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Article

Assessment of soil changes causing contamination with crude oil and mineralized liquids in the Middle Ob region (Western Siberia)

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Abstract. The influence of highly mineralized waters and crude oil on the properties of podzolic and alluvial soils in Western Siberia is analyzed. Soils contaminated with mineralized waters during oil production accumulate easily soluble salts, as shown by the amount of dense residue within the contamination halo (0.30–1.68%), including high content of toxic salts (toxic chloride-sulfate and sulfate anions and toxic cation sodium), which create an unfavorable environment for the growth and development of higher plants. Salt accumulation and the chemistry of soil salinization in oil production areas depends both on the type of pollution (crude oil, mineralized waters) and on soil-ecological conditions (landscape position, hydrological regime, genetic type of soils and their sorption properties, regime of salt supply). The discharge of mineralized waters during spillages in waterlogged taiga landscapes of Western Siberia leads to technogenic halogenesis (salinization) in areas where this process could never have occurred naturally. Soil salinization, which occurs in a humid climate, can be considered a superimposed soil-forming process, which forms an additional risk of the development of an accompanying solonchak process in soils. The changes revealed allow the ecological state of soils to be assessed. Proposals for the reclamation of oil-salt contaminated soils can be put forward, based on basic parameters of technogenically saline soils (chemistry, degree of salinization, and stock of toxic salts).

Keywords: oil and salt pollution, easily soluble salts, technogenic halogenesis, salinization chemistry, soil salt profile, reclamation methods, phytomelioration

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Научная статья

Изменения почв под влиянием загрязнения сырой нефтью и минерализованными жидкостями в условиях Среднего Приобья Западной Сибири

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Аннотация. Рассмотрено влияние высокоминерализованных вод и сырой нефти на свойства подзолистых и аллювиальных почв Западной Сибири. Специфическая особенность почв, загрязненных при добыче нефти минерализованными водами – накопление легкорастворимых солей, сопровождающееся высоким содержанием токсичных солей. Формирование солевых аккумуляций и химизма засоления почв на территориях нефтедобычи зависит как от вида загрязнения (сырая нефть, минерализованные жидкости), так и от почвенно-экологических условий (положения в ландшафте, гидрологического режима, типа почв, их сорбционных свойств, режима поступления солей). Сброс минерализованных вод в ходе аварийных разливов минерализованных жидкостей в условиях переувлажненных таежных ландшафтов Западной Сибири приводит к образованию техногенно засоленных почв на территориях, где естественное развитие этого процесса невозможно. Засоление почв в условиях гумидного климата можно считать наложенным почвообразовательным процессом, формирующим дополнительный риск развития в почвах техногенного солончакования. Обнаруженные изменения позволяют оценить экологическое состояние почв (химизм, степень засоления, запас токсичных солей) и разработать предложения по рекультивации почв нефтесолевого загрязнения.

Ключевые слова: нефтесолевое загрязнение, легкорастворимые соли, техногенный галогенез, химизм засоления, солевой профиль почв, методы рекультивации, фитомелиорация

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Introduction

The oil fields of Western Siberia are the main oil production area in the Russian Federation. With intensive development and exploitation of deposits, the natural environment experiences a significant technogenic load, which often leads to pollution and degradation of ecosystems.

The increase in the areas of technogenically saline soils is one of the urgent environmental problems of Western Siberia (Gennadiev, 2016; Seredina et al., 2017; Solntseva, 2002). Their origin is associated with spillages of highly mineralized waters used to maintain reservoir pressure in oil deposits. Salinization is also exacerbated by oil pollution of lands due to heavy watering of crude oil (Seredina et al., 2006; Nosova et al., 2020). Soils are the most valuable source of information about the ecological state of an oil-contaminated area.

To date, only a few studies have been published on assessment of the spatial distribution of technogenic salt contamination of soils (Capra et al., 2015; Nosova et al., 2021; Wiens, 2013). It is noteworthy that there is no large-scale practice of recultivation of technogenically saline lands, yet. The complexity of the issue lies both in the lack of techniques and methodology for assessing the nature and degree of environmental hazard of this type of pollution, and in the difficulties of visually determining the boundaries of oil and salt pollution.

