
DEGRADATION, REHABILITATION,
AND CONSERVATION OF SOILS

Soil Pollution with Polycyclic Aromatic Hydrocarbons and Petroleum Hydrocarbons in the North of Western Siberia: Spatial Pattern and Ecological Risk Assessment

M. G. Opekunova^{a, *}, A. Yu. Opekunov^a, S. Yu. Kukushkin^a,
S. A. Lisenkov^a, S. V. Vlasov^b, and V. V. Somov^a

^a Institute of Earth Sciences, St. Petersburg State University, St. Petersburg, 199178 Russia

^b Research and Production Association Taifun, Northwest Branch, Center for Ecological Monitoring ARLEKS,
St. Petersburg, 199397 Russia

*e-mail: m.opekunova@mail.ru

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Abstract—The assessment of soil pollution and soil toxicity in the area of oil and gas fields in tundra and northern taiga of Western Siberia was performed. The contents of petroleum hydrocarbons (HCs) and polycyclic aromatic hydrocarbons (PAHs) in soils were analyzed for four sites of sludge spills and along the winter road. Speciation of PAHs and its relationship with the HC content determined by the methods of infrared spectroscopy (HC_{IR}) and fluorimetry (HC_{FL}) were analyzed. The HC_{IR} content was several times higher than the HC_{FL} content. The high content of HC_{IR} in soils of oil and gas production areas attested to their contamination with crude oil during well construction. An increase in the HC_{FL} content was mainly related to the input of pyrogenic PAHs with emissions from heavy vehicles. The total PAHs content ranged from 95 to 22 114 $\mu\text{g}/\text{kg}$. Low-molecular-weight compounds—naphthalene (12%), phenanthrene (23%), and fluoranthene (16%)—predominated among PAHs, which was explained by soil contamination with light oil as a result of well drilling. The vertical migration of pollutants in the soil profile was weak, and they mainly concentrated in the upper part of the peat horizon. The distance of lateral migration of pollutants from the spill did not exceed 50–150 m and depended on the landscape and geochemical conditions. The ecological risk of soil toxicity was assessed using the contamination danger index based on the benzo[a]pyrene (BaP) toxicity equivalent and the schedule proposed by the authors. According to calculations, 62% of the studied soil samples were uncontaminated, 37% were characterized by moderate and low levels of environmental pollution risk, and one sample (<1%) corresponded to its high level.

Keywords: oil and gas production, permafrost, drilling sludge, contamination danger index, Entic Podzols, Gleysols

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INTRODUCTION

Pollution of the environment with crude oil and petroleum products is one of the most common types of anthropogenic impact. From 0.4 to 2% of oil is lost during the extraction, transportation, processing, and use of oil and petroleum products [12, 57]. Thus, about 18–90 million tons of oil per year now enter the environment in case of annual production of about 4500 million tons [46].

Exploration and development of oil and gas condensate fields (OGCF) in the north of Western Siberia result in environmental pollution and changes in tundra ecosystems [9]. One of the urgent problems is the release of petroleum products into the soil, which causes a change in its physicochemical and biological properties and a decrease (to complete loss) of fertility [2, 19]. Emergency sludge spills, containing petroleum

products, are one of the sources of adverse impact on landscape components at the stage of OGCF construction and operation.

Polycyclic aromatic hydrocarbons (PAHs) are assigned to the most toxic components of petroleum products, which are contained both in crude oil (to 4%) and in its refinery products. Special attention to the accumulation of PAHs in environmental components is explained by their carcinogenic properties and effect on human health [14, 21]. Priority pollutants for the assessment of environment contamination are represented by 16 substances of the PAH group [27], including 3,4-benz(a)pyrene (BaP), which is most often used as an indicator of anthropogenic pollution [7, 25, 47].

However, PAHs are widely spread in nature and enter the soil not only as a result of technogenic pollution, but also as ingredients of natural organic mat-

ter [37]. The ratios between polyarenes in soil may indicate both the sources of anthropogenic impact and natural processes [15, 49, 55].

Despite the great attention to environmental pollution with HC and PAHs, their migration and accumulation in soil horizons and along the catena in geosystems have not been sufficiently studied. The adsorption of PAHs as nonpolar hydrophobic compounds by various mineral and organic particles has not been completely determined. Polyarenes, entering the soil and natural waters, can migrate [42], bind to suspended particles [45, 48], and be transformed into other compounds [17, 31]. It is known that the capacity of soils to adsorb PAHs strongly depends on their solubility. Geochemical barriers exert a significant impact on the migration and accumulation of PAHs in environmental components [14]. Therefore, mechanical disturbances, destruction of the natural soil and plant cover of the Arctic regions accompanied by thawing of permafrost (PFR) are important factors, determining the accumulation of pollutants in landscape components [8].

There is a danger of persistent contamination with petroleum products for the northern regions of Western Siberia, since the degradation of petroleum hydrocarbons in acid, cold, waterlogged, and low-humus tundra soils is extremely slow. Predominating physicochemical processes here include their redistribution along the soil profile, evaporation, leaching, and ultraviolet irradiation [13]. Biodegradation of HCs and PAHs under the effect of soil microflora with the formation of complex hybrid molecules of the resinous-asphaltene series and new aliphatic structures takes decades at low temperatures. Soil pollution is preserved for many years [16]. Transformation of HCs may result in the formation of toxic compounds with carcinogenic properties and resistant to microbial destruction [6, 22, 44].

It is known that a continuous front of oil moving along the soil profile is formed in sandy soils. Oil is removed with soil- and groundwater [13, 51]. Oil is partially accumulated only in the humus horizon due to sorption and copolymerization of oxidized petroleum components. However, wide development of permafrost gleying, thixotropy, cryogenic retinization of technogenic organic substances, and metamorphization of salt solutions in combination with a high ability of peat horizons of soils in Western Siberia to absorb toxic HCs and their decay products favor fixation of petroleum products in soils [13]. Predominance of heavy fractions in the associated oil and high sulfur content (more than 0.5%) in combination with unfavorable natural conditions contribute to preservation and accumulation of persistent bituminous substances in soils for a long time [3]. Sulfates of mineralized production waters may be reduced to hydrogen sulfide, and bituminous substances are firmly fixed in hydromorphic soils on the hydrogen sulfide barrier [4].

The study of the behavior of HCs and PAHs in the Arctic zone during melting of PFR and the increase in the thickness of the seasonally melting layer (SML) under climate change is a topical issue. Currently, there are different hypotheses of their migration and accumulation in the environment. One of them presumes that the input of organic matter (OM) into natural waters, will increase due to melting of PFR [1, 20, 29]. According to another hypothesis, the input of organic matter into the surface waters will be reduced due to smaller content of dissolved OM in suprapermafrost waters as a result of a shorter period of their contact with permafrost [43].

The content of HCs and benz(a)pyrene is analyzed for environmental management in northern regions. Both the method of infrared spectrometry (IR spectroscopy) and the fluorimetric method are used to determine the content of HCs in environmental components of oil and gas fields [3, 5, 10, 11]. However, there is a significant difference between the measurement results obtained by these methods. Tundra soils contain a large amount of hydrocarbons in peat, including lignin, which is responsible for high concentrations of HCs determined by IR spectroscopy. This disadvantage is eliminated by the fluorimetric method, but does not provide a complete detection of soil contamination with crude oil.

The aim of this work is to determine the substances of the PAH group as indicators of soil pollution during the development of oil and gas fields under conditions of PFR and their relationship with HCs by different approaches—IR spectroscopy and the fluorimetric method—and to assess their informative value. Attention is paid to the study of migration and accumulation of pollutants during construction of wells, drilling waste spills, and the operation of vehicles, as well as to the effect of permafrost thawing on the vertical and horizontal migration of HCs in interrelated ecosystems.

OBJECTS AND METHODS

Research area and sampling. The studies were performed in September 2019 and 2020 in northern taiga and tundra of Western Siberia within the Yamalo-Nenets Autonomous Okrug on four plots of drilling sludge spills (transects 1–4), along the winter road (transects 5-1 and 5-2), and on background plots located under the same natural conditions outside the impact zone of the oilfields (Fig. 1). Sludge spills are allocated to several drilling sites, where walls of mud storage pits were broken during the spring snowmelt a year prior to the start of the research. The volume of spilled sludge was about 300–400 m³.

