PESTICIDES TOXICOLOGY

Toxicology : Is one of the oldest branches of ***Pharmacology***. Traditionally, it is the science of poisons affecting human lives and a branch of medical science that deals with the nature, propriety, effects and the detection of poisons.

This definition are included studies on the metabolism and excretion of poisons, on the action of poisons, on the treatment of poisoning.

Toxicology : The harmful effect of a poison to living system.

Classification of Insecticides Based on Mode of Action

1- Physical poisons : Heavy mineral oils, silica gel.

2- Protoplasmic poisons: Heavy metal (Hg), it prevent synthesis of RNA and DNA.

3- Respiratory poisons: HcN, H_2S, rotenone.

4- Stomach poisons: *Bacillus thuringiensis* in the digestive system.

5- Neuroactive agents:-

A- Effect on ion permeability to the nerve cell: DDT, pyrethroids.

B- Anticholinesterases : Organophosphorus, carbamate insecticides.

6- Insect hormones : Juvenile hormone, ecdysis.

NOEL (No Observed Effect Level): The greatest concentration of pesticide that cause **no** detectable change in functional capacity, morphology, biochemical changes on the animal under study. It is expressed in terms of weight of substance given daily per unit weight of test animal (mg / kg).

ADI (Acceptable Daily Intake) **=** $\dfrac{\textbf{NOEL}}{\textbf{Safety Factor(}10,\ 100,\ 1000 \text{ depend on compound).}}$

ADI : The daily intake during an entire lifetime (mg of substance per kg of animal body weight.

$$\text{Guide Line Value} = \frac{\text{ADI} \times (70)}{100 \times (0.2)}$$

70 – Mean weight of man.

0.2 Kg – consumption of cucumber per day.

100 – Safety factor.

MRL : **Maximum Residue Level**.

MRL should be less than ADI.

Routes of Insecticides Entry into the Insects

* **cuticle (insect skin) is the major route.**

* Respiratory system, mouth, antennae. eyes and tarsi.

* **Most modern insecticides are not water soluble (dissolve in oil) and therefore easily penetrate the insect cuticle.**

Factors Affecting Storage and Release of Pesticides

* storage is naturally high with stable (persistence) and oil soluble pesticides as chlorinated hydrocarbons.

Penetration and Distribution into Vital Organs and Tissues

* The most common site of insecticide attack is the nervous system.
* Highly oil soluble pesticides are expected to penetrate into the brain very rapidly.

Transfer to Fetus and Reproductive Organs

* The placental barrier is less selective and efficient thus even water soluble pesticides can harm the fetus.
* Oil soluble pesticides generally have no problem in reaching the fetus.

Elimination of Pesticides (Excretion and Secretion)

* It is necessary that the pesticide compound enter the blood stream.

- The renal (from Kidney to be eliminated in the urine)
- The liver (from intestine to be eliminated in the feces).

Secretion in Milk

* It has been found that the residue in milk were in the whole about 1:10 those in the fat of the cows. (10 ppm in fat ⟶ 1ppm in milk).

Movement of Insecticides in the Environment

* In general plants do not store oil soluble pesticides, such as chlorinated hydrocarbon more over the level found in the soil.

* For systemic pesticides to cause problem, it should be:
  - Persistence.
  - Translocated to edible part of the plant.
  - Able to be stored in tissues.

* Most of the systemic pesticides marked today are degradable (easily break down), and do not accumulate in other ecosystem.

* Oil soluble pesticides penetrate plant cuticle .

* Water soluble pesticides translocate inside.

Soils

Once pesticides droplets reach the soil, it could be:

1- Absorbed by soil particles as well as by the organic matter in the soil.

2- leached and washed off by water.

3- Evaporated into the air.

4- break down by the soil microorganisms.

5- break down by the soil PH.
6- break down by the light.
7- Translocated through plant and animals.

