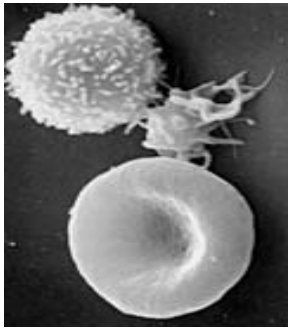
Environmental Chemistry

NIST & NanoEH&S

Three Major Areas

- **Standards**
- **Tools for Nanomaterial Characterization**
- **Methods/Data to inform health and environmental risk models**
  - **Robust methods to enable reliable toxicity testing**
  - **Metrology for evaluating transport and transformations of nanomaterials in biological and environmental systems**
  - **Methods to assess nanoparticle release and changes to nanocomposites from aging**



NIST Standard Reference Materials

Gold nanoparticles (10, 30, and 60 nm)
Single-wall carbon nanotube (raw soot) and dispersed into three length populations
Titanium dioxide nanoparticles (made from Degussa P25)
2 nm silicon nanoparticles
Silver nanoparticles (10 and 75 nm in preparation)
Multiwall carbon nanotube (in preparation)

Can be useful for interlaboratory comparisons, instrument validation and calibration, and positive and negative controls for nanotoxicity studies

Critical for establishing comparability of nano-related measurements.

Documentary Standards

NIST participates in standards organizations that provide validated documentary standards on a range of topics

- Carbon nanotube characterization (Raman, TEM, TGA, etc. for SWCNTs and MWCNTs)
- Nanoparticle characterization using a range of instruments for all nanoparticles (DLS, TEM, etc.) through the NIST/NCL protocols
- Sonication protocols that provide reproducible, traceable NP sonication between instruments and laboratories

Outline

- Solvent Properties
- Surface Tension
- Hydrogen Bonding

Solvent Properties

- Water is a substance that can almost dissolve anything. Salts such as sodium chloride (NaCl), dissolve in water by dissociating as each ion becomes surrounded by the polar water molecules. Shielded by a shell of water molecules, the ions stay in solution because they are no longer affected by attractive forces from other ions.

