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Article

Properties of Alluvial Soils of Taiga Forest under Anthropogenic Salinisation

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Abstract: The environmental impact of deposit development can be indirect and can cause combined geochemical processes in ecosystems. These must be taken into consideration under environmental forecasting and environmental risk assessment. Soil degradation in the Taiga Forest is considered, within the area of Verkhnekamskoye potash deposit (Russia), as an example of such environmental transformation. Here, the mechanism and characteristics of the anthropogenic salinisation of alluvial soils under potash deposit development are newly described. It was found that there is a strong anthropogenic impact of the potash industry on valley soils where the contaminated Na-Cl groundwater discharges or is close to the surface. The valley soils are characterised by high salinity, and the sum of toxic salts in soils has reached 26%. Alluvial gley humic clay chloride saline soil (Gleyic Fluvisols (Salic, Loamic, Technic)) and secondary solonchak on alluvial humic clay soil sulphate-chloride gypsum-containing surface-gleyed (Chloridic Gleyic Fluvic Solonchak (Hypersalic, Loamic, Technic)) were formed in hydromorphic conditions. Morphological, physicochemical and mineralogical analyses were carried out. Under hydromorphic conditions, Chloridic Gleyic Fluvic Solonchak (Hypersalic, Loamic) was described to show a hydrotroillite layer and reddish-yellow iron-rich precipitates on its surface. The top soil horizon has the highest content of iron minerals (up to 84.9%) and Fe-bearing plant residues (up to 20%). Additionally, the spongy and gel-like organic materials, as well as the siliceous remains of diatoms, are enriched in Ca, Fe, Cl, K, Na, S and P. The lower soil horizon consists of black gel-like phases and hydrogen sulphide settings with a high content of plant residues. The insoluble part of the samples contains up to 84% hydrogoethite. The sources of iron in soils and bottom sediments include the iron-enriched Sheshma sediments speckled rocks, slurry material, halite wastes and soil minerals of alluvial gley soils.

Keywords: potash mining; soil salinity; sulfidisation process; Fe-bearing minerals; leaching; ion exchange processes

1. Introduction

Environmental risk assessments of potash mining usually describe the anthropogenic salinisation of groundwater and surface water. The problems of brine distribution in groundwater and surface water were researched by reference [1,2] in Germany, reference [3] and reference [4] in Russia. These studies discovered saline drainage filtrations of slurry storage facilities and salt tailing piles into ground water and discharges of saline groundwater into local river valleys.

The interaction of saline drainages with rocks was studied by reference [5] in the Verkhnekamskoe potash deposit in Russia and reference [6] in the Upper Rhine Valley in France.

The analysis of soil salinisation is usually combined with vegetation research. Hulisz and Piernik [7] found very high and stable soil salinity values by analysing the electrical

conductivity, as well as the main anion and cation contents in an area affected by post-soda waste. They stated that soil salinisation was linked to the level of saline ground water and some species of halophytes could be indicators of soil salinity. Sommer et al. [8] also analysed electrical conductivity, as well as main anion and cation contents in soils in order to describe the holophilic algal communities near potash tailing piles in the Lower Saxony and Saxony-Anhalt regions (Germany). The general environmental issues related to the potash industry in Belorussia—including soil salinisation—were described by G.A. Kolpashnikov et al. [9] and V.S. Khomich et al. [10].

However, an increase in salt content in soils, groundwater and surface waters can cause different geochemical processes associated with water–rock interactions, such as element leaching, ion exchange, secondary mineral formation, etc. These processes have been described in arid ecosystems. For example, accumulation of iron-bearing minerals in soils in seepage areas and hydrogen sulphide settings in soil were generally described by A.I. Perel'man and N.S. Kasimov [11] in the Caspian lowland, and by R. Fitzpatrick el al. [12] and R.B. Salama et al. [13] in Australia.

The transformation of geochemical processes during anthropogenic soil salinisation was researched by V.S. Khomich [14]. Via a landscape–geochemical analysis near a slurry storage facility in Belorussia, V.S. Khomich described the appearance of hydrotroillite at a soil depth of 45–90 cm as a result of SO_4^{2-}-Na^+ drainage pollution.

We predict that soil salinisation in areas affected by the potash industry is a result of the complex interactions of waste, drainage water, groundwater, rocks and soils, which not only causes an increase in the content of salts, but also other elements, in addition to the formation of new soil conditions.

Research into geochemical processes was carried out in the territory of the Verkhnekamskoe potash deposit in Russia (Figure 1), where soil salinisation occurs due to the influence of potash mining. Soil salinisation has been identified in the area that is affected by the sludge storage and salt dumps of the Verkhnekamskoe potash deposit, and bare soils have acquired reddish-yellow iron-rich precipitates on their surface [15]. The presence of brines in the slurry storage facility and salt tailing piles represents the most serious environmental issue in potash mining regions.

Figure 1. Geographical location of the Verkhnekamskoe potash deposit.

The main goal of this study is to identify the physicochemical properties of saline soils and mineral formation and to describe the main causes of iron leaching from rocks and soils and hydrogen sulphide settings in the Taiga Forest. The study focuses on two types of soils that were observed in the Lyonva River valley, with different salt contents. Based on field observations, in addition to geochemical and mineralogical analyses, we hypothesised that saline ground water not only causes soil salinisation, but also causes

iron leaching from rocks and soils, iron mineral accumulation on the surface of soil, and hydrogen sulphide deposition in soil.

2. Materials and Methods

2.1. Site Description

The Verkhnekamskoe potash deposit is located on the left bank of the Kama River in Russia and has an area of about 6.5×10^3 km^2 (Figure 1). The ore contains between 18 to 34% KCl [16]. The geological reserve of carnallite is about 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.

The Verkhnekamskoe potash deposit has solid (more than 500 m in depth) salt strata with layers (from bottom to top) of underlying rock salt (URS) (320–400 m), potash deposits (70–100 m) and covering rock salts (CRS) (20 m). The salt stratum is underlain by clay–anhydrite deposits (200–220 m) and covered with salt-marl (SMS) and terrigenous-carbonate (TCS). A set of salts is related to the Iren horizon of the Kungurian strata of the lower Permian System [17]. The lens-shaped salt strata of the deposit acts as a regional aquiclude, dividing the supersalt and subsalt waters [17].

Active water exchange occurs in the upper part of supra-salt strata. The speckled (SS) and quaternary (Q) deposits are particularly vulnerable to potash mining activities [18].

