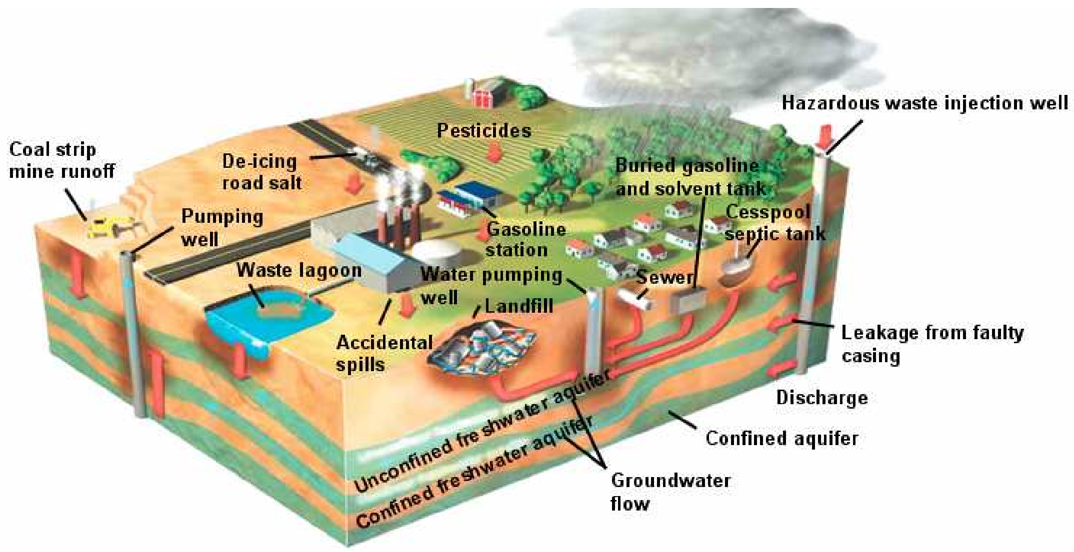
Water Pollution

Surface water is highly susceptible to contamination (contaminated by the municipal sewage effluent and industrial wastes from paper mills, chemical plants, tanneries, textiles, dye and pharmaceutical industries, food-processing plants etc). Dangerous chemicals, organic materials, and bacteria contaminate the surface water and so, much of the water we drink. Surface water which is found in lake, reservoir and streams are the source of majority of our water for all purposes - it is of direct use to humans.

One particular category of waste is oxygen demanding organic substances. Food-processing plants generally contain this type of waste. When biodegradable organic matter is released into a body of water, microorganisms, especially bacteria and fungi, break them down into simpler organic and inorganic substances- first in presence of oxygen and then in complete absence of oxygen.

Groundwater is also contaminated by the spillage from underground storage tanks, effluent from septic tanks, leachates (A product or solution formed by leaching, especially a solution containing contaminants picked up through the leaching of soil) from agricultural activities, municipal landfill, and abandoned hazardous waste sites. Persistent pesticides may leach through soil into groundwater and thus groundwater may be contaminated which is a continuing (growing) concern. Most commonly found contaminants from these sources are : nitrates, phosphates, pesticides (insecticides, herbicides), volatile organic compounds, petroleum products, metals and synthetic organic chemicals.

