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Selenium is a toxicant or antitoxicant

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ABSTRACT

The article deals with the issues of selenium content in plants, soil and human body, toxic and antitoxic properties of selenium. The studies were carried out on dried raw materials harvested in 2019 and 2021: stems, flowers and leaves of blueberries, chamomile, linden and oregano. The content of Se and other elements (Al, Fe, Mn, Ti. B, Pb, K, Mg, Ca, Zn, As and Cu) were determined both in plant material and in the soils of eastern Georgia (Abastumani) and western (Khulo), as well as in the hair of people living in this territory. The dependence of the selenium content on the type of plant and the time of its collection, the type of soil and distribution area was established, and an analysis was made of the Se coupling in these territories inhabitants hair. The influence of selenium on the accumulation of heavy metals in the objects of study was determined. It has been established that the largest amount of selenium is contained in the linden leaf, and the smallest – in the oregano leaf; selenium content increases in the order: leaf>flower>stem; the content of selenium in the soil of eastern Georgia (Abastumani) is 13 times higher than that in the soil of western Georgia (Khulo): Abastumani (0.051 μg/l)≫Khulo (0.039 μg/l). It has been established that selenium accumulates in the hair: the amount of selenium in the hair of a young girl (0.152 μg/l) is 70% higher than in the hair of a 60-year-old woman (0.055 μg/l). A high selenium to iodine ratio indicates gout and diabetes. It was found that an 18-year-old girl developed hypothyroidism due to an excess of selenium. It has been established that the amount of calcium and potassium is 2–5 times higher than the amount of magnesium. A relationship has been established between the content of selenium and lead: with an increase in the amount of lead, the amount of selenium sometimes decreases almost to a trace amount. In the objects of study, the amount of lead is 100-200 times higher than the amount of selenium. The largest amount of aluminum is found in the leaf, flowers of linden and oregano, the smallest – in the leaf of chamomile, iron in the flowers, and manganese in the leaves of the lind. The relationship between the content of selenium and arsenic, iron, phosphorus, zinc and manganese has been proven. An increase in phosphorus, zinc and manganese content reduces iron absorption and an increase in arsenic content causes a decrease in selenium content.

Keywords: heavy metals, selenism, elemental analysis, plants, toxicity.

INTRODUCTION

Global changes in the state of the environment also affect wild medicinal plants, therefore, since the last century, medicinal plant raw materials have become the object of environmental research. When using herbal medicines, the human body receives not only a complex of biologically active substances, but also a whole range of chemical elements that have a complex effect on it. They maintain the normal course of metabolism, and have high biological activity; however, potentially toxic compounds, in particular heavy metals, in high concentrations can be dangerous to human health. The study of the elemental chemical composition of medicinal plants is not only of great practical importance, but also helps to understand the influence of the environment on the plant adsorption of different forms of metals and non-metals. It is becoming very relevant to study the patterns of content, accumulation and distribution of the widest possible range of chemical elements in medicinal plants of various regions and to create a database on their elemental chemical composition. Also, research on medicinal plant raw materials growing in anthropogenically transformed areas is acquiring great theoretical and practical significance, which may further expand the raw material base of wild medicinal plants [Skorinova et al., 2020].

Currently, medicinal plant growing is developing very intensively, but in some cases, there is a deficiency of materials because of industrial and traffic pollution in towns and nearby areas [Kieliszek and Błażejak, 2016]. Organisms (animals and plants) are concentrators of chemical elements from soil, water and food. Plants are very sensitive to the microelements concentration in substrate because of they cannot withstand the penetration of high, often non-physiological amounts of metal ions into them [Duntas and Benvenga, 2015]. Despite the ability of selection, roots are constantly forced to assimilate heavy, undesirable and indifferent ions in certain quantities in conditions of their excess, when they are available for assimilation. Therefore, there is a positive correlation between the ion excess in substrate and their influence on plants. The concentration of chemical elements by plants depends on the presence in soils of elements whose salts are absorbed and accumulated by all plants living on these soils; the ash of such plants contains an increased amount of these elements.

Selenium is a trace element that is part of some enzymes and another proteins [Hanafi et al., 2022]. Selenium is a cofactor of glutathione peroxidase, which ensures the neutralization of free radicals in the body, and also protects the structure and functions of the cell membrane from damage. Cellular antioxidant enzymes prevent the formation of oxidative stress and the development of various diseases [Shahmiri et al., 2022]. Selenoproteins are part of iodine-thyronine and iodinase, so they normalize the synthesis of hormones by thymus. Se is also involved in immune response regulation and supplies the fertility. In recent years, it has been proven that Se takes an essential part in cancer protection of human's organism [Deepa and Lingappa, 2014].

Selenium – an antitoxicant – is an antagonist of As, that's why helps to protect from the action of heavy metals: Cd^{2+}, Pb^{2+} and Hg. According to studies, 80% of the population is deficient in selenium. There is another side to this problem, selenium as an antitoxicant can also be a toxicant, since in large doses it causes poisoning – the development of selenotoxicosis. Selenium enters the human body through food, drinking water and precipitation. Based on the foregoing, selenium, on the one hand, is a necessary element for the human body – an antitoxicant, and on the other hand, a toxicant, as it causes and contributes to the development of various types of serious diseases [Pandey et al., 2020]. Therefore, it was of practical and scientific interest to study the elemental chemical composition of medicinal plants, the soils of various regions in which they grow, and the hair of people living in these regions, that is, the study of the chain: soil – plant – person.

Selenium enters the human body through food and drinking water. The maximum daily and nightly dose is 300 mcg, for men – 70, for women – 55 and for children – 10–50 mcg [Hassan et al., 2020]. In adults, this is manifested by myxedema, in children – by violations of growth and development. Selenium deficiency can cause pancreatic fibrosis, bronchial asthma, diseases of the vascular system and other pathological conditions; Selenium deficiency leads to osteoarthritis, impaired growth of joints and bones [Xuan et al., 2020].

Selenium intoxication is manifested by the formation of a garlic taste in the mouth, palpitations, hair loss, brittle nails, dermatitis, and damage to the nervous system [Xia et al., 2015]. Selenium deficiency occurs in the human body if the selenium content in the soil is low. The reasons for the low level of selenium in the blood are: lack of selenium in food and water, alcoholism, unbalanced diet and increased consumption of selenium in the body [Bhattacharjee et al., 2017; Mary et al., 2016.].

