

## Aspects of the Environmental Monitoring on the Territory of Verhnekamskoye Potash Deposit (Russia)

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### Abstract

For effective environmental management the system of complex environmental monitoring has developed in the southern part of Verhnekamskoye Potash Deposit – one of the biggest potash salt deposits in the world. Environmental monitoring includes hydrochemical, soil and biological monitoring in terrestrial and aquatic ecosystems. The main factor of potash mining effect on the environment is high solubility of wastes. High concentrations of  $Na^+$ ,  $Cl^-$ ,  $K^+$ ,  $SO_4^{2-}$ ,  $Mg^{2+}$  in waste and active water migration of these chemical elements caused salinization of the environment.

There are two types of technogenic bio- and geochemical salt anomalies. The first type of anomalies is localized near the salt tailings and plants as a result of air migration of pollutants. The second type of technogenic anomalies is more intensive and developed in river valleys. The main transport of salt components is surface and groundwater ones. Technogenic bio- and geochemical anomalies are characterized by high content of  $Na^+$ ,  $Cl^-$ ,  $K^+$ ,  $SO_4^{2-}$ ,  $Mg^{2+}$ , decrease of soil microbial biomass and invasion of salt-resistance species of terrestrial and aquatic ecosystems. Hydrogen sulfide settings and precipitation of iron-rich minerals in soils are developed in discharge areas of saline ground water.

**Key words:** potash deposit, environmental monitoring, anthropogenic salinization, surface and ground water, iron-rich precipitates

### Introduction

Anthropogenic salinization of ecosystems was always serious problem for arid and semiarid environments and for cold and humid environments at last century. There are different sources of salt pollution, for example road salt (Kaushal *et al.* 2005), brines of old prospected oil wells (Svanidze *et al.* 2014) or salt production wells (Khayrulina & Maksimovich, 2015). Biggest salt source are associated with mining of evaporitic salt deposits, i.e. potash deposit (Rivers of Europe 2009, Beuer *et al.* 2005). Main factor of the environmental effect under mining of potash deposits is wastes of potash production that are accumulated in large amount in the field. For each tone of beneficiated ore 30 % becomes product, 70 % becomes waste (dry salt, slimes and brine). The wastes consist predominantly of high soluble potassium and sodium chlorides. These components are actively involved in the migration flows. Salinization of adjacent ecosystems has developed as a result of salt tailing piles deflation, plant emissions and drainage waters of salt tailing piles and slurry storage,

Intensive atmospheric precipitations percolate through the salt tailing piles and slurry storage and form saline drainage waters in great volume and may pollute the environment for long period after closing the mining (Beuer *et al.* 2005). Active migration of soluble components in water flows contributes salt pollution distribution trough ground- and surface water on considerable distance. Increase in salinity is a serious threat to the biodiversity of river ecosystems (Arle & Wagner 2013).

Effective environmental management must include a system of environmental monitoring. Monitoring has to consider special aspects of pollution distribution. Generally the environmental monitoring includes sampling of ground and surface water, biological monitoring of river ecosystems. The system of complex environmental monitoring is developing in the southern part of Verhnekamskoye Potash Deposit - one of the biggest potash deposits in the world.

### Study area

The deposit is situated mostly on the left bank of the Kama river, tectonically belongs to the central part of Solikamsk depression of the Pre-Ural foredeep and is represented by the salt of Low- Permian halogeneous formation.

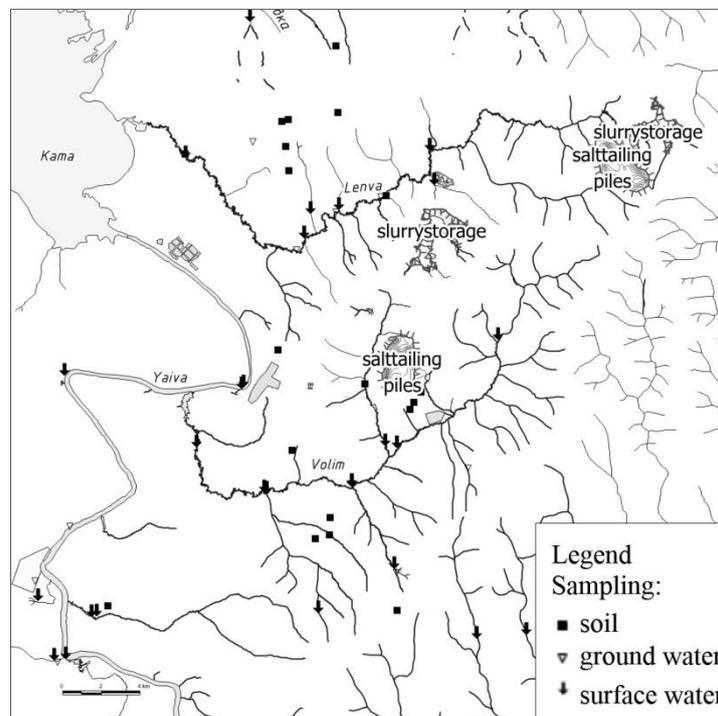
The area of deposit is about 6.5 thousand km<sup>2</sup>. The ore contains from 18 to 34% of KCl. Geological reserves of carnallite is up to 96,4 billion tons, sylvinite – 112,2 billion tons, halite – 4,65 trillion tons. Annual production of potassium-magnesium salts is about 40 million tons. Most of mines run flotation. Currently more than 270 million tons of halite wastes and 30 million m<sup>3</sup> of salt-clay slime have accumulated on the territory of the Verhnekamskoye Potash Deposit (Bachurin & Baboshko 2008).

