

## Organic contaminants in water



## Two Types of Contaminants

- Organic
  - Contain carbon
- Inorganic
  - Contain metals or metalloids



## Organics



- All organic means is that it is carbon based
- When you say organic contaminants in water- very wide range
- Plastic bag to dioxins to shampoo
- Big commonality is that they all eventually can turn into  $CO_2$  and that in order to do so, someone has to eat them

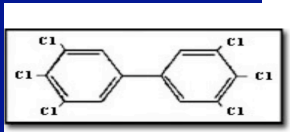
## Organics



- Eat them or burn them
- As all contain reduced carbon, they all store energy
- Energy can be used by bacteria eating them or can be dissipated by burning
- (think of wood)

## Revealing names

- For many organic contaminants
- The name is the same as the structure
- So for example
- **Hexa chloro bi phenol**



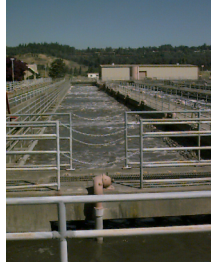
## Flame retardants

- PBDEs
- Poly brominated diphenol ethers
- poly brominated means that these compounds have a varying number of bromine atoms attached. Diphenol means that there are two phenol groups with a phenol group being a ring of carbon atoms with a hydroxyl group attached. Finally, an ether consists of two carbons with an oxygen in the middle.



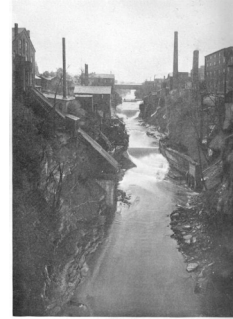
## Turn Carbon back to CO<sub>2</sub>

- Basic function of a Wastewater treatment plant
- To eat the carbon, you need O<sub>2</sub>
- That is why they bubble O<sub>2</sub> through the system- get the bugs to eat what is in there



But the bugs don't eat every thing- and not all water goes through the treatment plant

- Basic review of what organics do in water
- Different types of contaminants



Some organics don't mix with water

- Chemical formula of oil
- R-C-O-CH<sub>2</sub>



Others do

- Methanol
- 3CH<sub>3</sub>OH
- Ethanol
- C<sub>2</sub>H<sub>5</sub>OH

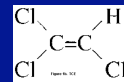


Not absolute

- There is an equilibria for all compounds
- They will each partition to solid, liquid, gas (Henry's Law)
- In the liquid phase- there will be a tendency towards hydrophobic or hydrophilic
- Kow- octanol water partition coefficient

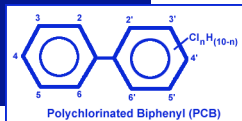
Two big factors

- Will it dissolve into water?
  - Kow
- Will it evaporate and become a gas?
  - Henry's law
- Tri chloroethylene
- Is both relatively soluble and has a high volatility



### Structure of the chemical will give you information

- More rings, larger, the less soluble (non polar not charged)
- More functional groups- things sticking off of the rings, greater the solubility in water
- (polar, charged)

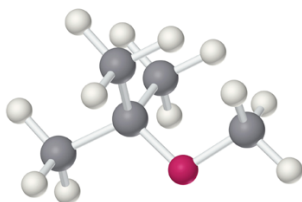


### Polar

- If it is polar- it will be soluble in water (remember that water is a polar molecule)
- It will have a low octanol water partition coefficient
- Low octanol: high water
- Your problem will be how to get it out of the water

### MTBE

- Added to gas as an octane enhancer
- Is soluble enough in water that it is now a big groundwater issue in CA
- <http://wps.prenhall.com>



Methyl *tert*-butyl ether

Solubility of MTBE is 5000 mg L in a gas that is 10% MTBE, increase Gas solubility as well

### MTBE

- MTBE smells and tastes bad
- It is detectable for people at 10-20 ppb
- This is about 10 000 times lower than the health threat concentration



