Relationship between soil fertility in foothills and inorganic components

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Abstract. In newly formed soils with low humus content, high concentrations of heavy metals do not have a positive effect on the development of green vegetation. In soils contaminated with crude oil, oil refining waste and heavy metals, green vegetation is not observed regardless of the concentration of heavy metals. However, in soils rich in humus and free from oil industry waste, restored or unpolluted by oil refining emissions, the development of green vegetation is directly proportional to the concentration of metals, including heavy metals. Fertile soils of mountainous and foothill areas are characterized by relatively high concentrations of mineral components and natural radionuclides. These results are in good agreement with the higher degree of development of herbaceous vegetation, green shrubs and trees observed in foothill areas, which is explained by both high soil fertility and the participation of microelements and natural radionuclides in accelerating photosynthesis processes.

Keywords: heavy metals, oil waste, natural radionuclides, green vegetation, mountainous and foothill areas.

1 Introduction

Soil is the upper layer of the lithosphere exposed to living organisms and the atmosphere. The main part of the soil is formed by chemical compounds in the form of various minerals. 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. 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, 2].

Systematic soil pollution with small volumes of anthropogenic emissions leads to an increase in the concentration of xenobiotics in other environmental objects (water bodies and vegetation). An increase in the technogenic load on the environment, the processing of minerals by outdated technological processes and, as a result, the pollution of environmental objects with small volumes of xenobiotics can cause the formation of ecological crisis zones. Therefore, systematic measurements and studies are necessary to obtain results on the distribution of radionuclides, heavy metals and other xenobiotics in the soil, vegetation, water bodies of the country, trends in the direction of the emergence of ecological crisis zones, information for predicting changes and the rate of change in the environment. The possibility of cleaning local areas of the Earth contaminated with radionuclides and heavy metals by

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various methods and studying the options for implementing these processes are the most important tasks of radiochemistry and are of great importance for solving many urgent environmental problems [3-5].

Radioactive elements and heavy metals, along with non-metals and light metals, are distinguished in the tables of chemical elements and are characterized by high density (more than 5 g/cm3), biological activity, toxicity, the ability to migrate in the environment of living organisms along the trophic chains "atmosphere – wind – rain – soil – plants – animals – humans", and to accumulate in environmental objects and organisms [6-8].

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 [7-9].

There is a redistribution and often an increase in the concentration of heavy metals in environmental objects as a result of the development of enterprises of mining and processing complexes, metallurgical, chemical, petrochemical, energy industries, intensive economic activity and intensification of the transport sector in many countries of the world. 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 or deficiency of absolutely and vital trace elements (iron, copper, zinc, cobalt, iodine, bromine, fluorine, chromium, cobalt), the normal vital activity of the body is disrupted, and in the absence or deficiency of probably necessary trace elements (nickel, selenium, vanadium, aluminum, molybdenum, strontium, manganese, silicon, scandium), the activity of enzymes decreases, the body functions on the verge of survival, with an increase in their concentration, an improvement in the life of activity is observed, and with an increase in their concentration, there is an improvement in the life of activity. excessive accumulation, their toxic effect is manifested.

Heavy metals include As, Hg, Pb, Cd, Sb, Sn, Zn, Al, Fe, Cu, Cr, Tl, Co, Sc, Ni, etc. Among them, the most highly toxic are mercury, lead, arsenic, aluminum and cadmium, the maximum permissible concentration (MAC) of which in water is 0.0005, 0.05, 1, 20 and 0.2 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 [8-10].

Heavy metals enter the atmosphere through technogenic emissions in the form of aerosols, settle on the upper part of land, pollute the soil and humus layer, enter large reservoirs with wastewater, pollute water and bottom sediments. Some goods (metal and enameled utensils produced for use in the household and food industry, polymer and plastic materials, products and toys, numerous synthetic dyes, etc.) contain certain amounts of heavy metals. Heavy metals that have entered living organisms, in addition to their toxic effect, can also lead to a decrease in the concentration of useful trace elements necessary for life due to participation in ion exchange processes. The negative effects of heavy metals on living organisms are described in detail in the scientific literature [9, 10].

Depending on the magnitude of their concentration in the body, microelements can have a "threatening, deficient, physiological, toxic and lethal" effect on the body [8-10].

The presence of radionuclides with a long half-life in uranium and thorium production wastes, the release of radioactive radon from these wastes, the occurrence of solid and liquid wastes during the mining and processing of uranium-ores creates local contaminated areas

with a high equivalent dose rate (more than 0.1 mSv/h) in the surrounding areas. Under the influence of atmospheric precipitation, waste leaching occurs. Radioactive mine water, industrial water effluents from chemical plants for the production of weapons-grade plutonium, reprocessing of nuclear fuel spent at nuclear power plants, production of phosphate fertilizer (traces of uranium in phosphorite and apatite) lead to contamination of groundwater and bottom sediments of water sources [11-14].

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 [15-18].

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 [7-10, 19-21].

The listed negative impacts of technological processes and their waste have led to a widespread violation of the ecological balance, impoverishment of biodiversity, varieties of vegetation and an increase in the number of occupational diseases.

