Chlorine and its Compounds Chapter 9

Issue #1: the production of Cl_2: the chloralkali process

$$2NaCl + 2H_2O \longrightarrow 2NaOH + Cl_2 + H_2$$

Economics of equal masses of NaOH and Cl_2 being produced

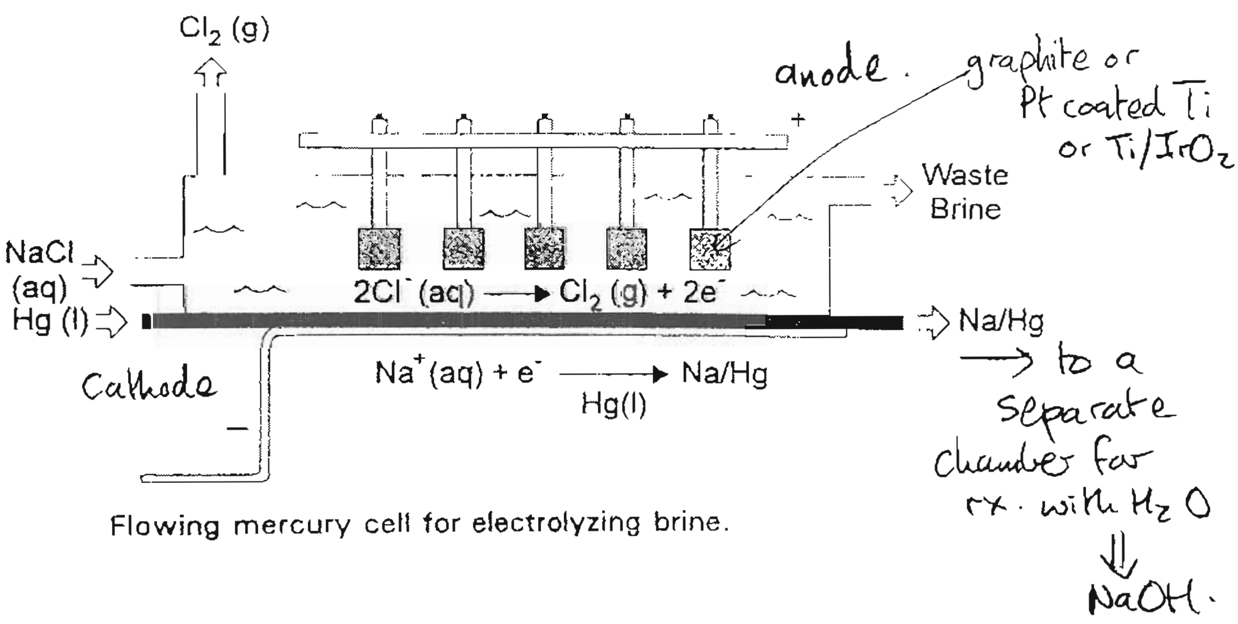
Electrolysis: Anode reaction

$Cl^-(aq) \longrightarrow \frac{1}{2}Cl_2 + e^-$ at a graphite anode (old style cells) or Ti/IrO_2 (newer cells)

Cathode reaction: old style mercury cell

$Na^+(aq) + e^- \longrightarrow Na/Hg$

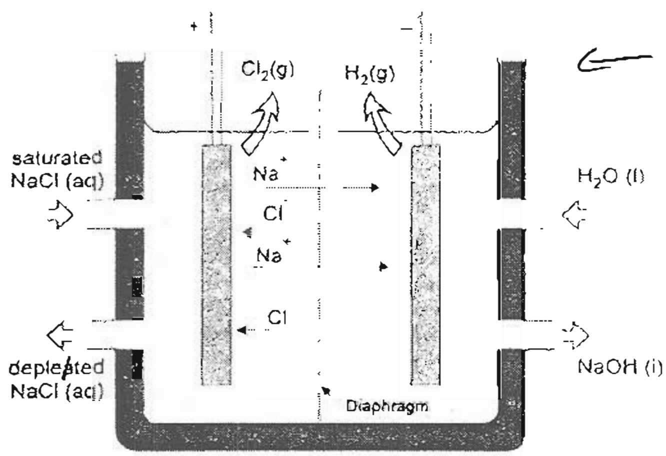
$Na/Hg + H_2O \longrightarrow NaOH + \frac{1}{2} H_2$ separate reaction



Flowing mercury cell for electrolyzing brine.

