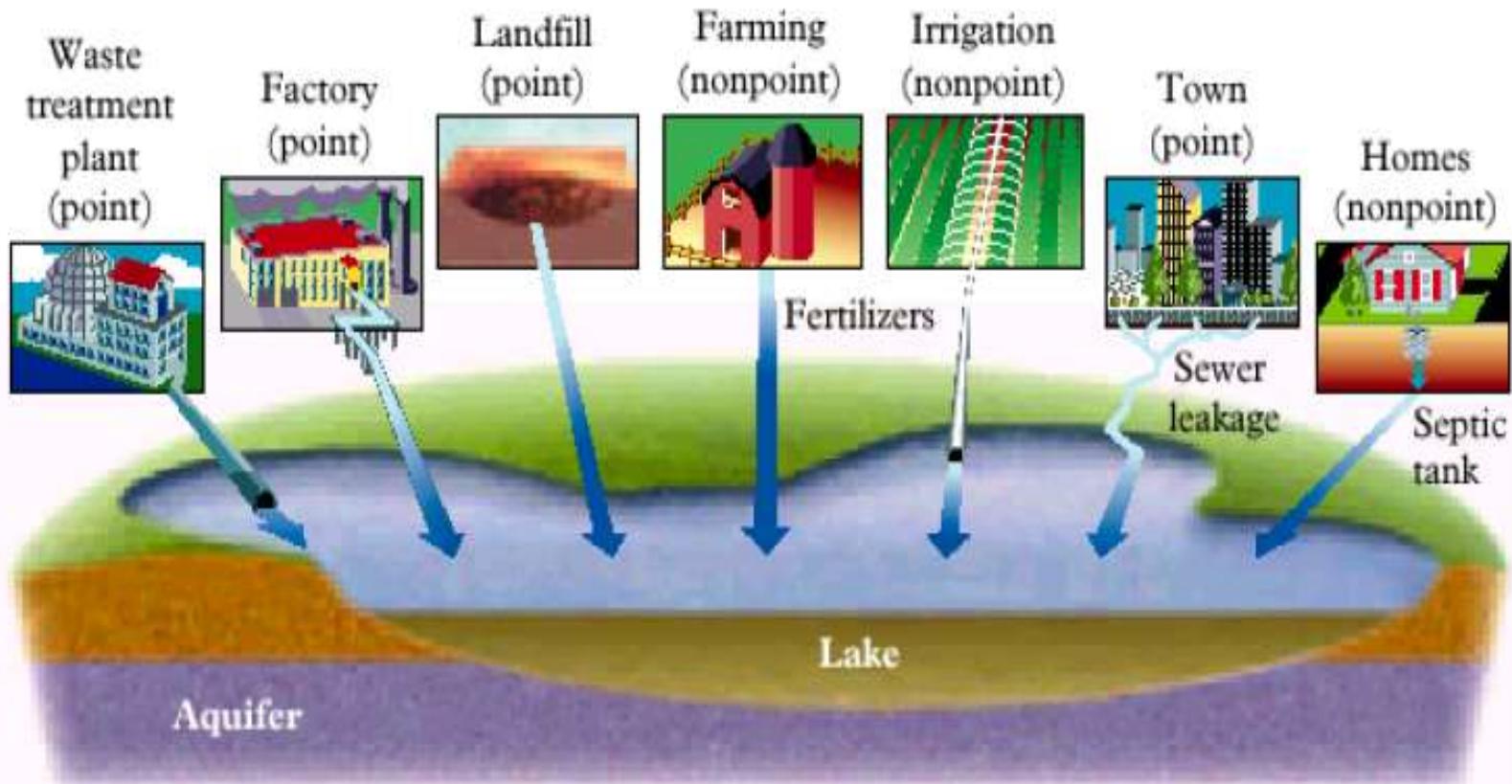


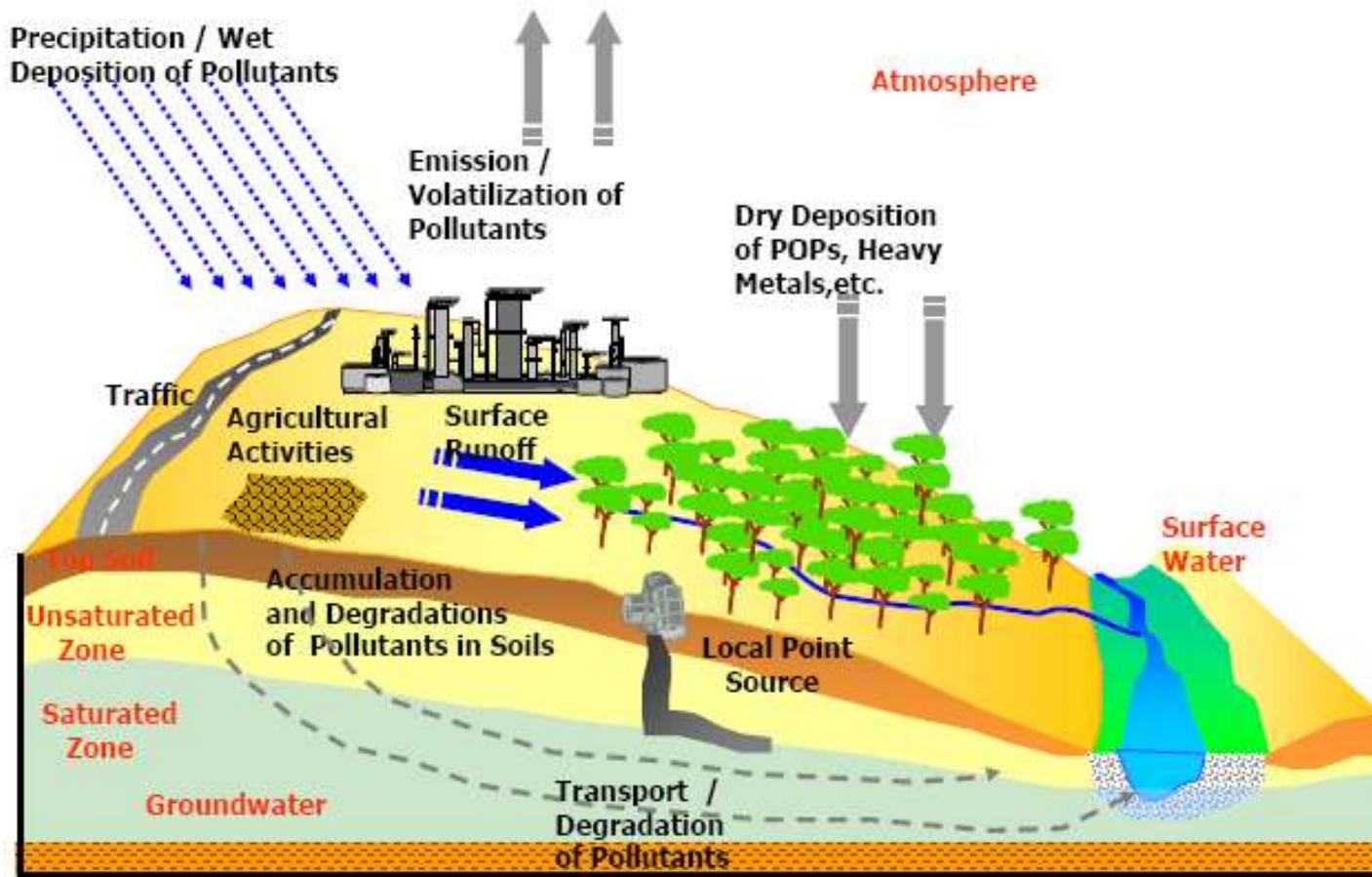
This material is for reference only. Points present in the slides are only for assistance and their elaboration are present in book. Examination questions will be in depth and can be solved by following text book only.

Water treatment: The Purification of Water

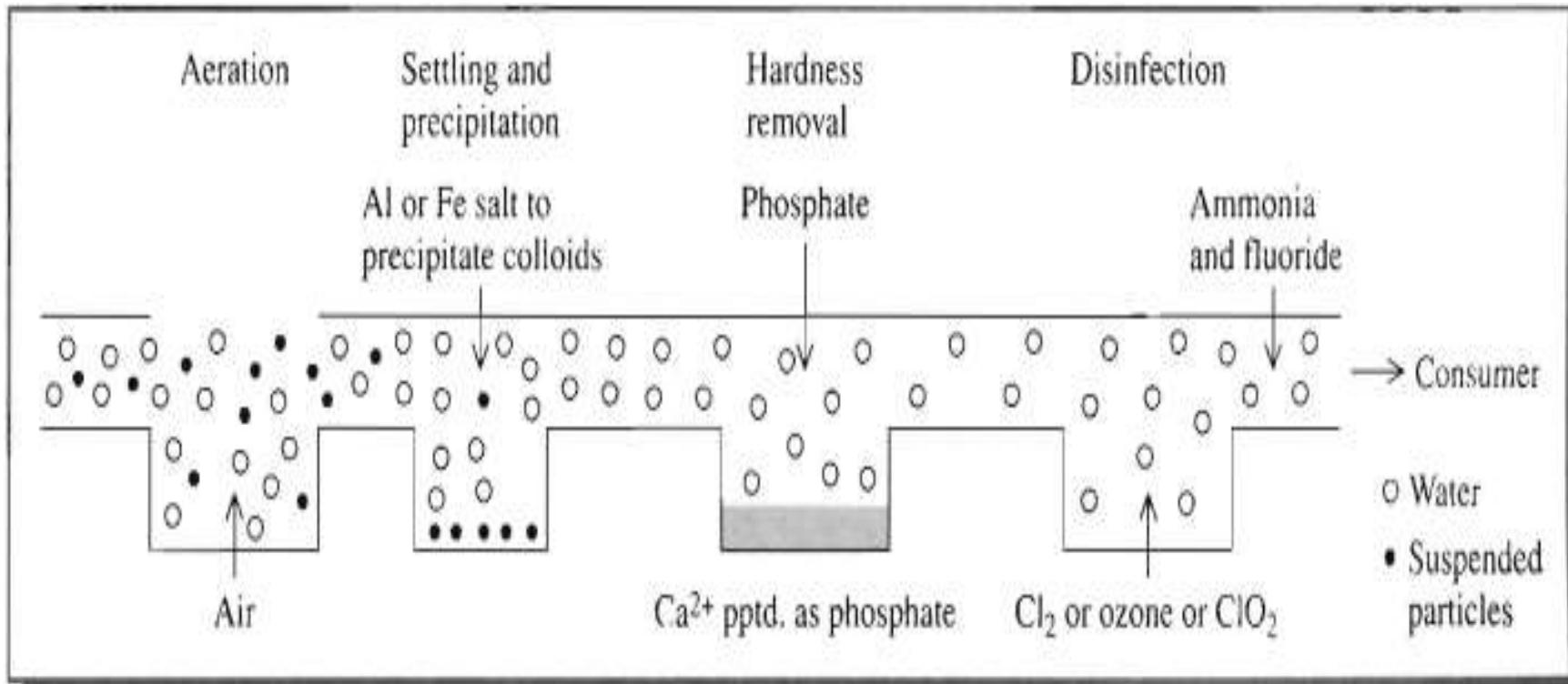
Hydrological Cycle - Pollutants



Hydrological Cycle – Pollutants II



Process flow of Treatment



Aeration of water

- To improve water quality.
- To remove dissolved gases like H₂S and organosulfur and VOCs.
- For oxidation of easily oxidizable organics.
- For oxidation of ferrous to ferric and then



- Organics can also be removed by activated carbons.
- Because both the type and quantity of pollutants in raw water vary, therefore the processes of purification also vary from place to place.

Removal of Calcium and Magnesium

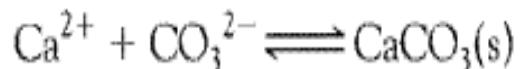
- From where these come?
- Why they should be removed?

How they can be removed:

- Adding phosphate ions to precipitate the cations
- More commonly removed as precipitates of calcium carbonate by adding sodium carbonate

Or

- If sufficient bicarbonate is present then hydroxide ion is added



Removal of Magnesium ion

- As precipitates of magnesium hydroxide, $\text{Mg}(\text{OH})_2$ when water is made alkaline.
- After this filtration of both type of precipitate is done.

Purification of Water

Aeration of water

To remove dissolved gases such as the foul-smelling hydrogen sulfide, and organosulfur compounds, as well as volatile organic compounds.

To oxidize easily oxidizable organic matters.

To oxidize water-soluble Fe^{2+} to Fe^{3+} , which then forms insoluble hydroxides (and related species) that can be removed as solids.



Removal of Calcium and Magnesium

Calcium ion is removed by adding phosphate anion, carbonate anion and hydroxide anion via precipitation, Calcium carbonate and calcium carbonate are insoluble.



Magnesium ion precipitates as magnesium hydroxide, $\text{Mg}(\text{OH})_2$,

After removal of Calcium and magnesium ions, pH of the solution is readjusted by bubbling carbon dioxide in water.

Removal of Colloidal Particles by Precipitation

- **Colloidal particles:** These are particles that have diameters ranging from 0.001 to 1 μm and consist of *groups of* molecules or ions that are weakly bound together.
- To capture the colloidal particles, a small amount of either iron(III) sulfate, $\text{Fe}_2(\text{SO}_4)_3$ or aluminum sulfate, $\text{Al}_2(\text{SO}_4)_3$, is deliberately dissolved in the water.
- These groups dissolve as a unit, rather than breaking up and dissolving as individual ions or molecules
- pH is adjusted around 7, both the Fe^{3+} and Al^{3+} ions produced from the salts form **gelatinous hydroxides** that physically incorporate the colloidal particles and form a removable precipitate (**Coagulation**).

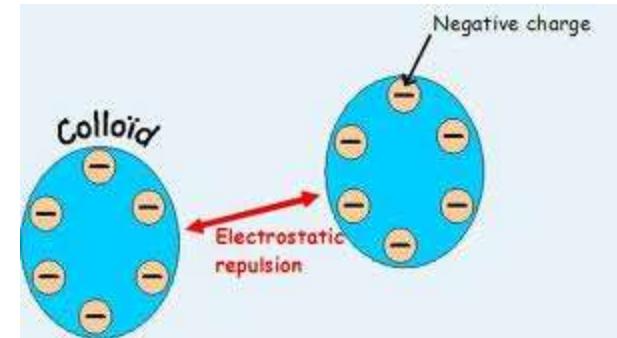
Removal of Colloidal Particles by Precipitation

How to remove?

Iron(III) sulfate $\text{Fe}_2(\text{SO}_4)_3$ or aluminum sulfate

$\text{Al}_2(\text{SO}_4)_3$ (alum) and making water neutral or alkaline.

Fe^{3+} and Al^{3+} from the salts form gelatinous hydroxides which physically incorporate the colloidal particles and form removable precipitates.



Water disinfection: Disinfection to Prevent Illness by physical and chemical methods

- Disinfection?
- Bacteria like *Salmonella* genus, *Escherichia coli*
- Viruses like polio, hepatitis-A etc.
- Protozoans (single celled animals)

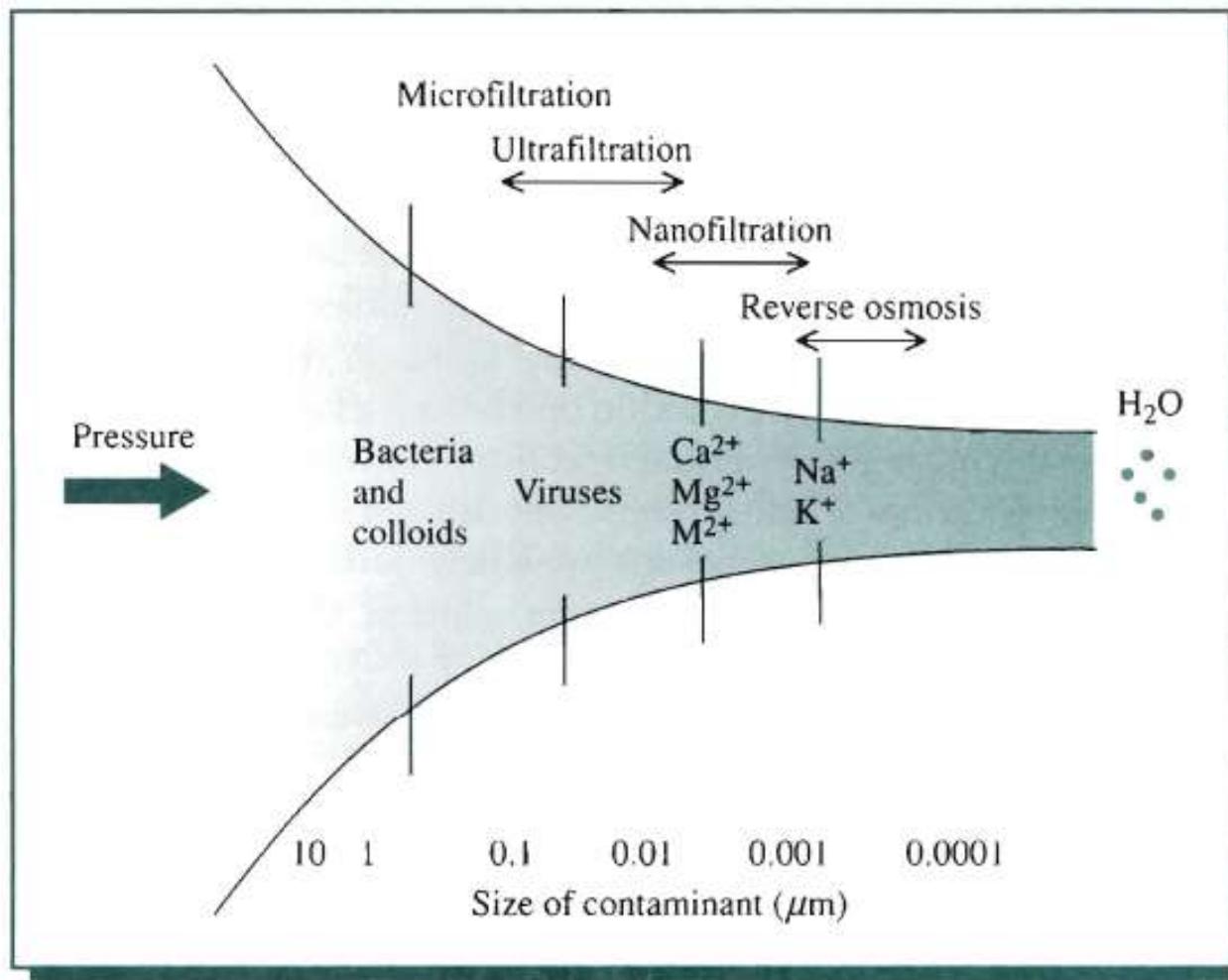
Filtering of Water

- Water contain multitude of tiny particles from natural or anthropogenic
- Natural?
- Anthropogenic?
- Effect?
- Large particles are often removed by filtration through sand filters ($10\mu\text{m}$).

Disinfection of Water by Membrane Technology

Membranes contain pores of uniform and microscopic size.

For a technique to be effective in providing a barrier, the pore size of the membrane must be smaller than the contaminant size.



Types of Filtration

- Microfiltration and Ultrafiltration: 0.002 to 10 μm diameters (2-10000 nm)
- Pressure or suction may be used for this.
- Thousands of strands of plastic tubing having tiny pores.
- Size of bacteria are as small as 0.1 μm and viruses 0.01 μm which require **ultra filtration**.
- Dissolved ions and organic molecules require **nanofiltration (1nm)** but **pretreatment is must**.
- Nanofiltration can also be used to soften the water?
- Hydrated monovalent ions such as Na and Cl can pass through nanofilters so require subnanometer pore size.

Purification of water by Reverse Osmosis (RO)

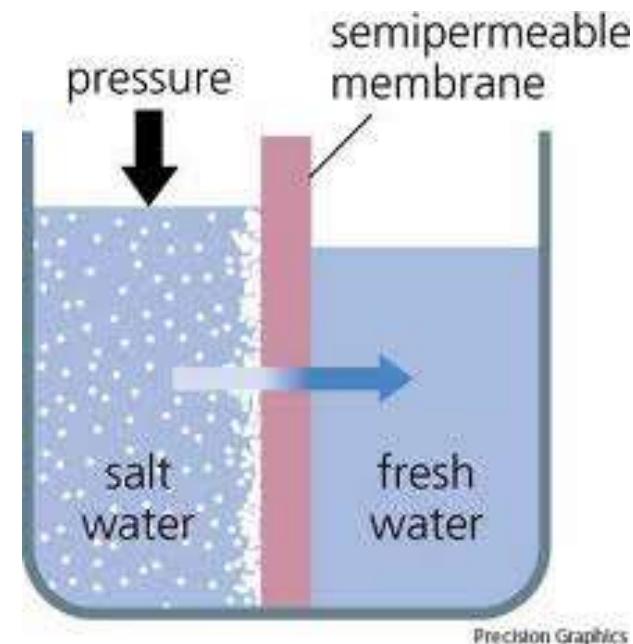
Water is forced under high pressure to pass through the pores in a semipermeable membrane, composed of an organic polymeric material such as cellulose acetate or triacetate or a polyamide.

Particles, molecules (including small organic molecules), and ions down to less than 1 nm (0.001 μm) in size, or about 150 g/mol in mass, are removed by reverse osmosis.

Desalination

Problems/Disadvantages

- Energy intensive process (2 atm pressure for domestic and higher for brines)
- Wasteful
- Accumulated discharge (concentrate)
- Drinking de-ionized water for long time is not good for health.



Disinfection by Ultraviolet Irradiation

Powerful lamps containing mercury vapor whose excited atoms emit UV-C light centered at a wavelength of 254 nm are immersed in the water flow.

About 10 seconds of irradiation are usually sufficient to eliminate the toxic microorganisms.

Action of UV light: disrupts the DNA in microorganisms, preventing their subsequent replication and thereby inactivating the cells.

Disruption during disinfection: dissolved iron and humic substances absorb the UV light and reduce the amount of UV available for disinfection.

Disadvantages:

- Complicated by the presence of dissolved ions and humic substances?
- Small solid particles?



Disinfection by chemical methods

Chlorination: hypochlorous acid, HOCl

At moderate pH: $\text{Cl}_2(\text{g}) + \text{H}_2\text{O}(\text{aq}) \rightleftharpoons \text{HOCl}(\text{aq}) + \text{H}^+ + \text{Cl}^-$

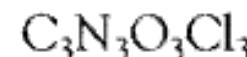
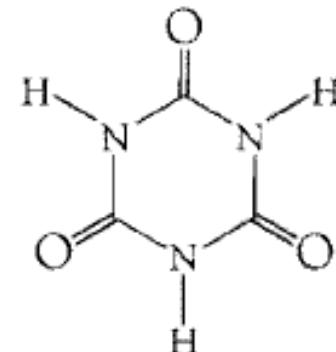
Kills microorganisms, as it readily passes through their cell membranes.

Once chlorination is complete, the pH of the water is adjusted upward, if necessary, by the addition of *lime*, CaO.

Sources of chlorine (HOCl/Cl₂): electrolysis of salty water, calcium hypochlorite, Ca(OCl)₂ an aqueous solution of sodium hypochlorite, NaOCl.



the reaction of isocyanuric acid with water



pH Maintenance

- pH is usually maintained above 7.
- Maintenance of an alkaline pH also prevents the conversion of dissolved ammonia to chloramines.
- Chemicals used to adjust pH of swimming pool are addition of acid (Sodium bisulfate). Or a base (sodium carbonate) or a buffer like sodium bicarbonate.
- Chlorine must be replenished outdoor as UV-A and UV-B can decompose hypochlorite ion.