2 Experimental part

The samples of oil refining waste were prepared for analysis by extraction with a mixture of hexane and toluene (2:1) from soil samples contaminated with oil refining waste. The content of elements in inorganic residues of crude oil and oil refining waste samples obtained by distillation at a temperature of 700°C for three hours was determined using X-ray fluorescence spectroscopy, X-ray spectral analyzer of a scanning electron microscope and analytical chemistry methods [11-14]. The soil samples taken 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. After radiometric measurements, the obtained dry mineral was analyzed by analytical chemistry, X-ray fluorescence, gamma, beta and atomic absorption spectroscopies and electron microscopy. 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). In the physicochemical analysis of minerals obtained through the evaporation of aqueous, slightly acidic, and slightly alkaline extracts from soil samples, as well as by treating plant samples with a nitric acid solution and heat treatment, and evaporating filtered and centrifuged aqueous samples, the following equipment was used: GFL-2304 distiller, TDL-5M and TD5A-WS centrifuges, a gamma spectrometer with an HP-Ge detector from Canberra, an SEM electron microscope (Carl Zeiss with an electron tube), an AA-6800 atomic absorption spectrometer (Shimadzu), Expert-3L and X-ray fluorescence spectrometers, pH meters, an STA-2900 thermal analyzer, automatic micropipettes, heaters for stirring, heaters for flasks, refractory glass and ceramic laboratory products, refrigerators, evaporators, metal stands with fixing clamps, and membrane filters [11-14].

3 Results and Discussion

Over the past 8 years, samples of crude oil from various fields in the country have been collected, as well as samples of newly formed soils contaminated with oil refining waste

with a low humus content, fertile soils with a high humus content, and samples of similar soils not contaminated with oil refining waste.

A detailed inspection of the studied land plots was carried out before taking soil samples. As a result of observations, it was found that in areas not contaminated with oil refining waste, newly formed soils with a low humus content, consisting mainly of dark brown color, had sparse, poorly developed weedy grassy vegetation, and in similar areas of land contaminated with oil refining waste, there was practically no vegetation [11-14].

TABLE 1. Relative content of elements in inorganic residues of oil and oil refining waste.

