Water pollution
Past and present:

In the past, pollution was mainly concerning drinking water:

- fecal pollution (fecal coliform bacteria)
- sewage (domestic, agricultural and farming)

Nowadays, additional concerns related to chemical pollutants involve all types of water:

- organic chemicals
- inorganic chemicals
- heavy metals (nomenclature to be discussed)

from industrial and urban run-off, and agricultural sources.
**Pollution markers**

**Markers** of water pollution: substances that show the presence of pollution sources (e.g. herbicides (=agricultural runoff), fecal bacteria (pollution from sewage), pharmaceuticals and their metabolites, caffeine (=contamination of domestic wastewater), etc.).

**Biomarkers** of water pollution: living organisms that live in, or are closely associated with, bodies of water and provide evidence of pollution from either accumulation of pollutants and/or their metabolites, or the effects on the organisms themselves as a consequence of exposure to pollutants (e.g. fishes, algae, etc.). Example: osprey (raptor bird).

- **Contaminant**: chemical substance at greater than background levels but with no detrimental effect.
- **Pollutant**: chemical substance at greater than background levels inducing a detrimental effect.
## Water pollutants

<table>
<thead>
<tr>
<th>Class of pollutant</th>
<th>Significance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trace Elements</td>
<td>Health, aquatic biota, toxicity</td>
</tr>
<tr>
<td>Heavy metals</td>
<td>Health, aquatic biota, toxicity</td>
</tr>
<tr>
<td>Organically-bound metals</td>
<td>Metal transport</td>
</tr>
<tr>
<td>Radiomuciles</td>
<td>Toxicity</td>
</tr>
<tr>
<td>Inorganic pollutants</td>
<td>Toxicity, aquatic biota</td>
</tr>
<tr>
<td>Asbestos</td>
<td>Human health</td>
</tr>
<tr>
<td>Algal nutrients</td>
<td>Eutrophication</td>
</tr>
<tr>
<td>Acidity, alkalinity, salinity (in excess)</td>
<td>Water quality, aquatic life</td>
</tr>
<tr>
<td>Trace organic pollutants</td>
<td>Toxicity</td>
</tr>
<tr>
<td>Polychlorinated biphenyls</td>
<td>Possible biological effects</td>
</tr>
<tr>
<td>Pesticides</td>
<td>Toxicity, aquatic biota, wildlife</td>
</tr>
<tr>
<td>Petroleum wastes</td>
<td>Effect on wildlife, esthetics</td>
</tr>
<tr>
<td>Sewage, human and animal wastes</td>
<td>Water quality, oxygen levels</td>
</tr>
<tr>
<td>Biochemical oxygen demand</td>
<td>Water quality, oxygen levels</td>
</tr>
<tr>
<td>Pathogens</td>
<td>Health effects</td>
</tr>
<tr>
<td>Detergents</td>
<td>Eutrophication, wildlife, esthetics</td>
</tr>
<tr>
<td>Chemical carcinogens</td>
<td>Incidence of cancer</td>
</tr>
<tr>
<td>Sediments</td>
<td>Water quality, aquatic biota, wildlife</td>
</tr>
<tr>
<td>Taste, odor, and color</td>
<td>Esthetics</td>
</tr>
</tbody>
</table>
trace elements
water pollutants (< ppm)

Typically essential plants and animals nutrients at low levels, toxic at high levels

Some labeled as “heavy metals”

Table 7.2. Important Trace Elements in Natural Waters

<table>
<thead>
<tr>
<th>Element</th>
<th>Sources</th>
<th>Effects and Significance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>Mining byproduct, chemical waste</td>
<td>Toxic(^1), possibly carcinogenic</td>
</tr>
<tr>
<td>Beryllium</td>
<td>Coal, industrial wastes</td>
<td>Toxic</td>
</tr>
<tr>
<td>Boron</td>
<td>Coal, detergents, wastes</td>
<td>Toxic</td>
</tr>
<tr>
<td>Chromium</td>
<td>Metal plating</td>
<td>Essential as Cr(III), toxic as Cr(VI)</td>
</tr>
<tr>
<td>Copper</td>
<td>Metal plating, mining, industrial waste</td>
<td>Essential trace element, toxic to plants and algae at higher levels</td>
</tr>
<tr>
<td>Fluorine (F(^-))</td>
<td>Natural geological sources, wastes, water additive</td>
<td>Prevents tooth decay at around 1 mg/L, toxic at higher levels</td>
</tr>
<tr>
<td>Iodine (I(^-))</td>
<td>Industrial wastes, natural brines, seawater intrusion</td>
<td>Prevents goiter</td>
</tr>
<tr>
<td>Iron</td>
<td>Industrial wastes, corrosion, acid mine water, microbial action</td>
<td>Essential nutrient, damages fixtures by staining</td>
</tr>
<tr>
<td>Lead</td>
<td>Industrial waste, mining, fuels</td>
<td>Toxic, harmful to wildlife</td>
</tr>
<tr>
<td>Manganese</td>
<td>Industrial wastes, acid mine water, microbial action</td>
<td>Toxic to plants, damages fixtures by staining</td>
</tr>
<tr>
<td>Mercury</td>
<td>Industrial waste, mining, coal</td>
<td>Toxic, mobilized as methyl mercury compounds by anaerobic bacteria</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>Industrial wastes, natural sources</td>
<td>Essential to plants, toxic to animals</td>
</tr>
<tr>
<td>Selenium</td>
<td>Natural sources, coal</td>
<td>Essential at lower levels, toxic at higher levels</td>
</tr>
<tr>
<td>Zinc</td>
<td>Industrial waste, metal plating, plumbing</td>
<td>Essential element, toxic to plants at higher levels</td>
</tr>
</tbody>
</table>
Types of water pollutants

Chemical pollutants:
- inorganic: nutrients (nitrates, phosphates), heavy metals (Hg, Cd, Pb), radionuclides (Th, U);
- organic: trichloroethylene, chloroform, carbon tetrachloride, herbicides, pesticides, oil, grease, hydrocarbons and polycyclic aromatic hydrocarbons (PAHs).

