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## САНОАТ ИФЛОСЛАНИШИ ЭКОЛОГИЯСИ

## ECOLOGY OF INDUSTRIAL POLLUTION

## ЭКОЛОГИЯ ПРОМЫШЛЕННЫХ ЗАГРЯЗНЕНИЙ

Z.A.Jabbarov<sup>1</sup>, I.Mamajanov<sup>2</sup><sup>1</sup>Z.A.Jabbarov*—Doctor of Biological Sciences, Professor of the National University of Uzbekistan.*<sup>2</sup>Mamajanov I.*— Teacher of the Department of Ecology, Fergana State University.***Аннотация**

Тупроқларнинг нефть билан ифлосланиши мураккаб кимёвий жараён бўлиб, асосий ҳолларда нефть конлари ва нефть узатиш тизими атрофида кузатилади. Нефть билан ифлосланиш билан бир вақтда тупроққа тузлар, оғир металллар, сульфид ва бошқа моддалар ҳам тушиши аниқланди. Бундай тупроқларни кўп йиллар давомида ўрганиш натижасида аниқландики, сур тусли қўнғир ва қумли чўл тупроқлар бошқа тупроқларга нисбатан озика элементлар, микроэлементлар ва гумус билан кам таъминланган ҳамда унумдорлиги паст эканлиги аниқланди. Aqua regia методи асосида As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sb, V u Zn элементларининг концентрацияси аниқланиб, ушбу хоссаларга боғлиқлиги очиб берилди. Бундан ташқари тупроқ рН муҳити, органик углерод ва гумуснинг ифлосланиш билан вариацияси ўрганилди.

**Annotation**

Oil pollution of soils is chemically complex process and it is mostly occurred around of oil drilling fields and pipeline systems. At the same time with oil hydrocarbons such compounds as salts, heavy metals, sulphides and other chemical mixture occur in the soil. The studied soils are long-term polluted. The grey-brown and sandy soils differ from other soils by low supplied chemical, humus, and micronutrients contents as well as their average fertility. The concentrations of As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sb, V and Zn elements in soils were determined by Aqua regia method. Furthermore, the variations in the contents of soil pH, organic carbon and humus contents under oil pollution were studied.

**Аннотация**

Нефтяное загрязнение почвы представляет собой химически сложный процесс, и в основном оно происходит вокруг нефтяных буровых месторождений и трубопроводных систем. В то же время с нефтяными углеводородами в почве встречаются такие соединения, как соли, тяжелые металлы, сульфиды и другие химические смеси. Изученные почвы подвержены многолетнему загрязнению. Серо-коричневые и песчаные почвы отличаются от других почв низким содержанием химических веществ, гумуса и микроэлементов, а также их средним плодородием. Концентрации элементов As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sb, V u Zn в почвах определяли методом Aqua regia. Кроме того, были изучены вариации содержания рН почвы, содержания органического углерода и гумуса при загрязнении нефтью.

**Таянч сўз ва иборалар:** сульфид, микроэлемент, гумус, концентрация, органик углерод, вариация.

**Keywords and expressions:** sulfide, trace element, humus, concentration, organic carbon, variation.

**Ключевые слова и выражения:** сульфид, микроэлемент, гумус, концентрация, органический углерод, вариация.

**Introduction**

Oil well drilling and oil processing industries are one of the main contaminants of an environmental condition. According to data, two billion oil drill over the world annually, of them 45-50 million t (about 2 %) contaminate of the environment [1].

Oil and oil products are not only effect on the soil properties, but on the other hand they influence of the grain plants. Oil products such as benzine (petroleum) affect on soil physicochemical and biological properties, at

the same time benzine seriously influences on the germination and growth of agricultural crops. Because it contains harmful compounds to human and animal health [2-7]. Concentrations of oil impacts differently on soil properties. For example when analysed four weeks after application of 0.2, 0.4, 0.6 and 0.8 mg/kg liquid oil on corn-cultivated soil there was found no change in soil condition and structure [8]. The concentrations of organic C, N and Mg increased than control, on the contrary the amount of phosphorus decreased<sup>3</sup>. When

increased the amount of oil simultaneously increased the doses of Fe, Cu, Zn and Pb in soil samples analysed. The change of soil properties after oil pollution depend on time of pollution. The microbiological population of short-term polluted soil significantly decreases at oil pollution than the soil polluted in long period [9].