Technological processes exclude brine release into the surface water. The main source of pollution on this deposit is uncontrolled discharge of drainage waters of salt tailing piles and slurry storage which were constructed 40-50 years ago without impermeable layer. Drainage water is a Cl – Na hydrochemical facies, has mineralization of about 300-400 g L<sup>-1</sup> and pH 6.6. The concentration of water soluble components are: Cl – 20.7 g L<sup>-1</sup>, SO<sub>4</sub> – 3.7 g L<sup>-1</sup>, Na – 128.8 g L<sup>-1</sup>, K – 20.6 g L<sup>-1</sup>. Drainage waters are filtrated into groundwater and spread salt pollution on the environment.

Necessity of environmental research is caused by very intensive mining. New potash plants, salt tailing piles and slurry storage are under construction. Local streams, as a main pollutant transport, drain into the Kama River used for drinking-water supply.

### Methods

Environmental monitoring includes hydrochemical, soil and biological monitoring in terrestrial and aquatic ecosystems. Samples of surface waters, springs were taken up 4 times in order to investigate fluctuations of salinity during the year. Sampling of soil, bottom sediments, plants and river biota was done once a year in July - August at different distance from plants and reservoir of wastes. Samples of snow were collected in the end of snow period (March) to analyze atmospheric pollution. Monitoring covers ecosystems in natural and impacted state (fig. 1).



**Figure 1** Schematic map of the southern part of Verhnekamskoye Potash Deposit with sampling sites of soil, surface and ground water.

Samples of surface and groundwater, soil- and bottom sediment were analyzed for  $NO_2^-$ ,  $NO_3^-$ ,  $NH_4^+$ ,  $Cl^-$ ,  $K^+$ ,  $SO_4^{2-}$ ,  $Ca^{2+}$ ,  $Na^+$ ,  $Mg^{2+}$  by using a capillary electrophoresis Capel-105, and  $pH$  of water extract,  $HCO_3^-$  and TDS – were investigating with traditional methods. Mineralogical analysis of soils and sediments was carried out by binocular microscope Nikon 104 with elutriation of soil and bottom sediment samples and removing of clay fractions less than 0.01 mm. Mineral components were analyzed by XRD using a D2 Phaser desktop diffractometer.