Surface Tension

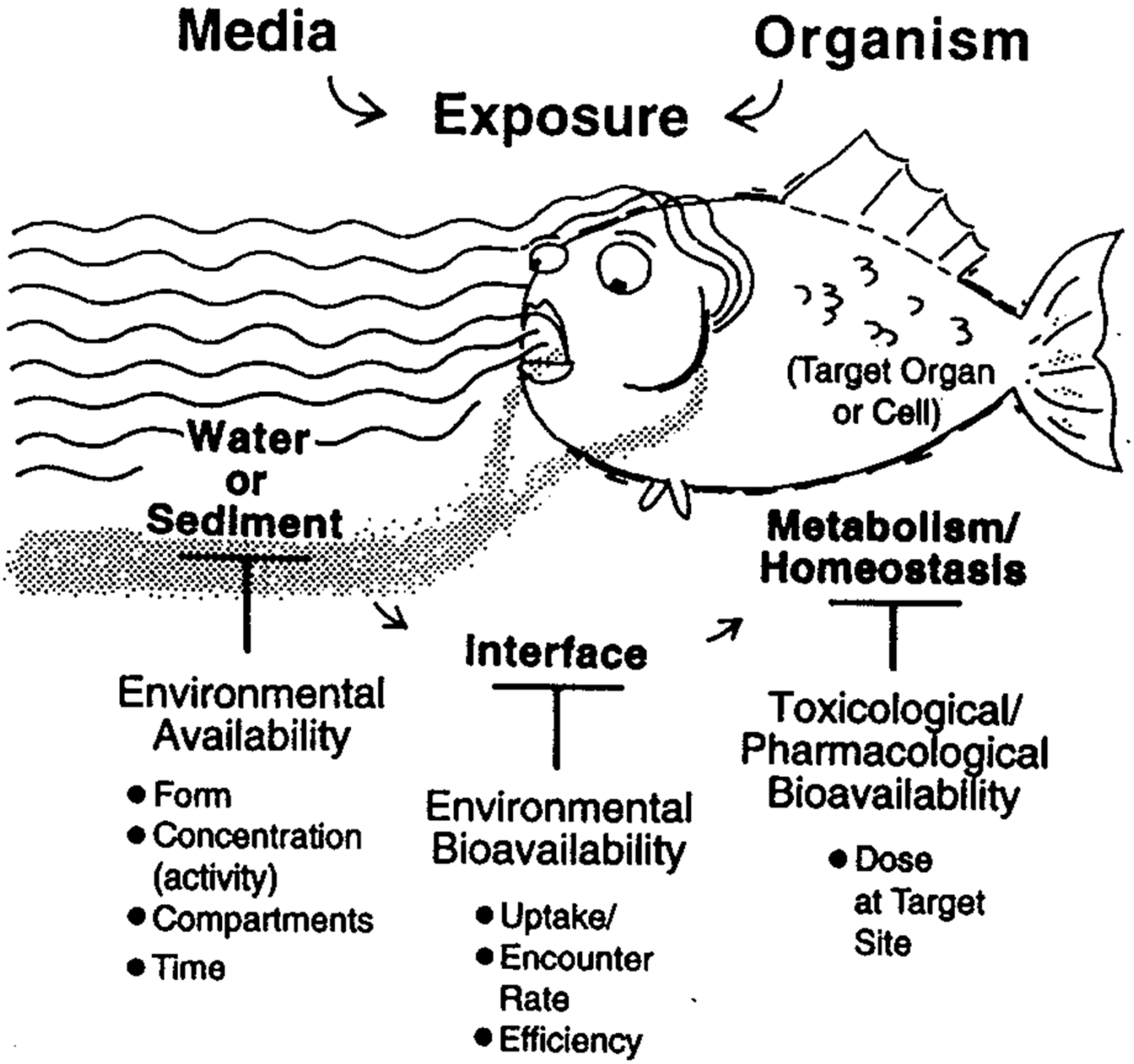
- Water has a greater surface tension than all other liquids except mercury. At the interface between water and air is an ordered arrangement of water molecules which are hydrogen bonded to one another and the water below. The result is an interface surface or film under tension. Students can observe the surface tension of water by overfilling a glass of water to the point where water stands above the rim.

Hydrogen Bonds

- Weak Bonds
- Plentiful
- Dictate solubility of solutes

Contaminant Solubility

- Hydrophilic Contaminants
- Hydrophobic Contaminants


Media
Organism
Exposure
(Target Organ or Cell)
Water or Sediment
Metabolism/ Homeostasis
Interface
Environmental Availability
• Form
• Concentration (activity)
• Compartments
• Time
Environmental Bioavailability
• Uptake/
• Encounter Rate
• Efficiency
Toxicological/ Pharmacological Bioavailability
• Dose at Target Site

Aquatic Ecosystems

Seawater (salinity = 33 - 37 ppt) and Freshwater (0.5 ppt)

- Conservative components (<99% of TDS):
  - chlorine, sodium, calcium, potassium, magnesium, sulfate
- Nonconservative components
  - dissolved gases
  - nutrients
  - dissolved silica
  - dissolved organic compounds
  - trace metals (< 0.05 µM)
  - colloids (< 0.45 µm in diameter)
  - particulate matter (sand, clay, excreta, nonliving tissues, organisms)

Aquatic Ecosystems

Oxygen regulates organism and community metabolism

O_2 solubility depends on temperature, partial pressure, and water salinity.

