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

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

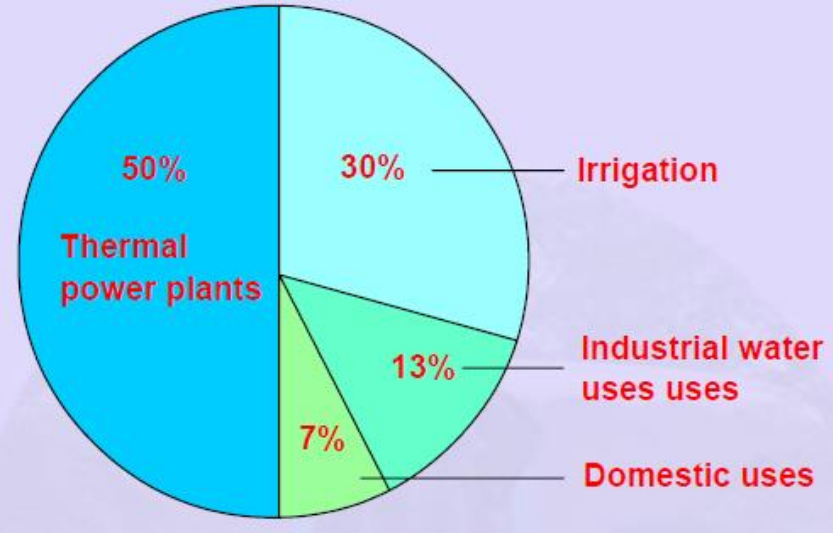
(ii) Irrigation for agriculture.

(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 (electroplat plants)*

- These wastewaters contain large proportion of suspended matter, which can be eliminated by sedimentation.
- Often together with flocculation means addition of iron or aluminium salts, flocculation agents and some kinds of organic polymers.

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.

Overall reaction $FeS_2 + \frac{15}{4}O_2 + \frac{7}{2}H_2O \rightleftarrows Fe(OH)_3 + 2H^+ + 2HSO_4^-$

Thus one mole of pyrite produces 2 moles of sulphuric acid and one mole of ferric hydroxide , which is removed from the solution as a brown precipitate. The ***pH of the streams receiving this drainage can be as low as 3.0***

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.

(1) Ground water is threatened with pollution from the following sources:

(a) ***Effluents from septic tanks***;

