Peculiarities of assessment of content of oil products in soils

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Abstract. The permissible content of oil and petroleum products in the soil must have a reasonable regional standard. It should be based on presence of specific and non-specific organic compounds in each specific soil, as well as the natural conditions that cause the ability of the soil to self-cleaning, and its provincial characteristics. The value of concentrations of petroleum products in the soil at a biologically safe level has not been established now. It is impossible to justify the maximum permissible concentration of petroleum products in the soil, since they include compounds that are a necessary component of any soil. We calculated the accumulation coefficient for 106 oil fields in 15 geographical regions of the Russian Federation. The accumulation coefficient varies in a narrow range of 1.19-1.21. It is necessary to compare the results of analysis of contaminated soil with the soil before pollution or with the background to establish the fact of a decrease in soil fertility in pollution. We believe it mandatory to consider the background concentration of petroleum products, which is understood as non-specific organic compounds of soils. The question of rationing of petroleum products in the soil remains open to the present time.

1 Introduction

Natural objective reasons such as the polyfunction and heterogeneity of soils, the variety of chemical forms of pollutants, the ability of soils to self-repair and self-purification significantly complicate the objective assessment of the content of oil and petroleum products in soils. The absence of standards, different quality composition of petroleum products, and provincial features of the soil cover make the study of regularities in assessing the content of petroleum products in soils relevant.

The work is aimed to increase the objectivity of the assessment of the content of petroleum products in soils.

2 Materials and methods

Objects of the research were light chestnut sandy loam soil on the territory of the sanitary protection zone (SPZ) of the chemical enterprise "HIMPROM" at a distance of 1 km from the enterprise, and meadow-chestnut light-loam soil of the Botanical nature monument Pakhotina Balka at a distance of 25 km from the enterprise.

In the international classification (Word Reference Base of Soil Resources, WRB, 1998), the studied soils are assigned to the group of chestnut soils (kastanozems) [1, 2]. In accordance to Classification of Russian soils [3], light-chestnut soils are distinguished at the type level in the department of accumulative-humus carbonate soils as "chestnut", and meadow-chestnut are distinguished in

the department of hydrometamorphyc soil called "humus-metamorphic".

Sampling and preparation of soils for analysis was carried out in accordance with the Russian State Standard 17.4.4.02-84.

Soil organic carbon was analysed using the method of I. V. Tyurin in the modification of D. S. Orlov and L. A. Grishina. A spectrophotometric termination and a fluorescent photometric analysis with "Fluorate 02-3M LUMEX" were used. The concentration of oil products (OP) was determined in n-hexane extract of soil samples.

3 Results and discussion

3.1 Assessment of soil organic carbon content

Oxidation of organic carbon to carbon dioxide – CO_2 is the basis of the method for determination of soil organic carbon by I. V. Tyurin and its modification. The calculation of the contain humus fraction is performed by multiplying of the obtained indicator by a coefficient of 1.724, which was introduced in 1864 on the basis of available data on the content of 58% organic carbon in humic acid [4].

The composition of oil includes organic compounds that can also be oxidized to carbon dioxide. The inertia of saturated hydrocarbons is well known. But they, in the presence of a tertiary carbon atom, are oxidized with a chromium mixture [5]. The effect of neighbouring alkyl radicals on the C-H bond leads to the fact that the bond

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of hydrogen with the tertiary carbon atom is weakened, this facilitates the substitution of hydrogen [6].

Organic carbon is determined by the method of I. V. Tyurin not only for humic acids, but also for many representatives of the non-specific organic part of the soil, including compounds of anthropogenic origin. The ratio of organic carbon in molecules of humic acid to the gross content of soil organic carbon is unknown.

The convention of this method is the assumption that all potassium dichromate reacts only with the carbon of the organic substance and all the carbon passes into carbon dioxide – CO_2. However, the composition of organic substances, along with carbon, includes water and other elements. The content of other elements influences on the overall balance of oxidative equivalents. Therefore, we obviously make some mistake when calculating the percentage of carbon. It is especially high for soils that contain chlorides (in an amount of ≥ 0.6 %) and for waterlogged soils containing Fe^{2+} compounds [7]. The oxidation process cannot be complete even under laboratory conditions.

When interacting with soil rather than humus, potassium dichromate reacts with hydrogen, which is a part of organic compounds. If the H:O ratio is ≥ 2 in organic soil compounds, then more oxidizer will be used for the oxidation of humus than it is required for the oxidation of organic carbon. If the H:O ratio is less, then less amount of oxidizer is required than it is necessary for the oxidation of organic carbon, which is a part of the humus [4,7,8,9]. Even K. K. Giedroyc noted [4], that to specify the amount of organic carbon in the soil is more correct, than to give a fictitious content of humus.