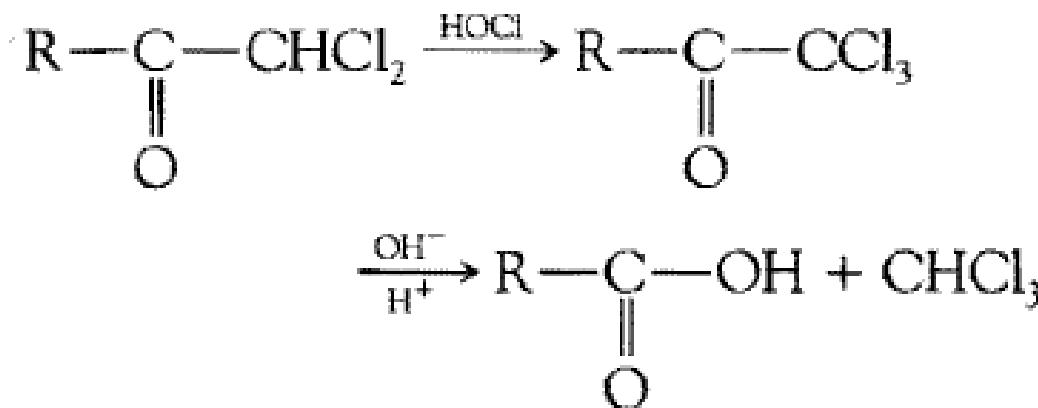
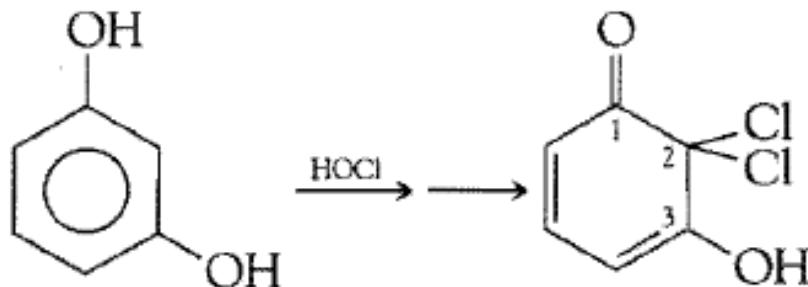
By products and their Health Effects

- **Chloramines** specially NCl_3 is an eye irritant and can cause respiratory problems.
- **Halogenated acetic acids** e.g. Dichloroacetic acid ($\text{CHCl}_2\text{-COOH}$) is a potent carcinogen than chloroform.
- If water contains phenol and a derivative thereof then **chlorinated phenols** are produced which have an offensive odor and taste and toxic.
- Trihalomethanes, **THM's** (CHX_3) e.g. chloroform which is a suspected liver carcinogen and can give rise to negative reproduction effects.

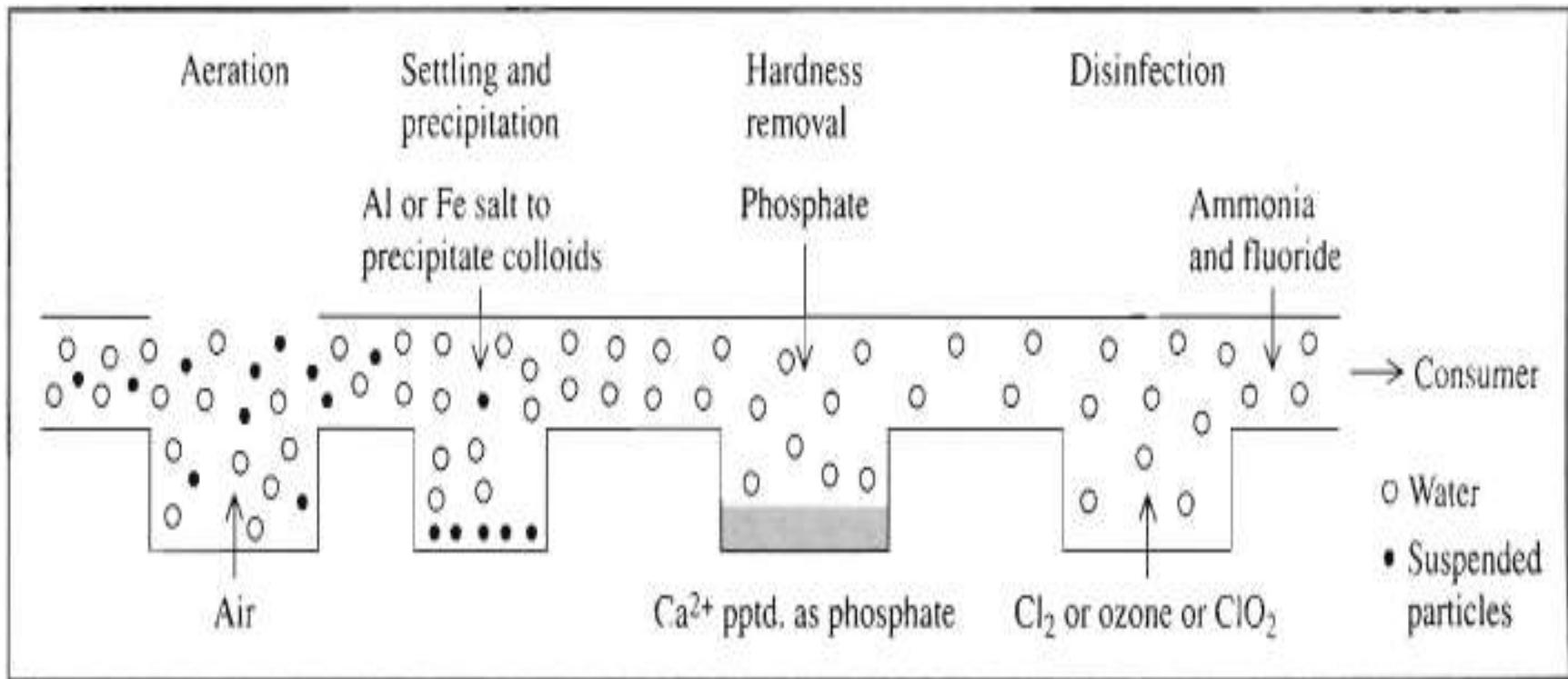
The Mechanism of Chloroform Production in Drinking Water

Humic acids: water-soluble nonbiodegradable components of decayed plant matter.

HOCl reacts with humic acids to form chloroform (carcinogenic).



Advantages of chlorination over other Methods

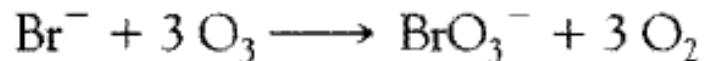


Disinfection by Ozone

- Chemical agent requires an oxidizing agent more powerful than O_2 .
- O_3 : cannot be stored or shipped?
- Generated onsite by relatively **expensive** process involving electrical discharge (20,000 V) in dry air.
- 10 minutes contact is sufficient.
- No residual protection?
- Some pollutants reacts with ozone itself and other with free radicals such as hydroxyl and hydroperoxy produced by ozone.

Continue...

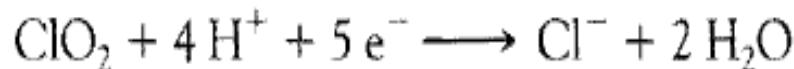
- Many unwanted reaction may occur specially with bromine in water in the formation of oxygen containing organic compounds (containing carbonyl such as formaldehydes and others).
- In addition the bromate ion, a carcinogen in test animals.



- Bromate ion can further react to form toxic organobromine compounds.
- **Disinfection by products:**
 - Disinfection by-products (DBPs) Carcinogens in nature

Disinfection by chlorine dioxide

The ClO_2 molecules, themselves free radicals, operate to oxidize organic molecules by extracting electrons from them:



- The organic cations created in the accompanying oxidation half reaction subsequently react with oxygen to become more fully oxidized.
- **Chlorine dioxide is not a chlorinating agent.**
- Less by products produced as it oxidizes organic matter.

Disadvantages

- ClO_2 can not be stored as it is explosive therefore generated on site (Sodium chlorite, NaClO_2).



- Chlorite and chlorate (ClO_3^-) have potential toxicity.

Waste water Treatment-Tertiary treatment (Chemical process-Chemical coagulation and flocculation)

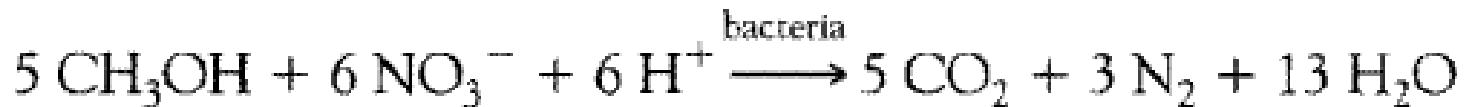
Results the most purified water even suitable for drinking purpose

- Use of aluminum salt to remove remaining colloidal contaminations.
- Removal of dissolved organic compounds (including chloroform) and some heavy metals by their adsorption onto activated carbon.
- Heavy metal removal by the addition of hydroxide or sulfide ions, to form insoluble metal hydroxides or sulfides.
- Removal of iron by aeration at a high pH to oxidize it to its insoluble Fe(III) state.
- Removal of phosphate (to be discussed)

- Removal of ammonia at high pH (11). At high pH ammonium ions turns to molecular form (gas) and can be removed by bubbling air in the water. Energy intensive and expensive
- Ammonium ion can also be removed by ion exchange, using certain resins.

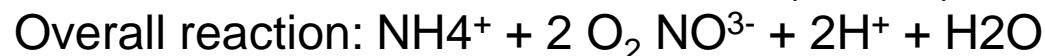
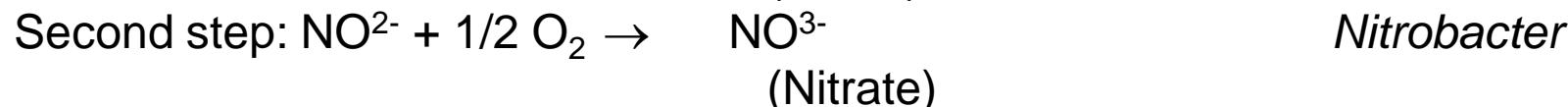
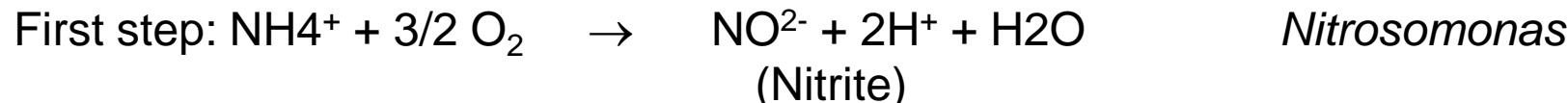


- Organic nitrogen and ammonia can be removed by first using nitrifying bacteria to oxidize all the nitrogen to nitrate ion. Then the nitrate is subjected to denitrification by bacteria to produced molecular nitrogen, N₂, which bubbles out of the water.



Biological Nitrification and denitrification

- ❑ Bacteria remove ammonia nitrogen from wastewater by a two step biological processes:
 - nitrification followed by denitrification to convert it finally to gaseous nitrogen
 - In this gaseous form N_2 is inert and does not react with the wastewater itself or with other constituents present in wastewater.
 - Since, treated wastewater is likely to be saturated with molecular nitrogen; the produced N_2 is simply released to the atmosphere



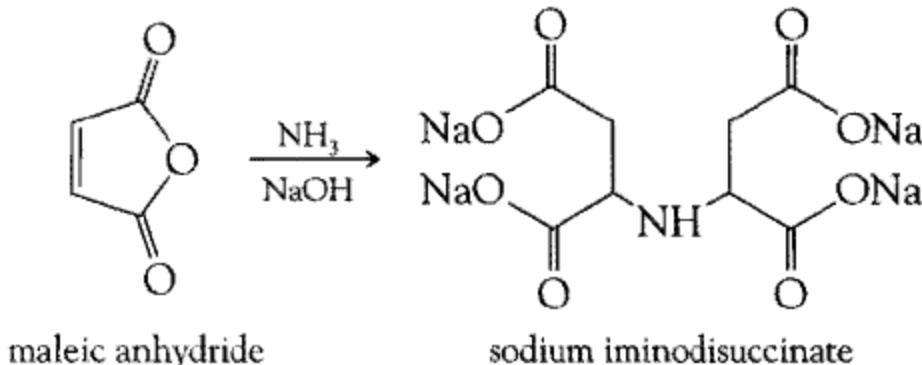
Denitrification

Nitrate, $NO^{3-} \rightarrow$ Nitrite, $NO^{2-} \rightarrow$ Nitric oxide, $NO \rightarrow$ Nitrous oxide, $N_2O \rightarrow$ Nitrogen, N_2

Phosphate removal

- Municipal wastewaters may contain from 5 to 20 mg/l of total phosphorous, of which 1-5 mg/l is organic and the rest in inorganic.
- The individual contribution tend to increase, because phosphorous is one of the main constituent of synthetic detergents.
- Controlling phosphorous discharged from municipal and industrial wastewater treatment plants is a key factor in preventing eutrophication of surface waters.
- Phosphorous is one of the major nutrients contributing in the increased eutrophication of lakes and natural waters.
- Its presence causes many water quality problems including increased purification costs, decreased recreational and conservation value of an impoundments, loss of livestock and the possible lethal effect of algal toxins on drinking water.
- **The usual forms of phosphorous found in aqueous solutions include:**
 - **Orthophosphates:** available for biological metabolism without further breakdown
 - **Polyphosphates:** molecules with 2 or more phosphorous atoms, oxygen and in some cases hydrogen atoms combine in a complex molecule.
 - Usually polyphosphates undergo hydrolysis and revert to the orthophosphate forms. This process is usually quite slow.

Sodium iminodisuccinate: A biodegradable chelating agent



- For absorption of agricultural nutrients
- Metal ion scavenging
- Groundwater remediation and
- As a builder in detergents

Treatment of Cyanides in Water

- Used for extraction of metals: mining, refining and electroplating
- Very poisonous
- Redox chemistry

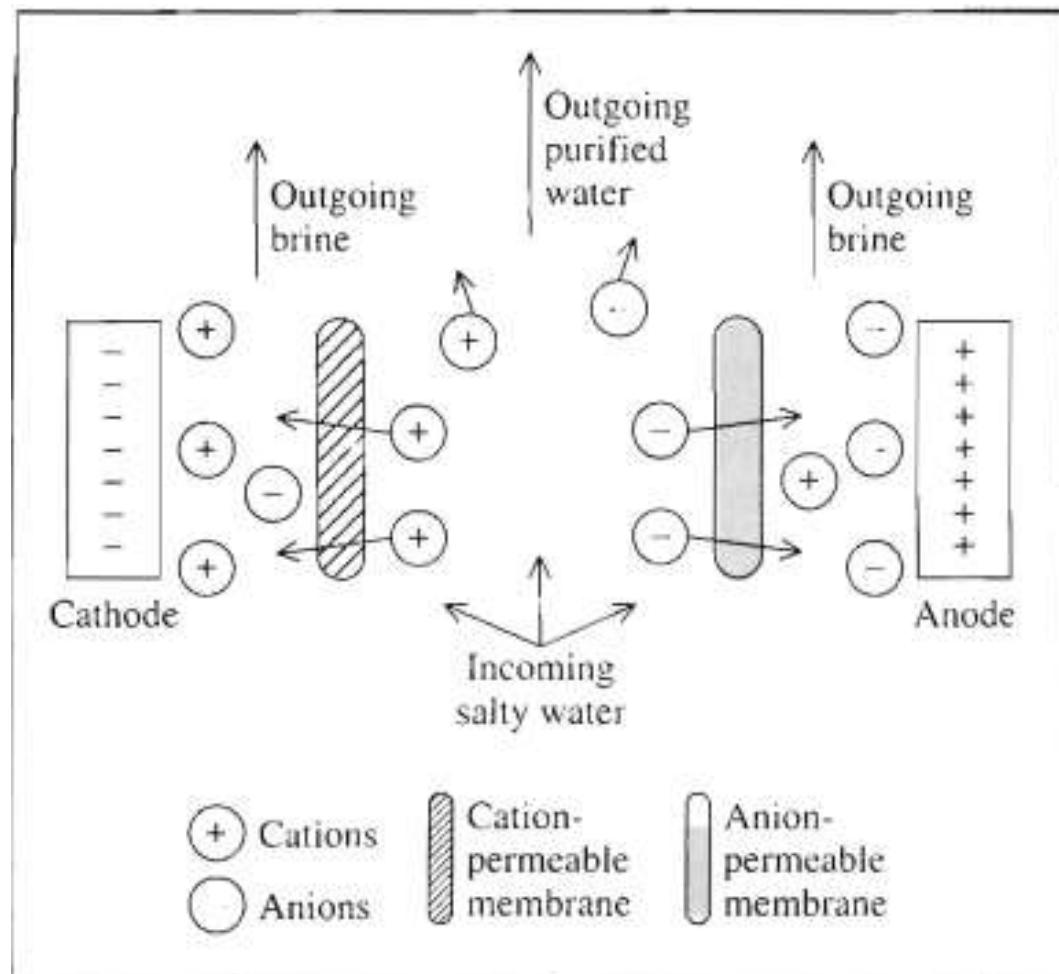
Oxidation Reaction	Chemical Equation	pH	ORP
(1) Cyanide → Cyanate	$\text{NaCN} + 2\text{NaOH} + \text{Cl}_2 \rightleftharpoons \text{NaCNO} + 2\text{NaCl} + \text{H}_2\text{O}$	10-11.5	(+) 250mV-400mV
(2) Cyanate → Carbon Dioxide & Nitrogen	$2\text{NaCNO} + 4\text{NaOH} + 3\text{Cl}_2 \rightleftharpoons 6\text{NaCl} + 2\text{CO}_2 + \text{N}_2 + 2\text{H}_2\text{O}$	8.5-9	(+) 300mV-600mV

Alternatives and Removal

- ✓ NTA: Sodium nitrilotriacetate
- ✓ Sodium citrate, sodium carbonate, sodium silicate
- ✓ Zeolites Removal:
- ✓ Using calcium hydroxide

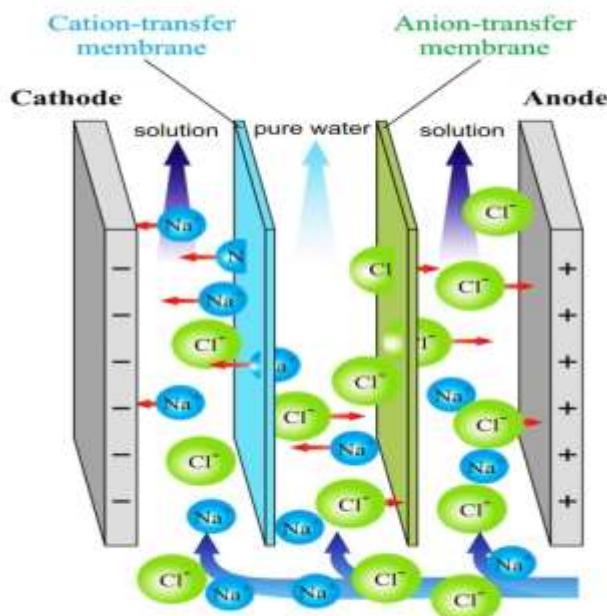
Reducing Salt Concentration in water

- Reverse Osmosis
- Electrodialysis
- Ion Exchange



Electro Dialysis (ED)

A membrane process, during which ions are transported through semi permeable membrane, under the influence of an electric potential. The membranes are cation (+) or anion (-) selective, which basically means that either positive ions or negative ions will flow through.

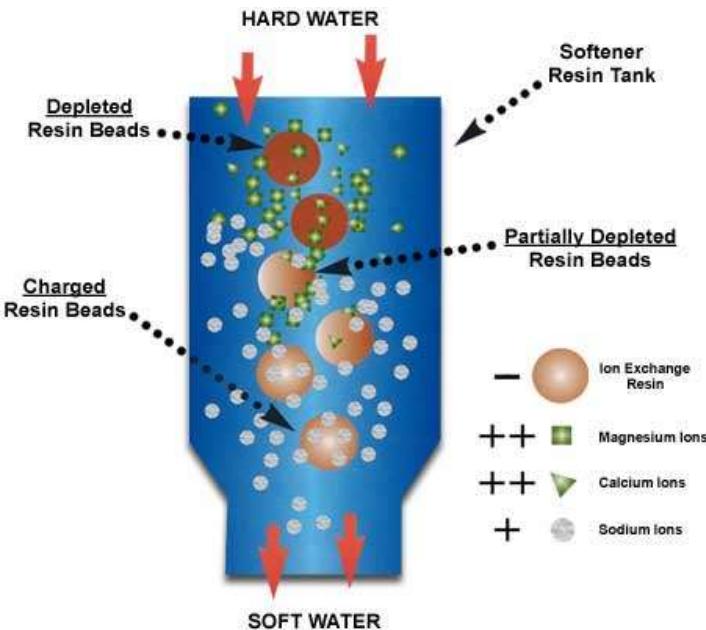
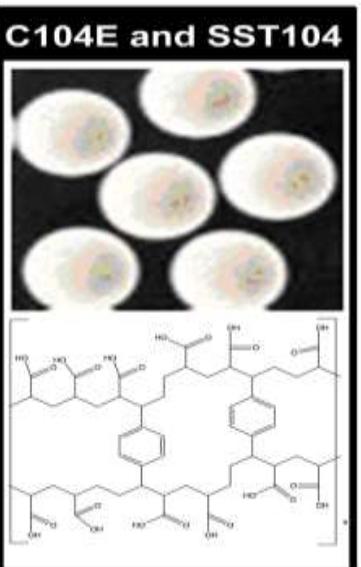
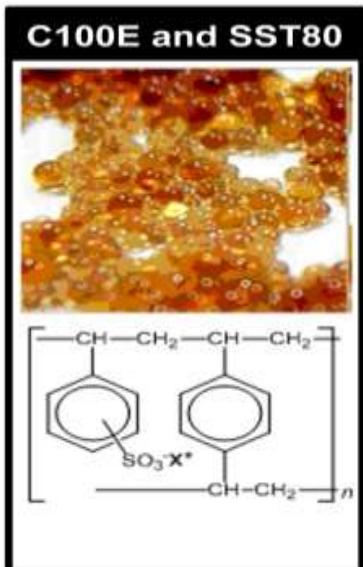


Electrodialysis (ED)
Electro Membrane Based Process
Electrodialysis Reversal (EDR)

