Transformation features of the main physicochemical and physical parameters of oil-contaminated alluvial soils in humid soil formation environment (Western Siberia)

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Abstract. This paper considers the results of the study of morphological and physicochemical parameters of floodplain ecosystem alluvial soils of Western Siberia, and reveals the features and their typical changes in different soil-contamination zones (the impact zone is the epicenter). Physicochemical parameters and morphological features of industrially contaminated soils are compared with reference analogs.

1. Introduction
Continuously increasing human intervention leads to the increase of contaminants emission to ecosystems. Among numerous environmental contaminants (EC), oil and oil products (OP) shall be mentioned as sufficiently hazardous, quickly propagating, slowly decomposing in natural conditions and capable of exerting a toxic effect on soil that is the central component of the ecosystem. At the same time, morphological properties of soils are the most representative signs of contamination, as they are indicators of changes in the agrophysical properties. Due to this fact, development of techniques, aimed at reduction of negative impact of hydrocarbons on natural ecosystems is a relevant objective. These developments are especially important for the soils formed in humid environment of Western Siberia, where soil self-regeneration is the most complex and long-term process [1-5].

Despite a significant number of works devoted to the study of the impact of oil pollution on the ecological state of soils in taiga eluvial landscapes of Western Siberia [5-9], few data is available on oil products typical behavior, as well as practical aspects of floodplain ecosystems soil reclamation. Due to this fact, the objective of this study is the analysis of specific oil contamination impact on morphological features and physicochemical parameters of alluvial soils.

2. Materials and methods
The study covered the soils of the territory of the crude oil spill in Alexandrovski and Kargasokski Districts of the Tomsk Region, and of Nizhnevartovsk District of the Khanty-Mansi Autonomous Area of Yugra. Soil contamination resulted from the field pipeline rupture in the central part of the Ob River.
floodplain. In each zone of different technogenic load (epicenter, impact zone, oil spill periphery), a soil cross section and a number of pits were made, and soil was classified based on the reference data. Soil sampling was carried out in accordance with GOST 28168-89, taking into account the thickness of the horizons of the described sections to a depth of 100 cm. Pit samples were taken from 0–10 and 10–20 cm layers. Biocenoses are represented by pine, larch, pine and birch forests; steppe cereal, forb cereal and leguminous cereal communities, as well as meadow forb associations of river valleys and interplanar depressions. For field studies of soils of the landscapes under study, soil-morphological, pedo-lithological, botanic, geological-geomorphological and comparative-geographic study methods were applied. Within the area, 5 soil cross sections and 25 soil pits were made and described. To identify the specific features of contaminated soil transformation, a cross-spectrum analysis of reference soils and soils contaminated with oil emulsions was carried out. Undisturbed soils are located in the immediate vicinity of the reference target and are represented by various types of alluvial soils. Diagnostics and classification was carried out in accordance with modern concepts of industrially transformed soil classification [10-11].

Air-dry soils samples were used for laboratory studies of properties of the main types of soils as per applicable GOSTs [12-14], and with the help of statistical methods and STATISTICA 6.0 software.

3. Results and discussion

The morphology of cross section objectively reflects soil formation trends and gives a clear idea of soil ecological state. Therefore, the primary indicator of oil contamination of the soil is the transformation of soil appearance.

The morphology of the reference soils quite clearly reflects the alluvial process trend. Under the sufficiently decomposed underlayer, an accumulative humic fine lumpy AY_{v,x} horizon up to 13 cm thick is formed. Medium horizon is not expressed as an individual genetic form: the middle part of the cross section does not show paedogenetic structure, and is amorphous. The root layer is not thick: the bulk of the roots is concentrated in the top part of the profile, in the organogenic and accumulative humus horizon; single roots only are observed deeper than 30 - 40 cm. According to the classification of soils of Russia [10], common alluvial pratal dirt/gley heavy-loamy soil formed in the central part of the floodplain land was used as reference soil. Cross section formula: AY_{v,x}(1-10 cm)+AY_{x}(13-23 cm)+AYC_{g,x}(30-40 cm)+IC_{1g}(45-55 cm)+ IIIC_{2g}(60-70 cm)+ IIIC_{3g}(90-100 cm).

