Transformation of the acid mine drainage composition of the Sibay chalcopyrite deposit on the geochemical barriers of the river system

Anatolii Opekunov, Marina Opekunova, Stepan Kukushkin, Vsevolod Somov, Vladimir Spasskij, Elena Yaskevich

Saint-Petersburg state university, 10th line of Vasiljevskiy island 33/35, 199178 Saint-Petersburg, Russia

a_opekunov@mail.ru

Abstract

This article focuses on the study of the Sibay copper-zinc deposit (South Urals) acid mine and dump drainage and on its transformation in the Karagaily river system. The runoff of the river is initially formed by underground water, dump drainage and mine drainage. The hydrochemical composition of water and the content of ore metals in bottom sediments have been examined. Special attention has been paid to the phase distribution of metals, which provides information about the forms and intensity of element mobilization into the solid phase. The effect of anthropogenic and natural geochemical barriers on the river self-purification ability has been estimated. It has been shown that the formation of a new artificial geochemical barrier in the river, caused by the discharge of alkaline waters from the treatment facilities, substantially increased the self-purification ability of the watercourse. This led to the fact, that the quality of river water in the lower course almost reached normative indicators.

Keywords: acid mine drainage, bottom sediments, potentially toxic metals, trace elements, geochemical barriers

Introduction

The development of polymetallic sulphide deposits leads to acidification of natural waters and contamination of landscape components with potentially toxic metals.

The mining of chalcopyrite deposits leads to contamination of landscape components with potentially toxic metals (PTM) and to natural water acidification (Liu et al. 2010; Perotti et al. 2017; Balci, Demirel 2018; Opekunov et al. 2018). This influence is especially noticeable for streams directly polluted with mine drainage (Opekunov et al. 2010, Canovas et al. 2017). Cu, Zn, Cd and other chalcophyles are the main elements of secondary dispersion haloes around chalcopyrite deposits. In the hypergenesis zone in presence of oxygen Fe2(SO4)3 and H2SO4 poorly soluble sulfides are transformed into hydrated metal sulfates. As a result of these reactions a sharp decrease in the pH of surface and soil water is observed, accompanied by an increase in Eh (Siegel 2002). The main forms of Cu, Zn and Cd in aqueous solutions are cations, as well as hydroxyl or mixed hydroxyl-sulphate complexes, which, with an increase in pH, pass into the solid phase, leading to a decrease in their concentration in water. This process is especially active on geochemical barriers. The Sibay copper-sulphidean (copper-zinc) deposit, located in the Bashkir Trans-Urals (Southern Urals), has been developed since 1939. Open-pit mining of the Sibay ore deposit (which contains the main reserves of Cu and Zn) was started in 1956. Since 2003 only shaft mining has been performed.

Before the construction began, the upper reaches of Karagaily river, were diverted to Kamyshly-Uzyak, (another small river of the study area) and in the middle stream a new channel has been dug, bypassing the future quarry. (fig. 1). In 2011, wastewater treatment facilities for the nearby Kamagan quarry were constructed. Alkaline wastewater discharge to the Karagaily led to a substantial change in the hydrochemical regime of the watercourse in the middle and lower reaches.

The article discusses the effectiveness of geochemical barriers in wastewater treatment. All barriers, including an artificial barrier, which arose as a result of the discharge of alkaline waters from treatment facilities, were formed spontaneously. However, their effect on water quality is quite substantial. Studies show that the construction of artificial geochemical barriers is a very effective and cheap way of reducing pollution of sour drainage waters.

