

# Environmental Toxicology (ET)

Course: ES 535

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# Stockholm Convention on POPs

- ❖ **The objective of the Stockholm Convention is to protect human health and the environment** from Persistent Organic Pollutants (POPs).
- ❖ The Stockholm Convention on Persistent Organic Pollutants (POPs) was adopted by the Conference of the Plenipotentiaries (Stockholm, 22 May 2001) and **entered into force on 17 May 2004 initially covering 12 chemicals**. These chemicals are three type by their use i) Pesticides, ii) Industrial chemicals and iii) By-products.
  - Pesticides:** Aldrin, Chlordane, DDT, Dieldrin, Endrin, Heptachlor, Hexachloro-benzene, Mirex, and Toxaphene;
  - Industrial chemicals:** Hexachloro-benzene, and Polychlorinated Biphenyls (PCBs); and
  - By-products:** Hexachloro-benzene, Polychlorinated Dibenzo-*p*-Dioxins (PCDD), Polychlorinated Dibenzo-furans (PCDF), and PCBs.
- ❖ Currently, 16 additional POPs have been added by Parties to the Stockholm Convention. Bangladesh did not ratify these additional 16.

# Pesticides

- Pest : A pest, broadly defined, is any organism - plant, animal or micro-organism that is distractive or living where it is unwanted.
- Pesticides: A pesticide is any substance or mixture of substances intended for preventing, destroying, repelling, or mitigating any pest (insects, mites, nematodes, weeds, rats, etc.), including insecticide, herbicide, fungicide, and various other substances used to control pests (EPA, 2009). At present there are more than 10,000 different pesticides.

# History of pesticide

The history of pesticides can be divided into three phases:

- (1) in the first phase (the period before 1870s) natural pesticides, for instance sulfur in ancient Greece, were used to control pests;
- (2) The second phase was the era of inorganic synthetic pesticides (the period 1870s-1945). Natural materials and inorganic compounds were mainly used during this period;
- (3) the third phase (since 1945) is the era of organic synthetic pesticides.
- (4) Sulfur has been known and used as a pesticide since very early times and has been registered for pesticidal use in the United States since the 1920s (US EPA).

# History of pesticide

- Since 1945, the man-made organic pesticides, e.g., DDT, 2,4-D, and later HCH, dieldrin, have terminated the era of inorganic and natural pesticides.
- Since then most pesticides have been synthesized by humans, and they were named chemical pesticides.
- The application of chemical pesticides, in particular the organic synthesized pesticides has been a significant mark of human civilization, which greatly protects and facilitates agricultural productivity.

# Classification of pesticides

**By target:** Insecticides, Herbicides, fungicides, rodenticides, algaecides, and nematocides.

**By chemical nature:** (a) Inorganic (b) Organic

(b) Organic:

(1) Natural organic Insecticides are two types:-

(i) Mineral: - e.g – Kerosine oil

(ii) Biopesticide:- Neembisidin

(2) Synthetic organic insecticides:-

(a) Organo chlorine ( DDT, Aldrin)

# Classification of pesticides

(b) Organo phosphorus ( Malthion, Sumithion, Nogos, Metasystox, Dimecron)

(c) Organo carbamate ( furadan, Sevin)

(d) Synthetic pyrethroid (Ripcord, Seembush)

**3. By physical state**:- Dusts, dissolved solution, suspended solution, volatile solids .

**4. By mode of action**:- contact poisons, fumigants, stomach poisons, systemic poisons.

# Classification of pesticides

- **Insecticides** - act pesticidally against the growth or survival of insects. Also includes specific types such as miticides, mosquito larvicides or adulticides;
- **Herbicides** - act pesticidally against plants, weeds, or grasses;
- **Rodenticides** - act pesticidally against rats or other rodents;
- **Avicides** - act pesticidally against damaging bird populations;
- **Fungicides** - act pesticidally against fungi on food or grain crops;
- **Nematicides** - act pesticidally against nematodes;
- **Fumigants** - gaseous pesticides used for invertebrate and fungal control





# Classification of pesticides

- **Antimicrobials** - act pesticidally against microscopic organisms on a variety of sites;
- **Plant Growth Regulators** - accelerate or retard plant growth rates;
- **Insect Growth Regulators** - retard insect growth;
- **Biopesticides** - naturally occurring substances with pesticidal properties, including microbial pesticides, biochemical pesticides and plant incorporated protectants;
- **Piscicides** - act pesticidally against unwanted or invasive fish populations; and
- **Molluscides** - act pesticidally against slugs, snails, or bivalves.



