Contaminants

**Contaminant**: substance present in greater than natural concentration due to man’s activities

100,000 chemicals are currently in use (US estimate).

~ 1,000 added annually

**TSCA** (Toxic Substances Control Act; 1976)
- regulates the introduction of new chemicals in the US
  - NOTE – most existing chemicals were “grandfathered” in

- **TSCA Inventory** contains >75,000 chemicals

  not included in TSCA:
  - pesticides
  - tobacco and tobacco products
  - nuclear materials
  - firearms and ammunition
  - food, drugs and cosmetics
Contaminants – Definitions

**Contaminant**: substance present in greater than natural concentration due to man’s activities

**Anthropogenic**: synthetic or man-made

**Pollutant**: a substance that occurs in the environment at least in part as a result of man’s activities, and which has a deleterious effect on living organisms.

**Xenobiotic**: a foreign chemical or material not produced in nature and not normally considered a constitutive component of a specific biological system. [Note – by this definitions, any xenobiotic compound is automatically considered a contaminant]

**Partitioning**: where a contaminant ends up; i.e. what phase (air, water, sediment, tissue type) the contaminant enters
Contaminants – Definitions

**Partition coefficient**: quantitative expression of concentration among phases at equilibrium:

\[ K_d \text{ or } K_p = \frac{[X_{\text{phase } b}]}{[X_{\text{phase } a}]} \]

**Sorption coefficient**: quantitative expression for the partitioning of a contaminant between the sorbed and dissolved phases.

\[ \text{e.g. } K_p = \frac{[X_{\text{sediment}}]}{[X_{\text{water}}]} \]

**Vapor pressure (P)**: the pressure exerted by a vapor in equilibrium with its solid and liquid phases

**Henry’s law coefficient (H)**: quantitative expression that describes a contaminant’s relative tendency to partition to the vapor phase or the dissolved phase:

\[ H = \frac{\text{vapor pressure (P)}}{\text{water solubility (C)}} \]; as H increases, so does the compounds’ tendency to partition into the vapor phase
Contaminants – Definitions

**Mineralization**: complete degradation of an organic molecule to inorganic components

**Weathering**: tendency for changes in relative concentrations of individual compounds in the mixture of contaminants over time

**parts per notation**: million (ppm = mg/kg, mg/L) billion (ppb = μg/kg, μg/L) trillion (ppt = ng/kg, ng/L)
Contaminants

Metals and metalloids; organometals
Inorganic gases
Nutrients
Radioactive isotopes
Volatile organic compounds (VOCs)
Polycyclic aromatic hydrocarbons (PAHs)
Polychlorinated biphenyls (PCBs)
also PCT, PBB
Chlorofluorocarbons (CFCs)
Organochlorine alkenes
Chlorinated phenols
Chlorination products
Polychlorinated dibenzodioxins (PCDDs; dioxin); also PCDFs
Insecticides:
  Organochlorines
  Organophosphates
  Carbamates
  Pyrethroids
  Aromatics
  Organometals
  Aromatic herbicides
Polybrominated diphenyl ether (PBDE)
Alkylphenols
Perfluorooctane sulfonates (PFOS)
Metals and Metalloids

**Metals** - left two-thirds of the periodic chart (minus hydrogen)
- lustrous appearance; malleability, ductility, conductivity

**Metalloids** – intermediate properties; semiconductors (silicon, arsenic, selenium)

**Heavy metals** – (old definitions) – specific gravity > 5 g/cm³; heavier than iron; atomic mass > Ca
- current: many metals; ionic forms or compounds are readily soluble in water
Generalizations about Metals

Metals are naturally-occurring elemental substances.
- what are the ecotoxicological implications of this fact?

Metals become contaminants when human activities raise their concentrations in the environment above natural levels.
- what are “natural levels”?

In the most cases, metals become pollutants through human activities, ......
- e.g. mining and smelting

... or are released as wastes or by-products; e.g.
- industrial manufacturing
- mining
- combustion products
  - coal, oil, wood
  - waste incineration
- agricultural pesticides
- phosphate fertilizers
- cement production

Many metals are used in normal physiological reactions as co-factors;
- however, in excess, they disrupt normal enzymatic reactions.