No	Content of elements in inorganic residues of oil samples (from 1 to 10) and waste oil refining (from 11 to 20)								
312	С	0	Na Na	Mg	Al	Si	S	P	
1.	54.2	14.5	1.8	0.4	12.4	9.8	0.9	0.5	
2.	52.5	11.8	2.1	1.2	7.5	3.6	0.7	0.2	
3.	55.7	14.4	1.5	1.8	3.4	7.1	0.3	0.2	
4.	56.4	14.9	1.7	1.1	5.3	5.2	0.2	0.1	
5.	51.1	14.5	2.4	1.8	9.5	6.7	1.1	0.4	
6.	52.0	12.2	2.8	1.8	3.3	4.5	2.0	0.2	
7.	49.5	15.2	3.1	1.6	1.9	5.2	1.8	0.4	
8.	49.8	13.9	3.0	1.8	2.5	5.8	1.9	0.3	
9.	49.4	14.0	3.9	1.9	3.8	7.7	1.5	0.3	
10.	49.9	13.8	3.2	1.8	5.6	5.3	2.2	0.4	
11.	46.0	12.7	5.1	2.2	7.1	4.9	2.4	0.1	
12.	46.7	12.3	4.4	2.1	6.8	4.4	2.5	0.2	
13.	46.1	12.8	4.2	2.4	3.7	4.8	2.1	0.4	
14.	45.7	12.0	3.9	2.3	2.6	5.2	1.8	0.2	
15.	46.0	12.5	4.0	2.5	1.8	8.0	1.7	0.3	
16.	44.9	12.2	4.1	2.6	1.9	7.2	2.2	0.1	
17.	45.2	12.3	3.8	2.7	3.4	6.5	2.6	-	
18.	46.1	12.0	4.0	2.9	5.1	5.8	2.1	0.1	
19.	44.4	12.1	3.7	2.8	2.5	6.1	2.8	0.1	
20.	45.0	12.0	3.9	3.0	6.6	6.3	2.9	-	
	Content of elements in inorganic residues of oil samples (from 1 to 10)								
	Conten	it of elem						1 to 10)	
№				e oil refin	ing (from	11 to 20))		
	K	Cr	and wast Ca	e oil refin Ti	ing (from Mn	11 to 20) Sr	Fe	1 to 10)	
1.	K 1.5	Cr -	Ca 1.7	e oil refin Ti 0.5	ing (from Mn 0.1	Sr 0.7	Fe 7.7	Pb -	
1. 2.	K 1.5 0.9	Cr - 0.3	Ca 1.7 3.4	e oil refin Ti 0.5 0.1	mg (from Mn 0.1 0.2	Sr 0.7 0.5	Fe 7.7 4.8	Pb - 1.2	
1. 2. 3.	K 1.5 0.9 2.0	Cr - 0.3 0.3	and wast Ca 1.7 3.4 2.9	e oil refin Ti 0.5 0.1 0.4	ing (from Mn 0.1 0.2 0.4	Sr 0.7 0.5 0.6	Fe 7.7 4.8 3.7	Pb - 1.2 1.9	
1. 2. 3. 4.	K 1.5 0.9 2.0 0.5	Cr - 0.3 0.3 0.4	and wast Ca 1.7 3.4 2.9 6.5	e oil refin Ti 0.5 0.1 0.4 0.1	Mn 0.1 0.2 0.4 0.1	Sr 0.7 0.5 0.6 0.8	Fe 7.7 4.8 3.7 4.4	Pb - 1.2 1.9 2.7	
1. 2. 3. 4. 5.	K 1.5 0.9 2.0 0.5 2.4	Cr - 0.3 0.3 0.4 0.5	and wast Ca 1.7 3.4 2.9 6.5 9.8	e oil refin Ti 0.5 0.1 0.4 0.1	Mn 0.1 0.2 0.4 0.1 0.2	Sr 0.7 0.5 0.6 0.8 0.6	Fe 7.7 4.8 3.7 4.4 8.1	Pb - 1.2 1.9 2.7 2.9	
1. 2. 3. 4. 5. 6.	K 1.5 0.9 2.0 0.5 2.4 2.1	Cr - 0.3 0.3 0.4 0.5 0.3	and wast Ca 1.7 3.4 2.9 6.5 9.8 2.2	e oil refin Ti 0.5 0.1 0.4 0.4 0.2	Mn 0.1 0.2 0.4 0.1 0.2 0.1 0.2 0.1 0.2 0.1	Sr 0.7 0.5 0.6 0.8 0.5	Fe 7.7 4.8 3.7 4.4 8.1 7.0	Pb - 1.2 1.9 2.7 2.9 2.8	
1. 2. 3. 4. 5. 6.	K 1.5 0.9 2.0 0.5 2.4 2.1 0.9	Cr - 0.3 0.3 0.4 0.5 0.3 0.4	and wast Ca 1.7 3.4 2.9 6.5 9.8 2.2 7.5	e oil refin Ti 0.5 0.1 0.4 0.1 0.4 0.2 0.3	Mn 0.1 0.2 0.4 0.1 0.2 0.1 0.2 0.1	11 to 20) Sr 0.7 0.5 0.6 0.8 0.6 0.5 0.5	Fe 7.7 4.8 3.7 4.4 8.1 7.0 6.8	Pb - 1.2 1.9 2.7 2.9 2.8 2.5	
1. 2. 3. 4. 5. 6. 7. 8.	K 1.5 0.9 2.0 0.5 2.4 2.1 0.9 2.3	Cr - 0.3 0.3 0.4 0.5 0.3 0.4 0.5	and wast Ca 1.7 3.4 2.9 6.5 9.8 2.2 7.5 2.5	e oil refin Ti 0.5 0.1 0.4 0.1 0.4 0.2 0.3 0.1	Mn 0.1 0.2 0.4 0.1 0.2 0.1 0.2 0.1	11 to 20) Sr 0.7 0.5 0.6 0.8 0.6 0.5 -	Fe 7.7 4.8 3.7 4.4 8.1 7.0 6.8 3.2	Pb - 1.2 1.9 2.7 2.9 2.8 2.5 1.8	
