EWC 105
Environmental Chemistry

Lecture 10

Instructor
Maj Kazi Shamima Akter, Ph.D, Engrs
Department of EWCE, MIST

Lecture Outlines

Topics	Sub-Topics	References
Organic Pollutants in Water	• Metal - Organic interaction • Pollution by Organometallic complexes • Persistent Organic Pollutants (POPs)	**1.** Environmental Chemistry Author – Stanley E. Manahan 8th ed., CRC Press **2.** Environmental Engineering Authors: Howard S. Peavy, Donald R. Rowe and George Tchobanoglous McGraw Hill International Edition **3.** Water Pollution – Causes, Effects and Control Author: P. K. Goel New Age International publishers

Metal – Organic Interaction

- Two major types of metal-organic interactions to be considered in an aquatic system are –

  ✓ **Metal - organic Complexation** – reversible bonding of metal ion with organic anions/ ligands

  ✓ **Organometallic compounds** – irreversible bonding of metal ion with organic ligands

Metal-organic Complexation

- Metals may exist in water reversibly bound to inorganic anions or to organic compounds as metal complexes.
- Example of metal complexation with inorganic anion, like CN^- is as follows:

$$Fe(H_2O)_6^{2+} + CN^- \Leftrightarrow FeCN(H_2O)_5^{+} + H_2O$$

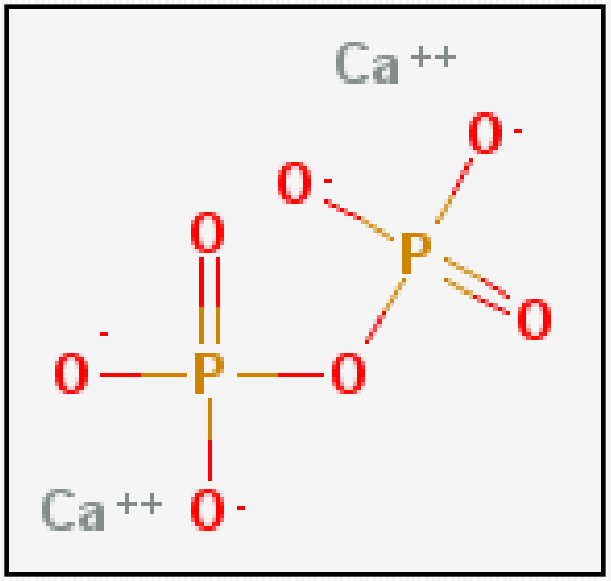
- Here, the species (CN^-) bound with the metal ion is called ***ligand***. CN- is a ***unidentate ligand***, which means it possesses only one site that bonds to a metal ion.
- And the product of ligand and metal ions is called ***complex, complex ion or coordination compound***.

Metal-organic Complexation

- A special case of complexation, in which a ligand bonds in two or more places to a metal ion is called ***chelation***.

- For example pyrophosphate ion, $P_2O_7^{4-}$, bonds to two sites on a Ca^{2+} ion to form a chelate.

- Complexes with chelating agents are of more importance in natural water compared to that with unidentate ligands.



- The importance is due to their more stable nature in water.

Organometallic Compounds

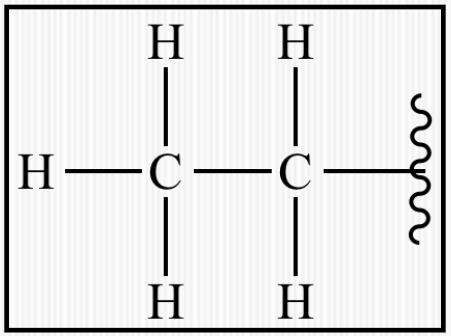
- Organometallic compounds contain metals bound to organic entities by way of a carbon atom and do not dissociate reversibly at lower pH or greater dilution.

- Furthermore, the organic component and sometimes the particular oxidation state of the metal involved, may not be stable apart from the organometallic compound.

