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Review

Two Faces of Chromium - Pollutant and Bioelement

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Abstract

Life and growth of plants and animals depends on some metals as micronutrients. However, certain forms of some metals can also be toxic, even in relatively small amounts, and therefore determine risk to the health of animals and people. Chromium is a heavy metal whose concentration in the environment is increasing. Chromium in inorganic systems occurs in several chemical forms. Only Cr(III) and Cr(VI) are significant in biological systems. Trivalent chromium is an essential nutrient component while excess chromium(VI) in biological systems has been implicated in specific forms of cancer.

Keywords: heavy metals, hexavalent and trivalent chromium, toxicant, bioelement

Introduction

Metals occur naturally in the environment in varying concentrations and are present in rocks, soil, plants, and animals. All metals at high concentration levels have negative impacts because they are easily accumulated in the food chain. Cadmium, mercury, lead, copper and zinc have received special attention in ecotoxicology in recent years. Some metals are necessary for the biological functions of organisms (e.g. cobalt, copper, manganese, molybdenum, zinc and chromium). They occur in different forms: as ions in water, as vapors, salts or mineral rock, sand, and soil. They can be bound by organic or inorganic molecules, or attached to particles in the air. Both natural and anthropogenic sources emit metals into air and water (Fig. 1) [1-5].

Metals, once emitted, can reside in the environment for hundreds of years or more. Evidence of human exploitation of heavy metals have been found in ice cores in Greenland and sea water in Antarctica. They are persistent environmental contaminations. Human activity has drastically changed the biogeochemical cycles and balance of some heavy metals in the environment. Therefore, a tendency towards their accumulation in the soils, seawater, freshwater, and sediments is observed. Excessive levels of metals in the marine environment can affect marine biota and are hazardous to human consumers of seafood.

During the recent three decades considerable attention has been given to problems concerning negative effects of heavy metals on various ecosystems in different environmental compartments. Numerous field observations indicate a significant increase of heavy metals concentrations in agricultural and forest soils as well as in marine and inland water sediments. This increase is frequently observed in remote areas thousands

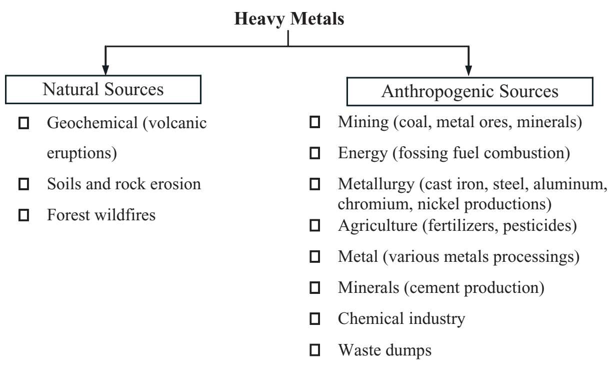

Fig. 1. Sources of heavy metals in the environment.

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of kilometers from major anthropogenic sources and can be explained by transboundary atmospheric long-range transport only. An assessment of the potential ecological and health risks associated with atmospheric fluxes of heavy metals requires an understanding of the relationship between sources of emission to the atmosphere and the levels of the concentrations measured in ambient air and precipitate.

The toxicity of heavy metals has also been documented throughout history: Greek and Roman physicians diagnosed symptoms of acute lead poisoning long before toxicology became a science. Today much more is known about the health effects of heavy metals. Exposure to heavy metals has been linked with developmental retardation, various cancers, kidney damage, and even death in some instances of exposure to very high concentrations. Exposure to high levels of mercury, gold, and lead has also been associated with the development of autoimmunity, in which the immune system starts to attack its own cells, mistaking them for foreign invaders.

In order to correctly estimate the risk caused by metal pollution it is important to know the bioavailability of the different chemical species of the metals. At least several heavy metals are more available when in organic compounds, e.g. dimethyl mercury or tetraethyllead, than as inorganic ions [1-5].

Chromium is one of the heavy metals whose concentration in the environment is still increasing. We do not need to be worry about global risk of chromium contamination, but for local environments it could be a serious problem.

Uses of Chromium

Chromium and its compounds are useful in common life, as presented in Fig. 2.