**Results**

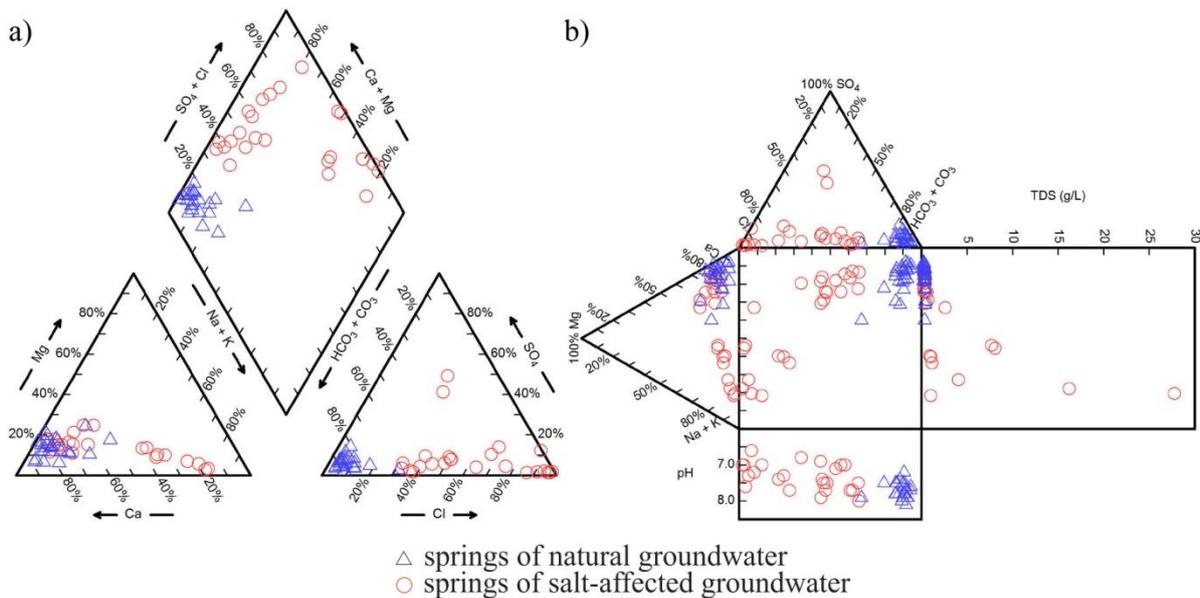
Our research of anthropogenic salinization during 2009-2015 years revealed two types of bio- and geochemical anomalies. The first type is localized near the tailings and potash plants. This salt anomaly caused by air pollution. Soil salinization is not persistent and high (tab.1), because rainfall are actively leaching watersoluble minerals into groundwater or underlying landscapes.

**Table 1** Range in contents of chemical elements in soils (mg 100g<sup>-1</sup>).

Location	pH	Sum of toxic salts, %	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Na <sup>+</sup>	K <sup>+</sup>
Near a salt piles (300 m)	5-6	0.090	1.4-7.5	0.6-4.8	0.8-1.8	1.4-5.6
Salt-affected valleys	4-8	1.582	22.6-1016.3	0.8-14.5	6.8-239.4	0.3-14.6
Background soils	4-6	0.011	1.1-2.3	0.8-1.9	0.6-1.0	0.3-1.7

Drainage waters entering into groundwater formed the second type of anthropogenic salt anomalies. Natural ground flows belong mostly to Ca – HCO<sub>3</sub> water type, in some cases – to Ca – SO<sub>4</sub> type. Drainage waters determine chemistry of groundwater: Na – Cl water type, high concentrations of K<sup>+</sup> (5.85 g L<sup>-1</sup>), SO<sub>4</sub><sup>2-</sup> (2.19 g L<sup>-1</sup>) and Mg<sup>2+</sup> (5.18 g L<sup>-1</sup>) (fig. 2). The ion exchange processes under the contact of saline water with carbonate and sulfate rocks set free Ca<sup>2+</sup> into the ground water (Lucas *et al.* 2010, Beuer *et al.* 2005) and transform water type to Ca, Na – Cl one.

Very large fluctuations in salinity were observed during monitoring. Some springs change the water type from Ca – HCO<sub>3</sub> to Ca – Cl and Na – Cl one for period of monitoring, salinity rose from background level of 256 mg L<sup>-1</sup> –up to 27 g L<sup>-1</sup>. These fluctuations may be determined by seasonal changes in the hydrodynamic regime.



**Figure 2** Groundwater hydrochemical data on **a** Piper diagram and **b** Durov diagram.

When saline groundwater meets confining beds it seeps to the surface in the river valleys and pollutes surface water. Chemistry of streams is derived from groundwater (fig. 3). Streams in natural state are  $Ca - HCO_3$  water type; salt-affected streams are  $Na - Cl$  and  $Ca, Na - Cl$  water types. Chloride concentration in salt-affected streams now already exceed the maximum limit ( $300 \text{ mg L}^{-1}$ ) recommended for protection of freshwater life. The maximum  $Cl^-$  concentration in salt-affected streams is up to  $34.63 \text{ g L}^{-1}$ . High  $K^+$  concentrations (up to  $4.23 \text{ g L}^{-1}$ ) attribute the river salinization to the impact of potash mining.

