Unit 4. Trace elements*

Cesium (Cs)

Various sources list the Cs abundance in the continental crust within the range from <1 to 6 mg kg^{-1}. It is a relatively rare element of the naturally occurring alkali metals in the terrestrial environment. It has lithophilic properties and behaves in the geochemical environments similarly to Rb, but appears to have a greater affinity to aluminosilicates. Thus, it is concentrated mainly in acidic igneous rocks and in argillaceous sediments where its contents range from 5 to 10 mg kg^{-1}. Most Cs, however, is dispersed in some common minerals, like micas and feldspars. Mean Cs content in coal is about 1 mg kg^{-1}.

Production and Use. Annual global production of Cs is estimated as 5.9 Mt [1]. There are relatively few commercial uses of metallic Cs. It is used in: vacuum tubes, rocket propellant, photovoltaic cells, and accurate atomic clocks. Compounds of Cs have also been employed as catalyst in organic synthesis.

Radioactive ^{137}Cs has been approved for the sterilization of some foods (e.g., wheat flour, potatoes), sewage, and surgical equipments, thus reducing the numbers of disease-causing bacteria.

Humans. Cesium occurs in tissues of all terrestrial and aquatic animals, and is distributed fairly uniformly in all types of tissues within the common range 0.01–0.05 mg kg^{-1}. The highest content is found in liver and heart tissues[2]. The mean concentration of Cs in soft tissues of “reference man” is given as 0.021[3] mg kg^{-1}. In human fluids Cs averages (in μg l^{-1}) in: blood, 3; serum, 1.5; and urine, 7. When its intake by organisms is increased, then it is likely to be accumulated in soft tissues.

Cesium exhibits an antagonistic reaction against potassium with respect to the biological availability. The daily dose of Cs with a regular adult’s diet is calculated as 10 μg and its content in an average diet is 9.4 mg kg^{-1}.

Cesium-137.

Radioactive isotopes, ^{134}Cs and ^{137}Cs, are produced by nuclear fission in nuclear power plants and occur also in fallout from nuclear weapons. Environmental concern with radiocesium in soils and food chain is largely a consequence of two events: *(i)* the worldwide fallout in the period 1952–1958, and *(ii)* the fallout from Chernobyl in 1986.

One of many Cs isotopes, ^{137}Cs is of special concern because it is a by-product of atomic energy production and nuclear weapons testing. Anthropogenic sources of this radionuclide include the mining and processing of contaminated

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[1] USGS. Mineral commodity summary. Reston VA: USGS, 2004.

[2] Jørgensen S.E. Principles of pollution abatement. Pollution abatement for the 21st century. Amsterdam: Elsevier, 2000.

[3] A compendium of geochemistry: From solar nebula to the human brain / ed. by Li Y.-H. Princeton, Oxford: Princeton Univ. Press, 2000.

ores. Also ash from coal burning and municipal waste incinerations may be a source of ^{137}Cs.

The geochemical characteristics of this long-lived radioisotope are fairly similar to those of the stable Cs. Thus, when it is deposited on soils it becomes strongly adsorbed by clay fractions, clay minerals and organic matter, and appears to migrate quite slowly in soil[4]. The fate of ^{137}Cs was widely studied after the fallout following the Chernobyl accident. At this accident, ^{134}Cs was also released, but this radionuclide is of a much less concern because it was released in a significantly smaller quantity and has a relatively short half-life ($t_{1/2}$ is 2.1 years) compared with ^{137}Cs ($t_{1/2}$ is 30 years). The deposition of both radionuclides was not only large in the zone surrounding the reactor, but also in several European countries, as well as on other continents.

Humans. The mean concentrations of ^{137}Cs in tissues of persons not exposed to this radionuclide vary from 0.106 to 2.440 pCi kg^{-1} FW, being the lowest in bones and the highest in gonads[5].

Strontium (Sr)

Strontium is a relatively common element in the Earth’s crust and its contents range between 260 and 730 mg kg–1. It is likely to concentrate in mafic igneous rocks and in carbonate sediments. Both geochemical and biochemical characteristics of Sr are similar to those of Ca. Strontium reveals lithophilic affinity and is associated with Ca, and in smaller extends with Mg. The Ca/Sr ratio, in particular environments, may reflect, to a certain extend, the abundance of Sr and its biogeochemical properties. Strontium occurs mainly as bivalent cation, but its chelated forms play an important role in the cycling.

Geological occurrence of Sr is associated mainly with calcareous rocks and sulfur deposits. The distribution of Sr in minerals is largely controlled by Ca, the ionic radius of which is fairly similar to that of Sr, thus it is likely to concentrate in calcium-rich minerals and to be incorporated in calcite and aragonite. Clay minerals have a large capacity to absorb Sr, and most argillaceous sediments are enriched in this element.

Commercially important minerals are strontianite, SrCO3; and celestite, SrSO4. Strontium occurs also in several other minerals, e.g., nordite or belovite, which are in association with Na and lanthanides. During weathering and transportation, Sr is incorporated in clay minerals and strongly fixed by organic matter. However, most Sr is likely to precipitate as biogenic carbonates, largely in the form of invertebrate shell material.

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[4] Meriwether I.R., Beck J.N., Keeley D.F., Langley M.P., Thompson R.H., Young J.C. Radionuclides in Luisiana
Soils // J. Environ. Qual.. – 1988. – 17. – P. 562–569.

[5] ATSDR (Agency for Toxic Substances and Disease Registry). Draft toxicological profile for several trace elements. Atlanta, GA: Registry, U.S. Dept Health Human Services, Agency for Toxic Substances and Disease, 2002.

Production and Use. Strontium world mine production in 2000 was 320 kt (USGS[6] 2004). Strontium does not have direct applications as a pure metal. However, its various compounds are broadly used (e.g., above 80% of all Sr consumed in the USA) in the manufacturing of ceramics and glass, i.e., television tubes, pyrotechnic materials. All color televisions in the USA are required by law to contain Sr in the faceplate glass of the picture tube to block X-ray emissions (ATSDR[7] 2002). Other uses of Sr compounds are in various technologies of metallurgy, luminescent paint pigments, and some medicines.

Humans. Strontium occurs in all mammalian tissues in the range from 0.09 to 0.24 mg kg^{-1}. It is accumulated mainly in bones (138 mg kg^{-1}) and other hard tissues (e.g., hair 4.2 mg kg^{-1}). In human fluids, Sr concentrations vary as follows (in μg l^{-1}): serum, 40; blood, 27; saliva, 11; and milk, 20 (ATSDR 2002).

Biochemical functions of Sr are not well known, but as reported D'Haese et al. (2002)[8], its small quantities are needed for proper processes of the calcification of bones and teeth.

There is not much evidence of Sr toxicity to man, other than in the biogeochemical provinces where increased level of Sr in the food chain, and especially in water is affected by bedrocks of increased Sr levels. Young organisms are more sensitive to Sr excess than older organisms. Inadequate levels of Ca and vitamin D in the diet increases the severity of skeletal effects, such as a reduction in bone mineralization, and alteration in the chemical composition of organic bone matrix.

Strotium-90. Strontium exists in the geological formations in several isotopic species, with atomic mass number from 79 to 102, of which ^{88}Sr is the most abundant stable isotope. Products of several nuclear processes are ^{89}Sr and ^{90}Sr, however the last radionuclide (^{90}Sr) is considered to be one of the most biologically hazardous for humans. The basis of the adverse effects of ^{90}Sr is related to ionizing radiation that is in the interaction of free radicals with cellular macromolecules, including DNA. Isotope ^{89}Sr is used as a cancer therapeutic to alleviate bone pain, while isotope ^{85}Sr has been used in various radiologic instruments (ATSDR 2002).