Biological pollutants:
- oxygen-depleting substances;
- pathogens.

Thermal pollution
Environmental toxicology: chemical aspects
Aquatic chemistry (7)

Heavy metals?

IUPAC Periodic Table of the Elements

[Periodic table highlighting elements like Cd, As, Pb, Hg]
Past and present:

In the past, pollution was mainly concerning drinking water:
- fecal pollution (fecal coliform bacteria)
- sewage (domestic, agricultural and farming)

Nowadays, additional concerns related to chemical pollutants involve all types of water:
- organic chemicals
- inorganic chemicals
- heavy metals (nomenclature to be discussed)

from industrial and urban run-off, and agricultural sources.
Heavy metals

Sources of heavy metal pollutants

- Mining
- Agriculture & forestry
- Smelting
- Fossil fuel combustion
- Metallurgical industries
- Waste disposal
- Corrosion
Environmental toxicology: chemical aspects

Aquatic chemistry (7)

Heavy metals

Bioremediation of Waters Contaminated with Heavy Metals Using Moringa oleifera Seeds as Biosorbent

Cleide S. T. Araújo, Dayene C. Carvalho, Helen C. Rezende, Ione L. S. Almeida, Luciana M. Coelho, Nivia M. M. Coelho, Thiago L. Marques and Vanessa N. Alves

Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/56157
“Heavy metals”—a meaningless term?

(IUPAC Technical Report)

Abstract: Over the past two decades, the term “heavy metals” has been widely used. It is often used as a group name for metals and semimetals (metalloids) that have been associated with contamination and potential toxicity or ecotoxicity. At the same time, legal regulations often specify a list of “heavy metals” to which they apply. Such lists differ from one set of regulations to another and the term is sometimes used without even specifying which “heavy metals” are covered. However, there is no authoritative definition to be found in the relevant literature. There is a tendency, unsupported by the facts, to assume that all so-called “heavy metals” and their compounds have highly toxic or ecotoxic properties. This has no basis in chemical or toxicological data. Thus, the term “heavy metals” is both meaningless and misleading. Even the term “metal” is commonly misused in both toxicological literature and in legislation to mean the pure metal and all the chemical species in which it may exist. This usage implies that the pure metal and all its compounds have the same physicochemical, biological, and toxicological properties, which is untrue. In order to avoid the use of the term “heavy metal”, a new classification based on the periodic table is needed. Such a classification should reflect our understanding of the chemical basis of toxicity and allow toxic effects to be predicted.
## Table 1 Terms often used to classify metals in biological and environmental studies (after [3]).

<table>
<thead>
<tr>
<th>Term</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal</td>
<td>Metals may be defined by the physical properties of the elemental state as elements with metallic luster, the capacity to lose electrons to form positive ions and the ability to conduct heat and electricity, but they are better identified by consideration of their chemical properties (see accompanying text). The term is used indiscriminately by nonchemists to refer to both the element and compounds (for example, reference by biologists to “the uptake of copper by...” does not distinguish the form in which the metal is absorbed).</td>
</tr>
<tr>
<td>Metalloid</td>
<td>See “semimetal”.</td>
</tr>
<tr>
<td>Semimetal</td>
<td>An element that has the physical appearance and properties of a metal but behaves chemically like a nonmetal [1]</td>
</tr>
<tr>
<td>Light metal</td>
<td>A very imprecise term used loosely to refer to both the element and its compounds. It has rarely been defined, but the originator of the term, Bjerrum [6], applied it to metals of density less than 4 g/cm$^{-3}$.</td>
</tr>
<tr>
<td>Heavy metal</td>
<td>A very imprecise term (see Table 2 for definitions), used loosely to refer to both the element and its compounds. It is based on categorization by density, which is rarely a biologically significant property.</td>
</tr>
<tr>
<td>Essential metal</td>
<td>Broadly, one which is required for the complete life cycle of an organism, whose absence produces specific deficiency symptoms relieved only by that metal, and whose effect should be referred to a dose–response curve. The term is often used misleadingly since it should be accompanied by a statement of which organisms show a requirement for the element. Again, it is used loosely to refer to both the element and its compounds.</td>
</tr>
<tr>
<td>Beneficial metal</td>
<td>An old term, now largely disused, which implied that a nonessential metal could improve health. Another term that has been used loosely to refer to both the element and its compounds.</td>
</tr>
</tbody>
</table>
Environmental toxicology: chemical aspects
Aquatic chemistry (7)

Heavy metals??

Heavy implies high density
Metal refers to pure element or an alloy

But...

- Knowledge of density contributes little to prediction of biological/toxicological effect of metals
- In most case the reactive species (exerting toxic effects on living organisms) are not elemental metals (e.g. Hg)
- Metals have each their own physico-chemical properties which in turn affect their transport, biological, toxicological and ecotoxicological properties/behaviour/effect → no categorization possible (e.g. Cr(0) and Cr(VI), Hg(0) and Hg(II), Sn(0) and [(C₄H₉)₃Sn]₂O TBTO (tributyltin oxide), wood preservative)
### Heavy metals

#### Table 1 (Continued)

<table>
<thead>
<tr>
<th>Term</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toxic metal</td>
<td>An imprecise term. The fundamental rule of toxicology (Paracelsus, 1493–1541) is that all substances, including carbon and all other elements and their derivatives, are toxic given a high enough dose. The degree of toxicity of metals varies greatly from metal to metal and from organism to organism. Pure metals are rarely, if ever, very toxic (except as very fine powders, which may be harmful to the lungs from whatever substance they may originate). Toxicity, like essentiality, should be defined by reference to a dose–response curve for the species under consideration. This is another term that has been used loosely to refer to both the element and its compounds.</td>
</tr>
<tr>
<td>Abundant metal</td>
<td>Usually refers to the proportion of the element in the earth’s crust, though it may be defined in terms of other regions, e.g., oceans, “fresh water”, etc.</td>
</tr>
<tr>
<td>Available metal</td>
<td>One that is found in a form which is easily assimilated by living organisms (or by a specified organism).</td>
</tr>
<tr>
<td>Trace metal</td>
<td>A metal found in low concentration, in mass fractions of ppm or less, in some specified source, e.g., soil, plant, tissue, ground water, etc. Sometimes this term has confusing overtones of low nutritional requirement (by a specified organism).</td>
</tr>
<tr>
<td>Micronutrient</td>
<td>More recent term to describe more accurately the second of the meanings of trace metal, above.</td>
</tr>
</tbody>
</table>
Possibility for a chemical classification of metals

Table 3: Biological significance of classification of metals based on the last electron subshell in the atom to be occupied (after [3]).

