Water constituents

What's in water

- **Suspended matter**
  - Mineral colloids; organic polymers; microorganisms
- **Dissolved inorganics**
  - Major vs. Trace
  - Nutrient vs. Contaminant
- **Dissolved organic matter (DOM)**
  - Simple vs. Polymeric
  - Biodegradable vs. Recalcitrant
  - Natural vs. Anthropogenic

Suspended matter

- **Not dissolved; potentially settleable (usually)**
  - Operationally defined: traditionally considered to be a material that retained on a 0.45 µm-filter
- **Mechanisms involved in fate**
  - Aggregation & sorption: dissolved → suspended
  - Deposited as sediment; sediment resuspension as suspended matter
- **Often found as aggregates**
  - Aggregates composed of mixtures of minerals, polymers, and microbial matter
  - Aggregates >0.45 µm may consist of many individual components <<0.45 µm

Suspended matter

- **Suspended mater influences:**
  - Contaminant fate
    - Contaminants attached follow the fate of suspended matter (transport/ deposition/resuspension)
  - Light attenuation
  - Disinfection efficiency

http://chasebc.ca

Microbes

- **Present in water in complex consortia**
- **$C_5H_7O_2N$ – approx. microbial chemical formula**
  - Dry weight basis; Cell is composed of ~90% water by weight
- **Other major constituents**
  - P: ~0.07 mole/mole cell material
  - S, Mg, Ca, K, Na: ~0.02-0.03 mole/mole cell material
  - Fe: more than trace, less than major
- **Trace constituents**
  - Cr, Co, Mn, Mo, Ni, Se, W, V, Zn
  - Constituents of enzyme systems
  - Need a little, but ***too much is toxic***

Dissolved inorganics

- **Major constituents of surface & groundwaters (ppm+)**
  - Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, HCO_3^-, SO_4^{2-}, SiO_2
- **Others important to life (ppb~ppm)**
  - O_2; Fe; N (NO_3^-, NH_3); P (PO_4^{3-})
    - N & P: rapid uptake by biota
    - P: strongly sorbed to minerals
    - Fe: low solubility in aerobic waters (Fe^{3+}) and moderate pH
- **Special cases**
  - Oxygen absent: high Fe^{2+}, S^{2-}
  - Low pH: high Fe^{3+}
- **Total dissolved solids (TDS): primarily ions**
  - Surface water < groundwater < seawater

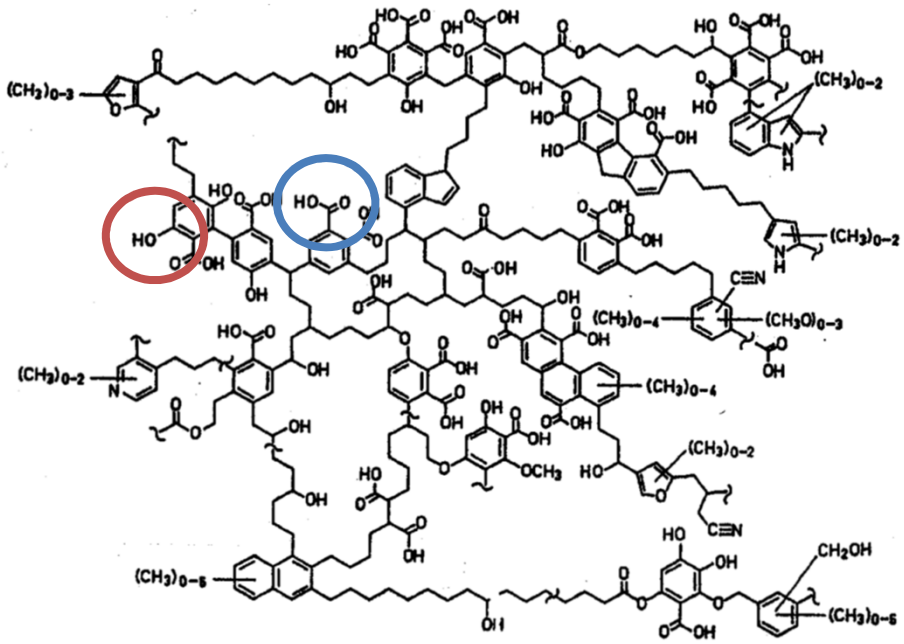
Organics in natural waters

- **Referred to as natural organic matter (NOM)**

- **Classification by origin: allochthonous vs. autochthonous**
  - Allochthonous NOM
    - Of terrestrial watershed origin
    - Influenced by the geology, land-use, and hydrology of the watershed
    - Exhibits humic character
  - Autochthonous NOM
    - Generated within the water column through microbial and algal activity
    - Includes glycolic enzymes, carbohydrates, polysaccharides, amino acids, peptides, enzymes, and toxins

