

# The Combination of Geoelectrical Measurements and Hydro-Geochemical Studies for the Evaluation of Groundwater Pollution in Mining Tailings Areas

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**Abstract** Sulfide-bearing mill wastes of the Salair Ore Processing Plant situated in the Kemerovo region (Russia) were investigated in the time period 1999–2011. Multipurpose studies of the Talmovskie mining tailings allowed the determination of the composition of the wastes, the acid mine drainages, and the affected groundwater. Geophysical sounding techniques (frequency sounding and electrical tomography) were used to trace the geoelectric zoning of the wastes, expressed as a consistent change of the electrical resistivity specific electrical resistance (SER) from zone to zone. Layers with low resistivity indicate areas with pore spaces filled by highly mineralized solutions. These layers extend to depths of 4–5 m, indicating the penetration of toxicants into the groundwater horizon. The pollution of groundwater was confirmed by chemical analysis, according to which the concentrations of Zn, Pb, and Cd in water samples from the wells are two to three orders of magnitude higher than the maximum permissible concentration (MPC). The authors provide an attempt to identify the correlation and quantitative relationships between SER and the total amount of various metal species present in the wastes and water extracts. The proposed approach permitted to estimate the amount of accumulated tailings, in order to predict changes in the total concentrations of Mn, Al, Fe, Cu, Zn, Cd, and Pb in waste and water extracts to a depth of 30 m.

**Keywords** Acid mine drainage, Geoelectrical zoning, Groundwater pollution, Metals, Sulfide-bearing wastes

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## Abbreviations

EFS	Electromagnetic frequency sounding
ET	Electrical tomography
ICP-MS	Mass spectrometry with inductively coupled plasma
MPC	Maximum permissible concentration
SB RAS	Siberian branch of Russian academy of sciences
SEM	Scanning electron microscope
SER	Specific electrical resistance
SER <sub>fs</sub>	Specific electric resistivity of the wastes according to frequency sounding
SER <sub>p</sub>	Specific electrical resistance measured by direct conductometry in the pastes
SOPP	Salair ore processing plant
XRD	X-ray diffraction analysis
XRF SR	X-ray fluorescence with synchrotron radiation

## 1 Introduction

Mining activity entails the accumulation of sulfide-bearing mill wastes with high concentrations of ore and impurity elements. Hundreds of thousands of tons of waste and mined ores with Fe, Cu, Zn, Cd, and impurities (As, Sb) lower than the industry level have been dumped in tailings and discharged spontaneously in river beds for decades. Oxidation of the sulfide minerals results in the formation of acidic solutions with high concentrations of  $\text{SO}_4^{2-}$ , Cu, Zn, Fe, As, Sb, and other soluble species. These elements migrate out of tailing dumps with drainage streams, are discharged into rivers, seep into groundwater, and are carried for tens of kilometers by wind [1–5]. Examples of such aggressive waste deposits and clinkers are the clinkers of the Belovo zinc processing plant, the cyanidation cakes of the Berikul and Komsomolsk ore-bearing plants (Kemerovo region), and the tailings of the Karabash copper smelting plant [6, 7]. As a consequence, zones of geochemical anomalies have formed in the vicinity of stored wastes. These areas are characterized by extremely high concentrations of Fe, Cu, Zn, Cd, Pb, As, and Sb

in surface and groundwaters, soils, snow and air compared with the background and with the MPC levels [8–12].

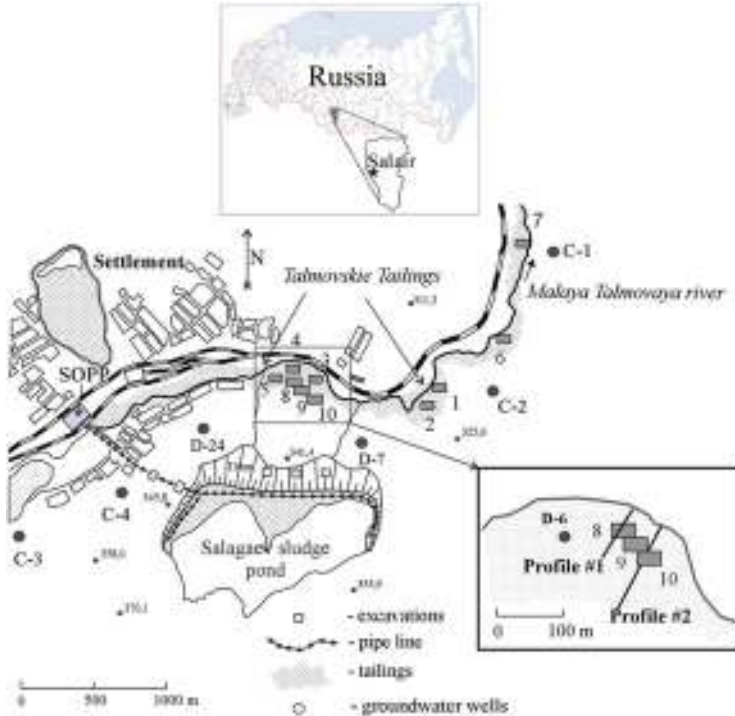
The main monitoring methods of mine tailings and polluted groundwaters consist in geochemical analyses, which include a series of activities, i.e. sample preparation, field and laboratory measurements of physical parameters, element and mineral composition, thermodynamic modeling for the species calculation, and interpretation of the actual data. Traditional geochemical approaches require significant investments of time and money and often do not allow the selection of optimum sampling sites. Vertical electrical sounding allows outlining the mine tailing dump location, detecting the depth of the waste and the penetration area of highly mineralized fluids into groundwater, calculating the resources of valuable components in technogenic deposits and, with the appropriate technology, assessing the feasibility of re-extraction [13–15]. It is also true that site-specific chemical characterisation is in any case necessary in order to calibrate the electromagnetic sounding results. In this context, geoelectric measurements are primarily used to address the choice of sampling points. So, the combination of the geochemical and geophysical techniques can be seen in terms of optimization of the direct chemical measurements.