Methods

Research on the Karagaily river has been conducted from 2004. During this period, wastewater, mine drainage water, river water and bottom sediments were sampled. Conductivity, pH, main cations and anions content, PTM (Cu, Zn, Pb, Cd, Fe, Mn, Ni, Co) concentration were measured in water samples. A total PTM content and content of their mobile forms were determined in bottom sediment samples. During the research period 30 water samples and 65 bottom sediments samples were analyzed. PTM total content was measured using mass spectrometry with inductively coupled plasma (ICP-MS) method («Optima-4300» spectrometer) with complete acid digestion. PTM concentration in water after filtration and PTM mobile forms content in bottom sediments (extracted with ammonium acetate buffer, with pH 4,8) as well as PTM phases content in bottom sediments were determined using atomic absorption spectrometry («AAS-novAA 300» spectrometer). The ion-cationic composition of water was determined by the titrimetric method. Phase analysis of PTM in 11 bottom sediments samples was done using sequential extraction and included determination of sorbed forms (0,25 mol/l MgCl2), carbonates and non-persistent organic matter (ammonium acetate buffer with pH 4,8), organic matter and sulfate (1 mol/l acetic acid and H_2O_2), PTM sorbed on iron and manganese hydroxides (hydroxylamine hydrochloride $NH_2OH{\cdot}HCl$), crystalline (0,3 mol/l HCl), residue (difference in total content and mobile phases content summary). Spatial distribution of PTM in bottom sediments was characterised using a multiplicative index (MI) calculated as a product of the Cu, Zn and Cd content (in%), additionally multiplied by 1000.

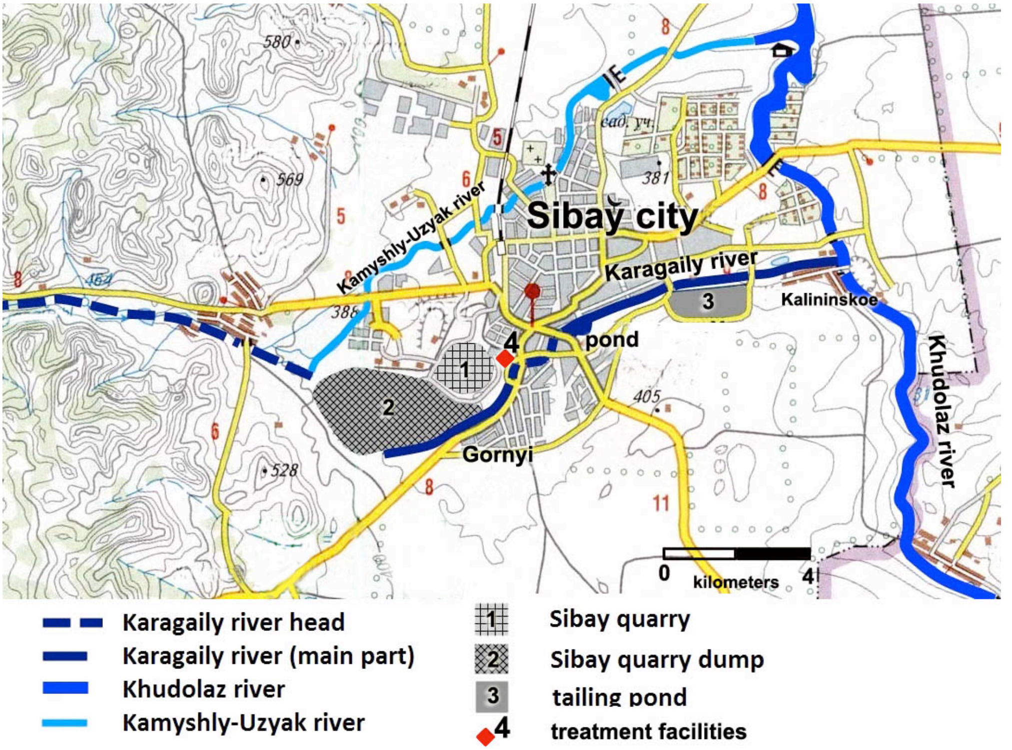


Figure 1 The study area

Discussion

Consumption of mixed waters in the summer is 15-30 l / s. At 1 km below the source, quarry waters are discharged into the river bed