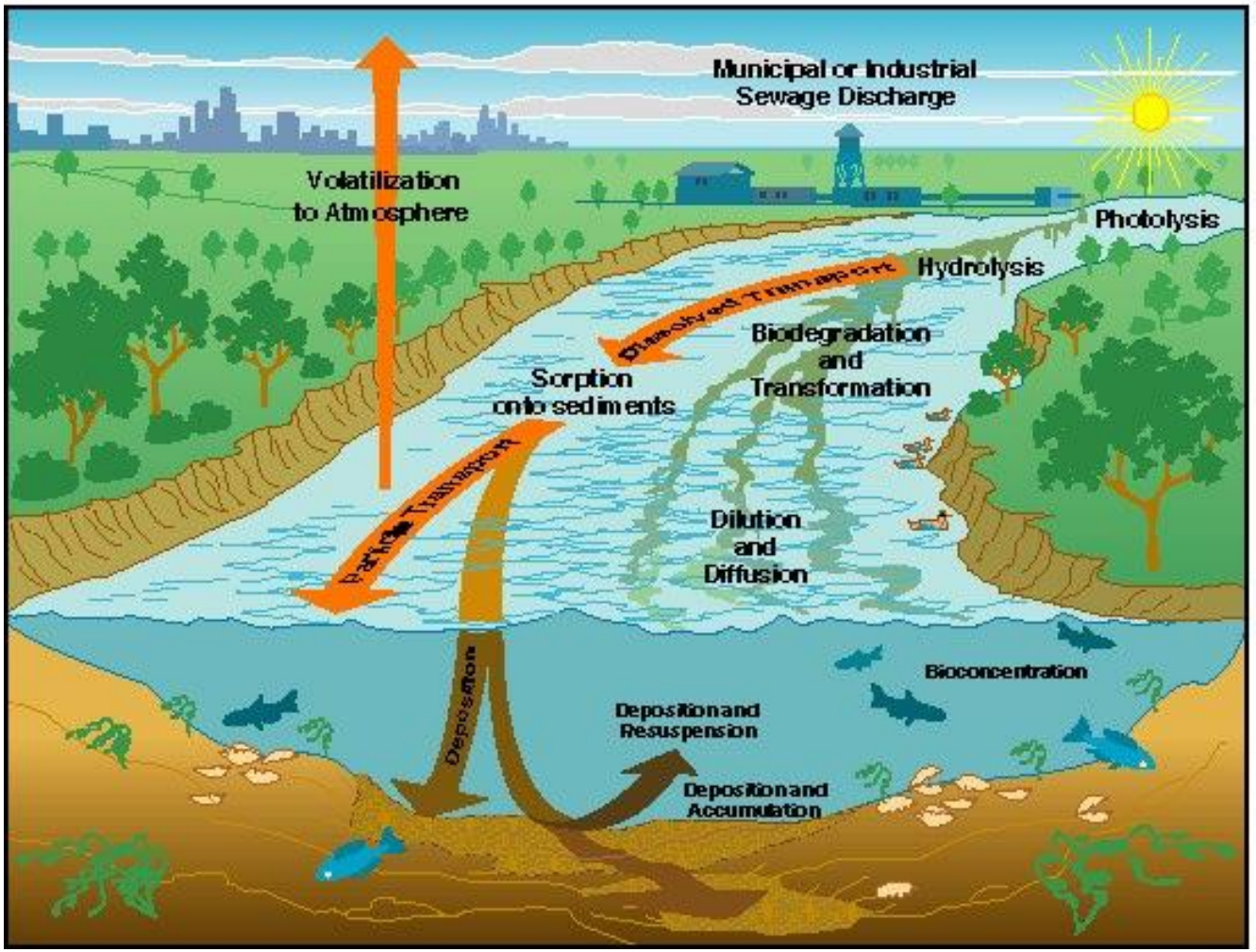
(b) ***Agricultural runoff like nitrates, phosphates*** (to fertilize plants), ***pesticides*** (insecticides, herbicides);

(c) ***Mine spills : Toxic substances from mining sites, and used motor oil also may seep into groundwater*** ;

(d) ***Leaky landfills*** to contaminate groundwater : ***Leaching and downward movement of pollutants like volatile organic compounds, petroleum products, metals and synthetic organic chemicals*** *which gets into groundwater by leaching process*

(e) ***Chemical spills at local industrial sites***

Fate of Contaminants in the River from Municipal and Industrial Wastewater



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*.

$$2Na[Au(CN)_2] + Zn \rightarrow Na_2[Zn(CN)_4] + 2Au \downarrow$$

- ***cyanide is used to make paper, textiles, and plastics*** (Manufacture of synthetic polymers, such as nylon and acrylics).
- It is present in the chemicals used to develop photographs.

Cyanide, a deadly poisonous substance, exists in water as HCN, a weak acid

(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.
Ammonia **itself** is used:

- ➢ **As a fertilizer, such as ammonium sulfate, ammonium nitrate**, ammonium hydrogen phosphate, and **urea**.
- ➢ In many alkaline cleansers, such as window and floor cleaners.
- ➢ **pulp and paper industry** uses ammonia for pulping wood.
- ➢ ***synthetic textile fibers such as nylon, rayon and acrylics***; and for the manufacture of certain ***plastics such as phenolics and polyurethanes***.

(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*);
- In petroleum cracking catalysts, and catalyst poisoning etc.

Wastes that come from ***chemical plants, paper mills, textile mills, and tanneries*** may also contain H_2S.