1. 2. 3. 4. 5. 6. 7. 8. 9.	K 1.5 0.9 2.0 0.5 2.4 2.1 0.9 2.3 2.2	Cr - 0.3 0.4 0.5 0.3 0.4 0.2 0.3	and wast Ca 1.7 3.4 2.9 6.5 9.8 2.2 7.5 2.5 2.1	e oil refin Ti 0.5 0.1 0.4 0.1 0.2 0.3 0.1 0.1	Mn 0.1 0.2 0.4 0.1 0.2 0.1	11 to 20) Sr 0.7 0.5 0.6 0.8 0.6 0.5 -	Fe 7.7 4.8 3.7 4.4 8.1 7.0 6.8 3.2 3.5	Pb - 1.2 1.9 2.7 2.9 2.8 2.5 1.8 1.9	
1. 2. 3. 4. 5. 6. 7. 8. 9.	K 1.5 0.9 2.0 0.5 2.4 2.1 0.9 2.3 2.2	Cr - 0.3 0.4 0.5 0.3 0.4 0.2 0.3 0.4	and wast Ca 1.7 3.4 2.9 6.5 9.8 2.2 7.5 2.5 2.1 7.8	e oil refin Ti 0.5 0.1 0.4 0.4 0.2 0.3 0.1 0.1 0.5	Mn 0.1 0.2 0.4 0.1 0.2 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.2 0.1 0.2 0.1 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.2 0.3	11 to 20) Sr 0.7 0.5 0.6 0.8 0.6 0.5	Fe 7.7 4.8 3.7 4.4 8.1 7.0 6.8 3.2 3.5 3.3	Pb - 1.2 1.9 2.7 2.9 2.8 2.5 1.8 1.9 1.9	
1. 2. 3. 4. 5. 6. 7. 8. 9. 10.	K 1.5 0.9 2.0 0.5 2.4 2.1 0.9 2.3 2.2 1.7	Cr - 0.3 0.4 0.5 0.3 0.4 0.2 0.3 0.4 0.1	and wast Ca 1.7 3.4 2.9 6.5 9.8 2.2 7.5 2.5 2.1 7.8 2.0	e oil refin Ti 0.5 0.1 0.4 0.4 0.2 0.3 0.1 0.1 0.1 0.1	Mn	11 to 20) Sr 0.7 0.5 0.6 0.8 0.6 0.5 0.4	Fe 7.7 4.8 3.7 4.4 8.1 7.0 6.8 3.2 3.5 3.3 6.5	Pb - 1.2 1.9 2.7 2.9 2.8 2.5 1.8 1.9 1.9 2.7	
1. 2. 3. 4. 5. 6. 7. 8. 9. 10. 11.	K 1.5 0.9 2.0 0.5 2.4 2.1 0.9 2.3 2.2 1.7 1.4	Cr - 0.3 0.4 0.5 0.3 0.4 0.2 0.3 0.4 0.1 0.1	and wast Ca 1.7 3.4 2.9 6.5 9.8 2.2 7.5 2.5 2.1 7.8 2.0 1.9	e oil refin Ti 0.5 0.1 0.4 0.1 0.4 0.2 0.3 0.1 0.1 0.1 0.5 0.1 0.1	ing (from Mn 0.1 0.2 0.4 0.1 0.2 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.2 -	11 to 20) Sr 0.7 0.5 0.6 0.8 0.6 0.5 0.4 0.5	Fe 7.7 4.8 3.7 4.4 8.1 7.0 6.8 3.2 3.5 3.3 6.5 7.8	Pb - 1.2 1.9 2.7 2.9 2.8 2.5 1.8 1.9 1.9 2.7 2.9	
1. 2. 3. 4. 5. 6. 7. 8. 9. 10. 11. 12.	K 1.5 0.9 2.0 0.5 2.4 2.1 0.9 2.3 2.2 1.7 1.4 1.1 0.6	Cr - 0.3 0.4 0.5 0.3 0.4 0.2 0.3 0.4 0.1 -	and wast Ca 1.7 3.4 2.9 6.5 9.8 2.2 7.5 2.5 2.1 7.8 2.0 1.9 2.5	e oil refin Ti 0.5 0.1 0.4 0.2 0.3 0.1 0.1 0.5 0.1 0.1 0.5 0.1 0.5 0.1 0.5	ing (from Mn 0.1 0.2 0.4 0.1 0.2 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.2 0.1 0.1 0.1 0.2 0.1 0.1 0.1 0.2 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1	11 to 20) Sr 0.7 0.5 0.6 0.8 0.6 0.5 0.4 0.5 0.4	Fe 7.7 4.8 3.7 4.4 8.1 7.0 6.8 3.2 3.5 3.3 6.5 7.8 6.7	Pb - 1.2 1.9 2.7 2.9 2.8 2.5 1.8 1.9 1.9 2.7 2.9 2.9 2.9	
1. 2. 3. 4. 5. 6. 7. 8. 9. 10. 11. 12. 13.	K 1.5 0.9 2.0 0.5 2.4 2.1 0.9 2.3 2.2 1.7 1.4 1.1 0.6 0.5	Cr - 0.3 0.3 0.4 0.5 0.3 0.4 0.2 0.3 0.4 0.1 0.1	and wast Ca 1.7 3.4 2.9 6.5 9.8 2.2 7.5 2.5 2.1 7.8 2.0 1.9 2.5 2.8	e oil refin Ti 0.5 0.1 0.4 0.1 0.4 0.2 0.3 0.1 0.1 0.5 0.1 0.5 0.1 0.5 0.1 0.1	ing (from Mn 0.1 0.2 0.4 0.1 0.2 0.1 0.1 0.1 0.1 0.1 0.1 0.2 - 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1	11 to 20) Sr 0.7 0.5 0.6 0.8 0.6 0.5 0.4 0.5 0.4 -	Fe 7.7 4.8 3.7 4.4 8.1 7.0 6.8 3.2 3.5 3.3 6.5 7.8 6.7 3.4	Pb - 1.2 1.9 2.7 2.9 2.8 1.9 1.9 2.7 2.9 2.7 2.9 2.7 2.9 2.9 1.7	
