Chemistry

STUDYING THE INFLUENCE OF OIL'S HEAVY METALS ON THE ENVIRONMENT

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Abstract. It was determined that the amount (activity) of radionuclides in coastal sands of Caspian Sea is 3-4 times lower than in the surrounding soils and the level of background radiation is 3-4 times below the maximum permissible directive value (0.12 μSv/hour). Accumulation of radionuclides and heavy metals are observed in soil areas, contaminated with oil refinety waste. Regardless of the concentration of heavy metals and radionuclides, neither any green vegetation nor microorganisms are observed in areas contaminated with oil waste. It has been established that in soils contaminated with oil waste, the amount of radionuclides is 2-3 times higher compared with clean land areas, and the levels of background radiation exceed the permissible directive values by 2 times. A detailed examination of soil plots in the study areas showed that a 2-3 fold change in the concentration of heavy metals does not affect the number of microorganisms in the soil unpolluted with oil waste. A comparative analysis of the concentrations of mineral components and natural radionuclides shows that fertile soils in mountainous and foothill areas are characterized by relatively high concentrations of the studied components. It is observed that the green vegetation is relatively more developed in unpollted fertile soils, where the amount of natural radionuclides is relatively large.

Keywords: *oil waste, radionuclides, heavy metals, radioactive background, green vegetation.*

Introduction

The main part of the soil is formed by chemical compounds in the form of various minerals. Soil is the upper layer of the lithosphere exposed to living organisms and the atmosphere. Studying the various forms of the presence of chemical elements in minerals, organic residues and emissions, soil colloids, determining the amounts of oxides, hydroxides, carbonates, bicarbonates, nitrates, nitrites, sulfates, phosphates in soil samples allow us to estimate the ecological state of the soil [1-3].

Systematic pollution of the soil with small amounts of anthropogenic emissions leads to an increase in the concentration of xenobiotics in other environmental objects (water reservoirs and vegetation). The increase in technogenic pressure on the environment, the processing of minerals by outdated technological processes and the consequent pollution of environmental objects with small amounts of xenobiotics can cause the formation of ecological crisis zones. Therefore, there is a need for systematic measurements and studies to obtain results on the distribution of radionuclides, heavy metals and other xenobiotics in the soil, vegetation, water reservoirs of the country, trends in the direction of the emergence of zones of environmental crisis, information for predicting changes and the rate of change in the environment. The ability to clean by various methods local areas of the earth contaminated with radionuclides and heavy metals and to study the options for implementing these processes are the most important tasks of radiochemistry and are important for solving many pressing environmental problems [3, 4].

Radioactive elements and heavy metals along with non-metals and light metals in the tables of chemical elements are distinguished and characterized by high density (more than 5 g/cm^3), biological activity, toxicity, and the ability to migrate in the habitat of living organisms through food chains

"atmosphere – wind – rain – soil – plants – animals – humans" accumulate in environmental objects and organisms. Concentrations exceeding the maximum permissible norms for these metals are capable of allergic, mutagenic, teratogenic, carcinogenic effects on the human body. Heavy metals participate as catalysts in numerous redox reactions, isomerization, hydration, and dehydration processes occurring in environmental objects. The mass fraction of macro-elements in the human body and food products is above 0.01% (potassium, sodium, calcium, magnesium, phosphorus, chlorine, sulfur). The mass fraction of microelements is below 0.01%, the mass fraction of ultra-microelements is below 0.00001%.

In the absence of vital trace elements (iron, copper, zinc, cobalt, iodine, bromine, fluorine, chromium, cobalt), the normal vital activity of the body is disrupted, and in the deficiency of necessary microelements (nickel, selenium, vanadium, aluminum, molybdenum, strontium, manganese, silicon, scandium), the activity of enzymes decreases, the body functions on the verge of survival and with an increase in their concentration, there is an improvement in the life activity [1-4].

