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

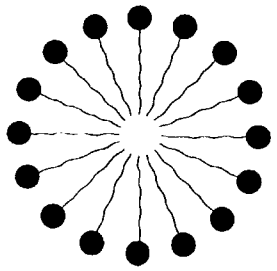
- tertiary treatment to remove specific contaminants
  - phosphorus (eutrophication problem since P is usually the limiting nutrient: ratios of C: N: P for optimal growth 100: 15: 1): see text pp. 238-240
  - major source of P in sewage is detergents, levels of which are now limited
  - P content of detergents is sodium tripolyphosphate (STP) which is used to sequester Ca^{2+}
  - complex chemistry of Ca–PO_4 systems:

- $Ca_3(PO_4)_2$ is highly insoluble (rock phosphate) and has to be solubilized to be used as a fertilizer (superphosphate)
- polyphosphates have the structure $-O-(PO_2-O)_n-PO_2-O-$ 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

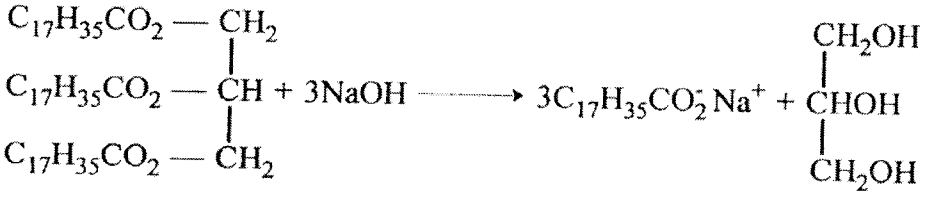
  - usual tertiary treatment for PO_4 is precipitation with either Al^{3+} or Fe^{3+} —> $AlPO_4$ or $FePO_4$ (insoluble)
  - other tertiary treatments include micro-straining and disinfection with chlorine (now out of favour): see also ammonia removal, later

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***

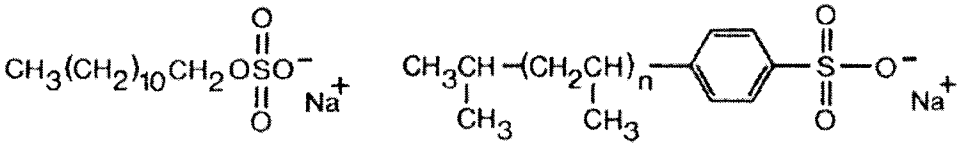


- soaps are long chain carboxylates: *e.g.*



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

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



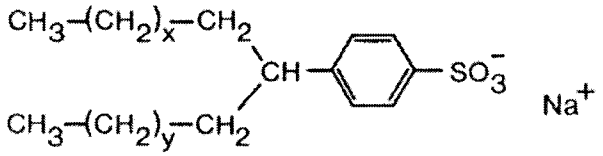
1

Dreft, an alkyl sulfate

alkylbenzenesulfonate

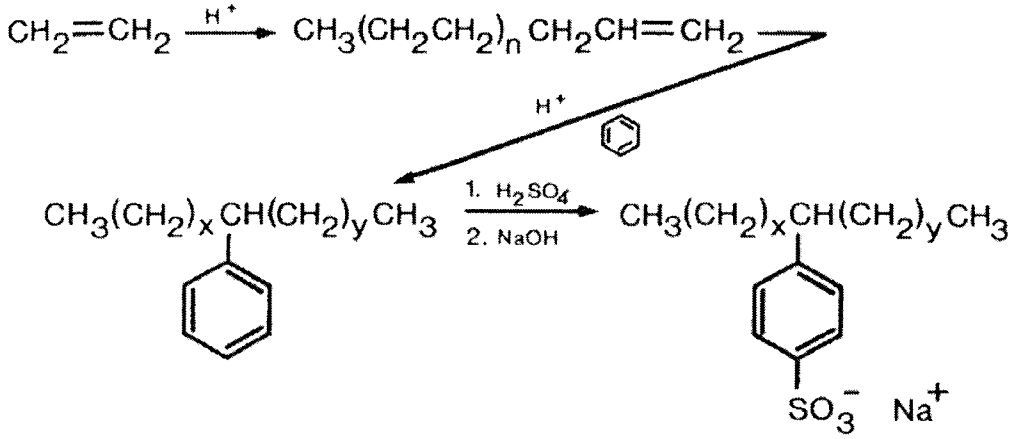
- this sulfonate is a ***branched chain*** alkylbenzenesulfonate

