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Transformation of oil-contaminated soils of cryolithozone

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ABSTRACT

The study of migration and transformation processes of spilled oil in permafrost soils was the goal of the paper. The work was the result of 13-year monitoring of oil contaminated soils at the oil pipeline area where the emergency oil spill had occurred in 2006.

The results demonstrated that at an overall trend towards decrease during 13 years of the spill despite the contamination level was still high. The obtained data showed that oil contamination composition had modified and became asphaltene-resinous character as result of oil transformation with domination of oxygen destruction processes. Without new spills an increase in the oil contamination level in different years may consider as oil's ability to migration in permafrost soils for a long time.

As appeared the presence of a permafrost layer determined the lateral character of oil contamination spreading. At the same time, during season thawing of grounds oil components partly transported up by thawed and ground waters in overlying soil layers in process of migration along permafrost layer. The process of oil contamination soils had become stable character as result of supposition of annual additions of new portions of oil components. High values of residual oil content in soil indicated formation of abnormal hydrocarbons technogenic fields.

KEY WORDS: Oil spill; Transformation; Cryolithozone; Permafrost soil; Hydrocarbons.

INTRODUCTION

The socio-economic development of the Republic of Sakha (Yakutia) is associated with the production and transportation of hydrocarbons. As practice shows, an operation of oil pipelines is often accompanied by accidental spills. According to the Ministry of Ecology, Nature Management and Forestry, over the past 12 years, the number of oil and oil products spills had amounted to more than 316 cases, including the Arctic zone (Government of the Republic of Sakha (Yakutia), 2020).

When oil enters the soil, the oil components mix with the native organic matter of the soil that leads to increase hydrocarbons content in soils. This process accompanied by formation of abnomal hydrocarbons surface geochemical fields of technogenic.

The nature of the distribution of oil components in permafrost soils and the level of their impact on the environment differ even in relatively small areas.

It is known the processes of oil contamination transformation proceed much more slowly in cryolithozone soils in comparison unlike with regions of favorable climatic conditions. It depends on of many factors. Such as morphological, structural, material and genetic features

of a concrete soil profile, its position in the system of geochemical interfaces of landscape facies, quantity and composition of the spilled oil, time since contamination are main. (Goldberg, et al., 2001; Jane, et al., 2011; Margesin and Schinner, 2001; Oborin, et al., 2008; Pikovsky, 1988; Stallwood, et al., 2005; Yang, et al., 2009). All this determines the picture of real distribution of oil components in the soil profile. It is difficult to estimate consequences of oil spills as oil contamination breaks natural processes and interrelations, changing conditions of dwelling of all live organisms.

The territory of the Republic of Sakha (Yakutia) characterizes by widespread permafrost soils. Under permafrost conditions, the processes of self-remediation of oil-contaminated soils are extremely slow (Camenzuli and Freidman, 2015; Filler, et al., 2008; Oborin et al., 2008; Yang, et al., 2009). This is due to a prolonged period of freezing temperatures in the surface layers of the soil, which determines the low flow rate of microbiological processes. The study of the transformation processes of oil pollution and the ability of oil-contaminated soils for self-remediation could give important information for the development of effective methods of cleaning and help maintain the ecological balance of soil ecosystems.

A purpose of the paper was the investigation of migration and transformation processes of spilled oil and its features in permafrost soils on base chemical composition of oil pollution and its change of thirteen years of monitoring results.

Materials and methods

The object of research was the oil-contaminated area at the territory of the emergency oil spill at the 'Talakan-Vitim'' oil pipeline, which occurred in May 2006. The total volume of the poured out oil from the oil pipeline was 244,68 tons. Field works to assess the ecological and geochemical condition of permafrost soils were conducted each year in summer at the emergency oil spill area (59º57′44,5″N 112º10′03,3″E). To that end monitoring platforms were arranged. At one of the platforms 0.5 ha in the area located in the influx of stream, 12 test sites in the area were chosen. During all the following years, soil samples were collected from these sites.

