COURSE
GUIDE

EMT 308
ENVIRONMENTAL ASPECTS OF PESTICIDE AND OTHER TOXICANTS USE

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UNIT 1 MOVEMENT AND ABSORPTION OF PESTICIDES IN SOIL

CONTENTS

1.0 INTRODUCTION

A pesticide is a toxic chemical substance or a mixture of substances or biological agents that are intentionally released into the environment in order to avert, deter, control and/or kill and destroy populations of insects, weeds, rodents, fungi and other harmful pests. Different pesticides have been used for crop protection for centuries (Imadi *et al.*, 2015). Pesticides released into the soil environment are subjected to various reactions with soil and environmental processes including adsorption, transfer and degradation. Transfer refers to processes that move the pesticides away from their target sites. These processes include volatilization, spray drift, runoff, leaching, absorption and crop removal. This unit intends to explain the movement and absorption of pesticides in soil.

2.0 OBJECTIVES

By the end of this module, you should be able to:

- explain the behaviour and fate of pesticides in soil.
- differentiate among the processes of pesticide dissipation
- outline the different types of pesticide degradation mechanisms.

3.0 MAIN CONTENT

3.1 Fate and Behaviour of Pesticides in Soil

Pesticides reaching the soil are subjected to diverse processes that sometimes may be beneficial in terms of control of target pests. For example, the leaching of some herbicides into the root zone can give better weed control. Conversely, releasing pesticides into the environment sometimes can be quite harmful, as not the entire applied chemical reaches the target site. For example, runoff can move a herbicide away from target weeds resulting in wastage of chemical and poor weed control as well as in more chance of damaging other plants and polluting soil and water. In addition, some of the pesticide may drift downward and outside of the application site. The fate processes of pesticides fall into three major types: adsorption, transfer, and degradation.

3.1.1 Adsorption

The adsorption process binds pesticides to soil particles and it often occurs because of the attraction between a chemical and soil particles. For example, positively charged pesticide molecules are attracted to and can bind to negatively charged clay particles. Adsorption of herbicides to soil colloids occurs due to the attraction between charges on soil colloid surfaces and herbicide molecule. In most situations, the charges are relatively weak and thus the process is reversible. An equilibrium is reached between the amount of herbicide bound to colloids and that found in solution (Hartzler, 2018). A number of factors influence pesticide adsorption. Soils rich in organic matter or clay are more adsorptive than coarse, sandy soils, partly because a clay or organic soil has more particle surface area, or more sites onto which particles can bind. Adsorption is also affected by soil moisture content. Dry soils tend to adsorb more pesticide than wet soils because water molecules compete with the pesticide for the binding sites.

Adsorption to soil particles varies amongst pesticides. For example, paraquat and glyphosate bind very tightly, whereas others bind only weakly and are readily desorbed or released back into soil solution. Reduced pest control could be a problem arising from pesticide adsorption. For example, weeds may not be controlled if a herbicide is held too tightly to soil particles and cannot be taken up by the roots of the target weeds. Some pesticide labels recommend higher application rates when the pesticide is applied to adsorptive soils. Plant injury can be another problem resulting from adsorption of pesticides to soil particles. Injury can result if a pesticide used for one crop is subsequently released from the soil in amounts large enough to cause injury to a sensitive rotational crop. This pesticide ‘carry-over’ can also culminate in the presence of illegal residues on rotational food or feed crops.

Adsorption is particularly important because it influences whether other processes are able to affect pesticides.

3.1.2 Pesticide Transfer

Pesticide transfer is sometimes necessary for pest control. For instance, certain preemergence herbicides need to move within the soil to reach germinating weed seeds for them to be effective. However, too much movement can move a pesticide away from the target pest. This can culminate in reduced pest control, contamination of surface water and groundwater, and injury of nontarget species, including humans. Five ways through which pesticides can be transferred are volatilization, runoff, leaching, absorption or uptake, and crop removal.

3.1.2.1 Volatilization

The conversion of a solid or liquid into a gas is called volatilization. A pesticide, once volatilized, can move in air currents away from the treated surface. An important factor that determines whether a pesticide will volatilize is vapour pressure. The higher the vapour pressure, the more volatile the pesticide.

Environmental factors that tend to increase volatilization include high temperature, low relative humidity, and air movement. A pesticide tightly adsorbed to soil particles is less likely to volatilize, thus soil conditions such as texture, organic matter content, and moisture can thus influence pesticide volatilization.

Volatilization can culminate in reduced control of the target pest as less pesticide remains at the target site. Vapour drift, the movement of pesticide vapours or gases in the atmosphere can lead to injury of nontarget species. For example, herbicide vapours can injure nontarget plants.

Pesticide volatilization can be reduced by avoiding the application of volatile pesticides when conditions are unfavourable, such as very hot, dry days or when the soils are wet. Labels on pesticide containers often provide warnings if there is a volatility hazard under certain conditions. Labels for volatile pesticides may suggest incorporating the pesticide into the soil by tillage or irrigation during or shortly after application. This helps to reduce the amount of exposed pesticide on the soil surface, thereby reducing volatilization. Low-volatile formulations are available for some pesticides.

3.1.2.2 Runoff

Runoff refers to the movement of water over a sloping surface. This occurs when water is applied faster than it can enter the soil. Pesticides can be transported in the water itself or bound to eroding soil particles. The magnitude of pesticide runoff depends on the slope or gradient of an area; the erodibility, texture and moisture content of the soil; and the amount and timing of rainfall and irrigation. Ordinarily, pesticide runoff is greatest when a heavy or sustained rain follows application. Over-irrigation can result in excess surface water as well as in pesticide runoff, particularly when an irrigation system is used to apply a pesticide.

The movement of runoff water tends to be slowed down by vegetation or crop residue. Certain physicochemical properties of the pesticide, such as how quickly plants absorb it or how tightly it is bound to plant tissue or soil, are also important.

Herbicide runoff can result in direct injury to nontarget plants. Insecticide and nematicide runoff into surface waters such as streams and ponds can be particularly harmful to aquatic organisms. Pesticide runoff also can lead to groundwater contamination and can cause injury to crops, livestock or humans if the contaminated is used downstream.

Practices to mitigate pesticide runoff include monitoring of weather conditions, careful application of irrigation water, using a spray mix additive to enhance pesticide retention on foliage, and incorporating the pesticide into the soil. Reduced-tillage cropping systems and surface grading, in addition to contour planting and strip cropping of untreated vegetation, can slow the movement of runoff water and help keep it out of wells, sinkholes, water bodies and other sensitive areas (Fishel, 2003).

3.1.2.3 Leaching

Leaching occurs when pesticides move through the soil rather than over the surface. Leaching is governed partly by the pesticide's physicochemical properties. For example, a pesticide held strongly to soil particles by adsorption is less likely to leach. Solubility is another factor influencing leaching. A pesticide that dissolves in water can move with water in the soil. Furthermore, the persistence of a pesticide also influences the likelihood of leaching. A pesticide that is rapidly broken down by a degradation process is less likely to leach because it may remain in the soil only a short time.

Soil factors influencing leaching include texture and organic matter partly because of their effect on pesticide adsorption. Another important factor is soil permeability that indicates how readily water moves through the soil. Soil permeability is directly related to leaching because the more permeable a soil, the greater propensity for pesticide leaching. For example, a sandy soil is much more permeable than a clay soil.

Pesticide leaching also can be influenced by the method and rate of application, the use of tillage systems modifying soil conditions, and the amount and timing of water a treated area receives after application. Ordinarily, the closer the time of application to a heavy or sustained rainfall, the greater the likelihood that some pesticide leaching will occur.

A certain amount of leaching may be essential for control of a target pest. Nevertheless, too much leaching can result in reduced pest control, injury of nontarget species and groundwater contamination.

Pesticide leaching also can be mitigated by monitoring weather conditions and the amount and timing of irrigation. Proper pesticide selection is vital because those pesticides that are not readily adsorbed, not rapidly degraded, and highly water-soluble are the most prone to leaching. Prior to pesticide application, labels must be read carefully for instructions on the rates, timing and methods of application. The label may also advise against applying the pesticide when certain soil, geologic or climatic conditions present. Pesticides can leach not only through the soil to groundwater from storage, mixing, equipment cleaning and disposal areas but also from normal applications.

3.1.2.4 Absorption or Uptake

Absorption or uptake refers to the movement of pesticides into plants and animals. Absorption of pesticides by target and nontarget organisms is influenced by environmental conditions and by the physicochemical properties of the pesticide and the soil. For example, a large portion of herbicide present in the soil is bound to soil colloids (clay, organic matter), and this herbicide is less readily available to plants than the herbicide present in the soil solution. Conditions that favour movement of the herbicide into soil solution tend to increase absorption by plants (Hartzler, 2018). Pesticides may be broken down or they may remain in the plant until tissue decay or harvest after plants absorb them.

3.1.2.5 Crop Removal

The presence of pesticides in soil may lead to their residues in plants grown in contaminated soil although the rate of uptake may differ for pesticides that are equally persistent. Accumulation of a pesticide in a plant is usually dependent upon the concentration of the residues in the soil. The total amount of the pesticide in plant may increase with time if the compound is long-lived (Khan, 1980). Crop removal transfers pesticides and their metabolites from the treatment site. Most harvested food commodities are subjected to washing and processing procedures that remove or degrade much of the remaining pesticide residue (Fishel, 2003).

3.1.3 Degradation

As soon as a pesticide is applied, it begins to break down or degrade into simpler compounds, which are usually less toxic. Each pesticide has its own speed of degradation, which depends on the active ingredient, the formulation, and environmental conditions. There are both advantages and disadvantages to a long degradation time. The longer a pesticide takes to break down, the longer it is present to control the insect, weed, or disease for which it was applied. This is called *residual activity*. One disadvantage of extended residual activity, or persistence, is that the pesticide may also be available for leaching or runoff over a longer period. Three types of pesticide degradation are microbial, chemical, and photodegradation.

3.1.3.1 Microbial Degradation

Microbial degradation is the breakdown of pesticides by fungi, bacteria, and other microorganisms utilizing pesticides as a food source. Most microbial degradation of pesticides occurs in the soil. The rate of microbial degradation is affected by soil conditions such as moisture, temperature, aeration, pH, and the amount of organic matter affect, because of their direct influence on microbial growth and activity.

Another factor that can influence microbial degradation is the frequency of pesticide application. Rapid microbial degradation is more likely when the same pesticide is used repeatedly in a field. Repeated applications can actually stimulate the buildup of organisms capable of effectively degrading the pesticide. The amount of pesticide available for pest control is reduced as the population of these organisms increases and degradation accelerates. In extreme cases, accelerated microbial degradation has been responsible for certain products being withdrawn from the market. The effectiveness of these chemicals is greatly reduced by microorganisms soon after application.

To reduce the possibility of very rapid pesticide breakdown is by using pesticides only when required and by avoiding repeated applications of the same pesticide. In order to minimize the potential for microbial degradation problems as well as for pest resistance, it is necessary to alternate between different classes, groups or formulations of pesticides.

3.1.3.2 Chemical Degradation

Chemical degradation is the breakdown of pesticides by processes not involving microorganisms. In addition to the physicochemical properties of the pesticide, temperature, moisture, pH and adsorption determine the chemical reactions that take place and how they quickly proceed.

Hydrolysis, a breakdown process involving the reaction of a pesticide reacts with water, is one of the most common pesticide degradation reactions. A large number of organophosphate and carbamate insects are particularly susceptible to hydrolysis under alkaline conditions. In fact, some are actually broken down in a matter of hours when mixed with alkaline water.

Instructions on product labels may indicate warning against mixing a pesticide with certain fertilizers, other pesticides or water with specific characteristics. Pesticide degradation and potential incompatibility problems can be prevented by observing these precautions. Buffers or other additives may be available to modify spray mix conditions and prevent or reduce degradation in some situations. By not allowing a spray mix to remain in a spray tank for a long period, pesticide degradation and possible corrosion of application equipment can be avoided.

3.1.3.3 Photodegradation

The breakdown of pesticides by light, particularly sunlight is termed photodegradation. Pesticides on foliage, on soil surface, and even in the air can be degraded through photodegradation.

Factors affecting pesticide degradation include the intensity of the sunlight, properties of the application site, the application method and the properties of the pesticide. By incorporating the pesticide into the soil during or immediately after application, pesticide losses from photodegradation can be minimized.

4.0 CONCLUSION

The understanding of fate and behaviour of pesticides in soil will enable agriculturists to fit pesticides to soil types and avoid the unpleasant consequences of ineffective control of target pests and environmental pollution.

5.0 SUMMARY

In this module, we have learnt that:

i. The factors influencing the availability of a pesticide in the soil determine how effective a treatment will be.
ii. The understanding of pesticide behaviour in soil is useful in diagnosing performance problems in the field; and
iii. The differences in chemical characteristics among pesticides are relatively small, and therefore soil type and environment will exert a greater impact on performance than does the specific pesticide applied.

6.0 TUTOR MARKED ASSIGNMENTS

1. Explain the following processes as they relate to pesticide transfer in the soil: volatilization, leaching, runoff, absorption, and crop removal.
2. Outline the various types of pesticide degradation mechanisms.

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UNIT 2 FACTORS AFFECTING THE MOBILITY OF PESTICIDES IN SOIL

CONTENTS

1.0 INTRODUCTION

Pesticide mobility may result in redistribution within the application site or movement of some amount of the pesticide off site. Following the application of a pesticide, it may: (i) attach to soil particles, vegetation, or other surfaces and remain near the site of deposition, (ii) attach to soil particles and move with eroded soil in runoff or wind, (iii) dissolve in water and be taken up by plants, move in runoff, or leach, (iv) volatilize or erode from foliage or soil with wind and become airborne (Tyriaki and Temur, 2010). Pesticide mobility is affected by its sorption, water solubility, vapour pressure, and other environmental and site characteristics including weather, topography, canopy and ground cover; and soil organic matter, texture and structure (Kerle *et al.*, 2007).

2.0 OBJECTIVE

By the end of this unit, you should be able to:

- outline the factors affecting pesticide mobility in soil;
- explain the soil properties affecting pesticide movement ;
- explain the site conditions affecting pesticide movement;
- outline the management practices that affect pesticide mobility in soil.

3.0 MAIN CONTENT

3.1 Pesticide Properties Affecting Its Mobility

To reduce the risk of contaminating the groundwater, it is essential to understand the factors that control the mobility of pesticides in the soil. The mobility of pesticides in the soil is not determined by a single property of the pesticide but controlled by a combination of properties including water solubility, adsorptivity, volatility, and pesticide half-life. The first two properties determine how much of the pesticide will be bound versus free, whereas the half-life relates to the persistence of the pesticide.