The purpose of this study is to determine the content of technogenic salts, to identify the nature and patterns of their distribution in soils of contrasting geochemical landscapes under conditions of local contamination with crude oil and mineralized waters, and to determine the most effective method of land recultivation.

Materials and methods

The objects of study were soils at spill sites of crude oil and mineralized liquids in the middle taiga of Western Siberia within the Khanty-Mansi Autonomous Okrug. The sources of pollution arose after breakage of field pipelines in the central part of the floodplain of the Ob River (oil pollution) and an failure of a high-pressure spillway on the watershed plain of the left bank of the Ob River (contamination with mineralized liquids). By agreement with the operating organization (PJSC NK Rosneft), we do not indicate the names of oil and gas fields or the exact coordinates of the location of contaminated sites.

Soils affected by each type of pollution were surveyed in July–August 2021 within a month of the pipeline accident. The boundaries of the distribution of oil pollution in the floodplain were determined by the presence of a bituminous crust on the soil surface and by the degree of inhibition of the vegetation cover. The latter indicator also served as an indicator of soil contamination of the watershed by mineralized formation waters.

At each site in the epicenter of pollution, a full-profile section was laid. Soil samples subjected to formation water pollution (s-1) were taken according to genetic horizons. It is difficult to distinguish the boundaries of horizons in oil-contaminated soil (Ss-2), so the samples were taken in layers every 10 cm to a depth of 1 m. A series of soil excavations was laid to study the lateral migration of oil products and easily soluble salts. Samples were taken at the epicenter of pollution, as well as at different distances from the source of pollution: in the impact zone (3 m) and at the boundary of pollution (5 m).

To assess the degree of change in soils in contaminated areas compared to natural soils, soil profiles were laid in the background areas 10 km from the contaminated area. Soil profiles were laid in the background areas 10 km from the contaminated area to assess the degree of change in soils in contaminated areas compared to natural soils. Samples of background soils were taken from the main genetic horizons throughout the entire depth of the section (background-1 and background-2). The systematic position of soils in each surveyed area was determined according to the Classification and Diagnostics of Russian Soils (Shishov et al., 2004) and the World Reference Base for Soil Resources (2014).

Petroleum products (PP) in the samples were determined by the fluorimetric method.The content and composition of easily soluble salts were determined in the aqueous extract in accordance with the standardized methods.

pH and solid residue according to GOST 26423-85[1],sulfate ion according to GOST 26426-85[2], sodium and potassium ions according to GOST 26427-85[3], chloride ion according to GOST 26425-85[4], calcium and magnesium ions according to GOST 26428-85[5], carbonate and bicarbonate ions according to GOST[6, 7]. The degree of salinity was estimated according to the generally accepted classification of F.R. Zeidelman (2017). The granulometric composi-

[1] GOST 26423-85 Soils. Methods for determining the specific electrical conductivity, pH and dense residue of aqueous extract.

[2] GOST 26426-85 Soils. Methods for determining the sulfate ion in water extract.

[3] GOST 26427-85 Soils. Method for determination of sodium and potassium in water extract.

[4] GOST 26425-85 Soils. Methods for determination of chloride ion in water extract.

[5] GOST 26428-85 Soils. Methods for determination of calcium and magnesium in water extract.

[6] GOST 26424-85 Soils. Method for determination of carbonate and bicarbonate ions in water extract.

[7] GOST 26424-85 Soils. Method for determination of carbonate and bicarbonate ions in water extract.

tion of the soil was determined by the pipette method. The normality of the distribution of the obtained results was assessed using the Kolmogorov-Smirnov test. The features have a normal distribution, so parametric statistics methods were used in the work (Pearson correlation coefficient – Rp). The data obtained were also grouped by pollution zones with the definition of the data range (min–max), mean and standard deviation (SD).