Heavy metals often block toxicant-degradation pathways.
# Elemental Composition

<table>
<thead>
<tr>
<th>Atomic Number</th>
<th>Element</th>
<th>Earth’s Crust (kg/kg)</th>
<th>Sea Water (kg/L)</th>
<th>Human Body (kg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>Chromium</td>
<td>1.0 X 10^{-4}</td>
<td>3 X 10^{-10}</td>
<td>2 X 10^{-7}</td>
</tr>
<tr>
<td>28</td>
<td>Nickel</td>
<td>8.4 X 10^{-5}</td>
<td>5.6 X 10^{-10}</td>
<td>2.14 X 10^{-7}</td>
</tr>
<tr>
<td>29</td>
<td>Copper</td>
<td>6.0 X 10^{-5}</td>
<td>2.5 X 10^{-10}</td>
<td>1.03 X 10^{-6}</td>
</tr>
<tr>
<td>30</td>
<td>Zinc</td>
<td>7.0 X 10^{-5}</td>
<td>4.9 X 10^{-9}</td>
<td>3.29 X 10^{-5}</td>
</tr>
<tr>
<td>33</td>
<td>Arsenic</td>
<td>1.8 X 10^{-6}</td>
<td>3.7 X 10^{-9}</td>
<td>1 X 10^{-7}</td>
</tr>
<tr>
<td>47</td>
<td>Silver</td>
<td>7.5 X 10^{-8}</td>
<td>4 X 10^{-11}</td>
<td>2.86 X 10^{-8}</td>
</tr>
<tr>
<td>48</td>
<td>Cadmium</td>
<td>1.5 X 10^{-7}</td>
<td>1.1 X 10^{-10}</td>
<td>7.14 X 10^{-7}</td>
</tr>
<tr>
<td>50</td>
<td>Tin</td>
<td>2.3 X 10^{-6}</td>
<td>4 X 10^{-12}</td>
<td>2.86 X 10^{-7}</td>
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<tr>
<td>80</td>
<td>Mercury</td>
<td>8.5 X 10^{-8}</td>
<td>3 X 10^{-11}</td>
<td>8.57 X 10^{-8}</td>
</tr>
<tr>
<td>82</td>
<td>Lead</td>
<td>1.4 X 10^{-5}</td>
<td>3 X 10^{-11}</td>
<td>1.71 X 10^{-6}</td>
</tr>
<tr>
<td>6</td>
<td>Carbon</td>
<td>2.00 X 10^{-4}</td>
<td>2.8 X 10^{-5}</td>
<td>2.29 X 10^{-1}</td>
</tr>
<tr>
<td>12</td>
<td>Magnesium</td>
<td>2.33 X 10^{-2}</td>
<td>1.29 X 10^{-3}</td>
<td>2.71 X 10^{-4}</td>
</tr>
<tr>
<td>15</td>
<td>Phosphorus</td>
<td>1.05 X 10^{-3}</td>
<td>6 X 10^{-8}</td>
<td>1.11 X 10^{-2}</td>
</tr>
<tr>
<td>16</td>
<td>Sulfur</td>
<td>3.50 X 10^{-4}</td>
<td>9.05 X 10^{-4}</td>
<td>2.0 X 10^{-3}</td>
</tr>
<tr>
<td>20</td>
<td>Calcium</td>
<td>4.15 X 10^{-2}</td>
<td>4.12 X 10^{-4}</td>
<td>1.43 X 10^{-2}</td>
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<tr>
<td>26</td>
<td>Iron</td>
<td>5.63 X 10^{-2}</td>
<td>2 X 10^{-9}</td>
<td>6 X 10^{-5}</td>
</tr>
<tr>
<td>53</td>
<td>Iodine</td>
<td>4.5 X 10^{-7}</td>
<td>6 X 10^{-8}</td>
<td>2.86 X 10^{-7}</td>
</tr>
</tbody>
</table>
# Nutritionally Important Metals

<table>
<thead>
<tr>
<th>Metal</th>
<th>Functional Association</th>
<th>Source</th>
<th>Toxicity (excess)</th>
<th>Recommended Daily Intake</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromium (Cr)</td>
<td>insulin</td>
<td>Food</td>
<td>Kidney, lung cancer (inhalation)</td>
<td>50 – 200 µg (Cr$^{3+}$)</td>
</tr>
<tr>
<td>Copper (Cu)</td>
<td>hemoglobin</td>
<td>Food</td>
<td>Toxicity rare, (-) anemia, (+) liver and kidney</td>
<td>1.5 – 3.0 mg</td>
</tr>
<tr>
<td>Iron (Fe)</td>
<td>hemoglobin</td>
<td>Food</td>
<td>Intestinal tract, liver</td>
<td>10 – 15 mg</td>
</tr>
<tr>
<td>Magnesium (Mg)</td>
<td>enzymes</td>
<td>Food</td>
<td>Inhalation</td>
<td>280 – 350 mg</td>
</tr>
<tr>
<td>Manganese (Mn)</td>
<td>enzymes</td>
<td>Food</td>
<td>Parkinson’s-like</td>
<td>2 – 5 mg</td>
</tr>
<tr>
<td>Selenium (Se)</td>
<td>deiodinases, anticancer</td>
<td>Food</td>
<td>Heart</td>
<td>55 – 70 mg</td>
</tr>
<tr>
<td>Zinc (Zn)</td>
<td>enzymes</td>
<td>Food</td>
<td>(-) impaired growth</td>
<td>12 – 15 mg</td>
</tr>
</tbody>
</table>