Sources of ^{90}Sr are associated with nuclear reactions, and have been tracked since nuclear energy became used on the global and regional scales. During the period 1945–1980, radioactive Sr was released into the atmosphere mainly from aboveground detonations of nuclear weapons. Its continuous sources increased greatly after the Chernobyl accident in 1986, and its relatively long live ($t_{1/2}$: 29 years) may lead to steadily increasing concentrations in various environmental compartments.

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[6] USGS – U.S. Geological Survey

[7] ATSDR – Agency for Toxic Substances and Disease Registry (USA)

[8] D'Haese P.C., Lamberts L.V., Broe M.E., Silicon. In: Elements and their compounds in the environment / Merian E., Anke M., Ihnat M., Stoeppler M. (eds). 2nd ed. Weinheim: Wiley-VCH, 2004. – Pp. 1273–1284.

Humans. The accumulation of ^{90}Sr in food and feedstuffs has been of a great concern. Milk and milk products can be one of the most serious sources of ^{90}Sr to humans in regions contaminated by this isotope.

The process of the discrimination of this radionuclide occurs during its transfer in the food chain, and the ratio of its concentrations in bones and soils is estimated to be relatively low, at value of 0.05. However, humans and animals are subjected to its additional sources from air dust and water. Radioactive Sr is mainly taken up into bone and retains there for a long time. At very high exposure to ^{90}Sr in bone, bone marrow is damaged (at critical average level 8 pCi l^{-1}). The health of organisms exposure to higher doses of ^{90}Sr is harmfully affected. Toxic effects of the ^{90}Sr are following:

- Development of various tumors, especially in bones
- Impaired bone mineralization
- Blood cells (red and white) reduction
- Leukemia
- Loss of platelets resulting in abnormal bleeding
- General fatigue and susceptibility to infection disease

The impact of radioactive Sr on human reproduction has not been observed yet. However, these effects are known to have occurred in animals. Similarly, as stable Sr, the radionuclide is relatively easily extracted from the organisms, especially by young, while in elders it is likely to be accumulated, especially in bones where Sr becomes relatively immobile.

Chromium (Cr)

The distribution pattern of Cr in rocks shows the tendency to its concentration in maficigneous rocks and in argillaceous sediments. In ultramafic rocks its content can be over 1 000 mg kg^{-1} and in felsic ones (e.g., granites) may be less than 20 mg kg^{-1}.

Chromium is precipitated from magma at an early stage, in the chromium spinel mineral group, with the general formula, $(Mg,Fe)O \cdot (Cr,Al,Fe)_2O_4$. All Cr minerals are resistant to chemical weathering and due to their high specific gravity and are usually concentrated in various types of intrusions and deposits. Chromite ores differ in composition mainly due to their variable proportion to silicate minerals. Cr-minerals are likely to be associated with pyroxenes, amphibolites and micas. Among these minerals chromite, $FeCr_2O_4$ has an economic importance. Crocoite, $PbCrO_4$, is also relatively common.

The geochemistry of Cr is complex because of its easy conversion from one oxidation state to another. The geochemical association of Cr with Fe and Mn is responsible for its elevated concentrations in ferromanganese nodules of sea bottom sediments as well as in Feconcretions of soils.

Production and Use. The main use of Cr is in metallurgical, refractory and chemical industries, however, it was first used as a pigment because of its yellow color. The major proportion of Cr is used for stainless steel and chromate plating.

In the chemical industry, Cr (both +3 and +6) is used primarily in pigments, metal finishing, leather tanning and wood preservatives. It is commonly used in the manufacture of green tints for paints, varnishes, glazes and inks. Leather tanning utilizes especially substantial amounts of Cr compounds. This metal is used in various phases of paper manufacture. It is a component of different refractory products, such as refractory bricks.

The main source of Cr pollution is considered to be from dyestuffs and leather tanning when wastes are discharged directly into waste streams, either as liquids or solids. Sewage treatment plants from industrial and residential sources discharge substantial amounts of Cr. Thus, COPR (chromite-ore processing residue) is of the greatest environmental risk in some regions.

Humans. Contents of Cr in mammalian tissues vary between 30 and 290 μg kg^{-1}. Normal endogenous Cr levels for the USA population have been reported as 0.01–0.17 μg l^{-1} in serum, 0.24–1.8 μg l^{-1} in urine, and 234 μg kg^{-1} in hair (ATSDR 2002). In workers exposed to Cr^{6}, the mean level of total Cr body's fluids significantly increases.

Amounts of Cr in many human organs decrease with aging, especially in the liver, whereas its concentration in the lungs is likely to increase with age. The Cr concentration in human milk is especially variable, with a range of 0.4–80 μg l^{-1}.

Chromium is an essential micronutrient for normal energy metabolism of humans and animals. It is reported to control the metabolism of glucose and lipids. It is a part of the glucose tolerance factor (GTF) and appears to affect some of the enzymes that regulate cholesterol synthesis. Although severe Cr deficiency is rare, marginal Cr deficiency is relatively common and results in:

- Increased cholesterol levels
- High blood sugar levels
- Coronary dysfunction
- Some changes in aortas
- Some abnormalities of nerve stimulation of the extremities

However, Cr^{6+} also exerts toxic effects and any exposure (oral, dermal and inhalation) to increased concentrations of Cr can be harmful (ATSDR 2002). Excessive doses of Cr may result in liver and kidney failure, anemia, muscle breakdown and abnormalities in blood clotting. When an excess of Cr compounds are inhaled, lung, nasal and possible stomach cancer may develop (ATSDR 2002). Also dermal allergy and asthma may occur under the exposure to Cr compounds.

The primary sources of dietary Cr are vegetables, whole cereal grains and nuts, followed by egg yolks, brewer's yeast, liver, and seafoods. Ascorbic acid (vitamin C) and glutathione are found to reduce Cr^{6+} to Cr^{3+} and thus may reduce toxic effects of the excess of Cr^{6+}.

Molybdenum (Mo)

The average content of Mo is given for the upper Earth's crust as 1.1 mg kg^{-1} (range 1–2 mg kg–1), and its concentration is elevated in granitic rocks and argillaceous sediments, up to 2.5 mg kg^{-1}.

Molybdenum exhibits unusual geochemical behavior since in most environmental compartments it is likely to form oxyanions, however, under reducing conditions it has a high affinity for sulfur. The most common Mo mineral is molybdenite, MoS_2, which occurs in several geological formations. Less frequent are: molibdite, MoO_3; wulfenite, $PbMoO_4$; and powellite, $CaMoO_4$. Several other Mo minerals, mainly oxidates, are known to be associated with various sediments. Especially Mn-Fe rich nodules have the ability to concentrate Mo up to 2 000 mg kg^{-1} (Fairbridge, 1972[9]).

Production and Use. Molybdenum is mined as a primary ore deposit, mainly as molybdenite, and as a byproduct, generally from copper mines. Annual production of Mo in 2003 was 127.4 kt (WMSY 2004[10]). Its main use is in metallurgy for the hardening of alloys. This metal is also widely used in electronics and chemistry (e.g., catalysts).

Humans. Molybdenum occurs in all human and animal tissues. Average values of Mo concentrations in human whole blood range from 3.4 to 14.9 μg l^{-1} and seem to be a little bit lower in women than in men.