For the study area, permafrost has an sporadic distribution. The thickness of the permafrost layer is 20-30 m, the depth of seasonal thawing is from 0,3 to 1,3 m (Savvinov, 1976). Experimental laboratory and field studies have been established (Gildeeva, 2003; Pikovsky, 1988; Guseva, 1996) that oil pollution extends to the depth of occurrence of the seasonally thawed layer and practically does not penetrate into the permafrost layer, therefore, in this work data on the content of hydrocarbons in permafrost layer are absent.

The oil content in the upper horizons of 0-20 cm was 6 or more times higher than in the lower horizons (up to trace concentrations at 40-60 cm depth in some points). As known, biodegradation processes of oil components proceed most active in the upper soil horizons (Aislabie, 1998; Kachinskii, 2014; Solntseva, 1998). Therefore in our work we studied transformation processes of the oil pollution in soil samples taken from depths of 0-10 and 10-20 cm.

In this work complex of physical and chemical methods was used. The content of OP in the soils was determined using cold chloroform extraction method by the extract yield. Soil extracts were studied by infrared spectrometry, liquid-adsorption chromatography, and gaschromatography-mass spectrometry (GC/MS). IR-spectra were recorded on the Nicolet Protege 460 FT-IR spectrometer. Liquid adsorption chromatography was used for fractional separation of soil extracts into hydrocarbons (HC), resinous, and asphaltene components.

The hydrocarbon fraction was studied by GC/MS. The studies were performed on a system including the Agilent 6890 gas chromatograph, which has interface with an Agilent 5973N high-performance mass-selective detector. The chromatograph is equipped with a quartz capillary column 30 m long, 0.25 mm in diameter, impregnated with the HP-5MS phase. Helium with a flow rate of 1 ml / min served as a carrier gas. Evaporator temperature 320 ° C. The temperature rise was programmed from 100 to 300 ° C at a rate of 6 ° C/min. The ionizing voltage of the source is 70 eV. More detailed research methods are given in the work (Glyaznetsova, et al., 2020; Jovančićević, et al., 2007).

The measurements were performed in triple repeatability. The figures and tables show the data on arithmetic mean values. The results obtained are statistically significant in comparison with the control.

Results and discussion

Oil contamination level determined at the selected sites revealed highly varying pollution rates. Apparently, this was due to the pit-and-mount microrelief with deeps and corresponding downward direction of runoff towards lower areas. Consequently, an average contamination level at all selected sites was calculated as integrated assessment of the oil contamination level of the area under study. Fig. 1 shows the average residual soil content of oil by observation years from 2006 to 2018. As seen, despite an overall trend towards decrease, after 13 years of observation, the contamination level varied strongly and remained very high both in the surface layer of 0-10 cm 86,7 g/kg, and at a depth of 10-20 cm 42,2 g/kg.
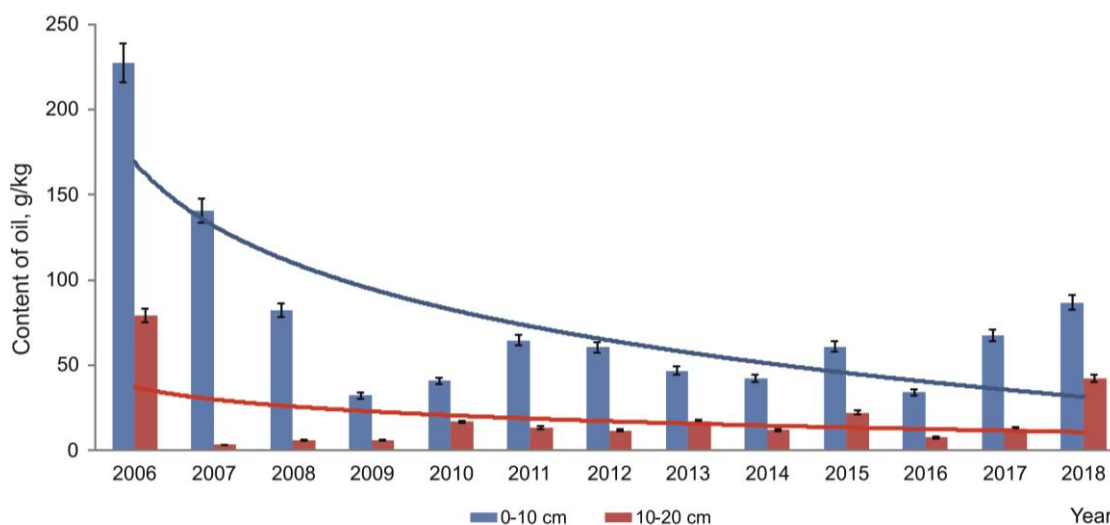

