Hydrocarbons content in soils of the northernmost taiga ecosystem of Komi Republic (North-East of Russia)

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Abstract
The background concentrations of hydrocarbons (HCs) were estimated for soils of the northernmost and northern taiga ecosystem of the Komi Republic. It was shown that accumulation and distribution of hydrocarbons in soil cover is regulated by following pedological factors: texture class, parent material and landform type and the type of soil forming process. In all studied soils of accumulative positions showed more pronounces accumulation of hydrocarbons than the soils of well-drained eluvial positions. Interprofile differentiation of hydrocarbons content is more expressed in clay-textured soils than sandy ones.

Key words: monitoring, background, Russian Subarctic, Komi

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Introduction

The global ecological issues related to the transboundary transfer of pollutants and the regional and local sources of environmental contamination require new approaches to the assessment of the specific ecological situations developed in natural ecosystems. Natural environments are overloaded with hydrocarbons (HCs). At present in the World, none of the oilfields belongs to "wasteless" production. Numerous of hydrocarbon polluted sites can be found worldwide (Sharma et al. 2000, Konečný et al. 2003, Shi et al. 2008, Panagos et al. 2013). This environmental problem occurs even in cold isolated and remote regions such as the Arctic and Antarctica (Aislabie et al. 2006, Gomez et Sartaj 2014, Karppinen et al. 2017) due to the hydrocarbon-based fuels which are used as energy source in these locations (Aislabie et al. 2004, Abakumov et al. 2014).

Petroleum HCs are one the most common contaminant, though a wide range of chemicals may be present (Towell et al.

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2011, Alekseev et al. 2016). Once released into the environment, petroleum hydrocarbons are subject to abiotic and biotic weathering reactions *e.g.* physical and biochemical transformations, interactions with soils. The HCs may change soil composition and toxicity, and thus influence their fate and biodegradation (Brassington et al. 2007, Jiang et al. 2016).

The extent of these transformations will vary according to the type of petroleum products present, the soil conditions (*e.g.* organic matter content, soil grain size and clay-type at the sites) (Stroud et al. 2007, Cabrerizo et al. 2016), and the bioavailability and susceptibility of the fractions of petroleum HCs (saturates, aromatics, resins and asphaltene) (Maletic et al. 2011).

Large oil fields and deposits are being intensively explored in the Komi Republic. The increase in production of raw HCs significantly complicates the environmental situation in this region (the far-northern and northern taiga). Anthropogenically-degraded soils are widely spread in the production areas of oil fields, at the sites of prospective and geophysical boring, and along the oil pipelines and transportation lines. They are developed because of mechanical disturbances of the soil cover, oil well accidents, pipeline damage and corrosion, breaches of pits with oil sludge and drill cutting waste, contamination with waste water, and emissions of toxic compounds. The contamination of soils with oil is a specific type of contamination, which results in profound changes in all the morphological, chemical, physical, and biological soil properties. The reasons for such phenomenon are related to the multicomponent composition of oil and its pulse input into soils, high mobility, capacity to circulate among different ecosystem components, and persistence (Beznosikov et Lodygin 2014).

According to the recent Russian regulations (State Sanitary Norms 2003 - [3]), the assessment of soil contamination with HCs requires the calculation of the pollutant concentration factor equal to the ratio between the content of the pollutant and its maximum permissible concentration (MPC). In the absence of an MPC, the background contents of the HCs are recommended to be used (Procedure for Determining Damage from Soil Contamination by Chemical Substances 1993 - [2]). The analysis of the methodological documents regulating the threshold limit value of HCs (oil products) in soils showed that the existing legislation of the Russian Federation on the contents of oil and oil products in soils is limited and not differentiated among the natural climatic zones. Therefore, it cannot be used for ecological expertise in a specific region.

The available data on the background concentrations of HCs in the soils of the Komi Republic are also limited and usually contradictive. Many of them are insufficiently related to the variation of the HCs content in the soil. Therefore, the assessment of the background content of HCs in soils is an urgent problem, whose solution will contribute to the detailed assessment of soil contamination and the timely limitation of industrial technologies of oil production, transportation, and processing. Under the extreme climatic conditions of the northern regions, the soils have a low cation exchange capacity and low self-purification capacity and, hence, require permanent control of their contamination with HCs. In this context, the aim of this study was to assess the background content of HCs and reveal their accumulation features in the organic (litter) horizons of different soils in the far-northern and northern taiga regions with consideration for the landscape geochemical features of the areas.