Humic substances

- **Acidic polymers**
  - ~3-15 mmoles/g, primarily
    - Carboxylic
    - Phenolic OH

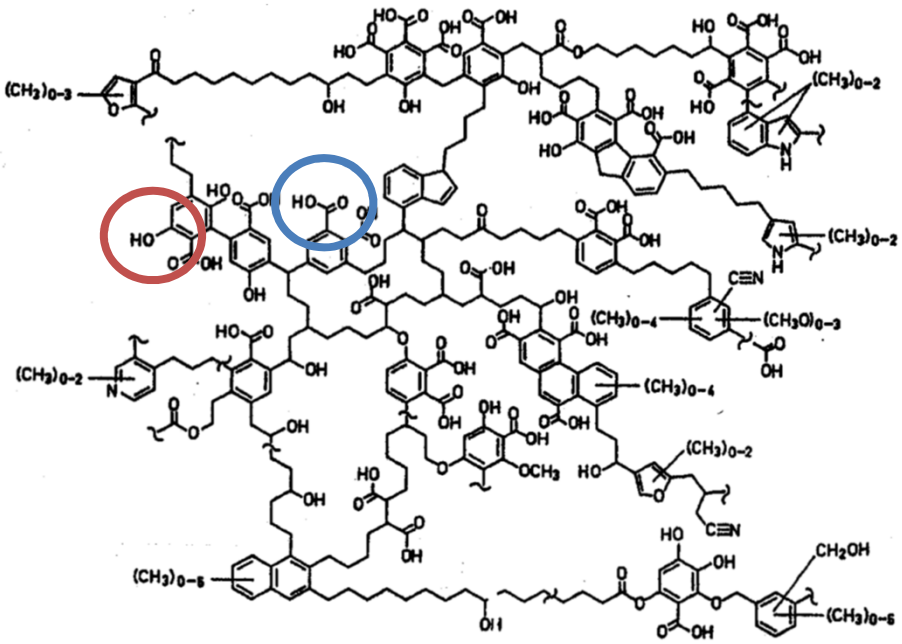


- **Wide varying composition**
  - There is no “humic molecule”
  - MWs from ~500 to >100,000

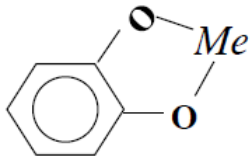
- **General classification**
  - Fulvic acid: soluble at all pH values
  - Humic acid: insoluble at pH<2 but becomes soluble at more alkaline pH
  - Humin: insoluble at all pH values

Humic substances

- **Hydrophilic/hydrophobic regions**
  - Binds a wide variety of chemicals
- **Molecular volume a function of pH, ionic strength**
  - Compact at high salinity, low pH
  - Extend at low salinity, high pH



Roles (impacts) of NOM - 1



- **Binds inorganic (e.g., metal ions) and organic chemicals via various mechanisms**
  - Chelation, complexation, hydrogen bonding, electrostatic interaction, hydrophobic interaction, etc.
- **Binding of chemicals by NOM may result in:**
  - Reduced bioavailability of the chemicals (i.e., reduced biodegradation rates, reduced toxicity)
  - Enhanced transport of hydrophobic organic chemicals
- **Absorbs light**
  - Light attenuation
  - Exhibits brownish color
  - Excited under sunlight to mediate transformation of other compounds (indirect photolysis)

Roles (impacts) of NOM - 2

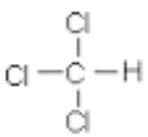
- **Mediates abiotic redox reactions**
  - Transfers electrons from and electron donor (i.e., oxidizing chemical) to an electron acceptor (i.e., reducing chemical)

- **In some cases, show adverse effects to aquatic organisms**
  - May accumulate on cell membranes
  - Toxic effects, deterioration of cell membrane structure, change in cell membrane permeability and functionalities