Molybdenum is an essential micronutrient being a component of several enzymes involved in oxydation-reduction processes and regulates the metabolism of purines and fats. The oxomolybdenum enzymes belong to the xanthine oxidase, sulfide oxidase and reductase families. It is relatively easily absorbed at all levels of intake and its whole blood levels vary directly with the dietary Mo intake. There is only one human case of the Mo deficiency described, that responded to Mo therapy.

The main sources of Mo in human diet are legumes, pulses, dark leafy vegetables and organ meats. The minimum daily requirement for Mo by adults is estimated at about 0.02 mg (Turnlung et al. 1993). The upper tolerable intake of Mo by children is established as 0.3–1.7 mg d^{-1}, depending on the age and by adults as 2 mg d^{-1} (WHO/IPCS[11] 2002).

The excess Mo in the human diet influences its accumulation in serum, urea, and hair. Apparently, it is also related to cancer of the stomach.

Manganese (Mn)

Manganese is one of the most abundant trace elements in the lithosphere. Its common occurrence in rocks ranges from 350 to 2 000 mg kg^{-1} and higher concentrations are associated with mafic rocks.

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[9] The encyclopedia of geochemistry and environmental sciences / Fairbridge R.W. New York: Van Nostrand Reinhold Company, 1972.

[10] World Metal Statistics Yearbook. World Bureau of Metal Statistics, London, UK (https://www.metaltorg.ru/)

[11] WHO – World Health Organization, IPCS - International Programme on Chemical Safety

Manganese is a member of the iron family and is closely associated with Fe in geochemical processes. Thus, the Mn cycle follows the Fe cycle in various geochemical environments. During weathering, Mn is oxidized in minerals, under atmospheric conditions and may be mobilized. The Mn oxides are reprecipitated and readily concentrated in forms of secondary Mn minerals, often in forms of concretions and nodules. Under weathering in tropical and subtropical conditions, Mn is concentrated in residual deposits, while under humid colder climate, Mn is leached by acid solutions from sediments and soils.

Complex behavior of Mn in sedimentation processes resulted in the accumulation of this metal in different layers of sediments. Polymetallic concretions in deep-sea sediments are effects of specific Mn properties. The genesis of deep-sea concretions is not fully understood, but recently the influence of microbes and organic matter has been recognized. Occurrence of Mn is highly associated with activities of microbes in both sediments and soils.

The redox state of Mn is very variable and is mediated by both geochemical and biological processes. The most common cation is Mn^{2+} that readily occupies the sites of other divalent cations (e.g., Fe^{2+}, Mg^{2+}). Several complex anions and cations of Mn as well as hydroxides of variable composition are also common.

The complex mineralogical and chemical behavior of Mn and its participation in oxidation-reduction processes resulted in the formation of the large number of oxides and hydroxides of variable stability and properties. The physical features of Mn compounds and minerals, especially the small size of crystals and large surface areas of amorphous forms have important geochemical and pedochemical implications.

Both Mn and Fe oxides are considered to be the most abundant compounds of the Earth’s surface that can serve as anaerobic terminal electron acceptors in microbial metabolism.

Production and Use. Global annual production of Mn in 2003 was 24.35 Mt (WMSY[12] 2004). Manganese ores are widely distributed in various geological and climatic environments and concentrated mainly in residual deposits, as various oxides and hydroxides; to a lesser extend as carbonates and silicates.

Manganese is used mainly in the metallurgical industry for steel and various alloys to provide hardness and toughness, and as an anti-oxidant. Alloys with Mn are used in the electrical industry (e.g., dry-cell batteries). It is also widely applied in the production of pigments, ceramics, and glass. Manganese sulfate ($MnSO_4$) is used as fertilizer and as a fodder supplement. It is relatively broadly used as fungicides, mainly for seed treatment (e.g., *Maneb*[13], manganese ethylene-bis-dithiocarbamate).

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[12] World Metal Statistics Yearbook. World Bureau of Metal Statistics, London, UK (https://www.metaltorg.ru/)

[13] A white compound used as a fungicidal powder on vegetables and fruit. Chem. formula: $C_4H_6N_2S_4Mn$.Origin: from elements of the name man(ganese) e(thylene) b(isdithiocarbamate). (according to ABBYY Lingvo)

Since 1970, Mn has been used in gasoline, first in Canada and the USA, as an antiknock agent (as replacement for Pb in unleaded fuel), in the form of an organic compound – methylocyclopentadienyl manganese tricarbonyl (MMT).

Potassium permanganate ($KMnO_4$) has long been used as an oxidizing catalyst in chemical processes, and in disinfection in medicine, as well as in the purification of various waters. Also several other Mn compounds (e.g., gluconate, sulfate) are used in pharmaceutical production.

Humans. Manganese occurs in all tissues of terrestrial and aquatic organisms. The physiological function of Mn is closely associated with some enzyme activities (e. g., superoxidase dismutase-SOD, arginase). The metabolism of Mn in the body is closely related to the metabolism of Fe that is manifested by a higher Mn absorption by women with low ferritin (Fe-protein) contents. This indicates an impact of Fe status of the organism on the Mn metabolism. In general, Mn is an activator of different enzymes that control the metabolisms of carbohydrates, proteins and lipids (including cholesterol), and nitrogen metabolism.

Symptoms of the Mn deficiency in humans are very rare. The Mn contents in human tissues, especially in bones, decrease with age, what can be associated with bone fractures (osteoroposis), dermatitis and hypochotesterolemia. Skeletal deformities and testicular dysfunctions can result from a Mn deficiency. At the normal, balanced diet, the Mn supply is adequate to meet its requirement.

The intake of Mn by adults varies from 0.1 to 10 mg d^{-1} in different countries. The estimated safe and adequate daily intake of Mn by adults was previously given to be between 2 and 6 mg d^{-1} whereas the recent EPA[14] recommendation is up to 10 mg d^{-1} for a 70 kg BW. The upper tolerable intake of Mn by children is established as 2–9 mg d^{-1}, depending on the age (WHO/IPCS 2002).

Some kinds of vegetarian diet, as well as Fe deficiency, anemia, and some hepatic dysfunction can promote chronic manganese toxicity. This can affect the Mn accumulation in brain that can be associated with neurological symptoms. Manganese, either ingested or inhaled is likely to concentrate in brain and causes a manganism – acute toxic symptoms of psychiatric disorders.

Oral Mn poisoning has not been observed often and is mainly related to drinking water. The ingestion of excess Mn can result in liver cirrhosis. The recent use of MMT in gasoline has prompted debates on the Mn potential health risk, especially since several studies have proven that the inhalation of Mn-rich dust by humans can increase susceptibility of the respiratory tract to infection and can induce Mn-pneumonitis and some damage to the central nervous system (Plumlee and Ziegler, 2003[15]; Schäfer, 2004[16]). Neurotoxicity of inhaled Mn depends on its particle size and species. In Germany, the MAK[17] value of Mn has been set at 0.5

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[14] Environmental Protection Agency

[15] Plumlee G.S., Ziegler T.L. The medical geochemistry of dusts, soils, and other earth materials. Treatise on geochemistry. – 2003. – 9. – P. 263–310.

[16] Schäfer U. Manganese // Elements and their compounds in the environment / Merian E., Anke M., Ihnat M., Stoeppler M. 2nd ed. Weinheim: Wiley-VCH, 2004. Pp. 901–930.