CO_2 serves as a buffer to prevent rapid shifts in acidity and alkalinity and it regulates certain biological processes

Calcium is most important and abundant dissolved solids

Ca > Mg > Na > K > P > Fe > S > Si

NOM: Allochthonous and autochthonous

Irradiation

Water is transparent

~ 90% of the radiation > 750 nm is absorbed at 1 m depth

Implications

plant and algal growth
contaminant fate
photosensitivity

Photochemical reactions

direct (UV energy is absorbed by the chemical's extended π-electron system and dissipated by bond-breaking)

indirect (a reactive species is generated photochemically from some UV-absorbing molecule and subsequently attacks the molecule of interest)

Acids and Bases

Strong Acids
HCl
H_2SO_4

Weak Acids
CH_3COOH
H_3PO_4

Strong Bases
NaOH

Weak Bases
NH_4OH

Autoprotolysis of Water

$H_2O <=> H^+ + OH^-$

$K_w = (H^+)(OH^-)/(H_2O)$

$K_w = 1.01 \times 10^{-14}$ @ 25°C

$pH = -\log[H^+]$

$pOH = -\log[OH^-]$

$p K_w = 14$

Carbonate System

$CO_{2(g)} + H_2O \rightarrow CO_{2(aq)}$

$P_{CO_2} = 10^{-3.5}$ atm

$K_H = CO_{2(aq)} / P_{CO_2}$

$K_H = 10^{-1.42}$ @ 25 ˚C

$CO_{2(aq)} = [H_2CO_3]$

$CO_{2(aq)} = 10^{-4.9}$ M

$K = [H_2CO_3]/CO_{2(aq)} = 1.6 \times 10^{-3}$

Carbonate System

$H_2CO_3 <=> HCO_3^- + H^+$ $\quad K_1 = [HCO_3^-][H^+]/H_2CO_3$, $pK_1 = 6.3$

$HCO_3^- <=> CO_3^= + H^+$ $\quad K_2 = [CO_3^=][H^+]/HCO_3^-$, $pK_2 = 10.25$

$C_T = [CO_3^=] + [HCO_3^-] + CO_{2(aq)} + [H_2CO_3]$

Total alk $= 2[CO_3^=] + [HCO_3^-] + [OH^-]$

Complexation

Ligands: Lewis bases that contain one pair of electrons that can form a coordinate covalent bond with metals

Water is a ligand, so are hydroxide, chloride, carbonate, and bicarbonate ions (monodentate ligands)

Glycine is a bidentate ligand

EDTA has 6 donor sites

Humic and Fulvic acids also contain oxygen donor atoms

(Salicylic acid is a good model)

Complexation

$Cd^{2+} + H_2O \iff Cd(OH)^{+} + H^{+}$ $\text{Log } K_1 = -10.08$

$Cd(OH)^{+} + H_2O \iff Cd(OH)_2^{o} + H^{+}$ $\log K_2 = -10.27$

$Cd(OH)_2^{o} + H_2O \iff Cd(OH)_3^{-} + H^{+}$ $\log K_3 = -12.95$

$Cd(OH)_3^{-} + H_2O \iff Cd(OH)_4^{2-} + H^{+}$ $\log K_4 = -14.05$

Contaminant

A substance released by man’s activities

A substance present in greater than natural concentration as a result of human activities.

Contaminant

Anthropogenic - man-made

Xenobiotic - foreign chemical or material not produced in nature

Major Classes of Contaminants

Metals and metalloids
Inorganic gases
Nutrients
Organics
Organometallic compounds
Pharmaceuticals
Nanoparticles (?)

Metals and Metalloids

- Most metals are malleable (can be pounded into thin sheets; a sugar cube chunk of gold can be pounded into a thin sheet which will cover a football field), and ductile (can be drawn out into a thin wire).
- All are solids at room temp (except Mercury, which is a liquid).
- Metals tend to have low ionization energies, and *typically lose electrons (i.e. are **oxidized**) when they undergo chemical reactions*.
- Alkali metals are always 1^+ (lose the electron in *s* subshell).
- Alkaline earth metals are always 2^+ (lose both electrons in *s* subshell).
- Transition metal ions do not follow an obvious pattern, 2^+ is common, and 1^+ and 3^+ are also observed.

Metals and Metalloids

Compounds of metals with non-metals tend to be ***ionic*** in nature.