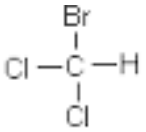
Roles (impacts) of NOM - 3

- **Impact on water & wastewater treatment**
  - Precursors for chlorine disinfection byproducts (THMs, HAAs)
  - Fouls membranes
  - Reduces efficiency of UV disinfection
  - Reduces longevity of activated carbon adsorption process by clogging pores

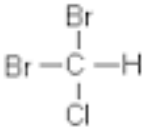
Trihalomethanes (THMs)



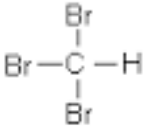
chloroform



bromodichloro methane

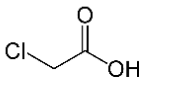


chlorodibromo methane

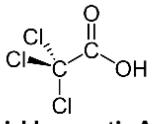


bromoform

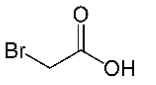
Halo acetic acids (HAAs)



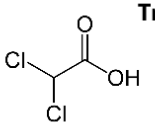
Chloroacetic Acid



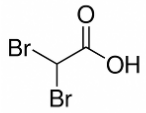
Trichloroacetic Acid



Bromoacetic Acid



Dichloroacetic Acid



Dibromoacetic Acid

Anthropogenic organics

- **A number of synthetic chemicals in daily use**
  - Estimated to be ~85,000 in the US and ~140,000 in the EU
  - Pesticides, solvents, dyes, personal care products, pharmaceuticals, anti-fouling agents, additives
  - >300,000,000 tons produced annually

- **Wide varying properties**
  - Size, aqueous solubility, volatility, degradability, toxicity

Terms referring to some set of organics

- Emerging contaminants or contaminants of emerging concern (CECs)
- Persistent organic pollutants (POPs)
- Trace organics
- Endocrine disrupting chemicals (EDCs)
- Pharmaceuticals and personal care products (PPCPs)
- Pesticides
- Surfactants
- Disinfection byproducts (DBPs)

Emerging contaminants

- Newly introduced chemicals and their transformation products, and chemicals (both synthetic and naturally occurring) with previously unrecognized adverse effects

- May include endocrine disrupting compounds (EDCs), pharmaceuticals and personal care products (PPCPs), plasticizers, surfactants, pesticides, detergents, nanoparticles, etc.

- Usually occur in ng/L to µg/L level

Persistent organic pollutants (POPs)

- Organic pollutants that are resistant to environmental degradation through chemical, biological, and photolytic processes

- **Mostly man-made chemicals**
  - Pesticides, solvents, pharmaceuticals, etc.
  - Often designed to be persistent; Exotic chemical structure for microbes

- **Stockholm Convention on POPs**
  - "To protect human health and the environment from POPs"
  - Adopted May 2001; 181 countries + EU approved (as of 2018)

POPs (continued)

Initial POPs under the Stockholm Convention (2001)

Name	Classification/origin	Name	Classification/origin
Aldrin	Organochlorine pesticide	Mirex	Organochlorine pesticide
Chlordane	Organochlorine pesticide	Toxaphene	Organochlorine pesticide
Dieldrin	Organochlorine pesticide	Polychlorinated biphenyls (PCBs)	Industrial chemical (e.g., coolant, insulating fluid)
Endrin	Organochlorine pesticide	Dichlorodiphenyltrichloroethane (DDT)	Organochlorine pesticide
Heptachlor	Organochlorine pesticide	Polycholrinated dibenzo-p-dioxins (PCDD or dioxins)	Unintentional byproduct of combustion
Hexachlorobenzene (HCB)	Organochlorine pesticide; industrial byproduct	Polychlorinated dibenzofurans (PCDF)	Unintentional byproduct of combustion & PCB production