The transects were laid from the spill spot down the terrain and ended on the local background. Two test plots were located on a gently undulating poorly drained plain in the northern taiga subzone. Transect 1 (TR 1) crossed a birch-larch woodland on iron-illu-

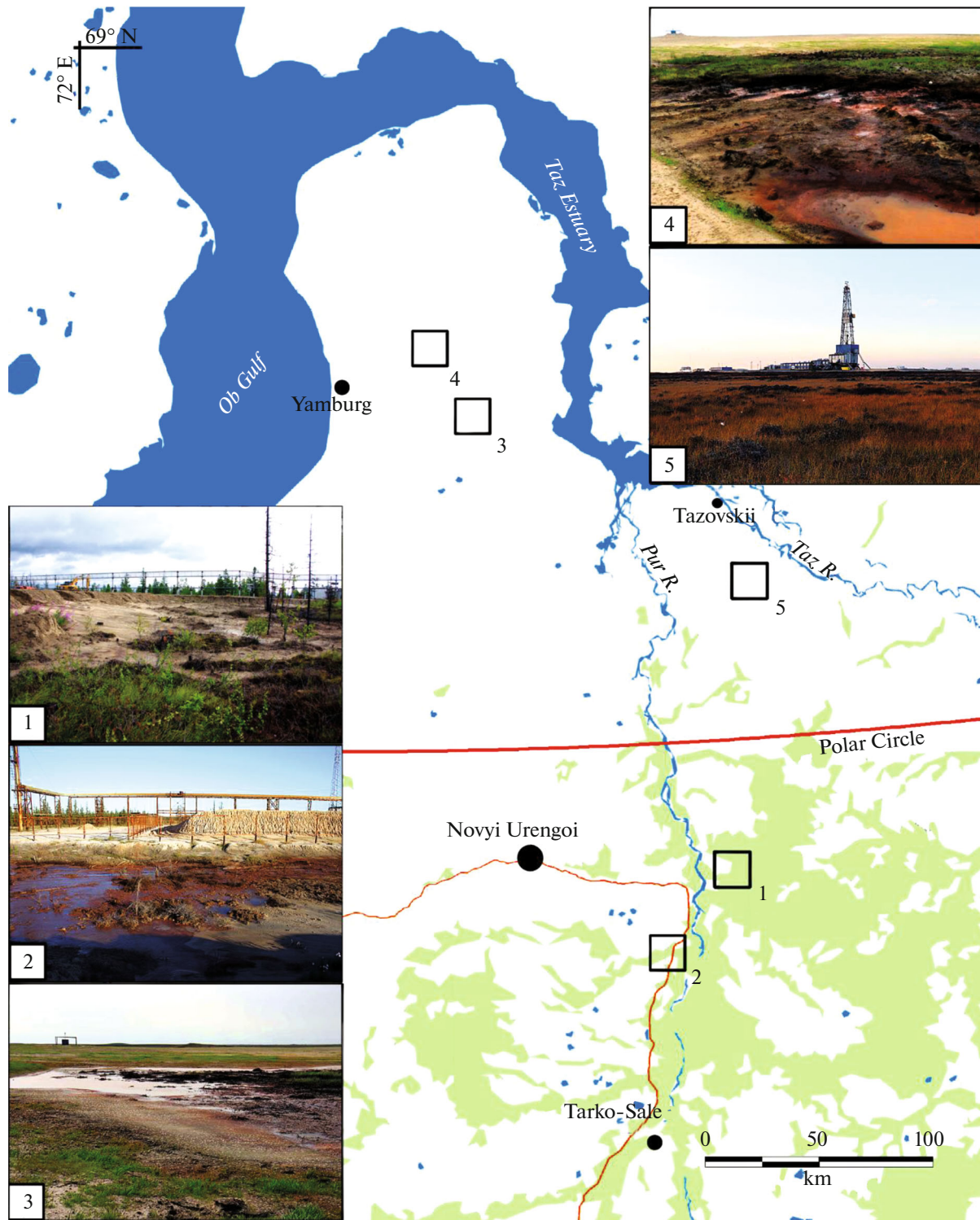


Fig. 1. Map of the study area.

vial medium-clay podburs (Entic Podzols). Transect 2 (TR 2) was located in a larch woodland on peat-gley heavy loamy soils (Histic Gleysols). Four test plots were located in the polygonal tundra of the Tazovskii

Peninsula. The transects on two plots passed from the sludge spill (exploration well sites) through tundra on the elevated inclined plain with heavy loamy (TR 3) and light loamy (TR 4) surface sediments.

Two transects (TR 5-1 and TR 5-2) were laid on the plot in the area of the overgrown winter road, by which equipment to the exploration well was seasonally delivered in 2008–2012. The first profile passed through undisturbed area, and sampling sites were set in various natural complexes: dwarf-shrub lichen tundra—moss tundra—patches of bare soil in the spotted tundra—hummocky peat bog—sedge swamp. The second transect was laid parallel to the road in the same, but mechanically disturbed natural complexes with pronounced thawing of PFR (Fig. S1).

Each profile comprised five sampling sites (SS) 20 × 25 m laid at a distance of 50–75 m from each other in different landscape-geochemical positions. Geoecological conditions were described in detail, the plant community was characterized, and soil pits were studied on each SS. Soil samples were taken by an auger through the entire depth of the SML to soil-forming rocks (55–200 cm), penetrating into the upper part of PFR. We studied 33 TPs and took 123 soil samples for chemical analyses.

Chemical analyses. The content of HCs and PAHs in soils was determined at a laboratory of the Research and Production Association Taifun. The mass fraction of petroleum products was measured, using infrared spectrometry (IR, HC_{IR}) and the fluorimetric method (FL, HC_{FL}) according to conventional certified procedures.

The samples for the analysis of the total HCs in soils by IR spectrometry were prepared according to the environmental regulatory document *PND F 16.1:2.2.22-98* and comprised three-fold ultrasonic extraction of lyophilized soil samples of 5 g with 10 mL of carbon tetrachloride followed by purification of extracts by column chromatography, using aluminum oxide. An AN-2 dispersion-free IR spectrometer (analyzer of petroleum products) with the measuring range of 50–100 000 mg/kg was used for the quantitative analysis.

Low concentrations of HCs in soils were determined by the fluorimetric method according to *PND F 16.1:2.21-98*. Lyophilized soil samples of 5 g were extracted three times by 10 mL of hexane with ultrasonic treatment, and the extract was then purified from polar compounds by column chromatography on aluminum oxide. A Flyurat-02 liquid analyzer was used for the quantitative analysis.

The concentrations of 16 individual PAHs were determined according to measuring method *FR. 1.31.2004.01279* by the HPLC approach on a LC-20 Prominence liquid chromatograph (Shimadzu, Japan) with a diode matrix and programmed detection of fluorescence in the UV region. A SPD-M20A spectrophotometric detector (diode matrix) was used to determine acenaphthylene and indeno[1,2,3-c,d]pyrene. The samples were extracted by hexane. After drying, the extracts were concentrated on a rotary evaporator, purified by the column chromatography on silica gel, and re-concentrated by evaporation on a rotary evap-

orator followed by bringing to an analytical volume by nitrogen flow in micro-vessels. The measurement range of benz[a]pyrene and other PAHs according to the method was 1.2–12 000 µg/kg. Standard samples produced by Ekroskhim (Russia), Ultra Scientific Analytical Solutions (USA), and Agilent (USA) were used for the analysis.

Blank samples were examined after analyzing each group of samples ($n = 5$) to control the error during sample processing. The analyte content in them was less than 5% of the mass concentration of the determined PAHs, which is acceptable for the control of contamination and interference during extraction, purification, and measurement of samples. One sample out of every ten ones was analyzed twice with additional dilution. The recoveries of 16 individual PAHs ranged from 77 to 110%.

The content of two-nuclear (naphthalene (Nap)), three-nuclear (acenaphthylene (Acy), acenaphthene (Ac), fluorene (Fl), phenanthrene (Phen), and anthracene (An)), four-nuclear (fluoranthene (Fln), pyrene (Py), benzo[a]anthracene (BaA), and chrysene (Chr)), five-nuclear (benzo(b)fluoranthene (BbF), benzo[k]fluoranthene (BkF), dibenzo[a,h]anthracene (DahA), and benzo[a]pyrene (BaP)), and six-nuclear (benzo[g,h,i]perylene (BghiP) and indeno[1,2,3-cd]pyrene (InP)) PAHs was determined in soils. We calculated the total content of 16 PAHs, the sum of high-molecular weight five–six-nuclear (HMW) and low-molecular weight two–three–four-nuclear (LMW) PAHs, and the sum of petrogenic (Petr) (Nap, Ac, Fl, Phen, Py, Chr, and BghiP) and pyrogenic (Prg) (Acy, An, Fln, BaA, BbF, BkF, BaP, DahA, and InP) PAHs.

