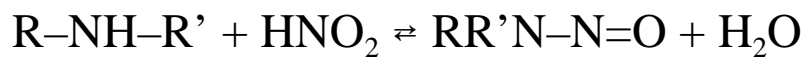


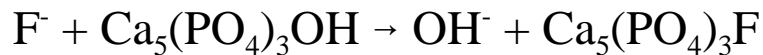
Metals in drinking water

- solubilization in acidic waters (acid mine drainage ... much later)
- concern because most are cumulative poisons (rate of excretion is slow): Hg, Pb, Cd, As
- lead a problem in older homes (“plumbing”/solder)
 - lead and mental retardation (also lead-based paints)
 - soft water more of a problem: Pb slightly more electropositive than hydrogen
 - “first draw” water
 - Pb concentrations reduced from 50 to 10 ppb
- cadmium a relatively recent problem, with the use of Cd in electroplating and Ni-Cd rechargeable batteries
- mercury as a problem more often associated with food intake than water
- arsenic a serious problem, especially in parts of Asia: Bangladesh, Taiwan, Vietnam
 - WHO limit: previously 50 ppb, lowered to 10 ppb
 - levels in Bangladesh recorded 1-5 ppm in some places
 - problem associated with wells drilled to avoid drinking microbially-contaminated surface water
 - skin eruptions, skin cancer, internal cancers, “blackfoot disease”, neurotoxicity: hundreds of thousands affected
 - testing of wells for those safe to drink
 - US controversy over reduction of limit to WHO standard
- nitrate generally a problem in rural areas:

- contamination of wells from fertilizer
- 45 ppm (10 ppm of nitrate nitrogen)
- methemoglobinemia in infants can result in mental retardation
- active agent is actually nitrite formed by reduction of nitrate by intestinal bacteria
- nitrite ion can nitrosate amines and amides - carcinogenic nitrosamines



- fluoridation: to medicate or not to medicate?



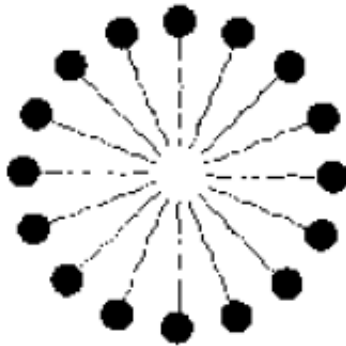
Sewage Treatment

- 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

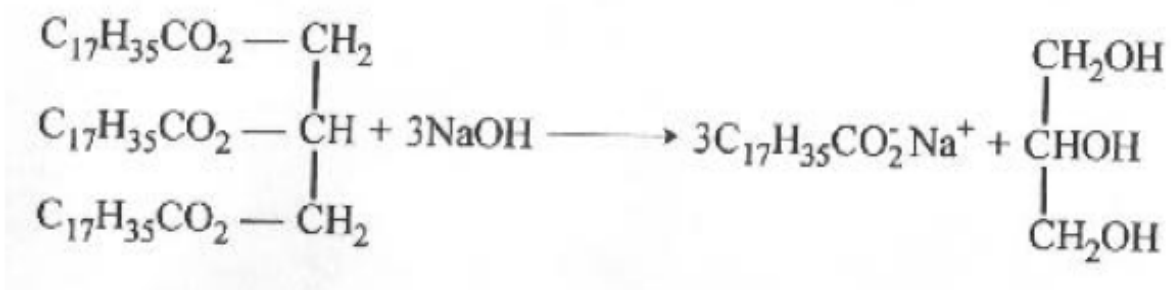
- phosphorus (eutrophication problem since P is usually the limiting nutrient: ratios of C: N: P for optimal growth 100: 15: 1): see text pp. 238-240
- major source of P in sewage is detergents, levels of which are now limited
- P content of detergents is sodium tripolyphosphate (STP) which is used to 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 $\text{Fe}^{3+} \rightarrow \text{AlPO}_4$ 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*

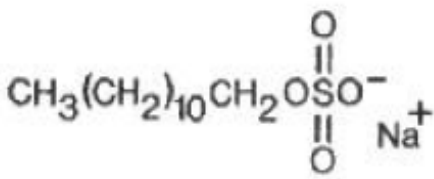


- soaps are long chain carboxylates: e.g.

