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ORIGINAL ARTICLE

A Review of germanium environmental distribution, migration and accumulation

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In this paper we summarized the published data on distribution, migration and accumulation of chemical forms of germanium in natural environment. Despite the germanium is found in lithosphere, hydrosphere and atmosphere it is one of the least studied elements. It belongs to rare scattered elements with a relatively high migration capacity in the earth's crust and on its surface. Depending on the physical and chemical conditions, germanium possesses different properties, which determines the variety of ways of its migration. The nature and form of migration of germanium is not determined only by its chemical properties but also by interaction with various underground water addendums, the granulometric and chemical-mineralogical composition of soil-forming rocks and soils, biogenic and technogenic processes. The content of germanium in natural waters, soils and plants can vary widely and depends on many factors. In particular, its concentration in groundwater and surface water depends on the natural geological environment, pressure, temperature, meteorological and anthropogenic factors; soil by their type, region, features of soil-forming processes, chemical composition of the parent rocks, climatic conditions and amounts of organic substances; in plants by their species and varietal facilities, the growth stage of the plants, the availability of soils by this element, the forms of germanium compounds in the soil (inorganic or organic), the ability of soil to retain labile form of germanium and climatic conditions. We also underlined the insufficient level of germanium in human body due to low concentrations in the food and water. However, we suggested that any products with a high content of germanium may pose a risk to human health through its toxic effects.

Key words: Germanium; Migration; Natural environment; Concentration; Water; Soil; Plants; Food; Human consumption levels

Introduction

The history of the discovery of germanium

Germanium as a chemical element has a very interesting history of discovery. This story began in the XIX century. In 1871 Dmitri Ivanovich Mendeleev predicted the existence of an element similar to silicon is ekasilicon (Eka-Si-licium) and suggested where to look for it. According to him, it can be found in ores containing titanium, niobium, zirconium and tantalum. He decided to search for this unknown chemical element on his own. But he couldn't find it. It took almost 15 years and ekasilicon was discovered. In 1885 a new mineral which was named argyrodite because it contained silver (Argentum) was found at "Himmelsfürst Fundgrube" mine in Germany by Carl Auer von Welsbach, a Professor of Mineralogy at the Freiberg mining Academy. The exact chemical composition of the mineral could not be immediately determined. Auer Von Welsbach asked the chemist Clemens Alexander Winkler to investigate and determine the composition of this mineral. Clemens Winkler was able quickly to determine its composition. It turned out that the main component of the new mineral was silver. In addition to silver, the composition also included sulfur, ferrous oxide, zinc oxide and mercury. The total amount of all mineral components did not exceed 93–94% of the weight of sample. No matter how hard the scientist tried, he could not find out what consists of the other 7%. Then he suggested that there was an unknown chemical element in the mineral that could not be detected by classical methods. This prompted him to do more research. After hard work in the beginning of February 1886 he discovered the salts of a new chemical element and even isolated a small amount of the element itself in its pure form. In the first report to the German society of chemists Clemens Winkler suggested that the new element is a non-metal and analogous to antimony and arsenic. The report was sent to many scientific institutions throughout Europe. This idea aroused a literary controversy that had not subsided until it was established that a new element ekasilicon was provided by D.I. Mendeleev.

Literature Review

Primarily, Clemens Winkler intended to call the new element neptunium meaning that the history of its discovery is similar to the history of the discovery of the planet Neptune the existence of which was predicted by the French astronomer Urbain Jean Joseph Leverrier. However, it turned out that the name neptunium had already been given to one discovered chemical element. And then

Clemens Winkler renamed the chemical element he discovered of germanium (Germanium) in honor of his homeland. The name has raised sharp objections from some scientists. For example, one of them indicated that this name is similar to the flower name geranium (Geranium). In the heat of debate Raymond jokingly suggested calling the new element Angularium that is one that causes controversy. However, D.I. Mendeleev in his letter to Clemens Winkler strongly supported the name germanium (Figurovskij, 1970; Enghag & Enghag, 2006; Burdette & Thornton, 2018). Subsequently, scientists have carried out a significant amount of work to further study the chemical and physical properties of germanium its distribution in the natural environment, the biological role and mechanism of action on living organisms and the possibilities of application in industry.

Physical and chemical properties of germanium

It is impossible to get a complete scientific understanding of the migration and distribution of germanium in the natural environment without consideration of their chemical nature and position in the periodic system of chemical elements of D.I. Mendeleev.