- ***linear*** alkylbenzenesulfonates are degraded more readily than branched analogs during sewage treatment



2

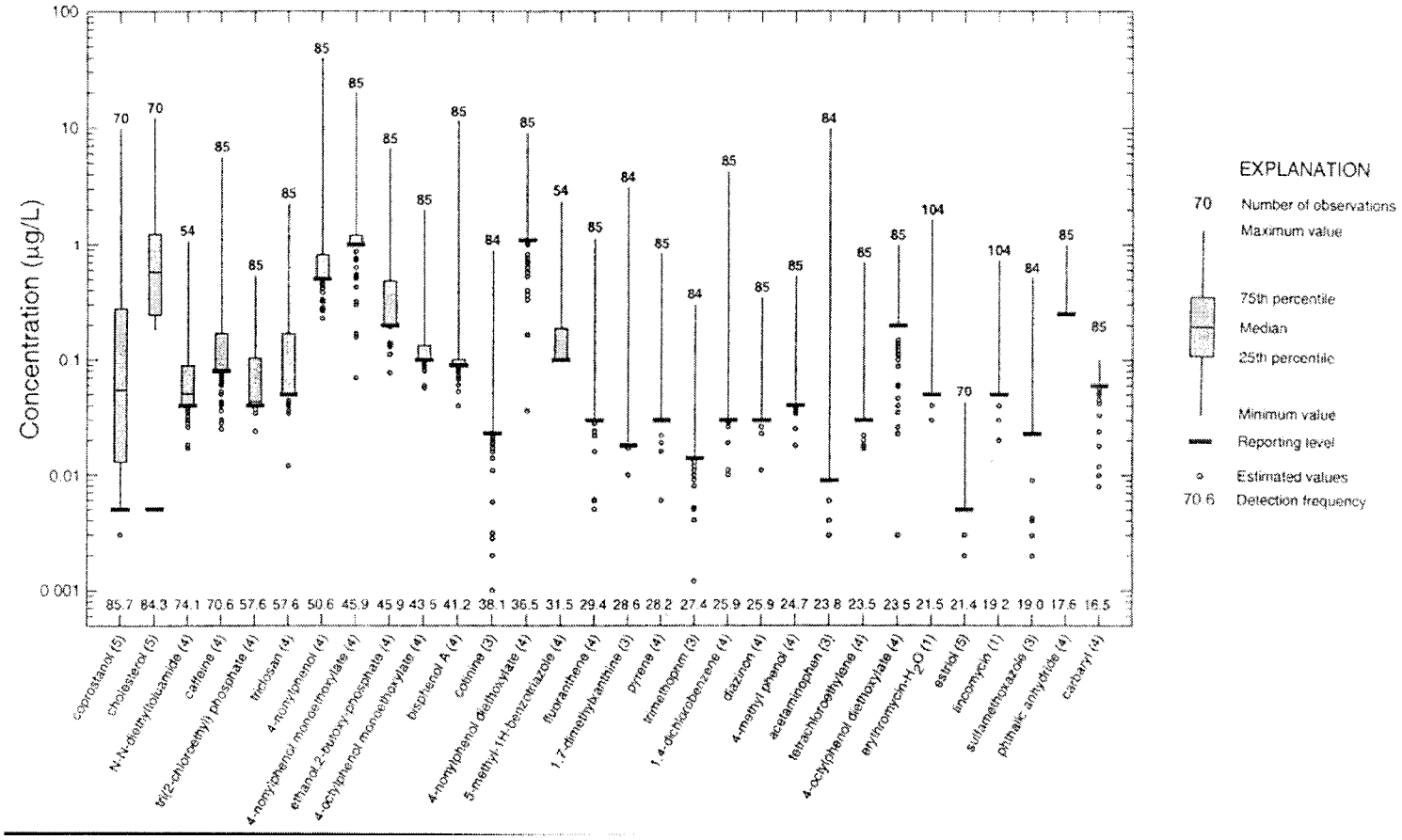
- alkylbenzenesulfonates are made by Friedel-Crafts alkylation of benzene, followed by sulfonation