Most metal oxides are basic oxides; those that dissolve in water react to form ***metal hydroxides***:

Metal oxide + water -> metal hydroxide

$Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq)$

$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(aq)$

Metals and Metalloids

- Metal oxides exhibit their ***basic*** chemical nature by reacting with ***acids*** to form ***salts*** and water:

Metal oxide + acid -> salt + water

$MgO(s) + HCl(aq) \rightarrow MgCl_2(aq) + H_2O(l)$

$NiO(s) + H_2SO_4(aq) \rightarrow NiSO_4(aq) + H_2O(l)$

Nutrients

- Nitrogen & Phosphorus
  - What is Eutrophication?

Polynuclear Aromatic Hydrocarbons

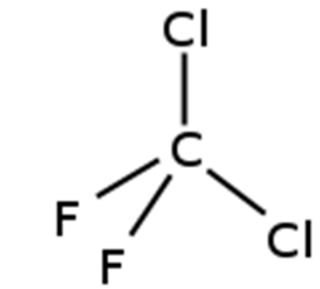
- Incomplete combustion of organic materials

Polychlorinated Biphenyls (PCBs)

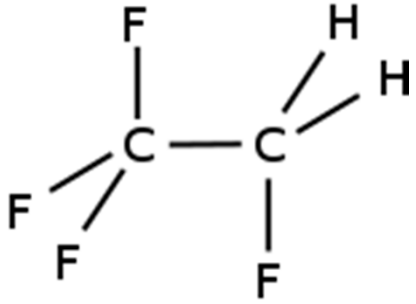
- Insulators, heat stabilizers in cooling oils

Chlorofluorocarbons

- refrigerants and production of styrofoam



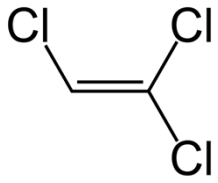
Dichlorodifluoromethane
(CFC-12)



1,1,1,2-Tetrafluoroetha
(HFC-134a)

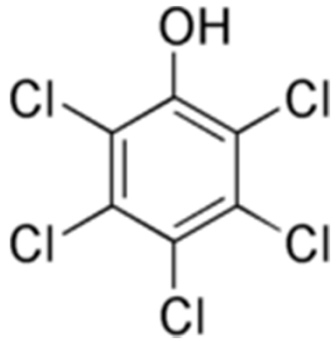
Organochlorine alkenes

- tetrachloromethane - dry cleaning solvent
- trichlorethylene - degreaser denser than water



Chlorinated Phenols

- Wood Preservatives
  - –Trichlorophenol
  - –Pentachlorophenol

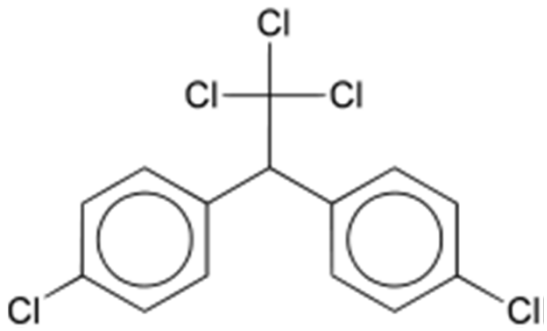


Chlorination Products

- Products of the reactions of chlorine with the organic compounds of wastewater effluents and natural organic matter – e.g. trihalomethanes

Organochlorine Pesticides

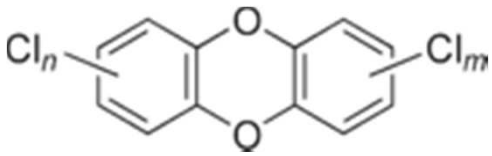
- First generation pesticides
- Insecticides
  - – lipophilic; high Kow; long half lives



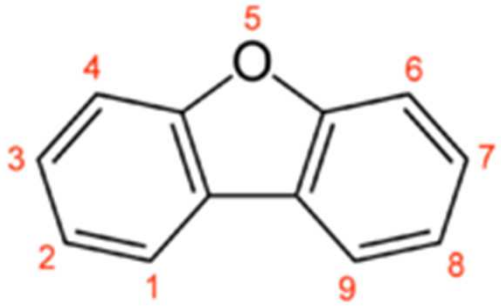
PCDD/PCDF

- By products of the incomplete combustion of PCBs, PVC, and other organochlrines

