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Heavy Metals and their Accumulation in the Planting Areas Irrigated with Wastewater in Ganja City

Sima Hasanova[1], Sevinj Ismayilova[2] and Sayyara Ibadullayeva[3*]
[1]Azerbaijan State Agrarian University, Ganja, Azerbaijan.
[2]Baku State University, Baku, Azerbaijan.
[3]Institute of Botany of ANAS, Baku, Azerbaijan.
[*]Corresponding author email id: ibadullayeva.sayyara@mail.ru

***Abstract* – The research work is devoted to the study of the distribution of iron, manganese and nickel in the agro-phytocenosis soils irrigated with wastewater around Ganja (Republic of Azerbaijan), as well as in plant organs. For the first time, the amount of a number of heavy metals (Fe, Mn, Ni) in the soil and in the underground and aboveground parts of plants growing in those soils (in the example of Beta vulgaris) in areas with excess and deficiency of elements was determined, the features of their accumulation in vegetative and generative organs were studied. According to the obtained results, the permissible concentration of toxic metals has reached the level of use, although it does not fully comply with the norms in all organs of the plant. High amount of biogenic metals such as iron and manganese are mainly characteristic for the leaves. The fact that the elements studied in the underground parts of plants used for food are close to the norm allows us to recommend their use.**

***Keywords* – Heavy Metals, Wastewater, Agrophytocenosis, Beta Vulgaris.**

I. Introduction

Heavy metals can accumulate and migrate in the soil. Metal contaminants in the soil can be absorbed through plant roots and the tube system. Accumulation of metals in the soil affects the safety of the ecosystem and poses a threat to animals, plants and humans. High concentration of metals adversely affect the synthesis of chlorophylls in plants, weaken the stomatal resistance and can cause oxidative stress [1]. Unnaturally formed heavy metals, such as chromium (Cr) and cadmium (Cd), impair plant growth, regardless of soil or air pollution. It is likely that heavy metals enter the human body through food and cause chronic diseases such as cancer [2], affecting the central nervous system in children [3]. Heavy metals are persistent pollutants, but many of them are essential for living organisms. As microelements, they are actively involved in important biochemical processes. Under natural conditions, both soil and plants contain a certain amount of heavy metals. It is known from the literature that heavy metals can enter the human body through the food chain and cause various tumors, including malignized ones [4; 5]. When the amount of heavy metals in the soil exceeds the allowable limits, there is a danger of contamination of grass with them.

Such a difficult situation and ecotoxic heavy metals and substances (Ag, Zn, Cu, Cr, Ni, Sn, Cd, Mo, Co, Fe, Mn, B, Sr, Hg) entering the ecosystem in the form of precipitation from the atmosphere has a phytotoxic effect on the productivity of agricultural crops. As a problem arising from all this, ensuring the production of ecologically clean products in agriculture should be solved in 2 aspects: 1- agronomic and 2- ecological cleanliness of the environment.

It should be noted that heavy metals, although poorly bioabsorbed by organic matter, are constantly migrating in the food chain, and are even selectively accumulated by some plants.

According to the obtained results, the composition of wastewater discharged from Ganja to the territory of Sa-

-mukh district can be characterized as follows.

1. Mechanical composition: mechanical mixtures as an indicator of the degree of light pollution;
2. Chemical composition: partial presence of organic and inorganic substances with toxic and non-toxic effects in wastewater;
3. Bacteriological and biological composition - the presence of pathogenic microbes, fungi and small algae in wastewater.

Quantitative and qualitative indicators of the mentioned composition are seasonally different and can change. For example, during the winter months, the temperature of wastewater is relatively high, so the water discharged directly into the sewerage system becomes hotter because the urban population uses more heated water. The solution and change of chemical compounds also vary depending on the temperature factor.

The highest toxicity in the composition of wastewater belongs to phenolic compounds. Phenol compounds are also formed from oil product wastes and inorganic substances in the composition of wastewater.