Originaly, Karagayly flowed from the ridges of the Irendyk mountain chain. Later the Karagaily upper course was buried under quarry dumps south-west of Sibay, where underground water comes to the surface and mixes with acid dump drainage. Water flow in summer is 15-30 L/s. About 1 km downstream mine drainage water, the volume of which exceeds the river's volume at this place approximately 1.5 times, is discharged into the river. Hydrochemical characteristics of mine drainage are close to those of dump drainage (table 1). Both are $Mg\text{-}SO_4$, mineralization is from 3,3 to 9,4 g/L. Water hardness is high, the sum of Ca^{2+} and Mg^{2+} reaches 139 mg-eqv/l. Anomalous concentration of Cu, Zn, Cd and other chalcophylic elements was discovered in the river water. Our estimation of Zn, Cu and Cd intake to the river is 53 t/yr, 3 t/yr and 0,1 t/yr respectively (Opekunov et al. 2018). Thus, for a long time the water flow in the upper and middle course of the Karagaily has almost completely been formed by mine and dump drainage.

Nowadays the Karagaily is 11 km long, The river flows through the southern outskirts of Sibay and into the river Khudolaz, which is a tributary of the Ural river. The river bed and floodplain morphology determines different hydrological regimes and sedimentation rate of suspended and dissolved matter. In the upper course near the village of Gornyi the river bed is 2-6 m wide (up to 20 m at maximum in several places). The flow velocity during the summer low-water period is 0,2-0,3 m/s. The River bed is a U-shaped valley, the height of the banks doesn't exceed 1,5 m. The sediment regime is predominantly accumulative or trans-accumulative. A wide (up to 200m) waterlogged floodplain covered with reed is located in the middle course of the river. In this area a pond has been constructed. It acted as a mechanical and sorption geochemical barrier, where suspended material and PTM accumulated. Downstream (near the tailing pond) the river has a narrow and relatively deep bed. The flow velocity reaches 0,8 m/s and provides a transitional sediment regime. In the lower course the floodplain expands and gets waterlogged again due to road construction. Close to the river mouth (near the village of Kalininskoe) the river bed is mature and the valley is relatively wide and the flow velocity is low (0,2-0,3 m/s). Such conditions determine an accumulative (in some places – erosional and accumulative) sediment regime.

Several natural and anthropogenic biogeochemical barriers have been formed along the river. To some extent they provide self-purification of the Karagaily and protection of the Khudolaz. Downstream from the mine drainage discharge site water acidity slowly decreases due to mixing with natural waters (pH 8,0-8,2) and contact with slightly alkaline soils (fig. 2). Alkaline and

***Table 1** Hydrochemical characteristics of dump and mine drainage.*

Characteristics	Dump drainage	Mine drainage
pH	4,95-6,25	3,32-4,95
K^+, mg/L	1,78-2,66	2,20-2,28
Na^+, mg/L	69,7-154,3	165,4-176,9
Mg^{2+}, mg/L	461,8-1463	358,9-450,4
Ca^{2+}, mg/L	363,2-369,2	248,7-256,2
Cl^-, mg/L	7,25-7,66	< 1,0
SO_4^{2-}, mg/L	2922-7392	2547-2917
HCO_3^-, mg/L	< 1,0-1,84	< 1,0
Σ ions, mg/L	3828-9381	3342-3783
Zn, mg/L	12,1-111,0	36,6-49,0
Cu, mg/L	0,20-21,0	5,4-8,1
Ni, mg/L	0,025-0,24	0,09-0,12
Cd, mg/L	0,03-0,59	0,13-0,15
Hardness, mg-eqv/l	56-139	42-49
Water type	$Mg\text{-}SO_4$	$Mg\text{-}SO_4$

sorption barriers are the most crucial for PTM immobilization.

The first anthropogenic alkaline barrier is located under the dumps, where acid dump drainage mixes with discharged underground water. At sampling point (SP) №1 mix pH reaches 6,0-6,5 (fig. 2). This barrier manifests itself in white powder-like sediment which covers the river bottom over 1 km downstream from the dumps (fig. 3). The white sediment is predominantly composed of hydrated sulfates of metals. The levels of SO_4^{2-} (19,8%), Cu (1,24%), Zn (1,57%) and Cd (13,3 ppm) substantially exceed background values. Compounds which sediment on the river bottom include copper sulfate, goslarite ($ZnSO_4 \cdot 7H_2O$), hydrosulfates of Fe, Zn and Cu. Cd is present as admixture. A high ratio of Cu, Zn and Cd mobile forms (33, 26 and 22% respectively) has been noted.