Chromium is resistant to ordinary corrosive agents at room temperature, which explains its uses as an electroplated, protective coating.

It is also used in ferrous and nonferrous alloys, in refractories, and in chemicals. Ferrous alloys, mainly stainless steels, account for most of the consumption. These steels have a wide range of mechanical properties as well as being corrosion and oxidation resistant. Cast irons may contain from 0.5% to 30% of Cr, which provides hardenability, toughness and corrosion and wear resistance. Chromium is also widely used in nonferrous alloys (nickel, iron-nickel, cobalt, aluminum, titanium and copper).

Chromium chemicals are used in a variety of applications. The largest amount is consumed to manufacture pigments for use in paints and inks. Other applications include leather tanning, metal corrosion inhibition, drilling muds, textile dyes, catalysts, wood and water treatment.

Chromite is used in the refractory industry to make bricks, mortar, and ramming and gunning mixes. Chromite enhances their thermal shock and slag resistance, volume stability, and strength [6].

Chromium Occurrence and Pathways in the Environment

Environmental concentration of chromium is known to increase due to industrial development. Two ionic forms of chromium, Cr(III) and Cr(VI), are present in various forms in soil, water and in the biota. Chromium and its compounds originate in the environment mainly from anthropogenic sources (industry emissions, combustion processes). Further, in plants, soil and in the waters chemical equilibrium between chromium speciation forms can exist (Fig. 3) [1,7-15].

The atmosphere has become a major pathway for long-range transfer of chromium to different ecosystems. Cr-containing particles in the atmosphere are carried over different distances by the wind, before they fall or are washed out from the air onto the terrestrial and water surfaces. The range of area covered by the metal depends on meteorological factors, topography and vegetation. Chromium wet precipitation and dry fallout from the atmosphere are greatly affected by particle size.

On the contrary, transport within the terrestrial and water systems is greatly affected by chemical speciation: chemical forms of Cr and their affinity to chemical and photochemical redox transformations, precipitation/dis-

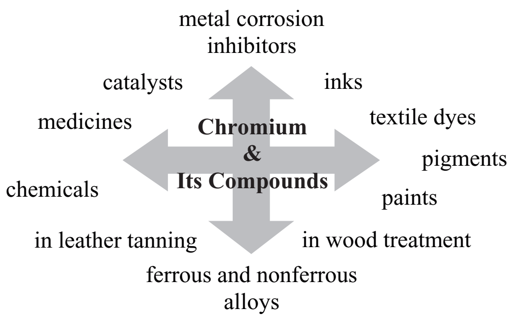

Fig. 2. Uses of chromium and its compounds.

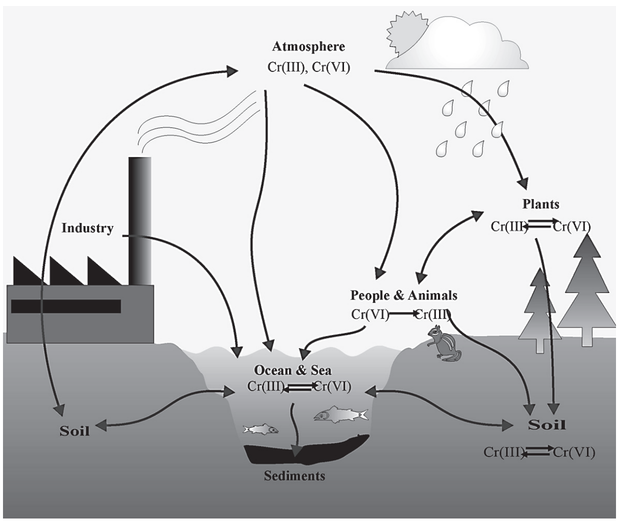

Fig. 3. Chromium circulation in the polluted environment.

solubility and adsorption/desorption processes occurring in individual compartments of the environment determine the biogeochemical cycle of this element.

The efficient adsorption of metals by soils tends to limit the effects of atmospheric input of chromium. The dumping of industrial waste materials significantly increases chromium concentration in soil and is usually accompanied by groundwater contamination. Hexavalent chromium is known as the most mobile chromium form in soil and water systems, whereas Cr(III) is generally not transported over great distances because of its low solubility and tendency to be adsorbed by solid particles in the appropriate pH range. Redox conversion of Cr(III) to Cr(VI) can increase the chromium dislocation from the soil into the water system.