The Se/I ratio of selenium and iodine in food and water directly depends on their ratio in the soil and naturally affects the content of selenium and iodine in the body of animals and humans (blood, hair, etc.). It was established that the Se/I ratio varies within 8–16; deficiency of these two trace elements provokes the development of endemic gout [Khurana et al., 2019]. Selenium concentration varies in surface and rainwater: the selenium content in surface water is determined by atmospheric precipitation and soil selenium [Mojadadi et al., 2021]. It has been established that arsenic and sulfur have a negative effect on selenium, since they reduce its binding to biological structures, thereby reducing the biological activity of selenium, while hydrochloric and ascorbic acids promote the absorption and circulation of selenium in the body [Biryukova, 2017].

It has been established that selenium deficiency in animals causes the same diseases as E-avitaminosis [Guan et al., 2019; Kumar and Prasad, 2021]. Selenium performs the following functions in the body: catalytic, structural, regulatory, interaction with vitamin enzymes. Participates in redox processes in the metabolism of fats, proteins and carbohydrates. The addition of selenium increases the activity of the diet, in particular the activity of the liver, heart, lungs, pancreas, and other organs [Xiao et al., 2023; Prilepsky, Yu et al 2019; Liao et al., 2021; Ranjbariuan et al., 2022].

Selenium is often enriched in food as a food additive, for example, they produce special bread and confectionery – croutons. Also, selenium is preliminarily introduced into yeast: 38 µg of selenium per 100 g [Mehanna et al., 2022]. For maximum activity of body tissues, the required rate of selenium is 0.85 mcg/1 kg of body. Men, unlike women, need more selenium, and if mother's milk is replaced with cow's milk, then the newborn's body lacks selenium. Stress, smoking, and drinking alcohol reduce selenium levels. Selenium is a part of pharmaceutical preparations, there are selenium capsules, liquids and tablets [Huang et al., 2014]. The content of selenium is higher in soils of volcanic origin and lower in clays. In acidic moist soils, there is more selenite (Se^{+4}) with iron and aluminum; it forms insoluble inactive complexes, as a result of which selenium becomes inaccessible to plants [Nasrolahi Shirazi et al., 2014; Loeschner et al., 2014; Pi et al., 2013].

The concentration of selenium in the soil depends on the type of soil and its genesis. As a result of research, it was found that the amount of selenium in the treated soil is reduced by 30%, in the untreated soil it is much more. This is due to the loss of humus and calcium from the soil as a result of anthropogenic impact [Gao et al., 2014; Cui et al., 2018.].

MATERIALS AND METHODS

Objects of study

This research was made on raw materials collected in 2019 and 2021 in two regions of western Georgia (Guria – Bakhmaro resort and Adjara – Charnali). The raw materials were dried under natural conditions. The analysis was carried out in prepared, dried raw materials, in particular, in the stems, flowers and leaves of blueberries (blueberries and Caucasian blueberries), chamomile, linden and oregano. Linden and oregano were collected in Adjara, the rest of the raw materials were collected in Guria.

The content of Se and metals Al, Fe, Mn, Ti. B, Pb, K, Mg, Ca, Zn, and Cu were determined both in plant material and in the soils of eastern Georgia – Abastumani and western – Khulo, as well as in the hair of people living in this territory (Fig. 1).

Research methods

The dried plant parts were ground into powder in a mortar; after that 500 mg of sample powder was taken and 8 ml of methanol was added for extraction. The mixture was subjected to ultrasonic disintegration at room temperature for 30 seconds at an amplitude of 60 %, immersing the rod of the disintegrator into the suspension. The obtained disintegrate was centrifuged at 1000 g for 3 minutes. The supernatant was collected and filled to a volume of 10 ml with methanol. Later, a 600 µl aliquot was taken and dissolved in 10 ml of distilled water. 5 ml of the tested solution was taken and transferred into a chromatographic vial with a sprayer. Analytes were purified by a flow of helium, which was supplied through an aqueous solution, at a rate of 40 ml/min at 35 ºC for 6 minutes. The separation was carried out by the method of gas chromatography. Before entering the gas chromatograph, the analytes, after passing helium, were fed to a column with silica gel and activated carbon (Tenax GC, 30.5·0.31 cm) at a temperature of 40 ºC. After concentration, the volatile compounds of Selenium were desorbed (within 3 min), raising the temperature to 210 ºC. The purification system was connected to the gas chromatograph, so the purified analytes were fed directly into the injector. Gas chromatography was performed on Agilent 6890 equipment, which is directly connected to an atomic emission detector. Injection temperature – 250 ºC; capillary column – Agilent DB-624 (30 m·0.32 mm·1.8 µm); carrier – helium with a flow rate of 4 ml/min; program – 40 ºC, 2 minutes – 150 ºC with a step of 20 ºC, 30 seconds. Emission detection conditions: the reagent was hydrogen, supplied at a pressure of 0.6 Bar; purging of the spectrometer – nitrogen with a flow rate of 2.5 ml/min; helium supply flow – 60 ml/min;

Figure 1. Plant objects of study

temperature -–250 ºC; the detection wavelength of Selenium was 196 nm. The obtained primary data was calculated by ChemStation G2360AA GC-AED software. Another cations content had been determined by analogy.

The dependence of the content of selenium and metals on the type of plant and the time of its collection, soil type and distribution area were studied, and determination of the cations quantity in the hair of residents was carried out.

RESULTS

The accumulation of selenium occurs in plants in which it comes from the soil, in the population living in areas with a high content of selenium, it accumulates in the hair. Based on this, the content of selenium and metals (Al, Fe, Mn, Ti. B, Pb, K, Mg, Ca, Zn and Cu) in plants was determined depending on the nature of the plant and the time of its collection. , in the soil, depending on its geographical location, namely the western (high-mountainous Adzharia – Khulo) and eastern (Abastumani) regions of Georgia, as well as selenium was determined in the hair of women living in these regions.

Figure 2 shows and compares the obtained data on the content of selenium in plants. As follows from the data obtained, the highest selenium content is in linden leaves collected in 2019 (0.174 μg/l), and the lowest is in oregano (0.03 μg/l). It has been found that the amount of selenium in chamomile leaves is 12% higher than in the stem, and when comparing the flower and leaf, the selenium content varies from year to year.

