

Major Chemicals and Plastics We Use Every Day

F803

Brian Martin

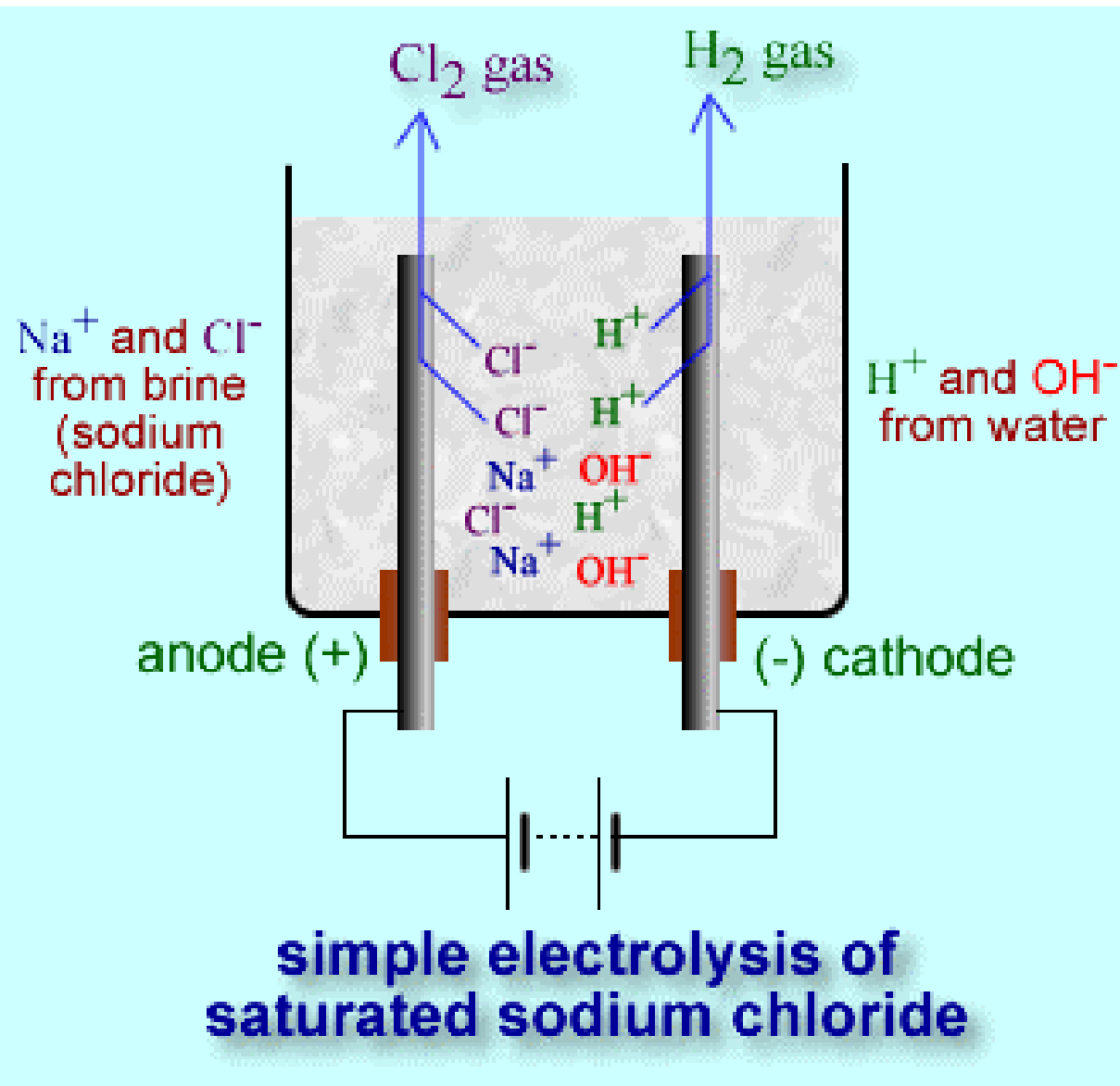
Topics

1. History of chemistry, and significant discoveries in the 19th century. Nitrogen fertiliser.
2. Plastics and rubber
3. (a) Polyethylene and (b) Silicones
4. Chlorine containing chemicals and polymers.