Data processing and statistical analysis. The statistical analysis included the descriptive statistics, the correlation and cluster analyses, and the factor analysis by the principal component method (PCM). STATISTICA 12.0 (StatSoft) and Microsoft Excel 16.22 (Microsoft) were used for the calculations. The normality was checked, using tests for asymmetry and kurtosis. The Spearman correlation coefficient was used for nonparametric data. The cluster analysis was performed for five samplings with 16 substances of the PAH, HC_{IR} , and HC_{FL} groups. The PCM was used for four statistical samplings with 18 variables (PAH, HC_{IR} , and HC_{FL}) for 123 soil samples.

The ratio between substances of the PAH group is an important parameter to determine the main pollution sources in soil. Eight indicator ratios were used in this work: fluoranthene/pyrene (Fln/Py), benzo[a]pyrene/benzo[g,h,i]perylene (BaP/BghiP), phenanthrene/anthracene (Ph/An), An/(An + Phen) in comparison with Fln/(Fln + Py), BaA/(BaA + Chr) in comparison with InP/(InP + BghiP), and LMW/HMW to characterize primary sources of soil PAHs.

Ecotoxicological risk assessment. Soil pollution with PAHs was determined, using the Nemerov complex

pollution index (NCPI). It is a conventional method for assessing pollutants. Based on one-factor P_i parameters, it evaluates not only their mean value, but also takes into account the maximum one [32]. The one-factor pollution index was calculated to determine the NCPI:

$$P_i = C_i/S_i,$$

where P_i is the index of one-factor pollution; C_i (mg/kg) is the measured concentration of individual substances of the PAH group; and S_i (mg/kg) is permissible amount of pollutants. Background PAH concentrations in soils of the studied region were used as a standard for soils. The Nemerov pollution index may be calculated, using the formula:

$$\text{NCPI} = \sqrt{\frac{(P_{i\max})^2 + (\bar{P}_i)^2}{2}},$$

where NCPI is the Nemerov pollution index; $P_{i\max}$ is the maximal unit pollution index among pollutants, and \bar{P}_i is the mean of unit pollution indices for all pollutants.

The gradations of the Nemerov pollution index for soil status are: NCPI = 0.7—safe; $0.7 < \text{NCPI} \leq 1.0$ —requires increased attention; $1.0 < \text{NCPI} \leq 2.0$ —slightly polluted; $2.0 < \text{NCPI} \leq 3.0$ —medium polluted; and $\text{NCPI} > 3.0$ —strongly polluted [23].

The Contamination Danger Index (CDI) was calculated to assess soil environmental risks according by the formula by Pejman et al. [39] and adapted for PAHs:

$$\text{CSI} = \sum_{i=1}^n w_i \left(\left(\frac{C_i}{\text{ERL}} \right)^{\frac{1}{2}} + \left(\frac{C_i}{\text{ERM}} \right)^2 \right),$$

where C_i is the content of substances of the PAH group in a particular soil sample; w_i is the weighted toxicity coefficient; ERL is the content, below which biological effects are seldom; ERM is the value, above which effects are often or constant.

The toxicity equivalent (TEQ, ng/g) [50] was determined for each sample to assess the ecotoxicological risk:

$$\text{TEQ} = \sum_{i=1}^n (\text{TEF}_i C_i),$$

where TEF_i is the benzopyrene equivalent of the toxicity of the i th polyarene (Table 1) [50]; and C_i is the content if the i th polyarene in soil, ng/g.

The weight coefficient of toxicity (w_i) was calculated by the formula:

$$w_i = \frac{\text{TEF}_i}{\sum_i \text{TEF}}$$

RESULTS AND DISCUSSION

The content of HCs and PAHs in soils. The concentrations of HCs determined by IR spectroscopy (HC_{IR}) and fluorimetric method (HC_{FL}) and the content of PAHs in soils are given in Table 1.

The HC_{IR} content in soils varies from <50 to 63000 mg/kg, depending on the genetic horizon and SS. Its median does not exceed 75 mg/kg in soil-forming rocks and illuvial (mineral middle-profile) soil horizons of tundra and northern taiga background areas and is below the sensitivity of the method (<50 mg/kg) in most samples. In peat horizons of tundra soils under background conditions, the median increases to 1300 mg/kg. The HC_{IR} content in the organic horizon of soils of the northern taiga is lower: 300–500 mg/kg.

The maximal HC_{IR} content (63000 mg/kg or 6.3%) is recorded in oil-containing drilling sludge on the sandy filling of a drilling well on PR 4. The HC_{IR} content in the peat horizon of contaminated soils is 2500–17000 mg/kg and reaches maximum near the spill on TR 4. The permafrost depth is the main factor, determining the migration of HCs in peat (Fig. 2). The HC_{IR} content sharply decreases with the distance from the discharge site of drilling mud: it is 270–1400 mg/kg at a distance of 200 m from the pollution source in tundra and 520–1800 mg/kg in northern taiga. The HC_{IR} content in illuvial horizons of tundra soils at a distance of 50 m from the spill reaches 400–1000 mg/kg and also sharply decreases with the distance from the pollution source. At a distance of 200 m from the contamination site, the HC_{IR} concentration does not exceed 200–240 mg/kg in illuvial horizons of heavy loamy soils and is <50–68 mg/kg in sandy loamy soils.

The HC_{IR} content in the peat of the hillock on the winter road slightly increases from 1300 to 1500 mg/kg as compared to the reference peat. Its level in peat of the sedge-sphagnum swamp in the disturbed area (1200 mg/kg) is close to the background. The HC_{IR} concentration in soils of disturbed tundra areas without vegetation and under wood reed-sedge communities is below the sensitivity of the method, but reaches 2200 mg/kg in the peat horizon of undisturbed tundra soil in the same natural complex.

Data on the content of HC_{FL} are very heterogeneous (Table 1, Fig. 2). It does not exceed 5 mg/kg in soil-forming rocks. The average concentrations in the peat and illuvial horizons on the background plots are 19.5 and 5.6 mg/kg, respectively, for tundra soils, and are slightly higher (34 mg/kg and 10.5 mg/kg, respectively) in soils of the northern taiga.

The median HC_{FL} content in areas near the sludge spill increases to 480 mg/kg in organic soil horizons and only to 27 mg/kg in illuvial horizons of soil in northern taiga and to 1100 mg/kg and 31 mg/kg, respectively, in tundra soils. In soils of the winter road, the HC_{FL} content is 79 mg/kg in the peat horizon and 20 mg/kg in the illuvial horizon.

Table 1. Total contents of petroleum hydrocarbons HC_{IR}, HC_{FL} (mg/kg), and PAHs (ng/g) in organic and illuvial soil horizons

Chemical substances and compounds	Number of nuclei	TEF	Median	Lower quartile	Upper quartile	Minimum	Maximum
Organic horizons, <i>n</i> = 39							
Petroleum hydrocarbons, HC _{IR}	–	–	1900	1300	3200	170	63000
Petroleum hydrocarbons, HC _{FL}	–	–	640	115	2500	27	91000
Naphthalene	2	0.001	25	8.9	58	<1.2	210
Acenaphthylene	3	0.001	<1.2	<1.2	7.7	<1.2	800
Acenaphthene	3	0.001	1.6	<1.2	5.6	<1.2	48
Fluorene	3	0.001	25	8.0	260	1.9	3100
Phenanthrene	3	0.001	64	33	365	<1.2	16000
Anthracene	3	0.01	6.5	1.9	26	<1.2	230
Fluoranthene	4	0.001	90	25	345	<1.2	5700
Pyrene	4	0.001	20	8.0	62	2.5	1100
Benz[a]anthracene	4	0.1	8.0	2.5	58	<1.2	1900
Chrysene	4	0.01	10	5.1	42	<1.2	2200
Benzo[b]fluoranthene	5	0.1	6.3	3.0	16	<1.2	670
Benzo[k]fluoranthene	5	0.1	1.3	<1.2	3.6	<1.2	62
Benzo[a]pyrene	5	1.0	1.5	<1.2	7.4	<1.2	250
Dibenzo[a, h]anthracene	5	1.0	<1.2	<1.2	3.5	<1.2	140
Benzo[g, h, i]perylene	6	0.01	1.9	<1.2	6.1	<1.2	90
Indeno[1,2,3-cd]pyrene	6	0.1	4.2	<1.2	16	<1.2	1700
Σ _{16PAH}			562	146	1709	91	22114
Illuvial horizons, <i>n</i> = 84							
Petroleum hydrocarbons, HC _{IR}	–	–	84	25	240	<50	7400
Petroleum hydrocarbons, HC _{FL}	–	–	25	9.0	51	<5	2100
Naphthalene	2	0.001	1.9	<1.2	8.7	<1.2	67
Acenaphthylene	3	0.001	<1.2	<1.2	1.4	<1.2	15
Acenaphthene	3	0.001	<1.2	<1.2	<1.2	<1.2	9.0
Fluorene	3	0.001	<1.2	<1.2	3.5	<1.2	350
Phenanthrene	3	0.001	5.4	3.2	12	<1.2	650
Anthracene	3	0.01	<1.2	<1.2	<1.2	<1.2	33
Fluoranthene	4	0.001	3.0	1.7	6.8	<1.2	270
Pyrene	4	0.001	<1.2	<1.2	1.9	<1.2	180
Benz[a]anthracene	4	0.1	<1.2	<1.2	0.8	<1.2	900
Chrysene	4	0.01	<1.2	<1.2	2.1	<1.2	1300
Benzo[b]fluoranthene	5	0.1	<1.2	<1.2	<1.2	<1.2	140
Benzo[k]fluoranthene	5	0.1	<1.2	<1.2	<1.2	<1.2	14
Benzo[a]pyrene	5	1.0	<1.2	<1.2	<1.2	<1.2	53
Dibenzo[a, h]anthracene	5	1.0	<1.2	<1.2	<1.2	<1.2	90
Benzo[g, h, i]perylene	6	0.01	<1.2	<1.2	<1.2	<1.2	46
Indeno[1,2,3-cd]pyrene	6	0.1	<1.2	<1.2	2.4	<1.2	61
Σ _{16PAH}			17	18	53	<1.2	2855