Presently a number of useful arable areas in the territory of Samukh district is irrigated by means of wastewater discharged from the territory of Ganja city. Here clover as a fodder plant; wheat, barley, corn from grain-crops; beets, tomatoes, cucumbers, eggplants, peppers, potatoes, onions from vegetables; grapes, apricots, raspberries, currants and others are grown from fruit plants. It is known that juicy fruits and vegetables, especially grains, beets, carrots, grapes, etc. plants accumulate more heavy metals [6].

Phytotoxic elements in forage plants migrate in meat and dairy productsin the form of food chains. Therefore, in areas irrigated with wastewater, toxic elements are observed in excess of the norm in food of animal origin.

The effect of metal on the plant organism depends on the nature of the element, its amount in the environment, the nature of the soil, the form of the chemical compound, the duration of pollution. The amount of the same chemical elements in different organs of a plant can vary.

The mobility of heavy metals and their characteristics in the soil-plant system, as well as migration, mainly depends on the sorption capacity of the soil. It is mainly determined by the acidity of the soil, the composition of organic matter, the granulometric and mineral composition of the soil and other chemical factors. For example, as the acidity of the soil increases, the mobility of heavy metals and their translocation in plants also increases.

Soil is a natural biological formation in which the processes of constant synthesis and decomposition of organic matter take place. Circulation of substances in the soil and detoxification of various polutants from the environment occur. The main feature of the soil is the activity of soil biota affecting the quality, productivity and environmental conditions of agricultural products. Decomposition of plant residues, especially cellulose, is a process of great importance in nature and occurs due to the activity of destructive microorganisms. This process is an important indicator of the ecological condition of the soil as one of its biological characteristics.

The effect of wastewater on the plant organism, its anatomical structure and general structural features has been little studied. The conducted research mainly focused on the functional changes that occur physiologically in plants irrigated with wastewater.

The response of plants to excess and deficiency of heavy metals was determined by us and the results obtaine-

-d are presented in Table 1.

Table 1. Importance of heavy metals for plants, the reaction of plants to their excess and deficiency.

Heavy Metal	Biological Significance of Heavy Metals	Reaction of Plants to an Increase in the Concentration of Heavy Metals	The Reaction of Plants to the Deficiency of the Heavy Metals
Iron	Participates in the synthesis of chlorophyll, included in thecomposition of respiratory enzymes, regulates the oxidation and reduction of complex organic compounds in plants	Delay of growth of the top part, thickened roots, formation of very large cells as a result of disruption of division in algae	The synthesis of growth substances is delayed (auxins), light yellow leaves are formed, and then completely whitens
Manganese	It is a catalyst for respiratory processes, participates in photosynthesis, accelerates hydrolytic reactions and, as a result, the amount of amino acids increases, ensures the transport of assimilates created as a result of photosynthesis from leaves to roots and other organs.	Chlorosis of leaves, damaged stems and stalks, drying and curling of leaf tips, leaf deformation	Diseases occur in plants, the formation of spots on the leaves and in the main vein is characterized by chlorosis of the leaves, which then turn into foci of necrosis. Plant productivity decreases, growth slows down and the plant dies.
Copper	Accumulates in chloroplasts in the leaf and is involved with photosynthesis process, participates in the synthesis of complex organic compounds such as anthocyanins, ferroporphyrin and chlorophyll, stabilizes chlorophyll, protects it from decomposition, enters to the composition of protein compounds as a structural component (misproteid), forms an oxidation enzyme.	The formation of spots on the tips of the lower leaves, leaf chlorosis, restriction of root growth, the formation of barren forms with a creeping stem in some species	The hydrophility of tissue colloids decreases, growth slows down, the tops of fruit plants dry out, damaged stems lose their leaves and dry out, the fruits are small with brown spots, leaf chlorosis and staining appear, protein synthesis becomes difficult.
Zink	It is the main component of the carbonic anhydrase enzyme, accelerates the development of the root system and increases resistance to cold, heat, drought and salinity, thus, under the influence of zinc, the amount of vitamin C, carotene, carbohydrates and proteins increases.	It slows down development and causes poisoning during the violation of the technology of zinc-containing pesticides. Chlorosis of young leaves is observed. Does not accumulate when ingested excessively and is excreted	Small leaves, fine and deformed fruits, and spots on the leaves are also observed. The leaves and root system stop growing and the plant dies.

