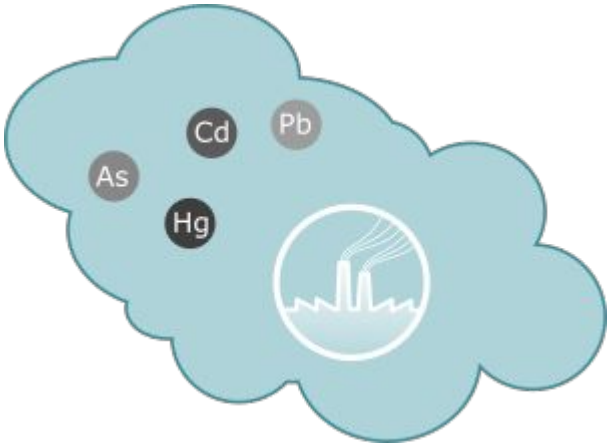


Chemical factors, Environmental toxicology

The Environment of the Czech Republic II

RNDr. Ondřej Zvěřina, Ph.D.

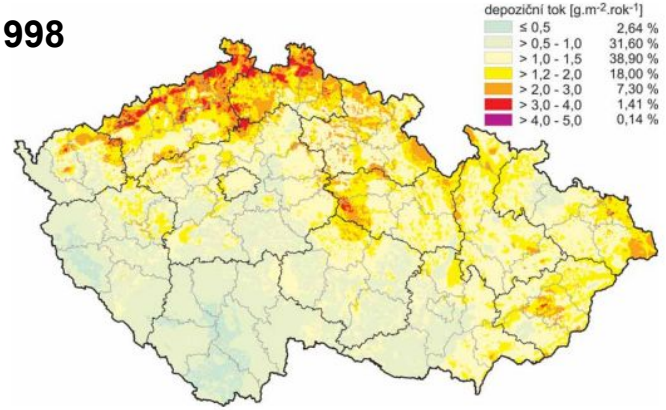
spring 2019

Development of environmental pollution in the Czechia

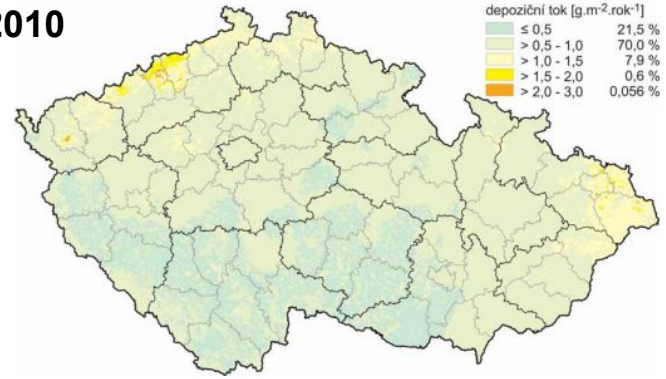
1960s	a huge increase in pollution load
1970s	Czechoslovakia: 3rd place in SO_2 emission (after Belgium and GDR), introduction of dust separators. Significant damage to the Krkonoše mountains and the Jizerské hory, increased incidence of allergies and respiratory diseases in children.
1980s	the peak of air pollution (Industry, local heating and transport)
1990s	significant decrease in emissions
present	further emission recutins, persistent problem: nitrogen deposition

Total Sulphur deposition

1998



2010

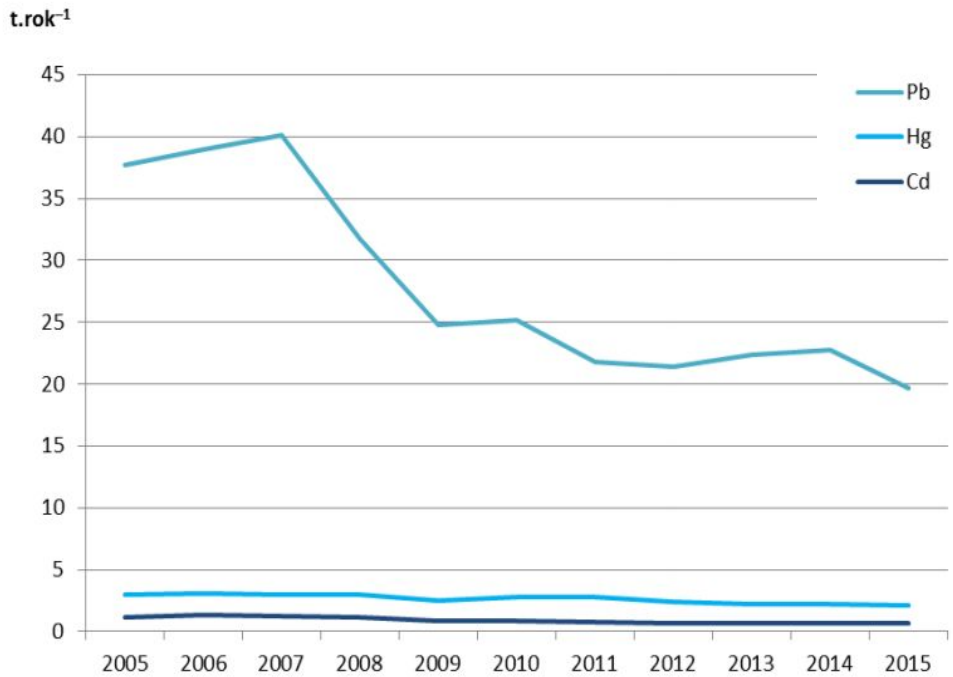


source: ČHMÚ

Emissions of heavy metals in the Czechia

a trend of last decades: **sustained decline** in heavy metal emissions

Currently the main sources:
public energy (Cd, Hg), heat generation (Hg), tire and brake abrasion (Pb), local heating (As)



A report on state of Czech Environment in 2017. MŽP

development of Pb level in children's blood

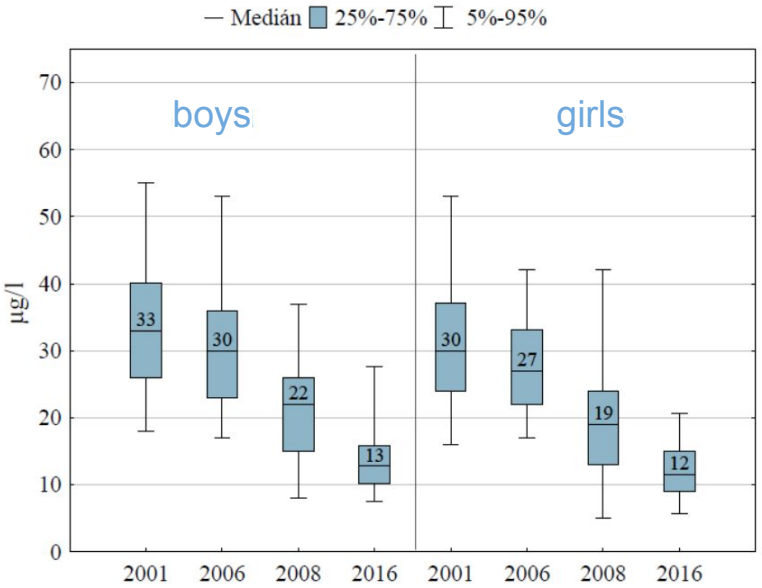
Since the ban on leaded petrol (2000), Pb has a **downward trend** in the blood of the population

Why continue to monitor the levels?