Figure 1. Dynamics of changes in the residual oil content in the soils of the study area at a depth of 0-10 cm and 10-20 cm

The maximum decrease twice in oil content was detected in the first year of observations. At this stage, according to Oborin et al. (2008) and Kachinskii et al. (2014), oil transformation in soil was mainly due by physical and chemical destruction, gas removal, dissolution, UV destruction. Further, in case of self-remediation of soils the transformation processes connected with biodegradation of oil hydrocarbons under an influence of self- soil oil-destructors microorganisms usually joined. In subsequent years, the level of oil pollution fluctuated both up and down. The decrease in the level of oil pollution could be associated with both the processes of its transformation and migration with flood, rain and melt waters.

The increase in the level of pollution in the absence of new spills could apparently be associated only with the ability of oil pollution to migrate. All this pointed to the high mobility of oil pollution in the soils of the permafrost zone.

According to some researchers (Goldberg, et al., 2001; Solntseva, 1998; Margesin and Schinner, 2001), during single oil spills for most types of soils, the bulk of oil was concentrated in the upper layer up to 10 cm thick. In all the years of monitoring at the study area, the oil content at a depth of 10-20 cm was lower than in the near-surface layer of 0-10 cm. The most significant decrease in the oil content in the soil horizon of 10-20 cm was detected in the first year after the spill, in subsequent years the content varied within 6-22 g/kg and by 2018 the residual oil content increased more than 5 times compared to previous 2016-2017 years of observations.

The study area was located at the mouth of the stream. The relief was gentle sloping, the microrelief was a depression, a small tubercle. Soils had a cold profile and below-zero temperatures for 7-8 months a year. The land cover at a depth of 0-10 (15) cm features peaty was humidified dark-grey (closer to black) clay loam with plant roots. Light-brown waterlogged clay loam with inclusions of peaty dark-grey clay loam was found at a depth of 16-60 cm. Seasonally thawed layer water entered the soil profile bottom. Watering can be the reason for the redistribution of oil along the soil profile. High water saturation of the soils during thawing could lead to the floating up of oil in the free phase. Thus as a result of vertical, lateral and radial migration of petroleum hydrocarbons, there was a constant redistribution of pollution in the soil profile, as a result of it the area of pollution could significantly exceed the initial one.

Consider the changes in oil composition over the period of observations. According to the data on the group composition of soil extracts and the type of IR spectra, oil pollution underwent oxidative degradation processes. Over 13 years of observation changes in the composition of soil extracts included a decrease in the composition of hydrocarbon components and increase resins and asphaltenes. By the end of observations, the contamination acquired asphaltic-resinous composition (fig. 2). The absorption of oxygen-containing groups 3300-3400, 1700-1740, 1170 cm^{-1} in the IR spectra of soil extracts increased (fig. 3).
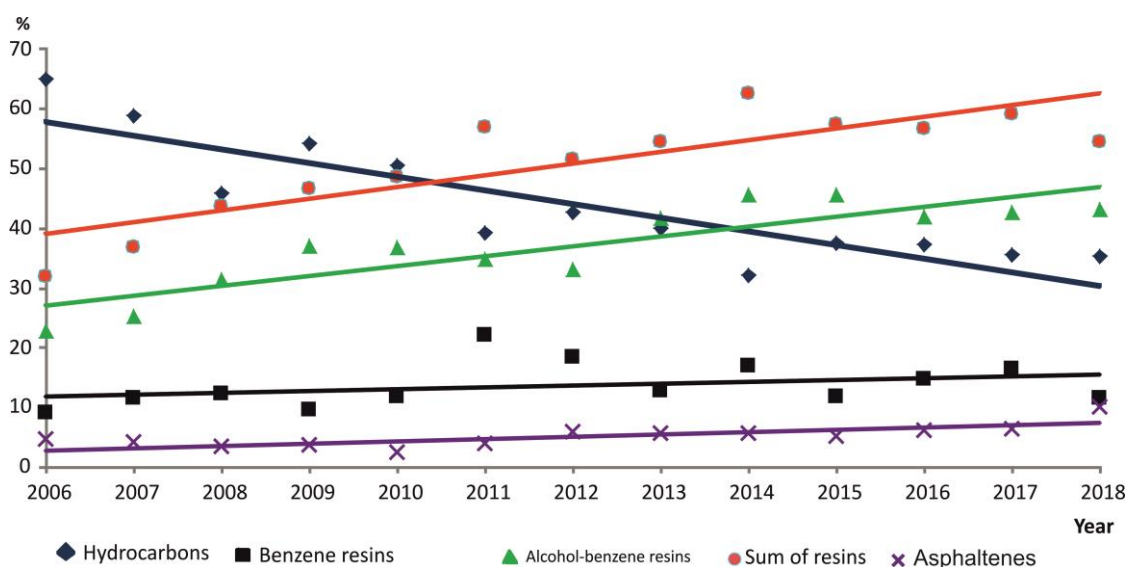