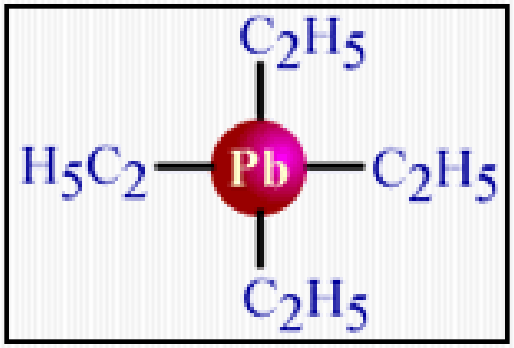
Organometallic Compounds

Examples:

- Compound in which the organic ligand is an alkyl group, such as ethyl in tetraethyllead, $Pb(C_2H_5)_4$.



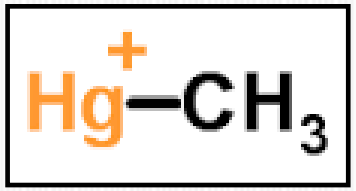
Ethyl Ligand



Organometallic Compounds

- A large number of compound exist that have at least one bond between the metal and a C atom on an organic group, as well as other covalent or ionic bonds between the metal and atoms other than carbon.

- An example is monomethylmercury chloride CH_3HgCl.



Metal – C bond



CH_3Hg^+ is ionically bonded to the chloride ion

Organometallic Compounds

Environmental Significance:

- Metal-organic interactions may involve organic species of both pollutants (such as EDTA: Ethylene Di-amin Tetra Acetic Acid)) and natural (such as fulvic acids) origin.

- These interactions are influenced by and sometime play a role in redox equilibria, formation and dissolution of precipitates, colloid formation and stability, acid-base reactions and microorganism mediated reactions in water.

- The interaction may increase or decrease the toxicity of metals in aquatic ecosystems and they have strong influence in the growth of algae in water.

Persistent Organic Pollutants (POPs)

Characteristics of POPs:

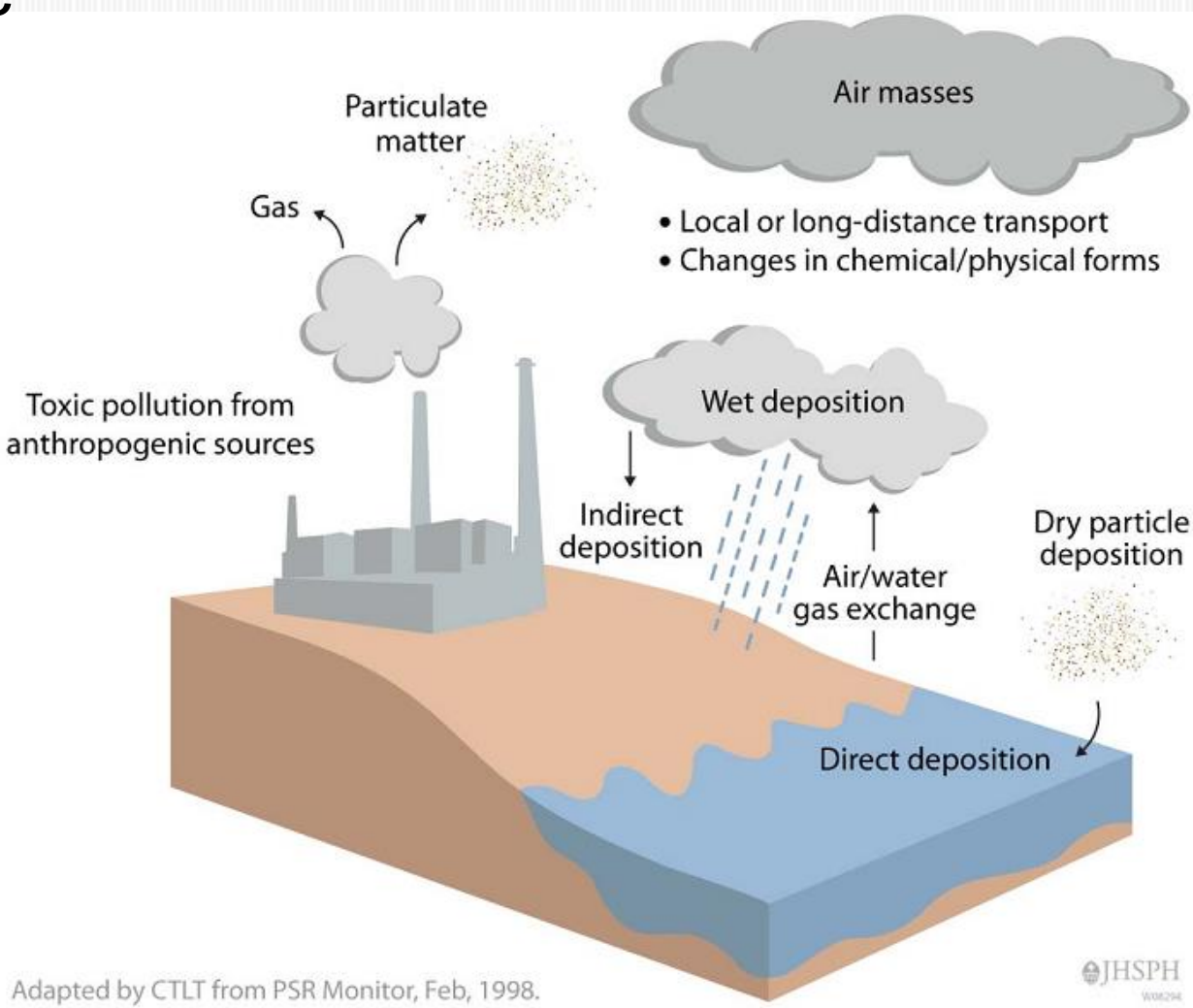
- Remain in the environment for a long time Š
- Resist chemical and biological degradation Š
- Can travel long distances Š
- Bioaccumulate and biomagnify up the food chain Š
- Have found their way into every living organism on earth

