Bituminous substances in soils of Baikal Rift zone

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Abstract. Parameters of hydrocarbon complex of the soils of lacustrine-alluvial plain and sandy uplands of the Baikal rift zone within the Barguzin Depression have been studied. Data were obtained on organic (non-carbonate) carbon, chloroform and hexane bitumoids, as well as on individual polycyclic aromatic hydrocarbons. The content, composition and properties of bitumoids vary depending on the intensity of endogenous activity. In soils located in the zone of active unload of hydrothermal waters and hydrocarbon fluids, atypical accumulation of organic carbon was noted; the concentrations of bitumoids do not correlate with its content. High values of the bitumoid coefficient, significant level of polycyclic aromatic compounds and their diversity, in combination with salts accumulation, indicate an additional influx of hydrocarbons and instability of the soil hydrocarbon system. The level of the indicators shifts towards background values in the soils of sandy hills with a complex combination of exogenous and endogenous factors of soil forming. Studied parameters of the soil hydrocarbon system in aggregate can serve as markers of the intensity of endogenous processes.

1. Introduction

Baikal Rift is the tectonically active zone with faults in earth crust and features of mud volcanism [1]. Free hydrocarbon gas, oil, petroleum bitumen, gas crystallohydrates, hydrocarbon gases dissolved in water are the main components of hydrocarbon systems found in the Baikal Rift basin [2]. Barguzin depression is the largest dry basin of this zone with dense network of tectonic faults [3], spontaneous emission of free gases and hydrothermal springs of the Kuldur type [4]. There are atypical soils in which "classical" alluvial, metamorphic and organic-accumulative processes are poorly developed, and characteristic system of genetic horizons of zonal soils is not appeared. Specific black viscous layers, interlayers, lenses are one of the features of soil morphology. These morphones are plastic in the wet state, and become solid when dried, sodium accumulates within these layers. Contrasting combination of soil pH values, texture, high salinity, turbidity are peculiar markers of endogenous activity in this area [5]. These specific soils are mainly confined to the Kuchiger thermal field (Ulyunkhan depression), the sandy upland "Nizhniy Kuytun", the close basin of the Nukhe-Nur lakes, the foothill of the Ikat ridge and the lacustrine-alluvial plain (Mondai tract). Soils are geochemically close both in terms of salt content and salinity chemistry, and in matter composition, with elevated or abnormal gross concentrations of a number of elements [6]. Along with the mineral components of thermal waters, the endogenous hydrocarbon gas fluids enrich soils with organic compounds. Our research was aimed to study bituminous substances fixed in soils. These results are important for the theory of endogenic impact on soil forming processes, and also are significant practically as markers of hydrocarbon emanations for exploration and environmental purposes.
2. Objects and Methods
The study was carried out in zones of active fluid dynamic processes within the Barguzin depression (North–West of the Republic of Buryatia, Russian Federation (figure 1). Climate of the study area is extra continental, cryo-arid. Average annual air temperature varies from –2.6 to –5.3 °C from south to north. Average annual precipitation in the basin is 160–300 mm. Soil profiles were laid within the several parts of the basin differ in manifestation of endogenous activity.

Organic–impregnated solonchakous slightly surface-saline humic psammozem, underlain by buried organic–impregnated sandy gley soil (Eutric Sodic Gleic Arenosol (Humic) (RF–1–4) and organic impregnated, gas-hydrothermally turbated surface solonchakous moderately saline sandy light-humus gley alluvial soil (Eutric Sodic Gleyic Pantofluvic Fluvisol (Alcalic, Epiloamic, Endoarenic, Humic, Sulfidic)) (RF–1–5) were studied in the North–Western part of the basin. These soils are formed in the zone of hydrothermal activity of Kuchiger hot spring. Soil morphology, classification, and preliminary data on hydrocarbons in these soils were presented earlier [7, 8]. Humus psammozem has a high content of organic carbon in the upper part of the profile, sandy texture, alkaline pH and low salinity level (table 1). There is dark viscous, plasticine-like horizon with the layer thickness of 40–45 cm in the middle part of the profile. It is sandy loam, lower saline, of slightly acidic pH. Light-humus gley alluvial soil is layered, has an uneven horizon boundary, and numerous dark inter layers and inclusions impregnated with a black oily substance. The soil from the surface is sandy clay loam, highly saline, pH value is 9.7. Degree of salinity, alkalinity, content of fine fractions, and organic carbon decreased down the profile.