One more anthropogenic alkaline barrier and one more maximum of PTM content in bottom sediments can be found on the acid mine drainage discharge site (fig. 2, SP 3). Here, unlike the first barrier place, mine drainage substantially acidifies the water (pH 4,75-4,85) and inhibits hydrosulfates formation downstream, where PTM are sedimented predominantly by sorption on clay minerals. It is proved by exchangeable forms ratio increase up to 70% for Cu (average – 25-30%), 82% for Zn (average – 50%) and 72% for Cd (average – 35-45%).

Before 2011 river water pH slowly rose downstream, up to 5,2-5,4 in the middle course (fig. 2; SP 11-18) and up to 6,85-7,12 near the mouth (fig. 2; SP 20, 21). This was mainly due to the lateral inflow and the formation of natural geochemical barriers. Changes of PTM concentration in water corresponded to pH changes (fig. 4). Cu and Cd sedimentation in hydrated sulfates forms in the upper and middle course reached 56-86% and 43-60% of total content respectively; however, in the river mouth it dropped to 15 and 7%. Zn hydrated sulfates ratio was lower: 22-29% in the upper and middle course and 9% in the river mouth.

Such a regime existed for about 50 years. There, at the confluence with the river Hudolaz, an alkaline barrier was formed, on which metals precipitated as sulfates and in the adsorbed state on iron oxyhydroxides. Their content in water was

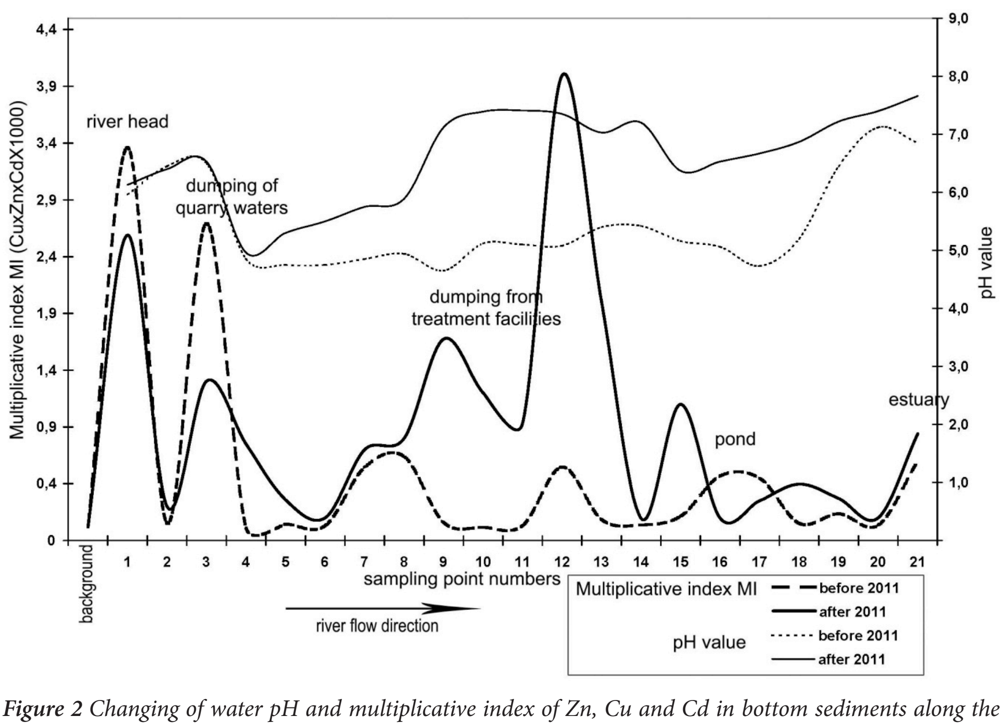


Figure 2 Changing of water pH and multiplicative index of Zn, Cu and Cd in bottom sediments along the Karagaily (Opekunov et al., 2018, revised and completed)

reduced to standard values. It all changed in 2011, when wastewater treatment facilities 2,2 km downstream of the river head were put in operation (fig. 2, SP 9). Now wastewater treatment is performed by water liming followed by flocculation. Discharged wastewater pH reaches 10,5. A sharp pH increase has intensified PTM sedimentation and river self-purification (fig. 2, SP 9-16).