Persistent Organic Pollutants (POPs)

- Persistent organic pollutants travel far from their source via –

✓ The hydrologic cycle

✓ The geologic cycle



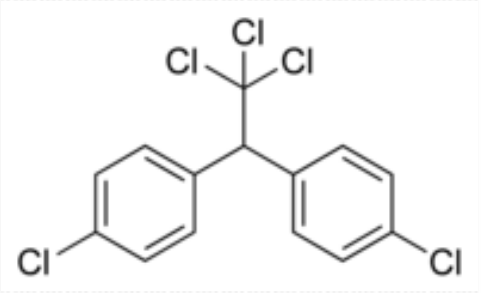
Persistent Organic Pollutants (POPs)

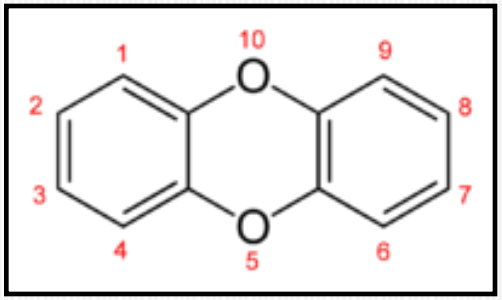
- The "**dirty dozen**" of POPs includes: PCBs, aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, hexachlorbenzene, mirex, polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans, and toxaphene.
- All of the Dirty Dozen are polychlorinated hydrocarbons
- They are stable and do not readily degrade to less toxic forms
- Persist in the environment for a long time and can bioaccumulate through the food chains
- Insoluble in water, soluble in fats

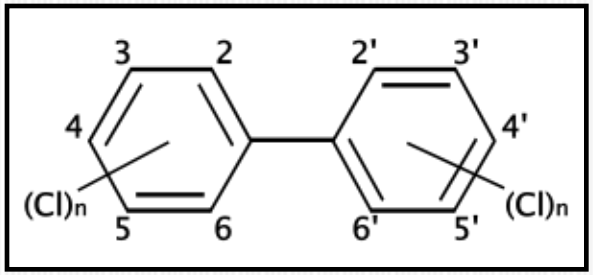
Persistent Organic Pollutants (POPs)

Polychlorinated hydrocarbons of particular concern are:

DDT ***dioxins*** ***PCBs***



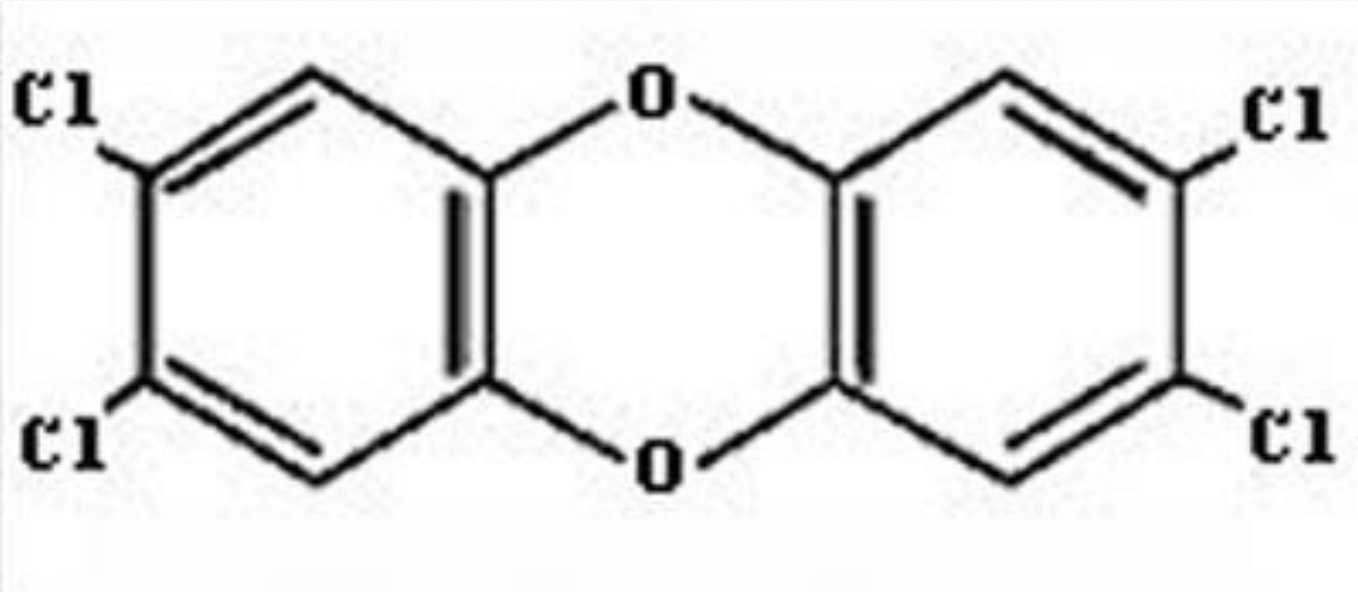




Persistent Organic Pollutants (POPs)

Examples = Dioxin, PCB, DDT (Chlorinated)