Material and Methods

Study sites

The region under study occupies an area of about 60.3 thousands km^2 and consists of plains and mountains. The forest-tundra (the northern forest-tundra boundary passes along the 67^{th} parallel north) has a flatridged-hilly topography with vast lows and dissected moraine hills. The vegetation is a combination of dwarf birch tundra, hummocky bogs, and insular thin spruce and birch forests, which develop not only in river valleys but also on hill slopes (predominantly on sandy soils). The far-northern taiga (its northern boundary passes along the Polar Circle), and the northern taiga (its northern boundary passes along the parallel of 65° 10' N) have a plain or gently ridged topography, which is more dissected near the rivers. Spruce forests and high-moor *Sphagnum* bogs prevail there. Lichen-dominated and moss-dominated pine forests occupy the high sandy terraces. Waterlogged spruce forests are predominant in the interfluves and weakly drained areas. Moss-dominated spruce forests prevail in the areas closer to the rivers and in the more dissected relief elements. The Timan Ridge is a band of smoothed hilly elevations extended in the northwestern direction. The relief of the Near-Polar Ural region is characterized by meridionally extended ranges separated by river valleys. Stone fields and polygonal and other forms related to frost weathering are widely developed on the tops and slopes of the mountains. The vegetation of the Near-Polar Ural mountain zone is characterized by the predominance of coniferous forests in the lower part and larch and birch forests in the upper part. A woodless mountain-tundra belt with large-herb meadows occupies the upper parts of the slopes. The lower boundary of the bald mountain zone in the Near-Polar Ural region occurs at the altitude of about 800 m a.s.l. The soils of the regions under study are shown in Fig. 1.

Soils of the northern and northernmost taiga of the Komi Republic were studied. Soils types were identified according to the IUSS Working Group WRB (2014) - [4]. For the landscape geochemical assessment of the background content of HCs in the soils, the State Soil Map of the Komi Republic on a scale of 1 : 1000000 (Zaboeva et al. 1982) was digitized. The digitized map formed the basis for the compilation of a taxonomic list of the soils, the calculation of their areas, the determination of the reference profile coordinates, and the sampling of mixed samples of the zonal and intrazonal soils. The mixed soil samples were composed of 15 individual samples from an area of 100 m^2. The range of the landscapes was from a watershed (automorphic soils) to geochemically subordinate landscapes of valleys (hydromorphic soils) in the northern and far-northern taiga and from hummocky and spotted hummocky complexes to flat-hummocky areas in the forest-tundra zone. On the basis of the analytical results, a database on the content of HCs in the organic (litter) horizons of the soils was developed with the use of GIS software (ArcView GIS 3.2a).