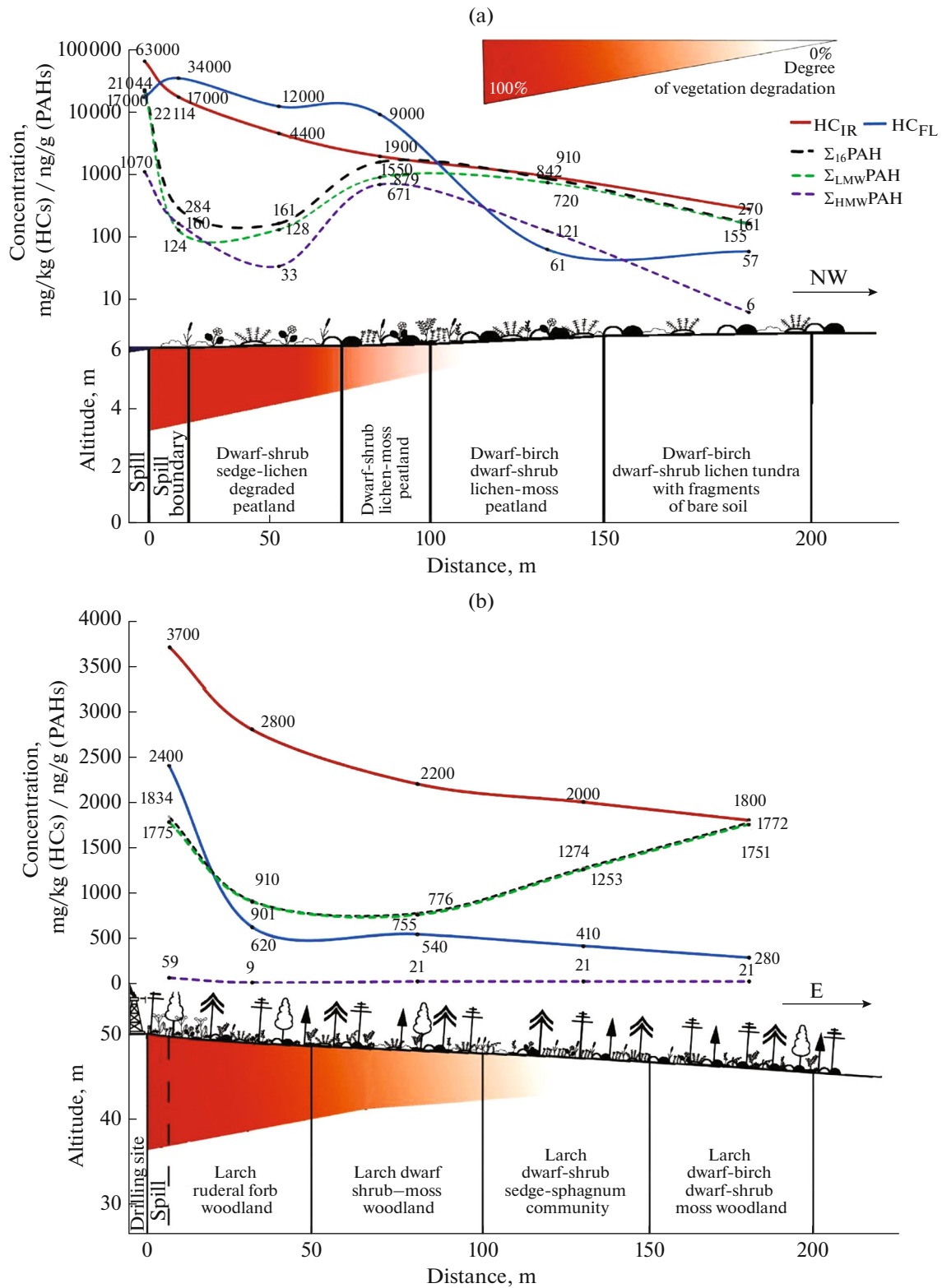


Fig. 2. Changes in the content of petroleum hydrocarbons and PAHs in surface horizons of soils of various transects: (a) TR 4, tundra and (b) TR 2, northern taiga.

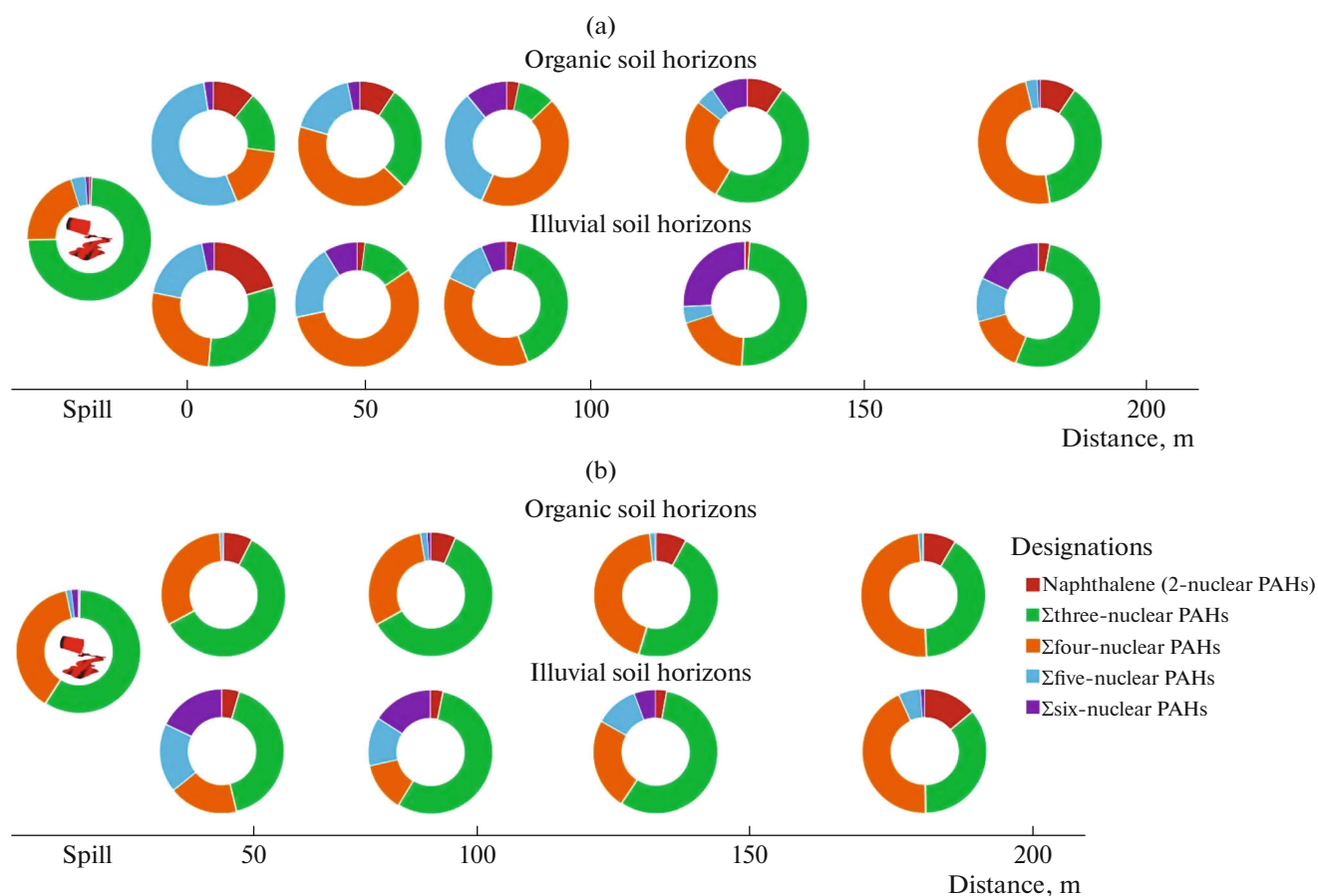


Fig. 3. Individual composition of PAHs in soil samples of the studied area: (a) TR 4, tundra and (b) TR 2, northern taiga.