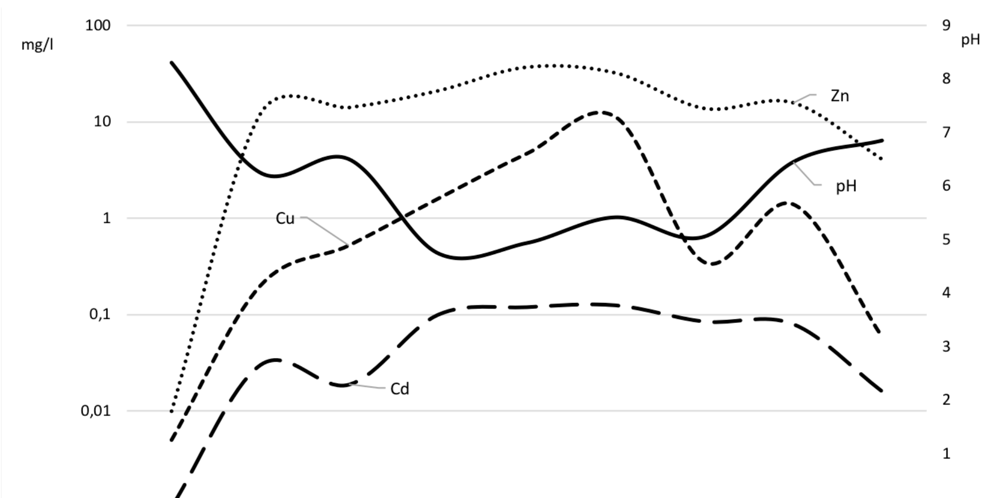
Directly at the discharge site (fig. 2, SP 9) PTM are immobilized in sulfate forms. Then iron sulfate is transformed into hydrocarbonate and later into hydroxide: $FeSO_4 + Ca(HCO_3)_2 \rightarrow Fe(HCO_3)_2 + CaSO_4$; $2Fe(HCO_3)_3 \rightarrow 2Fe(OH)_3\downarrow + 6CO_2$. The newly formed $Fe(OH)_3$ actively adsorbs ore metals. It is the basis for the complex sorption and alkaline barrier, which manifests itself in ochreous color of bottom sediment anomalously enriched with Fe (up to 21%), Cu (0,83%), Zn (1,92%) and Cd (0,0048%). Exchangeable forms content is maximum on the surface and decreases downward 1,3-1,8 times, due to Fe(OH)3 crystallization and consequential non-availability of PTM for the ammonium acetate buffer. Thus, the artificial barrier, which emerged spontaneously in 2011, causes active accumulation of PTM near discharge site and downstream (fig. 2, SP 10-15).

***Figure 3** Hydrated sulfates deposits in Karagaily river bed*

The high activity of the artificial barrier is proved by comparative data (tab. 2). The increase of PTM total content and exchangeable forms content in bottom sediments after 2011 is shown. However, it is accompanied by a decrease of exchangeable forms percentage. This highlights the role of iron hydroxides in chalcophylic metals sedimentation.