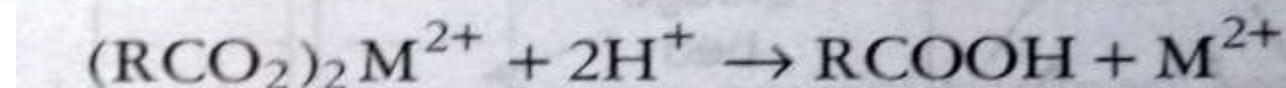
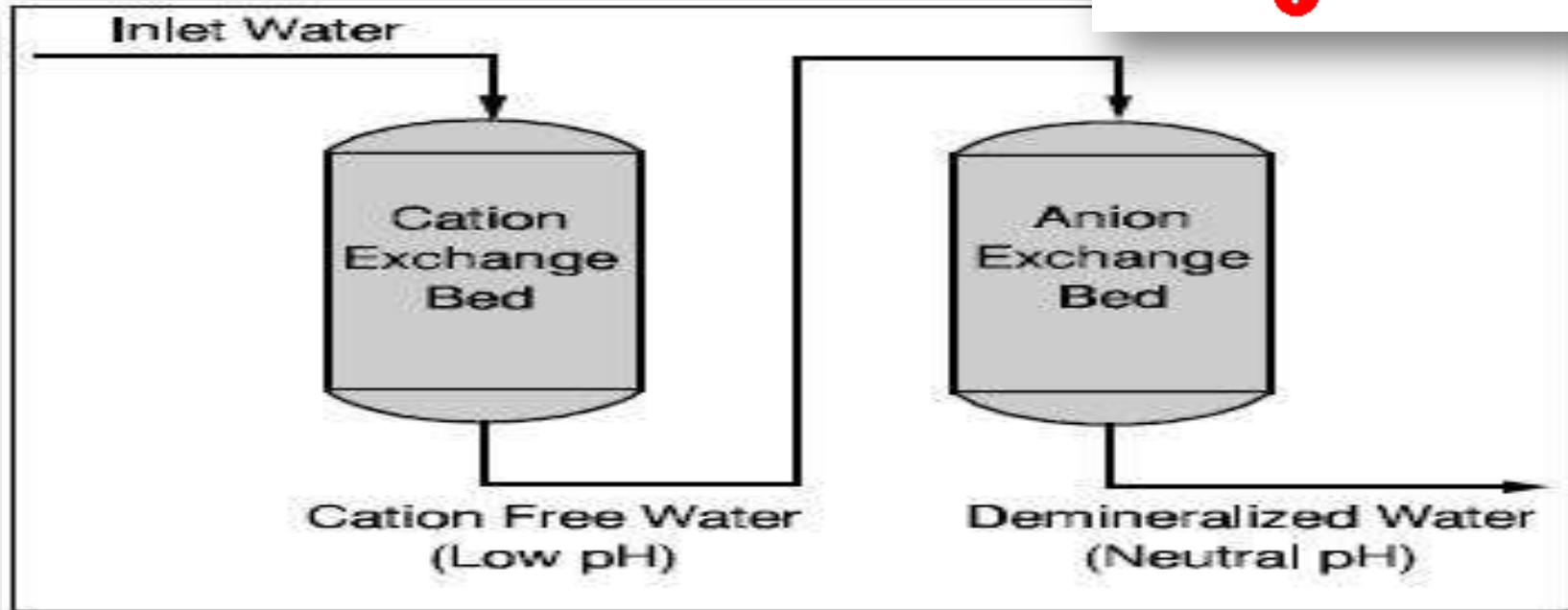
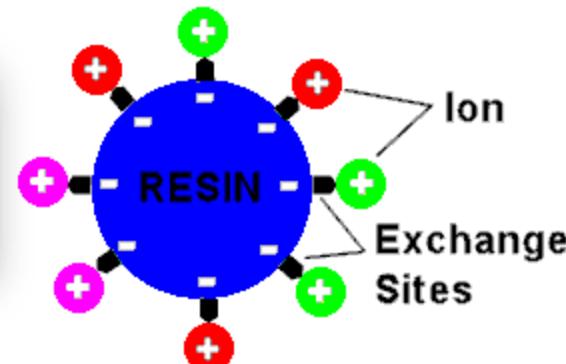
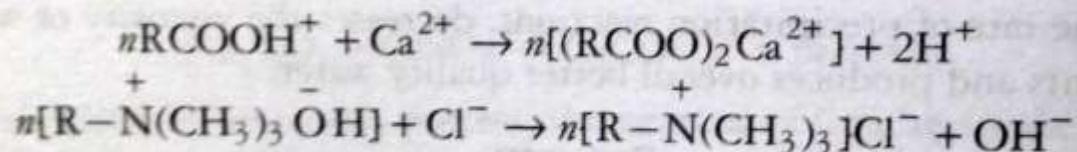


Ion exchange process

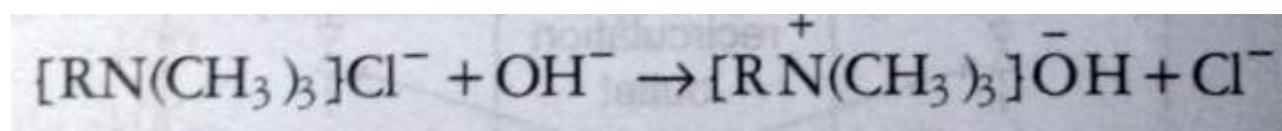
- Also known as **demineralization** of water
- Ion exchange resins are **high molecular weight cross-linked, porous polymers**
- Ion exchange property is due to **acidic** ($\text{R-SO}_3\text{H}$, R-COOH) or **basic** (R-N-OH , $\text{R-NH}_3\text{OH}$ or $\text{R-R'-NH}_2\text{OH}$) functional



- Acidic gr. exchange H^+ or Na^+
- Basic gr. Exchange OH^-



Regeneration



Advantage:

- easy to operate and control
- works well for variety of hardness of water
- takes less space, better quality and more economical

Disadvantage:

- corrosion may occur when cation exchange takes place with H exchanger
- Na exchanger when used TDS, alkalinity & silica are not reduced
- Ion exchange material should not be allowed to get contaminated

Heavy metal toxicity:

Toxic Heavy Metals

CHEMIX - PERIODIC TABLE



Graphics

Close

	<input type="radio"/> Atomic number	<input type="radio"/> First ionization potential V	<input type="radio"/> Electron configuration
	<input type="radio"/> Name	<input type="radio"/> Specific heat capacity Jg ⁻¹ K ⁻¹	<input type="radio"/> Oxidation states
Group	<input type="radio"/> Relative atomic mass u	<input type="radio"/> Electrical conductivity ×10 ⁶ Ohm ⁻¹ cm ⁻¹	<input type="radio"/> Phase 20 °C
1/A	<input type="radio"/> Melting point °C	<input type="radio"/> Thermal conductivity Wcm ⁻¹ K ⁻¹	<input type="radio"/> Crystal structure 18/VIIA
0.071	<input type="radio"/> Boiling point °C	<input type="radio"/> Electronegativity Pauling	0.126
H	2/IIA <input checked="" type="radio"/> Density g/cm ³	<input type="radio"/> Heat of fusion kJ/mol	He
0.530	1.850 <input type="radio"/> Covalent radius ×10 ⁻¹⁰ m	<input type="radio"/> Heat of vaporization kJ/mol	2.340 2.260 0.810 1.140 1.505 1.200
Li	Be <input type="radio"/> Atomic radius ×10 ⁻¹⁰ m	<input type="radio"/> Acid-base properties	B C N O F Ne
0.970	1.740 <input type="radio"/> Atomic volume cm ³ /mol	<input type="radio"/> Number of stable isotopes	2.700 2.330 1.820 2.070 1.560 1.400
Na	Mg 3/IIIB 4/IVB 5/VB 6/VIB 7/VIIB 8/VIII 9/VIII 10/VIII 11/IB 12/IIIB		Al Si P S Cl Ar
0.860	1.550 3.000 4.510 6.100 7.190 7.430 7.860 8.900 8.900 8.960 7.140 5.910 5.320 5.720 4.790 3.120 2.600		
K	Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr		
1.530	2.600 4.470 6.490 8.400 10.20 11.50 12.20 12.40 12.00 10.50 8.650 7.310 7.300 6.620 6.240 4.940 3.060		
Rb	Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe		
1.900	3.500 6.170 13.10 16.60 19.29 21.00 22.60 22.50 21.40 19.29 13.60 11.90 11.40 9.800 9.200		
Cs	Ba La Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn		
	5.000		
Fr	Ra Ac 6.670 6.770 7.000	7.540 5.260 7.890 8.270 8.540 8.800 9.050 9.330 6.980 9.840	
Lanthanides ->		Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu	
		11.70 15.40 19.07 19.50	11.70
Actinides ->		Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr	

Heavy Metal Toxicity

TABLE 15-1

Densities of Some Important Heavy Metals and Other Substances

Substance	Density (g/cm ³)
Hg	13.5
Pb	11.3
Cu	9.0
Cd	8.7
Cr	7.2
Sn	5.8–7.3
As	5.8
Al	2.7
Mg	1.7
H ₂ O	1.0

Heavy metals: having high density

Heavy metals are toxic as they do not undergo biodegradation like organic compounds.

Transportation of heavy metals: by water and air both.

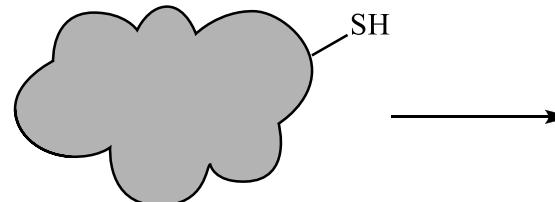
Continue...

- The toxicity for heavy metals depends very much on the chemical form of the element, i.e., upon its **speciation**
- The cationic and organometallic forms of heavy metals are more dangerous than condensed elemental forms

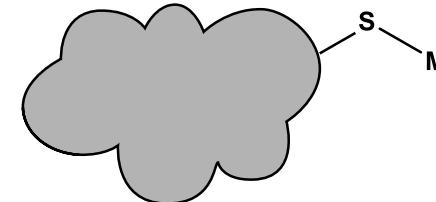


M = heavy metal, R = short alkyl chain

- Elemental heavy metals don't interact with biological system and are excreted from the body without doing much harm.
- Organometallics having short alkyl chains are more disturbing than cations as they pass through the skin membrane easily entering in to the biological system.
- After entering in to the biological system:



Enzyme having tethered SH group



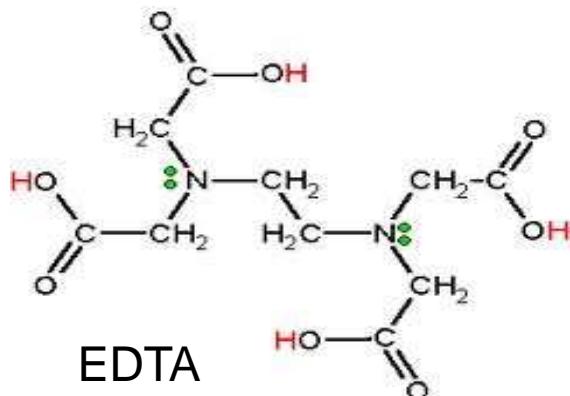
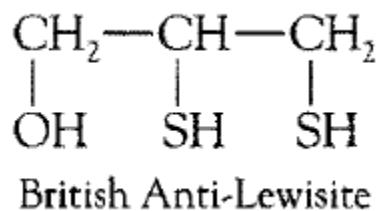
Metal bound enzyme

Water pH is also very important factor in determining heavy metal toxicity

□ Soluble forms of heavy metals

- cause immediate sickness or death (e.g., a sufficiently large dose of arsenic oxide) so that therapy cannot exert its effects in time, and
- can pass through the membrane protecting the brain—the blood-brain barrier—or the placental barrier that protects the developing fetus.

□ Treatment for acute heavy-metal poisoning



The metal ions are complexes with ligand to form a chelate which is subsequently excreted from the body.

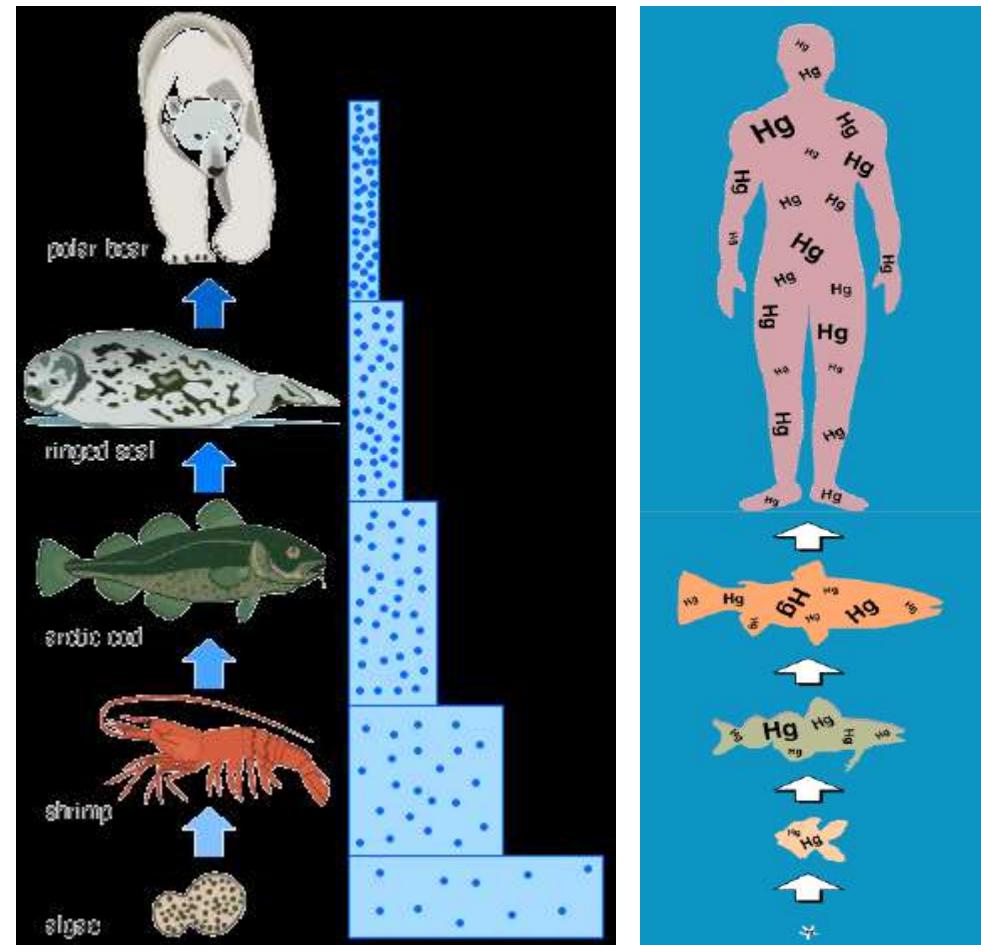
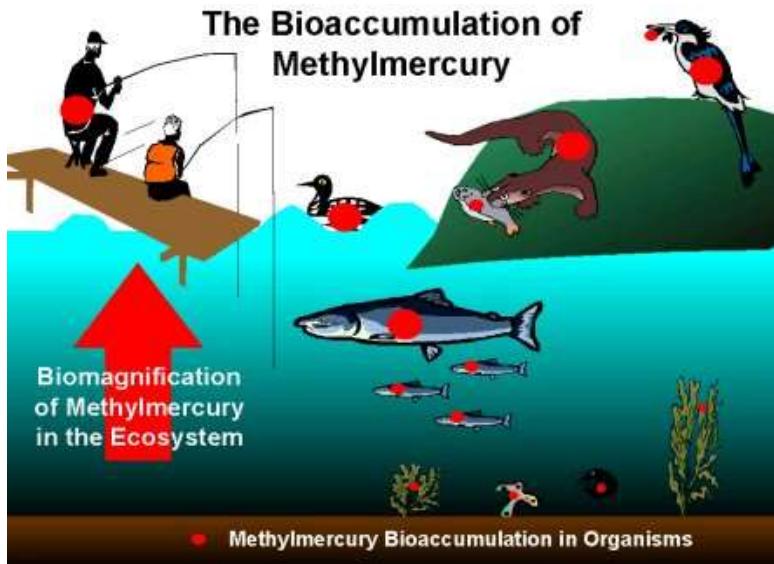
Di-calcium salt of EDTA is used.

Sources of Heavy metals

- Purification of metals (Metallurgy).
- Electroplating is the primary source of chromium and cadmium.
- **Bioaccumulation** and Biomagnification.

Biomagnification.

Bioaccumulation occurs when an organism absorbs a toxic substance at a rate greater than that at which the substance is lost.



Speciation and the Toxicity of Heavy Metals

- Although mercury vapor is highly toxic, the **heavy metals Hg, Pb, Cd, Cr, and As** are not
- Biochemically, the mechanism of the toxic action usually arises from the strong affinity of the cations for sulfur.
- Thus, sulfhydryl groups, -SH, which occur commonly in the enzymes that control the speed of critical metabolic reactions in the human body, readily attach themselves to ingested heavy-metal cations or to molecules that contain the metals.
- Because the resultant metal-sulfur bonding affects the entire enzyme, it cannot act normally and, as a result, human health is adversely affected, sometimes fatally.
- The reaction of heavy-metal cations M^{2+} (where M= Cr, Hg, Pb, or Cd) with the sulfhydryl units of enzymes R-S-H to produce stable systems such as R-S-M-S-R is analogous to their reaction with the simple inorganic chemical hydrogen sulfide, H_2S , with which they yield the insoluble solid MS.

- The toxicity for all four heavy metals depends very much on the chemical form of the element, i.e., upon its speciation. Substances that are almost totally insoluble pass through the human body without doing much harm.

The most devastating forms of the metals:

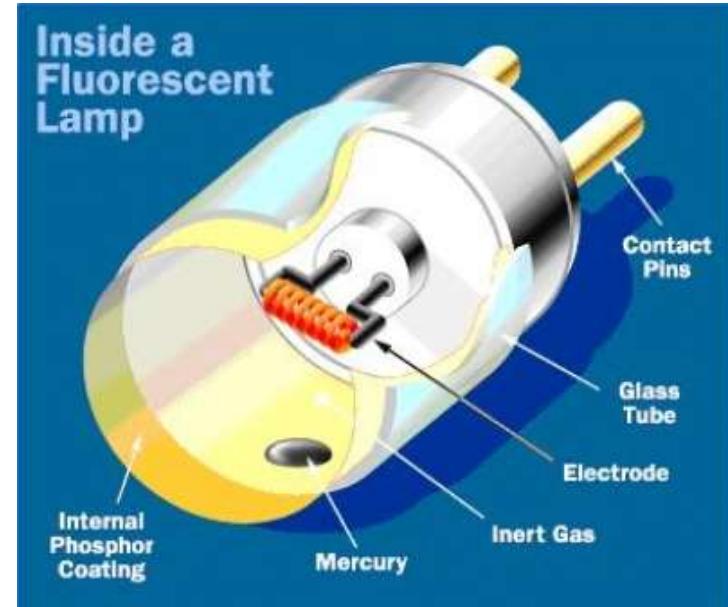
- cause immediate sickness or death {e.g., a sufficiently large dose of arsenic oxide} so that therapy cannot exert its effects in time, and
- can pass through the membrane protecting the brain-the blood-brain barrier-or the placental barrier that protects the developing fetus.
- **For mercury and lead, the forms that have alkyl groups attached to the metal are highly toxic.** Because such compounds are covalent molecules, they are soluble in animal tissue and can pass through biological membranes, whereas charged ions are less able to do so; e.g., the toxicities of lead as the ion Pb²⁺, and in covalent molecules differ substantially.
- **The toxicity of a given concentration of a heavy metal present in a natural waterway depends not only on its speciation but also on the water's pH and on the amounts of dissolved and suspended carbon in it,** since interactions such as complexation and adsorption may well remove some of the metal ions from potential biological activity.

Mercury

- Atomic Number: 80
- Atomic weight: 200.59
- Density: 13.5 g/cm³

Mercury Vapor:

- From Power Plants
- Incineration of municipal and medical waste
- Elemental mercury can conduct electricity therefore it can be found in Electrical switches, Trunk lighting and antilock brakes in automobiles
- Fluorescent light bulb
- Mercury can travel long distances in air before being oxidized and then dissolving in rain.



Continue...

- Mercury is the most volatile of metals and its vapors are highly toxic.
- It has very high vapor pressure.
- Vapors diffuse from lungs to blood stream and due to their electrical neutrality, they readily crosses blood brain barrier to enter brain.
- Serious damage to CNS: difficulties in coordination, eye sight and tactile senses are effected.
- Liquid mercury itself is not highly toxic, and most of what is ingested is excreted.
- Nevertheless, children should not be allowed to play with droplets of the metal because of the danger from breathing the vapor.

Mercury Amalgams

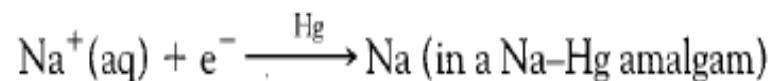
- Mercury readily forms amalgams, which are solutions or alloys with almost any other metal or combination of metals.
- Dental amalgam to fill cavities made up of mercury and variable amount of Cu, Sn and Zn. It is prepared by combining approximately equal proportions of liquid mercury and a solid mixture that is mainly silver with variable amounts of copper, tin, and zinc. The slight expansion of volume that accompanies its solidification ensures that the final amalgam fills the cavity.
- When the first filling is first placed in a tooth, and whenever the filling is involved in the chewing of food, a tiny amount of the mercury is vaporized.
- Some countries have banned for pregnant women and children.
- Mercury-free "amalgams" for use in dentistry are under development; porcelain fillings are already common, though expensive.
- Some fears have been expressed about the release of elemental mercury vapor into the atmosphere when **cremating deceased persons who had amalgam-filled teeth**, since the amalgam decomposes at high temperatures. In countries such as Sweden, crematoria are fitted with selenium filters that remove most mercury from emissions by forming mercury selenide crystals.

Continue...

- In some areas, dentists are now required to install a separator to capture mercury from their wastewater rather than have it flow down drains and become part of municipal sewage.
- Mercury is used to extract gold and silver by forming amalgam which is then roasted to distill off mercury.
- The health hazards to those whose work involves the vaporization of mercury are significant, since the element is so toxic in its gaseous form. Indeed, mercury vaporized from such operations currently makes up more than 10% of the anthropogenic emissions of mercury in air.
- People who live in mining regions often inhale air in which the concentration of elemental mercury exceeds 50 micrograms per cubic meters, which is 50 times the public exposure guideline of the World Health Organization (WHO).
- As a consequence, many "amalgam burner" workers exhibit tremors and other signs of mercury poisoning.
- In addition, mercury in surface sediments disturbed by slash-and-burn deforestation and agriculture in the region enters the aquatic environment, where some of it enters the food chain

Chlor-Alkali Process

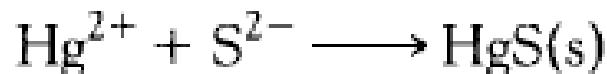
- An amalgam of sodium and mercury is used in some industrial chlor-alkali plants in the process that converts aqueous sodium chloride into the commercial products chlorine, Cl_2 , and sodium hydroxide, NaOH , (and gaseous hydrogen) by electrolysis.
- In order to form a concentrated, pure solution of NaOH , flowing mercury is used as the negative electrode (cathode) of the electrochemical cell. The metallic sodium that is produced by reduction in the electrolysis immediately combines with the mercury and is removed from the NaCl solution without having reacted with the aqueous medium.



- When metals such as sodium are dissolved in amalgams, their reactivity is greatly lessened compared to that for the free state, so that the otherwise highly reactive elemental sodium in the Na-Hg amalgam does not react with the water in the original solution.
- Mercury can escape as vapor into air while recycling process.
- Although liquid mercury is not soluble in water or in dilute acid, it can be oxidized to soluble form by the intervention of bacteria that are present in natural waters. By this means, the mercury becomes accessible to fish.

The +2 ion of Mercury

- Mercuric or Mercury (II) ion
- Red ore cinnabar, HgS, very insoluble salt
- Na₂S is sometimes used to precipitate soluble ion from effluents.