The content of Σ_{16} PAH in soils varies widely (Table 1). In soil-forming rocks, it ranges from 9.5 to 52 ng/g with the mean being 16 ng/g. The background content of PAHs in the illuvial horizons is similar—from 10 to 70 ng/g with the mean of 19 ng/g—and is almost by an order of magnitude greater (from 95 to 177 with the mean of 135 ng/g) in peat horizons of tundra soils. The Σ_{16} PAH content in the peat horizon is maximal on TR 4 near the pollution spot (22 114 ng/g) and varies from 2630 to 17 550 ng/g on other plots (Fig. 2). The migration of pollutants into the soil profile is determined by the SML thickness. In illuvial horizons of technogenically polluted tundra areas, Σ_{16} PAH sharply decreases and ranges from 58 to 810 ng/g with the mean of 109 ng/g. Its maximum is detected on TR 4 at a distance of 100 m from the sludge spill.

The individual composition of PAHs in soils on the SSs is different (Fig. 3). In general, low molecular weight (LMW) PAHs predominate in all studied samples. In peat horizons of the background soils, they are mainly represented (92–96%) by two–four-nuclear PAHs. Petrogenic polyarenes predominate (52–85% of Σ_{16} PAH). In areas of sludge spill, the portion of LMW PAHs in the peat horizon increases to 99%. The

amount of high molecular weight (HMW) PAHs is maximal on TR 4 (56%) and TR 3 (48–51%), which are adjacent to the sites of drilling wells with a pronounced effect of heavy vehicles. The composition of HMW PAHs is dominated by DahA and InP: their portion in the total pollution increases to 49 and 40–45%, respectively.

Anthropogenic pollution results in an increase in the portion of HMW PAHs in illuvial horizons of soils: their share reaches 28–48% on TR 3 and TR 4. The individual composition is characterized by a rise in BbF, as well as in BaP, DahA, and BghiP in some samples. However, this is not typical for all samples and depends on the composition of petroleum products in drilling fluid and on the impact of emissions of motor vehicles and diesel generators, operating at the well site. On TR 1 and TR 2, PAHs are mainly LMW: their portion is from 89 to 100%. They are represented by BaA (18%), Phen (17%), Fln, and BaA (18%) on TR 1 and by Phen (36%), Fln (33%), and Fl (22%) on TR 2. The increased role of BaA (25%), InP (22%), and Chr (18%) is detected in sludge solution on TR 3, and Phen accounts for 72% of the total composition of LMW PAHs on TR 4.

Analysis of HCs and PAHs patterns. Vertical migration of HCs and PAHs in the soil profile is weak both in background SSs (Fig. 4a) and in anthropogenically transformed areas. Their concentrations in polluted soils sharply decrease below the peat horizon. The content of individual PAHs in the illuvial horizon of most studied soil profiles is below the sensitivity of the method (Figs. 4b and 4d). However, moisture stagnation and gleying in deeply thawing soils result in an increase in the concentration of pollutants in the BHg humus-illuvial horizon (Fig. 4c). They probably precipitate on the sorption barrier during the downward migration of substances from the peat layer. There is an exception in the distribution of Σ_{16} PAH and individual PAHs in soil on TP 2 (PR 2): their concentrations are maximal in the illuvial horizon (1078 ng/g). This is probably related to the intensive migration of spilled drilling sludge in sandy sediments at the contact with close permafrost typical for this TP. It has been revealed that PFRs prevent migration of poorly soluble PAHs deep into the soil profile [26], but they function as a semi-permeable barrier for HCs [36]. This is confirmed by the results of our research. The downward water flow in the soil pit transports clay particles with adsorbed HCs and PAHs to the lower boundary of the SML (Fig. 4f). Only a small part of dissolved hydrocarbons enters the surface waters [26].

It has been shown under experimental conditions [41] that repeated cycles of freezing–thawing of soil waters cause a two–three-fold increase in the LMW fraction of organic carbon. Our research confirms that the thickness of the SML is important for the distribution of HCs and PAHs. The pollution with HCs in tundra soils with permafrost close to the surface is recorded in the surface part of the peat horizon, and HMW PAHs are partially fixed in the organic layer, partially migrate to the illuvial horizon, and are accumulated at the boundary of PFRs (Fig. 4e). In this regard, deeper PFR melting during climate warming may not affect the migration and accumulation of HCs in the soil profile, while redistribution of PAHs with depth and accumulation in different soil horizons will probably increase. This corresponds to the data [17, 26] on an increase in the concentration of HMW PAHs in the lower part of the soil profile during thawing of PFR.

An increase in the thickness of the active layer will favor an intensive water exchange due to seasonal downward and upward groundwater flows, which can cause the removal of dissolved substances. The intensive dynamics will be accompanied by a shorter contact period of above-permafrost waters with the solid soil phase and will reduce the probability of HCs desorption. Such patterns are observed in permafrost soils of Western Siberia [43].

Lateral migration of HCs and PAHs in the soil catena is weak and is more pronounced for coarse-textured soils (Fig. 2). Local pollution is in general spread

to a distance of 100–150 m from the spill, so the content of HCs and PAHs at a distance of 200 m corresponds to the background. Their concentrations are the highest in peat-gley soils. The content of HCs in the surface layer of iron-illuvial podburs is significantly smaller and is characterized by a gradual decrease with the distance from the sludge spill. For example, the amount of HCs on TR 1 at a distance of 50 m from the spill reaches the background. The main differences in the accumulation of pollutants in different soil types are related to the thickness of the SML, the percolative regime of podburs, and high accumulating capacity of the organic horizon in peat-gley soils. Topography plays an important role in the distribution of pollutants. They are spread uniformly on a gently undulating plain. The spotty and complicated tundra microtopography favors the removal of HCs into depressions and their fixation in peat (Fig. 2). The role of microtopography in the distribution of chemicals in tundra soils is described in [2, 38, 43]. This should be taken into account during researches in the Arctic areas to obtain representative results.

Comparative analysis of the content of HC_{IR}, HC_{FL}, and PAHs. There is a close correlation between the contents of HC_{IR} and HC_{FL} in illuvial soil horizons ($r = 0.99$). The patterns of changes in the concentrations of HCs in mineral deposits obtained by both methods are similar. In peat horizons, the relationship between the content of HC_{IR} and HC_{FL} is significantly weaker ($r = 0.42$, $r_{cr} = 0.22$, $p = 0.05$). The content of HC_{IR} is closely related to the sum of polyarenes and petrogenic and LMW PAHs ($r = 0.75$ – 0.84). The correlation of HC_{IR} with the total HMW PAHs is much weaker ($r = 0.43$). There is a close dependence of the content of HC_{FL} on the sum of pyrogenic and HMW PAHs ($r = 0.60$ – 0.89), and the relationship of their content with Σ_{16} PAH and Σ_{LMW} PAH is very low ($r = 0.23$ – 0.37).

The accumulation of HCs and PAHs in soil genetic horizons is different, which is related to the large role of OM in migration and accumulation of HCs and PAHs in the soil. Any correlation of the content of HC_{IR} in the peat horizon with the total amount and fractional composition of PAHs is absent. The HC_{IR} concentration correlates only with one polyarene—DahA ($r = 0.56$, $r_{cr} = 0.30$, $p = 0.05$). The content of HC_{FL} in peat soil horizons is closely related to the accumulation of all individual PAHs except for Nap. Illuvial soil horizons are mainly characterized by a reliable close correlation of the content of HC_{IR} and HC_{FL} with all groups of PAHs ($r = 0.92$ – 1.00 , $r_{cr} = 0.30$, $p = 0.05$). The correlation is only absent for the HC_{IR} with Ac, Fl, and Fln, as well as for the HC_{FL} with Ac, Fl, Phen, Fln, and Py.

