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SOIL CHEMISTRY

Alkanes as Components of Soil Hydrocarbon Status: Behavior and Indication Significance

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Abstract—Studies of soils on three key plots with different climatic conditions and technogenic impacts in Volgograd, Moscow, and Arkhangelsk oblasts have showed that alkanes in the soil exchange complex have some indication potential for the identification of soil processes. The following combinations of soil-forming factors and processes have been studied: (a) self-purification of soil after oil pollution; (b) accumulation of hydrocarbons coming from the atmosphere to soils of different land use patterns; and (c) changes in the soil hydrocarbon complex beyond the zone of technogenic impact due to the input of free hydrocarbon-containing gases. At the injection input of hydrocarbon pollutants, changes in the composition and proportions of alkanes allow tracing the degradation trend of pollutants in the soil from their initial content to the final stage of soil self-purification, when the background concentrations of hydrocarbons are reached. Upon atmospheric deposition of hydrocarbons onto the soil, from the composition and mass distribution of alkanes, conclusions can be drawn about the effect of toxicants on biogeochemical processes in the soil, including their manifestation under different land uses. Composition analysis of soil alkanes in natural landscapes can reveal signs of hydrocarbon emanation fluxes in soils. The indication potentials of alkanes in combination with polycyclic aromatic hydrocarbons and other components of soil hydrocarbon complex can also be used for the solution of other soil-geochemical problems.

Keywords: soil self-purification, hydrocarbons, alkanes, oil, soil gas phase, soil pollution, pollutants

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INTRODUCTION

Hydrocarbons in soils include a wide range of compounds, the study of which has received much attention in recent time because of their global distribution and effect on the quality of soils and the entire environment, including human health. In addition, hydrocarbons are indicators of current geochemical processes in landscapes, which is of great importance for increasing the efficiency of ecological prognoses and ecological monitoring.

Polycyclic aromatic hydrocarbons (PAHs) are most thoroughly studied individual hydrocarbons in soils [5]. Their importance for the indication of hydrocarbon biodegradation and the revelation of sources of hydrocarbon input into landscapes is shown by some authors [11, 12, 16].

Far fewer studies deal with the indication role of alkanes (saturated chain hydrocarbons, which are most abundant hydrocarbons in natural objects) in current landscape-geochemical processes.

In organic geochemistry, alkanes are widely studied in terms of the transformation of dispersed organic matter in hard rocks to oil hydrocarbons. High-molecular-weight alkanes of isoprenoid structure in ancient deposits are considered as petroleum biomarkers indicative of petroleum formation in presumable parent sedimentary rocks. Different coefficients are proposed for the indication of these processes. For example, the origin of alkanes from higher plants is indicated from the dominance of hydrocarbons with uneven numbers of carbon atoms in their composition. Gradual leveling of the mass concentrations of hydrocarbons with even and uneven carbon chains indicates the approach of compounds to the oil composition (CPI, Fillipi, OEP, and other indices). It is believed that the ratio between the isoprenois alkanes prystane ($C_{19}H_{40}$) and phytane ($C_{20}H_{42}$) points to less reductive conditions of organic matter transformation at the dominance of the former compound and to more reductive conditions at the dominance of the latter compound [10].

Another aspect of studying alkanes appeared after the works of Petrov, who divided the natural oils by the degree of their degradation on the basis of the ratio between normal alkanes and their isomers. It was showed that when the oil deposit approaches the soil surface, normal chains of hydrocarbon radicals are degraded first and isoalkanes become dominant; then, isoalkanes themselves are degraded, which results in the appearance of a class of biodegraded oil [8]. This aspect of alkane studies is widely used for assessing the degree of biodegradation of hydrocarbons during the remediation of lands polluted with oil and oil products.

The study of alkanes gradually becomes usual in soil-geochemical studies [13–15].

Krasnopeeva used data on the contents of *n*-alkanes and the carbon preference index (CPI) as parameters of hydrocarbon geochemical fields in soils of natural and natural-technogenic landscapes [7, 9].

Kachinskii et al. [6] used the ratio of the sum of pristane and phytane mass concentrations to the concentration of normal alkanes $C_{17}H_{36}$ and $C_{18}H_{38}$ to characterize the degree of biodegradation of residual diesel fuel in Arctic tundra soils of New Siberian Islands.

Gabov et al. [1] studied the ratio between the even and uneven alkanes C_{20}–C_{35} in peaty podzolic-gleyic soils of northern and middle taiga using the CPI value. It was shown that compounds with uneven number of carbon atoms prevail in organic soil horizons, which is due to the microbiological transformation of higher and lower plants. In mineral horizons, the concentrations of even and uneven alkanes become equal. In the opinion of the authors, the decrease of the CPI value to 1 is due to the decrease in the bioproductivity of soil horizons and the pollution of soil profile.

In published works, alkanes and polyarenes, with few exceptions, were considered separately. On the other hand, these hydrocarbon classes have different sources of input into the soil and specific physicochemical properties; therefore, their integrated interpretation makes it possible to more completely describe geochemical processes in soils and analyze affecting factors.