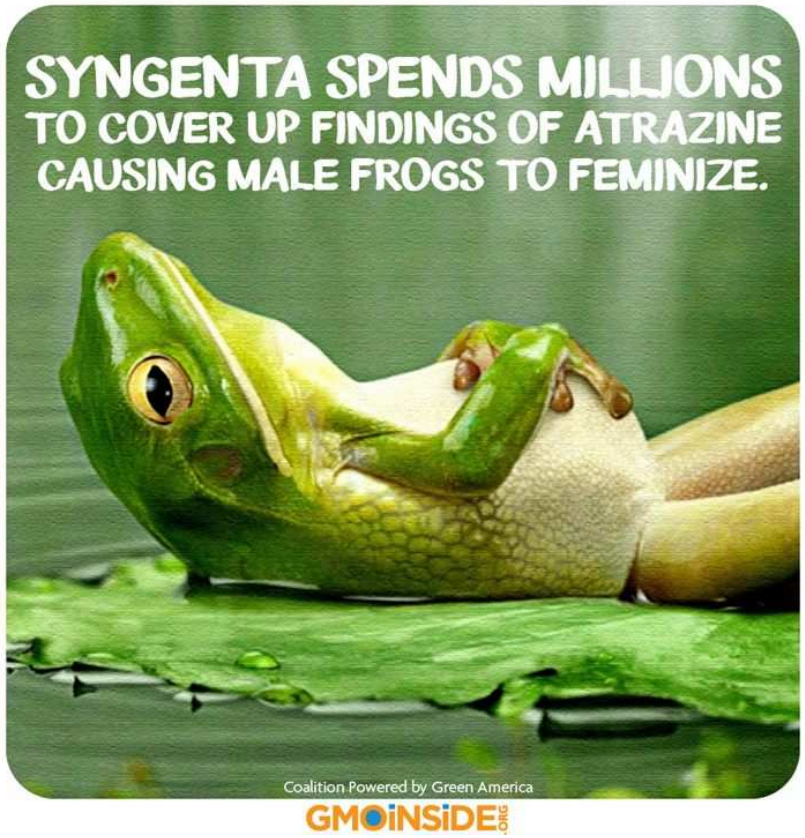
POPs (continued)

POPs added after 2011 under the Stockholm Convention

Name	Classification/origin	Name	Classification/origin
Polybromodiphenyl ethers (PBDEs); tetra-, penta-, hexa-, hepta-, deca-	Brominated flame retardant	Endosulfans	Organochlorine pesticide
Perfluorooctane sulfonic acid (PFOS)	Perfluorinated chemicals	Hexabromocyclododecane	Brominated flame retardant
Pentachlorobenzene	Industrial chemical (e.g., intermediate of pesticide production)	Hexachlorobutadiene	Solvent
Lindane	Organochlorine pesticide	Pentachlorophenol (PCP)	Organochlorine pesticide; disinfectant
Chlordecone	Organochlorine pesticide	Polychlorinated naphthalenes	Industrial chemical (e.g., insulation coatings)
α,β-hexachloro-cyclohexane (HCH)	Byproduct of pesticide production	Short-chain chlorinated paraffins	Industrial chemical (e.g., flame retardants, plasticizers)

Endocrine disrupting chemicals (EDCs)

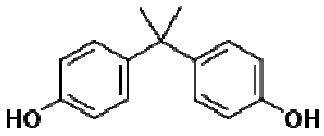
- **Chemicals that interfere with hormone systems**
- **May cause adverse effects to humans/other organisms at levels down to µg/L or ng/L**
- **Many are estrogenic**
  - Some anti-estrogenic, anti-androgenic, or androgenic EDCs also exist



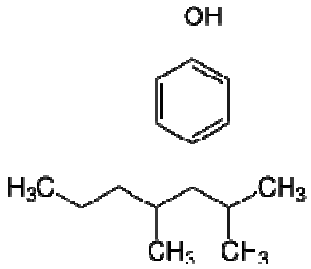
http://hines.blogspot.com/2013/06/frogs-feminized-but-atrazines-effects.html

EDCs – examples

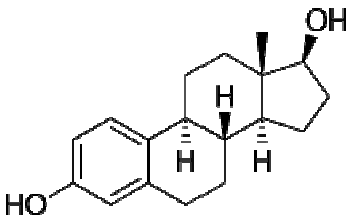
- **Chemicals that mimic the action of hormones**: bisphenol A, nonylphenol, octylphenol, triclocarbon, phthalates, atrazine, PCBs, …
- **Natural estrogens**: 17β-estradiol (E2), estrone (E1), estriol (E3)
- **Synthetic estrogen** (contraceptive pill): 17α-ethynylestradiol