Germanium (lat. Germanium) Ge is the 32th chemical element of the fourth period of group and IV of the main (A) subgroup of the periodic table with an atomic mass of 72.59 g/mol. Germanium can be attributed to both a semi-metal and a metalloid since it has the properties of both a non-metal and a metal. The atomic radius of germanium is 1.26 Å, the ionization potential is 7.85 EV, the electronegativity by Poling is 2.00, the melting point is 947.4°C, the boiling point is 2830.0°C, the density of solid is 5.323 g/cm^3 (25°C), the density of liquid is 5.557 g/cm^3 (1000°C). Germanium hardness according to the mineralogical scale is 6.0–6.5. The color is gray-white with a metallic sheen. Transparent for infrared rays with a wavelength of more than 2 microns. Germanium crystallizes in a diamond-type crystal lattice (unit cell parameter a=5.6575) but the Ge–Ge bond strength in a germanium crystal is less than in diamond crystals. Germanium metal at room temperature is resistant to oxygen but quickly oxidizes at high temperatures (600–700°C).

The germanium electronic formula has the form $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^2$. The germanium atom consists of a positively charged nucleus (+32) inside which there are 32 protons and 41 neutrons and 32 electrons move around the four orbits. General electronic configuration of valence sublevels of p-element atoms in the $ns^2 np^2$ ground state. Due to the presence of 2 unpaired p-electrons in germanium compounds it may exhibit an oxidation state of +2. Atoms can pass into an excited state with the formation of four valence electrons which causes the appearance of compounds with an oxidation state of +4. In some compounds, germanium may exhibit oxidation states of –4 and 0 (Rochow & Abel, 1973; Derry, 2018).

The distribution of germanium in the natural environment

In mineral and geochemical terms germanium is one of the least studied elements. It refers to scattered and relatively mobile elements in the earth's crust the so-called "trace" elements. The mass fraction of germanium in the upper part of the continental crust is in the range of $1{,}3 \times 10^{-6}$ to $1{,}40 \times 10^{-6}$% (Hu & Gao, 2008). Theoretically, the content of germanium in the earth's crust should allow the formation of large (>14000 t) or even giant deposits (>140000 t) (Hu & Gao, 2008). However due to its geochemical properties the bulk of germanium is scattered in various rocks and minerals of other elements. There are about 30 minerals that contain germanium are known (Ruiz et al., 2018). Due to its geochemical affinity with some common elements (Si, Zn, As, Fe, Cu, Sn, Ag) germanium shows a limited ability to form its own minerals. Therefore, the native germanium minerals in nature are extremely rare and mostly in the form of micro-inclusions. They are represented by sulphites and sulpho salt-germanite (9.1% Ge), argyrodite (6.4% Ge), canfieldite (1.8% Ge), renierite (6.6% Ge); double hydrated oxide of germanium and iron shtottit (13.4% Ge); sulfates itoit (7.6% Ge), fleisherit (7.2% Ge). They have almost no industrial significance.

A wide range of geochemical properties allows germanium to accumulate in significant quantities in deposits of various geological and industrial types. There are nine major natural sources of germanium: pyritic-polymetallic copper mineral assets; phyric and vein-stockwerk copper-gold-molybdenum; porflow and vein-stockwerk tin-silver; vein silver-lead-zinc (copper) mineral assets; stratiform copper-lead-zinc in terrigenic formations; stratiform mineral assets of nonferrous metals in carbonate formations; resultn polymetallic mineral assets; mineral assets of iron oxide ores; coal mineral assets (Höll et al., 2007; Frenzel et al., 2014).

Depending on the physico-chemical conditions of the mineral and lithogenesis of germanium can behave as a sidero-, lito-, chalco- and/or organophilic element which determines the variety of ways of its migration. Siderophil properties germanium shows in iron meteorites and the metal phase of other meteorites as well as in iron ores of sedimentary origin. Lithophile properties of germanium shows in silicon sedimentary rocks and post-magmatic products associated with granite magma. Therefore, the main amount of germanium in the earth's crust is in the form of solid solutions of germanates with silicates. Chalcophile properties of germanium shows in upper proterozoic sedimentary rocks where it is most often found in sulfide minerals. Organophilic properties of germanium shows in the formation of chelates with organic lignin derivatives in the process of peat formation and in the early stages of coalification and metamorphism of brown coals (Bernstein, 1985; Seredin & Finkelman, 2008; Rosenberg, 2009).