After TCE, MTBE was the most commonly found groundwater contaminant

### TCE

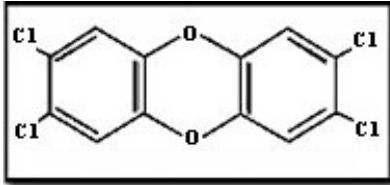
- Widely used as a solvent
- Is soluble enough in water that it is now a big groundwater across the country
- Phytoremediation
- Trees take up water, decompose compound



### Non-Polar

- If it is non polar- it will be insoluble in water (remember that water is a polar molecule)
- It will have a high octanol water partition coefficient
- high octanol: low water
- It will stick to the sediment
- Your problem will be how to get it out of the sediment

## Dioxins



## Hudson River, NY General Electric



## Non polar and water

### Immiscible liquids

- (cannot be mixed together, like oil and water)
- For example, a nonpolar liquid (e.g. carbon tetrachloride,  $CCl_4$ ) will not readily mix with water.
  - It will exist as a discrete liquid phase.
  - It is known as a *non-aqueous phase liquid* or *NAPL*.

## Non polar

- It is known as a *nonaqueous phase liquid* or *NAPL*.
- NAPLs with densities  $> 1$  kg/L are known as DNAPLs and those with densities  $< 1$  kg/L are known as LNAPLs.
- Why did the figure 1 kg/L get chosen as a separation point?
- Would LNAPLs sink?

## But remember...

- Even though  $CCl_4$  is considered to be a NAPL, a small amount of  $CCl_4$  will dissolve in  $H_2O$ . This doesn't involve a chemical change
- $CCl_4$  is also volatile so it can transfer to the gas or vapor phase.

## Non polar

- Will not be in water
- Will be in sediments
- Will this be a problem?



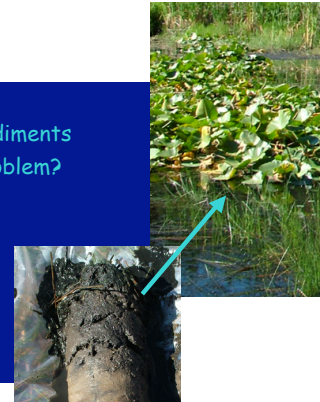
## Food chain transfer

- Bottom feeders
  - Will eat some of the sediment
  - Organic contaminants will be absorbed in fatty tissue
  - The fish or animals that eat the bottom feeders will eat the contaminants
  - biomagnification



## Polar

- Will be in water
- Will not be in sediments
- Will this be a problem?



## General categories of contaminants

- Industrial chemicals
  - Petroleum products
- Agricultural chemicals
- Household products

## Industrial chemicals

- Where would you expect to find these?
- Duwamish River
- (<http://yosemite.epa.gov/r10/cleanup>)



## Duwamish River

- South of Elliot Bay in Seattle
- Boat manufacturing and repair
- Airplane parts manufacture
- Combined sewer overflows
- Storm drains



## Contaminants include

- Polyaromatic hydrocarbons (PAHs)
- Polychlorinated bi-phenols (PCBs)
- Phthalates
- And mercury



## Site is listed

- Under US EPA's Superfund program
- Collect funds from responsible parties to pay for remediation
- These include Boeing, King County, City of Seattle, Port of Seattle



<http://yosemite.epa.gov/R10/CLEANUP.NSF>

## First step is to assess damage

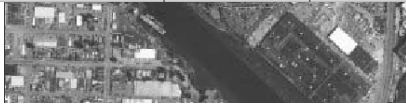
- Collect samples to determine extent and level of contamination
- Sediment toxicity assays
- Benthic community
- Salmon life history



<http://yosemite.epa.gov/R10/CLEANUP.NSF>

Clean up options:  
Consist of different degrees of removal and capping (for 1 small portion of the site)

	Material removed (in cubic yards)	Material placed for cap and fill (in cubic yards)	Estimated Cost
Alternative 1	8,100	27,000	\$ 6,000,000
Alternative 2	14,000	27,000	\$ 6,900,000
Alternative 3	27,000	20,000	\$ 8,700,000
Alternative 4	40,000	29,000	\$ 11,200,000