- 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

BH

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

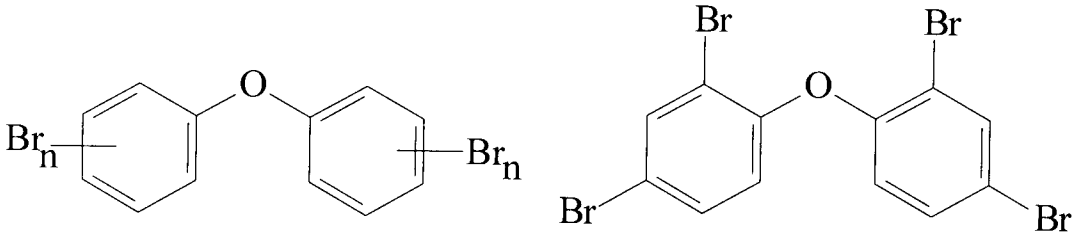
- problems of recalcitrant and toxic compounds

  recalcitrant = discharged untreated

  toxic = shuts down the reactor

Polybrominated diphenyl ethers (PBDEs): an emerging environmental problem

- widely used as flame retardants
- flame retardants are used in:
  - soft furnishings and bedding
  - childrens' sleepware
  - automobiles and aircraft
  - TV sets and computer housings
- current production > 67,000 tonnes per year; toxicity largely unknown
- long range transport
- found to bioconcentrate in:
  - human milk
  - seal and whale blubber



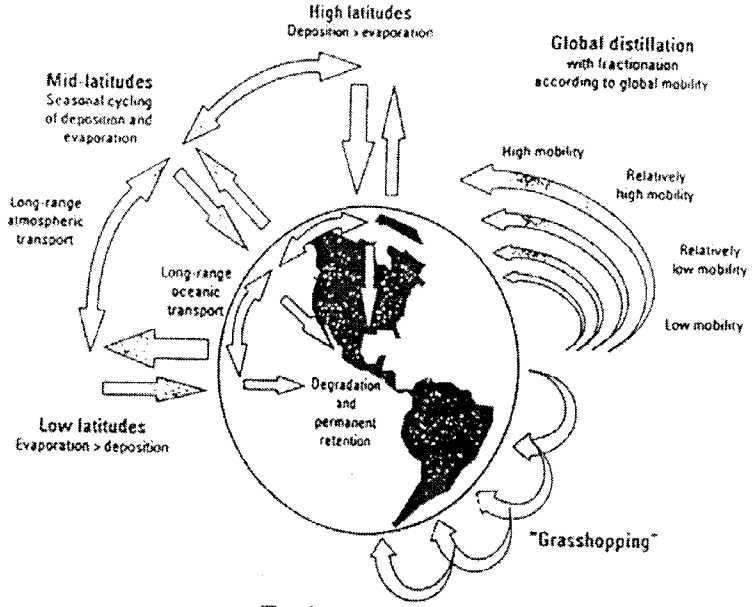
Left: generic PBDE structure
Right: a major component of the "penta" BDE mixture

As of May 2001, the European Union agreed to phase out the use of polybrominated diphenyl ethers as flame retardants because of their increasing environmental contamination

Issue #4: Long range transport of organochlorines: Persistent organic pollutants (POPs)

Environment Canada's *Toxic Substances Management Policy*: persistent if $t_{1/2}$ in the atmosphere > 2 days. Ancillary criterion: "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
- accumulate in the polar regions if they have low vapour pressure: "global distillation"



Environ. Sci. Technol., Sept. 1996

Canadian concern: Native Canadians and wildlife in the Arctic.

Issue #5: Toxic organochlorine aromatic compounds

Emphasis on polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-*p*-dioxins (PCDDs or "dioxins")

DDT (structure earlier) a 1940s/1950s insecticide

- effective against malaria mosquitos; cheap, readily applied

- synthesis = Friedel-Crafts alkylation of chlorobenzene (2 mol) with chloral hydrate $Cl_3C\text{-}CH{=}O$ ($Cl_3C\text{-}CH(OH)_2$)

- discovered to be persistent in the terrestrial environment, 1960s, and to be ubiquitous in biota, 1960s

- an emphasis in Rachel Carson's book *Silent Spring* (reduced fecundity of birds): biomagnification

- banned in developed countries 1969-1970; still in use in India for mosquito control: disease control *vs* environmental impact

- residues still found in Canadian biota, despite declines; reason is long range atmospheric transport

- technical product is mainly *p,p´*-DDT, but also contains *o,p´*- and *o,o´*- isomers: *o,p´*-DDT considered to be weakly estrogenic