In nature there are five isotopes of germanium with the following prevalence: ^{70}Ge (21.2% by weight), ^{72}Ge (27.7%), ^{73}Ge (7.7%), ^{74}Ge (35.9%), ^{76}Ge (7.5%). The first four isotopes are stable, the fifth (^{76}Ge) is weakly radioactive which is characterized by double beta decay with a half-life of 1.58×10^{21} years (Melcher & Buchhloz, 2014; Meija et al., 2016; Rouxel & Luais, 2017; Meng & Hu, 2018). To date 26 radioisotopes with atomic masses from 60 to 90 have been artificially obtained of which 11 are neutron-deficient and 15 are neutron-enriched isotopes. Radioactive isotopes of germanium were obtained by reactions of fusion-evaporation (FE) reactions, light particle reactions (LP), neutron capture reactions (NC) and shell fragmentation or shell separation (PF). The most stable of the radioisotopes is ^{68}Ge with a half-life of 270.95 days and the least stable is ^{60}Ge with a half-life of 30 months (Gross & Thoennessen, 2012).

Germanium in low concentrations identified in atmospheric air. The concentration of germanium in air solids can range from 0.01 to 1700 ng/m^3 (Braman & Tompkins, 1978). In regions with developed industry and infrastructure where the increased release of various chemical compounds into the atmosphere the concentration of germanium in the air increases significantly. So, a significant amount of germanium enters to the atmosphere from flue gases and fly ash as a result of burning coal. These emissions lead to an increase in the concentration of germanium in urban atmospheric air from 0.4 to 10 µg/m^3 (on average up to 2 µg/m^3) (Vouk & Piver, 1983). High concentrations of inorganic germanium (up to 300 µg/m^3) are recorded in the air above the working areas of enterprises where production processes are associated with the use of compounds of this element (Swennen et al., 2000). Low concentrations of germanium (0.011 µg/l) have also been found in rainwater (Eriksson, 2001).

In the hydrosphere the content of germanium is small. The concentration of germanium in the ocean varies from $7–10^{-12}$ mol/l on the surface to $1{,}2–10^{-10}$ mol/l in deep waters (Korzh, 1991). Its concentration in sea water is almost independent of the depth is 0.05–0.5 µg/l (Kabata-Pendias & Mukherjee, 2007). At the same time, there is evidence in the literature that the concentration of germanium in the waters of The world ocean increases with increasing depths (Hambrick et al., 1984). Scientists explain this fact by

the fact that the chemical composition of the waters of The world ocean is formed not only under the influence of atmospheric precipitation and river flow but mainly as a result of the receipt of various compounds from the depths of the Earth during volcanic activity and the formation of oceanic crust in tectonically active zones of the bottom. In seawater inorganic germanium is represented primarily as germanium hydroxide (H_4GeO_4), trihydrogen germanate ion ($[H_3GeO_4]^-$) and dihydro germanate ion ($[H_2GeO_4]^{2-}$) (Wood & Samson, 2006). In addition two other germanium species have been identified in seawater are monomethyl germanium ($CH_3Ge_3^+$) and dimethyl germanium ($(CH_3)_2Ge_2^+$). Both of these compounds are non-reactive and have a conservative concentration profile in depth. At the same time, their profile may change depending on the salinity of the water. The concentration of monomethyl germanium is in the range from 300 to 350 pmol/l and dimethyl germanium is in the range from 90 to 120 pmol/l which is significantly higher than the concentration of inorganic germanium (Lewis et al., 1988; Sutton et al., 2013).
It is known that the movement of chemical elements in the atmosphere, hydrosphere and lithosphere occurs according to a complex migration pattern: soil–water–plant–animal–human. This consistent migration path of germanium by trophic chains will be considered in order to get a complete picture of its significance for living organisms.