Some authors [10] studied the change of nutrients and carbon content in the soil. For example, in the soil polluted with 10 g/kg dose of diesel fuel the bacteria available nutrients such as carbon, nitrogen and phosphorus have decreased within 15-40 days. Experiments showed that the degradation was faster in forest soils than savannah soils.

Authors report [11] that oil pollution effects on soil physico-chemical and geotechnical properties of soils, that is soil pH, concentrations of cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$  and  $\text{K}^+$ ) and anions ( $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ ) change accordingly.

Studied the biochemical and physical properties of soils contaminated by diesel and petroleum in South Nigeria [12]. The soil acidity, organic carbon and nitrogen contents as well as clay rest have found to be higher than the control. At the same time with oil pollution, the heavy metals concentrations in soils increased, that are the concentrations of cadmium, iron, and lead were 0.25, 6311 and 1.67 mg/kg respectively.

Oil contamination in different amounts affects the physicochemical, respiration, enzyme activity of soils and mineralisation of nitrous compounds in grey forest and chernozem soils [13]. Such biological parameters as microbial complex, catalase, urease, invertase enzymes' activities indicate the biomonitoring and biodiagnosis of the ecological conditions oil polluted soils. Thus investigate of the oil chemical impacts on individual soil types is essential. In our research the effects of oil with different chemical contents on soil types formed in two soil-climatic conditions have been studied.

#### Materials and methods

The study objects are situated in southern regions of Uzbekistan, the grey-brown soils spread around the oil field "Kukdumalok" in Kashkadarya region (38.805544, 64.631047), the sandy soils spread around the oil field "Khovdak" in Surkhandarya region (37.936947, 67.571661).

The soil samples were collected 1, 3, 6, 9, 13 and 16 km far from the oil fields "Kukdumalok" and "Khovdak" and placed into special plastic packages, then air-dried and saved in  $\pm 11^\circ\text{C}$  until laboratory analyses. Soil samples were named as follows: PK-10-1; PK-10-4; PK-10-6; PK-10-9; PK-10-12 and PK-10-14 from "Kukdumalok", and PX-10-2; PX-10-5; PX-10-7; PX-10-10; PX-10-13 and PX-10-15 from "Khovdak" oil fields. The samples' names appropriate to the names of oil fields that is PK-Profile Kukdumalok, PX-Profile Khovdak.

The laboratory analyses were carried out in Czech University of Life Sciences and National University of Uzbekistan. The risk elements (heavy metals) were analysed in aqua regia method [14]. According to the method, 3 g of air-dried soil put into cone-shaped flask, then 0.5-1.0 ml water added. Then during gently shaking 21 ml of 12 mole/l chloride acid added while 7 ml of 15.8 mole/l nitrate acid added drop by drop until bubbles disappeared. Then the liquid leaved for 16 hours in room temperature in order to oxidize the organic matter. After all necessary procedure, the components in the solution were analysed by Atom adsorption spectrometer (ISP-AES).

The physicochemical properties of soil samples were analysed by following methods: soil pH according to standard method [15], organic carbon by Turin method's modification [16]. Statistical data analysis "T-test" was done.

#### Results and discussion

The soils in study area are arable and used in agriculture and animal husbandry by local people. In agriculture, local people cultivate cotton and wheat, besides these areas suitable for horticulture and livestock industry. The areas are naturally not polluted and not under irrigated or groundwater level.

Soil pH is one of the most important parameters of soil that effects on almost all processes and reactions taking place in soil. In order to determine the pH change in soil we studied the pH of oil polluted soils that seemed that oil pollution affected on soil pH in our case (table 1). The pH of grey-brown and sandy soils are usually neutral (pH 7.0) and alkaline (pH-7.6). So oil pollution influenced the pH of these soils by changing it into acidic condition. The laboratory analysis results of studied soil pH are given in table 1.

**Table 1. The pH of oil polluted grey-brown and sandy soils**

pH	Samples											
	PK-10-1	PK-10-4	PK-10-6	PK-10-9	PK-10-12	PK-10-14	PX-10-2	PX-10-5	PX-10-7	PX-10-10	PX-10-13	PX-10-15
pH <sub>H2O</sub>	6,6	6,5	6,2	5,9	5,8	7,0	6,2	6,4	6	5,2	5,7	6,8
pH <sub>KCl</sub>	6,3	6,5	6,0	5,6	5,9	6,9	6	6,1	5,7	4,9	5,4	6,7

According to results, the pH in all studied samples are acidic relatively on oil pollution level of soils.