[17] The MAK value is the maximum permissible concentration of a substance as a gas, vapour or aerosol in the air at the workplace which, according to current knowledge, does not normally affect worker health or

mg m^{-3}. The highest Mn concentration in drinking water, established by the WHO, is 0.5 mg l^{-1}. A much lower concentration of Mn, 0.05 mg l–1, has been recently proposed in the USA and Europe (Schäfer, 2004).

Cobalt (Co)

Cobalt, in the Earth's crust, is highly concentrated in mafic rocks, up to 200 mg kg–1, when compared to its content in acid igneous rocks, 1–15 mg kg^{-1}, and to its abundance in the upper continental crust, 12 mg kg^{-1}. It is also likely to concentrate in black shales.

As Co reveals siderophilic character it is likely to form minerals with S, As, and Se. Its common rock-forming minerals are: cobaltite, CoAsS; smaltite, $CoAs_{2-3}$; linneite, Co_3S_4; and arsenosulfide, CoAsS. In the hypergenic zones and in soils, the formation of erythrite, $Co_2(AsO_4)_2 \cdot 8H_2O$ is likely to occur.

The geochemical cycle of Co closely resembles Fe and Mn cycling, and is likely to be associated with several minerals of these metals. During weathering processes, Co^{3+} is unstable in the aqueous phase and precipitates as sulfides and/or adsorbed by hydrous oxides. In soils, however, Co behavior seems to be strongly influenced mainly by the Mn oxide phase formation.

Relatively easy interactions of Co with all metals that are associated geochemically or biochemically with Fe, have a significant impact on its behavior in soils and its phytoavailability. Especially exhibit are unique antagonistic reactions of Fe and Mn arise from their ability to occupy the same sites in crystalline structures and from the similarity of their metallo-organic compounds.

Production and Use. Global annual mining of Co in 2000 was 35.6 kt (USGS[18] 2004) and in 2003 was 43.03 kt (WMSY[19] 2004). Most of Co is used for special alloys. The application of Co is very broad and includes several industries such as stainless steel production, aerospace equipments, electroplating, and magnetic devices. This metal is also used in chemical catalyses and synthesis of fuels, in paints, and as a plastic hardener.

A significant branch of the pharmacy uses Co for medical and veterinarian drugs. The radionuclide ^{60}Co has been used for some medical treatments as a source of gamma radiation. This radionuclide has also been used in special equipments in steel production.

It is estimated that about 2% of Co used in the metallurgical industry is discharged to sewage sludge.

Humans. Cobalt occurs in all mammalian tissues and its contents vary from 5.5 to 230 μg kg^{-1}, with the highest value in the liver and the lowest in the brain. Cobalt is essential for humans and for most animals as a component of the vitamin B12. In the form of inorganic metal, Co is required for the synthesis of bacterial

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cause unreasonable nuisance even with repeated and long-term exposure, usually 8 hours a day, but assuming an average weekly working time of 40 hours.

[18] U.S. Geological Survey

[19] World Metal Statistics Yearbook. World Bureau of Metal Statistics, London, UK (https://www.metaltorg.ru/)

vitamin B12 by ruminants. Although inorganic Co (non-B12) is present in organs and fluids of a body, its other physiological functions are unknown. Cobalt is likely to be bound by some proteins and to replace other divalent cations (e.g., Zn, Mn) in various enzymes, without any effects.

The deficiency of Co may affect anemia and anorexia. Anemic patients show increased requirements for Co. Presumable Co binds to Fe-transport proteins and is involved in the formation of hemoglobin. The excessive ingestion of Co may cause polycythemia (increased red blood cells), cardiomyopathy, hypothyroidism, pancreas failure, bone marrow hyperplasia, and some types of cancer.

Most of Co is ingested in inorganic forms, while vitamin B12 accounts for a very small fraction of the total Co intake. Only a small fraction of Co is inhaled from air.

Nickel (Ni)

In the Earth's crust, the mean Ni abundance has been estimated at around 20 mg kg^{-1}, whereas in the ultramafic rocks Ni ranges from 1 400 to 2 000 mg kg^{-1}. Its concentrations decrease with increasing acidity of rocks, down to the range of 5–20 mg kg^{-1} in granites. Sedimentary rocks contain Ni in the range from 5 to 90 mg kg^{-1}, with the highest range being for argillaceous sediments.

Nickel reveals both chalcophilic and siderophilic affinity and readily combines with metallic Fe. Therefore, Ni-Fe compounds are common in the Earth's core and meteorites. Also the great affinity of Ni for S accounts for its frequent association with segregates of S bodies. The principal Ni metallic ore composed mainly of pentlandite, $(Ni,Fe)_9S_8$ and pyrrhotite, $Fe_{1-x}Ni$). In rocks, Ni occurs primarily as sulfides (millerite, NiS), arsenides (niccolite, NiAs), and antimonides (ullmanite, NiSbS). Nickel often forms sulfides and sulfarsenides together with Fe and Co, and is associated with several Fe minerals.

After weathering, most Ni is coprecipitated with Fe and Mn oxides, and becomes included in goethite, limonite, serpentinite, as well as in other Fe minerals. It is also associated with carbonates, phosphates, and silicates.

Organic matter exhibits a strong ability to absorb Ni, thus it is likely to be highly concentrated in coal and oil. This concentration is apparently an effect of the precipitation of Ni as sulfides in sediments rich in organisms and under reducing conditions.

Therefore, a significant proportion of Ni loads to the environment is from biolite combustion. Global emission of Ni from coal combustion is calculated to be around 20 kt yr^{-1}, and from oil products combustion it is estimated to range from 10 to >40 kt yr^{-1} (Kabata-Pendias and Pendias, 1999[20]).

Production and Use

Nickel has been broadly used in several industries. A great proportion of Ni goes into the production of variety of metal alloys for the aircraft and the plating

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[20] Kabata-Pendias A., Pendias H. Biogeochemistry of trace elements. 2nd ed. Warszawa: Wyd Nauk PWN, 1999.

industries. Most of Ni is used in various alloys (e.g., hastelloy, nickelbase, nickel-silver) that provide oxidation and corrosion resistance for use with acids and salts. Ni-alloys are also high-temperature and creep and stress resistant. Stainless steel usually contains Ni at 8–10%.

It is widely used for magnetic components (e.g., magnetic tapes, permanent magnets) and electrical equipments. Ni-alloys are used for different tools and vessels used in medicine and in food technology, as well as for kitchen equipment (e.g., cutlery). Its compounds are utilized as dyes in ceramic and glass manufactures, and in batteries containing Ni-Cd compounds. Nickel has been a common catalyst for hydrogenation of fats and oils, and for the oxidation of various organic compounds.

Humans. Investigations on the toxicity of Ni have indicated various effects of its excess, among which the most important are developmental, genotoxic, neurological, reproductive, and carcinogenic. Generally, the soluble compounds are more toxic than the less-soluble compounds. However, slightly soluble Ni compounds are likely to be carcinogenic at the site of deposition (ATSDR 2002a).

Nickel should be used with great precautions in industry since is exceedingly toxic when inhaled. Lung and nasal cancer were the forms of cancer commonly reported in the nickel-refinery workers. Up to 55% of the inhaled less-soluble Ni is retained in the lungs.