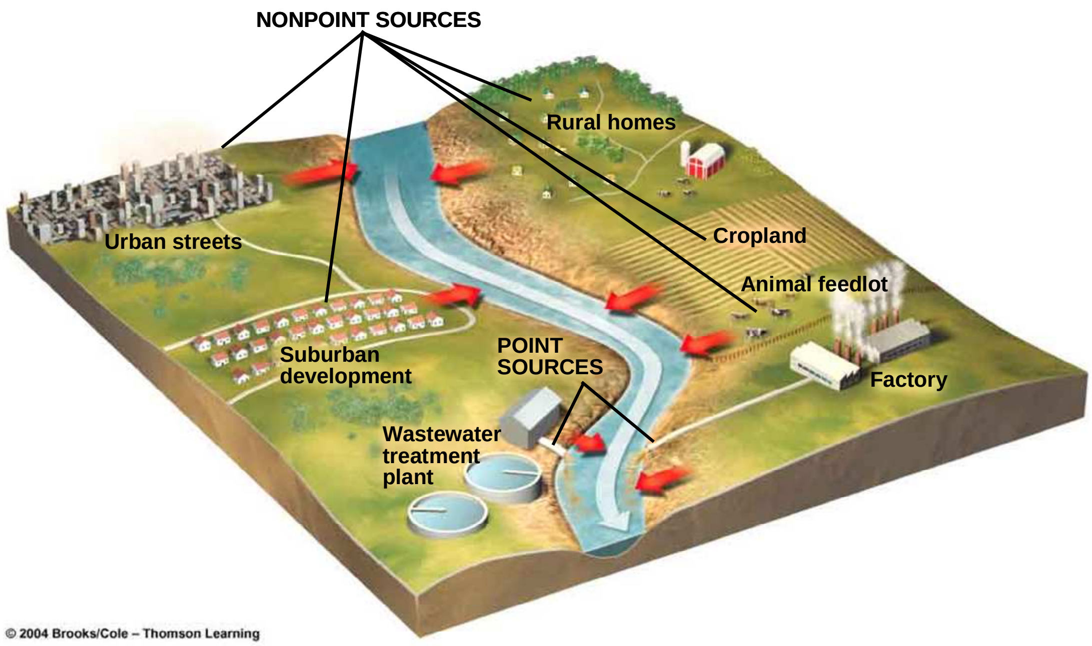


Because most groundwater is anaerobic, so remediation of organic wastes is almost impossible. Contaminants remain there for years decomposing slowly because of the cool, dark environment. That's why natural purification through flushing or biological decomposition is limited in groundwater. Once contaminated, groundwater is very difficult and expensive – in many cases impossible – to rehabilitate. For eg., benzene which comes from petroleum waste of which aerobic degradation is well known, but under anaerobic condition, it can be decomposed only in presence of nitrates.

$C_6H_6 + 9O_2 \rightarrow 6CO_2 + 3H_2O$

$$\underset{\text{(benzene)}}{C_6H_{6(aq)}} + 6NO^-_{3(aq)} + 6H^+_{(aq)} \longrightarrow 6CO_{2(aq)} + 3N_{2(g)} + 6H_2O_{(l)}$$

Point and Nonpoint Sources



1.1. METALS AS POLLUTANTS

When metals are present as pollutants in a body of water, it may exists in two forms ─ either in their elemental form or by forming the compounds with some organic groups or moieties.

A) METALS

(i) Heavy metals ─ some of the **heavy metals (**For example, Cd, Pb, Hg) are among the most harmful of the elemental pollutants and are of particular concern because of their toxicities to humans.

(ii) Metalloids ─ some of the **metalloids** (elements on the borderline between metals and nonmetals) are significant water pollutants, for example arsenic, selenium, and antimony are of particular interest.

B) ORGANICALLY BOUND METALS

Metal ions can be present in an aquatic system may form compounds with some organic moieties. These organic moieties may be the pollutant (such as CN^{-}, S^{-}, many aliphatic, aromatic groups, EDTA, humas etc).

1.2. INORGANIC SPECIES

Among inorganic pollutants CN-, is probably the most important. Others include ammonia, hydrogen sulfide, nitrite, and sulfite.

Cyanide

Cyanide, a deadly poisonous substance, exists in water as HCN, a weak acid. Cyanide is widely used in industry, especially for metal cleaning and electroplating.

The cyanide ion has a strong affinity for many metal ions. Volatile HCN is very toxic and has been used in gas chamber executions in the U.S.

Ammonia

Ammonia is produced during the anaerobic decay of nitrogenous organic wastes. 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.

Hydrogen sulfide, H_2S

i) It is produced during the anaerobic decay of sulfur containing organic matter and it requires other bacteria besides *Desulfovibrio* to oxidize organic matter completely to CO_2

$$SO_4^{2-} + 2\{CH_2O\} + 2H^+ \rightarrow H_2S + 2CO_2 + 2H_2O$$

ii) Seawater contains high concentration of sulfate ion which produces H_2S and causes pollution problems in some coastal areas. That is why in coastal areas waters, the sediment is often black in color due to the formation of FeS.

iii) Another source of H_2S is the 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. S^{2-} is not present in normal natural waters.

Nitrite ion, NO_2^-, Nitrite is added to some industrial process water as a corrosion inhibitor.

Sulfite ion, SO_3^{2-}, is found in some industrial wastewaters. Sodium sulfite is commonly added to boiler feedwaters as an oxygen scavenger:

$$2SO_3^{2-} + O_2 \rightarrow 2SO_4^{2-}$$

*A **scavenger*** in chemistry is a chemical substance added to a mixture in order to remove or inactivate impurities or unwanted reaction products.

