Inorganic contaminants of food

- Toxic anions (nitrites, nitrates)
- Toxic elements
  - Pb, Cd, Hg, As in the environment
  - Toxicity and chemical forms of toxic elements
  - Occurrence of toxic elements in foodstuffs

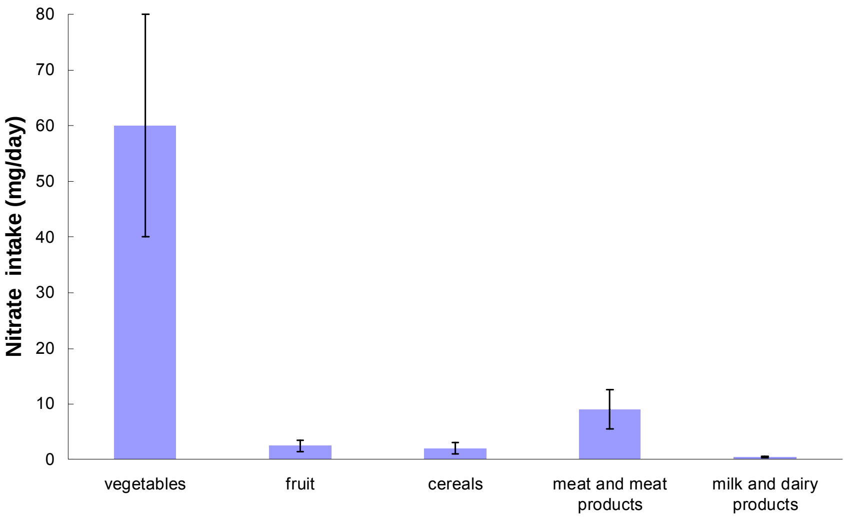
Nitrites and nitrates in food

- natural components of the environment and some plants (vegetables)
- toxic effects of nitrites (and nitrates after reduction to nitrites)
  - transformation of haemoglobin to methaemoblobin
    $4\ Hb(Fe^{2+})O_2 + 4\ HNO_2 \rightarrow 4\ metHb(Fe^{3+})OH^- + 4\ NO + 4\ O_2$
    metheamoglobinemia – dangerous for newborns and babies
  - formation of nitrosamines
- positive effects
  - antimicrobial action against *Clostridium*
  - stabilization of meat colour
    myoglobin (Mb) is converted to nitroxymyoglobin (MbNO)
    → use of $NaNO_2$ in salt to preserve meat products

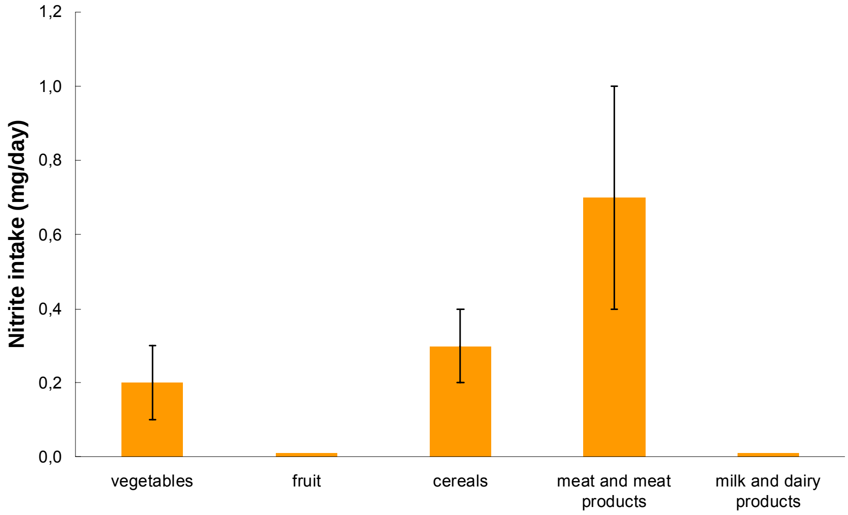
Toxicity and limits

- TDI for NO_3^- : 250 mg/day (70 kg body weight)
- limits in drinking water
  NO_3^- : 50 mg/l (6 mg/l in water for babies)
  NO_2^- : 0.1 mg/l