The specific features of the studied wastes are the multicomponent composition and heterogeneity of the tailings. Because the geoelectrical properties of wastes are determined by their mineral composition, moisture content, porosity, particle size, and pore water mineralization [16], the investigation of mine tailings using geophysical methods is a complex task.

The aim of this work is to estimate the groundwater pollution caused by mining activity using a complex geochemical and geophysical methodology, tested on the wastes of the Salair Ore Processing Plant (SOPP, Kemerovo region, Russia). The authors used electric prospecting to define areas with the lowest resistivities ( $\rho$ ) at depths of 0–40 m. These conductive zones were sampled for the waste and pore water composition in a range of depths 0–3 m. Groundwaters within the vicinity of the tailings were also collected. The physical properties, resistivity, and chemical composition of the waste samples, the element concentrations and their species in the pore and groundwaters were measured. The constraint equations were calculated to define the relationships among the resistivity, particle size, humidity, and chemical (elemental) composition of the sampled solids and solutions. These equations allowed the estimation of groundwater pollution. On the base of complex geochemical and geophysical investigations, we determined the penetration of highly mineralized solutions into groundwater.

## 2 Study Object

The Talmovskie tailings impoundment is located in the town of Salair, in the Kemerovo region of southwestern Siberia (Fig. 1). The Salair mine has been working since the 1930s, and gold- and silver-bearing barite-polymetallic sulfide



**Fig. 1** Schematic map of the study area with the geophysical profiles

ore bodies have been exploited. The sulfides are located within the subvolcanic series of dacite porphyries among Lower Cambrian limestones. The geological structure, mineralogy, and geochemical characteristics have been studied previously by numerous Siberian geologists. The Talmovskie tailings dump is the first tailing dump of the Salair Ore Processing Plant. Ore recovery was first performed at a gold-extracting plant, where quartz-barite ores from open pits in the oxidation zone were processed. Sulfide-bearing mill wastes were stored in the dammed stream of the Small Talmovaya River in 1932–1942 as a belt with a width of 30 m and a length of 8 km (Fig. 1). The thickness of the tailings does not exceed 3 m. Approximately 1 million tons of wastes have been accumulated in the channel of the Malaya Talmovaya river in close proximity to the town of Salair during the last 10 years. The stored waste is bulked by soil on the surface. The storage is dried during the summer and covered by water during floods. The M. Talmovaya River flows on the surface of the tailings impoundment. The described conditions support the intensive transformation of the sulfide-bearing wastes due to oxidation by atmospheric and water oxygen, and there is intensive removal of the dissolved metals in the river network and groundwaters [7]. Pyrite is the most common (75–90% of the total sulfide) of the sulfide minerals in the wastes. Less common are sphalerite (8–19%), galena (2–14%), and single grains of chalcopyrite [6].

### 3 Methodology

The methods include sampling, analyses of the bulk chemicals and the elemental and mineral composition, determination of the petro-physical properties, geophysical sounding of the wastes, statistical methods of data processing, calculations of the numerical relationships between resistivity and chemical composition, solution of the inverse problem (i.e., estimation of the chemical composition of the waste down to a depth of 40 m by combining the geophysical survey with geochemical measurements), and prediction of the groundwater pollution.

All works were performed in the following order:

- Electrical tomography and electromagnetic frequency sounding [16] for the construction of the storage sections on the two co-directional profiles (Fig. 1) and for revealing the geoelectric zoning in the subsurface environment. The length of profile no. 1 for electromagnetic frequency sounding is 45 m and the maximum probing depth is 8 m; the length of profile no. 2 for electro-tomography is 150 m, the distance between the electrodes is 5 m. The electro-tomographic method (profile no. 2) allowed us to reveal the geoelectric zoning in the subsurface environment at a depth from 0 to 30 m. Electromagnetic frequency sounding (profile no. 1) was used to clarify the geoelectric structure of the wastes in the upper 8 m.
- Sampling of pits in areas with the lowest resistivities to a depth of 1.6 m. Detailed sampling of the area included the collection of surface and subsurface material and pore water within the tailings, which was conducted in 2004–2011. The samples were collected, and measurements were made, in order to reveal the geochemical behavior of the elements during storage and, in particular, to determine the relative mobility of the metals (Zn, Cu, Pb, Cd, and Fe) under storage conditions. The study location and sample sites are shown in Fig. 1. Tailings were excavated in order to reveal vertical sections of the waste and were sampled in detail. Excavations were made using a shovel to dig through the tailings, in order to get a detailed record of layering in the different parts of the impoundment. Each pit extended to the bottom of the tailings. Samples were collected from each distinctive layer that was visually consistent for a thickness of more than 10 cm. The collected samples were placed in polyethylene bags. The stratigraphy of the tailings was constructed from exposures in the pits and was used to study the vertical zoning.
- Preparation of the pastes and pore waters; pH, Eh, and conductivity measurements; and transportation to the laboratory.