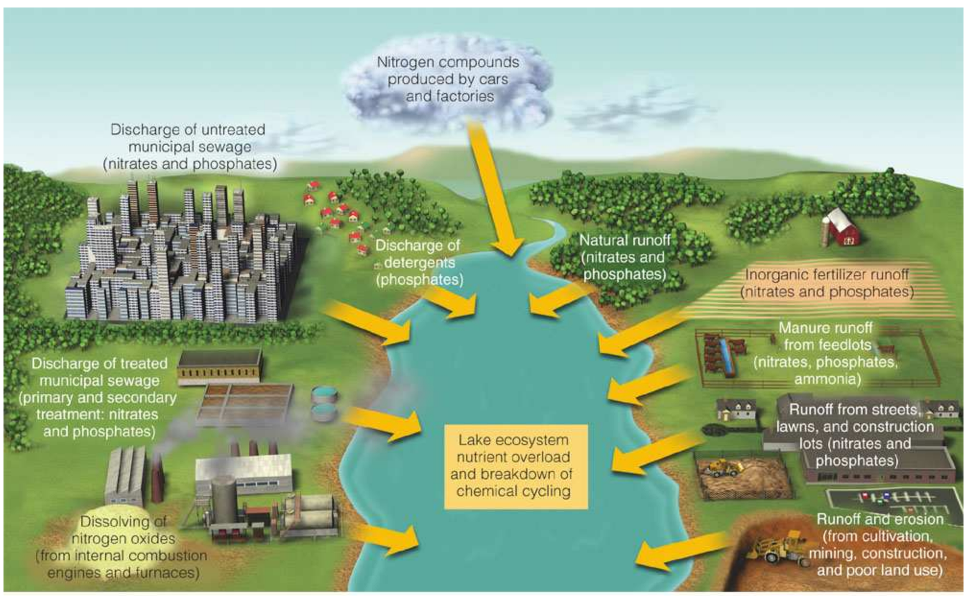


Table1.1. Essential Plant Nutrients: Sources and Functions

Nutrient	Source	Function
Macronutrients		
Carbon (CO_2)	Atmosphere, decay	Biomass constituent
Hydrogen	Water	Biomass constituent
Oxygen	Water	Biomass constituent
Nitrogen (NO_3^-)	Decay, pollutants, atmosphere (from nitrogen-fixing organisms)	Protein constituent
Phosphorus (phosphate)	Decay, minerals, pollutants	DNA/RNA constituent
Potassium	Minerals, pollutants	Metabolic function
Sulfur (sulfate)	Minerals	Proteins, enzymes
Magnesium	Minerals	Metabolic function
Calcium	Minerals	Metabolic function
Micronutrients		
B, Cl, Co, Cu, Fe, Mo, Mn, Na, Si, V, Zn	Minerals, pollutants	Metabolic function and/or constituent of enzymes

1.3. ORGANIC POLLUTANTS

Thousands of different organic chemicals are synthesized each year for use as insecticides, herbicides, detergents, soaps, insulating materials, plasticizers, solvents, cosmetics, and pharmaceuticals and for many other purposes. Among these some are easily biodegradable (for example - oil, grease, soaps, detergents etc). But unfortunately many of these materials cannot be broken down by microorganisms in water as they are very stable and persist for long periods in the environment. These are significant water pollutants.

Careful control of sewage sources is needed to minimize sewage pollution problems. Particularly, heavy metals and refractory organic compounds need to be controlled at the source to enable use of sewage, or treated sewage effluents, for irrigation, recycling to the water system, or groundwater recharge.

1.3.1. Biodegradable pollutans

<u>*Soaps (biodegradable)*</u>

Soaps may be present in the sewage. They are salts of higher fatty acids (week acid), such as sodium stearate, $C_{17}H_{35}COO^{-}Na^{+}$.

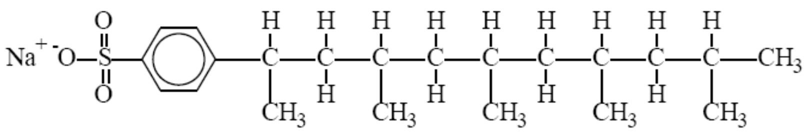
When the soap molecule comes in contact with the hardness ions like Ca^{2+}, Mg^{2+}, then they form ppt with ca^{2+}, Mg^{2+} / We know that soaps react with salts of magnesium or calcium to form insoluble salts of fatty acids:

$$2C_{17}H_{35}COO^{-}Na^{+} + Ca^{2+} \rightarrow Ca(C_{17}H_{35}CO_2)_2(s) + 2Na^{+}$$

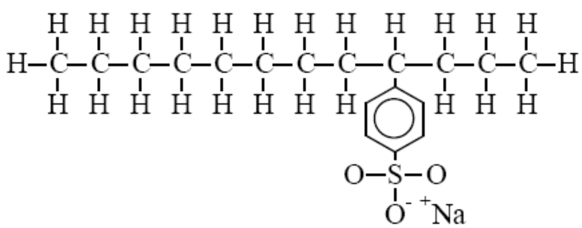
This reaction has distinct advantages from the environmental standpoint. As soon as soap gets into sewage or an aquatic system, it generally precipitates as calcium and magnesium salts. Hence, any effects that soap might have in solution are eliminated. With eventual biodegradation, the soap is completely eliminated from the environment.