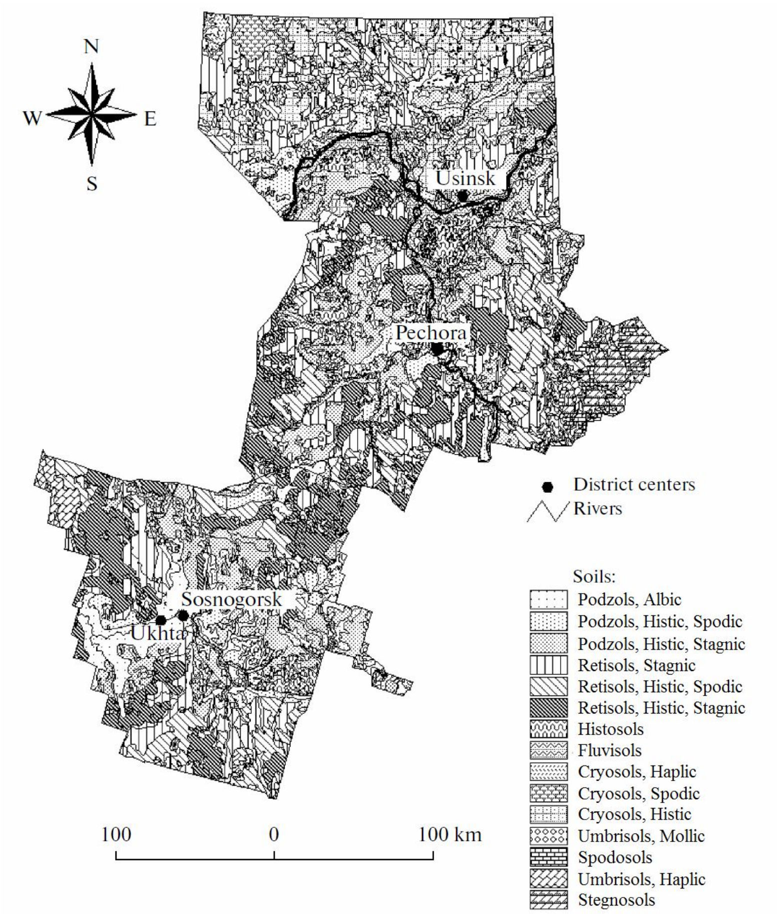

Fig. 1. Soil map.

Laboratory methods

The qualitative chemical analysis of the samples was performed in the Ecoanalytical Laboratory of the Institute of Biology of the Komi Research Center of the Ural Division of the Russian Academy of Sciences.

The concentrations of the HCs in the soil samples were determined from the fluorescence intensities of hexane extracts measured using a Fluorat-02-03M liquid analyzer (Lumex, Russia). The procedure is based on the extraction of oil products from a soil sample with chloroform, the evaporation of the extract, the dissolution of the dry extract in hexane, and the purification of the obtained solution on a column with alumina. The calibration of the analyzer and all the measurements were performed using color filter 1 (transmission maximum at 265 nm) in the excitation channel and color filter 3 (transmission maximum at 320 nm) in the recording channel (Environmental Protection Regulations 2007 - [1]). The state reference sample, a 1 $mg \cdot ml^{-1}$ solution of oil products in hexane (GSO 7950-2001) was used as a standard.

Results and Discussion

Soil morphology and general properties

The studied region is significantly extended in the meridional direction and experience a difference in the climate from the south to the north. Therefore, the drainage becomes lower, and the semihydromorphic and hydromorphic pedogenesis gets enhanced. The parent materials are clayey and loamy deposits, sands, and loamy sands or binary deposits (morainic loams overlain by sands and loamy sands), which changed by glaciofluvial sands near the rivers valleys. The pedogenesis in the mountain region is performed mainly on the loamy eluvium and eluvo-deluvium (colluvium) of acid crystalline rocks (Zaboeva 1975). Soils of northernmost and northern taiga of the Komi Republic are Podzols (on sandy textured substratas), various Retisols (on clayey and loamy textured materials), numerous Cryosols (Haplic, Spocid and Histic), Fluvisols, Umbrisols and Stagnosols. These soils types are quite different in terms of acidity levels (the most acidic are soils with pronounced Histic features, while the lowest acidity is typical for Umbrisols). All the soils investigated showed increased portions of organic carbon in superficial layers, which indicated high possible buffering capacity of the topsoils to the contaminants. The lowest base saturation degree was in soil with clear features of Histic material accumulation, while the highest were reveled for Umbrisols. The main chemical properties of the investigated soils are presented in Table 1.

Data on the background content of HCs in the organic (litter) horizons of the soils in the far-northern and northern taiga of the Komi Republic are given in Table 2. They were included in the database created using a GIS software (ArcView GIS 3.2a), a fragment of which is given in Fig. 2.