The pastes were prepared by mixing the sampled wastes and distilled water (1:2 by volume). We used distilled water (pH 5.6) to simulate the interaction between atmospheric precipitation and sulfide wastes with the AMD formation. The pH and Eh values of the pastes allow us to predict the acid production potential of the wastes and correct the selection of sampling points for further chemical analysis.

Pore water was squeezed from the samples for only the moist silty layers at each site. These samples were subjected to a pressure of 100 Pa using a sampling press, and the released water was filtered through 0.45- $\mu\text{m}$  Millipore filters. A fraction of each water sample was immediately acidified in the laboratory to  $\text{pH} < 2$  with concentrated  $\text{HNO}_3$  acid to analyze the cation and trace element concentrations. The pH values were measured in the field using the “Anion 410B” instrument (Infraspac-Analyt Company). Solid samples were dried and later used for the water extraction tests in the laboratory and the elemental analyses.

- X-ray fluorescence with synchrotron radiation (XRF SR) was used to determine elemental composition (Si, Ti, Al, Fe, Mn, Ca, Mg, K, Na, Ba, Cu, Zn, Cd, Pb, As, Sb) at the VEPP-3 station at the Institute of Nuclear Physics SB RAS, Novosibirsk [17].
- Preparation of the aqueous extracts at a water:waste ratio of 8:1 (by mass). Measuring pH and Eh by potentiometry and conductivity by conductometry. Determination of the anion ( $\text{Cl}^-$ ,  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ ) concentrations using the titrimetric and turbidimetric methods and determination of the concentrations of the elements Ca, Mg, K, Na, Al, Mn, Fe, Cu, Zn, Cd, Ni, Co, Pb, As, and Sb by mass spectrometry with inductively coupled plasma (ICP-MS) in the water samples.
- The element and mineral compositions of the wastes were analyzed using a Jeol JSM-638OLA scanning electron microscope (SEM) and by X-ray diffraction analysis (XRD).
- Determination of the resistivity, particle size distribution, density, porosity, and moisture content in the solid samples.

The accuracy and precision of these methods were estimated to be 10–15% or better.

## 4 Results and Discussion

### 4.1 Mineral Composition of Wastes

#### 4.1.1 Initial Minerals

The mineralogy of the investigated samples from the Talmovskie tailings is determined by the Salair ore composition and secondary alteration of the initial sulfides. The sulfide content reaches 5–7%, and the primary mineral is pyrite. The sulfides of Pb, Zn, and Cu are represented by small monomineral grains of galena (2–14%), sphalerite (8–19%), and trace amounts of chalcopyrite, tennantite, and tetrahedrite. Secondary rims on the surfaces of the sulfide grains mask the characteristic features of sulfides and prevent a more accurate estimation of the amount of a mineral. The remainder of the mass includes debris from host rocks

of different compositions (quartzites, limestones, and quartz-sericite schists) and mineral grains (quartz, calcite, dolomite, barite, and muscovite).

#### 4.1.2 Secondary Minerals

Amorphous Fe-hydroxides cover grains of pyrite, sphalerite, and chalcopyrite in the form of incrustations, rims, and films. As a rule, the amount of hydroxide increases in micro-layers containing a high percentage of sulfides and a medium coarse-grained texture, which allows the penetration of oxygen.

Amorphous silica was recorded by X-ray methods in efflorescences on the surface of the tailings. Gypsum is the most abundant secondary mineral, and it often cements a tailing bulk mass. Two different morphological forms of gypsum are observed. The first form is well-crystallized grains of “dovetail” with a size up to 1 mm. The second form is fine-grained semi-transparent gray aggregates, which can be identified by the X-ray method. Jarosite forms thin, loose rims, and porous reddish aggregates on oxidized sulfide grains. Rozenite was discovered on the tailings’ surface as intergrowth with other secondary sulfates. Anglesite forms rims and incrustation. An investigation with the help of a scanning microscope shows phosphorous and chlorine in the composition of these rims; consequently, we can conclude the occurrence of pyromorphite, i.e. chlorophosphanet of lead  $Pb_5Cl(PO_4)_3$ . Sulfates of Zn form efflorescences on the tailing surface and on pit walls. The amount of secondary minerals gives evidence of an active process of oxidation and the alteration of the tailings.

## 4.2 Geochemistry of the Tailings

### 4.2.1 Bulk Chemical Composition of the Tailings

The statistical summary of the chemical composition of the tailing samples presented in Table 1 shows that the bulk composition varies over a wide range. Thereinafter the average (mean) value is symbolized by  $\mu$ , the standard deviation by  $s$ , and the number of analyses by  $n$ . The major component is silica ( $\mu = 53$  wt% of  $SiO_2$ ,  $s = 11\%$ ). The next most abundant elements are Ba ( $\mu = 21.22$  wt% of  $BaSO_4$ ,  $s = 10.3$ ) and Al ( $\mu = 10.63$  wt% of  $Al_2O_3$ ,  $s = 3.0$ ).

The concentrations of these components are consistent with the mineral composition of the barite-polymetallic ore bodies observed with the debris of the host rocks.