Detergents

The key ingredient of detergents are – surfactant and builders. Surface-active agents basically improve the wetting qualities of water. Nowadays, biodegradable surfactants are used. A commercial solid detergent contains only 10-30% surfactant. Alkyl benzene sulfonate (ABS), it biodegrades very slowly because of its branched-chain structure (ie., contain the tertiary carbon). (<u>**structures are just for your information, not to memorize**</u>)



That's why ABS was replaced by a biodegradable surfactant known as linear alkyl sulfonate LAS. LAS is more biodegradable than ABS because the alkyl portion of LAS is not branched and does not contain the tertiary carbon which is so detrimental to biodegradability. Since LAS has replaced ABS in detergents, the problems arising from the surface-active agent in the detergents (such as toxicity to fish fingerlings) have greatly diminished and the levels of surface-active agents found in water have decreased markedly.



LAS

In addition, the builders added to detergents. Polyphosphates added to form complex with calcium and to function as builders. The builders added to detergents continued to cause environmental problems for a longer time.

Some detergents still contain polyphosphates. The polyphosphates have caused the most concern as environmental pollutants, although these problems have largely been resolved by using biodegradable builders (eg., Acrylic polymer, Unsaturated carboxylic acid polymer). Detergents are the salts of relatively strong acids and, therefore, they do not precipitate out.

1.3.2. Nonbiodegradable Organic Pollutants

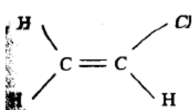
From Industrial sources

1.3.2. i) Volatile Organic Compounds

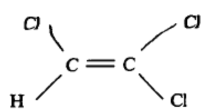
These are the organic compounds that are volatile (evaporate or vaporize readily under normal conditions). VOCs may be natural or synthetic. The compounds, the nose detects as smells, are generally VOCs.

Examples:

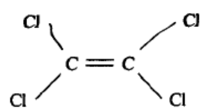
Benzene, methane, chlorofluorocarbons, vinyl chloride (chloroethylene), trichloroethylene, tetrachloroethylene, carbon tetrachloride, 1,2-dichloroethane etc.



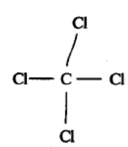
Vinyl chloride



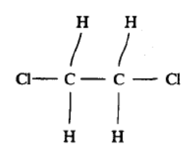
Trichloroethylene



Tetrachloroethylene



Carbon tetrachloride



1,2-Dichloroethane

Sources:

(i) The most abundant source of VOCs is fossil fuel products such as gasoline and fuel oil.

(ii) Volatile organic compounds are produced naturally through biological mechanisms such as metabolism.

(iii) VOCs can be found at airports and automobile service stations, machine print and paint shops, electronics and chemical plants.

(iv) Trichloroethylene is a solvent that was quite commonly used to clean everything from electronics parts to jet engines and septic tanks. It is a suspected carcinogen and it is among the most frequently found contaminants in groundwater.

<u>Uses :</u>

Modern industrial chemicals such as

(i) fuels, solvents, coatings, feedstocks, and refrigerants are usually VOCs.

(ii) They are used as solvents in laboratories, industrial processes and

(iii) in many household products, examples include: paints and lacquers, paint strippers, cleaning supplies, pesticides, building materials and furnishings, office equipment such as copiers and printers, correction fluids and carbonless copy paper, graphics and craft materials including glues and adhesives, permanent markers, liquefying agents in fuels, degreasers, solvents, polishes, cosmetics and photographic solutions.

<u>Toxic effects</u>

(i) Volatile organic compounds (VOCs) are among the most commonly found contaminants in groundwater. Once they enter groundwater, VOCs can remain there for years decomposing slowly because of the cool, dark environment. Since they are volatile, they are not often found in concentrations above a few $\mu g/L$ in surface waters, but in groundwater their concentrations can be hundreds or thousands of times higher.

(ii) A number of VOCs are either known or suspected carcinogens or mutagens. Benzene is a known human carcinogen (the main indoor sources of this chemical are environmental tobacco smoke, stored fuels and paint supplies, and automobile emissions in attached garages).

1.3.2. ii) Persistent Organic Pollutants (POPs)

These are the compounds which are mostly aryl or chlorinated hydrocarbons (frequently halogenated, usually with chlorine). Persistent Organic Pollutants (POPs) persist in the environment for long period of time, because, they are resistant to environmental degradation through chemical, biological, and photolytic processes. These substances are hard to be broken down in soil, air, and/or water, remaining in the environment for long periods of time. That’s why there is growing concern about them. POPs have high lipid solubility. When these compounds get into the water, they pose a threat to aquatic life, because they are stable and poorly biodegradable substances ie., they do not readily break into simpler, less toxic forms and have been found in drinking water.

So, the three main points about the POPs are as following :

i) They are very stable, so they do not break down into simpler less toxic form very easily in the environment, so they persist in the environment for long period of time.

ii) They are poorly biodegradable, they are resistant to environmental degradation through chemical, biological, and photolytic processes.

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

There are many different chemicals both natural and anthropogenic which may be defined as POPs. Though there are a few natural sources of POPs, most POPs are created by humans. But, 12 (or more) of these biorefractory compounds are especially referred to as **Persistent Organic Pollutants (POP)** because of their toxic effects to humans and environment. Of these 12 POPs, 10 are intentionally produced (in industrial processes, either intentionally or as byproducts of various combustion) and 2 are unintentionally produced.