The aim of this paper was to show the indication potentials of high-molecular-weight alkanes (C_{15}–C_{36}) in landscape situations, for which the soil hydrocarbon statuses were earlier characterized by the contents and composition of bituminous substances, PAHs, and hydrocarbon gases. The following landscape situations were considered: (a) self-purification of soils after oil pollution; (b) accumulation of hydrocarbons coming from the atmosphere to soils of different land use patterns; and (c) changes in the soil hydrocarbon complex beyond the zone of technogenic impact due to the input of free hydrocarbon-containing gases [2–4].

OBJECTS AND METHODS

The indication potentials of individual alkanes in soils were studied using soil samples collected on three key plots in differente landscapes with different types of hydrocarbon input into the soils: injection (oil spill in dry-steppe landscapes), atmosedimentation (deposition of aerosols from the atmosphere in the southern-taiga landscape), and emanation–biogeochemical (free hydrocarbon fluxes in soils of middle-taiga landscape).

In field studies, soil samples were collected from genetic horizons. Air-dry soil samples were ground and sieved through a 0.25-mm sieve. The contents of individual *n*-alkanes (from C_{14} to C_{36}) and isoalkanes (pristane and phytane) were determined at the Chemicoanalytical Center of the Faculty of Soil Science, Moscow State University.

Soil samples were extracted with chloroform. Filtered solutions were reextracted with *n*-hexane and passed through an adsorption column with aluminum oxide of Brockmann activity II. The contents of alkanes were determined using an Agilent 6890N gas chromatograph (Agilent Technologies, USA) and ChemStation HPChem. The gas chromatograph had the following parameters: column DB1-ms 30 m × 0.25 mm × 0.25 μm; evaporator injector; splitless injection mode; injector temperature 320°C; sample volume 1 μL; helium as carrier gas; carrier gas rate 1 mL/min; thermostat temperature range from 60 to 320°C. The absolute calibration method was used for the quantification of individual hydrocarbons. The C_{10}–C_{34} Connecticut *n*-hydrocarbon mix (Supelco, Switzerland) was used as a certified reference material. Calibration was performed for four calibration points; deviations from linearity did not exceed 10%.

RESULTS AND DISCUSSION

Alkanes as indicators of oil pollution degradation. In the area of an oil and gas production field (Archedinskaya field, Volgograd oblast), the contents and composition of alkanes were studied in three objects: (a) conventionally background soil with undisturbed profile not subjected to injection contamination (from visible indices): shallow dark loamy structural-metamorphic disperse-carbonate-accumulative agrozem on calcareous loess-like loams underlain by calcareous sands, on a flat plain (profile VFP10); (b) soil with a recent (no more than 4–5 months ago) contamination of the profile caused by an oil pipeline break at a depth of 0.5–1.0 m: oil-contaminated chemozem over postagrogenic dark structural-metamorphic disperse-carbonate-accumulative agrozem (profile VFK2); and (c) soil contaminated with oil at least 10 years ago: artificially stratified dark structural-metamorphic disperse-carbonate-accumulative agrozem (profile VPF11). The detailed morphological description of soils and the characterization of their PAHs, bitumoids, and hydrocarbon gases were reported earlier [3].

Results of analysis of alkanes supplemented with data from other studies of organic carbon, bitumoids, PAHs, and retained gases are given in Table 1.

Comparative consideration of the analytical parameters of three above soils allowed the following conclusions to be drawn.

The background soil (profile VFP10) is characterized by a gradual decrease in the contents of carbon, total alkanes, and retained gases down the profile,

Table 1. Alkanes in soils of different-aged injection contamination in the area of an oil and gas production field (dry steppe, Volgograd oblast)