3.1.1. Water Solubility

Water solubility is a measurement of how much of a chemical will dissolve in water, and typically is expressed in parts per million (Hartzler, 2018). It is perhaps the single most important property influencing a pesticide’s movement with water. When a pesticide enters soil, some of it will stick to soil particles, particularly organic matter, through a process called sorption and some will dissolve and mix with the water between soil particles, called “soil water.” As more water enters the soil through rain or irrigation, the sorbed pesticide molecules may be detached from soil particles through a process called desorption. The solubility of a pesticide and its sorption on soil are inversely related, meaning that increased solubility results in less sorption. The partition coefficient (K_{oc}) is one of the most useful indices for quantifying pesticide sorption on soils. The K_{oc} value is defined as the ratio of pesticide concentration in the sorbed-state (that is, bound to soil particles) and the solution-phase (that is, dissolved in the soil-water). Thus, for a given amount of pesticide applied, the smaller the K_{oc} value, the greater the concentration of pesticide in solution. Pesticides with small K_{oc} values are more likely to be leached compared to those with large K_{oc} values (Rao and Hornsby, 2001). In other words, the higher the water solubility value, the more soluble the chemical. For example, a pesticide with a water-solubility value of 33,000 ppm at 27°C is much more water-soluble than a pesticide with a water-solubility of 33 ppm at 27°C, and it is more likely to leach.

3.1.2 Adsorptivity

Adsorptivity is the electrical attraction between a chemical compound and soil. Pesticides strongly adsorbed to soil particles usually remain in the root zone, where they can be absorbed by plants or degrade. Weakly adsorbed pesticides move down through the soil profile with rain or irrigation water. The amount of adsorption depends upon a pesticide's chemical properties, its concentration in the soil water, and on the soil type and its holding potential.

3.1.3 Volatility

Volatility is the tendency for a liquid or a solid to change into a gas. Volatility measures how quickly a pesticide evaporates in air. Highly volatile pesticides vaporize into the atmosphere, thus reducing the leaching potential. Some pesticides, such as fumigants, must be volatile in order to move and provide uniform distribution through the soil profile. However, placing or sealing a pesticide in the soil reduces volatilization and increases leaching potential.

3.1.4 Pesticide Half-Life

The half-life of a pesticide describes the length of time it takes 50% of the pesticide to break down to secondary compounds. For example, if one kilogram of a product with a half-life of 90 days is applied, we would expect 0.5 kg to remain 90 days after application. After another 90 days, 0.25 kg should be left in the field. The half-life of a herbicide varies with soil characteristics and environment. For example, the half-life of atrazine in Georgia (USA) on a soil with a pH of 6.8 was reported to be 39 days, whereas in Minnesota (USA) the half-life was 261 days on a soil with 7.9 pH. It is important to ensure that half-lives were determined under similar conditions when comparing half-lives of different herbicides (Hartzler, 2018). In general, the longer the half-life, the greater the potential for pesticide movement. A pesticide with a half-life greater than 21 days may persist long enough to leach or move with surface runoff before it degrades.

3.2 Soil Properties Affecting Pesticide Mobility in Soil

Soil properties exert significant influences on the fate and transport of pesticides in croplands. Pesticide movement in soil is largely controlled by several factors including soil texture, soil moisture, organic matter, and soil pH.

3.2.1 Soil Texture

Soil texture describes the relative percentage of sand, silt and clay. Soil permeability, which is a measure of how fast water can move vertically through the soil, is affected by soil texture. Soils with coarse sandy textures are generally more permeable. Soils with higher permeability have greater potential for ground-water contamination than less permeable soils. Finer-textured clay soils have much more surface area, more adsorptivity, and limit pesticide and water movement better than sandy soils do.

3.2.2 Soil Moisture

Soil moisture affects how fast water can travel through the soil. If soils are already wet or saturated before rainfall or irrigation, excess moisture will runoff. Soil moisture also influences pesticide breakdown. Pesticide degradation is slow in dry soils. The rate of pesticide transformation generally increases with water content. In very wet soils, such as rice paddies, the rate of diffusion of atmospheric oxygen into the soil is limited and anaerobic pesticide transformation can prevail over aerobic degradation. Poor oxygen transfer at high moisture content can, however, accelerate or retard the degradation of pesticides (Pal *et al.*, 2006).

3.2.3 Soil Structure

Soil structure is another property that reflects the manner in which soil particles are aggregated and cemented. A soil with a weak structure is more likely to be eroded and have lower infiltration rates, and hence, sorbed pesticides are more likely to be discharged through runoff. Recent evidence indicates that at times soil macropores and cracks have a major effect on the movement of pesticides in soils (National Academy of Sciences, 2018). Macropores are formed by earthworms and decayed root systems, while cracks are formed by soil shrinkage. Under particular water application rate conditions, both water and chemicals in the dissolved and particulate forms tend to preferentially move through the macropores and cracks and reach the water table in a shorter period.

3.2.4 Organic Matter

Organic matter is the single most important factor affecting adsorption of pesticides in soils. Organic matter content of soils may be increased by the addition of manure and incorporation of crop residues. Many pesticides are adsorbed (bound) by soil organic matter, which reduces their rate of downward movement. Soils high in organic matter tend to hold more water, which may make less water available for leaching.

3.2.5 Soil pH

Soil pH can have a significant effect on the adsorption and therefore on mobility of many pesticides, particularly herbicides. pH is a measure of the availability of hydrogen ions (H^+) in a solution. As the pH decreases below 7 (acid conditions), the concentration of hydrogen ions found in the solution increases. Many herbicides can incorporate hydrogen ions into their molecular structure, therefore changing the charge of the herbicide molecule. At soil pH’s below 7, atrazine may pick up hydrogen ions from the soil solution causing the atrazine to take on a positive charge. The positive charge on the atrazine molecule under acid conditions increases the attraction between the herbicide molecule and negatively charged soil colloids. At soil pH’s above 7 most of the atrazine maintains a neutral charge and thus the herbicide is less tightly adsorbed and more available to plants (Hartzler, 2018).

3.3 Site Conditions Affecting the Mobility of Pesticides in Soil

The site conditions affecting the mobility of pesticides in the soil include groundwater table, hydrogeologic conditions, and climatic and weather conditions.

Generally, the groundwater table is shallower in humid regions than in regions that are more arid. A shallow depth to the groundwater offers fewer opportunities for pesticide sorption and degradation. The travel time of the pesticide to the water table may range from days to a week if the depth to the water table is shallow, and soil is permeable, and the amount of rainfall exceeds the water-holding capacity of the soil. In contrast, the travel time may be about decades in arid regions where the water table is tens of meters below the land surface.

Hydrogeologic conditions (underground plumbing) beneath the soil profile may dictate the direction and rate of chemical movement. The presence of impermeable lenses or layers in the soil profile and underlying strata may limit the vertical movement of pesticides. Such impermeable layers may, however, contribute to the lateral flow of shallow groundwaters and to the eventual discharge of groundwaters and its contaminants into surface waters. On the contrary, the presence of high-permeability earth materials such as sands and gravel may greatly accelerate the vertical and horizontal flows of contaminants. Of particular concern is the presence of karsts (limestone) and fractured geologic materials that generally transmit water and chemicals rapidly to the groundwater body.

Climatic and weather conditions other than rainfall may also influence the mobility of pesticides. Warmer temperatures tend to accelerate physical, chemical, and biological processes such as volatility, water solubility, and microbial degradation, respectively. High winds and high evaporation rates may accelerate volatilization and other processes that contribute to gaseous losses of pesticides (National Academy of Sciences, 2018).

3.4 Management Practices Affecting the Mobility of Pesticides in Soil

Irrigation and management practices such as the rate and timing of pesticide applications and the mode of pesticide application also affect pesticide transport processes. The recommended practices include pesticide use only when and where it is necessary and in amounts adequate to control pests. When applying pesticides, the directions on the labels should be carefully followed to minimize harmful effects to the applicator as well as potential losses to the environment. Pesticide users should select pesticides that are less likely to leach. Irrigation should be avoided shortly after pesticide application to reduce losses through runoff and leaching. The best management practices for pesticide use are location and crop specific.

4.0 CONCLUSION

From the above, it can be concluded that it is imperative to understand the diverse factors controlling the mobility of pesticides in the soil to achieve effective and efficient pest control while reducing the risk of groundwater contamination.

5.0 SUMMARY

In this unit we have learnt that:

i. The mobility of pesticides in the soil is not determined by a single property of the pesticide but controlled by a combination of properties including water solubility, adsorptivity, volatility, and pesticide half-life.
ii. Pesticide movement in soil is largely controlled by several factors including soil texture, soil moisture, organic matter, and soil pH;
iii The site conditions affecting the mobility of pesticides in the soil include groundwater table, hydrogeologic conditions, and climatic and weather conditions; and
iv. Irrigation and management practices such as the rate and timing of pesticide applications and the mode of pesticide application also affect pesticide transport processes.

6.0 TUTOR-MARKED ASSIGNMENTS

1. Outline the various soil properties affecting pesticide mobility in the soil.
2. Explain how pesticide mobility in soil is affected by water solubility and adsorptivity.

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UNIT 3 FACTORS AFFECTING THE MOBILITY OF OTHER TOXICANTS IN SOIL

CONTENTS

1.0 INTRODUCTION

Large application of fertilizers has been practiced on arable lands to improve crop production and recover inherent and induced soil nutrient deficiency (Kassir *et al*., 2012). Contamination of agricultural soils with trace elements, such as cadmium (Cd), lead (Pb), zinc (Zn) and copper (Cu), and with fluorine can occur as these elements are transferred during manufacturing from phosphate rock to phosphate fertilizers (Camelo *et al*., 1997). The accumulation of heavy metals in soil is of interest because of the adverse effect heavy metals may pose to food quality, soil health and the environment (Butkowska *et al*., 2015). While Cd and Pb are considered nonessential and toxic elements having no specific biological functions, Zn and Cu are micronutrients that could become toxic when exceeding certain limits (Kassir *et al*., 2012).

2.0 OBJECTIVE

By the end of this unit, you should be able to:

- understand the factors affecting the mobility of other toxicants, such as trace elements in soil;
- explain how trace element mobility is affected by soil pH and organic matter;
- understand how trace element mobility is influenced by clay content and soil structure.

3.0 MAIN CONTENT

3.1 Factors Affecting the Mobility of Trace Elements in Soils

The mobility of trace elements in soils depends on their interactions between the solid and liquid phases, which determine their partitioning. The underlying mechanisms regulating the partitioning of these trace elements include physicochemical and biological processes, which in turn are controlled by several factors including soil pH, chemical speciation, soil organic matter, fertilizer and soil amendments, redox potential, clay content and soil structure.

3.1.1 Soil pH

It is generally viewed that pH is the main variable controlling the solubility, mobility and transport of trace elements, as it controls metal hydroxide, carbonate and phosphate solubility (Carrillo-Gonzalez *et al*., 2006).

Soil pH controls the movement of trace elements from one soil compartment to another, since trace elements can be held in lattice of secondary minerals (1:1 and 2:1 clay minerals), adsorbed on Fe and Mn oxides, and carbonates, or precipitated as carbonates. For instance, while Maskall and Thornton (1998) found increases in the proportion of readily mobile form of Pb and Zn as pH fell below 5, Cattlet *et al.* (2002) observed a decrease of the Zn^{2+} activity in the soil solution as pH increased. They concluded that the organic matter adsorption and the formation of franklinite accounted for this trend (Carrillo-Gonzalez *et al*., 2006).

Many soil processes including trace element sorption are affected by soil pH. Cadmium sorption was observed to double for each 0.5 increase in pH from 3.8 to 4.9 (Boekhold *et al.*, 1993). In sandy soils, a unit increase in pH produced a 2- to 10-fold increase in ion sorption.. Nickel removal from the soil solution by pyrophyllite increased strongly when pH went from 6 to 7.5, or even higher (Scheidegger *et al.*, 1996). While the retention and release varied little for various cationic elements, they manifested large differences for those trace elements that form anionic chemical species such as As, Cr, or Se. The concentration of arsenate in solution, that is, the predominant inorganic species of As decreased at low pH because of its adsorption (Manning and Golberg, 1996). An increase was observed in the concentrations of As, Se, Mo, Cr, Sb, and U in soil solutions with increasing pH (Tyler and Olsson, 2001).

While the solubility of naturally occurring Cd and Zn from mineral soils depends upon pH, in some situations dissolved concentrations of Cd, Cu, and other elements, such as Pb, may not follow a single relationship with pH for polluted soils (Carrillo-Gonzalez *et al.*, 2006).

3.1.2 Chemical Speciation

Although the total trace element content determines the extent of elemental partitioning between the aqueous and solid phases in soils, the chemical speciation is likely one of the most important factors that influences trace element availability, solubility, and mobility (Carrillo-Gonzalez *et al.*, 2006). Trace element ions can combine with organic and inorganic ligands or substances in soil solution or in the rhizosphere. The ligands can be hydroxyl, carbonates, sulfate, nitrate, chloride, dissolved organic matter, or chelating agents. The distribution of metal ion species is apparently controlled by redox reactions, pH, and solubility of hydroxides, carbonates, oxides, and sulfides. Ion pairs, soluble metal-organic ligand complexes, and chelation are the three kinds of soluble complexes that can be formed between metal ions and ligands (Gao *et al.*, 2003). The first type is a weak electrostatic association while the second is a strong association that includes covalent bonding.

Trace element mobility is strongly restricted by carbonates in calcareous soils, presumably because of chemisorption or precipitation. However, the presence of humic acids increases Cd, Co, Cu, and Zn adsorption even at low pH, while at high pH they reduced the precipitation of trace elements, apparently due to the formation of metal humate species (Sparks *et al*., 1997a,b).

The stability of the metal-organic matter complexes is influenced by pH. Copper, Pb, and Cr form stable complexes, while Cu complexes dissociate at low pH. The association of trace elements to ligands in the soil is controlled by pH, with the ligand species ionic concentration increasing with higher pH (Carrillo-Gonzalez *et al*., 2006).

3.1.3 Soil Organic Matter

Organic matter (OM) can play a dual role in trace elements solubility (Carrillo-Gonzalez *et al*., 2006). Particulate OM, by virtue of its high cation exchange capacity (CEC), can effectively adsorb trace elements. High-molecular-weight organic compounds can also bind and strip trace elements from the solution, because they can be insoluble and therefore semi-immobile (Schmitt *et al*, 2002). Taylor and Theng (1995) reported that humic acids can increase Cd retention on kaolinite four times and the formation of stable organo-metallic complexes can lead to relatively lower mobility of Cu, Pb, Ni, Zn, and Cd.

It has also been observed that insoluble organic molecules reduced the availability of some elements, such as Cu or Pb, by the formation of insoluble complexes (Bataillard *et al*., 2003). Conversely, Temminghoff *et al*. (1998) found that humic acids enhanced Cu mobility, but the process was strongly affected by Ca concentration and pH of the soil solution. In general however, low-molecular-weight compounds, such as fulvic acids, could remain in the soil solution and thus increase the mobility of bound metals. It has been found that the naturally occurring DOM can increase the mobility of some elements such as Cd (Lassat, 2002). OM reduced Zn, Pb, and Fe adsorption onto kaolinite and montmorillonite at pH 5 and 7, presumably due to metal-complexes formation (Schmitt *et al*., 2002).

3.1.4 Fertilizers and Soil Amendments

Although fertilizers have been identified as a source of trace elements, the amounts of trace elements derived from fertilizers typically do not significantly increase trace element uptake by plants (Carrillo-Gonzalez *et al*., 2006). The main exception are possibly phosphate fertilizers.

According to He *et al*. (2005), phosphate rocks contain on average 11, 25, 188, 32, 10, and 239 mg kg^{-1} of As, Cd, Cr, Cu, Pb, and Zn, respectively. Cadmium is probably the main element of concern in this case since it can vary from near zero to more than 150 mg Cd kg^{-1} in some phosphate fertilizers. Cadmium is the most susceptible to be of concern in terms of crop accumulation from fertilizers and soil amendments.