![Figure 1](image-url)

**Figure 1.** Relief of the Barguzin depression and location of sampling plots: 1 – RF–1–4; 2 – RF–1–5; 3 – TNK–25; 4 – NK–8.
Salic solonet (TNK–25) (Salic Solonetz (Loamic, Cutanic, Humic)) is located in the center of the basin, on a sandy hill "Nizhniy Kuytun" area. The soil occupies an eluvial position, raised 180–200 m from the level of the lacustrine–alluvial plain. Salt deposits in this area do not agree with the classical (exogenous) factors of soil formation: climate, landscape position and the absence of salt sources in the parent rocks. In the soil profile, the lightened saline-eluvial horizon SEL is formed underlain by very dense, dark brown, of nutty-prismatic structure, intermittent low–thickness saline horizon (BSN). There is heavy texture and high salinity in this horizon.

There are large enough areas located in the central part of the lacustrine–alluvial plain, where channels of hydrocarbon emanations are well defined in soil morphology throughout the soil profile. There is humus psammozem (NK–8) (Eutric Arenosol (Humic, Alcalic)) location. Horizon W of this soil is sandy loam, not saline, and has a high organic carbon level. The soil texture is lightened sharply and organic carbon decreases deeper than 20 cm. Classification and diagnostics of soils was carried out according to [9, 10].

In soil samples, content of organic (non–carbonate) carbon was measured using potassium dichromate oxidation Tyurin method modified by Nikitin et al. [11]; pH, by potentiometry (soil : water ratio is 1 : 2.5); soluble salts amount and composition, in soil water extracts (1 : 5); soil texture by the pipette method [12].

| No | Plot | Horizon | Depth (cm) | pHw | Salts (%) | C<sub>org</sub> (%) | Particles <0.01mm (%) |
|----|------|---------|------------|-----|-----------|-----------------|---------------------|
| 1  | RF–1–4 | W       | 0–1.5      | 8.3 | 0.33      | 2.74            | 7                   |
|    |       | AC      | 1.5–3.7    | 9.1 | 0.25      | 0.76            | 7                   |
|    |       | IMP     | 40–85      | 6.6 | 0.20      | 1.37            | 13                  |
| 2  | RF–1–5 | AJimp   | 0–6        | 9.7 | 1.77      | 2.53            | 23                  |
|    |       | QCimp   | 6–20(41)   | 8.7 | 1.76      | 0.20            | 12                  |
|    |       | QCimp2  | 20(41)–55  | 6.3 | 0.37      | 0.74            | 13                  |
| 3  | TNK–25 | AJ      | 0–18       | 7.1 | 0.02      | 1.45            | 14                  |
|    |       | SEL     | 18–21      | 9.1 | 0.06      | 0.74            | 14                  |
|    |       | BSN     | 21–25      | 9.6 | 1.57      | 0.76            | 35                  |
| 4  | NK–8  | W       | 0–2(9)     | 8.6 | 0.06      | 2.77            | 14                  |
|    |       | C       | 20–33(37)  | 8.7 | 0.14      | 0.08            | 4                   |

Along with the general physical and chemical characteristics of soils, soil samples were analyzed for the total content of bituminous substances, hydrocarbons (HC), the amount of 14 individual polycyclic aromatic hydrocarbons (PAH) at the Analytical Center of the Faculty of Soil Science, Lomonosov Moscow State University.

In geochemistry, the term "bitumoid" (or bitumen–like) denotes the entire set of carbonaceous compounds extracted from natural objects, such as soils, rocks, water, etc., by non–polar or weakly polar organic solvents, mainly chloroform and n–hexane. Thus, bitumoid is an analytical concept, the composition of which depends on the type of solvent [13]. Hydrocarbons of all classes, low molecular weight heterocyclic compounds, resinous asphaltene substances, as well as chlorophyll and other plant pigments pass into these solvents.

Bitumoids of two types were investigated in soils under the study. The former type was extracted from soils with chloroform, then, redissolved in carbon tetrachloride. The content of chloroform bitumoid (CB) in the obtained extracts was determined by the Infrared Spectroscopy method. The
latter was extracted by treating of air-dry soils with n-hexane and mechanically shaking under normal conditions. After purification of the extract from macromolecular and bioorganic components on a column with a mineral sorbent (aluminum oxide), the concentration of the non–polar part of hydrocarbons, which is usually referred to as petroleum products, was determined using Gas Chromatography appliance with a flame ionization detector. The equipment calibration was performed using standard sample of petroleum products in n–hexane. High Performance Liquid Chromatography equipment was used for polycyclic aromatic hydrocarbons detection in hexane bitumoid (HB).