The contents of valuable components and their amounts are presented in Table 2 along with their concentrations in the ores, which were processed at the Salair plant until recent times. At the beginning of the deposit’s exploitation, the contents of nonferrous and precious metals in ores were several times higher than at present. Correspondingly, losses during the processing of ores were much

**Table 1** Bulk chemical composition of the tailings (wt% of dry matter) ( $n = 22$ )

	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	Ba	H <sub>2</sub> O
$\mu$	53.0	0.39	10.63	5.31	0.14	1.61	3.01	0.90	0.87	0.19	12.48	5.84
Min	27.35	0.19	4.59	2.50	0.035	0.71	0.79	dl	0.13	0.12	0.43	2.35
Max	66.78	0.95	15.66	11.04	0.25	2.76	6.79	2.63	1.88	0.32	18.35	10.88
$s$	10.53	0.27	3.0	2.12	0.06	0.65	1.84	0.71	0.57	0.05	6.09	2.34

**Table 2** Total concentration of metals in tailings

	Zn	Pb	Cu	Cd	Fe
$\mu$	1.05	3,100	870	45	3.6
Min	0.115	65	160	5	2.2
Max	2.4	7,990	3,420	240	7.6
$s$	0.51	2,290	620	34	1.6
Salair ore <sup>a</sup>					
Primary	2.30	3,200	800	10	3.2
Oxidized	0.32	4,300	670	6	3.8

Zn in wt%, other metals in ppm ( $n = 60$ )

<sup>a</sup>Archive data

higher in absolute magnitude than at present, resulting in considerable concentrations of useful components in the tailings, sometimes exceeding even their contents in the ores.

The differences in the metal concentrations throughout the tailing impoundments are not large (Table 2), but we detected a significant difference in the concentration range along vertical cross-sections. In the comparatively “young” part of the impoundment (cross-section nos. 7 and 1, Fig. 1), the max/min is 6–8 times (the highest range was measured for Cd); in the “oldest” parts (cross-section nos. 3 and 5, Fig. 1), the ratio reaches 180 (Table 3). This sharp increase of the ratio is an evidence of a more active metal redistribution in the old parts of the impoundments compared with the newer sections, which is found even after 70 years of age.

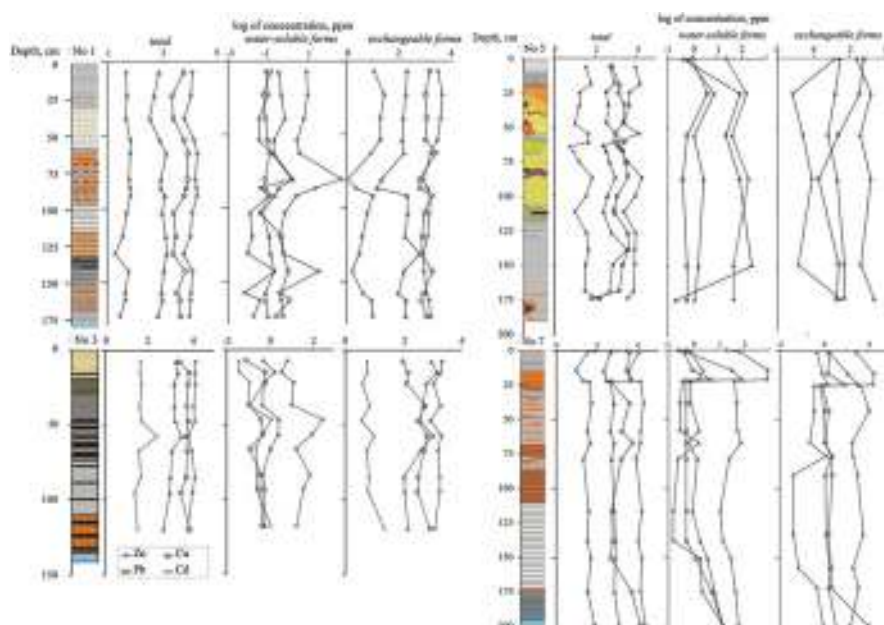
In the cross-section no. 7, which is located in the least altered (newest) part of the impoundment, the total metals are distributed quite uniformly. The distinctive feature of this particular cross-section structure is the presence of the concentrated layer SP-7/2 at a depth of 15–25 cm (Fig. 2). The layer consists of clay minerals and retains water migrated from the surface. As a result, the geochemical barrier described as “hardpan” [20] formed here. The hardpan is composed of secondary minerals and phases formed in the pore space and of cemented initial minerals. The water-soluble phases of the metals were precipitated on this layer, and the percentages of water-soluble Zn, Cu, and Cd are as high as 25% of their total concentrations (Table 4). In addition, clay minerals caused protonization. This process was identified during water extraction from samples of this layer (Fig. 2). After 15 min, the pH value of the extracted water decreased to 2.59, implying an acid media during the secondary mineral formation.

The second hardpan (less-pronounced) is located in cross-section no. 7 at a groundwater level of ~180–210 cm (layers SP-7/8a and 7/9). In this level,



**Table 3** Concentration of metals in particular cross-sections of the tailings

	Zn (%)	Pb (%)	Cu (ppm)	Cd (ppm)
Vertical section no. 7 ( <i>n</i> = 14)				
$\mu$	1.4	0.11	620	41
Min	0.36	0.016	220	9.4
Max	2.4	0.45	1,200	78
<i>s</i>	0.55	0.11	250	20
max/min	6.7	28	5.5	8.3
Vertical section no. 1 ( <i>n</i> = 15)				
$\mu$	1.1	0.46	900	51
Min	0.54	0.21	340	20
Max	1.7	0.79	1,300	69
<i>s</i>	0.35	0.20	300	15
max/min	3.1	3.7	3.8	3.4
Vertical section no. 3 ( <i>n</i> = 10)				
$\mu$	1.1	0.56	1,500	58
min	0.60	0.27	470	22
max	1.4	0.80	3,040	240
<i>s</i>	0.30	0.17	730	64
max/min	2.3	3.0	6.5	11
Vertical section no. 5 ( <i>n</i> = 18)				
$\mu$	1.2	0.20	930	43
min	0.058	0.065	42	1.3
max	1.96	0.41	3,400	240
<i>s</i>	0.52	0.12	730	30
max/min	34	64	81	180