Copper (Cu)

Copper occurs in the Earth’s crust at concentrations between 25–75 mg kg^{-1}. Its abundance pattern in rocks shows the tendency for the concentration in mafic igneous rocks and in argillaceous sediments, however, it is rather excluded from the carbonated rocks

Copper reveals a strong affinity for sulfur; hence its principal minerals are chalcopyrite, $CuFeS_2$; bornite, Cu_5FeS_4; chalcocite, Cu_2S; and covellite, CuS. The second group contains oxidized copper minerals, which are mainly formed during the weathering of copper sulfides exposed to erosion. Here, Cu is incorporated in oxide and carbonate minerals of which cuprite, Cu_2O; tenarite, CuO; malachite, $Cu_2CO_3(OH)_2$, and azurite, $Cu_2\ (CO_3)_2\ (OH)_2$ are the most common. Copper is often associated with sphalerite, ZnS; pyrite, FeS; and galena, PbS. Its deposits are commonly found in acid igneous rocks and various sedimentary deposits.

Production and Use. World primary production of Cu has increased from 9.2 Mt in 1990 to 13.7 Mt in 2003 (USGS, 2004). In the 20th century its utilization increased rapidly and now the mining and refining of Cu takes place on all six continents.

Due to its versatile properties, Cu has a wide range of applications. It is used for the production of conductor materials, wire, rod and bar; it is also used for current generation, transmission and conduction, and in the manufacture of motors and electrical equipment. Other applications of Cu include: fabrication of household articles, coins, art objects and ammunition. In the automobile industry, Cu has been partly replaced by Al. Copper wires and cables used for telecommunications are being nowadays displaced by microwave technology and fiber optics.

Copper is also widely used in agriculture (fertilizers, pesticides etc.). Due to its bacteriostatic properties, it is also used as a feed additive in livestock and poultry nutrition.

Humans. Copper is an essential element that is a component of several roteins and metalloenzymes. It is prerequisite in oxidation-reduction reactions and hemoglobin synthesis. Metallothionein is the main intracellular Cu-protein involved in Cu transport within the body. Copper is associated mainly with three distinctive phases, ceruloplasmin, albumins, and amino acids.

Copper deficiency in humans may affect several diseases such as: slow growth, anemia, and fertility, hair and weight loss, disorders of central nervous system, cardiovascular problems, osteoporosis and several other metabolic dysfunctions (ATSDR[21] 1990).

An excess of Cu has an adverse affect on several physiological processes such as: impairment of membrane properties, impairment of DNA and enzyme functions, especially those containing sulfhydryl groups, cellular injury due to the generation of hydroxyl radicals OH– and OH+ from hydrogen peroxide H_2O_2 which can lead to oxidative stress.

The main source of Cu for humans and animals are all kinds of food and water. However, the inhalation of atmospheric fine particles (<10 μm) which are carriers of Cu, can also be a significant source of Cu, in Cu-rich regions.

Copper in human diets does not generally exceed the human requirement. Several European studies indicated that intake of Cu is rather low among the populations of many European countries.

Zinc (Zn)

Zinc has been known as the metal since the Middle Ages, but industrial extraction and Zn refining only began in Europe in the late 18th Century.

Zinc is quite uniformly distributed in magmatic rocks, whereas in sedimentary rocks is likely to be concentrated in argillaceous sediments. It is very mobile during weathering processes and its easily soluble compounds are readily precipitated by reaction with carbonates, or it is sorbed by minerals and organic compounds, especially at the presence of sulfur anions. Some of the most common compounds are zinc chloride, $ZnCl_2$; zinc oxide, ZnO; zinc sulfate, $ZnSO_4$; and zinc sulfide, ZnS. This means that the metal has the potential for forming a variety of compounds with organic and inorganic groups. Most Zn minerals contain above 50% of pure metal.

Production and Use. The principal ores of Zn are composed of sphalerite and wutzite, ZnS, of the same chemical formula but with various crystallographic structures, cubic and hexagonal, respectively. Relatively common is also

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[21] ATSDR – Agency for Toxic Substances and Disease Registry

smithonite, $ZnCO_3$. Zinc ores contain different elements such as Pb, Cu, Ag and Cd of which Cd is most closely associated with Zn.

Zinc is used in many industries, mainly as corrosion protection on steel components and other metals. It is an important component of various alloys and is widely used as catalyst in different chemical production (e.g., rubber, pigments, plastic, lubricants, and pesticides). Due to its versatile properties, its use has been documented in different sectors such as batteries, automotive equipment, pipes and household devices. Different compounds of Zn have dental and medical applications.

Humans. Zinc plays several fundamental functions in metabolic processes. It is essential for growth, development, and reproduction. Its intake from food varies highly and depends on several factors, but often on intereactions between other metals. Important antagonistic relationship is between Zn-Cd and Zn-Cu.

Dietary reference values for Zn intake (in mg d^{-1}) as established by the WHO in 1996 are as follows: 5.5–7.5 for children (1–10 years), 12–13 for children (11–18 years), 9.5 for adult man, and 6.5 for adult female.

Meat products are a better source of Zn than plants. Meat contains Zn at the level of 19 to 90 mg kg^{-1}, in pork and pork-liver, respectively.

Zinc is relatively slightly toxic and therefore its deficiency occurs most commonly. At risk of the Zn deficiency are mainly infants and children, but also older adults, non-healthy adults, and some vegetarians.

The ingestion or inhalation of larger doses of Zn, especially in forms of inorganic compounds, can be harmful to individuals. It can damage alimentary tracts, and affect diarrhea and fever. A short-term illness called *metal fume fever* can result if workers breath very high levels of zinc dust or fumes at the working place. It may cause chills, fever, excessive sweating and weakness.

Cadmium (Cd)

The average content of Cd is given for the Earth's crust as 0.1–0.2 mg kg^{-1} and its abundance is fairly similar in both igneous rocks and sedimentary rocks. The metal occurs rarely in nature in the pure form. Its common minerals are: greenockite, CdS; octavite, CdSe; and monteponite, CdO. Its host minerals are Zn and Pb ores, sphalerite, biotite, and amphiboles.

Cadmium and Zn have similar ionic structures and electronegativities and belong to the chalcophile group. Although Cd has the same valence and similar ionic radius as Ca, it does not substitute for Ca in minerals.

During weathering processes, Cd forms simple compounds, such as CdO, $Cd(OH)_2$, $CdCl_2$ and CdF_2 that are easily mobile and follow Zn, especially in sedimentation processes.

Cadmium is considered as being one of the most ecotoxic metals that exhibits adverse effects on all biological processes of humans, animals, and plants. This metal reveals its great adverse potential to affects the environment and the quality of food.

Production and Use. Cadmium is produced mainly as a by-product in mining and refining of Zn. Therefore its supply is more dependent on the Zn production than on the Cd demand. Generally, 3 kilograms of Cd is produced from one ton of the Zn production (OECD[22], 1994).

Cadmium is also recovered from recycled materials such as Zn-Cd batteries. Approximately 10–15% of the Western World production stems from secondary materials. The main use of Cd is in the sector of Ni-Cd and Ag-Cd battery production. Relatively high amounts of Cd are used as pigments (yellow) and for coatings and stabilizers. Due to its unique physical and chemical properties, this metal is also added to alloys as stabilizers for various plastics, mainly for a purpose to provide protection from sunlight, chemical attack or heat degradation.

Humans. Cadmium is one of the most toxic metal to humans, mainly due to the ability to combine with sulfhydryl groups and thus disturb function of several SH-group enzymes that leads to changes in proteins. Recognized in 1960s in Japan, so-called *Itai-Itai* disease has increased the attention paid to environmental Cd pollution and its impact on health. *Itai-Itai* disease had occurred due to run off Cd containing mining tailings in the paddy fields. Thus, Cd uptaken by rice was subsequently ingested by humans. The Cd excess caused mainly the damage to skeletal structure, especially in elderly women. This phenomenon has brought important information on the Cd transfer in food-chain.