- Advantage of the old style cell: H_2 and Cl_2 formed in separate steps
- Disadvantage: cost of Hg and losses of Hg to the environment —> high concentrations of Hg in fish —> phase-out of this technology ('cos the plants were near cooling water)
- Newer technology: diaphragm or membrane separated cells: use of Nafion as a cation exchange membrane (cations can pass through, but neutrals and anions are repelled)

anode (oxidn) cathode (redn)



← Cl_2 and H_2 kept separate .... explosive mixture

Schematic of a diaphragm or membrane cell. ← fluorocarbon based.

Anode reaction

$$Cl^-(aq) \longrightarrow \tfrac{1}{2}Cl_2(g) + e^-$$

Cathode reaction

$$H^+(aq) + e^- \longrightarrow \tfrac{1}{2}H_2(g)$$

- NaOH forms because Na^+ ions cross the ion exchange membrane to restore charge balance due to loss of H^+
- the membrane separates the $H_2(g)$ and $Cl_2(g)$ streams
- no mercury is used

Overall rx:

$$H_2O(l) + Cl^-(aq) \longrightarrow \tfrac{1}{2}H_2(g) + \tfrac{1}{2}Cl_2(g) + OH^-(aq).$$

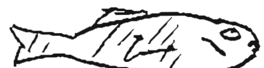
See section 9.1.2 for uses of Cl_2 ⇒ chlorinated solvents, PVC, CFCs, HCFCs, DDT, Aldrin, Mirex (insecticides), PCBs ... etc.

relatively inert to [O] and hydrolysis ... ∴ persistent environmental pollutants

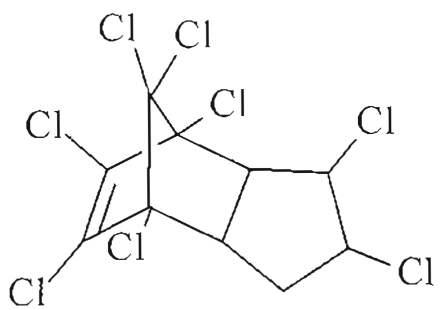
Issue #2: Lipophilicity of chlorinated organics

Lipophilic compounds are "fat-loving" and hydrophobic ("water-hating"). Organochlorine compounds are notorious for high lipophilicity. i.e. they just love to end up in fatty tissue.

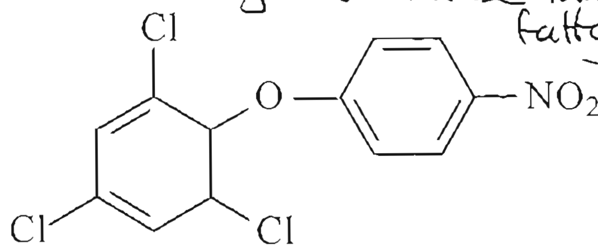
Some lipophilic pesticides



water containing organochlorines passes thru' gills. OrganoCls diffuse into the fatty tissue



Chlordane (insecticide)



Chlornitrofen (herbicide)

Partition Constant:

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

Solvent extraction, organic solvent = solvent 1; water = solvent 2

Octanol as Solvent 1: the octanol-water partition coefficient, K_{ow}

quantitative measure of the lipophilicity of a solute

Octanol as a model for fat. (e.g. fatty tissue in fish)

$$K_{ow} = \frac{\text{concentration of solute in octanol}}{\text{concentration of solute in water}}$$

Highly lipophilic substances, e.g. DDT, PCBs have $K_{ow} > 10^6$ i.e. strong tendency to partition out of water into lipids

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:

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

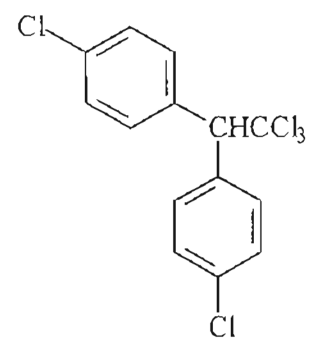
If fat is ~ 5% of wet weight: $BCF \sim 0.05 \times K_{ow}$

Environment Canada: $K_{ow} > 1000$, likely to bioconcentrate

Biomagnification:

- DDT in the Great Lakes back in the 1970s

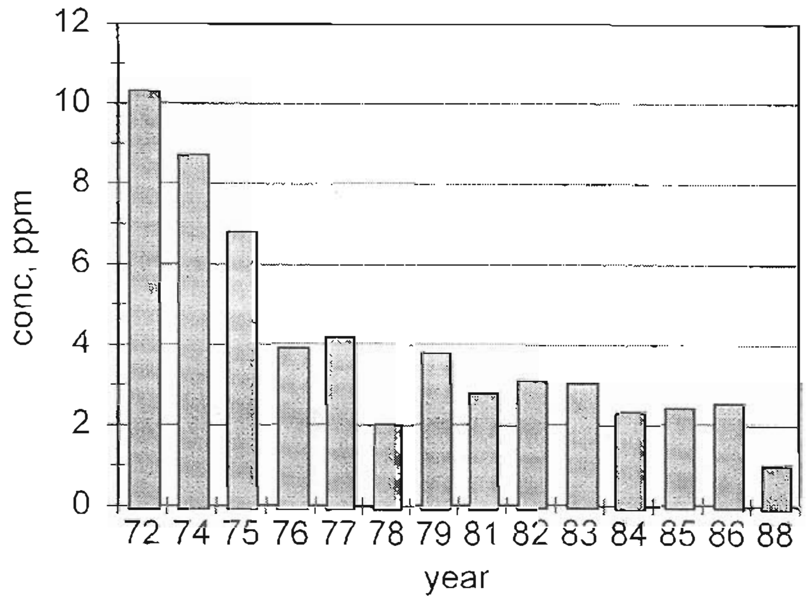
Source	[DDT] (ppb)
Water (L. Ontario)	0.03
Sediment	27
Plankton	400
Salmon tissue	8,000
Gull tissue	300000



para-dichlorodiphenyl-trichloroethane

The DDT just accumulates in the fatty tissue of e.g. the fish (i.e. not metabolised)
The older the fish, the more the accumulation

- PCBs in L. Ontario salmon (improvement due to phaseout)



Is biomagnification a real phenomenon?

G.E. Leblanc, *Environ. Sci. Technol.* 1995, *29*, 154: higher trophic organisms tend to have higher fat content —> possible reason for higher organochlorine concentrations

phytoplankton	0.5	% lipid
invertebrates	2 ± 1	
fish	5 ± 2	

Kinetics of uptake and depuration

→ removal of impurities from body

Example:

1.	c(aq)	→	c(fish)	k_1
2.	c(fish)	→	c(aq)	k_2
3.	c(fish)	→	metabolic products	k_3

- **depuration** is processes 2+3

rate[1] $= k_1$.c(aq)
rate[2] $= k_2$.c(fish)
rate[3] $= k_3$.c(fish)

(1) dc(fish)/dt = rate[1] − rate[2] − rate[3]
$= k_1$.c(aq) $- (k_2 + k_3)$.c(fish)

At the steady state:

(2) k_1.c(aq) $= (k_2 + k_3)$.c(fish, ss) → i.e. BCF = k(uptake) / k(depuration)

BCF = c(fish, ss)/c(aq) $= k_1/(k_2 + k_3)$ (defined in terms of rate consts (compare to equilibria, my p154))

- if the steady state has not been reached, eq. (1) must be integrated (see text: will not be tested).
- then measured BCF does not necessarily represent equilibrium (*e.g.* organochlorines in Great Lakes fish)
- bioconcentration is **always** associated with a low rate of depuration: rate[1] >> {rate[2] + rate[3]}

See Fig 9.6 (p293, text) regarding uptake and clearance of a dioxin by young trout placed first in dioxin water and then in clean water.