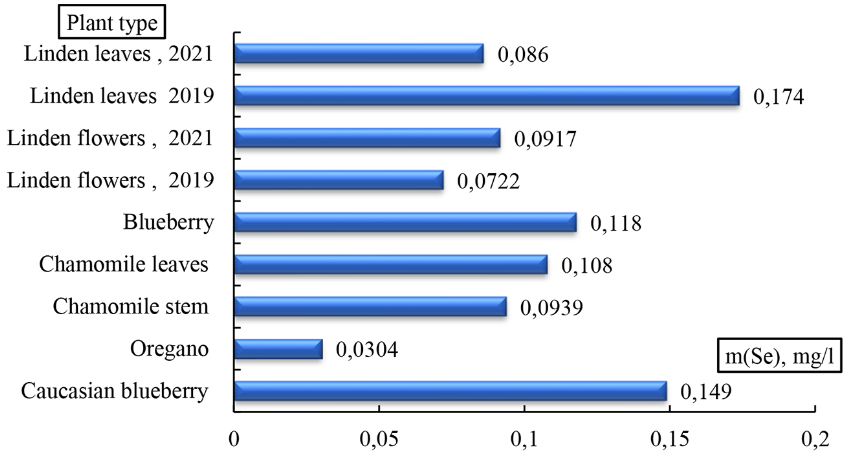

Figure 2. Selenium content in plants

It was found that the selenium content in linden leaves from the 2019 harvest (0.174 μg/l) is 2.5 times higher than in flowers (0.072 μg/l).

It follows from this that if a person uses the linden plant as an antipyretic, he should prepare a tincture from the linden leaves collected in 2019, since they contain 70% more selenium than the flowers. In 2021, according to the data obtained, the selenium content in the leaf and flower is almost the same: in the flower (0.092 μg/l) and in the leaf (0.086 μg/l). The smallest amount is found in the oregano plant (0.03 μg/l), which cannot be used to compensate for selenium deficiency, since its amount is less than the daily requirement.

Selenium deficiency occurs in the human body if its content in the soil is low. Therefore, at the next stage, the selenium content in the soil was determined, namely in the soils of the western (high-mountainous Adjara – Khulo) and eastern (Abastumani) regions of Georgia (Figure 3). Abastumani soil belongs to brown soils – this is a type of soil with a brown, gradually lightening color downwards, formed at variable conditions of humidity and temperature with flora resistant to permanent drought. This type of soil has also been formed under steppe forbs with xerophytic shrubs.

In terms of mechanical composition, brown soils are heavy; clay formation occurs in them at a depth of 0.3–0.6 meters, as a result of which the soil is saturated with calcium, which reaches up to 90% in the upper horizons. Soil acidity (pH) is neutral and as you move down the profile, the pH increases to alkaline. The amount of organic stuff is about 5%; it penetrates more than 100 cm inside. Thanks to the deep penetration of humus, a significant part of brown soils has high fertility.

The soil of high mountain Adjara (Khulo) is sandy. It contains 3–5% clay and more than 90% sand. Such soils, like a sieve, allow moisture to pass through, and with-it nutrients. Such soil is not fertile because it does not contain humus, that is, calcium, phosphorus and nitrogen, elements necessary for

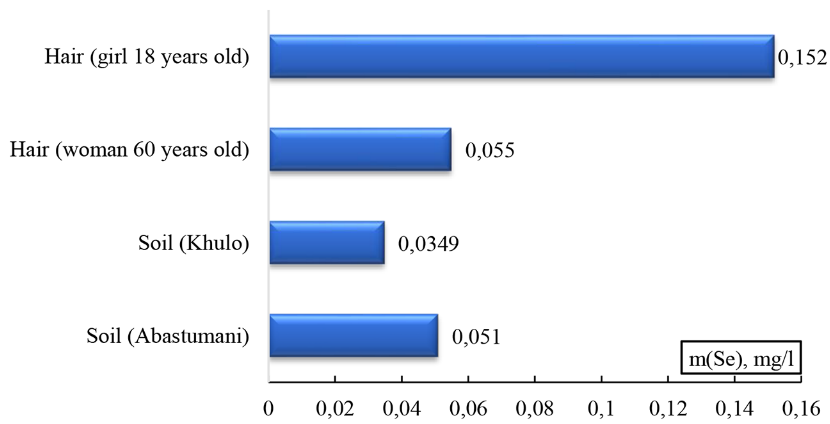

Figure 3. Selenium content in soil

plant growth. Selenium is located discretely in the soil: the amount of selenium in chernozems is higher than in silty soils, and, accordingly, the selenium content in plants grown on these soils is higher and corresponds to its content in the soil [Khan et al., 2019; Wang et al., 2016].

It was determined that the content of selenium in the soil of Khulo is only 0.039 μg/l, and in the soil of Abastumani – 0.051 μg/l, which is 13 times higher than the level of selenium in the soil of Khulo. In other words, people living in the highlands of Adjara will have a selenium deficiency.

The Se/I ratio of selenium and iodine in food and water directly depends on their ratio in the soil and naturally affects the content of selenium and iodine in animals and humans, that is, an excess amount of selenium accumulates in nails and hair. To do this, the authors analyzed women's hair for selenium content. It has been established that the amount of selenium in the hair of a woman living in Khulo for 60 years is less than the norm, which corresponds to the amount in the soil, which is why she has low immunity and complains of constant colds and inflammations.

As for an 18-year-old girl living in the same area, an increased selenium content (0.152 μg/l) – 3 times more than the norm, means the development of selenism in her body. As a result, she developed hypothyroidism. According to the literature, with an increase in the ratio of selenium and iodine, she may later develop diabetes mellitus and gout.

It is known that arsenic and selenium are antagonists, so the arsenic content in the soil was also determined [Yazdi et al., 2015].

According to the data obtained, the arsenic content in the soil is 20–23 times higher than the selenium content

This confirms the view that arsenic and selenium are antagonists. In soil where the arsenic content is high: 0.995 mg/l (Abastumani) and 0.786 mg/l (Khulo), the selenium content, on the contrary, is very low and amounts to 0.051 mg/l (Abastumani) and 0.035 mg/l (Khulo). Arsenic reduces the binding of selenium to biological structures, that is, it reduces its biological activity.

According to the data presented in Figure 4, in the soil of Abastumani, the amount of a toxic element – arsenic and non-toxic selenium – predominates, that is, selenium exhibits biological activity to a greater extent in the soil of western Georgia (Khulo).