10 intentionally produced POPs are as follows: PAHs, PCBs, DDT, heptachlor, chlordane, aldrin, dieldrin/endrin, Mirex, toxaphene, Hexachlorobenzene and 2 unintentionally produced POPs are — dioxins (both polychlorinated dibenzodioxins (PCDD) and polychlorinated dibenzofurans (PCDF)). Polychlorinated hydrocarbons are insoluble in water but soluble in fat. They become concentrated in the fatty tissues of fish, and also in birds and humans who eat fish.

If they enter waterways, they can cause serious environmental problems as well as health problems like neurologic disorders, genetic damage, cancer, they can suppress the immune system, infertility, reduced sperm count or other ill effects. Sometimes, there is growing concern because they may act as hormone disrupters (*the synthetic chemicals that block, mimic or otherwise interfere with naturally produced hormones*).

These POPs can be transported long distances by wind and water before they are finally deposited and have been found on every continent, at sites representing every major climatic zone and geographic area throughout the world. *They are not efficiently removed by primary and secondary sewage-treatment processes*.

The more chlorine groups a POP has, the more resistant it is to being broken down over time. Many of these compounds are known to cause taste and odor problems in water. That’s why the uses and disposal of POPs are strictly controlled and they should be disposed properly.

Most of these compounds have been banned in the developed countries (because they get into the soil, sediments and pollutes the water) but the under developed countries and some of the developing countries are still manufacturing/using these harmful chemicals. Since, POPs persist in the environment for many years and they bioaccumulate in fish in many lakes in the developed countries still contain significant levels of these kinds of contaminations. That's why learning about these harmful POPs is justified and we need to know about their harmful effects, their toxicities to humans.

(i). <u>Polynuclear aromatic hydrocarbons, PAHs</u>

The polycyclic aromatic hydrocarbons (or polynuclear hydrocarbon or poly-aromatic hydrocarbons) contain two or more fused aromatic rings and neither contain heteroatoms nor substituents.
Eight of the PAHs are considered to be possible or probable carcinogens.

<u>Examples:</u>

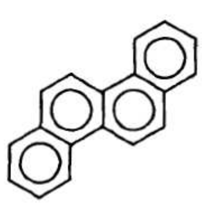
Naphthalene, anthracene, phenanthrene, chrysene, Benzo[α]pyrene etc.

<u>Sources :</u>

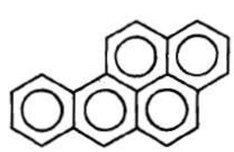
i) These compounds occur in natural crude oil, coal, and tar deposits, because of the chemical conversion of natural product molecules, such as steroids, to aromatic hydrocarbons.

(ii) Cereals, edible oils and fats contain PAHs. Benzo[α]pyrene has been found in various types of cereals, vegetables, fruits, and meats.

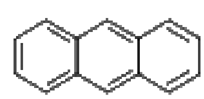
(iii) PAHs are also produced as byproducts of incomplete combustion of hydrocarbons. Natural sources include forest fires, prairie fires and volcanic eruptions.
Anthropogenic sources include motor vehicles (particularly diesel engines), cooking ovens, asphalt manufacture, fossil-fuelled furnaces, cigarettes and barbecues.



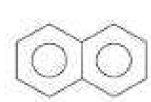
Chrysene



Benzo(a)pyrene



Anthracene



Naphthalene
$C_{10}H_8$

Structures of chrysene and benzo(a)pyrene, two examples of the polynuclear aromatic hydrocarbon, PAH, group of compounds.

Uses :

Many of these compounds have no use other than research. There are some, however, that are important 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). A mixture of phenanthrene and anthracene tar is used to coat water storage tanks to prevent rust.

Toxic effects

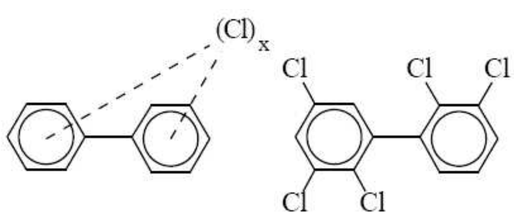
As a pollutant, they are of concern because

(i) Some compounds have been identified as carcinogenic. Naphthalene is a suspected human carcinogen, and has cause damage to the kidneys and to the liver.

(ii) Higher incidences of lung and skin tumors have been reported for people who have been occupationally exposed to naphthalene and other polynuclear aromatic hydrocarbons.

B. POLYCHLORINATED BIPHENYLS

Polychlorinated biphenyls (**PCB** compounds) are fat soluble and bioaccumulate through the food webs. Polychlorinated biphenyls (PCBs) are a class of organic compounds with 1 to 10 chlorine atoms attached to biphenyl. 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 United States Congress in 1979.