S. N. Chukov believes that humus substances in quantitative terms represent a little more than half of the organic carbon in the soil [10, p. 127]. According to K. Sh. Kazeev and co-authors [11, p. 44] about 10 % of the humus detected in laboratories is the sum of organic substances of a non-specific nature that have completely lost the morphological structures of the original organisms.

According to the literature, the content of humus in the soil varies from 1 to 10 %; the content of humus as calculated to carbon varies from 0.58 to 5.81 % (as divided by 1,724). The average carbon content in the in humus acids of chernozems is 55-61 % [9]. According to O. G. Rastvorova *et al.* [7] the part of organic and mineral carbon in the soil is about 2 %.

We would like to draw your attention to the following

1. D. S. Orlov provided data on the contain of carbon in the humus component, namely, in humic acids. So its part should be higher in humus (it also includes fulvic acids and humin).
2. The proposed methods for assessment of organic carbon determine not only the organic carbon of humus, but also non-specific compounds, including compounds of anthropogenic origin.
3. It is not appropriate to apply a conversion factor of 1.724 for any proportion of soil organic carbon. Carbon of organic compounds is not only humus.

Arable, recultivated, urban and polluted soils are characterized by the maximum difference in the values of organic carbon content assessed by the method of I. V. Tyurin [12].

N. G. Koronatov and co-authors [13] used the indirect determination of carbon in soils by I. V. Tyurin and direct method on the total carbon analyzer SHIMADZU TOC VCR (Japan). Their experiment on sod-podzolic soil has shown that the direct method gives results a third more than the method of I. V. Tyurin.

In our research, similar results were obtained. These results confirm the advantage of direct methods for determining of the content of the organic carbon of the soil. We determined the content of organic carbon in conventionally uncontaminated with petroleum products soils using two following methods: method by I. V. Tyurin and fluorescent photometric analysis of n-hexane extraction with "Fluorate 02-3M LUMEX" (table. 1).

Table 1. The content of soil organic carbon in soils, %.

Object, soil	Horizon	Fluorescent photometric analysis	Method by I.V. Tyurin
SPZ of "HIMPROM"	A1	2.56	1.78
	B1	1.82	1.68
Pakhotina Balka	A1	1.56	0.38
	B1	1.56	0.38

It is obvious that when we analyzed soils, the results of determination of organic carbon obtained by the fluorescent method are higher than results obtained by the I. V. Tyurin method. In light chestnut soils, the index was higher by 1.1-1.4 times; in meadow-chestnut soils the index was higher by 4 times [14].

When we use direct methods to determinate organic carbon in the soil, all substances are taken into account, regardless of which way (natural during soil formation or anthropogenic) they got into the soil.

Therefore, it is necessary to have data on the content of organic carbon in conditionally uncontaminated (background) soil to isolate organic compounds of xenobiotic origin. Terminologically, organic carbon of toxicants can be called as organic carbon of anthropogenic origin, and the compounds of anthropogenic origin can be called as pollutants of organic origin or xenobiotics [14].

The existing Russian State Standards and methods for determination of humus and soil organic matter are based on the method of I. V. Tyurin, namely, soil oxidation using an absolutely identical set of reagents and their concentrations (oxidizers such as potassium dichromate and potassium permanganate, Mohr's salt for titration, potassium hydroxide).

3.2 Calculations of oil products in soils by value of organic carbon

There are methods to assess the part of OP in the soil by the content of organic carbon in it. But OPs contain carbon and other elements and compounds. So, their concentration will be greater than the concentration of organic carbon. We propose to introduce the correction factor Kn to assess the amount of OP in the soil. This is

the accumulation coefficient of OP in the soil. The formula for its definition is below:

$$K_n = \frac{100}{n} \qquad (1)$$

where n is the total carbon fraction of all individual hydrocarbons that are the components of oil, %; 100 is correction coefficient.

$$n = \sum X_{(com)} = X_{(C_2H_6)} + X_{(C_3H_6)} + X_{(C_4H_{10})}, \quad (2)$$

where $\sum X_{(com)}$ is the total carbon amount of all compounds that are the components of oil; $X_{(C_2H_6)}$ is a part of ethane; $X_{(C_3H_6)}$ is a part of propane; $X_{(C_4H_{10})}$ is a part of butane (n-butane and isobutane) in the oil, %.

To determine the proportion of OP in the soil by the content of organic carbon of anthropogenic origin C_{antr}, we propose to multiply its value by the accumulation coefficient:

$$OP \% = C_{antr} K_n \qquad (3)$$

where OP is the content of oil products, %; C_{antr} is the value of organic carbon in contaminated soil,%; K_N is accumulati on coefficient.

