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Methodological aspects of a new method for determining the mass of oil in bottom sediments of water bodies

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Abstract. A method is proposed for determining the mass of oil pollution per unit area of bottom sediments of water bodies, which makes it possible to associate pollution not only with the concentration of pollutants, but also with the area of the reservoir. The approach relates to the field of environmental protection, in particular to the analytical control of the content of oil pollution in mineral, organogenic and mixed bottom sediments. It can be used for environmental monitoring of polluted water bodies, for assessing the damage caused to a water body, and for planning treatment works. The method for determining the mass of oil pollution per unit area of bottom sediments of water bodies includes sampling, drying the sample to an air-dry state, extraction of oil products from bottom sediments, chromatographic separation of oil products from associated organic compounds of other classes, quantitative determination of oil products by absorption intensity in the infrared spectrum. A survey of 88 oil-contaminated reservoirs within the Samotlor oil field in the north of Russia was carried out, in which the proposed method was tested.

Keywords: oil products, bottom sediments, water body

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Методологические аспекты нового метода определения массы нефти в донных отложениях водных объектов

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Аннотация. Предложен способ определения массы нефтезагрязнений на единицу площади донных отложений водных объектов, позволяющий ассоциировать загрязненность не только с концентрацией загрязняющих веществ, но и с площадью водоема.

Способ относится к области охраны окружающей среды, в частности к аналитическому контролю содержания нефтяных загрязнений в минеральных, органогенных и смешанных донных отложениях. Он может быть использован для экологического мониторинга загрязненных водоемов, оценки ущерба, нанесенного водному объекту, и планирования очистных работ. Способ определения массы нефтяного загрязнения на единицу площади донных отложений водоемов включает отбор проб, высушивание пробы до воздушно-сухого состояния, извлечение нефтепродуктов из донных отложений, хроматографическое отделение нефтепродуктов от сопутствующих органических соединений других классов, количественное определение нефтепродуктов по интенсивности поглощения в инфракрасной области спектра. Проведено обследование 88 нефтезагрязненных водоемов в пределах Самотлорского нефтяного месторождения на севере России, в рамках которого предложенный способ апробирован.

Ключевые слова: нефтепродукты, донные отложения, водный объект

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Introduction

Assessment of the ecological state of oil-polluted water bodies is a key factor in the development of measures for their cleaning and regeneration of biodiversity. The state of water bodies during long or accidental inflow of oil hydrocarbons is largely determined by the level of pollution of bottom sediments [1]. It is in the bottom sediments where the accumulation of oil by organic matter occurs, and when the bottom sediments stir up under mechanical impact (wind impact, removal of bottom sediments), the process of "secondary pollution" of the water phase is triggered [2]. In bottom sediments, oil hydrocarbons undergo biochemical degradation, which ensures natural restoration of the reservoir. However, in small, relatively stable lakes in oil-producing regions of the Russian Federation, in conditions of low temperatures, lack of oxygen and photo-oxidation, the degradation of oil and oil products occurs extremely slowly, and water bodies completely lose their fishery and recreational importance.

Despite the fact that oil-polluted bottom sediments have an uncertain legal status in Russian environmental legislation [3], the importance of taking into account their state is reflected in the methodological guidelines of the Ministry of Natural Resources of Russia, according to which environmental monitoring of bottom sediments of water bodies on land is an integral part of the general environmental monitoring of water bodies intended for their study and protection.[1]

[1] Act of Ministries and Departments "Guidelines for the Implementation of State Monitoring of Water Bodies in Terms of Organizing and Conducting Observations of the Content of Pollutants in the Bottom Sediments of Water Bodies" dated 24.02.2014 No. 112. *Bulletin of normative acts of federal executive bodies*. 29.09.2014. No. 39. (In Russ.)

It is known that objective control of oil pollution can be carried out only if there is an experimentally substantiated hygienic standard for oil hydrocarbons in the form of their maximum permissible concentration. The problem of the maximum permissible concentration for the content of oil products for bottom sediments is urgent. Often, researchers use maximum permissible concentrations approved for soils to work with bottom sediments of water bodies. These decisions, on the one hand, are forced, since the absolute majority of the Russian Federation regions do not have regional standards regulating the content of oil and oil products in the bottom sediments of water bodies. On the other hand, they remain a topic for discussion, since soils and bottom sediments have different genesis and differ in physical and chemical parameters. Standards for bottom sediments of water bodies are in force in St. Petersburg, the Nenets and Khanty-Mansiisk Autonomous Districts, active participation in the development of such standards is carried out by individual scientific groups, for example, in the Republic of Tatarstan [4].