Germanium in underground and surface waters

Studies of the mineral composition of natural waters conducted by scientists in different countries of the world have convincingly proved that germanium is present in both underground and surface waters. Its concentration in underground and surface waters can fluctuate within a fairly wide range and depends on the natural geological environment in which chemical reactions occur in the "rock–water–gas" system; pressure; temperature; meteorological and anthropogenic factors. The wide prevalence of germanium in underground water indicates its high mobility. Water migration of germanium depending on geochemical conditions occurs in the both form of simple ions and in complex compounds with various underground water adends.
The chemical composition of underground water is a consequence of the interaction of geological rocks with the underground hydrosphere where water as a universal solvent acts as the main agent for the removal of water migrants from minerals. It is established that an increased level of germanium is also observed in thermal waters that have a very low or very high pH as well as rich in CO_2 and N (Ivanov, 1996**;** Rosenberg, 2009). In thermal waters the concentration of germanium widely varies but rarely exceeds of 40–50 µg/l. For example in water samples from Iceland it ranges from 0.05–24 µg/l (Elmi, 2009), France (Vichy springs, Vals les Bains springs) it's from 0.5–47.9 (Criaud & Fouillac, 1986), Japan it's from 0.4–43.3 (Uzumasa et al., 1959), New Zealand it's of 52.5 (Koga, 1967), on the Juan de Fuca ridge (North-East Pacific ocean) it's from 10.9–18.9 (Mortlock et al., 1993), Poland (Sudetes Mountains) it's from 0.025–10.62 µg/l (Dobrzyński et al., 2018), Greece (Lesvos island) it's from 5.0–13.0 µg/l (Tziritis & Kelepertzis, 2011). According to scientists most of the germanium in thermal waters occurs in the form of pentahydroxogermaniate ($[Ge(OH)_5]^-$) but in salty waters at a water temperature of 200°C a significant amount of the element can be represented as germanium (IV) hydroxide ($Ge(OH)_4$) (Arnórsson, 1984).
Mineral waters contain less germanium than thermal waters. Thus, its concentration in the bottled mineral waters of the Caucasus are "Nazan" from 0.18–0.20 µg/l, "Yessentuki 17" from 6.1–6.6 µg/l, "Yessentuki 4" from 13.0µg/l (Vasil'ev & Amelin, 2016); Carpathian (Bieszczady mountains) from 0.08–35.8 µg/l (average 7.4 µg/l) (Dobrzyński et al., 2011); Sudet (Poland) from 0.025–10.62 µg/l (Dobrzyński et al., 2018).
Mine water are more enriched with germanium than underground water. This element is very typical for the mine waters of the coal seams of Donbass (Ukraine) where sometimes its content reaches industrial concentrations (up to 0.437 mg/l) (Shevchenko & Proskurnja, 2001; Sujarko, 2001).
In surface waters the concentration of germanium is low and in most cases it is characterized by relatively stable indicators for many years as evidenced by the results of regular studies of natural river waters in French laboratories. In the first publication it was noted that the concentration of germanium in river waters ranges from 0.008 to 0.012 µg/l (average 0.01 µg/l) (Yeghicheyan et al., 2001), in the second publication it was from 0.006 to 0.016 µg/l (average 0.015 µg/l) (Yeghicheyan et al., 2013). Along with natural factors human activity has a significant impact on the concentration of trace elements in river water. It was found that the concentration of germanium in river water samples taken near urban and industrial areas is much higher than in rural areas and ranges of 0.03–0.17 µg/l (on average 0.073 µg/l) (Ouyang et al., 2006). The waste water from leather processing materials can also be one of the sources of pollution of surface river waters by germanium. As a result of the discharge of such waters into rivers the concentration of germanium may exceed the permitted standards for surface waters by a factor of 3 or more (Zhang & Zhang, 2006).