Gilbert S.G. 2004
Hemoglobin – Fe Center

Heme
Anthropogenic metal contamination is superimposed on the natural biogeochemical cycle of a given element:

- **Bio**: biological systems affect metal cycling
- **Geo**: geological forces affect metal distribution
- **Chemical**: parameters/processes which affect the movement of metals
Kingston Fossil Plant,
Harriman, Tn. December 2008

Emory River → Clinch River →
Tennessee River → Ohio River →
Gulf of Mexico
US Steel Mill, Morgan Park, MN

runoff → St. Louis River → Lake Superior
# Metals of Concern

<table>
<thead>
<tr>
<th>RCRA 8¹</th>
<th>Priority Pollutants²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>Antimony</td>
</tr>
<tr>
<td>Barium</td>
<td>Arsenic</td>
</tr>
<tr>
<td>Cadmium</td>
<td>Beryllium</td>
</tr>
<tr>
<td>Chromium</td>
<td>Cadmium</td>
</tr>
<tr>
<td>Lead</td>
<td>Chromium</td>
</tr>
<tr>
<td>Mercury</td>
<td>Copper</td>
</tr>
<tr>
<td>Selenium</td>
<td>Lead</td>
</tr>
<tr>
<td>Silver</td>
<td>Mercury</td>
</tr>
<tr>
<td></td>
<td>Nickel</td>
</tr>
<tr>
<td></td>
<td>Selenium</td>
</tr>
<tr>
<td></td>
<td>Silver</td>
</tr>
<tr>
<td></td>
<td>Thallium</td>
</tr>
<tr>
<td></td>
<td>Zinc</td>
</tr>
</tbody>
</table>

1. Resource Conservation and Recovery Act
2. Clean Water Act
3. EPA regulations

## Target Analyte List³

- Aluminum
- Antimony
- Arsenic
- Barium
- Beryllium
- Cadmium
- Calcium
- Chromium
- Cobalt
- Copper
- Iron
- Lead
- Manganese
- Magnesium
- Mercury
- Nickel
- Potassium
- Selenium
- Silver
- Sodium
- Thallium
- Vanadium
- Zinc
Arsenic (As)

Metalloid; common oxidation states of -3, +3, +5
- trivalent (As$^{+3}$) state is more toxic than pentavalent (As$^{+5}$);
  e.g. AsO$_3$ more toxic than AsO$_5$

Ubiquitous element in earth’s crust

Natural sources: volcanoes, weathering, sedimentation, forest fires, groundwater
- *methylation* produces *organoarsenate* (Me-As = harmful form .... why?)
  - As methylated by fungi, bacteria, inverts, vertebrates (incl. humans)

Anthropogenic sources:
- smelting
- combustion of fossil fuels (most coal fly ash contains As)
- mining (Au, Pb)

Uses: metal alloys, pesticides (e.g. Pb$_3$(AsO$_4$)$_2$), wood preservatives, plant desiccants, herbicides (e.g. Na$_3$AsO$_3$), dyes, pigments, preservatives of animal hides, glass manufacture, pharmaceutical and veterinary nutritional supplement; veterinary acaricide
Arsenic Toxicity

Toxicity related to As solubility in water
- e.g. elemental arsenic almost insoluble in water
- toxicity: inorganic arsenites > organic trivalent compounds > inorganic arsenates > arsonium compounds > elemental arsenic

Cells accumulate As using the PO$_4$ active transport system

$As^{+3}$ forms interact with sulfhydryl (SH) enzyme systems
- e.g. arsenite ($AsO_3^{3-}$) interacts with two glutathiones (GSH);
  strong covalent bond eliminates GSH from further reactions

\[
\begin{align*}
\text{-O} & \text{- As} + 2\text{GSH} \rightarrow \text{-O} & \text{- As} + 2\text{OH}^- \\
\text{O}^- & \text{SG} & \text{SG}
\end{align*}
\]

As also uncouples oxidative phosphorylation and substrate-level phosphorylation

Glyceraldehyde 3-phosphate + HAsO$_4^{2-}$ \( \rightarrow \) AsO$_4^{2-}$-GAc-P
(arsenophosphoglycerate)

Carcinogenic
Cadmium (Cd)

Heavy metal; one to the most toxic trace elements

Used in steel plating, alloys, corrosion protection, solder, electrical parts, pigments, plastics, rubber, semi-conductors

Airborne exposure: occupational and general environment, cigarette smoke
Waterborne exposure: natural component; pollution from mining, motor oils, rubber tires, chemical industries