Moreover, application of fertilizers can further affect soil properties related to metal availability. Ammoniacal nitrogen fertilization has been shown to decrease soil pH in the rhizosphere, which could modify trace elements (Zn, Cu, and Mn) availability. Soluble phosphate, a rock phosphate, fertilizers such as monoammonium phosphate and diammonium phosphate decrease Cd, Pb, and Zn mobility, probably due to formation of metal minerals (McGowen *et al*., 2001). However, DOM present in the solution can coat the phosphate surfaces and thus inhibit the sorption on phosphate compounds, reducing the amount and rate at which phosphate becomes available for precipitation (Carrillo-Gonzalez *et al*., 2006).

Application of limestone and alkaline waste by-products such as beringite, a modified aluminosilicate produced from the fluidized bed burning of coal refuse, to the soil has increased pH and precipitated metals. Beringite depresses trace elements mobility, apparently by precipitation, ion exchange and crystal growth (Adriano *et al*., 2004).

3.1.5 Redox Potential

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Redox processes are controlled by the aqueous free electron activity, but certain microorganisms can modify and mediate most redox reactions in aquatic and terrestrial environments. Several elements, such as As, Cr, Mn, Fe, V, Mo, and Se manifest different oxidation states in the environment. Arsenic is found in -3, 0, +3, and +5 oxidation states (Carrillo-Gonzalez *et al*., 2006). At the soil surface, oxidizing conditions are favoured, so it allows the formation of either $As_{(V)}$ or $As_{(III)}$.

However, microbial activity could promote methylation, demethylation, or change in the oxidation state, while the presence of clay minerals, Fe, Al, Mn oxides, and OM can also modify the oxidation state. The most stable As chemical species are H_3AsO_4 up to pH 2.2, H_2AsO4^- in the pH range approximately between 2 and 7, and $HAsO4^{2-}$ above pH 7.

Chromium, Hg, Se, and Mn occur in more than one oxidation state, with their solubility in the soil depending on pH and mineral content. Cr $_{(III)}$ is an essential nutrient, it has a low solubility, it is mainly trivalent, it is specifically sorbed by Fe, Mn, and clay minerals, and its concentration in solution decreases with increasing pH and soil OM content. Cr $_{(VI)}$ on the other hand is anionic, relatively soluble and rep[resents a very mobile ion. Combined with its toxicity and carcinogenicity, this element certainly warrants careful speciation to differentiate trivalent from hexavalent chromium. The mobile and reactive chemical species of mercury are Hg^0, $(CH_3)_2Hg$. Hg^{2-} and $HgXn^{2-n-}$, where X could be OH-, Cl-, Br-, or organic ligands, hence more than one oxidation state could be present in the same environmental matrix. Selenate Se $_{(VI)}$ ($HSe04^-$) is the most mobile form of Se that can be leached to groundwaters.

Manganese occurs in two oxidation states: $Mn_{(IV)}$, which is the most stable in neutral to slightly alkaline conditions, and $Mn_{(II)}$, which is stable in reducing conditions. The solubility of Mn is highly sensitive to redox conditions; under oxidizing conditions Mn is precipitated as nodules or concretions of Mn oxides, but reduction of Mn oxides increases Mn solubility. Trace elements such as Cu, Co, Cr, Ni, Pb, and Zn associate to Mn oxides through coprecipitation and substitution, so when Mn is reduced the solubility of Pb, Zn, Cu, and Ni increases (Carrillo-Gonzalez *et al.*, 2006).

3.1.6 Clay Content and Soil Structure

Soils rich in clay generally have higher retention capacity than soils with little or no clay. Cation sorption on clay minerals varies depending on clay nature and cation properties. The adsorption of Pb and Cu was higher than the adsorption of Zn, Ni, and Cd on illite, beidellite, and montmorillonite (Carrillo-Gonzalez *et al.*, 2006). Desorption followed the trend Pb>Cd>Cu>Ni>Zn for beidellite and Pb>Cd=Cu>Ni>Zn for illite and montmorillonite (Rybicka *et al.*, 1995).

Selectivity of trace element cation adsorption varies with clay minerals. Vermiculite is very effective for adsorbing Cu^{2+}, Pb^{2+}, Cd^{2+}, Zn^{2+}, and Ni, and the selectivity is greater than in montmorillonite, apparently due to more specific adsorption sites (Malla, 2002). However, selectivity changes with cations as Brigatti *et al.* (2004) reported that montmorillonite adsorbed greater amount of Hg than vermiculite. Tiller *et al.* (1984) identified three reaction types, each having different affinities for cations: (1) those concerned with iron oxides, which appeared to be controlled by metal ion hydrolysis; (2) those associated with organic colloids; and (3) those associated with 2:1 clay minerals with lower sensitivity to pH.

Main factors affecting mobility or bioavailability of trace elements in soils are given in Table I. The most important factors affecting trace elements release from soil are pH, OM including DOM, and chemical speciation, while clay content and redox potential are less important.

Table I. Effects of Soil Factors on Trace Metal Mobility and/or Bioavailability

Soil Factor	Affected Process	Effect on Process
Low pH	Decreasing sorption of cations onto oxides of Fe and Mn	Increase
	Increasing sorption of anions onto oxides of Fe and Mn	Decrease
High pH	Increasing precipitation of cations as carbonates and hydroxides	Decrease
	Increasing sorption of cations onto oxides of Fe and Mn	Decrease
	Increasing complexation of certain cations by dissolved ligands	Increase
	Increasing sorption of cations onto (solid) humus material	Decrease
	Decreasing sorption of anions	Increase
High-clay content	Increasing ion exchange for trace cations (at all pH)	Decrease
High-swelling clays	Forming structured soils, which allow bypass flow	Increase
High OM (solid)	Increasing sorption of cations onto humus material	Increase
High-(soluble) humus content	Increasing complexation for most trace cations	Decrease/increase

Competing ions	Increasing competition for sorption sites	Increase
Dissolved inorganic ligands	Increasing trace metal solubility	Increase
Fe and Mn oxides	Increasing sorption of trace cations with increasing pH	Decrease
	Increasing sorption of trace anions with decreasing pH	Decrease
Low redox	Decreasing solubility at low Eh as metal sulfides	Decrease
	Decreasing solution complexation with lower Eh	Increase/decrease

Adapted from Adriano (2001).

4.0 CONCLUSION

From the above, it can be concluded that the most important factors affecting trace elements release from soil are pH, OM including DOM, and chemical speciation, while clay content and redox potential are less important.

5.0 SUMMARY

In this unit we have learnt that:

i. pH is the main variable controlling the solubility, mobility and transport of trace elements, as it controls metal hydroxide, carbonate and phosphate solubility
ii. Trace element mobility in soil is largely controlled by several factors including soil organic matter, redox potential, soil pH, clay content and soil structure;
iii With the exception of phosphate fertilizers, the amounts of trace elements derived from fertilizers typically do not significantly increase trace element uptake by plants.
iv. Cation sorption on clay minerals varies depending on clay nature and cation properties.

6.0 TUTOR-MARKED ASSIGNMENTS

1. Outline the various soil properties affecting trace element mobility in the soil.
2. Explain how trace element mobility in soil is affected by soil organic matter and redox potential.

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UNIT 4 SOIL HERBICIDE INTERACTION AND HERBICIDE EFFICACY

CONTENTS

1.0 INTRODUCTION

Herbicides reaching the soil are subjected to various reactions with soil and environmental factors. Herbicides reach the soil through preplanting and preemergence applications, as foliage run-off from postemergence applications, and through the return of crop residues to the soil. Interactions of a herbicide with soil and environmental factors determine its immediate phytotoxicity and subsequent degradation, and hence its persistence of activity and behaviour in the soil. Persistence in soils is an important feature of a herbicide as it determines its suitability or otherwise in a particular soil or cropping situation. Herbicides that decompose too readily are less desirable in some situations as they cannot be very effective on the weeds emerging later. Conversely, herbicides with longer persistence of activity are unsuitable as their toxic residues can injure the sensitive crops grown in rotation. Thus, a herbicide which becomes more desirable in some situations may not be useful in other situations (Rao, 2011).

2.0 OBJECTIVES

By the end of this unit, students should be able to:

- understand the various herbicide adsorption mechanisms in soils;
- understand the factors affecting the adsorption of herbicides in soils;
- explain the mechanisms of herbicide transport in soil; and
- understand the relationship between soil herbicide interaction and herbicide efficacy.

3.0 MAIN CONTENT

3.1 Herbicide Adsorption Mechanisms

Adsorption of herbicides by soil particles occurs through a number of mechanisms involving varying bond strengths. It is dependent on the herbicide characteristics, soil surface characteristics and competing solutes. The strength of adsorption affects molecule mobility along the soil profile and thus, its bioactivity, persistence, biodegradation, leaching, and the volatilization process. The adsorption of an agrochemical onto the soil components can be considered as the first step towards its chemical degradation (Blasioli *et al*., 2011).

Organic molecule adsorption modeling by soils is frequently done using adsorption isotherms, which are built by measuring the residual concentrations of pollutant in aqueous solution at the equilibrium point, after the adsorption on soil of different initial concentrations. For each concentration point, the adsorbed molecule concentrations are determined by the difference between initial and equilibrium concentrations. Adsorption data are commonly fitted using two different models described by the Langmuir and Freundlich equations (Blasioli *et al.*, 2011).

The physicochemical mechanisms governing adsorption of herbicides by soil include hydrophobic partitioning, London-van der Waals forces, hydrogen bonding, cation and water bridging, anion exchange, ligand exchange, protonation, cation exchange and covalent bonding (Harper, 1994).

3.1.1 Hydrophobic partitioning

This involves partitioning of an organic chemical from the aqueous phase into the more hydrophobic organic matter. Hydrophobic partitioning is the proposed mechanism of adsorption for chemicals in the soil though it is not widely applicable for herbicides (Rao, 2011).

3.1.2 London-van der Waals forces

These are short-range bonds, resulting from a correlation in electron movement between two molecules to produce a small net electrostatic attraction. This mechanism is characterized by low heats of adsorption (20 kcal mol^{-1} or less) or low binding strength and short residence time on the adsorptive surface (1×10^{-2} s or less). This indicates that the strength of these bonds is weak and decreases with distance. The interaction is additive, however, and increases with area of contact. As a result, interactions caused by London-van der Waals forces are particularly important for neutral high molecular weight compounds (Rao, 2011).

3.1.3 Hydrogen bonding

This involves dipole-dipole interactions involving an electrostatic attraction between an electropositive hydrogen nucleus or functional groups such as –OH and –NH and exposed electron pairs on electronegative atoms such as O^- and N^- electropositive atom. These bonds are stronger than London-van der Waals forces and can be both intra- and intermolecular. Hydrogen bonding is considered to be most prevalent in the bonding of herbicides to organic surfaces in the soil.

Hydrogen bonding is a significant binding mechanism for triazines, sulfonylureas and aryloxyphenoxypropionics.

3.1.4 Cation and water bridgings

These involve complex formation between an exchangeable cation and an anionic or polar functional group on the herbicide. In cation bonding, the organic functional group displaces hydrating water molecules around the cation to form the complex. Water bridging occurs when the organic functional group is unable to displace hydrating water molecules from the cation. Water bridging is more likely to occur with the larger, high valency cations such as Fe^{3+}, Al^{3+} and Mg^{2+}. Cation and water bridging are proposed mechanisms of adsorption for fluazifop-butyl, glyphosate, and picloram (Rao, 2011).

3.1.5 Anion bonding

This is a stronger adsorption mechanism caused by an electrostatic attraction of an anion to a positively charged site on the soil surface. This mechanism becomes significant only in acidic soils containing a pH-dependent charge from kaolinite or amorphous aluminosilicates and iron oxides. Anion bonding is a predominant adsorption mechanism in herbicides having dissociated functional groups such as carboxylates.

3.1.6 Ligand exchange

This mechanism involves displacement of an inorganic hydroxyl or water molecule from a metal ion at a hydrous oxide surface by a carboxylate or hydroxyl on an organic molecule. This is the mechanism proposed for adsorption of chlorsulfuron and possibly other sulfonylurea herbicides on iron oxides.

3.1.7 Protonation

In protonation, a charge-transfer complex is formed when a functional group like an amino or carboxyl group forms a complex with a surface proton. For herbicides with basic functional groups, protonation is a significant adsorption mechanism at acidic mineral surfaces at low pH and water content. These include fluazifop, chlorsulfuron and certain triazines.

3.1.8 Cation exchange

This involves exchange of cations through an electrostatic attraction on the soil surface. This mechanism is predominant in herbicides which are predominantly cationic, such as paraquat and diquat. Weakly basic herbicides with functional groups such as amines and heterocyclic N compounds may protonate to form the cationic form. Bypyridiliums, triazines and fluridone are adsorbed by the cation exchange mechanism (Rao, 2011).

3.1.9. Covalent bonding

This is an irreversible binding of herbicides and other metabolites to soil organic matter. It is formed by oxidative coupling and enzymatic polymerization. Covalent bonding reduces the availability and extractability of absorbed herbicides.

3.2 Factors Affecting the Adsorption of Herbicides

The ability of herbicides to adsorb on soils and sediments and their tendency to desorb are the most important factors affecting soil and water contamination (Blasioli *et al.*, 2011). Several factors affect the adsorption of herbicides by soils. These include: a) type of clay colloid, b) soil organic matter, c) soil pH, d) moisture content, e) chemical nature of the herbicide and f) leaching.

3.2.1 Clay colloid

Clay colloid refers to the microscopic (0.001 to 1 μ in diameter) inorganic and organic particles in the soil. These particles have an extremely large surface in proportion to a given volume. Clay particles have negative charges and hence can attract to their surface positive ions (cations).

There are three major groups of clays: montmorillonite, illite and kaolinite. Montmorillonite is an expanding lattice clay providing both external and internal adsorptive surfaces. It has three layers, with one layer of aluminium oxide lying between two layers of silicon oxides. Illite is also a three-layered clay, but it lacks the expanding lattice character which makes it less adsorptive of herbicide molecules than montmorillonite clay. On the other hand, kaolinite is only a two-layered clay, with alternate layers of aluminium and silicon oxides. There are few residual charges in kaolinite clay, making it the least adsorbent of the three clays. However, kaolinite has one hydroxyl surface, which makes it adsorb some organic chemicals more strongly than the other clays (Rao, 2011).

The strength of adsorption follows the order of montmorillonite>illite>kaolinite. Montmorillonite adsorbs considerably more of various herbicides than illite and kaolinite.

3.2.2 Soil organic matter

The most significant factor affecting adsorption and hence, the behaviour of herbicides in soils is soil organic matter. The organic matter is made up of humic materials, plant and animal residues, and soil microbes. Soil humic materials consists of three components: a) humic acid, the alkaline soluble and acid insoluble fraction, b) fulvic acid, the alkaline soluble and acid soluble fraction, and c) humin, the alkaline insoluble and acid insoluble fraction (Harper, 1994). The humic acids are responsible for stable bonding during herbicide adsorption. Plant residues, following decomposition in soil, have a much greater adsorption capacity than the soil itself. Dao (1991) reported that decaying wheat straw adsorbed metribuzin better than the undecayed wheat straw. This increase in soptive capacity was attributed to a decline in cellulose and its concomitant proportional increase in lignin. The humic material has a primary influence in the adsorption of several herbicides including 2,4-D, chlorsulfuron, picloram, linuron and metribuzin (Rao, 2011).