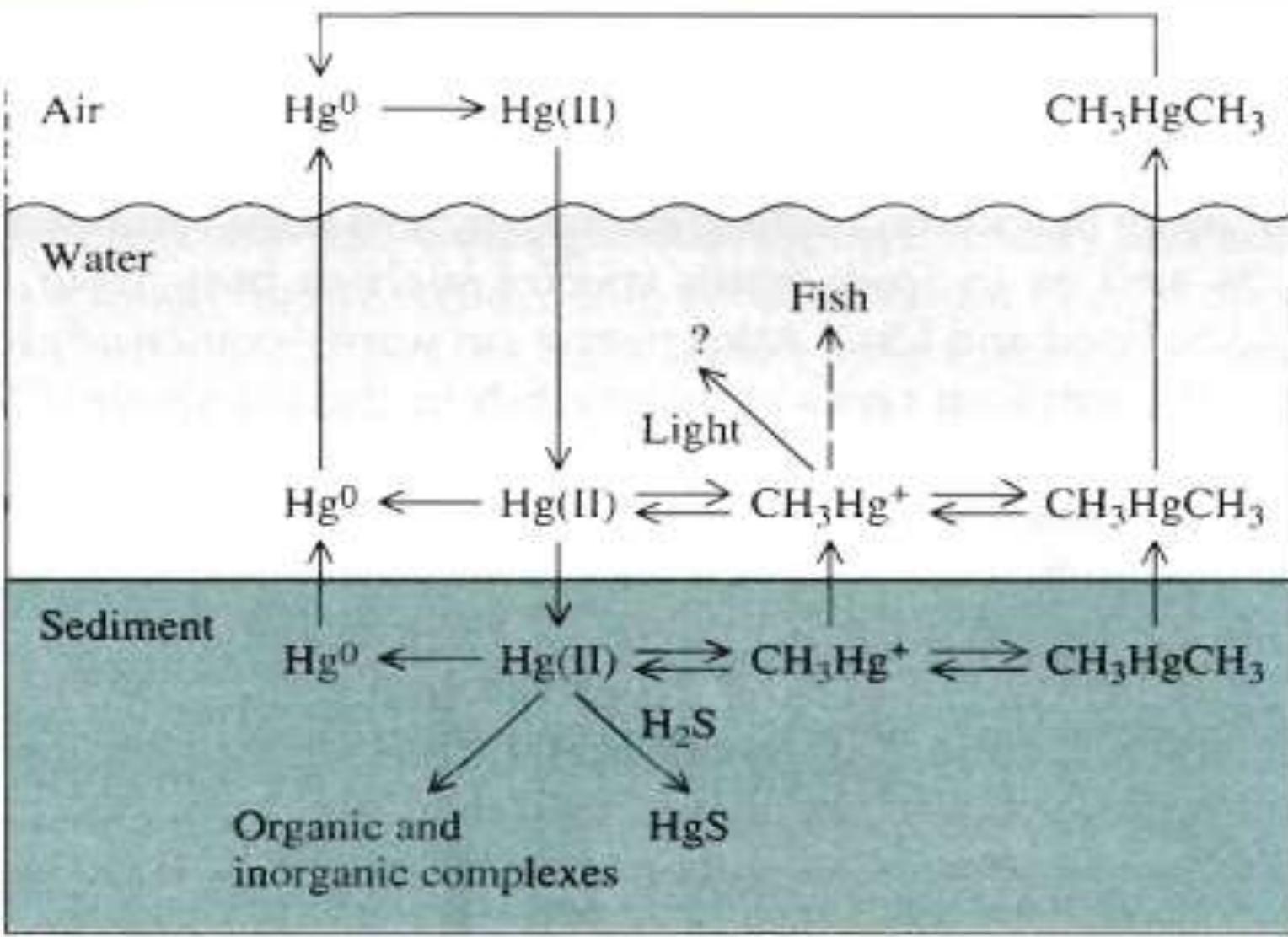
- Most of the mercury in the environment is inorganic, in the form of the Hg²⁺ ion. The levels of ionic mercury even in remote areas are two to five times as great as preindustrial values, with local polluted sites having levels 10 or more times greater. In natural waters, much of the Hg²⁺ is attached to suspended particulates, **so it is eventually deposited in sediments.**
- The nitrate salt of Hg²⁺ is water soluble and was at one time used to treat the fur used to make felt for hats. As a consequence of this constant exposure to mercury, workers in the felt trade often displayed nervous disorders: muscle tremors, depression, memory loss, paralysis, and insanity (giving rise to the expression "**mad as a hatter**" a concept familiar to fans of Lewis Carroll's Alice in Wonderland).

- Mercury vapor and, to a lesser extent, mercury salts attack the central nervous system, but the main target organs for HgH are the kidney and the liver, where it can cause extensive damage.
- Mercuric oxide, HgO , is present in a paste in mercury cell batteries such as those used in hearing aids. If the discarded spent batteries are subsequently incinerated as garbage, the volatile mercury can be released into the air.
- The other inorganic ion of mercury, Hg_2^{2+} , is not very toxic since it combines in the stomach with chloride ion to produce insoluble Hg_2Cl_2 .

Methyl Mercury Toxicity

- When in combination with anions that are capable of forming covalent bonds, the mercuric ion Hg^{2+} forms covalent molecules rather than an ionic solid.
- For example, HgCl_2 is a molecular compound, not a salt of Hg^{2+} and Cl^- . As chloride ion forms a covalent compound with Hg^{2+} , so does the methyl anion, CH_3^- , yielding the volatile molecular liquid dimethyl mercury, $\text{Hg}(\text{CH}_3)_2$.
- The process of dimethylmercury formation occurs in the muddy sediments of rivers and lakes, especially under anaerobic conditions, when anaerobic bacteria and microorganisms convert Hg^{2+} into $\text{Hg}(\text{CH}_3)_2$. The active agent in the **biomethylation process** is a common constituent of microorganisms; it is a derivative of vitamin B12 with a CH_3 anion bound to cobalt and is called **methylcobalamin**.

- The less volatile mixed compound CH_3HgCl and CH_3HgOH , collectively called **methylmercury** are often written as $\text{CH}_3\text{Hg}^+\text{X}^-$ as they consist of covalent molecules, not ionic lattices.
- In fact, the **methylmercury ion** CH_3Hg^- exists as such only in compounds with **anions such as nitrate or sulfate**. Methylmercury compounds are even more readily formed in the same way as dimethylmercury at the surface of sediments in anaerobic water.
- Methylmercury production predominates over dimethylmercury formation **in acidic or neutral aqueous systems**. Sulfate ions, stimulate the sulfate-reducing bacteria that methylate mercury; **in contrast, the presence of sulfide ion results in formation of mercury sulfide complexes that do not undergo methylation**.
- Due to its volatility, dimethyl mercury evaporates from water relatively quickly unless it is transformed by acidic conditions into the monomethyl form.
- Wetlands are also active sites of **methylmercury production**. Methylmercury in surface water is photodegraded (to as yet unknown products) and is the most important sink for this substance in some lakes.



- Mercuric ion itself is not readily directly transported across biological membranes. Methylmercury is a more potent toxin than are salts of Hg^{2+} because it is soluble in fatty tissue in animals, bioaccumulates and biomagnifies there, and is more mobile.
- Once ingested, the original covalent CH_3HgX compound is converted to substances in which X is a sulfur-containing amino acid; in some of these forms, it is soluble in biological tissue and can cross both the blood-brain barrier and the human placental barrier, presenting a twofold hazard.
- Methylmercury is, in fact, the most hazardous form of mercury, followed by the vapor of the element.
- The main toxicity of methylmercury occurs in the central nervous system. In the brain, methylmercury is converted to Hg^{2+} , which is probably responsible for the brain damage. Mercury vapor is also oxidized to this ion once it has entered the cell.
- Thus the usual barriers in the cell to Hg^{2+} are circumvented by Hg^0 and CH_3HgX , which by their electric neutrality can penetrate through the defenses and which later can be converted to the highly toxic +2 ionic form.
- Most of the mercury present in humans is in the form of methylmercury. Almost all methylmercury originates from the fish in our food supply:

Methylmercury Accumulation in the Environment and in Human body

- Half life of methylmercury compound in human is about 70 days, therefore it can accumulate in the body to a much higher steady state concentration.
- Case Study: **Minimata Disease.**
- ✓ **Minamata disease**, sometimes referred to as Chisso-Minamata disease, is a neurological syndrome caused by severe mercury poisoning. Symptoms include ataxia, numbness in the hands and feet, general muscle weakness, narrowing of the field of vision and damage to hearing and speech



Other sources of Methylmercury

- Used as fungicide in agriculture.
- Leached from rocks and soil into water system.
- Mercury based preservative (*Thimerosal*) in Vaccines, now removed.
- Phenylmercury ion with acetate or nitrite as the anion used as preservative in paints.
- As antiseptic and preservative in topical pharmaceutical preparations.

Lead (Pb)

- **Atomic Number:** 82
- **Atomic weight:** 207 and 206, two stable isotopes
- **Density:** 11.3 g/cm³

Lead's relatively low melting point of 327°C allows it to be readily worked.

- Use as structural metal in ancient times
- Weather proofing buildings
- In water pipes and ducts
- For cooking vessels
- For sound proofing
- When combined with tin, it form solder, the low melting point alloy.

Elemental Lead as Environmental Risk

- Elemental lead is also found in ammunition : “lead shot” used in huge amounts by hunters, especially of waterfowl (fresh water aquatic bird).
- **Condors** in California suffer from lead poisoning when they eat deer which is shot with lead and abandoned.
- **Lead sinkers Jigs** are still used for fishing.
- Although elemental lead is not an environmental problem to most life forms, it does become a real concern when it dissolves to yield an ionic species.



Ionic 2+ Lead in water and food as Hazard

- The stable ion of lead is the 2+ species, Pb(II) as Pb²⁺.
- For example, lead forms the ionic lead sulfide, PbS, Pb²⁺S²⁻, which is the metal-bearing component of the highly insoluble ore **galena**, from which almost all lead is extracted.
- Lead does not react on its own with dilute acids. Indeed, elemental lead is stable as an electrode in **the lead storage battery**, even though it is in contact with fairly concentrated sulfuric acid, H₂SO₄.

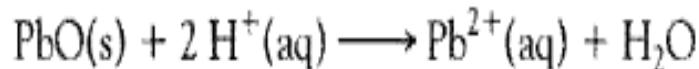


- Some lead in the solder which is used to seal tin cans dissolves in dilute acid of fruit acids and other acidic food once it is opened:
- Used in joints of domestic copper water pipes and earlier it was used to construct pipes even.

- The contamination of water by lead is less of a problem in areas of **Calcareous water**, because a layer of insoluble PbCO_3 is formed on the surface of lead which prevent further dissolution of metal in water.
- **Some times Phosphates are deliberately added to water in drinking water where lead is a component of water pipes.**
- Lead in water is more fully absorbed by the body than is lead in food.
- Now that many other sources of lead have been phased out, drinking water accounts for about one-fifth of the collective lead intake of Americans, whose major source is from food. Many domestic water treatment systems successfully remove the great majority of lead from drinking water.

Lead Salt as Glazes and Pigments

- PbO is yellow solid and has been used in glaze pottery.
- The oxide becomes hazard if applied incorrectly



- Lead silicate can be an alternative to PbO as it is almost insoluble and safer.



Pigments

- Lead chromate (PbCrO_4): yellow pigments used in paints (School buses and strips on road)
- Red Lead (Pb_3O_4) is used in corrosion resistant paints.
- Lead acetate used to cover gray hair. (Combines with SH)
- White Lead ($\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$) in white indoor paints. (Dangerous sweet taste)
- Lead Arsenate ($\text{Pb}(\text{AsO}_4)_2$) is used as pesticide is a source of lead in soil
- Lead pigments were also used to produce color used in glossy magazines and food wrappers and as a coloring agent for food.
- Used as stabilizer in various products of PVC including children's toys.

Drinking-Water Guidelines for Heavy Metals

Metal	U.S. EPA Maximum Contaminant Level (ppb)	Canadian Maximum Acceptable Concentration (ppb)	World Health Organization Guideline (ppb)
As	10	10	10
Cd	5	5	3
Cr	100	50	50
Hg (inorganic)	2	1	6
Pb	15	10	10

Ionic 4+ lead in Automobile

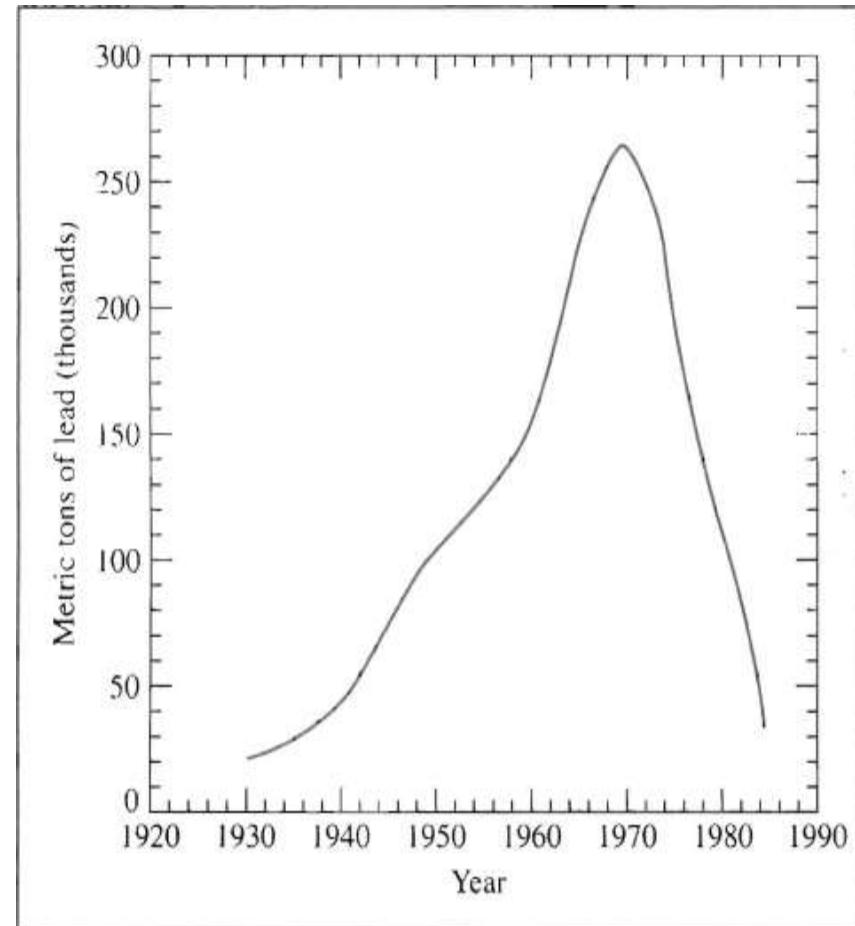
- Pb and PbO₂ in batteries. Also Pb₂O₃ and Pb₃O₄.
- Why problem from storage batteries?

Tetravalent Organic Lead Compounds

- Pb (II) for ionic but Pb (IV) forms covalent bonds similar to C, Si, Ge and Sn.
- Tetraalkyllead PbR₄.
- Used as additive in gasoline and still used in some aviation fuels.
- They are non water soluble but readily absorbed through skin.
- In human liver convert it to PbR₃⁺ which is a neurotoxin; can cross blood brain barrier.
- Little or no methylation of inorganic lead occurs in nature.

Environmental Lead from Gasoline

- Pb can damage the vehicle engine after the combustion of **tetraalkyllead** by forming metallic deposits.
- **Ethylene dibromide and ethylene dichloride** are used in leaded gasoline which can form dihalides of lead which ultimately converted to PbO and then exists as particulate which can enter the food chain.
- Lead in exhaust gas interfere with proper functioning of **catalytic converters**.



Effects of Lead

- Develop concentration plateau and then enters soft tissues including particularly in brain.
- Lead deposited in bone as it replaces calcium.
- At high levels Pb(II) is a metabolic poison.
- Lead remain in bones for decades therefore can accumulate in body and again come in blood at old age.
- Too much lead can slightly increase B.P.
- Children exposed to lead have more dental cavities.
- The metal readily crosses the placenta can effect the brain of the unborn.
- Interfere with the IQ level of brain

Synthetic organic chemicals and their toxicities

Principle of Toxicology

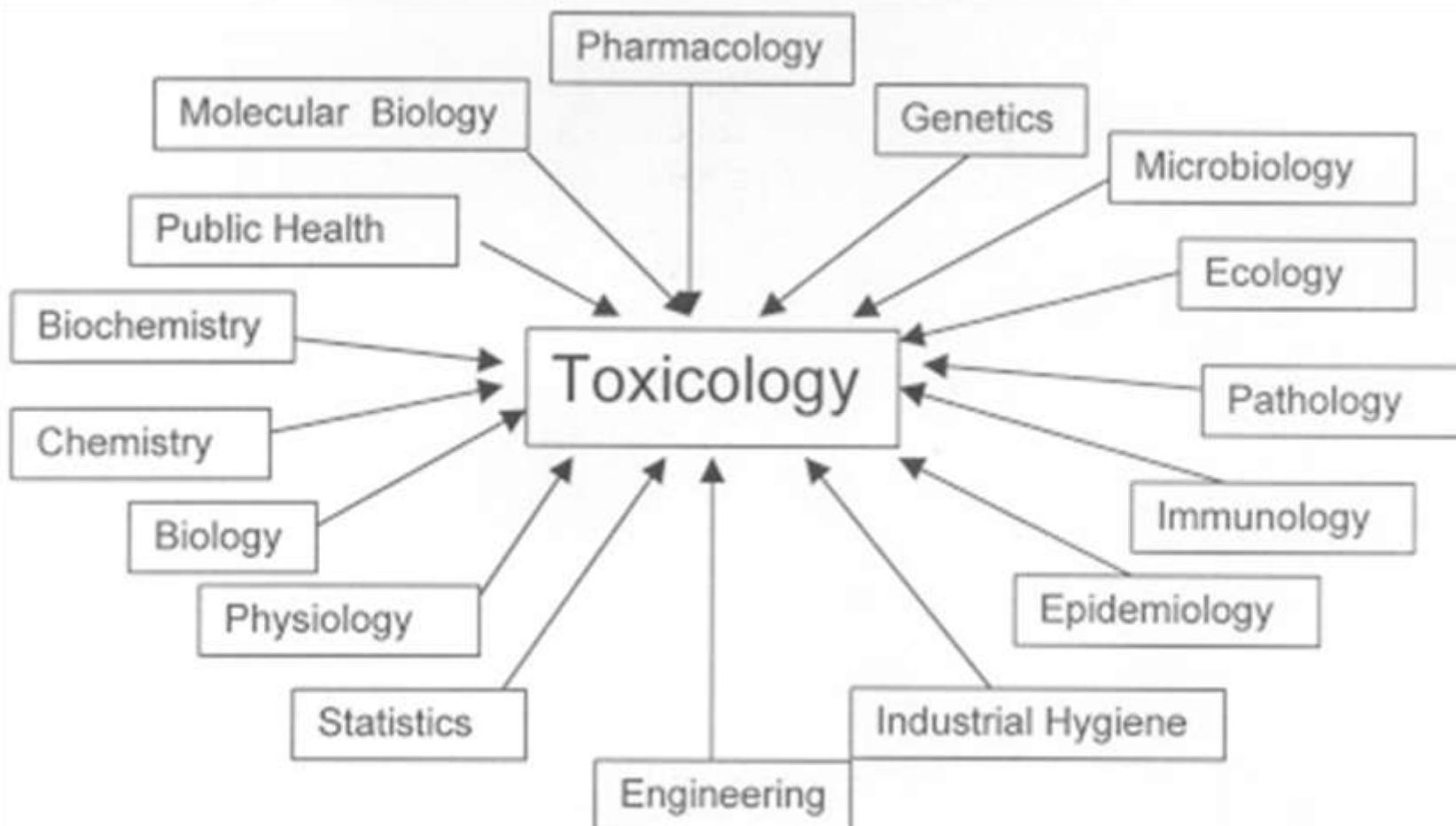
- Introduction
- Classification of Toxicants (Toxic organic Compounds)
- Characteristics of Exposures
- Route and Site Exposure
 - (a) Duration and frequency of Exposure
 - (b) Undesired Effects
- Interaction of Chemicals
- Dose Response
 - (a) Dose Response Relationship
 - (b) Comparison of Dose Response
- Variation in Toxic Responses
- Descriptive Animal Toxicity Tests
- Historical Control Incidence in Lab. Animals

Definitions

- Toxicology is the quantitative and qualitative study of the adverse effects of toxicants on biological organisms
- Toxicant is a chemical or physical agent that produces adverse effects on biological organisms.

Toxicant

Any agent capable of producing a deleterious(harmful) response in a biological system



Toxicology:

Study the adverse effects of toxicants in living organisms, and examine the toxic effects:

1. Cellular
2. Biochemical
3. Molecular mechanism of action
4. Occurrence
5. Risk assessment

Adverse effects

- Any change from an organism's normal state
- dependent upon the concentration of active compound at the target site for a sufficient time.

