1. Introduction

1.1 Definition of pesticide
According to FAO (1989) a pesticide is any substance or mixture of substances intended for preventing, destroying, or controlling any pest including vectors of human or animal diseases, unwanted species of plants or animals causing harm during, or otherwise interfering with, the production, processing, storage, or marketing of food, agricultural commodities, wood and wood products, or animal feedstuffs, or which may be administered to animals for the control of insects, arachnids or other pests in or on their bodies. The term includes chemicals used as growth regulators, defoliants, desiccants, fruit thinning agents, or agents for preventing the premature fall of fruits, and substances applied to crops either before or after harvest to prevent deterioration during storage or transport. The term, however excludes such chemicals used as fertilizers, plant and animal nutrients, food additives and animal drugs. The term pesticide is also defined by FAO in collaboration with UNEP (1990) as chemicals designed to combat the attacks of various pests and vectors on agricultural crops, domestic animals and human beings. The definitions above imply that, pesticides are toxic chemical agents (mainly organic compounds) that are deliberately released into the environment to combat crop pests and disease vectors.

1.2 Historical background of pesticides use in agriculture and public health
The historical background of pesticides use in agriculture is dated back to the beginning of agriculture itself and it became more pronounced with time due to increased pest population paralleled with decreasing soil fertility (Muir, 2002). However, the use of modern pesticides in agriculture and public health is dated back to the 19th century. The first generation of pesticides involved the use of highly toxic compounds, arsenic (calcium arsenate and lead arsenate) and a fumigant hydrogen cyanide in 1860's for the control of such pests like fungi, insects and bacteria. Other compounds included Bordeaux mixture (copper sulphate, lime and water) and sulphur. Their use was abandoned because of their toxicity and ineffectiveness. The second generation involved the use of synthetic organic compounds. The first important synthetic organic pesticide was dichlorodiphenyltrichloroethane (DDT) first synthesized by a German scientist Ziedler in 1873 (Othmer, 1996) and its insecticidal effect discovered by a Swiss chemist Paul Muller in
1939. In its early days DDT was hailed as a miracle because of its broad-spectrum activity, persistence, insolubility, inexpensive and ease to apply (Keneth, 1992).

\[ p, p'-DDT \]

\( p, p'\)-DDT in particular was so effective at killing pests and thus boosting crop yields and was so inexpensive to make its use quickly spread over the globe. DDT was also used for many non-agricultural applications as well. For example, it was used to delouse soldiers in the World War II and in the public health for the control of mosquitoes which are the vectors for malaria. Following the success of DDT, such other chemicals were synthesized to make this era what Rachel Carson (1962) in her book "The Silent Spring" described as the era of "rain of chemicals".

The intensive use of pesticides in agriculture is also well known to be coupled with the "green revolution". Green revolution was a worldwide agricultural movement that began in Mexico in 1944 with a primary goal of boosting grain yields in the world that was already in trouble with food supply to meet the demand of the then rapidly growing human population. The green revolution involved three major aspects of agricultural practices, among which the use of pesticides was an integral part. Following its success in Mexico, green revolution spread over the world. Pest control has always been important in agriculture, but green revolution in particular needed more pesticide inputs than did traditional agricultural systems because, most of the high yielding varieties were not widely resistant to pests and diseases and partly due to monoculture system (Vocke, 1986). Each year pests destroy about 30-48% of world’s food production. For example, in 1987 it was reported that, one third of the potential world crop harvest was lost to pests. A further illustration to the pest problem in the world is shown in table 1.1 (Hellar, 2002).

Insect pests and rodents also account for a big loss in stored agricultural products. Internally feeding insects feed on grain endosperm and the germ the result of which is the loss in grain weight, reduction in nutritive value of the grain and deterioration in the end use quality of the grain. Externally feeding insects damage grain by physical mystification and by excrement contamination with empty eggs, larval moults and empty cacoons. A common means of pest control in stored agricultural products has always been the use of insecticides such as malathion, chlorpyrifos-methyl or deltamethrin impregnated on the surfaces of the storage containers (McFarlane, 1989).

On the other hand malaria remains the major vector-borne infectious disease in many parts of the tropics. It is estimated that over 300 to 500 million clinical cases occur each year, with cases in tropical Africa accounting for more than 90% of these figures (WHO, 1995). Other vector-borne diseases that present a serious problem especially in the tropics include trypanosomiasis, onchocerciasis and filariasis. It is therefore quite apparent that, the discovery of pesticides was not a luxury of a technical civilization but rather was a necessity for the well being of mankind.
### Table 1.1 Estimated % losses caused by pests in some world’s major crops per year

