

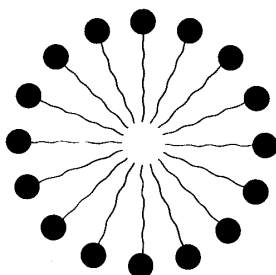
Sewage Treatment

- problem of whether sewage is treated at all – including in Canada – and mixed municipal storm/domestic sewers
- primary settling (“advanced primary treatment” by the addition of coagulants – same as in DW treatment)
- secondary treatment: biological treatment using trickling sand filters or activated sludge reactors: reduce BOD by means of microbial oxidation
- byproduct of secondary treatment is **sewage sludge** – (“biosolids”!), an excellent source of fertilizer elements N, P, K and of organic matter to amend soil *but* also contains toxic metals, including Cu, Cd, Pb, Hg, Zn, Cr, Ni, mostly because of deposition of industrial liquids into the municipal sewers
 - Ontario produces 400,000 t of sludge annually
 - alternative to land treatment is incineration or landfilling —> leachates
 - amount of sludge that can be applied safely depends on soil type: clays bind metal cations. Ontario MOE has *guidelines* for land application, but few analyses are done
 - sludge is *digested* in order to dewater it —> solid material *or* is spread directly as “liquid biosolids” —> concern about microbial contamination
 - possibility of entry of toxicants into human food supply through pathways such as soil —> plant —> human *or* soil —> plant —> animal —> human

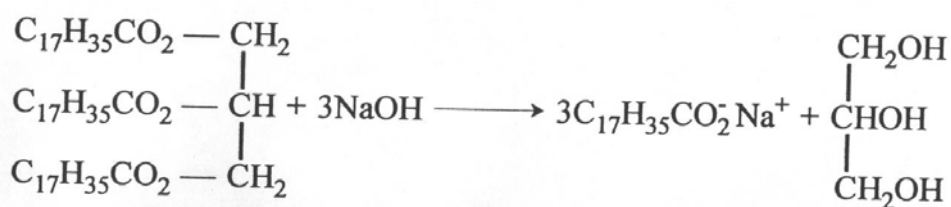
- tertiary treatment to remove specific contaminants
 - phosphorus (eutrophication problem since P is usually the limiting nutrient: ratios of C: N: P for optimal growth 100: 15: 1): see text pp. 238-240
 - major source of P in sewage is detergents, levels of which are now limited
 - P content of detergents is sodium tripolyphosphate (STP) which is used to sequester Ca^{2+}
 - complex chemistry of Ca-PO_4 systems:
- $\text{Ca}_3(\text{PO}_4)_2$ is highly insoluble (rock phosphate) and has to be solubilized to be used as a fertilizer (superphosphate)
- polyphosphates have the structure $-\text{O}-(\text{PO}_2-\text{O})_n-\text{PO}_2-\text{O}-$ and are analogous to ATP. Both linear and cyclic polyphosphates exist
- unlike monophosphate, polyphosphates form soluble complexes with Ca^{2+}
- like ATP, polyphosphates hydrolyze to monophosphate; monophosphate is discharged to the environment from sewage plants if untreated
 - usual tertiary treatment for PO_4 is precipitation with either Al^{3+} or $\text{Fe}^{3+} \longrightarrow \text{AlPO}_4$ or FePO_4 (insoluble)
 - other tertiary treatments include micro-straining and disinfection with chlorine (now out of favour): see also ammonia removal, later

Phosphates in the context of soaps and detergents

- surfactants: long chain hydrocarbon with polar head group – form *micelles* in water above the *critical micelle concentration*