PCDD

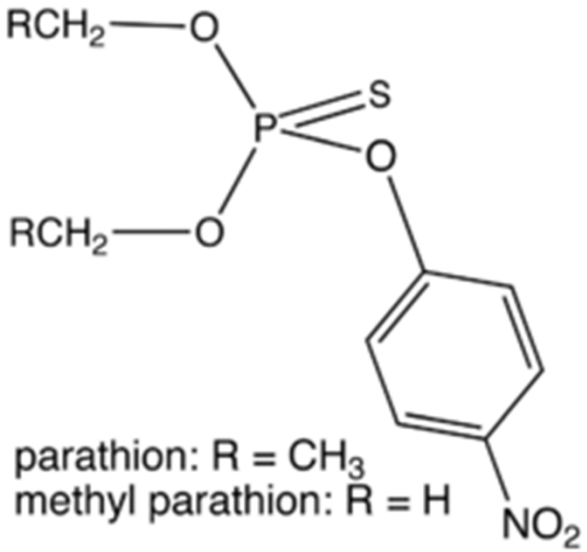


dibenzofuran



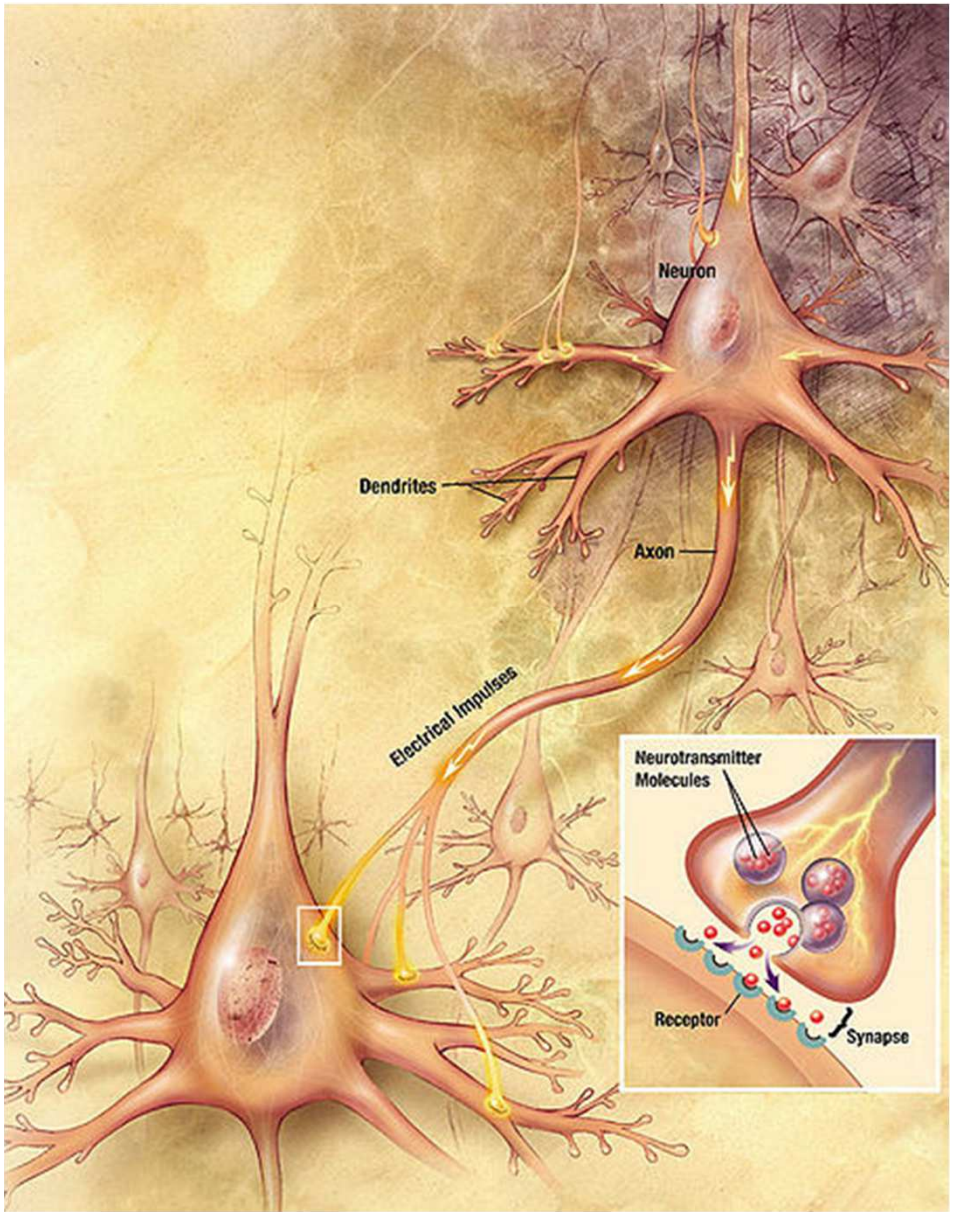
Organophosphate Insecticides

- Acetylcholinesterase inhibitors
  - – early OPs had high mammalian toxicity
  - – enzyme inhibition not reversible

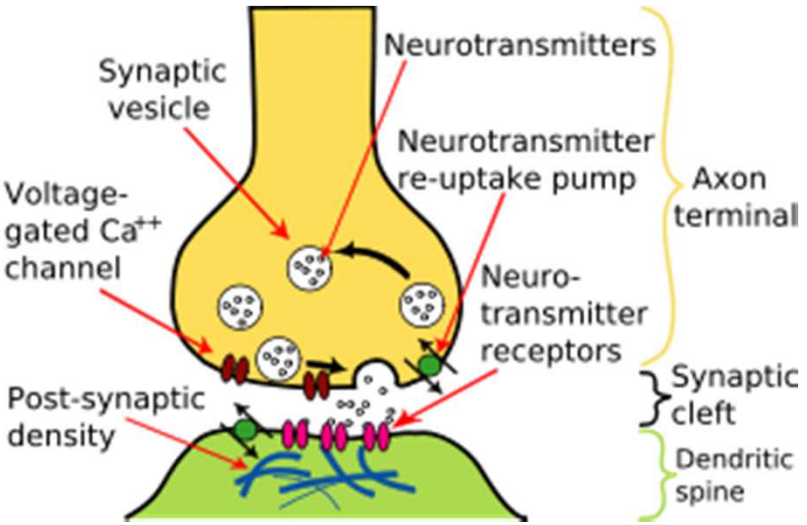


parathion: R = CH_3
methyl parathion: R = H

Anatomy of the Nervous System



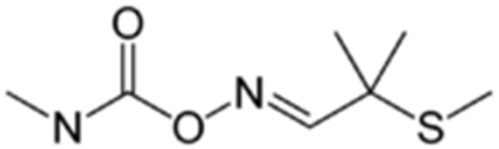
Synapse



Carbamate Insecticides

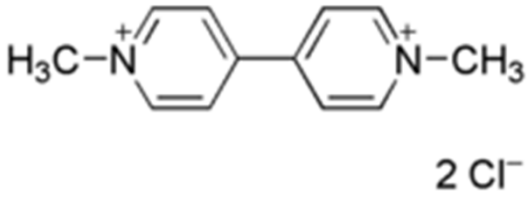
- Cholinesterase inhibitors
  - – enzyme inhibition is reversible

