Biochemical monitoring of soils in the area of development of subsurface energy resources

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Abstract. It was found that the sites of the drilling rigs are the most transformed and polluted areas of soils on the territory of the gas-condensate field. It was established that the soils of some of the sites of development of the gas-condensate field showed increased contents of oil products, lead, zinc, nickel and chromium exceeding background values and health standards. On the territory of the Nyuchakan base and of some boreholes of the gas-condensate field there occurred a change in the soil water composition, and chloride and sulfate salinization of soils was observed. Characteristic areas of technogenic soils formed 15 and 25 year after the accidents: ejection of highly mineralized oil-field pressure brine (natural brine) to the surface in the area of the valley of the Orlingskaya Nyucha (the Kovykta gas-condensate field), and oil spill in the vicinity of the village of Tyret (the Krasnoyarsk-Irkutsk pipeline). They show high contents of oil products, heavy metals and organic matter as well as the shift of the reaction of the medium toward the neutral and alkaline side. The study revealed an increase in the sum of exchange bases, salinization, a heavier granulometric composition, and enhancement in gleying, and a decline in biological activity of soils.

1. Introduction
The Kovykta gas-condensate field (KGCF), one of the largest on the territory of Eastern Siberia, is located in the northern part of the Lena-Angara Plateau. In 2004, on the KGCF drilling rig there occurred an accident with ejection of 2200 m³ of highly mineralized oil-field pressure brine (natural brine) to the surface from a depth of about 2000 m.

The territory of Irkutsk oblast is the home for more than 2 thou km of the Krasnoyarsk-Irkutsk and Omsk–Irkutsk oil pipelines and the Angarsk–Irkutsk kerosene pipeline. In March 1993, more than 32 thou t of oil were spilled on the surface because of the breaking at weld on the Krasnoyarsk–Irkutsk main oil pipeline in the vicinity of the village of Tyret. About 1 thou t of oil penetrated deep into the soil horizon and was localized in Lower Cambrian karst reservoirs 150–300 m from the operating groundwater intake facility. Residual oil saturation of earth materials and soils has been observed to date.

2. Models and methods
The object for study involves the soils of KGCF and of the territory of the Tyret accidental oil spill from the Krasnoyarsk–Irkutsk oil pipeline in the Zalarinskii district of Irkutsk oblast. The area of the
Kovykta license site on which the main extraction of gas is being conducted measures about 4.4 thou km².

The gas-condensate field is located in the interfluve of the Lena and its right tributary, the Kirenga. The Lena-Angara Plateau is the main morphostructure. The Zalarinskii district is located in the middle part of the Irkutsk-Chernemkhovo plain.

In March 1993, oil spill occurred due to an accident on the main oil pipeline in the vicinity of the village of Tyret. Oil spread along the right bank side of the Unga river inundating its channel and low areas of the floodplain, including agricultural lands. The territory of pollution was 700 m in width and 2 km in length.

During 2001–2012, soil-geochemical work was done on the Lena-Angara Plateau and in the Upper Angara region; soil samples were collected in accordance with effective State standards and with Methodological recommendations for identification of degraded and polluted lands [2]. A total of 300 soil profiles were established from which more than 700 samples were collected for physicochemical analyses.

The chemical analyses of soils were made according to generally accepted techniques in the Chemical-Analytical Center of Sochava Institute of Geography SB RAS and in Irkutsk State University. Total concentrations of metals were determined by the atomic-emission spectral method with the Optima 2000DV instrument. Total content and qualitative composition of readily soluble salts were investigated in the aqueous extract. The concentration of oil products in samples was analyzed by the fluorometric method. The proximate method of T.V. Aristovskaya and M.V. Chugunova [3] was used to determine the biological activity of soils.

3. Results and discussion
According to the soil-geographical regionalization [1], the territory of KGCF forms part of the Northern-Cisbaikalia mountain province, and the territory of oil spill forms part of the zone of Chernozems and Gray soils of the forest-steppe.

