

Metal contamination

The most common environmental contaminants include **risk elements originating from anthropogenic activity (pollution caused by human activities)**. If they get into the soil, they persist in it for thousands of years and it is difficult to eliminate their effects on plants and soil fertility. The permitted limits of the contents of risk elements for soils are specified in the legislative regulations: Decree No. 13/1994 Coll. and Decree No. 382/2001 Coll. define the levels of soil pollution in the Czech Republic. Higher contents of risk elements in soils have negative effects on biological and physical-chemical processes in soils, enter the food chain and have a negative effect on human health.

Risk elements

- **As, Cd, Cr, Cu, Hg, Ni, Pb** and Zn (Alloway (1990), Adriano (2001)) – belong

to the longest known toxic substances. Significant interest in metals and their behavior in the environment is caused by their extensive industrial use.

- **trace metals** – are present in the organism or in the environment in very low concentrations in units of ppm (e.g. Zn, Cr, Fe in the human organism)
- **heavy metals** – are metals with a specific weight higher than 5 g/cm³ (e.g. Cd, Hg, Pb)
- **toxic metals** – have a harmful effect on humans and other biotic components of ecosystems

Ecotoxicology prefers the term heavy metals for metals harmful to the environment: Cu, Zn, Cd, Hg, Pb, Cr, Ni, Mn and Fe and semi-metals (metalloids): As and Se.

The most important sources of environmental contamination with risk elements (Kafka, Punčochářová 2002)

Risk element	Source of contamination
Lead	Ore treatment plants, refineries, chemical industry, batteries, sheets, pipes, solder (metal packaging), paint pigments, leaded glass, glaze preparations, fertilizers, insecticides, combustion of fossil fuels, leaded gasoline
Arsenic	Ore Processing, Glass Additives, Fertilizers, Insecticides, Smoking, Veterinary Medicines, Wood Preservatives
Copper	Electrotechnical material, alloys (brass, bronze), municipal waste, chemical industry, fungicides, copper wires and sheets
Zinc	Galvanizing, pigments for paints and ceramic glazes, alloys (brass, bronze), agriculture, municipal waste, smoking
Cadmium	Companion metal in zinc and lead ores, phosphorus fertilizers, pigments for paints and plastics, batteries, burning of fossil fuels, smoking
Quicksilver	Ore processing, herbicides, fungicides, electrochemistry, catalytic processes, batteries, medicine (thermometers, dental amalgams), fossil fuel combustion
Chrome	Chemical industry, paint pigments, wood preservatives, leather processing, cement production, plating, alloys, fossil fuel combustion
Nickel	Ore treatment plants, smelters, refineries, batteries, plating, alloys, cosmetics (shampoo, hairspray), smoking

Lead

- Entering the human body through the digestive tract (5-10% Pb is absorbed), lungs and placenta .
- Absorbed lead is transported by blood, where 96-98% is bound to erythrocytes . **With long-term exposure, up to 98% of lead is deposited in the bones.**
- Damage to the hematopoietic system (anemia caused by inhibition of heme synthesis), the nervous system, both central (encephalopathy) and peripheral, digestive system and kidneys. Increase in blood pressure and blood cholesterol level, heart muscle damage .
- **Acute poisoning is rare today** . It is manifested **by a sweet taste in the mouth, salivation, nausea, vomiting, spasmodic stomach pains** .
- Chronic poisoning is manifested **by a lead rim** : a dark to black edge of the gums, an ashen coloration of the skin, a change in red blood cells, a decrease in body weight, weakness, psychological changes and retardation.
- Lead oxides, lead and lead salts are toxic with **lethal doses for humans of 10 g** . **Lead ions are carcinogenic** .
- Tetraethyl lead Pb (C₂H₅)₄, added as an anti-detonator to gasoline, is dangerous.
- Intoxication is manifested by headaches, loss of appetite, insomnia. The affected person gets tired quickly, vegetative disorders appear → slowing of heart activity (bradycardia), drop in body temperature. In case of acute poisoning, psychopathic symptoms increase, suicide attempts increase.
- For the human organism, the most risky entry of lead is ingestion, it leads to a higher retention (up to 60% of the amount received compared to 30% from inhalation).
- **Zinc- based preparations can act** as antagonists.
- The source of lead in the environment is emissions from gasoline engines, metallurgy, energy. It is contained in a large number of minerals (biotite, muscovite, feldspar, silicates), from rocks mostly in acidic igneous rocks, and also in clays and slates.

