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# Influence of High Molecular Mass Components of Oil on the Soil and Production Process of Potato Plants

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## Abstract

An effect of various concentrations of high molecular mass components of oil as wastes of petroleum production on the soil state and plant production processes was studied. From the standpoint of toxicity, its permissible concentrations values thereof for the normal vital function of plants were determined. A positive effect of oil on some agrochemical soil properties has been revealed, which opens up prospects for developing a biological method of utilization of oil wastes disposal.

Key words: high molecular mass oil components, disposal methods, toxicity, plant production process, agrochemical properties of soil, translocation effect

### INTRODUCTION

Sources of high molecular mass components of oil are the following: a) oil spills in the course of damaging the oil gathering networks after the evaporation of "light" fractions; b) significant amounts of oil contained on the water surface of sludge pits for many years; c) oil emissions to the surface as a part of the gel in the course of fracturing the oil-bearing layers; d) concentration procedure in technological barns under supplying as a result of repairing oil wells. Such oil is presented by hydrocarbons of alkane-naphthenic and aromatic series of in a wide range of the number of carbon atoms. Because of different origin, the componential composition of the high molecular mass ("heavy") oil is variable, however, the specifics of the chemical composition of oil is by the chemical structure to a greater extent is caused by the geographical location of oil fields.

Researchers in the field of the reclamation of oil-contaminated areas or of disposing it as a waste of oil-and-gas production most fre-

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quently deal with high molecular mass oil because light oil fractions are evaporated in the first hours and days after appearing on the exposed surface. The authors of [1] considered the reclamation of forest-swamp ecosystems contaminated with oil from one of the oilfields of middle Ob in West Siberia, and presented the group composition thereof. The fraction of paraffin-naphthenic hydrocarbons therein is 72 %, fraction of aromatic resins is 11 %, and the fraction of asphaltenes is 4 %. Therefore, the part of petroleum hydrocarbons that could be subjected to biodegradation is for 85 %.

The contemporary technologies for such oil utilization consist in sealing thereof at the sites of spills to a depth of 1 m or oil incineration after gathering from the surface of the spill in the form of oil-slime, which is associated with high energy consumption and the contamination of the atmosphere with pollutants. In this connection, it is necessary to develop a less costly and more environmentally safe technology for recycling this type of oil production wastes. The technology could comprise, for example,

introducing the wastes into the surface mineral soil horizon for naturally occurring oxidation of hydrocarbons, which is complicated to perform in the case of compact aggregation on the soil or water surface. The process of hydrocarbon decomposition could be significantly accelerated due to increasing the aeration in the course of distribution thereof over a large volume of soil and the subsequent cultivation of higher plants on the soil. However, in this case, it is necessary to determine permissible concentrations of "heavy" oil in the soil, those provide a normal activity of microorganisms and plants. It is also advisable to evaluate any possible transport of certain toxic elements (mainly heavy metals) inherent in the given pollutant from soil to plant vegetative organs.

For this purpose, in 2009-2011 we have carried out field research within the area of the middle Priob'ye in West Siberia over the territory of RN-Yuganskneftegaz and Gazpromneft-Khantos oil companies of the Khanty-Mansiysk Autonomous District (KhMAD-Yugra). This area is characterized by humid climate with annual precipitation level amounting to 450-600 mm, low evaporation level (400 mm/year) due to a high relative air humidity, which is facilitated by low summer average monthly air temperature values. The sum of active temperature values (the average daily temperature being higher than 10 °C) in this region does not exceed 1400 °C within the warmest period in the month of July. These climatic conditions allow the maturation of native plant species, whereas among the agricultural plants only perennial grasses and potatoes can ripen. The acceleration of ripening the plants is promoted only by a longer daytime duration in summer.

The region is characterized by a low temperature of soils, too, especially of peat-bog soil types and subtypes, which caused our choice for performing the experiments.

### EXPERIMENTAL

Field experiments were prepared on the plots with the area of  $3-6 \text{ m}^2$  with a regular location in triplicates [2] on the sod-podzolic soil oligotrophic with a medium-loamy grain-size distribution, attached to high relief elements directly within the boundaries of cluster-well pads. As the object of the study, we chose potato plants as the cultivar producing crops under the conditions of a low sum of active temperature values and of a short growing season in the region of the Middle Priob'ye.

As experimental variants we used plots where the soil heavy oil was introduced to a depth of 0-20 cm, with the volume concentration amounting to 0.5-4.0 %. A variant without introducing the oil into the soil served as the reference.

The oil impact on the properties of the soil was determined according to the biological activity of microorganisms [3], the content of organic matter (according to Tyurin) and the total nitrogen content (according to Kjeldahl), the concentration of mobile phosphorus species (according to Kirsanov) and the sum of exchangeable bases (according to the recommendations by E. B. Arinushkina [4]) with the registration of the content thereof using a C-115 atomic absorption photometer. The influence of the used oil concentrations in the soil was determined basing on the mass of the vegetative organs and on the yield of tubers; the content of toxic elements therein, including heavy metals, was determined with the use of an Optima 2000 DV atomic emission spectrometer.

