Heavy metal

Pentahydrate copper sulfate crystal . Copper is an essential micronutrient, but also toxic to most organisms at high levels.

A **heavy metal** is any one of a number of elements that exhibit metallic properties, which includes transition metals lanthanides actinides as well as the metalloids Arsenic and Antimony. Typically the term refers to elements of atomic number 21 or higher (e.g. Scandium or above) The term *heavy* metal chiefly arose with discussions of pollutants discharged to the environment in the form of air, water or soil contaminants. While many heavy metals have considerable toxicity, others are considered not deemed to possess significant toxic properties, and, in fact, several of these elements including zinc, iron, copper,chromium and cobalt are necessary for metabolic function for a large class of organisms.

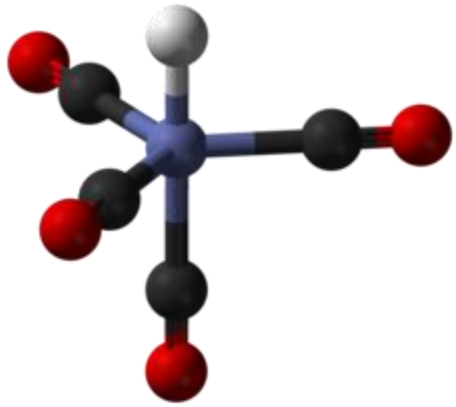
Although some heavy metals are essential micronutrients for animals, plants and many micro-organisms, depending on the route and dose, all heavy metals demonstrate toxic effects on living organisms via metabolic interference and mutagenesis. Animal health impacts range from reduction in fitness, to reproductive interference to carcinoma, with many exposures being lethal.

Definition

Manganese oxide-hydroxide, a monoclinic crystal. Source: Smithsonian Institute

There have been several schemes for designating heavy metals, based upon atomic number, toxicity or other factors; however, the usage of the term has centered on the treatment of certain metallic elements which have an impact upon plants or animals when discharged into the natural environment in relatively high concentrations. In terms of degree of interest, the chief heavy metals of note in the environmental science literature are lead,mercury, cadmium, chromium, copper, manganese, nickel, zinc,silver. Some schemes of classification for heavy metals exclude the lanthanides and actinides. The heavy metals are generally to consider all of the transition elements, eg. those elements with an incomplete d-shell.

Physical and chemical properties



Tetracarbonylhydrocobalt, a heavy metal ligand compound.

The heavy metals generally exhibit good electrical and thermal conductivity when in their pure form in many cases "heavy" refers literally to a metals specific gravity (ranging from 3.5-6 g/cm3), mass, and as indicated earlier, atomic number. The transition elements can manifest themselves as in varying chemical species or oxidation states;[1] moreover, many transition metals can be bound to a variety of species or ligands. All of the transition metals have two or more oxidation states.

Essential for life

While copper is an essential micronutrient, it also can manifest in disease syndromes with tissue accumulation, as seen in this iris eye-ring anomaly. Source Herbert L.Fred and Hendrik Dijk

There are no elements in the lanthanide or actinide series that are essential to life; however, among the transition metals the following elements play a fundamental role in metabolic function for a vast array of organisms: vanadium, manganese, iron, cobalt,nickel, copper, zinc and molybdenum. Each of these, however, can produce adverse impacts if ingested at sufficiently high concentrations. The most widespread human deficiency is noted in zinc, for which over two billion humans, mostly in developing countries, suffer from inadequate amounts of zinc in their diet. Resulting effects include growth retardation and increased susceptiblity to infection, with a net outcome of a contributory cause of death in more than 800,000 children per year.[2]

Heavy metals in plants

Plants have proven particularly effective for both bioremediation of metal contaminated sites and for studying the uptake, transport and toxicity of metals in general, and the following sections focus on heavy metals phenomena in plants.