The main source of the environmental pollution in this mining area is uncontrolled discharge of drainage waters of salt tailing piles and salt–clay slurry storage, which were constructed 50–90 years ago. Currently, more than 270 million tons of halite waste and 30 million m^3 of salt–clay slime have accumulated in the territory of the Verkhnekamskoye potash deposit [19]. Halite waste with over 90% NaCl is typically placed in piles, while clay slimes and brines drain into storage facilities (Figure 2). Clay–salt slurry contains 35–40% water—soluble salts and 60–65% insoluble clay materials. Brines have a Na–Cl composition and more than 300 g/L of total dissolved solids (TDS) [19]. The territory of the Verkhnekamskoe potash deposit is affected by seven potash mines (Figure 3).
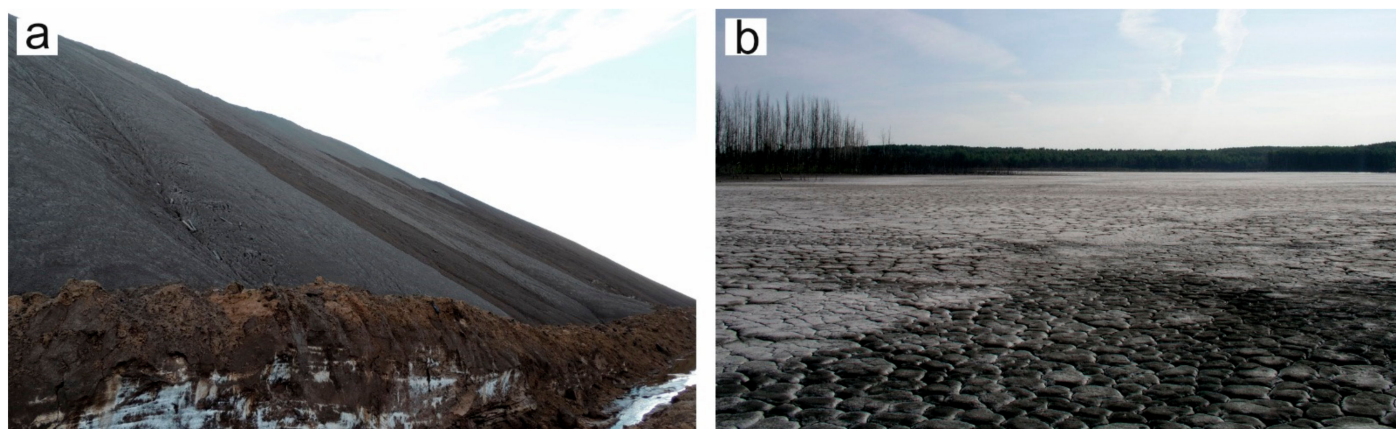

Figure 2. Potash waste storages: (**a**) slurry storage facility; (**b**) salt tailing pile with drainages.

Our studies were carried out in the territory of the Verkhnekamskoe potash deposit in the Lyonva River valley which has two potash mines, slurry storage facilities and salt tailings pile in the Lyonva catchment area. Subsidence processes and karst sinkhole formation have occurred as a result of mining activities in this area [20].

The Lyonva River valley is represented by quaternary sediments (fine alluvial–deluvial sands, loam, eluvial–deluvial clay, gruss–rock and coarse medium gravels) and Permian systems (interlaid siltstones and sandstones). The groundwater of quaternary sediments is found at a depth of 0.0–3.0 m in the Lyonva River valley. The groundwater and surface water are freshwater sources with a salinities of 0.23–0.50 g/L and a calcium—carbonate

composition (prior to mining activities). In the river valleys, according to the Russian soil classification [21], the soils are classified as alluvial grey humic gley [21].
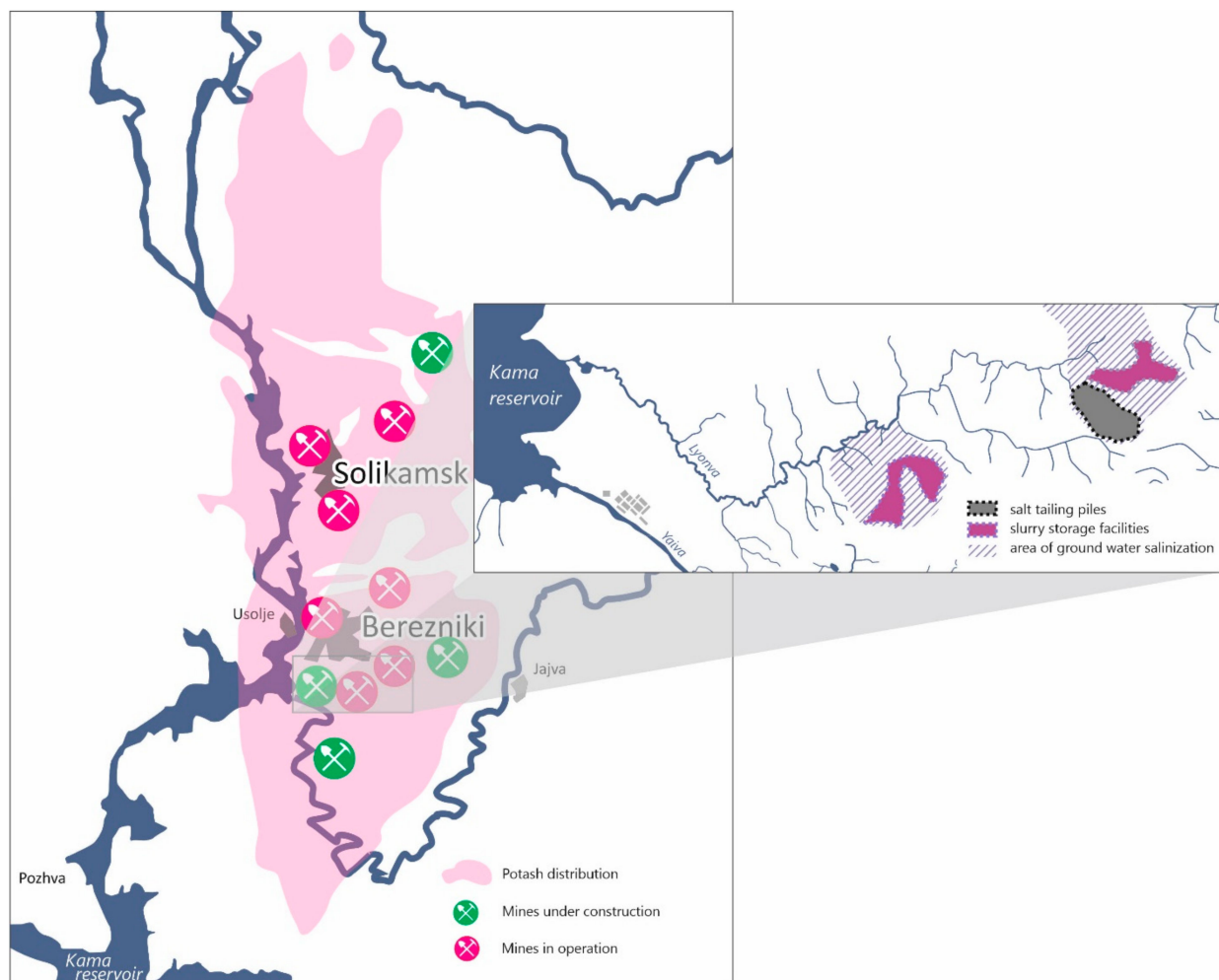

Figure 3. Scheme of the Verkhnekamskoe Potash deposit and research territory.

2.2. Sampling Procedures

Ecosystem degradation due to potash mining was studied during 2013–2016 in the southern part of the Verkhnekamskoe potash deposit. Observations of alluvial soils and their degradations were carried out [22]. For more detailed study, we selected two types of alluvial soils from the Lyonva River valley that represent different influences of saline groundwater.

The soil samples were collected at depths of 0–3 cm (4 samples) and 3–30 cm (3 samples) according to the different horizons and in 2 soil profiles in the Lyonva River valley in July 2016 (Figures 4 and 5). Soil samples were collected and stored in plastic bags.

