

## Drinking Water

- surface water vs ground water
- issues in making water fit for consumption
  - clarification
  - presence of microorganisms
  - presence of natural contaminants
  - presence of industrial and agricultural pollutants
- municipal water treatment
  - primary settling of particulate matter
  - aeration
    - removes easily oxidizable substances (*ie.* Fe)
  - coagulation
    - removal of pollen, bacteria, spores, many viruses, colloidal minerals
    - filter alum
  - disinfection
    - kills residual bacteria and viruses
    - “chlorine residual”

## **Disinfection with chlorine**

- cheap, effective, chlorine residual
- HOCl (aq) more effective than ClO<sup>-</sup>(aq)
- chlorine dose, chlorine residual, chlorine demand, free available chlorine
- Taste and odour problems - chlorinated phenols
- chlorination byproducts - trihalomethanes.

## **Chlorine dioxide**

- unstable, must be made in situ from sodium chlorite
- an oxidizing agent, not a chlorinating agent
- no taste and odour problems, no residual effect

## **Ozone**

- unstable, must be made in situ from O<sub>2</sub>
- expensive
- an oxidizing agent, not a chlorinating agent, pH dependant
- no taste and odour problems, no residual in the water, )

## **Chloramine, NH<sub>2</sub>Cl**

- only used in domestic applications ... cottages etc
- a source of “available chlorine”

## **UV radiation**

- uses UV-C at 254 nm – germicidal lamps
- causes photochemical cross-linking of DNA
- flow-through system, not influenced by pH or temperature
- water must be clear and free of absorbing solutes

## **Metals in drinking water**

- cumulative poisons

- lead
  - a problem in older homes
  - soft water more of a problem
- cadmium
  - recent problem
  - electroplating and Ni-Cd rechargeable batteries
- arsenic
  - serious problem, especially in parts of Asia
  - WHO limit: previously 50 ppb, lowered to 10 ppb
  - problem with wells drilled to avoid drinking microbially-contaminated surface water
- nitrate
  - rural areas - fertilizer
  - in infants can result in mental retardation
  - active agent - nitrite from reduction of nitrate by intestinal bacteria
- fluoridation

## Organics in Drinking Water

- natural compounds
- anthropogenic compounds
- often survive drinking water treatment
- potential for adverse health effects
- difficult to link cause and effect - exposure at levels below those known to cause toxic effects
- does the dose-response curve remain linear at lower doses?

### Geosmin

- monoterpene produced by *Actinomyces sp*
- smells

### Removal of organics

- activated carbon
  - removes most organics
  - finite capacity - must be reactivated
  - expensive
- aeration
  - only effective for volatile species
  - depends on Henry's law equilibration

## Sewage Treatment

- is sewage treated at all
- mixed municipal storm/domestic sewers
- primary settling
  - “advanced primary treatment” - coagulants
- secondary treatment
  - biological treatment
  - reduce BOD
  - byproduct - sewage sludge
    - source of fertilizer / organic matter
    - also source of toxic metals
    - land treatment / incineration / landfilling
- tertiary treatment - remove specific contaminants
  - phosphorus
    - eutrophication problem - P usually limiting nutrient
    - major source - detergents
    - complex chemistry of Ca-PO<sub>4</sub> systems:
    - treatment is precipitation with either Al<sup>3+</sup> or Fe<sup>3+</sup>
  - other tertiary treatments - micro-straining and disinfection with chlorine
  - emerging concern: pharmaceuticals in treated sewage
    - antibiotics, prescription and non-prescription drugs, steroids, “wastewater-related” chemicals

## Phosphates in the context of soaps and detergents

- surfactants
- micelles
- soaps
  - long chain carboxylates
  - calcium salts insoluble in water
- detergents
  - long chain sulfonates (alkylbenzenesulfonates)
  - linear are degraded more readily than branched
- builders
  - source of  $\text{OH}^-$
  - added to detergents to improve grease-cutting

# Waste Disposal

## Landfilling

- secured sites vs unsecured sites
- problems:
  - ground settles
  - methane released - air pollution
  - seepage, leachate finding way to aquifers - ground water pollution

## Industrial Waste

- e.g. Love Canal
  - big ditch used for disposal of 20 000 t of chemical waste
  - homes built around area, roads crossed it, school built on the site
  - 1970's, toxic chemicals found in school yard and basements of nearby homes
  - people evacuated, relocated, houses expropriated
  - US\$140 million spent in an attempt to rehabilitate the area
  - 2 areas still considered uninhabitable
- not an uncommon situation