## Agricultural Chemicals

- Include nutrients (next week)
- And herbicides and pesticides
- Surface and groundwater contamination

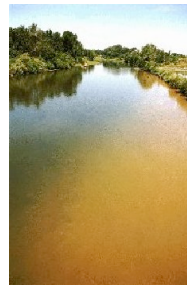


## Two pathways

- Erosion of surface soil into streams
- Movement through the soil profile into groundwater



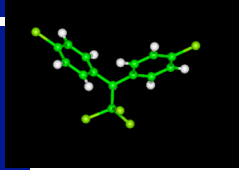
## Yakima River



[www.ecy.wa.gov](http://www.ecy.wa.gov)

## USGS - 1999

- 12 of 23 organo-chlorine compounds in unfiltered water samples detected
- DDT, DDE, Dieldrin, heptachlor epoxide exceeding water quality criteria

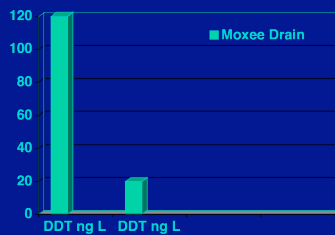


www.worldofmolecules.com

## Much improved

- In late 1980s fish in the Yakima had some of the highest DDT concentrations in the Nation
- Advisory issued
- Though much lower, still above for fish eating wildlife
- Use of DDT banned in late 1970s

## DDT concentrations over time



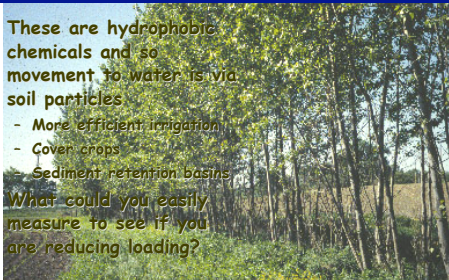
## Preventing flow to surface water

- Use of grassed or treed stream banks
- Set backs
- Active plant community will degrade compounds in addition to stopping particle movement



## Agricultural BMPs

- These are hydrophobic chemicals and so movement to water is via soil particles
  - More efficient irrigation
  - Cover crops
  - Sediment retention basins
- What could you easily measure to see if you are reducing loading?



## Groundwater

- Goes through the soil
- This will happen with more hydrophilic compounds
- Will happen in sandy soils where moisture is not limiting
- Why is this a concern?

## Temec in Long Island

- Used widely in the 1970s
- Initial testing showed more rapid decomposition
- Contaminated groundwater for large area of Long Island
- Drink bottled water



## Household products

- Things like perfumes, pharmaceuticals, detergents
- Things you use every day
- 'New organics'

## USGS Report

- Looked for a range of organic compounds downstream of CAFOs and WWTPs
- 95 Compounds looked for
- Found at least some of them in 80% of the streams sampled



## Compounds Identified

- Coprostanol (fecal steroid)
- Cholesterol (plant and animal steroid)
- N,N diethyltoluamide (insect repellent)
- Caffeine
- Triclosan (microbial disinfectant)
- Tri(2-chloroethyl)phosphate (flame retardant)
- 4-nonylphenol (nonionic detergent metabolite)

## The list includes

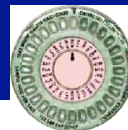
- Dehydronifedipine (prescription drug)
- Acetophenone (fragrance)
- Bis (2-ethylhexyl) phthalate (plasticizer)
- 17  $\alpha$ -ethynyl estradiol (ovulation inhibitor)
- Tri (dichloroisopropyl phosphate (fire retardant)



[www.cnn.com](http://www.cnn.com)

## Hormones

- WWTPs
- Primary source of hormones is birth control pills



- CAFOs
- Source of hormones supplements to diet





Though many of these compounds are from regular household products

- Their behavior in streams is not innocuous
- For example, 4-Nonylphenol (from detergents) is an endocrine disruptor and is known to cause damage to aquatic organisms



## Use of Endocrine disrupting chemicals



17% of frogs collected from farm ponds were deformed  
Rate on other ponds < 0.01%