<table>
<thead>
<tr>
<th>Grouping</th>
<th>Biologically significant chemical properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>s-block</td>
<td>The alkali metal ions are highly mobile, normally forming only weak complexes. Biologically, they act chiefly as bulk electrolytes. The alkaline earths form more stable complexes and have more specialized functional roles as structure promoters and enzyme activators. Neither group has any significant redox chemistry in vivo.</td>
</tr>
<tr>
<td>p-block</td>
<td>Some limited redox chemistry, e.g., Pb^{4+}/Pb^{2+} complicates the action of these metals. They generally form more stable complexes than the s block. The higher atomic number elements tend to bind strongly to sulfur; this is a major cause of their toxicity (see Section 4.3 on Class B metal ions).</td>
</tr>
<tr>
<td>d-block</td>
<td>Shows an extremely wide range of both redox behavior and complex formation. These properties underlie their catalytic role in enzyme action.</td>
</tr>
<tr>
<td>f-block</td>
<td>The lanthanide and actinide elements show a wide range of redox behavior and complex formation. Usually biologically unimportant, but some (the actinide group) may be significant pollutants.</td>
</tr>
</tbody>
</table>

2002 IUPAC, Pure and Applied Chemistry 74, 793–807
### Heavy metals

Bioremediation of Waters Contaminated with Heavy Metals Using *Moringa oleifera* Seeds as Biosorbent

[http://dx.doi.org/10.5772/56157](http://dx.doi.org/10.5772/56157)

<table>
<thead>
<tr>
<th>Element</th>
<th>US EPA Limit (mg L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antimony</td>
<td>0.006</td>
</tr>
<tr>
<td>Arsenic</td>
<td>0.010</td>
</tr>
<tr>
<td>Beryllium</td>
<td>0.004</td>
</tr>
<tr>
<td>Chromium (total)</td>
<td>0.1</td>
</tr>
<tr>
<td>Cadmium</td>
<td>0.005</td>
</tr>
<tr>
<td>Copper</td>
<td>1.3</td>
</tr>
<tr>
<td>Lead</td>
<td>0.015</td>
</tr>
<tr>
<td>Mercury</td>
<td>0.002</td>
</tr>
<tr>
<td>Selenium</td>
<td>0.05</td>
</tr>
<tr>
<td>Silver</td>
<td>0.1</td>
</tr>
</tbody>
</table>

*Table 1.* Maximum acceptable concentrations of metals in drinking water according to the US EPA [6].
Environmental toxicology: chemical aspects
Aquatic chemistry (7)

IUPAC Periodic Table of the Elements

<table>
<thead>
<tr>
<th>Element</th>
<th>Symbol</th>
<th>Atomic Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>H</td>
<td>1</td>
</tr>
<tr>
<td>Helium</td>
<td>He</td>
<td>2</td>
</tr>
<tr>
<td>Lithium</td>
<td>Li</td>
<td>3</td>
</tr>
<tr>
<td>Beryllium</td>
<td>Be</td>
<td>4</td>
</tr>
<tr>
<td>Boron</td>
<td>B</td>
<td>5</td>
</tr>
<tr>
<td>Carbon</td>
<td>C</td>
<td>6</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>N</td>
<td>7</td>
</tr>
<tr>
<td>Oxygen</td>
<td>O</td>
<td>8</td>
</tr>
<tr>
<td>Fluorine</td>
<td>F</td>
<td>9</td>
</tr>
<tr>
<td>Neon</td>
<td>Ne</td>
<td>10</td>
</tr>
<tr>
<td>Sodium</td>
<td>Na</td>
<td>11</td>
</tr>
<tr>
<td>Magnesium</td>
<td>Mg</td>
<td>12</td>
</tr>
<tr>
<td>Aluminum</td>
<td>Al</td>
<td>13</td>
</tr>
<tr>
<td>Silicon</td>
<td>Si</td>
<td>14</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>P</td>
<td>15</td>
</tr>
<tr>
<td>Sulfur</td>
<td>S</td>
<td>16</td>
</tr>
<tr>
<td>Chlorine</td>
<td>Cl</td>
<td>17</td>
</tr>
<tr>
<td>Arsenic</td>
<td>As</td>
<td>33</td>
</tr>
<tr>
<td>Antimony</td>
<td>Sb</td>
<td>51</td>
</tr>
<tr>
<td>Tellurium</td>
<td>Te</td>
<td>52</td>
</tr>
<tr>
<td>Iodine</td>
<td>I</td>
<td>53</td>
</tr>
<tr>
<td>Xenon</td>
<td>Xe</td>
<td>54</td>
</tr>
</tbody>
</table>

Environmental Toxicology, Master Sc. in Industrial Biotechnology

Silvia Gross
Trace elements: heavy metals

Cadmium - Cd(II)

- naturally-occurring as greenockite (CdS), about 0.1 ppm of the Earth's crust;
- mining wastes, industrial discharges (metal plating);
- chemical behavior very similar to Zn(II);
- effects of acute cadmium poisoning in humans: high blood pressure, kidney damage, destruction of testicular tissue, destruction of red blood cells.