Chemicals and Plastics Containing
Chlorine.

History

- Around 1900 bromide was a popular analgesic.
- Sodium bromide is found naturally, it is a minor component of natural salt (mostly sodium chloride)
- Herbert Dow began to produce bromine in Midland MI in 1899, by the **electrolysis** of brine.



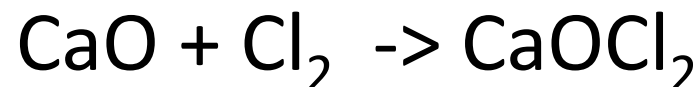
- After a few years, the production of chlorine was more profitable for Dow than bromide.

- Sold as bleach:



(this is what Clorox is today)

- Or Bleaching Powder:



- Bromides became obsolete medication, possibly replaced by aspirin.
- Principal use of bromine after 1920 was in the manufacture of tetra-ethyl lead.

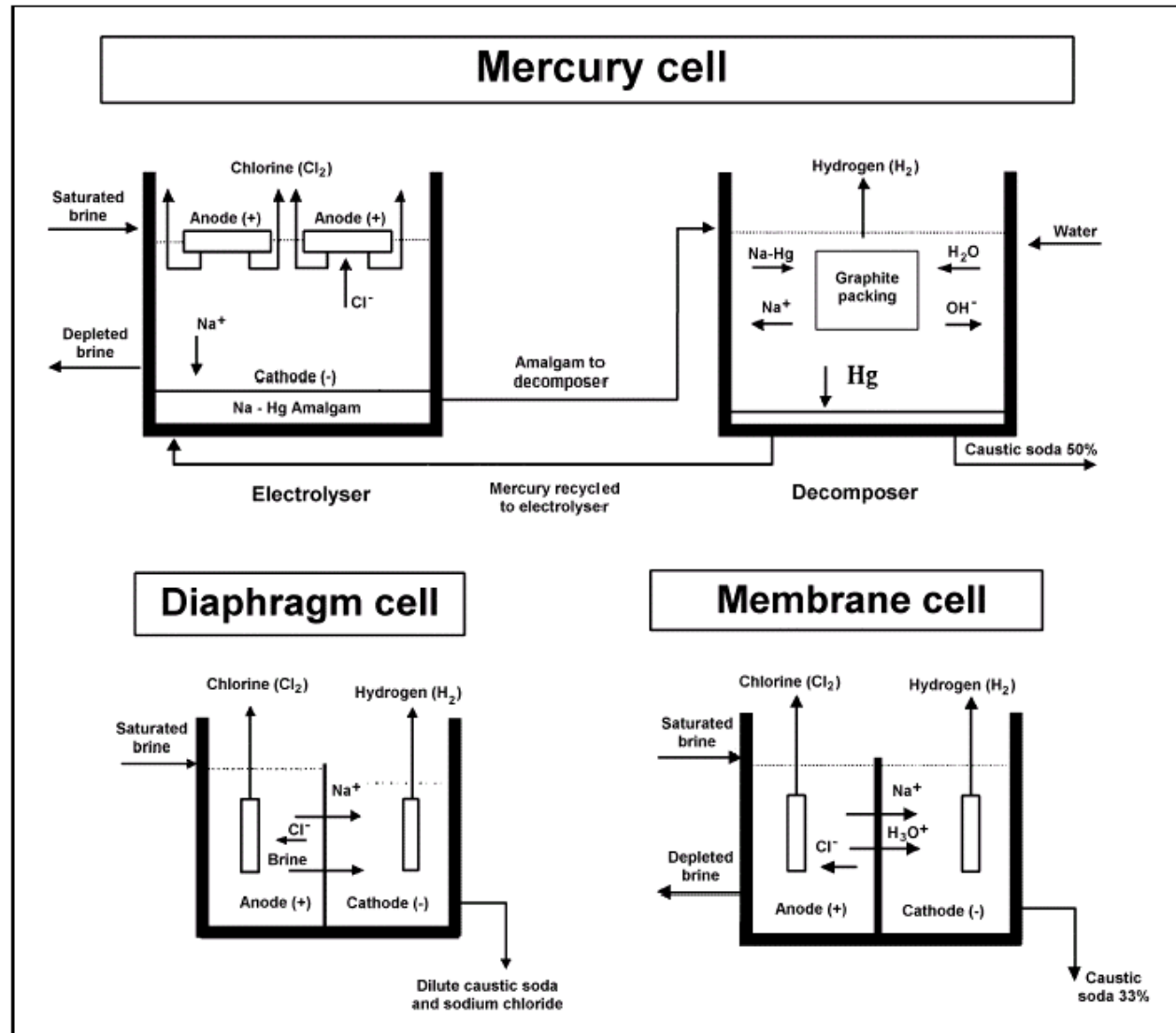


Figure 2.2: Simplified scheme of chlorine electrolysis cells after [Dutch report, 1998]

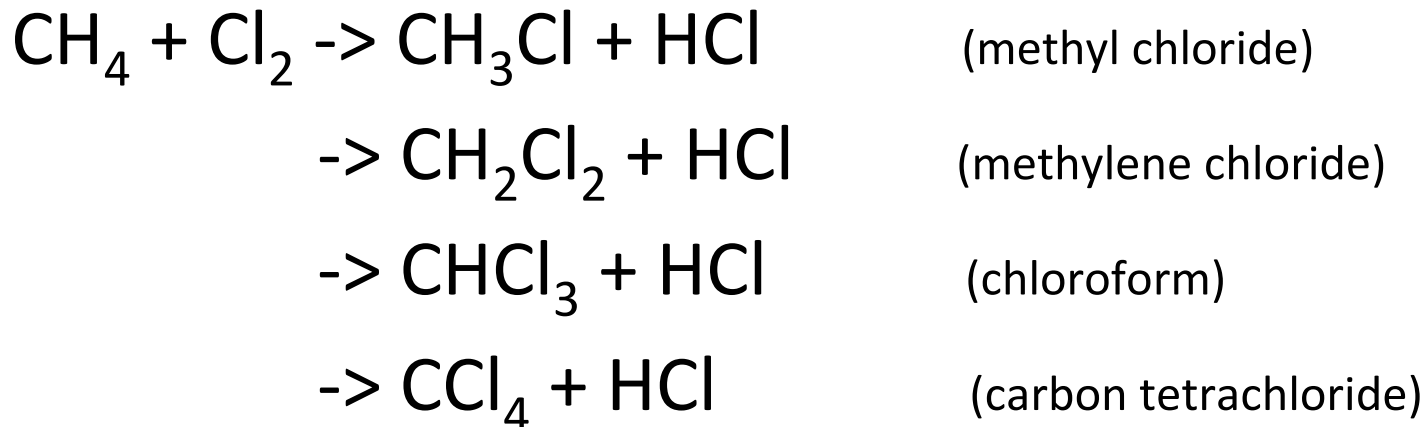


Principal Uses for Chlorine

1. 2008 US production about 10 million metric tons, declining trend.
2. Producing PVC and Saran
3. Biocide for municipal water supplies,
4. Bleach, for laundry, paper, fabrics etc.
5. Chemical intermediate.
6. Chlorine containing chemicals, notably DDT and other insecticides, and 2,4-D herbicide.
7. Producing chlorinated solvents.

Chlorinated Solvents

- Made from methane (natural gas) and chlorine.



- Production began in the 1920's
- Good solvents, volatile, nonflammable.
- But all affect human health.

Uses

- CH_3Cl - chemical intermediate (eg silicone mfg), refrigerant, affects CNS.
- CH_2Cl_2 - paint stripper, solvent in primers & adhesives, suspected carcinogen.
- CHCl_3 – (anesthetic), suspected carcinogen.
- CCl_4 – (dry cleaning solvent), fire extinguisher for electrical fires, causes cirrhosis of the liver.

2 Other Widely Used Solvents

Trichloroethylene

- Formerly used as anesthetic, extracting caffeine from coffee, solvent for vapor degreasing.
- CNS depressant, probable carcinogen.

Perchloroethylene

- Dry cleaning solvent
- Hazardous air contaminant, toxic.

