Long-Time Effect of Ancient Salt Production (Perm Krai, Russia)

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Abstract

On the territory of the outflow of ancient brine wells in the valley of the Usolka River, soils and vegetation, transformed under the long-term impact of highly mineralized waters on the soil pore, were studied. Brines from ancient brine-lifting wells flow in streams along the soil surface and flow into the Usolka River determining its Na-Cl composition. The study area is characterized by the presence of salt-tolerant plants. Long-term influence of sodium-chloride waters on alluvial soils of the Usolka River led to the formation of a secondary gley sulfate-chloride solonchak (Gleyic Fluvic Solonchak (Loam, Salic)).

Keywords: Salinity, Gleyic Fluvic Solonchak, Brine Wells, Halophyte, Terrestrial and Aquatic Ecosystems

Introduction

In Perm Krai (Russia) salt has been mined for about 500 years. For 400 years salt had been extracted from brine wells. Some of these wells exist to this day. Activization of karst processes leads to entry of saline ground water through the wells onto the earth surface (Kharitonov 2015). Verkhnekamskoe Potash Deposit opened only 90 years ago. Potash ores are extracted mainly by underground mining methods. The territory of the Verkhnekamskoe Potash Deposit territory has the current anthropogenic impact of potash mining is combined. Research of environmental consequences of ancient brine production allows determining long time influence of salinization on terrestrial and aquatic ecosystems.

The impact of highly mineralized waters on the ecosystem leads to a change in the chemical composition of surface water and groundwater, which affects the soil cover in their physical and chemical properties (Hulisz *et al*. 2013; Salama *et al*. 1999), the composition of vegetation with the change of native plant species to salt-tolerant ones, to the extent of halophytes emergence (Lavrinenko *et al*. 2012; Piernik *et al*. 2015; Sommer *et al*. 2020).

Ancient brine wells have retained their influence for a long time and determined salt-tolerant terrestrial and aquatic ecosystems. This research can help to forecast anthropogenic impact of potash mining.

The purpose of this work is to study properties of alluvial soils of the Usolka River valley in the area of influence of brine wells and to investigate the soil-forming process and the vegetation cover.

Study area

The studies were conducted in the north-east of the central part of Perm Krai in the Aleksandrovsky District on the territory of one of the first Russian settlements with the production of salt, Yaivinsky ostrozhok, founded in 1570, where a group of five historical wells in the Usolka River valley persist to this day (Khayrulina *et al*. 2017). Salt mining was carried out on the south-eastern periphery of the salt deposit and outside the potash deposit outline of the Verkhnekamskoe salt deposit (Fig. 1). Geologically, the study area is located in the Cis–Ural foredeep, in the southern part of the Solikamsk depression, within the Ust–Igumsky salt swell.

Natural outlets of saline waters in the Usolka River valley contributed to the active development of salt industry. Brine mining was carried out from a depth of 30–40 m with brine pipes. Salt production in the Usolka