undesirable effects even at exposure not exceeding the current limits

Lead and some other heavy metals toxic at each concentration

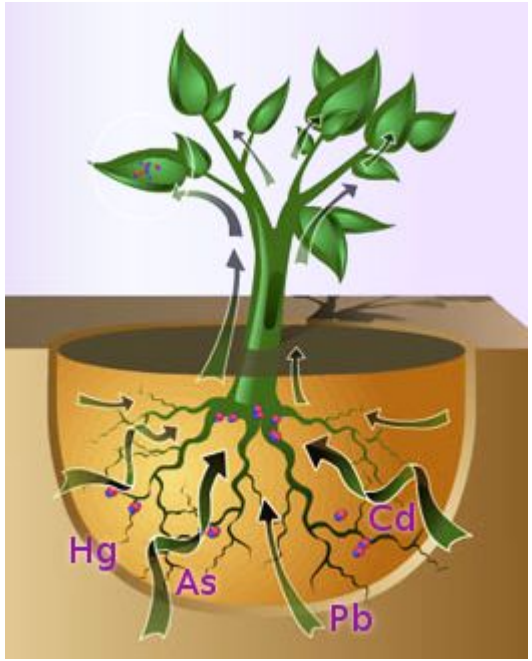
plumbemia trends
(Lead content in children's blood)



Source: *SZÚ: Systém monitorování zdravotního stavu obyvatelstva ČR ve vztahu k životnímu prostředí*

Characteristics of metals in the environment

- **nondegradable** (persistent) -
  It can only be changed between **forms** (species)
- **solubility controls their mobility**
  - **acid** solubility
    solubility in sulphuric or nitric acid → leaching from soils
- both **bioavailability** and **toxicity** is determined by the form
  - inorganic (elemental form, ions, compounds)
  - organic (humic-acids, organometalic compounds)
- especially risk elements: As, Cd, Hg, Pb



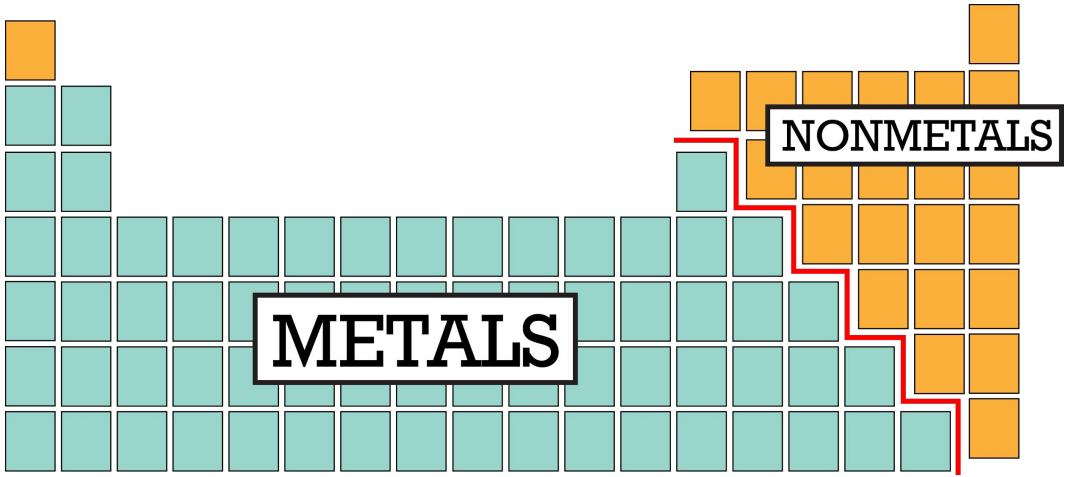
Metals in periodic table

There are 80 metal elements,

some are classified as

- trace metals
- heavy metals
- toxic metals

frequent confusion



trace metals
elements present in low concentrations ~ ppm

some heavy metals are essential at trace amounts
(e.g.: Fe, Zn, Cu, Cr^{III})

heavy metals
density > 5 $g.cm^{-3}$
(e.g. As, Cd, Hg, Fe, Cu)

density is interrelated with toxicity

little to do with density, but concerns chemical properties

toxic metals
metals that are toxic at *certain* concentrations

it depends on: dose, route of eposure, speciation
(e.g. As, Cd, Cr, Pb, Hg)

Fe

essential heavy metal
(hemoglobin, oxidoreduction processes)

the most widespread micronutrient deficit; > 1.5 billion

RDI: 10 mg men, 15 mg women in reproductive period
loss ~1 mg a day, women more (due to menstrueation)

iron deficiency adversely affects:
cognitive performance, physical growth, immune status and vulnerability to infections, may lead to anemia

meal patterns that enhance iron absorption

- separate tea drinking from mealtime
- include fruit juices to promote Fe absorption

absorption of iron from food

- ferrous form (Fe^{2+}) more easily absorbed than ferric (Fe^{3+})
- interaction with other components of the diet
  - ⇧ vitamine C ($\rightarrow Fe^{+II}$)
  - ⇩ oxalates, phytates, dietary fiber, tannins (tea, coffee)
- Resorption is regulated by iron reserves
- Iron absorption affects other elements: deficiency → inc. absorption of Cd, Pb

haem iron
(readily bioavailable)
- meat, guts

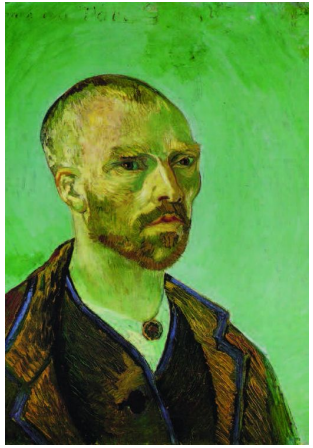
non-haem iron
cereals + pastry, green leafy vegetables, beans

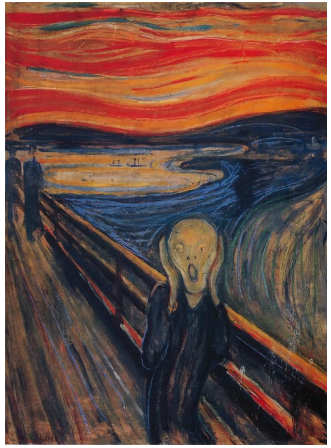
World Health Organization. "Iron deficiency anemia. assessment, prevention, and control (2001)

Toxic metals in human history

- people have known toxic metals for a long time;
  - Lead: at least 5K years, Bronze Age and antiquity (sweetening of wine, material of pipes)
  - Arsenic: a pigment in an old Egypt
  - toxicity of As described as far back as 1500 BC in Ebers papyrus
  - some discovered recently (Cd: 1817)
  - extensive industrial use ⇒ environmental burden