The cross-section of industrially transformed soils is similar to the reference one. According to the reference soil cross section, oil-contaminated soils are defined as chemical-contaminated occurring within gray/humic typical/gley medium-shallow soil. The color of the humified horizons of the contaminated soil (AY_{v,x}, AYC_{g,x}) is unnaturally dark compared to the reference, which is explained by the addition of organic contaminants. Observation data are confirmed by analytical studies: in oil-soaked freshly contaminated soil of oil spill center the total carbon content is as high as 10.7% in humus horizon, and 5.4% in the reference soil cross section. Tests of oil products content show their random distribution in soil cross section. In humus-accumulative horizons of soils, high concentrations of oil products are observed in all contamination zones, however, even in case of reclamation of these horizons, oil toxic effect on soil will persist for a long period. It should be noted that rating the contamination of deep mineral soil horizons is still problematic. In contaminated soils, oil products content ranges from 16.23 to 3.98 g/100 g of soil, decreasing laterally with the distance from the contamination source to the impact zone, and radially with the depth of soil horizons. Thus, oil carbon addition significantly increases content of soil total organic carbon, but deteriorates agrotechnical value of soils as a nutritious substrate for higher plants.

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The soil cross section top is sealed under dense technogenic material - bituminous crust. Soil consolidation varies from moderately cemented to highly cemented (AY_{v,x}, AY_{x}, AYC_{g,x}), overconsolidation is predominantly artificial. The humus horizons contain artifacts (> 20%) in the form of construction waste, synthetic solid waste, and crude oil, which enables reliable soil classification as Technosols [11] (table 1).
Table 1. Physicochemical parameters of oil-contaminated soils.

| Depth, cm | Oil g/100 g of soil | C opr lim | \( \bar{x} \) | r | pH | \( \bar{x} \) | r | toxic salts |
|----------|---------------------|----------|----------|---|----|----------|---|-------------|
|          | Reference values    |          |          |   |    |          |   |             |
| 0-10     | -                   | 5.4-3.27 | 4.88     | - | 4.6-4.7 | 4.73     | - | -           |
| 10-30    | -                   | 3.87-1.09| 2.62     | - | 5.2-4.1 | 4.93     | - | -           |
|          | Contamination source |          |          |   |    |          |   |             |
| 0-10     | 16.23               | 18.01-14.87 | 17.06     | 0.90 | 8.95-8.06 | 8.42     | 0.81 | NaCl, MgCl₂ |
| 10-30    | 11.82               | 12.82-6.98 | 9.33     | 0.71 | 6.81-6.28 | 6.36     | 0.72 | Na₂SO₄       |
|          | Impact zone         |          |          |   |    |          |   |             |
| 0-10     | 11.53               | 15.91-11.09 | 13.08     | 0.88 | 8.45-8.11 | 7.28     | 0.79 | NaCl, MgCl₂ |
| 10-30    | 7.06                | 9.61-6.47 | 7.98     | 0.83 | 6.34-6.01 | 5.98     | 0.71 | Na₂SO₄       |
|          | Pollution boundary  |          |          |   |    |          |   |             |
| 0-10     | 4.43                | 14.2-4.71 | 9.93     | 0.78 | 7.62-7.06 | 6.62     | 0.77 | NaCl, MgCl₂ |
| 10-30    | 3.98                | 8.02-2.76 | 5.17     | 0.91 | 6.91-5.34 | 5.03     | 0.81 | Na₂SO₄       |

In addition to unique morphology, the cross section of alluvial soils under consideration also shows specific physical and chemical properties. For reference soils, pH value of the root horizons varies from 4.6 to 5.2 (low acid). The values of pH of chemical-contaminated soil show opposite trends and varies from alkali values in the contamination source AY (8.95), to neutral values near the contamination periphery (7.62) that is directly related to freely soluble salts of Cenomanian water present in crude oil and causing its high water cut (98%). Statistical analysis data are indicative of a direct correlation between the content of freely soluble salts and oil products in contaminated soils: in the contamination source correlation factor (r) is 0.81 at p=0.08 (0–10 cm depth) and 0.72 at p=0.06 (10–30 cm depth).

Due to increasing industrial impact on topsoil, there is a change not only in the most dynamic agrochemical properties of soils, but also in such a conservative component as granulometric composition. Thus, as a result of short-term effect of oil flows, re-distribution of main fractions of granulometric composition in humus horizons and in horizons with heavier granulometric composition \((IIC_{2g}, IIC_{3g})\) is noted in comparison with natural analogues.

Silt fraction, which concentrates bulk of organic material (55-90%) and is a factor of its accumulation and stabilization in reference soils, and fixing of technogenic \(C_{org}\) (oil) in chemical-contaminated soil, is of special interest. As granulometric composition is one of the most important soil characteristic, deterioration of this parameter in industrially transformed soils affects soil structure \(K_{struct}=0.53\) (unsatisfactory) Initial lumpy-granular structure transforms into a blocky structure, which deteriorates agrophysical value of soils.