## **Industrial aqueous wastes**

- biological treatment for organic wastes - BOD reduction
- major industries: food; pulp and paper;
- aerobic and anaerobic reactors
- problems:
  - recalcitrant = discharged untreated
  - toxic = shuts down the reactor
  - solutions - advanced oxidation processes
    - source of reactive hydroxyl radicals to initiate oxidation
    - UV-ozone or UV-hydrogen peroxide
    - “Fenton” chemistry:  $\text{H}_2\text{O}_2/\text{Fe}^{2+}$
    - semiconductor assisted oxidation:  $\text{TiO}_2/h\nu$

## **Inorganic aqueous wastes**

- air stripping for ammonia - released to the atmosphere
- neutralization (waste acids and bases)
- breakpoint chlorination of ammonia
- oxidation/hydrolysis of cyanide ion

## **Remediation of contaminated soil**

- organics can be remediated; metals cannot
- usually industrial sites or dumps
- bioremediation is the preferred option
- “bugs in a bag”
- land farming
- “natural bioremediation”
- phytoremediation:
- soil washing, treatment of fines in a bioreactor
- incineration and vitrification
- costs

## **Remediation of ground water**

- flows often slow
- trichloroethylene (TCE) and tetra/per chloroethylene (PCE)
- pump-and-treat methods usually unsuccessful
  - continuing contamination from DNAPL sources
  - treatment usually involves oxidation: peroxide; Fenton’s reaction;  $\text{KMnO}_4$
- in situ permeable reactive barriers (PRBs)

## Chlorine and its Compounds

### The production of Cl<sub>2</sub>: the chloralkali process

- equal masses of NaOH and Cl<sub>2</sub> produced
- old style cell
  - H<sub>2</sub> and Cl<sub>2</sub> formed in separate steps
  - cost of Hg and losses of Hg to the environment
- Newer technology: diaphragm or membrane separated cells
  - membrane separates the H<sub>2</sub>(g) and Cl<sub>2</sub>(g) streams
  - no mercury is used

### Lipophilicity of chlorinated organics

- Organochlorine compounds- high lipophilicity.
- Partition Constant:

$$K_{\text{part}} = \frac{\text{concentration of solute in solvent 1}}{\text{concentration of solute in solvent 2}}$$

- octanol-water partition coefficient, K<sub>ow</sub>
- octanol as a model for fat.

## Relationship between $K_{ow}$ and bioconcentration factor, BCF

$$BCF = \frac{\text{concentration of toxicant in aquatic organism}}{\text{concentration of toxicant in surrounding water}}$$

$$BCF = K_{part} \times \% \text{ by weight of fat in the organism}$$

- if octanol is a good model for fat:  
 $BCF = K_{ow} \times \% \text{ by weight of fat in the organism}$
- if fat is  $\sim 5\%$  of wet weight:  $BCF \sim 0.05 \times K_{ow}$
- Environment Canada:  $K_{ow} > 1000$ , likely to bioconcentrate

## Kinetics of uptake and depuration

- measure rates of uptake and depuration

1.  $c(aq) \rightarrow c(fish)$   $k_1$
2.  $c(fish) \rightarrow c(aq)$   $k_2$
3.  $c(fish) \rightarrow \text{metabolic products}$   $k_3$

$$BCF = c(fish, ss)/c(aq) = k_1/(k_2 + k_3)$$

- measured BCF does not necessarily represent equilibrium
- bioconcentration is always associated with a low rate of depuration:  $\text{rate}[1] \gg \{\text{rate}[2] + \text{rate}[3]\}$

## **Chlorinated solvents: air and water pollution**

- Chlorinated alkanes, chlorinated alkenes
- degreasing solvents
- some covered by Montreal Protocol - concern is reaction rates with OH
- also ground water and drinking water contamination

## **Long range transport of organochlorines - Persistent organic pollutants (POPs)**

- Environment Canada: persistent if  $t_{1/2}$  in the atmosphere  $> 2$  days or "evidence of atmospheric transport to remote regions such as the arctic"
- low chemical and metabolic reactivity
- often associated with halogenated compounds
- able to distribute globally if even slightly volatile
- low volatility - polar deposition (DDT)
- high volatility - global distribution (CFC's)

## **Polybrominated diphenyl ethers (PBDEs)**

- widely used as flame retardants in
  - soft furnishings and bedding
  - childrens' sleepware
  - automobiles and aircraft
  - TV sets and computer housings
- toxicity largely unknown
- long range transport
- found to bioconcentrate
- being phased out in some jurisdictions