# Insecticides

- Insecticides are those compounds that are effective against insects. Many insecticides have been developed and used to control various species of insects. While most insecticides are applied as sprays, other are dusts, aerosols, fumigants and baits.
- The majority of insecticides used today are synthetic organic chemicals and most of them are nerve poisons. They act by inhibiting the organism's enzymes or interacting with other target sites vital to the proper functioning of the insect's nervous system.
- Although there are many synthetic organic insecticides, three main groups are: **(1)** chlorinated hydrocarbons **(2)** organophosphorus compounds or organophosphates and **(3)** Carbamates.

**(1) Chlorinated hydrocarbons:** chlorinated hydrocarbons also called organochlorines, were the first commercial organic insecticides to be developed. DDT, Aldrin, chlordane, dieldrin, endrin, lindane and heptachlor are some examples.

**DDT:** - DDT (Dichloro diphenyl trichloroethane), discovered as a pesticide in 1939, is probably the most widely known pesticide of the 20th century. The discoverer of DDT, **Dr. Paul Mullar**, received the Nobel prize in medicine in 1948.

# Where use DDT ?

- It was first used for controlling disease carrying insects, such as mosquitoes that spread malaria. As the range of DDT's effectiveness against insects became known, it was used by soldiers during world war II to control the body lice that spread typhus.
- After world war II , DDT was used in the home and applied to an agricultural crops, providing enormous success in pest control. DDT proved effective in the control of a large number of pests, including Gyps moth, potato pests, corn earth worm, etc.

# Effects of DDT

- Some 20 years later, when DDT's Environmental impacts became evident, its use was either limited or totally banned in industrialized countries, although it is still used in a number of less developed countries.
- Their residues persist in the environment for long periods, ranging from a few months to years. DDT can be readily absorbed through the skin into the fatty tissues of living organisms and it can pass through the food chain.

# Effects of DDT

- Many studies have provided evidence suggesting that chlorinated hydrocarbon residues found in the Environment may be responsible for interference with the functioning of the endocrine system and disruption of reproduction.
- Some scientists suggest that exposure to these chemicals could be related to the surge of disorders in human reproductive organs from falling sperm counts, to increasing rates of breast and prostate cancers.
- The adverse effects of organochlorine compounds on birds have been widely known since the publication of Rachel Carson's book *Silent Spring*.

# Solutions

- Delegates from 110 countries met in Geneva in September 1999 to work on a treaty to control 12 persistent organic pollutants (POPs).
- They decided to severely restrict the use of four others chlordane, dieldrin, heptachlor and mirex. They agreed to the international phase-out of the pesticides aldrin, endrin and toxaphene.

# Solutions

- These chemicals also are suspected of causing diseases of the immune system, reproductive disorders and abnormal child development in humans, even at low doses
- However, the countries were unable to make decisions on DDT and others. The WHO public health specialists some developing countries wanted DDT kept available for malaria control until equally inexpressive alternatives are developed.



# Organophosphorus Compounds

- Organophosphorus insecticides are the most toxic among the insecticides; they are dangerous not only to insects but also to mammals.
- Many of these compounds, such as parathion, Paraoxon, timet and tetram are in the super toxic category of human poisons. As little as 2mg of parathion has been known to kill children.
- Symptoms of poisoning in humans include vomiting, diarrhea, cramp's sweating, salivation, blurred vision and muscular tremors. Severe cases may be fatal due to respiratory failure.

# Carbamates

- In the same way that organophosphate insecticides such as parathion and malathion are derivatives of phosphoric acid, the carbamates are derivatives of carbamic acid ( $\text{HO-CO-NH}_2$ ).
- Carbamates are widely used for worm control on vegetables. Examples of carbamates include aldicarb and carbofuran.

# Herbicides ( Weedicides)

- During the Vietnam War, the U.S Air Force's defoliation program applied a huge quantity of undiluted 2,4-D( 2,4-Dichlorophenoxy acetic acid) and 2,4,5-T (2,4,5 Trichlorophenoxy acetic acid) on Vietnam's agricultural and forest land between 1965 and 1970.
- In addition to military use in Vietnams, Phenoxyherbicides (PHs) were widely used in the U.S for controlling weeds in agriculture, lakes, ponds and in forests.

- The biochemical actions of **Phenoxyherbicides** (PHs) in plants are complex. After application, the chemicals are absorbed primarily through stomata and secondarily through root hairs with water, in sensitive plants, the chemicals disrupt growth and various metabolic processes as they are translocated through vascular tissue.
- Clinical symptoms of severely poisoned farmers include pain and weakness in the lower extremities, slowed nerve conduction velocity and muscle spasms.

