The water can be used for different purposes as mentioned below:

(i) Domestic use for drinking, cooking and cleaning, etc.

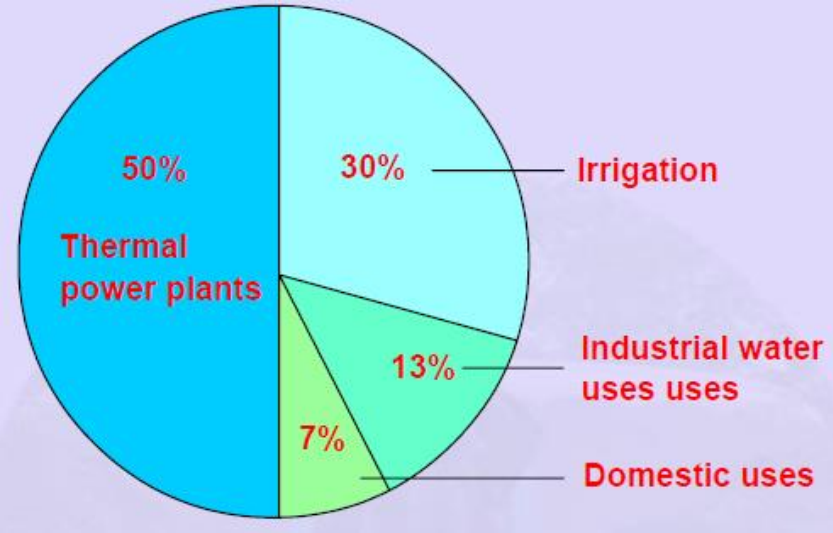
(ii) Irrigation for agriculture.

(iii) Power generation.

(iv) Industrial use for cooling, processing, cleaning, etc.

(v) For fisheries and acqua-culture.

(vi) Recreation.



Major use of fresh water

Waste water from industries

Inorganic industrial wastewater

- Wastewater produced mainly from
  - ✓ *Coal and steel industries*
  - ✓ *Commercial enterprises*
  - ✓ *Industries for surface processing of metals (electroplating plants)*

Acid Mine drainage

COAL WASHING

In the seperation of coal from dead rock large amounts of water is used, this water contains large amounts of coal and rock particles known as Coal washing water.

- Coal mines release substantial quantities of sulphuric acid and iron hydroxide into local streams.
- The first step in the process is the oxidation of pyrire (FeS_2), which is common in underground coal streams.
- Thiobacillus ferrooxidans is a highly acidophilic (pH 1.5 to 2.0), autotrophic bacterium that obtains its energy through the oxidation of ferrous iron (or in other words, reduced inorganic sulfur compounds.

Organic industrial wastewater pollution

- Wastewater produced mainly from
  - ✓ Chemical industries which mainly use organic substances for chemical reactions.
  - ✓ Pharmaceutical factories
  - ✓ Tanneries and leather factories
  - ✓ Textile factories
  - ✓ Paper manufacturing industries
  - ✓ Synthetic detergents
  - ✓ Organic dye stuff
  - ✓ Glue and adhesive industries

Water pollution nay be divided into the following categories:

1. **Ground water pollution;**
2. **Surface water pollution;**

How underground water is formed?

Groundwater forms when water from the surface seeps into the ground. This process is called recharge. The water is able to move underground through the rock and soil due to connected pore spaces.

Inorganic Species as Pollutants :

(i) Cyanide

Cyanide is a naturally occurring chemical that is found in low concentrations throughout nature including in fruits, nuts, plants, and insects. The edible parts of these plants contain much lower amounts of these chemicals.

- ❖ Cyanide is widely used in industry, especially for metal cleaning and electroplating.
- ❖ Cyanide, in the form of a very dilute sodium cyanide solution, is used to dissolve and *separate gold from ore*.

(ii) Ammonia

- ✓ *It is a normal constituent of groundwaters*
- ✓ *Most ammonia in water is present as* NH_4^+ rather than as NH_3.
- ✓ Excessive levels of ammoniacal nitrogen cause water-quality problems.

Ammonia is a very important industrial chemical, and is used widely in both its pure form and as a feedstock for a wide variety of other chemicals. Ammonia ranks *second behind sulfuric acid in the quantity* produced worldwide per year.

(iii) Hydrogen sulfide, H_2S

It occurs naturally in crude petroleum, natural gas, sour gases, in salt mines, in volcanic gases, hot sulfur springs, lakes, salt water ponds.