The evaluation of the oil chemical composition was carried by means of chromatographic analysis using a Clarus 500 chromatograph with a flame ionization detector. As the solvents in the course of the extraction of hydrocarbons we used *n*-hexane for low boiling alkanes (C7– C15) and *n*-pentatriacontanol for high boiling components (C30–C35). The molecular structure of the oil used was determined according to peak height and areas in the chromatographic profiles registered, whose substantial increase was observed since the components with the number of carbon atoms from 23–25 to 28–30. Additionally, the volumetric mass was determined, that was 940–960 mg/L.

#### **RESULTS AND DISCUSSION**

In the reconnaissance experiment in 2009 we studied the response of plants on introducing the oil into soil in concentrations of 1, 2 and 4 %. We used oil collected from the water surface of an old oil-slime pond, located near

Oil content, %	Total raw biomass (vegetative organs + tubers)		Mass of	tubers	Mass of tubers/ total biomass ratio	
	g/bush	% with respect to reference	g/bush	% with respect to reference		
0	200	100	110	100	0.55	
0.5	249	124	137	126	0.55	
1	177	88	106	96	0.60	
2	115	57	60	55	0.52	
$LSD_{05}$	-	-	34	-	-	
Sd	-	-	14	-	-	

Productivity of potato plants grown in soils with different content of	of "heavy" crude oil (field experiment, 2010)
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*Note.* Here and in the Table 2:  $LSD_{05}$  – Lowest Significant Difference, Sd – standard deviation from the arithmetic mean; dash means that the mathematical treatment was not carried out.

the town of Pyt-Yah (well cluster 52b of the RN-Yuganskneftegaz LLC).

TABLE 1

As an indicator of the impact of "heavy" oil on the soil in the year of its introduction, the value of microbial biomass was used [3]. It has been found that for the concentrations of oil of 1 and 4 % there are no significant differences in this indicator from the reference samples. An abrupt increase of the microbial biomass (8.4 vs. 3.8 mg/kg of dry soil in the reference sample) was observed for the oil concentration of 2 % and, to all appearance, could be caused by an enhanced carbon-oxidizing ability of microorganisms. In this case, it is reasonable to expect also an increase in plant productivity. However, when oil content is equal to 1 %, the yield of potato tubers remained at a level corresponding to the reference variant, whereas further increasing the oil concentration (2 and 4%), the plant productivity decrease to a considerable extent, especially in the case the of 4 % concentration. This could indicate a negative impact of oil at such concentrations on the physiological state of plants.

The effect observed was confirmed by the small-plot field experiment of 2010 that was prepared under the soil and environmental conditions identical with the experiment of 2009 (well closer pad No. 80 of the oil-and-gas company Gazprom Neft-Khantos near the Khanty-Mansiysk City). For the experiment, we used high molecular mass oil supplied to a specialized landfill for disposal of oil-and-gas production wastes mainly from technological oil sumps. The characteristics thereof are presented above. In this experiment, we investigated the influence of oil at the concentrations of 0.5, 1 and 2 % upon plants and soil. It has been found that the yield of tubers per one bush amounted to 54 % with respect to reference variant for 2 % oil content (Table 1); for 1 % oil content no effect was revealed, whereas in the case of 0.5 % oil content in the soil the tuber yield was by 26 % higher with respect to the reference variant. The mass of tubers was in direct correlation with the total biomass (vegetative organs + tubers).

The observations demonstrate that the accumulation of oil in large-scale amounts on the day surface (spills, oil-slime pits) results in the fact that the decomposition (oxidation) thereof under natural conditions requires for a very long period of time. However, the fractal distribution of an insignificant dose of oil over a great volume of soil could improve aeration conditions and promote the process of hydrocarbon oxidation.

In order to examine this hypothesis, we performed replanting the potato in 2011 on the same plots where the experiment was conducted in 2010, however, without additionally introducing the oil (after effect). It has been found (Table 2) that the potato crop increased by 13.5 % with respect to the reference variant already at the concentration of oil amounting to 1 %. The mass of the tubers was in direct correlation of the total biomass with the average mass of a tuber depending neither on the number of tubers per one bush nor on the mass ratio tuber/vegetative organs, called as "the coefficient of economic use of photosynthesis" (see Table 2).

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### TABLE 2

Structure of the potato crop of 2011, grown in soil with introducing oil in 2010 at different concentration values

Indicators	Oil cor	Oil content, %				Sd
	0	0.5	1	2		
Total crude biomass:						
g/bush	282	237	283	167	-	_
% with respect to reference	100	84	100	59	-	-
Mass of tubers:						
g/bush	208	172	235	144	46	19
% with respect to reference	100	83	113	69	-	_
Number of tubers per bush	8.0	6.7	7.7	6.7	-	-
Average mass of a tuber, g	27	28	32	27	-	-
Mass of tubers/total biomass ratio	0.74	0.73	0.83	0.82	-	_

Note. See Table 1 for notations.