Other elements were also determined in the samples. Figure 5 shows the content of zinc and copper in the research objects. Zinc is one of the most beneficial and necessary elements for the body. It affects several processes at the same time, in particular, it regulates the work of the immune system, promotes hair health, increases testosterone levels in the male body, regulates skin problems and sugar levels, participates in insulin secretion, stimulates collagen production, increases skin elasticity. The ions of Zn^{2+} are involved in some processes of hormones, acids and proteins formation.

It is established that the amount of zinc in hair is very high – practically 90–100% higher than the amount in other research objects and in the soil of Abastumni. The maximum amount of selenium was recorded in the hair of an elderly woman (94%), 20% less amount was recorded in the hair of a young girl and 37.9% in the soil of Abastumani. Copper is a vital (essential) microelement that maintains immune response, provides the protection against inflammation, inhibits the autoimmune reaction, binds toxic bacterial and fungal

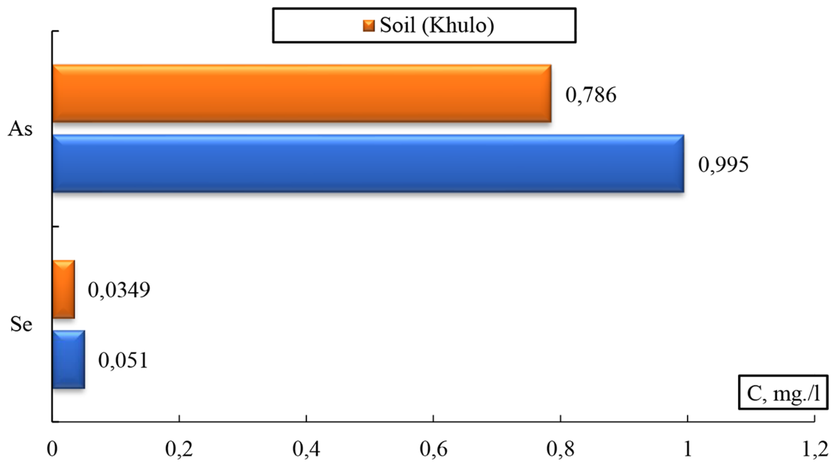

Figure 4. Selenium and arsenic content in soil

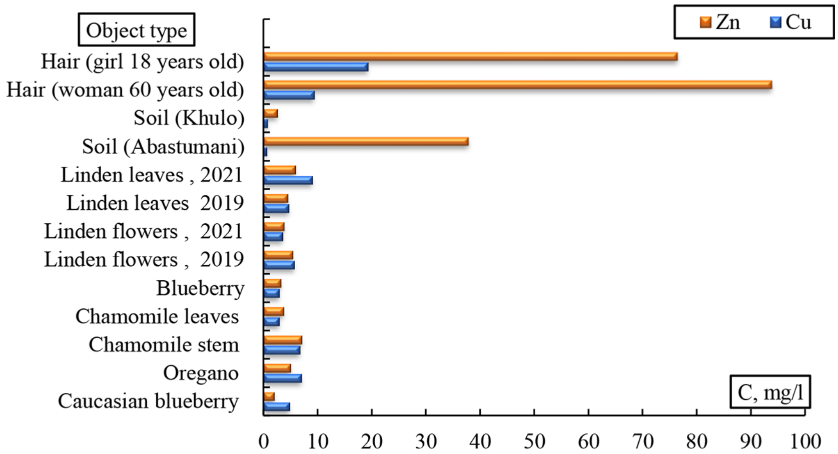

Figure 5. Dependence of Zn and Cu content on the type of research object

compounds, enhances the antibiotic action and alleviates ferric absorption. In different ionic forms – Cu^{2+}/Cu^{+}– these ions are able to make complexes with amino acids as well as another bioactive compounds. That's why copper is also represented as enzyme cofactor. In plants, together with sulfur, Cu^{2+} alleviates the N_2 fixation [Semenova et al., 2019; Karnaukhova et al., 2018].

The concentration of free copper in the cytoplasm is extremely low. The daily requirement is 2–4 mg of copper per day. The upper tolerable level of copper intake is 5 mg. When the copper supply falls less one mg per day – it leads to Cu^{2+} shortage. At the same time, Cu^{2+} income more than 0.2 g per day is toxic for human body.

As for the copper content, its amount is significantly less than its competing zinc. In the studied soils the copper content is less than 1 mg, that is, plants and people living on these lands will experience a copper deficiency. Unfortunately, copper deficiency causes anemia (loss of Fe^{2+} assimilation), diseases of joints and bones, decreased skin pigmentation, neurological disorders, cardiac dysfunction.

The maximum amount of copper contained in the hair of a young girl (19.3 mg) is significantly, 3.9 times higher than the upper permissible level of copper intake – 5 mg, which can cause serious complications as a result of the toxic effects of copper. Unfortunately, in a number of studied objects, in particular, leaves of linden (9.0), chamomile (6.74) and oregano (7.03), the copper content is also 1.5–2 times higher than the upper permissible level of copper consumption. These data should be taken into account when preparing and consuming medicinal decoctions from these leaves.

Great importance is attached to the content of the elements potassium and magnesium in the human body, since they strengthen the cardiovascular system. The daily intake of potassium is 2500–3500 mg/day, magnesium – 400–420 mg/day. Potassium transmits nerve impulses and is necessary to maintain the acid-base balance in the blood. With a lack of magnesium, neuromuscular tension increases and heart rhythm is disrupted. Some foods contain acetic acid and phytic acid, which react with magnesium and form salts that are not absorbed by the body [Karnaukhova et al., 2018].

Ca^{2+} is critically important ion for metabolism supply. The amount of calcium in human body is about 1.8 %. Different cells of plants and animals require the proper ratio of sodium, potassium and calcium cations in extracellular environments. According to Ca^{2+} demand, the plants are divided into calcephiles and calcephobes. The ions of calcium mediate membrane transport and blood coagulation cascade, stimulate muscle fiber contraction, activate some enzymes as cofactor, increase the heart rate, activate the phagocytosis by immune cells. Ca^{2+} ensures the supporting function of bones. Calcium deficiency is the cause of almost 150 diseases. The recommended daily intake is approximately 800 mg of calcium [Boulis et al., 2023].