The major industrial use of H_2S is -

- in the production of elemental sulfur and sulfuric acid.
- in metallurgy to precipitate copper, nickel and cobalt sulfides from ores (metals *are made precipitated as their sulfides*);

Non-Biodegradable ORGANIC Pollutants : REFRACTORY ORGANICS

1. Volatile Organic Compounds (VOCs)
2. Persistent Organic Pollutants (POPs) :

1. Volatile Organic Compounds (VOCs) :

- These are volatile compounds (evaporate or vaporize readily under normal conditions).
- The compounds, the nose detects as smells, are generally VOCs.
- These compounds are of low-molecular weight and have high vapor pressure.
- VOCs may be natural or synthetic (man-made).

They include a variety of chemicals, some which may have short and long-term adverse health effects.

Examples:

Methane, chloroflurocarbons, trichloroethylene, formaldehyde, Acetone, Ethylene glycol, 1,3-butadiene

Sources:

- (i) Extraction and distribution of fossil fuels : VOCs are released from burning fuel (gasoline, oil, wood coal, natural gas, etc.), and automobiles are a major source of VOCs.

(ii) Volatile organic compounds are produced naturally through metabolism (called *metabolites*).
Plants synthesize many organic molecules and release some VOCs (*terpenes, isoprene, which give them characteristics smell*) into the atmosphere.

Trees emit VOCs for a variety of reasons:

- To repel harmful insects and animals.
- To attract pollinators.

2. Persistent Organic Pollutants (POPs)

(10 + 2)

NOT naturally occurring -- Produced by Industries.

Three main points about the POPs ---

(i) Mostly these are chlorinated aromatic compounds.

(ii) Very stable, so do not break down into simpler less toxic form very easily in the environment -- Poorly biodegradable. Hence persists in the environment for long period of time. These are resistant to environmental degradation through chemical, biological, and photolytic processes.

(iii) Soluble in fat , hence, bioaccumulative, ie., they accumulate in the fatty tissues of the organisms and can pass from one species to the next through the food-chain.

Persistent Organic Pollutants (POPs) :

10 intentionally produced POPs are as follows:

(i) PAHs, (Polynuclear Aromatic Hydrocarbons)

(ii) PCBs, (Poly Chlorinated Biphenyls)

(iii) DDT,

(iv) heptachlor,

(v) chlordane,

(vi) aldrin,

(vii) dieldrin/endrin,

(viii) Mirex,

(ix) toxaphene,

Insecticides

(x) Hexachlorobenzene (raw materials for pesticides) and

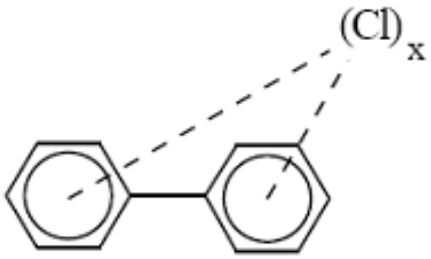
2 unintentionally produced POPs are –

(i) Polychlorinated dioxins and

(ii) Polychlorinated dibenzofurans (PCDF).

(ii). POLYCHLORINATED BIPHENYLS

- Polychlorinated biphenyls (PCBs) are a class of organic compounds with 1 to 10 chlorine atoms attached to biphenyl.



- The chemical formula of PCB's can be presented as : $C_{12}H_{10-x}Cl_x$ where x is a number of chlorine atoms within the range of 1 to 10

Sources:

- PCBs, a by-product of coal tar. Coal tar is a thick black liquid that is a byproduct of coke production. Coal tar contains hundreds of chemical compounds that will have varying amounts of Polycyclic Aromatic Hydrocarbons (PAHs)
- .

(iii). DDT and other Organochlorine Insecticides

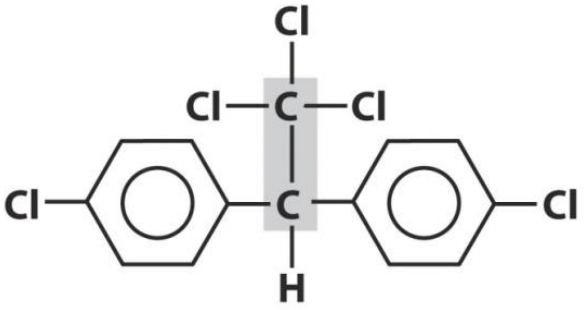
Pesticides :

These are chemicals or biological agents used to control, repel, attract or kill pests.

Pests are organisms that include **insects,**
weeds or other unwanted plants,
birds, mammals, fishes and
microorganisms
that compete with humans for food, destroy properties, spread disease or are considered a nuisance.