The chemical formula of PCB's can be presented as $C_{12}H_{10-n}Cl_n$, where `n' is a number of chlorine atoms within the range of 1-10.

They are made by substituting from 1 to 10 Cl atoms onto the biphenyl aryl structure as shown on the left in the above Figure. This substitution can produce 209 different compounds (congeners) of which one example is shown on the right in the above Figure.

Polychlorinated biphenyls have very high chemical, thermal, and biological stability; low vapor pressure; and high dielectric constants.

Sources:

PCBs, a by-product of coal tar.

Uses:

PCBs were widely used in

(i) hydraulic fluids,

(ii) plasticizers,

(iii) inks,

(iv) lubricants,

(v) waxes, and

(vi) adhesives,

(vii) in addition to being used to insulate electrical capacitors and transistors (PCBs are used as insulating materials (coolant-insulation fluids) in transformers and electrical capacitors).

(viii) PCBs are fire resistant and have a high electrical resistance;

(ix) for the impregnation of cotton and asbestos;

(x) as additives to some epoxy paints; and as plasticizers in plastic industries. Plastics tend to brittle; the addition of PCBs makes tem more flexible and resistant to cracking. They are still present in older equipments.

The extraordinarily stability once made PCBs useful but, this stability contributes to their bioaccumulation in the environment.

Toxic effects:

(i) Disposal of PCBs are problematic because PCBs are volatile and they will escape from ordinary incinerator as vapors. When plastic wastes and other PCB-containing materials are burned, PCB vapors condense on airborne particles that then fall directly onto water or reach water in runoff from the land. So, special kinds of incineration processes are needed to destroy them.

(ii) There is growing concern that many of PCBs interfering with the endocrine system (they mimic, block or otherwise interfere with naturally occurring hormones) in both animals and humans and disrupting reproduction and fetal development.

(iii) PCBs make eggshell thin and cause neurologic damage in birds.

(iv) In humans, they cause liver damage and most important, they can be transferred from mother to fetus through the placenta.

C. DDT and other Organochlorine Insecticides

We all know that DDT is a pesticide. Pesticides are chemicals or biological agents used to control, repel, attract or kill pests. Pests are organisms that include insects, weeds or other plants, birds, mammals, fishes and microorganisms that compete with humans for food; destroy properties, spread disease or are considered a nuisance. Pesticides are the significant water pollutants.

Pesticides includes ─ **Insecticides** are used to kill the insects. **Herbicides** are used in the control of weeds and to kill plants. **Fungicide**s are used against fungi, **bactericides** against bacteria and **algicides** against algae.

Insecticides and herbicides are the most important pesticides with respect to human-exposure-in-food because they are applied shortly before or even after harvesting. That's why there is a high chance of the foods to be contaminated by the pesticides and water also gets polluted by the runoff from treated land.

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 pyrethrums flower,

(iii) rotenone extracted from tropical derris plants (certain legume roots) and

(iv) garlic oil.

The massive use of pesticides began at the end of World War II with the introduction of DDT. There are other types of pesticides also, which I will describe after this segment.

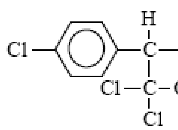
DDT

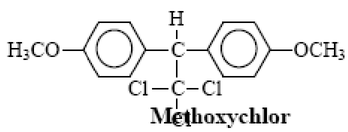
DDT dichlorodiphenyltrichloroethane or 1,1,1-trichloro-2,2-bis(4-chlorophenyl) ethane.

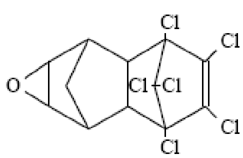
When DDT was first introduced in late 1940s, it appeared to be an ideal insecticide. It was cheap to produce and because it was stable, that's why its effect used to remain for long period of time. Apparently it was non-toxic to humans and other mammals because, it did not break down easily.

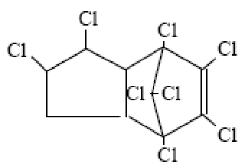
However, later it was discovered that runoff from treated land was having devastating effect on fishes, fish-eating birds. In 1973, the use of DDT was banned in USA and since then (since that time) fish-eating birds have made a dramatic recovery.

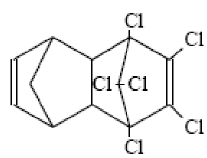
You need to remember the structure of DDT only, not the others.