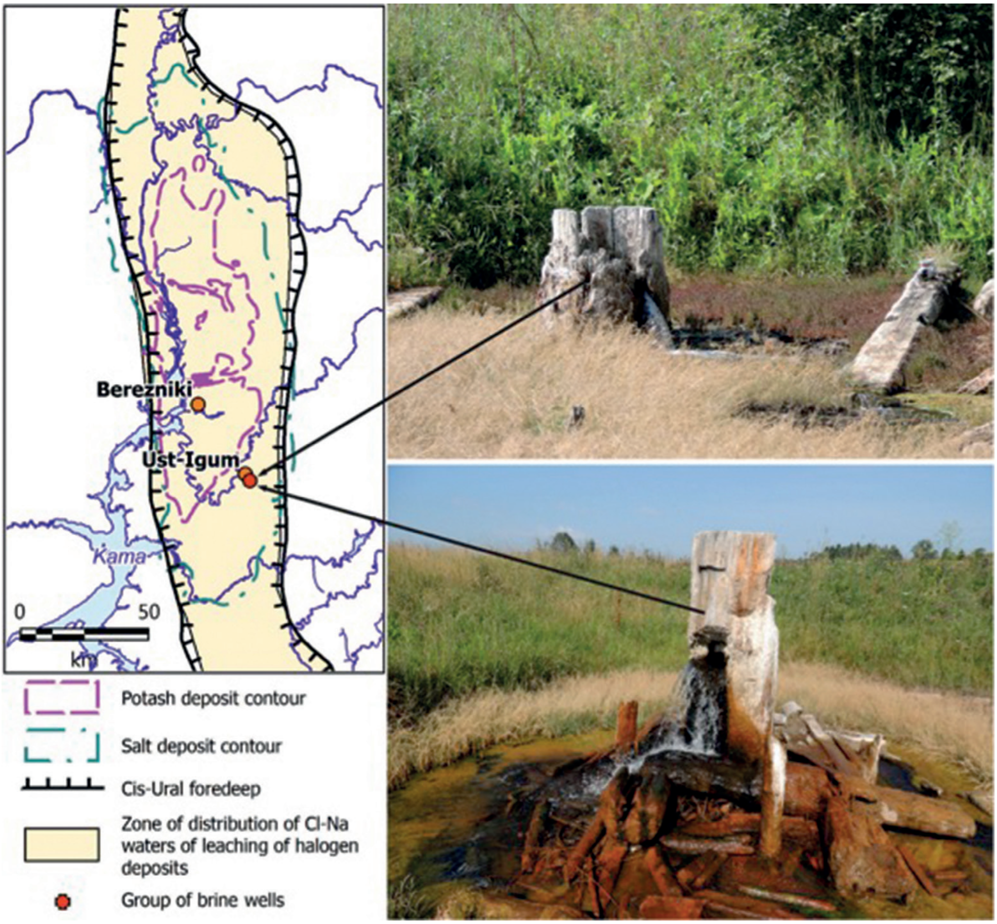

Figure 1 Distribution of potash and salt deposits of the Verkhnekamskoe salts deposit and location of objects of observation (images: E.A. Khayrulina).

River valley was stopped in the 18th century. The study area is significantly remoted from industrial enterprises and settlements that excludes modern anthropogenic influence.

Methods

Five wells are located on a floodplain terrace 80–120 m from the Usolka River. Sampling of water from brine-lifting wells, streams and rivers was carried out in 2015, 2016 and 2017. In water, the following criteria are determined: pH – by potentiometric method, HCO_3^- – by titration method according to GOST 31957-2012; Fe_{total} – by photometric method; Cl^-, K^+, SO_4^{2-}, Ca^{2+}, Na^+, Mg^{2+}, NO_3^-, NO_2^- – by capillary electrophoresis using Kapel-104 (Russia); dry residue – by gravimetric method according to PND F 14.1: 2: 4.261-10; mineralization – by calculation method; specific electrical conductivity – using conductometer Hanna HI 8733 (Germany).

Soil samples were taken in the floodplain of the Usolka River in 2016 at a distance of 15–20 cm from the channel of a salty stream pouring out from brine-lifting wells. The soil types were determined according to World Reference Base for Soil Resources (World reference base 2015). Physicochemical research of soils included (Theory and practice 2006; Mineev 2001): determination of organic matter according to Tyurin; determination of pH_{H_2O} and pH_{KCl} using potentiometric method according to GOST 26483-85; determination of hydrolytic acidity using Kappen method; determination of exchangeable cations using Kappen-Gilkowitz method; determination of the cation exchange capacity (CEC) in carbonate samples using the barium chloride method; determination of mobile potassium using flame photometry; the quantity and quality of soluble salts was determined in water extractions: Na^+ and K^+ – using flame photometry; Cl^- – titration with silver nitrate; Ca^{2+}, Mg^{2+} – by trilonometric method; the amount of sulfate ions was calculated as a difference between the amounts of cations and anions; the amount of toxic salts – using the calculation method. The sodium adsorption ratio (SAR) was used to isolate sodium soils; SAR is the ratio of the concentration of Na^+ to the square root of the sum of Ca^{2+} and Mg^{2+}. Agrochemical properties are determined only in the surface layers. The content of water-soluble ions was determined throughout the soil profile.

Result and Discussion

At the present stage, mineralization of the waters pouring out from the wells is 30–34 g/L for the brine-lifting wells of the Yaivinsky ostrozhok; chloride and sodium ions prevail; the flow rate of the wells is 0.009–0.011 m^3/s. The chemical composition of the waters of the brine wells was stable. The content of Cl^- in brines exceeded the MPC (Maximum allowable concentration) by 49 times and reached 14700 mg/L, while the content of Na exceeded the MAC by 82 times and amounted to 9800 mg/L (Table 1). Outflows of wells form hydromorphic conditions in the area of the floodplain terrace and flow into the Usolka River in the form of two streams.

The inflow of brines into natural waters transforms the Ca^-HCO_3 composition of rivers into Na^-Cl composition. Mineralization of water in rivers, into which saline underground springs are discharged, is much lower due to dilution with fresh waters and amounts to 1.2–1.3 g/L. The predominance of Na and Cl in the chemical composition of the Usolka River waters above the influx of well outflows indicates the presence of salt sources that we have not yet discovered.

As a result of long–lasting inflow of highly mineralized groundwater onto the surface from brine wells of the Yaivinsky ostrozhok, in the floodplain of the Usolka River, a secondary gley humus solonchak with a sulfate-chloride sodium type of salinity (Gleyic Fluvic Solonchak (Loam, Salic)) was formed. The examined secondary solonchak was formed from the alluvial humus gley soil typical of floodplains of taiga landscapes, the upper horizon of which is characterized by heavy granulometric composition, a weakly acidic or acidic reaction of the soil medium, and a low adsorption capacity (Vasiliev *et al*. 2014).