3.2.3 Soil pH

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Soil pH affects the detoxification of herbicides by affecting the ionic or molecular character of the chemical, the ionic character and the CEC of soil colloids, and the inherent capacity of soil microorganisms to react with the herbicides.

Hydrogen ions have a positive electrical charge, indicating that they can be bound to the negatively charged soil and organic matter particles. The more free sites clay and organic matter particles have on them, the more hydrogen and other ions that can be bound to these particles. These binding sites, also called exchange sites, indicate the cation exchange capacity (CEC) of the soil. Thus, soils with greater CEC have more exchange sites. Additionally, the more exchange sites a soil has, the more hydrogen ions that can be held to the soil for eventual release into the soil solution (Rao, 2011). This is referred to as reserve acidity, which explains why an acid soil with high CEC needs more time for neutralization than an acid soil with low CEC.

Many herbicides are ionic which enables them, when in solution, to give off or attract hydrogen ions depending on the pH of the solution. For example, 2,4-D, MCPA, dicamba, chloramben, picloram, etc., which are acidic in character, can release hydrogen ions in a neutral or basic solution, while herbicides such as s-triazines, substituted ureas, phenyl carbamates, amides, etc., which are chemically basic in nature, can accept hydrogen ions in an acidic solution. Other herbicides, such as diquat and paraquat, are so basic that they are positively charged in virtually all soil pH values.

3.2.4 Soil moisture

The soil moisture content has a pronounced effect on both the degree of adsorption and the phytotoxicity of herbicides present in the aqueous phase. Herbicides reaching the soil are partitioned into adsorption and solution phases, moving through the soil either by molecular diffusion or by mass flow with the movement of water.

The amount of herbicide present in solution depends on the solubility of the herbicide in water and the amount adsorbed by soil colloids. The availability of a herbicide for plant uptake is related to its desorption into water solution. Thus, if a herbicide moves with the water, it may be completely removed from the soil profile and leached down to groundwater and streams.

Most of the herbicides have lower phytotoxicity at lower soil moisture contents. This is related to the degree of competition of the organic compound for adsorption sites at different moisture levels. Water is a polar compound and is strongly adsorbed by mineral colloids. At low moisture levels, the number of water molecules present to compete for adsorption sites is relatively small and fewer polar organic molecules may be able to compete more favourably for the available sites to be adsorbed. As the moisture content increases, the number of water molecules increases, resulting in reduced adsorption of the organic molecules. If the organic molecules have been adsorbed under conditions of low moisture and then the moisture level is increased, the adsorbed organic molecules may be displaced by water molecules and made available in soil solution for plant absorption (Rao, 2011).

3.2.5 Chemical nature of herbicides

Herbicides are classified into several groups depending on base structure of the herbicide molecule. Herbicides within the principal group can be loosely categorized as permanently ionized (i.e. quaternary ammonium compounds), ionizable (i.e. triazines) or neutral (carbamothioates) (Harper, 1994). Different functional groups on the base structure lead to a range of polarity and ionizability within a herbicide group. Substitution of functional groups on the base chemical structure also brings about changes in water solubility, volatility, adsorption strength and adsorption mechanisms as also charges in herbicidal activity (Rao, 2011).

Generally, soil and organic matter particles have negative electrical charges. Herbicides having positive charges are attracted and bound to them. Most organic molecules ionize only under certain pH conditions. The pH of ionization may range from -0.5 to 11.2 depending on the functional group. Compounds that ionize at these extremes would be unlikely to occur as ions in soils. Within the normal pH range of soils, 4.0 to 9.0, dissociation usually takes the form of H^+ loss by acids and H^+ gain by bases.

The weakly basic herbicides such as triazines and triazoles, which are less effective in soils of low pH, adsorb hydrogen ions in an acidic solution and become cationic. More atrazine is adsorbed by a muck soil at pH 3.2 than at 5.3, as little atrazine (ionization constant, pKa, 1.85) would exist as cation at pH 5.3. Adsorption is generally more pronounced when the pH of the soil is near the pKa of the herbicide. In high pH soils, triazines are desorbed into the soil solution, which results in greater availability of the chemical for uptake by plants and possible risk of injury even at rates considered safe. The strongly basic herbicides such as paraquat and diquat are so rapidly and tightly bound to montmorillonite clay and organic matter that they are virtually inactivated as soon as they come into contact with the soil (Rao, 2011).
The strongly acidic herbicide glyphosate is adsorbed more at low pH. It is readily bound to kaolinite, illite and bentonite clays, and to charcoal

and muck. The strongly acidic herbicides such as benzoic acids, phenols, aliphatics and nitriles posess carboxyl, phenolic or phosphonic functional groups and ionize in soil solution to become anions. The weakly acidic herbicides such as 2,4-D, dicamba and dinoseb are less active at a soil pH 5.0 or below. They tend to be repelled by, rather than attracted to, the negatively charged soil and organic matter surfaces. With the decrease in percentage of negatively charged herbicide molecules at low pH, adsorption increases, and hence their low activity at pH below 5.0.

The non-ionic herbicides such as diuron and other urea herbicdes, and trifluralin and other dinitroanilines, which do not ionize significantly in soil solution can also be affected by soil pH, but to a much lesser extent than the basic and acidic herbicides. These non-ionic herbicides are adsorbed through physical adsorption forces (Rao, 2011).

3.2.6 Leaching

Leaching refers to the movement of herbicides with water within the soil profile. This is influenced by the chemical nature of a herbicide, the adsorptive capacity of the soil and the amount of water available for downward movement through the soil. These aspects have earlier been discussed.

Leaching affects the selectivity of herbicides and by extension their relative efficacy. Excessive leaching to the deeper soil layers may render the herbicide less effective on shallow-rooted weed species, but could make it effective on deep-rooted ones. In such a situation, a shallow-rooted crop species may exhibit tolerance while deep-rooted crop plants become susceptible. Irrigation or rainfall following herbicide application has a profound effect on leaching and crop and weed tolerance to a herbicide.

3.3 Herbicide Transport in Soil

Herbicide absorption by plants occurs primarily from free herbicide content available in soil water. The processes that control the concentration of herbicide in soil water are: a) solubility of the herbicide, b) adsorptive capacity of the soil for the herbicide and c) water content of the soil. However, there is no general correlation between the water solubility of herbicides and the concentration of herbicides that remain free in equilibrium soil solution, because the adsorption of herbicides by soil is the main factor controlling the concentration of the solution. Soil water content affects the rate of transpiration, mass flow and molecular diffusion in the liquid phase, thus controlling the rate at which herbicide is transported in the liquid phase to the site of action in plants. Soil water content also determine the pore space diffusion in the vapour phase, which affects the rate of herbicide uptake by roots (Rao, 2011).

3.3.1 Diffusion transport

Diffusion is the movement of nutrients to the root surface in response to a concentration gradient. Herbicides are distributed in soil among solid, air and liquid phases. Herbicide molecules in the liquid or gas phase are in a state of random motion with more molecules moving out of the high concentration region to the dilute region along the concentration gradient. The diffusion rate in a very dry soil increases rapidly as the soil moisture content increases, while the diffusion rate in moist soils increases as the temperature increases.

Herbicides diffusing primarily in soil air are not active in extremely dry soil. Hence, incorporation of herbicides such as trifluralin and triallate may not lead to satisfactory weed control in dry soils, with soil moisture content below the permanent wilting point, unless soil moisture content is increased by way of rainfall or irrigation. The slight activity of herbicides at low vapour pressure in dry soils may be due to diffusion in the vapour phase. The efficacy of herbicides with low vapour pressures increases as the soil moisture content increases. The lack of herbicidal efficacy in dry soil may be attributed to insufficient water content to move the herbicide into the root zone or due to reduced diffusion of some herbicides in soil water to the emerging roots (Rao, 2011).

3.3.2 Mass flow transport

Mass flow is the movement of dissolved nutrients into a plant as the plant absorbs water for transpiration. The process is responsible for most transport of nitrate, sulphate, calcium and magnesium. The amount of herbicide that reaches the roots by mass flow is calculated by the volume of water transpired from leaves. The water flow through the soil-plant system occurs along a potential gradient, which must decrease continuously from the soil through the plant to the atmosphere for transpiration to occur. However, the mass flow of water and dissolved herbicide to the plants varies greatly depending on soil and atmospheric conditions.

The rate of water transfer in the soil-root-leaf part of the pathway to the air is described by the following equation (Nye and Tinker, 1977):

$$\text{Rate of transpiration (Q)}=\frac{\text{Water potential in soil (Ws)-Water potential in leaf (Wl)}}{\text{Resistance to water flow in plant (Rp)+Resistance to water flow in}}$$

The resistance in plant and soil (Rp+Rs) increases greatly as the soil water content falls and as the relative transport rate also decreases (Rao, 2011). Generally, water will be transported through the soil-plant system fast enough to meet the potential transpiration demands only when the soil water potential is at a very small absolute value. The potential transpiration rate will depend on meteorological parameters such as incident radiation, temperature and wind speed. Normally, there is good correlation between the uptake of herbicides by plants and the rate of transpiration at varying soil moisture contents. The concentration of a herbicide in plant leaves is related to total uptake and rate of plant growth.

3.3.3 Effect of Rainfall on Herbicide Transport

Rainfall is necessary for the activation of soil-applied herbicides as the downward flow of water transports herbicides to the root zone. The placement or position of the herbicide moving along the water flow is dependent on the amount of rainfall, amount of moisture in the soil, soil composition, adsorption of the herbicide by soil, speed of adsorption and desorption, permeability and amount of dispersion (Rao, 2011).

Movement of herbicides after rainfall depends on their relative mobility in soil. The herbicides range between those which move freely (moving with a wetting point) to those which are almost immobile. The herbicides with lowest adsorption coefficients move into the 5 to 10 cm soil layer, while those with higher adsorption coefficients will remain above 5 to 10 cm depth. However, herbicides with lower adsorption coefficients move readily into the root zone, in which case herbicide selectivity is based on depth protection. Herbicides with higher adsorption coefficients remain in the surface layer, although these may flow through the large soil pores and cracks to the root zone even with a moderate rainfall (Rao, 2011).

For most soil-applied herbicides, rainfall shortly after application is important for good herbicidal activity. Soil incorporation tends to improve weed control under all climatic conditions for herbicides that are highly volatile and strongly adsorbed by soil or absorbed into plants primarily by roots.

4.0 CONCLUSION

The prediction of the movement and the fate of herbicides in soils constitute an important strategy in limiting their environmental impact. The understanding of soil phase characteristics and the mechanisms involved in herbicide transformation can help to understand the fate of herbicide in soil. The physicochemical properties of herbicides affect their behaviour in soil and regulate their interaction mechanisms with organic and inorganic soil phases.

5.0 SUMMARY

In this unit we have learnt that:

i. Adsorption of herbicides by soil particles occurs through a number of mechanisms including hydrophorbic partitioning, hydrogen bonding, cation and water bridgings, protonation, cation exchange, covalent bonding, etc;
ii. Several factors affecting the adsorption of herbicides by soils include: a) type of clay colloid, b) soil organic matter, c) soil pH, d) moisture content, e) chemical nature of the herbicide and f) leaching;
iii. Herbicide transport in soil occurs through diffusion and mass flow transport; and
iv. Rainfall is necessary for the activation of soil-applied herbicides.

6.0 TUTOR MARKED ASSIGNMENT

1. Explain any five of the physicochemical mechanisms governing adsorption of herbicides by soil.
2. Explain how adsorption of herbicides by soil is affected by soil organic matter, soil pH and soil moisture.
3. Discuss the effect of rainfall on herbicide transport in soil.

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UNIT 5 FUMIGANT ACTION AND SYSTEMATIC ACTIVITY

CONTENTS

1.0 INTRODUCTION

Fumigation is the use of poisonous gases to kill pests in an enclosed area. It is the most effective way to reach pests in their most remote hiding places. Fumigants are broad-spectrum pesticides, killing all species of arthropods and rodents that are likely to be found in a building. To be effective, fumigants must reach target pests as gases entering the insect’s body through the body wall or respiratory system. Fumigants penetrate into many areas of a building not accessible by sprays or dusts, even penetrating into the burrows of wood-infesting insects, as well as into the centre of tightly packed commodities, such as tobacco in hogsheads, bales, cases or grain in large silos or storage bins. A fumigant gas generally does not leave unsightly, odorous, or hazardous residues.

2.0 OBJECTIVES

By the end of this unit, students should be able to:

- explain what fumigants are and how they work.;
- outline the factors modifying the effectiveness of fumigants; and
- understand the principles behind storage, handling and disposal of fumigants.

3.0 MAIN CONTENT

3.1 Types of Fumigation

Fumigants are Restricted-Use pesticides because of their high acute toxicity, primarily by inhalation. They can act as respiratory poisons, anesthetics or narcotics or enzyme poisons. The two types of fumigation commonly used are space fumigation and soil fumigation.

3.1.1. Space fumigation

The term “space fumigation” is convenient for the designation of a wide range of treatments in enclosed spaces, which either contain infested materials or residual insect populations. Space fumigation includes empty building fumigation, farm grain storage fumigation, rodent burrow fumigation, vehicle fumigation, tarpaulin fumigation, etc.

3.1.2 Soil fumigation

Soil fumigation involves the use of pesticides that, when applied to soil, form a gas to control pests that live in the soil and can disrupt plant growth and crop production. Soil fumigants are used on many high value crops and provide benefits to growers in controlling a wide range of pests including nematodes, fungi, bacteria, insects and weeds. Soil fumigation can be carried out on field, nursery, greenhouse and seed or transplant bed soils. It can also be achieved through non-tarp fumigation by injection.

3.2 Types and Nature of Fumigants

All space fumigant products and several soil fumigant products, especially those containing chloropicrin and/or methyl bromide, are now labeled Restricted-Use. A number of fumigant active ingredients formerly used have either been cancelled or have had their uses strictly limited in the US (Rodriguez, undated).

Fumigants are broad-spectrum pesticides that can act as respiratory poisons, anesthetics or narcotics, or enzyme poisons. They are chemically simple molecules, but they can exert potent and wide-ranging effects on the target organisms. On account of their gaseous nature and acute inhalation toxicity, fumigant products are labeled as Toxicity Category I with signal word Danger, or Danger-Poison with the skull and crossbones symbol.

Outlined below are some of the active ingredients that are still available and legal to use.

Methyl bromide is formulated as a liquid and vapour under pressure. It is odourless, non-flammable, and generally not corrosive nor irritating to eyes as a vapour. Because of its high toxicity and odourlessness, many formulations contain chloropicrin as a warning agent on non-food products. Methyl bromide products are used both for space and soil fumigation. If trapped inside tight clothing next to skin, methyl bromide can cause severe skin burns. It should not be used to fumigate materials containing sulphur (e.g., hair, fur, leather, and rubber goods) because of an undesirable chemical reaction with sulphur. It might also be necessary to actually conduct a small-scale fumigation on a suspect material to determine if it might react.