Its presence is easily detected by its characteristic rotten-egg odor.

Toxic effect

Low concentrations irritate the eyes, nose, throat and respiratory system

Repeated or prolonged exposures *may cause eye inflammation, headache, fatigue, irritability, insomnia, digestive disturbances and weight loss*.

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
vinyl chloride, tetrachloroethylene ,
carbon tetrachloride,
1,2-dichloroethane ,
Benzene, Toluene and Xylene ⇨ ***widely used as solvent*** etc.

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.
- They are found at airports and automobile service stations, machine print and paint shops, electronics and chemical plants.

(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.**

Uses :

1. ***They are used as solvents in laboratories, industrial processes***

2. Many household products emit VOCs

Toxic effects of VOCs:

- A number of VOCs are ***either known or suspected carcinogens***. Some organics can cause cancer in animals, while some are suspected to cause cancer in humans.
- **Most toxic** of the five is ***vinyl chloride (chloroethylene), is a known human carcinogen***.
- Many have been shown to have both short and long term health effects, including:

  Eye, nose, and throat irritation

  Headaches

  Loss of coordination

  Nausea

  Damage to liver, kidney, and central nervous system

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. H***ence ***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,
(x) Hexachlorobenzene ***(raw materials for pesticides)*** and

Insecticides

The extraordinarily stability once made these compounds useful, at the same time the stability contributes to their bioaccumulation in the environment.

2 unintentionally produced POPs are –

(i) Polychlorinated dioxins and

(ii) Polychlorinated dibenzofurans (PCDF).

(i). Polynuclear aromatic hydrocarbons, PAHs

The polycyclic aromatic hydrocarbons (or polynuclear hydrocarbon or poly-aromatic hydrocarbons) contain two or more fused aromatic rings and neither contain heteroatoms nor substituents.

Examples:

Naphthalene, anthracene, phenanthrene, chrysene, Benzo[α]pyrene etc.

How do PAHs get in the Environment?

- ***PAHs are released to the environment through natural and man made processes***.
- ***Also produced from incomplete combustion of organic compounds***
- ***Man-made sources contribute far more PAHs to the environment than natural sources***.
- **Burning of wood**
- **Vehicle exhaust**
- **Coal burning power plants**
- **Grilled/smoked foods**
- **Cigarette smoke**

Uses :

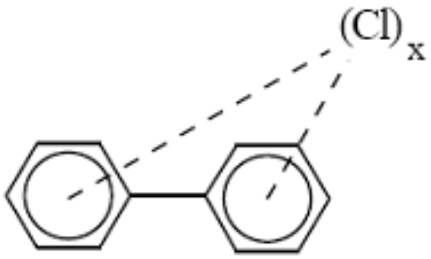
- **In the making of *pharmaceuticals, dyes, plastics, and pesticides*.**
- ***Naphthalene*** is the most abundant distillate of coal tar. Its most common use is as a household fumigant against moths (hence the name mothballs), **Cockroaches Repeller**.
- ***A mixture of phenanthrene and anthracene is used to coat water storage tanks to prevent rust***
- ***Anthracene, phenanthrene*** is used in the production of ***fast dyes*** *as well as fibers and plastics*.

PAHs and Your Health

- **Some PAHs have been shown to be cancer causing: *These compounds directly damage DNA and initiate mutations that can lead to the development of cancer*.**
- **Chronic Bronchitis**
- **Skin Problems**
- **Allergies**

(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***
- *PCBs* were discovered in 1865 and first synthesized in 1881
- **These compounds were first discovered as environmental pollutants in 1966, they have been found throughout the world in water, sediments, bird tissue, and fish tissue.**
- **PCB production was banned by the Stockholm Convention in 2001.**

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)

Uses:

PCBs were widely used in

(i) Used ***as insulating materials.***

(ii) Coolants and lubricants in electrical equipment such as transformers and voltage regulators.