In the profile of the studied secondary solonchak, we identified three horizons: solonchak, gleyed, and alluvial rock. S[AYg] – solonchak horizon, 0–45/45 cm, with signs of gleying; Gs – gleyed horizon, 45–95/52 cm, dark-gray-glaucous, with an emerging prismatic structure; at a depth of 80–90 cm, we found decaying wood and stones. Cgs – alluvial gley rock, occurring from a depth of 95 cm, light gray-glaucous; moist, structureless with a smell of hydrogen sulfide.

In the surface soil layers (thickness of layer 10 cm) of three different pits of the solonchak, the content of organic carbon varied from 0.9 to 2.9%, the neutral and slightly alkaline reaction of the soil is explained by the influx of sodium chloride water from the brine wells. The studied solonchaks are characterized by an average adsorption capacity of 25.2–36.3 mmol/100 g (Table 2), which is typical for alluvial soils and, seemingly, is associated with low values of organic matter. The amount of mobile potassium compounds varied from

Table 1 *Chemical composition of surface waters in the area of outflowing brine wells.*

Sampling site	pH	Content, mg/L								
		HCO_3^-	SO_4^{2-}	Cl^-	Ca^{2+}	Mg^{2+}	Na^+	K^+	Fe_{total}	TDS
MAC	6,5–8,5	–	100	300	180	40	120	50	0,1	–
Wells	7,08	285	3176	14732	1179	12	9886	26	1.4	29417
The Usolka River	8,1	222	161	492	94	17	352	1.4	–	1342

***Table 2** Agrochemical properties of solonchak.*

Soil name	№	Layer, cm	C_{org}, %	pH_{H2O}	pH_{KCl}	CEC mmol/100 g	K_{HCl} mg/100 g	SAR
Gleyic Fluvic	1	0–10	2.88	7.15	7.06	36.3	12.5	13.8
Solonchak (Salic,	2	2–12	2.9	7.72	7.16	25.2	50	19.8
Loam)	3	2–12	0.9	8.2	7.59	29.6	50	17.9

12.5 to 50 mg/100 g; it appears that this is due to the supply of potassium from the waters of brine wells.

The maximum content of toxic salts – 1.1% – was noted in the 0–10 cm layer and 1.2% – in the 100–115 cm layer; the minimum amount of toxic salts – 0.55% – was noted in the 27–40 cm layer. The amount of toxic salts indicates a high degree of soil salinity; the surface soil layer was characterized by chloride sodium type of salinity, from a depth of 11 cm – by sulfate-chloride sodium type; from a depth of 60 cm, sulfate ions and sodium cations prevailed (Fig. 2), which is associated with a change in the prevailing anions in the water extract from soil. The waters of the brine wells with chloride type of salinization determined the chemical properties of the soil profile.

We noted the highest content of Cl^- and Na^+ in the 0–10 cm layer – 613 and 425 mg/100 g of soil, respectively; the content of Cl^- decreased by 1.5–2.3 times with the depth of the soil profile; the content of Na^+ also decreased with depth by 1,4–2 times, but at a depth of 100–115 cm it increased to the surface horizon values (Fig. 2). We observed the highest content of Ca^{2+}, Mg^{2+} and SO_4^{2-} in the solonchak in 100–115 cm layer; it amounted to 91, 10 and 609 mg/100 g, respectively. We found gypsum at a depth of 60 cm. The formation of gypsum can be associated with exchange reactions in soil as a result of the interaction between calcium of the soil adsorption complex and sulfate–sodium solutions (Yamnova *et al.* 2013). As a result of the impact of salt water on the surface layer of the soil, at a depth of 27–40 cm, we observed a minimum content of almost all ions.

The sodium adsorption ratio (SAR) for the surface layer of sample 1 (0–10 cm) is 13.2, the highest value of the ratio – 17.1 – was observed in the 11–21 cm layer, the lowest SAR value – 12.8–11.2 – at a depth of 60–115 cm. In the surface layers of samples 2 and 3, SAR values were 19.8 and 17.9, respectively. SAR values over 13 indicate a significant