lead was the material of wine storage vessels in ancient Rome



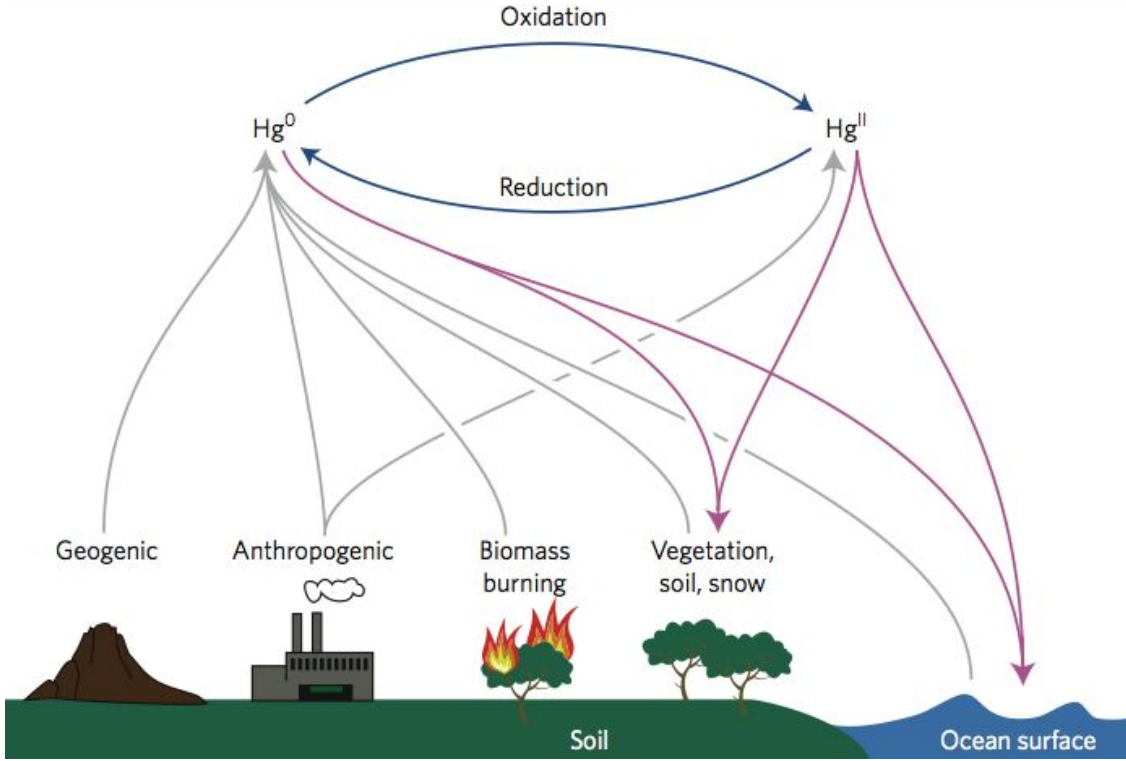


Green Arsenic Pigments (Vincent van Gogh), Cadmium Sulfides: Yellow, Orange and Red (Monet, Munch)
Many heavy metals form colorful compounds - pigments, used in painting.

Cycling of Heavy Metals

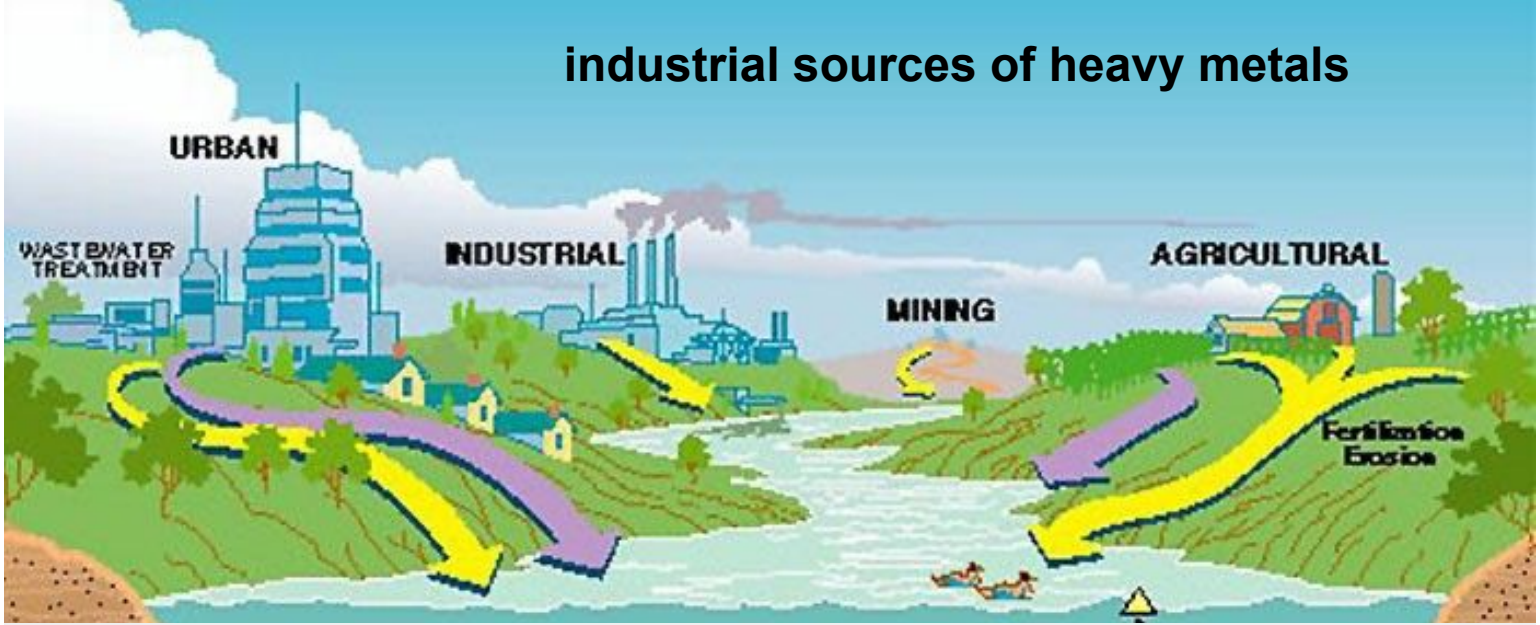
metals are not-degradable ⇒ **persistent**
In environment they only can move

- they occur in different forms - species (pure metals / solid, liquid, gaseous compounds)
- In ecosystem they cycle in **BioGeoChemical cycles**.
  Leaving cycle → **accumulation**
- Natural + anthropogenic influence.
- **industrial activity redistributed** many metals from earth's crust to environment → increase of exposure



Global mercury cycle according to Holmes et. al.

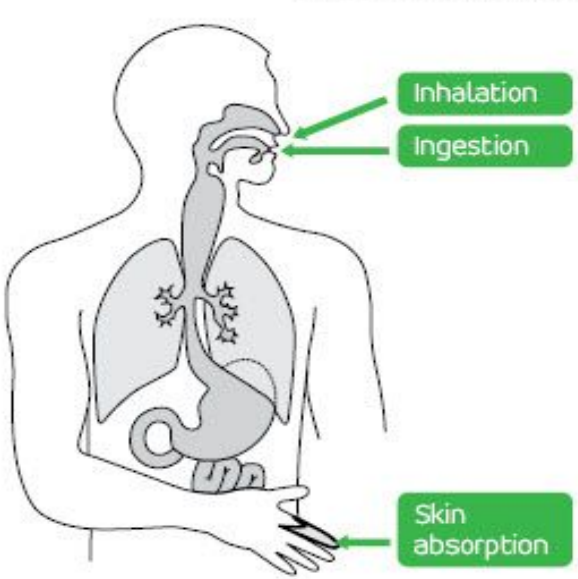
Holmes, C. D. (2012) Nature Geoscience 5, 95-96, doi:10.1038/ngeo1389.



priority metals of public health significance: **As, Cd, Pb, Hg** (due to high industrial use)

- **metal processing** in refineries
  professional exposures (e.g. metal fume fever caused by inhalation of fumes of certain metals)
- **coal burning** in power plants
  emissions of Pb, Se, Cd, Hg, Cr, ..
- **agriculture**
  fertilizers (phosphate - Cd, Pb)
  pesticides (As, Pb, Hg, Cu, Cd)
- **other**
  - conservation of wood (Cr)
  - electrochemical processes (Hg)
  - tobacco smoke (Cd, Ni)
  - formerly: leaded fuel (Pb)

Entry routes for Heavy Metals



Heavy metals enter human tissues via:

- **air inhalation**
  traffic is source of airborne As, Cd, Pb, Pt
- **diet (including drinking water)**
  polluted groundwater
  exposed plants uptake metals from soil → animals → human
- **manual handling**
  contact with polluted soil, nickel allergy (pictures)

absorption is necessary for entering circulatory system (blood,lymph) M during transport bind to erythrocytes/plasma proteins
→ **target organs**

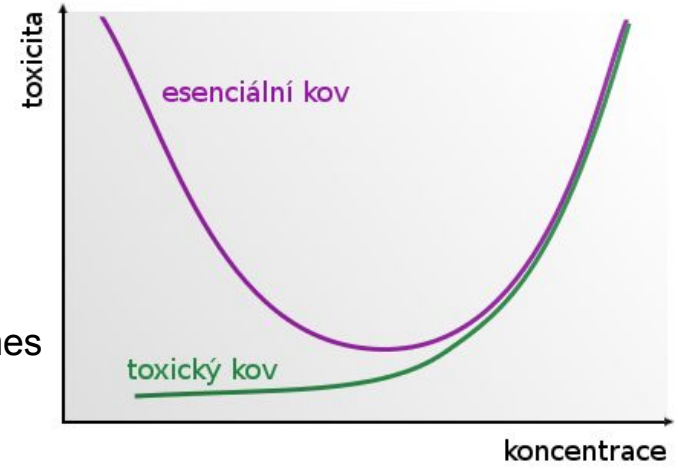
heavy metal	target organ(s)	biological half-life
Arsenic	skin, central nervous system	hours-days
Cadmium	bones, kidneys, liver, testicles	20-30 years
Lead	bones, brain, liver, kidneys, placenta	20-30 years
Mercury	brain, kidneys, liver	months

Toxic metals - **Health effects**

- multilateral, often non-specific effects
  (dermatitis, gastrointestinal disorders, organ damage, tumors, binding to cell walls and limiting nutrient penetration
  As, Cr^{VI}, Pt carcinogens
  Cd, Pb, Th spermiotoxicity
  Hg teratogenicity, embryotoxicity

- binding to **-SH, -COOH a -NH_2 groups** of biological structures → function alternation, inactivation of enzymes

- **replacement of other elements**
  Pb and Sr vs. Ca in bones
  Cd vs. Zn in enzymes
  As vs. P

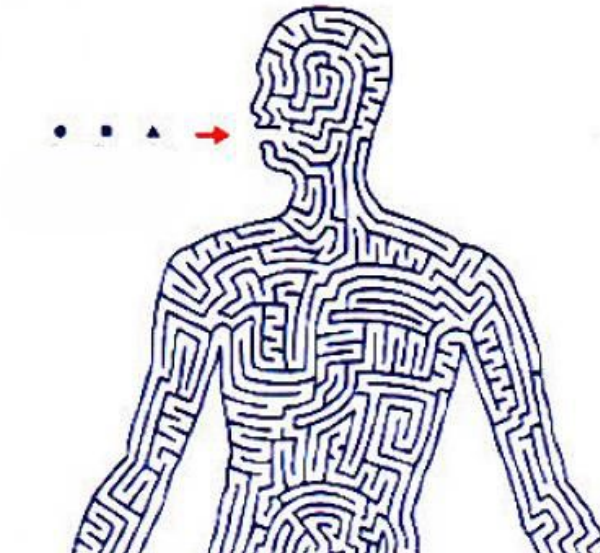


non-specific effects of heavy metals

bioavailability
a fraction of an ingested trace element ultimately presented to tissues

- metal cations are eletrophiles
  ⇒ they bind to negative charged ions like:
  -SH (thiol), -COOH a -NH_2 groups of biological structures ⇒ deactivation

- **replacing other elements**
  Pb, Sr vs. Ca in bones
  Cd vs. Zn in enzymes

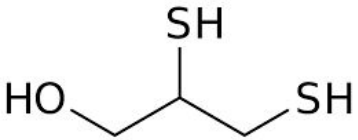


Metal poisoning

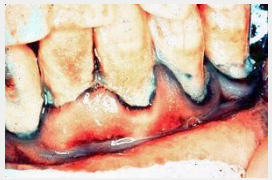
Accute intoxication is rare,
mostly of professional origin

The most common is intoxication with lead, arsenic and mercury

Chelation therapy
chelated metals are excreted in urine



symptoms of poisoning



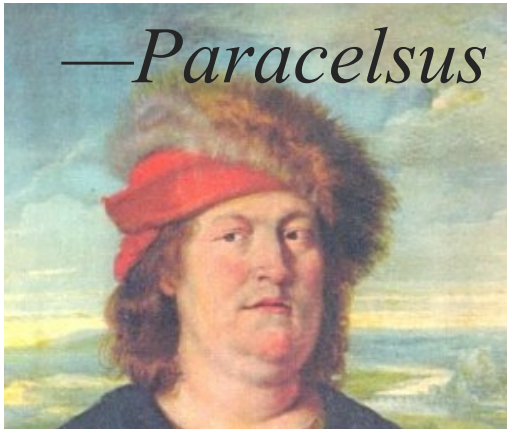
hyperpigmentation *(hyperpigmentosis)* of teeth and gums - symptoms of poisoning with heavy metals
left: lead, right: copper

colouration	**metal**
black	Silver, Iron, Manganese
gray	Lead, Mercury
Blue-Green	Copper, Nickel
Yellow	Cadmium

chelating agent	metal
EDTA	Pb
British Anti-Lewisite (**BAL**, or **dimercaprol**)	As, Au, Hg, Pb
DMSA	As, Hg, Pb

All things are poison and nothing is without poison, only the dosage makes a thing not poison.

—Paracelsus



Mercury

(Hg, hydrargyrum)

used by mankind over 3000 years

gradually gaining experience with its toxicity

mercury harms several organ systems

neurotoxicity = **critical toxic effect** of mercury

expression of the adverse effect depends on availability

(physico-chemical properties of the specific forms)

Mercury and its physico-chemical forms

Hg^0

elemental mercury: metal or in the form of vapor

Hg^{2+}

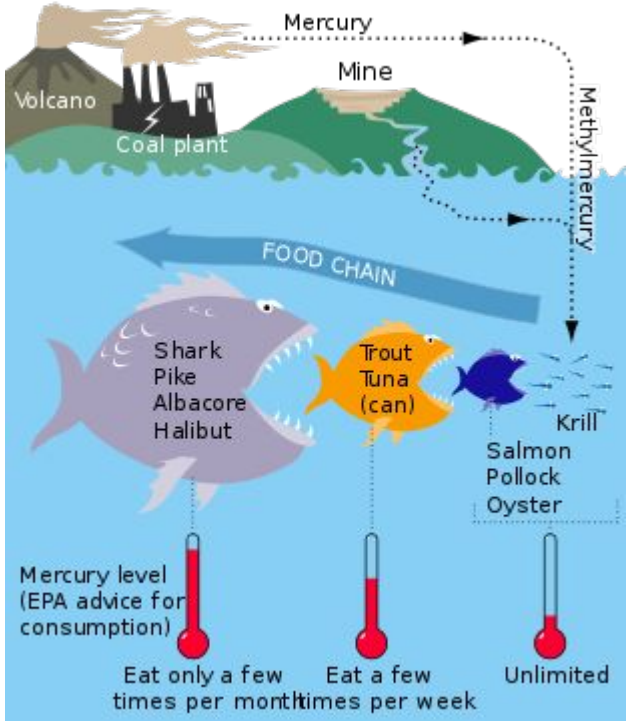
inorganic compounds

organic Hg

organic forms, especially methylmercury (MeHg, CH_3Hg)

these forms most easily passes through the blood-brain barrier (hematoencephalic barrier)

EPA: what to do with broken themometer



Mercury in the aquatic environment

Diagram of the journey of mercury from its **emission sources** (volcano, coal-burning power station) into the **aquatic environment**.