Problems

- Volatile and readily inhaled in the [workplace](#).
- Fat soluble, retained in the body
- Toxic, some are carcinogenic
- Except for chloroform, don't readily biodegrade. Persistent in the environment.
- Most chlorinated solvents were used by small operations: garages & aircraft maintenance ([for metal cleaning](#)), dry cleaners, furniture refinishing. Not set up for proper waste disposal; led to air, ground and drinking water contamination.
- Reduction of pollution is via recycling. Waste from recycling is burned in [cement](#) kilns.
- Several solvents banned, use and emissions [much reduced](#) over 25 years.

PVC and Saran

To make vinyl chloride monomer:



Polymerise as a latex to make PVC or Saran, as dry white powders.

Saran

- Originally developed as an strippable coating for the mothballed US Fleet after WW11.
- Film has low permeability to oxygen.
- Good for wrapping meat or fruit which would be spoiled by oxygen.

PVC Plastisol

- Mix 1:2 with a **plasticiser** -> smooth paste, like pancake batter. This is a **Plastisol**.
- Pour into a mold, or coat fabric, wood, or paper etc.
- Heat 15 minutes at 350°F → tough, leathery, but not resilient, thermoplastic.

Key Properties

- Tough, wear resistant and durable
- Inexpensive
- Versatile in use, performance can be varied by proportion of PVC:plasticizer:filler.
- Fire resistant
- UV and oxidation resistant, weathers well.
- Blood compatible – preferred material for catheters and blood bags.

Applications

Coated Products:

- Paper → Wallpaper (washable)
- Knitted fabric → Synthetic leather for seating, handbags, shoes, furniture.
- Fiberglass web → Vinyl floor tiles and sheet floor covering.
- Wood → weather and rot resistant covering for window and door frames.
- Film for decorative decals, trim.

Applications (contd)

- Extrusions: Major application is for pipe and siding in home construction. Insulation for telephone cords.
- Moldings: Toys, beach balls, etc. Soft, flexible plastic parts.

2007 PVC Production

in thousands of metric tons
(millions of kilograms)