Contribution of food commodities to dietary intake of nitrates



Contribution of food commodities to dietary intakes of nitrites



Groups of vegetables according to nitrate content

1. very high content (> 1000 mg/kg fresh matter): lettuce, spinach, endive, beetroot, radish, Chinese cabbage…
2. intermediate content (> 250 mg/kg fresh matter): cabbage, kale, cauliflower, carrot, broccoli, potato…
3. low content (<250 mg/kg fresh matter): tomato, Brussels sprouts, peas, cucumber…

Chemical changes of nitrates

- the most important: reduction to nitrites
- in vegetables, the rate of NO_3^- to NO_2^- conversion depends on the conditions of storage:
  - at 5°C: NO_3^- is not reduced
  - at 25°C: one third of nitrate content is reduced to nitrite during a day
- NO_3^- to NO_2^- conversion can take place inside a human body (e.g. in stomach of newborns – enzyme catalysed reduction caused by microorganisms)

1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104														

58 Ce	59 Pr	60 Nd	61 Pr	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Origin of toxic elements in food

- from raw materials (agricultural products)
  result of bio-geochemical processes and environmental contamination
  - rocks weathering, volcanic activity…
  - transfer of elements from soil to plants
  - air pollution (metallurgy, power plants, traffic)
    → transport → fallout →
    → deposition on the surface of soil and plants →
    → animals
  - water pollution (metallurgy, other industrial activities, waste disposal…) → deposition in sediments and accumulation in aquatic organisms (bio-accumulation)
  - excessive use of mineral fertilizers
- contamination during food processing
- contamination from packaging materials

Lead

The use in industry

- batteries
- additives to petrol (in past)
- paints, pigments
- alloys, sheets and tubes, glass

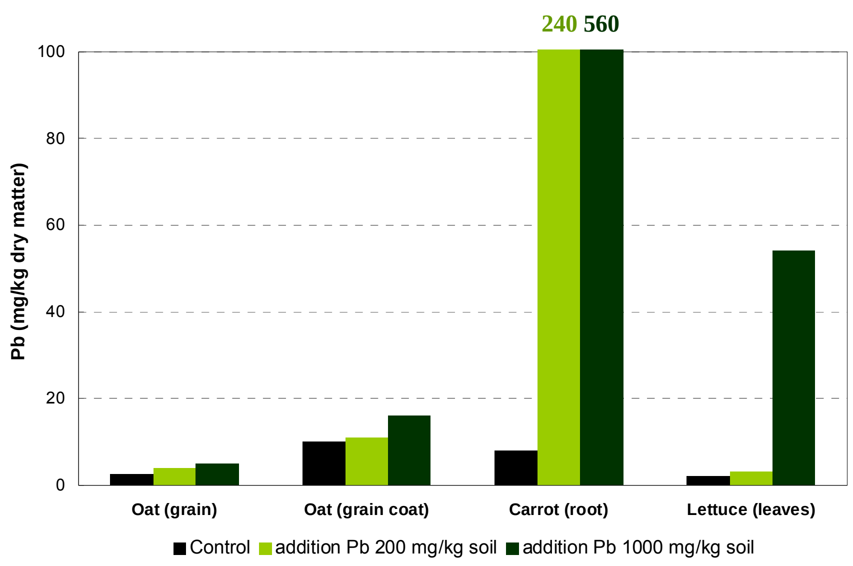
Lead in the environment

- air: ng/m^3 in non-polluted areas,
  in big cities up to 2−3 μg/m^3
- natural waters: <1-10 μg/l (drinking water should contain ≤ 10 μg/l)
- soil: non-polluted 10−40 mg/kg dry matter

Lead in plants

- coming into plants:
  - deposition on leaves surface
  - uptake from soil via roots
    more effective from acidic soils
    variable ability of lead transfer in individual plant species
    root and leaf vegetables – usually higher lead contents
- lead distribution in plant parts is not uniform

