Ecological State of Technogeneous Saline Soil of Oil-Contaminated Alluvial Ecosystems and Their Remediation Techniques

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Abstract. The article discloses the trends of technogenic salts distribution in alluvial soils contaminated with oil and petroleum products. The salt distribution was examined in the lateral direction – impact zone, oil contamination boundary, as well as radial salts distribution within the soil profile (to 100 cm depth). Specifics and chemistry of technogenic halogenesis process (freely soluble including phytotoxic salts content, qualitative composition, migration and distribution trends) has been identified for soils of different contaminated zones. It was revealed that technogenic salinization of alluvial soils (that is the end body of the cascaded geochemical systems) is an essential geoecological factor contributing to formation within oil-contaminated areas of new technogenic soil-geochemical successions – chemical-contaminated soils, showing the features of salinity not typical for humid climate. The technique of technogeneous saline soil remediation was suggested based on indigenous halophyte plants phytomelioration sowing.

1. Introduction
The Western Siberian superaquial landscapes are the end point of organic pollutants accumulation, where the intense technogenic stream flow of petroleum hydrocarbons typical for oil pipeline accidents produces maximum impact to soil landscape [1–3], which indirectly affects the state of the hydrological network. At shallow groundwater occurrence, the presence of freely soluble salts may result in soil salinization, and no proven salinized soil remediation technique is currently available. In the conditions of growing technogenic environmental load, its ecological status issues are of high priority. According to multiple studies [3–6], oil contamination impact on natural ecological systems is a function of geochemical and physical loads. Soils are a natural barrier and a center of accumulation of all pollutants and various chemicals. In this respect, the soil landscape investigation in the technogenic zone is essential, as the contaminants upset the balance of natural processes resulting in a change in soil system parameters [6–9].
The issues of radial and lateral salts distribution within the arid zone soil were the subject of numerous surveys [1–11]. In areas of humid soil genesis, salts migration during accidental oil spills as well as their secondary (post-technogenic) redistribution has not been actually studied yet. Hence, for the zone of excessive humidification, the technogeneous saline soils may provide the models for prediction of geochemical changes related to oil contamination; this makes the study of the above issues relevant and essential.

Therefore, this study is focused on identification of specifics of halogeochemical phenomena in alluvial ecosystems of Western Siberia under circumstances of soil local contamination with oil and petroleum products, and selection of the most effective salinized soil remediation technique.

2. Material and methods
Actual data originate from field studies and laboratory tests fulfilled by this article authors in Aleksandrovsky and Kargasoksky districts of the Tomsk Region, and in Nizhnevartovsk District of the Khanty-Mansi Autonomous Okrug – Yugra. To reveal soil morphological transformations, a routing method was applied with subsequent comparative/geographic and profile/genetic analysis of reference and contaminated soil. The trends of radial and lateral salts and oil distribution were revealed with the help of reference sections (2 full-scale sections) and trenching (26 samples) in different technogenic impact zones. The contamination source area is the zone affected with the heaviest oil contamination and closest to the technogenic impact source (a field pipeline). The impact zone is the area of oil contamination impact from the contamination source area contour (abrupt drop of petroleum products content) to contamination diffuse halo (bitumen cake thickness reduction). The morphological boundary of the contamination diffuse halo was assumed the lack of visible petroleum products (bitumen cake) on soil surface, and the vegetation condition (signs of oppression or disturbance).

According to soil classification of Russia [12], common alluvial gley heavy loamy soil formed in the central part of the flood plain land was used for reference. Oil-contaminated soils are defined as oil-contaminated chemical-contaminated soils occurring within the areas of gray typical/gley medium-shallow soil. To specify vertical soil characteristics, main genetic horizons were sampled, and to assess salts lateral migration, the envelope technique was used as per national standard [13]. Petroleum products content in soil was determined by the fluorimetric method using a Fluorat-02 fluorometer. Acidic reaction (aqueous extract pH), as well as analytical studies of readily soluble salts content and composition were fulfilled as per national standard [14]. Statistica 6.0 software package was used for data mathematical processing.