Horizon	Depth, cm	C_{org}, %	$\sum C_{16-36}$	C_{20}	C_{25}	C_{I-15} + C_{I-16}	$\frac{C_{i-15}}{C_{i-16}}$	$\frac{C_{i-15}+C_{i-16}}{C_{17}+C_{19}}$	$\frac{C_{i-15}+C_{i-16}}{C_{19}+C_{20}}$	$\frac{\sum C_{16-23}}{\sum C_{24-36}}$	CPI	Bitumoid	$\sum$ PAHs	Retained gas $\sum \Sigma C_{1-4}$, ppmv
			mg/kg									mg/kg		
Background soil. Dark loamy structural-metamorphic disperse-carbonate-accumulative agrozem (developed dark chestnut soil), profile VFP-10														
PUpa	0–32	1.8	5	0.056	0.787	0.03	0.40	1.1	0.39	0.1	1.3	12	0.12	7.4
BCAdc	55(62)–105	0.5	1.5	0.042	0.217	0.03	0.16	1.2	0.39	0.2	1.4	9	0.04	5.5
D	140–145	0.2	1	0.075	0.145	0.08	0.05	2.2	0.62	0.7	1.3	120	0.32	3.2
Recent (4–5 months) oil spill. Oil-contaminated chemozem over dark structural-metamorphic disperse-carbonate-accumulative agrozem (developed dark chestnut soil), profile VFK-2														
PUpa.x	6–15	5	512	45.25	9.94	240	1.12	3.8	3.18	11	1.0	15000	92.2	17.7
BCAdc.nc	45–74(76)	5.3	677	57.44	38.84	252	1.06	4.2	2.29	5	1.6	23000	95.19	720
D2	115–140	1.1	132	13.47	7.91	30	0.51	3.5	1.42	2	1.2	11400	25.54	99
Old (10–15 years) oil spill. Artificially stratified dark structural-metamorphic disperse-carbonate-accumulative agrozem (dark chestnut soil), profile VFP-11														
AUad	15–30(33)	2	3	0.09	0.55	0.02	0.13	0.8	0.14	0.3	1.5	90	0.07	2.3
BCca	105–131(135)	0.7	1	0.040	0.155	0.00	0.16	0.6	0.05	0.3	1.6	36	0.02	2.3
D	131(135)–160	0.5	1	0.079	0.142	0.03	0.08	2.4	0.24	0.5	1.3	30	0.02	3.3

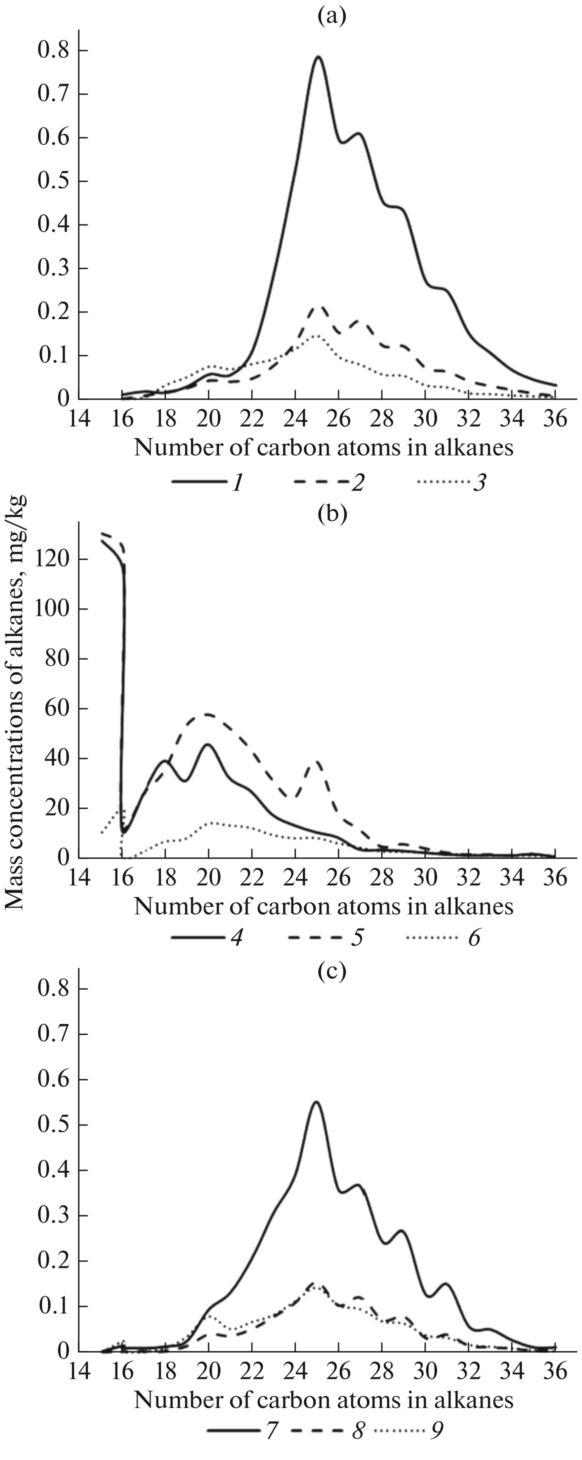

Fig. 1. Distribution of the mass concentrations of alkanes in soils as a function of the time of soil contamination with oil: (a) no contamination; age of contamination: (b) 4–5 months; (c) 10–15 years (horizons: (*1*) PUpa; (*2*) BCAdc; (*3*) D; (*4*) AUad; (*5*) BCca; (*6*) D; (*7*) Pupa,x; (*8*) BCAdc,nc; (*9*) D2).

from the PUpa to the D horizon. The mass concentrations of even and uneven alkanes in the horizons PUpa, BCAdc, and D gradually increase from C_{16} to higher-molecular-weight compounds and reach a maximum for pentacosane ($C_{25}H_{52}$); then, the mass concentration curves go down simultaneously, with insignificant steps for uneven structures: C_{27}, C_{29}, and C_{31} (Fig. 1a). The CPI values are similar in all horizons: 1.3–1.4. The contents of pristane and phytane isomers are minor, with a significant dominance of phytane.