Main toxic effects of the excess of Cd on humans are related to:

- renal damage
- hypertention
- emphysema
- carcinogenic changes, mainly of kidney and prostate
- skeletal deformation due to impaired Ca metabolism
- low reproduction functions

Cadmium intake by humans is mainly by inhalation and ingestion of food and drink. Other mechanism is “hand-to-mouth” which generally occurs at the working place. Also the smoking is a significant root of the Cd exposure to general population. The dietary exposure of population varies highly between countries and is affected by local conditions and occupations.

The concentration of Cd in the atmosphere does not appear to pose a great threat to human unless one lives close to a zinc-lead smelter. But still, physicians are concerned about Cd exposure in Pb-Zn smelter, Ni-Cd battery factories or other manufacturings that use Cd compounds, especially when the operation involves heatings. These persons can build up Cd level in the liver over time. Cadmium is not very well absorbed (it may be about 20%), but still it is high comparing with other metals in the environment.

The acute toxicity of Cd is rather rare. With the Zn deficiency, more Cd is stored in human body. With long body retention time, the concentration of Cd in target organs will increase in time. The target organ is generally kidney or more specifically the renal cortex.

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[22] OESD - Organization for Economic Co-operation and Development

Mercury (Hg)

Mercury has been known since prebiblical times and this element occupies a unique place in the human civilization. It has been known by alchemists in China, perhaps since 2 000 years BC. For over a century it has been known as an environmental pollutant. Mercury abundance in the Earth's crust is very low, in the range of 0.02–0.06 mg kg^{-1}, but is it likely to be concentrated in argillaceous sediments and in coal.

There are several Hg host minerals such as amphiboles, sphene, sphalerite, and other sulfides. It may evaporate from some compounds release to various ecosystems. It is chalcophilic and shows the affinity to several metals, such as Ag, Zn, Cd.

In the 1950s, it was established that emissions of Hg to the environment could have serious effects on human health. In the United States, the 1990 US Clean Air Act Amendments have identified Hg as one of the trace elements listed in the legislation as “hazardous air pollutant” because of its toxicity, availability, and potential bio-accumulation within the environmental compartments.

Increased Hg load into the environment is additionally due to its use in Au-mines for amalgamation process became of a real risk of its transfer to the food chain. This is a serious threat in the Amazonian region and in the Siberian subregion.

Production and Use. Due to toxic properties of Hg and strict regulations, primary Hg production and its uses have been restricted in many countries. In Finland, virgin Hg is recovered from roaster gases by precipitation-filtration methods at the Kokkola Zinc Plant. In the West, secondary Hg production (e.g., recycling) can be accomplished by chemical or thermal treatment. The most common method is thermal treatment where Hg-containing scrap is sized and heated in furnaces or retorts at about 538 °C to vaporize the Hg.

In the EU-25 states, Spain and Finland still produce virgin Hg. The old Hg mine in Almadén, Spain, operating since 4th Century BC, the largest Hg producer in the world, has been stopped in recent years.

Main uses of Hg are in the caustic soda and chlorine production and in the Au-ore processing (amalgamation). There is a tendency to replace Hg by other metals or compounds, as for example, in Northern Europe; an organic compound has replaced Hg-amalgam for teeth feelings. Also Hg free thermometers or Hg free batteries are quite common in the western countries. However, Hg is still used in many products including: fluorescent lamps, batteries, instruments, manometers, electric conductors, metal recovering processes, dental fillings, bactericides, fungicides, insecticides, pharmaceuticals and also in paints. The use of Hg in both interior and exterior paints is prohibited in the USA and in many other countries in Europe (particularly in the north Europe).

Humans. The biochemistry of Hg has received significant attention because of the toxicity of Me-Hg, its accumulation in biota and biomagnification in the human food chain.

Both forms of Hg, elemental and organic have acute or chronic effects on humans. In a brief summary, Hg toxicity to humans is related to:

- Mutagenic, carcinogenic, and teratogenic effects
- Immunology impaired
- Coronary disease
- Central nervous system damage
- Deformation of DNA
- Low reproduction
- Disturbance of the development of a child

The Me-Hg compounds irreversibly damage neurons of the central nervous system. At high sublethal Hg doses in man, it may also cause: nervous disorders, brain damage, cancer, cerebral palsy, gross motor and mental impairment, speech disturbances, blindness, deafness, microcephaly, intestinal disturbances, tremors, and tissue pathology (Drasch et al., 2004[23]).

The Hg concentration in fish tissues is of great health risk. Dietary intake of Hg has been studied recently for 14 countries, including the USA. Intake of Hg depends, to a great extend, on dietary habits. In the Nordic countries, especially in Sweden and Finland, high intake of Hg has been observed.

Several human populations, around the world, have been identified as being in high risk groups due to the consumption of fish with elevated Me-Hg contents. However, higher consumption of cereals and other foods contribute more or less about the same amount of Hg intake as that from fish. As a result of dietary habits, fish cannot be blamed as the highest source of Hg for human diets. Nevertheless, fish food is usually considered to contribute a great proportion of Hg in a diet.

The concentration of Me-Hg in fish is of a special concern. It is regulated by restrictions of the consumption, especially for pregnant woman and children, when the concentration in fish is higher than 1 mg Hg kg^{-1}.

Since the 1950s, when Hg compounds were commonly used as fungicides, several Hg intoxications have been observed in humans. It was known as *Minamata* disease and has occurred in Japan, after the consumption of fish and shellfish with increased Hg contents, in the range of 2.6–6.6 mg kg^{-1} (Adriano, 2001[24]).

Aluminum (Al)

Aluminum is the third most abundant element in the Earth’s crust, occurring at about 8%. It reveals lithophile properties, one oxidation state (+3) and is slightly mobile in hypergenic zones. However, in an acidic environment, its solubility increases and Al becomes toxic to terrestrial and aquatic species. Naturally occurring Al compounds exist mainly in undissolved forms.

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[23] Drasch G., Horvart M., Stoeppler M. Mercury // Elements and their compounds in the environment / Merian E, Anke M, Ihnat M, Stoeppler M (eds.). 2nd ed. Weinheim: Wiley-VCH, 2004. – P. 931–1005.

[24] Adriano D.C. Trace elements in terrestrial environments: biogeochemistry, bioavailability and risk assessments. 2nd ed. Berlin Heidelberg: Springer-Verlag, 2001.

Aluminum is either main or secondary component of many minerals, especially of all silicates. Minerals composed only of Al are: boehmite -AlOOH; diaspore - AlOOH; corundum - Al2O$_3$; and hydrargilite/gibbsite - Al(OH)$_3$ that is the main component of bauxite rocks. Possible host minerals of Al are: feldspars, micas, and all layer silicates.

Aluminum reacts with mineral acids and strong alkalis due to its amphoteric character. It exhibits a strong relation to electronegative groups (e.g., OH^-) and to some ions (e.g., F^-). Its partitioning between solid and liquid phases has been cited as results of reactions between water molecules and electron-rich anions, e.g., chloride, fluoride, sulfate, nitrate, and negatively charged functional groups of humic materials and clays (WHO, 1997).

Production and Use.