Taking into account all this, the aim is to study the accumulation of heavy metals in agrophytocenoses irrigated with wastewater.

II. Materials and Methods

Distribution of iron, manganese and nickel in the experimental lands of Samukh region irrigated with Ganja waste water, as well as in plant organs was studied.

In order to determine the degree of purity of plants in the cameral stage, expeditions were carried out in their distribution areas and the accumulation of iron, manganese and nickel in the soil, as well as in the underground and abovegroundorgans of plants was studied in accordance with generally accepted methods in populated areas. Atomic absorption method is mainly used for determination of heavy metals [7].

Biological accumulation coefficient (BAC) was calculated to reveal the characteristics of metal accumulation in plant organs:

BAC = the amount of the element in the plant the amount of the element in the soil.

When BAC > 10, the species is considered to be the concentrate of the element being studied. If 10 >BAC ≥ 1, the metal belongs to the element of weak accumulation, and if 1 >BAC ≥ 0,1, it belongs to the element of weak retention [8].

Statistical processing of data was carried out using generally accepted methods by means of Microsoft Excel 2003, Statistics 6.0 computer software package.

In the relief of the geobotanical area under study, two western and eastern strips of the foothills were selected. According to elongated tectonic zones between them there is a system of mountain ranges extending parallel to each other in the submeridional direction. The relief is mainly composed of sedimentary rocks and is characterized by a flat area. It is a specific biogeochemical province, characterized by the diversity of the polymetallic mining sector and the rare adaptation of the areas to different levels of anthropogenic impactshowever, some phytomeliorative measures have been taken in the area as contaminants sometimes lead to complete destruction of plants [9].

Technogenic wastes, biogenic metals through rivers enter the area and accumulate in riverine valleys. In relatively lowland areas, the soil is highly saline.

Extensive use of experimental planting areas, determination of ecological purity of raw materials, clarification of the accumulation of specific pollutants in plants make the research work relevant. In order to achieve the set goal, soil cutting was done in each experimental area.

After being separated into organs, the plants were dried separately in accordance with the purpose [10]. At the time, soil samples were taken from deep layers in each planting area irrigated with wastewater: drying was carried out to a light-dry state, the material was crushed and sifted through a 1 mm sieve.

The amount of iron, manganese and nickel in soil samples, as well as in the root, leaf, stalk, flower and seed of the plant was determined in the laboratory. In the same way, samples were taken from areas irrigated with clean water.

Since the normative-technical document regulating the quality of plant raw materials does not contain PCI (permissible concentration limit), we used the literature data as the permissible limits of iron, manganese and nickel in the bodies of the studied species [11].

The plant's reaction to the toxic effects and deficiency of iron is extremely variable, depending on its genotype and species [12].

III. Discussion of Experimental Results

Agrophytocenoses irrigated with Ganja waste water are mainly areas of Samukh region. The beet plant planted in different directions in this area was studied as an object of research. First of all, the concentration of iron in plants and soil was studied. Iron is essential for the formation of green leaves. Iron deficiency slows photosynthesis and respiration and causes deep chlorosis in developing leaves. High pH (>6.0) is also observed in extremely humid soils with iron deficiency, its actual insufficiency, as well as with high levels of phosphorus in the basal zone. The normal amount of iron in dry weight of grass plants is considered from 50.0 to 240.0 mg/kg, and the critical amount is 750.0 mg/kg. The background amount of iron in the soil was accepted 3800.0 mg/kg as a control [4, 13]. The response of plants to the toxic effects of iron and its deficiency is very different (or variable) depending on the species and genotype of the plant [12]. In all the studied experimental soils, the iron concentration does not reach the background amount.

Samples from four agrophytocenoses were taken for the study of heavy metals. Two of them are cenoses irrigated with clean water and the other two with waste water. The main plants planted in cenoses irrigated with wastewater were various graminaceous species, beets, various greens and pomegranate plantations. In the 1st and 2nd agrophytocenoses irrigated with clean water, the iron concentrationin the seeds of plants did not exceed the norm, and this amount was above the norm in the agrophytocenoses irrigated with wastewater.