Electronic configuration similar to Zn (however, greater affinity for SH than Zn)

Similar to Ca$^{2+}$ in size and charge density

Toxicity:
- operates as sulfhydryl binding agent (like arsenic)
- competes with Zn binding in metalloenzymes

Human carcinogen
Mercury (Hg)

Hg is rare in earth’s crust (avg. $8.5 \times 10^{-8}$ kg/kg)
- not uniformly distributed
- however, ubiquitous over large scales

Liquid at room temperature; highest volatility of any metal

Many metals dissolve in Hg (form amalgams); many industrial uses
- batteries, electrical apparatus, lab equipment, switches, relays, catalysts, electrolysis, paint preservatives, jewelry, lamps

Environmental sources:
Natural (30%): volcanoes, erosion, weathering, gaseous emissions

Anthropogenic (70%):
- fossil fuel combustion (Hg content of coal ~ 1 mg/kg)
- mining
- smelters
- pesticides (Hg seed dressings)
- pulp and paper processing
- gold mining
- lab chemicals
- waste incineration
- batteries
- sewage effluents

- also - fungicides for seeds; fungal growth inhibitors in pulp mills, etc.
Hg Biotransformation and Toxicity

Form of compound (species) influences transport, bioavailability, and toxicity
- elemental mercury is not readily absorbed
- but organic forms (e.g. methylmercury) are quickly taken up by organisms

**Biotransformation**: bacteria transform elemental Hg into organic forms; e.g.
- \( \text{CH}_3\text{Hg}^+ \) (methylmercury)
- \( (\text{CH}_3)_2\text{Hg} \) (dimethylmercury)

- e.g. sulfur-reducing bacteria (such as those found in wetlands) methylate Hg as a substitute for SH

- these organic forms have increased water solubility, volatility
  - soluble metals are much easier for cells and tissues to absorb

Toxicity: Hg and organic Hg compounds inhibit SH-containing enzymes

\[
\text{RSH} + \text{CH}_3\text{Hg}^+ \rightarrow \text{R-S-Hg-CH}_3 + \text{H}^+
\]

- NOTE – this mechanism is similar to Pb and Cd toxicity
- affected systems: Na/K ATPase, mitochondria, mitosis
- also mutagenic
Lead (Pb)

Lead has been used for 7000 years

Lead poisoning has been noted since at least Greek and Roman times
  Lead pipes for water transport (Pb from the Latin *plumbum*)

Lead acetate - used in ancient Rome as a sweetener for wine
Lead (Pb)

Increased use since the Industrial Revolution (circa early-mid 1800s);
- traced in Greenland snowpack

Modern industrial and commercial applications:
- gasoline additive (tetraethyl-lead used as an anti-knock agent)
- batteries (> 70% of US lead consumption is in batteries)
- solders (pipes, cans)
- plumbing
- pigments (yellow and red pigments; lead chromate)
- paints (paint chips and dust - leading cause of lead toxicity)
- ceramic glazes (mainly red and yellow); also leaded glass
- caulking
- ammunition (ingestion of lead shot causes severe toxicity in waterfowl)

Bones and teeth contain > 95% of body burden; Pb released during stress

Lead Toxicity
- central nervous system (primary target)
- inhibits hematopoiesis (interferes with heme synthesis*)
- anemia
- renal dysfunction
- carcinogen
Selenium (Se)

Se required nutritionally (trace mineral)
- component of some rare amino acids (selenocysteine, selenomethionine)
- enzyme cofactor; e.g. glutathione peroxidase, thyroid deiodinases
- biochemically similar to sulfur
  - replaces S in elevated concentrations
- toxic at concentrations not much higher than those required nutritionally
  (evolutionary implications?)

Natural sources – volcanoes, weathering, erosion

Anthropogenic sources: fossil fuel burning (found in coal fly-ash), irrigation, waste disposal and incineration, smelting, burning vegetation,
- byproduct of gold, copper, and nickel mining

Microbial transformation produces alkylselenides
- alkylated forms are more volatile
  - however, alkylated forms are also less toxic than elemental forms

Uses include: electronics, glass manufacturing, electrical applications, pigments, alloys

Se is antagonistic to both Hg and Cd; reduces their toxicity
- selenohydryl group binds Hg 100X tighter than SH group
Inorganic Gases
Carbon Dioxide (CO₂)
Carbon Monoxide (CO)

CO₂ - from combustion; linked to global warming through the greenhouse effect.