US	6625
Europe	6888
Japan	2162
South Korea	1161
Total	16836

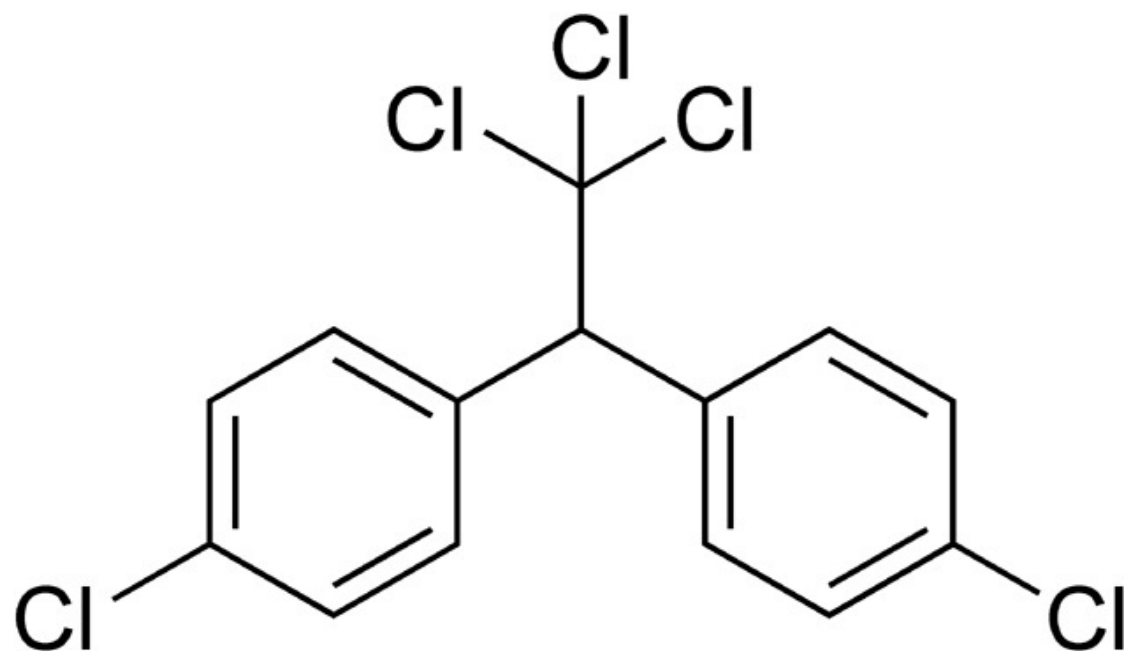
Problem Areas

- Toxicity of **di-octyl phthalate** (LD₅₀ is 30gm/kg in rats). But under investigation as a possible carcinogen, and may cause adverse reproductive effects. There is a very large amount in circulation.
- Waste disposal – **burning** PVC, except at very high temperature, produces some dioxin.
- Not biodegradable.

DDT

- Invented by Swiss Company Geigy in 1939.
- Spectacularly successful in the control of diseases transmitted by insects (typhus, malaria).
- In insects, a respiratory poison and a lipid soluble narcotic.
- Has saved 50 million lives (World Health Org).

Dichlorodiphenyltrichloroethane



DDT

- 1945-1960, used to control agricultural pests as well as disease-carrying insects.
- Massive insect-control projects undertaken.
 - Gypsy moth (4 million acres sprayed '54-'58), Dutch elm disease, Fire ant.
- Growth in DDT production:
 - 1953 38 million pounds;
 - 1959 125 million pounds.

DDT (continued)

- 675,000 tons used in US, a lot on cotton.
- Not biodegradable, built up in the environment,
- Accumulated in fatty tissues of fish.
- Caused eggshell thinning in birds which ate fish. Bird populations declined.
- Widely present in human body fat.
- Additional chlorinated insecticides developed and produced, many more toxic than DDT.

- “Silent Spring” published in 1962.
- Written by Rachel Carson, a respected marine biologist.
- An expose of the damage to the environment from **indiscriminate** use of chlorinated pesticides.

Silent Spring

- Birth of environmental movement in America can be traced to the publication of Silent Spring.
- (1992) Picked as the “most influential book” published in past 50 years.

Greatest contribution:

- Call for a new attitude toward nature. A recognition of the possibly destructive effects of humanity’s actions on the environment.

Retrospective

- EPA was formed in 1970.
- DDT was **banned** in 1972.

What were DDT's faults?

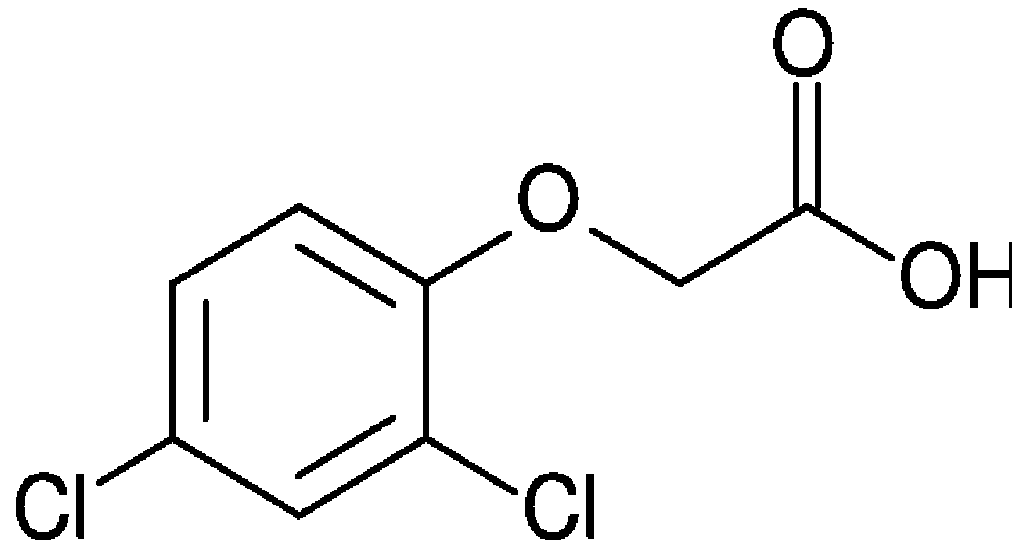
- Too great a persistence in the environment.
- Bioaccumulation and biomagnification in food chain.
- Lack of toxicity of DDT to humans no guarantee of safety for other species.