In the underlying rock (D horizon) of the background profile, some increase in the mass concentrations of light alkanes (C_{17} to C_{23}) is observed compared to the overlying soil horizons, as well as a higher $\sum C_{\le 23} : \sum C_{>23}$ ratio than in the higher horizons. The sum of phytane and pristane and its ratio to normal alkanes with the same numbers of carbon atoms in the chain also increase. An increase in the content of bitumoid is observed in the D horizon compared to the soil horizons. It may be suggested that alkanes in the D horizon of background soil fix hydrocarbon emanation from a deep oil deposit.

Significantly different qualitative and quantitative distributions of alkanes are observed in the soil relatively recently contaminated with oil (profile VFK2) (Table 1, Fig 1b). Most oil was squeezed out upward and spilled on the surface; a part of oil infiltrated down to the D horizon or even deeper. The total amount of alkanes increased in more than 10 times in the Pupa,x and D horizons and in 450 times in the BCAdc,nc horizon (the pollution focus). The content of phytane and pristane increased in 8000 times in the upper and middle horizons and in almost 400 times in the D horizons compared to the background soil. The mass concentrations of pristane and phytane prevail over all other individual compounds. In the agro-dark humus and middle horizons, pristane and phytane are present in almost similar amounts; in the underlying rock, phytane is dominant.

Under oil contamination, the major part of normal alkanes covers the homological series in the range from C_{16} to C_{28} with the maximum contents of C_{18} and C_{20} in the agro-dark humus horizon and C_{20} and C_{25} in the middle horizon. In general, the middle horizon, where the pollution focus occurred, remains most contaminated. The maximum concentrations of bitumoids, PAHs, and retained gases (dominated by butane) are observed in the same horizon.

The distribution of the light ($\sum C_{\le 23}$) to heavy ($\sum C_{>23}$) alkane ratio among soil horizons is characteristic. Light alkanes exceed heavy alkanes in the D horizon, in 5 times in the BCAdc,nc horizon, and in 11 times in the Pupa,x horizon. This is a convincing proof of the differentiation of light and heavy molecules during migration up and down from the pollution focus.

Thus, signs of oil hydrocarbon biodegradation are observed already in the first month after pollution. They include changes in the ratios of normal alkanes,

Table 2. Alkanes in soils of different land use at different distances from the source of atmosedimentation pollution (southern taiga, Moscow oblast)

Land use	Horizon	Depth, cm	C_{org}, %	$\sum C_{16-36}$	$C_{i-15} + C_{i-16}$	C_{i-15}/C_{i-16}	$(C_{i-15} + C_{i-16})/(C_{17} + C_{18})$	$(C_{i-15} + C_{i-16})/(C_{19} + C_{20})$	$\sum C_{16-23}/\sum C_{24-36}$	CPI	Bitu-moid	$\sum$ PAHs	Ben-zo[*a*]py-rene	Retained gas, ppmv	
				mg/kg							mg/kg			C_2H_4	CH_4
100 m from the industrial zone, source of atmosphere pollution															
Industrial zone	X2	10–20	6.7	53.4	1.66	0.2	0.75	0.24	0.7	0.7	2500	190	8.4	2	5.5
2 km from the industrial zone															
Forest	AY	0–5	6.2	7.3	0.03	0	0.75	0.2	0.2	2.1	26	5.2	0.1	3	1.5
Plowland	P	5–27	2.5	3.5	0.07	0.4	1	0.4	0.5	1.3	3.5	1.4	0.013 (to 0.13)	1	2.1
4 km from the industrial zone															
Forest	AY	0–5	11.0	19.7	0.12	0.2	1.09	0.35	0.2	5.9	13	1.8	0.03	21	2.6
Plowland	P	5–25	5.9	4.4	0.01	0	0.5	0.1	0.3	1.7	12	0.1	0.001	16	2.2

which degrade more rapidly than isoalkanes, which become thus dominant. Lighter alkanes degrade more rapidly.

A study of alkanes in the soil subjected to oil pollution 10 years ago (profile VFP11) showed that the biodegradation of hydrocarbons in the soil was deep. As a result, the concentrations and distributions of alkanes became almost analogous to those in the background profile (Table 1, Fig. 1c). The presence of additional carbon portions stimulated a higher activity of oil-oxidizing microorganisms than in the unpolluted soil. The deep degradation of alkanes and then isoalkanes resulted in a decrease in their concentrations to a lower level than in the background soil. The concentrations of retained gases were also lower than the background level. The maximums of uneven alkanes in the range C_{25}–C_{31} became more contrast. The distribution curve of alkane mass concentrations in the underlying rock became identical to the curve for the overlying soil horizon. Products of hydrocarbon biodegradation could dissipate in the soil profile, as evidenced by the approaching of carbon concentrations in the old contaminated soil to those in the background soil.

Thus, the evolution of hydrocarbon biodegradation is clearly traced by the distribution of alkanes in the oil-contaminated soil.

