


# Classification of Pollutants

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## Priority Pollutants

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- Amount Produced/Released
- Persistence
- Bioaccumulation
- Toxicity
- Other Effects

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## Amount Produced or Released

- Some pollutants are produced in large amounts but only released accidentally (e.g. chlorinated solvents, benzene)
- Others are released intentionally in large amounts (e.g. pesticides)
- Some very toxic pollutants are only produced in very small amounts (e.g. dioxins)

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## Persistence

- Resistance to transformation in the environment either chemical or biological
- Persistent chemicals can migrate widely
- Measured as residence time or as "half-life"
- Chlorinated/halogenated compounds are typically persistent (e.g. DDT, PCBs, CFCs)
- Rate of degradation depends on environmental conditions

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### Bioaccumulation

- Uptake of pollutant by organisms
- Depends on hydrophobicity (i.e. water-hating), persistence and toxicity of pollutant
- Concentration may increase more than 100,000 times from water to fish
- Concentration is "biomagnified" going up the food chain

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### Bioaccumulation

Sample Type	Approximate Concentration Range (mg/kg)
Sea water	10 <sup>-7</sup> - 10 <sup>-5</sup>
Fresh water	10 <sup>-5</sup> - 10 <sup>-3</sup>
Sediments	10 <sup>-3</sup> - 10 <sup>-1</sup>
Sewage	10 <sup>-1</sup> - 10 <sup>0</sup>
Plankton	10 <sup>-1</sup> - 10 <sup>0</sup>
Aquatic invertebrates	10 <sup>0</sup> - 10 <sup>1</sup>
Fish	10 <sup>0</sup> - 10 <sup>2</sup>
Birds	10 <sup>1</sup> - 10 <sup>3</sup>
Bird eggs	10 <sup>1</sup> - 10 <sup>3</sup>
Marine Mammals	10 <sup>1</sup> - 10 <sup>3</sup>

(from Pearson, 1982)

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## Toxicity

### ■ Acute toxicity:

- concentration which kills 50% of a given population (usually determined in lab)
- expressed as Lethal Dose to 50%: LD50, in units of mg chemical/kg body weight
- also depends on exposure

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## Toxicity

### ■ Chronic toxicity

- "Sub-lethal" tests
- adverse effects: cease to feed, grow more slowly, unable to reproduce or just abnormal behavior
- typically occurs at dosages 10 to 100 times smaller than acute toxicity; more difficult, controversial & expensive to test

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## Toxicology

- Solvents as a general class
  - Usually have high vapor pressures, so they form vapors: major intake route is through inhalation
  - Toxicity usually expressed as LD<sub>50</sub> in terms of air concentration
  - Most solvents depress the central nervous system => anesthetic effect

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## Toxicology

- Solvents
  - CNS depression symptoms:
    - dizziness, confusion
    - headaches
    - loss of coordination
    - convulsions
    - coma
    - death

**Central Nervous System (CNS)**

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## Toxicity

### ■ Genotoxicity

- Carcinogenic or mutagenic
- New tests are constantly developed, but given low dosage and exposure, it is always difficult to determine increased risk
- Short-term, high dosage test vs. long-term, low dosage in real life
- Additional environmental factors also genotoxic

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## Other Effects

- Ability to influence large-scale biogeochemistry (e.g. CFCs, acid rain)
- Alter availability of nutrients or other needed organic chemicals
- Odor (e.g. sulfur compounds)
- Color (e.g. organic dyes)
- Foaming (e.g. detergents)
- Interfere with visibility (e.g. SO<sub>2</sub> particulates)

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## Classification of Pollutants

- What is the best criteria for classification?
  - Physical properties
  - Chemical properties
  - Chemical structure
  - Effect on the environment
  - Organic vs. Inorganic

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## Classification of Pollutants

- Organic Chemicals
  - Hydrocarbons
  - Halogenated hydrocarbons
  - Oxygenated hydrocarbons
  - Nitrogen compounds
  - Sulfur compounds
  - Phosphorus compounds

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## Classification of Pollutants

- Inorganic pollutants
  - Arsenic
  - Lead
  - Copper
  - Cadmium
  - Mercury
  - Chromium
  - Chlorine
  - Cyanide
  - Nitrate
  - Ammonia

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## Hydrocarbons

- Formed by biogenic processes: microbes, vegetation, animals
- Contamination from oil spills, refineries and fuel transport and use
- Only slightly soluble in water, very hydrophobic: Hexane about  $10 \text{ g/m}^3$
- Linear hydrocarbons are easily degraded by microbes; branched are resistant

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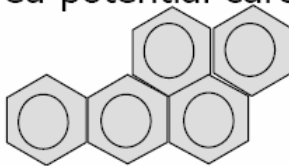
## Hydrocarbons

- Hydrocarbons with double or triple bonds (alkenes, alkynes) are highly reactive: short lives in the environment
- Aromatics: fairly toxic (e.g. benzene, xylenes, ethylbenzene, toluene). They are considerably more soluble in water (e.g. benzene =  $1780 \text{ g/m}^3$ ) which is a big concern for ground water supplies.