The nearer to the contamination source, the more even the distribution of granulometric composition fractions becomes, which leads to reduction of soil profile differentiation. Thus, in oil-contaminated soils, the degradation of genetic horizons is extremely expressed, up to the complete erasing of the distinctive primary features of the natural soil cross section. The nature of contaminated soil contours change: tongues and pockets are observed, bituminous crust is formed on the surface. Besides, silty fraction shows a certain rearrangement trend: its content grows in root horizons of soils (reference – 11.5%, chemical-contaminated soil – 18.5 %). This feature is explained by oil impact on soil under reductive conditions, which contribute to the increase of quantity of fine-dispersed particles in contaminated soils. These processes are a consequence of uneven distribution of the contaminant over cross section, and appearance of strongly pronounced mosaic structure under influence of oil contamination. Changes in structural aggregates are traced: within the same genetic horizon \((AY_v,x, AY_x, IC_{1g,x}, IC_{2g,x})\) the areas of different types of structural separates appear.
In the lower hydromorphic horizons of the studied oil-contaminated soils (IC1g, IIIC2g,x, IIIC3g,x) an increase in the grain size distribution and in the number of ochre spots confirming the intensification of gleying is observed. Heavy oil fractions have a significant effect on the aggregate state of soils. In reference soils, Kd (dispersion coefficient) is at its peak in humus horizons (8%), while in chemical-contaminated soil its values reach 22% that is indicative of a high water resistance of reference samples. This trend was also observed during field visual analysis of soils: an increase in lumpiness is noted in line with a decrease in the content of agronomically valuable mesoaggregates. Such changes cannot be attributed to positive phenomena, since unnatural, independent of soil genesis growth of agronomically valuable fraction of soil structure due to the adhesion of microaggregates with oil is accompanied by the appearance of a number of extremely negative properties and processes deteriorating the index of quality and yield of soil.

Index of quality and yield of soil is the integral assessment of soil capabilities. Transformation of alluvial soils into anthropogenically transformed chemical-contaminated soils is manifested through a system of diagnostic morphological, agrochemical and agrophysical indicators reflected in the evaluation score scale. According to FAO rating method, the index for assessing reference alluvial soils calculated as the geometric mean of the total number of points (indices) LUI = 67 (Land Unit Index) makes it possible to attribute the soil to suitability class II (moderately suitable). Soil within no more than 1/4 of the area shows slight restrictions; lands are suitable for hay harvesting.

Oil-contaminated soils have LUI = 14, and may be attributed to lands category IV (subclass ‘a’) (unsuitable). The possibility of further use of soils requires additional significant material costs (reclamation), there are severe restrictions on 2/3 of the territory.
4. Conclusion
Hydrocarbon contaminant impact on soils of inundable ecological systems cause the changes in morphological and physicochemical properties of soils. This results in the following changes: darker color of the entire soil cross section, intense specific petrochemical odor, cementation of soil aggregates with heavy oil fractions, and formation of bituminous crust on the soil surface, which, in turn, leads to sharp changes of physical and chemical properties (pH, C_{org}). An important feature of soil contamination with technogenic hydrocarbons is not only destruction of morphological properties, but also transformation of an important agrophysical component of soils, their granulometric composition, and, consequently, general ecological state of soils as well.

Therefore, soil reclamation shall involve the mechanisms of soil natural purification. The factors affecting oil products migration and degradation in soil are: amount of precipitations, area topography, air temperature mode, depth of soil seasonal freezing and filtration properties. The soils under consideration require additional irrigation with fresh water, which will ensure salts outwashing from top and bottom soil horizons.

Besides, inundable ecological system soils accumulate extra amount of various chemical compounds including various contaminants arriving from topographic highs. Groundwater may cause soil recontamination, because groundwater table rising will initiate post-technogenic soil transformation: migration of technogenic contaminants from the underlying horizons to biogenic accumulative ones. Hence, oil-contaminated alluvial soils are of high danger for hydrographic network, and even after soil reclamation monitoring and inspection is a must. Based on the study data, it is recommended that new standard maps are plotted for disturbed soils reclamation, and monitoring program of environmental impact during oil fields development shall include the section covering the investigation of technogenic soil salinization and agrophysical parameters of soils.

Acknowledgments
We are grateful to JSC «TomskNIPIneft» for the opportunity to publish this article to the sponsors, as well as the staff of the Department of Soil Science and Soil Ecology of the National Research Tomsk State University.

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