Before, 1940, only a few insecticides were available. Many of them were naturally occurring insecticides extracted from plants, these are
(i) nicotine sulfate from tobacco,
(ii) pyrethrins from pyrethrum flower,
(iii) rotenone extracted from certain legume roots
(iv) Azadirachtin from Neem etc.

DDT



(DDT): *para-d*ichloro*d*iphenyl*t*richloroethane

Unnumbered Figure, pg 313
Environmental Chemistry, Third Edition

- It was cheap to produce
- Stable
- DDT is very persistent and remained in the environment for long periods without being broken down
- Apparently it was non-toxic to humans and other mammals
- Banned in 1973 in most countries for agricultural use

Devastating effect on ***fishes, fish-eating birds***

- DDT interferes with the calcium metabolism in birds,
- and as a result, eggshells become thin and
- break when parent birds attempt to incubate the eggs.
- As a result of this, population of fish-eating birds was decreasing at high rate.
- In 1973, the use of DDT was banned in USA and since then fish-eating birds have made a dramatic recovery.

Octanol-water partition coefficient (K_{ow})

K_{ow} is defined as the molar concentration of an organic compound in n-octanol (organic phase) and in water (aqueous phase), in dilute solution and K_{ow} is expressed as

$$K = \frac{C_{octanol}}{C_{water}}$$

- K_{ow} value indicates the tendency of fat solubility of a contaminant ie., it provides us information about how much a pesticide is bioaccumulative

$(\log K_{ow})_2 = (\log K_{ow})_1$ + "Pi-value" (it is also called reference index)

What is “Pi-value” or PREFEENCE INDEX ?

(i) “Pi-value” describes the lipophilic nature of a substituent (or functional group).

(ii) ***+ve Pi-values indicate a preference for octanol ie., organic medium*** and ***-ve Pi-values indicate a preference for aqeuous medium***

(iii) Pi-value is different for different functional groups (substituent).

Pi-values			
NH_2	−1.23	F	0.14
OH	−0.67	$N(CH_3)_2$	0.18
CN	−0.57	CH_3	0.56
NO_2	−0.28	Cl	0.71
COOH	−0.28	Br	0.86
OCH_3	−0.02	C_2H_5	0.98
H	0.00	$CH(CH_3)_2$	1.35

1. logK_{ow} value for a trichlorobiphenyl is 6.19, what will be the logK_{ow} value for tetrachlorobiphenyl? Between them which one is more lipophilic?

Ans : We will add the Pi-value for chlorine (0.71) to the log K_{ow} value and get,

$(\log K_{ow})_{tetrachlorobiphenyl} = (\log K_{ow})_{trichlorobiphenyl}$ + "Pi-value" of "Cl"

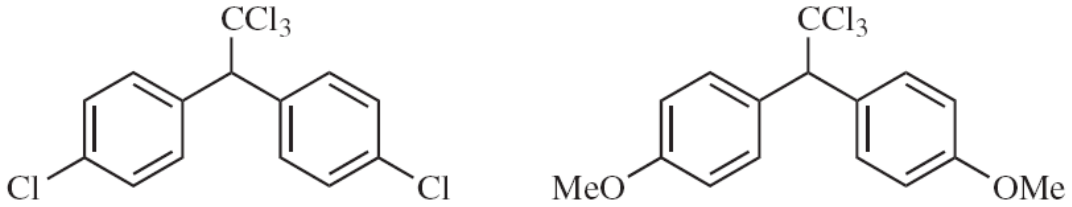
$= 6.19 + 0.71 = 6.90$

$\therefore (K_{ow})_{tetrachlorobiphenyl} = 10^{6.19} = 1.54 \times 10^{6}$

And $(K_{ow})_{trichlorobiphenyl} = 10^{6.90} = 7.94 \times 10^{6}$

Therefore, obviously, tetrachlorobiphenyl is more fat soluble, ie., more bioaccumulative.

2. The structures of DDT and methoxychlor are given below (left and right, respectively). Given that the log K_{ow} value for DDT is 5.87, what is the logK_{ow} value of methoxychlor ? By what factor is it more or less lipophilic than DDT ?



$(\log K_{ow})_{methoxychlor} = (\log K_{ow})_{DDT}$ – "Pi-value" for "Cl" + "Pi-value" for methoxy

$= 5.87 - 2\,(0.71) + 2\,(-0.02)$

$= 4.41$

$\therefore (K_{ow})_{methoxychlor} = 10^{4.41} = 2.57 \times 10^4$

And $(K_{ow})_{DDT} = 10^{5.87} = 7.41 \times 10^5$

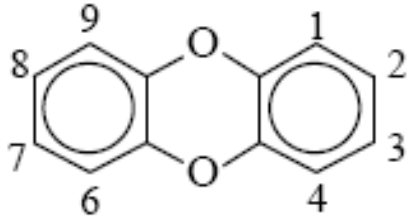
$$\therefore \quad \frac{7.41 \times 10^5}{2.57 \times 10^4} = 29$$

Because it has a higher K_{ow} value, DDT is the more lipophilic of the two compounds, and it is more lipophilic by a factor of 29. ie., DDT is more bioaccumulative.