Alkanes as indicators of the pollution level of soils under different land use. The study of soil hydrocarbon status under the hydrocarbon contamination of the atmosphere by an industrial object showed appreciable differences in the contents of pollutants at the same distance from the pollution source depending on the land use pattern: forest, plowland, area with increased hydromorphism, etc. In particular, the reserves of heavy PAHs on the plowland were significantly lower than under forest [2], which was attributed to different conditions of hydrocarbon accumulation and transformation after deposition from the air basin: better aeration and conditions for the photodestruction of polyarenes because of plowing. The behavior of alkanes in soils under forest and plowland under atmogenic contamination is considered below.

Studies were performed in the southern taiga subzone, Noginsk district, Moscow oblast. Chemozem on gray humus soil was studied in the industrial zone of a plant producing technical carbon (atmospheric pollution source) (profile MU-3-A). At 2 and 4 km from the pollution source, the following soils were tested: podzolized soddy podbur (profile MU-10-B) and soddy-podzolic soil (profile MU-12-A) under forest; Al-Fe-humus agrozems (profiles MU-10-A, MU-12-B) on plowland. A detailed description of these soils is reported earlier [2].

The dominance of even carbon chains over uneven chains (CPI = 0.7) is a specific feature of alkane composition in industrial emissions from the enterprise. The ranked homological series are dominated by hydrocarbons with the following numbers of carbon atoms C_{22}, C_{24}, C_{26}, C_{28}, and C_{32}. The C_{28} hydrocarbon (octacosane) has the maximum concentration: 8 mg/kg. The ratio of light to heavy molecules $(\sum C_{\le 23}) : (\sum C_{>23})$ is 0.7. The sum of alkanes in the soil in the close vicinity of the emission source is 53.4 mg/kg (Table 2, Fig. 2a).

The content of alkanes in the soil at 2–4 km from the industrial zone is lower than in soils of the industrial zone (3.5–19.7 mg/kg); the compositions of alkanes in forest and arable soils differ significantly: uneven chains prevail in alkanes. CPI is 2.1–5.9 in the forest and 1.3–1.7 on the plowland. The peaks of uneven alkanes (C_{21}, C_{23}, C_{25}, C_{27}, C_{29}, and C_{31}) are clearly distinguished in the ranked series of these compounds. The $(\sum C_{\leq 23}) : (\sum C_{>23})$ ratio is lower than near the industrial zone (0.2–0.5). The content of phytane and pristane isoalkanes does not exceed that of their normal analogues and is significantly lower than in heavier analogues (Table 2; Figs. 2b, 2c).

In soils under forest, the distribution of mass concentrations in the homological series is characterized by clear maximums of uneven alkanes. In plow horizons, these maximums are also present, although they are less sharp (Figs. 2b, 2c). An important feature of alkane distribution in soils under forest is that the mass concentrations of alkanes and the CPI value at 4 km from the industrial zone are higher than in closer soils (at 2 km) in more than 2 times. The concentrations of bitumoids and PAHs in soils regularly decrease with increasing distance from the industrial zone.

This distribution of alkanes may be explained as follows.

The composition of alkanes in the studied soils at longer distances from the pollution source differs from that near the industrial zone. This can be indicative of the biogeochemical, rather than atmosedimentation, origin of alkanes at 2 km and more from the industrial source. The dominance of uneven chains occurs, when alkanes form in the soil due to the microbiological transformation of plant material. The dominance of long-chain alkane homologues with uneven numbers of carbon atoms indicates that aboveground plant biomass, which has a similar spectrum of *n*-alkanes, is their main source in the upper soil horizon.

The productivity of this process increases with decreasing content of toxic substances, including benzo[*a*]pyrene, in the soil (Table 2). An analogous process, although slower, occurs in the plow horizon; however, the accumulation of uneven homologues in the arable soil is less manifested because of the permanent soil turbation and the regular withdrawal of aboveground biomass. In the topsoil of agrocenosis, the contribution of root and microbial biomass, for which the dominance of uneven homologues in the spectrum of *n*-alkanes is less pronounced, to the hydrocarbon pool becomes more significant.

This supposition is confirmed by the composition of retained gases in the studied horizons. In the soil at 2 km from the industrial zone, the content of ethylene of plant origin in the gas is only 1–3 ppm. In the soil at 4 km, which contains an almost background concentration of benzo[*a*]pyrene in the retained gas, the content of ethylene reaches 16–21 ppm, which indicates enhancement of biochemical processes in the soil.