A considerable part of mercury and its methylated form ends (due to its physical properties) **absorbed** by small aquatic organisms or **adsorbed on particles** of organic matter that are **eaten**.

In a sea, for example, these tiny organisms then become food for krill.
Krill becomes food for larger fish and at the end of the food chain there are predators such as shark or swordfish.

Symbolic thermometer shows how the concentration of mercury increases on the way up the food chain due to **bioaccumulation**.

Mercury Levels in Fish

HIGH

- Bluefish
- Crab *(Blue)*
- Grouper*
- Mackerel *(King, Spanish, Gulf)*
- Marlin*
- Orange Roughy*
- Salmon** *(Farmed, Atlantic)*
- Seabass *(Chilean*)*
- Shark*
- Swordfish*
- Tilefish*
- Tuna *(Ahi,* Yellowfin,* Bigeye, Blue, Canned Albacore)*

*Overfished **May Contain PCBs

MEDIUM

- Bass *(Striped, Black)*
- Carp
- Cod *(Alaskan)*
- Croaker *(White Pacific)*
- Halibut *(Pacific, Atlantic*)*
- Lobster
- Mahi Mahi
- Monkfish*
- Perch *(Freshwater)*
- Sablefish
- Skate*
- Snapper*
- Tuna *(Canned Chunk Light, Skipjack*)*
- Sea Trout

Data from: nrdc.org

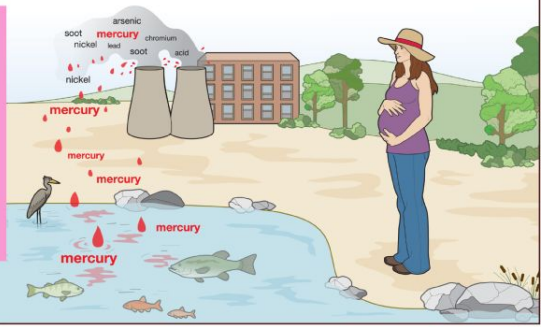
LOW

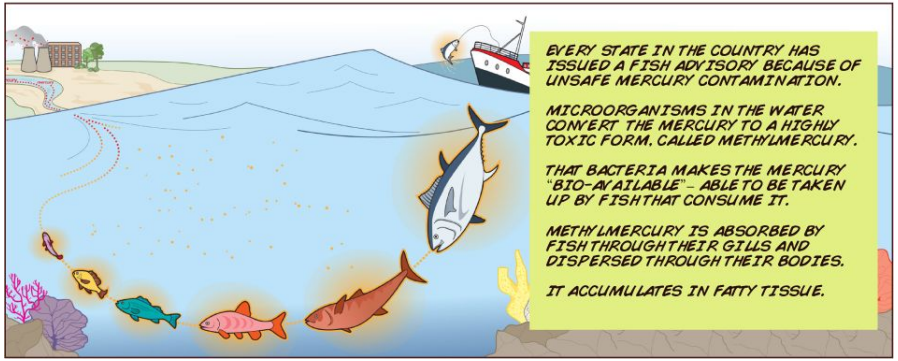
- Arctic Cod
- Anchovies
- Butterfish
- Catfish • Clam
- Crab *(Domestic)*
- Crawfish/Crayfish
- Croaker *(Atlantic)*
- Flounder*
- Haddock *(Atlantic*)*
- Hake • Herring
- Mackerel *(N. Atlantic, Chub)*
- Mullet • Oyster
- Perch *(Ocean)*
- Plaice • Pollock
- Salmon** *(Canned, Fresh, Wild)*
- Sardine • Scallop*
- Shad • Shrimp*
- Sole • Squid
- Tilapia • Trout
- Whitefish
- Whiting

COAL-FIRED POWER PLANTS ARE THE LARGEST SOURCE OF TOXIC MERCURY: THEY EMIT 72% OF ALL MERCURY AIR POLLUTION IN THE UNITED STATES.

WHEN A COAL SMOKESTACK IS NOT FILTERED, MERCURY AND OTHER POISONS–ARSENIC, LEAD, NICKEL, CHROMIUM, AND ACID GASES–ARE RELEASED INTO THE AIR.

THAT MERCURY DRIFTS THROUGH THE AIR ACROSS THE GLOBE AND RAINS DOWN INTO RESERVOIRS, RIVERS, LAKES, AND THE OCEAN.





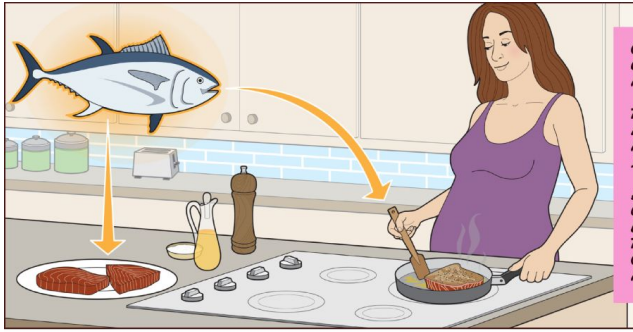
EVERY STATE IN THE COUNTRY HAS ISSUED A FISH ADVISORY BECAUSE OF UNSAFE MERCURY CONTAMINATION.

MICROORGANISMS IN THE WATER CONVERT THE MERCURY TO A HIGHLY TOXIC FORM, CALLED METHYLMERCURY.

THAT BACTERIA MAKES THE MERCURY "BIO-AVAILABLE"– ABLE TO BE TAKEN UP BY FISH THAT CONSUME IT.

METHYLMERCURY IS ABSORBED BY FISH THROUGH THEIR GILLS AND DISPERSED THROUGH THEIR BODIES.

IT ACCUMULATES IN FATTY TISSUE.



CONTAMINATED FISH IS EATEN BY OTHER FISH, BIRDS, AND MAMMALS – INCLUDING HUMANS.

TYPICALLY, THE LONGER A FISH LIVES, AND THE LARGER IT IS, THE MORE MERCURY ACCUMULATES IN ITS FLESH.

KING MACKERAL, TILEFISH, RAY, GROUPER, HALIBUT, SWORDFISH BARRAMUNDI, SHARK, GEMFISH, TUNA, AND ORANGE ROUGHY ALL CONTAIN HIGH LEVELS OF MERCURY.

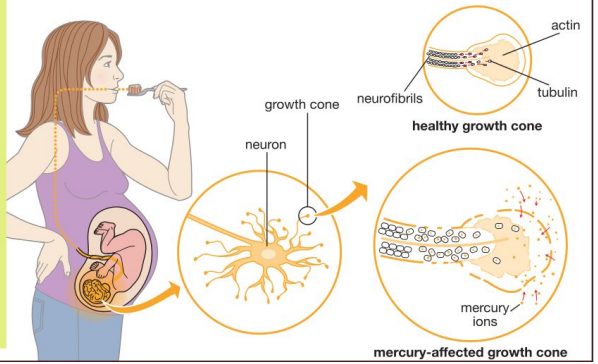
ONCE WE EAT CONTAMINATED FISH, METHYLMERCURY GOES DIRECTLY INTO THE ORGANS THAT HAVE THE MOST FATS, WHERE IT ACCUMULATES.