**Fig. 2** Vertical sections showing layering patterns and total concentrations of water-soluble and exchangeable elements in the tailings

**Table 4** Percentage of water-soluble metals in layers of vertical sections

Sample	Depth (cm)	% of water-soluble species				pH
		Zn	Pb	Cu	Cd	
Vertical section no. 7						
SP-7/1	1	0.54	0.031	0.1	2.2	6.68
SP-7/2	15	24	0.092	15	24	2.86
SP-7/2a	22	15	0.32	27	8	2.80
SP-7/3	23	0.29	0.31	0.16	0.86	6.85
SP-7/4	39	0.25	0.038	0.11	0.52	6.35
SP-7/4a	60	0.39	0.089	0.35	0.85	6.39
SP-7/5	69	0.53	0.026	0.086	3.5	6.48
SP-7/5a	81	0.30	0.093	0.26	1.1	6.17
SP-7/6	120	0.069	0.28	0.12	0.40	6.18
SP-7/7	142	0.13	0.25	0.21	0.47	6.34
SP-7/8	155	0.19	0.75	0.45	3.6	6.15
SP-7/8a	180	0.32	0.3	0.88	5.8	5.77
SP-7/9	205	3.7	0.58	4.50	2.8	4.86

**Table 5** Percentage of water-soluble metals in layers of vertical sections

Sample	Depth (cm)	% of water-soluble species				pH
		Zn	Pb	Cu	Cd	
Vertical section no. 1						
SP-1/1	7	0.080	0.0024	0.049	0.17	8.07
SP-1/2	23	0.097	0.0028	0.096	0.20	8.06
SP-1/3	39	0.11	0.0032	0.21	0.075	8.05
SP-1/4	54	0.022	0.0017	0.026	0.052	8.14
SP-1/5a	63	0.023	0.0016	0.015	0.24	8.13
SP-1/5b	81	3.7	0.00094	0.21	2.6	5.47
SP-1/5B	87	0.15	0.0010	0.042	0.060	7.19
SP-1/5r	92	0.017	0.0022	0.020	0.15	8.07
SP-1/6a	104	0.0064	0.0018	0.0053	0.025	7.98
SP-1/6b	120	0.0042	0.017	0.0092	0.046	8.21
SP-1/6B	132	0.011	0.027	0.010	0.048	7.92
SP-1/7	144	0.31	0.016	0.019	0.40	7.65
SP-1/8a	159	0.0038	0.015	0.0084	0.014	8.26
SP-1/8b	164	0.0047	0.030	0.00785	0.089	8.16
SP-1/9	175	0.0069	0.0066	0.015	0.065	8.25

water-soluble metals increase (as do the concentration and the percentage), and the pH value of water extraction decreases in comparison with the upstream layers. This pattern means that with water ingress in these hardpans (seasonal rains, snow melting, and raising of the groundwater level), cationic exchange leads to the rapid acidification of water. As a result, water-soluble and weakly sorbed metal species may be released in the solutions.

In the vertical section no. 1, the distribution of metals is similar to that in cross-section no. 7, which is proved by the high correlation coefficients among the metals (Table 5). Two geochemical barriers were found in this cross-section

**Table 6** Percentage of water-soluble metals in layers of vertical sections

Sample	Depth (cm)	% of water-soluble species				
		Zn	Pb	Cu	Cd	pH
Vertical section no. 3						
SP-3/1	7.5	0.05	0.009	0.03	0.08	8.68
SP-3/2	15	0.03	0.024	0.08	0.10	8.37
SP-3/3	22.5	0.10	0.028	0.04	0.26	7.85
SP-3/4	37.5	0.09	0.006	0.03	0.24	7.92
SP-3/5a	47.5	2.36	0.020	0.16	2.78	5.75
SP-3/5b	57.5	1.52	0.027	0.08	0.18	6.87
SP-3/5B	67.5	0.18	0.006	0.10	0.63	8.32
SP-3/6	85	0.06	0.021	0.05	0.63	8.56
SP-3/6b	95	0.37	0.038	0.07	1.07	7.50
SP-3/7a	120	0.30	0.016	0.13	3.75	7.76

and are marked by a sharp increase of water-soluble species. The first barrier is located at a depth of ~60 cm and the second at ~130 cm (Fig. 2, Table 5). The upper barrier accumulated a higher quantity of secondary minerals than the lower barrier. In contrast to the cross-section no. 7, the percentage of water-soluble species here is less than 3.7% for Zn and 2.6% for Cd. It is possible that mobile species had leached from the tailings to this part of the impoundment and that the measured concentrations of water-soluble phases represent the remainders.

Cross-section no. 3 is represented by dry material with an insignificant quantity of ocher lenses in the middle part (layers 3/5 and 3/6). The metals are distributed irregularly, with concentrations increasing downward, except Pb, which decreases up to the last layer (Table 6). In this cross-section, we find three concentrated layers, although the concentration of exchangeable metals here is not high compared with the layer from cross-section nos. 7 and 1. Obviously, in this cross-section, sorb barriers, which are able to accumulate high amounts of migrated metals, are absent. Additionally, the redistribution of secondary minerals takes place along the whole of the section in more or less suitable layers, but a significant accumulation of secondary minerals does not occur (Fig. 2).