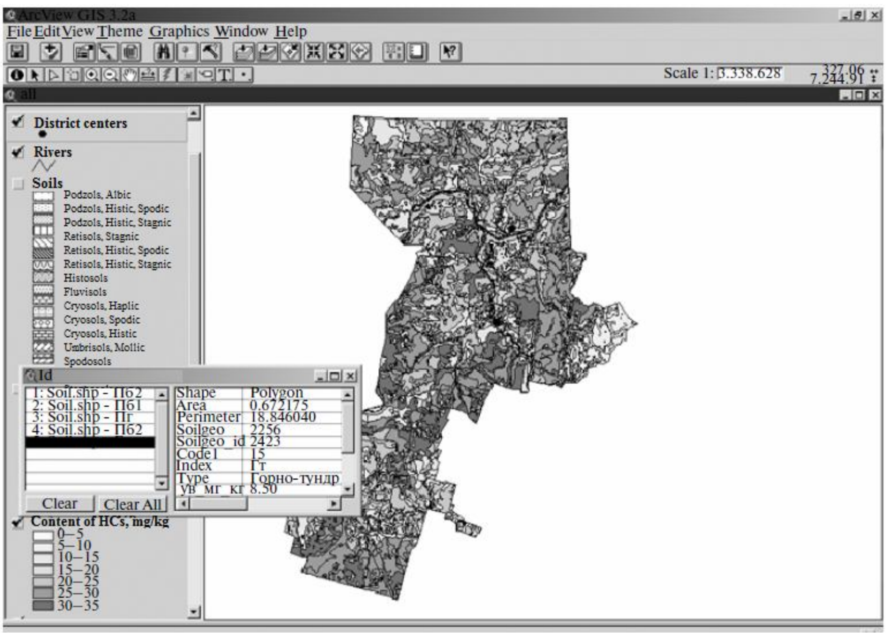

Fig. 2. Fragment of the database on the content of hydrocarbons in the soils.

Soils	pH		C_{org}, %	Ca+Mg, mmol/ 100 g
	H_2O	KCl		
Podzols Albic	4.0	3.4	24.5	19.6
Podzols Histic, Spodic	3.7	3.0	28.1	15.9
Podzols Histic, Stagnic	3.8	3.2	30.8	13.7
Retisols, Stagnic	5.0	4.4	33.5	37.6
Retisols Histic, Spodic	4.8	3.7	42.7	23.3
Retisols Histic, Stagnic	4.5	3.8	38.9	26.8
Histosols	4.1	3.0	41.2	23.4
Fluvisols	4.7	3.6	7.4	24.1
Cryosols Haplic	3.7	3.1	35.0	12.8
Cryosols Spodic	4.2	3.7	20.8	33.4
Cryosols Histic	3.9	2.8	36.7	20.6
Umbrisols Mollic	5.6	4.8	32.4	46.7
Spodosols	4.3	3.2	27.6	12.6
Umbrisols Haplic	5.1	4.2	26.1	30.9
Stagnosols	4.5	3.3	21.9	14.7

Table. 1. Soil chemical properties.

Soils, sample size	Arithmetic mean, mg/kg	Confidence interval (0.95)	Variation coefficient, %	Asym-metry
Podzols, Albic, n = 19	12.7	2.0	33.1	-0.29
Podzols, Histic, Spodic, n = 15	13	3	45.7	0.57
Podzols, Histic, Stagnic, n = 13	22	4	30.9	0.37
Retisols, Stagnic, n = 22	30	10	75.8	1.26
Retisols, Histic, Spodic, n = 13	26	4	44.3	0.14
Retisols, Histic, Stagnic, n = 36	32	6	38.7	0.28
Histosols, n = 18	19	5	52.9	2.35
Fluvisols, n = 36	21	4	43.3	1.26
Cryosols, Haplic, n = 9	2.6	0.8	39.7	0.19
Cryosols, Spodic, n = 12	11	5	69.2	1.92
Cryosols, Histic, n = 12	22	9	65.2	1.49
Umbrisols, Mollic, n = 15	6.0	2.5	16.7	0.00
Spodosols, n = 5	5	3	40.0	-0.75
Umbrisols, Haplic, n = 5	9.7	1.1	10.7	-0.37
Stegnosols, n = 5	8.5	2.8	20.4	-0.58

Table 2. Weight portion of hydrocarbons in the organic (litter) horizons.

The accumulation and distribution of HCs in the soil cover depended on several factors. The texture of the parent materials, the relief of the area, and the type of pedogenesis. The analysis of the entire data set showed that the distribution of HCs in the soils has a positive asymmetry. Positive asymmetry usually indicates that most variations in the weight portion of the HCs correspond to the values lower than the arithmetic mean. It was found that the background variation ranges of the HCs in the organic horizons were similar for the different Retisols at a significance level of 0.5. This is suggeste to be caused related to the similarity of parent rocks, particle-size composition of the soils on the mantle loams, and the common features governing the HC migration in the landscape. The same distribution of HCs in the forest floor horizons was found for the soils developed on old alluvial and glaciofluvial sandy deposits and poorly drained watershed ridges and glaciofluvial terraces covered by sandy deposits. Absolute content of HCs in these soils (Podzols, Albic; Podzols, Histic, Spodic; Podzols, Histic, Stagnic), however, was lower than that in the soils developed on loamy soil-forming rocks. The mountainous soils (Umbrisols and Spodosols) were characterized by negative asymmetry values (A from –0.75 to –0.29) and an insignificant accumulation of HCs.