The main regulatory document which is used to calculate damage to a water body is the methodology for calculating the amount of damage caused to water bodies as a result of violation of water legislation, introduced by the Order of the Minprirody of Russia. The methodology also reflects the need to take into account bottom oil pollution, however, it does not regulate the process of determining oil at the bottom of a water body, while explaining in sufficient detail the assessment of the pollution of the surface of a reservoir by an oil slick. Currently, when assessing oil pollution of bottom sediments of water bodies, only the concentration of oil or oil products in the composition of sediments is used, which is estimated in grams of oil (oil products) per kilogram of air-dry state of bottom sediments (g/kg, mg/kg, etc.). Chemical analysis of samples for the carbon content of oil is a reliable method, but methodically insufficient for assessing the pollution of bottom sediments of reservoirs with oil, expressed in absolute mass in a water body. With the initial data in the form of pollution concentration, it is impossible to estimate the volumes of oil that are at the bottom of the water body, which makes the engineering cleaning affairs more difficult and distorts data on the amount of damage caused.

In the Russian Federation, there are several regional standards related to bottom sediments: the standard for the city of St. Petersburg, which is based on the standards and criteria proposed by the Dutch Environmental Protection Agency;[2] governmental decree of Khanty-Mansiisk Autonomous District – Yugra; the standard for the permissible residual content of petroleum hydrocarbons in bottom sediments of water bodies of the Nenets Autonomous District; governmental decree of Khanty-Mansiisk Autonomous District – Yugra (2018). The last one, from January 1, 2022, enters the standard of permissible residual content of oil and oil products in bottom sediments.

All the unsolved problems in the field of ecological regulation of bottom sediments of surface water bodies gives rise to the search for new approaches in assessing the ecological state of oil-polluted water bodies. The purpose of this study was to develop a new method for determining the mass of oil at the bottom of the reservoir, expressed in the amount of pollution per unit area of bottom sediments.

[2] Regional Standard. Norms and criteria for assessing the pollution of bottom sediments in water bodies of Saint Petersburg. Saint Petersburg; 1996. (In Russ.)

Materials and methods

The methods for determining oil products in bottom sediments, in a generalized form, include the following mandatory steps: sampling bottom sediments, drying the sample to an air-dry state, extracting oil products and determining the concentration of pollutants. As a rule, sampling is regulated and should be carried out by a sampling device. Bottom sediment samples are characterized by the presence of a certain sampling area. As we know, compulsory accounting of the sampling area is used in hydrobiological research to determine the quantitative indicators of food organisms per unit area. Similarly, our proposed method[3] includes: 1) fixing the sampling area; 2) weighing the entire sample after the drying step.

After determining the content of the mass concentration of oil pollution in the analyzed sample of bottom sediments, *Cf*, g/kg, this indicator is compared with the established regional background value for this type of bottom sediments, or with the standard for the permissible residual content of oil and oil products in bottom sediments *Cf*, g/kg. If the value of $Cx > Cf$, then anthropogenic pollutants are most likely present in the bottom sediments, and then the oil content $C0$, g, in the entire sample of bottom sediments is calculated using following formula:

$$Cs = C0 / Sn = Mn(CxCf)) / (1000Sn),$$

Mn – the mass of the entire sediment sample at point n, g; $C0$ – the mass of petroleum products in the entire sediment sample from point *n*, g; *Sn* – the area of seizure of the bottom sediment instrument when sampling, m^2; *C* – the mass concentration of petroleum products measured by the instrument, g/kg; *Cf* – the fuel mass concentration of the specified regional background values for this type of bottom sediment or the allowable residue of the sediment in sediment, g/kg.

Table 1

Calculation of the oil mass per 1 m^2 organogenic bottom sediments

Subject of measurement	Measure	Calculation
The area of the sampled bottom sediments	m^2	0.025
Weight of the whole sample in air-dry state	g	478.0
The concentration of oil in bottom sediments	g/kg	38.5
Regional standard for organogenic bottom sediments[4]	g/kg	4.0
Oil mass in the selected sample of known weight with a specific area	g	16.491 = (38.5 – 4.0)478 / 1000
Oil mass per 1 m^2	g/m^2	659.64 = 16.491 / 0.025

We conducted a survey of 88 oil-contaminated water bodies within the Samotlor oil field, North Russia. For selection sediment samples used corer Petersen capture area 1/80 m^2 and sampler for peat deposits P 04.09 (EIJKELKAMP, Netherlands) with a sample volume of 0.5 litters. To determine the type of bottom sediments was analysed organic matter content gravimetrically. The total oil content was determined by infrared spectrophotometry. Application example is listed in Table 1.

[3] Vorobev DS, Perminova VV, Pokrovskii OS. *Method for determining the mass of oil pollution per unit area of bottom sediments of water bodies.* Patent RU2711119. Application No 2019113925; date of filing: 08.05.2019; date of publication: 15.01.2020. Bull. No 2. (In Russ.)

[4] Decree of the Government of Khanty-Mansiisk Autonomous District – Yugra No 432-p of November 2018. (In Russ.) Available from: http://publication.pravo.gov.ru/Document/View/8600201811300004 (accessed: 20.08.2021).

