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DISTRIBUTION CHARACTERISTICS OF TRACE ELEMENTS IN SOILS AND PLANTS

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Abstract.

The article gives a brief description of current knowledge on geochemical and biogeochemical processes that influence directly or indirectly the distribution of chemical elements in soils and plants under natural and man-made conditions. The sampling of soils and plants as research objects is not accidental. Soil and plants are the most important, most complex and dynamic components of the biosphere. Revealing their geochemical and biogeochemical role is interesting and important. Man-made input of trace elements into the environment has a negative effect on soil and plants, which requires serious study. On the other hand, it is possible that all kinds of chemical elements can enter the food chain in the conditions of pollution, which is dangerous for the human body. The role of trace elements, including heavy metals, is undeniable in terms of their physiological importance in living organisms. When the concentration of heavy metals, which are important for life, exceeds the norm, it becomes dangerous for human life. That is, the main issue depends on the concentration of chemical elements in the environment: for living organisms, it is considered as a trace element in the case of a lack of an element, and it is considered as a heavy metal in the case of its excess. It has already been proven that their intensive distribution in the biosphere and atmosphere and the observation of high concentrations in the soil pose a great threat to biota. When the amount of toxic heavy metals or biophilic trace elements exceeds the maximum allowable concentration (MAC) in living organisms, biological processes are disturbed. Especially lead, mercury, cadmium are considered more dangerous pollutants among heavy metals. The source of heavy metals in soils are rocks of various origins. Features of their distribution in soils are different depending on the origin and granulometric composition of the rocks.

Key words: soil, vegetation, trace elements, biogeochemistry

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İntroduction.

Research on the chemical properties and interactions of trace elements in the environment has been increasing in recent decades. Rapid industrialisation, the stream of people from rural to cities is constantly increasing all over the world. Population growth leads to an increase in metal concentration in an atypical natural way.

The study of trace elements has become widespread throughout the world. The body of such works should be included in the results of research conducted in other countries. Summarizing the knowledge on geochemical and biogeochemical processes at the present level of science has an adequate impact on the knowledge about the distribution of trace elements in soils and plants.

Soils and plants are important components of the biological environment. They can be characterized as extended and constantly changing parts of the biosphere. The distribution peculiarities of trace elements in soils, their man-made input into living organisms also effect, which is of great importance for environmental protection and health [1, 2, 4].