1. 2. 3. 4. 5. 6. 7. 8. 9. 10. 11. 12. 13. 14.	K 1.5 0.9 2.0 0.5 2.4 2.1 0.9 2.3 2.2 1.7 1.4 1.1 0.6 0.5	Cr 0.3 0.4 0.5 0.3 0.4 0.2 0.3 0.4 0.1 0.1	and wast Ca 1.7 3.4 2.9 6.5 9.8 2.2 7.5 2.5 2.1 7.8 2.0 1.9 2.5 2.8 2.0	e oil refin Ti 0.5 0.1 0.4 0.1 0.2 0.3 0.1 0.1 0.5 0.1 0.5 0.1 0.1 0.2 0.3 0.2	ing (from Mn 0.1 0.2 0.4 0.1 0.2 0.1 0.1 0.1 0.1 0.1 0.2 0.1 0.1 0.1 0.2 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1	11 to 20) Sr 0.7 0.5 0.6 0.8 0.6 0.5 0.4 0.5 0.4 -	Fe 7.7 4.8 3.7 4.4 8.1 7.0 6.8 3.2 3.5 3.3 6.5 7.8 6.7 3.4 3.4 3.4	Pb - 1.2 1.9 2.7 2.9 2.8 1.9 1.9 2.7 2.9 2.7 2.9 2.7 2.9 2.9 1.7 1.6	
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1. 2. 3. 4. 5. 6. 7. 8. 9. 10. 11. 12. 13. 14. 15. 16. 17.	K 1.5 0.9 2.0 0.5 2.4 2.1 0.9 2.3 2.2 1.7 1.4 1.1 0.6 0.5 0.7 0.4 0.5	Cr 0.3 0.4 0.5 0.3 0.4 0.2 0.3 0.4 0.1 0.1 0.2 0.4 0.2	and wast Ca 1.7 3.4 2.9 6.5 9.8 2.2 7.5 2.5 2.1 7.8 2.0 1.9 2.5 2.8 2.0 3.3 8.4	e oil refin Ti 0.5 0.1 0.4 0.1 0.4 0.2 0.3 0.1 0.1 0.5 0.1 0.1 0.5 0.1 0.5 0.1 0.5 0.1 0.5 0.1 0.5 0.1 0.5 0.1 0.5 0.5	ing (from Mn 0.1 0.2 0.4 0.1 0.2 0.1 0.1 0.1 0.1 0.2 - 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1	11 to 20) Sr 0.7 0.5 0.6 0.8 0.6 0.5 0.4 0.5 0.4 - 0.3 0.7	Fe 7.7 4.8 3.7 4.4 8.1 7.0 6.8 3.2 3.5 3.3 6.5 7.8 6.7 3.4 3.1 8.0	Pb - 1.2 1.9 2.7 2.9 2.8 1.9 1.9 2.7 2.9 1.7 1.6 1.5 2.4	
1. 2. 3. 4. 5. 6. 7. 8. 9. 10. 11. 12. 13. 14. 15. 16. 17.	K 1.5 0.9 2.0 0.5 2.4 2.1 0.9 2.3 2.2 1.7 1.4 1.1 0.6 0.5 0.7 0.4 0.5 0.6	Cr 0.3 0.4 0.5 0.3 0.4 0.2 0.3 0.4 0.1 0.1 0.2 0.4 0.1 0.1 0.2 0.4 0.1	and wast Ca 1.7 3.4 2.9 6.5 9.8 2.2 7.5 2.5 2.1 7.8 2.0 1.9 2.5 2.8 2.0 3.3 8.4 3.0	e oil refin Ti 0.5 0.1 0.4 0.1 0.4 0.2 0.3 0.1 0.1 0.5 0.1 0.5 0.1 0.1 0.2 0.3 0.2 0.3 0.2 0.3	ing (from Mn 0.1 0.2 0.4 0.1 0.2 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1	11 to 20) Sr 0.7 0.5 0.6 0.8 0.6 0.5 0.4 0.5 0.4 - 0.3 0.7 0.3	Fe 7.7 4.8 3.7 4.4 8.1 7.0 6.8 3.2 3.5 3.3 6.5 7.8 6.7 3.4 3.1 8.0 3.2	Pb - 1.2 1.9 2.7 2.9 2.8 2.5 1.8 1.9 2.7 2.9 2.7 2.9 2.9 1.7 1.6 1.5 2.4 1.6	
1. 2. 3. 4. 5. 6. 7. 8. 9. 10. 11. 12. 13. 14. 15. 16.	K 1.5 0.9 2.0 0.5 2.4 2.1 0.9 2.3 2.2 1.7 1.4 1.1 0.6 0.5 0.7 0.4 0.5	Cr 0.3 0.4 0.5 0.3 0.4 0.2 0.3 0.4 0.1 0.1 0.2 0.4 0.2	and wast Ca 1.7 3.4 2.9 6.5 9.8 2.2 7.5 2.5 2.1 7.8 2.0 1.9 2.5 2.8 2.0 3.3 8.4	e oil refin Ti 0.5 0.1 0.4 0.1 0.4 0.2 0.3 0.1 0.1 0.5 0.1 0.1 0.5 0.1 0.5 0.1 0.5 0.1 0.5 0.1 0.5 0.1 0.5 0.1 0.5 0.5	ing (from Mn 0.1 0.2 0.4 0.1 0.2 0.1 0.1 0.1 0.1 0.2 - 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1	11 to 20) Sr 0.7 0.5 0.6 0.8 0.6 0.5 0.4 0.5 0.4 - 0.3 0.7	Fe 7.7 4.8 3.7 4.4 8.1 7.0 6.8 3.2 3.5 3.3 6.5 7.8 6.7 3.4 3.1 8.0	Pb - 1.2 1.9 2.7 2.9 2.8 1.9 1.9 2.7 2.9 1.7 1.6 1.5 2.4	