Results and discussion

The morphological structure of the soil profile reflects the direction of the soil-forming process and suggests the ecological state of the soils. Below we discuss the structural features of the profile of the studied background and technogenically polluted alluvial and podzolic soils.

Background site 1 (background-1) is located on the watershed area under the pine forest (*Pinus sibirica* Du Tour) with an admixture of aspen (*Populus tremula* L.). Forb-shrub associations are represented by mountain ash (*Sorbus* sp.), wild rosemary (*Ledum palustre* L.), lingonberry (*Vaccinium vitis-idaea* L.), sedge (*Carex* sp.), hair moss (*Polytrichum* sp.), with thin forest litter. The soil profile is represented by a system of horizons O (0–2 cm) – OT (2–7 cm) – EL (7–12 cm) – BEL_{Fe} (12–30 cm) – BT_{1Fe} (30–50 cm) – BT_{2Fe} (50–60 cm) – BT_{3Fe} (60–70 cm) – BC_{Fe} (70–100 cm). The upper soil horizons are formed by peaty sod (horizons O and OT). The granulometric composition of the soil is differentiated by the eluvial-illuvial type, especially by the clay fraction. Thus, the upper part of the illuvial horizons shows fairly pronounced features of illuviation: a nutty structure, a denser structure in horizons $BEL_{Fe,}$ $BT_{1Fe,}$ $BT_{2Fe,}$ $BT_{3Fe.}$ In combination with a light granulometric composition, the intensity of podzol formation is especially clearly manifested in the light gray unstructured EL horizon characteristic of this soil type. The soil is diagnosed as podzolic typical illuvial-ferruginous finely clarified light loamy (*Retisols Gleyic*).

Background site 2 (background-2) is located on a lowered flat drained periodically flooded section of the Ob River floodplain. Shrub-forb communities of the site are formed by willows (*Salix* sp.), blackcurrant (*Ribes nigrum* L.), bridewort (*Spiraea salicifolia* L.), meadowsweet (*Filipendula ulmaria* (L.) Maxim.), tufted vetch (*Vicia cracca* L.), and also creeping buttercup (*Ranunculus repens* L.), marsh-marigold (*Caltha palustris* L.), and sedge. The profile contains the following horizons: AY_v (1–10 cm) – AY (13–23 cm) – AYC_g (30–40 cm) – IC_{1g} (45–55 cm) – IIC_{2g} (60–70 cm) – $IIIC_{3g}$ (90–100 cm). The gray-humus (turf) horizon of brownish-gray color (AY_v), is lumpy, densely permeated with root systems of meadow vegetation. Traces of the activity of soil fauna are noticeable. Organogenous horizons (AY_v, AY) are gradually replaced by gleyed horizons (AYC_g, IC_{1g}, IIC_{2g}, $IIIC_{3g}$). The soil is diagnosed as alluvial gray humus typical gleyic unsaturated medium fine heavy loamy (*Stagnosols Fluvic*).

Below we consider the manifestation of each type of pollution in the morphological appearance of soils.

Saline podzolic soils (s-1) do not have pronounced morphological changes in the structure of the profile compared to the background soils. The most characteristic sign of salt contamination of soils is the complete degradation of the vegetation cover over the entire area of distribution of mineralized liquids. In the epicenter, dried aspens are found sporadically, the degradation of the tree-shrub layer is pronounced, and salt efflorescence is observed on the soil surface. In the impact zone of pollution, in the grass-shrub layer, there are May lily (*Maianthemum bifolium* (L.) F.W. Schmidt), twinflower (*Linnaea borealis* L.), stone bramble (*Rubus saxatilis* L.), wood horsetail (*Equisetum sylvaticum* L.), and reed grass (*Calamagrostis obtusata* Trin.). The total projective cover is up to 30–45%. At the pollution boundary, the tree layer is represented by cedar with an admixture of aspen; Siberian Mountain ash is noted in the shrub layer (*Sorbus sibirica* Hedl.), wild rosemary, and lingonberry. The herbaceous layer is dominated by sphagnum mosses. (*Sphagnum* sp.), and hair moss. The projective cover increases to 75–100%. According to the accepted classifications, the soil should be classified as technogenically saline chemozem over to podzolic soil (*Solonchaks Gleyic Toxic*).