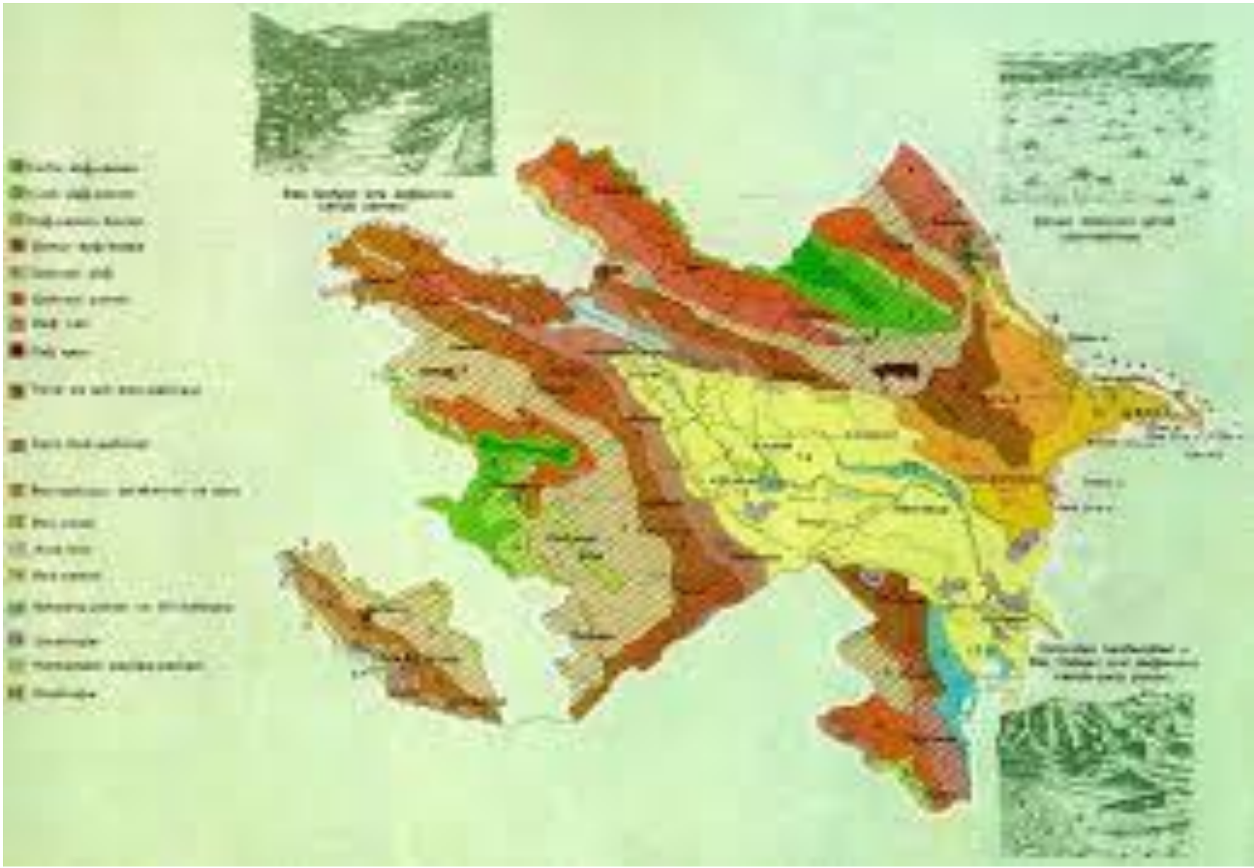

Fig. 1. Land map of Azerbaijan

The term “trace elements” does not have a strict definition, because it is not widely distributed in the Earth’s crust (often below 0.1%), and is present in very small amounts in living matter. They are called “trace” elements because they are nutritional minerals for cellular processes. The main issue depends on the concentration of chemical elements in the environment: for living organisms, it is considered as a trace element in the case of a lack of an element, and it is considered as a heavy metal in the case of its excess. An excess of any element in the environment or food is undesirable.

Objects and methods of research.

The metabolism of trace elements in plants is studied very intensively. Basic information on this problem can be obtained from studies on plant physiology and nutrition. The characteristic behavior of the role of any trace elements in plants is explained by several main processes: absorption and transport through plants; enzymatic processes; concentrations and forms of finding, deficiency and toxicity; their concentration and interactions.

These processes have been relatively well studied for many elements, and the study of these processes for a number of elements is the work of the future. Chemical stress in plants cannot be considered as fully studied based on trace element deficiency or excess data, because such mechanisms have been developed in the lives of individuals (ontogeny and phylogeny) that lead to adaptation and chemical imbalance in the environment in the course of evolution in plants. Therefore, the response of plants to soil trace elements should always be studied for specific soil-plant processes.

The chemical composition of plants reflects the chemical composition of the plant nutrient medium. However, the degree of expression of this relationship is extremely variable, depending on many different factors. Concentrations of trace elements in plants growing on different soils (without contamination) have wide fluctuations [6].

The main source of trace elements for plants is their nutrient medium, i.e. nutrient solutions or soils. The source of heavy metals in soils are rocks of various origins. Features of their distribution in soils are different depending on the origin and granulometric composition of the rocks. The binding of trace elements with soil components is one of the most important factors that ensures their physiological availability. In general, plants absorb readily ionic and chelate complexes dissolved in soil solutions.

According to the accepted norms, if the amount of trace elements in the soil exceeds 2-3 times the clarke quantities (average amount in soils) of these elements, it has a toxic effect, and such soils are considered contaminated [2,3].

The root system of plants is very active in transporting trace elements. Trace elements adsorbed from clay minerals are more favorable for plants. The ability of different plants to absorb trace elements is very variable: Cd, B, Br, Cs, Rb are absorbed extremely easily, while Ba, Ti, Zn, Se, Bi, Ga are poorly available to plants.

The bioavailability of trace elements (fluorine absorption) penetrated through leaves from air sources can greatly influence plant infestation. Some of the trace elements penetrated through the leaves can be washed away or transferred to other plant tissues, transferred through the roots, accumulate, etc.