Difference in pH of soil samples has no pattern of relationships on the distances from the oil fields that is our results suggest that remoteness of oil fields does not effect on soil pH (Table 1). Probably it depends on soil chemical property and oil concentration in soil. When soil pH has acidic condition, some reactions may go more intensive such as adsorption of heavy metals on soil organic matter can be easier etc. Thus, it is necessary to have a neutral pH in the soils during the recultivation of oil pollution. Our results showed that the soil pH at oil pollution was decreased until 5.2 in grey-brown and sandy soils.

The results of aqua regia analysis (table 2) of the soil samples showed that the concentrations of heavy metals and toxic elements reached the maximum allowable concentration in soil.

**Table 2. The Aqua-regia analysis of oil polluted grey-brown and sandy soils (mg/kg)**

Samples	As	Cd	Co	Cr	Cu	Ni	Pb	Sb	V
PK-10-1	5.95±0.06*	0.18±0.02	4.4±0.18	28.3±0.94	64.5±0.52	24.4±0.9	31.8±0.8	3.94±0.3	23.4±0.9
PK-10-4	6.05±0.18	0.17±0.01	0.9±0.05	22.5±0.57	30.5±0.85	0.5±0.04	2.0±0.1	3.64±0.1	0.9±0.05
PK-10-6	5.93±0.04	0.19±0.03	4.2±0.1	16.6±9.63	28.8±0.42	16.4±0.04	24.7±0.4	14.7±0.03	17.8±0.4
PK-10-9	5.94±0.05	0.17±0.01	5.1±0.19	22.8±0.57	30.3±0.81	16.9±0.31	25.3±0.7	3.80±0.3	17.4±0.3
PK-10-12	5.94±0.05	0.17±0.01	6.1±0.05	29.3±0.46	42.5±0.42	23.9±0.52	36.5±0.6	25.34±0.7	22.6±0.4
PK-10-14	6.41±0.64	0.17±0.01	7.5±0.3	26.8±0.51	48.6±0.57	22.4±0.53	31.5±0.7	15.91±0.5	21.7±0.5
PX-10-2	18.27±0.64	0.54±0.07	2.6±0.05	2.1±0.12	13.2±0.33	1.4±0.04	6.0±0.1	11.24±0.5	2.5±0.04
PX-10-5	15.69±0.62	0.38±0.05	4.7±0.04	28.6±0.64	59.0±0.47	22.2±0.5	33.2±0.5	12.26±0.1	22.2±0.8
PX-10-7	10.73±0.46	0.30±0.02	3.5±1.7	24.3±0.45	60.2±0.31	19.3±0.4	28.2±0.7	3.62±0.1	21.0±0.5
PX-10-10	6.30±0.09	0.19±0.01	4.5±0.04	26.1±0.51	63.3±0.60	22.4±0.8	31.3±0.6	16.15±0.6	22.0±0.7
PX-10-13	6.16±0.06	0.18±0.01	4.6±0.03	24.3±0.46	38.2±0.45	19.5±0.38	25.2±0.5	3.6±0.05	20.3±0.6
PX-10-15	6.14±0.07	0.15±0.01	4.6±0.05	23.2±0.53	35.9±0.23	21.1±0.5	26.7±0.3	3.62±0.1	23.2±0.4

The soil samples were collected in similar remoteness from the oils fields while the soil types and the chemical contents of oil are different. The maximum allowable concentration (MAC) for the soils of Uzbekistan is as follows: As 2.0, Cd 0.05, Co 5.0, Cr 200.0, Cu 55.0, Ni 85.0, Pb 32.0, Sb 4.5.

There are no any special relationship in the accumulation of the elements in soil on the distances was not found whether their concentrations increased or decreased by the distance from the pollution source. Besides, no pollution was found on the soil layers because of automorphic conditions in the study areas.

The reason is that in the automorphic conditions around the oil fields pollution could occur in top soil layers rather than sub soil layers, vice versa in hydromorphic conditions.

The heterogeneity in pollution character and lack of any regular occurrence might be explained in two basis: First basis is difference of soil-climatic conditions, soil forming rocks and oil chemical contents that "Kukdumalok" and "Khovdak" oil fields are situated in separate areas. Second basis can be seen in technological perfectness and working efficiency of the oil fields that could cause an

environmental contamination in surrounding areas.

The concentrations of analysed elements were higher in the samples taken from sandy soils (optionally first area: PX-10-2, PX-10-5, PX-10-7, PX-10-10, PX-10-13 and PX-10-15) than the samples of grey-brown soils (optionally second area: PK-10-1, PK-10-4, PK-10-6, PK-10-9, PK-10-12 and PK-10-14). The reason is that there was an accident in oil pipeline system 48 years ago causing a pollution in the territory. Furthermore, any of recultivation measures have not been carried out in these territories. The scenario is little more different in the territory of “Kukdumalok” that the pollution was not so serious because of technological efficiency of the oil field during the past period.