The contrasting change in the content of HCs with the domination of HC_{IR} or HC_{FL} is related to different composition of hydrocarbons and their origin, as well

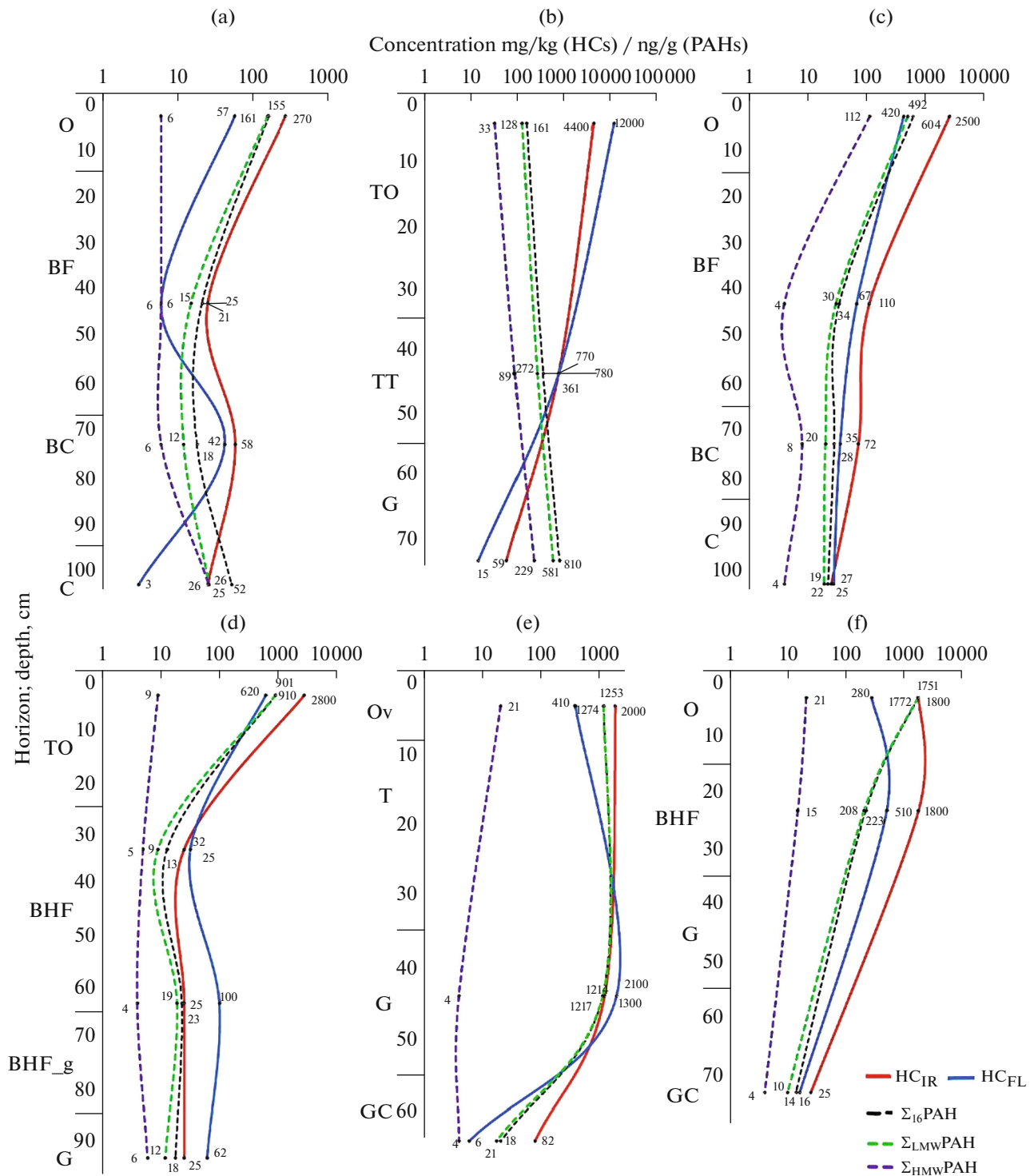


Fig. 4. Distribution of HCs and PAHs in soil profiles with depth: (a) iron-illuvial podbur (Entic Podzol), background, TR 4; (b) oligotrophic peat gley soil (Histic Gleysol), TR 4; (c) iron-illuvial podbur (Entic Podzol), TR 1; (d) gleyed peat podbur, (Histic Gleyic Entic Podzol), TR 2; (e) peat gleyzem (Histic Gleysol), TR 2; and (f) gleyed podbur (Gleyic Entic Podzol), TR 2. Soil horizons: O—peaty litter, Ov—moss debris, T—peat, TO—oligotrophic peat, TT—peat deposit, BF—iron-illuvial, BHF—Al-Fe-humus, BHF_g—gleyed Al-Fe-humus, BC—transitional iron-illuvial, G—gley, and C—soil-forming rock.

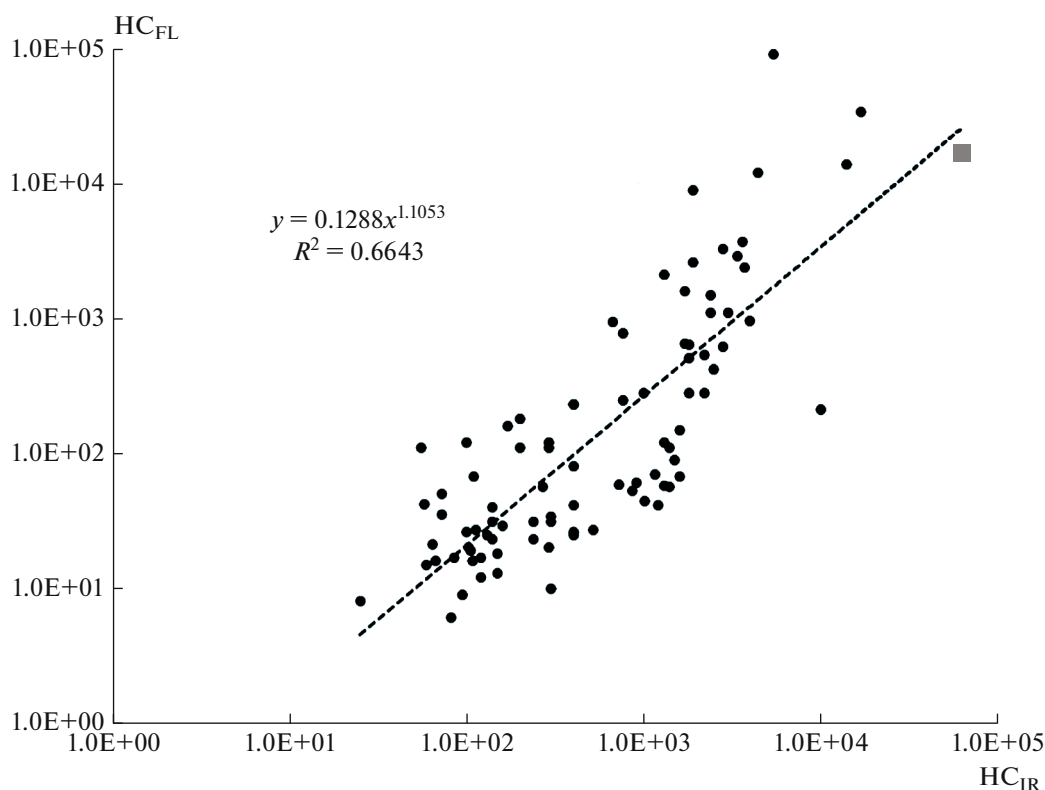


Fig. 5. Regression dependence between the content of petroleum hydrocarbons determined by the infrared spectroscopic (HC_{IR}) and fluorimetric (HC_{FL}) methods.

as to the pollution source. The increase in the HC_{IR} concentration in soils is caused by a combination of a high content of plant residues enriched with lignin and contamination with crude oil with the domination of LMW PAHs, which is typical for deposits in the north of Western Siberia. The predominance of HC_{FL} over HC_{IR} is primarily seen in soils contaminated with HMW PAHs formed during fuel combustion. This is well pronounced on TR 4 in tundra, where the work of diesel equipment significantly contributes to pollution (Fig. 2a).

The regression analysis was used to reveal general regularities in the distribution of HCs content obtained by two methods. A power dependence is revealed between these two parameters: $y = 0.1288x^{1.1053}$ (x is the content of HC_{IR} , and y is the content of HC_{FL}). The reliability of the approximation of the dependence ($R^2 = 0.66$) is not very high, but the large sampling size ($n = 123$) and diversity of ecological-geochemical environments, where soil samples were taken, enable us to assess the relationship between the analyzed variables. The approximation equation with a degree close to one (1.1053) indicates that the portion of aromatic hydrocarbons (HC_{FL}) is 13–18% of the total composition (HC_{IR}), which is the sum of aliphatic, alicyclic, and aromatic hydrocarbons. This corresponds to the fact that the content of aromatic groups in the hydrocarbon

oil composition rarely exceeds 15% [24]. Basing on the fact that high concentrations of aromatic hydrocarbons in the environment are caused by anthropogenic pollution, it may be concluded that samples above the regression line are significantly polluted (Fig. 5). Soil samples below the line contain a high portion of natural hydrocarbons formed as a result of peat diagenesis. The soil sample marked by a square in Fig. 5 was taken in a fresh oil spill on sandy soil. It is characterized by the maximal content of HC_{IR} and is practically located on the regression line. So it may be concluded that the infrared method is most useful for detecting fresh oil spills.