- It is believed that much of its physiological action arises from its chemical similarity to zinc. Specifically, cadmium may replace zinc in some enzymes, thereby altering the their structure and impairing their catalytic activity.
Trace elements: heavy metals

Summertime: microbial reduction of sulfates by organic matter \(\{\text{CH}_2\text{O}\}\) (which is oxidized) in the anaerobic bottom layer of stagnant water (e.g. harbor):

\[
2 \{\text{CH}_2\text{O}\} + \text{SO}_4^{2-} + \text{H}^+ \rightarrow 2 \text{CO}_2 + \text{HS}^- + 2 \text{H}_2\text{O}
\]

Formation of insoluble CdS:

\[
[\text{CdCl}]^+ + \text{HS}^- \rightarrow \text{CdS}_{(s)} + \text{H}^+ + \text{Cl}^-
\]

Bacteria transform \(\text{Cd}^{2+}\) in insoluble form: decreasing the active pollutant concentration

Wintertime: Mixing of water, variation in pH, T: desorption of Cd compounds from sediments and speciation, \(\text{Cd}^{2+}\) available.
Environmental toxicology: chemical aspects
Aquatic chemistry (7)
Environmental toxicology: chemical aspects
Aquatic chemistry (7)

Trace elements: heavy metals

Lead – mainly as Pb(II) in water

- naturally-occurring primarily as galena (PbS), cerussite (PbCO\(_3\)), and anglesite (PbSO\(_4\));
- mining wastes, industrial discharges and, formerly, from leaded gasoline;
- acute lead poisoning in humans causes severe dysfunction in the kidneys, reproductive system, liver, and the brain and central nervous system (possibly causing mental retardation in children); (saturnism)
- burdens have decreased over recent decades because of reduced use in plumbing and other products that come in contact with food or drink.
Environmental toxicology: chemical aspects
Aquatic chemistry (7)
Thimerosal in vaccines

Thimerosal is a mercury-containing organic compound (an organomercurial, ethylderivative). Since the 1930s, it has been widely used as a preservative in a number of biological and drug products, including many vaccines, to help prevent potentially life threatening contamination with harmful microbes.

Recently eliminated, for precautional reasons, from most of children vaccines

Trace elements: heavy metals

Mercury – mainly as Hg(II) in water

- naturally-occurring primarily as cinnabar (HgS), corderoite (Hg₃S₂Cl₂), and livingstonite (HgSb₄S₈);
- gold extraction (many in developing countries), electrodes, thermometers, vacuum apparatus (elemental), batteries, laboratory chemicals (inorganic compounds), pesticides, fungicides (organomercury compounds); fossil fuels (100 ppb), preservative substances (also in vaccines, but…)
- acute mercury poisoning in humans causes severe neurological damage; chromosome breakage, birth defects, behavioural problems (low Hg poisoning not detected)
- most inorganic derivatives of mercury are relatively insoluble in water so, in the past, it was assumed that mercury was not a serious water pollutant, but…
...the unexpectedly high concentrations of mercury found in water and in fish tissues result from the formation of soluble monomethylmercury ion, \([\text{CH}_3\text{Hg}]^+\), and volatile dimethylmercury, \([(\text{CH}_3)_2\text{Hg}]\). Mercury in these forms is extremely toxic and concentrates in fish lipid (fat) tissue. Anaerobic bacteria synthesizing methane produce the intermediate methylcobalamin (vitamin B\(_{12}\) cofactor), commonly acknowledged as methylating agent of inorganic mercury:

\[
\text{HgCl}_2 + \text{MetB}_{12} \rightarrow [\text{CH}_3\text{HgCl}] + \text{Cl}^-
\]

In neutral or alkaline waters, the volatile \([(\text{CH}_3)_2\text{Hg}]\) forms.
Minamata disease was first discovered in Minamata city in Kumamoto prefecture, Japan, in 1956. It was caused by the release of mercury waste in the industrial wastewater from the Chisso Corporation's chemical factory, which continued from 1932 to 1968. This highly toxic chemical bioaccumulated in shellfish and fish in Minamata Bay and the Shiranui Sea, which, when eaten by the local populace, resulted in mercury poisoning (111 cases and 43 deaths, 5-20 ppm)
Minamata Mercury Convention (2013)

Minamata Convention on Mercury.
The Minamata Convention on Mercury is a global treaty to protect human health and the environment from the adverse effects of mercury. It was agreed at the fifth session of the Intergovernmental Negotiating Committee in Geneva, Switzerland at 7 a.m. on the morning of Saturday, 19 January 2013. The major highlights of the Minamata Convention on Mercury include a ban on new mercury mines, the phase-out of existing ones, control measures on air emissions, and the international regulation of the informal sector for artisanal and small-scale gold mining. The Convention draws attention to a global and ubiquitous metal that, while naturally occurring, has broad uses in everyday objects and is released to the atmosphere, soil and water from a variety of sources. Controlling the anthropogenic releases of mercury throughout its lifecycle has been a key factor in shaping the obligations under the convention.

http://www.mercuryconvention.org/
Environmental toxicology: chemical aspects
Aquatic chemistry (7)
Environmental toxicology: chemical aspects
Aquatic chemistry (7)

Trace elements: heavy metals

Arsenic – mainly arseniate (As$^V$O$_4^{3-}$) and arsenite (As$^{III}$O$_3^{3-}$)

- naturally-occurring (2-5 ppm in the Earth crust) primarily as native arsenic (As, rare), arsenopyrite (FeAsS), orpiment (As$_2$O$_3$), realgar (a-As$_4$S$_4$), tennantite (Cu$_{12}$As$_4$S$_{13}$), and in several phosphate minerals;
- mining wastes, former pesticides (lead arsenate, Pb$_3$(AsO$_4$)$_2$, sodium arsenite, Na$_3$AsO$_3$, and Paris Green, Cu$_3$(AsO$_3$)$_2$); combustion of fossil fuels.
- suspect carcinogen, acute exposure induces death by poisoning, whereas mild consumption leads to serious skin damage; Bangladesh: 35-77 million people exposed