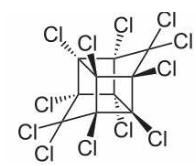

DDT

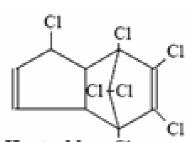

Methoxychlor

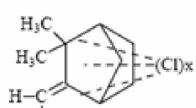

Dieldrin/Endrin


Chlordane


Aldrin


MIREX

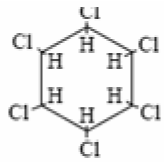

Heptachlor


Toxaphene

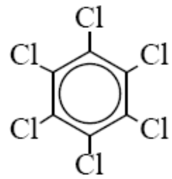
Because of the high rates of application and because these are nonbiodegradable, the organochlorine insecticides polluted surface water and groundwater still found from fields where they were formerly applied. The soil half-life is 2-15 years, and 150 years in the aquatic environment. The organochlorine insecticides used in the 1960s have been largely phased out of because of their toxicities, and particularly their accumulation and persistence in food chains.

D. Hexachlorobenzene

Hexachlorobenzene is used as a raw material for the synthesis of many pesticides and it is degradation-resistant. It is has often been found in water.



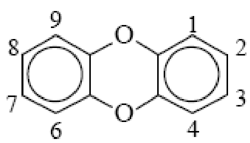
1,2,3,4,5,6-Hexachloro-cyclo-hexane, gamma isomer (Lindane)



Unintentionally produced POPs.

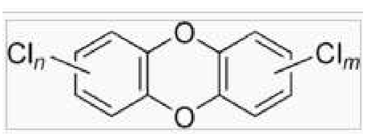
E. Polychlorinated dibenzo-*p*-dioxins (PCDDs) or simply DIOXINs

Polychlorinated dibenzo-*p*-dioxins are not produced intentionally.

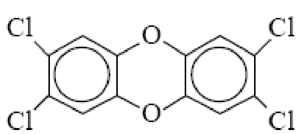


Dibenzo -*p* -dioxin

In PCDDs, chlorine atoms are attached to this structure at any of 8 different places on the molecule, at positions 1–4 and 6–9 and give 75 possible chlorinated dioxins (giving a total of 75 possible chlorinated derivatives). These are commonly referred to as “dioxins”.



General structure of PCDDs where *n* and *m* can range from 0 to 4, but m & n cannot be zero at the same time.



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

Of the dioxins, The most toxic chemical in the class is 2,3,7,8-tetrachlorodibenzo-para-dioxin (TCDD).

Sources:

➢ Dioxins are produced during the manufacture of items such as preservatives, fungicides, and herbicides (ie., it is the byproducts of 2,4,5-T herbicide manufacture). As a result of this concern, the use of has been banned in 1985.

➢ Its major source is the burning of chlorine containing medical and municipal wastes in municipal incinerator, because, chlorine from organochlorine compounds reacts with carbon in the incinerator.

➢ During the incomplete combustion of chlorine containing hydrocarbons, dioxins are produced, examples include wood stove fires, barbecues, forest fires and other natural burning methods also produce dioxins.

➢ Power plants, and heavy metal recycling plants also produce dioxins.

<u>Toxic effects of TCDD :</u>

(i) TCDD is of especial concern among the dioxins. TCDD is a known carcinogen for many animals (TCDD shows the highest toxicity to mammals). Humans are primarily exposed to dioxins by eating food contaminated by these chemicals.

(ii) It can cause skin disease, reproductive and developmental problems and also, increase risk of cancer, heart disease and diabetes.

(iii) Dioxin accumulates in the fatty tissues, where they may persist for months or years. People who have been exposed to high levels of dioxin have developed chloracne, a skin disease marked by severe acne-like pimples.

(iv) Studies have also shown that chemical workers who are exposed to high levels of dioxins have an increased risk of cancer.

(iv) Other studies of highly exposed populations show that dioxins can cause reproductive and developmental problems, and an increased risk of heart disease and diabetes. More research is needed to determine the long-term effects of low-level dioxin exposures on cancer risk, immune function, and reproduction and development.

(v) TCDD has a very high vapor pressure (volatile), a high melting point of 305°C, and a water solubility of only 0.2 μg/L. It is stable thermally up to about 700°C, has a high degree of chemical stability, and is fat soluble, thus poorly biodegradable.

Please see the class note for **lipophilicity**.

<u>1.5. Less persistent insecticides</u>

Chlorinated hydrocarbons kill a wide range of insect types including many that are beneficial, that’s why chlorinated insecticides are known are broad-spectrum insecticides.

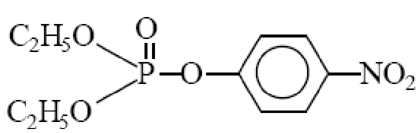
There are other types of insecticides which are known as narrow-spectrum insecticides – example of this type are organophosphates and carbamates in general. Narrow-spectrum means these are toxic only to a few types of insects. These are also considered to be non-persistent because they break down rapidly once they have been released into the environment.

But, these classes of insecticides also cause water pollution, because of their widespread use, the contamination of drinking water or food by these pesticides has been reported. At the same time, they are still toxic to humans and other animals. Exposures occur when farmers spray insecticides and herbicides, farmers can inhale the pesticides while spraying, or some pesticides can be absorbed through the skin. But with masks and protective clothing this contamination can be avoided.