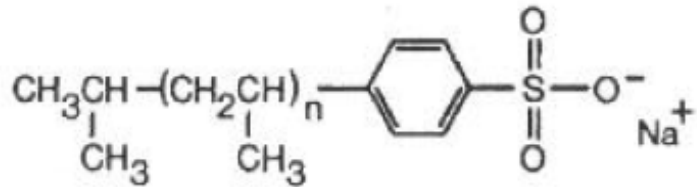


- calcium salts of carboxylic acids are insoluble in water
→ scum

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



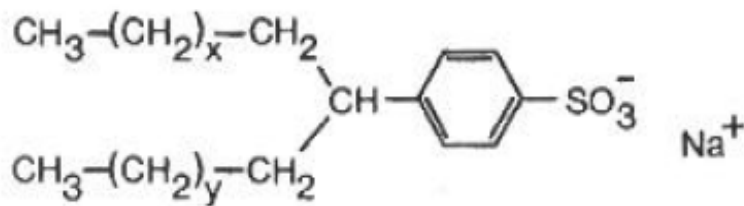
Dreft, an alkyl sulfate



1

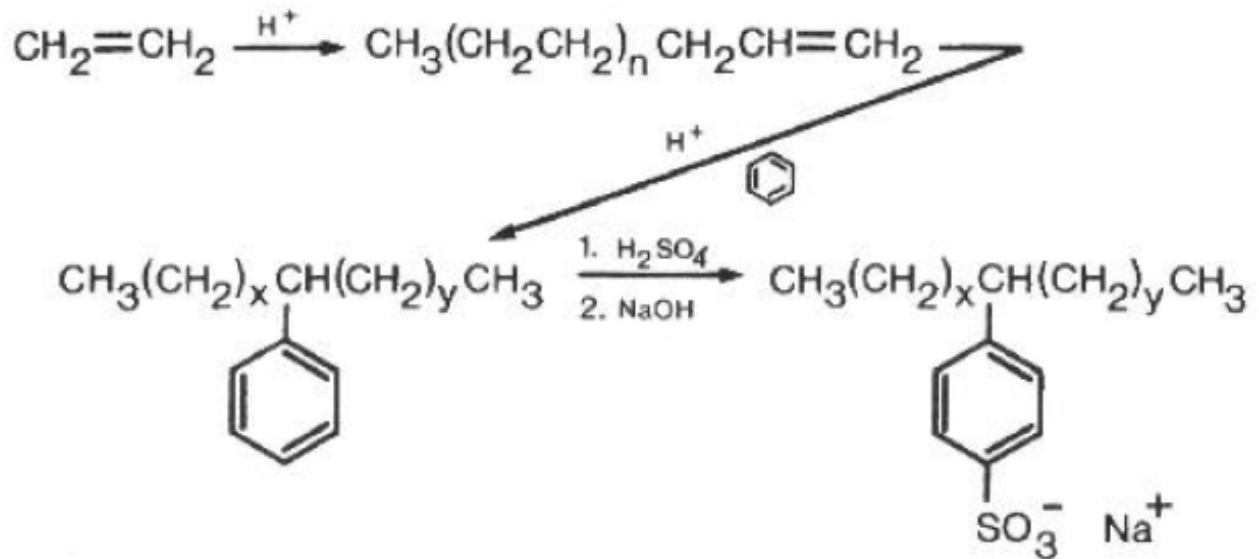
alkylbenzenesulfonate

- this sulfonate is a *branched chain* alkylbenzenesulfonate
- linear* alkylbenzenesulfonates are degraded more readily during sewage treatment