# World Production of Pesticides

- **Annual world production:** The annual world production of pesticides grew from 6000 million pounds (1954) to over 24000 million pounds (1973). Of these, about 600 million pounds were Organochlorine insecticides which persist in the environment.

**Table 1** Changes of pesticide consumption worldwide

Category	1960		1970		1980		1990		2000		2005	
	Sale	%	Sale	%	Sale	%	Sale	%	Sale	%	Sale	%
Insecticides	310	36.5	1002	37.1	4025	34.7	7655	29	7559	27.9	7798	25.0
Herbicides	170	20.0	939	34.8	4756	14.0	11625	44	12885	47.5	14971	48.0
Fungicides & Bactericides	340	40.0	599	22.2	2181	18.8	5545	21	5306	19.6	7486	24.0
Others	30	3.5	159	5.9	638	5.5	1575	6	1354	5.0	936	3.0
Total	850	100	2700	100	11600	100	26400	100	27104	100	31191	100

Sale: million US dollars (Xu, 1997; <http://www.docin.com/p-55305172.html>)

# Bad effect of pesticides

- When we apply a pesticide to crops, plants and animals absorb most of it. But a portion of the pesticide is vaporized in atmosphere and deposited in rainwater.
- Another portion of it remains in the soil. It also gets mixed up with the surface water that runs off to rivers and lakes. Still some of it reaches groundwater via leaching by rain.

# Bad effect of pesticides

- Rain can carry pesticides far away. Once the water of a lake in Japan was found to be contaminated by a pesticide. Japan at the time did not use any pesticide. It was then found that the pesticide used in China and Korea about 1500 km away from the lake caused the contamination by rainfall.
- Fog is thicker than rain, so fog can contain more pesticide than rain. In cold countries, therefore pesticide contamination by fog is a serious environmental problem.

# Benefits and risks of pesticide application

- Worldwide approximately 9,000 species of insects and mites, 50,000 species of plant pathogens, and 8,000 species of weeds damage crops.
- Insect pests cause an estimated 14% of loss, plant pathogens cause a 13% loss, and weeds a 13% loss.
- About one-third of the agricultural products are produced by using pesticides.
- Without pesticide application the loss of fruits, vegetables and cereals from pest injury would reach 78%, 54% and 32% respectively.
- Crop loss from pests declines to 35% to 42% when pesticides are used.



# Benefits and risks of pesticide application

- In view of the world's limited croplands and growing population, it is necessary to take all measures to increase crop production in order to ensure food safety.
- Most pesticides are not spontaneously generated. Most of them are high toxic to humans and the environment.
- Pesticides and their degraded products would flow into the atmosphere, soils and rivers, resulting in the accumulation of toxic substances and thus threatening human health and the environment.
- The environmental pollution caused by pesticides in Asia, Africa, Latin America, the Middle East and Eastern Europe are now serious.

# Benefits and risks of pesticide application

- There were four aspects of issues in pesticide production and application worldwide:
- (1) some countries still produced or used highly toxic pesticides;
- (2) pesticides were overused to a variety of crops like cotton, vegetables and rice;
- (3) the quality of pesticides was poor, for instance, some countries were not able to effectively regulate pesticides and thus result in the production and consumption of counterfeit and unqualified pesticides, and
- (4) pesticide residue standards were not implemented effectively.

# Worldwide Situation of Pesticide Pollution

- Globally 4.6 million tons of chemical pesticides are annually sprayed into the environment.
- There are currently about 500 pesticides with mass applications, of which organochlorinated pesticides, some herbicides and the pesticides containing mercury, arsenic and lead are highly poisonous to the environment.
- Only 1% of the sprayed pesticides are effective. 99% of pesticides applied are released to non-target soils, water bodies and atmosphere, and finally absorbed by almost every organism.

# Worldwide Situation of Pesticide Pollution

- According to a report from the EPA of the United States, many of rural wells in the nation contain at least one of 127 pesticides.
- A research panel of Indiana University analyzed barks from 90 sites from the equator to high latitude cold regions, and detected DDT, aldrin and lindane residuals.
- High-residual pesticides like DDT have been detected in the Greenland ice sheet and the bodies of Antarctic penguins which were resulted from atmospheric circulation, ocean currents and biological enrichment of pesticides.
- According to a report of WHO and UNEP, worldwide there are more than 26 million human pesticide poisonings with about 220,000 deaths per year.