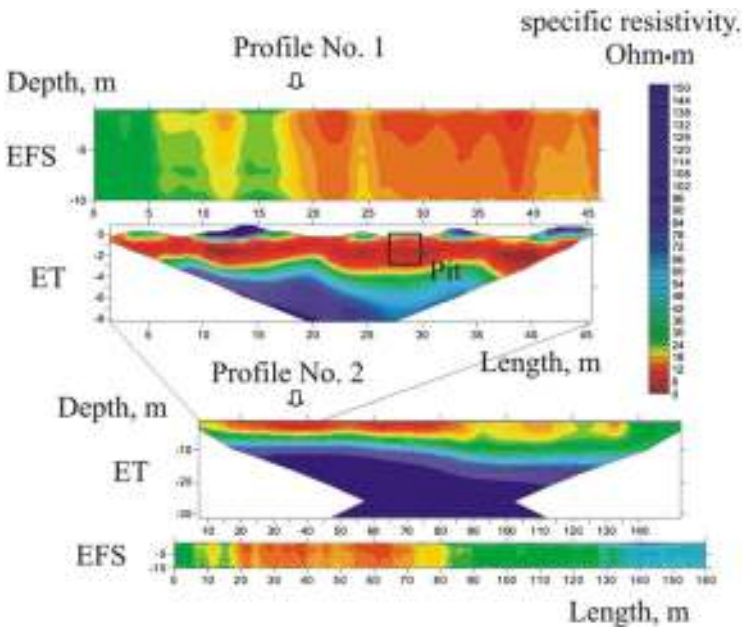
Vertical section no. 5 is located in the oldest part of the tailing impoundments, where the first wastes of the Salair ore processing were stored. In this part of the tailings, substance oxidation is manifested most clearly in the abundance of red ochre.

Trace elements Cu and Cd are distributed irregularly, with a max/min ratio = 180 and 81, respectively; for Pb and Zn, these ratios are 64 and 34, respectively (Fig. 2, Table 7). These ratio values can serve as a mark of the degree of redistribution of each element along the vertical direction. We can also observe the reverse order between the mobility of these metals (Cd > Cu > Pb > Zn) and their content in the tailings (Zn > Pb > Cu > Cd). Correlation between metals is absent in this vertical section, except for Pb–Cu.

A high amount of secondary metals form precipitates on the concentrated barriers (hardpans), especially Cu and Cd (more than 40% for Cd, Table 6).

**Table 7** Percentage of water-soluble metals in layers of vertical sections

Depth (cm)	% of water-soluble species					
	Zn	Pb	Cu	Cd	pH	
Vertical section no. 3						
SP-5/1	1	0.18	0.012	0.051	1.5	7.89
SP-5/3	26	2.9	0.308	19	39	5.45
SP-5/7	56	0.33	0.014	2.5	2.5	6.87
SP-5/8	88	8.6	0.0014	19	42	4.58
SP-5/16	150	0.54	0.022	30	4.3	7.86
SP-5/18	175	0.96	0.88	0.080	0.86	8.64

**Fig. 3** Vertical zoning of the Talmovskie Mine Tailings according to the data of the electromagnetic frequency sounding (EFS) and electrical tomography (ET)

### 4.3 Geophysical Data

Geophysical methods have been applied in order to further clarify the structure of the waste to a depth of 7 m and find evidence of infiltration drainage to groundwater. The section on profile no. 1 is characterized by a range of resistivities of 1–150 Ohm m. The upper part of the section (0–5 m vertically) is represented by the most conductive rocks with resistivities 1–20 Ohm m (Fig. 3). This layer is apparently confined within the highly mineralized wastes of the Salair Ore Processing Plant in the range 2–3.5 m. High-impedance (70–150 Ohm m) heaps

**Table 8** Specific electric resistivity of the wastes according to frequency sounding ( $SER_{fs}$ ) and parameters of the pastes and aqueous extracts (average values for pits nos. 8–10)

Depth (cm)	$SER_{fs}$ (Ohm m)	Humidity (%)	Parameters of the pastes			$\Sigma$ (Al, Mn, Fe, Cu, Zn, Cd, Pb, Sb) in aqueous extracts (mg/L)
			$SER_p$ (Ohm m)	Eh (mV)	pH	
2	16	8	13	646	3.1	30
25	9.0	7	8.0	693	3.0	110
45	10	8	4.8	738	2.8	110
70	4.8	3	4.3	729	2.9	80
120	4.0	29	3.4	719	3.1	370
160	4.0	32	3.2	642	3.7	760

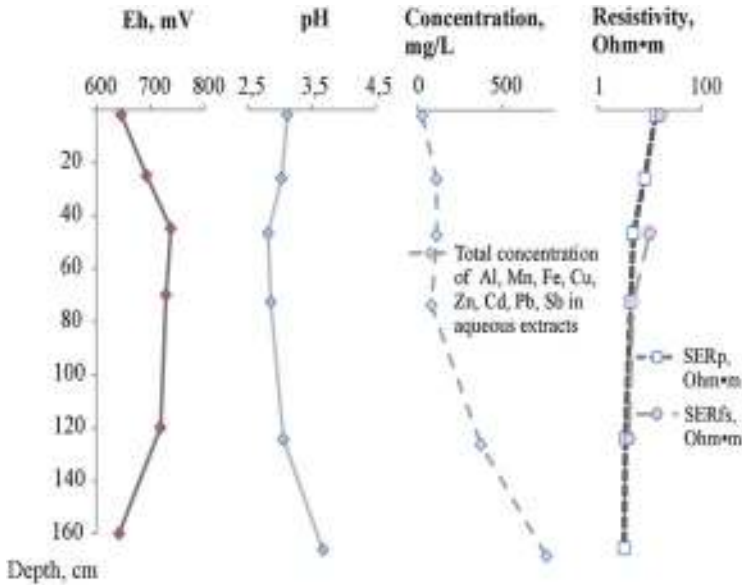
located at elevations of 10–18, 32–35, and 40–45 m on the profile represent bulk soil. Deeper (3.5–5 m vertically), there is a layer with a resistivity from 25 up to 35 Ohm m belonging to the waterproof horizon. At the bottom of the section, at 5–8 m in depth, the resistivities vary from 40 to 150 Ohm m, which is typical for low-conductive bedrock.