Lead accumulation by plants



Lead in animal body

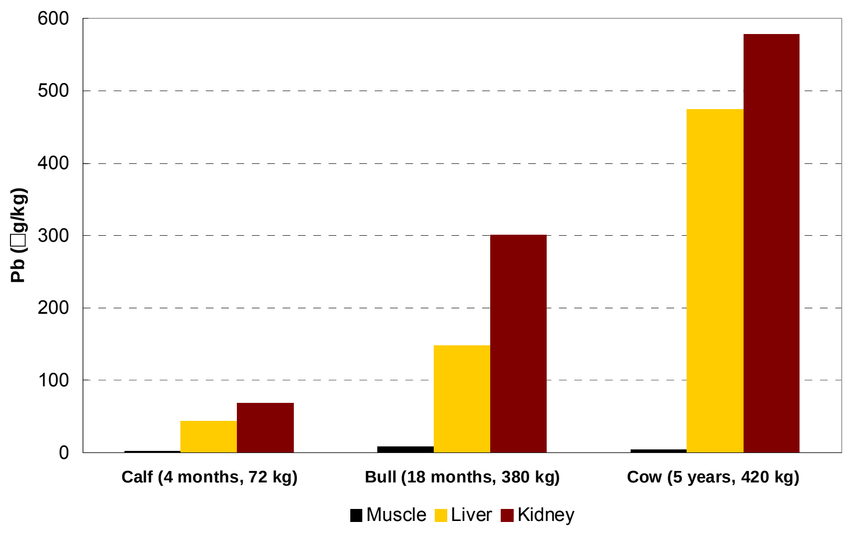
blood: usual range for humans 50−200 μg/l

higher contents in liver and kidney (the content rises with age)

muscle – very low content

long-term exposure → higher contents in bones and teeth

Lead in animal (cattle) tissues



Toxic effects of lead

- impaired red blood cells production
  (inhibition of haem synthesis) → anaemia
- impaired liver, kidneys, pancreas
- impaired nerve system

Lead intoxication from food is very unlikely.
Lead content in foodstuffs is low (tens of μg/kg to units mg/kg) and lead absorption is limited.
Lead intoxications – practically only in the case of professional exposure (e.g. workers in foundry factories…)

Cadmium

Contamination sources

- industrial production of metals
- coal combustion
- fertilizers
- use of Cd and its compounds
  - batteries, pigments
  - electroplating
- industrial waste disposal

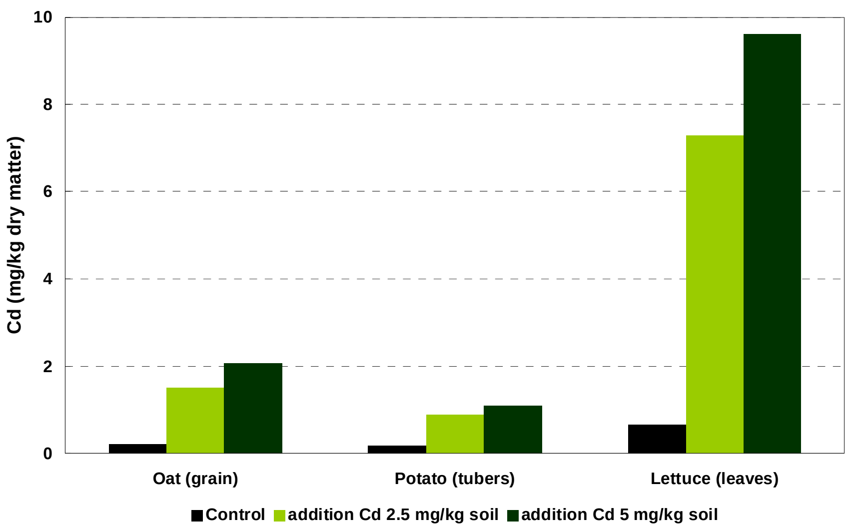
Cadmium in the environment

- air: max. conc. several ng/m^3
- natural waters: < 1 μg/l, (drinking water should contain ≤ 5 μg/l)
  higher Cd content in sediments
- soils: non-polluted 0.01–0.2 mg/kg dry matter
  limits of Cd for agric. soil are 0.5–1 mg/kg dry matter