(iii) ***Plasticizers***.

(iv) Inks

(v) lubricants,

(vi) adhesives,

PCBs in the Environment

- **Where does it go?**
  - Deposition in river/lake sediments
  - Enters food stream, bio accumulation
- **Life span**
  - Do not readily degrade
  - Can exist in environment for decades

Toxic effects:

There is growing concern that many of PCBs

(i) These chemicals ***interfere with the endocrine system*** (***they mimic, block or otherwise interfere with naturally occurring hormones***) in both animals and humans

(ii) ***Disrupt reproduction and fetal development.***

(iii) Most important, these chemicals can ***be transferred from mother to fetus through the placenta and from mother to infant through breast milk***

(iv) ***In birds, PCBs make eggshell thin ⇨ reduction in birds' population***

(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.

Pesticides includes –

- **Insecticides** are used to kill the insects.
- **Herbicides** are used in the control of weeds and to kill plants.
- **Fungicides** are used against fungi,
- **bactericides** against bacteria and
- **algicides** against algae.

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,

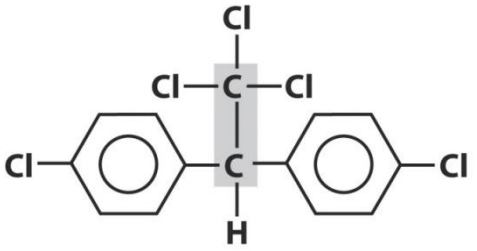
(ii) pyrethrins from pyrethrum flower,

(iii) rotenone extracted from certain legume roots

(iv) Azadirachtin from Neem etc.

DDT

- **Insecticidal activity discovered by Müller in 1939**
- **Between 1940 - 1960, DDT was a commonly used pesticide**
- ***Broad spectrum usefulness***
- Found to be **effective against malaria and typhus (carried by lice)**
- **Saved lives of millions of people**
- **Even its creator earned a Nobel Prize in 1948**