Conclusion

The artificial geochemical barrier formed spontaneously as a result of alkaline discharge from wastewater treatment facilities substantially increased the self-purification ability of the Karagaily river



	background	1	3	6	8	14	16	19	21
Zn	0,01	12,1	14,1	21	37	32,2	13,8	15,8	4,1
Cu	0,005	0,2	0,525	1,6	4,7	11,3	0,35	1,4	0,059
Cd	0,001	0,03	0,0188	0,1	0,12	0,1255	0,085	0,08	0,016
pH	8,3	6,25	6,5	4,75	4,94	5,42	5,06	6,45	6,85

***Figure 4** Changing of pH and PTM content in water along the Karagaily river (sampling points numbers are given in fig. 1)*

Table 2 Ore metals total content and mobile forms content in bottom sediments of the Karagaily, mean and

Time period	Forms	Cu		Zn		Cd	
		x	S	x	S	x	S
Before 2011	Total, ppm	5353	5082	5141	4109	8,9	8,2
	Mobile forms, ppm	1916	3019	2943	3848	5,0	5,9
	Mobile forms ratio %	36	-	57	-	56	-
After 2015	Total, ppm	6848	4369	9180	3746	15,9	9,8
	Mobile forms, ppm	1980	1400	4437	3128	6,4	4,7
	Mobile forms ratio %	29	-	48	-	40	-

in regard to sulfate and PTM. The creation of this barrier led to a 5-fold decrease of Zn, Cu and Cd concentration downstream from 4,1 mg/L, 0,059 mg/L and 0,016 mg/L respectively before 2011 to 0,826 mg/L, 0,0125 mg/L and 0,003 mg/L after 2011. After 2011 the quality of water in the mouth of the river Karagaily satisfied the standards for river water for drinking and water supply. It also means that removal of PTM to the Khudolaz river decreased correspondingly in 2011. According to preliminary estimation of the river self-purification ability, before 2011 about 25% of Zn that had come with mine and dump drainage, was carried from the Karagaily downstream to the Khudolaz. After the artificial barrier - wastewater treatment facility - construction this ratio dropped to 5%. For Cu this value changed from 1,2% to 0,3% and for Cd – from 10% to 2%. Simultaneous increase of PTM total content and decrease of their mobile forms ratio in bottom sediments is an important factor (tab. 2). It can be claimed, that after the described changes of physic and chemical conditions the risk of secondary pollution of the river water has decreased.

Acknowledgements

The research was performed with support of RFBR grant 18-05-00217 «Biogeochemical indicators of anthropogenic transformation of potentially toxic metals flow in landscapes».

References

Balci N, Demirel C (2018) Prediction of acid mine drainage (AMD) and metal release sources at the Küre copper mine site, Kastamonu, NW Turkey - Mine Water and the Environment. Vol. 37, № 1: 56-74. DOI: 10.1007/s10230-017-0470-4

Canovas CR, Macías F, Olias M, Lopez RP (2017) Restoration measures of an AMD polluted watershed based on mixing and geochemical models - Proceedings13th International Mine Water Association Congress, Vol. 1, June 25–30, 2017 Lappeenranta, Finland: 588-594

Liu L, Wu L, Luo Y, Zhang C, Jiang Y, Qiu X (2010) The impact of a copper smelter on adjacent soil zinc and cadmium fractions and soil organic carbon - J. the Soils and Sediments. V. 10, № 5: 808-817

Opekunov AY, Opekunov MG, Somov VV, Mitrofanova ES, Kukushkin SY (2018) Influence of the exploitation of Sibay deposit (the Southern Urals) on the transformation of metal migration in subordinate landscapes -Vestnik Mosk. un-ta. Serija 5:Geografija, № 3: 14-24 (in Russian)

Opekunov AYu, Leont'eva LV, Kuprina MS (2010) The geochemical features of modern sedimentation in the development area of Sibay massive sulfide deposit (Southern Urals) - Vest. S.-Peterb. un-ta, ser. 7, vyp. 2 (№ 15): 84-98. (in Russian).

Perotti M, Ghezzi L, Casiot C, D'Orazio M, Giannecchini R, Petrini R (2017) The geochemistry of pore waters in riverbed sediments in a mining-impacted landscape: sources of potentially toxic elements - Proceedings13th International Mine Water Association Congress, Vol. 2, June 25–30, 2017 Lappeenranta, Finland: 732-736

Siegel FR (2002) Environmental Geochemistry of Potentially Toxic Metals, Springer-Verlag, Berlin, 218 pp.