CO – formed by:

1) Incomplete combustion of carbon or carbon-containing compounds
   \[ 2C + O₂ \rightarrow 2CO \]
   \[ 2CO + O₂ \rightarrow 2CO₂ \]

2) Reactions between CO₂ and C
   \[ CO₂ + C \rightarrow 2CO \]

3) Dissociation of CO₂ at high temp
   \[ CO₂ \rightarrow CO + O \]

Toxicological effects:
- interferes with O₂ transfer
- CO forms carboxyhemoglobin; affinity >200X O₂; \( t_{1/2} = 4 \) h

Exposure routes (humans):
- CO in ambient environment; exhaust gases, occupational exposure; cigarettes
Nitrogen Oxides

Six forms of NO\textsubscript{x} present in the atmosphere; e.g.

Nitrogen dioxide (NO\textsubscript{2}) formed from nitric oxide (NO; from combustion):
- participates in smog formation

\[
\text{UV light energy}
\]

\[
\begin{array}{c}
\text{NO}_2 \\
\text{NO} \\
\text{O} \\
\text{O}_2 \\
\text{O}_3 \\
\text{O}_2
\end{array}
\]

Nitric acid formed via: \(\text{NO}_2 + \text{OH}^\cdot \rightarrow \text{NOH}_3\); contributes to acid precipitation

Nitrous oxide (N\textsubscript{2}O) has 290X warming effect per kg as CO\textsubscript{2}
- contributes \(\sim\)4% of total greenhouse effect
**Ozone** ($O_3$)

Ozone is a natural constituent of the upper atmosphere; trace in lower atmosphere

\[
O_2 \xrightarrow{hv} O + O_2 \rightarrow O_3
\]

Interaction with nitrogen oxide pollutants:

\[
NO_2 \rightarrow NO + O
\]
\[
O + O_2 \rightarrow O_3
\]

net: $NO_2 + O_2 \rightleftharpoons NO + O_3$

UV light energy

hydrocarbon free radicals react with and remove NO

results in a buildup of $O_3$

$O_3$ is the major component of smog
Sulfur Dioxide (SO$_2$)

SO$_2$ originates mainly from volcanoes, fossil fuel burning, and industrial activities.
- coal = 0.3 – 7% sulfur (organic and inorganic)
- oil = 0.2 – 1.7% sulfur (organic)

SO$_2$ dissolves in water; forms sulfuric acid (H$_2$SO$_4$)
- returns as acid rain

[Map of 1992 annual precipitation-weighted mean hydrogen ion concentrations as pH]

[Photo of acid rain withering trees in a coniferous forest in Europe]

ga.water.usgs.gov/edu/acidrain.html
Nutrients

Nutrients = phosphorus and nitrogen compounds

Sources:
- ag. and rural watersheds dominated by diffuse non-point sources
- urban watersheds dominated by point sources

Nitrogen:
- *nitrate* (cation-NO$_3^-$) enter water from runoff or sewage discharges
- high concentrations of nitrates can be converted into *nitrites* (NO$_2^-$) in the gut (human infants)
  - nitrites bind to hemoglobin to form methemoglobin = reduced O$_2$ transport; *methemoglobinemia*
- nitrosamines can form from N compounds in drinking water
  - carcinogenic
- nitrite is very toxic to aquatic biota
- ammonia (NH$_3$) found near sewage discharges; toxic to aquatic biota

Phosphorus:
- fertilizers, industrial, commercial, and consumer products
- adheres to particulates; contributed to water via erosion
Nutrients

N and P can change the structure and functioning of ecological communities - eutrophication: excess N and P accelerated plant production; accumulation of organic matter, e.g. algae bloom; decomposition leads to severe $O_2$ depletion.
Contaminants

Metals and metalloids; organometals
Inorganic gases
Nutrients
Radioactive isotopes
Volatile organic compounds (VOCs)
Polycyclic aromatic hydrocarbons (PAHs)
Polychlorinated biphenyls (PCBs)
also PCT, PBB
Chlorofluorocarbons (CFCs)
Organochlorine alkenes
Chlorinated phenols
Chlorination products

Polychlorinated dibenzodioxins (PCDDs; dioxin); also PCDFs

Insecticides:
- Organochlorines
- Organophosphates
- Carbamates
- Pyrethroids
- Aromatics
- Organometals

Aromatic herbicides
Polybrominated diphenyl ether (PBDE)
Alkylphenols
Perfluorooctane sulfonates (PFOS)
Volatile Organic Compounds (VOCs)

VOCs – organic compounds which have boiling points within the range 50-100 to 240-260 C

EPA designates VOCs as one of six “Criteria Air Pollutants”

VOCs include:
- Aliphatics - methane, pentane, hexane, heptane, ethylene, etc.
- Aromatics - benzene, toluene, xylenes, naphthalene, styrene
- Halogenated - chloroform, dichloromethane, trichloroethylene
- Alcohols - 2-butylalcohol, 1-dodecanol
- Aldehydes - decanal, nonanal
- Esters - ethyl acetate, 1-hexyl butanoate