In land plots contaminated with oil refining waste, with fully formed fertile soil and a low humus content, few and poorly developed species of weeds were observed. In areas not contaminated with oil refining waste, fully formed fertile soils with a high humus content, covered with green, well-developed herbaceous vegetation, as well as green shrubs and trees, are observed. At the same time, in different areas and on different soil plots on the territory of the studied lands of the country, there is a significant difference in the degree of development of green vegetation. The relative content of elements in percentages in inorganic residues of oil samples (samples with numbers from 1 to 10) and oil refining waste (samples with numbers from 11 to 20) is given in Table 1.

Table 1 shows that the relative total content of elements in the inorganic residues of various samples of crude oil and oil refining waste is 26-47% and 26-41%, respectively. The results obtained and the comparison of the relative content of metals in the inorganic residues of crude oil and oil refining waste extracted from soil samples contaminated with oil waste clearly indicate the accumulation of metals, including "heavy metals", in the soil when it is contaminated with oil refining waste.

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.

Daniana	Components, mg/kg							
Regions	Sulphates	K	J	Sr	NO ₃	Fe; Mn	Zn	
Yardimli	790	8820	0.9	21	206	332, 18	2.4	
Lerik	780	8210	1,4	42	212	333; 23	2,2	
Astara	690	7600	0.9	19	95	230; 15	2,5	
Lankaran	680	6650	0.9	24	86	190; 46	2,5	
Masalli	750	6580	1.0	22	75	164; 25	2,5	
Nakhchivan city	460	6500	2,0	110	25	30; 20	1,2	
Quzanli	460	7605	1.4	42	78	71; 16	2.2	
Goranboy	380	7240	1.8	48	65	54; 29	1.8	
Ordubad	600	9800	3,0	110	313	220; 30	2,2	
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	

Table 2. Concentrations of components in the composition of soil samples taken from country's regions.

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 (Yardimli, Lerik, Astara, Lankaran, Masalli, Quzanli, Goranboy, Ismayilli, Ordubad, and Qabala) is 7.62-10.19 g/kg and common concentrations of components in the composition of soil samples taken from other regions of country (Nakhchivan and Sumgayit cities) is 5.47-7.15 g/kg.

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 (Yardimli, Lerik, Astara, Lankaran, Masalli, Quzanli, Goranboy, Ismayilli, Ordubad, and Qabala) is 0.03- $0.15~\mu Sv/hour$ and the intensity of alpha radiation is 0-0.03~Bq/cm2. The value of the radioactive background in other regions of country (Nakhchivan and Sumgayit cities) is $0.08~\mu Sv/hour$ 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 (Yardimli, Lerik, Astara, Lankaran, Masalli, Quzanli, Goranboy, Ismayilli, Ordubad, and Qabala) is 7.3-10~Bq/kg and common

activity of all natural radionuclides in soil samples taken from other regions of country (Nakhchivan and Sumgayit cities) is 5.3-6.7 Bq/kg.

A comparative analysis of the concentrations of mineral components and natural radionuclides (Tables 2 and 3) shows that fertile soils in mountainous and foothill areas (Yardimli, Lerik, Astara, Lankaran, Masalli, Quzanli, Goranboy, Ismayilli, Ordubad, and Qabala) are characterized by relatively high concentrations of the studied components.

These results are in good agreement with the higher degree of development of herbaceous vegetation, green shrubs and trees observed in mountainous and foothill areas, which is explained both by the high fertility of the soil and by the participation of microelements and natural radionuclides in the acceleration of photosynthesis processes [12].

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 - $\mu Zv / h$;	Isotopes, Bq / kg					
alpha ray Bq / sm^2)	11Na ²²	19 K ⁴⁰	$_{26}\text{Fe}^{60}$	27Co ⁵⁷	30Zn ⁶⁵	
Yardimli (0,14; 0,01)	3.0	2.4	1.1	0.9	0.2	
Lerik (0,13; 0,02)	2.7	2.5	0.9	0.9	0.2	
Astara (0,14; 0,01)	2.7	2.5	0.8	0.9	0.2	
Lankaran (0,14; 0,02)	2.7	2.0	1.0	0.8	0.2	
Masalli (0,11; 0,01)	2.7	2.5	1.1	0.8	0.2	
Nakhchivan city (0,08; 0,01)	1.0	2.0	0.9	0.9	0.2	
Quzanli (0,03; 0)	1.3	2.4	0.68	0.75	0.2	
Goranboy (0,04; 0)	1.5	2.4	0.7	0.8	0.2	
Ordubad (0,09; 0,03)	1.5	2.5	1.0	1.1	0.4	
Ismayilli (0,13; 0,01)	2.8	2.5	1.2	0.9	0.2	
Qabala (0,15; 0,01)	2.6	2.0	1.1	0.8	0.2	
Sumgayit (0,08; 0,01)	1.0	1.7	0.5	0.5	0.2	
Regions (background - $\mu Zv / h$;	38 Sr ⁹¹	50 Sn ¹¹³ ,	63Eu ¹⁵⁴	88Ra ²²⁶	90Th ²²⁸	
alpha ray Bq / sm²)		50Sn ¹²⁶				
Yardimli (0,14; 0,01)	0.5	0.2; 0.3	0.6	0.6	0.04	
Lerik (0,13; 0,02)	0.5	0.2; 0.3	0.6	0.6	0.05	
Astara (0,14; 0,01)	0.7	0.1; 0.3	0.5	0.6	0.02	
Lankaran (0,14; 0,02)	0.8	0.1; 0.3	0.7	0.6	0.01	
Masalli (0,11; 0,01)	0.8	0.2; 0.3	0.7	0.7	0.05	
Nakhchivan city	0.4	0.1; 0.2	0.3	0.6	0.05	
(0,08; 0,01)						
Quzanli (0,03; 0)	0.5	0.1; 0.2	0.5	0.8	0.05	
Goranboy (0,04; 0)	0.5	0.1; 0.2	0.6	0.8	0.05	
Ordubad (0,09; 0,03)	0.5	0.2; 0.3	0.4	0.8	0.06	
Ismayilli (0,13; 0,01)	0.7	0.3; 0.2	0.5	0.7	0.05	
Qabala (0,15; 0,01)	0.5	0.4; 0.2	0.6	0.8	0.05	
Sumgayit (0,08; 0,01)	0.4	0.1; 0.2	0.30	0.4	0.05	