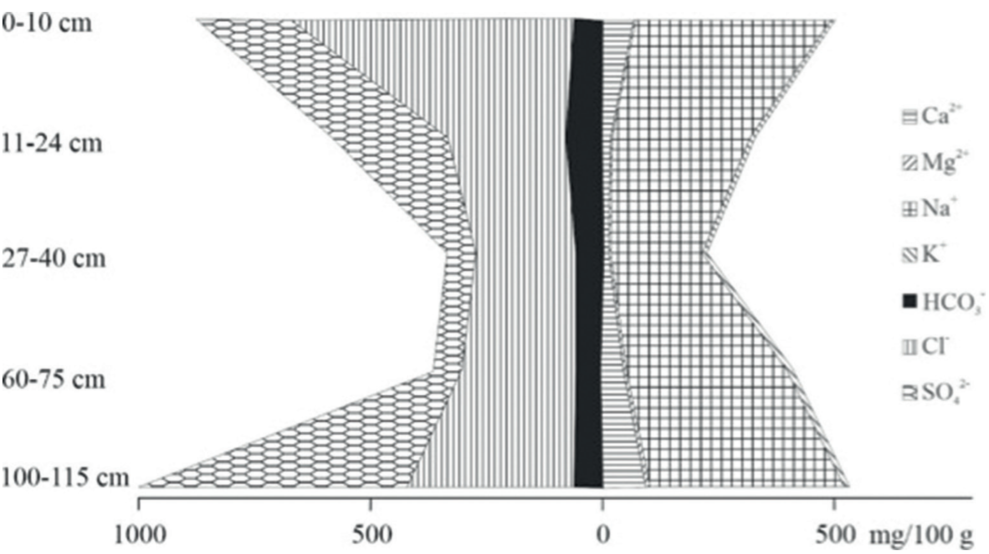

***Figure 2** Salt profile of solonchak.*

proportion of sodium in the soil adsorption complex and a soil alkalinization.

The content of water-soluble sodium and the sodium adsorption ratio (SAR) in solonchak indicated the transition of sodium into the soil adsorption complex; sodium, displacing other cations, mainly calcium and magnesium, from the soil adsorption complex, contributed to the deterioration of the physicomechanical properties of the soil, which caused its viscosity, stickiness, lack of structure in the wet state and firmness in the dry state.

The secondary solonchak is formed from alluvial soil that is quite mature. The main soil-forming factors in solonchak formation in the valley of the Usolka River in the brine outlet area were saline waters, relief, climate and the duration of the brine impact on the soil cover. Despite the fact that saline waters are classified as eventual soil-forming factors, in our study they were the main cause of the emergence of solonchaks. However, in spite of the genetic and chemical changes in the soil, with the limitation or complete absence of the influence of brines, the soil evolution can go the opposite way, desalinization of saline soils will occur, the soil will again become alluvial humic.

The vegetation cover of the study area is represented by species associated with floodplain meadow landscapes. The floodplain tallgrass of the study area includes meadow fescue *Festuca pratense* Huds., alsike clover *Trifolium hybridum* L., common yarrow *Achillea millefolium* L., meadow vetchling *Lathyrus pratensis* L., cock's-foot *Dáctylis glomerata* L., timothy-grass *Phleum pratense* L. meadow buttercup *Ranunculus acris* L., autumn hawkbit *Leontodon autumnalis* L., smooth meadow-grass *Poa pratensis* L., garden angelica *Angelica officinalis Hoffm*., meadowsweet *Filipendula ulmaria* (L.) Maxim, parsnip *Pastinaca sylvestris* Mill. The plant community is represented mainly by salt tolerant plant species.

High salinity of soils along the salty stream led to the appearance of glasswort *Salicornia perennans* **WILLD**. It belongs to the group of obligate halophytes with the highest resistance to salts that grow well and develop on saline soils, absorb a large amount of salts from the soil.

Usually, halophytes grow on highly saline soils on the sea coasts, along the shores of salt lakes. Halophytes form red "glades" and "paths" in places where highly mineralized waters are discharged; in this case, they grow along the banks of a stream formed by the waters of ancient brine wells. In a humid climate with a leaching water regime, the appearance of halophytes is possible with a long-term impact of saline waters on soils; most often this process has anthropogenic origin.

The distribution area of the obligate halophyte Salicornia perennans Willd in Perm Krai is local. Currently, we are working on creating a natural monument to protect this ecosystem, which comprises brine wells, soils and vegetation.

Conclusions

As a result of long-term unloading of ancient brine wells in the floodplain of the Usolka River, in the area of alluvial gley humus soils, secondary solonchak with sulfate-chloride sodium type of salinization was formed. In Perm Krai, due to the humid type of climate and leaching water regime, the formation of saline soils is associated only with the natural discharge of saline springs in floodplains of rivers in areas of salt mass bedding, as well as with the consequences of the industrial extraction of potash salts.

In addition to transformation of the soil cover of the Usolka River valley, there was a change in the ionic composition of natural waters of the Usolka River, a change in plant species to more salinization resistant: in the immediate vicinity of the streams flowing from the wells, the obligate halophyte Salicornia perennans Willd appeared, which is a plant unique for Perm Krai.

Ancient brine wells have retained their influence for a long time and determined transformation of terrestrial and aquatic ecosystems. This research can help to forecast ecosystem changes due to potash mining influence.

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