Trace elements are vital for plants and cannot be replaced by other elements [6]. This is such a specific role that it affects the organism directly. They have a specific biochemical role that affects the organism directly, i.e. a number of metabolic cycles cannot occur, in short, the plant cannot live without them. There are elements that need new facts to prove their importance.

Tolerance, which is a common property of plants, is the ability to maintain viability during the excess of trace elements in the environment, mainly in the soil. This is the quick adaptation of plants to chemical stresses, although they are more sensitive to the excess of certain elements. Determining harmful concentrations of these elements in plant seeds is difficult.

Research results and discussion.

So, it has been partially shown that the ability of different plants to absorb trace elements is very variable. The article presents the results of modern research on the distribution peculiarities of a number of elements in soils, plants, etc.

Zinc (Zn) is one of the main biogenic elements. Its clarke (i.e. the average amount in the Earth's crust) is 8.3·10-3%. Its most important minerals are sphalerite (ZnS) and smithsonite ($ZnCO_3$). Zn is weakly enriched in basic eruptive rocks ($8\text{-}12{\cdot}10^{-3}$) and poor in acidic rocks ($4\text{-}6{\cdot}10^{-3}$%). Its valence is stable, it is inaccessible to plants in soils with a weak alkaline reaction. Zn is poor in sandy soils, and Zn is second only to manganese in surface water. High biophilia and flexibility in natural waters provide the important physiological importance of Zn for humans, animals and plants.

The average amount of Zn in the top layer of the soil is 6-7%, i.e. a little less than clarke, the background amount of Zn in the plant ash of the continents is $100{\cdot}10^{-3}$%. Technogenic anomalies of Zn in soils, plants and bottom sediments are contrasted and cover a significant area.

Copper (Cu) occurs in monovalent, divalent (Cu^{2+}) and free state in the Earth's crust. The most widespread in the biosphere are divalent compounds, the main minerals of which are sulfides (chalcopyrite, chalcosine, covelline, etc.). Cu is the best complexing agent among metals, sorbed easily with clay and organic colloids. Its biophilia is high, higher than that of many heavy metals (0.04). It helps in protein synthesis and photosynthesis in plants. Its amount in plant ash (dry residue) is 20-$25{\cdot}10^{3}$, or 10-15 mg/kg.

Cu participates in hematogenesis of animals, is part of enzymes as a coloring pigment (hemocyanin is part of the respiratory pigment of hemolymphs).

Cu migrates more strongly in sulfuric acid landscapes, for example, in the oxidation zone of sulfide ores, where its readily soluble sulfate – copper sulfate ($CuSO_4 \cdot 5\,H_2O$) is formed.

Nickel (Ni) – clarke is $5.8{\cdot}10^{-3}$ %. It is a siderophile element of the Earth's depths. Its highest amounts are in ultramafic rocks (20-30 KK). In acid rocks (0.1-0.3 KK. It is high in clays and shales among sedimentary rocks (1-2 KK), much less in sandstones, limestones and dolomites (0.1-0.3 KK). It occurs together with Fe and in the form of silicates, sulfides, and arsenides in the Earth's crust. Its biophilia is very low, but it is higher than that of Fe. The amount of Ni in the ash of land plants is close to or lower than the lithospheric clarke. Systemic conditions have a weak effect on the amount of Ni in plants under background conditions.

Ni is a toxic and carcinogenic element for animals. Its source is the mining of sulphide and silicate Ni ores.

Lead (Pb) – clarke is $1.6{\cdot}10^{-3}$ %.This element gravitates to the upper part of the Earth's crust – granite and sedimentary layers. Pb is a typical chalcophilic element, about 90 minerals are known – sulfides (galena) – PbS, sulfates, carbonates, etc. Migration of Pb, like other heavy metals is closely related to alkaline-acidic conditions. It is equal to $4{\cdot}10^{-3}$ % (2-2.5 KK) in the ash of dry plants. Its biological absorption coefficient is close to unit in background landscapes.

The clarke of Pb in soils is about 10 mg/kg, and it is 20-25 mg/kg in loamy and clayey soils, i.e. it is slightly higher than the lithosphere clarke. It has the weakest flexibility among heavy metals.