Heavy metals include As, Hg, Pb, Cd, Sb, Sn, Zn, Fe, Cu, Cr, Tl, Co, Sc, Ni, etc. Among them, the most highly toxic are mercury, cadmium, arsenic, and lead, the maximum permissible concentration (MAC) of which in water is 0.0005, 0.001, 0.005, and 0.05 mg/l, respectively. More stringent requirements are imposed on children's and dietary products. Substances are classified according to toxicity in the following order: extremely toxic – LD50 (a dose that causes the death of 50% of experimental animals with a single oral administration) less than 5 mg/kg, highly toxic – 5-50 mg/kg, moderately toxic 50-500 mg/kg, low-toxic 500-5000 mg/kg, practically non-toxic 5000-15000 mg/kg, practically harmless – more than 15000 mg/kg. Sodium-22, sodium-24, potassium-40, uranium-238, thorium-232, radon-222, etc. are present in many objects of inanimate nature and living organisms. The problem of the impact of artificial radionuclides (carbon-14, cesium-137, strontium-90, 89, ruthenium-106, cerium-144, iodine-131, zirconium-95, etc.) on the human body has arisen as a result of the operation of nuclear power facilities. These radionuclides enter the human body by inhaling polluted air, through the gastrointestinal tract with food and water, and through the skin.

Chemical bonds in organic molecules of protein, DNA, RNA and lipids are broken (physical damage to cells), when exposed to ionizing rays. Further, there is an interaction of the resulting radicals with water, oxygen and water radicals, as a result of which there is the formation of hydroperoxides, changes in molecules and enzyme activity, and destruction of biological membranes. The absorbed dose of ionizing radiation equal to 1 Grey after 30 minutes leads to a violation of the process of oxidative phosphorylation, as a result of which there is damage to the ATP generation system, a decrease in vitality and a slow cessation of vital processes [3].

The intensive development of oil and gas fields on the continental shelf of the Caspian Sea leads to an increase in the environmental burden on the Caspian region. Oil waste and heavy metals (iron, copper, aluminum, zinc, etc.) are the main sources of pollution. The produced oil contains aromatic compounds that are stable in the environment. The spread of an oil film on the sea surface leads to the death of fish and other aquatic organisms [1-4].

Experimental part

Preparation of oil waste samples were obtained by extraction with hexane and toluene (2:1) mixture from soil, contaminated with oil waste. The contents of elements in the inorganic residues of samples of crude oil and oil waste obtained by distillation at 700°C for three hours were determined using X-ray fluorescence spectroscopy unit of a scanning electron microscope and methods of analytical chemistry.

For conducting microbiological rapid tests, we used express test napkins - certified ISO 9001 and 13485 quality control systems - manufactured by R-Biopharm (Germany). To determine the number and types of microorganisms in stationary laboratory conditions, we used selective nutrient media produced by Hi-Media (India) and Condalab (Spain), incubators with an automated thermostat [5]. Chemical and biological parameters of comprehencive analysis, the degree of contamination with

anthropogenic xenobiotics of sea water samples were determined in accordance with the requirements of sanitary and hygienic norms and rules. Sea water samples were taken from coastal water areas. Chemical and microbiological express tests of sea water were performed at the place of sampling. Later, long-term (24-48 hours) microbiological analyzes were carried out in stationary laboratory conditions [3, 6].

The soil samples were treated with distilled water, weak solutions of acid and alkali with periodic mixing and filtration, isolation of sparingly soluble particles in a centrifuge with further evaporation to obtain minerals, heavy metals and radionuclides [6-8].