Pollution sources. Isomeric ratios. Various indicator ratios are now used to identify the main sources of soil pollution with PAHs [52, 54]: BaP/BghiP, An/(Ph + An), Fln/(Fln + Py), BaA/(BaA + Chr), InP/(InP + BghiP), Petr/Pyrg, and LMW/HMW. They are characterized by significant variability in samples from the studied plots (Table 2, Fig. S2). The results confirm that the main role in soil pollution is played by the input of crude oil. From 77 to 90% of contamination with LMW PAHs, including petrogenic ones, are related to oil.

The most informative ratios for pollutants in tundra soils include LMW/HMW, Phen/An, and Petr/Prg for drilling waste; LMW/HMW, Fl/Py, BaP/BghiP, and Fln/(Fln + Py) for stratal waters; BaP/BghiP and

Table 2. Diagnostic ratios of PAHs for soil samples

Parameter	BaP/BghiP	An/ (Ph + An)	Fln/ (Fln + Py)	BaA/ (BaA + Chr)	InP/ (InP + BghiP)	Petr/Pyrg	LMW/ HMW
TR 1							
Mean	0.93	—*	0.85	0.79	0.69	1.81	6.68
Median	0.91	—	1.00	0.69	1.00	1.67	3.84
Maximal	1.35	0.06	1.00	1.00	1.00	5.61	29.2
TR 2							
Mean	1.17	0.10	0.84	0.45	0.58	1.66	27.3
Median	0.82	0.01	0.91	0.53	0.64	1.12	8.53
Maximal	4.00	1.00	1.00	0.73	1.00	7.92	136
TR 3							
Mean	1.09	0.10	0.77	0.58	0.89	1.34	43.5
Median	1.00	0.02	0.85	0.59	1.00	1.55	11.2
Maximal	2.56	0.81	1.00	1.00	1.00	2.96	135
TR 4							
Mean	1.37	0.10	0.55	1.24	1.50	2.19	36.5
Median	1.15	0.04	0.62	0.44	0.96	1.64	8.51
Maximal	2.90	0.54	1.00	67.0	70.0	8.33	281
TR 5 background							
Mean	0.80	—	0.31	0.26	0.26	3.63	29.3
Median	0.92	—	0.33	0.22	—	2.59	25.6
Maximal	1.68	0.10	0.55	1.00	1.00	8.33	107
Value at the source and coefficient according to Kavouras et al. [28]; Larsen and Baker [30]; Wang et al. [52]; Yunker et al. [55], and Zhang et al. [56]							
Pyrogenic (prg)	—	>0.1	>0.5	—	—	—	<1
Petrogenic (petr)	—	<0.1	<0.4	<0.2	<0.2	—	>1
Combustion of fossil fuel	—	—	0.4–0.5	—	<0.5–0.2	—	—
Emissions from diesel fuel combustion	—	—	>0.5	—	—	—	—
Emissions from vehicles	>0.6	—	—	>0.35	—	—	—
Carbon combustion	—	—	>0.5	0.2–0.35	>0.5	—	—
Oil combustion	—	—	—	—	0.2–0.5	—	—
Oil	—	—	<0.5	—	<0.2	—	—

* The content of individual PAHs is below the sensitivity of the method.

BaA/ (BaA + Chr) for the impact of heavy diesel machines; and An/(Ph + An), BaP/BghiP, InP/(InP + BghiP), and BaA/(BaA + Chr) for combined effect during drilling operations (Table 2). The An/(Ph + An) < 0.10 ratio is usually considered as evidence of crude oil pollution, and the ratio >0.10 indicates the pyrogenic factor [52, 55, 56]. In our studies, it is <0.1 in 90% of samples, which indicates the petrogenic contamination source. From 7 to 10% of soil samples on the studied plots undergo contamination during fuel combustion (An/(Phen + An) > 0.1). The contribution of heavy vehicle emissions to soil pollution with

PAHs in the areas of crossroads of tracked vehicles increases to 40%.

The cluster analysis revealed specific features of PAHs and HCs distribution in soils near drilling mud spills and along the winter road (Fig. S3). In general, four groups of SSs may be distinguished. The first one includes the SSs, where soils are characterized by background contents of HCs and PAHs. In the dendrites constructed for peat and illuvial horizons, they became isolated into a core formed at the first clustering stage. Then SSs with increased contamination with

Table 3. Paragenetic associations of HCs and PAHs in generalized factor loads, characterizing the distribution of HCs and PAHs in soils of background and polluted areas in the North of Western Siberia

Parameter (factor)	Paragenetic association	Factor portion, %
Soils of the studied area, $n = 123$		
Affinity of HCs and PAHs to organic matter	$BbF_{96}BaA_{92}Py_{92}BkF_{89}Chr_{89}An_{74}HC_{FL73}InP_{73}HC_{69}Phen_{69}$ $DahA_{67}BghiP_{66}Acy_{65}BaP_{58}$	49.4
Anthropogenic pollution with LMW PAHs of sludge solutions	$\frac{Acy_{55}HC_{FL49}InP_{47}}{Fl_{77}Ac_{73}Fln_{69}Phen_{49}An_{47}}$	19.0
Nature factor	$\frac{Ac_{52}Fln_{51}Fl_{49}}{HC_{65}Phen_{47}Chr_{30}}$	11.6
Anthropogenic pollution from diesel vehicles	$BaP_{71} BghiP_{68}$	8.2
Soils of the contaminated area of sludge spill, $n = 77$		
Affinity of HCs and PAHs to organic matter	$BbF_{97}BaA_{94}Chr_{93}Py_{92}BkF_{88}HC_{FL74}An_{73}InP_{73}HC_{68}Phen_{68}$ $DahA_{65}BghiP_{62}Acy_{66}BaP_{56}$	49.0
Anthropogenic pollution with LMW PAHs of sludge solutions	$\frac{Acy_{54}HC_{f49}InP_{46}}{Fl_{78}Ac_{75}Fln_{70}Phen_{51}An_{49}Nap_{46}}$	19.6
Nature factor	$\frac{Ac_{54}Fln_{52}Fl_{50}}{HC_{65}Phen_{46}}$	12.0
Anthropogenic pollution from diesel vehicles	$BaP_{72} BghiP_{71}$	8.6
Pollution with naphthalene	Nap_{75}	4.1
Soils of background test plots, $n = 56$		
Affinity of HCs and PAHs to organic matter	$Fl_{95}HC_{92}Fln_{91}BbF_{91}Py_{90}Phen_{87}Chr_{75}HC_{FL60}Nap_{50}InP_{57}$ $BghiP_{72}BaP_{71}An_{47}BkF_{44}$	45.8
Nature factor	$\frac{BkF_{81}InP_{53}BaP_{64}DahA_{56}}{Nap_{58}}$	19.6

slurry solutions are sequentially added to them. Separate groups are formed by test plots, where the input of PAHs is related to emissions of heavy vehicles and combustion of fossil fuel. The last group includes SSs of mixed contamination with combustion products and waste drilling mud.

The principle component method of the factor analysis enables us to identify four leading paragenetic associations (Table 3). The first association (49.4%) includes all the studied PAHs and HCs, indicating the relationship of pollutants with organic matter. Maximal loads of this factor are typical for peat horizons of soils adjacent to sludge spills. The second factor (19%) testifies to the domination of light fractions of PAHs in drilling mud, including Fl, Ac, Fln, Phen, and An. This factor is the most pronounced in peat horizons of soils on TR 3 and TR 4 in the spill area and in areas at a distance of 50–100 m from it. The third factor (12%) is interpreted as natural one responsible for the accumulation in the peat horizon of Phen, Ac, Fl, and Chr genetically related to terrestrial higher vegetation. The fourth factor (8%) is the input of pollutants from diesel

vehicles used during the construction of wells. The high content of Acy, InP, DahA, and BaP also indicates vehicle emissions [30].

The naphthalene distribution in soils is related to both natural processes of peat formation and contamination with petroleum products [53]. The features of its accumulation in various natural complexes are reflected in an independent paragenetic association. Its weight increases from 4% in the background area to 20% on anthropogenically disturbed plots. Positive loads of this factor are related to the intensive formation of peat and peatbogs.