H_2O and occurs mainly in tropical and sub-tropical areas. There are also some bauxite deposits in Europe. The commercial deposits are mainly gibbsite, and boehmite.

Scrap Al has significant value and can be recycled repeatedly. The recycling of Al requires only 5% of the energy as compared to primary production and as such generates only 5% of the “green house” gas emissions (http://www.world-aluminium.org/production/recycling/index.
html).

In 1998, global recycling of Al scrap was about 11.6 Mt, which fulfilled close to 40% of the global demand. In Europe, average recycling of Al cans and other scrap is about 40%. In some countries, such as Sweden and Switzerland, Al scrap recycling is over 80%.

Aluminum ores, most commonly bauxites, contain up to 55% of Al_2O_3. Due to versatile properties of Al, it is used in different industrial sectors including: metallurgical, packaging, transportation, construction, and electrical and chemical productions. Its compounds are used in paper manufacturing, water purification, sugar refining, wood preservation, leather tanning, waterproofing textiles and many others.

Aluminum is a component of cathode ray tube heating elements, is used as a corrosion inhibitor, cement accelerator, and has several others applications (HSDB[25]).

Humans. There is increasing awareness and concern of the Al toxicity to world population and ecosystems due to acid rain/precipitation (Matsumoto 2000). Although there is much debate on Al effects on humans, so far no positive conclusions have been made. It has been cited that there is a risk of Alzheimer’s disease (AD) when one is exposed to Al-dusts at work (WHO 1997). Aluminum is relatively easily excreted from human body, however at kidneys’ disorders, Al may be accumulated in brain cells and in bones.

Lead (Pb)

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[25] Hazardous Substances Data Bank (HSDB) - Comprehensive, peer-reviewed toxicology data for about 5,000 chemicals: http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB

Of the known environmental pollutants, Pb has few competitors as a persistent pollutant, which causes harmful effects to humans, animals and ecosystems. However, it is also a useful metal. It occurs in the environment mainly as Pb^{2+} and its compounds are mostly insoluble in waters. There are still large quantities of Pb, mainly as $PbSO_4$ and $PbCO_3$ released into the environmental compartments. This metal is remobilized in ecosystems causing toxic effects to terrestrial and aquatic species.

In the 1970s and 1980s, most Pb pollution was emitted from the use of leaded gasoline, and the emission of Pb was higher from anti-knock additives in gasoline than it was from pollution point sources. In the 1990s, strict regional regulation has virtually eliminated the use of Pb in gasoline in the developed countries. However, it is still use in several African countries, such as in Nigeria, where Pb in gasoline is about 0.6 g l^{-1} that is the highest concentration noted in the world.

Production and Use. The most important Pb ore is the heavy black mineral galena, PbS. Other common minerals are: anglesite, $PbSO_4$; cerussite, $PbCO_3$; minium, Pb_3O_4; pyromorphite, $Pb_5(PO_4)3Cl$; and mimetesite, $Pb_5(AsO_4)3Cl$. Lead ores are widely distributed throughout the world, but only fifty countries have Pb-ores that can be mined commercially.

Normally, Pb is obtained from galena deposits. The Pb-concentrate is roasted at a temperature of 600 °C in a limited supply of air and the product, PbO, is mixed with coke and limestone (as a flux) and reduced to liquid Pb in the blast furnace at 1 250 °C. The product contains different metals as impurities: Cu, Ag, Au, Zn, Sn, As, and Sb, which must be removed to obtain 99.99% of pure Pb.

In the USA, 92% of all Pb is produced from secondary sources, i.e., Pb scrap from spent lead-acid batteries. In the near future, the EC will adopt a new battery directive, which requires collection of all used batteries in the EU and the recovery of metal used in car and industrial-type lead-acid batteries.

The largest use of Pb worldwide is for lead-acid batteries known as the SLI battery (starting, lighting and ignition). In addition, it is used in solders, alloys, chemicals, cables, lead weights, lead wool, and for many other purposes, due to its special physical and chemical properties. Nowadays, the use of Pb in petrol as an anti-knock additive in developed countries has been phased out in an effort to reduce the atmospheric Pb pollution. Hence the overall market for tetraethyl and tetramethyl lead (TEL and TML) has declined considerably, but still there is some market for these chemicals in the developing countries.

There are strict regulations in many countries on the release of Pb to the environment, but still it continues to be one of the most serious global human hazards.

Humans. The exposure pathway of Pb for the adult population is from food, water, and air. The Pb inhalation is the major pathway for workers of various industries, particularly of persons working at Pb-Zn smelters and mines.

The ingestion of soil and house dust is a major pathway for the exposure of young children to Pb, due to hand-to-mouth activity (pica-soil). Amounts of Pb intake depend on several factors, such as children behavior and age, and the bioavailability of Pb compounds.

Lead in drinking water may be its significant source that is especially important for both children and pregnant women. The Pb concentration in drinking water is generally safe when at <5 μg l^{-1}. However, sometimes in many old houses, water pipe lines are still made of Pb that may increase its content in tap water above the maximum WHO recommendation value of 10 μg l^{-1}, and even be above the EU statutory limit of 50 μg l^{-1}.

Various foodstuffs have been, and still may be, a serious source of Pb in diets. However, the Pb contamination of most foodstuffs has recently declined substantially. Previously, leaded solders in food cans and wine bottles contributed to the Pb in foods. Also some ceramic articles may contain leaded glazers.

The toxicity of Pb and its adverse effects have been known for many centuries. Even the Romans were familiar with some of the toxic effects of Pb. The excess of Pb to the Roman population was from broadly used leaded glazers, and in addition, from the sweet precipitation of Pb acetate, $Pb(CH_3COOH)_2 \cdot 3H_2O$, that was consumed (Kabata-Pendias and Pendias, 1999).

Young children can absorb up to 50% of the Pb from the diet whereas the adult population takes only about 10% (WHO, 1995). The absorption of Pb by humans is a function of both, forms of Pb and kind of a diet. When the diet is low in Fe, Ca, and proteins then absorption of Pb is higher.

The absorbed Pb is distributed in blood, soft tissues, and in particular in bones, including teeth. The human body cannot differentiate between Pb and Ca; hence the majority of Pb is stored in the bones and teeth, where up to 90% of absorbed Pb may be accumulated. The excess of Pb may cause several health effects:

- Damage to nervous systems
- Inhibition of heme formation
- Kidney damage
- Anemia (inhibitiona hem synthesis)
- Impaired mental development of young children
- Carcinogenicity and genotoxicity
- Impaired reproductivity

Some other Pb sources, such as soft water and Pb paints has still affected increased Pb exposure of the population in some areas of the Western Europe.

Arsenic (As)

Arsenic is widely distributed in the environment. It occurs in the Earth’s crust at levels between 0.5 and 2.5 mg kg^{-1} and is likely to be concentrated, up to 13 mg kg^{-1}, in argillaceous sediments. Its concentration in coals causes environmental problems and it exhibits extreme variability among coals of different origin.

Arsenic is associated with several ores of metals, most often as arsenite minerals where occurs as anions, As^{2-} and As^{3-}. It is likely to combine with several metals (e.g., domeykite, Cu_3As; nikieline, NiAs; sperrylite $PtAs_2$). Its common minerals are: arsenopyrite, FeAsS; orpiment As_2S_3; realgar, AsS; arenolite, As_2O_3, and some other polymorphous forms of minerals.

Due to similar ionic radii, the geochemical behavior of $As5^+$ is very similar to that of P, especially in phosphates (Goldschmidt, 1958[26]).