Chloropicrin is a heavy, colourless, non-flammable chemical with an irritating tear gas odour. In similarity to methyl bromide, it is highly toxic by inhalation. If added to methyl bromide formulations at a concentration of 2% or less, it is considered to be only a warning agent but at a concentration exceeding 2%, it is considered an active ingredient that enhances the fumigant activity of the methyl bromide.

Aluminum phosphide and **magnesium phosphide** are space, commodity, and rodent burrow fumigants. They are formulated as pellets, tablets, prepacs, prepac ropes, bags and plates. They are solids that react with moisture to liberate hydrogen phosphide (phosphine) , which is a gas highly toxic to insects**,** humans, rodents, and other animals. It is thus absolutely necessary to keep aluminum phosphide and magnesium phosphide products DRY in storage. Since magnesium phosphide is more reactive aluminum phosphide, it is generally recommended for fumigation under cooler and/or drier conditions.

Sulfuryl fluoride is a space fumigant used primarily to control wood-destroying insects. It is a colourless, odourless, non-flammable gas formulated in cylinders under pressure. Sulfuryl fluoride is the active ingredient contained in Vikane, which requires special monitoring equipment for its use. Registration is expected soon to permit sulfuryl fluoride under the trade name Profume to be used for fumigating flour mills and similar areas.

DDVP, also known as **dichlorvos**, is a contact and stomach insecticide with some fumigant action and is used to protect stored products. It is an organophosphorus insecticide requiring special precautions when used with other organophosphate products. DDVP is somewhat corrosive and should be kept dry in storage. It is under Special Review by the Environmental Protection Agency.

Ethylene oxide is a colourless, toxic, flammable liquefied gas that can be used as a fumigant on spices, black walnuts, and copra. It is formulated with carbon dioxide or dichlorodifluoromethane to reduce flammability.

3.3 Advantages and Disadvantages of Fumigation

Because fumigants are broad-spectrum pesticides, space fumigation, done properly, will kill all species and life stages of insects and rodents that are likely to be found in the structure being fumigated. Soil fumigation will kill soil microorganisms, nematodes, and many weed seeds and seedlings. As gases, fumigants penetrate into nooks and crannies of buildings, including the galleries of insects that infest interior wood that cannot be reached by pesticide sprays and dusts. Pests are rapidly killed and the fumigant gas does not leave unsightly, odourous, or hazardous residues if the site is properly aerated after fumigation.

Fumigation has certain disadvantages. Fumigants are broadly toxic and hazardous to use, and thus fumigations must be done by highly skilled and experienced, licensed fumigators. For space fumigation to be done successfully, it must be carried out in enclosed spaces, structures or sites that must be tightly sealed. All humans and other non-target organisms vacate the area until the fumigation period is over and aeration has been completed. Items that may be damaged by the fumigants should also be removed. Another disadvantage is that fumigation may cost more than other methods of pest control. Also, fumigants leave no protective residue and pests may reinfest the fumigated site immediately after treatment. Corrosion is a real concern when fumigating with the metal phosphides.

3.4 Factors that Modify Fumigant Effectiveness

Fumigants are used in various formulations and dosages according to the nature of the commodities and pests involved. Factors that modify fumigant effectiveness that must be considered when selecting a formulation include the following: i) pests to be controlled, ii) temperature, iii) moisture, iv) structure to be fumigated, and v) method of application.

3.4.1 Pests to be controlled

A pest’s susceptibility to fumigants depends on the species, its stage of development, and its habitat. Generally, fumigant gases reach the insects’ tissues through the respiratory system. Most insects breathe through a series of openings, called spiracles, in the outer skeleton. Once inside the insect’s body, oxygen from the air and fumigant gases are diffused through the insect’s thin cell membranes. Some primitive insects and mites, close relatives of insects breathe by taking in air through the cuticle, which covers the whole body.

The life stage of the insect that is least active metabolically (e.g. , pupae, hibernating adults) is the most difficult to kill by fumigation. Fumigant labels give dosages needed for different species of insects and different life stages of those species. For this reason, a fumigator should know some pest biology.

Insects that been fumigated with methyl bromide die slowly. At first, they may be unable to walk or fly normally. They usually come to rest on their backs and eventually are unable to recover from that position; however, they may move their heads, legs, or antennae for as long as several days before they finally die.

3.4.2 Temperature

Sub-lethal concentrations of the fumigant gas may result if fumigation is done at abnormally high or low temperatures. At low temperatures, the fumigant vapourizes and diffuses more slowly. Insect activity and metabolism are likewise slow. These factors tend to retard killing action, especially at temperatures below 10°C (50°F); thus, at lower temperatures, higher dosages and longer exposure time must be used for a successful fumigation.

On the contrary, at excessively high temperatures, fumigants vapourize faster and may dissipate too soon for lethal concentrations to be maintained long enough to kill pests, especially if the seal of the fumigation site is not perfect.

In the range of normal fumigating temperatures (60° to 80°F), the fumigant concentration needed to kill a given stage of an insect species decreases with the rise in temperature. Death occurs faster in the higher end of the normal temperature range.

3.4.3 Moisture

Adequate moisture is required for release of the actual toxicant, phosphine, in aluminum phosphide and magnesium phosphide products. At relative humidities below 25%, or grain moisture below 10%,, release of phosphine requires more time. Excessive moisture may interfere with fumigant action by reducing fumigant concentration within a commodity, or by retarding aeration during soil fumigation. Do not fumigate extremely dry soils because a certain amount of moisture is needed so that weed seeds will germinate and can be killed while actively growing.

3.4.4 Air Movement

Fumigation should be carried out when there is little air movement. Regardless of how well the enclosure to be fumigated is sealed, wind can create problems due to leaks. Leaks in an enclosure are the single most likely cause for fumigation failures.

3.4.5 Structure, Site or Commodity

The most important step in a structural fumigation is the proper sealing of the structure – the more tightly sealed the structure, the more efficient the fumigation. Because wood is porous, wooden structures, even well-sealed ones, will not retain fumigant gases as well as those made of metal, plastic, masonry, or concrete. Cement blocks are also porous and likewise are a problem for efficient fumigation.

The loss of gas through diffusion into porous building materials can be compensated for by increasing dosage levels and exposure times. Tarpaulin fumigation under gasproof sheet or cover is more effective than sealing a building with paper or tape and holding a fumigant within structural walls. Tarpaulin fumigation has the advantage of reaching the exterior wood areas (doors, sills, etc.) which may be infested.

According to federal or state law, a pesticide label is a legal document, and use of a pesticide in a manner that is inconsistent with the label directions is illegal. Thus, use a fumigant only on sites or commodities listed on the label, the other parts of the labeling, or the applicator’s manual. Product label directions discuss the factors that affect the fumigant’s efficiency on a particular commodity.

Ordinarily, a fumigant should not change the quality of or damage the treated commodity in any way, or leave any hazardous residue during processing of the commodity that could harm the consumer. In fumigation, as in any pesticide treatment of a raw agricultural commodity or packaged food product, the “tolerance” must be considered. The tolerance, or tolerated residue, is the amount of the pesticide’s active ingredient that is considered safe to consume and is legally permitted to remain in the commodity. Tolerances are expressed in parts per million, which is the same value as milligrams per kilogram (1000 grams).

Grain fumigation can be affected by type and condition of the grain: size, shape and permeability of the kernels, and the amount of dockage (chaff, dust, etc..) in the grain. “Sorptive capacity” of stored grain refers to adsorption , the adhesion of the fumigant gas molecules to the external surface of the grain, plus absorption, the holding of gas molecules within the kernel by capillary action. Other factors being constant, sorptive capacity of a grain increases with a decrease in kernel size and a corresponding increase in surface area. Permeability of seed coat is also a factor. Increased sorptive capacity means less gas fumigant in the surrounding air, hence, recommended dosages are generally higher for smaller grains such as wheat, rye, or sorghum than they are for corn.

3.4.6 Methods of Application

Soil fumigants may be applied under a tarpaulin (methyl bromide products) or by chisel injection into the soil (Telone, Vorlex), according to label directions.

Solid space fumigants that release phosphine may be added directly as pellets or tablets to animal feed, feed ingredients, and raw agricultural commodities stored in bulk. Commodities not stored in bulk (e.g., bagged) should be treated in the same way as processed foods; these should not come in contact with tablets, pellets or residual dust except for brewer’s rice, malt and corn grits for use in the manufacture of beer.

3.5 Safety Recommendations

The most dangerous and common route of exposure to fumigants is through inhalation. Most fumigants are highly toxic and can cause serious illness or death if small amounts are inhaled. Exposure also can occur through the eyes, mouth or skin. Below are the some of the safety recommendations for fumigators in terms of personnel and protective equipment.

3.5.1 Personnel

- Assign at least two persons to each fumigation job and use a “buddy system” of at least two persons when a fumigated area must be entered.

- Ensure that employees actively taking part in a fumigation are in good physical conditions. Fumigators should have (i) a physical examination at least once a year and more often if health conditions require such, while fumigation businesses should maintain up-to-date health records for each employee, (ii) abstain from alcoholic beverages and medical or recreational drugs for 24 hours before and after a fumigation job, (iii) not participate in a fumigation if they have colds or other respiratory problems that make breathing difficult, and (iv) not participate in a fumigation while undergoing continuing medical or dental treatments unless authorized to do so by the physician or dentist in charge.
- Instruct all personnel in first aid and other emergency procedures, including personal decontamination.
- Make sure fumigators understand the use of specific antidotes, first aid procedures and symptomatic relief measures.
- Instruct employees to report all accidents immediately to the employer or supervisor. Caution personnel to report all indications of illness or physical discomfort regardless of their apparent minor nature. Signs of illness may include but not be restricted to any or all of the following: dizziness, diarrhea, nausea, headaches and lack of coordination.
- Make sure employees understand the hazards that may be encountered because of carelessness or misuse of fumigants.
- Teach employees in the selection, operation, and maintenance of all protective equipment and safety procedures required by the fumigant of choice.

3.5.2 Protective Equipment

Fumigators must use protective equipment to prevent injury or loss of life if they are likely to be exposed to gas levels above the allowable limits. It is necessary to follow exactly the label recommendations concerning specific protective equipment and clothing for each fumigant product.

Label requirements for protective clothing and equipment are related to threshold concentrations of the fumigants in fumigated spaces. Therefore, fumigators need reliable detection devices to ensure health and safety of personnel, as well as to comply with the law, because the pesticide label is a legal document.

If the fumigant concentration in the fumigated area, as measured by a direct reading detector device, is above the threshold concentration specified by regulation for that fumigant, all persons in the area must wear the protective equipment specified on the label.

Respiratory protection must be available at the site of application in case it is needed when applying aluminum phosphide within a structure; it does not have to be available for outdoor applications.

3.6 Storing, Handling and Disposing of Fumigants

All fumigant products must be stored in a locked, dry, well-ventilated place away from heat. Do not risk contamination of water, food, or feed by storing these products in the same area as other pesticides. Fumigants should not be stored in buildings that animals or humans occupy. It should be remembered that all pesticides and their empty containers should be kept out of reach of children.

Specifically, methyl bromide cylinders should be handled with care; they should not be dropped, bumped, or dragged or slid from one place to another. Only transport these cylinders on hand trucks, or similar devices to which the cylinders can be firmly secured. Do not remove the valve protection bonnet and safety cap until immediately before use, and always ensure that the cap is in place when the cylinder is not in use. Empty cylinders should be closed securely with safety cap. Make sure the protection bonnet is in place and return the empty cylinder to the shipper. THESE CYLINDERS MUST NOT BE USED FOR ANY OTHER PURPOSE.

Some aluminum phosphide products are supplied in relatively gas-tight, resealable aluminum flasks, which should not be opened and exposed to atmospheric moisture any longer than is absolutely necessary to remove the products. Tightly reseal partially empty containers and mark them as partially used. Triple-rinse empty flasks and stoppers with water and offer them for recycling or puncture and dispose of the flasks in an approved sanitary landfill or use other local and state approved procedures. Dispose of the rinsate in the same way or by other means given in the labeling.

If properly exposed, the dust remaining after fumigation with hydrogen phosphide products will be gray-white and contain only a small amount of unreacted aluminum or magnesium phosphide. Residual dust from an incompletely exposed product, the so-called “green dust” needs special deactivation and disposal procedures. Small amounts may be disposed of by a “dry” method, while large quantities must be disposed of by a “wet” method, in which the residual dust is deactivated in a detergent or surfactant and water solution. Follow the detailed directions EXACTLY as they are on the product labels.

Triple-rinse liquid soil fumigant containers and dispose of the rinsate in the field just treated. The containers can then be offered for recycling or punctured and disposed of in the same way as other pesticide containers.

3.6.1 Hazardous materials management

The United States Environmental Protection Agency (EPA) has compiled a list of extremely hazardous materials for which records must be kept by the local Emergency Planning Committee and the State Emergency Response Commission. EPA has also set up Threshold Planning Quantities (TPQs) and Reportable Quantities (RQs) for each material on the list. The TPQ is the amount which if held instorage at a facility, must be reported to the local Emergency Response Commission. The RQ is the amount which, if accidentally released into the environment through misapplication or spillage, must be reported to the Commission. Among the hazardous materials on the EPA list are numerous pesticide active ingredients.

Facilities that use or store the TPQ of any of the chemicals on the list of extremely hazardous materials must furnish Material Safety Data Sheets (MSDS’s) for those chemicals and file annual inventories with the local Emergency Planning Committee and the State Emergency Response Commission. The MSDS’s are provided by the chemical manufacturers.

3.6.2 Spill and leak procedures

Methyl bromide product directions recommend that if a spill or leak occurs, fumigators should evacuate the immediate area of the spill or leak, then use a respirator to go back into the affected area to correct the problem. The spill should be allowed to evaporate and no one should enter the spill area without respiratory protection until the concentration of methyl bromide isles than 5 ppm. Remove leaking containers to an isolated area and cover them with a polyethylene sheeting (tarp) at least

4 mm thick. Place the edges of the tarp in a trench and seal them with soil, tamped down tight.

Contaminated soil, water, and other cleanup debris comprise a toxic/hazardous waste. If the Reportable Quantity is 1,000 pounds of methyl bromide is exceeded, the spill must be reported to the local Emergency Response Commission.

A spill of aluminum or magnesium phosphide products may generate high levels of phosphine gas, hence all personnel must wear a respirator for spill cleanup. DO NOT USE WATER AT ANY TIME to clean up these spills; water speeds up the production of phosphine, which could result in a toxic or fire hazard. The RQ for phosphine is 100 pounds.

If aluminum flasks have been damaged enough to leak, temporarily repair them with aluminum tape, or transfer the undamaged product to a sound metal container. If a spill is only a few minutes old, return intact products to the original flasks, or to another sound metal container stoppered tightly. Remember to properly label the alternate container. If you do not know the age of the spill, or if the product has been contaminated with soil, water, or debris, gather up the spillage and place it in a small ope bucket of less than 1 gallon capacity, with no more than 2 or 3 pounds of spillage per bucket. Carry out wet deactivation if feasible; if not, carry spillage in an open vehicle to a suitable area and deactivate it there. Small amounts of spillage (up to 18 pounds of product) may be spread out in an open area to be deactivated by atmospheric moisture.