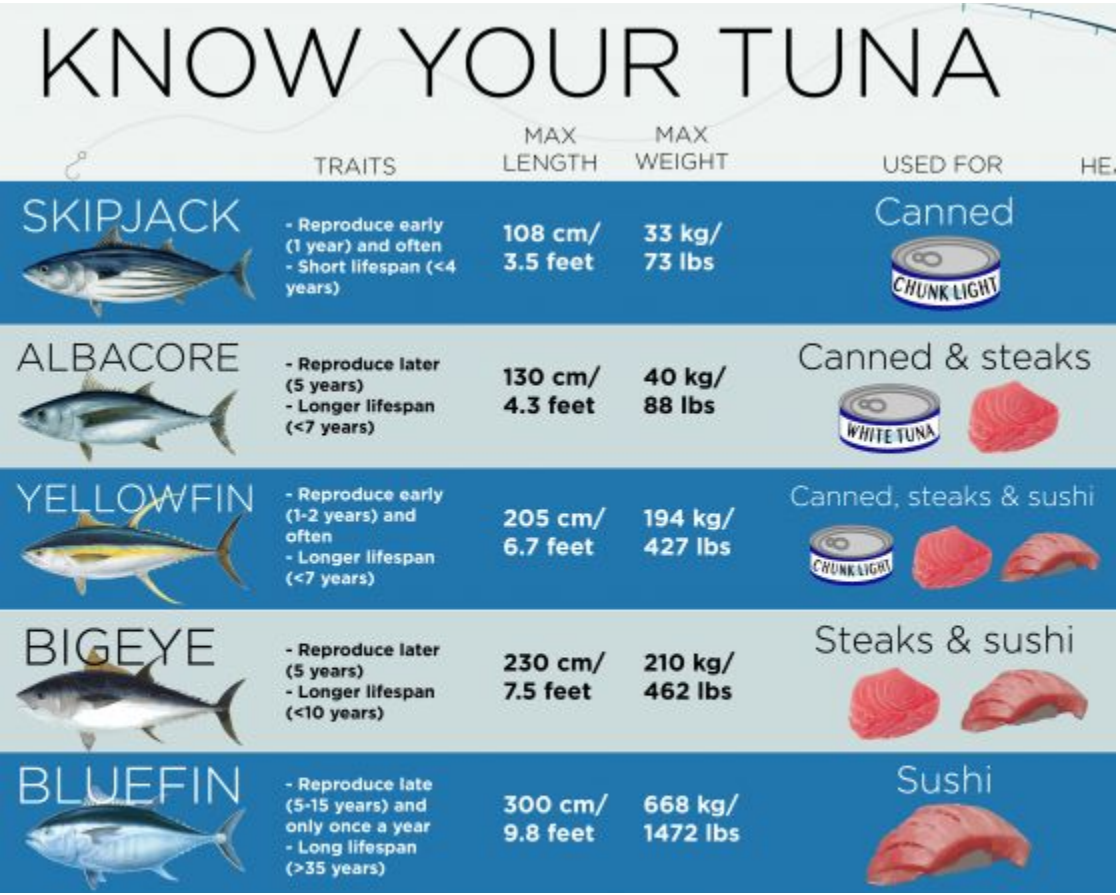
BREASTS: MERCURY IS FOUND IN BREAST MILK.

BRAINS: METHYLMERCURY IS ABLE TO BREACH THE BLOOD-BRAIN BARRIER.

UMBILICAL CORD: METHYLMERCURY REACHES THE FETUS AND THE BABY'S DEVELOPING BRAIN.

FETUSES AND YOUNG CHILDREN ARE ESPECIALLY VULNERABLE TO POISON, WHICH CAUSES CAUSES BRAIN NEURON DEGENERATION AND IMPAIRS LEARNING AND GROWTH.





What about canned tuna?

individual types of tuna differ in Hg content

- smaller species contain less Hg

  (often in cans)

- bigger species contain much more Hg

  (usually consumed as steaks or in sushi)

Minamata (JAP)

mercury poisoning - Minamata story

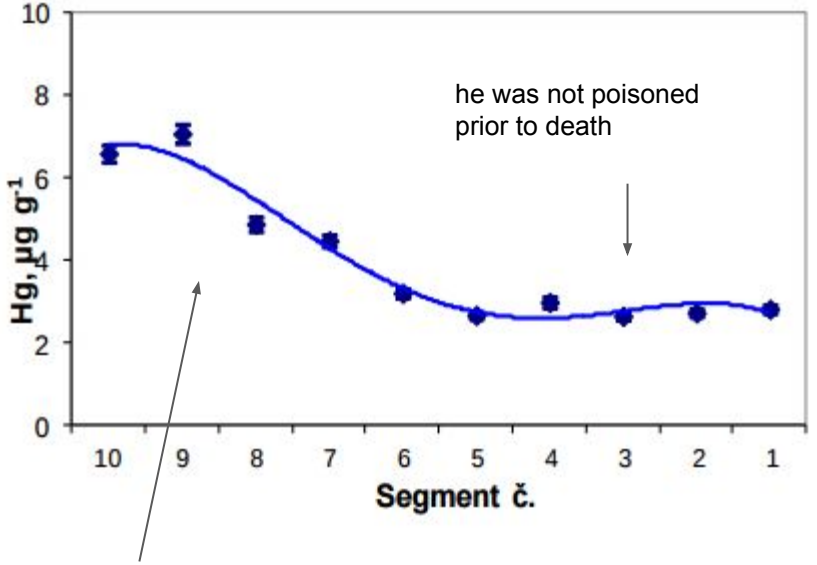
In the Iraq poisoning, of an estimated 50,000 people exposed to the contaminated bread, 459 died, and 6,530 were hospitalized.

MeHg Poisoned Wheat


Collecting a hair sample from a mother

Photographs from *Neurotoxicology*, 1995, Vol. 16, No. 4

Tycho Brahe had 7.5 cm long hair.
Daily growth rate of hair: 0.27 mm,
thus record of 6-9 months



he was developing (and probably using) the elixir *Medicamenta tria.* One of the three components was mercury

it seems Tycho Brahe was not poisoned by Hg

Hair as a bioindicator for trace elements exposure

Suitable for estimation of exposure to:
Se, Cd, Hg, Pb, …

time integration: according to length of hair

(exposure in recent years can be monitored)

easy sampling and handling and storage

risk of external contamination

(The more distant parts often contain higher metal levels than those close to the head.)

Hair care can distort results.
The ideal condition of hair near the head
(at the cost of losing long-term information).

Hair as a bioindicator for trace elements exposure

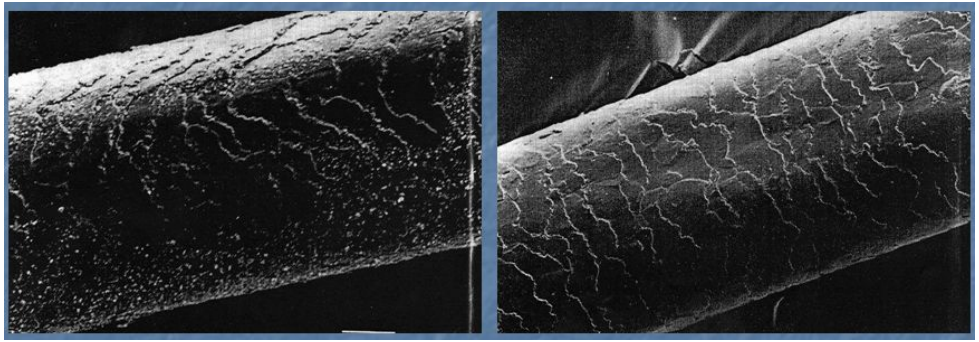
sample collection

collection from the back of the head
<5 cm of hair, cca 0.5 g of a material

Sample cleaning from an external contamination (according to WHO):
- acetone,
- 3x deionised water,
- acetone
(ten minutes each step)