(DDT): *para-dichlorodiphenyltrichloroethane*

Unnumbered Figure, pg 313
Environmental Chemistry, Third Edition
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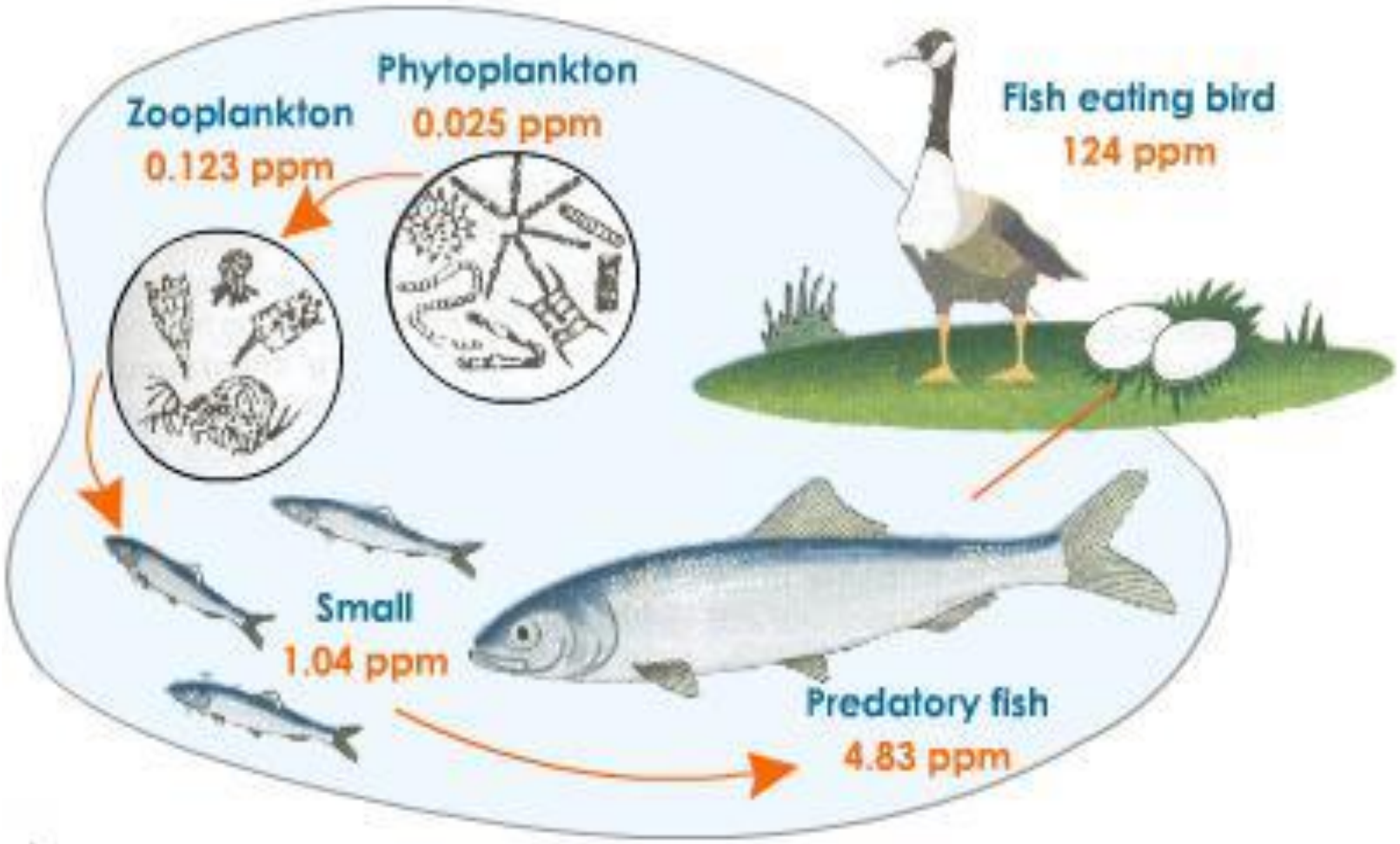
- **It was cheap to produce**
- **Stable**
- ***DDT is very persistent and remained in the environment for long periods without being broken down***
- ***Apparently it was non-toxic to humans and other mammals***
- **Banned in 1973 in most countries for agricultural use**

DDT Bioaccumulation

DDT accumulated across the food chain and had devastating effects on carnivores at the top of the food chain