According to our results, the amounts of some compounds have reached the MAC in soil. For example, concentration of the toxic elements were found to be higher in the samples of the second area PX-10-2, PX-10-5 and PX-10-7 that As 8 times, Cd 9 times, S 6 times and Sb 5.3 times higher than MAC.

Such elements As, Pb and Cd can highly be accumulated in soil during the burning of oil. Heterogeneous of pollution of the soils in the second area can be explained by miscellaneous allocation of petroleum on the soil surface. For example, in the control points where the samples PX-10-2, PX-10-5 and PX-10-7 taken from appear such large massive soil fragments as “oiled soil”.

The concentration of Co was found to be lower in both studied areas that in the samples PK-10-12 and PK-10-14 of the first area its amount was 1.4 times higher than MAC while others concentration were not reached the MAC level.

That is why we can say the oil pollution among other pollutants as “a big complex pollution”. Thus, during the oil pollution many toxic compounds like heavy metals, sulphides, salts, minerals, water and other additives can appear in the environmental components. Even though the heterogeneous of chemical contents of oil drilling from different oil fields is a limitation factor for such view in this system.

Manganese's concentration did not reach the MAC level in any samples analysed. There is almost no chrome Cr pollution of the soils in the oil fields and oil industry, thus in oil polluted acidic soils Cr is in immobile form. Cuprum Cu usually

accumulates in the upper soil horizons and has average mobility. Cu forms a steady polymer in combination with humus in soil. In middle and low oil polluted soils the polymer forms much more because of high contents of organic carbon and humin matters in soil and impacts on soil chemical and biological properties adversely.

Appearance of mentioned above heavy metals in soils decreases of the mobile forms of N/NO<sub>3</sub>, P<sub>2</sub>O<sub>5</sub> and K<sub>2</sub>O [17]. Therefore, in the second area under the long-time toxic effect of oil pollution the amounts of nutrients in soil have decreased resulting in negative change of plant cover and microflora. Besides, the soil fertility has also decreased and even been ineligible in agricultural use.

In grey-brown and sandy soil in the result of oil pollution the concentrations of As, Cd reached the MAC level while the concentrations of Cr, Ni did not reach the level in soils. We can say that sandy soils are highly polluted even during a long period giving a chance to accumulate of toxic compounds in soil.

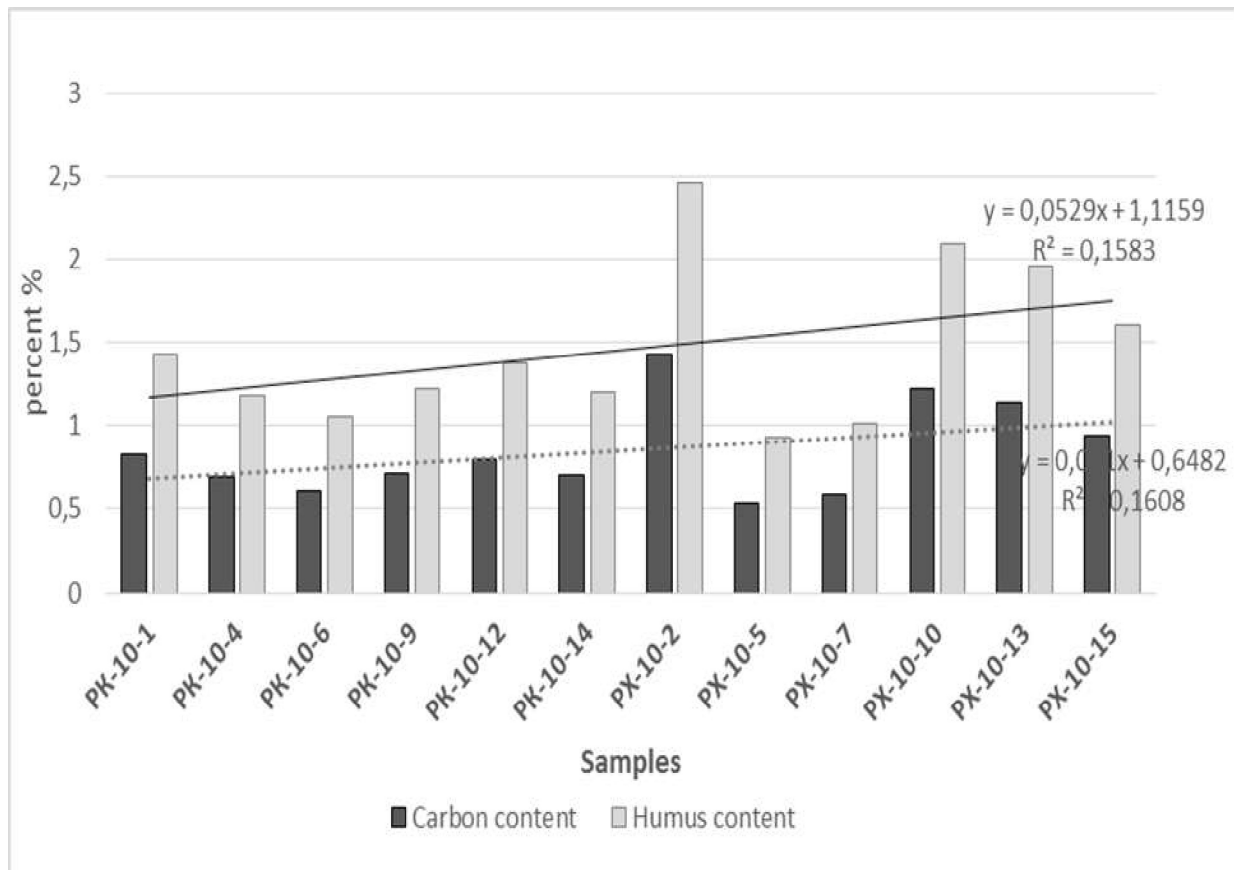
The microbiological community of soil affected under oil pollution that some amounts of microorganisms and physiological groups dead. Then plant cover are dramatically decreased and the biomass less accumulated.