Sampling of infiltration through the dam of the slurry storage facility was carried out to investigate the chemical composition of drainage water of potash mining wastes. The Lyonva River was studied at 1 km (18 samples) downstream from the slurry storage facility (Figure 4). Water from two springs (11 samples) was taken in the Lyonva River valley (Figure 4) to assess groundwater pollution and its role in soil salinisation (Figure 4). Samples of surface waters and springs were collected four times a year in plastic bottles during periods of low–water levels in December and July and high-water levels in May and October. Additionally, water samples were collected for Fe_t analysis. Water samples for analysis of elemental composition were filtered, acidified with pure HCl and stored in a refrigerator.

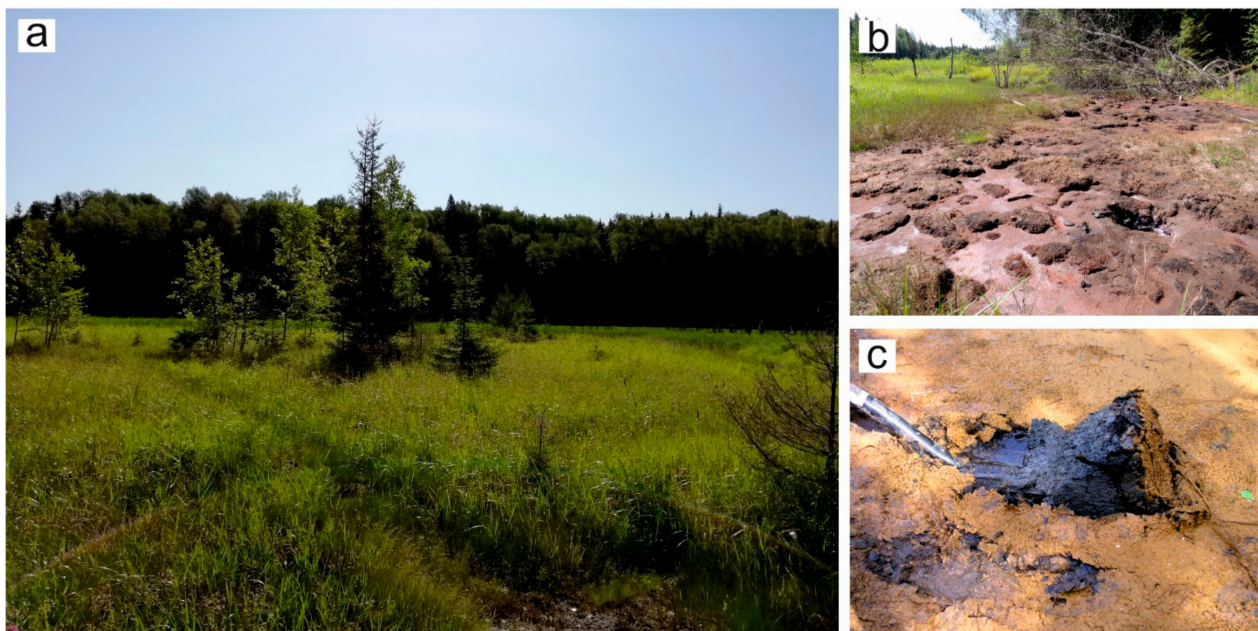**Figure 4.** Locations of water and soil sampling sites.

Figure 5. Soil sampling sites: (**a**) Gleyic Fluvisols (Salic, Loamic); (**b**) Chloridic Gleyic Fluvic Solonchak (Hypersalic, Loamic); (**c**) iron–bearing crust on the surface of the soil and black gel–like phases in lower sulphide horizon of Chloridic Gleyic Fluvic Solonchak (Hypersalic, Loamic).

2.3. Analytical Procedures

Morphological and physicochemical methods were used to assess the ecological state of the soils. Morphological analysis was carried out according to the "Classification and Diagnosis of Soils of Russia" [21].

The soil samples had been air-dried at room temperature for two weeks, then crushed and sieved through a 2 mm screen. This fraction was used for the physicochemical analysis of soils. Soil pH was analysed by a pH–meter [23]. Soil organic matter was determined by the wet-combustion Tyurin method [24]. Soil hydrolytic acidity was determined by the Kappen method, based on treating the soil sample with sodium acetate at a concentration

of 1 mol/L, followed by titration of soil extract with alkaline solution. Exchangeable cations were determined by the Kappen–Gilkowitz method, which is a treatment of soil samples with a certain amount of 0.1 N HCl, followed by titration of soil extracts with 0.1 N NaOH [23]. The cation exchange capacity (CEC) in carbonate samples was determined by the barium chloride method [24]. Mobile phosphates and potassium were determined by the Kirsanov method [24] based on the extraction of mobile phosphates and potassium from the soil with a solution of 0.2 M HCl. Then mobile phosphates were determined as a blue phosphorus–molybdenum complex on a photoelectrocolorimeter and potassium on a flame photometer [25]. Soluble salts were determined in water extractions of soil samples, followed by determination of anions and cations. Carbonates were determined by back-titration with sulphuric acid. The Na^+ concentrations in water extraction were analysed by flame photometer and concentrations of Ca^{2+} and Mg^{2+} were analysed by the titration method with Trilon B (disodium dihydrogen ethylenediaminetetraacetate), and sulphate ions were calculated as the difference between the amounts of cations and anions [24]. H_2S was analysed by the titration method which is based on the oxidation of H_2S with iodine released during the interaction of potassium iodide with $KMnO_4$ [26].

Samples of groundwater and surface water were analysed for NO_2^-, NO_3^-, NH_4^+, Cl^-, K^+, SO_4^{2-}, Ca^{2+}, Na^+, Mg^{2+} by capillary electrophoresis Kapel-104. The pH of the aqueous extract and the HCO_3^- and TDS contents were determined by titration [25].

The soil samples were pretreated by removal of less than 0.01 mm clay fractions with wet preparation. Soil mineralogy was then determined by using a Nikon 104 binocular microscope and XRD using a D2 Phaser desktop diffractometer "Bruker" at the Center for collective use at Perm State National Research University.

The morphology and microstructure of the samples were investigated using a TES-CAN MIRA 3 LMU and LEO 1430VP high-performance, variable pressure, analytical scanning electron microscope (SEM). Energy-dispersive X-ray spectroscopy (EDS; Oxford Instrument X-Max 80 EDS-system) was used for microanalysis of the solid phases viewed by SEM. Microphotography of the sand–aleurite part of a number of samples was carried out using a Leica-MZ-16 microscope.

2.4. Soil Salinity Estimation

The estimation of soil salinity was based on calculating the levels of toxic and non-toxic salts, taking into account the binding of ions in a certain sequence to hypothetical salts, starting with less soluble salts and ending with more soluble ones. First of all, cations and anions of carbonates bind in the following order Na_2CO_3, $MgCO_3$, $Ca(HCO_3)_2$, $NaHCO_3$, $Mg(HCO)_2$; next, with SO_4^{2-} anions in the sequence: $CaSO_4$, Na_2SO_4, $MgSO_4$; last Cl^-: NaCl, $MgCl_2$, $CaCl_2$ [27].