3. Results
Due to specific genesis conditions, the West Siberian soils show low ecological/geochemical immunity from technogenic impacts and low potential of autopurification and self-regeneration [4]. Hence, oil can migrate laterally from eluvial and downslope landscape locations, as shown in the diagram suggested by V. P. Seredina and M. E. Sadykov (Fig. 1). Immediately after an accident, oil is accumulated in soil near the area of accident within the contamination halo center.

![Figure 1. Oil pollutant migration pattern in geochemically related landscapes of the study area [4].](image)
However, pollutants content growth is observed towards the contamination halo periphery and in deeper soil horizons that is indicative of oil seeping in the contamination central area and its lateral migration via migration paths (Table 1). Biogenic accumulative chemical-contaminated soil horizons (0-10 cm) of the entire contamination halo typically show higher content of petroleum products fixed with the soil humus matrix forming a toxic mixture of soil organic matter and hydrocarbon pollutant (NaCl, Na$_2$SO$_4$, MgCl$_2$).

Table 1. Oil content in various pollution zones. Oil products content in g/100 g of soil.

|                  | Epicenter of pollution | Impact zone | Pollution boundary |
|------------------|------------------------|-------------|--------------------|
|                  | 0–10 cm | 10–30 cm | 0–10 cm | 10–30 cm | 0–10 cm | 10–30 cm |
| Min              | 16.23   | 11.82    | 11.53   | 7.06     | 4.43    | 3.98     |
| Max              | 41.37   | 17.48    | 26.56   | 12.24    | 13.74   | 7.08     |
| Mean             | 36.78   | 10.15    | 22.42   | 6.54     | 13.3    | 7.69     |

Contamination heterogeneity is a function of pollutants accumulations in microdepressions. Such oil products diffusion creates spotty contamination pattern. Therefore, morphological features of contamination are the sensitive indicator of physical/chemical changes in soil: soil horizons gleying as a result of anaerobic conditions establishing; bluish shades of cutan; ferromanganese nodulous neoformations; humus/aluminum nodules; oil strong smell; generation of a compact bituminous cake on soil surface.

Any accidental crude spill is accompanied with high-mineralized salts discharges to the ecological system; these cause soil technogenic salinization and create bituminous varieties of soils. Statistical analysis data are indicative of a direct correlation between the content of freely soluble salts and petroleum products in contaminated soils: correlation factor (r) is 0,87 at $p=0,91$ (at 0–10 cm depth) and 0,83 at $p=0,076$ (at 10–30 cm depth).

Maximum discharged salts quantity is accumulated in the root layer (Table 2).

Technogenic liquids migration inside the soils is associated with ion composition fractionation. In a contamination source zone salts distribution shows prismoidal configuration: essential quantities of freely soluble salts are found within the entire soil profile showing the highest accumulation level in biogenic accumulative soil horizon.

Table 1. Oil content in various pollution zones. Oil products content in g/100 g of soil.

|                  | Dense residue, % | The amount of toxic salts, % | pH  | Salinity | Anionic salinity type | Type of salinity according to cationic composition |
|------------------|------------------|-----------------------------|-----|----------|----------------------|-----------------------------------------------|
| Epicenter of pollution (0–10 cm) |
| Min              | 0.35             | 0.28                        | 7.7 | medium   | sulfate              | sodium chloride                                |
| Max              | 1.12             | 0.33                        | 8.5 | medium   | sulfate              | sodium chloride                                |
| Mean             | 0.54             | 0.31                        | 7.6 | medium   | sulfate              | sodium chloride                                |
| Epicenter of pollution (10–30 cm) |
| Min              | 0.45             | 0.18                        | 6.9 | low      | sulfate              | sodium                                        |
| Max              | 0.65             | 0.29                        | 8.5 | low      | sulfate              | sodium                                        |
| Mean             | 0.48             | 0.26                        | 7.3 | low      | sulfate              | sodium                                        |