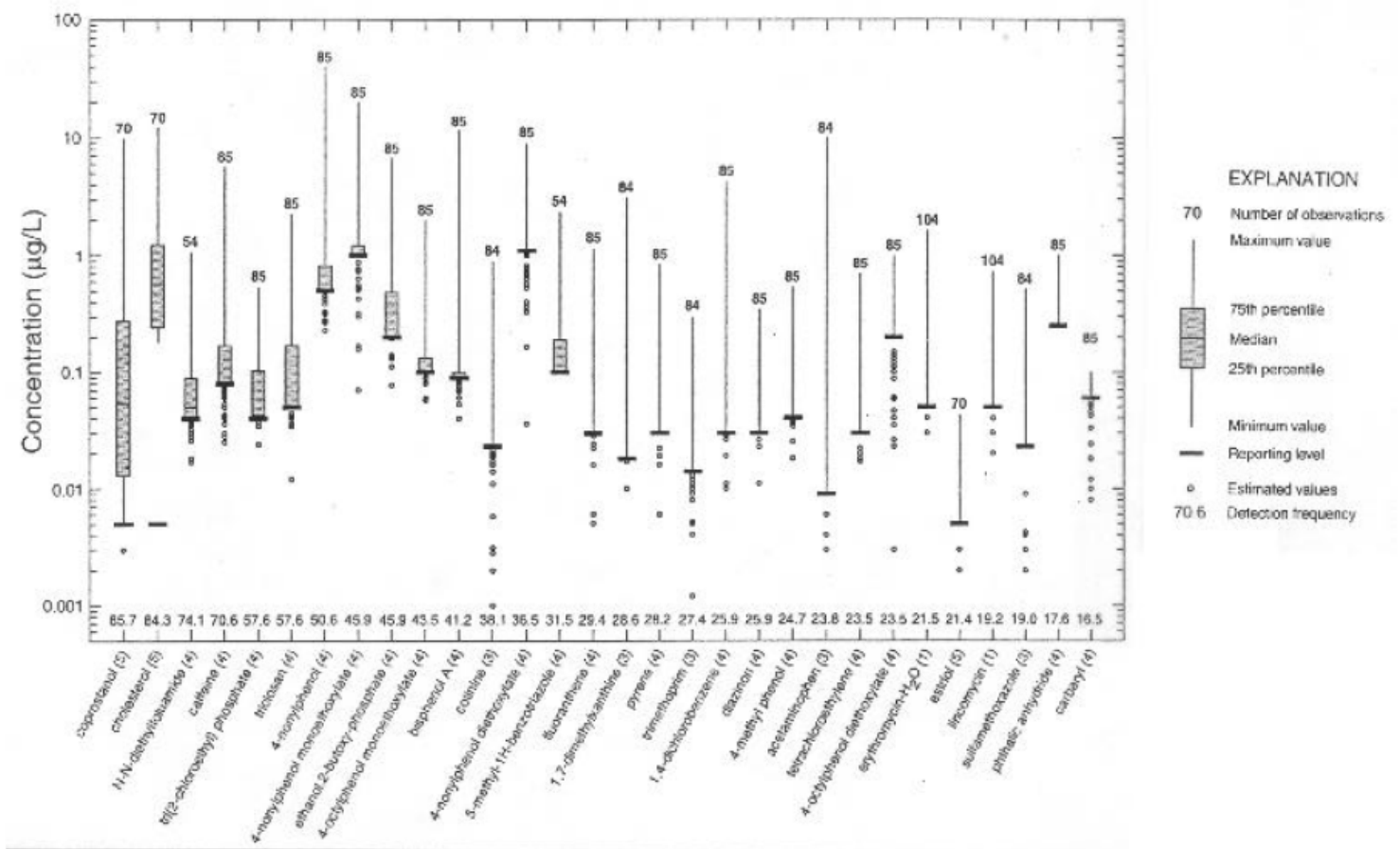
2

- alkylbenzenesulfonates are made by Friedel-Crafts alkylation of benzene, followed by sulfonation



- Detergent 1 (previous page) made from propene
- builders (source of OH^-) are added to detergents to improve grease-cutting
 - RCO_2^- acts as its own builder
 - phosphates have a dual role: builder and Ca sequestration
 - sodium carbonate is a non-phosphate builder, but precipitates Ca
 - “industrial” detergents often contain NaOH (pH >12)

- 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 CO₂ + 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

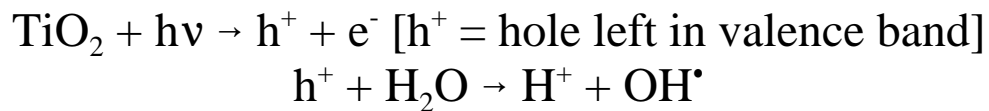
- “Advanced Oxidation Processes” for recalcitrant and toxic wastes
 - UV-ozone or UV-hydrogen peroxide: source of reactive hydroxyl radicals



- initiate oxidation by H-abstraction or addition to double bonds (cf Chapt. 3)
- “Fenton” chemistry: $\text{H}_2\text{O}_2/\text{Fe}^{2+}$



- semiconductor assisted oxidation (much hyped!)