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## Hydrocarbons

- Fusion of benzene rings produces polycyclic aromatic hydrocarbons (PAHs) = polynuclear aromatic hydrocarbons (PNAs). Many are considered potential carcinogens.



benzo(a)pyrene

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## Hydrocarbons

### ■ Effects on Living Organisms

#### ■ Physical

- smothering
- reduced light
- inability to swim, fly, etc
- fur or feathers cannot function properly

#### ■ Habitat

- decrease dissolved oxygen
- decrease food availability

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## Hydrocarbons

### ■ Effects on Living Organisms

- Toxicity of most hydrocarbons is usually low at low concentrations, given their biodegradability; may affect internal organ functions (liver, kidney, etc) if ingested
- PAH's cause cancerous and non-cancerous tumors in fish, reptiles, amphibians and mammals in lab studies

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## Toxicology of Alkanes

- Highly lipophilic so they target fatty tissue
- CNS depressants
- Direct aspiration causes chemical pneumonitis
- Concentrated gasoline vapors cause cardiac arrhythmia
- Typical half-life of hexane in body is 2h, but 10 d to remove hexane from fat tissue
- Some of the metabolites of hexane may cause other functional disturbances

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## Toxicology of Aromatic Hydrocarbons

- Benzene and derivatives
  - Principal exposure route is by inhalation
  - 30 to 80% absorbed by circulating blood
  - Concentrates in fat
  - Destroys bone marrow and affects blood cells
  - Considered a carcinogen (lungs, leukemia)
  - Acute exposure depresses CNS (3000 to 5000 ppm)
  - Higher concentrations cause death

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## Halogenated Hydrocarbons

- Halogens: Chlorine, Bromine, Iodine, Fluorine
  - halogens are highly reactive as gases
  - form very stable organic compounds, less flammable, more persistent in the environment
  - less hydrophobic => more soluble in water

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## Toxicology of Chlorinated Hydrocarbons

- Chloroform
  - discontinued use as anesthetic in medicine due to effect on liver and heart
  - used in lacquers, plastics and refrigerant manufacture
  - exposure routes: inhalation, ingestion, dermal
  - suspected animal carcinogen (liver, renal)
  - present in drinking water as a byproduct of chlorination to disinfect water

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## Toxicology of Chlorinated Hydrocarbons

### ■ Carbon Tetrachloride

- anesthetic and antihelmintic agent
- used in dry cleaning and degreasing
- classified as carcinogen
- acute exposure depresses CNS
- chronic exposure affects liver and kidney

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## Toxicology of Chlorinated Hydrocarbons

### ■ Trichloroethylene (TCE)

- dry cleaning, degreasing, solvent
- used to extract caffeine from coffee
- discontinued use as anesthetic in medicine
- classified as carcinogen
- direct exposure irritates eyes, nose, throat
- acute exposure affects CNS
- chronic exposure affects liver and kidneys

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## Toxicology of Chlorinated Hydrocarbons

### ■ Tetrachloroethylene (PCE)

- dry cleaning, degreasing, grain fumigant
- exposure routes: inhalation and dermal absorption
- distributes through body, stored in fats
- classified as carcinogen
- acute exposure affects CNS

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## Halogenated Hydrocarbons

### ■ Chlorinated aromatics

- biologically active, i.e. they interfere with normal processes
- persistent
- useful as pesticides and disinfectants
- Pentachlorophenol
- Chlorobenzenes, dichlorobenzenes

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## Halogenated Hydrocarbons

### ■ Polychlorinated biphenyls (PCBs)

- Large family (209) of compounds
- Very stable, used as electrical insulator fluids in power transformers until ~ 20 years
- fluorescent light until 1970s
- hydraulic fluids, brake fluids, heat transfer, plastizicers, lubricants, flame retardants
- base for pesticides



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## Halogenated Hydrocarbons

### ■ PCBs

- persistent and significant bioaccumulation
- low *acute* toxicity
- incident in Japan in 1968 brought them attention (1291 individuals affected by contaminated rice oil)
- from 1979 on, total ban on use of PCBs except in completely enclosed systems
- river sediments are a major reservoir (e.g. Upper Hudson, St. Lawrence)

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## Halogenated Hydrocarbons

- Fluorinated and chlorofluorinated hydrocarbons are extremely stable
  - best example is TEFLON, a fluorinated polymer with extreme stability, temperature resistance and hydrophobicity (usually not a pollutant)
  - CFCs are used as refrigerants due to their stability. Their persistence in the lower atmosphere allows transport to stratosphere where they interact with ozone formation. Half-lives of decades in the atmosphere.