After pollution of soils the amount of oil under the effect of photochemical, chemical, physical and biological processes in soil has been degraded and decreased. In these soils, the heavy fractions of oil like pitch, asphalt kept collapsed the soil processes. Providing of recultivation measures in these soils may create difficulties than short-term polluted soils.

Even if oil is organic matter containing more carbon amount it does not increase carbon content and humus in soil. Because, if oil amount is up to 1 g per kg, then carbon and humus contents are increased, when oil concentration reaches the MAC level it might destroy soil chemical, physical and biological processes leading to decrease organic matter and humus in soil.

Oil as organic matter could not directly become humus in soil. Besides, other toxic compounds do not allow to form humus in soil.

Additionally, the amounts of organic carbon and humus in these soils were determined (table 3). The total amounts of organic carbon and humus were calculated according to methods used in Czech Republic [18].



**Fig.2. Organic carbon and humus content in oil polluted grey-brown and sandy soils**

The results suggested that the amounts of organic carbon and humus decreased. There is no any regulatory that carbon and humus contents either change or not. Because the oil dose and chemical content, soil-climate condition, soil microflora, plant cover change depending on soil physicochemical properties. Such process goes in sandy and grey-brown soils of the study areas. In the soil samples closer the oil field PK-10-1, PX-10-2, PK-10-4 and PX-10-5 the humus contents were 1.43, 2.46, 1.12 and 0.93 % respectively. PK-10-1 sample was less contaminated than PX-10-2, that is why the microbial community, plant cover and soil properties were less damaged. According to these, humus and organic carbon contents much higher in these soils. PX-10-2 sample highly contaminated, therefore the microorganisms and their physiological groups decreased as well, soil water-physical properties affected increasing bulk density and decreasing moisture.

According to results, there were found homogeneous in humus and carbon contents in

the studied soils. Therefore, general approach in the recultivation of these oil-polluted soils would not be given the expected results if there were not an individual approach according to locality and soil-climate conditions.

#### **Conclusion**

In conclusion, at the same time with oil pollution of grey-brown and sandy soils the heavy metals, toxic compounds and other mixtures have been entered into soils ruining of the soil processes. Results suggested that the soil processes after oil pollution depended on oil and soil chemical contents. Oil pollution changed the soil pH turning it into acidic condition. Grey-brown and sandy soils are naturally low supplied with humus and nutrients. Nevertheless, due to oil pollution, the whole soil physical, chemical, biological properties affected negatively as well as the microbial community amounts and enzyme activities were considerably slowed down resulting to decrease the contents of organic carbon and humus.

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(Reviewer: G. Yuldashev – doctor of agricultural sciences, professor).