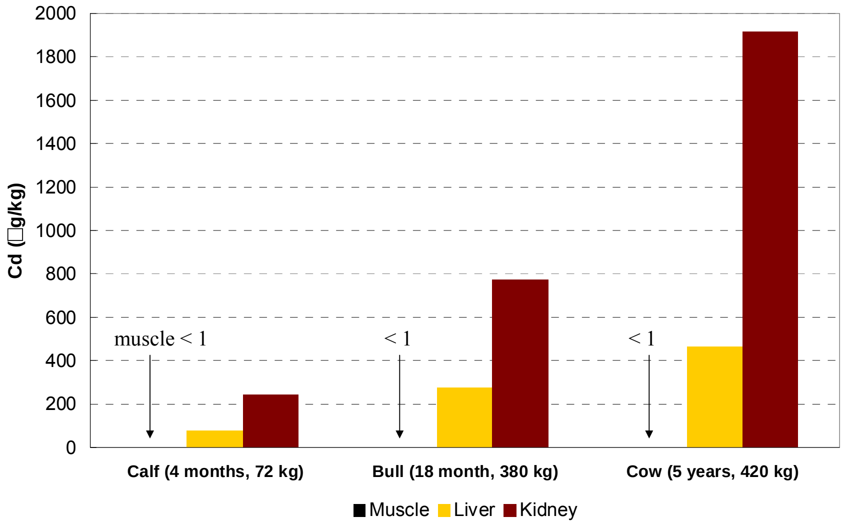
Cadmium in plants

- coming-in: mainly *via* root uptake from soil (surface deposition is less important)
- soil-plant transfer depends on the plant species e.g. tobacco – efficient Cd accumulation
- uptake is higher from acidic soils
- distribution of Cd in plant parts: roots > leaves > stalks > fruits = tubers > seeds

Cadmium accumulation by plants



Cadmium in animal (cattle) tissues



Toxic effects of cadmium

- impaired kidney function → kidney failure
- impaired liver
- sexual organs: → decreased sperm production, limited mobility of sperm cells
- lungs (in the case of inhalation exposure)
- bones decalcification
- carcinogenic effects, teratogenic effects

Acute intoxication is very unlikely.
Long-term exposure → accumulation of Cd in the body.
Only low portion of Cd (2–8 %) is absorbed from the diet.
Smokers are exposed via inhalation → increased health risk.
Protection mechanisms: synthesis of metallothioneins

Mercury

Sources of contamination

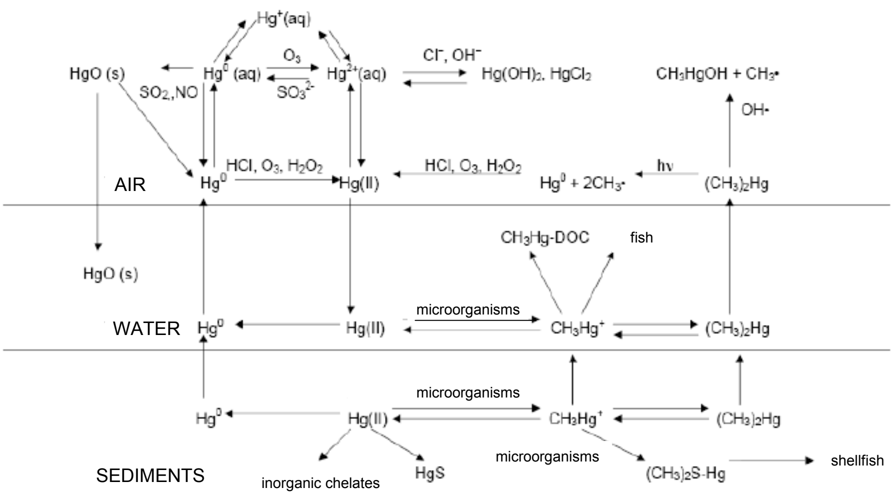
- natural sources
  (volcanic activity, rock weathering, forest fires)
- coal combustion
- use of sewage sludge as a fertilizer
- use of Hg and its compounds
  - electrochemical production
  - electrical engineering
  - measuring instruments
  - catalysers
  - fungicides (phenylmercury chloride)
  - medicine