## **Toxic organochlorine aromatic compounds**

### **DDT**

- a 1940s/1950s insecticide

- effective against malaria mosquitos; cheap, readily applied
- discovered to be persistent in the terrestrial environment, , and to be ubiquitous in biota
- banned in developed countries 1969-1970
- residues still found in Canadian biota- long range transport

### **Polychlorinated Biphenyls (PCBs)**

- Produced ~1930-1970
- final North American ban 1976
- “closed uses” - dielectric fluids in transformers and capacitors
- “open uses”: plasticizers, de-inkers, golf ball interiors, carbonless copy paper
- 209 possible congeners

### **Why are PCBs still a problem?**

- improper disposal - leaching and volatilization
- very unreactive chemically - persistent
- highly lipophilic ( $\log K_{ow} > 5$ ): bioaccumulate
- Analysis - separation followed by GC-MS

### **Are PCBs toxic?**

- Acute toxicity very low: LD50 values ~ 1 g/kg
- “Coplanar” congeners - dioxin like toxicity
- chloracne

## **Destruction of PCBs**

- Incineration = high temperature combustion
  - $T > 1000^{\circ}\text{C}$  and contact time  $> 2$  s
  - Dioxin formation  $\sim 10^{-10}\%$
  - Storage vs transport
- combination with cement manufacture
- reaction with active metals
- photo-induced radical chain chemistry

## **Alterations in PCB congener distributions**

- Grasshopper effect - depletes more volatile congeners close to the source
- Microbial action - preferentially consumes less chlorinated congeners

## **“Dioxins”**

- PCDDs and PCDFs
- never intentionally manufactured - trace byproducts
- 75 PCDD congeners: 135 PCDF
  - 2,3,7,8-positions all substituted- high toxicity
- Historical background
  - Introduction of the herbicide 2,4,5-T
  - Explosions at chlorophenol manufacturing facilities
  - Pulmonary chick edema: “toxic fat syndrome”
  - Spraying of “still bottoms” from 2,4,5-T manufacture
  - Agent Orange in Vietnam
  - Underbrush spraying of forest lands in Oregon
  - Explosion at 2,4,5-trichlorophenol plant at Seveso, Italy
  - dioxins formed municipal and hospital waste incinerators

## **Toxicological issues**

- Extreme lethal potency, but not uniform across species
- Many other toxic endpoints are observed besides lethality
  - chloracne, teratogenicity, carcinogenicity, porphyria and immune suppression
- Mechanism of action involves binding to the Ah receptor

## **PCDDs are not the only “dioxin-like” substances**

- Concept of “toxic equivalency factors” (TEFs) and Toxic Equivalence (TEQ) =  $\sum(c_i \times TEF_i)$
- structure activity relationships

## **Endocrine disrupting compounds**

- substances that interfere with hormone action (agonists, or antagonist)

- estrogen mimics the most widely studied to date: androgens and thyroid hormone mimics becoming a research focus
- concerns about:
  - sewage works effluents
  - pulp and paper effluents
  - industrial spills
  - natural compounds
- a key issue is that hormones act at minuscule concentrations

### **Steroid hormones**

- biosynthesized in vertebrates from cholesterol
- the most important sex hormones estradiol and testosterone
- important in development esp. fetal development

### **Mechanism of action of steroid hormones – estradiol**

- binding to a steroid hormone receptor
- estrogen mimics bind to the ER
- to be an estrogen mimic, the molecule must:
  - be the correct size and shape
  - normally have polar groups (especially –OH) located to hydrogen bond with amino acids in the active site
- ER binding site described as “catholic”
- TEF of estradiol = 1

## **Effects possibly linked to endocrine disruptors**

- reproductive effects
- thyroid malfunction
- neurological disorders
- immunological disorders

## **Vitellogenin Production in Fish**

- vitellogenin - egg yolk protein produced by estrogenic stimulation
- vitellogenin production observed in fish exposed to domestic and industrial effluents

## **The pulp and paper industry**

- cellulose fibers vs lignin.
- hardwoods contain vs softwoods
- paper-making requires removal of the lignin
- Separated pulp is **bleached** to make fine paper
  - bleaching with chlorine → traces of dioxins
  - bleaching with chlorine dioxide and hydrogen peroxide
- endocrine effects down stream of pulp mills are similar for bleached and unbleached pulp → a natural component of the wood. Most likely candidate is  $\beta$ -sitosterol

## **Metals in the Environment**

- cannot be “destroyed”
- speciation may significantly affect toxicity

### **Mercury**

- Mercury occurs as the element or as the sulfide
- significant vapour pressure at ambient temperatures
- toxicity of mercury
  - metal and inorganic salts <<toxic than alkylmercury compounds
  - arylmercury compounds are not as toxic
  - neurotoxins and renal toxins
  - cumulative poison
- methylmercury compounds formed by microbial alkylation
- C-Hg bonds are non-polar - organomercury compounds are lipophilic and bioaccumulative

