Determination of the state of oil-contaminated soils

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Abstract. This study has a great practical and economic significance for regions with oil-contaminated soil. The concentration of oil products in the studied soil samples was determined by four methods: extraction from soil samples with n-hexane using a fluorescent photometric analyzer «Fluorat 02-3M LUMEX», carbon tetrachloride using an analyzer «AN-2», and chloroform using a gravimetric method. The data obtained make it possible to estimate the effectiveness of the application of the methods of analysis. There are also identified the advantages and disadvantages of direct and indirect methods for determining soil organic carbon, the effect of oil pollution on soil pH and carbon content in the soil. Evaluation criteria are proposed to improve the objective assessment of the state of oil-contaminated soils.

1. Introduction
The aim of the concentration of oil products in the soil at a biologically safe level has not been established, since nonspecific organic compounds of soils are also found in the composition of oil.

2. Subject matter of the study and research method
Studies objects and research methods. LLC «Lukoil-Volgooliprocessing» is located in the Krasnoarmeisky district of Volgograd. The facilities are divided into several zones include the virgin lands in the north of the enterprise, sanitary protection zone (less than 1 km), light chestnut light loamy (virgin lands), Higher Education and Research Center «Gornaya Polyana»; light chestnut sandy loam, sanitary protection zone, Volgograd Joint Stock Company «Himprom», meadow chestnut light loamy botanical monument of nature Pahotin’s balka. Sampling and preparation of soils for analyzes were carried out in accordance with Federal standard 17.4.4.02-84. Soil organic carbon was analyzed by the method of I V Tyurin modified by D S Orlova and L A Grishina with a spectrophotometric end and on a fluorescent photometric analyzer «Fluorat 02-3M LUMEX». The concentration of oil-products was determined by several methods, like extraction from soil samples with n-hexane using an analyzer «Fluorat 02-3M LUMEX», with carbon tetrachloride using an analyzer «AN-2» device or with chloroform using a gravimetric method.

We offer a criteria for improving the objective assessment of the state of oil-contaminated soils.

3. Accounting of methods of analysis of oil-products
The content of oil-products in the soil was determined using extractants differing in properties: n-hexane, chloroform, and carbon tetrachloride. When determining the oil-products on analyzer «Fluorat 02-3M LUMEX», n-hexane served as the extract. First of all, it extracts the most soluble organic...
compounds from the soil. Then, the destruction of chelates, organic colloids, and organomineral compounds occurs [1][2].

To analyze the content of oil-products by the gravimetric method, multiple extraction with chloroform is used. Chloroform is a stronger solvent than n-hexane. This can explain the large values in comparison with the method for determining the oil-products with the analyzer «Fluorat 02-3M LUMEX», and smaller values in comparison with their analysis on the analyzer «AN-2».

Extraction with n-hexane in the determination of oil-products with the analyzer «Fluorat 02-3M LUMEX» showed the lowest values of all three methods. The highest values of oil-products, when they are determined with the help of carbon tetrachloride (analyzer «AN-2»), may indicate their complete extraction. The data for the determination of oil-products on the analyzer «AN-2» are 2.8-4.3 times higher than on the analyzer «Fluorat 02-3M LUMEX» and 1.1-4.3 times higher than by the gravimetric method. The analysis of oil products by the gravimetric method gives results 1.5-3.7 times higher than those for the analyzer «Fluorat 02-3M LUMEX» (table 1).

Table 1. The content of oil-products in soils, wt ppm.

| Object, bedrock | Fluorat | AN-2 | Gravimetric method |
|-----------------|---------|------|--------------------|
| Virgin lands    |         |      |                    |
| (A)             | ND      | 48.0 | ND                 |
| (B1)            | ND      | 21.6 | ND                 |
| Section 1       |         |      |                    |
| (A1)            | 75.8    | 146.4| 112                |
| (B1)            | 16.0    | 64.5 | 59                 |
| (C)             | 39.0    | 215.4| 78                 |
| Section 2       |         |      |                    |
| (A1)            | 42.7    | 347.0| 80                 |
| (B1)            | 23.0    | 51.1 | 44                 |

When determining the concentration of oil-products in the soils of 11 objects located on the territory of the industrial zone of the refinery. Their average concentration was 264 wt ppm on the analyzer «AN-2» device and 179 on the analyzer «Fluorat 02-3M LUMEX» [3].