In oil-contaminated alluvial soils (s-2), the greatest morphological transformations were noted in the root-inhabited layer. The upper part of the soil profile is sealed under a dense bituminous crust. Root-inhabited horizons ($AY_{v,\ x}$, AY_x, $AYC_{g,\ x}$) are strongly compacted. Humus horizons ($AY_{v,\ x}$, $AY_{g,\ x}$) contain anthropogenic inclusions (> 20%) in the form of construction debris, synthetic solid waste and crude oil. Based on these features, the studied soils should be classified as oil-contaminated chemozem over to the alluvial soil (*Technosols Urbic Toxic (up to a depth of 40 cm) or Solonchaks Fluvic Toxic)*.

In the very epicenter of pollution, complete degradation of the tree-shrub layer is observed. There are occasional specimens of bridewort, tufted vetch, creeping buttercup, and marsh marigold with pronounced morphological changes: dark color, violation of normal proportions, dried stems and leaves. Partially degraded shrub associations are confined to the impact zone of pollution. These include Siberian Mountain ash, Russian spiraea (*Spiraea media* L.), prickly wild rose (*Rosa acicularis* L.) with projective cover up to 45–65%. At the boundary of pollution in herbaceous associations there is an understory of silver birch (*Betula pendula* Roth.) and aspen. Projective cover in this zone increases up to 80–100%.

The content of PP in *Solonchaks Gleyic Toxic* and in background soils is below the detectable level (Table 1). In the humus-accumulative horizons of *Technosols Urbic Toxic (up to a depth of 40 cm) or Solonchaks Fluvic Toxic*, the maximum content of PP was recorded in the epicenter of pollution. As we move towards the boundary of the impact zone, the content of PP decreases on average by 1.2 times. The data obtained are consistent with field studies. Due to the input of oil hydrocarbons, the humus horizons ($AY_{v,\,x}$, $AYC_{g,\,x}$) of *Technosols Urbic Toxic (up to a depth of 40 cm) or Solonchaks Fluvic Toxic* are darker in color compared to the background.

The bottom settlement water of crude oil and highly mineralized liquids used in the extraction of oil are sources of salinization in the examined technogenically polluted soils. The results of the analysis of water extract show that the impact of mineralized waters has a stronger effect on soils than the impact of oil and oil products (Table 1).Compared to the background soils, in polluted soils, the reaction of the environment shifts to the neutral or weakly alkaline side. The zone of accumulation of easily soluble salts is confined to the epicenter, as they move towards the boundaries of the spill, their content decreases. In all studied soils, there is a wide gradient of salinity levels – from weak to strong.

Solonchaks Gleyic Toxic are characterized by a strong degree of salinity. The removal of chlorides is noted with a slight migration of carbonates in the profile (Fig. 1).

The Cl^-/SO_4^{2-} ration ranges from1.96/1.77 mmol(eq)/100 g of soil in a layer 0–10 cm to 12.4/4.56 mmol(eq)/100 g of soil in the lower part of the profile, suggesting the absence of progressive salt accumulation. Two zones are expressed in the profile: the upper 60 cm, where the active removal of ions occurs, and the underlying horizons, where the removal products accumulate. The type of chemistry throughout the profile is sulfate-chloride sodium, which is typical of pollution by mineralized waters. The concentration of Cl^- and Na^+ increases and decreases with depth from the epicenter of the spill to its periphery. The share of chloride ion in migration flows is about 80%.

Technosols Urbic Toxic (up to a depth of 40 cm) or Solonchaks Fluvic Toxic) are characterized by a medium level of salinity in the epicenter and a weak degree of salinity in the impact zone (Table 1). Oil-contaminated soils are characterized by a sulfate-sodium type of salinity due to the sulfur content of oil and the composition of bottom settlement waters. Correlation analysis revealed a statistically significant positive relationship between the content of readily soluble salts and PP ($R_p = 0.87$ (at a depth of 0–10 cm) and 0.83 (at a depth of 10–30 cm), $p < 0.05$).