Impact zone (0–10 cm)

|                  | Dense residue, % | The amount of toxic salts, % | pH  | Salinity | Anionic salinity type | Type of salinity according to cationic composition |
|------------------|------------------|-----------------------------|-----|----------|----------------------|-----------------------------------------------|
| Min              | 0.45             | 0.19                        | 6.3 | low      | sulfate              | sodium                                        |
| Max              | 0.55             | 0.25                        | 7.5 | low      | sulfate              | sodium                                        |
| Mean             | 0.48             | 0.22                        | 6.9 | low      | sulfate              | sodium                                        |
The trend of high-mineralized stream flows accumulation is observed in soil top horizons and in contamination impact zone; however, another zone of salts accumulation is observed in the heavy grain size horizons at their general low content in the remaining soil thickness (Fig. 2).

As the total salinization impact is caused with different salts and ions toxicity for plants, qualitative salts composition is essential for salinized soils agronomical value. After pollutants batch-like discharge, the most mobile ion $\text{Cl}^-$ prevails in aqueous extracts from soil bottom horizons within the spill source and contamination zone periphery; note that total less mobile ions $\text{Ca}^{2+}$ gradually decrease from top to bottom soil layers. Such ions distribution within the soil stratum causes high cation $\text{Na}^+$ and anion $\text{SO}_4^{2-}$ content. Therefore, salinization typically shows sulfate and chloride/sulfate nature. Despite of low soil salinization, total toxic salts content is assumed the main diagnostic feature of the salts environmental impact. In the soils under consideration, technogenic salts are represented by compounds of the toxic salts $\text{NaCl}$, $\text{Na}_2\text{SO}_4$, $\text{MgCl}_2$. These salts inhibit plants growth that is an essential factor during phytomelioration sowing of grass at a biological remediation phase, since humid areas vegetation, unlike that of arid areas, is not adapted for periodic soil salinization.

One of the critical diagnostic features of oil contamination is soil acidic reaction. In reference soils, pH values vary from 4.6 to 5.2 that is indicative of acidic and low acidic reaction. Unlike the reference
samples, the oil-contaminated soils show low alkaline reaction. Hence, in the contamination source area, two months after the oil spill, the top soil layer shows pH equal to 7.82 that is indicative of the maximum oil and petroleum products content in the layer, as well as of the fact that crude has a certain content of freely soluble salts. So, acidic/alkaline properties are sensitive to oil contamination. Changes in absorbing soil complex, such as H⁺ and Al³⁺ ion exchange for Na⁺ resulting from soil contamination with oil (especially with crude showing high salinity) cause the shift in alkaline/acidic conditions: alkalinization of originally acidic and low-acidic soils is observed.

Hence, primary geochemical structure of infiltration bodies is formed: gradual reduction of the contamination core salinization towards its periphery, and simultaneous growth of chlorides percentage in salts. This differentiation of salts at contaminants single injection discharge to soil is indicative of progressive salinization, aggravating soil salinization in line with main phenomena forming the alluvial soil profile (turfy, alluvial, gleying).

The landscape features of the Western Siberian alluvial soils, such as poor drainage and shallow groundwater table contribute to forming the high-contrast and stable salt accumulations creating toxic environment for plants growth and development. Besides, shallow occurrence and subsequent rising of groundwater table may result in soil resalinization in presence of freely soluble salts. In this respect, alluvial soil technogenic salinization is an essential geocological factor, because these soils accumulate extra amount of different chemical compounds including different pollutants incoming from the elevated sites and contributing to forming new technogenic soil-geochemical successions (chemical-contaminated soils) in oil-contaminated areas.

Over the past ten years, different remediation technologies for technogeneous saline areas of the oil fields were put forward more than once. Contaminated lands irrigation with fresh water and its subsequent pumping-off and disposal at landfills may be a promising technique. This technique has been proven in practice, and is typically use for agricultural lands [14]. However, technical procedures involving irrigation of technogeneous saline areas have certain specifics: the irrigation rate of 5 l/m² is not capable of significant reduction of toxic water-soluble salts content in top soil, and is comparable with natural rainfalls. Contaminated irrigation water shall be accumulated to special tank trucks and removed; this activity involves extra costs and makes the technique extremely expensive and labor consuming.