- like mercury, arsenic may be converted to more mobile and toxic methyl derivatives by bacteria first by reduction of H$_3$As$^V$O$_4$ to H$_3$As$^{III}$O$_3$, which is then methylated to CH$_3$AsO(OH)$_2$, (CH$_3$)$_2$AsO(OH) and (CH$_3$)$_2$AsH (dimethylarsine).
- Occurrence together with Fe, S, organic matter
Interaction metal/organic matter relevant in aquatic environment (waters and wastewaters)

- Coordination compounds (complexation, chelation, can be reversible)
- Metallorganic compounds (not reversible)

- These interactions influence redox equilibria, formation/dissolution of precipitates, acid/base reactions, colloids stability
- Influence the toxicity/availability/transport properties of metals
Organometallic compounds

Classically compounds having direct bonds between one or more metal atoms and one or more carbon atoms of an organyl group. Organometallic compounds are classified by prefixing the metal with organo-, e.g. organopalladium compounds.

http://goldbook.iupac.org/O04328.html
Trace elements: organometallic compounds

Major categories of organometallic compounds encountered in the environment:

- containing alkyl groups (e.g. \([\text{Pb}(\text{CH}_2\text{CH}_3)_4]\));
- containing carbonyl groups (M-C=O);
- containing unsaturated ligands (e.g. ethylene, benzene).
- combination thereof (e.g. arene + carbonyl)

Typical example: organotin compounds

- tin has the greatest number of organometallic compounds in commercial use;
- major industrial uses include fungicides, acaricides, disinfectants, antifouling paints, stabilizers in several polymerization reactions, wood, leather and textiles preservation;
- endocrine disruption in shellfish, oysters
- toxicity: inorganic < methylnitnt < alkyltin << aromatic derivatives.
Environmental toxicology: chemical aspects

Aquatic chemistry (7)

Past and present:

In the past, pollution was mainly concerning drinking water:

- fecal pollution (fecal coliform bacteria)
- sewage (domestic, agricultural and farming)

Nowadays, additional concerns related to chemical pollutants involve all types of water:

- organic chemicals
- inorganic chemicals
- heavy metals (nomenclature to be discussed)

from industrial and urban run-off, and agricultural sources.
Inorganic pollutants

Inorganic pollutants that do not contain heavy metals or metalloids.

- **Cyanide (CN−):** a deadly poisonous substance, exists in water as HCN and has strong affinities for many metals and forms several metal complexes (e.g. \([\text{Fe}^{II}(\text{CN})_6]^{4−}\)). Widely used in industry, especially for metal cleaning and electroplating, and in certain mineral-processing operations.

- **Ammonia (NH₃):** mainly present in water as ammonium ion (NH₄⁺), is a normal constituent of low-pE groundwaters and is the initial product of the decay of nitrogen-containing organic wastes.

- **Carbon dioxide (CO₂):** produced by the decay of organic matter, it is also added to softened water during water treatment as part of a recarbonation process. Excessive carbon dioxide levels increase acidity and may make water more corrosive and may be harmful to aquatic life.
Inorganic pollutants

- **Hydrogen sulfide (H$_2$S):** produced by the anaerobic decay of organic matter containing sulfur and the anaerobic reduction of sulfate by microorganisms, is also evolved from geothermal waters. Wastes from chemical plants, paper mills, textile mills, and tanneries may also contain H$_2$S. The sulfide ion has tremendous affinity for many heavy metals, and precipitation of metallic sulfides often accompanies production of H$_2$S.

- Other inorganic pollutants, such as nitrite (NO$_2^-$), sulfite (SO$_3^{2-}$) and perchlorate (ClO$_4^-$), are less common.

- **Asbestos:** asbestos fibers are believed to induce a rare lung cancer (mesothelioma).
### Plant nutrients: sources and function

<table>
<thead>
<tr>
<th>Nutrient</th>
<th>Source</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Macronutrients</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon (CO₂)</td>
<td>Atmosphere, decay</td>
<td>Biomass constituent</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>Water</td>
<td>Biomass constituent</td>
</tr>
<tr>
<td>Oxygen</td>
<td>Water</td>
<td>Biomass constituent</td>
</tr>
<tr>
<td>Nitrogen (NO₃⁻)</td>
<td>Decay, pollutants, atmosphere</td>
<td>Protein constituent</td>
</tr>
<tr>
<td></td>
<td>(from nitrogen-fixing organisms)</td>
<td></td>
</tr>
<tr>
<td>Phosphorus (phosphate)</td>
<td>Decay, minerals, pollutants</td>
<td>DNA/RNA constituent</td>
</tr>
<tr>
<td>Potassium</td>
<td>Minerals, pollutants</td>
<td>Metabolic function</td>
</tr>
<tr>
<td>Sulfur (sulfate)</td>
<td>Minerals</td>
<td>Proteins, enzymes</td>
</tr>
<tr>
<td>Magnesium</td>
<td>Minerals</td>
<td>Metabolic function</td>
</tr>
<tr>
<td>Calcium</td>
<td>Minerals</td>
<td>Metabolic function</td>
</tr>
</tbody>
</table>

| Micronutrients         |                                 |                                         |
| B, Cl, Co, Cu, Fe, Mo, Mn, Na, Si, V, Zn | Minerals, pollutants | Metabolic function and/or constituent of enzymes |

**Limiting growth factors**

**Sea water**

**Environmental toxicology: chemical aspects**

**Aquatic chemistry (7)**
Past and present:

In the past, pollution was mainly concerning drinking water:

- fecal pollution (fecal coliform bacteria)
- sewage (domestic, agricultural and farming)

Nowadays, additional concerns related to chemical pollutants involve all types of water:

- organic chemicals
- inorganic chemicals
- heavy metals (nomenclature to be discussed)

from industrial and urban run-off, and agricultural sources.
Organic pollutants

- Millions of tons of organic compounds are manufactured globally each year.
- Most of these compounds, particularly the less biodegradable ones, are substances to which living organisms have not been exposed until recent years.
- Consequently, effects are not well-known, particularly for long-term exposures at very low levels.
- Biorefractory organics are poorly biodegradable organic compounds and, among all, aromatic and/or chlorinated hydrocarbons represent a major concern, in particular because they have been found in drinking water.