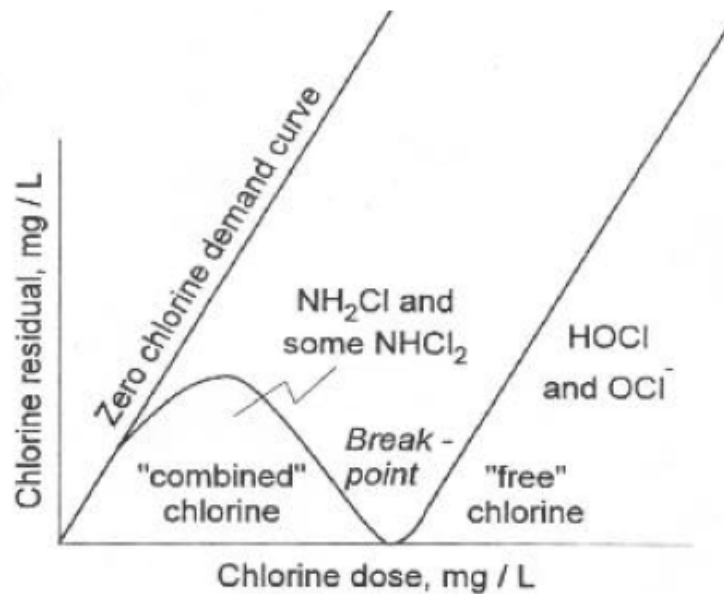


- The idea is that sunlight could be used because TiO_2 absorbs in the UV-A region
- electrochemical oxidation: a “green” approach as only electrons are involved. Problems include the need for a supporting electrolyte; electrodes made of inexpensive materials free from fouling
- mediated electrochemical oxidation e.g. Ag^+

$$[\text{Ag}^+ \rightarrow] \text{Ag}^{2+} + \text{H}_2\text{O} \rightarrow \text{Ag}^+ + \text{H}^+ + \text{OH}^\bullet$$

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

- oxidation/hydrolysis of cyanide ion

$$\text{CN}^- + \text{Cl}_2/\text{H}_2\text{O} (\equiv \text{HOCl}) \rightarrow \text{OCN}^- + (2)\text{HCl}$$

$$\text{OCN}^- + \text{H}_3\text{O}^+ \rightarrow \text{NH}_3 + \text{CO}_2$$
- oxidation can also be done electrolytically

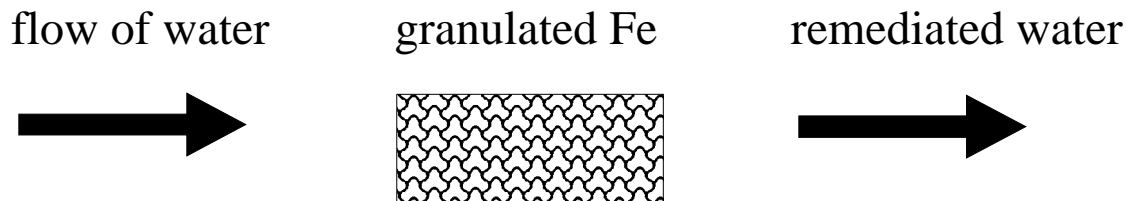
$$\text{CN}^- + \text{H}_2\text{O} \rightarrow \text{OCN}^- + 2\text{H}^+ + \text{e}^-$$

Remediation of contaminated soil

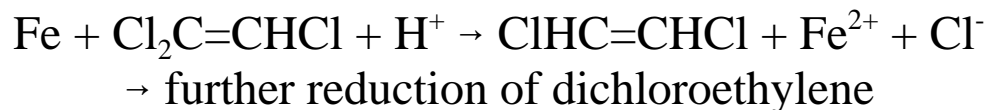
- organics can be remediated; metals cannot. Bioremediation is the preferred option. Most contaminated areas are former industrial sites or dumps; gas stations; wood treatment. Unremediated “brownfields” sites cannot be redeveloped.
 - in situ remediation by stimulating microbial growth: limitation of “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

Remediation of ground water

- flows often slow: m yr; 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
 - treatment usually involves oxidation: peroxide; Fenton's reaction; KMnO_4
- in situ permeable reactive barriers (PRBs) involving granulated iron (R.W. Gillham): useful for chlorinated aliphatics



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



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