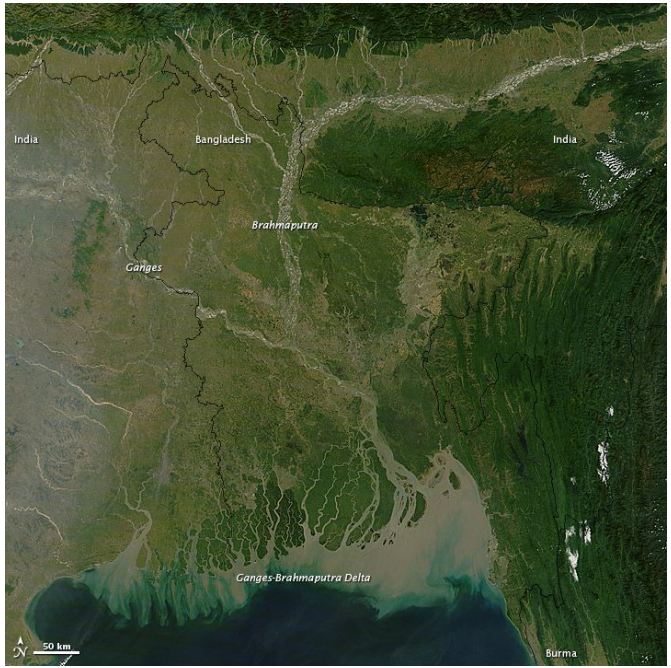
Mineralization of the sample
Usually involves dissolving the sample ‘
in nitric acid (microwave assisted extraction)

Determination of elements
Atomic absorption spectrometry, ICP-MS



before wash

after wash



Arsenic in the waters of Bangladesh

deltas of the rivers Ganges and Brahmaputra are biologically polluted

solution: depth drilling for groundwater 10-70 m to reduce disease from ingestion of pathogen-laden surface waters

→ significant reduction of parasitic diseases

but: occurrence of **arsenic poisoning.**

Later it turned out that almost 5 millions of these water sources are contaminated with As

result: 35-77 million people in the country have been chronically exposed to As in drinking water = largest pass poisoning in history

WHO guideline value of 10 µg As/l same limit in Czech Republic)

source: WHO

Arsenic in waters of the Czech Republic

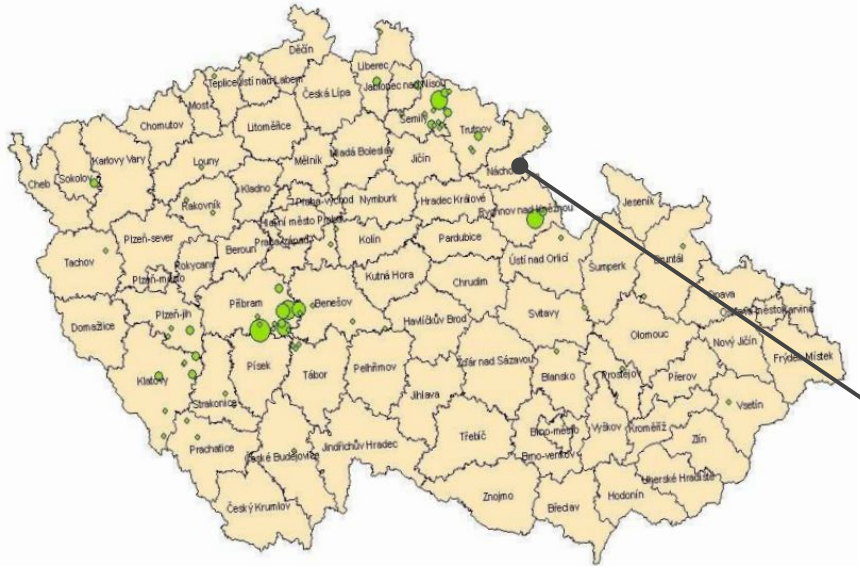
The situation is generally favorable.

However: **diverse geological bedrock**
→ In certain regions, the issue of Arsenic is current.

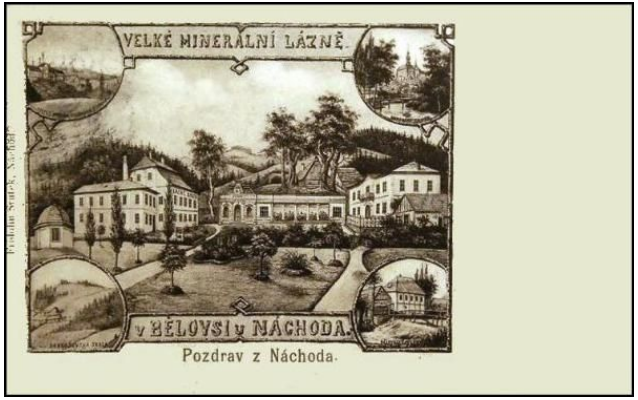
In ca. **1 %** of areas, exposure may be significant

Relatively **high As levels occur in Krkonoše** mountains and also in **Orlické hory**.

There is a possibility of **water treatment** using special filters.



Běloves in Náchodsko
mineral water with up to 2,7 mg As/l
formerly: curative springs, spas



iDNES.cz / Hradecký kraj

iDNES.cz 〉 Zprávy | Kraje | Sport | Kultura | Ekonomika | Bydlení | Technet | Ona | Revue

Hradecký kraj | Zprávy | Sport | Jízdní řády MHD | Práce | Reality | DO TOHO

Lidé pili čtyři roky arzen v minerálce, město přehlédlo zákaz inspekce

20. února 2016 7:50

people have been drinking arsenic in mineral water for four years, the city has overlooked the ban

Arsenic toxicity

toxicity is associated with **arsenic speciation** (oxidation state, binding and solubility):

- arsenic sulphide (As_2S_3) insoluble ⇒ nontoxic
- organoarsenic compounds (as arsenobetaine in marine foods) are non-toxic
- **the most toxic: inorganic As(III) compounds**

chronic effects: skins lesions, hyperkeratosis, skin cancer
acute effects: nausea, vomiting, abdominal pain, skin problems
LD_{50} As_2O_3: 70-180 mg

Rezaul Morol, a young Bangladeshi man, nearly died from arsenic poisoning caused by drinking arsenic-laden well-water for several years. The doctor advised Rezaul to stop drinking contaminated water and eat more protein-rich food such as fish. Since then Rezaul feels a lot better and is happy that his skin is healing (Photo and original story: Asia Arsenic Network)

Arsenic poisoning is manifested by skin patches that go into hyperkeratosis, often skin cancer.