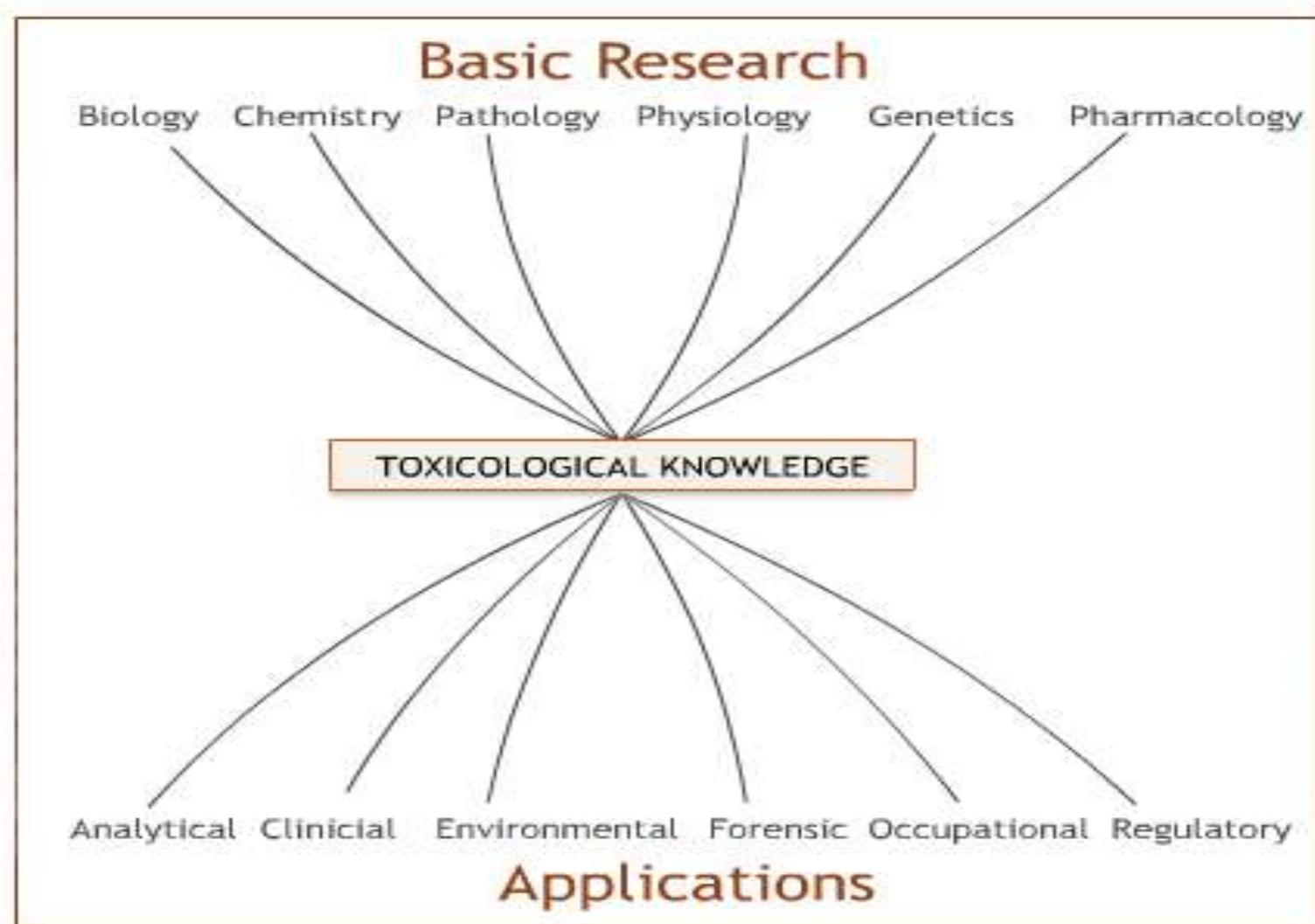
Effect of Toxicants

Effects of Toxicants

Irreversible Effects

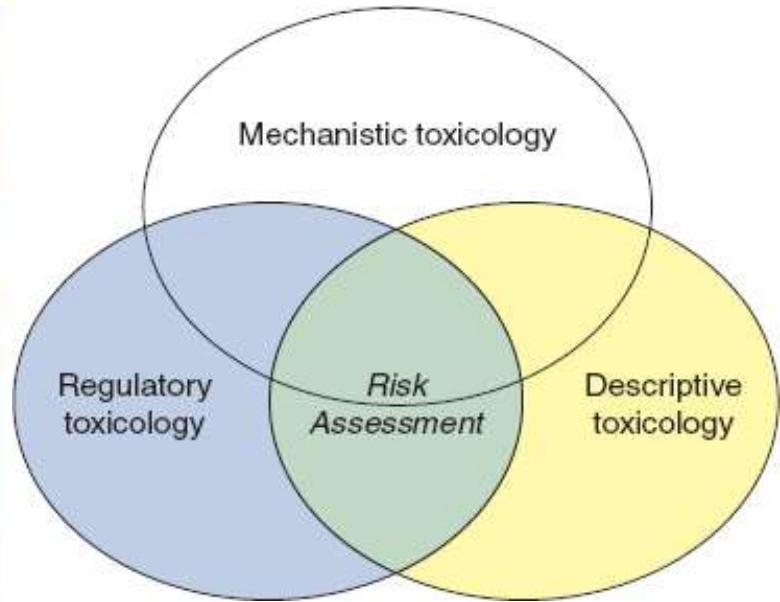
- Carcinogen - causes cancer
- Mutagen - causes chromosome damage
- Reproductive hazard - damage to reproductive system
- Teratogen - causes birth defects

Area/Branches of Toxicology

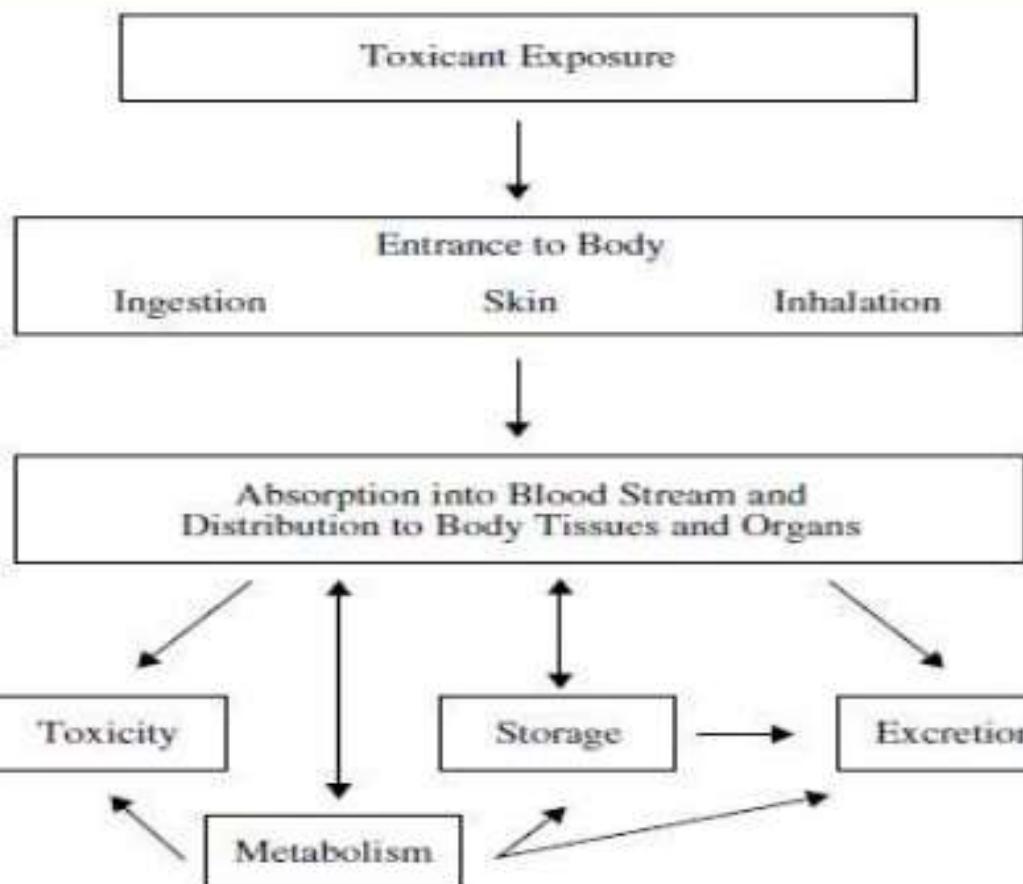


Branches of Toxicology

- 1. Mechanistic**—cellular, biochemical and molecular mechanisms by which chemicals cause toxic responses
- 2. Forensic**—cause of death, legal aspects
- 3. Clinical**—treatments for poisonings and injuries caused by xenobiotics
- 4. Environmental**—environmental pollutants, effects on flora and fauna
- 5. Food**—adverse effects of processed or natural food components
- 6. Regulatory**—assigns risk to substances of commercial importance.



Toxicology



Classification of Toxicants (Toxic organic Compounds)

Classification of chemical substance based on toxicity

Toxicity class	LD ₅₀ mg/kg b.w.	Probable lethal oral dose for humans
Supertoxic	<5	a taste (less than 7 drops)
Extremely toxic	5-50	between 7 drops and teaspoonful
Very toxic	50-500	between teaspoonful and ounce (1/3 dl)
Moderately toxic	0.5-5 (g/kg)	a glass
Slightly toxic	5-15 (g/kg)	0.5-1 liter
Practical nontoxic	>15 (g/kg)	>1 liter

DEFINITIONS

PEST

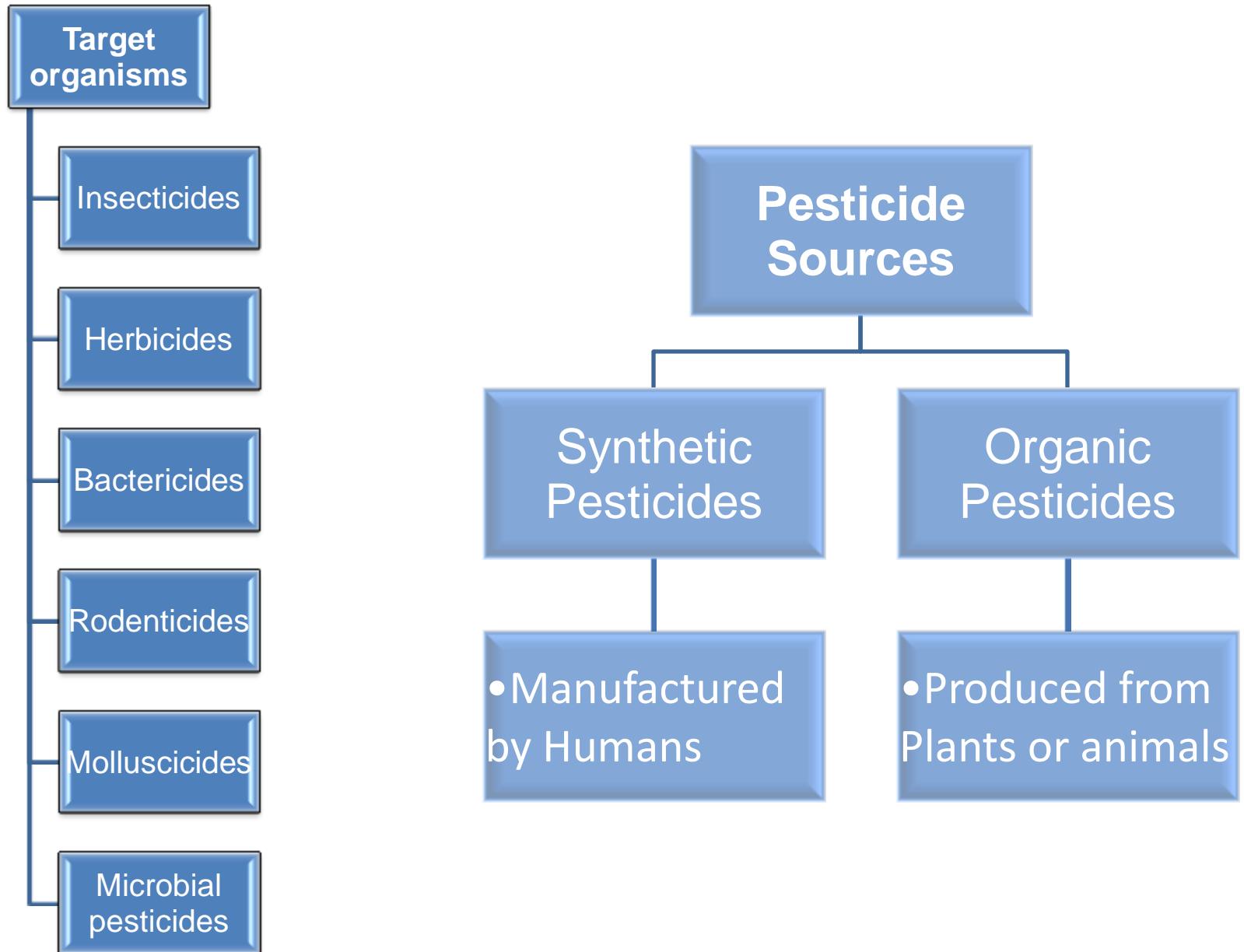
- Injurious, noxious or troublesome Insect, fungus, bacterial organism, virus, weed, rodent etc.
- Includes any injurious, noxious or troublesome organic function of a plant or animal.



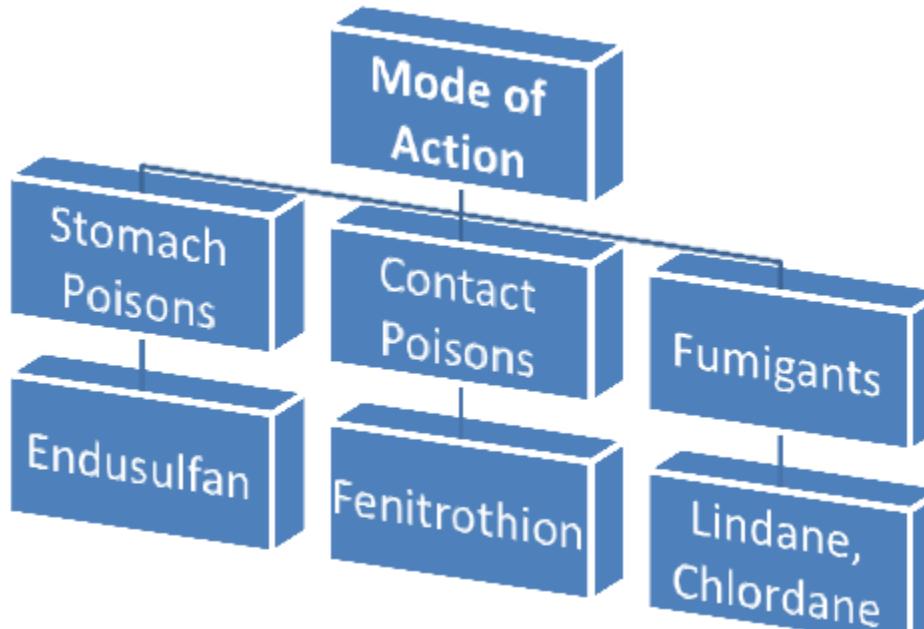
PESTICIDE

- A substance or mixture of substances, chemical or biological agent (viruses or bacteria):
 - For preventing, destroying, repelling or mitigating a pest
- Compete with humans Food, destroy property, spread disease

Classification of Pesticides



Classification of Pesticides/Insecticides



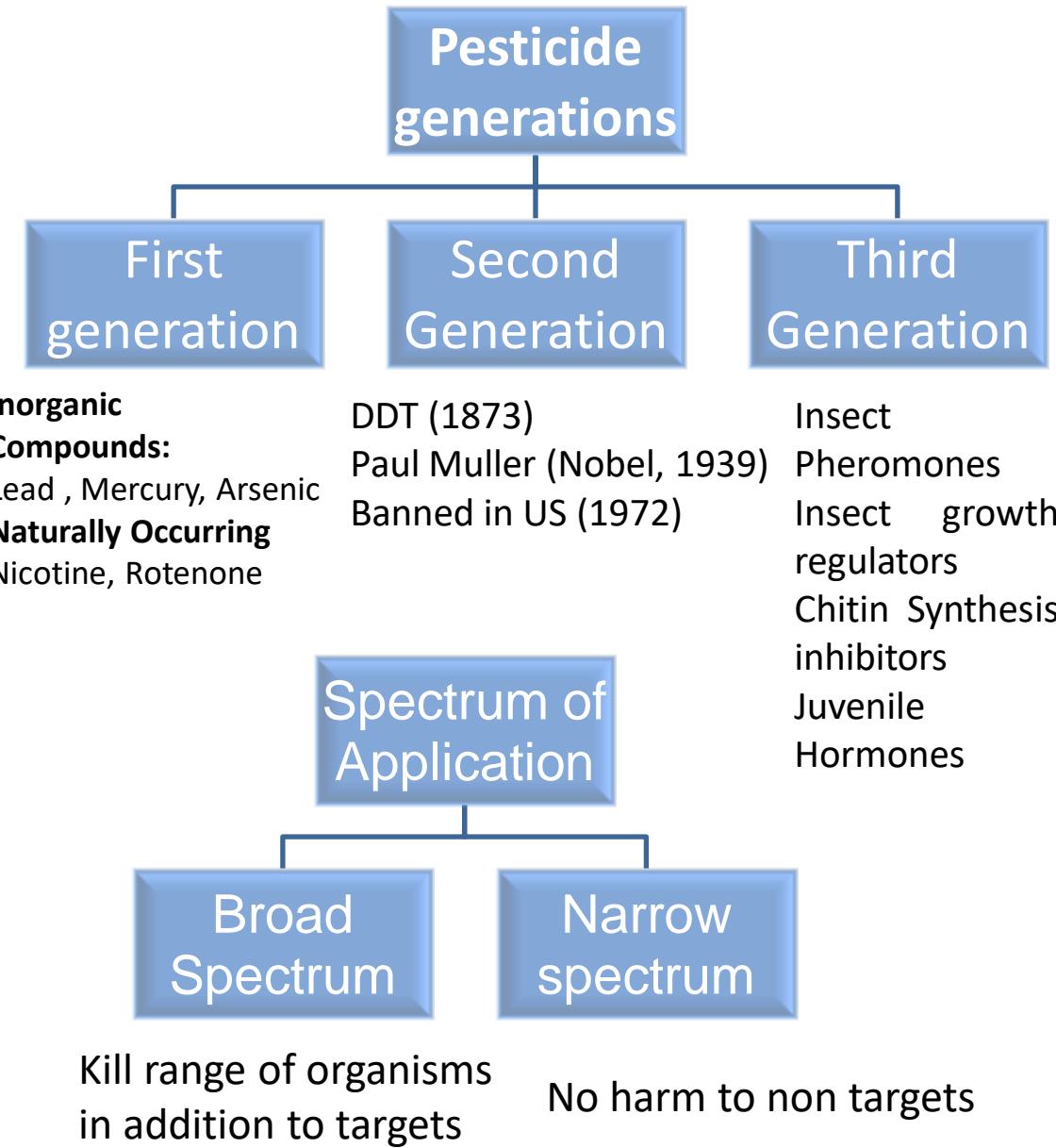
Stomach Poisons: Arsenic compounds (Arsenates and arsenites) e.g. acid lead arsenate, basic lead arsenate, calcium arsenate, copper acetate metaarsenate , Inorganic fluorine compounds Cryolite, sodium fluoride etc and **mercury compounds :** mercuric chloride.

Contact Poisons: Chlorinated hydrocarbons, organophosphates, carbamates etc. e.g.DDT, Malathion, Sevin etc.

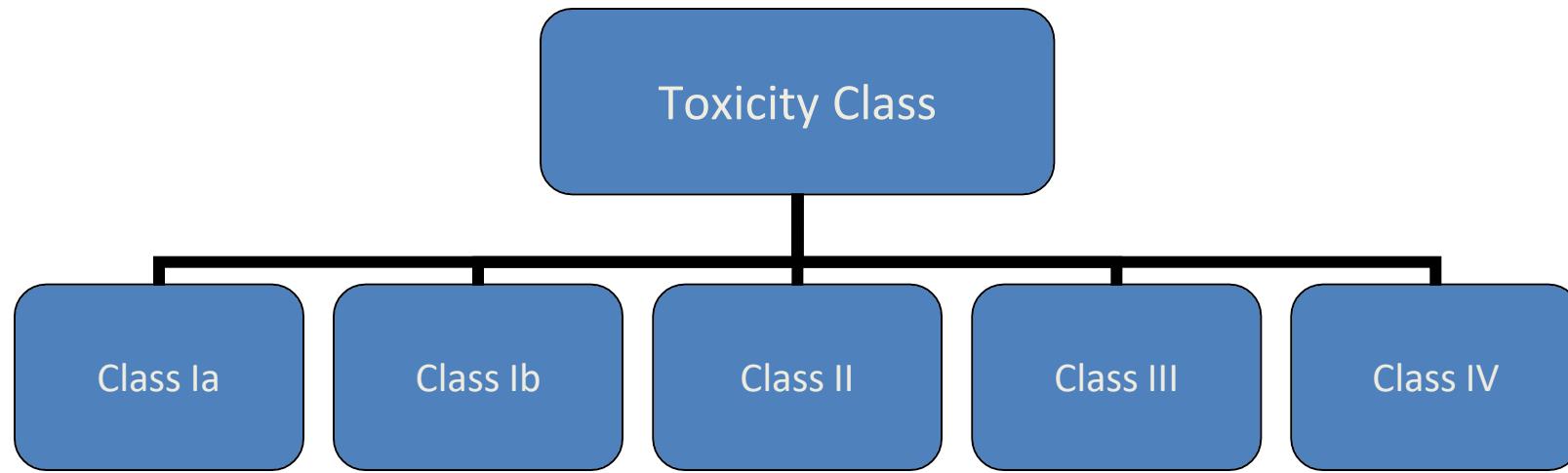
Fumigants: HCN released from calcium cyanide, methyl bromide, CCl_4 , Carbon disulphide, Naphthalene, nicotine etc.

Fenitrothion : Phosphorothioate (organophosphate) insecticide that is inexpensive and widely used worldwide

Continue...



Continue...



Extremely Hazardous

Highly Hazardous

Moderately Hazardous

Slightly Hazardous

No acute Risk

Allowance of Use

Registered Pesticides

Banned Pesticides

Continue...

Active Ingredients

Carbamates

Disturb PNS (short acting): Sevin

Organochlorines

Disturb CNS (long acting): DDT, DDD, BHC
Dieldrin, aldrin, methoxychlor, mirex, chlordane

acetyl cholinesterase inhibitor

Organophosphates

Disturb PNS (long acting): Malathion, Parathion,
Thimet, tetram, phosdrin etc.

Irritant to eye, skin,
and respiratory tract

Pyrethroids

Irritant of skin, upper
respiratory tract

Thiocarbamates

Pesticide Ingredients

➤ ACTIVE INGREDIENT (A.I)

Part of the pesticide that has the pesticidal properties: kill, impair, repel or affect

➤ INERT INGREDIENTS

Part of the pesticide formulation that act as emulsifiers, solvents, carriers, stabilizers, surfactants, preservatives, sticking agents, spreading agents or defoamers, depending on the need of the product and supposedly will not affect the pest if used by itself .

Can be more toxic than active ingredients

Traditional Insecticides

- Burning of sulfur to fumigate Greek homes around 1000BC. Sulfur sometimes incorporated in candles was used till 19th century.
- NaF to control ant populations at domestic level.
- NaF along with Boric acid were used to kill cockroaches.
- Various types of oils have also been used to kill insect eggs.
- Toxic Chemicals like arsenic, mercury and Lead applied to crops.
- 17th Century: Nicotine Sulphate (Tobacco leaves) used as insecticide

Organochlorine Insecticides

organochlorines, which are organic compounds that contain chlorine. Many organochlorines share several notable properties:

- stability against decomposition or degradation in the environment;
- very low solubility in water, unless oxygen or nitrogen is also present in the molecules;
- high solubility in hydrocarbon-like environments, such as the fatty material in living matter;
- relatively high toxicity to insects, but low toxicity to humans.

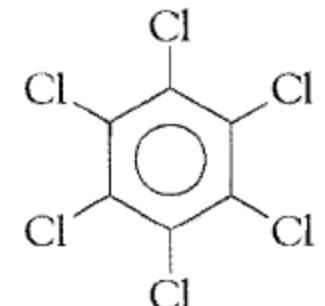
Example is C_6Cl_6 used as agricultural fungicide.

Suspected liver carcinogen.

It is a member of “dirty dozen” listed by UNEP.

Another example is 1,4 isomer of dichlorobenzene

It is used as insecticidal fumigant



hexachlorobenzene (HCB)

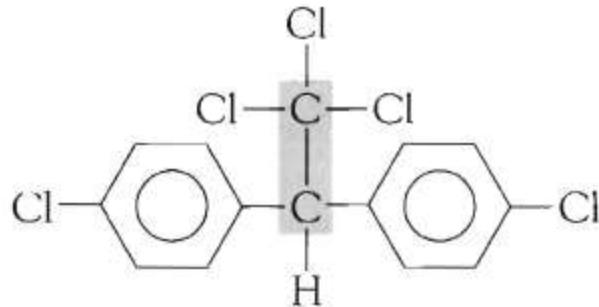
**U.N.'s Persistent Organic Pollutants (POP) "Dirty Dozen"
and Their Status in Several Countries**

POP	U.S.	Canada	U.K.	Mexico	China	India	Use
DDT	X	X	X	R	R	R	Mosquitoes
Aldrin	X	X	X	X	OK	OK	Termites
Dieldrin	X	X	X	X	OK	R	Crops
Endrin	X	X	X	X	OK	X	Rodents
Chlordane	R	X	X	OK	R	OK	Termites
Heptachlor	R	X	X	X	OK	OK	Soil insects
Hexachlorobenzene	X	X	X				Fungicide
Mirex	X	X		R	R		Ants, termites
Toxaphene	X	X	X	X	OK	X	Ticks, mites
PCBs*	X	R	R	OK			Many uses
Dioxins*	BP	BP	BP	BP	BP	BP	
Furans*	BP	BP	BP	BP	BP	BP	

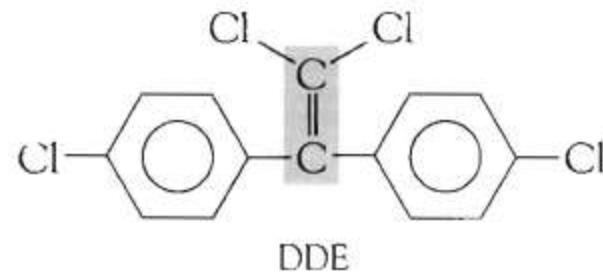
Codes: *not pesticides; X = banned or no registered uses; R = severely restricted uses only; OK = not restricted; BP = by-product, not produced deliberately.