The toxicity threshold is the limiting amount of salts in the soil, above which inhibition of the growth and development of salt resistant plants begins. Toxicity thresholds for individual ions: (mEq/100 g of soil) CO_3^{2-}—0.03; HCO_3^-—0.8; Cl^-—0.3; SO_4^{2-}—1.7 [28]. We used the sodium adsorption ratio (SAR) [29] to determine sodium soils which may be an alternative to the exchangeable sodium percentage of the cation exchange capacity (CEC).

3. Results and Discussion

The rainfall level in the area of the Verkhnekamskoe potash deposit is around 650 mm/year and the average temperature is 0 °C. This climatic condition promotes formation of a clay–salt slurry and halite waste drainage water that discharges into the groundwater. A change in the groundwater composition from Ca–HCO_3 to Na–Cl was observed in close proximity to the slurry storage facility. The highest level of salinisation was detected in the groundwater from quaternary (Q) sediments (up to 26.1 g L^{-1} of Cl) [15]. This aquifer was the most affected by potash mining activities. A part of the drainage water enters into the speckled (P_1ss) aquifers, increasing the Cl content in the groundwater up to 5.3 g L^{-1} [15].

The discharge of contaminated groundwater as springs, as well as areal, subaqueous and surface discharge of high salinity waters in the Lyonva River valley (Figure 6), leads to

the salinisation of previously fresh river and valley water. The water of the Lyonva River has a sodium–chloride composition, neutral pH, and concentrations of Cl^-, SO_4^{2-}, Ca^{2+}, Mg^{2+}, Na^+, K^+, Fe_t (Table 1).
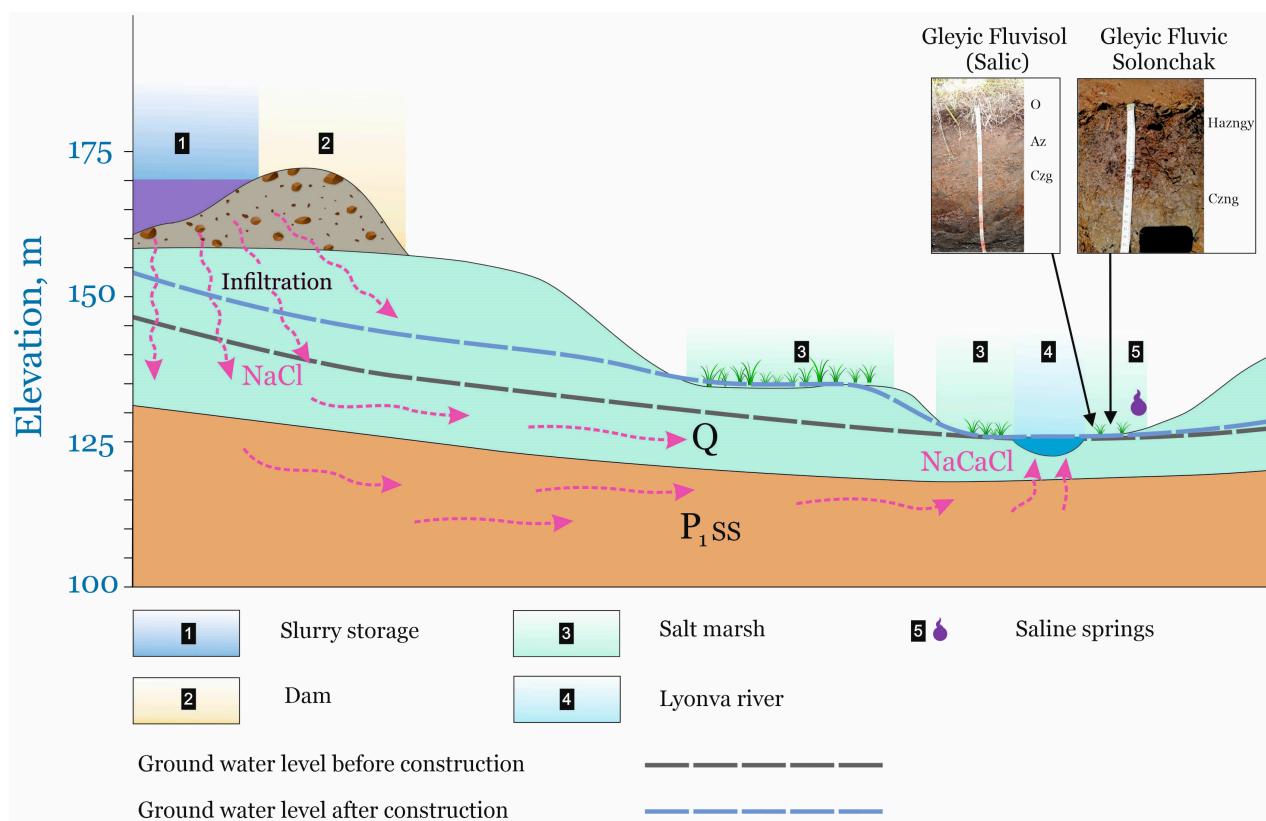

Figure 6. Cross section of the Lyonva River valley illustrating the multi-process formation of saline soils.

Table 1. Water chemistry in the vicinity of the slurry storage site [15].

Components	Infiltration through the Dam of Slurry Storage Site	Saline Spring (Q) in the Lyonva River Valley	Saline Spring (P1ss) in the Lyonva River Valley	The Lyonva River 1 km from the Slurry Storage Site Downstream	MAC
pH	6.9 * 6.3–7.2 **	6.9 6.8–7.0	7.1 7.0–7.1	7.2 6.8–7.7	6.5–8.5
HCO_3^- (mg/L)	341 293–458	153 11.0–186	129 99–148	137 99–174	
SO_4^{2-} (mg/L)	1830 646–4190	374 191–598	106 84–122	600 73–1793	100
Cl^- (mg/L)	33.400 5540–66.700	15.000 6950–26.200	3210 2370–5310	7931 3320–15.290	300
NO_2^- (mg/L)	6.1 0.34–10.3	<0.2	<0.2	3.3 0.1–12.3	0.08
NO_3^- (mg/L)	78.0 15.0–127	27.2 0.2–65.0	25.4 10.8–62.0	15.7 2.8–32.4	40
Ca^{2+} (mg/L)	1530 721–2710	1240 552–2170	418 275–627	1179 561–1593	180
Mg^{2+} (mg/L)	270 146–727	947 117–5190	76 49–116	281 122–383	40
Na^+ (mg/L)	16.700 7060–32.100	6400 2560–11.000	1200 866–1920	3083 781–6422	120

Table 1. *Cont.*

Components	Infiltration through the Dam of Slurry Storage Site	Saline Spring (Q) in the Lyonva River Valley	Saline Spring (P1ss) in the Lyonva River Valley	The Lyonva River 1 km from the Slurry Storage Site Downstream	MAC
K^+ (mg/L)	10,800 5170–23.700	3230 1230–5860	489 339–894	1259 158–4237	50
Fe_t (mg/L)	0.5 0.14–0.98	0.6 0.11–1.38	0.8 0.46–1.38	0.8 0.6–0.9	0.1
NH_4^+ (mg/L)	53.0 5.0–193	16.2 15.3–17.0	<0.5	23.1 0.6–93.5	0.5
TDS (mg/L)	45.000 11.600–77.200	29,400 11.700–46.100	5950 4570–9540	12,888 5294–21.840	1000
Number of samples	10	7	4	18	

Note: MAC—maximum allowable concentration; *—average; **—minimum and maximum values.