Sources:
- natural – petroleum, forest fires, transformation of biogenic precursors
- anthropogenic – high-temperature combustion of fuels, emissions from crude and refined oil, municipal incineration, burning croplands

VOCs contribute ~ 14% of air pollution species
VOCs - Aromatics

Benzene
- starting point for many industrial and agricultural products
- solvent, thinner, degreaser
- fuel additive
- source – combustion of fossil fuels; industrial emission
- toxicological **Mode of Action (MOA):** narcosis
  - affects CNS
  - high concentration – inhalation fatal
  - low concentration – blood abnormalities, bone marrow damage
  - carcinogenic

Toluene
- primarily precursor for synthesis of other chemicals
  - substitute for benzene (less toxic)
- MOA – narcosis
  - skin irritation; damage to blood, CNS

Xylene(s)
- replaces benzene and toluene
- MOA: narcosis (CNS)
- virtually insoluble in water (very lipophilic)
- rapid biodegradation

*para*-xylene
1,4-dimethylbenzene
Polycyclic Aromatic Hydrocarbons

(PAHs, polyaromatic hydrocarbons, polynuclear aromatic hydrocarbons)

Composed of carbon and hydrogen with two or more fused aromatic rings

Naphthalene

Anthracene

Phenanthrene

Natural components of petroleum products
- aromatization of saturated compounds at relatively low temperatures and high pressures (diagenesis or categenesis); e.g. naphthalene, phenanthrene

Anthropogenic - incomplete combustion of organic matter (pyro genesis);
- e.g. chrysene, benzo[a]pyrene

Chrysene

Benzo[a]pyrene

16 PAHs are on the EPAs list of 126 priority pollutants
**PAHs**

Environmental sources:

Natural – forest fires, breakdown of natural organic matter under elevated temp and pressure
- may be some direct biosynthesis by microbes and plants

Anthropogenic – residential heating, aluminum production, coke manufacture (creosote; 90% PAH), incineration, power generation

NOTE – regardless of formation method, related molecules are always present; therefore, a suite of related PAHs can be expected; 15 – 17 compounds typical

Higher MW PAHs tend to be more stable;
- less amenable to biodegradation or metabolism

Highly lipophilic – easily penetrates cell membranes
- subsequent metabolism can increase water solubility; more amenable to excretion
- however, metabolism can make PAHs more toxic

Some PAHs (e.g. benzo[a]pyrene) are carcinogenic, or are precursors to carcinogenic metabolites

Vertebrates can metabolize PAHs; invertebrates generally do not; therefore, can accumulate in inverts
Low v. High MW PAHs

**Low molecular weight**
- Few rings
- Partitions to air (volatile)
- Water soluble (toxic to fish & plankton)
- Less carcinogenic
- Less bioaccumulative
- Naphthalene: 2 rings
  - MW 128, H₂O sol. 30 mg/L

**High molecular weight**
- Many rings
- Partitions to particulates
- Water insoluble (impacts benthic invertebrates)
- More carcinogenic
- More bioaccumulative
- Benzo[a]pyrene: 5 rings
  - MW 252, H₂O sol. 6.0 mg/L
Polychlorinated Biphenyls (PCBs)

PCBs
- synthetic chemicals developed in the 1920s
- stable, unreactive viscous fluids; low volatility
  - used as hydraulic fluid, coolant-insulation in transformers
    plasticizers in paints, oils and lubricants

Biological properties
- highly lipophilic
- extremely stable (and barely metabolized)
- therefore accumulate in biological tissues (fats)

Toxicity
- problems evident in 1950s – 60s
- carcinogenesis, immune suppression, endocrine disruption
- banned from all use in 1979
  (worldwide production in 1976 estimated to be 1.64 billion pounds)
Polychlorinated terphenyls (PCTs)

Polybrominated biphenyls (PBBs)

- flame retardants in thermoplastics
- lipophilic
- poorly metabolized
- slowly excreted

1973 Michigan livestock feed contamination...

... resulted eventually in > 90% of Michigan population with PPB concentrations > 10 ppb in body fat

- general population had undetectable levels
Organochlorine Alkenes

Alkene - unsaturated CH compound with at least one C=C double bond
e.g. ethylene $C_2H_4$ (ethene)

**Tetrachloroethene** $Cl_2C=CCl_2$
(tetrachloroethylene, perchloroethylene, perc)
- used as dry-cleaning fluid, degreaser
- often associated with groundwater pollution

**Trichloroethene** $ClCH=CCl_2$
(trichloroethylene)
- industrial solvent; degreaser
- common groundwater and drinking water pollutant
Chlorinated Phenols

e.g. *Trichlorophenol* (TCP), *pentachlorophenol* (PCP)
- some chlorinated phenols manufactured
- some are by-products from paper mill processing, bleaching kraft wood pulp
- formed from degrading natural organic matter and chlorine used in bleaching
- accumulates in sediments downstream from discharges