Germanium in soils

The distribution of germanium in the soil is determined by various factors. Studies have shown that the content of germanium in the soil depends on its type (sandy soils adsorb less germanium than clay), region, features of soil-forming processes, chemical composition of parent rocks, climatic conditions (average annual temperature and precipitation), the amount of organic matter and so on. The concentration of germanium in soils increased in the presence of Si and decreases in the presence of Fe. Germanium in soils is sedentary. Its migration occurs when soluble germanium compounds are formed which it is further included in the complex with humic acids and move with them. Either in the process of weathering of rocks the destruction of germanium minerals occurs with the formation of simple compounds and most often in secondary silicates. During the weathering of germanium is mobilized in the form of $Ge(OH)_2$. Mainly in soils germanium is found in the form of divalent cations as well as in anionic complexes such as $HGeO_2$, $HGeO_3$ and GeO_3 (Eriksson, 2001; Kabata-Pendias & Szteke, 2015).
Analytical literature about germanium content in soils of various types is not numerous. It is believed that its concentration in soils ranges from 0.5 to 2.5 mg/kg (Kabata-Pendias & Mukherjee, 2007). At the same time the study of the distribution patterns and geochemical behavior of germanium in various soil types in some regions revealed a fairly wide range of its concentrations from <0.1 to 15 mg/kg (Wiche et al., 2018). Thus, the average values of germanium content in agricultural soil (Ap-horizon, 0–20 cm) and pasture lands (Gr-horizon, 0–10 cm) of some European regions (in Scandinavia, Germany, France, Spain and the Balkans) are almost the same ranges of 0.037 and 0.034 mg/kg (Negrel et al., 2016). At the same time scientists have noted the existence of places with abnormal concentrations of germanium in the soil. The high concentrations of germanium are found in clay soils in the Central part of the Scandinavian Peninsula, particularly in the South and the South-East of Finland (in samples of peat soils), along the entire Western coast of Norway, along the Eastern coast of Sweden and in the Melaren region (Ladenberger et al., 2012). The germanium content in the upper soil horizons of the United States averages of 1.1 mg/kg with minor variations from 0.8 mg/kg in light organic soils to 1.5 mg/kg in clay and loamy soils (Kabata-Pendias & Pendias, 2001). In the soils of the island of Maui (Hawaii, USA) the germanium content is higher and ranges from 1.7 to 4.5 mg/kg. The lowest concentrations of trace elements were found

in the upper soil horizons of the island (Scribner et al., 2006). The results of studies of samples of upper soil horizons taken in the South of Middle Saxony (Germany) showed that the germanium content in them varied from 1.0 to 4.3 mg/kg (average of 1.9 mg/kg). The higher germanium concentrations were typical for wet pasture soils with low pH and high organic matter content (Wiche et al., 2017). On the territory of the municipality of Freiberg (Saxony) the soils polluted with mining waste were characterized by high concentrations of germanium (to 7.91 mg/kg) (Midula et al., 2017). The results obtained by studying the Geochemistry of trace elements in the upper soil horizon of (2–4 cm) from Eastern China indicate that the concentration of germanium in the samples ranged from 1.3 to 3.4 mg/kg (average 2.0 mg/kg). Chinese scientists say that the concentration of trace elements in soils mainly depends on the chemical composition of the parent rock as well as on the climate which determines the intensity of weathering of rocks (Yang et al., 2010). Comparatively low germanium concentrations were found in various types of soil in Gyeongnam province (South Korea) in particular in the loam of 0.27 mg/kg in sandy loam of 0.23 mg/kg (Lee et al., 2005). The data provided in the geochemical Atlas of England and Wales indicate that the average concentration of germanium in the soils of these countries are 1.1 mg/kg. However, there are several areas with high concentrations of trace elements in the soil (>2.4 mg/kg) in particular these are industrial areas between Liverpool, Manchester, Derby, Nottingham and Lid and between Durham and Newcastle and also in the Lake district (North-West England) and the Pennines. Areas with the low concentrations of germanium in the soil is found in North-East England (Rawlins et al., 2012). Germanium is unevenly distributed in Irish soils with minimum concentrations of 0.1 mg/kg and maximum concentrations of 2.58 mg/kg. The level of germanium is 1.5 mg/kg and higher typical for sandy soils are found in the South-West and North-East of Ireland and concentrations below of 0.9 mg/kg which are gray brown podzolic soils that occur in the Center and West of the country (Fay et al., 2007). Unfortunately, similar data characterizing the mineral composition of soils in other countries of the world including Ukraine have not been found.

Lithium in plants and plant products

Plants uptake germanium from the soil is the most significant beginning of the element's biological migration path. The amount of germanium uptake by plants depends on its participation in biological processes and the availability of forms that are easily accessible to plants. Plants absorb germanium by the root system in the form of GeO_2 or Ge $(OH)_4$. The root systems of plants raise germanium in dissolved form from the lower layers of the soil to the upper ones. After germanium is raised, it is transferred to the stems and leaves of plants where it precipitates as a result of supersaturation with silicon. Germanium is deposited in the form of opal phytoliths in the cell walls, the cells themselves and the intercellular space near the plant surface (Prychid et al., 2003; Blecker et al., 2007). When plants die off it accumulates in the surface horizon. A small amount of it accumulates in the humus layer. Germanium in plant tissues forms stable complexes with a large number of functional groups (Wiche et al., 2018). However the high germanium concentrations (above 5 ppm) are toxic to most plants (Keith et al., 2015). An excess of germanium plants have various anomalies of development: gigantism of individual organs (most often-flowers) irregular thickening of the stem, the heterogeneity of color and others. Germanium is found in the tissues of many plants. Germanium accumulation by plants depends on their species and varietal facilities the growth stage of the plants, the soils in this element, the forms of germanium compounds in the soil (inorganic or organic) the ability of soil to retain labile form of germanium and climatic conditions (Halperin et al., 1995; Lee et al., 2005; Choi et al., 2013; Wiche et al., 2017). In addition it was found that plants grown on neutral soils (pH=6.6) accumulate germanium more than on slightly alkaline (pH=7.8) (Wiche & Heilmeier, 2016). However, some scientists believe that germanium accumulation in plants does not depend on its reserves in soils (Hara et al.,1990).