Unlike *Solonchaks Gleyic Toxic*, the salt concentration in *Technosols Urbic Toxic (up to a depth of 40 cm) or Solonchaks Fluvic Toxic*, reaches a maximum in the surface layer and then gradually decreases with depth (Fig. 2). Such a pattern of salt distribution can be associated with the seasonal rise of groundwater and the migration of salts to the horizons of heavy granulometric composition. The danger of technogenic salinization is associated not only with the total salt content in the root-inhabited soil horizons, but also with their toxicity to higher plants. The main diagnostic sign of the ecological effect of technogenic halogenesis is considered to be the total amount of toxic salts.

The degree of toxicity of salts is determined by their composition and solubility – the easier salts enter the plant body, the more pronounced the negative impact. In *Solonchaks Gleyic Toxic*, toxic technogenic salts are represented $NaHCO_3$, Na_2SO_4, $MgCl_2$. Their total amount ($\sum_{tox}$) in the profile increases with depth and reaches 1.15% in the lower horizons. This may indicate the leaching of salts from the soil profile with a decrease in the level of groundwater. Such a salt profile is characteristic of the solonchak type of salinization.

In *Technosols Urbic Toxic (up to a depth of 40 cm) or Solonchaks Fluvic Toxic)*, toxic technogenic salts are represented by $NaCl$, Na_2SO_4, $MgCl_2$. High concentrations of toxic salts in the underlying soil horizons, when they gradually enter the root-inhabited horizons with groundwater, can cause secondary salinization. Thus, oil-salt pollution enables the development of an accompanying solonchak process along with the main processes that form the profile of alluvial soils (soddy, alluvial).

Due to the annual increase in the areas of contaminated land, technologies for the recultivation of saline areas have been repeatedly proposed, however, these methods lead only to local improvements and are not complex measures for soil restoration. No generally accepted system of criteria for assessing the degree and danger of salinization has been developed for technogenically saline soils, hence, there are no standards for the acceptable residual salt content after recultivation. These parameters are necessary to monitor the state of recultivated soils after restoration work. The main goal of systematic monitoring is constant control over the decrease in the degree of salinity relative to the initial state, the development of the potential for self-purification of soils and the restoration of natural flora.

Based on the analysis of open literary sources (Fominykh, 2013; Mustafaev et al., 2015; Shirokova et al., 2007), field observations and their own laboratory studies, the authors offer recommendations for the recultivation of technogenically saline soils.

To determine the depth of salt penetration, as well as the stage of salinization/desalinization of soils, it is proposed to lay a soil section before the start of recultivation work. It is advisable to locate it in the lower part of the cascade-geochemical system of landscapes – in the zones of maximum accumulation

Table 1. Salt composition and type of soil salinization in various pollution zones. The mean ± SD is shown above the line, and the limits (min–max) are shown below the line.