### **Exposure to mercury compounds:**

- Historically, gilding mirrors, alchemy, hatmaking
- Mining and refining mercury
- Gold mining
- Dental amalgams
- Scientific equipment and old science labs

### **Mercury in the wider environment:**

- Burning coal, volcanoes - not trapped as a flue dust
- Garbage incineration- Hg batteries
- chloralkali process
- in fish
- use as an industrial catalyst: Minamata Disease (Japan)

### **Principal problem remaining today:**

- air pollution due to coal burning and incineration (major)
- non-combustion sources chloralkali, cement production
- natural (volcanoes and flooding) and anthropogenic releases of Hg are of similar orders of magnitude

## **Lead**

- ancient times: plumbing systems, roofing
- modern uses:
  - solder: Pb-Sn alloy
  - paints
  - lead-acid batteries
  - gasoline anti-knock agents
  - crystal glass
  - lead shot
- Toxicity of lead:
  - $\text{Pb}^{2+}$  substitutes for  $\text{Ca}^{2+}$  in bone
  - organoleads are more toxic than inorganic lead
  - Pb can cross blood-brain barrier - neurotoxicity in adults and children; mental deficits in children
  - lead recycling - air pollution

## **Lead in gasoline**

- “straight run” gasoline – tendency to knocking/pinging
- addition of tetraalkyl lead compounds as “antiknock agents”
- roadside dusts are high in inorganic Pb compounds
- catalytic converters incompatible with leaded gasoline → unleaded gasoline
- Related issue: oxygenates and MTBE
  - MTBE
  - ethanol

## **Lead-acid battery (in cars)**

- electrochemistry

- Problems with lead-acid batteries:
  - low energy density
  - recycling – secondary lead smelters
  - improper disposal:
    - landfill leachate
    - poisoning of cattle

## **Arsenic**

- abundant element but few uses
- toxic: essentially no known role as micronutrient
- organoarsenicals are less toxic than inorganic arsenic
- shellfish contain arsenobetaine and arsenocholine - non-bioavailable, water-soluble, readily excreted.

## **Issues in many parts of Asia**

- UNICEF program to provide new wells - reduce water-borne disease
- thousands of cases of skin disorders - arsenicosis
- levels up to 1-5 mg/L
- no good (cheap) methods for arsenic removal
- no simple test for As

## **Origin of arsenic in water**

- naturally occurring arsenopyrite ( $\text{FeAsS}_2$ )
- details of the solubilization chemistry are unclear and controversial
  - If oxidation chemistry predominates, dig the wells deeper
  - If reduction chemistry predominates, deeper wells mean more anaerobic conditions

## **Uptake**

- Efficient for soluble inorganic As
- Low for insoluble salts, and from soil.

## **Inhalation toxicology**

- Dusts of  $\text{As}_2\text{O}_3$  are the commonest form in air - metal smelters
- clear evidence of increased risk of lung cancer
- Uptake: 40-60% of the amount inhaled.

## **Effects**

- low doses for weeks or months - GI upset
- Acute doses - neurotoxin
- Dermal effects
- Long term oral exposure- skin cancer, also lung, bladder, liver

## **Metabolism and mechanism of action**

- Humans more susceptible to As intoxication than lab animals

## **Biomarkers for exposure**

- Analysis of hair and fingernails
- Analysis of blood does not give useful data.
- No preferential accumulation in specific organs

## **Acid Mine Drainage (AMD)**

- Major problem, Canada and elsewhere, (abandoned) mine sites – both metal ore mines and coal mines
- Biological origin of AMD – microbial oxidation of sulfides
- AMD problems are:
  - toxicity due to low pH
  - toxicity due to solubilization of metals Cu, Pb, Zn, Cd, Ni etc
  - deposition of  $\text{Fe}(\text{OH})_3$  downstream

## **Dimensions of the AMD problem**

- The Clark-Fork site, Montana
  - 50,000 acres
  - contaminated with As, Cu, Cd, Pb, Zn
- Richmond Mine, Iron Mountain, California
  - subsurface - extreme acidity pH to  $-3.6$
  - metal concentrations to 200g/L

## **AMD remediation**

- Exclude air through:
  - submersion of tailings
  - cover the tailings with soil and grow grass
- Cathodic protection using sacrificial Fe or Zn anode
- Remediate seepage via:
  - neutralization
  - wetlands as filters
  - phytoremediation using engineered wetlands
  - electrochemical technologies