- The average content of lead in soils is 5–50 mg·kg⁻¹.
- **In plants, it is mostly deposited in the roots**, in the above-ground parts of plants the concentrations are low even in soils heavily contaminated with lead.
- Phytotoxicity is manifested only at extremely high concentrations.
- Of the entire group of heavy metals, lead is **the least toxic to small crustaceans**, which are the main test organisms in environmental monitoring.

Arsenic

- Arsenic is one of the most toxic metals. **Arsenic compounds are more toxic than arsenic.**
- The most well-known poison is arsenic oxide, As₂O₃, arsenic or opium. Since ancient times, it has been among the feared herbal remedies. **The lethal dose for humans is 60-200 mg.**
- Acute poisoning after ingestion is manifested by a metallic taste in the mouth, scratching and burning in the pharynx. This is followed by persistent vomiting and severe pain in the abdomen, later diarrhea associated with dehydration occurs as in cholera. Convulsions, anuria, tachycardia, paralysis, and death later occur. These symptoms are the result of a primary effect on the nervous system. At higher doses, poisoning can also take a paralytic form, manifested by general weakness, convulsions, loss of consciousness and paralysis of the respiratory and vasomotor centers.
- Another target organ is the immune system, which manifests itself especially in chronic poisonings.
- Arsenites have similar effects. **Arsenates are less toxic.**
- hydrogen arsenic, arsine, now arsenic AsH₃ is a gas that appears as an impurity in some technical gases.
- As AsH₃, arsenic was proven by the so-called Marsh test, where gaseous AsH₃ formed after the thermal decomposition of the material is precipitated on the wall of a glass tube as metallic As.
- JM Marsh used the findings of Scheele and Serullas in 1836 and thus laid the foundations of toxicological analytical chemistry with the discovery and introduction of this analysis.
- Modern methods of atomic absorption spectrometry AAS, neutron activation analysis NAA are used today.
- AsH₃ intoxication is characterized by burning in the face and nausea. Chronic poisoning manifests itself mainly in the CNS with polyneuritis.
- Cirrhosis of the liver and nephritis are the consequences of any serious arsenic poisoning, **later effects include skin, lung and upper respiratory tract cancer.**
- The least toxic arsenic compounds include sulfides that are almost insoluble in water - arsenic sulfide As₂S₃ and arsenic sulfide As₂S₂.
- Arsenic in solution is shown to be more toxic than undissolved, probably because of its better absorption. Also, trivalent arsenic compounds are more toxic than pentavalent ones.
- Arsenites **can interact with thiol groups in enzymes** and form very stable thioarsenites, which can inactivate some enzymes (alanine amino-transferase - ALT).
- Arsenates cannot directly interact with thiol groups, however, they can be reduced to arsenites by mitochondria.
- Arsenates and arsenic acid methyl esters, however, react with thiols in vitro to produce disulfides and thioarsenites.
- Arsenates can displace phosphorus in phosphorylating agents and thus significantly affect their activity. Pentavalent and trivalent As have been shown to exhibit certain effects in inhibiting mitochondrial respiration and uncoupling oxidation from the phosphorylation of ADP to ATP.
- High As contents are often found in coal. In the USA, the average As content in coal ranges from 1-10 mg·kg⁻¹ while up to 1500 mg As·kg⁻¹ was found in coal mined in the Czech Republic
- It is therefore obvious that **the main sources of arsenic pollution of the air and, through surface fallout, of agricultural soils are the burning of coal and the smelting of metals.**
- Uncontaminated soils usually contain 0,2–40 mg As·kg⁻¹, in contaminated soils the As content increases up to 550 mg·kg⁻¹.
- In soils, arsenic occurs mainly in the form of arsenites and arsenates of iron and aluminum, which are poorly soluble, especially in more acidic soils.
- The mobility of arsenic is determined by the intensity of sorption in the soil and is determined by the grain size of the soil, humus content, content of active iron and aluminum oxides, pH and soil moisture.
- In dry climates, arsenic compounds are practically immobile. A low redox potential increases the mobility of soil arsenic by reducing As⁵⁺ to As³⁺, which is then easily leached from the subsoil.
- At comparable soil total arsenic levels, As from clay soils with high clay minerals and iron and aluminum oxide content is less acceptable to plants compared to lighter soils.
- A level of As in plants of 0,01–1 mg·kg⁻¹ is considered normal and contents of 3–10 g·kg⁻¹ as phytotoxic. **Of the agricultural crops, legumes are the most sensitive to the effects of As.**