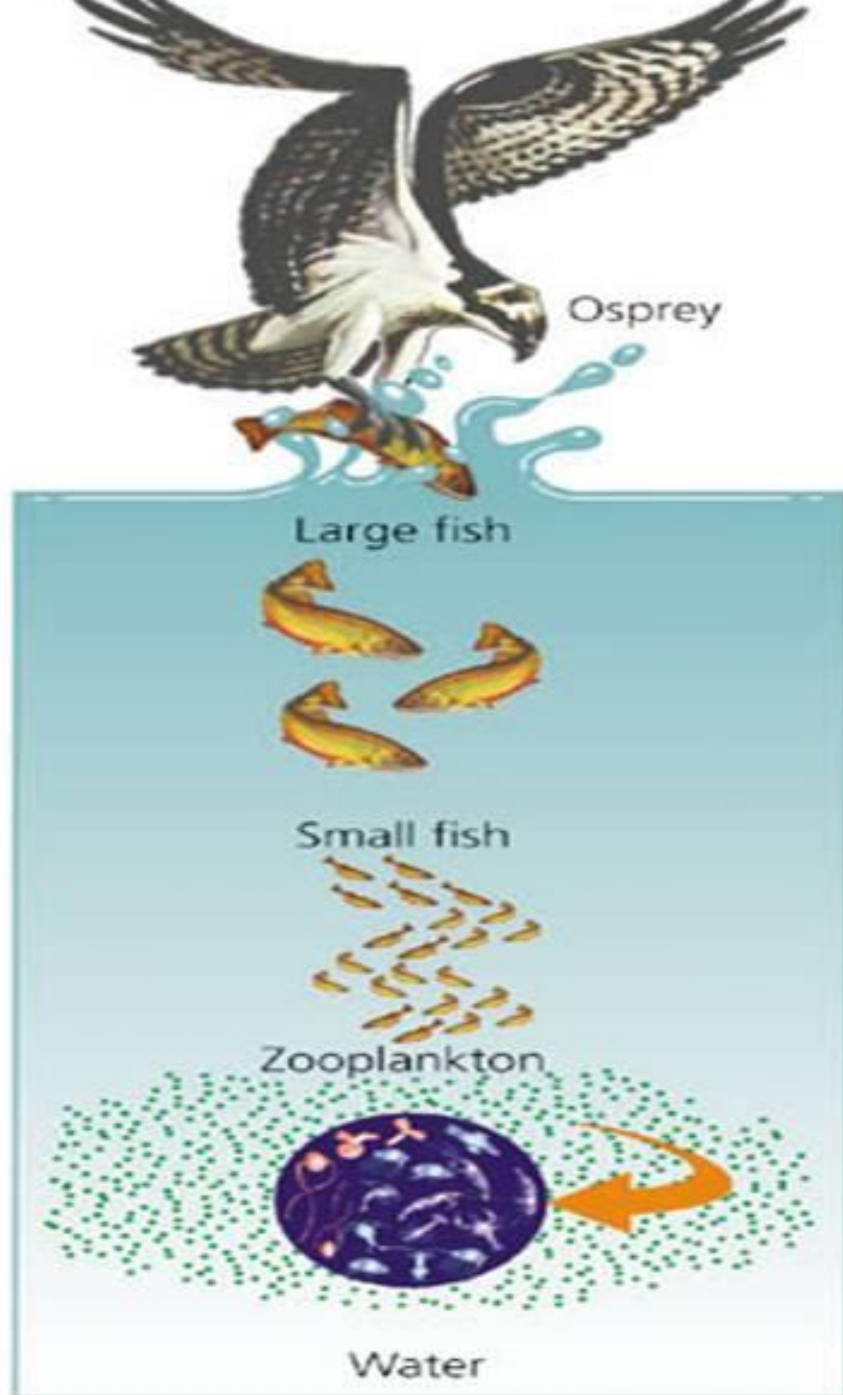


# Nontoxic Chemical Spills



- Sept. 10, 2013
- 233,000 gallons molasses spilled (1400 tons)
- Matson Pier on the Sand Island side of Honolulu Harbor westward into Ke'ehi Lagoon
- 30,000 fish dead