Inorganic minerals of polluted soil, green grass and water samples obtained by evaporation of aqueous, weakly acid and weakly alkaline extracts of soil samples, by treatment of plant samples by nitric acid's solution and heat treatment, and by evaporation of filtered and centrifuged water samples. The obtained dry mineral was analyzed by methods of analytical chemistry and physical chemistry. The "GFL-2304" distiller, centrifuge "TDL-5M", gamma spectrometer with HP-Ge detector manufactured by Canberra, Scanning Electronic Microscope (manufactured by Carl-Zeiss), atomic absorption spectrometer (AA-6800 manufactured by Shimadzu), Expert-3L X-ray fluorescence spectrometer, STA-2900 simultaneously thermal analyzer were used for analysis of heavy metals and radionuclides in obtained inorganic minerals.

Radiometric measurements were carried out using the "İnSpector-1000" and "Radiagem-2000" radiometers (manufactured by Canberra and equipped with alpha, beta and gamma detectors) and the "İdentiFinder" radiometer-identifier (manufactured by Thermo Scientific) [6-8].

Results and discussion

To eliminate side complications in the analysis, soil samples with humus, a layer of oxidized plant debris from trees and contaminated with random organic debris and emissions were not taken.

Samples of crude oil have been taken from various fields of the country, as well as samples of newly formed soils contaminated with oil refining wastes with low humus content, fertile soils with rich humus, as well as samples of similar soils uncontaminated with oil refining wastes. A detailed inspection of the studied land plots before taking soil samples was carried out [9, 10].

As a result of the observations, it was found that in areas uncontaminated by oil refining waste, newly formed soils with a low humus content and consisting mainly of a dark brown color had rare, underdeveloped weed herbaceous vegetation, and in similar areas of land contaminated by oil refining waste there was practically no vegetation of any kind [11, 12].

The relative content of elements in percentage in inorganic residues of oil samples (samples numbered 1 and 2) and oil refining waste (samples numbered 3 to 5) are given in Table 1.

Table 1

Relative content of elements in inorganic residues of oil and oil refining waste.

№	Content of elements in inorganic residues of oil samples (from 1 to 10) and waste oil refining (from 11 to 20)															
	C	O	Na	Mg	Al	Si	S	P	K	Cr	Ca	Ti	Mn	Sr	Fe	Pb
1.	55.7	14.4	1.5	1.8	3.4	7.1	0.3	0.2	2.0	0.3	2.9	0.4	0.4	0.6	3.7	1.9
2.	56.4	14.9	1.7	1.1	5.3	5.2	0.2	0.1	0.5	0.4	6.5	0.1	0.1	0.8	4.4	2.7
3.	46.0	12.5	4.0	2.5	1.8	8.0	1.7	0.3	0.7	0.1	2.0	0.2	0.1	-	3.4	1.6
4.	44.9	12.2	4.1	2.6	1.9	7.2	2.2	0.1	0.4	0.2	3.3	0.3	0.1	0.3	3.1	1.5
5.	45.2	12.3	3.8	2.7	3.4	6.5	2.6	-	0.5	0.4	8.4	0.5	0.3	0.7	8.0	2.4

It can be seen from Table 1 that relative common content of elements in inorganic residues of different samples of crude oil and oil refining waste is 26-30% and 26-41%, respectively. The results obtained and a comparison of the relative content of metals in inorganic residues of crude oil and oil refinery wastes extracted from soil samples contaminated with oil wastes clearly indicate the accumulation of metals, including "heavy metals" in soil, when it is contaminated with oil refinery wastes.

Soil samples were taken in summer and autumn from green grass meadows, pastures or forest edges at a distance of at least 10 kilometers from residential areas or industrial enterprises. Soil samples were also taken from these areas by digging the soil to a depth of 10–20 cm. If one site had sandy and fertile soil, samples were taken from both sites. When taking soil samples, areas were selected that were not contaminated with volleys of foreign emissions, remains of dead organisms, rotten and oxidized plant matter. Determination of mineral components and natural radionuclides was carried out in order to explain the serious difference observed in the degree of development of green vegetation in different soil areas in the regions of the country. The determined mineral components in the soil samples taken from the different regions of the country are shown in table 2.