On Figures 6–7 show the determination of K, Mg and Ca in the objects of study. It was found that in all samples the content of calcium and potassium is significant, 2–5 times higher than the amount of magnesium. The highest amount of calcium and potassium is recorded in linden flower. The amount of magnesium in the leaves and flowers of plants is almost the

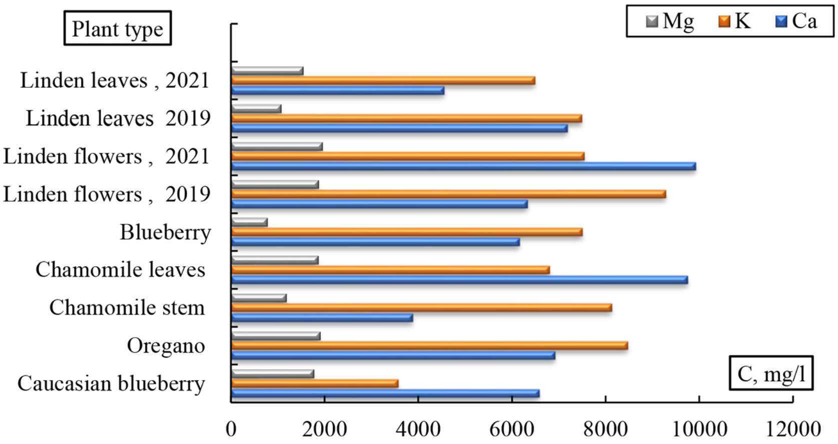

Figure 6. K, Mg and Ca content in plants

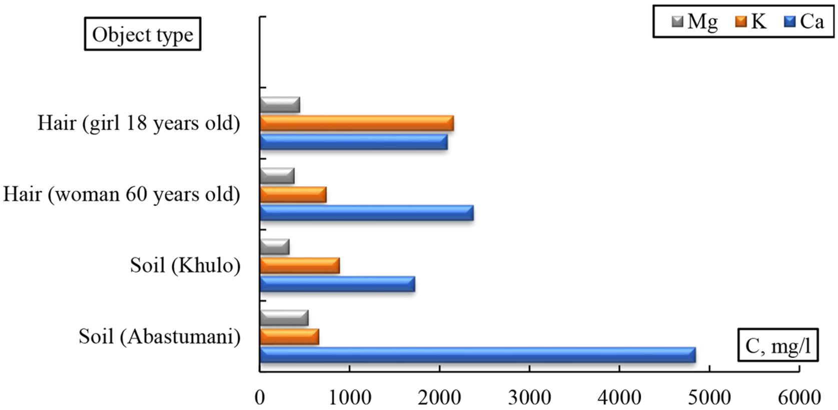

Figure 7. K, Mg and Ca content in soil and hair

same. As for soil and hair, the same distribution of Ca>K>Mg is maintained.

Installed, that in the soil of Abastumani the calcium content is 2.8 times higher than in Khulo, the potassium content in the soils differs by 20%, the amount of magnesium in the soil of Abastumani is 60% higher. The results obtained correspond to the nature of the soils: the soil of eastern Georgia (Abastumani) is brown, fertile, rich in essential elements, which from the soil will enter the plants and then into the human body.

For estimation the nutrient body state, the calcium amount in samples of urine, skin appendages and blood has been determined. Because of hair accumulates Ca^{2+} for extended time, the concentration of calcium in hair is a significant index for determination of chronic calcium metabolism discord. The chronic diseases caused by calcium lack are osteomalacia, sarcopenia and osteoporosis [Skalny et al., 2023]. Installed: a young girl's hair contains equal amounts of calcium and potassium, while a woman's hair contains 30% more calcium than potassium. The magnesium content in both types of hair is almost the same.

Figure 8 shows the relationship between selenium and lead levels. It has been established that the content of selenium and lead are interdependent, in particular, if the amount of lead in the test object increases, then selenium decreases, sometimes to trace amounts, since selenium binds lead, reducing its negative effect.

Based on the data obtained, it was established that the amount of lead in the research objects is 100–200 times higher than the amount of selenium, and titanium is significantly less than the amount of lead. Sugar slows down the absorption of selenium, and by reducing the boron content, the processes of formation and absorption of sugars slow down, that is, selenium and selenium are interrelated in this process. Therefore, it was important to determine the boron content in the studied objects [Blaurock-Busch et al., 2012].

Boron is the most important microelement for plants. It is classified as a conditionally essential

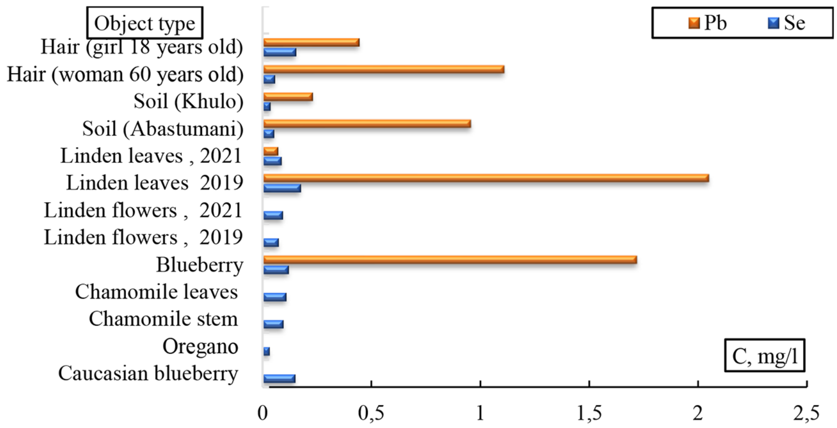

Figure 8. Relation between selenium and lead

element, biologically useful for humans. Boron deficiency is often detrimental to plants. Responsible for the formation of sugars [Namkoong et al., 2013]. Under the influence of boron, the formation and transport of sugars from leaves to fruiting organs and roots are improved.

It also promotes better use of calcium in metabolic processes in plants. Boron, together with calcium, participates in the formation of the plant cell wall; the plant spends 90% of the boron coming from the soil on this. Plays an essential role in fertilization processes. Many functional diseases of cultivated plants are caused by insufficient amounts of boron [Batyrova et al., 2021; Mutonhodza et al., 2022; Li et al., 2021].

The boron content in plants varies greatly in different species of plants and their growing conditions (Figure 9).