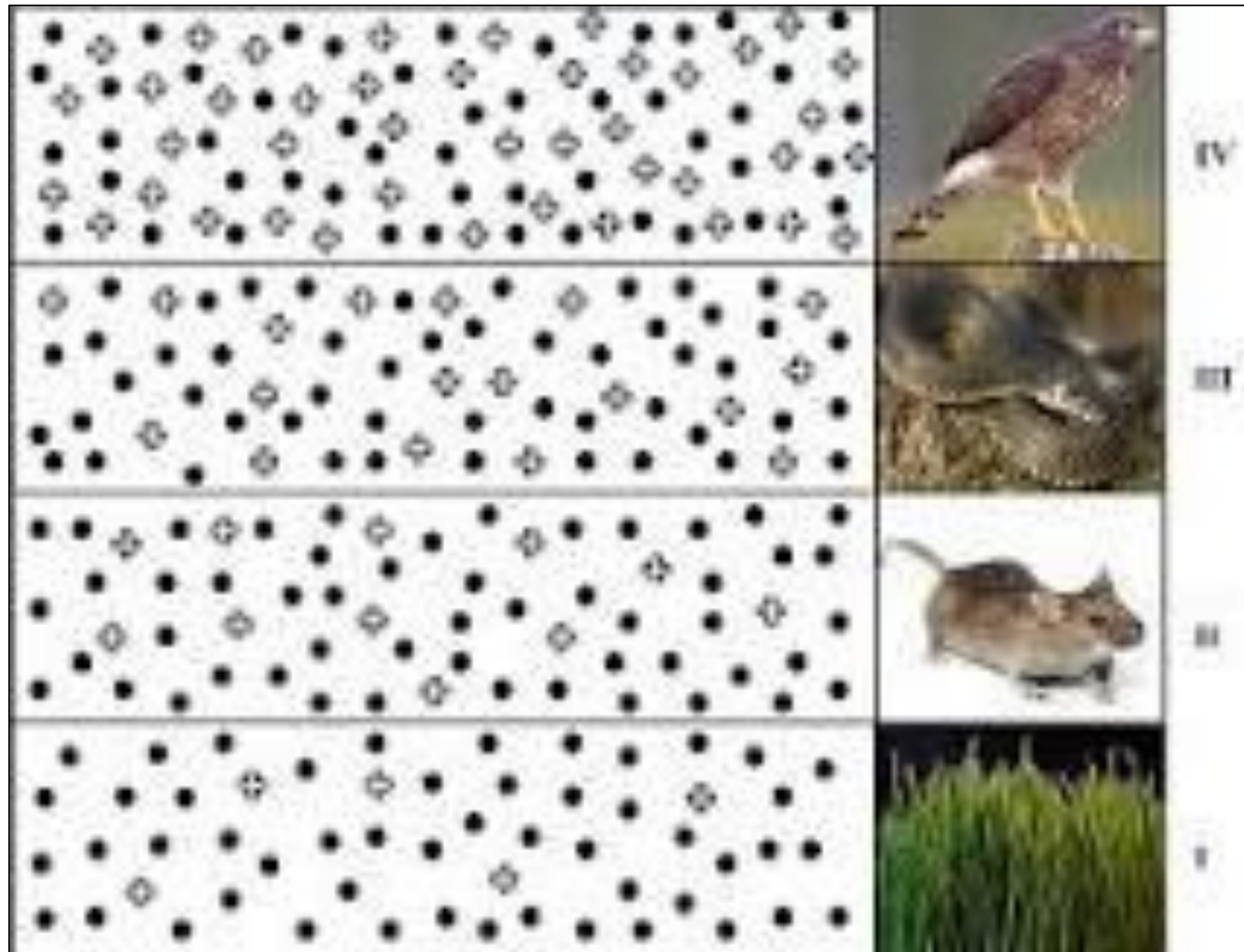
# Biomagnification



Biomagnification, or biological magnification, is the increasing buildup of toxic substances within organisms that happens at each stage of the food chain.

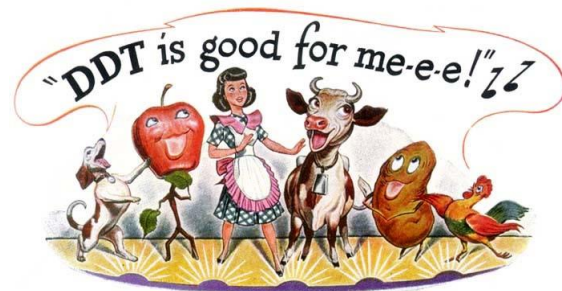


# Biomagnification



# Pesticides, Herbicides & other organochlorines

- PCBs
- DDT



**Bioaccumulation → biomagnification**



# Toxic Metals

Heavy metals resist biodegradation

**Natural occurrence-** volcanoes

- **Mercury** (Hg)
- **Copper** (Cu)
- **Lead** (Pb)
- **Cadmium** (Cd)



Heavy metal

# Mercury

## Minamata Disease (1953-1960)– Japan