The section on profile no. 2 is characterized by resistivities varying within a range of 1–150 Ohm m. There is an upper layer (0–3 m vertically) with highly conductive waste followed by the waterproof horizon and the bedrock, which is deeper than 10 m. Three pits of 1.6 m depth were excavated and tested. Their location is 28 m from the beginning of the profiles in the area of the highly conductive material (Fig. 3).

The waste material is heterogeneous, has a bright red and brown color, and smells of sulfuric acid. The upper layers are composed of coarse sand with a predominantly quartz, barite and pyrite mineral composition. After a depth of 30 cm, the waste matter is represented by red and bright red coarse-grained sands, and the main mineral phases are barite and pyrite. The lower horizon is composed of dense gray-brown watered material with a particle size of 1.1 mm, and the mineral composition is dominated by quartz, plagioclase, potassium feldspar, and pyrite.

The pH values of the field-prepared pastes vary within the range of 2.8–3.6, and the redox potential ranges from 640 to 740 mV, which indicates oxidation of the waste material. The specific electrical resistance measured by direct conductometry in the pastes ( $SER_p$ ) varies within the range 3.2–13 Ohm m and correlates well with the results of the  $SER_{fs}$  obtained by frequency sounding (Table 8, Fig. 4).

The plots of pH and resistivity values vs. depth are substantially specular reflections with respect to the distribution of Eh: horizons with the lowest pH values are characterized by a high redox potential and low resistance (high conductivity, Fig. 4). The pH values increase and the Eh and resistivity decrease with depth due to the flow of the slightly alkaline groundwater in the pit after a depth of 1.2 m. The total Cu, Zn, Cd, and Pb concentrations in the aqueous extracts and the humidity of the wastes in the lowest horizon increase (760 mg/L and 32 %, respectively, Table 8), which indicates intense leaching.



**Fig. 4** Eh, pH of the pastes, total concentration of the elements in aqueous extracts, specific electric resistivity of the pastes ( $SER_p$ ), measured in-situ by conductometry, and in the wastes according to frequency sounding ( $SER_{fs}$ )

The lowest resistivities are also in the lowest water-bearing horizons with the highest concentrations of  $SO_4^{2-}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$ ,  $Cd^{2+}$  in the aqueous extracts. Intensive leaching reduces the metal content in the solids and increases concentrations in the solutions (Table 9). The percentage of the water-soluble species of Cu, Zn, and Cd in the lower horizon is much higher than in the upper layers, reaching 14% for Zn, 5.7% for Cd, and 3.5% for Cu in % of the total content of all species. The low mobility of lead in the acid sulfate-bearing solutions is associated with the formation of the insoluble anglesite  $PbSO_4$ . Obviously, flooding of the tailings by groundwater and intense leaching of the metals occurs at a depth greater than ~160 cm.

#### 4.4 Pore- and Groundwater Composition

The pore waters coexisting with the solids have a highly variable composition (major components and trace elements), which is determined by the local physico-chemical conditions in the different areas and layers (Table 10). The pore solutions are weakly acidic (pH 5–6).  $Ca^{2+}$  and  $Mg^{2+}$  dominate in the cation composition,  $SO_4^{2-}$  prevails among the anions, and concentration of sulfate-ions reaches 4,500 mg/L. The increased acidity and sulfate of the solutions indicate the active oxidation processes of sulfides in the waste and the dissolution of secondary sulfate

**Table 9** Composition of the wastes, aqueous extracts, and percentage of the soluble species (average values for pits nos. 8–10)

Depth (cm)	Content of the elements in the wastes (ppm)					
	Cu	Zn	Cd	Pb		
2	980	5,000	13	3,600		
25	320	6,000	14	4,800		
45	1,500	19,000	52	8,800		
70	1,300	41,000	120	14,000		
120	220	2,500	14	150		
160	290	4,800	39	220		
Depth (cm)	Aqueous extracts (mg/L)					pH
	Cu	Zn	Cd	Pb	SO <sub>4</sub> <sup>2-</sup>	
2	0.89	14	0.07	0.06	570	2.5
25	2.4	66	0.13	0.12	530	2.8
45	1.5	104	0.26	0.65	500	2.8
70	1.3	58	0.13	3.3	420	2.1
120	6.9	311	0.78	0.05	1,000	2.4
160	10	660	2.2	0.04	1,200	3.0
Depth (cm)	% of water-soluble species					
	Cu	Zn	Cd	Pb		
2	0.09	0.28	0.55	0.001		
25	0.74	1.09	0.96	0.002		
45	0.10	0.54	0.49	0.007		
70	0.10	0.14	0.11	0.02		
120	3.15	12	5.53	0.03		
160	3.53	14	5.73	0.02		