Higher amounts of iron are characteristic of underground parts and stem. According to the results obtained, the amount of iron in plant organs decreases in the following order: underground parts > leaves > flowers > stalk (stems) > seeds.

The underground parts of the plant are characterized by a high concentration of iron and act as a barrier. In the 4th agrophytocenosis, where beets are planted, characterized by the maximum amount of iron in the soil, the main amount of iron accumulates in the leaves of the plant, ie the foliar pathway predominates in the entry of the element. This is due to air pollution with dust during the movement of vehicles on a dirt road (Figure 1).

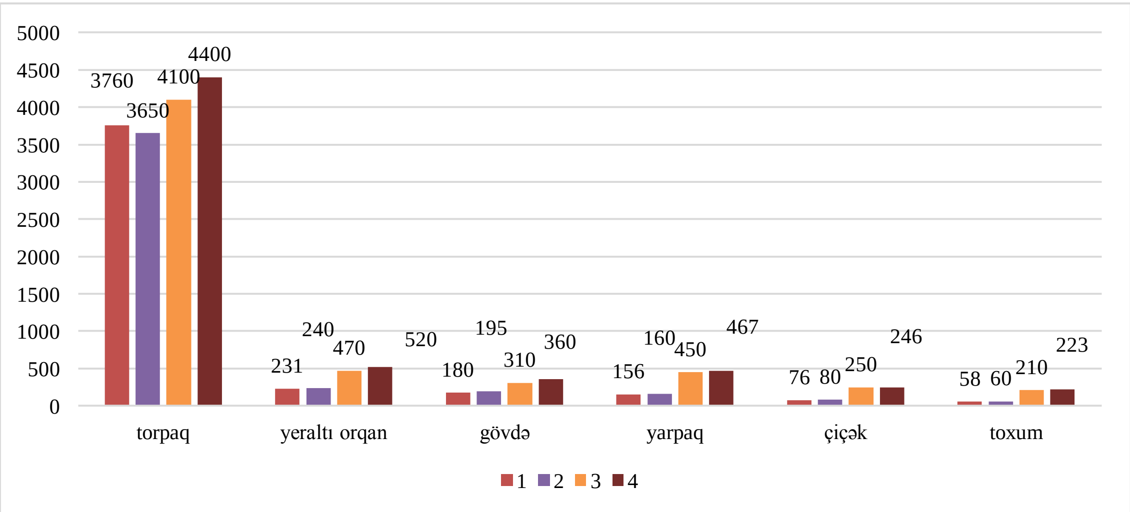

Fig. 1. Amount of iron (mg/kg) in the organs of the beet plant (*Beta vulgaris*) and in the experimental soil.

As can be seen from the figure, in agrophytocenoses irrigated with wastewater, although the amount of iron in plant organs, as well as in the soil, exceeded the norm, it did not exceed the permissible level.

The next stage of the research was devoted to the study of the distribution properties of manganese. It is known that manganese is involved in the biosynthesis of chlorophyll and increases the intensity of the process. It has a positive effect on the formation and accumulation of terpenoids, including essential oils, steroid and triterpenoid saponins, as well as cardiac glycosides, alkaloids.

It plays an important role in regulating the genetic functions of plants. Manganese plays a key role in the biosynthesis and maintenance of DNA structure in the nucleus [7].

At first glance, the high content of manganese is similar to iron deficiency and is accompanied by the formation of chlorosis between the veins in the leaves. Yellowing of leaf tissues between the veins is called intraveinal chlorosis. The main difference for these cases is that in the absence of manganese, chlorosis begins to manifest itself on the upper side of the leaf, and in the case of iron deficiency, it begins to manifest itself more on the old leaves. The normal amount of manganese for grass plants is accepted as 25.0-250 mg/kg by dry weight. Concentration (or amount) greater than 500 mg/kg by dry weight is considered toxic [10].