Plant root uptake

The transport and cell wall diffusion theory of plant root uptake of heavy metals is fundamentally similar to processes governing other minerals in solution. Availability at the root surfaces is limited by diffusion of the metal cations (only molybdenum is taken up in anion form); by the interception of growing roots; and by mass transport of solute flowing toward the root, driven by evapotranspiration. Thus, in the case of rapid root uptake, a depletion zone of the heavy metal may form near the root uptake sites, unless evapotranspiration and root growth rate overwhelm the diffusion process.The actual crossing of the root membrane may occur by ionic diffusion, but in many cases may be aided by a protein or other biochemical transporter mediary.

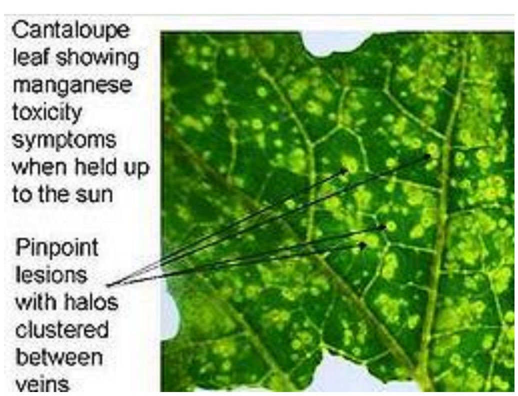
A variety of factors influence the rate of uptake by plant roots. Obviously the solubility of the chemical species plays a dominant role; beyond that, pH has a relatively systematic effect, with higher pH levels facilitating uptake of all metals, including heavy metals. One of the chief reasons for this systematic bias is that hydrogen ions compete with metal cations at the root uptake sites.[3] Again from a mechanism of competition at the root zone, there is also a general depression of heavy metal uptake in the presence of high concentrations of soil nutrients, e.g.calcium. In the case of salinity variation, the results vary widely depending upon the precise species (or valence) of the heavy metal cation. Increased light levels are clearly correlated to higher root uptake of heavy metals.

There is a significant amount of filtering or rejection of unwanted heavy metals due to the architecture of the root tissues. Once the heavy metal ion has penetrated the outer root membrane, it is forced to navigate the crossing of the Casparian Strip, a waxy impregnated layer of the endodermis that forces all solute materials diffusing across the root epidermis to enter a before entering the xylem, which serves as a veritable freeway of solute transport driven by evapotranspiration. Thus each plant species has its own highly specialized filter mechanism to limit the inflow of harmful chemicals.

The presence of mycorriza (the result of a symbiotic relationship between plant roots and a fungus) inhibit the uptake of toxic heavy metals for some combinations of metal and fungal species. This phenomenon is thought to be due to the presence of certain peptides, organic acids and polyphosphate grains in the fungalmycelium (vegetative filaments.)

Efflux mechanisms also operate at the plant root surfaces to expel heavy metals from the plant; moreover, these efflux processes appear to be governed by ionic diffusion. These elimination processes seem to be very important in regulating the cellular concentrations of essential metals such as zinc.

Plant foliar uptake



Manganese lesions on cantaloupe leaves. Source: University of Delaware

Leaf surfaces can act as points of uptake for heavy metals, both bystomatal and cuticle pathways. Stomates allow passage of gaseous heavy metals, e.g. mercury, whereas cuticle intake is applicable toionic forms of heavy metals. High relative humidity promotes cuticle intake, since those conditions create a swollen cuticle, subject to easiest penetration. There is a pronounced difference on cuticular uptake rate for different heavy metals. For example, copper, zinc and cadmium are found to be taken up at high rates by cuticles of many plants, whereas lead is transmitted in very low quantities.

As in the case of root tissue, leaves also have a reverse process of efflux. Remarkably some stomata have shown this to be a mechanism for eliminating ionic mercury, by conversion to gaseous form in the stomata and effluxing the resultant gas. A more common manifestation of this reverse or efflux process is the expulsion of heavy metal ions through the cuticle. The phenomenon is particularly important when acid rain is deposited on leaf surfaces. Then, due to high hydrion concentrations, there can be significant cation exchange with a result of expulsion of considerable amounts of heavy metals onto leaf surfaces, and eventual washing of the leaves by the precipitation itself.