The determined contents of HCs in the soils under study allowed revealing their accumulation in the organic (forest floor) horizons. These horizons serve as a geochemical barrier for the migration of HCs within the soil profile. The differentiation of the HCs among the genetic horizons was more pronounced in the soils developed on loams (Retisols, Stagnic) and less pronounced in the soils on sandy parent rocks (Podzols, Albic). The profile accumulation of the HCs in the Podzols, Albic was significantly lower than in the Retisols, Stagnic. The comparison of the downward migration of the HCs in the Podzols, Albic and the Retisols, Stagnic showed that they were more uniformly distributed along the profile and leached from the podzolic horizon of the Podzols, Albic while an accumulation of HCs in the O and EB horizons and a decrease of their content in the E, B, and BC horizons occurred in the Retisols (Stagnic) (Fig. 3).

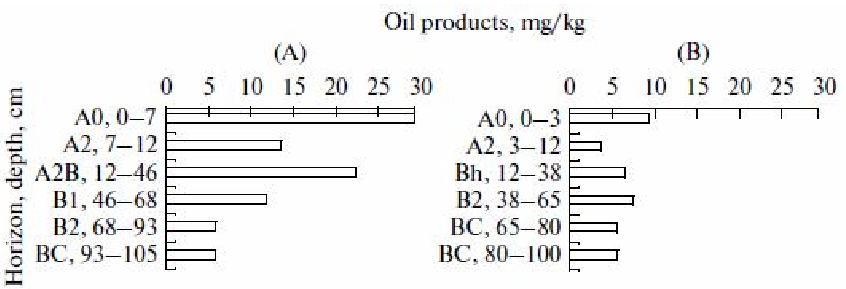

Fig. 3. Distribution of hydrocarbons along the soil profiles, $mg \cdot kg^{-1}$: (A) Retisols, Stagnic, (B) Podzols, Albic.

The background concentrations of the HCs varied among the soils in the different landscape elements. The Retisols (Histic, Spodic) and the Retisols (Histic, Stagnic) were characterized by an increased content of HCs. These soils occupied accumulative and eluvial-accumulative landscapes (flat depressions and watersheds, poorly drained ridges and gentle slopes, and interreges lows and bog edges), where the natural accumulation of HCs during pedogenesis occurred under conditions of periodic anaerobiosis and slow decomposition of plant residues. The accumulation of HCs in the Retisols (Histic, Spodic) and the Retisols (Histic, Stagnic) can also be related to the active lateral inflow from the surrounding landscapes. In the organic horizons of the Retisols (Histic, Spodic) and the Retisols (Histic, Stagnic) developed on mantle loams, the content of HCs varied in the range from 26 ± 4 to 32 ± 6 $mg \cdot kg^{-1}$.

In the superficial layers of the Podzols, Albic developed on the different-aged terraces of rivers with old-alluvial mainly fine quartzsands. The average content of HCs was 12.7 ± 2.0 $mg \cdot kg^{-1}$. In the Retisols (Histic, Spodic) and the Retisols (Histic, Stagnic) on poorly drained plain watershed ridges and glaciofluvial terraces covered by sandy deposits, the content varied in the range from 13 ± 3 to 22 ± 4 $mg \cdot kg^{-1}$. It should be noted that an increase in the HC accumulation was found in the Retisols (Spodic) of the mountain landscapes.

Conclusions

Data obtained on the background concentrations of hydrocarbons in various soils of the northern most and northern taiga of European north-west of Russia with taking into account the landscape-geochemical peculiarities of the region give a possibility for the first time to estimate the pollution level for natural and antropogenically affected soils. It was shown that soil of eluvial positions are less enriched by hydrocarbons in comparison with soil of accumulative territories. Differentiation of hydrocarbons content within the soil horizons was more pronounced in soil, formed on clay textured parent materials than in sandy ones. Database on hydrocarbons content in soil has been created with the use of GIS technologies. Data obtained could be used as background data for further investigation and environmental impact assessment.

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