Figure 2. Dynamics of changes in the group composition of soil extracts

As seen from fig. 3, the following hydrocarbon groups and bonds prevail in the chemical

structure of the extract of oil contaminated sample collected in 2006 almost right after the spill: compounds with long methylene chains - absorption band (a.b.) 720cm^{-1}, aromatic hydrocarbons - a.b. 750, 810 and 1600cm^{-1}. With time, absorption of oxygen groups and bonds increased in spectra compared to hydrocarbon structures. Intensity of typical for carbonyl groups a.b. 1700cm^{-1} and a.b. in the range of 3300-3400cm^{-1} for hydroxyl groups increased whereas intensity of bands 1460cm^{-1} (methyl and methylene groups) and 1600cm^{-1} (aromatic cycles) decreased.
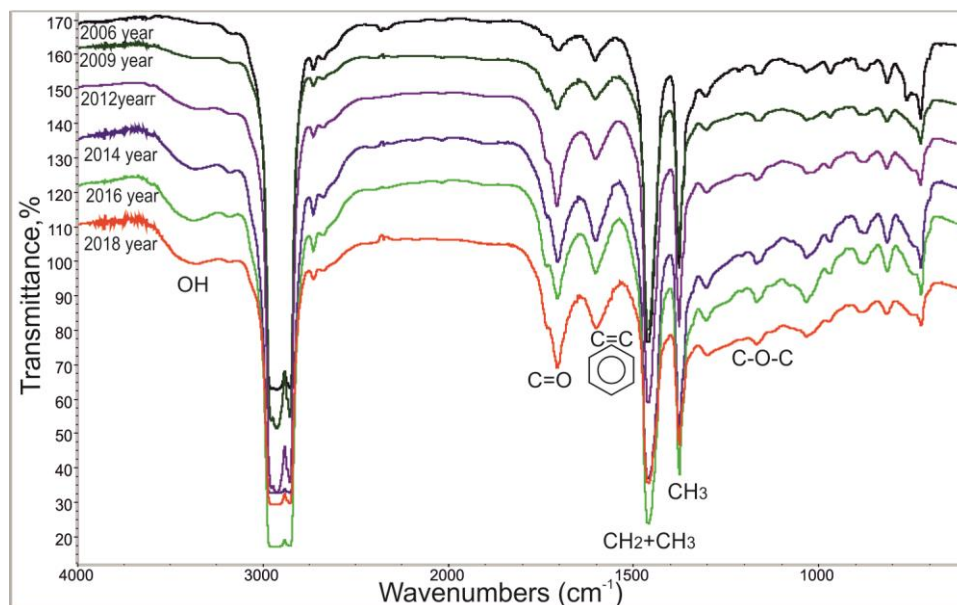

Figure 3. IR spectra of soil extracts collected over different years of observations

All the above changes in the nature of IR spectra of oxygen groups compared to hydrocarbon ones was the evidence of oil oxidative destruction processes in soils.