Review of literature sources indicates the absence of regular large-scale studies on the content of germanium in various plants as well as the inconsistency of some experimental data on this issue. The comparison of research results are complicated by the fact that the authors in their articles do not always indicate the genus, species or plant variety, time of planting (autumn or spring), cultivation (field, greenhouse or laboratory), growing region (country), the vegetation phase of the plant, time of harvest, conditions of processing and storage and do not provide information regarding the type and chemical composition of the soil in which plants were grown. Besides the scientists use different methods of preparing samples for analysis, different techniques and different devices to determine the concentration of germanium which are not always certified. It is not always possible to understand from the text of the article the value of germanium concentration in plants based on the natural moisture content of the dry substance or in ash.

Ginseng is a leader in plants that can adsorb germanium and its compounds from the soil. According to research results the germanium concentration in a 4-year-old ginseng root that can range from 0.20 to 5.34 µg/g and in leaves from 0.31 to 6.11 µg/g depending on its content in the soil (Kang et al., 2011). Germanium is found in some medicinal plants and preparations based on vegetable raw materials, for example in dandelion root (0.01–0.23 µg/g) thousand-leaf grass (0.06 µg/g), Angelica roots (0.2 µg/g), burdock roots (0.02 µg/g), divesilu roots (0.003 µg/g), comfrey medicinal (0.02 µg/g), oat seeds of milk ripeness (0.03 µg/g), aloe room, natural (0.005 µg/g) (Komarov et al., 2014), aloe tree (0.697–1.219 µg/g) (Hui et al., 2004), aloe Vera tablets (20.83 µg/g), ginseng tablets (5.48 µg/g), ginger tablets (9.96 µg/g) (McMahon et al., 2006). The germanium content in samples of winter and spring garlic grown in various agricultural zones in Russia was at a low level. According to some data it was 0.007 µg/g (64) while according to others it was less than of 0.0042 µg/g (Poljakov et al., 2018). At the same time, the high concentrations of germanium were found in garlic grown in China and Ukraine of 2.79 and 3.2 µg/g (McMahon et al., 2006; Ivanyca et al., 2016).

It is a common pattern for agricultural crops that the germanium content is reduced in the following order: cereals > vegetables > fruits (Rawlins et al., 2012). According to the literature data the concentration of germanium in cereals and legumes: barley and lentils are 0.007 µg/g, soy and durum wheat are 0.09 µg/g, peas are 0.02 µg/g, legumes are 0.15 µg/g (Konovalova et al., 2012); brown rice are 0.097 µg/g and polished rice are 0.23 µg/g (Kim et al.,2019). The concentration of germanium in vegetables and fruits are about two orders of magnitude lower. There is evidence that the content of this trace element in cabbage are 0.893 ng/g, spinach are 0.864 ng/g and cucumber are 0.597 ng/g (Jinhui & Kui, 1995), depending on the type of banana are 0.53–1.03 ng/g (Delvigne et al., 2009). As for herbs, cereals accumulate much more (169–449 ng/g) than legumes (15–50 ng/g) (Wiche & Heilmeier, 2016).

Mushrooms are well known for their ability to accumulate various metals and methoids in their fruit bodies. Germanium is no exception. Germanium content in the most common types of mushrooms collected in Ukraine varies in a wide range of concentrations. The highest values were recorded for white mushroom (50–60 µg/g of ash), champignon and fly agarics (25–40 µg/g of ash) and the lowest for Polish mushroom and mossiness mushroom (0.5–3 µg/g of ash) (Ponomarenko et al., 2019). The concentration of this trace element in dried white mushroom (humidity of 12%) collected in Russia is 0.01 µg/g (Komarov et al., 2014).