At the same time, it should be noted that there is a paradoxical decrease of plant productivity in the experiment of 2011 (see Table 2) with 0.5 % oil content, although in the experiment of 2010 this concentration was optimal. This fact could be explained basing on the following concepts. With increasing exposure of any environmental factor with respect to the plants, they undergo changing the physiological condition toward the: stimulation of functions  $[5] \rightarrow a$  spontaneous adaptation  $[6, 7] \rightarrow a$ reversible damaging [8]  $\rightarrow$  a death. It could be assumed that in the course of oxidation of the oil within the period from 2010 to 2011 the initial concentration thereof gradually decreased. In the experiment of 2010 the concentration of oil equal to 0.5~% could induce an increase enhancing the plant resistance (adaptation), which promotes increasing the productivity thereof under extreme environmental conditions inherent in the boreal zone of the West Siberia. In the case of the experiment of 2011, the initial concentration of 0.5 % decreased with time to become a factor of the stimulation of a state that is always connected with reducing the resistance of plants [9]. It is that resulted in the decrease of the plant productivity for this variant in the experiment of 2011. As far as the indicators are concerned, for 1 % oil content it can be assumed that with decreasing the initial (1 %) concentration of oil during a year there were formed the same conditions formed for the adaptation of plants, just as in the experiment with 0.5 % oil content immediately within the year introducing the oil to the soil.

The ability of the quite fast mineralization (oxidation) of oil in the course of spills is confirmed by studies conducted over the territory of the Yamalo-Nenets Autonomous District by the authors of [10]. Their results demonstrated that an almost complete oxidation of oil in the soil requires for one month at a temperature of 25-30 °C with artificially introducing a specific microflora, whereas under naturally occurring conditions (at summer temperature ranging within 10-15 °C) with introducing the microbiological preparation into the soil this requires for two years.

Another reason for increasing the productivity of potato plants in some cases consists in the fact that high molecular mass oil fractions affect the physicochemical properties of the oligotrophic soil. The analysis of soil samples

### TABLE 3

Effect of introducing high molecular mass oil fractions exerted on some agrochemical properties of oligotrophic soil (field experiment, 2011)

Indicators	Content in dry soil				
	at the oil content in soil, $\%$				
	0	0.5	1	2	
N gross, %	0.029	0.028	0.029	0.031	
Organic C, %	0.82	1.34	2.75	1.98	
$P_2O_5$ , mg/100 g	3.10	2.25	4.70	5.70	
Sum of exchangeable bases, mgEq/100 g:					
К	0.11	0.15	0.09	0.09	
Na	0.50	0.52	0.46	0.48	
Ca	0.85	0.77	0.58	1.36	
Mg	0.22	0.20	0.17	0.19	

### TABLE 4

Content of toxic elements and heavy metals in potato tubers grown in soil with different oil content (field experiment, 2009), mg/kg

Elements	Characteristics	Oil co	ntent,	%	
	and Sanitary Standard	0	1	2	4
	(SanPin 2.3.2.560–96	)			
Copper	5.0	2.0	1.4	0.4	1.9
Lead	0.5	0.4	0.2	0.4	0.2
Cadmium	0.03	0.04	0.03	0.02	0.04
Nickel	ND	0.6	0.4	0.2	0.7
Vanadium	ND	< 0.4	< 0.4	< 0.4	< 0.4
Arsenic	0.2	< 0.4	< 0.4	< 0.4	< 0.4

Note. ND - no data.

taken in the experiment of 2011 demonstrates that with increasing the concentration of oil in the soil, and in the absence of significant differences with the reference in the content of total nitrogen and total exchangeable bases (K, Na, Ca, Mg), there occurs an increase in the content of organic carbon and mobile phosphorus species (Table 3). The latter could have a positive influence on water-physical properties of soil and on the optimization of the mineral nutrition of plants.

It is known that the oil is characterized by an increased content of nickel and vanadium. In this regard, we investigated the possibility of transporting certain toxic elements and heavy metals from the soil into vegetative organs of plants. It has been found (Table 4) that there is no specific transfer of the mentioned elements.

It should be noted that at the oil concentration of 2 %, the yield of tubers in the year when the oil was introduced in the soil decreased by 46 % (see Table 1), and after a year passed there was a 31 % decrease observed (see Table 2). To all appearance, this could be caused by a rapid mineralization of high molecular mass oil at the expense of alkane-naphthenic components and reducing the initial concentration thereof as a whole.

### CONCLUSION

In the course of experimental studies, it has been found that the permissible content of "heavy" oil in soil to provide the normal vital function of potatoes does not exceed 1 % in volumetric ratios oil/soil ratio. Introducing the corresponding amount of the macromolecular components causes an increase in the content of organic matter and mobile phosphorus species in soil. It has been found that the transport of toxic and heavy elements from the soil to the vegetative plant organs does not occur.

The logical continuation of research in this field should be in-process testing aimed at replacing the technogenous method of disposing the high molecular mass components of oil (oilslime) by a biological method based on the principle of waste oil "dilution" *via* introducing them to the surface horizon of mineral soil at the heightened elements of the relief.

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