Results

A surface water body – an unnamed lake on the territory of the Nizhnevartovsk region of the Khanty-Mansiisk Autonomous District – Yugra, with an area of 15.4583 hectares – was examined.

According to the terms of reference, the survey of the reservoir was carried out at 8 stations and 8 samples of bottom sediments were taken to determine the content of oil products. The depths at the survey points varied from 1.5 to 3.5 m. The average depth was 2.0 m. Samples were taken with a Petersen bottom grab, with a capture area of 1/80 m^2. Each sample consisted of two bottom grabs, which corresponded to the sampling area (*Sn*) 2 / 80 m^2 = 0.025 m^2. The average content of oil products in the lake was 6.6901 ± 1.1058 g/kg. All bottom sediments were represented by peat of varying degrees of decomposition, with a "loss on ignition" (LOI) of 71.4–91.6%. The calculations are presented in Table 2.

Table 2

Calculation of the mass of oil in the bottom sediments of an unnamed lake

Substances, units of measurement		Sampling points for bottom sediments							
		1	2	3	4	5	6	7	8
1	*Sn*, m^2	0.025	0.025	0.025	0.025	0.025	0.025	0.025	0.025
2	*Mn*, g	56.69	20.69	67.68	32.56	34.93	38.63	40.7	21.61
3	*Cx*, g/kg	5.568	5.570	12.056	3.828	7.311	2.129	9.245	7.814
4	*Cf*, g/kg	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000
5	*C*0, g	0.089	0.032	0.545	0	0.116	0	0.213	0.082
6	*Cs*, g/m^2	3.556	1.299	21.809	0	4.626	0	8.539	3.297
7	*Cs*, t/ha	0.0356	0.013	0.2181	0	0.0463	0	0.0854	0.033

The arithmetic mean value of the excess *Cs* oil content in the lake was 5.3908 ± 2.5448 g/m^2 (0.0539 ± 0.0254 t/ha). When multiplying this indicator by the area of the lake (15.4583 ha), we obtain the mass of oil at the bottom of the reservoir – 0.8332 ton.

Discussion

The proposed method makes it possible to calculate the amount of oil products at the bottom of the reservoir. A particularly important step in the application of the method is weighing each sample of bottom sediments in a complete sampled volume, after the stage of drying to the possibility to determine the concentration of petroleum hydrocarbons (and not just taking a sample for chemical analysis). There is experience of conducting the survey and cleaning the Lake Shchuchye located beyond the Arctic Circle in the Komi Republic from oil, in 2004–2006 [5]. During conducting the work, the weighing of each sample of bottom sediments in an air-dry state was not carried out, which does not allow the calculations to be carried out using the proposed method.

The data that an unnamed lake (Nizhnevartovsk district of the Khanty-Mansiisk Autonomous District – Yugra), with an area of 15.45 ha, contains 0.83 t of oil, allow us to classify the reservoir according to the degree of pollution, and also take this important information into account when engineering cleaning affairs. The next step is to adapt the information on the mass content of oil in bot-

tom sediments into the systems for classifying water bodies by the degree of pollution by oil and oil products. So, generally accepted in world practice, as well as successfully applied in Russia are "Dutch sheets," according to which there are 4 regulatory levels [6], depending on the concentration of pollutants, and not on the amount (weight) of pollution. The Order of the Minprirody of Russia "On Approval of Instructions for Determining the Lower Level of an Oil and Oil Product Spill for Classifying an Accidental Spill as Emergency Situations" is in force, which regulates the values of the lower level of an oil and oil product spill for classifying an accidental spill as an emergency. For surface water bodies (except for swamps), the indicator for light oil products is from 0.5 to 1 t, for heavy oil products from 1 to 1.5 t, depending on the category of water bodies, the water area is not less than 1 hectare. The methodology approved by order[5] makes it possible to assess the situation by the total oil content in the reservoir, measured in tons without reference to background concentrations. The force of the order is relevant for emergency situations, but most water bodies with oil-polluted sediments are characterized by chronic pollution, positioned as a 'historical heritage' [7]. The results obtained by the proposed method must be synchronized with the existing classifications of bottom sediment contamination, which will significantly expand the approaches to assessing the ecological state of water bodies polluted with oil and oil products.

Conclusion

The proposed method for determining the mass of oil pollution per unit area of bottom sediments of water bodies makes it possible to carry out calculations necessary not only to assess the degree of pollution of the bottom of a water body, but also to determine the amount of damage caused to a water body. The method has commercial potential; therefore, it is patented, that also confirms its modernity and originality.[6] This algorithm is convenient to use when developing projects of technical documentation for the cleaning of water bodies from oil and oil products. With the development of methods for cleaning bottom sediments of water bodies, more attention will be paid to the aspects of rationing the content of these pollutants.

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