<table>
<thead>
<tr>
<th>Crop</th>
<th>Insects</th>
<th>Diseases</th>
<th>Weeds</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rice</td>
<td>26.7</td>
<td>8.9</td>
<td>10.8</td>
<td>46.4</td>
</tr>
<tr>
<td>Maize</td>
<td>12.4</td>
<td>9.4</td>
<td>13.0</td>
<td>34.8</td>
</tr>
<tr>
<td>Wheat</td>
<td>5.0</td>
<td>9.1</td>
<td>9.8</td>
<td>23.9</td>
</tr>
<tr>
<td>Millet</td>
<td>9.6</td>
<td>10.6</td>
<td>17.8</td>
<td>38.0</td>
</tr>
<tr>
<td>Potatoes</td>
<td>6.5</td>
<td>21.8</td>
<td>4.0</td>
<td>32.3</td>
</tr>
<tr>
<td>Cassava</td>
<td>7.7</td>
<td>16.6</td>
<td>9.2</td>
<td>33.5</td>
</tr>
<tr>
<td>Soybeans</td>
<td>4.5</td>
<td>11.1</td>
<td>13.5</td>
<td>29.1</td>
</tr>
<tr>
<td>Peanuts</td>
<td>17.1</td>
<td>11.3</td>
<td>11.8</td>
<td>40.4</td>
</tr>
<tr>
<td>Sugarcane</td>
<td>9.2</td>
<td>10.7</td>
<td>25.1</td>
<td>45.0</td>
</tr>
</tbody>
</table>

1.3 Impacts of pesticides use in agriculture and public health

The use of pesticides in agriculture has led to a significant improvement in crop yield per hectare of land. Studies have established a possible correlation relationship between the quantity of pesticides used per hectare and the amount of crop yields per hectare (Hellar, 2002); table 1.2. Pesticides like DDT and others proved their usefulness in agriculture and public health. Economies were boosted, crop yields were tremendously increased, and so were the decreases in fatalities from insect-borne diseases. Insecticides have saved the lives of countless millions of people from insect-borne diseases (Youdeowei, 1983).

1.4 Side effects of pesticides use to the environment and public health

Despite the good results of using pesticides in agriculture and public health described above, their use is usually accompanied with deleterious environmental and public health effects. Pesticides hold a unique position among environmental contaminants due to their high biological activity and toxicity (acute and chronic). Although some pesticides are described to be selective in their modes of action, their selectivity is only limited to test animals. Thus pesticides can be best described as biocides (capable of harming all forms of life other than the target pest). Further details on the side effects of pesticides are discussed in the following chapter (ecological effects of pesticides).

### Table 1.2 Pesticides use and the corresponding crop yield in some countries/areas

<table>
<thead>
<tr>
<th>Country/Area</th>
<th>Pesticide Use (kg/Ha)</th>
<th>Crop Yield (Ton/Ha)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Japan</td>
<td>10.8</td>
<td>5.5</td>
</tr>
<tr>
<td>Europe</td>
<td>1.9</td>
<td>3.4</td>
</tr>
<tr>
<td>USA</td>
<td>1.5</td>
<td>2.6</td>
</tr>
<tr>
<td>Latin America</td>
<td>0.2</td>
<td>2.0</td>
</tr>
<tr>
<td>Oceania</td>
<td>0.2</td>
<td>1.6</td>
</tr>
<tr>
<td>Africa</td>
<td>0.1</td>
<td>1.2</td>
</tr>
</tbody>
</table>

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2. Identity of pesticides

2.1 How can pesticides be identified?
Many of the pesticides that we use in our crops, gardens or domestic animals, are often a mixture of several chemicals mixed together in desired proportions suspended in appropriate carrier or diluent materials. These chemicals are called active ingredients that are responsible for killing or otherwise affecting the pests. Apart from the active ingredients, there are other chemicals that are formulated together with the active ingredients that usually do not kill pests. These are called inert ingredients that serve as carriers, diluents, binders, dispersants, prolong the shelf life of active ingredients or make the pesticide smell better. It is often the case that active ingredients on the container labels are named using common names. However, common names are not the only way to identify pesticides and in fact common names do not give complete information on the chemical nature of the pesticides. When chemists want to give a specific and unambiguous name to a chemical, they use what is called “systematic name”. These names are usually long and complicated, but they are necessary for naming the millions of known chemicals. There are two main systems for deriving the systematic names of chemicals, one from the International Union of Pure and Applied Chemistry (IUPAC) and the other from the Chemical Abstracts Service (CAS). As an example of the two systematic naming described above, the following insecticide is names respective as;
IUPAC systematic name: \((E)-1-(6\text{-chloro}-3\text{-pyridylmethyl})\text{-}N\text{-nitroimidazolidin-2-ylideneamine}\)
The same insecticide has the following CAS systematic name:
\((2E)-1\text{-}[(6\text{-chloro}-3\text{-pyridinyl})\text{methyl}]\text{-}N\text{-nitro-2-imidazolidinimine}\)
In addition to a systematic name, CAS assigns a registry number to each chemical which is different from one chemical to another. For example the insecticide just described above has a CAS registry number of 138261-41-3
As pointed out earlier, systematic names are long and complicated for a mere user of pesticides (layman). For that matter, systematic names are more used by experts in the field of pesticides who pursue specific researches in which a proper identification of the chemical is needed. For many purposes, a relatively short and simple name would be helpful than a systematic name or registry number, and that is the role of common names.

2.2 How are the common names of pesticides derived?
What most people need when reading, writing or talking about a pesticides is a short, fairly simple and reasonably memorable name. Common names are approved by the International Organization for Standardization (ISO) based on given guidelines. For example the common name for the insecticide \((E)-1-(6\text{-chloro}-3\text{-pyridylmethyl})\text{-}N\text{-nitroimidazolidin-2-ylideneamine}\) is given as “imidacloprid” derived from parts of the systematic name. The process of registering common names usually starts with the pesticides manufacturers submitting proposals for names to ISO and the ISO committee checks that the proposed names comply with the rules, not misleading, and are not likely to be confused with the existing names of pesticides or drugs. Once common names are approved by ISO, they no longer belong to the company, but rather they can be used in other countries.

2.3 Classification of pesticides
The word "pesticide" is an umbrella term for all insecticides, herbicides, fungicides, rodenticides, wood preservatives, garden chemicals and household disinfectants that may
be used to kill some pests. Since pesticides varies in identity, physical and chemical properties, it’s therefore logical to have them classified and their properties studied under their respective groups. Synthetic pesticides are classified based on various ways depending on the needs. However, there are three most popular ways of classifying pesticides which are; classification based on the mode of action, classification based on the targeted pest species and classification based on the chemical composition of the pesticide (Drum, 1980).

2.3.1 Classification of pesticides based on the mode of action
Under this type of classification, pesticides are classified based on the way in which they act to bring about the desired effect. In this way pesticides are classified as contact (non-systemic) and systemic pesticides. The non-systemic pesticides are those that do not appreciably penetrate plant tissues and consequently not transported within the plant vascular system. The non-systemic pesticides will only bring about the desired effect when they come in contact with the targeted pest, hence the name contact pesticides. Examples of contact pesticides are paraquat and diquat dibromide. On the other hand, the systemic pesticides are those which effectively penetrate the plant tissues and move through the plant vascular system in order to bring about the desired effect. Examples of systemic pesticides include 2, 4-D and glyphosate (Buchel, 1983). Under this classification, also are stomach poisons that bring about the desired effect after being eaten eg. Rodenticides. Fumigants are those pesticides that produce vapour which kills the pests.

2.3.2 Classification of pesticides based on the targeted pest species
In this type of classification, pesticides are named after the name of the corresponding pest in target as shown in table 2.1

<table>
<thead>
<tr>
<th>Type of pesticide</th>
<th>Target organism/pest</th>
</tr>
</thead>
<tbody>
<tr>
<td>Insecticides</td>
<td>Insects</td>
</tr>
<tr>
<td>Herbicides</td>
<td>Weeds</td>
</tr>
<tr>
<td>Rodenticides</td>
<td>Rodents</td>
</tr>
<tr>
<td>Fungicides</td>
<td>Fungi</td>
</tr>
<tr>
<td>Acaricides and Miticides</td>
<td>Arachnids of the order Acarina such as ticks and Mites</td>
</tr>
<tr>
<td>Molluscicides</td>
<td>Mollusks</td>
</tr>
<tr>
<td>Bactericides</td>
<td>Bacteria</td>
</tr>
<tr>
<td>Avicides</td>
<td>Bird pests</td>
</tr>
<tr>
<td>Virucides</td>
<td>Virus</td>
</tr>
<tr>
<td>Algicides</td>
<td>Algae</td>
</tr>
</tbody>
</table>

Table 2.1 Classification of pesticides based on the target organisms

2.3.3 Classification of pesticides based on the chemical composition
Under chemical classification, pesticides are categorized according to the chemical nature of the active ingredients. The chemical classification of pesticides is by far the most useful classification to researchers in the field of pesticides and environment and to those who search for details. This is because, it is from this kind of classification that gives the clue of the efficacity, physical and chemical properties of the respective pesticides, the knowledge of which is very important in the mode of application, precautions that need to be taken.
during application and the application rates. Based on chemical classification, pesticides are classified into four main groups namely; organochlorines, organophosphorous, carbamates and pyrethrin and pyrethroids (Buchel, 1983).

Organochlorines pesticides are organic compounds with five or more chlorine atoms. Organochlorines were the first synthetic organic pesticides to be used in agriculture and in public health. Most of them were widely used as insecticides for the control of a wide range of insects, and they have a long-term residual effect in the environment since they are resistant to most chemical and microbial degradations. Organochlorine insecticides act as nervous system disruptors leading to convulsions and paralysis of the insect and its eventual death. Some of the commonly used representative examples of organochlorine pesticides are DDT, lindane, endosulfan, aldrin, dieldrin and chlordane and their chemical structures are presented hereunder.

Organophosphorous insecticides on the other hand contain a phosphate group as their basic structural framework as defined by Schrader's formula:

$$\text{R}_1^1 \text{R}_2^2 \text{P} = \text{O(S)} \text{O} \text{X}$$

Where, \( \text{R}_1^1 \) and \( \text{R}_2^2 \) are usually methyl or ethyl groups, the O in the OX group can be replaced with S in some compounds, whereas the X group can take a wide diversity of forms. Organophosphorous insecticides are generally more toxic to vertebrates and invertebrates as cholinesterase inhibitors leading to a permanent overlay of acetylcholine neurotransmitter across a synapse. As a result, nervous impulses fail to move across the synapse causing a rapid twitching of voluntary muscles and hence paralysis and death. Unlike organochlorines, organophosphorous insecticides are easily decomposed in the
environment by various chemical and biological reactions, thus organophosphorous insecticides are not persistent in the environment (Martin, 1968). Some of the widely used organophosphorous insecticides include parathion, malathion, diazinon and glyphosate.

![Chemical structures of parathion, malathion, diazinon, and glyphosate](image)

Carbamates are organic pesticides derived from carbamic acid with the general formula

![General structure of carbamates](image)

Where, $R^1$ is an alcohol group, $R^2$ is a methyl group and $R^3$ is usually hydrogen. Both oxime and aryl carbamates have fairly high insect and mammalian toxicities as cholinesterase inhibitors. The cholinesterase inhibitions of carbamates differ from that of organophosphorous in that, it is species specific and it is reversible (Drum, 1980). Some of the widely used insecticides under this group include carbaryl, carbofuran and aminocarb.

![Chemical structures of carbaryl, carbofuran, and aminocarb](image)

Pyrethroids are synthetic analogues of the naturally occurring pyrethrins; a product of flowers from pyrethrum plant (*Chrysanthemum cinerariaefolium*). The insecticidal components of pyrethrum flowers are the optically active esters derived from (+)-trans-chrysanthemic acid and (+)-trans-pyrethroic acid.
Pyrethroids are acknowledged of their fast knockdown effect against insect pests, low mammalian toxicity and facile biodegradation. Although the naturally occurring pyrethrins are effective insecticides, their photochemical degradation is so rapid that their uses as agricultural insecticides become impractical. The synthetic analogues of the naturally occurring pyrethrins (pyrethroids) were developed by the modification of pyrethrin structure by introducing a biphenoxo moiety and substituting some hydrogens with halogens in order to confer stability at the same time retaining the basic properties of pyrethrins. The most widely used synthetic pyrethroids include permethrin, cypermethrin and deltamethrin.

Other miscellaneous groups of pesticides that are worth mentioning particularly in this book include among others phenoxyacetic acid under which the herbicide 2,4-D belongs and bipyridyls under which the herbicides paraquat and diquat belong.
Fungicides are pesticides that are used for the control of fungal infections in crops. There are inorganic and organic fungicides. Inorganic fungicides include Bordeaux mixture, Cu(OH)$_2$.CaSO$_4$ and malachite, Cu(HO)$_2$.CuCO$_3$. Organic fungicides on the other hand include among others, benomyl and oxine copper (Manahan, 2001).

2.3.4 Other minor classes of pesticides
2.3.4.1 Activity spectrum of the pesticide
In this system of classification, pesticides are classified into two groups as broad spectrum pesticides and selective pesticides. Broad spectrum pesticides are those pesticides that are designed to kill a wide range of pests and other non target organisms. They are non-selective and are often lethal to reptiles, fish, pets and birds. Some examples of broad spectrum pesticides are chlorpyrifos and chlordane. Selective pesticides on the other hand are those pesticides which kill only a specific or group of pests leaving other organisms with a little or no effect at all. A good example in this case is a herbicide 2,4-D which affects broad-leaved plants leaving the grassy crops unaffected.

2.3.4.2 Mode of formulation
**Emulifiable concentrates (EC)** are fine suspensions of oil droplets in water and appears milky in colour. They do not require constant agitation prior to each application.

**Wettable Powders (WP)** are suspensions of fine particles suspended in water. These suspension require constant agitation prior to each application.

**Granules (G)**. Granules are obtained by mixing the active ingredient with clay for outdoor applications.

**Baits**. These are obtained by mixing the active ingredient with food base especially used for the control of rodents.

**Dusts (D)**. Dusts cannot be mixed with water and they must be applied dry. The common carriers for dusts are clay, talc, silica gel or diatomaceous earth.

**Fumigants**. These are gaseous insecticides usually packaged under pressure and stored as liquids. Some are tablets or pellets that release gas when mixed with water.

2.3.4.3 Toxicity level
The World Health Organization (WHO) has developed a classification system that group pesticides according to the potential risks to human health caused by accidental contact to human being and they are grouped into the following classes;
Class Ia = extremely hazardous
Class Ib = highly hazardous
Class II = moderately hazardous
Class III = slightly hazardous
Class IV = products unlikely to present acute hazard in normal use

3. Physical properties of pesticides

The biological activity of a pesticide to the target pest species is greatly influenced by its physical and chemical properties. The physical properties of a pesticide in particular determine the pesticide mode of action, dosage, mode of application and the subsequent environmental chemodynamics. The physical properties of pesticides varies greatly according to their chemical nature and formulation. For simplicity, here are discussed some general physical properties of pesticides without going to specifics and then in table 3.1 are discussed the specific physical properties of the named representative pesticides.

3.1 General physical properties of pesticides

3.1.1 Molecular weight and form

In some references such as pesticide manual, the molecular weight (MW) and the physical form (appearance and odour) of the active ingredient (AI) is usually given. Molecular weight of a substance is a summation of individual atomic weights of all the atoms making up the molecule in question. The molecular weight of a pesticide is an inherent property that distinguish one pesticide from the other except for stereoisomeric pesticides which share similar molecular weights differing only on the group spatial orientations at given chiral centres. The common gas-phase pesticides for example have a molecular weight of about 103 or less. However, it become very difficult to predict the state and form of complex molecules with molecular weight that are substantially greater than 500.

3.1.2 Vapour pressure (VP)

The vapour pressure of a substance is the measure of how easy it can volatilise and turn into vapour (gas state). For pesticides, the easy with which a pesticide can volatilise may be considered advantageous with respect to a particular mode of action on one hand but it can be of negative influence on the other hand. For example, a pesticide with a fumigant mode of action can have a useful penetrative power and thus it is advantageous to have higher vapour pressure. However, a high vapour pressure can cause vapour drift and environmental pollution. Pesticides with high vapour pressure need to be handled in such a way so that the vapours do not escape into the atmosphere. A pesticide with low vapour pressure does not move into air, so there is a potential to accumulate in water if it is water soluble. If it is not water soluble, the pesticide may accumulate in soil or biota. The usually preferred SI-unit for vapour pressure is millipascal (Mpa = g.m⁻¹ or 0.001 N.M⁻²).

3.1.3 Solubility

Solubility is a measure of how easily can a given substance dissolve in a given solvent. Unless stated otherwise, the unit for solubility in water are given in ppm (parts per-million) which is the same as milligrams per litre (mg/L). When the solubility is too low, the units are given in ppb (parts per-billion) which is the same as micrograms per liter (µg/L). Measurements of solubility are influenced by temperature, pH, polarity of the substance, hydrogen bonding, molecular size and the method used. The following is an expression for ppm (Linde, 1994);
The significance in environment fate of solubility of pesticides is that, a pesticide which is very soluble in water will tend not to accumulate in soil or biota because of its strong polar nature. This suggests that it will degrade via hydrolysis which is a favored reaction in water.

### 3.1.4 Octanol/Water partition coefficient - $K_{ow}$ (Log $K_{ow}$)

Partition coefficient is a measured ratio (at equilibrium) of the dissolved mass of the substance between equal layers of n-octanol and water.

$$K_{ow} = \frac{\text{Concentration in n-Octanol Phase}}{\text{Concentration in Water Phase}}$$

$K_{ow}$ is a unitless parameter which provides a useful predictor of the other physical properties for most pesticides and other organic substances with molecular weight less than 500. Values of $K_{ow}$ for organic chemicals can be quite large, and therefore for convinience it is often expressed as Log $K_{ow}$ (which is log to the base 10 of $K_{ow}$) and the values range from -3 to 7. $K_{ow}$ is considered to be a good indicator of bioaccumulation of pesticides in organisms and food chains. Pesticides with a positive correlation to Log $K_{ow}$ are more likely to have bioaccumulation effects to organisms and food chains. The parameter is also a good indicator of systemic mode of action of a pesticide. Pesticides with low $K_{ow}$ values (generally ≤2) indicate the likely systemic translocation of such pesticides or their metabolites in the plants transvascular system. $K_{ow}$ values are generally influenced by the polarity of the pesticide and the general physical factors. Polar pesticides tend to be more soluble in water and hence low values of $K_{ow}$. For the general physical factors, $K_{ow}$ will increase when the following physical properties increase; molecular surface area, molar volume, molecular weight, and density (Mallhot & Peters, 1988).

### 3.1.5 Soil adsorption coefficient $K_{oc}/K_d$

Adsorption of pesticides on soils and sediments is a major factor that determines the destination of pesticides in the environment and their eventual degradation processes. Most pesticides are non polar and hydrophobic meaning that they are not very soluble in water. The non polar pesticides tend to be pushed out of water onto soils and sediments which contain non polar organic matter. $K_d$ is called the sorption coefficient and it measures the amount of pesticides adsorbed onto soil per amount of water without considering the organic matter content of the soil. The values for $K_d$ vary greatly because the organic matter content of the soil is not considered in the equation. The preferred parameter to determine the soil’s ability to adsorb pesticides is $K_{oc}$ since it considers the organic matter content of the soil. $K_{oc}$ is the ratio (at equilibrium) of the mass of a substance, adsorbed onto a unit mass of soil, relative to the mass of the substance remaining in water solution. $K_{oc}$ is also a unitless parameter and its value is dependent on the organic matter content of the soil, polarity of the chemical and soil pH.
3.1.6 Henry’s law constant-H^*

Henry’s Law Constant (HLC) is a measure of the concentration of a chemical in air over its concentration in water. It expresses the tendency of a material to volatilise from aqueous solution to air. It is sometimes measured, but more usually calculated as the ratio of vapour pressure (in pascals) x molecular weight / solubility (mg/L).

\[
H^* = \frac{16.04 \times P \times M}{T \times S}
\]

Where
\( P = \) Vapour pressure,
\( M = \) Molecular mass
\( T = \) Temperature
\( S = \) Solubility

The environmental significance of Henry’s law constant is that, a pesticide with a high HLC value will volatilize from water into air and distribute over a large area. Conversely, a pesticide with a low HLC value tend to persist in water and may be adsorbed into soil and sediment. The HLC value is also an integral part in calculating the volatility of a chemical.

3.2 Specific physical properties of selected representative pesticides

<table>
<thead>
<tr>
<th>Pesticide Name</th>
<th>Synonym/trade name</th>
<th>Type</th>
<th>Physical properties</th>
<th>Health effects</th>
<th>Handling procedures</th>
<th>Route of entry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlordane C_{10}H_{8}Cl_{3}</td>
<td>Toxiclor, Niran, Octachlor, Synklor, Corodane</td>
<td>Organochlorine insecticide</td>
<td>Viscous amber to colourless liquid with a mild odour</td>
<td>Suspected carcinogen, affect central nervous system, gastrointestinal tract and liver.</td>
<td>Goggles, chemical/solvent resistant gloves, apron</td>
<td>Inhalation, ingestion, skin, eye</td>
</tr>
<tr>
<td>Chlorpyrifos C_{5}H_{11}Cl_{3}NO_{3}</td>
<td>Dowco179, Dursban, Lorsban, Pyrinex, Killmaster</td>
<td>insecticide</td>
<td>White or colourless granular crystals, gas like odour</td>
<td>May affect the central nervous system and liver</td>
<td>Gloves, dust proof goggles</td>
<td>Inhalation, ingestion, skin</td>
</tr>
<tr>
<td>DDT C_{12}H_{8}Cl_{3}</td>
<td>Dicophane, Agritan, Gesapon, Gesapex, Citox, Detox, Anoflex</td>
<td>Organochlorine insecticide</td>
<td>Colourless solid or white to slightly off-white powder with faint odour</td>
<td>Probable carcinogen, reproductive, liver, and kidney problems, eye, nose, skin, throat irritant</td>
<td>Respirator, gloves, goggles and face shield</td>
<td>Inhalation, ingestion and skin</td>
</tr>
<tr>
<td>Identity, Physical and Chemical Properties of Pesticides</td>
<td>Diaznon C₁₂H₂₁N₂O₃ PS</td>
<td>Basudin, Dazzel, Gardentox, Royazol, Out, Nucidol</td>
<td>Organophosphate insecticide</td>
<td>Oily colourless liquid</td>
<td>Eye and skin irritant, may cause gastrointestinal symptoms</td>
<td>Glove, long pants, sleeves, face shield, goggles</td>
</tr>
<tr>
<td>---</td>
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<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Dichlorvos C₆H₇Cl₂O₄P</td>
<td>Unitox, Lindan, DDVP, Vapona, Nuvan, Cypona</td>
<td>Organophosphate insecticide</td>
<td>Clear, slightly yellow liquid with a mild odour, combustible</td>
<td>Suspected carcinogen, can affect the central nervous system</td>
<td>Nitrile gloves, Tyvek clothes, respirator, safety glasses</td>
<td>Inhalation, ingestion, skin</td>
</tr>
<tr>
<td>Ethion C₆H₂₁O₄P₂S₄</td>
<td>Ethanol, Hylmox, Nialate, Rhodocide</td>
<td>Organophosphate insecticide</td>
<td>Colourless or light brown to pale yellow liquid or dust</td>
<td>Affect central nervous system and gastrointestinal system, chest, nose</td>
<td>Dust masks, gloves and safety glasses</td>
<td>Inhalation, ingestion, skin</td>
</tr>
<tr>
<td>Lindane C₆H₆Cl₆</td>
<td>Aficide, Agroicide, Benzene hexachloride, Bexol, Celanex</td>
<td>Organochlorine insecticide</td>
<td>White or colourless crystalline solid with slight musty odour</td>
<td>Suspected carcinogen, affects central nervous system, respiratory, reproductive systems</td>
<td>Goggles, gloves and respirator</td>
<td>Inhalation, ingestion and skin</td>
</tr>
<tr>
<td>Malation C₁₀H₁₃O₆P₂S₂</td>
<td>Chemathion, Malacide, Detmol, o,o-dimethyl thiophosphate</td>
<td>Organophosphate insecticide</td>
<td>Clear brown to colourless liquid with mild skunk-like odour</td>
<td>Skin, eye, nose irritant, affects respiratory and central nervous system</td>
<td>Nitrile gloves, Tyvek clothing, respirator, splash-proof goggles</td>
<td>Inhalation, ingestion, skin</td>
</tr>
<tr>
<td>Pentachlorophenol C₆Cl₅OH</td>
<td>PCP, Dowside 7, Permacide, Permagard, Pentakil</td>
<td>Organochlorine fungicide</td>
<td>Colourless to white crystalline solid with benzene-like odour</td>
<td>Possible carcinogen, eye, skin, nose, throat irritant, liver and kidney damage</td>
<td>Glove, safety glasses</td>
<td>Inhalation, ingestion, skin, eye</td>
</tr>
<tr>
<td>Permethrin C₂₁H₂₀Cl₃O₃</td>
<td>Ambush, Ectban, Pounce, Nix Dragnet, Spartan</td>
<td>Pyrethroid insecticide</td>
<td>Odourless colourless crystalline solid or pale brown viscous liquid</td>
<td>Eye, skin, respiratory irritant, affect central nervous system</td>
<td>Gloves, face shield</td>
<td>Inhalation, ingestion, skin</td>
</tr>
<tr>
<td>Rozol (Chlorophacinone) C₂₃H₁₅ClO₃</td>
<td>Amvac, Romix special, Mouse seed®</td>
<td>Rodenticide</td>
<td>Bluish green solid, odourless</td>
<td>Skin, eye irritant, may affect liver</td>
<td>Gloves</td>
<td>Ingestion</td>
</tr>
<tr>
<td>Thymol C₁₀H₁₄O</td>
<td>6-isopropyl-m-cresol</td>
<td>Fumigant</td>
<td>White crystal, aromatic odour, combustible</td>
<td>Skin and eye irritant</td>
<td>Mask, respirator, rubble gloves, safety glasses</td>
<td>Inhalation, ingestion, skin</td>
</tr>
</tbody>
</table>

Table 3.1. Specific physical properties of selected representative pesticides
4. Chemical properties of pesticides

Following the release of pesticides in the environment, they undergo a complex series of interdependent processes that are collectively called chemodynamics of pesticides. The chemodynamic processes that a pesticide undergoes is essentially determined by its inherent physico-chemical properties and partly by environmental parameters such as pH, temperature, moisture, precipitation, salinity, light intensity and topography. The major chemodynamic processes that determine the pesticides persistence, distribution and their ultimate fate in the environment include transportation, retention, degradation and biota uptake. Among all these chemodynamic processes, degradation is of much relevance with regard to this section as it entails the chemical transformations of pesticides in the environment, hence chemical properties of pesticides.

Degradation of pesticides is the breakdown or chemical transformation of pesticide molecules into other forms that are not necessarily simpler and less toxic compared to the parent molecule. In some cases the degradation products are also toxic and have some pesticidal effects as well. A good example of this is the degradation of DDT to DDD, which is itself a pesticide. The rate of degradation of pesticides is usually measured in terms of half-life ($t_{1/2}$), which is the time required for the depletion of half (or 50%) of the amount of pesticide present initially. The degradation processes that bring about pesticides transformation can be categorized into two major groups; chemical degradation and biological degradation. Chemical degradation generally occur in water or atmosphere and it follows one of four reactions namely; oxidation, reduction, hydrolysis and photolysis. Biological degradation generally occurs in soil and in living organisms and it utilizes one of four reaction; oxidation, reduction, hydrolysis and conjugation. The type of the reaction in which a pesticide undergoes is largely determined by the pesticide inherent phyco-chemical properties and the environmental compartment (water, soil, air, biota) in which it is hosted.

4.1 Oxidation reaction of pesticides

Oxidation of pesticides is a reaction process whereby the dissolved oxygen in the environment reacts with pesticides. This oxidation process can also be achieved by Singlet oxygen, ozone, hydrogen, peroxide, or other hydroxy radicals. Hydroxy radical ($\cdot$OH) are the primary agents that bring about chemical oxidation of pesticides in water or atmosphere. The radical can be formed from either the pesticides or from other molecules in the environment. $p,p^\prime$-DDT for example undergoes both reduction as well as oxidation reactions in the soil under the aid of Enterobacter aerogenes microorganisms in the presence of UV light and/or iron catalyst to form reduced products; $p,p^\prime$-DDE and $p,p^\prime$-DDD as well as oxidized derivative which ultmately form $p,p^\prime$-dichlorobenzophenone.
4.2 Reduction reaction of pesticides
Reduction of pesticides is a chemical reaction in which the substrate (pesticide) undergoes a reduction in oxidation state. The reducing agents in the environment are usually +H. For example, malathion undergoes a reduction reaction in acidic aquatic environment which proceed by the substitution of one of the ethyl group with +H resulting into the formation of two functional isomeric molecules of malathion monoacid at the end of one half life. However, malathion diacid would be the product at extended reaction time (Wolfe et al, 1977).