- BCF: bioconcentration factor: ratio of a substance concentration in the tissue of an aquatic organism/concentration of the substance in the water the organism is living in
- BAF: bioaccumulation factor: ratio of a substance concentration in the tissue of an aquatic organism/concentration of the substance in the water the organism is living in, but assuming both are exposed similarly to a pollutant over a long period of time
Sewage from domestic, commercial, food-processing, and industrial sources contains a wide variety of pollutants, including organic pollutants.

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Potential sources</th>
<th>Effects in water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen-demanding</td>
<td>Mostly organic materials, particularly human feces</td>
<td>Consume dissolved oxygen</td>
</tr>
<tr>
<td>substances</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Refractory organics</td>
<td>Industrial wastes, household products</td>
<td>Toxic to aquatic life</td>
</tr>
<tr>
<td>Viruses</td>
<td>Human wastes</td>
<td>Cause disease (possibly cancer); major deterrent to sewage recycle through water systems</td>
</tr>
<tr>
<td>Detergents</td>
<td>Household detergents</td>
<td>Esthetics, prevent grease and oil removal, toxic to aquatic life</td>
</tr>
<tr>
<td>Phosphates</td>
<td>Detergents</td>
<td>Algal nutrients</td>
</tr>
<tr>
<td>Grease and oil</td>
<td>Cooking, food processing, industrial wastes</td>
<td>Esthetics, harmful to some aquatic life</td>
</tr>
<tr>
<td>Salts</td>
<td>Human wastes, water softeners, industrial wastes</td>
<td>Increase water salinity</td>
</tr>
<tr>
<td>Heavy metals</td>
<td>Industrial wastes, chemical laboratories</td>
<td>Toxicity</td>
</tr>
<tr>
<td>Chelating agents</td>
<td>Some detergents, industrial wastes</td>
<td>Heavy metal ion solubilization and transport</td>
</tr>
<tr>
<td>Solids</td>
<td>All sources</td>
<td>Esthetics, harmful to aquatic life</td>
</tr>
</tbody>
</table>

**Organic pollutants: sewage**

Some, particularly oxygen-demanding substances (oil, grease, and solids) are removed by primary and secondary sewage-treatment processes. Others (salts, heavy metals, degradation-resistant organics) are not efficiently removed.
Environmental toxicology: chemical aspects

Aquatic chemistry (7)

Organic pollutants: sewage

Disposal of inadequately treated sewage: beds of sewage residuals

Offshore disposal of sewage, commonly practiced by coastal cities: the warm sewage water rises in the cold hypolimnion and forms a cloud from which the solids fall down on the ocean floor, thus giving rise to colloids and the subsequent formation of sludge-containing sediment.
Organic pollutants: soaps

- Soaps are salts of higher fatty acids, such as sodium stearate, $C_{17}H_{35}COONa$:

- The cleaning action results largely from its emulsifying action: the “tail” of the anion can dissolve the insoluble organic matter, (e.g. oil, fats) whereas the ionic “head” makes it water soluble.

- Disadvantage: reaction with divalent cations to form insoluble salts of fatty acids $((C_{17}H_{35}COO)_2M$, $M = Ca, Mg)$.

- Not a big deal if such insoluble residues are, eventually, biodegraded by microorganisms.
Organic pollutants: synthetic detergents

- Synthetic detergents have good cleaning properties and do not form insoluble salts with either calcium or magnesium.
- The key ingredient of detergents is the surfactant, an amphiphilic compound in which the “head” is polar or ionic (hydrophilic), and the “tail” is a hydrocarbon (hydrophobic).
- A typical example is represented by alkyl benzene sulfonates (ABS):

![Chemical structure of alkyl benzene sulfonates (ABS) with sodium ion (O^-Na^+)](image)

- Very slowly biodegradable, forms a massive bed of foam.
Organic pollutants: synthetic detergents

- ABS were then replaced by the more biodegradable linear alkyl sulphonates (Linear LAS, that is, no branched side chains), such as a-benzenesulphonates:

- Some surfactants are non-ionic and are still in use or under consideration.
Organic pollutants: synthetic detergents

➢ Most of the environmental issues currently attributed to detergents are not related to surfactants themselves but to the other components (detergent-builders, 70-80% content, bind hardness ions).

➢ Ingredients include polyphosphates, ion exchangers, alkalis (sodium carbonate), anticorrosive sodium silicates, amide foam stabilizers, soil-suspending carboxymethylcellulose, bleaches, fabricsofteners, enzymes, optical brighteners, fragrances, dyes, and diluent sodium sulfate.

➢ Builders bind to hardness ions, making the detergent solution alkaline.

➢ Among all, polyphosphates have caused the most concern but now they are being phasing out.
Organic pollutants: pesticides

Pesticides are chemicals used to control:

- invertebrates: insecticides (insects), molluscicides (snails and slugs), nematicides (roundworms);
- vertebrates: rodenticides (rodents), avicides (birds repellers), piscicides (fish);
- plants: herbicides, plant growth regulators, defoliants, desiccants;
- lower organisms: fungicides (fungi), bactericides (bacteria), slimicides (slime-causing organisms in water), algicides (algae).
- US in the Nineties: 365 million kg/year pesticides + 900 million kg/year insecticides

Insecticides and fungicides are the most important pesticides with respect to human exposure in food because they are applied shortly before or even after harvesting.
Organic pollutants: pesticides

Concerns about pesticides as water pollutants:

- highly biodegradation-resistant;
- known or probable carcinogens;
- toxicants with adverse reproductive or developmental effects;
- some are proven/potentially neurotoxic;
- some show high acute toxicity;
- groundwater contaminants.