Table 2

Concentrations of inorganic components in the soil samples taken from country's regions.

Regions	Components, *mg/kg*						
	Sulphates	K	J	Sr	NO_3	Fe; Mn	Zn
Bibiheybat settlement	320	3960	1.8	28	34	162; 6	2.1
Goranboy	380	7240	1.8	48	65	54; 29	1.8
İsmayilli	700	8360	1.3	42	126	64; 6	2.1
Qabala	710	7490	1.2	40	114	72; 6	2.5
Sumgayit	300	5008	1,4	28	43	84; 6	1,5

It can be seen from Table 2 that common concentrations of components in the composition of soil samples taken from country's mountainous and foothill areas (Goranboy, Ismayilli, and Qabala) is 7.6-10 g/kg and common concentrations of components in the composition of soil samples taken from other region of country (Sumgayit city) is 5.5 g/kg.

A comparative analysis of the concentrations of mineral components and natural radionuclides (Tables 2) shows that fertile soils in mountainous and foothill areas are characterized by relatively high concentrations of the studied components.

The results of radiometric measurements and the activity of radionuclides in soil samples taken from the green plains and mountainous regions of the country are shown in table 3.

It can be seen from Table 3 that the value of the radioactive background in country's mountainous and foothill areas (Goranboy, Ismayilli, and Qabala) is 0.03-0.15 μSv/hour and the intensity of alpha radiation is 0-0.03 Bq/cm^2. The value of the radioactive background in other regions of country (Sumgayit city) is 0.08 μSv/hour and the intensity of alpha radiation is 0-0.01 Bq/cm^2. The common activity of all natural radionuclides in soil samples taken from country's mountainous and foothill areas is 7.3-10 Bq/kg and common activity of all natural radionuclides in soil samples taken from other region of country (Sumgayit city) is 5.3 Bq/kg.

In areas uncontaminated by oil refinery waste, fully formed fertile soils with a high humus content are observed as green, well-developed herbaceous vegetation, as well as green shrubs and trees. At the same time, in different areas of the soil on the territory of the studied lands of the country, there is a significant difference in the degree of development of green vegetation.

On land plots contaminated with oil refinery waste, with fully formed fertile soil and low humus content, few and underdeveloped species of weeds were observed. The results of radiometric measurements and the activity of radionuclides in soil samples taken from the green plains of regions of the country are shown in table 4.

Table 3

The results of radiometric measurements and the activity of radionuclides in soil samples taken from green plains and mountainous regions of country

Regions (background - *μZv / h;* alpha ray *Bq / sm²*)	Isotopes, Bq / kg									
	$_{11}Na^{22}$	$_{19}K^{40}$	$_{26}Fe^{60}$	$_{27}Co^{57}$	$_{30}Zn^{65}$	$_{38}Sr^{91}$	$_{50}Sn^{113}$, $_{50}Sn^{126}$	$_{63}Eu^{154}$	$_{88}Ra^{226}$	$_{90}Th^{228}$
Bibiheybat settlement	1.0	1.7	0.7	0.8	0.2	0.4	0.4; 0.3	0.6	0.7	0.05
Goranboy (0.04; 0)	1.5	2.4	0.7	0.8	0.2	0.5	0.1; 0.2	0.6	0.8	0.05
Ismayilli (0.13; 0.01)	2.8	2.5	1.2	0.9	0.2	0.7	0.3; 0.2	0.5	0.7	0.05
Qabala (0.15; 0.01)	2.6	2.0	1.1	0.8	0.2	0.5	0.4; 0.2	0.6	0.8	0.05
Sumgayit (0.08; 0.01)	1.0	1.7	0.5	0.5	0.2	0.4	0.1; 0.2	0.3	0.4	0.05

Table 4

The results of radiometric measurements and the activity of radionuclides in soil samples taken from territory of regions, polluted with oil refining waste