On the basis of published material [4-10] and results of investigations, we identified the following main types of soils: Podzols, Folic Podzols, Histic Podzols, Retisols, Folic Retisols, Burozems, Burozems Umbric, Cryosols, Histic Cryosols, Podburs, Folic Podburs, Histic Podburs-gleyic, Umbrisols, Humus Umbrisols, Cambisols, Regosols Calcaric, Arenosols Calcaric Humic, Gray, Dark Gray, Fluvisols Humus, Fluvisols Aridic, Fluvisols Umbric, Fluvisols Mollic-gleyic, and Fluvisols Histic-gleyic. Technozems and Technosols occur locally on the sites of the drilling rigs and on the territory of oil spill.

On the basis of field investigations using thematic maps as well as satellite images and aerial photographs, maps were compiled for separate licensed sites of the gas-condensate field [5, 6] and for the entire Baikal region [11].

It was found that the medium reaction of soil suspension (pH_{H_{2}O}) showed a broad range from acidic to alkaline values. The upper soil horizons on calcareous material showed a reaction close to neutral. Folic Retisols are distinguished by a constantly weakly acidic reaction throughout the profile. The low acidity of these soils reflects the provincial feature of Middle-Siberian soils with a differentiated profile and may be attributed to the recent replacement of moss dark-coniferous forests by grass light-coniferous forests and the lithological inhomogeneity of earth materials [7].

The soils on the territory of the drilling rigs often show an alkaline reaction due to the removal of the upper horizons or their mixing with parent rocks as well as technogenic salt flows. The content of organic carbon in the upper soil horizons of natural landscapes is high (more than 5%). Technozems and Technosols on the sites of the drilling rigs show lower contents of organic carbon, varying from 0.1 to 1.7%. According to the analysis of the aqueous extract, the natural soils are not salinized. The aqueous extract from the sites of the long-operated drilling rigs and the Nyuchakan base shows the chloride-calcium and chloride-potassium composition. The total amount of mineral salts in the aqueous extract of soils reaches 0.15%. A high mineralization was observed in 2005–2006 in the soil in the vicinity of the unrecultivated drilling rig in the upper reaches of the Tipui river (1.7%) and in
the area of the drilling rig 18 (5.6%) on which the accident occurred in 2004. The accident involved the ejection of highly mineralized oil-field pressure brine (natural brine) to the surface from a depth of about 2000 m (the contact zone of the Bil’skaya Usol’skaya formations of the Lower Cambrian) and the runoff of brine flow to the valley of the Orlingskaya Nyucha river. The liquid phase of the flow showed a highly acidic medium (pH 3.3–3.5) due to a high concentration of Cl (370–390 g/dm³). In the total mineralization of this brine (700–730 g/dm³), the cations were dominated by Ca²⁺ (about 200 g/dm³). A few days after the accidental ejection, the aqueous extract from the upper soil layer beneath the brine contained in mg eq./100 g: Cl⁻ – 370–800, Ca²⁺ – 290–600, NH₄⁺ – 80–260, Mg²⁺ – 60–200, Na⁺ and K⁺ – 25–200, with the total amount of mineral salts varying from 825 to 2886.

The background areas commonly show hydrocarbonate-calcium and (more rarely) sulfate-calcium soil solutions. The concentrations of ions in mg eq./dm³ are: HCO₃⁻ – 0.1–0.5 (averaging 0.2), Ca²⁺ – 0.2–0.8 (0.4), SO₄²⁻ – 0.02–0.21 (0.06), Cl⁻ – 0.01–0.20 (0.05), and Na⁺ – 0.01–0.06 (0.02).

According to results of the chemical analyses, the ecological status of the soils on the sites of the drilling rigs is largely characterized as relatively unsatisfactory. The content of Mn, Zn, Ni, Cr and Pb in the soils of the drilling rigs exceeds the regional background of Cisbaikalia [12] by factors of 1.2–12. On the sites of some of the drilling rigs, the content of zinc, nickel, chromium and lead in the soils exceeds the health standards by factors of 1.2, 1.3, 1.6 and 3.7, respectively. In the soils from the areas of development of the gas-condensate field which have been in operation for more than 30 years, increased contents of chemical elements were recorded at a depth of more than 20 cm.