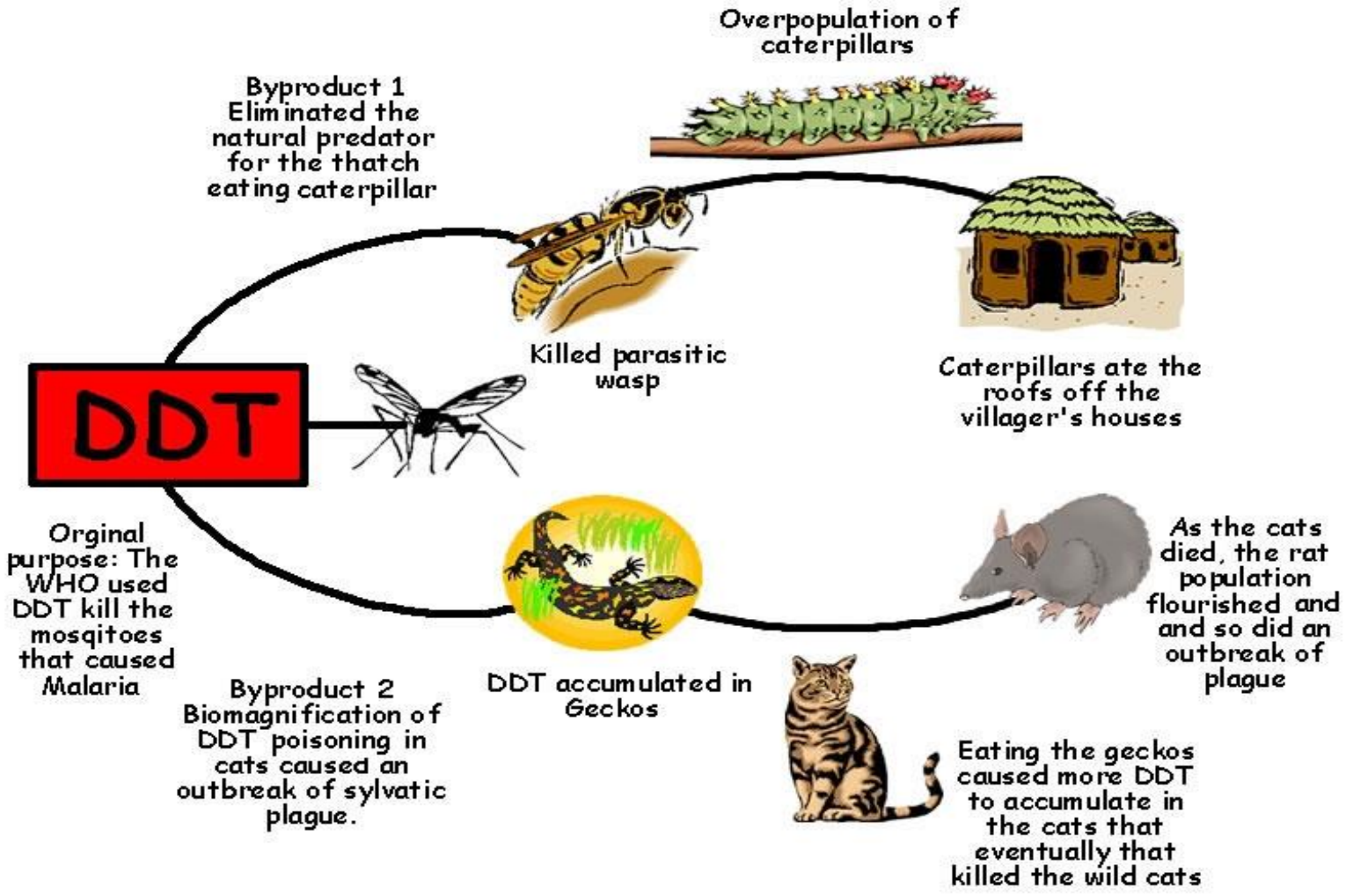
Process of Biological Magnification;
DDT concentrations increase in organisms along the food chain

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***.

Effect of DDT Use in Borneo

In the early 1950's the people in Borneo, suffered from Malaria the World Health Organization had a solution, kill the mosquitoes with DDT. This is what happened.



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"

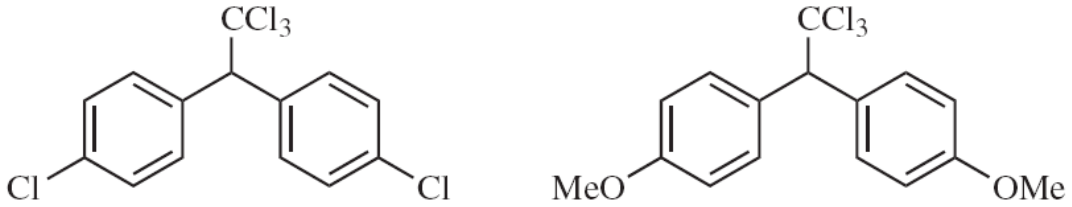
$= 6.19 + 0.71 = 6.90$

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

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

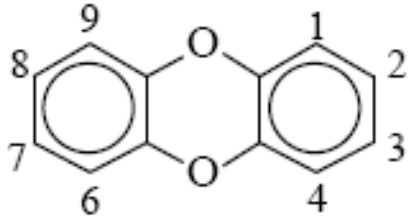
$$\therefore \quad \frac{7.41 \times 10^5}{2.57 \times 10^4} = 29$$