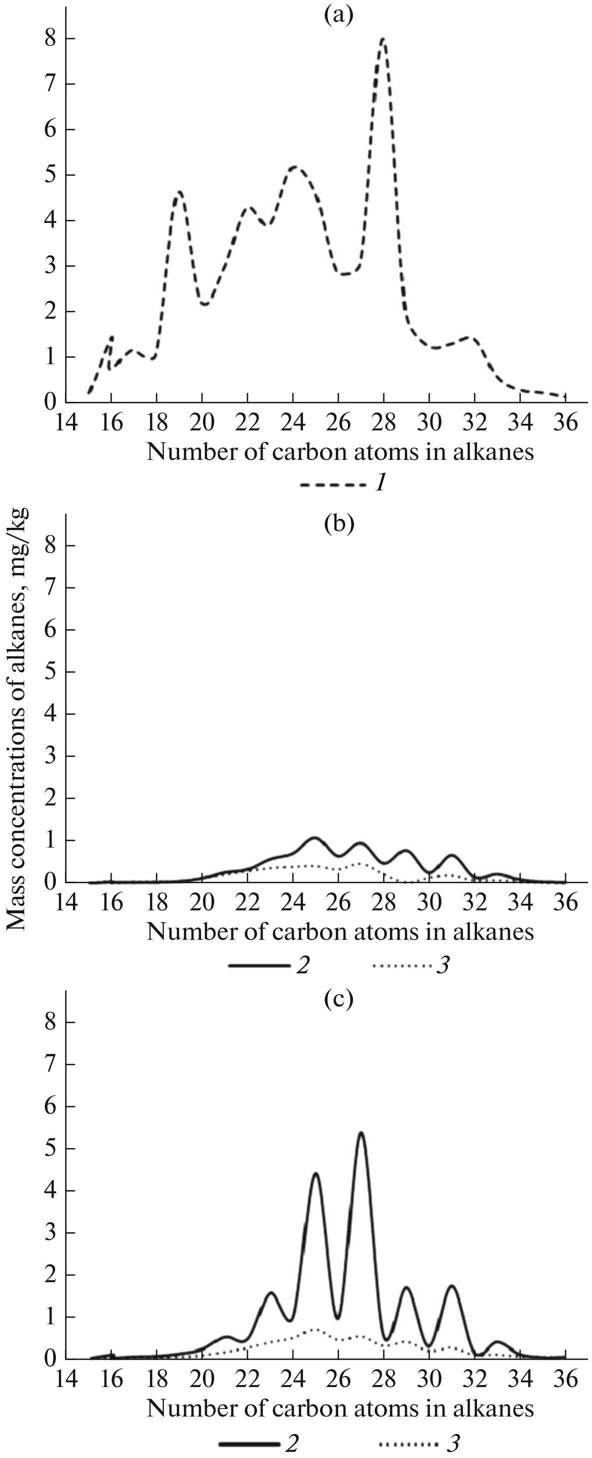

Fig. 2. Distribution of the mass concentrations of alkanes in soils as a function of vegetation and land use: (a) industrial zone; (b) 2 km from the industrial zone; (c) 4 km from the industrial zone ((*1*) horizon X, industrial zone; (*2*) horizon AY, forest; (*3*) horizon P, plowland).

Thus, the study of the concentrations and composition of alkanes in soils under different land use patterns significantly supplements our knowledge about the nature and formation of soil hydrocarbon status.