The drainage waters entering into the groundwater formed a large saline plume between the storage facility and the river channel. The background groundwater belongs mainly to the Ca–HCO$_3$ water type, in some cases under contact with gypsum—to the Ca–SO$_4$ type [17]. The drainage waters from the dam of slurry storage site affects the groundwater composition: $Na - Cl$ water type, high concentrations of K^+(5.85 g L^{-1}), SO_4^{2-} (0.59 g L^{-1}) and Mg^{2+} (5.18 g L^{-1}) (Table 1).

Another indicator of pollution is the high content of nitrogen compounds in drainage water, groundwater and surface water (Figure 7). The NH_4^+, NO_2^- and NO_3^- concentrations exceeded the maximum allowable concentration (MAC) in groundwater by 400, 128 and 3 times, respectively. High concentrations of nitrogen in groundwater were caused by the presence of a wide range of N–bearing heterocyclic compounds in the tailings that were used as flotation reagents [30].
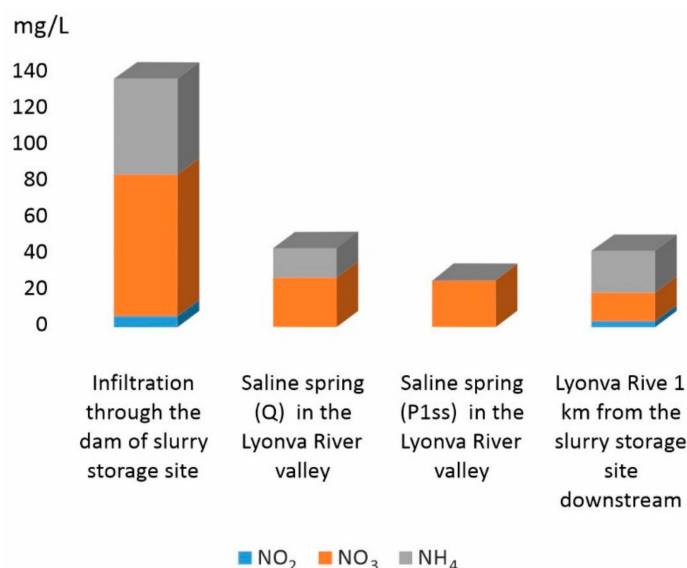

Figure 7. Concentrations of nitrogen compounds in drainage, groundwater and surface water in area effected by slurry storage site.

When saline groundwater meets confining beds, it seeps into the surface in the river valleys and pollutes the surface water (Figure 6). The streams have a Ca–HCO$_3$ water type; the salt-affected streams have Na–Cl and Ca, Na–Cl water types. The chloride concentration in the salt-affected streams exceeds the maximum limit (300 mg L^{-1}) recommended for the protection of freshwater life by more than 20 times. The TDS of the river water ranged from 3.4 g/L to 12.9 g/L, and the Cl$^-$ concentration in the salt-affected streams

was up to 34.6 g L^{-1}. The high K concentration (up to 4.23 g L^{-1}) is attributable to river salinisation caused by the drainage waters of potash mining [22]. The background soil in the researched area is classified as an alluvial grey humic gley soil according to the classification of soils of Russia [21]. While, according to the World reference base (WRB) for soil resources 2014 [31], the soil is called Gleyic Fluvisols (Loamic). Underground mining causes subsidence processes, karst sinkhole formation and an increase in the water table in the surrounding area. The presence of shallow groundwater of the Na–Cl type develops waterlogging processes in the river valley which promotes soil salinity (Figure 6). The presence of dead trees in the river valley indicates that marsh forming developed relatively recently (Figure 8).
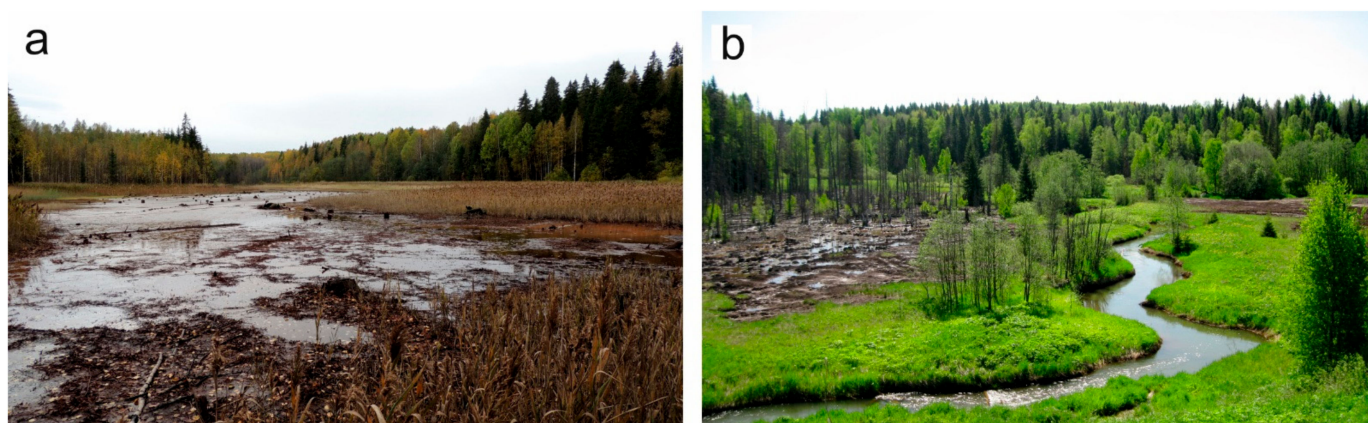

Figure 8. Different stages of ecosystem transformation to marsh: (**a**) a salt marsh forming after salt tailing pile construction; (**b**) seepage areas in the river valley with bare soils.

Two types of soils were identified in the Lyonva River valley depending on the ground water influence and according to the WRB Classification (2015) [31] (Figures 5 and 6): (1) Gleyic Fluvisols (Salic, Loamic, Technic) (alluvial gley humic clay chloride saline soil according classification soils of Russia); (2) Chloridic Gleyic Fluvic Solonchak (Hypersalic, Loamic, Technic) (secondary solonchak on alluvial humic cley soil sulphate–chloride gypsum–containing surface–gleyed according to classification soils of Russia).

The physicochemical properties of the investigated soils are presented in Table 2.

Gleyic Fluvisols (Salic, Loamic, Technic) consist of three horizons and are covered by vegetation, dominated by plants of the families Poáceae and Apiáceae. The top 20 cm was a grey-humus horizon (grey–brown coloured). It was densely intertwined with roots at a depth of 10 cm, and the roots were rare below 10 cm. The soil colour became darker at a depth of 14 cm and the soil structure was cloddy. A pale grey colour and rust-stains were observed at a depth of 18 cm. Gleyed horizon Czg was formed at a depth of 20–70 cm. This horizon had a brown colour, rust-stains and iron-manganese nodules. An alluvial gleyed horizon Czg with blue–grey colour and rust-stains was identified at a depth of 70 cm. Below 100 cm, a blue-grey colour without rust-stains was observed.