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

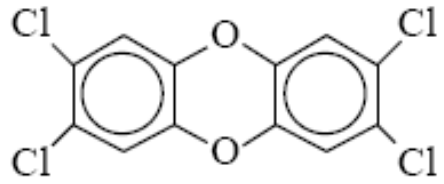
DIOXINs : Polychlorinated dibenzo-*p*-dioxins (PCDD)

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



Dibenzo -*p*-dioxin

Of the dioxins, *the* *most toxic chemical in the compound is 2,3,7,8-tetrachlorodibenzo-para-dioxin (TCDD)*. It is stable ***thermally up to about 700°C***



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

Sources:

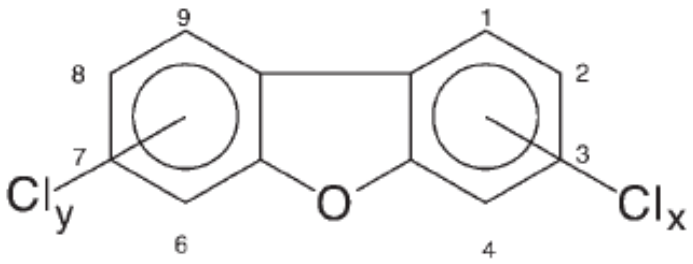
- Dioxins and furans are produced in the manufacture of ***trichlorophenoxyacetic acid herbicide (2,4,5-T)***, ***polychlorinated biphenyls (PCBs***) etc.
- During ***burning of chlorine containing medical and municipal wastes*** in municipal incinerator.

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

- Sometimes *beneficial insects are destroyed together with the target pests*.
- By the repeated of a particular pesticide, *slowly, pests develop resistance against them*. *A*fter a few years, ***those pesticides will not be effective anymore*****. Then *new more potent pesticides are required***.

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

- **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 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
- ***Limonene, a terpene (VOC)***
- Linalool, found in small quantities in citrus peel
- **Target pests**: Fleas, aphids, mites, flies, paper wasp
- **Mode of action**:
- **Limnonene** act as nerve toxin and stomach poisons
- **Linalool** affects ion transport and release of acetyl choline esterase

❖ 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

- All the ***living organisms***, which are ***cultivated*** in the laboratory on large scale and are used and exploited experimentally for the control of harmful organisms are, called ***biopesticides.***

1st Biopesticide discovered in the year 1835

Why are biopesticides useful?