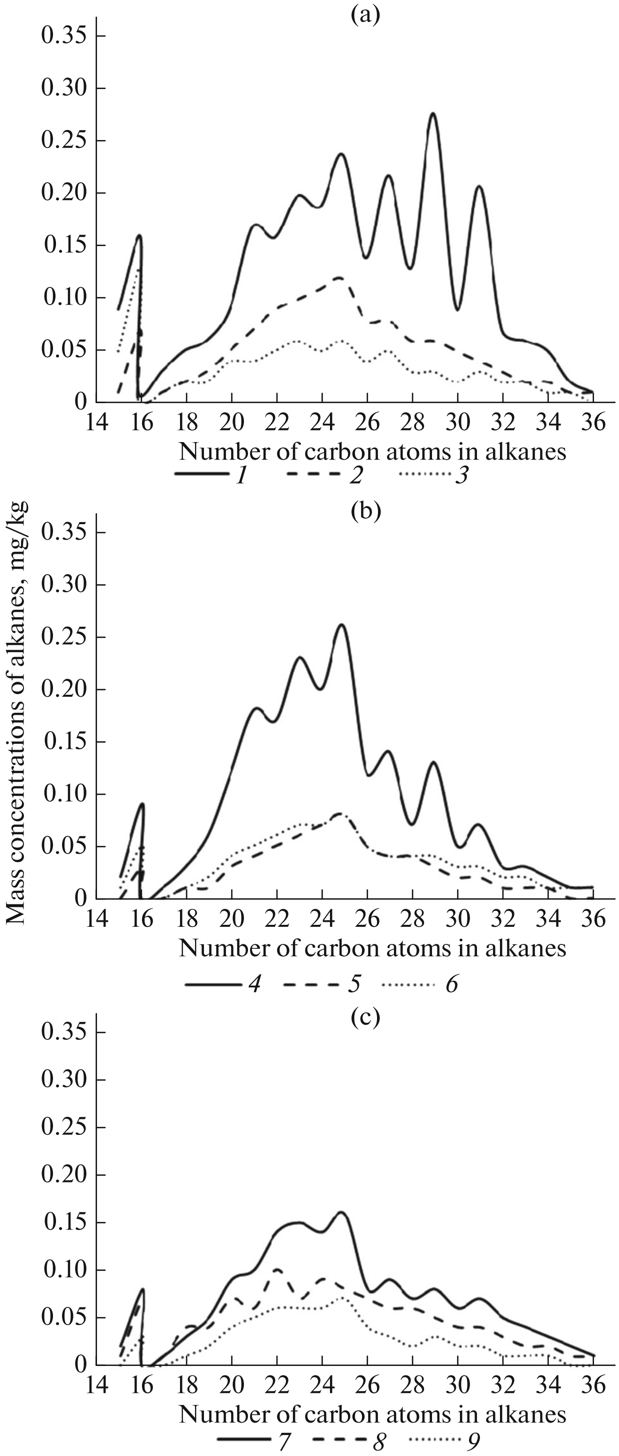

Fig. 3. Distribution of the mass concentrations of alkanes in soils with different intensities of free hydrocarbon gas fluxes (Ust'yanskii district, Arkhangelsk oblast, middle taiga). Hydrocarbons in soil air: (a) up to 14 ppm; (b), (c) absent (horizons: (*1*) AYe; (*2*) BHF; (*3*) C; (*4*) AY[e-hf]; (*5*) BHFfn; (*6*) C; (*7*) AYe; (*8*) BF; (*9*) D).

Alkanes as indicators of soil alteration by hydrocarbon emanations. The contents and composition of alkanes were determined in soils of middle-taiga landscapes developed on the Kokshenga River terraces in the Ust'yanskii district of Arkhangelsk oblast. Steady fluxes of free gas with increased content of hydrocarbons were detected in soil profiles by gas analyzers. The area is far from industrial objects and occupied by natural landscapes. The source of these hydrocarbon fluxes, which have a high variability, is not clearly determined. The area is characterized by abrupt and frequently contrast changes of parent rocks, vegetation types, and soil wetting conditions, as well as the presence of buried peat horizons. The study of soil hydrocarbon status on this area showed very low concentrations of light bitumoid and low concentrations of PAHs, with the dominance of light 2–3-ring molecules. Morphological study of soils revealed no clear confinement of hydrocarbon gas emissions to a specific factor, except sandy soil texture [4].

On the area of gas showing, profile AKTs3 was established on iron-illuvial humus soddy podzol. At several meters from it, profile AKTs2 was established on iron-illuvial humus peat podzol in the area free from gas showing. The both profiles are developed on old alluvial sands of the Kokshenga River terrace. A lithobarrier clay-illuvial soddy podzol (profile AKS10) confined to the watershed surface and developed on binary deposits (loamy sands underlain by loams) was also studied on the same plot in the area free from gas showing.

In addition to the earlier studies, the distribution of alkanes in soils was studied at sites with and without hydrocarbon gas showing in order to reveal its potential changes in relation to the release of free gases. The results of study are given in Tables 3 and 4 and Fig. 3.

In general, the soils of the studied area are characterized by low contents of alkanes. Their maximum content (2.7 mg/kg) is confined to the humus horizon of the "gas" profile AKTs3. A slightly lower concentration of alkanes (2.1 mg/kg) is found in the nearest profile AKTs2, where no hydrocarbons from gas emanations were revealed. Even a lower concentration of alkanes (1.6 mg/kg) is in the "gas-free" profile AKS10 on binary deposits. Analysis of alkane distribution parameters among soil horizons shows that each soil horizon can be characterized by indices that distinguish the soils with the circulation of free gases containing increased concentrations of hydrocarbons from the soils where no such gases were revealed (Table 4). Most of these indices are related to the ratio between the isoalkanes (pristane and phytane) and normal alkanes. In addition, an increase in the maximum concentrations of uneven alkanes, especially among compounds with the longest chains (C_{27}–C_{31}), can be seen in the soil with the circulation of free gases, which is reflected in the mass ratio between these compounds in "gas" and "gas-free" soil profiles.

It may be suggested that the circulation of free gases containing hydrocarbons in the soil profile hampers the biochemical transformation of plant mortmass

Table 3. Alkanes in soils of the area with local hydrocarbon gas exhalations (middle taiga, Arkhangelsk oblast)