Selenium

- The toxicity of selenium and its compounds has been known since 1935, but its essentiality for mammals was only identified in 1957, when its protective role in liver necrosis caused by avitaminosis E was discovered.
- There are many organisms in nature that take it from the environment and are able to incorporate it into their body structures **instead of sulfur, which is chemically very similar to selenium.**
- Currently, the average intake of the population of the Czech Republic is around 45 µg Se/day.
- In the body, Se is found mostly bound in selenoproteins or amino acids, where **it replaces sulfur**, e.g. selenomethionine, selenocysteine.
- Se is part of some enzymes and enzyme systems as well as nucleic protein and membrane complexes.
- Se is a microbial element, in living organisms it acts as an antioxidant even in minute concentrations. It is toxic in higher doses.
- **Acute poisonings are uncommon in humans.** They resemble arsenic compounds in their effect. The garlic

smell of exhaled air is characteristic.

- Selenium dioxide is strongly irritating, affects the immune system (sensitizing effect). Selene (hydrogen selenide, H_2Se) is among the most toxic compounds of selenium. Tellurium compounds have similar toxicological properties.
- It belongs to the semi-metals, it ranks among the essential elements.
- It is part of metalloenzymes in the human body and acts as an effective antioxidant.
- **Reduces the toxicity of cadmium, mercury, methylmercury, thallium and silver** by altering their metabolism.
- From a medical point of view, the direct relationship of Se to cardiovascular, tumor and some metabolic diseases is of great importance.
- Currently, the most accepted theory is the protection against free oxygen radicals through the enzyme glutathione peroxidase.
- Recently, a significant effect of Se on iodine metabolism has also been found. In this case, Se deficiency inhibits the utilization of iodine by the organism and actually causes its secondary deficiency.
- Se enters the human body through food chains from grain products, meat and dairy products.
- Se poisoning is rare, symptoms are various **dermatitis, damage to nails, teeth, hair loss, CNS involvement**.
- A biologically accessible form of Se for plants and animals is the soluble selenates $SeSO_4^{2-}$, which are formed in nature in an alkaline environment under oxidizing conditions.

Copper

- Copper is a biogenic element. Copper deficiency manifests as anemia, which results from the loss of the ability to absorb Fe^{2+} from food.
- Even mild chronic Cu deficiency causes neurological disorders.
- **The daily requirement for humans is 2-5 mg.**
- It is toxic in vapors during welding and in higher concentrations. **It irritates the skin locally**, causes fever, nausea, develops gastroenteritis, liver and kidney damage.
- **The lethal dose of copper (soluble copper salts) is 10 g.** In addition to anemia, soluble copper salts can cause damage to the liver, kidneys, indigestion **associated with bleeding into the digestive tract**.
- Cu^{2+} ions have astringent and fungicidal effects.
- Cu is an accumulative xenobiotic, **it accumulates mainly in the liver and bone marrow**.
- A set of health problems related to chronic accumulation of Cu in the liver, kidneys, brain and cornea is referred to as Wilson's disease. There is damage and functional insufficiency of organs.