Lead(Pb)

together with mercury the longest known and used metal with no essential importance - only toxic

calcium antagonist → **cumulation in bones**,
anemia of lead poisoning (disrupts hemoglobin synthesis)

in a period of calcium deficiency (e.g. pregnancy), Pb can be mobilized in the blood and penetrate placental barrier

causes mental retardation

source: WHO

Lead in the Roman Empire: period of chronic lead poisoning

fatal taste for wine
the acidic wine gradually dissolved
the walls of the lead vessels,
in addition: lead acetate added
⇒ rich Romans often had advanced poisoning

symptoms of dementia, insanity (Neron, Caligula?)
less pronounced manifestations: madness,
sadness, reduced sexual performance
- common among aristocrats

poor people threatened with water
lead pipelines, leaded food containers,
writing with a lead-pencil,

slaves worked in lead mines

Lead intake

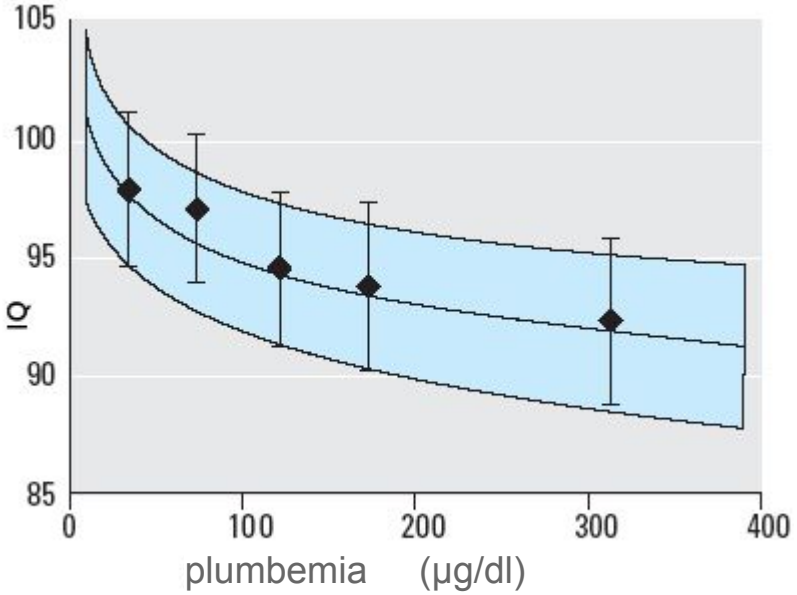
main sources: **water and food** (bread, cereals)

Contamination of foods by lead from **cans** is gradually decreasing, **glazed ceramic** cooking utensils can contribute.

Contamination of drinking water by **lead from piping** is still the issue.

level of lead in blood = **plumbemia** (µg/l)

elimination half-life
from blood - tens of days
from bones - tens of years



At lower levels of exposure: intelligence quotient(IQ) decrements of cca. 3 points at reference value of plumbemia 50 µg/dl.

There is no really safe level.

Lead in drinking water

The use of lead piping in the 19th and first half of 20th century
At present several percent of houses in Czech Republic are still equipped with Pb pipes

Lead pipeline = **inexhaustible lead source**

Aggressivity of water (soft, acidic, by chlorination) and its stagnation
influences the significance of the source.

Layer of **orthophosphates** (simply from phoshoric acid)
can **prevent lead** getting into the water.

Concentration of Pb in water is variable:
Pb ve vodě variabilní - units up to hundreds of µg/l
after night even up to mg/l

Limit Pb in water
WHO recommendation **10 µg/l**
(nor does this limit exclude unfavorable effects)

Cadmium

long elimination half-life (10-30 years)
main sources: food and smoking

Crops take in cadmium readily from soils

Population groups that are especially vulnerable
to increased exposure of cadmium:

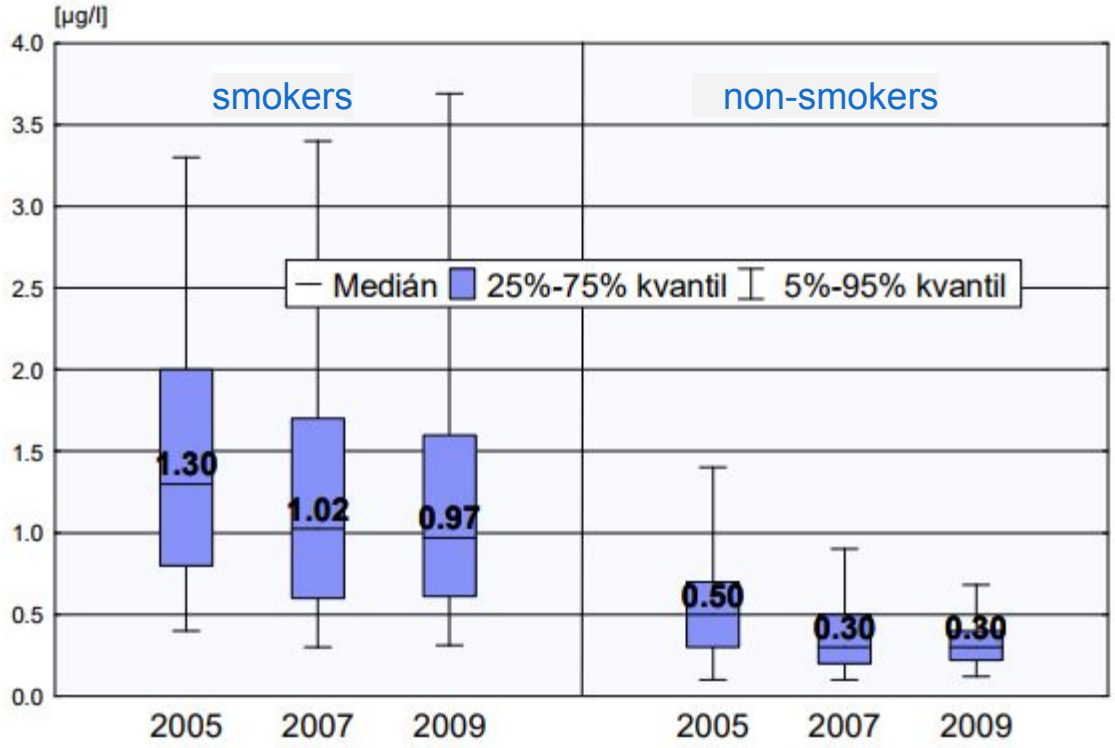
- vegetarians (consume amounts of cereals and rice)
- smokers (tobacco plants absorb Cd from soil)

itai-itai disease
Firstly described in Japan in the 1940s among people who had eaten rice grown on fields irrigated with cadmium-polluted water. Low calcium diet plus high cadmium exposure led to kidney disease followed by bone disease.

source: European Commission: Soil contamination: Impacts on Human health

One cigarette
contain 1-2 µg Cd of which about 10% is absorbed

Levels of Cadmium in blood of smokers and non-smokers



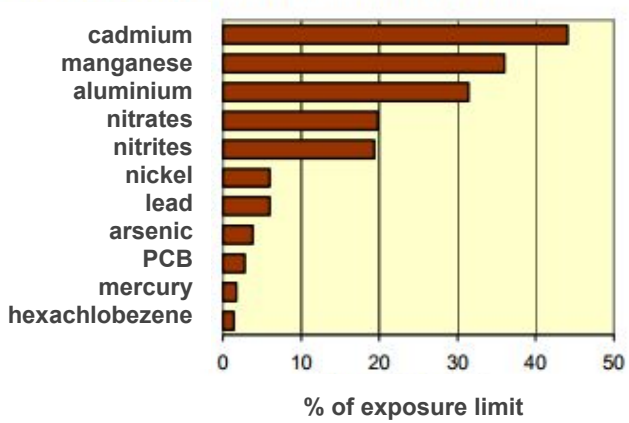
source: National institute of Public Health

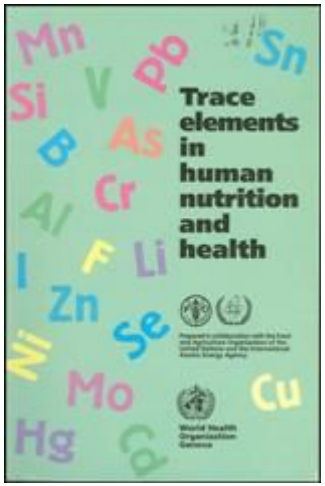
positive **conclusion**

key message

For people with average consumption and composition of food, the intake of any monitored metal does not exceed an acceptable value.

[National Institute of Public Health]





Recommended literature

If anything in this presentation is unclear,
try to find the answers in this book:

Trace elements in human nutrition and health
by World Health Organization