Microsoft Excel and Statistica 12 software was used for data processing [14].

3. Results and Discussions

The results of the analysis show that maximum organic carbon ($C_{org}$) values are typically confined to the upper humus horizons and consisted of 1.45–2.77% (table 1) in soils of the Barguzin Depression. High concentrations of $C_{org}$ in humus psammozems are not characteristic for soils of this type. Radial decreasing profile distribution of organic carbon was noted in salic solonetz (TNK–25) and humus psammozem (NK–8). In soils of the hydrothermal unloading zone, $C_{org}$ is unevenly distributed throughout the profile, increasing in the impregnated horizons to a high level, and even at a depth of 2 m and more is 0.7–0.8%.

The content of chloroform bitumoids in soils varies within 48 – 483 mg / kg (table 2). The average value among all studied samples, regardless of horizon and depth, is 242.66 mg / kg (n = 12). CB content in humus horizons of soils of different natural zones varies from 0.01 to 3.0 g / kg [15]. Content of bitumoids and their qualitative composition are closely related to the conditions of soil formation, differ in soil genetic horizons, and depend on landscape position.

Table 2. CB, HC and total PAH concentrations in soils of the Barguzin Depression.

| No | Plot | Horizon | Depth (cm) | CB | HC (mg / kg) | ΣPAH |
|----|------|---------|------------|----|--------------|------|
| 1  | RF–1–4 | AC      | 1.5–3.7    | 250.0 | 51.6±13.9 | 0.009±0.004 |
|    |       | IMP     | 40–85      | 373.8 | 27.3±7.4 | 0.020±0.008 |
|    |       | AJimp   | 0–6        | 346.5 | 15.4±4.2 | 0.503±0.170 |
| 2  | RF–1–5 | QCimp1  | 6–20(41)   | 49.5 | 15.0±4.1 | 0.020±0.008 |
|    |       | QCimp2  | 20(41)–55  | 99.5 | 93.9±25.4 | 0.024 0.009 |
|    |       | AJ      | 0–18       | 483.1 | 97.5±26.3 | 0.019±0.008 |
| 3  | TNK–25 | SEL     | 18–21      | 357.1 | 74.4±20.1 | 0 |
|    |       | BSN     | 21–25      | 255.1 | 38.4±10.4 | 0.019±0.008 |
| 4  | NK–8  | C       | 20–33(37)  | 346.5 | 67.6±18.3 | 0.018±0.007 |

In some soils of the Baikal Rift zone the chloroform bitumoids accumulated in horizons with black viscous plastic material saturation. In humus psammozem (Eutric Sodic Gleyic Arenosol (Humic)), these are lower non–saline organic–impregnated horizons of black color with an oily gloss, similar to bitumen. In light–humus gley alluvial soil (Eutric Sodic Gleyic Pantofluvic Fluvisol (Alcalic, Epiloamic, Endoarenic, Humic, Sulfidic)), CB are concentrated in the upper horizon with black viscous films of organic matter. The pH of these horizons is strongly alkaline. They have average value of sulfate sodium salinity (aNa 80–90 mmol / l, aCl 3–4 mmol / l) and noticeable content of fluorides (aF 4–5 mmol / l). Humus psammozem of the lacustrine–alluvial plain (NK–8) has the high CB content throughout the profile. The minimum concentrations of CB were found in the humus
horizon of humus psammozem (RF–1–4) and in the middle horizon of light-humus gley alluvial soil (RF–1–5). The maximum CB index was noted in salic solonetz (TNK–25).

The distribution of chloroform bitumoids in the soil profile is uneven. In humus psammozems (RF–1–4 and NK–8) and light-humus gley alluvial soil (RF–1–5), CB concentrations are low, at the background level, even in horizons, the PAH concentrations are low, at the background level, even in horizons.

Polycyclic aromatic compounds were found, including heavy ones, consisting of 5–6 rings, as well as benzo(a)pyrene in the high concentration, exceeding the MPC level for soils. In some soils, the

The content of hydrocarbons, or petroleum products, in the purified hexane bitumoid varies from 15 to 114 mg / kg. The maximum HC content is confined to the humus horizons of soils (92.4–114.9 mg / kg). The obtained indicators are higher than in the soils of natural landscapes [16]. HC radial distribution is uniformly decreasing, excepting the light-humus gley alluvial soil, in which oil products accumulated in the middle QCimp2 horizon at the depth of 20(41) – 55 cm.