		Dense residue, %	Salinity level	Type of salinity by anion composition	Type of salinity by cation composition	Toxic soil content, %	PP content in g/100 g of soil	pH_{water}
Contamination with mineralized liquids (s-1)								
Epicenter of pollution	Depth 0–10 cm	1.22 ± 0.09 / 1.58–1.66	high	sulfate-chloride	sodium	0.25 ± 0.13 / 0.17–0.33	< 2.5	6.32–6.81
	Depth 10–30 cm	0.76 ± 0.31 / 0.58–0.88	from medium to low	sulfate-chloride	sodium	0.26 ± 0.05 / 0.23–0.3	< 2.5	6.26–7.28
Impact pollution zone	Depth 0–10 cm	0.74 ± 1.17 / 0.34–1.68	from high to low	sulfate-chloride	sodium	0.22 ± 0.1 / 0.17–0.35	< 2.5	6.04–6.73
	Depth 10–30 cm	0.46 ± 0.51 / 0.30–0.84	from medium to low	sulfate-chloride	sodium	0.26 ± 0.04 / 0.20–0.33	< 2.5	5.94–6.39
Pollution by oil emulsions (s-2)								
Epicenter of pollution	Depth 0–10 cm	1.02 ± 0.34 / 0.35–1.57	from medium to high	sulfate	sodium	0.45 ± 0.09 / 0.28–0.59	66.45 ± 13.16 / 16.23–72.26	7.6–8.5
	Depth 10–30 cm	0.58 ± 0.71 / 0.45–1.15	from low to medium	sulfate	sodium	0.37 ± 0.11 / 0.18–0.44	50.72 ± 12.75 / 11.82–65.61	6.9–8.5
Impact pollution zone	Depth 0–10 cm	0.48 ± 0.03 / 0.45–0.55	low	sulfate	sodium	0.28 ± 0.08 / 0.19–0.35	52.02 ± 8.98 / 11.53–68.12	6.3–7.6
	Depth 10–30 cm	0.36 ± 0.09 / 0.3–0.75	low	sulfate	sodium	0.23 ± 0.04 / 0.15–0.27	43.47±9.09 / 4.43–50.23	5.9–6.7

of pollutants. The study of salt migration in the soil section will make it possible to assess the depth of salt penetration, the stage of salinization, and the reserve of salts, and to compile a set of typical measures in the recultivation process map. This will determine the feasibility of soil remediation and will optimize the set of preparatory work for a particular kind of pollution.It is proposed to divide the entire subsequent complex of works into three standard stages: preparatory, technical, and biological.

The preparatory stage is based on ready-made technical solutions for soil recultivation and the proposals of authors with practical experience in the recultivation of technogenically saline soils (Fominykh, 2013; Mustafaev et al., 2015; Shirokova et al., 2007). The primary task at this stage is to create favorable conditions for accelerating soil desalinization. Hence, it is necessary to equip a system of temporary drainage trenches on the entire area of the saline territory. The saline washing water enters the intercepting ditch, equipped along the pollution contour of the site. The depth of the drainage ditch must be below the level of the trench system. In order to avoid unnecessary operational investments for irrigation of technogenically saline soils with fresh water, it is advisable to supplement the trench system with snowbanks placed on the site. In the spring, when the snow stored in the snowbanks melts, the soil profile will gradually be washed through with melt water lowering the salt concentration in the soil horizon.

With repeated migration of salts as a result of groundwater level fluctuations from the lower part of the soil profile to the root-inhabited layer, there is a risk of formation of new salt-saturated horizons and dense salt crusts in soils. These horizons can become a source of formation of new compounds of toxic salts in soils. Therefore, the next stage in the recultivation of technogenically saline soils is a technical set of works to improve the agronomic state of soils using milling. Mechanical processing of the upper soil layer accelerates the surface removal of salts, and improves the granulometric composition and water-physical properties of the soil (permanent wilting point of plants, the range of active moisture).

During the biological stage of land recultivation, use of soil gypsum is recommended to eliminate the residual effect of toxic salts. In case of low soil supply with nutrients (N, P, K), it is necessary to apply mineral fertilizers, followed by phytomelioration of the site with halophyte plants. Importantly, recultivation in a humid climate uses native plants or those adapted to the local natural and climatic conditions (members of the families Chenopodioideae, Plantaginaceae, and Gramineae). The application of the entire range of remedial measures will make it possible to reduce