Considering chromium transport in natural waters, three subsystems (river, lake and ocean water) are distinguished. The transport mechanism of metal in rivers is associated mostly with suspended adsorbing particles. Chromium enters the oceans in two ways – riverine and atmospheric. In the ocean and sea waters the precipitated and dissolved chromium exist in an equilibrium. Dissolved Cr is lost from the oceanic water through its incorporation into biologic material and adsorption onto sediment particles. Dissolution of this incorporated chromium occurs both in the water and at the sediment – water interface, leading to deep and bottom water enrichment in the dissolved chromium. Chemical reduction of hexavalent chromium occurs in anoxic basins and the oxygen – free zones, where increased Cr removal may be due to Cr(III) adsorption onto bottom sediments. The remobilization of Cr(III) from sediment can also occur by its oxidation, carried out mostly by manganese dioxide. The high level of organic matter creates the reductive and complexing medium, which favours reduction of Cr(VI) to Cr(III), which is afterwards rapidly precipitated or adsorbed onto the sediments. Chromium contained in sediments may be remobilized into the surrounding pore water via oxidizing or via solubilization of Cr(III) sediments.

Living organisms can also play a role in metal transport. Plankton in costal areas may have an influence of chromium transport in ocean. High – standing crops of zoo- and phytoplankton may absorb some part of this metal. Further, it can be flocculated with faecal pellets or dead organisms and become incorporated into sediment instead of being transported. The hexavalent anionic form is more available for living organisms than is Cr(III), and plays a main role in removing this metal from water and soil systems [1,7,8,9,16].

The main source of chromium in natural soils is weathering of their parent materials. The chromium content in soil varies greatly from traces to 250 mg/kg and more. Chromium present in soil is mostly trivalent and is relatively little absorbed by the plants. An increase in local chromium concentration in soils originates from fallout and washout of chromium containing particles as well as from chrome – bearing sludge and refuse from industrial activity.

Chromium in waters originates from natural sources, such as weathering of rock constituents, wet precipitation and dry fallout from the atmosphere, and washed out from the terrestrial systems. The local increase in chromium concentration in waters (mainly in rivers) is caused by discharge of wastewater from metallurgical industry, electroplating and tanning industries, from dying and other chemical industries. The quantity and types of chemical chromium forms present in effluents depend on the character of the individual processes using chromium.

Chromium concentration in the rivers and freshwater lakes range commonly between 1.0 and 10.0 μg/l, in the ocean water between 0.1 and about 5.0 μg/l, irrespective of an estimated 6.7×10^6 kg of chromium flowing annually in the sea with industrial waste effluents.

In the neutral pH conditions the trivalent chromium cations present in water tend to form hydroxide colloids. The trivalent chromium ions have a tendency to bind with the suspended solids and are thus detectable in the sediment (Fig. 4) [9,16]. The hexavalent form is almost exclusively present as oxo-anions which can persist only in the absence of substances that are oxidizable by them at given pH. The hexavalent chromium is toxic for fish as well as protozoa, but in wastewater it tends to be rapidly reduced to the biologically less active trivalent form, owing to abundance of organic matter present in this type of water.

Chromium present in the atmosphere originates from anthropogenic sources which account for 60-70%, as well as from natural sources which account for the remaining 30-40%. The main human activities contributing to the chromium increase in the atmosphere are: metallurgical industries, refractory brick production, electroplating, combustion of fuels and production of chromium chemicals, mainly chromates and dichromates, pigments, chromium trioxide and other. The cement industry, production of phosphoric acid in a thermal process, and combustion of refuse and sludge are other potential sources of atmospheric chromium. The main natural sources are volcanic eruptions and erosion of soils and rocks, airborne sea salt particles and smoke from forest wildfires.