The results of analysis of uncontaminated virgin soil are of particular interest. The presence of oil-products on virgin soil, in light chestnut soil 25 km away from the city and major highways, can definitely be considered as a fraction of nonspecific organic compounds of the soil itself. Then the truth content of oil-products ($OP_{\text{truth}}$) in the contaminated soil will be

$$OP_{\text{truth}} = OP_{\text{cont}} - OP_{\text{uncont}}$$

Where: $OP_{\text{truth}}$ – truth oil content, $OP_{\text{cont}}$ – amount of oil products in the contaminated soil, $OP_{\text{uncont}}$ – proportion of organic compounds in virgin uncontaminated soil.

Our understanding is that such discrepancies are based on the properties of the extractants themselves and organic compounds, which serve to create a calibration graph and the properties of the extractant. On the analyzer «Fluorat 02-3M LUMEX» determine oil-products by extracting with n-hexane. For the calibration graph, 5 ml of oil products with a concentration of 100 ppm are brought to 50 ml with hexane [4]. Infrared photomtery (analyzers «AN-1», «AN-2», «KN-1», «Evrika», IKF) takes into account aromatic hydrocarbons included in oil-products using an artificial standard containing 25% benzene [5].

4. Account for the properties of extragents

The proposed methods are based on the extraction of oil and oil products from samples with organic solvents. When choosing a solvent, it is necessary to take into account the complex chemical composition of both the substance being determined an oil product, and the object under study – soil [6].

Oil and oil-products can be extracted from the soil with various solvents: petroleum ether, hexane, benzene, alcohol-benzene, chloroform, methylene chloride, carbon tetrachloride, acetone,
dichloromethane [7]. Almost all reagents partially dissolve natural organic compounds. At the same time, complete extraction of all oil components does not always take place [2].

A A Buzuluktaev and L H Sangadzheva determined oil products in the light chestnut soils of Kalmykia by gravimetric and fluorimetric methods [8]. The results obtained with the extraction with chloroform are 1.5-2 times higher than with the extraction with hexane. Chloroform extracts have a high concentration of hydrocarbons in contrast to hexane extracts. According to the strength and activity of the reagents under consideration, they can be put in ascending order in the following row: hexane → chloroform → carbon tetrachloride.

Our understanding is that significant discrepancies in the analysis results are primarily associated with their solubility and reactivity of the extractants (table 2). From the data presented, it is obvious that the solubility of carbon tetrachloride in water is in $0.57 \times 10^{11}$ times greater than that of diopropyl, and that of chloroform is in $0.7 \times 10^{12}$ times higher, and in $0.8 \times 10^{11}$ times lower than carbon tetrachloride.

| Compound             | Formula | Solubility, kg / CM Water | Ethanol | Ether |
|----------------------|---------|---------------------------|---------|-------|
| Hexane               | CH$_3$$(CH_2)_4CH_3 | 1.413                      | 5030    | soluble |
| Chloroform           | CHCl$_3$ | 1.015                      | ∞       | ∞     |
| Carbon tetrachloride | CCl$_4$  | 0.824                      | ∞       | ∞     |

It can be assumed that carbon tetrachloride and chloroform extract not only the organic carbon of oil-products, but also the carbon of a specific and nonspecific organic part of the soil, and n-hesan extract its soluble part.

5. Accounting of soil organic carbon content

According to the method of I V Tyurin, organic carbon is determined not only by humic acids, but also by many representatives of the nonspecific organic part of the soil, including compounds of anthropogenic origin. Significant increases in soil organic carbon due to oil-products have been identified by Kucharski and Jastrzêbska [9], Caravaca and Roldán [10], and Riffaldi [11]. N G Koronatova [12] used the indirect determination of carbon according to I V Tyurin and direct determination on the analyzer «SHIMADZU TOC V» (Japan). The experiment on sod-podzolic soil showed that the direct method gives results by 1 / 3 more than the method of I V Tyurin.

In our studies, similar results were obtained. This confirms the advantage of direct methods for determining soil organic carbon. We have determined the content of organic carbon in the soils conventionally not contaminated with oil products by two methods according to I V Tyurin and on the analyzer «Fluorat 02-3M LUMEX» with extraction with n-hexane (table 3).

| Object                                | Bedrock | Fluorat | Method according to I V Tyurin |
|---------------------------------------|---------|---------|-------------------------------|
| Volgograd Joint Stock Company «Himprom» | A1      | 2.56    | 1.78                          |
| Volgograd Joint Stock Company «Himprom» | B1      | 1.82    | 1.68                          |
| Pahotin’s balka                       | A1      | 1.56    | 0.38                          |
| Pahotin’s balka                       | B1      | 1.56    | 0.38                          |