Lead is mined from deep underground, and its technophilicity is very high. At the same time, it is one of the main toxicants, the contrast creates man-made anomalies. Automotive pollutions produce flexible contrast anomalies of Pb in air, plants and soils.

Cadmium (Cd) – clarke is $1.3 \cdot 10^{-3}$%. It is a typical cationic chalcophilic element, close to Zn according to its properties. Poor concentrators of Cd in rocks are clay shales. It accumulates up to 2.5-1% in sphalerite. Its migration in natural waters is regulated by alkaline-acidic conditions. The biophilia of Cd is not great because of its toxicity. Its amount in the ash of land plants is 3-7 mg/kg, i.e. 30-50 KK. This shows its flexibility and accessibility to plants. Many concentrators of Cd are known – spinach, carrot, potato.

The clarke of Cd in soils is 0.3-0.5 mg/kg. It is a more toxic heavy metal and has carcinogenic properties. It penetrates into the environment through coal, polymetallic ores, phosphorites. Man-made anomalies of Cd are particularly strong in industrial cities. Its average amount in soil can reach 60 KK.

High concentrations of Cd in animals lead to skeletal deformation.

Mercury (Hg) – clarke is 3-9·10-6%. It is one of the rarest elements. Its relatively high concentrations are typical for sedimentary rocks (clays). The source of Hg for the biosphere is magma and crustal rocks. Hg is released from these during heating.

Elementary univalent and divalent forms are typical for this element in nature, which depend on the pH and Eh of the environment. The most important feature of Hg geochemistry is its formation of sulfur compounds.

Hg is easily absorbed through plants due to its flexibility up to certain levels and is close to other chalcophiles (Cu, Pb) in terms of biophilia [7].

Aluminum (Al) – is one of the most important components of the Earth's crust, it is 0.45-10% in rocks. A series of Al hydroxide compounds are formed (from $Al(OH)^{2+}$ to $Al(OH)^{-3}$) during the weathering of primary rock minerals, which later become structural components of clay minerals. In general, the solubility of Al hydroxides is low (especially at pH= 5-8).

Aluminum is a common component of all plants. Its amount is about 200 mg/kg of dry matter in higher plants. The complex nature of Al toxicity for plants is reflected in a number of interactions. In general, absorption of cations in plants decreases during Al excess. It is known that the excess of this element in plants causes Ca deficiency or weakens its transport. Its mass percentage in the Earth's crust is 0.05.

Silicon (Si) is the most common element in the Earth's crust. This element is soluble and able to migrate under some specific conditions. Quartz (SiO_2) is the most stable mineral of the soil, it occurs in a non-crystalline form - in the form of opal, the latter is named for its biological origin. According to the data, the presence of monomer silicic acid in the solution increases the sorption of cations of heavy metals (Co, Ni, Zn). In general, Si transfers readily from minerals to soil solution. It participates in H_2SiO_3 soil solution at 1-200 mg/l. Some plant species can accumulate significant amounts of Si.

Titanium (Ti) – this element is a common component of rocks, their concentration ranges from 0.03 to 1.4%. This element has valence of 4 in minerals. Ti minerals (rutile and ilmenite) are resistant to weathering. Its amount in the surface layer of the soil is 0.1-0.9% (average amount 0.35%), there is no exact information about its biochemical role. Its minerals are the most stable in the soil environment. It is considered that this element is of little value to plants and is transported poorly in them. Its mass percentage in the Earth's crust is 0.45%.

Chromium (Cr) – this element occurs in the soil in the form of Cr^{2+}, penetrates into the composition of minerals, and forms Cr^{3+} oxides. It is inert in an acidic environment (pH= 5.5), it precipitates rapidly. It is considered very stable in soils. Its behavior depends on soil pH and Eh. Organic complexes (in the soil) can also have a great effect on it. A decrease in its flexibility in soils can lead to its deficiency in plants. Chromium is an essential element of nutrition because it is vital for animals and humans. Its penetrating into soils has a positive effect on the productivity of agricultural food plants.

The occurrence of chromium in plant metabolism has not been fully proven. Its amount in plants is also controlled by the amount of its compounds that are mostly soluble in soil. Penetrating chromium into the soil leads to a significant increase in its amount in plants. Its mass percentage in the Earth's crust is 0.083%.