There is an impressive number of pesticides formerly and/or currently used, belonging to several classes of compounds (e.g. pyrethrins, pyrethroids, organochlorines, organophosphates, carbamates, bipyridyls, nitrogen-containing heterocyclic derivatives, chlorophenols, polychlorinated biphenyls, etc.).
DDT (1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane)
DDT (1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane)

Any discussion about pesticides must start with 1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane (DDT), the first synthetic organic substance massively used as insecticide.

- 1874: first synthesized by Othmar Zeidler (Austria);
- 1939: Paul Müller discovered its insecticidal properties (malaria, awarded the Nobel Prize in medicine in 1948);
- 1949 onwards: mass introduction into agriculture and public health programs;
- 1950-1960: development of trace analytical techniques;
- 1960-1970: recognition of ecological and physiological effects;
Environmental toxicology: chemical aspects
Aquatic chemistry (7)

**DDT (1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane)**

DDT is a chlorinated hydrocarbon, which means that it is not soluble in water, but does dissolve in oils and fats. It is not easily biodegraded, and therefore remains in the soil long after it has been applied to agricultural crops (39% remaining 17 years since treatment). Banned 1972.

- Low acute toxicity for mammals
- Very persistent, accumulates in food chains.
- Severely affected several bird species.
- Carcinogenic aspects may result from metabolites (es. phosgene Cl₂C=O)
Eutrophication ( = well nourished)

A condition of waters involving excess algal growth may eventually lead to severe deterioration of the body of water.

1. excess input of plant nutrients;
2. large amounts of plant biomass produced upon photosynthesis, along with a smaller amount of animal biomass;
3. dead biomass accumulates in the bottom of the body of water and partially decays, making nutrients again available;
4. plants begin to grow abnormally, accelerating the accumulation of solid material in the basin (bottom-rooted plants begin to grow);
5. eventually, a marsh is formed, which finally fills in to produce a kind of forest.

Eutrophication is often a natural phenomenon but human activity can greatly accelerate the process.
The two most acute symptoms of eutrophication are hypoxia (or oxygen depletion) and harmful algal blooms, which among other things can destroy aquatic life in affected areas.
Aquatic biota are sensitive to extreme pH as well as to abnormal amounts of salts (largely because of osmotic effects; for instance, a fresh-water fish soon succumbs in the ocean, and the other way around).
Acidity, alkalinity and salinity

pH Value Scale

- Caddisflies and mayflies die.
- Salmonid eggs and alevin die.
- Bass and trout begin to die.
- Snails and tadpoles begin to die.

Best level for most fish

All Fish Dead

Acidic

0 1 2 3 4 5 6

Battery Acid
Lemon Juice
Vinegar
Tomatoes
Carrots
Normal Rain
Milk

Basic

8 9 10 11 12 13 14

Human Blood
Ammonia
Bleach

All Fish Dead

www.ecy.wa.gov
Acidity, alkalinity and salinity

- **Pollutant acids**: acid mine drainage (microbial oxidation of pyrite), acid rains and industrial wastes (mainly sulfuric acid from SO$_2$);

- **Excess alkalinity**: generally not anthropogenic, the soil and mineral strata are alkaline and impart a high alkalinity to water (human activity can make the situation worse).

- **Salinity**: lots of human activities may contribute, including urban run-off (softeners), industrial wastes, leaching, etc.
Environmental toxicology: chemical aspects
Aquatic chemistry (7)

Oxygen depletion

Oxygen in water is rapidly consumed by the microorganism-mediated oxidation of organic matter:

\[
{\{\text{CH}_2\text{O}\}} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}
\]

Unless the water is reaerated efficiently, it rapidly loses oxygen and will not support higher forms of aquatic life.

Oxygen in water may be also consumed by (determined by BOD):

- biooxidation of nitrogen-containing material

\[
\text{NH}_4^+ + 2 \text{O}_2 \rightarrow 2 \text{H}^+ + \text{NO}_3^- + \text{H}_2\text{O}
\]

- chemical or biochemical oxidation by reducing agents

\[
4 \text{Fe}^{2+} + \text{O}_2 + 10 \text{H}_2\text{O} \rightarrow 4 \text{Fe(OH)}_3(s) + 8 \text{H}^+
\]

\[
2 \text{SO}_3^{2-} + \text{O}_2 \rightarrow 2 \text{SO}_4^{2-}
\]
Oxygen depletion

- Initially, the oxygen level is high; and the (anaerobic) bacterial population is relatively low.
- With the addition of oxidizing pollutant, $O_2$ level drops because reaeration cannot keep up with oxygen consumption and the bacterial population rises.
- In the septic zone there are high bacterial population and very low oxygen levels (until the oxidizable pollutant is consumed).
- In the recovery zone, the bacterial population decreases and the dissolved oxygen level increases until the water regains its original condition.
- TOC readily determined instrumentally by catalytically oxidizing carbon ($CO_2$ evolution)
Emerging water (stable) pollutants

- Radionuclides (nuclear weapons, nuclear reactors, radiotherapeutics).
- Nanomaterials (electronics, cosmetics, pharmaceuticals): very little is known about their toxicity and potential environmental impact.
- Silicones (protective encapsulating materials in semiconductors, lubricants, coatings, sealants, cosmetics): extremely resistant to biodegradation, persistent in waters. Thermal/chemical stability.
- Disinfection products: mainly halogenated hydrocarbons (e.g. chloroform, trihalometanes $\text{CHCl}_2\text{Br}$, $\text{CHBr}_3$, $\text{CHCl}_3$), suspect carcinogens, bactericides. Limit in drinking water: 100 $\mu$g/L.
- Discarded pharmaceuticals and their metabolites (steroids, hormones): evidence of feminization of male fishes.
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Emerging water (stable) pollutants: nanomaterials

Nanotechnologies:  
the science and technology for the realization of objects of nanometric dimensions  
(nanometer = a billionth of a meter)

nano = $10^{-9}$

Nanosystems  
structures characterized by a low dimensionality (clusters, nanocomposites, materials in thin layer, systems in molecular base) in which at least one of the dimensions is included between 1 and 100 nm
Le nanotecnologie sono l’insieme di metodi e tecniche per la manipolazione della materia su scala atomica e molecolare e hanno l’obiettivo di costruire materiali e prodotti con speciali caratteristiche chimico-fisiche.