The risk of boron deficiency occurs in sandy soils, which are initially acidic, and whose pH level has been excessively increased by the addition of lime (pH>6.5). The author's data confirms this fact: the sandy soil of western Georgia (Khulo) contains only 0.377 mg/l, while the brown soil of eastern Georgia (Abastumani) contains boron an order of magnitude higher (2.03).

Hair accumulates boron and therefore serves as a good biomaterial for assessing long-term exposure to this element. It is believed that the concentration of boron in the hair reliably reflects its concentration in the body, but it is possible that boron can enter the hair from external sources, for example, from boron-containing shampoos, dyes and other hair products. The study of boron content in hair is used to assess the microelement status of the body and to diagnose possible boron intoxication.

Oversaturation with boron causes hair loss. It has been established: women's hair does not contain boron, on the one hand they are not at risk of hair loss, but on the other hand, the absence of boron in the hair is an indicator of its absence in the body of these women, which is undesirable for their health. The content of aluminum, iron and

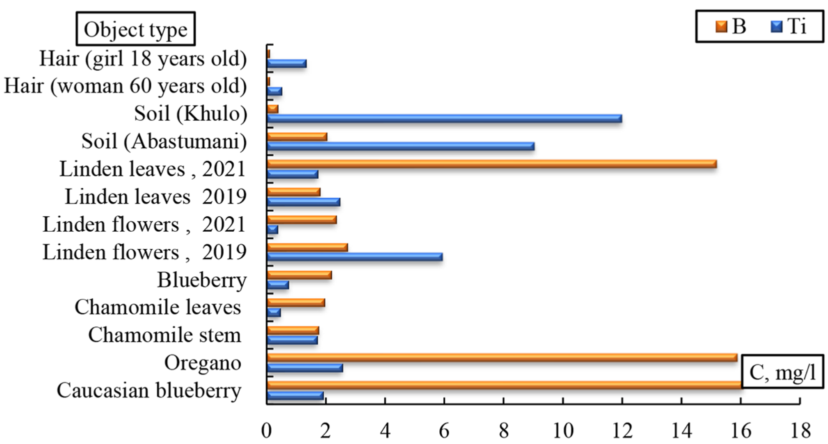

Figure 9. Boron and titanium content in research objects

manganese was also determined (Figure 10). To date, there is no any data proving the Al^{3+} necessity for plant metabolism. In some cases it has been detected, that excess of Al^{3+} concentration about 0.001 g/l is harmful for plants, mainly in the first period of their life. The effect of aluminum is associated with the introduction of phosphorus.

It has been established that the aluminum content is several orders of magnitude lower than the phosphorus content, which confirms the interaction of phosphorus with aluminum and the formation of insoluble salts, from which aluminum does not enter plants. The greatest amount of aluminum is contained in soils, for example, the soil of the western region of Georgia – Khulo contains 1540 mg/l Al, and the soil of Abastumani – 984 mg/l, respectively, the phosphorus content in these soils is ~3 times lower. In plants with a high phosphorus content, the aluminum content is an order of magnitude lower and in some cases reaches trace amounts. As for hair, the content of both phosphorus and aluminum is low, but it should be noted that the hair of a young girl contains these elements in equal quantities, and in a woman's hair the phosphorus content predominates (223 mg/l), it is ~3 times higher than the aluminum content (80.9 mg/l).

Manganese supports the processes of photosynthesis and respiration, carbohydrate and protein metabolism, and is necessary for the synthesis of ascorbic acid and sugars.

This element is involved in chlorophyll formation, immune response, nitrogen accumulation from nitrate salts: the higher the level of nitrogen nutrition, the more manganese is needed for plants; it increases the plant's resistance to adverse factors. Mn cations are also responsible for the fruits taste, crops development and seeds maturation. But critically high concentrations of manganese are harmful for plant metabolism.

Most of the manganese is in the form of sparingly soluble compounds. Low acidity and high humidity are the reasons of lack of available Mn cations. According to the data obtained, the studied objects have a high content of Ca^{2+}, Mg^{2+}, PO_4^{3-}, Cu^{2+}, Zn^{2+}, K^+ and Fe^{2+}. In these conditions, the adsorption of manganese become complicated. Under high Ca^{2+} concentration, the ions of Mn^{2+} transform into MnO_2, which becomes inaccessible for plant accumulation.

Iron is a vital element for plants, involved in the process of photosynthesis and accumulated mainly in the leaves. It plays a role of enzyme cofactor and is involved in processes of SO_4^{2-} and NO_2^- restoration, nitrogen fixation, synthesis of proteins and chlorophyll, plant respiration and photosynthesis. The ferric lack manifests in chlorophyll destruction: leaves and shoots become pale and yellow, with brown areas. The apical point growth surceases. The ferric absorption is readily available only in Fe^{2+} oxidation stage, but not in Fe^{3+}.

Excess iron can have a toxic effect – decay of nucleic acids, proteins and lipids at conditions of extremely low acidity. At the same time, in conditions of over high soil humidity, the Fe^{2+} ions are oxidized into Fe^{3+}. In this form, ferric cations reach the critical concentrations and damages the roots. Excess of Fe leads to a deficiency Mn and P because of these elements accumulation blocking. Iron and its compounds are among the most important components of the chemical composition of soils.

According to the classification of geochemists, iron is a siderophile element. These elements

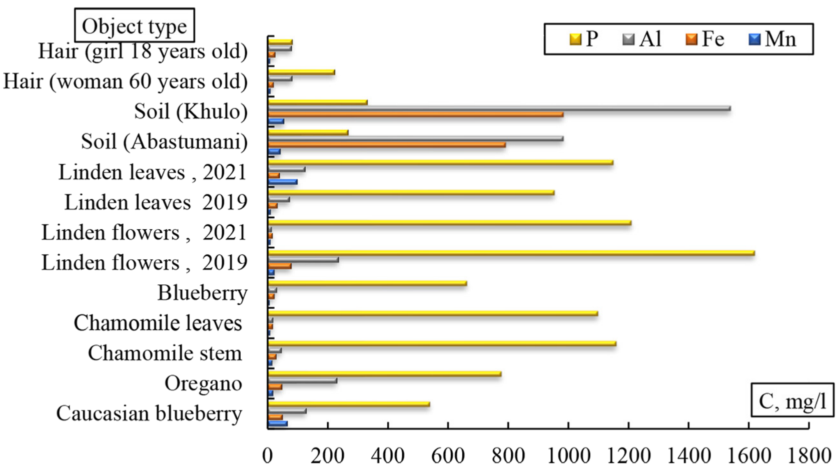

Figure 10. Al, Fe, P and Mn content in the research objects

include, in addition to iron, its satellites: cobalt, nickel, molybdenum and some others. These elements have a chemical affinity for carbon (form carbonates), phosphorus (numerous phosphates), as well as sulfur and silicon (sulfates, sulfides, silicates). It is the various minerals and compounds of iron and manganese that cause the bright colors of various soil. Manganese is a catalyst for iron absorption and a regulator of hormonal synthesis. It oxidizes iron. The correct proportion is Mn: Fe = 1:2–5, that is, this ratio should be 0.2–0.5. Too much manganese will hinder the absorption of iron and vice versa