TCP and PCP widely used as fungicides (wood preservatives); banned in 1987

Health effects:
- respiratory (oxphos) uncoupler; major target - CNS
- reproductive effects; damage to liver and kidneys
- carcinogen
Chlorination and Disinfection
Byproducts

Chlorine products or gas (and ozone) are used to disinfect drinking water; toxic byproducts can include:

**Trihalomethanes** – e.g. chloroform CHCl$_3$
- liver, kidney, CNS
- carcinogen

**Haloacetic acids**
- carcinogen

**Chlorite** (chlorite ion: ClO$_2^-$)
- CNS effects (infants, young children; fetuses in pregnant women)

**Bromate** (BrO$_3^-$)
- carcinogen
Polychlorinated Dibenzodioxins (PCDDs, PCDFs)

Dioxins are not intentionally manufactured; no commercial value
- byproducts of other processes (e.g. herbicide production)
- also formed during combustion (natural, industrial, and small-scale)
- paper production
- persistent, thermally stable, do not readily degrade

210 possible dioxin compounds
- PCDDs – 75 possible congeners
- PCDFs – 135 possible congeners

Toxicity - wide range of effects
- “most toxic compound” (rats)
- virtually no effect (humans)

- 17 congeners considered toxic
  - rats – carcinogen
  - humans - chloracne

Dioxin-related:
“Agent Orange” (Vietnam)
Times Beach, MO
Pesticides
Pesticides - Historical Perspective

1000 BCE – Chinese used sulfur as a fumigant

1500s – Japanese treated rice with a whale oil-vinegar mix to inhibit development of insect larvae

1600s - the seed of *Strychnos nux vomica* (containing strychnine) used to kill rodents

1800s - insecticidal pyrethrum extracted from chrysanthemums

1800s - Bordeaux Mixture (copper sulfate, lime [calcium oxide], water) used to combat vine downy mildew

2000s - Bordeaux Mixture still used in vineyards
Organochlorine Pesticides

e.g. lindane, toxaphene, methoxychlor, chlordane, aldrin, dieldrin, DDT

Some of the earliest manufactured pesticides
- produced prior to regulation by FIFRA (Federal Insecticide, Fungicide,
  and Rodenticide Act)

Synthetic compounds
- slow degradation
- low water solubility/ high lipid solubility

*These characteristics make organochlorines quite persistent

**Organochlorine pesticides**

\[
\begin{align*}
\text{1,2,3,4,5,6-Hexachloro-cyclohexane} \\
\text{Lindane} \\
\text{Methoxychlor}
\end{align*}
\]
**Organochlorine Pesticides - DDT**

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

$dichloro$-$diphenyl$-$trichloroethane$

![Chemical structure of DDT](image)

**Toxicity:**
- Invertebrates – acetylcholinesterase inhibition
- Vertebrates – breakdown product (DDE) may act as an endocrine disruptor

- Developed as an insecticide in 1939
- Banned in most industrialized countries in the 1970s (US – 1972)
  - Low vapor pressure
  - Low water solubility
  - High lipid solubility
- Highly resistant to breakdown or metabolism
- Persistent ($t_{1/2} = 7 - 30$ y)
- Accumulates in biological tissues
Organochlorine Pesticides - DDT

- extremely persistent
- endocrine disruptor (estrogen mimic)
  - related to feminization of male alligators, fish
  - bird eggshell fragility
  - delayed puberty (mice)
Organophosphate Pesticides

e.g. methyl parathion, diazinon, chlorpyrifos, malathion
  - derivatives of orthophosphoric acid ($H_3PO_4$)
  - developed from early research on nerve agents for warfare
  - higher water solubility than organochlorines
  - less likely to accumulate in sediments
  - more easily degraded
    - $t_{1/2}$ – days to weeks

MOA - inhibition of acetylcholinesterase
  - irreversible inhibition (same mechanism as nerve gas)
Acetylcholinesterase Inhibitors

Neurotransmitter **acetylcholine** must be broken down rapidly by the receiving neuron - continued stimulation - uncoordinated muscle movement, seizures, and death
**Acetylcholinesterase** binds ACh by donating a proton from serine, resulting in the release of the choline group.
- acetyl group is released
- serine reactivated by a proton donated by H$_2$O
Organophosphates inhibit AChE by initially binding to serine at the active site - allows *irreversible* binding of organophosphate and an active site glutamyl residue - acetylcholine is prevented from entering the active site = no degradation

- Methyl Parathion
- Diazinon
Carbamate Insecticides

Synthetic derivatives of carbamic acid
e.g. carbaryl, primacarb, carbofuran
- more polar and much more water soluble than chlorinated hydrocarbons