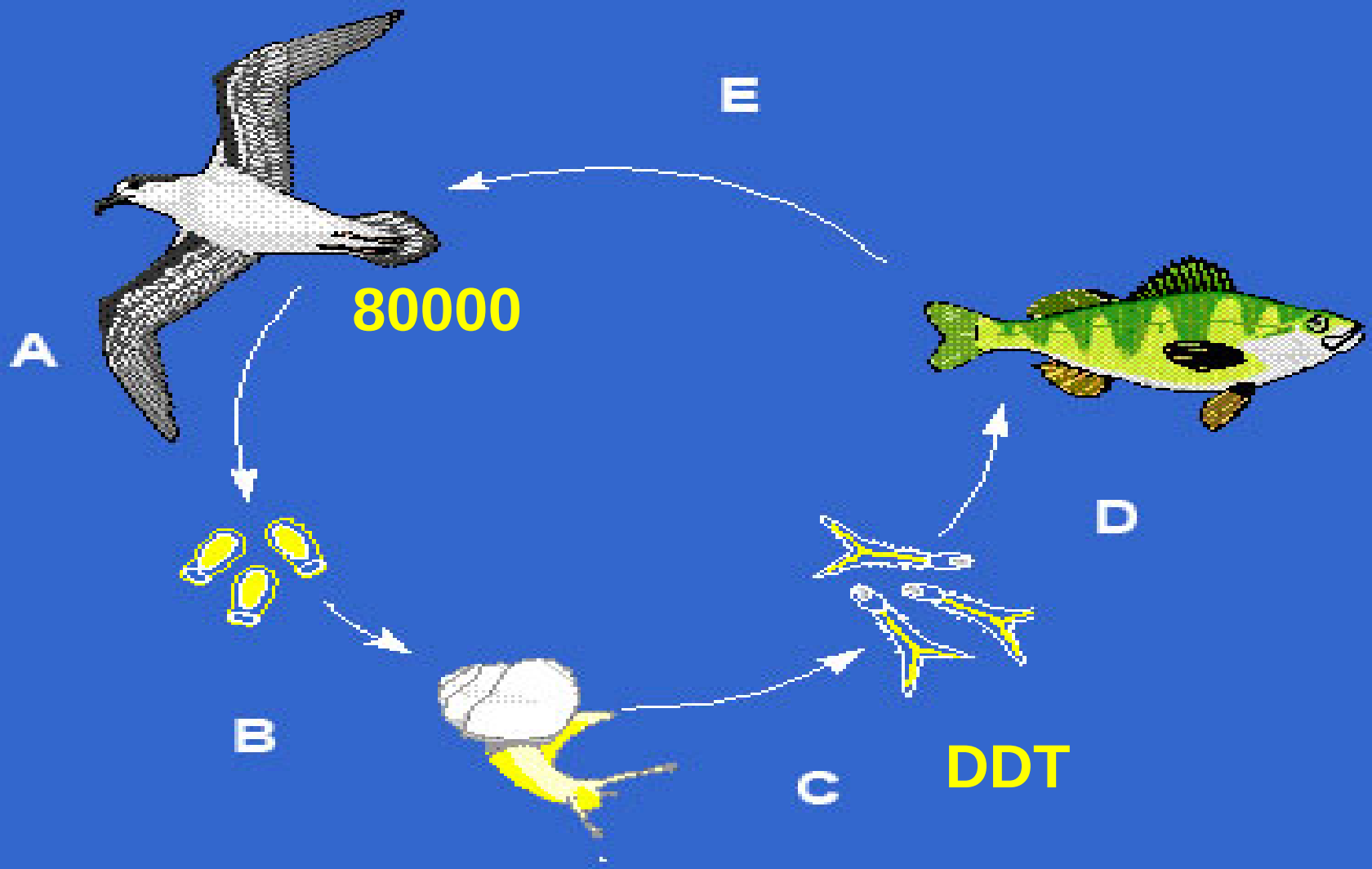
Among all these processes, only those belonging to 4,5,6 and to some extent 7 can actually reduce the total amount of pesticides in the environment.

Movement of Residue in the Environment

* Water transport pesticides.
* Some pesticides can stay in water as a suspension, although the presence of soil particles in water accelerate the process of precipitation.
* Air (water particles, dust, evaporation).

* Evaporation from soils containing high concentrations of organic matter was less than from soils with low concentrations. Organic matter adsorb (stick) more pesticides.