The data obtained confirm this conclusion, namely, the soil of Khulo contains 984 mg/l of iron and 53.6 mg/l of manganese, and the soil of Abastumani contains 792 mg/l of iron and 41.5 mg/l of manganese. The Mn/Fe ratio in the first and second cases is 0.05, that is, it does not correspond to the correct proportion Mn/Fe, necessary for the absorption of these elements. Since the iron content in both soils is significantly, 18-19 times higher than the manganese content, manganese will not be absorbed by plants, and, as a result, their immunity, the absorption of nitrate nitrogen and the plant's resistance to adverse factors will decrease. That is, the data the authors' received – the high content of calcium and iron –wwwwwwwwwwwwwwwwwwwwwwwwww confirms the fact that they limit the absorption of manganese [Skalny et al., 2019; Favorito et al., 2021; Li et al., 2018].

It has been established that in all plants the manganese content is 2–3 times lower than the iron content, that is, the classic ratio Mn:Fe = 0.2 –0.4 is observed, which means. that all plants absorb iron well, except for Caucasian blueberry and Linden leaves, 2021, in which the manganese content is (65.5) and (97.8), respectively, which is 1.4 and 2.5 times higher than the iron content (48.6) and (39.1), that is, iron will be poorly absorbed by blueberries.

As for hair: the ratio Mn:Fe = 0.4 for hair (woman 60 years old) and 0.26 for hair (girl 18 years old), that is, as can be seen from the data obtained, both women have no problems with the absorption of iron. Zinc and iron are antagonists. The relationship of these elements is shown in Figure 11.

It has been established that in all samples, except for hair and soil samples, the zinc content is 4–25 times lower than iron, which confirms the antagonism of these elements. Caucasian blueberry Fe:Zn = 25 contains the most iron and the least zinc. In Linden leaves 2019 and 2021, regardless of their collection time, the Fe:Zn ratio is the same and equal to 7, that is, the iron content in them is 7 times higher zinc content. And in Linden flowers in 2019 Fe:Zn = 17, and in 2021 it is 4. The same ratio Fe:Zn = 4 in Chamomile stem and Chamomile leaves. In soil, this ratio in soil (Abastumani) is 792/37.9 = 20.8, in soil (Khulo) – 984/2.54 = 387. The exception is hair samples, in which the zinc content exceeds the iron content: in hair (woman 60 years old) – 5 times, and in hair (girl 18 years old) – 3 times.

DISCUSSION

Mainly, the content of selenium in a specific ecotope is determined by the type of soil that represents a certain ecotope. The main factor affecting the accumulation of Se by the human body is the soil. Mutonhodza et al. [2022] showed that in the conditions of the subequatorial climatic zone, where red soils with an insignificant content of

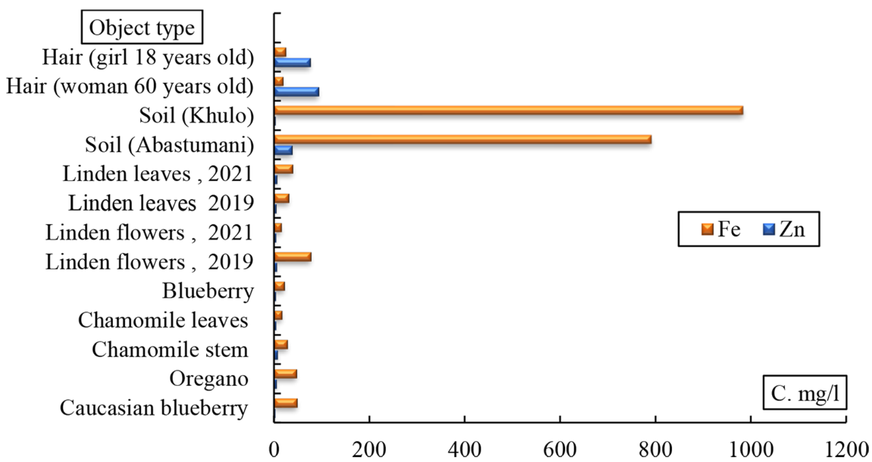

Figure 11. Comparison of zinc and iron content

humus (about 3%) dominate, the concentration of selenium is 0.4 mg/kg on average. Instead, the obtained results of the current work determine an order of magnitude lower content of Se in sandy or brown soil. Obviously, this phenomenon is due to the different elemental composition of soils and the different amount of precipitation per year in subtropical and subequatorial climate zones. On the other hand, despite the higher content of selenium in soils, the maximum quantity of Se was found in agricultural crops in the amount of 0.205 mg/kg (sorghum), but on average less than 0.045 mg/kg was accumulated in the most common crop, *Zea mays.* In the current study, a maximum of 0.17 mg/l was found in the leaves of *Tilia cordata.* Taking into account the much lower content of selenium in soils, it can be assumed that in the conditions of a subtropical climate on brown soil, plants absorb selenium better than in the conditions of a subequatorial climate on red soil. In some children and women – residents of the subequatorial belt – Se content in the blood was also determined as below normal (29–69 μg/l). Selenium deficiency was noted in an average of 60% of children. Obviously, this phenomenon is related to poor accumulation of this element by agricultural crops and farm animals, as well as social living conditions.