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## Oxygenated Compounds

- Alcohols (OH group)
  - very widely used industrially
  - usually water soluble
  - usually highly degradable in the environment
  - only an issue if spilled in large quantities
  - large-chain alcohols (e.g. octanol) can be solvent for hydrophobic and hydrophilic organics.

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## Toxicology of Alcohols

- Rapidly absorbed through lungs, gastrointestinal tract and skin
- Distributed through body tissues and fluids
- CNS depressants at high doses (e.g. ethanol !)
- Methanol => formaldehyde => formic acid, which affect optic nerve, causing blindness
- Ethanol in large doses or repeated ingestion causes hepatic or cardiac toxicity

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## Oxygenated Compounds

- Phenols
  - aromatics with alcohol group
  - may disrupt biological processes
  - chlorinated phenols are particularly toxic; used in wood preservation (e.g. telephone poles) which has led to widespread contamination of certain sites

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## Oxygenated Compounds

### ■ Ketones and Aldehydes

- usually only a problem in atmospheric pollution, where they contribute to ozone formation in urban areas
- fairly reactive in aquatic systems
- formed by incomplete combustion
- industrial use is relatively small
- carcinogenicity of aldehydes

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## Oxygenated Compounds

### ■ Organic acids

- usually quite reactive, so they are not of major environmental concern

### ■ Dioxins and dibenzofurans

- form by oxidation/combustion of chlorinated organics at high temperatures
- possibly the most toxic organics

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## Nitrogenated organics

- Amines, amino acids, proteins, etc.
  - most are formed in biological processes
  - can be quite toxic, but typically produced only in small quantities
  - biologically active but degradable
  - some are formed during incomplete combustion of fossil fuels (e.g. nitro PNAs)
  - explosives manufacture and use (TNT)

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## Inorganic Pollutants

- Metals
  - most are essential for biological activity
    - macronutrients: calcium, magnesium, iron, potassium, sodium
    - micronutrients: chromium, cobalt, copper, manganese, nickel, selenium, zinc
  - toxic in large doses
  - mercury and lead form organometallic compounds which disrupt normal biological processes

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## Inorganic Pollutants

- Natural releases via volcanoes
- Human sources:
  - mining
  - fuel combustion, cement production
  - foundries
  - refuse incineration
  - industrial products, processes and waste
  - pesticides or fertilizers

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## Toxicology of Metals

- Arsenic
  - "Substitutes" for phosphate, disrupting metabolic processes (e.g. in ADP-ATP energy cycle of cells)
- Cadmium
  - Affects renal, pulmonary, skeletal, testicular and nervous systems
  - Disrupts zinc-dependent enzymes

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## Toxicology of Metals

- Lead
  - Inhibits hemoglobin synthesis => anemia
  - Substitutes for Calcium, reducing cellular functions (e.g. ATP production)
  - Stored in bones, where it becomes a life-long source of lead to the blood
  - organic lead compounds affect brain function

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## Toxicology of Metals

### Clinical Signs and Symptoms Following Et<sub>4</sub>Pb or Et<sub>3</sub>Pb Exposure<sup>a</sup>

Phase I	Lethargy
Phase II	Inappetance, tremor, hypermotility, hyperexcitability, aggression
Phase III	Hypothermia, convulsion, incoordination, ataxia, paralysis
Phase IV	Death

<sup>a</sup> Symptoms and signs resemble those observed in trimethyltin (TMT) intoxication.

Source: Basic Env. Toxicology, Cockerham and Shane, 1994

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## Toxicology of Metals

- Mercury
  - Mercury vapors and organomercury enter central nervous system
  - Affects brain and nerve cells
  - Sensory disturbance, reduced field vision and ataxia
  - Impairment of speech, hearing and mental functions

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## Toxicology of Metals

### Metal-Induced Carcinogenesis

Metal Carcinogen	Tumor
Cd	Testicular
Ni, Pb	Lung adenoma
Ni <sub>3</sub> S <sub>2</sub>	Muscle
Ni, Cd, Pb	(Various)
Cu	Lung

Source: Basic Env. Toxicology, Cockerham and Shane, 1984

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## Inorganic Pollutants

### ■ Nitrate ( $\text{NO}_3^-$ )

- good fertilizer, toxic at high concentrations
- easily leaches out to rivers, ponds, lakes
- cause of lake eutrophication

### ■ Ammonia ( $\text{NH}_3$ )

- good fertilizer
- in high concentrations affects pH of soil

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## Biological Pollutants

- Human pathogens
- Medical Waste
- Animal pathogens

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