Pesticides Bioaccumulation

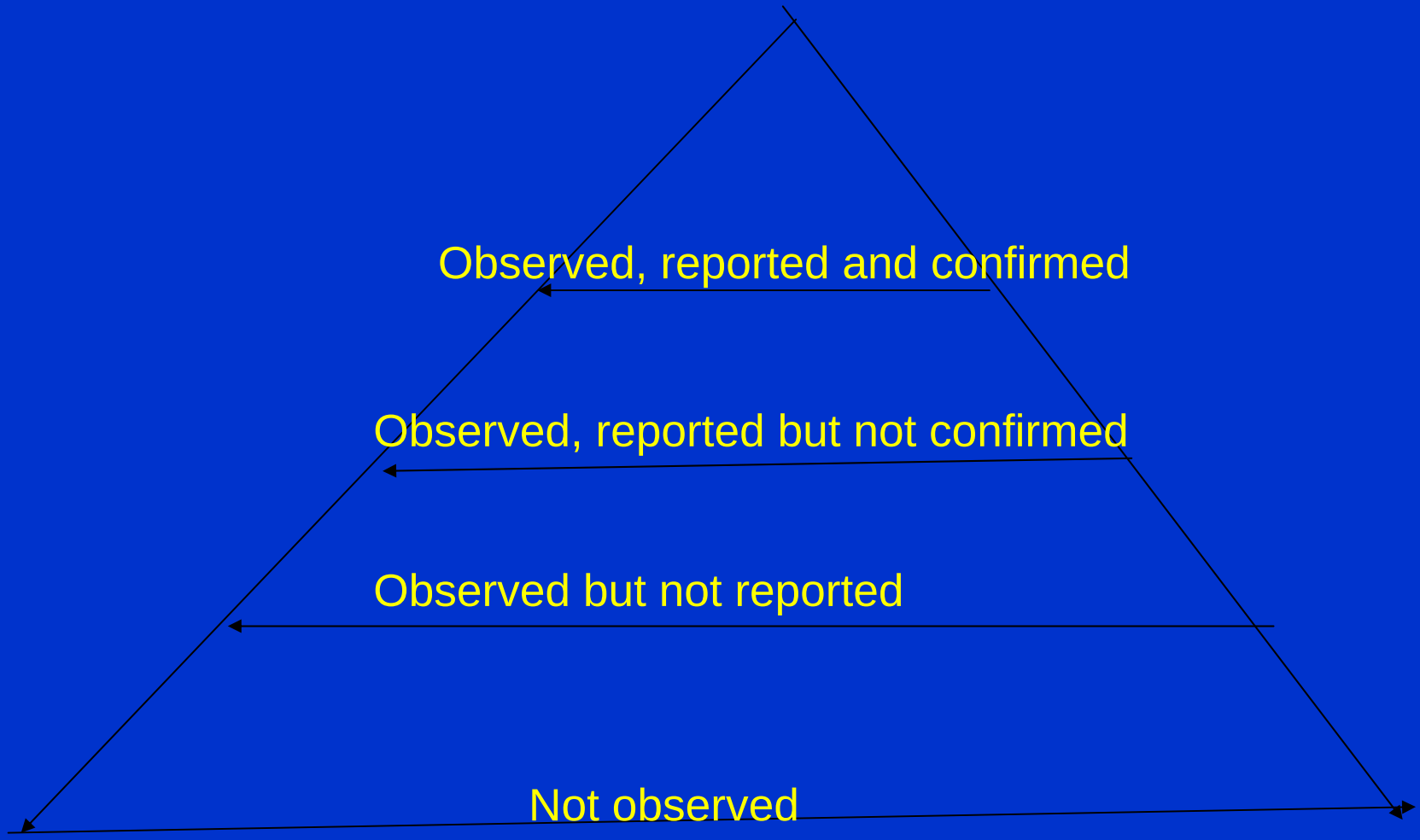


Effect of Pesticides on Birds

Egg shell thickness. They observe that the egg shell of wild birds generally decrease as the level of environmental contamination increased.

Thinner egg shell cause declining reproduction rate in several species of birds (**Imidacloprid**).

Birds die from CB insecticides within a few hours of exposure but mortality from OP insecticides exposure may extend over 5 days.



Our current knowledge of pesticide effects on wildlife. (Wildlife mortality).

Toxicology of Common Pesticides

Imidacloprid Toxicology

Effects on Reproduction:

In rats, gave birth to smaller offspring.

Effects on Birds:

The LD_{50} is 152 mg/kg for bobwhite quail.

Breakdown in Vegetation:

Imidacloprid penetrates the plant, and moves from the stem to the tips of the plant. The most important steps in break down were loss of the nitro group.

(LD50) is 450 mg/kg body weight in rats.

NOEL: 5.7 mg/kg/day.