4.0 CONCLUSION

From the foregoing, it can be concluded that since fumigants are broadly toxic and hazardous to use, fumigations must be done by highly skilled and experienced, licensed fumigators. For space fumigation to be done successfully, it must be carried out in enclosed spaces, structures or sites that must be tightly sealed. Fumigators must use protective equipment to prevent injury or loss of life if they are likely to be exposed to gas levels above the allowable limits. It is necessary to follow exactly the label recommendations concerning specific protective equipment and clothing for each fumigant product.

5.0 SUMMARY

In this unit students have learnt that:

i. Fumigation is the use of poisonous gases to kill pests in an enclosed area and it is the most effective way to reach pests in their most remote hiding places.;
ii. The two types of fumigation commonly used are space fumigation and soil fumigation;
iii Factors modifying fumigant effectiveness when selecting a formulation include 1) pests to be controlled, 2) temperature, 3) moisture, 4) structure to be fumigated, and 5) method of application;
iv. Most fumigants are highly toxic and can cause serious illness or death if small amounts are inhaled;
v. All fumigant products must be stored in a locked, dry, well-ventilated place away from heat; and
vi. A spill of aluminum or magnesium phosphide products may generate high levels of phosphine gas, hence all personnel must wear a respirator for spill cleanup.

6.0 TUTOR-MARKED ASSIGNMENTS

1. List some problems with fumigants.
2. List some of the advantages of fumigants.
3. Outline the factors modifying fumigant effectiveness.

7.0 REFERENCES AND OTHER RESOURCES

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UNIT 6 PESTICIDE CONVERSION MECHANISMS IN THE ENVIRONMENT ENZYMATIC CONVERSION

CONTENTS

1.0 INTRODUCTION

The transformation of the different types of pesticides to various degradation products is brought about by physical, chemical, and biological agents (Coats, 1991). Microbial metabolism is however responsible for the degradation of a vast majority of pesticides in the environment. Microbial degradation is the breakdown of pesticides by fungi, bacteria, and other microorganisms that use pesticides as a food source, and most microbial degradation of pesticides occurs in the soil. According to the definition by the International Union of Pure and Applied Chemistry, the term biodegradation is “Breakdown of a substance catalyzed by enzymes in vitro or in vivo”. The biodegradation of these pesticides, is often complex and involves a series of biochemical reactions. These reactions are catalyzed by enzymes, hence they are termed enzymatic conversion.

2.0 OBJECTIVES

By the end of this module, you should be able to:

- explain the term pesticide conversion in the environment.
- differentiate among the processes involved in enzymatic pesticide degradation
- explain how the process of enzymatic degradation had been harnessed by man to facilitate enhanced pesticide degradation

3.0 MAIN CONTENT

3.1. Enzymatic Conversion

The potential to use enzymatic treatment in biodegradation is a modern technology, which is currently receiving attention as a step ahead of the use of microorganisms for bioremediation. An array of enzymes and other natural substances have proved highly effective in the breakdown of pesticides and other xenobiotic compounds in the soil. Enzymes are catalytic in nature and therefore speed up the rates of biochemical reactions by lowering the activation energy needed to drive these reactions. These enzymes can detoxify many times their own weight of agent within very short time. The advantages of enzymatic treatment over microbial biodegradation include (1) no acclimation phase, (2) use over a wider range of environmental conditions (pH, moisture, temperature), (3) effectiveness at high and low pollutant concentrations, (4) movement of enzymes readily into soil micropores and their protection from inactivation, and (5) little effect of inhibitors of microbial metabolism on enzymes (Dec and Bollag 2001). The limitations of enzymatic treatment in bioremediation include the high cost of isolation and storage, the difficulty in maintaining enzyme stability, the requirement for expensive cofactors, and the lack of xenobiotic mineralization (Dec and Bollag 2001). Microbial enzymes with potential for pesticide metabolism include hydrolases, oxidoreductases, hydroxylases, amidases, and esterases. However, enzymatic treatments are not ideal for complete xenobiotic mineralization because mineralization usually requires many enzymes and several cofactors such as NAD(P)H and FAD. Enzymatic treatment holds great promise in bioremediation of contaminated soil and water (Van Eerd et al., 2003).

Enzymes with activity against nerve agents were first discovered during World War II, which include numerous organophosphorus pesticides. Some others were researched into very recently. Below is a list of some of enzymes with potentials to detoxify pesticides in the environment:

3.1.1 Organophosphorus Hydrolase

Organophosphorus Hydrolase (OPH) is a known Nerve Agent Detoxifying Enzymes which enhances activity of the Bacteria *Pseudomonas diminuta*in degradation process. OPH is an enzyme found in a number of bacterial isolates that has optimal activity against a variety of organophosphorus pesticides (originally called parathion hydrolase) in addition to its activity against nerve agents. The gene for this enzyme has been cloned, sequenced, and expressed in a number of prokaryotic and eucaryotic host organisms. The three-dimensional crystal structure of OPH also has been determined revealing that the native enzyme is a homodimer and contains two Zn2+ ions per sub-unit. The Co2+ substituted enzyme has greater activity on nerve agents and substrates with P-F and P-S bonds.

3.1.2 Organophosphorus Acid Anhydrolase

Organophosphorus Acid Anhydrolase (OPAA) is another Nerve Agent Detoxifying Enzymes which enhances activity of the Bacteria *Alteromonas*sp. in degradation of hosphorus base pesticides. OPAA was originally identified in the obligate halophilic bacterium *Alteromonas*sp. that was isolated from Grantsville Warm Springs in Utah. Unlike OPH, OPAA has very little activity against pesticides. The OPAA gene has been cloned, sequenced, and expressed at very high levels in *Escherichia coli* (up to 50% of cell protein). The enzyme can be freeze-dried and survive for many years at room temperature with no loss of activity. From the amino acid sequence of OPAA and functional studies on a variety of dipeptides, it was identified as an X- Pro dipeptidase (or prolidase) having nothing at all to do with phosphorus metabolism. Through serendipity, it is ideally positioned for hydrolytic attack on the phosphorus atom. This class of enzymes can be found throughout nature in organisms as primitive and diverse as Archea and bacteria all the way up to humans.

The gene for squid enzyme Diisopropylfluorophosphatase (DFPase) also a Nerve Agent Detoxifying Enzymes which aid the microbe *Loligo vulgaris* has been cloned, sequenced, and expressed in both *E. coli* and the yeast *Pichia pastoris*. The squid-type DFPase has only been found in cephalopods, requires Ca2+ for activity and stability, and hydrolyzes DFP five times faster than soman. Its chemical and biological properties are completely different from those of all other types of DFPases as well as OPH and OPAA.

3.1.3 Phenoloxidases (peroxidases and laccases)

Phenoloxidases are produced by microbial activity in biobeds with straw-degrading fungi being the driving force. Here the straw is the main substrate for pesticide degradation and microbial activity, especially from lignin-degrading fungi such as white rot fungi, which produce phenoloxidases (peroxidases and laccases). The broad specificity of these enzymes makes them suitable for degradation of mixtures of pesticides.

The degradation of individual pesticides by white rot fungi/peroxidases has been demonstrated in several studies. Moreover in laboratory scale biobeds, the dissipation of most of the pesticides in a mixture is correlated with phenoloxidase activity and/or basal respiration and both activities are correlated to the levels of straw. Therefore, a high amount of straw in the biomixture is recommended, although in practice not more than 50 vol-% due to the requirement to achieve a homogeneous mixture.

The lignin-degrading system of many white rot fungi is nitrogen-regulated. At low nitrogen levels the fungi activate the production of phenoloxidases, while higher nitrogen levels can enhance growth but inhibit the production of enzymes. Therefore, addition of nitrogen to biomixtures is not recommended.

3.1.4 Esterases

The esterases involved are somewhat characterized, but relatively little is known about which ones modify xenobiotics. Many of these enzymes are non-specific and reside in cuticles and cell walls. Herbicides applied as esters are fairly lipophilic and mobile in the cuticle; however, de-esterification is required prior to entry of the herbicide (now an acid) into the phloem via ion trapping. De-esterification will also increase or maintain the concentration gradient because the ester is converted into an acid and therefore, the gradient is steeper for entry of additional ester. De-esterification can be viewed as a form of bioactivation because the herbicide will not be translocated as readily in the ester form. In some cases, the de-esterified form of the herbicide is more toxic as well (i.e. fenoxyprop is more toxic to grassy weeds than fenoxyprop-ethyl).

3.1.5 Oxidoreductases

Oxidoreductases, such as laccase, tyrosinase, and horseradish peroxidase, can be used to decontaminate soil and water. These enzymes oxidize the substrate to free radicals, which are susceptible to chemical coupling, forming oligomers. For example, oligomer formation reactions can take place between humic acid and xenobiotics, resulting in the polymerization of the substrate to soil, as was observed with 2,4-dichlorophenol. In another experiment, horseradish root tissue and hydrogen peroxide (an electron acceptor) decontaminated water containing 850 ppm of 2,4- dichlorophenol and other chlorinated phenols. Depending on the concentration of hydrogen peroxide, up to 100% of the contaminants were removed by polymerization. Furthermore, horseradish root tissue contributed to the irreversible binding of 2,4-dichlorophenol to soil.

3.2 Enzyme immobilization

For enzymatic treatment to be effective in bioremediation, the enzymes must be stabilized. The most effective way to stabilize enzymes is by immobilization. Immobilization can be accomplished by enzyme linkage to organic or inorganic solid supports by adsorption on solid surfaces such as glass, entrapment in polymeric gels, encapsulation, or intermolecular cross-linking. Although preparing supports can be time-consuming and expensive, the support can generally be reused. The use of immobilized enzymes to metabolize pesticides is not new. For example, enzymes from crude *Pseudomonas* cell extracts immobilized on glass beads hydrolyzed 95% of parathion (10 to 250 ppm) from wastewater. The same enzyme preparation hydrolyzed parathion at 2,500 ppm in soil and was also effective in hydrolyzing other organophosphate insecticides (triazophos, diazinon, and fenitrothion).

4.0 CONCLUSION

From the above, it is obvious that though the cost of pesticide conversion with enzymes may be quite prohibitive, it is an efficient and eco-friendly technology for pesticide cleanup in the environment. The prospects of this technology in pesticide breakdown is also vast because more classes of enzymes can be explored for future use in bioremediation of pesticide contaminated environment.

5.0 SUMMARY

In this unit, we have shown that pesticide conversion in the environment is mainly by microorganisms of which enzymatic breakdown forms a major aspect. The use of enzymes as biodegradation agents presents many advantages. However, enzymatic treatments are not ideal for complete xenobiotic mineralization because of certain limitations, which include high cost of enzyme isolation and storage, difficulty in maintaining enzyme stability, and the requirement of many enzymes and several cofactors such as NAD(P)H and FAD to achieve mineralization. We have also shown that the limitations associated with the use of enzymes for pesticide conversion can be overcome by adopting the technology of enzyme immobilization.

6.0 TUTOR-MARKED ASSIGNMENTS

1. Explain the term pesticide conversion in the environment.
2. Differentiate among the processes involved in enzymatic pesticide degradation
3. Explain how the process of enzymatic degradation had been harnessed by man to facilitate enhanced pesticide degradation

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UNIT 7 PESTICIDE CONVERSION MECHANISMS IN THE ENVIRONMENT: NON-ENZYMATIC CONVERSION

CONTENTS

1.0 INTRODUCTION

Apart from microbial degradation, pesticides are also converted in the environment through many different mechanisms. Physical and chemical agents play significant roles in the transformation of insecticide, herbicide, and fungicide molecules to various degradation products. Transformation mechanisms include oxidation, hydrolysis, reduction, hydration, conjugation, isomerization, and cyclization. Resultant products are usually less bioactive than the parent pesticide molecule, but numerous cases have been documented of metabolites with greater bioactivity. The physical and chemical properties of the degradation products are also different from those of the parent compound, and their fate and significance in the environment also are altered with the structural changes. The concept of "environmental activation" describes the transformation of a pesticide to a degradation product that is of significance in the environment as a result of its environmental toxicology or chemistry (Coats, 1991).

2.0 OBJECTIVES

By the end of this unit, students should be able to:

1. understand the various mechanisms of pesticide conversion other than enzymatic conversion
2. describe the components of non enzymic conversion of pesticides in the environment; and
3. understand the various products of non-enzymatic conversion of pesticides.

3.0 MAIN CONTENT

3.1. Non-Enzymatic Conversion

Processes involved in the conversion of pesticides outside the biological processes previously discussed are termed non-enzymatic conversion. They are mainly physical and chemical processes. A combination of factors usually influence the breakdown of a pesticides over a time period of hours, days, weeks, months, or years, and through many of the situations enumerated above. Factors that influence the relative importance of the various transformation agentsdepend to a great extent on the chemical's use pattern, physical properties, and chemical structure. The two primary physical agents involved in the degradation process are light and heat.

Photolysis of pesticide residues is extremely significant on vegetation, on the soil surface, in water, and in the atmosphere (Matsumura, 1985) · Thermal decomposition of the chemicals often occurs concomitantly with the photodegradativereactions; solar radiation, therefore, is directly responsible for the decomposition in two ways, through photolysis and thermal decomposition. Cold, especially freezing, temperatures can also contribute occasionally to pesticide degradation if certain formulations are allowed to freeze, and the pesticide is forced out of solution, suspension, or microencapsulation, making it more susceptible to degradative forces before and after application. Chemical degradation occurs as a result of the various reactive agents in the formulations, tank mixes, and in the environment. Water is responsible for considerable breakdown of pesticides in solution, especially in conjunction with pH extremes. Even slight variance from a neutral pH can elicit rapid decomposition of pH-sensitive compounds. Molecular oxygen and its several more reactive forms (e.g., ozone, superoxide, peroxides) are capable of reacting with many chemicals to generate oxidation products. In all but the most oxygen-poor environments, oxidative transformations are frequently the most common degradation pathways observed. Other chemical oxidations, as well as reductions, can progress in the presence of certain inorganic redox reagents (Manahan, 1990). These reactive species of metals function as highly effective catalysts which effect pesticide transformations in soils and in aquatic and marine environments.

3.1.1 Hydrolysis Reaction

For many pesticide molecules, hydrolysis is a primary route of degradation. Many types of esters are hydrolytically cleaved, yielding two fragments with little or no pesticidal activity. Hydrolysis of esters can occur by chemical means; even mildly alkaline solutions can cause hydrolytic decomposition of some esters (organophosphorus, carbamate, pyrethroid), while acidcatalyzed hydrolysis typically is induced only by strongly acidic solutions.Chemical hydrolysis of chlorides and bromides can occur, yielding a hydroxylated product. Hydrolysis of an epoxide, by an epoxide hydratase, produces a diol (Sipes andGandolfi, 1986). Oximecarbamates can be hydrolyzed to an oxime and a carbamic acid (Kuhr, 1975).

3.1.2 Oxidation

The mechanisms of oxidation vary. Physical and chemical oxidations involve molecular oxygen or more reactive species including various acids, peroxides, orsinglet oxygen, and are often enhanced by light, heat, or oxidized metals in soil or water. Ring hydroxylation occurs on aromatic rings in pesticides of several types, as well as polycyclic aromatic hydrocarbons (PAH). It is easily accomplished on single or multiple-ring molecules that are unsubstituted or activated. Substitution with bulky or multiple groups can sterically inhibit the reaction, as can the presence of deactivating substituents such as halogens.Any methylene group in an aliphatic side-chain is susceptible to oxidation. Carbofuran undergoes hydroxylation of a methylene in the furan ring to form 7-hydroxycarbofuran, followed by further oxidation to 7-ketocarbofuran. Terminal methyl groups are also susceptible to hydroxylation.