The content of organic matter in the investigated soils varied from 5.4 to 5.9, which is a typical value for natural alluvial soils [32,33]. The active (pH_{H2O}) and exchangeable (pH_{KCl}) acidity of soils changed slightly with depth. Gleyic Fluvisols (Salic, Loamic, Technic) had an acid pH_{H2O} = 4.16–5.18; the hydrolytic acidity also confirms this (13.3 meq/100 g) (Table 2). The cation exchange capacity of the surface layer of Gleyic Fluvisols (Salic, Loamic, Technic) was 68.5 meq/100 g. The content of mobile phosphates in Gleyic Fluvisols (Salic, Loamic, Technic) soil was 3.5 mg/100 g in layers of 3–20 cm, the content of mobile potassium in the upper layer was 27 mg/100 g.

Table 2. Physicochemical properties of soils.

Soil Type	Horizon	Layer cm	Corg %	H_2S mg/kg	pH–H_2O	pH–KCl	CEC	Sum of Exchangeble Bases meq/100 g	Hydrolytic Acidity	P_2O_5 HCl mg/100 g	K-HCl mg/100 g	Amount of Toxic Salts %	SAR
Gleyic Fluvisols (Salic, Loamic, Technic)		3–20	5.4	<0.32	4.69	5.42	82.7	69.4	13.3	3.5	27	0.4	1.5
	Az	20–30	-	<0.32	4.47	4.48	-	-	-	-	-	0.2	1.6
		32–42	-	-	5	4.78	-	-	-	-	-	0.25	1.9
		50–60	-	-	4.16	3.97	-	-	-	-	-	0.45	1.6
	Czg	70–80	-	-	4.68	4.72	-	-	-	-	-	1.3	2.1
		95–105	-	-	5.18	5.22	-	-	-	-	-	1	1.9
Chloridic Gleyic Fluvic Solonchak (Hypersalic, Loamic, Technic)	Hazngy	0–3	5.9	0.52	5.91	5.84	71	68.5	2.5	15.7	550	26.9	14.5
		3–15	5.8	17	6.75	6.7	37.3	36.1	1.1	0.8	150	17.1	36.3
	Czng	15–70	-	14.2	5.8	5.8	-	-	-	-	-	9.3	10.2

- not observed. SAR: sodium adsorption ratio.

Gleyic Fluvisols (Salic, Loamic, Technic) had a calcium–sodium chloride type of soil salinisation. The top soil horizon (5–15 cm) had high ion concentrations in the soil–water extract (mg/kg): Cl^-–330; Na^+–39.1; K^+–7.8 (Figure 9a). However, at a depth of 50 cm, the ion content increased and in the lower soil horizon–at a depth of 70 cm–contents of Cl^- and Na^+ reached 902 and 108 mg/kg, respectively. The highest ion concentrations (excluding HCO_3^-) were detected in the low horizon at a depth of 70–80 cm.
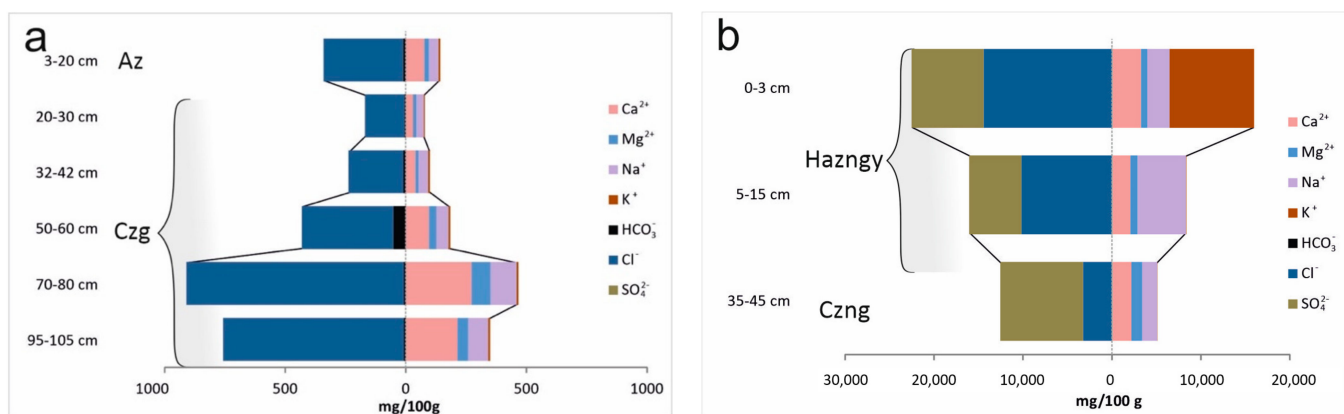

Figure 9. The content of water-soluble ions in: (**a**) Gleyic Fluvisols (Salic, Loamic, Technic); (**b**) Chloridic Gleyic Fluvic Solonchak (Hypersalic, Loamic, Technic).

Chloridic Gleyic Fluvic Solonchak (Hypersalic, Loamic, Technic) was slightly acidic (pH_{H2O} = 5.8–6.75) (Table 2). The surface layers of Chloridic Gleyic Fluvic Solonchak (Hypersalic, Loamic, Technic) were characterised by a high cation exchange capacity and amounted to 71–37 meq/100 g, which is associated with an organic matter content of 5.9%; the sum of exchangeable bases indicates the saturation of soils with bases. The content of mobile phosphates in Chloridic Gleyic Fluvic Solonchak (Hypersalic, Loamic, Technic) was 3.5 mg/100 g the 0–3 cm layer, and 0.8 mg/100 g in the 3–15 cm layer. The content of mobile potassium in the upper layer of Chloridic Gleyic Fluvic Solonchak (Hypersalic, Loamic, Technic) was 550–150 mg/100 g which is five to 20 times higher than that in Gleyic Fluvisols (Salic, Loamic, Technic), which is associated with salinisation of the soil by groundwater. In Chloridic Gleyic Fluvic Solonchak (Hypersalic, Loamic, Technic), the SAR exceeds 13, which indicates a high percentage of exchangeable sodium (Table 2).

Chloridic Gleyic Fluvic Solonchak (Hypersalic, Loamic, Technic) was characterised by a sulphate–chloride calcium–sodium type of soil salinisation. The content of water-soluble ions in the Chloridic Gleyic Fluvic Solonchak (Hypersalic, Loamic, Technic) significantly exceeded the amount in the Gleyic Fluvisols (Salic, Loamic). The top layer of Chloridic Gleyic Fluvic Solonchak (Hypersalic, Loamic, Technic) (~3 cm) was an iron-bearing crust without any vegetation. A salt–sulphide horizon Hazngy (3–15 cm) consisted of black gel-like phases with high contents of plant residues, we noted a gypsum content of 8.5%. A gley loam horizon Czng (15–70 cm) had a grey colour with rust-stains. In the 0–3 cm layer, the maximum content of water-soluble ions was observed in the top layer of the soil (mg/100g): Cl^-–1400, K^+–9500, Na^+–2500 (Figure 9b). These extremely high ion concentrations are associated with salt water-logging. The soil–water extract had much higher concentrations of Cl^-, Na^+ and K^+ than the background soil (e.g., (mg/100 g) Cl^- 0.6–2.5, K^+–1.48, Na^+–2.0) [15]. The maximum content of water-soluble ions decreased slightly with depth (Figure 9b). The sum of toxic salts was equal to 26%, which corresponded to a very high degree [34] of soil salinity (Table 2).