The results of the analysis table 3, reveal a higher content of soil organic carbon in light chestnut soils compared to meadow chestnut soils. It can be assumed that this is the result of a lower content of carbon of mobile and water-soluble forms in meadow chestnut soils. Obviously, when analyzing soils, the results of carbon determination on the analyzer «Fluorat 02-3M LUMEX» are higher than those obtained by I V Tyurin, in light chestnut soils 1.1-1.4 times, in meadow chestnut soils 4 times [3].
6. Accounting for organic soil compounds

A S Yakovlev and Y G Nikulina believe that «the background oil content in the soil is the sum of the results of natural deep emission of oil and gas, as well as the transformation of vegetation and organic matter in the upper part of the soil profile» [13].

The concept of «background oil content» can be hardly considered correct, since it is an obvious xenobiotic for any soil. Representatives of the main classes of nonspecific compounds are similar to oil-products in chemical structure and in relation to solvents (n-hexane, chloroform, carbon tetrachloride). We propose to understand the background as the presence in any unpolluted (reference, background) soil of nonspecific organic compounds and specific, as humus [14]. A H Chukparova in unpolluted salt marshes of Western Kazakhstan revealed a concentration of oil-products equal to 0.013 g / kg, at the Kosshagyl deposit of Atyruu oblast to 130.61 g / kg [15]. To identify organic compounds of a xenobiotic nature, it is necessary to determine the content of nonspecific and specific compounds in the samples under study [16].

7. Increasing the content of organic carbon in soil contaminated with oil products

Analysis of our data revealed a tendency with an increase in oil products in the soil, the content of organic carbon increases due to the share of organic carbon of anthropogenic origin (table 1). With an increase in the proportion of carbon from 0.90% to 1.78%, the concentration of oil products increases from 48 wt ppm to 369 wt ppm [17]. The resulting pattern is confirmed by our later studies. In light chestnut and alluvial soils, with an increase in oil-products from 0.40 wt ppm to 4.13 wt ppm, the carbon concentration increased from 0.55% to 3.98% [14].

In the soils of the Irkutsk region, an increase in the humus content in the oil-contaminated horizons was noted from 1-5% in the gray forest soil, to 1-10% in the meadow-boggy soil, and from 3-15% in the dark gray soil [18]. According to the data obtained by E V Prosyannikov, a six-hour stay on the soil surface of 4.32 l / m² of oil increased the total carbon content from 3.44% to 9.14% in the mountains (A) [19]. An increase in organic carbon in oil-contaminated meadow soils of the Tyumen region was noted by A S Nikiforov [20]. In the salt marshes of the deposit (Western Kazakhstan), an increase in the content of organic carbon in oil-contaminated soils from Kosshagyl from 0.68% to 1.9% was noted with an oil concentration of 0.013 g / kg (uncontaminated site) and 130.61 g / kg, respectively [15]. The content of organic carbon in terms of total carbon and humus in contaminated soils increases due to oil carbon, according to A V Shamraev [21]. A sharp increase in carbon indicates its technogenic nature in the soil [8].

8. Increasing pH with increasing concentration of oil products in soil

With the appearance of oil-products in soils (1.93%), pH increases from 7.87 to 8.26 in light chestnut soils of Kalmykia [8]. Oil-contaminated horizons of soddy-podzolic soils [22]. Results of studies of oil fields in China have shown that oil pollution increases soil pH [23] [24].

9. Conclusion

Criteria for improving the objective assessment of the state of oil-contaminated soils are proposed. Soil organic carbon analysis was carried out by the method of I V Tyurin modified by D S Orlova and L A Grishina with a spectrophotometric end and on a fluorescent photometric analyzer «Fluorat 02-3M LUMEX». The deviation of the obtained data on the content of oil products in the soil is based on the properties of the extractants themselves and organic compounds, which serve to create a calibration graph and the properties of the extractant. Also, the content of organic carbon in the soils conventionally not contaminated with oil products was determined by two methods. First method is according to I V Tyurin. Second method is on an analyzer «Fluorat 02-3M LUMEX» with extraction with n-hexane. The results of the conducted studies confirm the advantage of direct methods for determining soil organic carbon using the total carbon analyzer «SHIMADZU TOC V».
Analysis of the experimental data obtained revealed a tendency - with an increase in oil products in the soil, the content of organic carbon increases due to the proportion of organic carbon of anthropogenic origin.

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