5	80
$MeCO^0_{3aq}$, $MeHCO^+_3$	33	6.0	95	60	2
$MeSO^0_{4aq}$	6.0	10	1.0	0.5	18
$Me(OH)^0_2$, $MeOH^+$	1.0	0	1.0	34	0
$MeCl^+$	0	1.0	0	0	0

TABLE 6

Mass concentrations of the metals and their water-soluble [W] and exchange [S] forms in bottom sediments of the M. Talmovaya and Talmovaya rivers, % mass

Value	Zn			Cd			Pb			Cu			Fe			Ba		
	Total	[W]	[S]	Total	[W]	[S]	Total	[W]	[S]	Total	[W]	[S]	Total	[W]	[S]	Total	[W]	[S]
Mean (n = 11)	0.73	0.085	13	0.0036	0.08	25	0.12	0.1	7.7	0.029	0.16	18	1.9	0.12	3	7.0	0.07	0.05
Minimal	0.3	0.015	0.12	0.0012	0.016	0.55	0.069	0.01	0.1	0.014	0.12	0.28	1.3	0.009	0.35	3.5	0.0025	0.01
Maximal	1.9	0.22	26	0.0087	0.24	67	0.31	0.17	11	0.057	0.26	44	3.1	0.65	6.1	14	0.011	0.09
Standard deviation	0.45	0.078	9.3	0.0022	0.083	23	0.072	0.065	3.6	0.013	0.052	14	0.56	0.24	2.1	3.6	0.0034	0.025
Background	0.017	–	–	0.00005	–	–	0.0036	–	–	0.0038	–	–	2.5	–	–	1.0	–	–

Mass concentrations Me[W] of all elements are close by values, their maximal level makes up 0.65 % except barium which is inert under the given conditions. The Me[S] fractions are the highest for Cd which occurs by more than a half in weakly sorbed forms. The fraction of weakly sorbed forms of copper, zinc and lead is also significant – 18, 13, 7.7 %, respectively. Hence, under slight changes in the conditions, *i.e.*, with acidifying, metals (especially Cd, Zn, Cu, Pb) intensively start to transfer into solution, some times causing shock pollution of reservoirs.

Since local population fishes in the M.Talmovaya and uses its water for economic purposes, in order to estimate the ecological danger, it is necessary to compare concentrations of the metals in the river with maximum permissible concentration (MPC) for potable water and fishery reservoirs (pH 6–9), μg/l:

Zn	Cd	Pb	Cu	As	Ba	Ref.
$5\ 10^3$	1.0	30	$1\ 10^3$	50	100	[16]
10	5.0	100	1.0	50	200	[17]

An excess over the MPC for potable water was revealed for Cd 2.9 – 5-fold, Pb – 2–5-fold, Ba – 3–13-fold. MPC for the water of fishery reservoirs is exceeded for Zn 88–190-fold, Pb – 1.5, Cu – 34 – 80, Ba – 1.5 – 6.5-fold. In water-pipe water of Salair, MPC level for potable water is not exceeded for Zn, Cd, Pb, Cu, Fe, As, but it is exceeded for Ba – 2–3-fold. This is more likely linked with water chlorination which requires additional studies.

CONCLUSIONS

1. Man-caused load on the M. Talmovaya and Talmovaya rivers is expressed in a several orders of magnitude increase in the concentration of the elements in water over the background contents. Taking into account the use of water by local population, one can speak about high danger of metals for the region.

2. A mobility row of the elements in surface water is established: Ba, Fe < Pb < Cu < As < Zn, Cd.

3. Bottom sediments, being a geochemical barrier, accumulate toxic elements. Heavy metals, especially Cd, present in bottom sediments, are the real danger for bottom inhabitants;

they can become a cause of secondary pollution in the case of acidification of the medium.

4. Ba, Zn, Cu, Cd and Pb are the most dangerous metals for the region because their concentration in the river exceeds the MPC for potable water and fishery reservoirs. Ba is especially dangerous because its content in water-pipe water exceeds the MPC for potable water 2–3 times.

5. Surface water of the M. Talmovaya cannot be used for economic purposes, especially as potable water. It can be recommended to carry out works for clearing the river channel, *i.e.*, to strew the bank slopes and the river with ground limestone which is spread in this area, especially as these actions do not require considerable expenses.

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