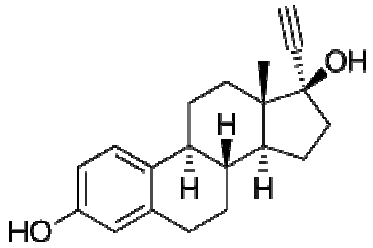
bisphenol A (BPA)



nonylphenol



E2



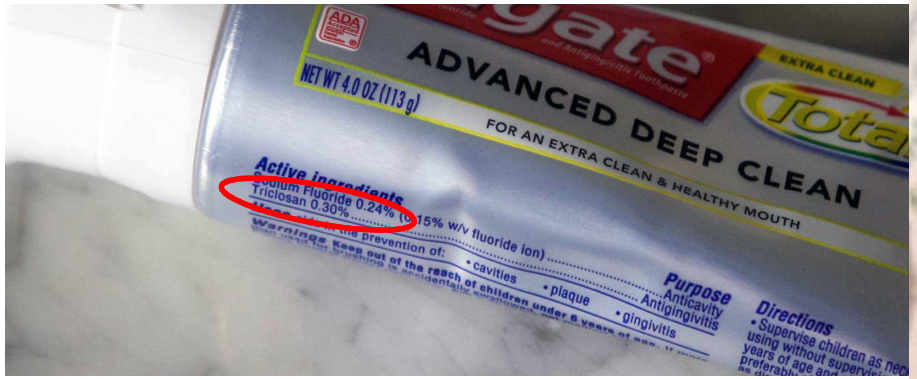
EE2

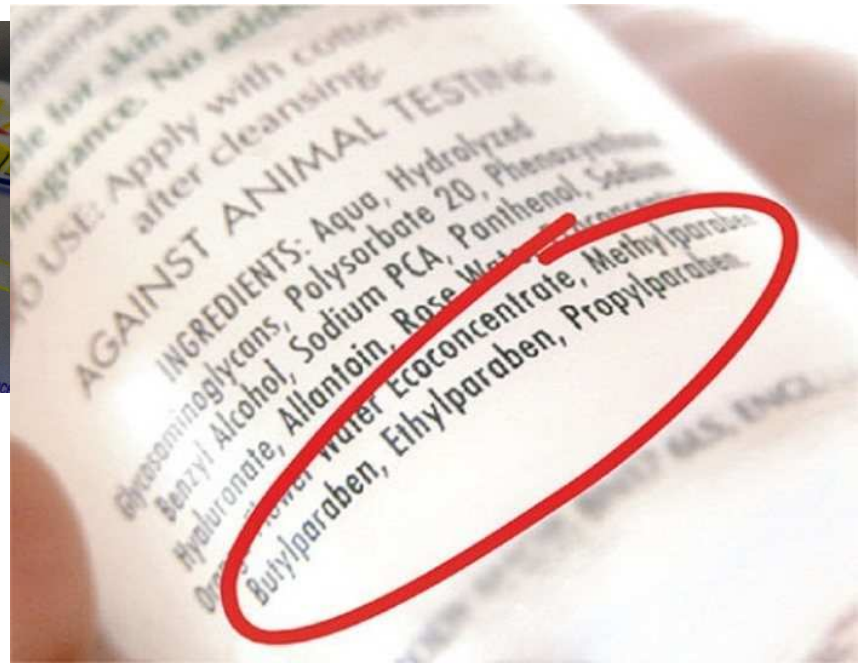
PPCPs – examples

- **Pharmaceuticals frequently found in wastewater**
  - acetaminophen (relieves pain/fever), ibuprofen (anti-inflammatory), naproxen (anti-inflamm.), diclofenac (anti-inflamm.), atenolol (treats high blood pressure), carbamazepine (anticonvulsant), sulfamethoxazole (antibiotic), **...**

PPCPs – examples (continued)

- **Chemicals used in personal care products that are frequently found in wastewater**
  - triclosan (antibacterial agent), parabens (preservative), synthetic musks (fragrances), caffeine (drinks), …