Aldicarb



Aromatic Herbicides

- Diquat & Paraquat



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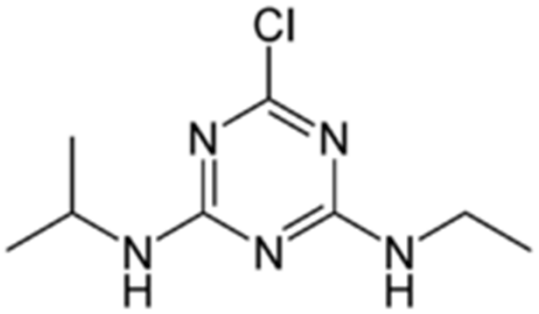
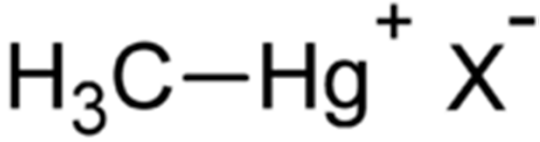
- Triazines

  – atrazine



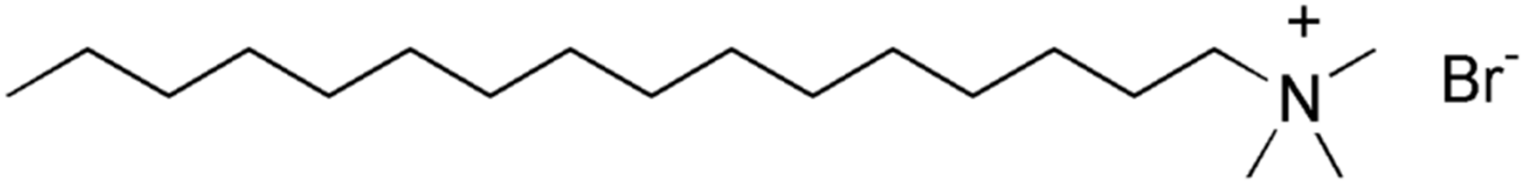
Organometallic Compounds

- Tributyltin
- Tetraethyl lead
- Organomercury

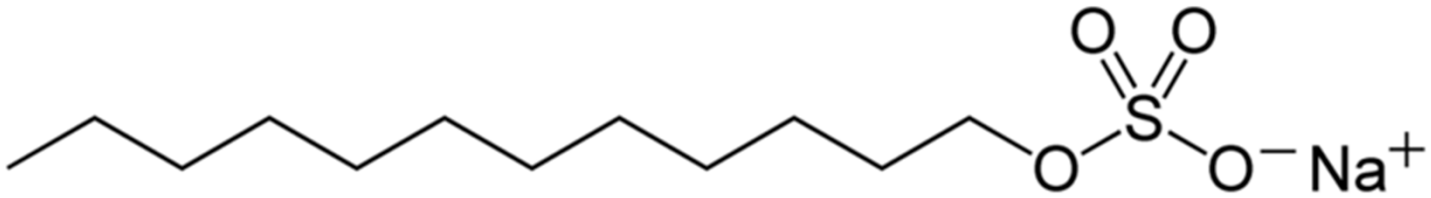


Surfactants

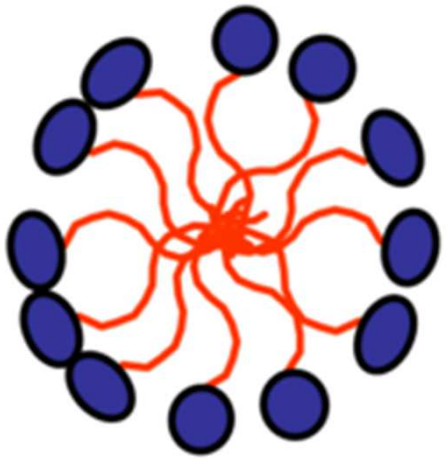
- Cationic – e.g. Cetrimonium bromide (CTAB)



- Anionic – e.g. sodium dodcyl sulfate (SDS)