Toxic salts of the root layers may be removed by means saline soil cutting and transportation from the area under consideration. This land remediation technique requires the use of special machinery, such as excavation equipment and trucks; this approach is extremely expensive and ineffective for organogenic soils and large areas. Besides, salinized soil landfill shall be authorized by law. Removed soil shall be replaces with pure soil (peat, sand). Such an approach is also ineffective due to salt accumulation in the underlying soil horizons, which may instigate resalinization in future.

The technique of acceleration of freely soluble salts surface carry-over with thaw water [15] is known; it may be rather effective for contaminated land remediation, as the major part of precipitations is accumulated in a form of snow cover in humid climate of Western Siberia. To intensify snow thawing, top soil mulching with peat or ash may be used. This technique may have a dual effect: despite of the fact that snow water washes the top soil horizons and salt concentration is somehow reduced, in general the technique does not actually influence the surface water composition and results in forming the strips of various concentration of water-soluble salts in surface horizons. Mobile drainage systems may be effective. In bogged and waterlogged areas, where near-surface water table is close to the day light, salinized groundwater inflow may be increased to natural or artificial microdepressions [16].

Efficient remediation of salinized areas may be achieved by means of combination of a number of techniques with consideration of environmental conditions, such as salinization level, area dimensions, topography, soils physical and mechanical properties, and watering conditions. Summarizing the lessons learned, it may be concluded that the methods combined with the techniques used for oil-contaminated land remediation may be effective. Based on field observations and qualitative chemical analysis data on freely soluble salts content and distribution the systems of drain ditches may be recommended with their subsequent washout with thaw water; and indigenous halophyte species seeds shall be used for phytomelioration. The use of indigenous (local) plant species or those adapted for a
specific climate and environment is an essential feature of remediation in humid climate conditions. The plants of Carex, Taraxacum, Artemisia, Ranunculus, Poa, Plantago families are capable of freely soluble salts accumulation in the Western Siberian environment. The technique provides for subsequent phytomass removal, and perennial grasses resowing till freely soluble salts content in soil achieves permissible values. The technique is also based on the landscape geochemical potential involvement into soil remediation making it essentially relevant at soil resalinization, when the groundwater table rises. Freely soluble salts will be carried-over with water to biogenic accumulative soil horizons and then will be accumulated in phytomass.

4. Conclusion
In reducing conditions of the middle forest of Western Siberia, in the event of accidental oil spills, the technogenic halogenesis causes highly mineralized flows, wherein sulfates and sodium are significant. Salt compounds create phytotoxic environment during phytomelioration at biological phase of land remediation. Chloride/sodium type of salinization and toxic salts content in soil profile governs the salinization that is not typical for soils of alluvial genesis type, and is indicative of the initial stage of technogenic halogenesis. Therefore, remediation activities shall involve the mechanisms of natural soil demineralization. The factors affecting chloride ions migration in soil are: amount of precipitations, area topography, air temperature mode, depth of soil seasonal freezing and its filtration properties. The soils under consideration require additional irrigation with fresh water, which will ensure salts removal from top and bottom soil horizons.

Besides, alluvial ecosystem soils accumulate an extra amount of various chemical compounds including various pollutants arriving from elevated sites. Groundwater may cause soil recontamination, because groundwater table rising will initiate post-technogenic soil transformation, that is migration of freely soluble salts from the underlying horizons to biogenic accumulative ones. Hence, alluvial soils are of high danger, and even after remediation activities monitoring and inspection is a must. Based on the study, it is recommended to compile new standard maps for technogeneous saline soil remediation, and it is necessary to include a section on studying the processes of technogenic soil salinization in the monitoring programs for oil-contaminated areas.

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