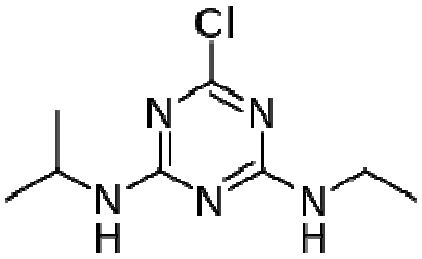




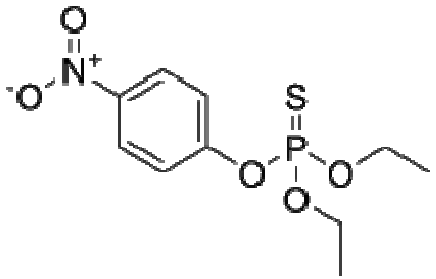
Pesticides

- **Herbicides, insecticides, fungicides, bactericides, rodenticides, nematicides, …**

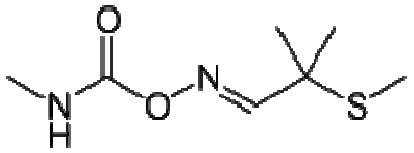
- **Examples**
  - Organochlorines: DDT, atrazine, aldrin, dieldrin, chlordane, mirex, toxaphene, diuron, …
  - Organophosphates: parathion, malathion, chlorpyrifos, …
  - Carbamates: aldicarb, carbofuran, carbaryl, …



Atrazine



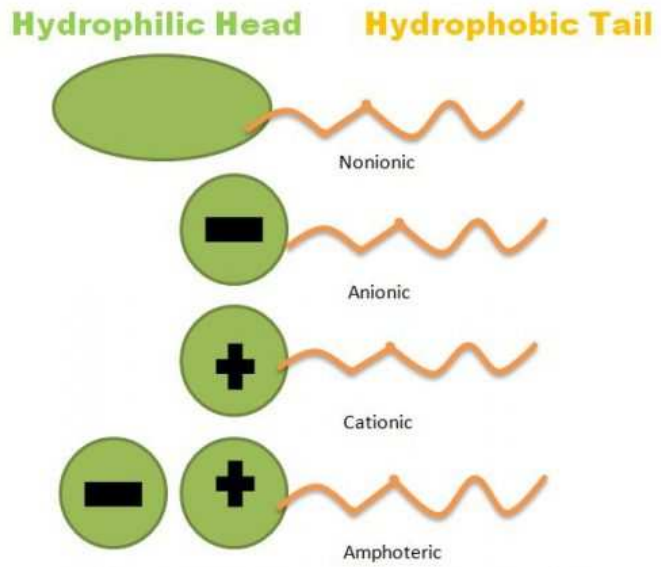
parathion

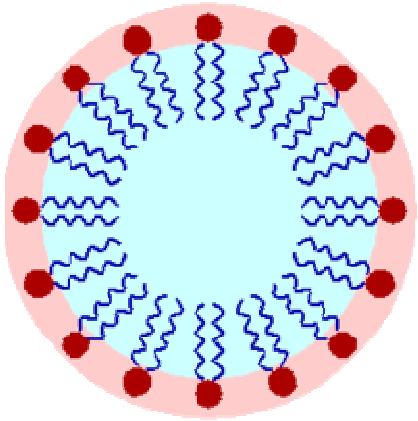


aldicarb

Surfactants

- **Surface-active agents**
- Compounds that lower the surface tension between two liquids, between a gas and a liquid, or between a liquid and a solid
- Usually organic compounds with amphiphilic property
  - Hydrophilic head + Hydrophobic tail
- Critical micelle concentration (CMC): concentration of surfactants above which micelles form

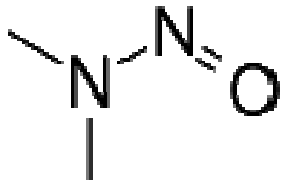




a micelle

Disinfection byproducts (DBPs)

- **Substances produced by chemical reactions during water disinfection process**
- **Chlorination DBPs**
  - Trihaolomethanes (THMs), haloacetic acids (HAAs)
  - Regulation history of > 40 years



NDMA

- **Nitrogenous DBPs**
  - Occurs in chloraminated water (or chlorination of ammonia-containing water)
  - Rather classified as emerging contaminants
  - N-nitrosodimethylamine (NDMA), N-nitrosodiethylamine (NDEA), etc.
- **Others**
  - Iodinated DBPs, inorganic DBPs (bromate, chlorite, etc.)