Zinc

- Zinc is a distinctly essential element, playing a vital role **in all aspects of cellular metabolism**.
- Zn is part of more than 200 enzymes or enzyme systems (e.g. alcohol dehydrogenase, alkaline phosphatase, aldolase, lactate dehydrogenase, RNA and DNA polymerase, reverse transcriptase or Zn-dependent superoxide dismutase).
- It is generally known that Zn is a component of insulin, but the paradox is that it has very little influence on its biological effect.
- **The daily requirement for humans is 25 mg.**
- Zinc ions have an astringent and disinfecting effect. Zinc deficiency is manifested by growth retardation and skin disorders.
- Zinc ions are toxic, **the lethal dose for humans is 10 g of $ZnSO_4$** .
- Chronic exposure to zinc can lead to anemia based on a decrease in serum ferrous ions.
- **Zinc metal fumes are particularly toxic.**
- The source of zinc in the environment is metallurgy, urban agglomerations, sludge from sewage treatment plants. Plant acceptability of zinc increases with decreasing soil pH and with excess Fe in the soil.
- In plants, it accumulates mainly in the roots, in higher concentrations it is phytotoxic.

Cadmium

- Cadmium is a **highly toxic metal**. It causes inhibition of many enzymes by binding to sulfanyl groups or by competing with biogenic elements such as iron, zinc, and copper.
- The route of entry is decisive for the toxicity of Cd (both in metallic form and cadmium salts). Both Cd and Cd^{2+} ion have a strong emetic effect. After ingestion of acutely toxic doses, a significant proportion is vomited. The lethal dose ranges from 0.3–8.9 g.
- **Inhalation of dust and fumes is more dangerous.** The lethal concentration for humans is 40–50 mg/m^3 . Symptoms include respiratory tract irritation, tightness in the throat, metallic taste in the mouth, cough, flu-like symptoms, gasping for breath, stinging under the ribs, pulmonary edema, and death by respiratory arrest. Surviving victims are left with long-term damage to their liver, kidneys and reproductive organs. Of the chronic effects, the most important are carcinogenicity (lungs, prostate), damage to reproductive organs - infertility, damage to the liver, lungs and bones. Cd accumulates in the kidneys.
- The retention of cadmium taken in food in humans does not exceed 25%, **the median lethal dose has not yet been clearly determined**.
- Critical organs are the testicles, lungs, kidneys and liver.
- Up to 40% of inhaled Cd^{2+} is absorbed in the lung alveoli during long-term exposure.
- 50-75% of a subtoxic dose accumulates in the liver.
- At a Cd concentration of $30 mg \cdot kg^{-1}$, the metal is immobilized as **metallothionein**, at a concentration higher than $40 mg Cd \cdot kg^{-1}$, a toxic effect is manifested by changes in hepatocytes and necrosis of the parenchyma.

- The critical concentration of Cd in the kidney cortex is $200 \text{ mg}\cdot\text{kg}^{-1}$, **toxicity is manifested by changes in the cells of the proximal tubules or degeneration of these tubules.**
- The teratogenic and mutagenic effect of cadmium ions has been demonstrated and chromosomal aberrations have been observed .
- The main sources of soil contamination are waste and fallout from the energy, metallurgical and chemical industries, as well as phosphorous fertilizers, sludge from sewage treatment plants and some industrial composts.
- The solubility of cadmium in soil increases with decreasing pH (at a pH value lower than 5, more than 80% of soil cadmium is able to migrate).