Dioxin: stable; slow to degrade



POPs - Dioxin

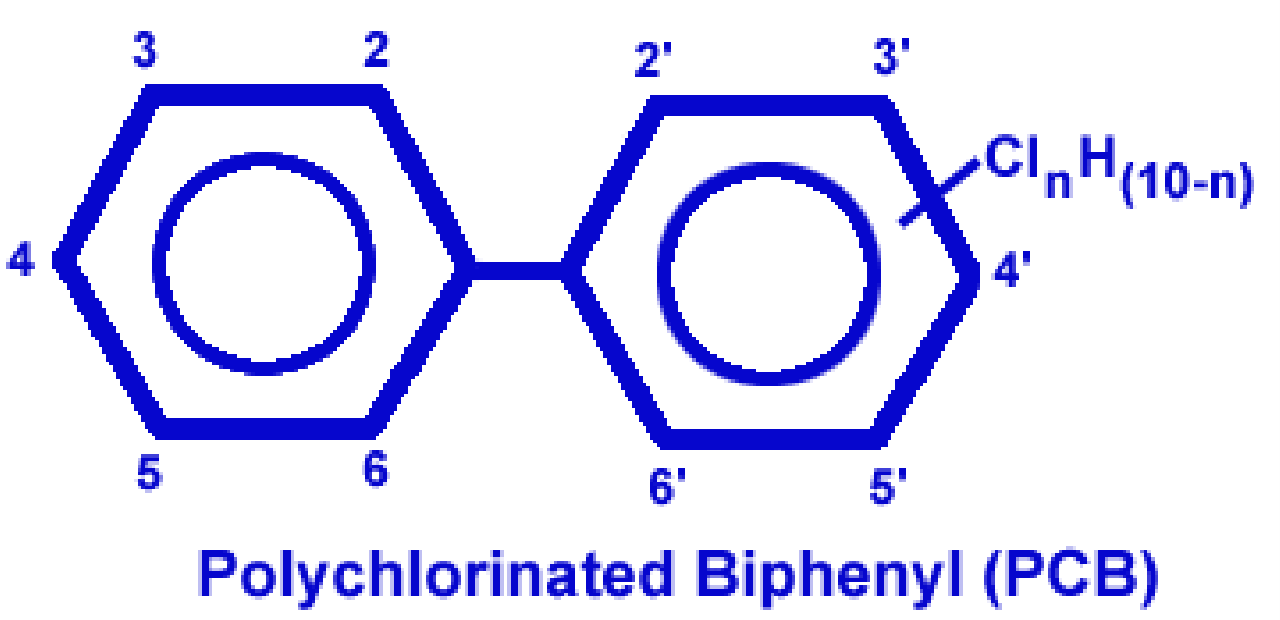
Generated from: Burning wood, coal, oil, household trash, and chlorine bleaching of pulp and paper

Accumulates in fat of animals → biomagnification

Causes: **cancer**
weakened immune response

POPs - PCBs

- non-flammable;
- not dissolved in water;
- high boiling points;
- does not conduct electricity well. Therefore, used for **transformers and capacitors**.



Polychlorinated Biphenyl (PCB)

POPs - PCBs

More than one **billion pounds** of PCBs have been made.

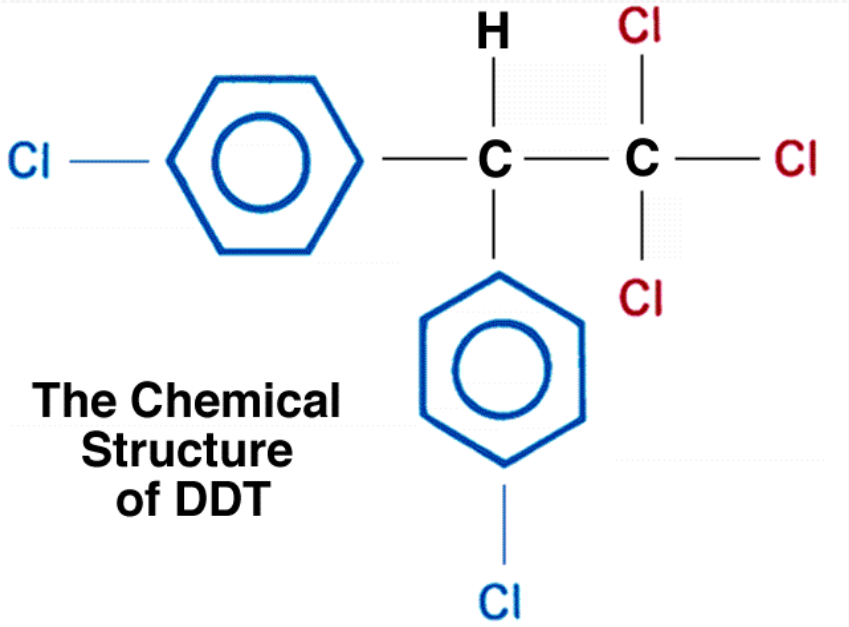
Accumulates in fat of animals → biomagnification

Causes: **cancer**
hormonal and reproductive disruptions
decrease cognitive abilities (dopamine)

POPs - DDT

- DDT is an insecticide;
- stable and slow to degrade.