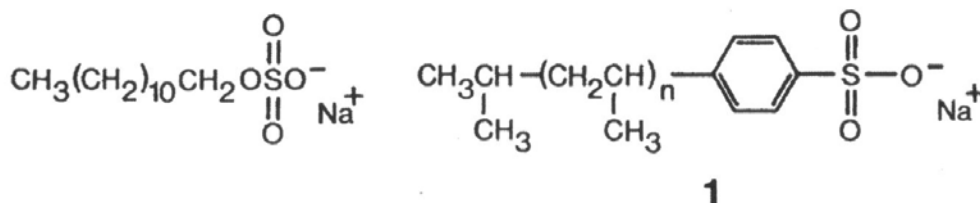


- soaps are long chain carboxylates: *e.g.*



calcium salts of carboxylic acids are insoluble in water
 —> scum

- detergents are long chain sulfonates or, less frequently, sulfate monoesters

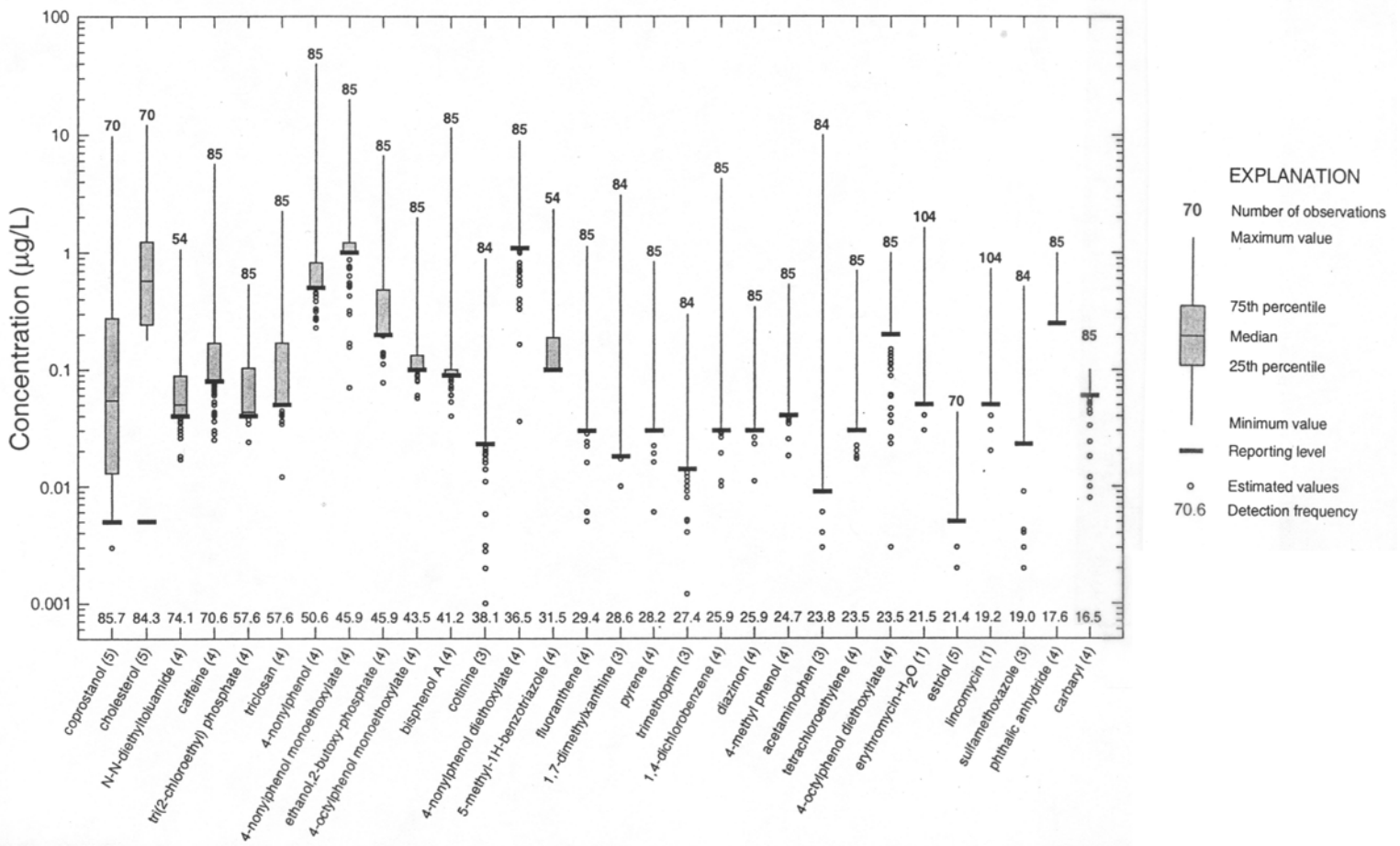


Dreft, an alkyl sulfate

1
 alkylbenzenesulfonate

- this sulfonate is a *branched chain* alkylbenzenesulfonate

- emerging concern: pharmaceuticals in treated sewage (*Environ. Sci. Technol.*, 36, 1202, 2002)
 - bigger issue in Europe than North America (population density)
 - compounds detected include antibiotics, prescription and non-prescription drugs, steroids (see later: endocrine disrupters), as well as “wastewater-related” chemicals