Plant internal transport

Mouse ear syndrome leaf damage to River birch by excess nickel uptake. Source: Carl Rosen

Within the plant structure there is considerable variation in the mobility of heavy metals, depending on the plant species and the particular metal. For example, cadmium and zinc are much more mobile than copper or lead. Young plants are usually more efficient at internal transport of heavy metals, since the Casparian Strip is not well developed, such that the rejection filter in the root structure is less effective. In addition, young plants have a high shoot to root mass ratio, so that the upward movement of metals is governed more by root pressure and less by the transpiration process.[4]

Plant toxicity

See main article: Absorption of toxicants

Wholesale ecological damage from zinc contaminated soils, Palmerton, Pennsylvania; low pH is a concomitant issue. Source: Keith Weller/USDA

Adverse impacts to plant metabolism appear at elevated concentrations of all heavy metals. These effects manifest in decrease in germination, increase in seedling mortality, inhibition of growth rates and reduction in reproductive capability. For the essential micronutrients, there is usually a threshold concentration, below which no adverse effects are observed, but with elevation of levels above the threshold, monotonically increasing toxic impacts are evinced.

As an example, studies of copper and cadmium exposure indicated no adverse effects for cation concentrations of up to .01 mg/liter; however, with increasing concentrations in the root zone, there was a steady decline in germination rates.[5] Cadmium was somewhat more toxic than copper in the cases analyzed; moreover, the combined effects of copper and cadmium provided a negative synergistic effect on seed germination.

Plants have proved to be such reliable indicators of heavy metal toxicity that they have demonstrated clear advantages over sacrificing fauna in laboratory testing. For example, many of the effect relationships (e.g. mortality versus concentration) are not only monotonic, but quite linear; in addition, use of common duckweed (*Lemna minor*) for toxicity assays of water pollution stemming from heavy metal concentrations showed greater sensitivity to metals by a factor of eight relative to published 96 hour fish bioassays.

The mechanisms of heavy metal toxicity can be traced to metabolic interferences related to enzyme synthesis or DNA replication itself. Specific interference phenomena include down-regulation of essential protein synthesis appurtenant to enzyme production, but also include oxidative damage of nucleobases and mutagenesis phenomena. Mutageneses have been observed in both plants and animals for all of the following heavy metals: cadmium, copper, chromium, nickel, lead, mercury, platinum and zinc.[6]

Serpentine soils

California pitcher plant growing on serpentine soils rich in nickel, chromium and certain other heavy metals. Source: Sydney Carothers/U.S.Forest Service

Serpentine soils are defined as unusual soil types which are rich in such heavy metals as nickel and chromium and deficient in calcium. Correspondingly plant associations thrive on these soils which are specially adapted to these soil mineral conditions. While serpentine soils are often noted for their plant associations which are rich in rare wildflowers, there are numerous shrubs and trees that have emerged as specialists to these soils; the California endemic treeLeather Oak is an example of such a larger plant. In fact, serpentine soils are the loci of highly restricted range species and many rare species of not only plants, but insects and even higher fauna.[7]

Heavy metals in animals

Most heavy metals, even those essential for life, have thresholds above which toxic effects are evidenced. Pathways of entry for animal exposure include respiratory, ingestion and dermal contact. Effects of elevated heavy metal concentration vary, and may include fitness reduction, impacts to reproductive success and production of carcinomas.

Pathways of entry

Respiratory intake may occur in the form of atomic or molecular gases, an example being mercury vapor; however a more common form of respiratory intake is heavy metal attachment to particulate matter. This circumstance is common in many industrial and energy generation applications, particularly from combustion of coal and from metal refining. The most severe health risk is posed when the particulate matter is extremely fine; in these instances, the particulate matter can penetrate deeply into the lungs, with increasing risk of long residence lodging. A special risk is posed when the heavy metal is also a radioactive substance; this case is notable for many forms of tobacco smoking, where traces of uranium are present in the phosphate rock fertilizers commonly used in tobacco growing.