Thus, in the near-surface soil layer, pollution had already acquired an asphalt-resinous, inactive nature. Therefore, the preservation of the ability of oil to migrate for 13 years was apparently associated with the vertical and lateral movement of oil components during seasonal freezing-thawing cycles of soils.

According to chromatography-mass spectrometry data, oil transformation processes also characterized by changes in the hydrocarbon composition, namely, by redistribution of hydrocarbons both inside homologous rows and between different homologous rows (Table 1, fig. 4).

In the initial contaminated samples collected in 2006 and not yet exposed to transformation, prevailing saturated hydrocarbons were alkanes of regular structure among, which relatively low-molecular homologous compounds with distribution maximum of nC_{15}, nC_{17} prevailed (table 1, fig. 4 a). The ratio of n-alkanes with an odd number of carbons to n-alkanes with an even number (CPI) was about 1. Isoprenoids amounted to 19,81%. Phytane (iC_{20}) dominated over pristane (iC_{19}) and n-octadecane (nC_{18}). The iC_{19}/nC_{17} ratio was about 1. This distribution of saturated hydrocarbons is typical for oils of the Vendian-Cambrian deposits of the Nepsko-Botuobinskaya oil and gas-bearing region, where the Talakanskoye oil-gas condensate field is located (Kashirtsev, 2003). Oil from this field was the source of contamination.

Table 1. Composition of saturated hydrocarbons in extracts of soil samples

Parameters	Year					
	2006	2009	2011	2014	2016	2018
Group composition of alkanes, % for $\sum$ of identified alkanes: n-alkanes	52,39	30,03	30,20	28,26	27,94	not detected
isoprenoids	19,81	25,76	41,12	28,92	20,76	not detected
12- and 13-methylalkanes	14,8	16,37	14,34	44,00	not detected	not detected
$\sum b.b.t\text{-}nC_{20}/ \sum nC_{21}\text{-}e.b.t^{*}$	1,5	1,17	1,03	0,65	not detected	not detected
max n-alkanes	$nC_{15,17}$	nC_{17}	$nC_{17,18}$	nC_{19}	$nC_{17,18}$	not detected
isoprenoids/n-alkanes	0,35	0,86	1,36	1,00	0,74	not detected
CPI	1,10	1,20	1,38	1,40	0,93	not detected
iC_{19}/ iC_{20}	0,60	0,71	0,56	0,37	0,50	not detected
iC_{19}/nC_{17}	0,57	1,87	4,92	3,29	0,72	not detected
iC_{20}/nC_{18}	1,34	3,54	8,56	10,17	1,55	not detected
$Pr+Ph/nC_{17}+nC_{18}$	0,90	2,58	6,76	6,50	1,12	not detected

* – b.b.t. temperature of beginning boiling; e.b.t. temperature of end boiling

It is known petroleum hydrocarbons to have different resistance to biodegradation processes (Aislabie, et al., 1998; Oborin, et al., 2008; Jovancicevic et al., 2008; Margesin and Schinner, 2001). First of all n-alkanes and among them nC_{17}, nC_{18}, monomethyl-alkanes subject to a process of biodegradation and only then to isoprenoids. As can see from the mass chromatograms (Fig. 4) and the data in Table 1 over time, the content of n-alkanes, 12- and 13-methylalkanes in the composition of hydrocarbon fractions decreased and isoprenoids increased. This indicated changes in the individual composition of the hydrocarbon fractions of soil extracts had occurred under the influence of microbical biodegradation processes.

Kachinskii et al. (2014), Margesin and Schinner (2001), Ibatullina et al. (2012), Philp (1994) use a ratio of the sum of isoprenoids pristane (Pr) and phytane (Ph) to the sum of a number of eluted alkanes nC_{17} and nC_{18} as a biodegradation coefficient. Kachinskii et al. (2014) also use this ratio for determination of oil aging degree. The more intense biodegadation processes the higher values of this ratio.