The study of the chemical composition of 5 species of fungi of the genus Phellinus which are used in traditional Eastern medicine showed that the concentration of germanium in them ranged from 0.32 to 1.70 µg/g of ash (Chenghom et al., 2010). A slightly higher concentrations of germanium (1.32 and 3.18 µg/g) were detected in 2 species of fungi of the genus Ganoderma which are also used in folk medicine as a broad-spectrum drug (Zhong et al., 2013). In the fruit bodies of the fungi Ganoderma lucidum and Pleurotus ostreatus which were grown in experimental systems with the addition of germanium its maximum levels reached of 80 and 70 µg/g (Siwulski et al., 2019).

The data on germanium content in tea leaves is limited. There are reports in the scientific literature that a high concentration of germanium (9 ng/g) was found in green tea (Goodman, 1988).

Germanium in animals and food products of animal origin

The main ways of getting germanium into the body of farm animals and poultry with food it’s drinking water and air, additional enter to the body of farm animals it's intramuscular and intra-abdominal injections. It is experimentally proved that germanium compounds both organic and inorganic are quickly absorbed through the mucous membrane of the gastrointestinal tract and distributed in the tissues and body fluids of animals. Germanium compounds have expressive lipophilic properties, so they easily penetrate cell membranes and the blood-brain barrier. Germanium accumulation in animals can occur in cells of all tissues. At the same time, no organ was identified in which its concentration was significantly higher than in others. Germanium stays longer in the kidneys, liver, gastrointestinal tract, peripheral nerves and thyroid gland. Organs and tissues that can accumulate germanium can be arranged in such a decreasing sequence: kidneys, liver, lungs, stomach, intestines, muscles, heart and brain (Kobayashi & Ogra, 2009; Stewart et al., 2012; Keith et al., 2015; Gutyj et al., 2017; Sobolev et al., 2017; Darmohray et al., 2019; Ivankiv et al., 2019). In addition, germanium has been found in many body enzymes such as guanase, cytochrome oxidase, carbonic anhydrase as well as in cell membranes and some subcellular organelles including mitochondria and chromosomes (Song et al., 2005).

The main factors that determine the content of germanium in livestock products are the level in the diets of farm animals and poultry. If the natural background of germanium is low then its concentration in animal products will also be low for example in beef and poultry meat are 0.001 and 0.0007 mg/kg, in offal are 0.002 mg/kg, in milk are 0.0003 mg/kg, in eggs are 0.001 mg/kg (Song et al., 2005). At the same time, the results of research by French scientists indicate that the level of germanium in animal products may be higher and fluctuate within certain limits in particular in beef are 0.0024–0.0035 mg/kg, poultry meat are 0.0014–0.0027, offal are 0.0048–0.0052, milk are 0.0005–0.0020 and eggs are 0.0012–0.0025 mg/kg (French Agency for Food, 2011).

In products obtained from regions with high germanium content in soils, water and as a result in forage plants its concentration will be even higher. One of these areas is Silesia (Poland) on the territory of which the Upper Silesia coal basin was located as well as iron, zinc, silver-lead and copper ores are mined. The average germanium content in the milk of cows kept in Upper Silesia are 37.81 µg/l and in Lower Silesia are 19.75 µg/l (Dobrzański et al., 2005). The experimental data obtained that allow us to state with a high degree of confidence that the amount of germanium deposited in poultry products also depends on the level of germanium in mixed feeds for poultry. Thus, when Ge-132 additives were added to the feed mix for laying hens, the germanium concentration in the egg increased and ranged from 26.16 to 48.91 µg (Zhaoxin, 1995).

Fish occupies an important place among the food products of animal origin. Fish with germanium content is not inferior to the meat of farm animals and poultry and sometimes it has an advantage in this indicator. Scientists found that the concentration of germanium in fish ranges from 0.0023 to 0.0033 mg/kg (French Agency for Food, 2011). However, other scientific evidence suggests that certain fish species such as sardines can accumulate up to 0.009 mg/kg of germanium in muscle tissue. In other seafood (shell fish and crustaceans) the average germanium content is 0.002 mg/kg with a maximum level of 0.005 mg/kg in mussels and crabs (Guerin et al., 2011).