1.5.1. Organophosphate Insecticides

Unlike the organohalide compounds, the organophosphates readily undergo biodegradation and do not bioaccumulate. This property makes then disadvantageous also because, as they break down rapidly in the environment, they must be applied frequently to be effective.

Organophosphates are cheap to produce and are very effective against many different insects. Organophosphate insecticides contain pentavalent phosphorus atom, examples include paraoxon, parathion, malathion.



(**Structure is for your information, not to memorize**)

Parathion

Toxic effects :

(i) Parathion is very toxic to humans. Most accidental poisonings have occurred by absorption through the skin. But this kind of contamination can be avoided if farmers wear respirators and protective clothing when applying them. As little as 120 mg of parathion has been known to kill an adult human, and a dose of 2 mg has killed a child. Most accidental poisonings have occurred by absorption through the skin. Since its use began, several hundred people have been killed by parathion. Parathion is 20 times more toxic to rats as compared to DDT. Parathions are used on fruits. Pesticide residue in foods may cause adverse health effects.

(ii) Parathions are used on fruits. Pesticide residue in foods may cause adverse health effects.

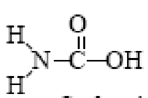
(iii) In contrast, malathion is relatively nontoxic to humans. Mammals possess a particular enzyme that can hydrolyse malathion.

(iv) Exposure of organophosphates by humans can result in irregular heartbeat and even death.

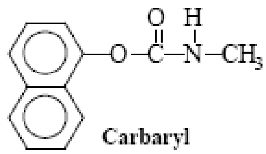
1.5.2. Carbamates

Another type of insecticides is carbamates.

Carbamates are made by the derivatives of carbamic acid**,** shown below (not to memorize).



Carbamic acid



Carbaryl

Carbamate pesticides have been widely used because some are more biodegradable than the organochlorine insecticides, they are rapidly broken down in animal tissues and in the environment and have lower dermal toxicities than organophosphate pesticides.

They are of three types –

Carbaryl has been widely used as an insecticide on lawns or gardens.

Carbofuran is highly soluble in water – it is taken up by the roots and absorbed by the leaves of plants so that insects are poisoned by the plant material on which they feed.

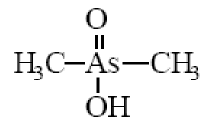
Pirimicarb has been widely used in agriculture as a systemic aphicide (kills aphides, means insects which damages the plants). Unlike many carbamates, it is rather persistent, with a strong tendency to bind to soil.

Carbamates have toxic effects to animals if they are ingested or by inhalation of spray, skin contact, because they inhibit some enzymic activity.

1.6. Herbicides

In addition to animal pests, farmers also need to control weeds, (competes with crops for nutrients and water). Herbicides are applied on farmland worldwide and they are widespread water pollutants.

Earlier inorganic chemicals used for weed control and they were non-selective eg., solutions of sodium chlorate ($NaClO_3$), sulfuric acid, copper salts (Paris Green, $Cu_3(AsO_3)_2$), arsenic trioxide and other arsenic compounds includes lead arsenate, $Pb_3(AsO_4)_2$ etc. Organic arsenicals, such as cacodylic acid, have also been widely applied to kill weeds (Structure is only for your information).



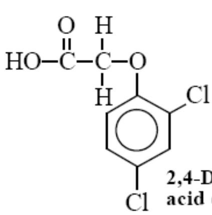
Hydroxydimethylarsine oxide, cacodylic acid

Because of the high rates of application and because arsenic is nonbiodegradable, the arsenic polluted surface water and groundwater still found from fields where inorganic arsenic compounds formerly applied.

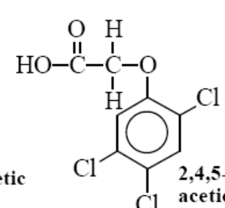
Most selective herbicides are systemic herbicides. They are absorbed by leaves or taken up by roots and then are transferred through the plant. They act like growth hormones and cause the plant to grow so fast that it dies. Sometimes, they work by inhibiting the enzymes necessary for the synthesis of essential amino acids (*this amino acid protects the plants from predators such as insects*). By stopping this essential biosynthetic pathway kills the plant. Animals are unaffected by these systemic herbicides because, their biosynthetic pathways are different from those of plants.

1.6.1. Chlorophenoxy Herbicides

The chlorophenoxy herbicides, including 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) shown below (structures are only for your information). 2,4-D is very effective against emerging broad-leaved weeds and 2,4,5-T used to control woody plants.



2,4-Dichlorophenoxyacetic acid (and esters), 2,4-D



2,4,5-Trichlorophenoxy-acetic acid (and esters), 2,4,5-T

Mixture of 2,4-D and 2,4,5-T in equal quantities is known as **Agent orange**. It is a defoliant (which causes leaves to fall-off) used during the Vietnam War. Because of health problem associated with its use, it has been banned in 1985.