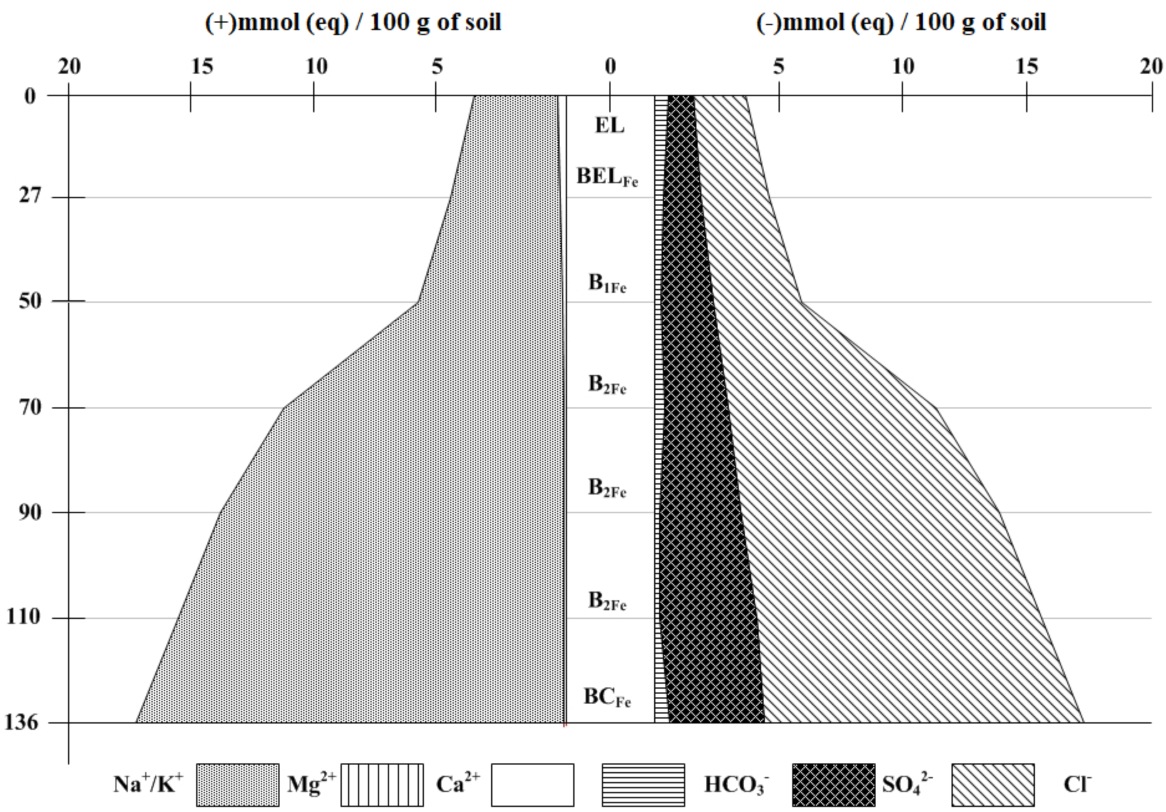

Fig. 1. Soil salt profile of *Solonchaks Gleyic Toxic*.