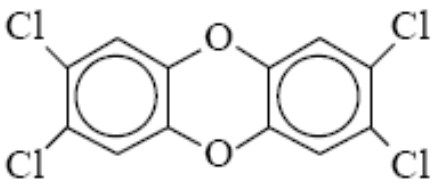
Unintentionally produced POPs

DIOXINs : Polychlorinated dibenzo-*p*-dioxins (PCDD)

These Compounds are not commercially produced (not produced intentionally) but are formed as byproduct of some industrial procedure.



Dibenzo -*p* -dioxin



2,3,7,8-Tetrachlorodibenzo-*p* -dioxin

Of the dioxins, the most toxic compound is 2,3,7,8-tetrachlorodibenzo-para-dioxin (TCDD).

Sources:

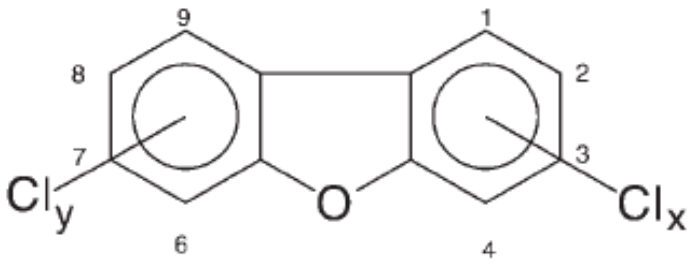
- Dioxins and furans are produced in the manufacture of herbicide, polychlorinated biphenyls (PCBs) etc.
- During burning of chlorine containing medical and municipal wastes in municipal incinerator.

There is no known technical use for PCDDs

TCDD shows the highest toxicity to mammals

As a result of these concerns, the use of 2,4,5-T has been banned in 1985.

Polychlorinated dibenzofurans (PCDF)



Polychlorinated dibenzofurans

PCDF

Sediments are the ultimate sink for PCDD/PCDF

Environmentally attractive approach to control the pests

- *By applying pheromones & VOCs (naturally occurring chemical substances)*
- *Biological controls*

A. Natural Chemical Defenses: Application of PHEROMONES

- Pheromones are the chemical substances that released by insects and other animals as a means of communication;
- they differ from species to species, hence they are species-specific.
- Pheromones can be used as bait,
- it will be kept (placed) in a trap; and these traps are coated with a sticky substance.
- The insects follow the pheromone trail into the trap. Insects will be attracted towards the trap and thus insects are trapped.
- Since these traps are coated with a sticky substance, thus insects are trapped.

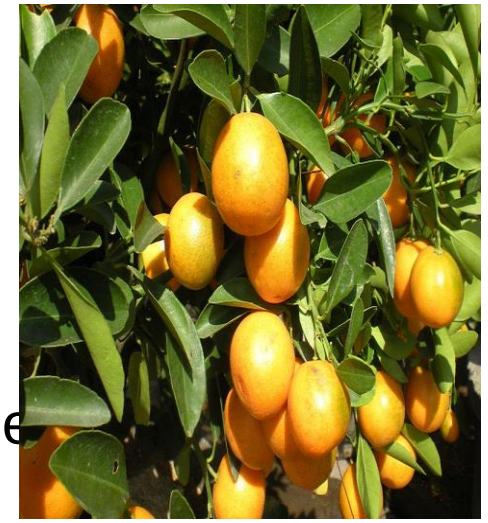
A. Natural Chemical Defenses

- Trees produce nearly ***1,000*** different chemical compounds (VOCs)

Trees emit VOCs for a variety of reasons:

- To repel harmful insects and animals.
- To attract pollinators.

Botanical insecticides



Limonene and linalool

- Extracted from orange and other citrus fruits, found in small quantities in citrus pe
- Limonene, a terpene (VOC)
- Target pests: Fleas, aphids, mites, flies, paper wasp

❖ Biological controls : BIOPESTICIDE

- **What are bio pesticides?**

Bio means involving life or living organisms

Pesticide includes substance or mixture of substances intended for preventing, destroying or controlling any pest

Why are biopesticides useful?

- Often very specific.
- Compatible with other control agents.
- Little or no residue.
- Inexpensive to develop.