Transformation of Trace Element Composition of Fresh Natural Waters in the Central Part of Upper Kama Potash Deposit

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Abstract

Potash salts primarily used in the manufacturing of potash fertilizer are an important and highly valuable commodity in our modern economy. This study includes analysis of trace element composition of fresh natural waters (rivers, springs) in the area of the Upper Kama potash deposit. Indicators of the change in the trace element composition of water affected by potash mine effluents were determined. The results of the study will allow a more comprehensive approach to environmental monitoring and to a list of environmental protection measures in such regions.

Keywords: groundwater, surface water, chemical composition, potash deposits, techno-genesis, geochemical indicators

Introduction

As with all mining activities, the extraction of potash has the potential to cause a change in the composition of natural water. The influence of potash ore deposits on the chemical composition of fresh water has been identified in the beginning of the XX century. Since the 1860s, the activity of potash mines in Germany has resulted in contamination of drinking water in the Weser River and some other rivers in the Rhine basin (Rauche 2015).

The chemical composition of fresh surface water and groundwater is studied in all regions, manufacturers of potash fertilisers. The goal of these studies is to ensure drinking water safety and quality control. These studies revealed the following changes in the water composition: an increase in TDS, total hardness, and concentrations of major anions and cations (e.g., sodium chloride, potassium chloride). These changes occur naturally when salts anmd their products are dissolved. However, analysis of the trace element composition of surface water and groundwater often remains beyound the scope of research.

It should be noted that the most substantial change in the composition of fresh water occurs in areas with humid climate conditions. The high humidity and surface disposal of soluble wastes contribute to the transformation of the hydrosphere. At the same time, the largest potash deposits, which are currently being developed, are located in such regions. These are Canada (Saskatchewan), Russia (Perm Region), Belarus, and Western Europe (U.S. Geological Survey 2018).

Let us briefly consider the results of trace element studies of natural waters and wastewater from a variety of potash ore deposits.

Studies on the composition of wastewater from waste storage facilities, as well as their further effect on the composition of groundwater were conducted on the example of Upper Kama potash deposit (Khayrulina & Maksimovich 2012; Khayrulina 2014). They revealed the extremely high concentrations of sodium and potassium chlorides and elevated contents of a wide range of trace elements (Sr, Mn, Pb, Ba, Cr, Zn, Li, and V).

Bachurin (2007) presents the data on potentially toxic metal contents in anthropogenically-generated wastewater at the mining sites of the Urals. He showed that the concentrations of the following elements (Mn, Fe, Pb, Zn, Co, Ni, Cu, and Cr) in wastewaters generated at the Upper Kama potash deposit are much higher than the background.

Similar results were obtained for groundwater in Spain, Germany, France and other countries (Otero & Soler 2002). This study presents the results of wastewater and natural water monitoring in the Llobregat River basin in the north-east of Spain. Among trace elements, strontium is present in high concentrations, whille manganese, zinc, copper and lead are present in elevated concentrations. Studies of the composition of natural waters were carried out in the Upper Rhine region, where the potash mines of Alsace have been operated for a long time (Bauer et al. 2005, Durand et al. 2005, Lucas *et al.* 2010). Rubidium, strontium and barium are found in the trace element composition of waters from this area. Similar data were obtained for Thuringia, Germany (Siefert *et al.* 2006).

We investigated the hydrochemical influence of the potash mine at the Upper Kama deposit (Belkin 2018). The work summarizes the data on monitoring of the groundwater chemical compositionin in the area slated for development, and the data on multi-year monitoring of springs in the vicinity of existing enterprises. Comparison of the average chemical compositions of natural and wastewaters using statistical methods showed substantial changes in the composition of waters. The major ion composition of groundwater is enriched in chlorides, bromides, sodium, potassium, calcium, magnesium and ammonium cations. Hydrochemical indicators of microelemental changes are manganese, cobalt, arsenic, vanadium, nickel, antimony, barium, strontium, and selenium.

The results of this work confirmed the potential effect of potash fertiliser production on the trace element composition of fresh natural waters, which has been identified during monitoring (Belkin 2018) at specific natural sites. A total of 11 groundwater samples from springs were studied. In addition to groundwater sampling, surface water samples were taken from the Usolka River.

Study area

The Upper Kama potash deposit, located in the Perm Region, is an important global resource due to its large size. The study area located in the central part of the field, in the vicinity of Solikamsk, in the middle and lower reaches of the Usolka River (fig. 1). Potash mines under operation are located on the left bank of the river, while on the left bank any major production facilities are absent. The main aquifer in this area is the Upper Solikamsk subformation (P_1sl_2)> it is represented by terrigenous-carbonate rocks (limestones, marls) and is extensively used for water supply. The Sheshma aquifer (P_1šš) represented by sandstones, clays, siltstones, and mudstones occurs locally. Groundwater has a salinity of 0.2-0.5 g/L, the predominant ions are bicarbonates and calcium.

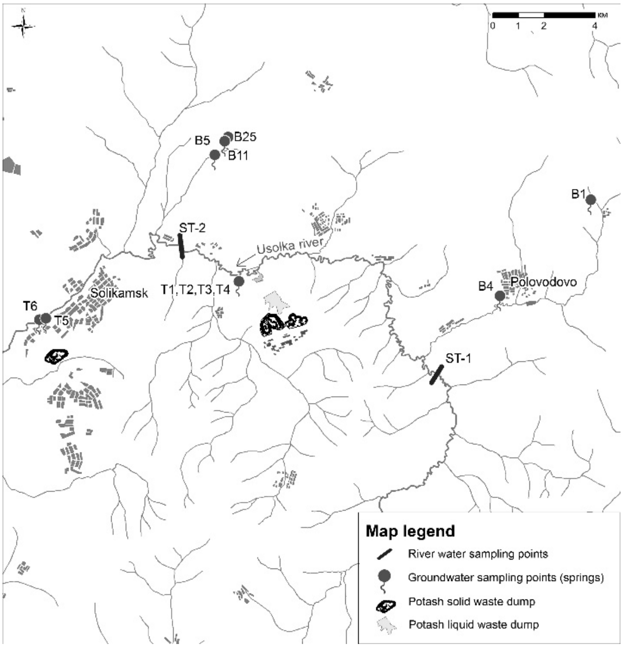

Figure 1 *Schematic map of the central part of Upper Kama potash deposit with surface water and groundwater sampling localities.*

Methods

Surface water and groundwater samples were taken in March 2018. The study of natural waters not affected by potash mining was carried out in springs on the right bank of the Usolka River. Springs B1, B5, B11, B25 are confined to the Upper Solikamsk terrigenous-carbonate aquifer (P_1sl_2), spring B25 is confined to the Shesha aquifer (P_1šš). Groundwater is fresh (0.4-0.5 g/L TDS), of a calcium-bicarbonate type. Surface water samples (ST-1) were collected 9 km upstream of the plant (fig. 1).

Water samples collected from the area affected by potash mining activities were taken in close proximity to waste disposal facilities. Two groundwater discharge zones were studied. The first zone is located 800 m northwest of the potash liquid waste storage dam. The zone comprises a group of five springs (of which four were sampled). Springs discharge on the southeastern side of the man-made lake. The second zone comprises springs discharging on the left bank of the Usolka River, in the town of Solikamsk. Two springs were sampled at a distance of 1000-1200 m from the salt dump. Surface water sampling (ST-2) is carried out 2 km downstream of the plant (fig. 1).

The trace element composition (Li, Be, B, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Rb, Sr, Zr, Mo, Ag, Cd, Sn, Sb, Cs, Ba, W, Tl, Pb, Bi) of water samples was analyzed by inductively coupled plasma mass spectrometry (ICP-MS).

The change in the concentration of each trace element in the composition of groundwater is analyzed by comparing the element concentrations with its background value. Due to the similar chemical composition of all sampled springs, the arithmetic mean of the analyzed samples is taken as a reference background. The data were compared with the results of groundwater monitoring (Belkin 2018). Changes in the concentration of each trace element in surface water were quantified by comparing its content in the background sample (ST-1) and that in the sample taken downstream of the mining sites (ST-2).

Results and Discussion

The results of comparison between trace element concentrations in surface water and groundwater samples collected in the study area are given in Table 1. We determined the concentrations of trace elements present in concentrations higher than the background value (groups "sharp increase" and "significant increase") and the concentrations of trace elements not related to the effect of potash mining (groups "slight incrrease", "no increase or decline"). The elements shown in bold are those present in elevated concentrations in surface water and groundwater sample, according to the 2018 monitoring and summary of monitoring data.

Analysis of the data revealed the following patterns. A sharp increase in the element concentrations in natural waters is typical of a limited number of elements. *Arsenic, barium, rubidium, strontium,* and *titanium* show the most significant increase. This set of elements is typical of both surface water and groundwater. Boron, cobalt, gallium, germanium, lithium, and nickel also show a significant increase in their concentration (from 2 to 8 times). The concentrations of manganese, which increases substantially in groundwaters affected by potash mining, remains almost unchanged in surface waters. This can be explained by the geochemical

Table 1 *Grouping of trace elements by the degree of change in concentration*

	Sharp increase (> 8 times)	Significant increase (2-8 times)	Slight increase (< 2 times)	No increase or decline
Groundwater (monitoring)	**As, Ba, *Mn*, Rb, Sr, Ti**	**B, Co, Ga, Ge, Li, Ni**, Sb, Se, V, Zn	Be, Bi, Cd, Cr, Sn, Tl, Zr	Cs, Cu, Mo, Pb, W
Groundwater (2018)	**As, Ba, Rb, Sr, Ti**	**B,Co**, Cu, **Ga, Ge, Li, *Mn*, Ni**	Be, Cd, Cr, Se, Sn, Tl, V, Zr	Bi, Cs, Mo, Pb, Sb, W, Zn
Surface waters (Usolka River, 2018)	**As, Ba, Rb, Sr, Ti**	**B,Co, Ga, Ge, Li, Ni**	Cd, Cr, Cu, Mo, Se, Tl, W	Be, Bi, Cs, Mn, Pb, Sb, Sn, V, Zn, Zr

mobility of this element in different environments.

The results of groundwater studies conducted in March 2018 using a single sampling and single laboratory analysis method confirmed the previously identified set of specific trace elements characteristic of natural waters in the potash mining area. In addition, the study of the surface waters of the Usolka River shows that the same set of elements is also present in river waters.

Conclusions

A series of specific components determined in this study is consistent with the elements, indicators of the effect of potash mining activities on the chemical composition of natural waters presented in Belkin & Kataev (2018). Studies showed that the same elements are found both in grounwaters and surface natural waters in the area affected by potash waste storage facilities.

Therefore, the results of the study were used to assess and identify a number of trace elements in natural waters, the concentration of which is influenced by potash mining activities. This indicates the need to add the environmental monitoring programs for these areas with the analysis of trace element composition of water and to take into account the possibility of their high concentrations in implementation of environmental protection measures.

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