The part of organic carbon of anthropogenic origin C_{antr} is determined by the formula:

$$C_{antr} = C_{com} - C_f \qquad (4)$$

where C_{com} and C_f, respectively, are the concentrations of organic carbon in the researched and background soil, %.

The calculation of the total carbon fraction is presented on the example of the qualitative composition of the oil of the Korobkovskoye oil field of the Volgograd region. The part of ethane (C_2H_6) was 2.30% by mass, the part of propane (C_3H_8) was 19.60%, the part of isobutane (C_4H_{10}) was 21.00%, the part of n-butane (C_4H_{10}) was 57,10 [15].

The part of carbon in the molecule of ethane was calculated by the formula

$$A = (24/30)\ 100 = 80 \qquad (5)$$

where A,% is the part of carbon in the ethane molecule; 24 is the atomic mass of two carbon atoms, 30 is the atomic mass of ethane.

We composed the proportion to determine the mass content of ethane in the composition of oil (x):

$$2.30 - 100\ \%;\ x - 80\ \% \qquad (6)$$

then we get X=1.84 g

Similarly, we calculated the part of carbon in the molecule of propane (81.82%), butane and isobutane (83.0%). Their mass contents were 16.04 g and 64.92 g respectively. The part of carbon C_{org} in the oil was calculated as n = 1.84 + 16.04 + 64.82 = 82.70 g.

Then we can find the accumulation coefficient K_n:

$$K_n = 100 / 82.7 = 1.2 \qquad (7)$$

We calculated the accumulation coefficient for 106 oil fields in 15 regions using data on the qualitative analysis of oils located in different geographical regions of the Russian Federation published in the Information Databank [15].

We demonstrated that it is possible to assess the concentration of oil and petroleum products in the soil for the main regions of Russia. The accumulation coefficient varies in a narrow range of 1.19-1.21. To determine the part of oil or petroleum products in the soil by the content of organic carbon of anthropogenic origin, we suggested multiplying its value by the accumulation coefficient, which is on average equal to 1.2 [14].

The hydrocarbons listed in the reference book are gaseous components of associated (or dissolved) gas, but they are not direct components of oil. It is more correct to calculate liquid hydrocarbons because they are predominant. In addition to saturated hydrocarbons with the general formula C_nH_{2n+2}, the composition of oil includes unsaturated hydrocarbons with the general formula of C_nH_{2n} (up to 15%), and aromatic hydrocarbons (up to 35 %), in which the proportion of carbon is even greater. For example, in naphthalene ($C_{10}H_8$), the carbon fraction is 93.75%. For such oils, the coefficient Kn will differ in a smaller direction from 1.2. In general, for the average oil, this coefficient will be in the range of 1.15-1.19. For approximate calculations it can be rounded to 1.2 only.

It is more correct to call Kn the conversion factor or correction factor, since this term is already taken to assess the accumulation of pollutants in nutrition chains of ecosystem. That coefficient does not characterize the accumulation of OP s in the soil, but it is used to calculate their content, by the proportion of carbon in OP.

We recognise that if we have more detailed data on the qualitative composition of oil, in particular, liquid hydrocarbons, the value of the accumulation coefficient will be clarified.

3.3 Account of organic compounds of soil

A. S. Yakovlev and Yu. G. Nikulin consider that the background content of oil in the soil is the sum of the results of the natural deep emanations of oil and gas, as well as the transformation of vegetative and organic matter in the upper part of the soil profile [16, P. 237].

The very concept of "background content of oil in the soil" can hardly be considered as correct term, since oil is a clear xenobiotic for any soil. Representatives of the main classes of nonspecific compounds of soil are similar to petroleum products in chemical structure and in relation to solvents (n-hexane, chloroform, carbon tetrachloride). We suggest to consider the presence of non-specific organic compounds and specific ones – humus components in any uncontaminated (etalon, background) soil as a background.

It is necessary to determine the content of nonspecific and specific compounds in the studied samples of soils for the objective identification of

xenobiotic organic compounds, in this case, oil and petroleum products [14].

3.4 Increase of the organic carbon content in the oil contaminated soil

The mass content of organic carbon in oil and petroleum products is 83-87%. Therefore, the content of organic matter per total carbon and humus in oil contaminated soils increases due to oil carbon [17, p. 643]. Organic carbon content in soils increases with increasing oil pollution. A lot of increase in organic carbon and a decrease in total nitrogen indicates the technogenic origin of carbon [18]. The final products of oil oxidation are carbon dioxide, which can be transformed into bicarbonates and carbonates, as well as oxygen-containing organic compounds (such as alcohols, acids, aldehydes, ketones), which partially enter the soil organic substance, partially dissolve in water on evaporate. They can be removed from the soil profile. Solid insoluble metabolic products are the result of further compaction of products with high molecular weight or their binding to organo-mineral complexes [19].