Ingestion of heavy metals is a significant pathway of exposure. Particularly common pathways are ingestion of water contaminated by heavy metals from industrial wastewater discharge, and ingestion by eating higher level predators, who have concentrated heavy metals from successive food chain predation levels. High mercury levels in fish are common examples of this phenomenon. Typically the concentration of heavy metals in predators becomes more elevated at higher rungs of the food chain. Ingestion of metal contaminated plants is also a significant pathway of entry

Dermal exposure is generally a lower risk pathway, generally more relevant in industrial settings, where workers are cautioned to wash down exposed areas after work shifts. The dermal pathway is potentially significant for situations where heavy industrial plants are sited near residential uses in developing countries that lack the land use controls and emission controls of Western Countries. There is also a great deal of interest in potential exposure to consumers using sunscreen products based on nanoized titanium dioxide and zinc.

Transport and storage within animals

Once within the animal organism, there are a myriad of internal transport, storage and metabolic interference effects. At the transport level, one of the most significant transitions is migration from the lung tissue to bloodstream; for example, almost forty percent of inhaled lead enters the circulatory system. Subsequent to entering the bloodstream, there are many intermediate storage areas, the longest residence time being in bone. Again, using lead as an example, half life storage in human bone is approximately 25 years.

Specific organs are subject to elevated sensitivity to certain heavy metals. For example the brain is sensitive to lead poisoning, and there is widespread occurrence of permanent reduction of brain performance, particularly for children exposed to high levels of lead in the environment.

Metabolic impacts on animals

There are a vast variety of metabolic impacts of heavy metals upon animals.[8] Some of the chief effects are enzyme inhibition, immune system degradation, neuron signal interference and organ specific degradation. One of the fundamental issues in cell metabolic interference is the ability of some heavy metals to mimic other metals essential in enzymatic processes. For example lead often displaces zinc or calcium in enzyme processes; these effects can lead to minor impacts such as fitness reduction ranging to lethal impact for some very high exposure.

An example of organ failure effects is from hexavalent chromium which exerts acute oral toxicity for dosages as low as 50 µg/kg. The high toxicity of hexavalent chromium is based upon the strong oxidative effects of this metal. Subsequent to bloodstream transport hexavalent chromium impairs the liver, kidney and blood cells via oxidation, with high concentrations of chromium leading to complete shutdown of renal or liver organs.

An example of lung damage is via cadmium exposure; cadmium, a heavy metal with no constructive value to animal organisms, can induce not only acute renal and liver failure, but also cause pneumonitis, and pulmonary edema in mammals.

References

1. ^ Allison A. Lewinsky. 2007. *Hazardous materials and wastewater: treatment, removal and analysis*.Nova Publishers. 375 pages
2. ^ Ananda.S.Prasad. 2003. "Zinc deficiency". British Medical Journal. **326** (7386): 409
3. ^ Arthur Jonathan Shaw. 1990. *Heavy metal tolerance in plants: evolutionary aspects*. CRC Press. 375 pages
4. ^ Majeti Narasimha Vara Prasad. 2004. *Heavy metal stress in plants: from biomolecules to ecosystems*. Springer. 462 pages
5. ^ S.k.Agarwal. 2009. *Heavy Metal Pollution*. APH Publishing. 270 pages
6. ^ Joseph W.Gorsuch. 1991. *Plants for toxicity assessment*. ASTM Committee E-47 on Biological Effects and Environmental Fate. 401 pages
7. ^ Majeti Narasimha Vara Prasad and Kazimierz Strza?ka. 2002. *Physiology and biochemistry of metal toxicity and tolerance in plants*. Springer. 432 pages

8. ^J.C.Merrill, J.J.P.Morton and S.D.Soileau. 2007. *Metals*. In A.W.Hayes. Principles and Methods of Toxicology, 5th edition. CRC Press. ISBN 084933778X.

Source: http://www.eoearth.org/view/article/51cbee017896bb431f6956d3/?topic=51cbfc79f702fc2ba8129ed6