The content of selenium in the human body varies, depending on age, living conditions, gender, body mass index. Li et al. [2021] screened a Chinese population of 2,155 individuals (from 15 regions with varying amounts of Se in the environment) for hair selenium concentrations. In middle-aged people, the median value was 0.36 μg/g, in eldery people it was higher in twice (0.6 μg/g). The most selenium content was found in the inhabitants of the southern plains, where a high concentration of selenium in the dominated red soil was recorded – 0.5 μg/g, regardless of age. At the same time, a higher content of selenium was recorded in the hair of men, compared to women; body mass index did not correlate with the content of this element. In the received current data, on the other hand, there is a deficiency of Se in the hair samples of the elderly and an excess in the hair samples of young people. However, in current research, it is not possible to ascertain the relationship between age and selenium content in hair due to the narrow sample. In a study by Skalny et al. [2019] also has not been proven a correlation between age and selenium index.

In conditions of moderately continental or continental climate with black soil type, where a sufficient amount of selenium accumulates, 0.3 μg/g of this element was found in the hair of residents. Food products such as milk, goat cheese, pork, and rye bread were found to be rich in selenium in this region. The inhabitants consumed an average of 84 μg of Se per day. Selenium was detected in the soil at a concentration of 0.256 mg/kg, and in water – 168 mg/kg. Given that the minimum Se requirement is 55 μg/day, and the critical maximum is 400 μg, under these conditions, the population is not at risk of diseases associated with selenium deficiency. On the other hand, in conditions with a subtropical climate and sandy soil (for example, Adjara), such a threat exists.

As for plants, the accumulation of selenium by representatives of the *Asteraceae* family has been described. In particular Favorito et al. [2021] studied the nature of Se accumulation by a representative of this family – *Symphyotrichum ascendens* (american asters). This plant is considered a hyperaccumulator of selenium in its ecotope. This ecotope is enriched with selenium and phosphates, because of formation in the place of the former phosphate deposit. As a result of the reclamation of phosphorus minerals, a process of Se release occurred, followed by its accumulation in the soil has been detected. The degree of selenium contamination in the soil ranges from 3 to 435 mg/kg. It has been recorded that american aster can accumulate from 4.5 to 6.8 mg/kg of Se in own tissues. This amount is critical for the consumers of these plants. The bioavailability of selenium in this case is determined by redox processes and the level of sorption by the ground cover. The germination of hyperaccumulators is a marker of selenium pollution. On the contrary, in Ajaria and Abastuman ecotopes, the representatives of *Malvaceae* family were dominant in terms of selenium accumulation, while the representatives of *Asteraceae* took the last places in the accumulation row: in their tissues, a magnitude lower of Se concentration has been found: 0.108 and 0.03 mg/l.

Since selenium is an indispensable trace element of plant metabolism, cultivated plants are often artificially treated with it. In the case described by Li et al. [2018] the blueberry plantations were artificially sprayed with solutions of selenate or selenite by applying the spray to leaves at the stages of young berries and ripening berries. A concentration of 200 g/ha has been used for processing. In the experiment, two lines of blueberries has been tested. They differed in the nature of selenium accumulation by 1.4 times. At the stage of young berries, plants accumulated approximately twice concentration of Se in comparison with plants at the stage of berries maturation. The content of organic selenium in plants was more than 77%. In the leaves of the line that accumulated better, after spraying the solutions to the leaves at the stage of young berries, 0.7 mg/kg Se (IV) and 0.9 mg/kg Se (VI) has been determined; in stems – 0.2 mg/kg. Under spray conditions, the leaves accumulate higher concentrations of Se than the stem. Foliar spraying of selenates and selenites contributed to the accumulation of a higher concentration of anthocyanins in fruits and an increase in the percentage of intact berries. Under natural conditions, as shown in this work, blueberries accumulated 0.12–0.15 mg/kg of Se.

This experiment had shown the relationship between the accumulation of selenium and other elements, depending on the type and elemental composition of the soil. In the perspective of future research – the discovery of new relationships in other ecotopes.

CONCLUSIONS

The accumulation of selenium occurs in plants into which it comes from the soil; in populations living in areas with high selenium content, it accumulates in the hair. Based on this, the content of selenium and other elements (Al, Fe, Mn, Ti. B, Pb, K, Mg, Ca, Zn, As and Cu) in plants was determined depending on the nature of the plant and the time of its cultivation. collection, in the soil, depending on the geographical location, namely the western (high mountainous Adjara – Khulo) and eastern (Abastumani) regions of Georgia and in the hair of women living in these regions.

It has been established that the amount of selenium in chamomile leaves is 12% higher than in the stem, and the selenium content varies from year to year. It has been established that the selenium content in linden leaves from the 2019 harvest (0.174 mg/l) is 2.5 times higher than in flowers (0.072 mg/l). In 2021, according to the data obtained, the selenium content in the leaf and flower is almost the same. The smallest amount of selenium is contained in oregano (0.03 mg/l), this is less than the daily human requirement, i.e., oregano cannot be used to replenish selenium deficiency.

The selenium content in Abastumani soil was found to be 0.051 μg/l, which is 13 times higher than the selenium level in Khulo soil. those. people living in the mountainous regions of Adjara will experience selenium deficiency. It has been established that the amount of selenium in the hair of a 60-year-old woman (Khulo) is less than normal, which corresponds to the amount in the soil, and therefore she has developed low immunity. An 18-year-old girl living in the same area has an increased selenium content (0.152 μg/l) – 3 times higher than normal, which means the development of selenism in her body and, as a consequence, hypothyroidism. The arsenic content in the soil is 20–23 times higher than the selenium content. This confirms that arsenic and selenium are antagonists; arsenic reduces the binding of selenium to biological structures, that is, reduces its biological activity.

It has been established that the amount of zinc in hair is very high – almost 90–100% higher than in other research objects. The maximum amount of copper was found in the hair of a young girl (19.3 mg), which is 3.9, as well as in the leaves of linden (9.0), chamomile (6.74) and oregano (7.03), which is 1.5–2 times higher than the maximum permissible. copper level – 5 mg. and can cause serious complications as a result of its toxic effects. These data should be taken into account when preparing and consuming medicinal decoctions from the leaves of these plants.

It was found that in all samples the content of calcium and potassium significantly, 2–5 times, exceeds the amount of magnesium. The greatest amount of aluminum is contained in the leaves and flowers of linden and oregano, the smallest in chamomile leaves, iron in flowers, manganese in linden leaves. The connection between the content of iron, phosphorus, zinc and manganese has been proven: with an increase in the content of phosphorus, zinc and manganese, the absorption of iron decreases.

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