As far as we know, there is no data in the scientific literature on the content of germanium in honey. Probably, the concentrations of this trace element in honey are very low and are below the detection limits of all known analytical methods.

The levels of consumption of germanium with food and the person's need for it

In view of the above, water and food are the main sources of germanium in the human body. Analysis of the actual consumption of germanium by the population of some countries of the world has shown that most people get a small amount of this trace element with food and water. For example, in the UK the average daily consumption of germanium by adults are in the range of 0.001-0.018 µg/kg bw, children (1.5–4.5 years) are 0.002–0.053, adolescents (4–18 years) are 0.001–0.032 and elderly people are 0.001–0.016 µg/kg bw (Rose et al., 2010). Analysis of the trace element composition of daily diets selected from France showed that the average values of germanium intake in adults and children are slightly higher than in the UK and are 0.042-0.088 µg/kg bw and 0.058–0.1218 µg/kg bw (French Agency for Food, 2011). Scientific research has proved that microdoses of germanium are necessary for the normal functioning of the antioxidant and immune systems of living organisms. Scientists and doctors are of the opinion that the daily rate of germanium consumption for a person is 0.8–1.6 mg. However, to date the experts of FAO/WHO have not yet established official food consumption standards for various categories of the population, according to which it is possible to draw a conclusion about the usefulness of their diets. In this regard, some countries in particular Russia have offered to their citizens adequate and upper acceptable levels of the consumption of germanium are 0.4 and 1.0 mg/day. Despite the imperfect and largely formal approach to the formation of an indicator of an adequate level of germanium consumption, it can be considered as a reference point for calculating the physiological needs of each person in this trace element. It should also be noted that a person's need for germanium is individual in nature and is a variable that depends on the physiological state of the body, the type of activity (mental or physical), the level of physical activity and health status which requires constant correction of their intake with food. If there is insufficient intake of germanium in the human body the risk of infection and development of cardiovascular diseases (coronary heart disease, insultus), osteoporosis, cancer, arthritis, and various states of immunodeficiency increases. In the blood the level of cholesterol are raised (Stadnyk et al., 2006; Sahanda, 2014). It is assumed that germanium deficiency is one of the factors that contributes to the development of a rare endemic disease-Kashin-Beck's disease (Peng et al., 2000).

Experts from the food standards Agency concluded that germanium contained in small amounts in people's diets does not cause toxic effects (COT, 2008). However, long-term use of inorganic germanium preparations, the main component of which is germanium dioxide or germanium lactate-citrate leads to serious side effects, including various organ dysfunction and even death. The main target organs of germanium are the kidneys, muscles, nerves and liver. The primary symptoms of intoxication are weight loss, fatigue, gastrointestinal disorders (nausea, vomiting, lack of appetite and diarrhea), anemia and muscle weakness. Prolonged intoxication causes acute renal failure (Nagata et al., 1985; Asaka et al., 1995; Chen & Lin, 2011). In some patients, renal function remained impaired even after the abolition of germanium drugs (Van der Spoel et al., 1990). In the case of chronic germanium intoxication, high concentrations of germanium were found in the thyroid gland, brain and spinal cord, lumbar muscle, gluteal nerve, hollow gut, liver and kidneys (Nagata et al., 1985; Chen & Lin, 2011). In this regard, it has been suggested that any products with a high content of germanium may pose a risk to human health.

Discussion and Conclusion

Analyzing the data already established at this time, we made an attempt to systematize the results of scientific research and discoveries of scientists from different branches of science, about the patterns of distribution, migration and accumulation of germanium in the natural and social environment. Review of literature sources indicates that there are no regular large-scale studies on the content of germanium in various components of the environment. The concentrations of germanium in water, soil, plants and food products have been established its indicate that not only the chemical and mineralogical component of natural waters and soils, but also biogenic and technogenic processes determine the level of this trace element entering the human body. At the same time, some experimental data on this issue are either single or contradictory and require further explanation or research. In addition, different scientists use different methods of preparing samples for analysis, different techniques and different instruments to determine the concentration of germanium in the same biological objects, which makes it difficult to compare the results of research. According to scientists, the difficulties of quantitative analysis are related with the variety of forms of germanium and their crystal modifications, as well as ways to verify the correctness of the definition of forms and concentrations. Further comprehensive ecological and toxicological studies of the levels and patterns of migration and accumulation of germanium in the environment are necessary primarily to minimize the negative consequences for human health associated with dangerous concentrations of trace elements.

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