Mercury in the environment

- air: normal conc. – units ng/m^3
- freshwater (rivers, lakes, wells: < 0.2 μg/l)
  drinking water – Hg limit 1 μg/l
- river sediments: tenth μg/kg to units mg/kg dry matter
- sea water:
  normal concentrations: units ng/l
  bays polluted by industry (in past): units μg/l →
  → bioaccumulation in fish and shellfish →
  → mass intoxication (Japan 1953)
- soil: normal levels <0.1 mg/kg dry matter

Transformations of mercury chemical species in aquatic eco-systems

- methylation of Hg^{II} *via* microbial activity
  → methylmercury CH_3HgX (main mercury species in fish)
  → (dimethylmercury $(CH_3)_2Hg$ – volatile compound)
- oxidation-reduction reactions
  – reduction of Hg^{II} to low soluble compounds of Hg^{I} (Hg_2Cl_2)
  – disproportionation of Hg^{I}
- precipitation reactions – namely formation of mercury sulphide (HgS)



Toxic effects of mercury

depend on the chemical form of mercury

- inorganic monovalent mercury – low toxicity
- inorganic divalent mercury – highly toxic
  induce namely kidney damage and CNS damage
- methylmercury – extremely toxic,
  it affects nerve system and sense organs,
  teratogenic effects!
- arylmercury compounds (phenylmercury chloride) – less toxic

Arsenic

Sources of contamination

- natural: volcanic activity, forest fires
- anthropogenic:
  - ore mining
  - metals production
  - coal combustion
  - use of pesticides containing arsenic (in past)
  - combustion of wood treated by arsenic-containing fungicides

Arsenic in the environment

- air
  in non-polluted areas: tenths ng/m^3
  big cities: up to units μg/m^3 according to the season
  (autumn, winter → heating → increase of As)
- natural waters
  rivers and lakes: < 0.5 μg/l (drinking water: limit 50 μg/l)
  sea: 0.02−1 μg/l
- soil: normal contents 2−10 mg/kg dry matter
  limits of As for agricultural soil is 20 mg/kg dry matter

Transformations of arsenic chemical species

- oxidation-reduction reactions
  $As^{III} \rightleftarrows As^{V}$
  is important, because As^{III} is more toxic than As^{V}
- formation of methylated species (less toxic than inorg. species)
  $CH_3AsO(OH)_2$ methylarsonic acid (MMA)
  $(CH_3)_2As(O)OH$ dimethylarsinic acid (DMA)
  are formed from arsenate (arsenic acid H_3AsO_4) in aquatic organisms; they are also produced via metabolic transformation in bodies of mammals when some inorg. As compound is taken
- formation of trimethylarsonium compounds, e.g. in fish
  $(CH_3)_3As^+\text{-}CH_2\text{-}COO^-$ arsenobetaine (non-toxic compound)

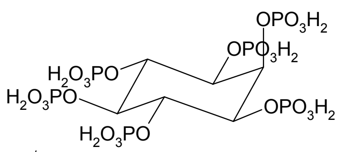
Values of PTWI and TDI for toxic elements

Element	**PTWI*** (mg/(kg. week))	**TDI**** (μg/day)
Pb	0.025	250
Cd	0.007	70
Hg	0.005 (MeHg 0.0016)	50 (16)
As	0.015	150

*   provisional tolerable weekly intake per 1 kg of body weight
** tolerable daily intake at the body weight of 70 kg

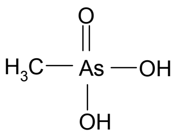
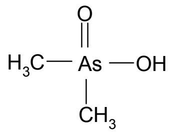
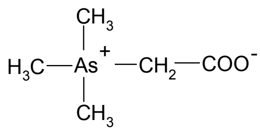
Factors affecting the actual toxic effect of the element

- occurrence of the element species in food (speciation)
  CH_3Hg^+ *vs.* Hg^{2+}, H_3AsO_3 *vs.* arsenobetaine (AsB)
  Cr^{VI} *vs.* Cr^{III}
- composition of diet
  - proteins
  - vitamins
  - phenolic compounds
  - dietary fibre
  - phytic acid