Regions (background - *μZv / h;* alpha ray *Bq / sm²*)	Isotopes, Bq / kg									
	$_{11}Na^{22}$	$_{19}K^{40}$	$_{26}Fe^{60}$	$_{27}Co^{57}$	$_{30}Zn^{65}$	$_{38}Sr^{91}$	$_{50}Sn^{113}$, $_{50}Sn^{126}$	$_{63}Eu^{154}$	$_{88}Ra^{226}$	$_{90}Th^{228}$
Soil sample from an area covered with oil waste in the village of Bail (0.15; 0.03)	1.6	1.2	1.2	0.7	0.2	0.7	0.6, 0.6	0.6	0.9	0.12
Soil contaminated with oil waste in the area adjacent to the highway in the village of Bibiheybat (0.11, 0.02)	1.5	1.8	1.1	0.5	0.2	0.6	0.6, 0.5	0.6	0.7	0.08
Sand contaminated with oil waste in the area adjacent to the highway in the village of Bibiheybat (0.03, 0.01)	1.0	0.8	0.3	0.4	0.2	0.3	0.1, 0.32	0.3	0.4	0.05
Soil contaminated with oil waste around treatment facilities in the Surakhani region (0.08, 0.01)	1.2	1.4	1.3	0.8	0.2	0.6	0.5, 0.5	0.6	0.8	0.08
Soil contaminated with oil waste from local areas around oil refineries (0.09, 0.01)	1.4	1.6	1.1	0.6	0.2	0.6	0.5, 0.5	0.5	0.8	0.06

It can be seen from Table 3 that the value of the radioactive background in Baku city is 0.03-0.15 μSv/hour and the intensity of alpha radiation is 0-0.03 Bq/cm^2. The common activity of studied natural radionuclides in soil samples taken from Baku city areas is 5-10 Bq/kg.

It was determined that the activity of radionuclides in coastal sands is relatively small. There are approximately 1.5-2 times larger amounts of radionuclides and the value of radioactive radiation background is 1.5-2 times greater, than the permissible directive indicator, in the soil samples covered with oil waste. In areas contaminated with oil waste, regardless of the concentration of heavy metals and radionuclides, neither any green vegetation nor microorganisms are observed (*Escherichia coli, Citrobacter, Salmonella, Shigella, Nag-vibrions, Vibrio Cholerae, Rizopus, Candida, Aspergillus, Staphylacoccus, Streptococcus* etc.). It is observed that the green vegetation is relatively more developed in unpollted fertile soils, where the amount of natural radionuclides (K^{40}, Na^{22}, etc.) is relatively large.

Conclusions

1. It was determined that the amount (activity) of radionuclides in coastal sands is 3-4 times lower than in the surrounding soils, and the level of background radiation is 3-4 times below the maximum permissible directive value (0.12 μSv/hour).
2. The amounts of radionuclides in soil samples covered with oil waste are approximately 1.5-2 times larger than for unpolluted soil and the value of radioactive radiation background is 1.5-2 times greater than the permissible directive indicator.
3. In areas contaminated with oil waste, regardless of the concentration of heavy metals and radionuclides, neither any green vegetation nor microorganisms are observed (*Escherichia coli, Citrobacter, Salmonella, Shigella, Nag-vibrions, Vibrio Cholerae, Rizopus, Candida, Aspergillus, Staphylacoccus, Streptococcus* etc.). In addition to oil waste, accumulation of radionuclides is also observed in those areas to a certain extent.
4. A detailed examination of soil plots in the study areas showed that a 2-3 fold change in the concentration of heavy metals does not affect the number of microorganisms in the soil.
5. It is observed that the green vegetation is relatively more developed in unpollted fertile soils (in the established range of concentrations of microelements in the soil's cover remedied by transporting and adding clean soil or by other methods), where the amount of natural radionuclides (K^{40}, Na^{22}, etc.) is relatively large.

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Accepted: 07.11.2024