Fonte: Forrester Research, In realis
Nanomaterials: electronic effects

Molecular Cluster

Large Cluster

Metal
Nanomaterials: surface effects

Cobalto

Rapporto

atomi superficie/atomi volume F

n = 139 atomi
R = 0.65 nm
F = 0.77

n = 369 atomi
R = 0.90 nm
F = 0.56

n = 3043 atomi
R = 1.82 nm
F = 0.28
Nanomaterials: health, toxicological effects

http://www.nanosafetycluster.eu/

About the NanoSafety Cluster

The EU NanoSafety Cluster is a DG RTD NMP initiative to maximise the synergies between the existing FP6 and FP7 projects addressing all aspects of nanosafety including toxicology, ecotoxicology, exposure assessment, mechanisms of interaction, risk assessment and standardisation.

Participation in the NanoSafety cluster is voluntary for projects that commenced prior to April 2009, and is compulsory for nano-EHS projects started since April 2009.

The terms of reference of the NanoSafety Cluster define its role and are included as an appendix to all new projects.
Emerging water (stable) pollutants

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- Discarded pharmaceuticals and their metabolites (steroids, hormones): evidence of feminization of male fishes.
Emerging water (stable) pollutants: silicones

Octamethylcyclotetrasiloxane

http://www.ncbi.nlm.nih.gov/books/NBK44789/
Emerging water (stable) pollutants

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- Nanomaterials (electronics, cosmetics, pharmaceuticals): very little is known about their toxicity and potential environmental impact.
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- Disinfection products: mainly halogenated hydrocarbons (e.g. chloroform, trihalometanes CHCl₂Br, CHBr₃, CHCl₃), suspect carcinogens, bactericides. Limit in drinking water: 100 µg/L
- Discarded pharmaceuticals and their metabolites (steroids, hormones): evidence of feminization of male fishes.
Humic substances and trihalomethanes (THM)

- THM carcinogenic substances
- Seem to be formed in the presence of humic substances during disinfection of water by chlorination
- Humic substances produce THM by reaction with chlorine
Humic substances and trihalomethanes (THM)

Chlorine reacts with humic substances (dissolved organic matter) present in most water supplies, forming a variety of halogenated disinfectant by-products (DBPs) such as THMs, HAAs, HANs, chloral hydrate and chloropicrin, as follows:

\[
\text{HOCl} + \text{Dissolved Organic Carbon} \rightarrow \text{DBPs}
\]

It is generally accepted that the reaction between chlorine and humic substances, a major component of natural organic matter (NOM), is responsible for the production of organochlorine compounds during drinking-water treatment.

Humic and fulvic acids show a high reactivity towards chlorine and constitute 50–90% of the total DOC in river and lake waters.
### Table 3. Disinfectant by-products present in disinfected waters

| Disinfectant                  | Significant organohalogen products | Significant inorganic products                                      | Significant non-halogenated products |
|-------------------------------|------------------------------------|----------------------------------------------------------------------|
| Chlorine/hypochlorous acid    | THMs, HAAs, HANs, chloral hydrate, chloropicrin, chlorophenols, N-chloramines, halofuranones, bromohydrins | Chlorate (mostly from hypochlorite use)                              | Aldehydes, cyanoalkanoic acids, alkanoic acids, benzene, carboxylic acids |
| Chlorine dioxide             |                                    | chlorite, chlorate                                                   | unknown                              |
| Chloramine                   | HANs, cyanogen chloride, organic chloramines, chloramino acids, chloral hydrate, haloketones | nitrate, nitrite, chlorate, hydrazine                                | aldehydes, ketones                   |
| Ozone                        | bromoform, MBA, DBA, DBAC, cyanogen bromide | chlorate, iodate, bromate, hydrogen peroxide, hypobromous acid, epoxides, ozonates | aldehydes, ketoacids, ketones, carboxylic acids |

**Humic substances and trihalomethanes (THM)**
Emerging water (stable) pollutants

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- Discarded pharmaceuticals and their metabolites (steroids, hormones): evidence of feminization of male fishes. Common levels 1 $\mu$g/L.
Emerging water (stable) pollutants: Per- and Polyfluoroalkyl Substances (PFAS)
PFAS can be found in:

- **Food** packaged in PFAS-containing materials, processed with equipment that used PFAS, or grown in PFAS-contaminated soil or water.
- **Commercial household products**, including stain- and water-repellent fabrics, nonstick products (e.g., Teflon), polishes, waxes, paints, cleaning products, and fire-fighting foams (a major source of groundwater contamination at airports and military bases where firefighting training occurs).
- **Workplace**, including production facilities or industries (e.g., chrome plating, electronics manufacturing or oil recovery) that use PFAS.
- **Drinking water**, typically localized and associated with a specific facility (e.g., manufacturer, landfill, wastewater treatment plant, firefighter training facility).
- **Living organisms**, including fish, animals and humans, where PFAS have the ability to build up and persist over time.

https://www.epa.gov/pfas/basic-information-pfas
Environmental toxicology: chemical aspects
Aquatic chemistry (7)

Thermal pollution

Degradation of water quality by any process that changes the normal water temperature.

A common cause is the use of water as a coolant by power plants and industrial manufacturers.

- Elevated temperature decreases the level of dissolved oxygen in water, thus harming aquatic organisms and favoring anaerobic conditions (increased levels of bacteria).
- Elevated temperature increases the metabolic rate of aquatic animals, resulting in higher consumption of food in a shorter time, leading to fewer resources.
- Release of unnaturally hot water can dramatically change the fauna of rivers, and reduce river productivity.