The lowest atmospheric concentrations of chromium (5–16 $pgCr/m^3$) have been observed over the South Pole. Average atmospheric concentrations of this metal are much higher: they range from 1 ng/m^3 in rural to 10 ng/m^3 in polluted urban areas. The amount of chromium

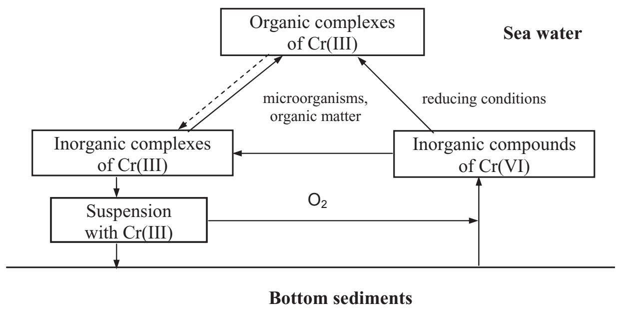

Fig. 4. Chromium circulation in sea water.

at any particular time and location depends on the intensity of industrial processes, proximity to the sources, the amount of chromium released and meteorological factors. [1,8,9,16,17].

Chromium in Biological Systems

Chromium occurs in inorganic systems in several chemical forms. Only Cr(III) and Cr(VI) are significant in biological systems [Fig. 5].

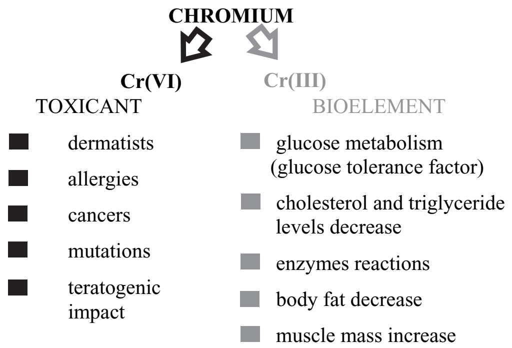

Fig. 5. Cr(III) positive and Cr(VI) negative effects for humans.

Toxicity of Hexavalent Chromium

Severe and often deadly pathological changes are associated with excessive intake of Cr(VI) compounds. Cr(VI) exerts toxic effects on biological systems. It has been found that occupational exposure to hexavalent chromium compounds leads to a variety of clinical problems. Inhalation and retention of materials containing Cr(VI) can cause perforation of the nasal septum, asthma, bronchitis, pneumonitis, inflammation of the larynx and liver and increased incidence of bronchogenic carcinoma. Skin contact of Cr(VI) compounds can induce skin allergies, dermatitis, dermal necrosis and dermal corrosion [9].

Hexavalent chromium compounds are irritating and corrosive when allowed to come in contact with skin, the digestive system or lungs. Chromium trioxide (CrO_3) is a common toxic hexavalent chromium compound. In fact, chromic baths used to soak and clean laboratory glassware are very toxic and are a safety risk to use in common laboratory situations. Chromium(VI) connected with long-term occupational exposure (such as workers in the chromate industry) is a chemical carcinogen that can cause carcinomas of the bronchial systems. Epidemiological studies of workers working at the chromate industry have found a large increase in bronchogenic carcinomas among workers involved in the isolation and manufacture of dichromates from ores. The mechanism of cancer formation caused by Cr(VI) is not known for certain; however, it has been postulated that Cr(VI) binds to double-stranded deoxyribonucleic acid (DNA), therefore altering gene replication, repair, and duplication [7].

The toxic and genotoxic nature of the Cr(VI) ion was established long ago. Workers exposed to Cr(VI) compounds in stainless steel welding, pigment production and other industrial occupations can suffer skin lesions, lung disease and various forms of cancer.

However, these problems are not restricted to chromium-industry workers. During the process of production a relatively large quantity of chromium is released to the atmosphere, earth, lakes and rivers. Hexavalent chromium in air is a human carcinogen and toxicant. In soil and water the less toxic Cr(III) ion can be oxidized to carcinogenic, teratogenic and mutagenic Cr(VI). It is generally assumed that in living organisms only the reduction process Cr(VI) to Cr(III) takes place. The hexavalent chromium ion is not genotoxic *per se*. A fundamental feature of chemistry of the chromium(VI) ion is its redox behavior. The most important and known reason of the mutagenic activity of Cr(VI) is exactly the oxidation properties of the ion. Cr(VI) ions are easily transported through the cellular membrane. Once they enter the cell, they oxidize its constituents and undergo a metabolic reduction, Cr(VI) to Cr(III). Migration to the nuceli of various chromium metabolite complexes and interaction with DNA cause the final negative effect.