DDT

- *para-dichlorodiphenyltrichloroethane.*
- Termed as “*Elixir of death*” by writer *Rachel Carson*.



(DDT): *para-dichlorodiphenyltrichloroethane*



- *DDE, dichlorodiphenyldichloroethene.*
- DDE interfere with the enzyme that regulates the distribution of calcium in birds.
- Elixir of death

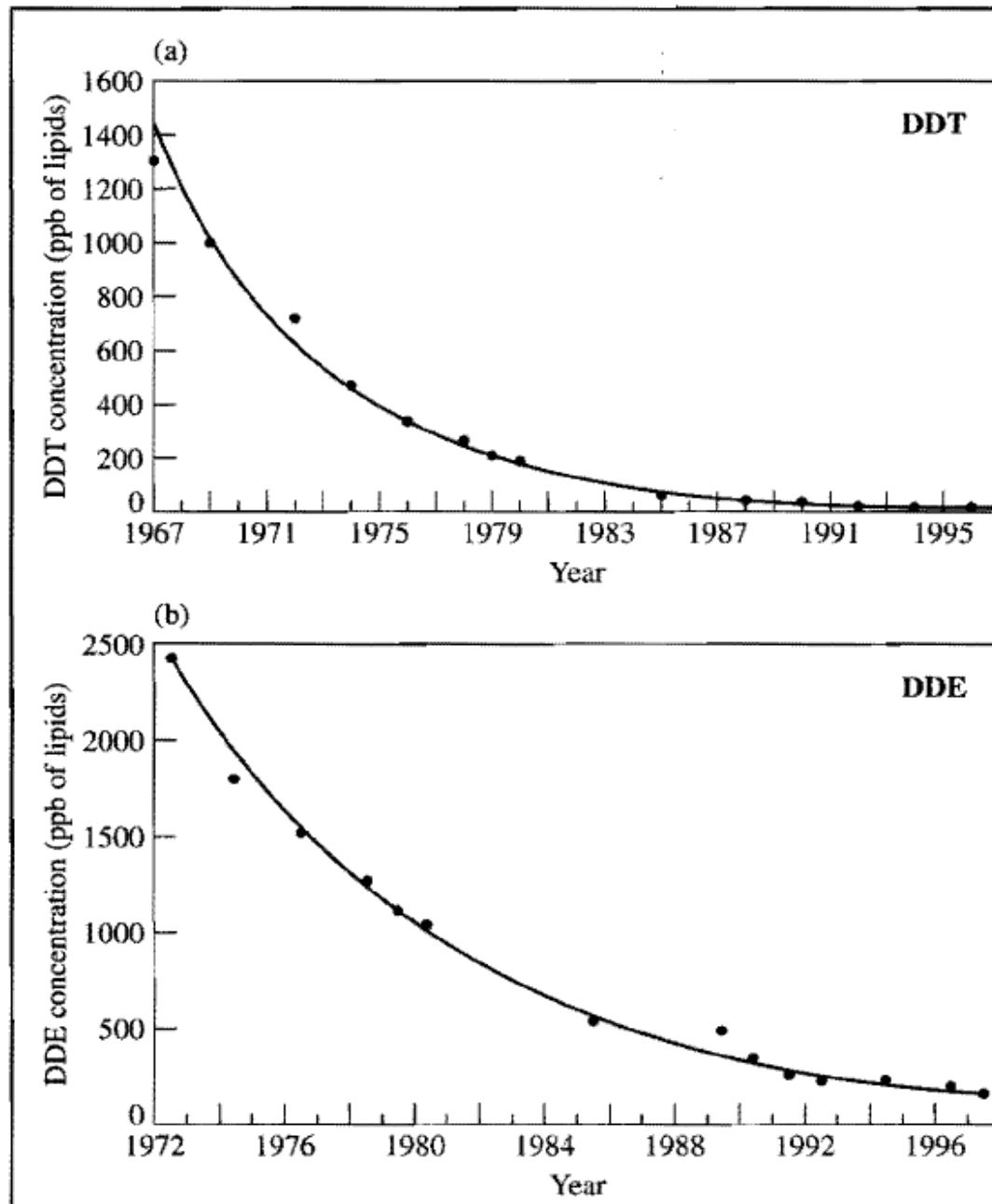
DDE in Body Fat

Its persistence is due to

- its low vapor pressure and its consequent slow rate of evaporation;
- its low reactivity with respect to light and to chemicals and microorganisms in the environment; and
- its very low solubility in water.

We all have some “DDT” (to the extent of about 3 ppm for North American adults) stored in our body fat. In humans, most ingested DDT is slowly but eventually eliminated. Most of the “DDT” stored in human fat is actually the DDE that was present in the food we have eaten, having previously been converted from DDT that was originally in the environment. Unfortunately DDE is almost nondegradable biologically and is very fat-soluble, so it remains in our bodies for a long time.

FIGURE 10-1 Trends in (a) DDT and (b) DDE concentrations in breast milk of Swedish women. [Source: K. Noren and D. Meironyte, "Certain Organochlorine and Organobromine Contaminants in Swedish Human Milk in Perspective of Past 20–30 Years," *Chemosphere* 40 (2000): 1111.]



Less Persistent Analogs of DDT

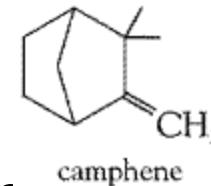
- A number of compound having same general molecular structure as DDT.
- This is due the same molecular shape.
- The shape is determined by two tetrahedral carbons in the ethane unit and by two flat benzene rings. DDT like molecule become wedged in the nerve channel that leads out from the nerve cell.
- This mechanism is not occurred to warm blooded animals like humans.
- DDD (TDE): para-dichlorodiphenyldichloroethane.
- It also bioaccumulates.

Other Organochlorine Insecticides

Toxaphene: for cotton and Soyabeen.

It is a mixture of hundreds of similar substances, all of which are produced when the hydrocarbon camphene (from pine trees) is partially chlorinated

Extremely toxic to fish.

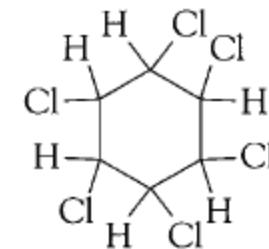


Bioaccumulates in fatty tissues and causes cancer in test rodents.

It is a member of dirty dozen.

Hexachlorinated Cyclohexane: Lindane, BHC

Gamma isomer actually kills insects

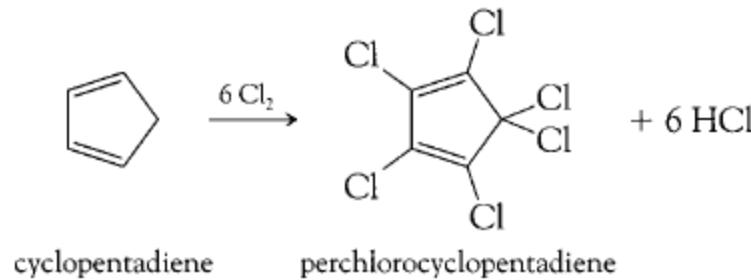


1, 2, 3, 4, 5, 6-hexachlorocyclohexane

Bioaccumulates.

It was also used in medical preparations to treat lice and scabies and also to treat seeds.

Chlorinated Cyclopentadiene Insecticides:



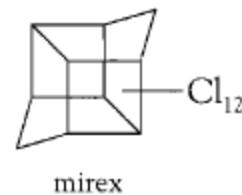
Soil insects, fire ants, cockroaches, termites, grasshoppers etc.

Highly persistent.

Aldrin and Dieldrin.

Accumulate in fatty acids and were causing mortality to bald eagles.

Member of dirty dozen.



Mirex is still used to fight giant termites. It is also listed in **Persistent organic pollutants** (POP) list.

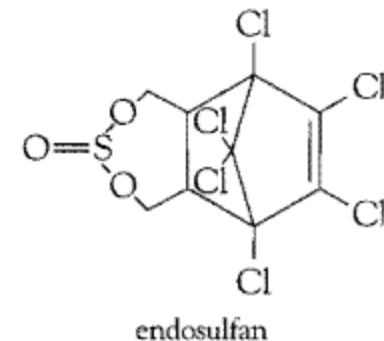
Endosulfan

- Acaricide.

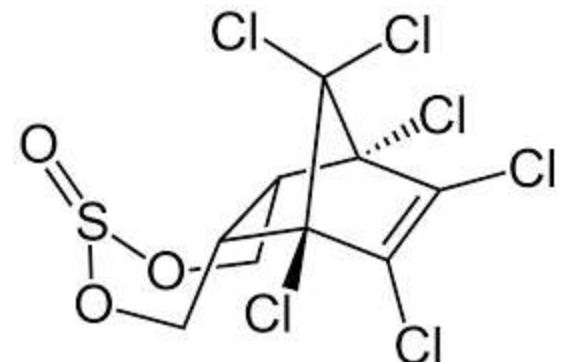
In nature it get converted to endosulfan sulfate and sulfur free diol (which degrade further)

Its only concern is its effects on workers.

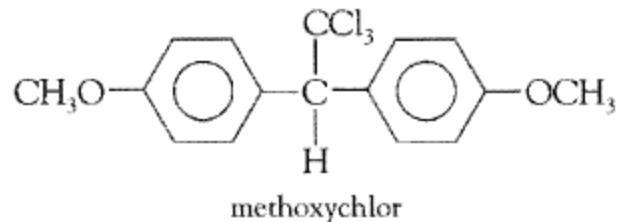
Can attack non-target animals.



Example of Sri Lanka



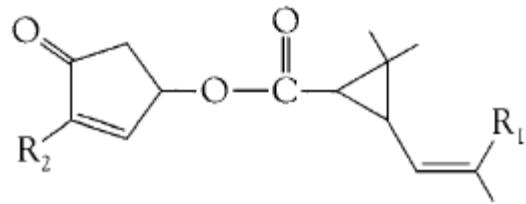
- Methoxy Chlor



- Used for flies and mosquitoes.
- Methoxy group has the same size as that of chlorine.
- This compound excreted from the body than accumulating.

Natural and Green Insecticides

- Pesticides from Natural Sources
- Plants themselves manufacture certain molecules
- e.g. Nicotine, Rotenone, the pheromones and juvenile hormones.
- Pyrethrins: obtained from flower of a species of *chrysanthemum*.



general pyrethrin structure

- Pyrethrins were used in Napoleonic time and still being used.
- They generally considered to be safe.
- These compounds are unstable in sunlight, therefore several synthetic pyrethrin-like insecticides have been developed.
- Pyrethroids-semisynthetic are very common to find in household.
- Mixed with piperonyl butoxide (from sassafras plants).

- **Rotenone:** a complex natural product from roots of tropical **bean plants**, used as crop insecticide and to paralyze or kill fish.
- Decomposed by sunlight.
- Chronic exposure to rotenone can contribute the onset of Parkinson's disease.
- Pyrethrins and rotenone are classified as moderately hazardous, since they have acute toxicity.
- **Greener insecticide** may refer to a chemical remedy which has lesser effect on the environment or include less toxins as compared to the conventional insecticides but having same potential effect on the target organism.

Accumulation of Organochlorides

- Hydrophobic nature is one of the several reasons of bioaccumulation of substances like DDT.
- Bioconcentration factor, BCF: *presents the equilibrium ratio of the concentration of a specific chemical in a fish relative to that in surrounding water, provided that the diffusion mechanism represents the only source of the substance to the fish.*
- The BCF of a chemical can be predicted, to within about a factor of 10. *1-octanol, an alcohol is used.*

$$K_{ow} = [S]_{\text{octanol}} / [S]_{\text{water}}$$

octanol-water partition coefficient, K_{ow}

TABLE 10-5

Selected Data for Some Pesticides

Pesticide	Solubility in H ₂ O (ppm)	log K _{ow}
HCB	0.0062	5.5–6.2
DDT	0.0034	6.2
Toxaphene	3	5.3
Dieldrin	0.1	6.2
Mirex	0.20	6.9–7.5
Malathion	145	2.9
Parathion	24	3.8
Atrazine	35–70	2.2–2.7

For HCB, $\log K_{ow} = 5.7$. What would be the predicted concentration of HCB due to bioconcentration in the fat of fish that swim in waters containing 0.000010 ppm of the chemical?

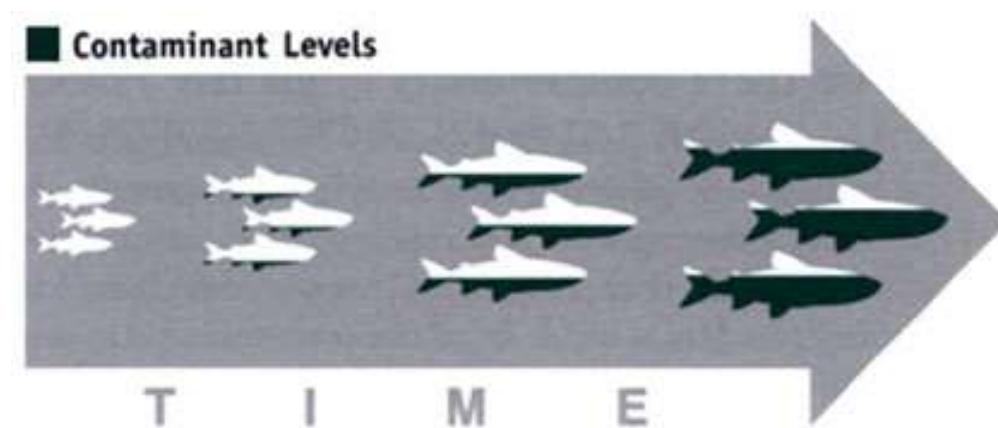
- ❑ The bioconcentration factor is referred as a particular concentration of specific chemical inside biological tissues to that of surrounding environment.
- ❑ The bioaccumulation is referred as the chemical concentration of aquatic organism reach a level when it exceeds in water due to uptake of chemicals when it is exposed to chemicals by transport of respiratory surface

Pesticides

Persistence + Lipid solubility = Bioaccumulation

Bioaccumulation

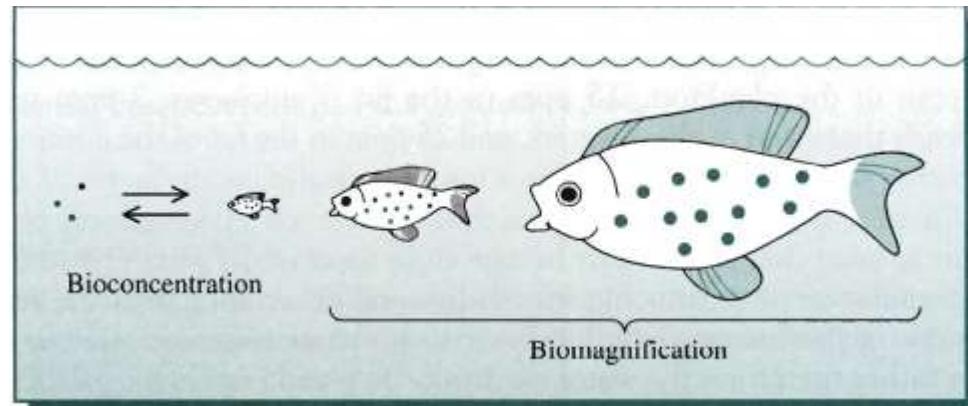
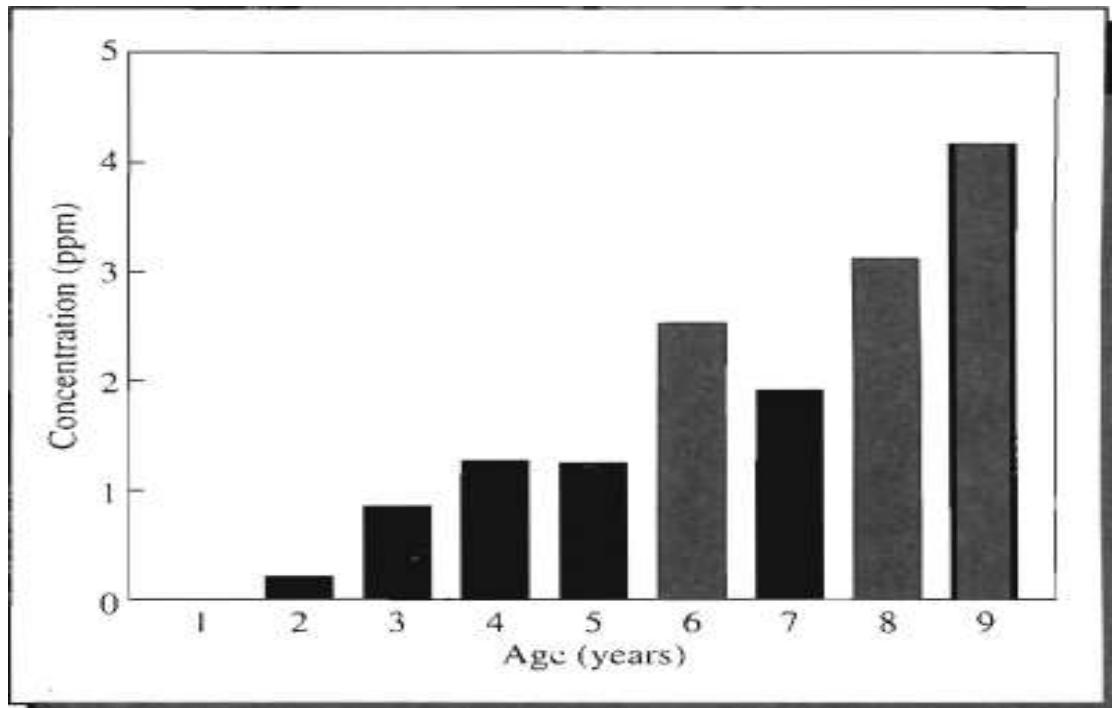
E.g DDT

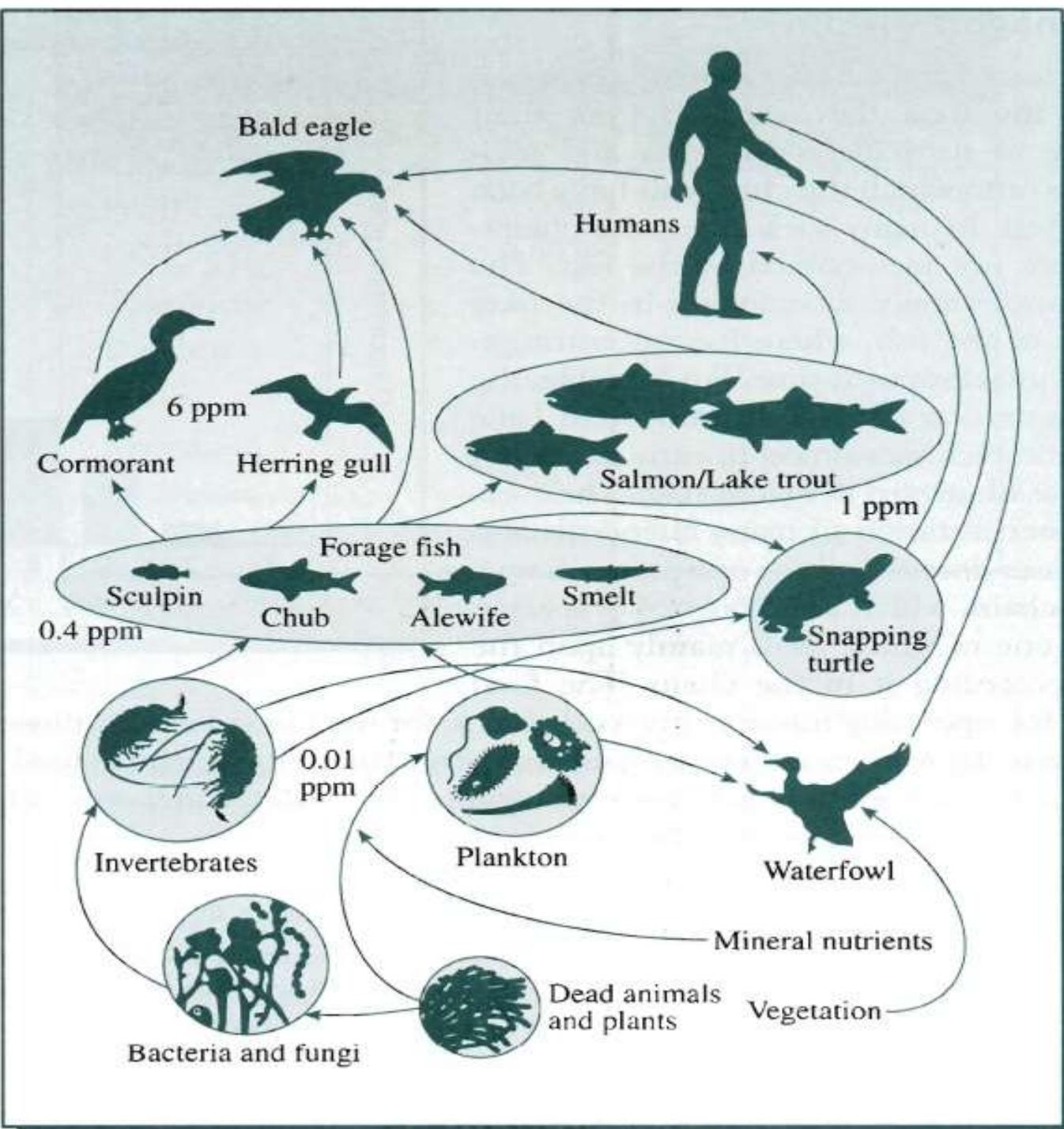


Biomagnification

Bioamplification or biological magnification:

Increasing concentration of a substance, such as a toxic chemical.