The evidence of oil pollution biodegradation was also the maximum displacement in the distribution of n-alkanes to a higher molecular weight area from $nC_{15,17}$ to nC_{19} in 2014. The ratio of relatively low molecular weight n-alkanes to high molecular weight $\sum b.b.t\text{-}nC_{20}/\sum nC_{21}\text{-}e.b.t$ decreased. Then biodegradation processes affected an ever wider range of hydrocarbons. There was a redistribution in the content of various groups of acyclic alkanes and their almost complete disappearance. Since 2015, the area of unseparated components appears on the mass chromatograms. Usually, this area is represented by unseparated

polycyclic methane-naphthenic and naphthenic-aromatic hydrocarbons, in this case probably - the products of transformation of oil hydrocarbons.

A peculiar feature of all samples was the presence of hydrocarbons of row of 12- and 13-methylalkanes among isoalkanes. They are typical compounds in oils of the Vendian-Cambrian deposits of Western Yakutia (Kashertsev, 2003; Petrov, 1984). Presence of these hydrocarbons served one of the indicators for identification oil contaminants of this type.

The changes in the individual composition of saturated hydrocarbons in comparison to the initial pollution indicated that processes of biodegradation of oil hydrocarbons had taken place.

Many researchers differ three types of oil transformation in soils specifically physical and chemical destruction; microbiological transformation of oil hydrocarbons and the stage, when the most stable, high-molecular compounds remaining in soils and weakly undergoing to microbial attack. As a result, in the soil there is a biocenosis different from background. The duration of each stage is a result of a group of factors, affecting the oil destruction rate: temperature, moisture content, oil composition and concentration, oxidation-reduction conditions, soil type, presence of native hydrocarbon oxidizing microorganisms, etc. Despite the common trend of oil transformation, these processes could vary to a certain degree, in different bioclimatic zones. For example, Pikovsky (1993) ascertained that the first degradation stage lasted 1-1,5 years but this period could be significantly longer subject to the oil spill volume. In time, during oil transformation in the soil extracts content of hydrocarbon fractions decreases and the amount of asphaltic-resinous components increases. Resins and asphaltenes are more stable compounds almost inaccessible to microorganisms; their degradation is very slow; it could be last a few decades.

Our data over thirteen years of monitoring of the area disturbed by the oil spill allowed also to distinguish the main stages of oil transformation in soils. During the first year, a decrease in the oil content in soil was mainly due to physical and chemical destruction, gas removal, dissolution, UV destruction. During the second year observations, the oil contamination level remained almost the same. Only on the third year, significant decrease of oil content became an evidence, which was perhaps due to the activation of self-soil oil-degrading microorganisms.