Not only toxicity, but also the mobility and bioavailability of chromium, depend fundamentally on its chemical form. Cr(VI) compounds are usually highly soluble, mobile and bioavailable compared to sparingly soluble trivalent Cr species [7,8,9,18].

Chromium as Bioelement

On the other hand, the trivalent chromium is an important bioelement and plays an exceptional role in metabolic processes [7,8,19-22].

Chromium occurs in the tissues of human fetuses and infants. From birth on its content continues to decrease with increasing age in all body organs except the lungs, in which a slight rise in chromium content is detectable from the 10th year of life, apparently as a consequence of inhaled Cr deposits in the lungs. The highest accumulation of chromium (0.2 – 2 mg/kg) was found in the hair.

In the 1950s scientists described chromium as an important bioelement. In the organisms, the trivalent chromium was found to act in the metabolism of insulin, and is likely to play an important role in various enzyme reactions.

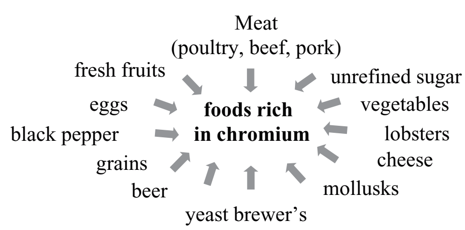

Fig. 6. Food sources of chromium.

Table 1. Chromium content of selected food [mcg/ 100 grams of product].

Food	Chromium content [mcg/100 g]	Food	Chromium content [mcg/100 g]
Brewer's yeast	112	Butter	13
Liver, calf	55	Cheese	13
Whole-wheat bread	42	Banana	10
Wheat bran	38	Carrot	9
Rye bread	30	Navy bean, dry	8
Potato	24	Fresh fish	6
Wheat germ	23	Orange	5
Egg	20	Blueberry	5
Green pepper	19	Green bean	4
Apple	14	Cabbage	4

Chromium is an active component of GTF (Glucose Tolerance Factor) and has a beneficial effect on blood sugar regulation mechanisms. Chromium helps to regulate blood sugar levels by collaborating with insulin in facilitating the uptake of glucose into cells. Insulin is secreted in response to the rise of glucose level in blood after the consumption of a meal. If chromium is not present, insulin's action is blocked and glucose level is elevated.

Trivalent chromium is necessary for normal development of humans and animals. The commonest source of chromium for man under normal conditions is food (Fig. 6). The estimated and safe daily dose for chromium is 50 to 200 micrograms. For good health we shouldn't take more than 200 µg of chromium daily [7,11,19-23].

Chromium-rich food includes entrails, meat, mollusks, lobsters, vegetables, and unrefined sugar. Edible parts of fish, vegetable oil and fruits contain smaller amounts of Cr (Table 1) [17,21].

Chromium is also used to promote weight loss. In health food stores and drugstores we can find plenty of chromium products ranging from body-building powders to slimming shakes and tablets. Organic Chromium (trade mark - Chrom Organiczny), Bioslank, Biodiet, Chromdiet, Bio-Slim and Bio-Chrom are the most popular chromium supplementations available on the Polish market. The chromium supplementations enhance weight loss by increasing the sensitivity of the organism to insulin and helping to control appetite. Chromium decreases weight yet increases lean body mass [22].

Conclusions

However, chromium is thought to be necessary for a normal functioning of living organisms but the necessity of chromium may still be a controversial subject. Some laboratory studies have also shown that the trivalent chromium can cause allergy, some of the Cr(III) compounds are toxic, even genotoxic for humans. The oxidation of Cr(III) to Cr(VI) and migration of CrO_4^{2-} or $Cr_2O_7^{2-}$ ions through the cellular membranes in living organisms are still under examination.

Also due to environmental toxicity of hexavalent chromium it is crucial to limit its further discharge into the environment and the presence of Cr in wastewater or sludge, especially when utilized for agricultural purposes, should receive similar attention to other potentially toxic trace elements (Hg, Cd, Pb).

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