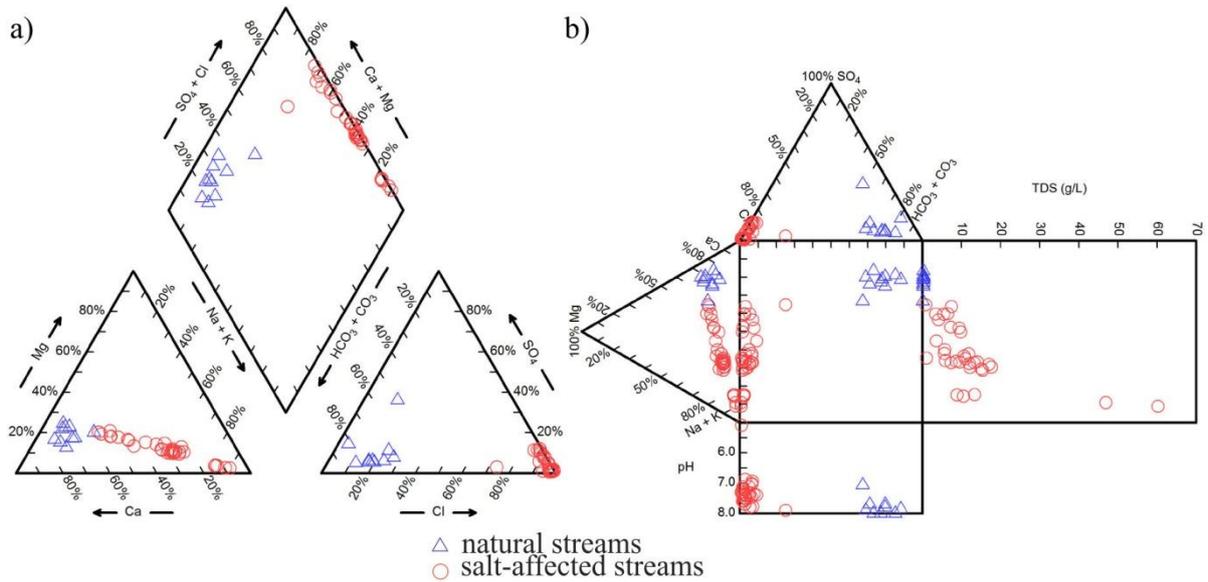


Figure 3 Hydrochemical data of streams on a Piper diagram and b Durov diagram.

Small rivers are experienced more intensive salt pressure, salinity some of them were up 100 times greater than salinity of natural flows. Concentration of water soluble salts of larger rivers gradually reduced by dilution of the non-affected streams. However increased chloride concentration can be propagated at substantial distance from salt sources, leading to negative effect on aquatic ecosystems.

Other aspect of groundwater salinization is sharp increase of  $Cl^-$ ,  $K^+$ ,  $SO_4^{2-}$ ,  $Na^+$  contents in valley soils (tab. 1). Water table in these landscapes is on 0-2 m depth. Saline ground water evaporates and causes minerals to precipitate. Increased concentrations of  $Cl^-$  and  $Na^+$  in soils decrease soil microbial biomass and facilitate invasion of salt-resistance species of plants (Yan & Marschner 2012, Eremchenko & Lyman' 2007, Khayrulina 2015).

Some soil-change processes are associated with saline water-logging in seepage areas developed because of rising of water tables. In seepage areas bare soils acquired reddish-yellow iron-rich precipitates on their surface. This processes is described for arid ecosystems (Salama, Otto & Fitzpatrick 1999) High content of sulfates in the saline waters and microbiological activities lead to hydrogen sulfide settings in the soils. Mineralogical analysis of the upper soil horizons (0-3 cm depth) showed that the maximum total content of iron minerals was 84.9%, ferruginated plant - 20% (in the insoluble part of the samples). In the lower soil horizons (3-30 cm depth) hydrogoethite content reached up to 84% in the insoluble part of the sample. Other iron minerals (hematite and magnetite) were indentified. Source of iron in the soils is the iron-enriched rocks and saline ground water. The presence of dead trees in bare seepage areas was observed that this processes have been developing recently.

### Conclusion

The system of complex environmental monitoring including hydrochemical, soil and biological monitoring in terrestrial and aquatic ecosystems revealed that the most damage of soil and water salinization were caused by drainage water filtration into groundwater. Saline groundwaters spread high concentrations in  $Na^+$ ,  $Cl^-$ ,  $K^+$ ,  $SO_4^{2-}$ ,  $Mg^{2+}$  and pollute streams and soils in river valleys. The

salt pressure on terrestrial and aquatic ecosystems changed the species composition of vegetation for salt-resistant and decreased microbial communities.

Sulphurous settings in soils are formed with iron-rich precipitates on the surface of soils in areas of saline groundwater discharges. Appearance of reddish-yellow iron-rich precipitates may indicate increasing of polluted ground water zone.

### **Acknowledgements**

This project was funded partly by Russian Fund of Basic Research 15-05-07461.

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