The insoluble part of the samples, collected from the uppermost horizon (0–3 cm depth), had the highest content of iron minerals of amorphous form (up to 84.9%) and Fe-bearing plant residues (up to 86.8%) (Table 3, Figure 10).

Table 3. Mineralogical composition of soil of Chloridic Gleyic Fluvic Solonchak (Hypersalic, Loamic, Technic) in seepage areas in the Lyonva River Valley (%).

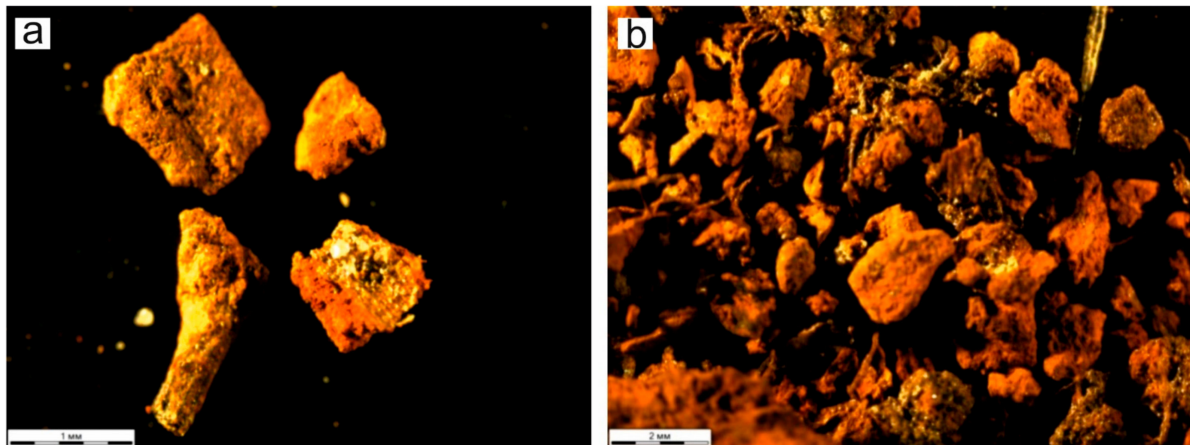| Depth of Sample	No Sample	Quartz	Fe-Bearing Plant Residues	Iron Minerals	Hydrogothite	Hematite	Oxides of Mn	Organic Residues	Other Minerals
0–3 cm	4.1	0.1	10.0	84.9	-	-	-	-	5.0
	6.1	2.5	86.8	6.0	-	-	-	-	4.7
	8.1	1.0	20.0	73.9	-	-	-	-	5.1
	11.1	0.5	30.0	-	68.2	-	-	-	1.3
3–30 cm	4.2	57.6	9.0	25.0	-	-	-	-	8.4
	6.2	78.2	3.0	8.0	-	-	0.3	-	10.5
	8.2	5.0	5.0	-	84.8	-	-	-	5.2

- not observed.

Figure 10. Images of iron-bearing phases: (**a**) Fe-bearing plant residues; (**b**) Fe-bearing minerals.

The scanning electron microscope images of the reddish-yellow iron-rich precipitates on the surface of upper soil horizon showed cubic halite crystals, flaky particles, a crust of iron oxides-hydroxides (Figure 11) and spongy residues. The spongy siliceous residues are remains of diatoms and are enriched in Ca, Fe, Cl, K, Na, S, and P (Figure 12).
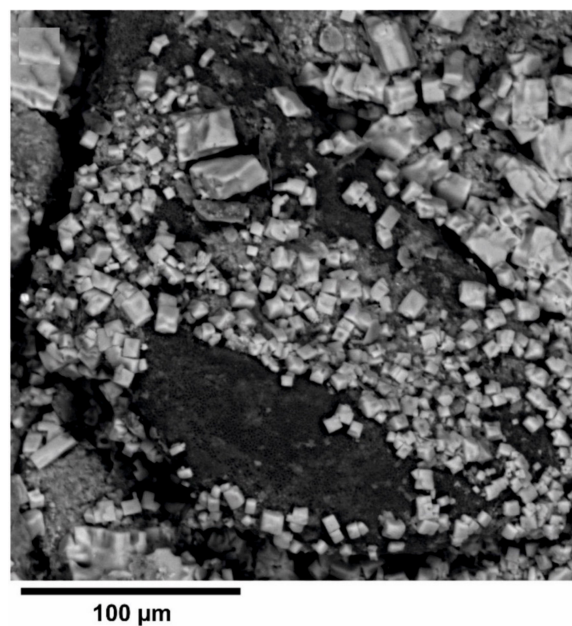

Figure 11. Upper soil horizon (0–3 cm depth) with reddish-yellow iron-rich precipitates and cubic halite crystals on the surface of soil.
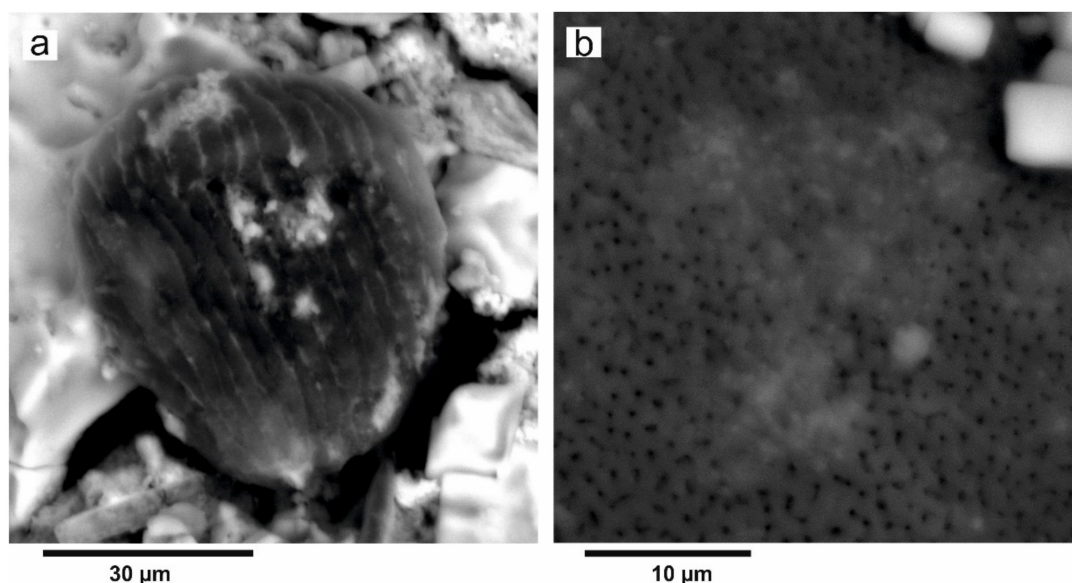
Figure 12. Upper soil horizon (0–3 cm depth) with organic material: (**a**) layered organic formation; (**b**) spongy residue.