- data refer to 139 US rivers and streams

Industrial aqueous wastes

- biological treatment the best option for organic wastes
- “biox” reactors = aerobic, analogous to activated sludge reactor for sewage
- major industries: food; pulp and paper; BOD makes these wastes damaging to the environment if untreated. Major goal is BOD reduction
- organic matter converted to CO_2 + microbial biomass
- anaerobic reactors less common: slower (hence less throughput), “off gases” are odorous amines and sulfides
- volume of reactor depends on treatment time and volume of waste to treat per unit time

$$V(\text{reactor}) = \text{Flow rate (m}^3 \text{ h}^{-1}) \times \text{Residence time (h)}$$

- problems of recalcitrant and toxic compounds
 - recalcitrant = discharged untreated
 - toxic = shuts down the reactor

“Advanced Oxidation Processes” for recalcitrant and toxic wastes: generally involve aqueous hydroxyl radicals

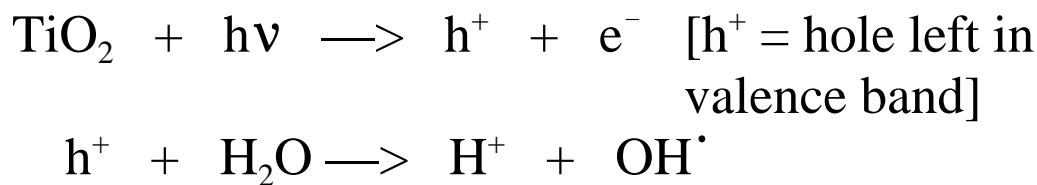
- UV-ozone or UV-hydrogen peroxide: source of OH_{aq} which initiate oxidation by H-abstraction or addition to double bonds (*cf* Chapter 3)



- “Fenton” chemistry: $\text{H}_2\text{O}_2/\text{Fe}^{2+}$



- semiconductor assisted oxidation (much hyped!)



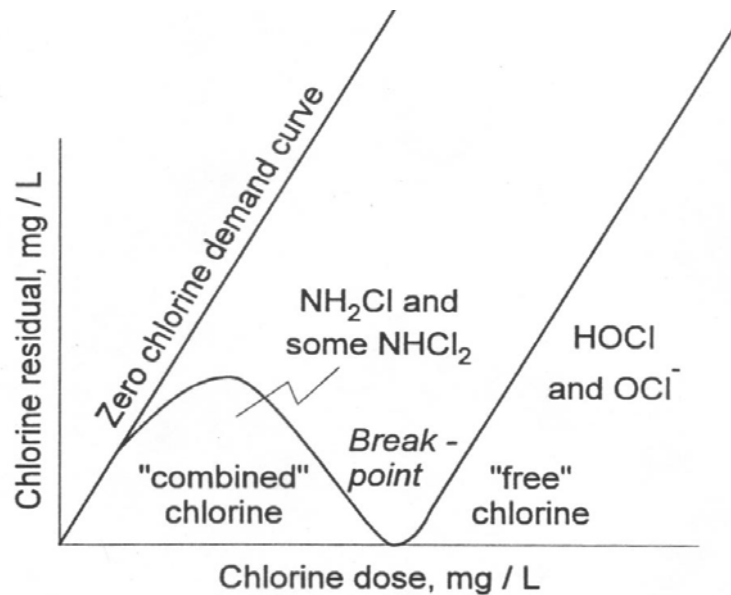
The idea is that sunlight could be used because TiO_2 absorbs in the UV-A region

- electrochemical oxidation: a “green” approach as only electrons are involved. Problems include the need for a supporting electrolyte; electrodes made of inexpensive materials free from fouling
- mediated electrochemical oxidation *e.g.* Ag^+



Inorganic aqueous wastes

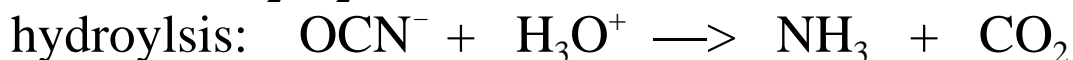
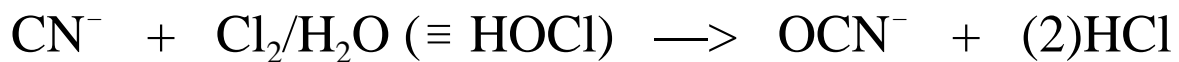
- air stripping (Henry's Law) for ammonia (and also for low molar mass organics): undesirable because it releases material to the atmosphere
- neutralization (waste acids and bases)
- breakpoint chlorination of ammonia