Mechanism of action (MOA) – acetylcholinesterase inhibition (reversible)
- metabolic hydrolysis reverses AChE inhibition
  - generally less toxic to mammals than are organophosphates

Carbamate insecticides degrade rapidly in water
- \( t_{1/2} = \) weeks

Carbamic acid

\[
\begin{array}{c}
\text{O} \\
\text{H}_2\text{N} & \text{C} & \text{OH} \\
\text{Carbamic acid}
\end{array}
\]

Carbaryl

\[
\begin{array}{c}
\text{O} \\
\text{H}_3\text{C} & \text{N} & \text{C} & \text{O} & \text{O} & \text{O} \\
\text{Carbaryl}
\end{array}
\]
Pyrethroid Insecticides

Synthetic analogs of natural pyrethrins

- pyrethrins are produced by chrysanthemum (pyrethrum) plants
e.g. pyrethrin, permethrin, fenvalerate

- generally degrade quickly
- low mammalian toxicity

![Permethrin structure](Permethrin.png)
Aromatic Herbicides

Diverse group; many aromatics
- those based on nitrogen heterocyclic molecules are very polar
- produces high water solubility, potential for contamination

**Bipyridines**
e.g. diquat, parquat

![Diquat](image)

**Triazines**
e.g. atrazine, simizine, metrabuzin

![Atrazine](image)

**Phenoxy herbicides**
(2,4-dichloro-phenoxy)-acetic acid

![2,4-D](image)

(2,4,5-trichloro-phenoxy)-acetic acid

![2,4,5-T](image)
Organometals

Many metal ions are so *insoluble* that they are relatively non-toxic to animals
- bioavailability (and toxicity) can be greatly enhanced when metals are bound to an organic ligand
- some organometals occur naturally
  - e.g. methylmercury
- others synthesized
  - e.g. tetraethyl lead, tributyl tin

**Organomercury**
- methylmercury, dimethylmercury

**Organolead**
- tetraethyl lead - anti-knock agent for gasoline

**Organotin**
- tributyltin – industrial antifungal agents, marine anti-fouling agent
- trimethyltin, triethyltin – neurotoxins; used as mitocides and acaracides
- triphenyltin – antifungal paints; agricultural fungicides
- dibutyltins – (low toxicity; no antifungal, antibacterial activity)
  - industrial plasticizers
(NOTE – tetraorganotins are very stable and non-toxic)
Contaminants

Metals and metalloids; organometals
Inorganic gases
Nutrients
Radioactive isotopes
Volatile organic compounds (VOCs)
Polycyclic aromatic hydrocarbons (PAHs)
Polychlorinated biphenyls (PCBs)
also PCT, PBB
Chlorofluorocarbons (CFCs)
Organochlorine alkenes
Chlorinated phenols
Chlorination products

Polychlorinated dibenzodioxins (PCDDs; dioxin); also PCDFs

Insecticides:
  Organochlorines
  Organophosphates
  Carbamates
  Pyrethroids
  Aromatics
  Organometals

Aromatic herbicides
Polybrominated diphenyl ether (PBDE)
Alkylphenols
Perfluorooctane sulfonates (PFOS)
Polybrominated Diphenyl Ether (PBDE)

2,2’,4,4’-Tertrabrominated-diphenylether (BDE-47)

Flame retardants – clothing, plastics
  - synthetic (possibly some natural sources)

Mehran Alaee, Environmental Science and Technology, 2001

Toxicity: not well established
  - possible liver, thyroid, neuro-developmental
Alkylphenols are degradation products of ethoxylated phenols; used extensively as surfactants in detergents

Synthetic chemicals

Alkylphenol ethoxylates (APEs) are widely used as industrial surfactants

NOTE – the APE nonoxynol 9 – common spermicide

Toxicity – suspected as an estrogen mimic (endocrine disrupting chemical)
Perfluorooctane Sulfonates - PFOS

Perfluorooctane sulfonate [PFOS]

PFOS - synthetic chemical; primarily used as a surfactant

- repels water (like other fluorocarbons)
- principle ingredient in Scotchgard ®
  (NOTE – reformulated in 2003 to remove PFOS)
- manufacture of carpets, apparel, furniture, paper, cleaning products
- component of fire-fighting foams
PFOS initially thought to be non-toxic, due to inability to enter tissues

- however, recent analysis found uptake and bioaccumulation

- global distribution; found in Arctic marine mammals

Related: perfluorooctanoic acid, perfluorobutanoic acid

- PFBA recently found in municipal wells in St. Paul, MN

Toxicity: unclear; possible developmental effects; possible carcinogen

PFOS is of concern because of:

- persistence
- bioaccumulation
- biomagnification