Hydrocarbons are an integral part of soil organic matter and usually depend on the organic content of the soils. Our study confirm close correlation between the content of HC and Corg only in salic solonetz (R² = 0.88, P < 0.05). This may indicate indirectly intraprofile supply of hydrocarbons to other soil types, since the content of hydrocarbon components in the background soils of plakors usually correlates with the total carbon content. In soils under the study, definite regularities between the content of HC and other soil properties, such as pH, readily soluble salts concentrations, and texture were not found.

The value of the ratio of HB and CB is a diagnostic feature of natural bitumoids, regardless of the type of soil and genetic horizon. For background soils, this indicator does not exceed 0.5. In the upper horizons of humus psammozems (RF–1–4) this ratio exceeds 2.0, in QCimp2 horizon of light-humus gley alluvial soil, it is 0.94. High values of the ratio serve as an indicator of the input of the hydrocarbon fluids into the soil, which are usually passes into hexane bitumoid.

Polycyclic aromatic compounds are substantial part of soil bitumoids [17]. In soils of the Barguzin Basin, 11 individual PAHs were identified: phenanthrene, anthracene, pyrene, benz(a)anthracene, chrysene, fluoranthene, benz(b)fluoranthene, benz(k)fluoranthene, dibenz(ah)anthracene, benz(a)pyrene, and benzo(ghi)perylene. Total PAH content varies in the range of 0.008–0.503 mg / kg (table 2). The background concentrations of polycyclics in polyarenes in soils change significantly depending on the location, horizon, and texture: from 0.01–0.02 to 0.23–0.37 mg / kg in horizons with a heavy texture [18].

In most soil samples, the PAH concentrations are low, at the background level, even in horizons with a predominance of hexane bitumoids. The maximum total PAH level was found in the humus horizon of the light-humus gley alluvial soil (RF–1–5), comparable to PAH content in petroleum hydrocarbons (0.5 mg / kg or 3–4%). High enough content of polycyclics was also noted in the upper horizon of humus psammozem (NK–8) with bitumen outcrops. PAH were not found in the SEL horizon of salic solonetz, possible because of its eluvial properties and light texture. It was noted that PAH accumulation is associated with humus and/or impregnated soil horizons and directly related to the fine soil fractions (R² = 0.85, P < 0.05).

The qualitative composition and profile distribution of polycyclic aromatic compounds is not uniform. In all horizons, in which PAH were detected, phenanthrene was mainly found in the amount of 13.7–94.7% of total PAH. In salic solonetz, pyrene was also detected. Pyrene and dibenz(ah)anthracene were revealed in humus psammozem (RF–1–4). Six different PAH were identified in the soils of lacustrine-alluvial plain (NK–8), including acenaphthene and fluorine. In light-humus gley alluvial soil of the hydrothermal activity zone, with maximum PAH total content, 11 polycyclic aromatic compounds were found, including heavy ones, consisting of 5–6 rings, as well as benzo(a)pyrene in the high concentration, exceeding the MPC level for soils. In some soils, the
predominance of phenanthrene over the sum of other PAH is accompanied by increased concentrations of hydrocarbon gases [19]. High PAH content in combination with their diversity in soil horizons was noted in the zones of geodynamic activity [16], along with the high pH values and concentrations of readily soluble salts it implies the hydrothermal origin.

4. Conclusions
Data on chloroform, hexane bitumoids, and polycyclic aromatic hydrocarbons in the soils of the Baikal rift zone within the Barguzin Depression were obtained. Studied indicators of the hydrocarbon state in the soils of the lacustrine–alluvial plain and sandy uplands can serve in the aggregate as markers of the intensity of endogenous processes.

In soils of the North–Western part of the basin, located in the zone of active unload of thermal waters and hydrocarbon fluids, atypical accumulation of organic carbon appears throughout the profile. High concentrations and distribution of chloroform bitumoids do not correlate with carbon content. Elevated bitumoid coefficient (HB/CB), increased concentrations of polycyclic aromatic compounds and their variety in combination with the accumulation of readily soluble salts indicate an additional influx of hydrocarbons and instability of hydrocarbon system of the soils.

Intensity of endogenous processes is less pronounced in soils of the central part of the lacustrine–alluvial plain: low values of the bitumoid coefficient, decreased concentrations of polycyclic aromatic compounds and their incomplete spectrum.

Salic solonettes of sandy uplands formed with a complex combination of exogenous and endogenous factors. High content of chloroform bitumoids in the soil profile may be associated with spontaneous hydrocarbon emanations from the fault zone and organic–accumulative processes. Close correlation between the bitumoid level and organic carbon, low bitumoid index, background concentrations of PAH and their narrow spectrum reflect natural conditions of soil development.

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