**Table 10** Major ion composition in pore waters of the Talmovskie tailings (mg/L)

Component	P-1	P-2	P-3	P-4	P-6
pH	5.98	5.09	6.44	5.54	6.36
Ca <sup>2+</sup> +Mg <sup>2+</sup>	570	1,500	1,000	540	570
Na <sup>+</sup>	53	28	52	55	26
K <sup>+</sup>	36	8.0	11	18	20
HCO <sub>3</sub> <sup>2-</sup>	Not detected	Not detected	130	Not detected	120
SO <sub>4</sub> <sup>2-</sup>	1,600	4,500	3,400	2,800	1,800
Cl <sup>-</sup>	78	29	27	28	33
F <sup>-</sup>	360	10	24	6.0	6.0
NO <sub>3</sub> <sup>-</sup>	140	Not detected	Not detected	Not detected	58

minerals, such as jarosite KFe<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>, orthoserpierit Cu<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>2</sub>·2H<sub>2</sub>O, and magnesiocopiapite MgFe<sub>4</sub>(SO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>·20H<sub>2</sub>O.

The variations of Zn in the pore water are notably broad; its concentrations are mostly high, reaching 1,000 mg/L (Table 11). It is necessary to take into account the peculiarities of the pore water solutions, i.e., the low content of HCO<sub>3</sub><sup>-</sup> and the high

**Table 11** Concentrations of metals in pore water of the Talmovskie tailings (mg/L)

	Zn	Pb	Cu	Cd	Fe
P-1	16	8.5	2.3	0.05	0.5
P-1/9	203	0.046	1.0	1.0	0.27
P-2	1,000	5.7	0.35	3.5	140
P-2/13	128	0.022	0.7	0.35	0.11
P-2/14	142	0.085	0.8	0.81	0.25
P-3	177	4.4	1.0	4.1	1.1
P-4	750	18	1.2	1.6	100
P-6	0.02	1.0	0.02	0.01	1.3
P-6/10	29	0.007	0.21	0.52	0.08
P-6/15	0.54	0.13	0.36	0.0004	0.67
P-6/16	1.3	0.15	0.44	0.0014	0.44
P-6/18	0.8	0.24	0.5	0.0013	0.52

**Table 12** Concentrations of elements in water samples from wells

	Concentration ( $\mu\text{g/L}$ )			
	Cu	Zn	Cd	Pb
D 6	64	98,000	410	15
D 7	125	10,000	5,900	1,000
D 24	8.7	8,800	5.3	3.0
C 1	4.0	7,300	1.4	0.7
C 2	6.7	5,900	1.3	190
C 3	5.5	5,200	0.61	0.7
C 4	110	3,900	0.34	0.5
MPC <sup>a</sup>	1,000	1,000	1.0	10
Average in river waters <sup>b</sup>	7.0	20	0.01	1.0

<sup>a</sup>Maximum Permissible Concentration for Chemical Compounds in Water Reservoirs, accepted in Russia (HN 2.1.5.1315-03) [18]

<sup>b</sup>According to Taylor and McLennan [19]

level of  $\text{SO}_4^{2-}$ . Therefore, instead of the formation of smithsonite  $\text{ZnCO}_3$  on the surface of sphalerite  $\text{ZnS}$ , zinc remains in the solution. The lead concentrations are not high because of its easy coupling with sulfate and the consequential formation of  $\text{PbSO}_4$ ; in some cases, however, concentration of lead may increase up to 10–17 mg/L. The concentrations of Cu, Cd, and Fe are lower than those for zinc, but in isolated samples, 100–140 mg/L of iron was detected (Table 11).

The chemical analyses of the groundwater samples from the wells located in close proximity to the Talmovskie tailings (Fig. 2) indicate high contents of Cu, Zn, Cd, and Pb in the groundwater (Table 12). The copper concentrations range from 4 to 125  $\mu\text{g/L}$ , and the Cd and Pb concentrations range from 0.5 to 5,900  $\mu\text{g/L}$ . The zinc concentrations are the highest compared with the other elements: up to 98 mg/L (sample D6, Table 12). It is important to note that the concentration of zinc in all the analyzed samples is higher than the MPC by 4–100 times. The Cd concentrations significantly exceed the MPC (up to 5,900 times) in five of the seven



samples. The concentration of Pb increases compared with the MPC by 3–1,000 times in three of the seven samples. The concentrations of all elements (except for copper in three samples) are significantly higher than the average content in river waters [19].

## 5 Conclusions

It should be emphasized that significant amounts of water-soluble forms were observed over the vertical sections. In the lowest layers, however, the concentration of water-soluble species decreased, obviously due to the removal of mobile forms by groundwater below the water table. The percentage of exchangeable species varies in a wide range along the vertical sections – from traces up to very high values, especially for Pb. All of these factors provide evidence of a high degree of oxidation and alteration of tailings in this part of the impoundment and consequently the redistribution, removal, and precipitation of secondary metal minerals and phases.

Electrical tomography and electromagnetic frequency sounding allowed the delineation of the tailings of the Salair Ore Processing Plant and the prediction of changes in the composition of waste with depth. The existence of secondary modified and oxidized zones of the waste material with a high proportion of water-soluble, mobile forms of elements, was estimated down to a depth of 7 m, based on data from the geophysical surveys and geochemical analyses. The authors made the first attempt to develop and test this approach, in order to quantify the resources of the valuable components in the tailings and to evaluate the environmental risks presented by underflooding of the stored wastes by seasonal streams and groundwaters.

As expected, the leaching of metals from the tailings stockpiled in the Talmovskie tailings and the migration of drainage solutions lead to a significant pollution of local groundwater, causing irreparable damage to the supply of clean drinking water at the regional level and, thus affecting the health of local residents.

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