As is known, photosynthesis is a complex chemical process of converting light energy and infrared radiation into the energy of chemical bonds of organic substances with the participation of photosynthetic pigments (plant chlorophylls, bacteriochlorophyll bacteria, archaea bacteriorhodopsin).

In one year, green algae release 3.6×10^{11} tons of oxygen into the Earth's atmosphere, which is about 90% of all oxygen produced during photosynthesis on Earth. As you can see, photosynthesis is the largest biochemical process on Earth. It is assumed that about 3 billion years ago, the process of splitting a water molecule by quanta of sunlight occurred with the formation of an oxygen molecule. The binding energy of the hydrogen atom with the hydroxyl group of the water molecule is 5 eV / molecule. The established low values of the energy of light quanta allow us to conclude that the nature of the course of photosynthesis is complex and the complex mechanisms of the process of splitting water molecules in plants are proposed. In general, photosynthesis can be represented in the following image and equation [12]:

$$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$$
 (1)

Two types of pigments were found in living organisms (the retinal vitamin A derivative is less common, and chlorophylls are involved in photosynthesis in most organisms). In accordance with this, chlorine-free and chlorophyll photosynthesis are isolated. The efficiency of chlorophyll-free photosynthesis is relatively low (one H⁺ is transferred to one absorbed quantum of light). This process is found in the mating membrane of halobacteria. As a result of the operation of the light-dependent proton pump (bacteriorhodopsin) of the membrane, the energy of sunlight transforms into the energy of the electrochemical gradient of protons on the membrane. Chlorophyll photosynthesis is more energy efficient. At least one H+ is transferred to each absorbed light quantum against the gradient and energy is stored in the form of reduced compounds (ferrodoxin, etc.). Oxygen-free chlorophyll photosynthesis (purple, green bacteria and heliobacteria) proceeds without oxygen evolution. Oxygenic chlorophyll photosynthesis (plants, algae, cyanobacteria, etc.) is accompanied by the release of oxygen. In the initial (photophysical) stage of photosynthesis, light quanta are absorbed by pigments, they transition to an excited state and energy is transferred to other molecules of the photosystem (plastoquinone). In the photochemical stage, charge separation occurs in the reaction center. A water molecule loses an electron under the influence of a radical-cation formed from a chlorophyll molecule transfers its electron to plastoquinone in the first stage of photosynthesis:

$$H_2O - e - \rightarrow H + + \cdot OH \tag{2}$$

Hydroxyl radicals formed under the influence of positively charged manganese ions are converted into oxygen and water:

$$4 \cdot OH \rightarrow O_2 + 2H_2O \tag{3}$$

Light quantum is absorbed by another chlorophyll molecule and it transfers its electron to ferrodoxin in the chemical stage [22-24].

Next, biochemical reactions of the synthesis of organic substances using energy accumulated at the already described light-dependent stages take place.

The energy of gamma rays (1.45 MeV) emitted by the K^{40} isotope is many times higher than the value of the binding energy of hydrogen with a hydroxyl group in water molecules (5 eV). In addition, K^{40} isotopes were found in all samples without exception taken from the environment, and the geometric dimensions of the studied vegetation specimens were directly proportional to the activity (concentration) of K^{40} detected in them.

Therefore, we concluded that along with the multi-stage processes of splitting water molecules in the proposed photosynthesis mechanisms, the cause of the splitting of hydrogen atoms from water molecules, in addition to the complex process of photolytic decomposition of water, is also the radiolytic decomposition of water under the influence of gamma rays of natural isotopes (in mostly K^{40} , having the greatest / activity / concentration in vegetation).

A comparative analysis of the geometric, qualitative, organoleptic characteristics of the vegetation cover of different areas is in good agreement, proportional to the concentration of K⁴⁰ in these plants. The high energy of gamma rays irradiated with K⁴⁰ and the relatively high activity (relatively high concentration) are the reason for the increase in the current concentration of radicals in the mass of the plant, which is equivalent to the acceleration of high-barrier endothermic process of the splitting of hydrogen atoms from water molecules.

The analysis of numerous samples of water, soil, vegetation, livestock products showed the presence of Na^{22} and K^{40} radioisotopes in all samples, without exception.