In the following years, the oil contamination level varied both downwards and upwards. The decrease of the oil contamination level was due to transformation processes. An increase of contamination level in the absence of new spills was apparently due to the ability of oil contamination to migration. Made studies showed that oxidative destruction of oil contamination was developing in subsurface soils (0-20 cm) over these years, due to which oil contamination acquired asphaltic-resinous composition and thus slow-moving character. Most possibly, oil components migrated up to the surface from underlying soil layers (where they had accumulated) to the permafrost layer. Due to lower temperatures, lack of oxygen and UV, transformation processes at depth were very slow or were absent.
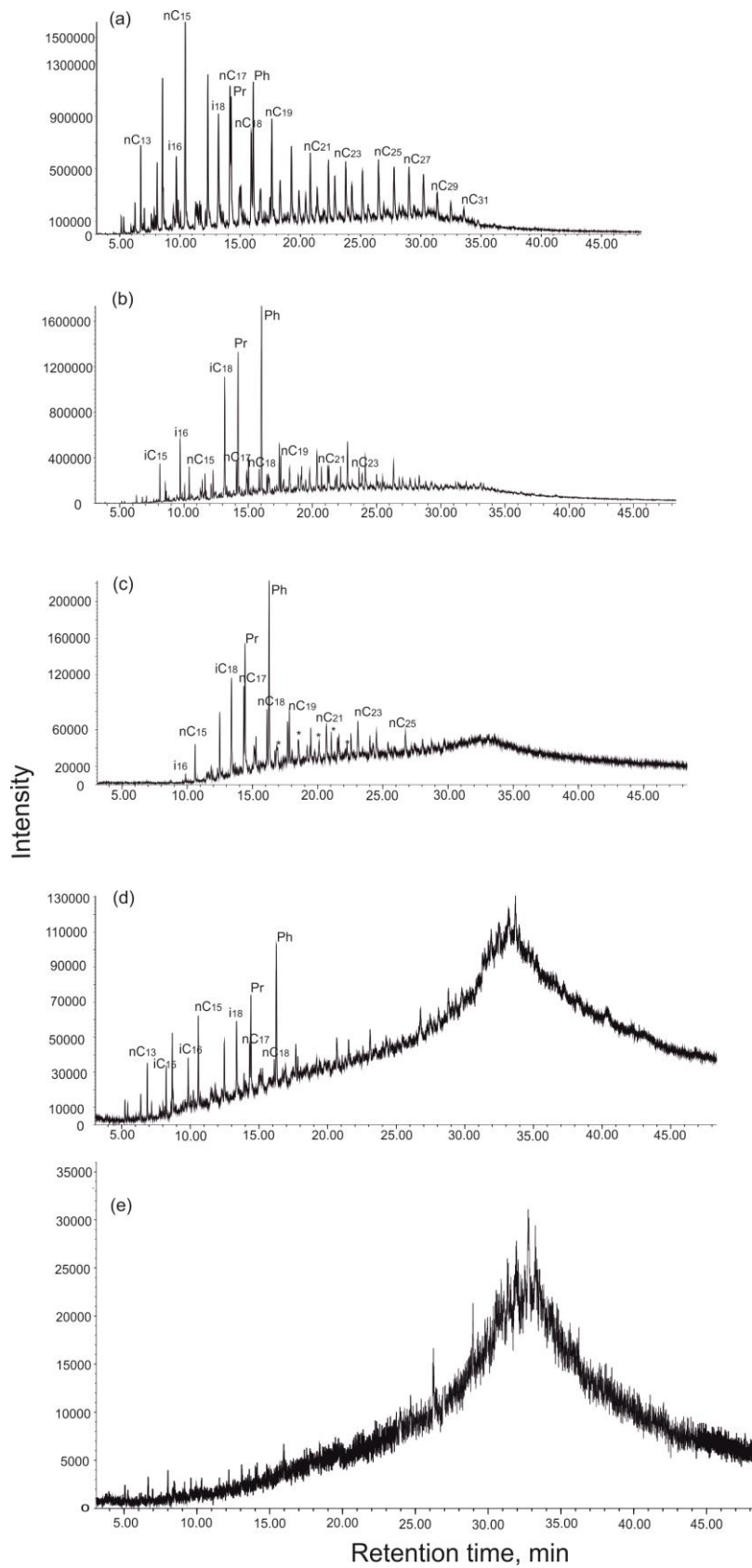
Figure 3. Mass fragmentograms (m/z) of saturated hydrocarbons in soil extracts samples taken in different years: (a) - 2006; (b) – 2009; (c) –2011; (d) –2015; (e) – 2018
$C_{13}… C_{27}$ – n-alkanes, i-C_{15}…i-C_{20} – isoprenoids, * - 12- and 13-methylalkanes.

CONCLUSIONS

It is shown that the processes of biodegradation of permafrost soils (Western part of Yakutia) under the influence of their own hydrocarbon-oxidizing microflora were activated only 2-3 years after oil spill. At the same time, for the soils of the middle zone, the activation of microflora observed already after 2-3 months. Biodegradation processes in soil of cryolithozone slowed down after about 11 to 12 years. By this time, there were practically no hydrocarbons available for the vital activity of microorganisms of the soils, but the level of pollution was still high.

Oil contamination acquired asphaltic-resinous composition and steady character. If no new spills occurred, an increase of the oil contamination level in observation years (2011, 2015, 2017) indicated oil's ability to migrate in permafrost soils for a long time. At seasonal thawing of soil oil components from a permafrost layer partially moved up to overlying soil layers, migrating with thawed and ground waters along a permafrost layer. Thus, oil contamination became chronic due to annual additions of oil components.

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