2,4-D Herbicide

- Developed during WWII to enhance yield of cereal crops, by killing competing weeds.
- Commercially released in 1946.
- Has properties of a growth hormone in broad leaved plants, causes unequal growth, then death.
- First successful, effective selective herbicide.
- Most widely used herbicide in the world.

2,4-D Herbicide

2,4-Dichlorophenoxyacetic acid



Uses

- Weed control in lawns and other turf, hayfields and pastures.
- Control of weeds and brush along fences, highways and railroad rights of way.
- Conifer release (control of broad-leaf trees in conifer plantings).
- In admixture with another herbicide, for defoliating the jungle in Vietnam (Agent Orange).

Health Effects

- Low order of toxicity in a single dose
- International Agency for Research on Cancer (IARC) has classified 2,4-D as a class 2B carcinogen - possibly carcinogenic to humans.
- **Different agencies** -> differing conclusions on safety
- Breakdown in soil; half life 1.5-16 days. Faster in waterways. Not persistent.

Dioxin

- Agent Orange toxicity is now attributed to a previously unknown contaminant called Dioxin.
- Found also in body fluids (eg fish, birds) wherever DDT is found.
- But Dioxin has never been manufactured!

Dioxin: Toxicity and Health Effects

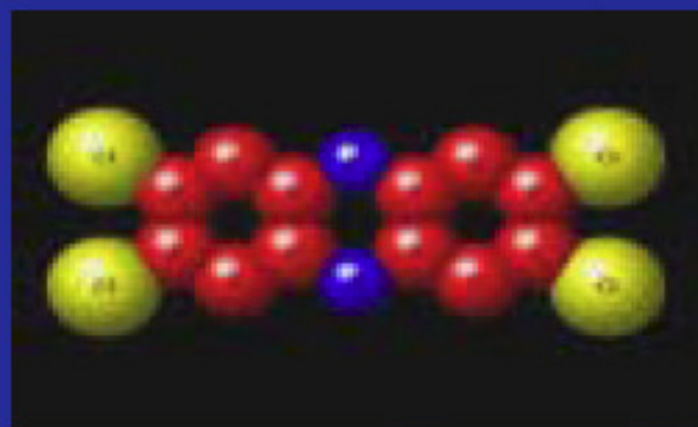
Suzanne White, M.D.

Children's Hospital of Michigan Regional Poison
Control Center

Detroit Medical Center-Wayne State University

What is Dioxin?

- Chlorinated dibenzo-p-dioxins = a family of 75 chemicals
- Colorless, odorless solids
- Prototype is 2,3,7,8-TCDD (most toxic)
- Exist as mixtures (TEQ)
- Not intentionally manufactured



Sources

- Chlorine bleaching processes at pulp and paper mills
- Waste & drinking water treatment
- Chemical manufacturing contaminants
- Released into air in emissions
- Uncontrolled combustion of household wastes

Fate of CDDs

- Persistent
- Emissions: may be transported in air long distances
- Waste water: most attaches to soil- sediment
- Concentrate in food chain
- Overall environmental levels declining in US

Human Exposure

- 95% diet (meat, dairy, fish, breast milk)
- Proximity to hazardous waste site or incinerator
- Air, water, skin contact: less significant
- Occupational
- Half-life ~ 8.5 years





Dioxin Toxicity

- Potent animal toxicants
- Tremendous species variability
- Dioxins have a common toxic mechanism
- Alter basic steps for cell growth and development
- Results in broad impact in animals:
 - Reproductive/developmental
 - Immunologic
 - Skin
 - Cancer

Summary

- Chlorine containing chemicals have a large economic footprint; form a range of useful materials.
- Cl₂/water-treatment and DDT have been very beneficial to human health and wellbeing.
- Non-biodegradable/non-flammable: difficult to dispose of. Persistent in the environment.
- Bio-accumulate, and mostly toxic.
- Facilitate formation of Dioxin, a dangerous toxin.