Benefits = Controlled spread of malaria; Provided crop protection

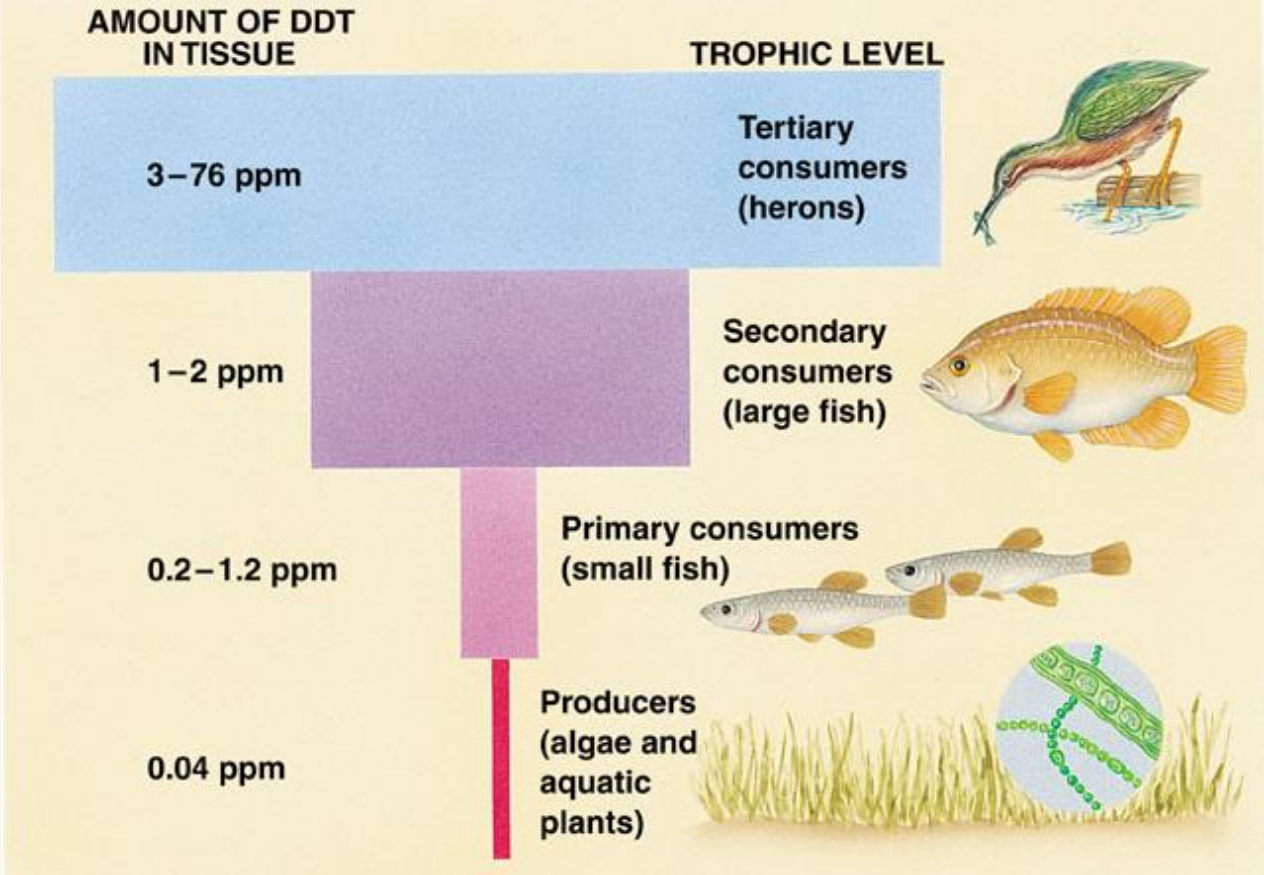


The Chemical Structure of DDT

POPs - DDT

Problems with DDT:

- DDT is not metabolized very rapidly by animals;
- instead, it is deposited and stored in the fatty tissues → biomagnification



POPs - DDT

Problems with DDT:

- Toxic to fish

- Increased mortality in birds: calcium decreased in egg shells

POPs - DDT

Unintentional Pathways:

