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Guest Articles

Chemical Nature of Pesticides

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The phrase, "The Granary of the East" was used to describe the success of agriculture-based economy of our ancient nation. After European invasion, we lost our self-sustaining golden era, and gradually we started begging from developed countries and now we depend on their monetary loans and products. Pesticides are one of the major hazardous products, which we import without proper specifications, guidelines and monitoring. Today, it seems that these pesticides are making us sick or killing silently, particularly those who live in cultivating areas of Sri Lanka.

The substances or mixtures that use for controlling, preventing, destroying, repelling or attacking any biological organism are known as "**pesticides**". First historical evidence of pesticides came from Sumerian civilization, 2000 BCE. According to the archeologists, they have used sulfur to control mites and insects. Presently, about 2 million tons of pesticides are utilized globally, out of which 47.5% are herbicides, 29.5% are insecticides, 17.5% are fungicides and 5.5% are other pesticides.

Pesticides can be classified into two main groups based on;

- **Targeted use** - *e.g.* Algaecide (foralgae), Acaricide (for mites), Avicide (for birds), Bactericide (for bacteria), Fungicide (for fungi), Herbicide (for weeds), Insecticide (for insects), Biopesticide (derived from natural materials, *e.g.* baking Soda), *etc.*
- **Chemical nature** - This article intends to shine some light in this regard.

Pesticides based on chemical nature

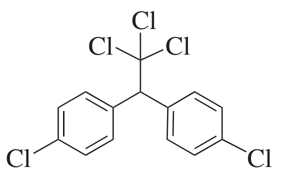
Pesticides are classified depending on their chemical compositions, and are broadly classified as either organic or inorganic pesticides.

Inorganic pesticides are simple compounds which have a crystalline, salt-like appearance; these are environmentally stable and usually soluble in water. These are the earliest chemical pesticides, *e.g.* sulphur, aluminium phosphide, lime, arsenic, copper and mercury salts. They are generally toxic and can remain in the environment for a long period of time.

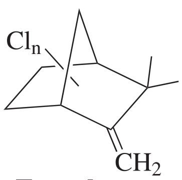
Organic pesticides are water insoluble, but readily soluble in fatty acids. Most of the modern pesticides are organic chemicals, which often contain oxygen, phosphorus, or sulphur in their molecules. They are further classified as either organochlorines, organophosphates or carbamates *etc*.

1. **Organochlorines (OCs)**

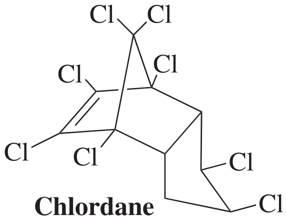
This broad-spectrum pesticide group contains chlorinated organic compounds. Nowadays, most pesticides belong to this group are banned or restricted in many countries as it is labeled as **persistent organic pollutants** (POPs). Organochlorines are mostly used as insecticides and its usage ranging from pellet application in field crops to sprays for seed coating and grain storage. These are strong neurotoxins; though it can be harmful to mammalians as well as insects. Dichlorodiphenyltrichloroethane (DDT) is one of the infamous banned insecticides that successfully used to control malaria. Endrin, Methoxychlor, Chlordane, Endosulfan, Chloropropylate, Aldrin, Toxaphene (Camphechlor) are some of the popular examples among OCs.



DDT



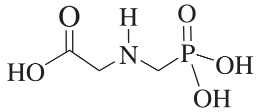
Toxaphene



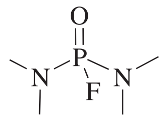
Chlordane

2. **Organophosphates (OPs)**

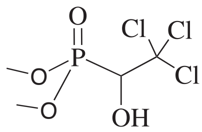
Esters of phosphoric acid and its derivatives are included in this group. These chemicals consist of phosphoric (P=O) or thiophosphoric (P=S) bond, and a leaving group, which can be replaced by the oxygen of serine in the acetylcholine esterase (enzyme that responsible for the metabolism of the neurotransmitters) active site. Toxicity of the pesticide depends on the leaving group. Today in Sri Lanka, **glyphosate** has become the main controversial OP pesticide that contains arsenic. However, OPs degrade rapidly by hydrolysis on exposure to moisture, air and soil; though small amounts can be detected in food and drinking water, *e.g.* Methyl Parathion, Dimefox, Malathion, Fenthion, Trichlorfon, glyphosate *etc*.



Glyphosate



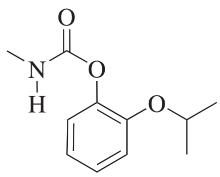
Dimefox



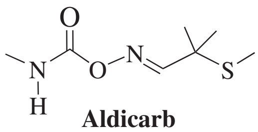
Trichlorfon

3. **Carbamates**

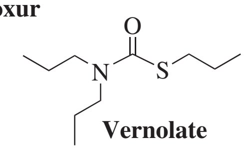
Carbamates are derivatives of carbamic acid, which has a similar structure to phosphoric acid. Carbamylating of the active site of acetycholine esterase is the main inhibition mechanism used by this pesticide group. Though carbamates are biodegradable, it is not as fast as OPs. Prupoxur, Carbofuran, Aldicarb, Vernolate, Thiourea are few examples of carbamates.



Propoxur



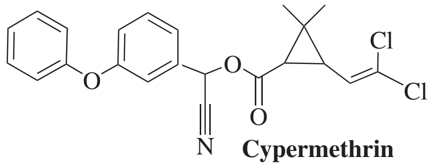
Aldicarb



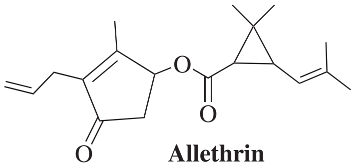
Vernolate

4. **Pyrethroids**

Chrysanthemum coccineum and *C. cinerariaefolium* flowers are used to isolate pyrethroids, as it exhibits natural insecticidal properties. Pyrethroids affect the sodium channels and lead to paralysis of the organisms. These types of pesticides have high biodegradable capacity, *e.g.* Allethrin, Tetramethrin, Cypermethrin, Furethrin, Tetramethrin



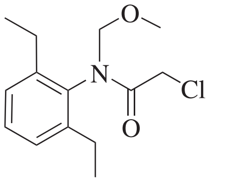
Cypermethrin



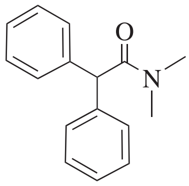
Allethrin

5. **Phenyl amides**

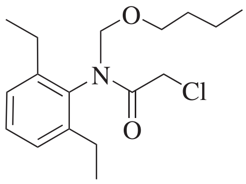
These are well-known fungicides, which added to the soil to enhance plant growth and yield. Barban, Alachlor, Diphenamid, and Butachlor are some examples for the pesticides which belong to this category. These fungicides have an impact on mitosis and cell division in target fungi.



Alachlor



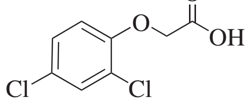
Diphenamide



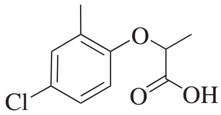
Butachlor

6. **Phenoxyalkonates**

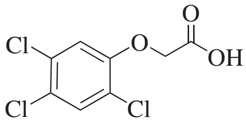
This herbicidal group is mainly used to control weeds in agriculture. Nearly almost all of the compounds of this group are degraded by microorganisms. Mecoprop, Erbinox, 2,4-D (2,4-dichlorophenoxyacetic acid), 2,4,5-T (2,4,5-trichlorophenoxyacetic acid), Sesone, and Dichloroprop are some of the members of this category.



2,4-D



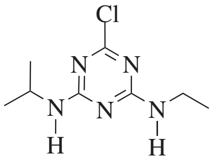
Mecoprop



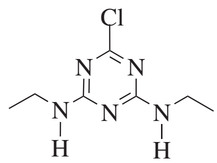
2,4,5-T

7. **Trazines**

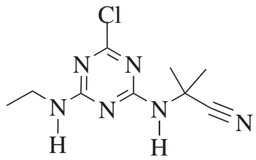
Atrazine, Simazine, Ametryn, Atratone, Chlorazine, Cyanazine can be included under this wide range of herbicide category. These chemicals are also used as insect chemo-sterilants.



Atrazine



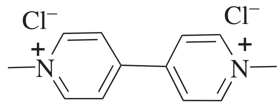
Simazine



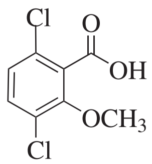
Cyanazine

8. **Others**

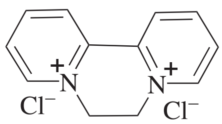
Benzoic acid and dipridyl derivatives which include paraquat and diquat are used as herbicides. Captan, Folpet and Captafol are fungicides which consist of the phthalimide moiety. Heavy metal elements such as iron, lead, arsenic, mercury, zinc, tin, *etc*. and both inorganic and organometallic compounds (*e.g.* Methyl mercuric chloride, sodium arsenate, calcium arsenate, zinc phosphide) are used as pesticides.



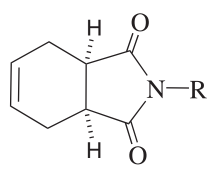
Paraquat



Dicamba

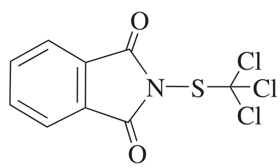


Diquat



Captan R = $-SCCl_3$

Captafol R = $-SCCl_2CHCl_2$



Folpet

Threats and concerns

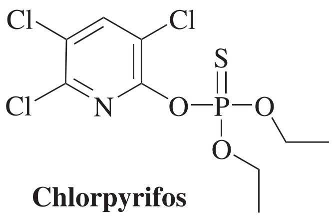
Pesticides are well known carcinogenic agents. These toxins can enter the human body *via* ingestion (swallowed or eaten), inhalation (as a mist, dust, fumes or smokes), or dermal contact (absorbed through skin or eyes). The toxic effect varies with the quantity, quality and potency of the pesticide, time of exposure, type of the injury and health state of the victim.

Short-term effects of pesticides are headache, skin-irritation, eye-irritation, muscle pain, fever, and weakness. It also adversely effects on nerve system (*e.g.* Alzheimer's disease, Parkinson's disease) and cardiovascular system, decreasing immunity, and cause infertility and severe birth defects. Pesticides are also known to cause gene mutation, chromosomal alteration and DNA damage. Unfortunately, some Sri Lankan farmers use pesticides to suicide.

Chronic kidney disease of unknown origin (CKDu) in rural areas of our country (especially in Polonnaruwa and Anuradhapura) is one of the tragic examples which imply the hazardous nature of pesticides. According to the latest researches, arsenic is the possible etiological factor for this emerging epidemic of CKDu. Phosphate agrochemicals are the main source of arsenic in Sri Lanka; and long-term application of this contaminated agrochemicals lead to the accumulation of arsenic in the soil.

Today, pesticide manufacturing companies use latest gene technology to produce "pesticide resistant crops". Roundup Ready crops are type of genetically modified crops invented by the Monsanto Company. However, researchers have revealed that these GM Crops are the main reason for many diseases including various types of cancers, infertility, birth defects and autism.

Chloropyrifos is an OP which has become the latest controversial pesticide as, it traces back to nerve agents developed in a Nazi laboratory.



Chlorpyrifos

Pesticides adversely effect on the complete eco-systems. There are many micro-organisms, invertebrates and vertebrates that support to improve the soil-structure and soil fertility. Most of pesticides that farmers are using today belong to the broad-spectrum category. Hence, these friendly creatures also get eliminated with the pests due to the chemical activities. Thus, soil has become a barren land. According to the Darwinian Theory, well adopted organisms will survive from the struggle of living. Mainly organochlorines act as an air pollutant; chlorinated compounds create free radicals and ultimately cause the depletion of the ozone layer. Eutrophication of water bodies is one of the serious water polluting method. Downstream drift of the pesticides is another way of polluting water. This polluted water runoff *via* drinking water sources and finally every water drop that we consume could become poisonous.

How to control the effects of pesticides

It is important to rinse vegetables and fruits with saltwater or vinegar or turmeric water or baking soda, followed by clean water, before cooking or consuming. The best possible way to reduce the intake of pesticides is to grow your own food in your garden. If you do not have enough garden space, you can use a hydroponic system.

Unlike most Sri Lankans, Europeans buy organically grown food for their daily usage to keep them healthy. Usage of many pesticides is banned in European countries, though they are selling low quality pesticides to third world countries. It should be mentioned that Sri Lanka has banned some of the toxic/harmful pesticides such as 2,4,5 T, arsenic, chlordane, DDT, dibromoethane, ethyl parathion, fluoroacetamide, mercury, thallium sulphate, methyl parathion, captafol, endrin, aldicarb etc.

Nanotechnology is the latest revolutionary trend in the modern world. Scientists have revealed that action in pesticides can be controlled with the help of nanotechnology. Engineered nanoparticle in the nano pesticides can be formulated to control the release of its active ingredients. This may reduce the environmental contamination through the reduction of pesticide application rates. Inventors of these nano-pesticides believe that development of this latest method will help to minimize the misuse. The other ways of avoiding exposure to toxic pesticide are to develop pest-resistant crop varieties, use of traditional agricultural methods such as crop rotation with locally produced fertilizers, and use of effective biopesticides.

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Guest Articles

Coke Reactivity and Its Applications in Blast Furnace Iron Making

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Greenhouse gas emission is the biggest challenge for the blast furnace iron making process. Even though intensive research has been undertaken in developing new iron making technologies, the blast furnace process still dominates in the iron making.

The iron making blast furnace is a smelting reaction chamber. It is a counter-current reactor where raw materials are added to the top of the furnace and gases are injected into the bottom. The raw materials consist of iron-bearing materials (oxides), fluxes and coke.[1] A low carbon operation in the blast furnace is a possible solution to reduce greenhouse gas emission. Low carbon usage means optimising the metallurgical coke usage in the blast furnace. Coke is the fuel and the primary source of the reductant (CO) of iron oxide in the blast furnace. It also gives the structural support to the furnace to ensure high permeability for high productivity.[1] One way to reduce coke usage is to inject supplementary fuels such as coal, natural gas and oil. These supplementary fuels can provide the heat and reductant for the iron making process but unable to provide the mechanical support to the burden and hence cannot be replaced entirely. Understanding coke reactivity and effect of coke mineralogy lead to optimise the coke usage to achieve high production rates required for profitable iron making in a blast furnace.

Coke characterisation

Coke is a complex material composed of organic components, inorganic minerals and pores. Further, it often displays significant heterogeneity in any metric(s) used to characterise its mineralogy, phase desperation, morphology and porosity.[2]