The conversion of alkenes to epoxides does not radically alter the polarity of the substrate, nor the biological activity in some cases, e.g., aldrinls epoxidation to dieldrin. Epoxide formation may be, in fact, critical to bioactivity, e.g., precocenes require activation to be cytotoxic to the corpora allatum of insects to inhibit the production of juvenile hormone (Bowers, 1982). Epoxides can be hydrolyzed to form diols; the net effect of the arene oxide formation followed by hydrolysis, is ring hydroxylation.

3.1.3 Reductions.

Pesticides undergo reduction reactions in reducing environments, characterized by low oxygen concentrations, low pH's, and anaerobic microorganisms. Examples of situations in which pesticides are reduced include stagnant or eutrophic ponds and lakes, bogs, flooded rice fields, the rumens of ruminant livestock, and lower intestines of some species, including man. Reduction of a nitro group has been observed in flooded soil. The fungicide pentachloronitrobenzene has also been shown to undergo reduction to an amino analog.

3.1 4 Photo-degradation is the breakdown of pesticides by sunlight. All pesticides are susceptible to photo-degradation to some extent. The rate of breakdown is influenced by the intensity and spectrum of sunlight, length of exposure, and the properties of the pesticide. Pesticides applied to foliage are more exposed to sunlight than pesticides that are incorporated into the soil. Photo-degradation can destroy pesticides on foliage, on the soil surface, and even in the air. Pesticides may break down faster inside plastic-covered greenhouses than inside glass greenhouses, since glass filters out much of the ultraviolet light that degrades pesticides. Factors that influence pesticide photo-degradation include the intensity of the sunlight, properties of the application site, the application method, and the properties of the pesticide.

4.0 CONCLUSION

From the above, it is obvious that natural processes are capable of converting pesticides from one form to another. Knowledge of these processes is therefore important as this will be useful in pesticide storage, application and cleanup.

5.0 SUMMARY

In this unit, we have shown that different pesticide group are subject to degradation and conversion by one or more natural process. We have also shown in details the mechanisms of action of these processes as it relates to how they are able to convert pesticides to form the degradation products.

6.0 TUTOR-MARKED ASSIGNMENTS

1. Discuss some natural processes that are capable of bringing about pesticide conversion.
2. Differentiate the processes of non-enzymatic conversion from the enzymatic conversion.

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UNIT 8 DEGRADATION OF PESTICIDES IN SOILS

CONTENTS

1.0 INTRODUCTION

Alongside sorption, degradation is the second most important process used to predict the fate of pesticides in soils (Boesten and van der Linden,1991). Many pesticides dissipate rapidly in soils. This process is mineralization and results in the conversion of the pesticide into simpler compounds such H_20, $C0_2$, and NH_3. While some of these processes are as a result of chemical reactions such as hydrolysis and photolysis, microbiological catabolism and metabolism is usually the major route of mineralization. Soil micro biota utilize the pesticide as a source of carbon or other nutrients. Some chemicals (for example 2,4-D) are quite rapidly broken down in soil while others are less easily attacked (2,4,5-T). Some chemicals are very persistent and are only slowly broken down (atrazine)".

Standard laboratory and field dissipation studies are performed to assess the rate of degradation (often expressed as a first-order half-life or

DT50, the time required for 50% of the initial dose to disappear). Rates of degradation are influenced by physicochemical properties of the soil [such as pH and organic carbon (OC) content], biological properties (activity and distribution of microorganisms), and environmental conditions that control soil temperature and moisture content. Both route and rate of degradation also depend on properties of the chemical. Variability in degradation rate is expected, and numerous studies have provided evidence for field-to-field variation in the degradation rates of pesticides (Walker et al., 2001). Extrapolation from measurements on a set of soils to prediction for a different soil is therefore a common problem in environmental assessment. A greater understanding of the factors that influence degradation rates is required to support this extrapolation and thus ensure the safe use of new and existing products.

2.0 OBJECTIVES

By the end of this unit, students should be able to:

1. identify the types of degradation that take place in the soil
2. identify the factors influencing rate of pesticide degradation in soils
3. make pesticide selection based on the prevailing factors for effectiveness and sustainability

3.0 MAIN CONTENT

3.1 Pesticide degradation in soil

Soil constitutes a major environmental sink for many pesticides from which they are taken up by plants, move into the bodies of invertebrates, pass into water or air, and are broken down. However, pesticides applied do not remain in the soil forever. The degradation of a pesticide in soil is dependent on a host of conditions, such as soil type, organic matter content, clay content, pH, the nature of soil colloids, the microflora and microfauna present in soil, liquid and air flow through the soil, the cultural practices, and the exposure to wind, sunlight, rain and temperature, etc. Superimposed on all these factors is the chemical nature of the pesticide. Most of these conditions and factors are often interrelated and have been discussed in earlier chapters. Pesticide degradation, or the breakdown of pesticide, usually is beneficial. Pesticide-destroying reactions change most pesticide residues in the environment to nontoxic or harmless compounds. However, degradation is detrimental when a pesticide is destroyed before the target pest has been controlled. The three types of pesticide degradation are microbial, chemical, and photo-degradation.

3.2 Types of pesticide degradation in the soil

3.2.1 Microbial degradation

Microbial degradation: is the breakdown of pesticides by fungi, bacteria, and other microorganisms that use pesticides as a food source. Most microbial degradation of pesticides occurs in soil. Soil conditions such as moisture, temperature, aeration, pH, and the amount of organic matter affects the rate of microbial degradation because of their direct influence on microbial growth and activity.

The frequency of pesticide application also is a factor that can influence microbial degradation. Rapid microbial degradation is more likely when the same pesticide is used repeatedly in a field. Repeated application can actually stimulate the buildup of organisms that are effective in degrading the chemical. As the population of these organisms increases, degradation accelerates and the amount of pesticide available to control the pest is reduced. In extreme cases, accelerated microbial degradation has led to certain products being removed from the marketplace. Microorganisms greatly reduce the effectiveness of these chemicals soon after application.

The possibility of very rapid pesticide breakdown is reduced by using pesticides only when necessary and by avoiding repeated applications of same chemical. Alternating between different classes, groups or formulations of pesticides can minimize the potential for microbial degradation problems as well as pest resistance

3.2.2 Chemical degradation of pesticides in the soil

Chemical degradation is the breakdown of pesticides by processes that do not involve living organisms. Temperature, moisture, pH, and adsorption, in addition to the chemical and physical properties of pesticide, determine which chemical reactions take place and how quickly they occur.

One of the most common pesticide degradation reactions is hydrolysis, a breakdown process in which the pesticide reacts with water. Many organophosphate and carbamate insecticides are particularly susceptible to hydrolysis under alkaline conditions. Some are actually broken down within a matter of hours when mixed with alkaline water.

Product labels may warn against mixing a pesticide with certain fertilizers, other pesticides or water with specific characteristics. Following these precautions can help prevent pesticide degradation and potential incompatibility problems. In some situations, buffers or other additives may be available to modify spray mix conditions and prevent or reduce degradation. Pesticide degradation and possible corrosion of application equipment can be avoided by not allowing a spray mix remain in a tank for a long period of time.

3.2.3 Photo-degradation of pesticide in the soil

Photo-degradation is the breakdown of pesticides by light, particularly sunlight. Photo-degradation can destroy pesticides on foliage, on the surface of the soil, and even in the air.

Factors that influence pesticide photo-degradation include the intensity of the sunlight, properties of the application site, the application method and the properties of the pesticide. Pesticide losses from photo-degradation can be reduced by adding the pesticide to the soil during or immediately after application

3.3 Factors influencing pesticide degradation in soils

Several factors determine the length of time herbicides persist. These factors fall into three categories: soil factors, climatic conditions, and herbicidal properties. Factors from each category strongly interact with one another.

3.3.1 Soil factors

Soil factors affecting pesticide degradation include soil composition, soil chemistry, and microbial activity. Soilcomposition is a physical factor determined by the relative amounts of sand, silt, and clay in the soil (the soil texture), as well as by the organic matter content. An important chemical property of soil that can influence herbicide persistence is pH. The microbial aspects of the soil environment include the types and abundance of soil microorganisms present in the soil.

3.3.1.1 Soil composition

Soil composition affects pesticide breakdown through soil-herbicide binding (adsorption and desorption). Generally, soils high in clay, organic matter, or both have a greater potential for adsorption because of increased binding of the herbicide to soil particles, with a corresponding decrease in availability of the pesticide in soil mostore to be accessed by microbial degrading agents. This “tie-up” results in decreased in microbial breakdown, initial plant uptake and herbicidal activity. More herbicide is held in reserve, potentially injuring susceptible crops in the future.

In general, medium- and fine-textured soils with an organic matter content of more than 3 percent have the greatest potential to bind or hold herbicides and injure sensitive rotation crops. Coarse- to medium-textured soils with a lower organic matter content (less than 3 percent), are less likely to retain herbicides and have carryover problems. Under the right circumstances, however, herbicide carryover can occur in any type of soil.

3.3.1.2 Soil pH

Soil pH can influence the persistence of some herbicides, especially the triazines and sulfonylureas. Chemical and microbial breakdown, two ways herbicides degrade in soil, often are slower in higher-pH soils.In particular, the chemical degradation rate of the triazine and sulfonylurea herbicide families slows as the soil pH increases, particularly above 7.0. In addition, in higher-pH soils, lesser amounts of these herbicides are bound to soil particles, making more available for plant uptake. So in higher-pH soils, the triazine and sulfonylurea herbicides persist longer, and more is available for plant uptake. (Some triazine and sulfonylurea herbicides do not persist and carry over regardless of how high the soil pH is.) Low pH also can affect the persistence of both the triazine and the sulfonylurea herbicides. Soil pH levels below 6.0 allow a more rapid dissipation of both these herbicide families. In acid soils, herbicides like atrazine become bound to soil particles, making them unavailable for weed control; but at the same time, they are chemically degraded more quickly. This makes liming an acid soil important for achieving an adequate performance form these two herbicide families. In contrast, a low soil pH increases the persistence of the imidazolinone herbicides imazaquin (Scepter) and imazethapyr (Pursuit). As the soil pH drops below 6.0, imazaquin and imazethapyr become increasingly bound, or adsorbed, to soil particles. Adsorption of these herbicides appears to reduce their availability to soil microorganisms, the primary mechanisms of degradation. Even though adsorption is greater in lower-pH soils, the herbicide can still be released several months later, becoming available for plant uptake and potentially injuring a sensitive follow crop. Sorption processes may affect biodegradation mainly bymodifying chemical bioavailability. A positive relationship between sorption coefficient (Kd) and half-life has been reported for many ionizable pesticides (Kah and Brown, 2006).However, several factors might counterbalance the influence of sorption on degradation, and the link between sorption and degradation is not always obvious (Barriuso, *et al.*, 1997; Radosevich *et al.*, 1996; Shaw and Burns, 1998).

Degradation processes by soil microorganisms probably are the most important pathways responsible for the breakdown of herbicides. The types of microorganisms (fungi, bacteria, protozoans, etc.) and their relative numbers determine how quickly decomposition occurs. Microorganisms require certain environmental conditions for optimal growth and utilization of any pesticide. Factors that affect microbial activity are moisture, temperature, pH, oxygen, and mineral nutrient supply. Usually, a warm, well-aerated, fertilesoil with a near-neutral pH is most favorable for microbial growth and, hence, herbicide breakdown.

3.3.2 Climatic factors

The climatic variables involved in herbicide breakdown are moisture, temperature, and sunlight. Herbicide degradation rates generally increase as temperature and soil moisture increase because both chemical and microbial decomposition rates increase with higher temperatures and moisture levels. Cool, dry conditions slow down herbicide degradation. Carryover problems are always greater the year following a drought. If winter and spring conditions are wet and mild following a previously dry summer, the likelihood of herbicide carryover is lower. Sunlight is sometimes an important factor in herbicide degradation. Photodecomposition or degradation catalyzed by sunlight (photolysis) has been reported for many herbicides, especially in liquid solution (i.e., water) or on plant leaf surfaces. But for most of the more persistent soil-applied herbicides, once soil contact is made, losses due to photolysis are small. The exception may be the dinitroanilines, including trifluralin (Treflan) and pendimethalin (Prowl). These can be lost if they remain on the soil surface for an extended period without rainfall. A sensitivity to sunlight and losses through volatilization are primary reasons for incorporating the dinitroanilines at application time.

3.3.3 Pesticide properties

A herbicide's chemical properties affect its persistence. These properties include water solubility, vapor pressure, and the molecules' susceptibility to chemical or microbial alteration or degradation. Leaching is one mechanism responsible for herbicide dissipation. The solubility of a herbicide in water helps determine its leaching potential. Leaching occurs when a herbicide is dissolved in water and moves down throughthe soil profile. Herbicides that readily leach may be carried away from crop and weed germination zones.

Herbicide leaching is determined by other factors as well. These include herbicide-soil binding properties, soil physical characteristics, rainfall frequency and intensity, herbicide concentration, and time of herbicide application. In general, herbicides that are less soluble in water and strongly attracted to soil particles are less likely to leach, particularly in dry years. The *vapor pressure* of a herbicide determines its volatility.

Volatilization is the process whereby a herbicide changes from a liquid or solid to a gas. Volatile herbicides(those with higher vapor pressures) generally dissipate more rapidly than herbicides with lower vapor pressures.Volatilization increases with temperature and moisture. Most herbicides are relatively nonvolatile under normalfield-use conditions. The more volatile herbicides are generally incorporated to avoid gaseous losses. Volatile herbicides include members of the thiocarbamate family EPTC (Eradicane, Eptam) and butylate (Sutan+); the dinitroanilinestrifluralin (Treflan) and ethalfluralin (Sonalan); and clomazone (Command). A herbicide's chemical structure dictates how the herbicide will degrade in soil. Some herbicides are rapidly decomposed by microorganisms if the right kind and number are present and if soil conditions are favorable for their growth. But herbicides vary greatly in their susceptibility to microbial decomposition. The chemical structure of 2,4-D,for example, allows microbes to quickly detoxify the molecule into inactive metabolites, whereas atrazine is not as prone to microbial attack; hence, degradation is slower. Some herbicides are prone to chemical reactions. Members of the sulfonylurea herbicide family, for example, are degraded through chemical hydrolysis as well as through microbial processes. Remember that for the sulfonylureas as well as the triazines, the rate of chemical hydrolysis is dependent on soil pH. Although it is less sensitive than microbes to fluctuations in soil physical characteristics and often soil moisture, the rate of chemical reaction also will vary dependingon the surrounding soil environment. Several families of herbicides are degraded through both chemical and microbial pathways. Others less prone to chemical breakdown are lost primarily through microbial alteration.

4.0 CONCLUSION

The unit concluded that there is the need for proper understanding of the types of degradation and factors that influence degradation in soils. This will inform the choice of pesticide to be applied based on soil and pesticide properties as well as the prevailing climatic condition.