Abamectin Toxicology

Reproductive effects:
Increased stillbirths, decreased pup viability, decreased lactation, and decreased pup weights.

Effects on birds:
Nontoxic to birds. The LD_{50} in bobwhite quail is >2000 mg/kg.

Breakdown in soil and groundwater:

Abamectin is rapidly degraded in soil. At the soil surface, it is subject to rapid break down by sunlight, with half-lives of 8 hours to 1 day.

Breakdown in Vegetation:

Plants do not absorb abamectin from the soil. Abamectin is subject to rapid break down by sunlight when present as a thin film on treated leaf surfaces.

The oral LD_{50} in rats is 650 mg/kg .

ADI: 0.0001 mg/kg/day.

Methomyl Toxicology

Reproductive effects:

No adverse effect on reproduction.

Effects on birds: Highly toxic to birds. The acute oral LD_{50} in bobwhite quail is 24 mg/kg.

Breakdown in soil and groundwater:

* Methomyl has low persistence in the soil with a half-life of approximately 14 days .

* Because of its high solubility in water, and low soil binding, methomyl may contaminate groundwater.

* only slight leaching was observed in a silt loam and in a sandy soil.

Breakdown in vegetation :

Following soil treatment, plants take up methomyl through their roots and move it throughout the plant .

When methomyl is applied to plants, its residues are short-lived (3 to 5 day half-life).

ADI: 0.03 mg/kg/day.

Chlorpyrifos Toxicology

Reproductive Effects:

No adverse affect reproduction .

Effects on Birds:

It is moderately to very highly toxic to birds. The oral LD_{50} is112 mg/kg in mallard ducks,

and 32 mg/kg in chickens.

Breakdown of Chemical in Soil and Groundwater:

It adsorbs strongly to soil particles and it is not readily soluble in water.

Breakdown in Vegetation:

Residues remain on plant surfaces for approximately 10-14 days.

NOEL: 0.03 mg/kg/day for dogs.

ADI: 0.003mg/kg/day

Deltamethrin Toxicology

Reproductive Effects :

No adverse effect

Effects on Birds : Slightly toxic.

LC_{50} for ducks was greater than 4,640 mg/kg.

Breakdown of Chemical in Soil and water :

In soil, break down occurs within 1-2 weeks.

In water it was rapidly adsorbed, mostly by sediment.

Breakdown in Vegetation:

There were no residues on plants 10 days after use,

ADI: 0.01 mg/kg/day.

Benomyl Toxicology

Reproductive Effect:

No adverse effect.

Effects on Birds: moderately toxic

Breakdown in Soil and Groundwater:

Benomyl is strongly bound to soil and does not dissolve in water.

Residues did not accumulate from one year to the next.

Breakdown in Vegetation:

Since benomyl is a systemic fungicide, it is absorbed by plants through the roots or the above-ground tissues.

It accumulates in veins and at the leaf margins.

The residues are easily extracted from the plant in hot water.

ADI: 0.02 mg/kg/day

Mancozeb Toxicology

Reproductive Effects:

Toxic effects on animals were observed only at high doses.

Effects on Birds: Slightly toxic

LC_{50} for bobwhite quail is greater than 10,000 ppm.

Breakdown in Soil and Groundwater:

Insoluble in water, do not reach groundwater.

Breakdown in Vegetation: A 24-hour reentry interval is required in mancozeb-treated crops because: break down product has been shown to produce tumors, birth defects, cell mutations and thyroid effects.

NOEL : 0.25 mg/kg/day.

Paraquat Toxicology

Reproductive effects:

No effects in humans at expected exposure.

Effects on birds: Moderately toxic

LD_{50}, 981 mg/kg in bobwhite quail.

Breakdown in soil and groundwater:

Highly persistent in the soil, field half-lives greater than 1000 days. It is strongly adsorbed by soil particles and organic matter , do not accumulate in plants, earthworms, and microorganisms.

Thus, it does not present a high risk of groundwater contamination.

Breakdown in vegetation: Paraquat droplets break down when exposed to light.

ADI: 0.004 mg/kg/day.

Glyphosate Toxicology

Reproductive effects :

Produce reproductive changes at very high doses .

Effects on birds: Slightly toxic.

The LC_{50} in both mallards and bobwhite quail is greater than 4500 ppm.

Breakdown in soil and groundwater:

It is strongly adsorbed to soil.