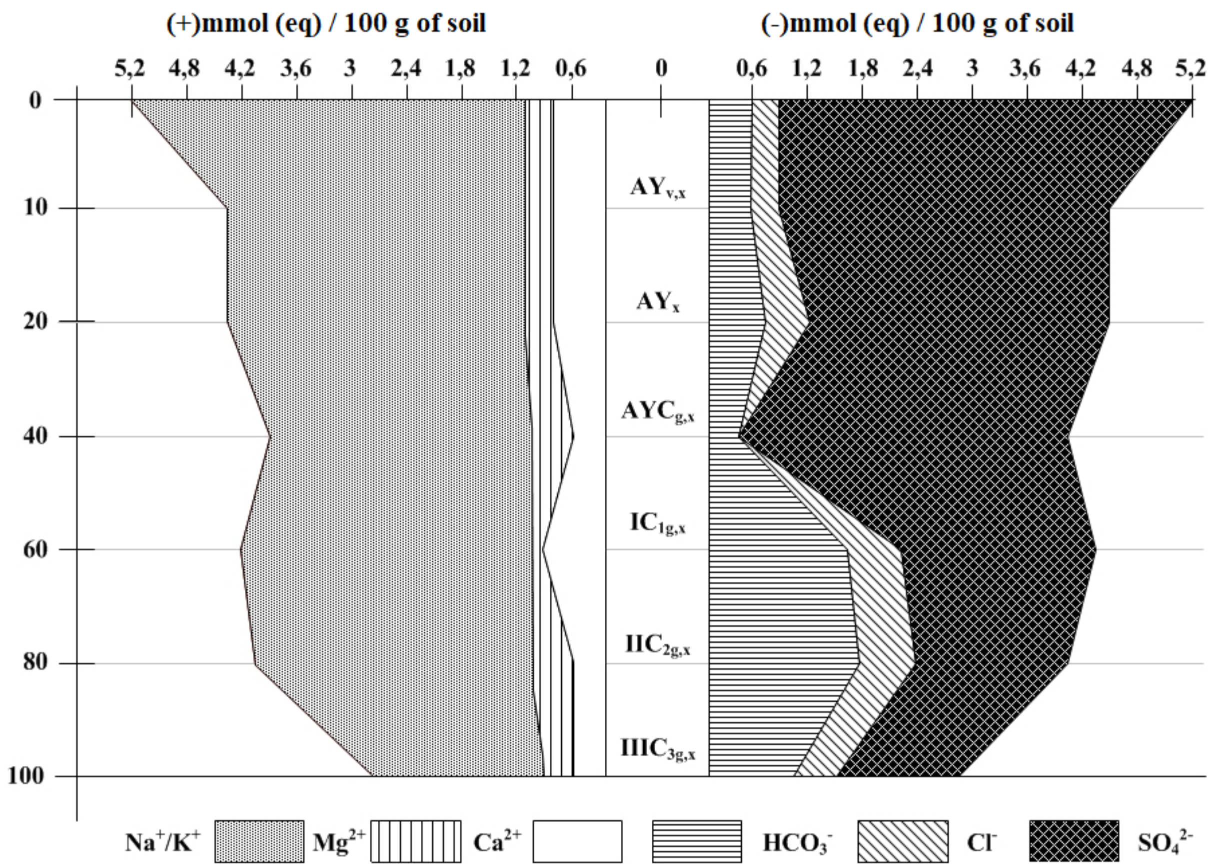

Fig. 2. Soil salt profile of *Technosols Urbic Toxic (up to a depth of 40 cm) or Solonchaks Fluvic Toxic.*

the content of easily soluble salts to acceptable values, no more than 0.3% in the most saline horizon (Zaidelman, 2017).

Conclusions

Comparison of two types of soil pollution reveals the following features. On spills of crude oil, the maximum salt content is confined only to the upper root-inhabited horizons, and their concentrations in the underlying horizons are low. SO_4^{2-} and Na^+ ions play the leading role in the process of salt fractionation. In general, the distribution of salts within the soil profile is uniform. In soils contaminated with mineralized liquids, on the contrary, the maximum of salts is displaced to a depth of 130 cm, forming a salt accumulation horizon due to the intense removal of Cl^- and Na^+.

At the same time, in the soils of each type of pollution, secondary soil salinization is possible. This can lead to transformation into technogenic surface formations (SST) and technogenic solonchaks. Due to natural reasons (humid climate, leaching type of water regime), this phenomenon is impossible in the study area.

Objective assessment of the ecological state of anthropogenically transformed soils is possible through monitoring the migration and accumulation of salts. Easily soluble salts entering ecosystems due to local spillages accumulate in the root- inhabited layer and have a toxic effect on higher plants. Toxic salts can also accumulate in soils at considerable depths, contributing to the secondary salinization of soils due to the additional influx of salts into the upper soil horizons due to the rise of groundwater during spring floods. Therefore, the main problem when transferring recultivated plots to regulatory authorities is the difficulty of creating a plant layer that is uniform in density and area. When developing approaches and methods for restoring oil-salt soils, it is necessary to take into account the type of soils, the nature of pollution (the degree of salinization, the chemical composition of salts, and the supply of salts in the soil profile), the type of pollutant (crude oil, mineralized liquids), and the position of soils in landscape-geochemical catenas. Taking into account all these parameters will allow processes of soil restoration to be fulfilled.

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