Production and Use. Until the 1970s, about 80% of As was used in the manufacturing of pesticides. Due to its toxicity, the use of As in pesticides has decreased to about 50%, but organic As compounds still dominate the pesticides production by 90% (Matschullat, 2000[27]). The rest of the amount is used in wood preservation, photoelectric devices, glassware, and Pb-acid batteries. It is also used to improve corrosion resistance and tensile strength in Cu alloys.

Humans. Arsenic is known to be highly toxic to humans and animals. Both cations, As^{3+} and As^{5+} may cause similar toxicological effects, but the former is considered to be more mobile and toxic for living organisms (NRC[28], 1999).

Since the 13th Century, As has been used as a medicine while at the same time it is known to be poisonous. Several compounds of As may interfere with activities of some enzymes, especially those with sulfhydryl groups.

The toxicology of As is quite complex and is highly dependent upon its species. Species of As^{3+} and inorganic compounds are more toxic than As^{5+} and organic compounds.

In Bangladesh over 50 million people are at risk due to As in waters. It is reported by the WHO that 1.0 mg of inorganic As per day may give rise to skin lesions within a few years. In the affected areas of Bangladesh and West Bengal, As concentrations in ground waters vary between >50 and 1 000 mg l^{-1}, whereas the maximum permissible level of As in drinking water in Bangladesh is 50 $\mu g\ l^{-1}$.

Arsenic toxicity from food and drinking water can cause several health problems: mutagenic, carcinogenic and teratogenic effects that affect various disfunctions:

- Neurological effects
- Cardiovascular disease
- Respiratory disorders
- Hypertension
- Diabetes mellitus
- Keratosis

Fresh water fish may be serious dietary source of As in some regions. However, most of As in seafood is in organic compounds that are less toxic than inorganic species.

Some metallurgic industries (e.g., brass production) are also known as a source of increased concentration of As in workers.

Antimony (Sb)

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[26] Goldschmidt V.M. Geochemistry / Muir A. (ed.). Oxford: Clarendon Press, 1958.

[27] Matschullat J. Arsenic in the geosphere – a review // Sci. Total Environ. 2000. V. 249. P. 297–312.

[28] NRC - National Research Council (USA)

Antimony exhibits chalcophilic properties for which it combines readily with sulfides and occurs mainly at 3^+ and 5^+ oxidation stages. Its contents in igneous rocks range between 0.1 and 0.9 mg kg^{-1} and in sediments are likely to be increased, up to 2 mg kg^{-1} in argillaceous rocks.

Common Sb minerals are stibnite, Sb_2S_3 and valentinite, Sb_2O_3. Antimony may substitute for As in several minerals, although there is a difference in ionic radii (Sb^{3+}, 76 pm; As^{3+}, 58 pm). Common minerals also are: pyrargyrite, Ag_2SbS_3; and bourmite, $PbCuSbS_3$. It also easily forms soluble thiocomplexes, like SbS_2^{2-} and SbS_4^{3-}, depending on pH. Antimony is associated with over 100 Sb-bearing minerals. Therefore, increased levels of Sb are observed in many regions of the world, especially around smelters, chemical facilities, and mining, and mineralized areas, particularly with ores of Cu, Ag, and Pb.

In recent years, Sb and its compounds are considered to be an important pollutant by the US EPA and the EU. Especially, Sb released from coal combustion is an important pollutant due to its high solubility and reactivity.

Chemical and toxicological properties of Sb are similar to those of As. There is not much information on the toxicity of Sb and on its effects on the environment and human health. In ancient times, Sb compounds were used for medical purposes.

Production and Use. The main source of Sb is stibnite, Sb_2O_3. Antimony is also recovered from primary concentrates, recycled scrap, and antimonial Pb-battery scrap. Primary production of Sb has been ceased in many countries due to its low price (http://minerals.usgs.gov/minerals/ pubs/commodity/antimony/).

Antimony increases the strength and hardness of Pb alloys and is used as an alloying element for Pb-acid batteries. It also is used in solders and bearings, as alloying element.

Hard Pb (3–9% Sb) is used in the grids and Pb-oxide paste for automobile batteries. In recent years, its uses in high-tech applications are increasing. Sb-containing lead lining is used to protect pipes, valves, and pumps in the chemical industry. This metal is used for the manufacturing of flame-retardants in plastics, vinyl and synthetic fibers.

Humans. Most common health effects of Sb intoxication, as cited by Abbaspour and Baramakeh (2005)[29], are:

- Carcinogenic and mutagenic problems
- Diarrhea
- Nephropathy
- Encephalopathy
- Muscles/joint pain
- Gastrointestinal problems
- Anemia

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[29] Abbaspour A., Baramakeh L. Simultaneous determination of antimony and bismuth by beta correction spectrophotometry and an artificial n151al network algorithm // 1st Intern Workshop on Antimony in Environ. Heidelberg, 2005. 52 p.

– Heart problems

The general population is rarely exposed to Sb, but in smelter and mining regions some individuals and especially workers can be affected *via* skin and inhalation of Sb.

Bromine (Br)

The Br abundance in crustal rocks is about 2 mg kg^{-1} and it is relatively uniformly distributed among igneous rocks, whereas in argillaceous sediments it is likely to be concentrated up to 10 mg kg^{-1}. Minerals containing Br are not very common, due to its low abundance and high solubility. The common minerals are: bromyrite, AgBr; embolite, Ag(Cl,Br); and iodobromite, Ag(Cl,Br,I). The close correlations of Br and Cl in various rocks have often been observed. Bromine is a very volatile element and its salts are readily soluble and mobile in most environments. However, it is likely to be accumulated by coals and organic matter.

Bromine is very reactive chemically and can have several valence states. However, as only one-electron atom it can form compounds mainly with oxygen (e.g., Br_2O, BrO_2, BrO_3^-).

Production and Use. The major commercial source of Br is the sea, especially from K-salt water, although some amounts are also obtained from brine deposits.

The primary use of Br was as ethylene dibromide, a gasoline anti-knock additive, together with Pb. Due to recent environmental legislation, Br addition to gasoline has been significantly reduced.

Considerable amounts of Br (methyl bromide and ethylene dibromide) are used in agriculture as pesticides (fungicide, herbicide, and insecticide). It has been utilized in the pharmaceutical industry and also has been used in fire-retardant compounds and for dyestuff production. In photosensitive compounds, Br has been used for many years in the photographic industry.

New persistent chemicals, polybrominated diphenol ethers (PBDEs) are presently widely used as flame-retardants in a great variety of products.

All bromine-based compounds are very persistent and seem to travel over long distances in both the atmosphere and water.

Humans. After oral ingestion, Br is rapidly absorbed and distributed in the extracellular fluids and no particular accumulation in any organ has been noted. It is relatively easily excreted from the body. Average Br intake by adults is estimated at around 8 μg d^{-1}. An antagonistic interaction between Br and I intake has been observed. With a deficiency of I, Br may concentrate in the thyroid gland.

There have been many reports of cases of methyl bromide (CH_3Br) poisoning in humans, involving skin and eye injuries, gastric irritation, kidney lesions, damage to the central nervous system and toxic effects to immune system.

Excess inhalation of Br triggers allergic reactions, especially of mucous membranes. Deficiency symptoms of Br have not been observed, neither in humans nor in animals.

Task

Choose one of the chemical elements described above and write down the information about it:

- Name of an element
- Natural associations, rocks and minerals, containing this element
- Directions of use
- Biological impact