Micelles



Pharmaceuticals

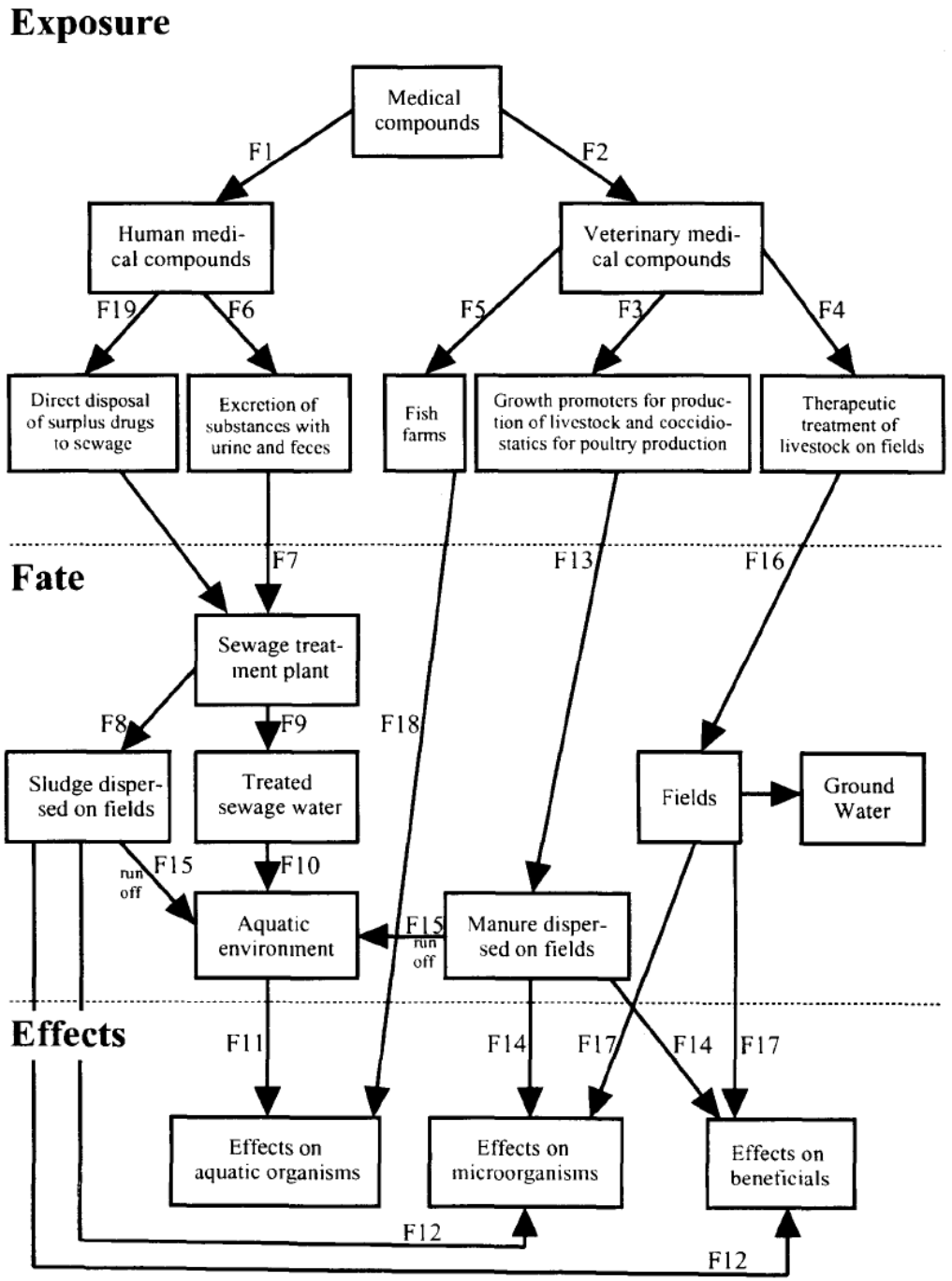


Figure 1. Anticipated exposure routes of both veterinary and human medicinal substances in the environment.

Sources of Pollutants

- Unintended Release
- Waste Disposal
- Deliberate Release

Contaminant Degradation

- ABIOTIC
- BIOTIC