\[
\begin{align*}
\text{malathion} & \rightarrow (\text{CH}_3\text{O}_2)\text{P} - \text{S} - \text{CH}_2\text{COOC}_2\text{H}_5 + (\text{CH}_3\text{O}_2)\text{P} - \text{S} - \text{CH}_2\text{COOH} + (\text{CH}_3\text{O}_2)\text{P} - \text{S} - \text{CH}_2\text{COOH} \\
\end{align*}
\]

4.3 Hydrolysis reaction of pesticides
Hydrolysis is a pH dependent reaction in which pesticides react with water (i.e. Hydrogen ion and hydroxy ion). Hydrolysis is one of the most common reactions that most pesticides undergo in the environment. Most organophosphates and carbamates have particularly shown to be highly responsive to hydrolysis reaction under alkaline condition. A pesticide that is very soluble in water will tend not to accumulate in soil or biota because of its stronger polar nature. This suggest that it will degrade via hydrolysis which is the reaction that is favoured in water. The following example shows the hydrolysis of atrazine in water.

\[
\begin{align*}
\text{Cl} & \quad \text{H}_2\text{O} \\
\text{C}_6\text{H}_7\text{HN} & \quad \text{OH} \\
\text{N} & \quad \text{N} \\
\text{N} & \quad \text{N} \\
\text{NH}_2\text{C}_2\text{H}_5 & \quad \text{NH}_2\text{C}_2\text{H}_5 \\
\end{align*}
\]

4.4 Photodegradation of pesticides
Photodegradation or photolysis is the breakdown or transformation of pesticides by sunlight that causes a rupture of chemical bonds. The organic molecule absorbs photons and become excited with the ensuing release of electron thus changing the molecule. Photolysis reactions are important for degrading organic molecules in the upper atmosphere, in shallow aquatic environment, on foliage and on the surface of soils. Pyrethrroids are particularly susceptible to photolysis reactions. The total decomposition of a pesticide in the
air can take several steps which is illustrated by the following photo-decomposition of parathion (Linde 1994).

4.5 Biodegradation
Biodegradation is the breakdown or transformation of pesticides by microbial agents which normally occurs in water and soil. The rate of microbial degradation depends highly on the amount and nature of pesticides present in the soil, the microbial population in the soil and soil conditions that favours microbial activities, such as warm temperature, favourable pH, adequate soil moisture, aeration and high organic matter content. The microorganisms participating in biodegradation include fungi, bacteria and other microorganisms that use pesticides as their substrate. Pyrethroids, organophosphates and some carbamates have been found to be more susceptible to biodegradation. However, most organochlorines have shown to be formidable to biodegradation due to the strength of C-Cl bond. The following is a example of microbial degradation of 2,4-D. The microbial degradation of 2,4-D can follow different pathways depending on the types of microbes present. Path “a” occurs when the bacteria Flavobacterina and Arthrobacter sp are present. Path “b” occurs when the fungus Aspergillus Niger is present (Linde, 1994).
Furthermore, oxidation process in the environment is brought about by mixed function oxidases (MFO). MFO is a complex enzymatic system which contains an enzyme called cytochrome P-450 that is responsible for the oxidation of lipophilic compounds (Garvish, 1999). Enzymatic oxidation of parathion for example is achieved by mixed function oxidases (MFO) which involve conversion of P=S to P=O to form paraoxon which is further hydrolyzed to phosphoric acid and p-nitrophenol.

5. References
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Linde, C. D. (1994). Physico-Chemical Properties and Environmental Fate of Pesticides, Environmental Hazards Assessment Program, California, USA
Garvish, J. F (1999)., Introduction to Boitransformation, Texas University Press, USA,
The book offers a professional look on the recent achievements and emerging trends in pesticides analysis, including pesticides identification and characterization. The 20 chapters are organized in three sections. The first book section addresses issues associated with pesticides classification, pesticides properties and environmental risks, and pesticides safe management, and provides a general overview on the advanced chromatographic and sensors- and biosensors-based methods for pesticides determination. The second book section is specially devoted to the chromatographic pesticides quantification, including sample preparation. The basic principles of the modern extraction techniques, such as: accelerated solvent extraction, supercritical fluid extraction, microwave assisted extraction, solid phase extraction, solid phase microextraction, matrix solid phase dispersion extraction, cloud point extraction, and QuEChERS are comprehensively described and critically evaluated. The third book section describes some alternative analytical approaches to the conventional methods of pesticides determination. These include voltammetric techniques making use of electrochemical sensors and biosensors, and solid-phase spectrometry combined with flow-injection analysis applying flow-based optosensors.

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