The content of organic carbon and OP in the upper layer of light chestnut soils of the Volgograd oil refinery was compared. Analysis of the data revealed the following trend. The content of organic carbon in the soil increases with the increase in the content of OP due to the part of organic carbon of anthropogenic origin. As the part of total organic carbon increases from 0.90 to 1.78%, the concentration of OP increases from 48 to 369 mg/kg of soil.

The described regularity wass confirmed by our later studies. According to studies conducted in 2011, if the content of OP was low in light chestnut and alluvial soils of the Volgograd-Volzhsky agglomeration, and it formed 0.47-0.61 mg/kg, then the part of organic carbon ranged from 1.67 to 2.00%. In 2015, the pattern was confirmed. The content of OP increased in soils from 0.40 to 4.13 mg/kg, and the concentration of organic carbon increased from 0.55 to 3.98%.

In the soils of the Irkutsk region, the humus content in oil-contaminated horizons increased from 1-5 % in grey forest soil, to 1-10% in meadow-swamp soil, and to 3-15 % in dark grey soil [20]. In accordance to data obtained by E. V. Prosyannikov and co-authors [21], the six-hour presence of 4.32 l/m^2 of oil on the soil surface increased the total carbon content from 3.44 to 9.14% in horizon A, and from 2.45 to 5.47 in horizon A1 and A2 of grey forest soil.

In the salt marshes of the oil field (West Kazakhstan), an increase in the organic carbon content was observed from 0.68 % to 1.9%, when a concentration of OP, respectively, was 0.013 g / kg (non-polluted area) and 130.61 g / kg in oil-contaminated soils from Kosshagyl [22].

3.5 The increase of pH with growth of the concentration of oil products

The pH increases from 7.87 to 8.26 with an increase in concentration of OPs in soils to 1.93 % (fluorometric method, hexane) in light chestnut soils of Kalmykia [19]. The highest pH values were observed in oil-contaminated horizons of sod-podzolic soils [23].

Light chestnut soils were characterized by neutral and slightly alkaline conditions. Values of pH varied from 7.0, if the content of OP was 48 mg / kg (selenium) to 8.21, if the content of OP was 369 mg/kg, tank farm).

Alkalization of the soil may be the result of disruption of the processes of natural mineralization and oxidation. Ammonium form of nitrogen prevail over nitrate one [19], which contributes to an increase in pH. The possibility of increasing the content of carbonate anions in the soil increases alkalinity.

3.6 Choice of horizon where sampling is performed

Sampling of soils is use to be done from the surface horizon for engineering and environmental surveys. In areas that have been reclaimed, the illuvial horizon becomes surface one, because the fertile soil layer is removed. Therefore, it is advisable to do sampling both in the surface horizon and in the illuvial horizon before the construction and operation of the site.

In the Resolution of the Government of the Russian Federation No. 612 dated 22.07.2011 "On approval of criteria for a significant decrease in the fertility of agricultural soils" noted that change of the numerical values of at least 3 of the following criteria is a significant decrease in soil fertility:
- decrease in content of organic matter in the arable horizon by 15% or more;
- decrease in acidity in acidic soils (pH of salt extract, KCl) by 10% or more;
- decrease in soil alkalinity (pH of water extract) by 10% or more;
- decrease in mobile phosphorus content (mg / kg of soil) by 25% or more;
- decrease in the content of exchange potassium (mg / kg of soil) by 25% or more.

Conclusions about the decrease in soil fertility of the study area on the basis of this Resolution are not substantiated for the following reasons.
1. It is necessary to compare the results of analysis of contaminated soil with the soil before pollution or with the background to establish the fact of a decrease in soil fertility.
2. Environmental engineering surveys do not provide for determining the agrochemical characteristics of soils as well as the properties of the illuvial horizon.
3. When the fertile soil layer is removed, the comparison should be based on the underlying illuvial horizon.
4. Indicators characterize the arable layer. This Resolution is not correct for agricultural soils used for pasture and hayfields.

The stocktaking of removing of the fertile soil layer is obligatory for environmental engineering surveys and

monitoring. Therefore, it is necessary to determine the content of organic carbon and OP in the fertile and illuvial horizons before removing the fertile horizon, because the after the removal of the upper layer illuvial horizon will become surface.

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