Molybdenum (Mo) – the distribution of this element in soils in the Earth's crust indicates that Mo is associated with granite and other acidic igneous rocks. The amount of molybdenum in soils is close to its concentration in parent rocks (bedrock). Mo is vital for plants, but its physiological demand is relatively small. It is absorbed through plants mainly as molybdate, its adsorption is proportional to the concentration of this element in the soil solution. Although Mo is actively transported from soils to plants in easily soluble forms, and some plants are considered its collectors, phytotoxicity of this element occurred in field conditions (in case of large concentrations in feed). Its mass percentage in the Earth's crust is $1.1 \cdot 10^{-4}$%.

Manganese (Mn) – this element is one of the most widespread trace elements in the lithosphere. Its amount in rocks is 350-2000 mg/kg. Its highest concentrations are usually observed in bedding rocks. Manganese forms a series of minerals in which this element occurs in the form of Mn^{2+}, Mn^{3+}, or Mn^{4+} ions. The Mn^{2+} cation has the ability to replace divalent cations (Fe^{2+}, Mg^{2+}) in a number of silicates and oxides. Manganese compounds are of great importance for the soil, because this element is important for plants, besides it controls the behavior of other nutritional trace elements.

The degree of solubility of manganese in soils depends on the pH and Eh of the environment. Its distribution in the soil layer is multifaceted. Globally, the amount of Mn in soils varies from 10 to 9000 mg/kg. Its maximum range is 200-800 mg/kg.

There are many works devoted to the processes of absorption of Mn through plants and its distribution in plant tissues. Absorption occurs as a result of metabolic processes. It is transported to plants in the form of Mn^{2+}. Its soluble forms are extracted from the soil through plants, its amount in the latter depends on the soluble concentration of this element in the soil. Toxic effects of some agricultural crops can occur in acidic soils. Its interaction with heavy metals has not been fully studied. Its mass percentage in the Earth's crust is 0.10%.

Iron (Fe) – this element is one of the main components of the lithosphere and accounts for about 5% of its mass. It accumulates in the main series of igneous rocks. The geochemistry of iron in the environment is complex and, to a large extent, it changes easily its valence depending on the physicochemical conditions of the environment. This element occurs mainly in the form of oxide and hydroxide in soils. Iron is often in chelated form in horizons of soil rich in organic matter [8].

Soil-forming minerals of iron include hematite (Fe_2O_3), magnetite (Fe_3O_4), pyrite (FeS_2) and others.

Mechanisms of absorption and weathering of iron are the main processes in providing plants with this element. Its absorption through plants occurs metabolically. The ability of plant roots to recover Fe3+ to Fe2+ provides the basis for the use of this cation through most plants.

Iron deficiency affects various physiological processes, which leads to growth retardation and reduced productivity. Also, its deficiency becomes a problem for many agricultural plants. So, adequate amount of Fe are essential for their normal nutrition. The distribution of iron in the Earth's crust – the average mass percentage is 4.65%.

Cobalt (Co) – the relative amount of Co, which is associated with clay minerals or organic matter in sedimentary rocks, ranges from 0.1 to 20 mg/kg. This element has no specific rock-forming mineral. It includes arsenic cobaltite (Co·AsS), sulfur, selenium, often iron and nickel minerals. Its geochemical cycle is closely related to Fe and Mn. Soils formed in bedrock and clay sediments have the highest Co concentrations.

The absorption of cobalt through plants depends on its mobile forms in the soil: although this element varies widely in natural conditions, its toxic effects are not often observed. Absorption of Co in soils depends not only on soil properties but also on plant species. Its average mass percentage in the Earth's crust is 4.65%.

Conclusion.

The distribution of Ni, Co and Fe in the Earth's crust is very similar. They range from 5 to 90 mg/kg in sedimentary rocks. Their largest values are typical for clay rocks and sandstones. According to its geochemical properties, Ni is a siderophile element. Ni is associated with oxides of iron and manganese in soils – and with oxides of Mn for most soils [9.10]. It is an active pollutant, penetrating into the environment as waste from metal processing enterprises. Its absorption through plants and biochemical functions are unclear. It can be assumed that this element performs certain functions in plants. It is able to form organic compounds and complexes like other divalent cations (Co^{2+}, Cu^{2+}, Zn^{2+}).

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