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

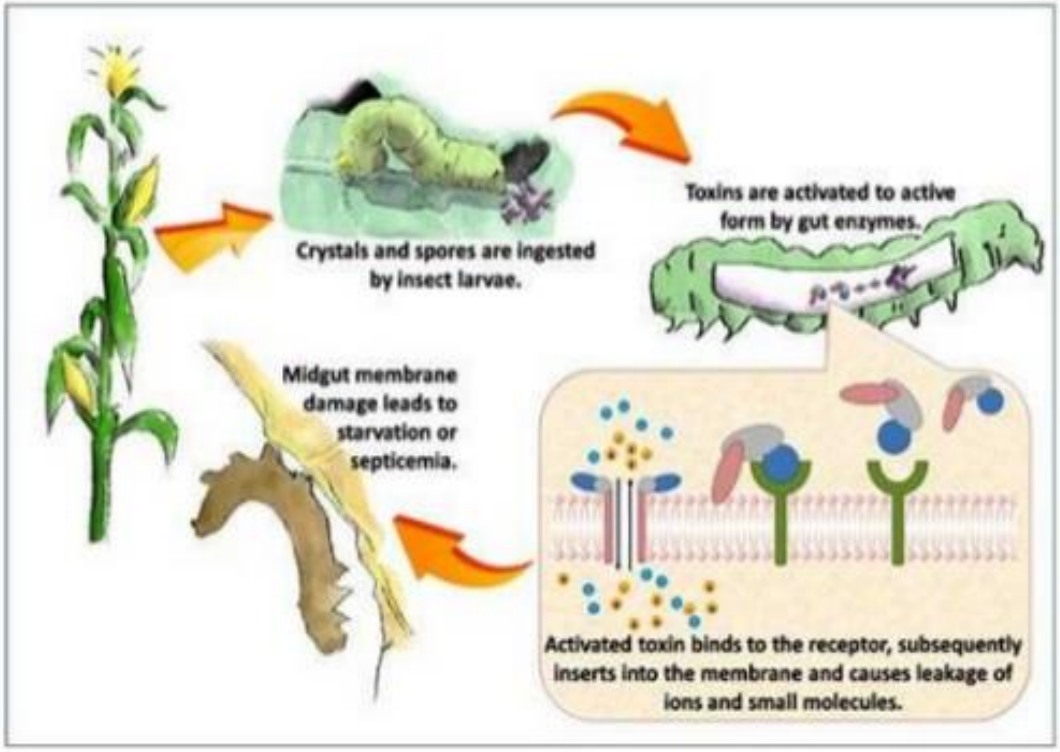
B. LIVING ORGANISMS AS BIOPESTICIDES

(i) Some Important Biopesticides and Bio control Agents

Bacillus thuringiensis (Bt).

- ***Bacillus thuringiensis*** (most commonly used biopesticide globally) ***is a bacterium that produces proteins which are toxic to insects.***

DIAGRAMS are ONLY for your information



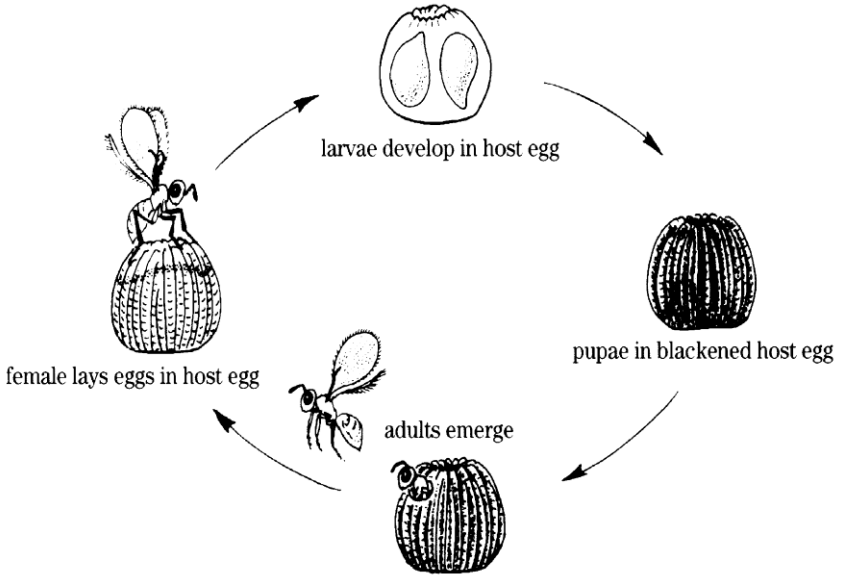
When ingested by pest larvae, Bt releases toxins which damage the midgut cell of the pest, **(**punching holes in the lining. The *Bt* spores spills out of the gut and germinate in the insect causing death within a couple days**) eventually killing it.**

B. LIVING ORGANISMS AS BIOPESTICIDES

(ii) Some Important Biopesticides and Bio control Agents

Trichogramma.

- **Trichogramma are tiny wasps which are exclusively egg-parasites.**
- They lay eggs inside (within) the eggs of various lepidopteran pests as the wasp larva develops, the host egg turns black. After hatching, the Trichogramma larvae feed on and destroy the host egg**.**
- **Ensure that the parasite is destroyed before any damage is done to the crop.**



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