The amount of manganese in the soil was determined to be PCI 600 mg/kg [14]. In the agrophytocenoses 5 and 6 of the studied agrophytocenoses irrigated with clean water, the amount of manganese in the soil and in individual plant organs did not exceed the PCI, and even manganese deficiency occurred. It should be noted that the amount of manganese in plant organs is in the range of 28-150 mg/kg. Agrophytocenoses 7 and 8, irrigated with wastewater, had high levels of manganese. Foliar type is characteristic for the entry of manganese into plant organs. Therefore, the amount of the element in plant organs varies as follows: stem > underground parts > leaves > flowers > seeds (Fig. 2).

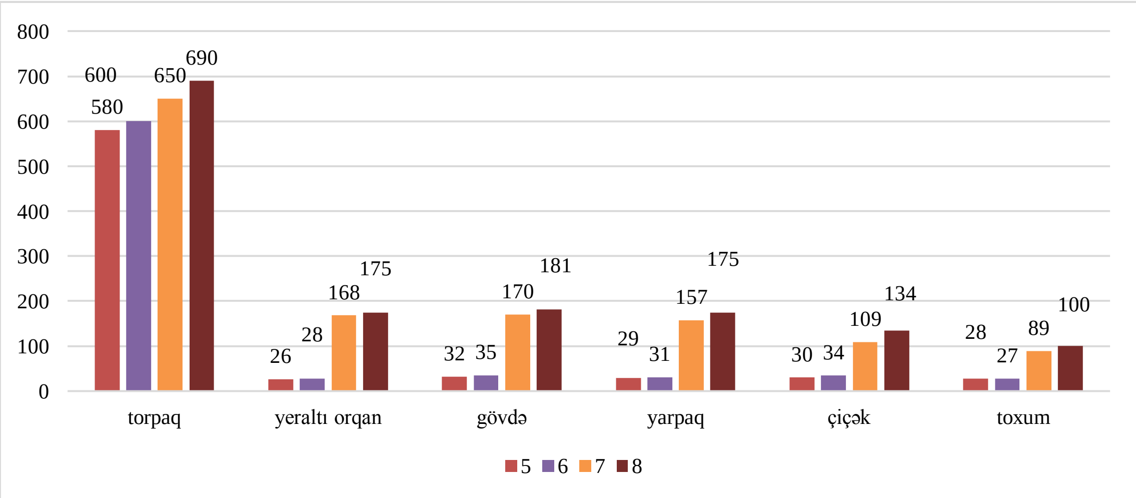

Fig. 2. The amount of manganese in the organs of the beet plant (Beta vulgaris) and in the soil (mg/kg).

Chemical elements in the soil have a complex effect on plants: they demonstrate antagonism by weakening each other’s influence or synergism by strengthening their influence. Determining the Fe/Mn ratio is crucial in assessing plant resistance to iron toxicity: For normal plant growth, the Fe/Mn ratio should not exceed 1.5-2.5, since at higher values the plant experiences manganese deficiency. In the study areas, this ratio was higher than that accepted in all plant organs (Table 2).

Table 2. Fe/Mn ratio in the organs of beet plant (Beta vulgaris).

SP	**Fe/Mn (mr/kg) in the Underground Part**	**Fe/Mn (mr/kg) in the Stalk (Stem)**	**Fe/Mn(mr/ kg) in Leaves**	**Fe/Mn(mr/kg) in the Flower**	**Fe/Mn(mr/kg) in the Seed**
1	43,4	34,4	15,5	24,9	22,7
2	18,0	32,2	9,65	20,8	-
3	13,7	27,0	36,6	22,2	-

SP	Fe/Mn (mr/kg) in the Underground Part	Fe/Mn (mr/kg) in the Stalk (Stem)	Fe/Mn(mr/ kg) in Leaves	Fe/Mn(mr/kg) in the Flower	Fe/Mn(mr/kg) in the Seed
4	21,9	45,5	59,7	21,0	22,0
5	19,0	33,1	30,6	13,9	7,2
6	13,3	26,4	5,5	15,5	8,6
7	26,8	18,3	10,7	20,0	53,1
8	17,7	10,4	4,5	28,3	14,3

SP-senopopulation.