Moderately persistent in soil, average half-life of 47 days.

In water, it is strongly adsorbed to suspended organic and mineral matter and is broken down primarily by microorganisms.

Breakdown in vegetation:

Glyphosate may be translocated throughout the plant, including to the roots.

Breakdown in plants is by a variety of biological and chemical pathways.

ADI: 0.3 mg/kg/day.

2,4-D Toxicology

Reproductive Effects:

No adverse effects.

Effect on Birds: Slightly toxic.

LD_{50} to Mallards 472 mg/kg.

Breakdown in soil and groundwater:

Half-life in soil are seven days.

Soil and water microbes are primarily responsible for its disappearance in soil and in the water.

Breakdown in vegetation:

Uptake of the compound is through leaves, stems and roots; however, it is generally non persistent.

Breakdown in plants is by a variety of biological and chemical pathways.

NOEL (rats):1 mg/kg/day.

ADI: 0.3 mg/kg/day.

Questions About Pesticide Environmental Fate

What is pesticide environmental fate ?.

A pesticide’s fate is described by how and where it enters the environment, how long it lasts, and where it goes.

How does pesticide application determine fate ?.

- Method of application,
- The amount, timing, frequency and placement.
- Weather conditions during application.
- Land form (topography).
- Vegetation type and density.
- Soil conditions.

What happens to a pesticide after application ?.

(1) Break down.

(2) Be redistributed within the application site.

(3) Move off site.

* Off site movement includes movement to groundwater, surface water, and to atmosphere.

*Off site movement also includes crops or livestock when it is removed from the site.

How do pesticides break down ?.

All pesticides react in the environment to form new chemicals,

* React with oxygen (oxidation)
* React with water (hydrolysis).
* Breakdown in the presence of sunlight.
* Microorganisms (bacteria, fungi, etc.) in soil and sediments.
* Some pesticides may enter plant roots or foliage and break down through plant metabolism.
* Pesticides applied directly to animals are also subject to uptake and metabolism.

What determines how fast pesticides breakdown ?.

Environmental conditions can influence reaction rate:

* For air, conditions include temperature, moisture, and sunlight intensity.
* For water, conditions include temperature, pH, sunlight intensity, and sediment microbial activity.
* For soil, conditions include temperature, soil type, organic matter, moisture, pH, aeration, and microbial activity.
* For plants and animals conditions include rates of uptake, metabolism and elimination.

How long does it take pesticides to break down ?.

Pesticides can be divided into 3 categories based on half- lives:

Non persistent (< 30 days).

Moderately persistent (30 – 100 days).

Persistent (> 100 days).

What happens to pesticides when they breakdown ?.

* The complete breakdown of pesticides form carbon dioxide, water, and minerals which commonly include sulfur, phosphorus, nitrogen, and the halogens: (chlorine, fluorine, and bromine).

* Some pesticide break down products are incorporated into soil organic matter.

* Usually the initial break down products are much less toxic than the pesticide, but sometimes they are of similar or greater toxicity.

How do pesticides move in the environment ?.

* In air and water (including air and water in soil) pesticides move only short distances by diffusion.
* To travel longer distances pesticides move by mass transfer, usually in moving water or air.
* Pesticides may attach to soil, vegetation, or other surfaces. The strength of the adsorption often determines a pesticide's availability to mass transfer.

How do pesticides get into the atmosphere ?.

* Volatilization occurs when pesticide surface residues change from solid or liquid to a gas.
* The media also influences vapor pressure: the more tightly adsorbed the lower the vapor pressure.
* Temperature also effects vapor pressure: higher temperature results in a higher vapor pressure.
* Pesticides can also move into the air as particles, adsorbed onto dust, or as droplets or aerosols during application.

How do pesticides get into ground and surface water ?.

* The more strongly a pesticide adsorbs to soil, the lower the tendency to move to ground water.
* Soils high in clay and organic matter adsorb pesticides better than sandy soils low in organic matter.

What happens to pesticides applied indoors ?.

* Pesticides applied indoors (glass or greenhouses) usually breakdown at a slower rate due to the lack of sunlight indoors (UV light is filtered out by glass).
* Pesticides applied indoors are not effected by wind or rain, and are less likely to move by mass transfer from the point of application.
* Vapor loss may also be less.

How does plant uptake effect pesticide movement?.

* If the plants are harvested some pesticide may move from the site with the crop.