Multiplication
par 10 millions de
la concentration
de DDT



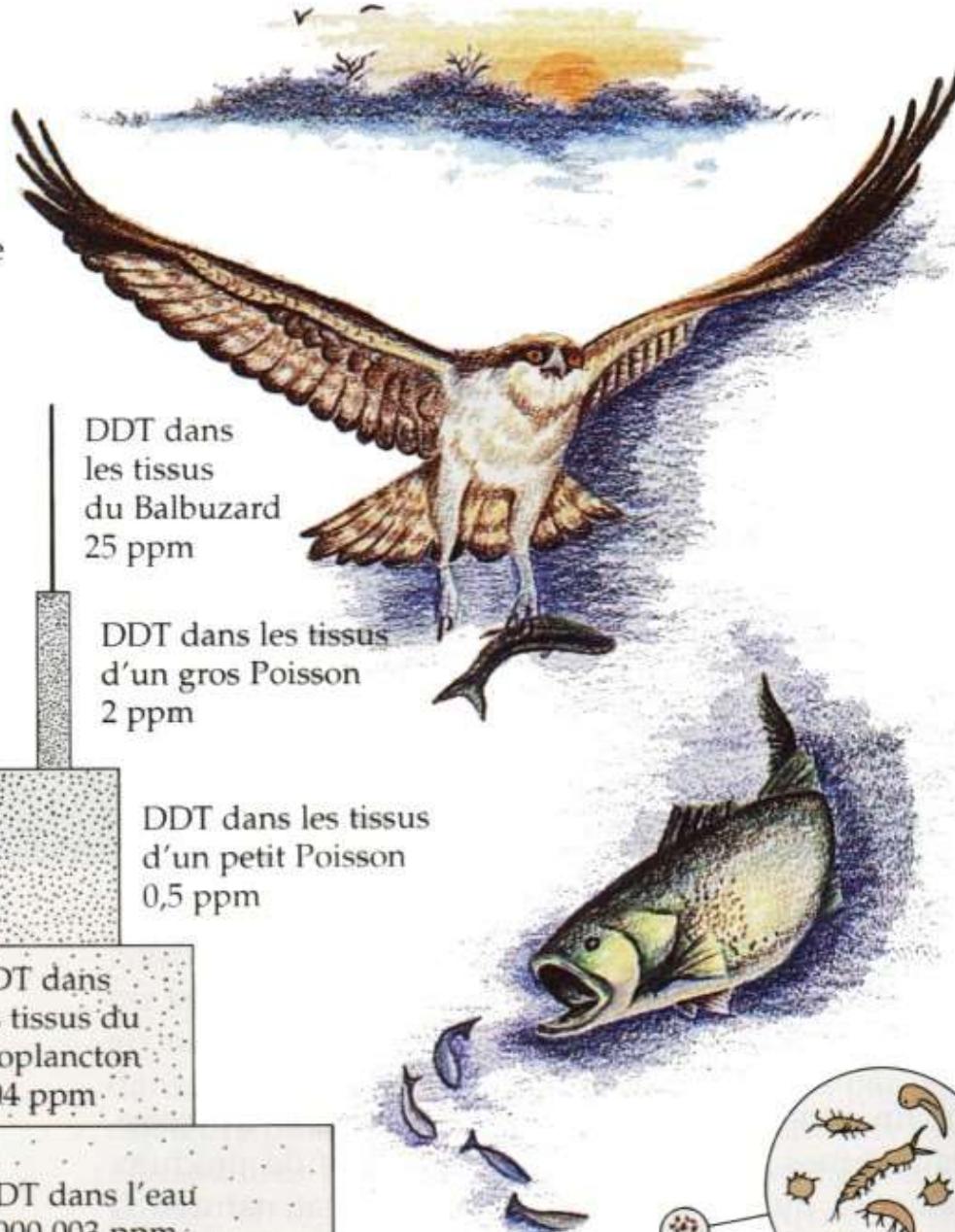
DDT dans
les tissus
du Balbuzard
25 ppm

DDT dans les tissus
d'un gros Poisson
2 ppm

DDT dans les tissus
d'un petit Poisson
0,5 ppm

DDT dans
les tissus du
zooplancton
0,04 ppm

DDT dans l'eau
0,000 003 ppm





POTENTIAL EFFECT OF PESTICIDES & INTEGRATED PEST MANAGEMENT

CHEMICAL PESTICIDE POLLUTION

(A MAJOR BOTTLENECK IN OUR FIGHT AGAINST PESTS)

- Development of resistance in pests to pesticides
- Recovery of target and non target species
- Destruction of beneficial organisms like honeybee, pollinators, parasitoids, predators etc.
- Pesticide residue in food, fodder and feed (food grain, fruits, vegetables, meat, fish egg, milk and milk products and even human milk.)

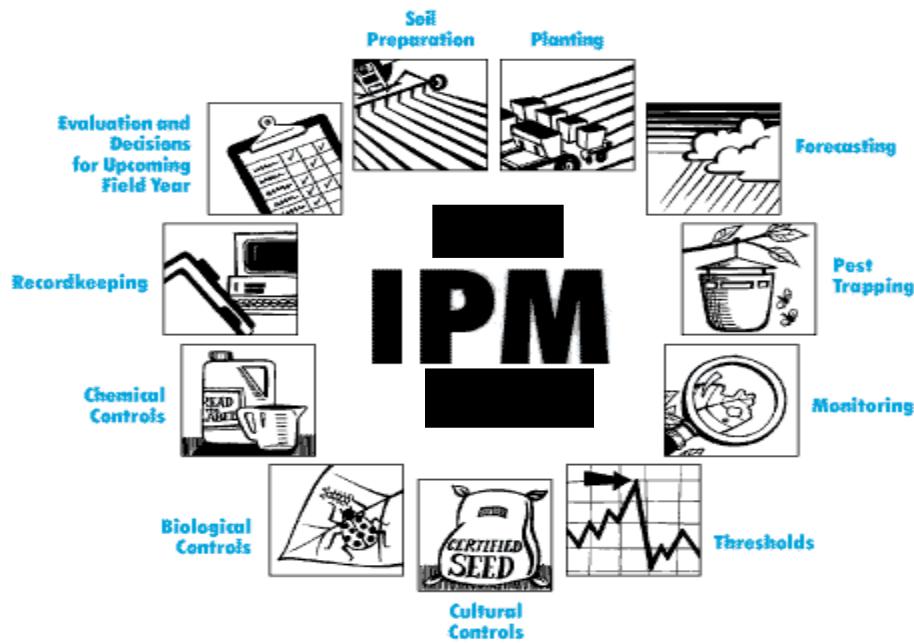
Secondary pest outbreak.

- Bioaccumulation
- Biomagnifications
- Pesticide persistence
- Economic problems

Integrated Pest Management (IPM)

Integrated Pest Management is the coordinated use of pest and environmental information along with available pest control methods, including cultural, biological, genetic and chemical methods, to prevent unacceptable levels of pest damage by the most economical means, and with the least possible hazard to people, property, and the environment.

- Six principles of IPM are:
1. Prevention
 2. Pest identification
 3. Monitoring
 4. Treatment/ Injury thresholds
 5. Treatment options and selections
 6. Post treatment Evaluation



What is IPM?

- Ecosystem-based strategy that focuses on long-term prevention of pests or their damage through a combination of techniques such as biological control, habitat manipulation, modification of cultural practices, and use of resistant varieties.



Reasons for IPM

- Chemical pesticides can impact the human health and ecosystems
- Example: DDT, a pesticide, can accumulate in the fatty tissue of animals and affect bird reproduction
- Insects can become resistant to chemical pesticides
- Approximately 500 species of insects are resistant to one or more pesticides



How does IPM work?

- Reduces the amount of chemical pesticides by using three possible approaches:
 1. Mechanical
 2. Biological
 3. Chemical



Mechanical approach:

- Limits the pest's access to food, water and harborage sites (i.e. proper storage of food/water supplies or installation or repair of physical barriers to future pest intrusion use of mechanical devices (i.e. traps)
- Example – Japanese beetle traps



Biological approach:

- Introduction of a natural enemy of the pest
- Example – Lady bugs feed on aphids and can be introduced to reduce the aphid population on crops



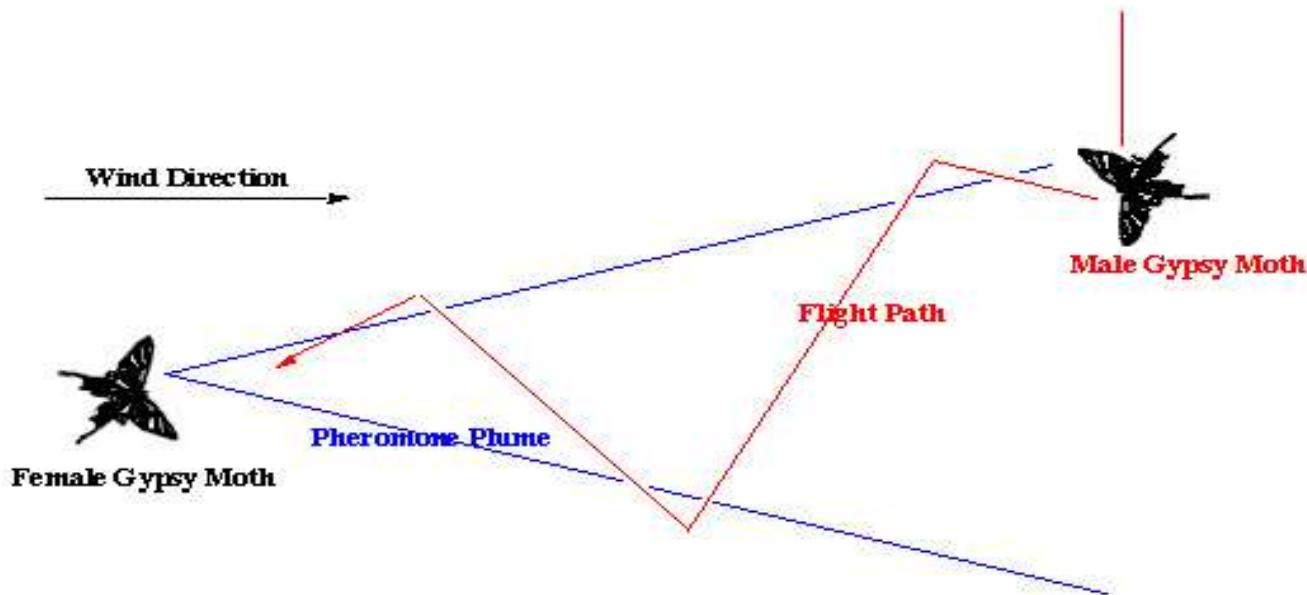
Chemical approach:

- Pesticide applications that have minimal risks associated with their use
- Using the least amount of chemicals that will still be effective



Insects use of Pheromones

- Pheromones are chemicals emitted by an animal that signals another animal of the same species.



Pheromones and IPM

- Pheromones can be utilized to catch or deter insects
- Example: Pheromone “traps”, which contain the pheromone emitted by the female gypsy moth can be set to catch male moths



Advantages & Disadvantages of IPM

- Reduce chemicals being used
- May reduce of pesticide resistant insects
- Only uses chemicals if necessary
- Long term benefits (lower cost for chemicals, better for environment and human health)
- Individual using IPM must be educated about the options
- Takes more time to initiate than simply “spraying for pests”
- Must be closely monitored for best results
- Natural enemies of pests may become pests themselves

IPM

- chemical control—the use of chemical pesticides, both synthetic and natural;
- biological control—reducing pest populations by the introduction of predators, parasites, or pathogens;
- cultural control—introducing farm practices that prevent pests from flourishing;
- host-plant resistance—using plants that are resistant to attack, including plants adapted by genetic engineering to have greater resistance;
- physical control—using nonchemical methods to reduce pest population; and
- regulatory control—preventing the invasion of an area by new species.

Risk Assessment

- Risk assessment Analysis

In order to perform a risk assessment on a chemical, it is necessary to know

- **hazard evaluation** information; i.e., the types of toxicity (acute? cancer? birth defects?) that are expected from it;
 - quantitative **dose-response** information concerning the various possible modes of exposure (oral, dermal, inhalation) for it; and
 - an estimation of the potential **human exposure** to the chemical.
-
- To find threshold level for the most sensitive members of human population, it is common to divide the **No-observed-adverse-effect level** (NOEL) from animal studies by a *safety factor*, typically 100. This value is called maximum **Acceptable daily intake (ADI)** or **toxicity Reference dose, (RfD)**.

OVERVIEW

Why is Cyanide Wastewater Treatment Important?

Several modern industrial processes produce cyanide-containing wastes, including metal plating, case hardening of steel, and refining of gold and silver ores. Wastewater from these processes that contains even trace amounts of cyanide must be treated before discharge into sewage systems. Cyanide wastewater treatment is critical, because cyanide wastes are toxic to living organisms. Specifically, cyanide may reduce or eliminate oxygen utilization in organisms, including human beings, making cyanide poisoning potentially fatal. Aquatic life, including microorganisms involved in natural water purification streams, is particularly susceptible to cyanide poisoning. Cyanide toxicity presents a direct human hazard if cyanide containing wastes enter agricultural or municipal water supplies. A lethal dose of cyanide in human beings is approximately 4mg/lb of body weight.

Alkaline Chlorination Systems

The predominant mode of cyanide wastewater treatment is alkaline chlorination. This treatment proceeds in two steps. First, cyanide is oxidized to

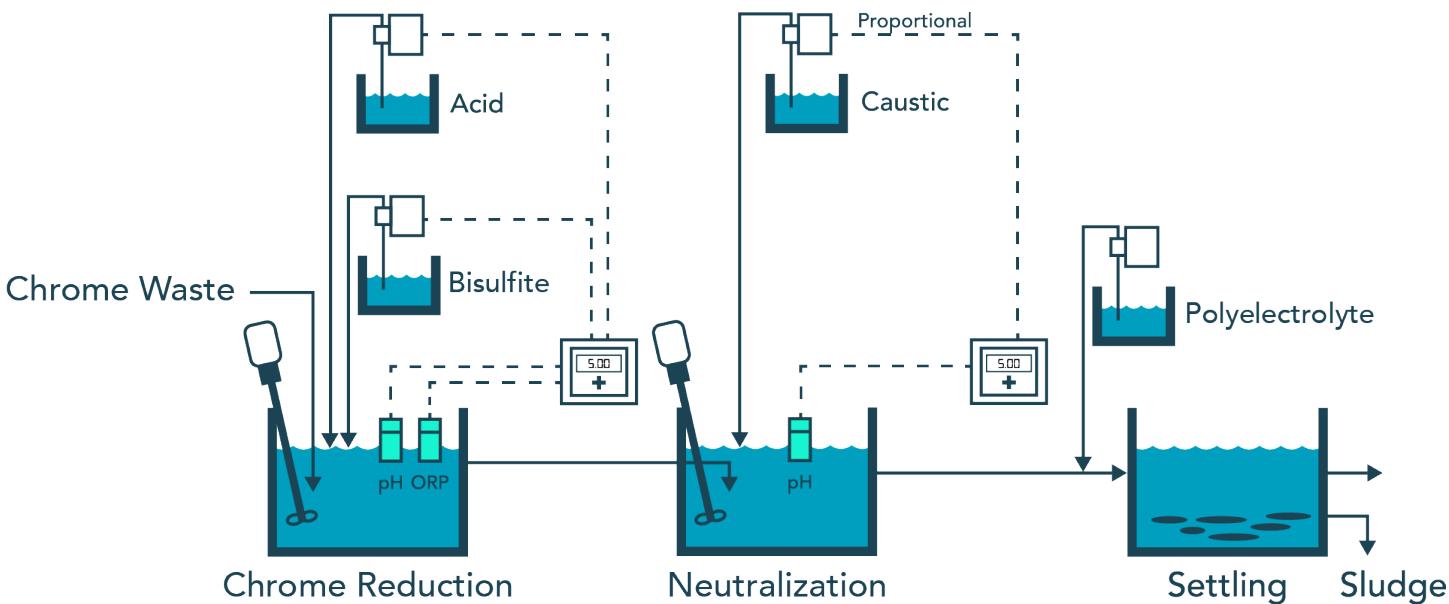


cyanate by sodium hypochlorite. This reaction may be brought about through direct addition of sodium hypochlorite or by addition of chlorine gas and sodium hydroxide. In the second step, cyanate is oxidized to carbon dioxide and nitrogen by further addition of the chosen oxidizing agents.

pH and REDOX (ORP) Control in Cyanide Wastewater Treatment Systems

In order to ensure that the alkaline chlorination process proceeds safely and efficiently, it is important to monitor pH and ORP during each oxidation step.

CYANIDE WASTEWATER TREATMENT PROCESS DIAGRAM



DESIGNED AND ASSEMBLED IN CALIFORNIA, USA

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PARAMETERS AND MONITORING

pH Control

During the oxidation of cyanide to cyanate, pH control is critical. If pH is too low (acidic) during this step, the reaction may produce toxic cyanogen chloride. Poor pH control can also lead to reaction inefficiency: sub-optimal pH may negatively impact reaction speed and prompt addition of oxidation reactants in excess of stoichiometric requirements.

ORP Control

ORP is monitored during each oxidation step to track reaction progress and ensure that oxidation has gone to completion before waste discharge. As each oxidation reaction proceeds, ORP increases and eventually plateaus. The exact ORP value where each plateau occurs depends on the specific reaction conditions for an individual cyanide waste treatment scenario. Typical pH and ORP ranges are listed in the table below.

Cyanide Wastewater Treatment Monitoring Systems

A typical cyanide wastewater treatment monitoring system will consist of two pH sensors, two ORP sensors, and four controllers. Sensors with well protected reference junctions are an ideal choice for cyanide waste treatment applications, as preventing reference poisoning will extend sensor lifetime. ORP sensors with a gold electrode – as opposed to the usual platinum – are also recommended, as they provide the most accurate measurements for effective reagent control.



Cyanide Wastewater Treatment Monitoring Products

The Sensorex S8000 Series provides a modular cyanide waste treatment solution that can be adapted to fit various system configurations. For maximum sensor lifetime, the S8000 Series is designed with Enhanced Reference Path (ERP) technology, creating a complex path to protect the reference cell. Sensor maintenance is also minimized with a self-cleaning flat surface design and quick change replacement cartridges. Deploy the [S8000CD pH sensors](#) and [S8000CD-ORP-AU](#) gold ORP electrodes with the controller of your choice to optimize your cyanide waste treatment process.

Oxidation Reaction	Chemical Equation	pH	ORP
(1) Cyanide → Cyanate	$\text{NaCN} + 2\text{NaOH} + \text{Cl}_2 \rightleftharpoons \text{NaCNO} + 2\text{NaCl} + \text{H}_2\text{O}$	10-11.5	(+) 250mV-400mV
(2) Cyanate → Carbon Dioxide & Nitrogen	$2\text{NaCNO} + 4\text{NaOH} + 3\text{Cl}_2 \rightleftharpoons 6\text{NaCl} + 2\text{CO}_2 + \text{N}_2 + 2\text{H}_2\text{O}$	8.5-9	(+) 300mV-600mV

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Module 23 : Tertiary Wastewater Treatment
Lecture 38 : Tertiary Wastewater Treatment

23.1 Introduction

Secondary treatment removes 85 to 95 percent of BOD and TSS and minor portions of nitrogen, phosphorus, and heavy metals. Tertiary treatment is the next wastewater treatment process after secondary treatment. This treatment is sometimes called as the final or advanced treatment and consists of removing the organic load left after secondary treatment for removal of nutrients from sewage and particularly to kill the pathogenic bacteria. The effluents from secondary sewage treatment plants contain both nitrogen (N) and phosphorus (P). N and P are ingredients in all fertilizers. When excess amounts of N and P are discharged, plant growth in the receiving waters may be accelerated which results in eutrophication in the water body receiving such waste. Algae growth may be stimulated causing blooms which are toxic to fish life as well as aesthetically unpleasing. Secondary treated effluent also contains suspended, dissolved, and colloidal constituents which may be required to be removed for stipulated reuse or disposal of the treated effluent.

The purpose of tertiary treatment is to provide a final treatment stage to raise the effluent quality before it is discharged to the receiving environment such as sea, river, lake, ground, etc., or to raise the treated water quality to such a level to make it suitable for intended reuse. This step removes different types of pollutants such as organic matter, SS, nutrients, pathogens, and heavy metals that secondary treatment is not able to remove. Wastewater effluent becomes even cleaner in this treatment process through the use of stronger and more advanced treatment systems. It includes sedimentation, coagulations, membrane processes, filtration, ion exchange, activated carbon adsorption, electrodialysis, nitrification and denitrification, etc. (Figure 23.1). Tertiary treatment is costly as compared to primary and secondary treatment methods.

23.2 Need of Tertiary treatment

Tertiary treatment may be provided to the secondary effluent for one or more of the following contaminant further.

- To remove total suspended solids and organic matter those are present in effluents after secondary treatment.
- To remove specific organic and inorganic constituents from industrial effluent to make it suitable for reuse.

- To make treated wastewater suitable for land application purpose or directly discharge it into the water bodies like rivers, lakes, etc.
- To remove residual nutrients beyond what can be accomplished by earlier treatment methods.
- To remove pathogens from the secondary treated effluents.
- To reduce total dissolved solids (TDS) from the secondary treated effluent to meet reuse quality standards.

One or more of the unit operation/ process mentioned in Figure 23.1 will be used for achieving this tertiary treatment.

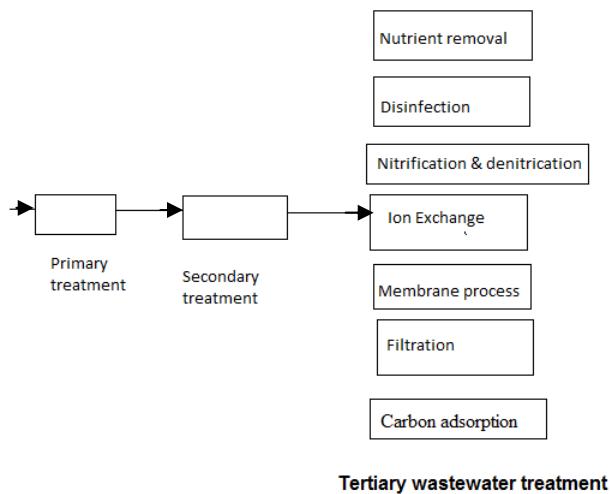


Figure 23.1 Process involved in tertiary wastewater treatment

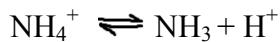
23.3 *Tertiary Treatments*

In advanced wastewater treatment, treatment options or methods are dependent upon the characteristics of effluent to be obtained after secondary treatment to satisfy further use or disposal of treated wastewater.

23.3.1 Nitrogen removal

Wastewater containing nutrients includes sewage, agriculture runoff and many of the industrial effluents. The nutrients of most concern are N and P. The principal nitrogen compounds in domestic sewage are proteins, amines, amino acids, and urea. Ammonia nitrogen in sewage results from the bacterial decomposition of these organic constituents.

The nitrogen compounds result from the biological decomposition of proteins and from urea discharged in body waste. This nitrogen is in complex organic molecules and is referred simply as organic nitrogen. Organic nitrogen may be biologically converted to free ammonia (NH_3^0) or to the ammonium ion (NH_4^+) by one of several different metabolic pathways. These two exist in equilibrium as



Ammonia nitrogen is the most reduced nitrogen compound found in wastewater, which can be biologically oxidized to nitrate if molecular oxygen is present (under aerobic condition). In wastewater, the predominant forms of nitrogen are organic nitrogen and ammonia. The nitrification may take place in biological treatment units provided the treatment periods are long enough. Generally, for the HRT used in secondary treatment conversion of organic nitrogen to ammonia is significant and nitrification may not be significant. Because of oxygen demand exerted by ammonia (about 4.6 mg of O_2 per mg of NH_4^+ -N oxidized) and due to other environmental factors, removal of ammonia may be required. The most common processes for removal of ammonia from wastewater are

- i) Air stripping,
- ii) Biological nitrification and denitrification.

23.3.1.1 *Air stripping*

It consists of converting ammonium to gaseous phase and then dispersing the liquid in air, thus allowing transfer of the ammonia from wastewater to the air. The gaseous phase NH_3^0 and aqueous phase NH_4^+ exist together in equilibrium. The relative abundance of these phases depends upon both the pH and the temperature of the wastewater. The pH must be greater than 11 for complete conversion to NH_3 . Since, this pH is greater than pH of normal wastewater, adjustment of pH is necessary prior to air stripping. Addition of lime is the most common means

for raising the pH. Enough lime must be added to precipitate the alkalinity and to add the excess OH⁻ ions for pH adjustment.