Horizon	Depth, cm	C_{org}, %	$C_{i\text{-}15}$	$C_{i\text{-}16}$	$\frac{C_{i-15}}{C_{i-16}}$	$\frac{C_{i-15}+C_{i-16}}{C_{17}+C_{18}}$	$\frac{\sum C_{16-23}}{\sum C_{24-36}}$	CPI	Bitumoid	$\sum$PAHs	Free gas, ppm	Retained gas, ppmv		
			mg/kg						mg/kg			$\sum C_{1-4}$	C_2H_2	C_2H_4
Iron-illuvial humus soddy podzol (profile AKTs3)														
AYe	3(8)–9(19)	0.2	0.09	0.16	1.8	3.13	0.6	2.0	96	0.13	>13.5	21	17	3
BHF	50(53)–64(75)	0.1	0.01	0.07	7.0	3.65	0.7	1.3	8	0.02		0.7	0.2	0.5
C	64(75)–110...	–	0.05	0.14	2.8	5.24	1.2	1.6	<5	–		0.1	0.1	0.8
Iron-illuvial humus peat podzol (profile AKTs2)														
AY[e-hf]	b6–10(12)	0.8	0.02	0.09	4.5	2.81	0.9	1.8	160	0.08	<0.5	24	17	4
BHF fn	61–80	0.1	0.004	0.03	7.5	3.42	0.6	1.2	<5	0.01		2	0.2	2
C	80–90	–	0.01	0.05	5.0	3.61	0.7	1.2	<5	–		3	0.1	3
Lithobarrier clay-illuvial soddy podzol (profile AKS10)														
AYe	5–18(22)	0.2	0.02	0.08	4.0	2.48	0.7	1.4	10	0.02	<0.5	4	2	2
BF	37(44)–73	–	0.01	0.07	7.0	1.91	0.8	1.1	20	0.03		2	0	2
D3	130–145	–	0.004	0.03	7.5	1.78	0.9	1.3	<5	0.02		2	0	2

Table 4. Alkane proportions in soils with and without signs of free hydrocarbon gases

Horizon	Profile	$\sum C_{16-36}$	$C_{i-15} + C_{i-16}$	$\frac{C_{i-15}}{C_{i-16}}$	$\frac{C_{i-15} + C_{i-16}}{C_{19} + C_{20}}$	$\frac{C_{27}AKTs3}{C_{27}AKTs2}$	$\frac{C_{27}AKTs3}{C_{27}AKS10}$	$\frac{C_{29}AKTs3}{C_{29}AKTs2}$	$\frac{C_{29}AKTs3}{C_{29}AKS10}$	$\frac{C_{31}AKTs3}{C_{31}AKTs2}$	$\frac{C_{31}AKTs3}{C_{31}AKS10}$
		mg/kg									
AYe	AKTs3 (gas)	2.7	0.25	0.56	1.7						
	AKTs2 (no gas)	2.1	0.11	0.22	0.6	1.6		21.5			3.0
	AKS10 (no gas)	1.6	0.10	0.25	0.8		2.4		3.5	3.0	
BHF, BF	AKTs3 (gas)	1.2	0.08	0.14	1.1						
	AKTs2 (no gas)	0.6	0.03	0.13	0.8	2.0		2.0		2.0	
	AKS10 (no gas)	1.1	0.08	0.14	0.8		1.3		1.2		1.0
C. D	AKTs3 (gas)	0.8	0.19	0.36	3.3						
	AKTs2 (no gas)	0.7	0.06	0.20	0.9	–1.3		0.8		1.0	
	AKS10 (no gas)	0.6	0.03	0.13	0.5		1.7		1.0		1.5

and results in the relative accumulation of normal alkanes with uneven carbon chains, the dominance of which is typical for higher plants, mosses, and some fungi. This is especially pronounced in the humus horizon of soil.

Biogeochemical processes of hydrocarbon formation in the soil are confirmed by the increase in the concentrations of retained gases (containing 80% ethylene) in the humus horizon. An active formation of ethylene is observed in retained gases of peat interlayers. Increased ethylene concentrations are also noted in profile AKTs2 adjacent to the "gas" profile. It is quite possible that the gas flux sometimes passes through this profile.

However, the nature and location of the source of free gases with the increased concentration of hydrocarbons remain unclear. It was supposed earlier [4] that gas fluxes are generated below the soil profile and below the buried peat horizons. This supposition is also confirmed by the distribution of alkanes. Signs of gas fluxes in the form of specific alkane distributions are observed in the "gas" profile AKTs3 not only in the humus horizon, but also in the parent rock.

Thus, the indication properties of alkanes are also manifested in the situation considered above, where the genesis of soil hydrocarbon status is far from being obvious.

CONCLUSIONS

The performed study allows a conclusion to be drawn that data on alkanes in soils have some indication potential for the identification of natural and technogenic processes affecting the soil hydrocarbon status.

Changes in the composition and proportions of alkanes under the injection input of hydrocarbon pollutants make it possible to trace the degradation trend of pollutants get into the soil from their initial level to the final stages of soil self-purification, when the background concentrations of the added hydrocarbons are reached. At the atmosedimentation input of hydrocarbons into the soil, the composition and mass distribution of alkanes are indicative of the effect of toxicants on biogeochemical processes in the soil, including their manifestation under different land use patterns. Analysis of the composition of soil alkanes in natural landscapes can reveal signs of hydrocarbon emanation fluxes in soils. The indication potentials of alkanes in combination with PAHs and other components of soil hydrocarbon complex are undoubtedly suitable for the solution of other soil-geochemical problems.

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