It was found that the background levels (mean content on a conventionally clean territory of KGCF) for Fe, Mn, Ba, Zn, Cu, Ni, Cr, Pb and Cd in the soils of the central zone of KGCF were 37 539, 683, 308, 42, 19, 48, 92, 18 and 0.8 mg/kg, respectively. The concentration of manganese, barium, zinc, copper, nickel, chromium, lead and cadmium in the soils of the drilling rigs exceeds the background values determined for the territory of KGCF by factors of 1.9, 2.5, 2.2, 3.6, 2.6, 1.7, 6.3 and 3.1, respectively.

Increased contents of oil products (184 mg/kg) in the soil exceeding the background content by a factor of 8 but not exceeding the health standards were recorded in the area of the mobile automated gas-turbine power plant. The background content of oil products for the territory of KGCF not affected by human activity averages 21.7 mg/kg [5].

In 1993, oil spill occurred as a result of a serious accident on the Krasnoyarsk-Irkutsk main oil pipeline, in the vicinity of the village of Tyret. The immediate measures undertaken to eliminate the consequences of that accident made it possible to minimize the negative effects. However, oil spread along the right bank side of the Unga river and penetrated deep into the soil. At the center of the oil slick, the content of oil products exceeded the background level by a factor of 7500 [13].

A peculiar area of pollution formed on the study territory within 25 years after the accidental ejection. The content of oil products in the 30–40 cm Dark-Gray soil layer is 5600 mg/kg; in the waterlogged horizons of Histic-gleyic soils, 8990 mg/kg. The background contents of oil products within the Irkutsk-Cheremkhovo plain lie in the range 20–130 mg/kg [6].

Soil pollution by oil leads to the shift of the medium reaction toward alkalization. Thus, in the Dark-Gray forest soil there occurs the shift of pH_H₂O to weakly alkaline and in the Gray forest soil, to alkaline.

An excess of specific organic matter forming part of composted oil disturbs the overall regularity of humus distribution with depth. All oil-polluted soils are characterized by the occurrence of horizons with increased humus content within the soil profile. The humus content can vary over a significant range 1–5% in Gray, 1–10% in Fluvisols Histic-gleyic and 3–15% in the Dark Gray soil.

It was found that the granulometric composition becomes heavier in the oil-saturated horizons. The exposed Fluvisols Histic-gleyic soil is characterized by a pungent, persistent smell of oil, which is indicative of high contents of residual oil products. In the lower waterlogged horizons, the granulometric composition becomes heavier and the number of ochreous spots increases confirming an enhancement in the gleying process. With the increasing period of composting, there is an increase of the number of exchange cations in the oil-polluted horizons.
At the time of oil spill into the soil and groundwater, a large number of chloride-ions and sulfate-ions were brought in by oil, and they can serve as an additional source of soil salinization. According to the anion composition, we categorized the soils from the study territory as salinized soils, with a different intensity of manifestation of the process. The neutral sulfate-chloride and chloride-sulfate types of salinization are dominant. The soil profile shows layers with the chloride type of salinization. The upper horizon of the Dark-Gray forest soil exposed near the protection dike shows the alkaline threshold and weak sulfate-chloride-soda salinization. Solonetization is recorded from a depth of 60–70 cm in the oil-saturated soils.

Thus 25 years after the pollution the concentration of toxic oil products has decreased. The study territory shows a stable vegetation cover. Currently the main mass of oil products is composed of low-toxic hydrocarbons and resinous asphaltenic components that are not toxic for colonization by most plant species.

The indicators of biological activity of the soils used in this study vary from 7.5 to 19 hours (до 19 часов (henceforth referred to as units) [14]. The upper horizon, like most of the lower horizons, showed a comparatively low activity. At depths of 6–24, 24–39 and 45–3 cm the degree of biological activity of soils lies within 7.5–8.5 units. The general indicators in the control area fluctuate from 9 (5–15 cm) to 23 units (65–80 cm). Of interest is a very low activity of the upper horizon. This can be explained by a large amount of oil in this surface layer which, like a filter, received the first result of the Tyret oil spill accident shows a natural directedness of natural recovery processes. Vegetation shows no signs of suppression, and sustainable grass stands are observed. However, oil pollution gave rise to a peculiar area of technogenic soils. Composting of oil products involves changes in the soil properties: an increase in content of organic matter in the horizons to 80–90% of the mass, an enhancement in gleying processes. The degree of biological activity of the oil-saturated soil decreases considerably and can lead to a disturbance of the nitrogen cycle.