Quicksilver

- Mercury and its compounds are known poisons. **The only metal that is liquid at normal temperatures** . If the atmosphere is saturated with metallic mercury at a temperature of $20 \text{ }^\circ\text{C}$, it contains about $19 \text{ mg}/\text{m}^3$ Hg. It is an acutely non-toxic concentration, but **mercury has the ability to significantly accumulate in the body** , which is why chronic poisoning occurs when mercury vapor is inhaled. There is a particularly significant risk of intoxication where mercury is worked at higher temperatures.
- Mercury binds to sulfanyl groups and thus inhibits a number of enzymes non-competitively.
- It affects the nervous system, kidneys, lungs, skin.
- After ingestion, metallic mercury induces vomiting , it is often excreted without affecting the organism.
- **Due to the accumulation in the tissues, however, poisoning is possible with repeated smaller doses.**
- Soluble salts are highly toxic. Among the most toxic are mercuric chloride, a sublimate whose lethal dose is $0.1\text{-}0.5 \text{ g}$. Less toxic are mercuric chloride (Hg_2Cl_2 , calomel) and mercuric sulfide (vermillion), due to their low solubility in water.
- Acute mercury salt poisoning is manifested by a metallic taste in the mouth, a dark rim of mercury sulfide around the teeth, bleeding and suppuration of the gums, nausea, vomiting, later diarrhea, sometimes nephritis , tremors , speech and walking disorders. **Ulcers form on the skin and on the mucous membrane of the stomach and duodenum . Chronic poisonings are more significant than acute poisonings.**
- Intake of mercury by the organism is possible both through the lungs and the digestive system, methylmercury is absorbed 100% here, but also through the skin and the placental barrier .
- Acute intoxication with inorganic compounds of mercury causes damage to the digestive system and kidneys, intoxication with organic compounds of mercury leads to damage to the nervous system (degeneration of neurons in the cerebral cortex, atrophy of the cerebral cortex).
- The carcinogenic effect of methylmercury has been demonstrated.
- The source of mercury in the environment is metallurgy, energy (combustion of fossil fuels), sludge from sewage treatment plants. Significant ability of methylation of mercury by the action of certain microorganisms and accumulation of organic compounds of mercury in plant and animal organisms.
- The mercury content in the soil is in the range of $0.002\text{-}0.2 \text{ mg}\cdot\text{kg}^{-1}$, the transformation of mercury in soils is influenced by microbial activity in the soil.
- The phytotoxic effect is manifested by disturbances in the internal arrangement of chloroplasts, enlargement of the endoplasmic reticulum and mitochondria .
- It affects photosynthetic reactions, more so in the organic form than in the inorganic form.

Chrome

- **Chromium is slightly toxic in its metallic form** , the toxicity of the compounds depends on the degree of oxidation. Chromium compounds are very little toxic, chromium and chromite are little toxic, but they have **an irritating effect on the skin and mucous membranes of the digestive tract**, causing allergies .
- The most toxic are chromium compounds, chromium oxide, chromates and dichromates. They are significant carcinogens, lead to lung cancer, some have mutagenic effects, **damage the liver and kidneys and cause internal bleeding.** They can also strongly irritate the skin and mucous membranes, causing ulcers on the skin, stomach and duodenum.
- Chronic inhalational intoxication of chromium compounds causes irritation of the nasal mucosa, sneezing and nosebleeds . Larger doses cause perforation of the nasal septum. Severe acute poisoning is manifested by dizziness, vomiting , chills, increased heart rate and stomach pain.
- Inhaling dust irritates the respiratory tract, causing shortness of breath and cyanosis .
- **Cr is a biogenic element, its need is 20 mg per day.**
- Cr^{6+} compounds are classified as one of the most important contaminants of the environment, especially the atmosphere, but also other abiotic components such as the hydrosphere and pedosphere.
- The hexavalent cation Cr^{6+} is very mobile in the environment, especially in soil water.
- For most plants, Cr^{6+} is quite toxic, with a high content, soil fertility decreases.
- **Some plants (including industrial ones, e.g. grain) can receive a concentration of chromium from the soil, they usually retain it in their root system, so chromium does not pass into other tissues forming the above-ground part of the plant.**
- Foods contain increased amounts of chromium, e.g. some spices, meat, unrefined sugar.

Nickel

- Nickel is a toxic element. **All nickel salts** (chloride, nitrate, phosphate or sulfate), oxide and tetracarbonylnickel ($\text{Ni}(\text{CO})_4$) are toxic .
- Nickel locally irritates and causes skin inflammation, characteristic **dermatitis.**

- Dust generated during the processing of nickel components can cause lung cancer or cancer of the nasal and throat mucosa.
- Mutagenicity of Ni has only been demonstrated in test animals.
- **Acute poisoning after ingestion results in dizziness, labored breathing, cyanosis , pulmonary edema, damage to the digestive tract, blood vessels, kidneys, heart and CNS.**
- Chronic exposure causes damage to the myocardium, kidneys and CNS, causes allergies , erosion of the nasal septum and **lung cancer**.
- Sources of nickel exposure are metallurgy, electroplating, production of nickel-cadmium cells, municipal waste incinerators and smoking.
- The most toxic nickel compound is **nickel tetracarbonyl**.
- Nickel can occur as a contaminant in all types of abiotic environments.
- **Nickel contamination of soils is more significant than that of waters.** These are localities near nickel smelters and refineries, where natural vegetation is often completely devastated.

Links

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