Finally, change in the amount of nickel were investigated in the study. According to the literature, nickel is involved in the structure and function of DNA, RNA and proteins, as well as in the hormonal regulation of the body. Excess nickel in the plant inhibits the processes of photosynthesis and transpiration, signs of chlorosis appear on the leaves. The toxic effect of the element on living organisms is accompanied by a decrease in the activity of a number of iron enzymes, disruption of the synthesis of DNA, RNA and proteins, and damage to many organs and tissues.

The amount of nickel in the soil is PCI-85 mg/kg [14]. The biological content of nickel in plant organs and soil was determined in the range of PCI-85 and 80 mg/kg, respectively [10]. The results of the analysis are shown in the diagrams for agrophytocenoses 9, 10 irrigated with clean water and 11, 12 irrigated with wastewater (Fig. 3).

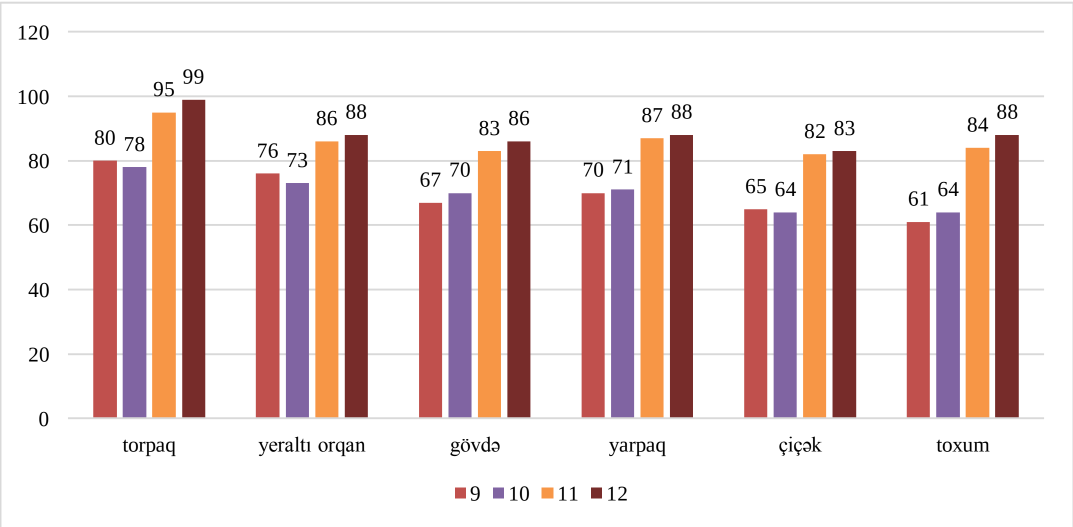

Fig. 3. Amount of nickel (mg/kg) in the soil and in the organs of beet plant (*Beta vulgaris*).

The amount of Ni in both soil and plant organs (9 and 10) irrigated with clean water was almost below normal. In soils and plants exposed to wastewater, the PCI was moderately higher than normal, but this amount did not have a toxic effect on organs and tissues, especially the underground parts of the plant with nickel content of 82-88 mg/kg. According to the results, the amount of nickel in all organs of the plant practically corresponded to the required standards.

Thus, according to the results obtained, the amount of heavy metals in the soil is not toxic, and vegetables and greens grown in these areas can not harm the human body. However, from a microbiological point of view, the accumulation of helminths, viruses and protozoa on plants can be observed. In order not to become infected with various diseases or intoxication when eating fruits and vegetables irrigated with wastewater, their toxicity or pathogenicity can be prevented if, after washing, the plants are kept for several hours in vinegar.

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AUTHOR'S PROFILE

First Author
Sima Hasanova, Scientific Worker, Department of Ecology, Azerbaijan State Agrarian University, Ganja, Azerbaijan. Contact: +994558434454. email id: sima1982h@gmail.com

Second Author
Sevinj Ismayilova, Phd, Associated professor, Department of Plant Physiology, Baku State University, Baku, Azerbaijan. Contact: +994502346633. email id: sevinc.abduyeva@gmail.ru

Third Author
Sayyara Ibadullayeva, Doctor of science, professor, General Director Institute of Botany of Azerbaijan National Academy of Science. Contact: +994558231571. email id: ibadullayeva.sayyara@mail.ru