The lower soil horizon (3–30 cm depth) consists of black gel-like phases with a high content of plant residues. The high concentrations of sulphate in the saline waters (Table 2) and microbiological activities led to hydrogen sulphide formation in this horizon (Figure 5). Content of H_2S varied from 17 mg/kg, Eh decreased up to -156–-197 which corresponded to a reducible condition. Siliceous remains of diatoms, halite, plant residues and iron-bearing phases were found in samples (Figure 13).
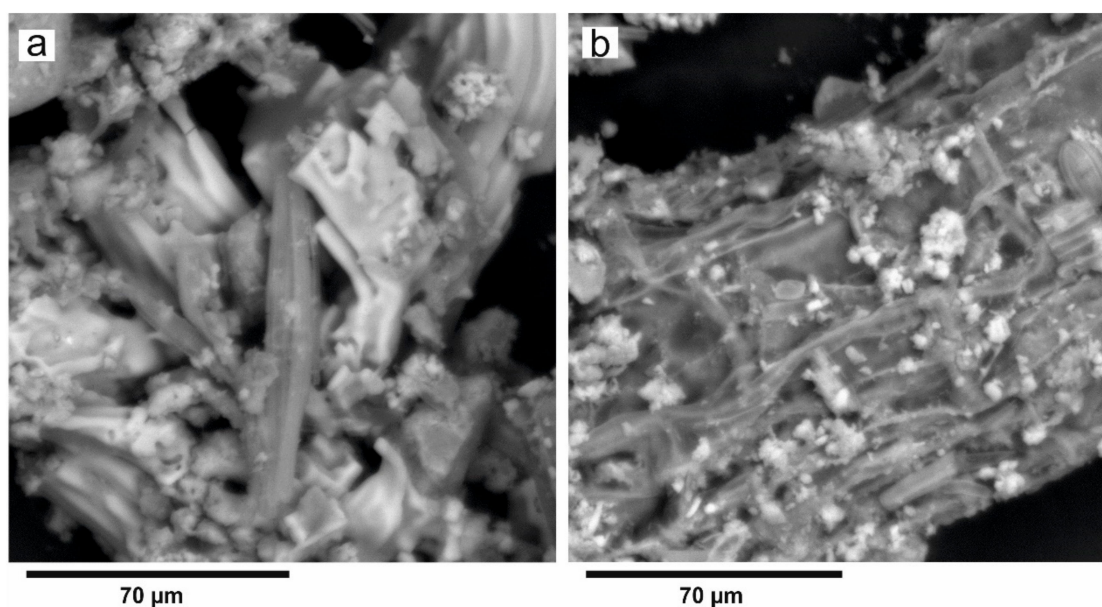

Figure 13. Lower soil horizon (3–15 cm depth) black gel-like phases, hydrotroillite horizon: (**a**) siliceous remains of diatoms, halite, iron-bearing formation; (**b**) plant residue covered by siliceous remains of diatoms and iron-bearing phases.

The inflow of sulphate ions with seepage drainages into groundwater and river waters promotes sulphate reduction in the anaerobic settings of soils due to the activity of sulphate-reducing bacteria. Desulphurisation and the formation of H_2S is a common process under natural conditions, for example, in sulphate water bodies of steppes and deserts [11], under the conditions of saline groundwater inflow [13], along the seashore [35], along the low swampy shores of Sakhalin Island in conditions of flooding by sea waters [36].

The H$_2$S released during sulphate reduction interacts with highly mobile iron species, forming an insoluble aqueous iron hydrate—hydrotroillite (FeS·nH$_2$O). This mineral forms a black gel-like soil layer. Hydrotroillite is an unstable mineral and various geochemical settings are required for its formation: anaerobic settings, presence of organic matter, iron and sulphates [14].

The insoluble part of the samples contained up to 84% hydrogoethite (Table 3), which was the result of iron oxidation during sample preparation. We suggest that hydrotroillite was the predominant iron-bearing mineral in this horizon. Other iron minerals (hematite and magnetite) were also identified in the samples (Table 3).

Carbonaceous and organic residues, manganese oxides and gypsum were identified in the soil profile of Chloridic Gleyic Fluvic Solonchak (Hypersalic, Loamic, Technic). Gypsum formed during the interaction of calcium in the parent rocks and sulphate in highly mineralised waters. The biogenic type of gypsum formation may be associated with the activity of thionic bacteria [37].

The observations during 2013–2016 showed that the hydrotroillite horizon is extremely unstable and its thickness varied depending on the amount of precipitation and the groundwater level. The underlying horizon at the depth of 40–80 cm had a gley condition. The low organic content limited the growth of sulphate-reducing bacteria and hydrogen sulphide was not formed.

The sources of iron in the soils and bottom sediments include the iron-enriched Sheshma sediments (P1ss) speckled rocks, slurry material and halite wastes and soil minerals of alluvial gley soils.

The main source of Fe and other metals in potash rocks is a continental runoff water [38]. Hypergenic destruction of carnallite and sylvinite rocks leads to the concentration of these elements in the salt layer [39]. In the water-soluble part of the salts, the Fe content is n $\times$ 10^{-5}% [38]. Fe (III) was found as FeCl$_3$ and as an isomorphic replacement of Mg in carnallite; Fe (II) was mainly found in the form of rinneite minerals, less often in douglasite, widely represented in the German Zechstein in the lower Cambrian of Siberia, and in the Khimiset deposit (Morocco) [38].

At many deposits of potassium salts, gypsum-clay caps were uncovered and composed of dark grey brecciated clays with interlayers, lenses and inclusions of transparent and brownish-red grains of gypsum films, lenses and streaks of red, reddish-orange, orange–yellow ferruginous substances, which were named hematite layers. They were formed as a result of salt rock destruction [40]. The hematite layers, with thicknesses from a few millimetres to 5–25 cm, were formed at the Verkhnekamskoe potash deposit [39].

Iron-bearing minerals were concentrated in waste as a result of the enrichment of potash ore. In the halite waste of the Verkhnekamskoe potash deposit, the iron content varied from 380 to 990 mg/kg, and in the clay-saline sludge—from 1450 to 4200 mg/kg [17]. In clay minerals of halite waste, the iron content can reach 38.7 wt.% and in the material of sludge—from 2.9 to 6.8 wt.% [17]. The pyrite content ranges from 1.3 to 1.8% [15].

Soils are a source of iron, for example, Fe (II) is oxidised with the formation of hydrogetite, goethite, hematite and other Fe-bearing phases in Taiga landscapes under the oxidizable conditions of the upper soil horizons [41,42]. In the alluvial soils of the floodplains of the Perm Krai, the main Fe-bearing minerals are goethite and Mn-feroxyhyte, with the total Fe$_2$O$_3$ content reaching 62 wt.% [33].

The Fe release from the bottom sediment and soil might be caused by an increase in the NaCl content [43], which was found along with an increase in the NaCl content in water, the Fe (II) concentration increased in the pore water of bottom sediments. Saline drainage and saline groundwater more active than fresh groundwater at leaching Fe from the iron-rich speckled aquifer, slurry material, and soil minerals.

4. Conclusions

The formation of Gleyic Fluvisols (Salic, Loamic, Technic) and Chloridic Gleyic Fluvic Solonchak (Hypersalic, Loamic, Technic) in the territory of the Verkhnekamskoe potash

deposit was determined by the close occurrence of Cl–Na groundwater with a high content of sulphates. As a result of the interaction between technogenic brines and parental rocks and soils, the contents of sulphate and iron increased, leading to the formation of sulphide salt marshes with the deposition of Fe-bearing minerals on the surface and hydrotroillite horizon under anaerobic conditions. The sources of iron in the soils include speckled rocks, slurry material and soil minerals. The intensity of technogenic salinisation and subsidence of the Earth's surface in mining areas contribute to the formation of large areas of soil salinisation in valley landscapes.

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