4. Conclusion
The soil cover of the territory of the Kovykta gas-condensate field and of the Krasnoyarsk-Irkutsk pipeline is quite varied. As a result of doing the research and analyzing published data, we identified 26 main types and subtypes of soils on the study territory.

The sites of the drilling rigs are the most transformed and polluted areas of soils on the territory of the gas-condensate field. The soils of the sites of the drilling rigs show a weak salinization and increased contents of zinc, chromium and lead exceeding the health standards.

The study territory of the Tyret oil spill accident shows a natural directedness of natural recovery processes. Vegetation shows no signs of suppression, and sustainable grass stands are observed. However, oil pollution gave rise to a peculiar area of technogenic soils. Composting of oil products involves changes in the soil properties: an increase in content of organic matter in the horizons to which oil penetrated and became entrenched in it; the shift of the reaction of the soil medium toward alkaline reaction; soil solonetization and an enhancement in gleying processes. The level of biological activity of the oil-saturated soil decreases considerably and can lead to a disturbance of the nitrogen cycle.

References
[1] Dobrovol’skii G V and Urusevskaya I S 2004 Soil Geography (Moscow: Kolos) p 460
[2] Methodological Recommendations for Identification of Degraded and Polluted Lands 1995 (in Russian) Income accessed online on 10th September 2019 via http://pandia.ru/text/78/664/70746.php
[3] Aristovskaya T V and Chugunova M V 1989 Proximate method of determining biological activity of soils Pochvovedenie 11 142-7 (in Russian).
[4] Abalakov A D, Nechaeva E G and Shchetnikov A G 1997 Soil-geochemical mapping for purposes of the environmental protection Geography and Natural Resources 1 25-33
[5] Belozertseva I A 2012 Soil transformation in cryogenic-taiga conditions in the area of development of the gas-condensate field Geokologiya, Inzhenernaya Geologiya, Gidrogeologiya, Geokryologiya 3 221-8 (in Russian)
[6] Belozertseva I A and Ryzhov Yu V 2017 Chemical composition of natural and anthropogenically disturbed soils of the right-bank forest-steppe Angara region (exemplified
by the Bokhanskii district of Irkutsk oblast) Izvestiya of Irkutsk State University Series, Biology and Ecology 20 47-60 (in Russian)

[7] Vorobyeva G A 2009 Soils of Irkutsk Oblast: Questions of Classification, Nomenclature and Correlation (Irkutsk: ISU) p 149 (in Russian)

[8] Kuzmin V A and Belozertseva I A 2004 The current state of soil cover in Ecologically Oriented Land Use Planning in the Baikal Region (Kovykta Gas-Condensate Field) eds. E G Suvorov and S A Makarov (Irkutsk: IG SO RAN) pp 91-9 (in Russian)

[9] Nechaeva E G 1997 Landscape-geochemical changes in the taiga as identified during geological surveys of subsurface resources Geography and Natural Resources 4 81–7 (in Russian).

[10] Sazonov A G 1969 Soil cover and soils of the Khand and Kirenga interfluve Doklady Instituta Geografii Sibiri i Dal’nego Vostoka 21 40-7 (in Russian)

[11] Ubugunov L L, Ubugunova V I, Belozertseva I A, Gyninova A B, Sorokovoi A A and Ubugunov V L 2018 Soils of the Lake Baikal drainage basin: Results of research for 1980–2017 Geography and Natural Resources 4(39) 332-42

[12] Grebenshikova V I, Lustenberg E E, Kitayev N A and Lomonosov I S 2008 Geochemistry of the Baikal Environment (Baikal Geocological Test Site) ed. M I Kuzmin (Novosibirsk: Geo) p 234 (in Russian)

[13] Blokhin Yu I 1993 Project of the Conduct of Priority Hydrogeological Work in the Section of the Accident on the Oil Pipeline in the Village of Tyret for 1993–1994 (Irkutsk: GGP Irkutskgeologiya) p 28 (in Russian)

[14] Granina N I and Naprasnikova E V 2014 The ecological state of soils after the oil spill accident in Irkutsk oblast Vestnik Tambovskogo Universiteta Seriya: Estestvenye i Tekhnicheskie Nauki 5 1393-6 (in Russian)