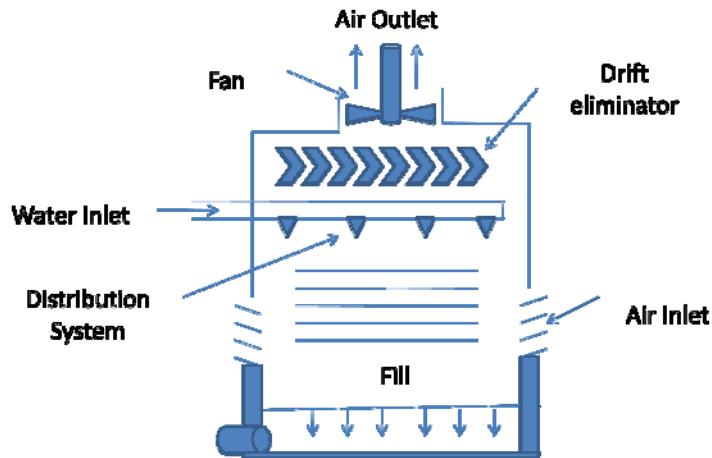


Figure 23.2 Spray tower

The most important and efficient reactor for air stripping is counter current spray tower. Larger quantity of air is required, and fan must be installed to draw air through tower (Figure 23.2). Packing is provided to minimize the film resistance to gas transfer by continuously forming, splashing and reforming drops.

The air to wastewater ratio ranging from 2000 to 6000 m³ of air/m³ of wastewater is used for design. Air requirement is more at lower temperature. Tower depths are generally less than 7.5 m, and hydraulic loading vary from 40 to 46 L/min.m² of tower. The limitation to this process occurs at temperature close to freezing temperature. Drastic reduction in efficiency is observed and preheating of gas is not possible because of high volume.

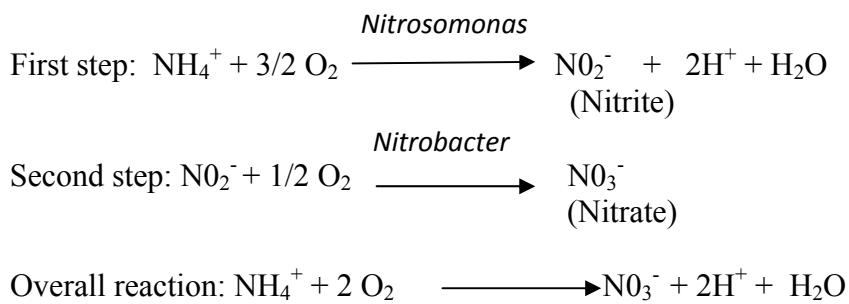
The other problems associated with this include noise and air pollution and scaling of the packing media. Noise pollution problem is caused by roar of the fan. The odor problem is due to dispersion of ammonia gas in atmosphere, due to which this technique may not be permitted at some location. This problem can be minimized by locating the facility away from the populated area. Precipitation of calcium carbonate scale on the packing media as a result of wastewater softening can be minimized by the use of smooth surface PVC pipe as packing material. The occasional cleaning of packing media is still required.

23.3.1.2 Biological Nitrification and denitrification

Bacteria remove ammonia nitrogen from wastewater by a two step biological processes: nitrification followed by denitrification to convert it finally to gaseous nitrogen. In this gaseous form N_2 is inert and does not react with the wastewater itself or with other constituents present in wastewater. Since, treated wastewater is likely to be saturated with molecular nitrogen; the produced N_2 is simply released to the atmosphere. These two steps involved require different environmental conditions and hence generally they are carried out in separate reactors.

Nitrification

It has important role in nitrogen removal from wastewater during treatment. The biological conversion of ammonium to nitrate nitrogen is called Nitrification. It is autotrophic process i.e. energy for bacterial growth is derived by oxidation of nitrogen compounds such as ammonia. In this process, the cell yield per unit substrate removal is smaller than heterotrophs. Nitrification is a two-step process. In first step, bacteria known as *Nitrosomonas* can convert ammonia and ammonium to nitrite. These bacteria known as nitrifiers are strictly aerobes. This process is limited by the relatively slow growth rate of *Nitrosomonas*. Next, bacteria called *Nitrobacter* finish the conversion of nitrite to nitrate.



Nitrosomonas and *Nitrobacter* use the energy derived from the reactions for cell growth and maintenance. Some of ammonium ions are assimilated into cell tissues. Neglecting this ammonium ion used in cell synthesis the O₂ required to oxidize ammonia to nitrate is 4.57 mg O₂/mg ammonium nitrogen. If the ammonium used in cell, O₂ required is considered it is 4.3 mg O₂/mg ammonium nitrogen and about 7.14 mg of alkalinity is needed to neutralize the H⁺ produced.

Nitrification may be used to prevent oxygen depletion from nitrogenous demand in the receiving water. Nitrification requires a long retention time, a low food to microorganism ratio (F/M), a high mean cell residence time (MCRT), and adequate alkalinity. Wastewater temperature and pH affects the rate of nitrification.

Under favourable conditions, carbon oxidation and nitrification may occur in a single reactor called single stage under favourable conditions. In separate stage carbon oxidation and nitrification occur in different reactors. It can be accomplished in both suspended and attached growth process such as trickling filter, ASP, rotating disc biological contactor (RBC), SBR, etc. Also, nitrifying organisms are present in almost all aerobic process sludge but they are less in number. In nitrification, when ratio of BOD_5 to TKN is greater than 5, the process is called as combined carbon oxidation and nitrification, whereas, when ratio of BOD_5 to TKN is less than 3, the process is called as separate stage carbon oxidation and nitrification.

For single stage carbon oxidation and nitrification, plug flow, completely mixed and extended aeration ASP can be used. Oxidation ditch is also one of option for this process. The attached growth processes like TF and RBC are commonly used. Nitrification can be achieved by reducing applied loading rate, increasing the mean cell residence time (θ_c) and air supply.

Nitrifying bacteria are sensitive organisms. A variety of organic and inorganic agents can inhibit the growth and action of these organisms. High concentration of ammonia and nitrous acid can be inhibitory. The effect of pH is also significant with optimal range of 7.5 to 8.6. The system acclimatize to lower pH can also work successfully. The temperature also has considerable impact on growth of the nitrifying bacteria. Dissolved oxygen concentration above 1 mg/L is essential for nitrification. Below this DO, oxygen becomes the limiting nutrients and nitrification slows down or ceases.

Denitrification

In some applications, such as discharge of effluent into enclosed water bodies or recycle to water supplies, nitrification may not be sufficient. When nitrogen removal is required, one of the available methods is to follow biological nitrification with denitrification. Denitrification is

accomplished under anaerobic or near anaerobic conditions by facultative heterotrophic bacteria commonly found in wastewater. Nitrates are removed by two mechanisms: (1) conversion of NO_3^- to N_2 gas by bacterial metabolism and (2) conversion of NO_3^- to nitrogen contained in cell mass which may be removed by settling. Denitrification occurs when oxygen levels are depleted and nitrate becomes the primary electron acceptor source for microorganisms.



Denitrifying bacteria are facultative organisms, they can use either dissolved oxygen or nitrate as an oxygen source for metabolism and oxidation of organic matter. This is carried out by heterotrophic bacteria such as *pseudomonas*, *spirillum*, *lactobacillus*, *bacillus*, *microaoccus*, etc. For reduction to occur, the DO level must be near to zero, and carbon supply must be available to the bacteria. Because of low carbon content is required for the previous nitrification step, carbon must be added before denitrification can proceed. A small amount of primary effluent, bypassed around secondary and nitrification reactor can be used to supply the carbon. However, the unnnitrified compounds in this water will be unaffected by the denitrification process and will appear in effluent. When complete nitrogen removal is required, an external source of carbon containing no nitrogen will be required. The most commonly used external source of nitrogen is methanol. When methanol is added the reaction is



For treatment plant above 3 mg/L of methanol is required for each milligram per litre of nitrate, making this process an expensive. Alkalinity is generated in this process. Denitrification can be carried out as attached growth (anaerobic filter) and suspended growth process (expanded bed or UASB reactor).

23.3.2 Phosphorus removal

Normally secondary treatment can only remove 1-2 mg/l of phosphorus, so a large excess of phosphorus is discharged in the final effluent, causing eutrophication of lakes and natural water bodies. Generally it appears as orthophosphate, polyphosphate and organically bound phosphorus. Phosphorus is required for microbes for cell synthesis and energy transport, maintenance as well as it is stored for subsequent use by microbes. During secondary treatment process about 10 to 30 % of influent phosphorus is removed (Metcalf & Eddy, 2003). Phosphate

removal is currently achieved largely by chemical precipitation, which is expensive and causes an increase of sludge volume by up to 40%. An alternative is the biological phosphate removal (BPR), which is accomplished by sequencing and producing the appropriate environmental condition in the reactors.

Acinetobacter organisms are helpful for removal of phosphorus from effluent. Under anaerobic conditions, phosphorus accumulating organisms (PAO) assimilate fermentation products (i.e. volatile fatty acids) into storage products within the cells with the concomitant release of phosphorus from stored polyphosphates (Gray, 2005). Release of phosphorus occurs under anoxic condition. The BPR requires both aerobic and anaerobic zones in reactors for efficient treatment. Generally, lime precipitation is most commonly used for phosphorus removal. Phosphorus is removed in the waste sludge from the system.

Treatment technologies presently available for phosphorus removal include (de-Bashan and Bashan, 2004):

- A) Physical:
 - a) filtration for particulate phosphorus
 - b) membrane technologies
- B) Chemical:
 - a) precipitation
 - b) other (mainly physical-chemical adsorption)
- C) Biological
 - a) assimilation
 - b) enhanced biological phosphorus removal (EBPR)

23.3.3. *Ion exchange*

Ion Exchange can be used in wastewater treatment plants to swap one ion for another for the purpose of demineralization. The widest application of this process is in domestic water softening, where sodium ions are removed on cation exchange resin and chlorides are removed on anion exchange resin. Ion exchange is a unit process in which ions are removed out of an aqueous solution and is replaced by another ionic species. The basic principle behind ion exchange is that a weakly bound ion can preferably be displaced by a stronger binding ion. This effect is called the principle of selectivity. A more selective ion binds more strongly than a less selective ion. The effect of selectivity can be used to remove distinct ions from water and to

replace them with others. It can be operated in a batch or continuous mode and has been used for removal of nitrogen, heavy metals and TDS in wastewater applications. It has also been used selectively to remove specific impurities and to recover valuable trace metals like chromium, nickel, copper, lead and cadmium from industrial waste discharges.

A number of naturally occurring minerals have ion exchange properties. Among them the notable ones are aluminium silicate minerals, which are called zeolites. Synthetic zeolites have been prepared using solutions of sodium silicate and sodium aluminate. Alternatively synthetic ion-exchange resins composed of organic polymer with attached functional groups such as $-SO_3^-$, H^+ (strongly acidic cation exchange resins), or $-COO^- - H^+$ (weakly acidic cation exchange resins) or $-N^+(CH_3)_3OH^-$ (strongly basic anion exchange resins) can be used. Synthetic and industrially produced ion exchange resins consist of small, porous beads that are insoluble in water and organic solvents. The most widely used base-materials are polystyrene and polyacrylate.

23.3.4 Membrane process

Membrane technology can be used to treat a variety of wastes, including sanitary landfill leachate containing both organic and inorganic chemical species, water-soluble oil wastes used in metal fabricating and manufacturing industries, solvent-water mixtures, and oil-water mixtures generated during washing operations at metal fabricating facilities. Depending upon the material used for membrane, nature of driving force and separation mechanism, the membrane processes can be classified into sub-processes such as electrodialysis (ED) or electrodialysis reversal (EDR), microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO).

MF, UF, NF and RO use pressure to transport water across the membrane. MF removes particulate matter while RO removes many solutes as water permeate through the membrane. MF membranes have the largest pore size and typically reject large particles and various microorganisms. UF membranes have smaller pores than MF membranes and, therefore, in addition to large particles and microorganisms, they can reject bacteria and soluble macromolecules such as proteins. RO membranes are effectively non-porous and, therefore, exclude particles and even many low molar mass species such as salt ions, organics, etc. NF membranes are relatively new and are sometimes called loose RO membranes. They are porous

membranes, but since the pores are of the order of ten angstroms or less, they exhibit performance between that of RO and UF membranes. Different membrane processes are being used in water treatment since 1960.

The driving forces for the use of membrane technology are increased regulatory pressure to provide better quality water, increased demand of water requiring exploitation of low quality water resources as source and development and commercialization of membrane processes. Application of membrane processes for wastewater treatment is increasing worldwide day by day with reduction in cost of process and increased water charges. Membrane processes are used for about 70 % of the total installed capacity of desalination worldwide and percentage is increasing (for drinking water). In Japan, more than 30 MLD wastewater is used as toilet flushing water in building. It has application in many industrial wastewater treatment plants to produce reusable quality water from the effluents.

23.3.4.1 Types of membrane operation

The membrane is defined as the thin film separating two phases and acting as a selective barrier to the transport matter. Chemical potential difference exists between the two phases (Figure 23.3). **Retentate** contains non permeating species (Figure 23.4). **Permeate** forms the produced water from the membrane filtration. Membrane operation is recommended nomenclature than membrane process. The relevant main membrane operations used in water treatment are summarized in Table 23.1.

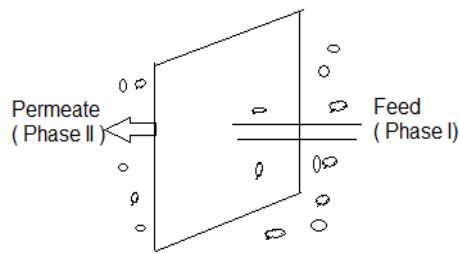


Figure 23.3 Mechanism of membrane operation

Table 23.1 Technically relevant main membrane operations in water treatment

Membrane	Driving force	Mechanism of separation	Membrane structure	Phases in contact
Microfiltration (MF)	pressure	Sieve	Macropores	Liquid-liquid
Ultrafiltration (UF)	pressure	Sieve	Mesopores	Liquid-liquid
Nanofiltration (NF)	pressure	Sieve + solution + diffusion + exclusion	Micropores	Liquid-liquid
Reverse Osmosis	pressure	Solution/diffusion + exclusion	Dense	Liquid-liquid

Advantages of membrane operation:

- Separation takes place at ambient temperature without phase change.
- Separation takes place without accumulation of product inside membrane (unlike ion exchange resins, which needs replacement/regulations).
- No need of chemical additives for separations.

**Figure 23.4** Three end modules

23.3.4 .2 Membrane operations

The transmembrane flux for each element is given by

$$\text{Flux} = \text{Force} * \text{concentration} * \text{mobility}$$

In most cases, concentration will vary with distance from the membrane surface along the boundary layer. Hence above equation is local equation where local forces are used to estimate gradient of chemical potential $d\mu/dx$ of every component that can be transported.

The variation of chemical potential of component 'i' can be expressed as a sum of the terms

$$d\mu_i = RTd \ln a_i + V_i dP + Z_i Fd\Psi$$

where, activity a_i (product of concentration by activity coefficient) is not under the control of operator. The pressure P and electric potential Ψ can be varied in order to improve the separation between the mobile components. The applied pressure of every component is proportional to its molar volume V_i . Electric field acts on every ionic species according to its valency Z_i and does not affect non-ionic species.

23.3.4.3 Reverse Osmosis

Reverse osmosis (RO) is a most commonly used membrane filtration method that removes many types of large molecules and ions from effluents by applying pressure to the effluents when it is on one side of a selective membrane. RO is used to remove specific dissolved organic constituents from wastewater remaining after advanced treatment with depth filtration or MF. RO system can operate at 90 % efficiency or better with respect to TDS. In addition, it also removes residual organic molecules, turbidity, bacteria and viruses.

The solvent of the solution is transferred through a dense membrane tailored to retain salts and low molecules weight solutes. When concentrated saline solution is separated from pure water by such a membrane, difference in chemical potential tends to promote the diffusion of water from the diluted compartment to the concentrated compartment in order to equalize concentration. At equilibrium, the difference in the levels between two compartments corresponds to the osmotic pressure of the saline solution. The demineralization of water can be accomplished using thin, microporous membranes. There are two basic modes of operation in use. One system uses pressure to drive water through the membrane against the force of osmotic pressure and is called RO. The pressure applied is several orders of magnitude in excess of natural osmotic pressure. The membrane commonly used in reverse osmosis is composed of cellulose acetate and is about 100 μm thick. The film contains microscopic openings that allow water molecules to pass through but retain dissolved solids by either molecular sieving (or by some other mechanism which is not yet completely understood). The process results in a concentrated solution of the ions on the pressure side of the membrane and product water relatively free of ions on the other side of the membrane.

For the producing pure water from the saline solution, osmotic pressure of the solution must be exceeded in the brine. For economically viable flows, at least twice the osmotic pressure must be exerted e.g. for seawater pressure of 5 -8 MPa is used in practice.

22.3.4.4 Nanofiltration (NF)

Nanofiltration (NF) is a rapidly advancing membrane separation technique for water and wastewater treatment as well as concentration/separation of antibiotics and pharmaceuticals due to its unique charge-based repulsion property and high rate of permeation. This process is also called as low pressure RO or membrane softening. It lies between RO and ultrafiltration in terms of selectivity of membranes, which is designed for removal of multivalent ions (Ca, Mg, etc.) in softening operation. Monovalent ions are poorly rejected. Hence, osmotic back pressure is much lower than that in RO. The operating pressure used in NF is typically 0.5 to 1.5 MPa.

It is a pressure driven process wherein the pore size of the membrane is in the range of 0.5-1 nm. Due to the lower operating pressure and higher flow rates, nanofiltration is inexpensive when compared to reverse osmosis. NF membranes allow partial permeation of monovalent salts such as sodium chloride while rejecting bivalent salts and hardness to a greater extent from aqueous solutions. NF can lower TDS and hardness, reduce color and odor, and remove heavy metal ions from groundwater. Other possible applications include treatment of effluents from textile dyeing, bulk drug and chemical process industries.

NF process is useful for raw water containing TDS in the range 700-1200 ppm and has exhibited two advantages over RO. NF allows sufficient permeation of essential salts while keeping the total dissolved solids (TDS) in accordance to BIS drinking water standards, whereas RO removes almost all the minerals essential for the human body. NF can be operated at lower pressure while RO requires higher operating pressure and therefore higher running cost.

23.3.4.5 Ultrafiltration (UF)

It is a clarification and disinfection membrane operation. UF membranes are porous and allow only coarser solutes (macromolecules) to be rejected. All types of microorganisms as viruses and

bacteria and all types of particles can be removed by this process. Since, the low molecular solutes are not retained by UF, osmotic back pressure can be neglected and operating pressure is kept low as 50- 500 KPa.

23.3.4.6 Microfiltration (MF)

Microfiltration (MF) membranes are having $0.1 \mu\text{m}$ or more pore size. It is generally used for particulate matter removal. The pressure used in this process is similar to that of UF.

23.3.5 Classification of membranes

23.3.5.1 According to separation mechanism: Three mechanisms exist for separation of ions and other particulate matter from the membranes, and accordingly the membranes are classified as below:

- Sieve effect: In this mechanism, separation is based on difference in pore size e.g. MF, UF.
- Solution-diffusion mechanism: In this mechanism, separation is based on difference in the solubility and diffusivity of materials in the membrane e.g. RO.
- Electrochemical effect: In this mechanism, separation is based on difference in the charges of the species to be separated e.g. ED (electrodialysis).

The classification based on separation mechanism leads to three main classes of membranes.

i) Porous membranes

Fixed pores are present in these membranes. These pores are sub-divided into three types' viz.

- Macropores: Theses are larger than 50 nm
- Mesopores- These are in the range of 20 to 50 nm
- Micropores- These are in the size less than 2 nm.

MF and UF are porous membranes while, NF could be classified in an intermediate class between porous and non porous membranes. Since, solution diffusion and even electrochemical effect have to introduce in equilibrium of mass transfer.

ii) Non Porous membranes

These are dense media membranes. The diffusion of species takes place in the free volume which is present between the macromolecular chains of the membrane material. RO is non porous membrane.

iii) Ion exchange membranes

These are specific types of non porous membranes. They consist of highly swollen gels carrying fixed positive or negative charges. A membrane with fixed positive charges (e.g. $-\text{NR}_3^+$) is called as anion exchange membranes, whereas cation exchange membranes have fixed negative charges (e.g. $-\text{SO}_3^-$).

23.3.5.2 Classification based on morphology

i) Asymmetric membranes

These are anisotropic membranes prepared from the same material (Figure 23.5 a).

ii) Composite membranes

These are anisotropic membranes where top layer and sub-layer originate from different materials. Each layer can be optimized independently. Generally porous layer is asymmetric membranes.

The anisotropic membrane consists of very thin top layer called skin supported by a thicker and more porous supporting sub-layer (Figure 23.5 b). Skin has main function of membrane. Overall flux and selectivity depends upon the structure of skin. Skin has thickness in the range of 0.1 to 0.5 μm , which is about 1% of the thickness of porous sub-layer. Supporting layer offers negligible resistance to mass transfer and imparts mechanical strength to the membrane forming integral part of the membrane.

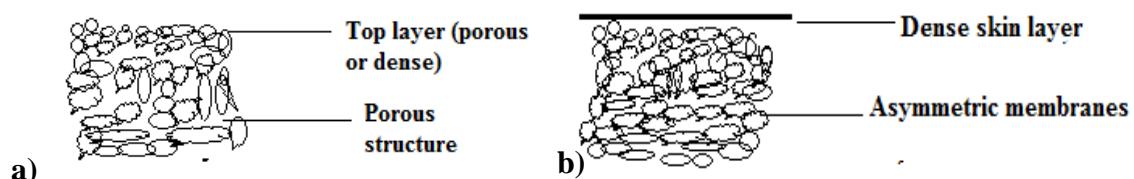


Figure 23.5 a) Asymmetric membrane and **b)** Composite membrane.

23.3.5.3 Classification based on geometry

According to the geometry, the membranes can be classified as flat sheet membrane and cylindrical membrane. The cylindrical membrane can be further classified as (a) Tubular membranes having internal diameter >3 mm, and (b) Hollow fiber membranes having internal diameter <3 mm. They are available in market with outer diameter ranging from 80 to 500 μm . They are used in RO with larger diameter. Also hollow fiber membranes are used in MF and UF in which they are also called as ‘capillary membranes’.

23.3.5.4 Classification based on chemical nature

On the basis of chemical nature of the material used for membrane these are classified as: organic (polymers) membrane and inorganic membranes made from metals, ceramics, glasses, etc.

a) *Polymer (organic) membranes*

Cellulose and its derivatives are more widely used. These hydrophilic polymers are low cost and they are having low tendencies for adsorption. Polyamides, a hydrophilic polymers, are second type of polymer (aromatic polyamides) used for making membrane after cellulose diacetate. It has better thermal, chemical and hydraulic stability than cellulose esters. Amide group (-CO-NH-) cannot tolerate exposure to trace of Cl_2 , hence they are not suitable for chlorinated water. Poly acrylonitrile (PAN) are used in UF but not in RO.

Polysulphone (PSF) and Poly ethersulphone (PES) - These two are not hydrophilic and hence they have high adsorption tendency. They have very good thermal, chemical and mechanical stability. Polytetra fluoro ethylene (PTFE), Polyvinylidene fluoride (PVDF), Polyethylene (PE), Polycarbonate (PC) or isotactic Polypropylene (PP) are hydrophilic polymers that are used for membranes.

b) *Inorganic membranes*

These membranes have superior thermal, chemical and mechanical stability relative to polymer materials. The disadvantage of this membrane is that they are brittle and more expensive. Ceramic membranes are oxides, nitrides or carbides of metals such as Al, Zr, Ti, etc.