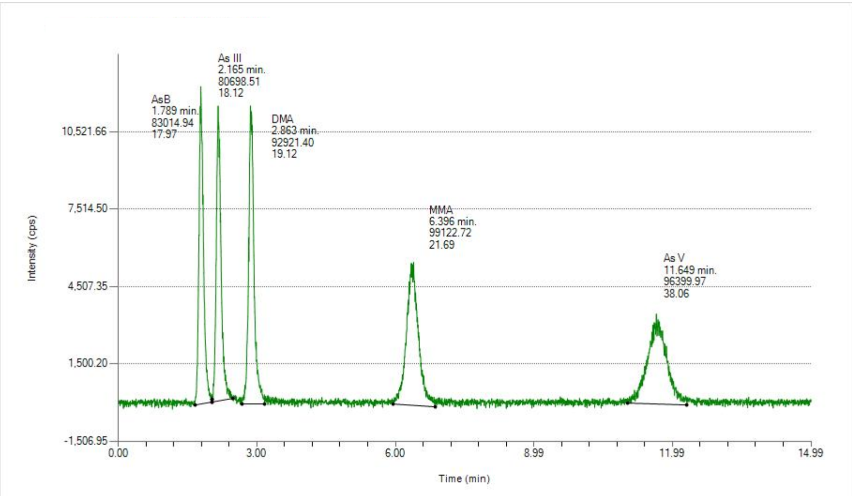


- interactions among the elements
- individual factors (age, health state…)

Arsenic: effect of chemical species on acute toxicity

		LD_{50}
As^{III}	H_3AsO_3	**4** mg/kg
As^{V}	H_3AsO4	**15** mg/kg
MMA		**1 800** mg/kg
DMA		**2 500** mg/kg
AsB		**10 000** mg/kg

Determination of arsenic species

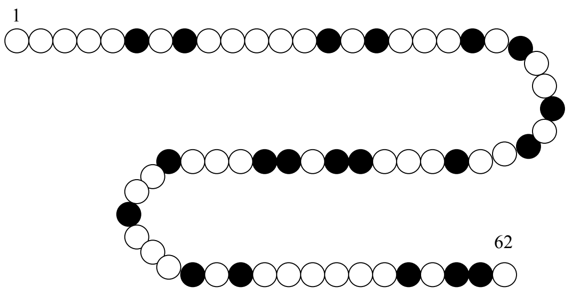


Metabolism of elements

- absorption from diet
  - metals that form cations (Cd, Pb, Hg…): low efficiency (3−20 %)
  - non-metals and metalloids that form anions (halogens, As, Se): higher efficiency (50−90 %)
- transport and fate in the body
  - metals (Cd, Pb, Zn…): deposition in liver, kidney as chelates with metallothioneins (detoxification)
  - As, Se: transformation to methylated compounds
- excretion: urine (As, Se…)

Metallothioneins

- polypeptides (M_r = 6000–8000) synthetised in liver, kidney, pancreas, intestinal mucosa, brain
- peptide chain: 60−63 AA, 20 Cys



- a molecule of MT can bind up to 7 atoms of Cd, Zn…

Food and beverages that could contain higher quantities of lead
(approx. >0.1 mg/kg)

- offal of animals (kidney, liver)
- carrot
- spinach, lettuce
- some mushrooms
- tea
- wine
- cocoa powder
- (rarely: wholemeal cereal products)

Food and beverages that could contain higher quantities of cadmium
(approx. > 0.07 mg/kg)

- kidney (namely bovine kidney and game kidney)
- liver
- shellfish (crustaceans, molluscs)
- carrot
- spinach, lettuce
- poppy-seed, sunflower seed, nuts
- rice
- some mushrooms
- tea, cocoa powder

Food that could contain higher quantities of arsenic

- sea fish
- crustaceans and molluscs
- seaweed
- (freshwater fish)
- (rice)
- (poultry)

The majority of As in fish and seafood is represented by low toxic organic compounds.

Food containing higher quantities of mercury

(0.05−2 mg/kg)

- fish (especially predatory marine species)
  crustaceans, molluscs
  - result of bio-accumulation of Hg in aquatic environment
  (the main chemical form is methylmercury)
- (some mushrooms)

Mercury contents in most other food are much lower
(units μg/kg or less).

Determination of mercury species in fish