Schematic of the progress of a breakpoint chlorination

overall chemistry: $2\text{NH}_3 + 3\text{HOCl} \longrightarrow \text{N}_2 + 3\text{HCl} + 3\text{H}_2\text{O}$

- oxidation/hydrolysis of cyanide ion



CN⁻ can also be oxidized electrolytically



Remediation of contaminated soil

- Organics can be remediated; metals cannot. Bioremediation is the preferred option.
- Most contaminated areas are former industrial sites or dumps; gas stations; wood treatment. Unremediated “brownfields” sites cannot be redeveloped.
- In situ remediation by stimulating microbial growth: limitation of “bugs in a bag”
- Land farming: issues of VOC release and accumulation of high molar mass compounds including PAHs
- “Natural bioremediation” = do nothing
- Phytoremediation: both inorganics and organics: for metals need “hyperaccumulators”. Also applicable to aqueous streams: engineered wetlands
- Soil washing followed by treatment of the fines in a bioreactor: expensive and destroys soil structure; horseradish peroxidase as an enzymatic approach
- Incineration and vitrification: “last resort” methods, but guaranteed as permanent solutions
- Costs per site usually tens of million \$\$: US Superfund legislation for “orphaned” sites

Solidification – cement and lime-based technologies

Cement manufacture: $\text{CaCO}_3(\text{s}) \longrightarrow \text{CaO}(\text{s}) + \text{CO}_2$ Typically contains 60-65% CaO, 20-25% SiO_2 (see text, p. 272)

Making concrete: $\text{CaO} + \text{H}_2\text{O} \longrightarrow \text{Ca}(\text{OH})_2$

Setting concrete: $\text{Ca}(\text{OH})_2 + \text{CO}_2 \longrightarrow \text{CaCO}_3 + \text{H}_2\text{O}$

Examples:

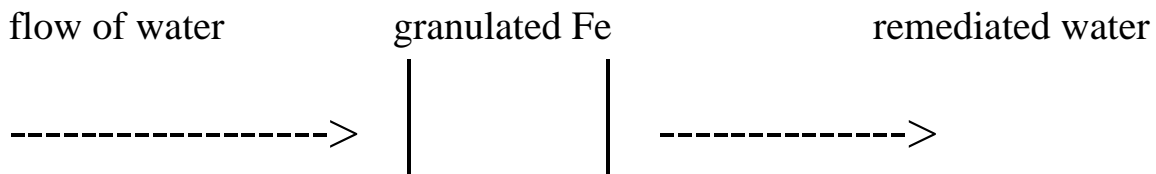
- setting the finely divided solids from flue gas desulfurization
- radioactive wastes: combination of vitrification and concrete encapsulation: Yucca Mountain, Nevada

For a story on Yucca Mountain in *Chem Eng News* see:

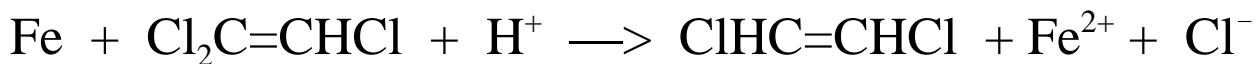
<http://pubs.acs.org/subscribe/journals/cen/81/i01/html/8101gov1.html>

Remediation of ground water

- flows often slow: m yr^{-1} ; slowest in clay
- commonest contaminants trichloroethylene (TCE) and tetra/per chloroethylene (PCE)
- pump-and-treat methods usually unsuccessful, due to DNAPL sources continuing the contamination [DNAPL = **dense non aqueous phase liquid]**
- treatment usually involves oxidation: peroxide; Fenton's reaction; KMnO_4
- in situ permeable reactive barriers (PRBs) involving granulated iron (Gillham, U of Waterloo): useful for chlorinated aliphatics



$\text{Fe}(0)$ acts as **reductant**



—> further reduction of dichloroethylene

- Read descriptive material in the text pp. 258-280