As is known, after completion of reactions in spurs, the values of the primary radiation-chemical yield of water gamma radiolysis products at pH = 4–9 are: G(H+aq) = 3.4; G(e-aq) = 2.9; G(H) = 0.6; G(.OH) = 2.9; G(.O) = 0.0067; $G(H_2) = 0.45$; $G(H_2O_2) = 0.75$; $G(OH^-aq) = 0.6$ ion / 100 eV [22-24].

In some sources the value of $G(H+aq) = 4.25 \ H^+ / 100 \ eV$ is indicated [11]. Taking into account the average value of K^{40} activity in 1 kg of plant mass (1.2-3.0 Bq / kg), exposure to

this isotope during the year leads to the formation of (2,5 quanta / (s.kg)) \times (4,25 H⁺_{aq} / 100 eV) \times (1.46 \times 10⁶ eV / quanta) = 15 \times 10⁴ H⁺_{aq} / s.kg = 4.7 \times 10¹²H⁺ / (year. kg).

As can be seen from Table 3, in addition to K^{40} radioactive isotopes of other elements were detected in plant mass. Thus, the total value for 1 kg of plant mass formed during one year under the influence of natural gamma rays of all isotopes and cosmic radiation will be 10^{15} H⁺_{aq}. This is lower than the value of the resulting H+ ions involved in photosynthesis.

In the 1980s, the radiation-chemical chain process of hydrogen conversion into carbon monoxide was studied [23-26].

Similar to the radiation-chemical process convertion of molecular hydrogen in reaction with carbon dioxide to carbon monoxide and water, where after the radiation initiation of the process in the energy region above the potential barrier of the limiting reaction stage the chain process begins, and after radiation initiation (formation of radicals, atoms and ions) in the presence of K⁴⁰ and Na²² take place closed cycles of elementary reactions [22-24]:

common process

$$H_2 + CO_2 \rightarrow CO + H_2O \tag{4}$$

radiation initiation

$$H_2 \rightarrow H + \dot{H}$$
 (5)

$$H_2^* + CO_2 \rightarrow CO + \cdot OH + \cdot H$$
 (6)

the chain process

$$H + CO_2 \rightarrow CO + OH$$
 (7)

$$\cdot OH + H_2 \to H_2O + \cdot H \tag{8}$$

$$H^+ + CO_2 \rightarrow CO^+ + \cdot OH \tag{9}$$

$$R^+ + CO_2 \rightarrow CO^+ + RO^- \tag{10}$$

$$H^+ + RR \to R^+ + RH \tag{11}$$

$$CO^+ + RR \rightarrow RCO + R^+ \tag{12}$$

chain reaction's break

$$R + R \to RR \tag{13}$$

$$R + CO \to RCO \tag{14}$$

$$R + OH \to ROH \tag{15}$$

$$CO^+ + e^- \to CO \tag{16}$$

Taking into account the multiplicity of intermediate products of water radiolysis (the radiation-chemical yields of which are given above), the little exothermicity (2.8 kJ / mol) of the total reaction of the radiolytic conversion of a mixture of hydrogen and carbon dioxide into carbon monoxide and water, the possibility of multiple participation of radiolysis products of water and the organic matrix (H., \cdot OH, R $^{+}$, H $^{+}$, H $^{+}$ _{aq}, e $^{-}$ _{aq}, R $^{+}$, CO $^{+}$) in the above repeated cycles of elementary reactions that occur with the resumption of the starting radicals and ions, a direct contribution of water's radiolysis radicals and ions in the course of many elementary reactions occurring in the plant mass - the role of gamma radiation of the natural radioisotopes Na²² and K⁴⁰ should be taken into account in a comprehensive analysis of photosynthesis.

This conclusion is consistent with the presence of Na²² and K⁴⁰ radioisotopes in all analysed samples of water, soil, vegetation, livestock products without exception, with the revealed facts of increasing plant fertility in soils with relatively high concentrations of natural radioisotopes, observation of photosynthesis in the mating membrane of extreme halobacteria, under thick layers of water and in the presence of only long-wave infrared rays or in the absence of chlorophyll and oxygen.

A comparative analysis carried out using physical chemistry methods shows that the fertile soils of mountain and foothill areas are characterized by relatively high concentrations of mineral components and natural radionuclides.

4 Conclusions

- 1. In the soils of regions of the country with a low humus content, large concentrations of radionuclides and heavy metals in the established range of concentrations of microelements in the soil's cover of the planet do not have a positive effect on the development of green vegetation.
- 2. Green vegetation is not observed in soils contaminated with crude oil or oil refinery waste, regardless of the concentration of heavy metals.
- 3. In fertile soils that are not contaminated by oil refinery emissions, the development of green vegetation is directly proportional to the concentration of microelements and natural radionuclides, in the range of concentrations of microelements formed in the soil cover of the planet.
- 4. The land areas that are fertile and uncontaminated by oil refining emissions are soils of mountainous and foothill areas with relatively high concentrations of mineral components and natural radionuclides.
- 5. The high development of herbaceous vegetation, green shrubs and trees in mountainous and foothill areas is explained by the stimulation of photosynthesis by high concentrations of microelements and natural radionuclides.

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