The toxicity and environmental risk were assessed by the comparison of absolute concentrations with the maximum permissible concentrations (MPCs) and by the calculation of the CDI, NCPI, and TEQ indices. The rate of soil contamination with PAHs is specified into four levels [35]: unpolluted (less than 200 ng/g), slightly polluted (200–600 ng/g), polluted (600–1000 ng/g), and strongly polluted (more than 1000 ng/g). Based on these criteria, all soil samples on TR 5 near the winter road were assigned to non-polluted. More than

Table 4. Soil pollution according to the scale by Maliszewska–Kordybach [35]

Soil pollution class	TR 1	TR 2	TR 3	TR 4	TR 5
	% of soil samples				
Unpolluted	70	47	50	54	100
Slightly polluted	0	12	19	14	0
Polluted	30	17	0	14	0
Strongly polluted	0	24	31	18	0

Table 5. Danger level classification according to CDI thresholds and TEQ value

Danger level	Contamination danger index	Criterion	Threshold CDI	ng TEQ/g
Safe background level	Background level	BEL	≤0.06	<1.5
Low level	Threshold effect level	TEL	0.06–<0.5	1.5–125
Medium level	Effects range low	ERL	0.5–<1.0	125–550
High level	Probable effects range	PEL	1.0–<1.6	550–1500
Very high level	Effects range median	ERM	1.6–<4.3	1500–12000
Extremely high level	Effect range—maximal values	ERM	≥4.3	12000

30% of soils on each plot of sludge spill are contaminated or strongly contaminated with PAHs (Table 4). In general, 16 of 123 samples are strongly polluted with the maximal concentration of 22 114 ng/g. The BaP content exceeds the MPC for soils (20 ng/g) in nine samples (7% of the total) taken near the polluted sites. It exceeds the MPC for peat: two times at the spill boundary and 2–12 times at a distance of 50–100 m from it. This indicates lateral migration of the substance in the peat horizon with surface waters. However, the maximal BaP content in the studied samples (250 ng/g) is lower than the MPC accepted in the United States and the European Union (300 ng/g).

The NCPI range in the studied soils is 0.21–116 at the mean of 5.59. According to this index, soils along the winter road on TR 5 are not polluted with PAHs and correspond to the background (Fig. S4). The NCPI for all soil samples taken from the sludge spill spots and at a distance of 50 m from them is 3–47.5, which indicates a strong contamination.

A formal schedule with an interval 0.5–1 is now used to assess the contamination danger index (CDI) [39, 40]. We propose a scale of threshold values of CDI for PAHs, based on the concentrations of individual substances obtained by the study of biological effects. The low, moderate, high, and very high danger is determined, using the values of the low (ERL) and medium (ERM) effect ranges according to Long et al. [33]. Threshold effect levels (TEL) and probable effect levels (PEL) are taken according to Macdonald et al. [34]. The safe (background) level (BEL) is the regional background content of PAHs in soils of the Yamal-Nenets autonomous district (own data) (Table 5). The CDI varies from 0.06 to 1.13 with the mean of 0.13. According to the schedule in Table 5, one soil sample

is characterized by the high, and five samples are assigned to the moderate danger level. Uncontaminated soils compose 62% of the samples studied, and 33% are characterized by a low pollution. Peat-gley soils and iron-illuvial podburs practically do not differ from each other according to the absolute values of the danger index. Thus, the revealed vegetation degradation (Fig. 2) is mainly related not to the high content of HCs and PAHs, but to the effect of neutral and alkaline solutions (pH 6.70–8.69) on acidophilic plants, as well as to possible change in physicochemical properties of the substrate.

The calculated CDI and TEQ are closely interrelated ($r = 0.93$, $r_{cr} = 0.17$, $p = 0.05$). This enables us to use the previously proposed CDI scale, because such gradations are absent for the toxicity equivalent. According to the regression analysis performed for this purpose, the revealed dependence is described by a power regression equation $y = 547x^{2.1}$ (x is CDI, and y is TEQ) with $R^2 = 0.97$ (Fig. S5). The TEQ scale is constructed, using this dependence (Table 5).

The benzpyrene toxicity equivalent varies from 1.46 to 646 ng TEQ/g with the mean of 22.8, which indicates a relatively low content of five–six-nuclear polycyclic aromatic hydrocarbons of the greatest carcinogenic danger in most soil samples. The data obtained are close to those in soils of the Al-Ahdab oil field in the Waset region, Iraq [18]. According to the proposed scale, all TEQ values are in the range from low to high danger. The last gradation includes six samples taken within 50 m from the spill spots on TR 3 and TR 4. With the distance from the source, the TEQ values naturally decrease from 2 to 2–4 times. On TR 5 and at a distance of more than 150 m from the drilling mud spill, the danger is low everywhere and is close to the safe content of polycyclic aromatic hydrocarbons.

The calculated CDI, NCPI, and TEQ basically display similar regularities. A high correlation between CDI and TEQ values is pointed out above. The correlation of NCPI with CDI ($r = 0.29$, $r_{cr} = 0.17$, $p = 0.05$) and TEQ ($r = 0.33$) is considerably slighter, which makes NCPI less effective for assessing soil contamination with PAHs (it was originally elaborated for metals).

CONCLUSIONS

Our studies have shown that tundra soils in the north of Western Siberia are locally contaminated with HCs and PAHs. Their accumulation and distribution in soils are related to both natural processes of peat formation and anthropogenic impact. Pollution affects the organic peat horizon; the radial migration of pollutants down the soil profile is weak and is mainly caused by mechanical soil disturbances during the passage of heavy machines.

Several sources of soil pollution have been identified. Spills of drilling waste and its discharge into the elements of topography result in soil contamination with HCs and low molecular weight PAHs, including fluorene, acenaphthene, fluoranthene, phenanthrene, and anthracene. Emissions of heavy vehicles are the sources of benzo[ghi]perylene and benz[a]pyrene. Indeno[123-cd]pyrene and acenaphthylene are the indicators of diesel fuel combustion. Combined soil contamination with exhaust gases and waste drilling fluids causes an increase in the concentration of HC_{IR}, benzo[a]anthracene, benzo[b]fluoranthene, chrysene, pyrene, and phenanthrene in soils.

Lateral migration of pollutants usually does not exceed 100 m and is more intensive in coarse-textured (sandy) soils of the northern taiga with deep seasonal thawing. The migration activity of pollutants in peat-gley soils is limited by the high buffering capacity of the peat horizon. Cryogenic conditions minimize the downward matter flow during the radial migration, which enhances the transportation of pollutants with upward water flows during seasonal melting of PFRs.

Infrared spectroscopy and the fluorimetric method are characterized by different information value for determining the content of HCs in soils within oil and gas production areas. The HC_{IR} content in soils is closely related to the amount of petrogenic PAHs and of plant residues enriched with lignin. Its high concentration in soils of licensed oil and gas production sites indicates pollution with crude oil during the construction of wells. The increase in the HC_{FL} content is mainly determined by the input of pyrogenic high-molecular weight PAHs during diesel fuel combustion.

When assessing soil pollution in the Arctic, it should be taken into account that the fluorimetric method is characterized by a narrow range of detectable petroleum hydrocarbons represented by aromatic compounds. In case of analyzing the petroleum prod-

ucts (the transformed oil composition), it is reasonable to use the fluorimetric method for assessing the pollution level, taking into account the relative exceeding of the background, but not absolute values. The infrared method enables the determination of almost the entire spectrum of HCs, but the data obtained include a large amount of natural hydrocarbons, in peat soils in particular. It should be used in case of crude oil spills, as long as its primary composition is preserved, and the content of natural hydrocarbons on the background of oil concentration becomes insignificant. Determination of the regression dependence between the contents of HC_{IR} and HC_{FL} may be an efficient method for separating the natural and technogenic HCs.

The results of the study of the environmental danger of the content of PAHs in soils of sludge spills enable us to conclude that the observed vegetation degradation is mainly related not to a high content of hydrocarbons, but to the effect of neutral and alkaline solutions (pH 6.70–8.69) on acidophilic plants. Soils along the abandoned winter road underwent almost complete self-purification from HCs and PAHs during the ten-year period.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

SUPPLEMENTARY INFORMATION

The online version contains supplementary materials available at <https://doi.org/10.1134/S1064229322110102> and accessible for authorized users.

SUPPLEMENTARY MATERIALS

Fig. S1. Background (5-1) and disturbed (5-2) profiles along the winter road.

Fig. S2. Changes in indicator ratios of the content of PAHs in soils.

Fig. S3. Dendrogram of the hierarchical cluster analysis of Σ_{16} PAH and HCs in organic (A) and illuvial horizons (B) of soils.

Fig. S4. Distribution of the Nemerov index on test plots of profiles at sludge spills and along the winter road.

Fig. S5. Regression relationship between the contamination danger index (CDI) and the toxicity equivalent (TEQ).

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