5.0 SUMMARY

In this unit students have leant that:

- Degradation of pesticide in the soil environment happens in three ways; viz: microbial, chemical, and photo-degradation;
- Pesticide degradation in the soil is governed by several factors, which include soil properties, pesticide properties, as well as weather conditions.

6.0 TUTOR-MARKED QUESTIONS

1. Explain the pros and cons of pesticide degradation in agriculture.
2. Discuss the three types of pesticide degradation in the soil.
3. Briefly explain the factors governing pesticide degradation in the soil.

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UNIT 9 FATE OF PESTICIDES IN WATER

CONTENTS

1.0 INTRODUCTION

Pesticides are frequently found in surface and ground water and concentrations have been found that could affect small aquatic organisms or animals that feed on fish.Pesticides may enter surface waters directly through runoff, spills, or various effluents.Contamination also may be indirect, with pesticides first entering the atmosphere or ground water, and then transported to surface waters. Once in surface water, some pesticides can be deposited in sedimentation areas, which can then act as a long-term source to the water column through resuspension, biotic uptake, and diffusion. Irrespective of the manner in which the water got contaminated, pesticides may undergo a degradation process, which converts the parent chemical to either toxic or non-toxic products.

In the following sections, the various sources of pesticides to surface waters are discussed. The fate of these chemicals once in water as well as their dissipation are also discuss.

2.0 OBJECTIVES

By the end of this module, students should be able to:

- explain the behaviour and fate of pesticides in water.
- differentiate among the processes of pesticide dissipation in water
- outline the different types of pesticide transformation mechanisms in the water environment.

3.0 MAIN CONTENT

3.1 Behavior and fate of pesticides in waters

The behavior, transport, and fate of an organic chemical in surface waters is controlled by the properties of the chemical and the environmental conditions in the water. The structure of the organic chemical determines its physical, chemical, and biological properties. The surface water environment that surrounds the organic chemical consists of physical, chemical, and biological components. The interaction of the chemical structure and environmental conditions controls the chemical's behavior and ultimately its effect on the environment. The environmental processes that control an organic chemical's behavior and fate in surface water can be classified into three types: (1) transformation processes, which change its chemical structure; (2) phase-transfer processes, which control its movement between water, biota, suspended sediments, bed sediments, and the atmosphere; and (3)transport processes, which move it away from its initial point of introduction to the environment and throughout the surface water system.

3.2 Transformation processes

The transformation of a pesticide results in changes in its chemical structure. One or more new chemicals are produced, and the original pesticide disappears. These new chemicals can be organic or inorganic molecules and ions. From an environmental-effects point of view, the ideal fate for a pesticide is ultimate transformation to inorganic species, such as water, carbon dioxide, and chloride ions (termed mineralization). However, in many instances, the chemicals formed from transformation reactions are long-lived intermediates, which themselves can have a negative impact on the environment. Often the initial transformation products undergo subsequent transformation reactions before mineralization. By this process, a large number of transformation products can potentially be formed, some of which may retain pesticidal properties. Some pesticide formulations are applied as inactive agents and gain pesticidal properties only after transformation. The transformation of pesticides in water is brought about by chemical and biological reactions. Another process (photolysis) involves the breakdown of chemical by light.

3.2.1 Chemical transformation

Chemical transformations can be mediated by chemical, biological, or physical means. In surface waters, chemically induced abiotic hydrolysis and oxidation-reduction reactions often occur. Biodegradation is the general term for biologically mediated reactions. Microorganisms can induce pesticides to undergo both hydrolytic and oxidation-reduction reactions. Photolysis is a chemical reaction induced by the energy from sunlight.

3.2.1.1 Hydrolysis

Hydrolysis is the chemical (sometimes biologically mediated) reaction of a pesticide with water, usually resulting in the cleavage of the molecule into smaller, more water-soluble portions and in the formation of new C-OH or C-H bonds. This process is important for many organophosphorus and carbarnate pesticides. The hydrolysis rate of a given organic compound is dependent on the characteristics of the solution. The strongest factor is pH. Hydrolysis reactions can be a result of direct attack by the water molecule (H_20), the hydronium ion (H_30^+), or the hydroxide ion (OH^-). These are termed neutral, acid, and base hydrolysis, respectively. At low pH, reactions are dominated by acid-catalyzed hydrolysis, whereas at high pH, reactions are dominated by base-catalyzed hydrolysis. At intermediate pH values, both neutral and acid, or neutral and base-catalyzed reactions, can be important to the overall rate of hydrolysis. It should be noted that acid or base catalysis does not necessarily occur in all hydrolysis reactions, and that neutral catalyzed reactions alone sometimes may govern the overall rate of reaction. In these cases, the rate will not depend on pH. Temperature also is an important factor. Generally, a temperature rise of 10°C increases the reaction rate twofold to fourfold. The presence of certain metal ions, humic substances, and particles can catalyze hydrolysis for some compounds. The structure of the pesticide determines which of these processes, if any, are important in its hydrolysis.

Organic chemicals that can undergo hydrolysis on time scales important for consideration of this process in surface water systems (half-lives of days to years) include alkyl halides, aliphatic and aromatic esters, carbamates, phosphoric esters, and phosphoric acid esters. Some pesticides, such as dichlorvos, undergo hydrolysis at rates too fast (halflives of minutes) to ever be present at significant concentrations in surface waters. Other pesticides, such as DDT and chlordane, undergo hydrolysis at rates too slow (half-lives of years to decades) to warrant consideration of this transformation process. Others, such as pentachlorophenol (PCP) and benfluralin (benefin), contain no hydrolyzable functional groups.

3.2.1.2 Oxidation-reduction reactions

Oxidation-reduction reactions are chemically or biologically mediated reactions that involve a transfer of electrons. The process requires two chemical species to react as a couple: one chemical undergoes oxidation (loses one or more electrons) while another undergoes reduction (gains one or more electrons). Many oxidation reactions of pesticides in surface waters are biologically or photolytically induced. In reduced environments, such as bed sediments and the hypolimnion of lakes, abiotic reduction reactions can occur when organic or inorganic reducing agents are present, such as certain transition metals (iron, nickel, cobalt, chromium), extracellular enzymes, iron porphyrins, or chlorophylls. The rates of reduction reactions are dependent on pH and the magnitude of the reduction potential. The reduction half-life of the organophosphorus insecticide (OP) parathion, for example, is on the order of minutes in strongly reducing environments.

3.2.2 Biodegradation

Biodegradation is the transformation of pesticides mediated by living organisms using enzymes. Chemical transformation reactions can cause structural changes in an organic chemical, but biodegradation is the only transformation process able to completely mineralize the pesticide. Microorganisms degrade (transform) organic chemicals as a source of energy and carbon for growth, although most of their degradative enzymes are not used directly for growth and energy processes, but rather are part of a metabolic sequence that terminates in energy release. All naturally produced organic compounds can be biodegraded, though this is a slow process for some chemicals. On the other hand, some synthetically produced organic chemicals, including most pesticides, have structures totally unfamiliar to microorganisms, which may not have the enzymes needed for degradation of these compounds. This is the primary reason why some pesticides, such as DDE, hexachlorobenzene (HCB), and mirex, are recalcitrant (very long lived) in the environment. However, even these synthetic compounds are observed to slowly biodegrade, probably owing to a process called cometabolism. In cometabolism, the microorganisms are using other substrates (carbon sources) for growth and energy, and the unfamiliar synthetic compound enters into the process and is transformed. The microorganisms derive no particular benefit from the degradation of this compound.

The rate of biodegradation of a pesticide is dependent on chemical structure, environmental conditions, and the microorganisms present. The structure of the organic chemical determines the types of enzymes needed to cause its transformation. The concentration of the chemical also can affect its rate of degradation. At high concentrations, a chemical may be toxic to microorganisms; at very low concentrations, it can be overlooked by the organisms as a potential substrate. The environmental conditions (temperature, pH, moisture, oxygen availability, salinity, and concentration of other substrates) determine the species and viability of the microorganisms present. Finally, the microorganisms themselves control the rate of biodegradation depending on their species composition, spatial distribution, population density and viability, previous history with the compound of interest, and enzymatic content and activity (Scow, 1990).

3.2.3 Photolysis

Photolytic transformations of pesticides are caused by the addition of energy from sunlight. The earth's atmosphere filters out light with wavelengths shorter than 290 nm; only wavelengths greater than this reach the earth's surface. Pesticides can undergo a direct reaction with sunlight (direct photolysis) or a secondary reaction with a photoactivated, sunlight-induced, short-lived reactive chemical species (indirect photolysis). The type of photoinduced reaction is dependent on the structure of the pesticide and specific environmental conditions.

3.2.3.1 Direct photolysis

Direct photolysis is the result of absorption of sunlight by a pesticide, causing a chemical transformation, such as cleavage of bonds, dimerization, oxidation, hydrolysis, or rearrangement.
This reaction will occur only if the pesticide absorbs light at wavelengths present in solar radiation. The light absorption spectrum of most pesticides falls outside or near the fringes of the solar spectrum; therefore, direct photolysis is not an important transformation process for many pesticides. Notable exceptions to this are DNOC, fenitrothion, and metoxuron.

3.2.3.2 Indirect photolysis

Indirect photolysis is usually a photo-induced oxidation reaction. Sunlight excites a photon absorber, such as nitrate or dissolved organic matter, which in turn reacts with dissolved oxygen to form potential photoreactants such as singlet oxygen ($1O_2$), hydroxyl radical (OH), superoxide anion (027, peroxy radical (ROO), and hydrogen peroxide (H_20_2). These highly reactive species randomly attack water, dissolved organic matter, dissolved oxygen, or pesticides, if present. Another type of indirect photolysis, triplet photosensitization, occurs when a photon absorber, such as humic acid, transfers excess energy to a pesticide molecule, which then photodegrades. The two most important indirect photolysis reactions are singlet oxygen and nitrate-induced photooxidation. Singlet oxygen is a very efficient photoreactant for specific types of chemical structures, including many OPs. The more general reaction is the nitrate-induced photooxidationthat proceeds through the hydroxy radical intermediate and affects all organic molecules. For any specific surface water, the rate of this reaction is a function of the nitrate concentration.

3.3 Phase-transfer processes

Phase-transfer processes involve the movement of a pesticide from one environmental matrix to another. The important processes that can occur in the water environments include water-to-solid transfer (sorption), water-to-biota transfer (bioaccumulation), and water-to-air transfer (volatilization from water). In addition to these processes, air-to-solid transfer (vapor sorption) is important in soil environments. Although the physical movement of the chemical is involved, these transfer processes should not be confused with transport processes. Transfer processes are important on the scale of molecular distances (nanometers to micrometers). Once the organic chemical has passed through the physical interface (environmental compartment boundary), it may undergo transport over much larger distances. The phase-transfer processes of sorption and volatilization largely control the overall transport of many pesticides in water.

3.3.1 Pesticide sorption in water

Pesticides are distributed between particle surfaces and the water to varying degrees. This process, termed sorption, can play a pivotal role in the environmental behavior, transport, and fate of a pesticide in surface water. An organic chemical sorbed to a particle surface behaves differently than it does in the dissolved phase. Chemicals associated with particles generally are less available for biodegradation and are not available for volatilization to the atmosphere. Some particle-associated pesticides, such as atrazine (in soil), undergo sorbent-catalyzed hydrolysis. The extent of sorption of a pesticide is a function of its physicalchemical properties and the properties of the particle and the solution. Relevant aspects for the solution include pH (especially for organic chemicals having a pKa, from 4 to 8), ionic strength, concentration of dissolved organic carbon (DOC), and, to a lesser extent, temperature. The ionic strength of the solution affects the activity coefficient of the organic chemical in water. As the ionic strength of an aqueous solution increases, the chemical's solubility decreases and the extent of sorption slightly increases. The presence of DOC in the water also can affect the activity coefficient of the pesticide, decreasing the extent of sorption. Because sorption is a surface process, the characteristics of the particles that have the greatest influence on the extent of sorption are surface area and surface coverage by organic films. In most surface waters, the majority of the particulate surface area is contributed by silt, clay, and colloidal size particles. In addition to having large surface areas, these sizes of particles are generally the most enriched with organic surface films. It has been shown that organic coatings on particles essentially control the extent of sorption for many organic chemicals (Chiou, 1990). The hydrophobicity of an organic chemical, which can be quantified to some extent by its water solubility or octanol-water partition coefficient, also controls the extent of sorption. The extent of sorption at equilibrium is commonly defined in terms of a distribution coefficient, Kd, defined as the ratio of the concentrations of the pesticide between the suspended sediments and the water.

An organic carbon-normalized distribution coefficient, K_{oc}, defined as $K_d$divided by the fractional content of organic carbon in the suspended sediment, also is used widely. For a wide range of pesticides and other organic chemicals, their sorption distribution coefficients have been shown to be correlated strongly with their water solubilities. This provides a tool for predicting the extent of sorption of a particular chemical in a particular environment where the organic coatings of the particles dominate the sorptive process. **A** number of structure activity relations have been derived for these types of predictions (Lyman, 1990). Sorption is an extremely complex process. With limited information on sorption and relatively few environmental observations of the process, researchers have often assumed that sorption of organic chemicals is completely reversible, linear (with respect to chemical concentration), and at equilibrium in surface waters. Studies have shown, however, that sorption and desorption are not completely reversible, at least in the laboratory, and that chemical equilibrium may not be reached for biotic particles in surface waters. For most environmental situations, organic contaminants are present at concentrations low enough that a linear K_d value adequately describes its sorptive behavior. Given the numerous uncertainties in environmental observations of organic chemicals, the quantification of nonequilibrium, nonlinear, and nonreversible sorptive behavior has been difficult.

3.3.2 Bioconcentration and bioaccumulation

Some pesticides concentrate in the living tissues of aquatic organisms, such that the concentration in the organism is greater than in the water. The pesticide can accumulate in tissues by two routes. One route is through the process called bioconcentration, which is direct water/ tissue partitioning governed by the same mechanisms as sorption of pesticides to organic matter on particles. The second route is through the organism's diet. When one organism eats another that has accumulated pesticides in its tissue, some fraction of that pesticide burden is available for accumulation by the consumer. The combination of these two routes, both of which are thought to be important in the environment, is termed bioaccumulation. It has been observed by many investigators that bioconcentration can be related to hydrophobicity for many persistent chemicals. Thus, numerous structure-activity relations have been developed that relate bioconcentration to a chemical's water solubility or octanol-water partition coefficient (Bysshe, 1990**).** The two most important parameters determining the extent of bioconcentration for a particular compound are the lipid content of the organism and the rate at which the chemical is metabolized in the organism. Differences of up to two orders of magnitude in bioconcentrationcan be expected for a single compound because of variations in biotic species, sex, life stage, and size (Bysshe, 1990).

3.3.3 The Henry's Law constant

Pesticides can be transferred from the dissolved aqueous phase to the vapor phase in the atmosphere as a result of volatilization from water. This transfer is controlled by the chemical nature of the air-water interface and the mass transfer (advective) rates of the chemical in water (velocity of water flow, etc.), the pesticide's molecular diffusion coefficients in air and water, and its Henry's Law constant. Thomas (1990) has suggested that the importance of volatilization for a given chemical can be generalized from its Henry's Law constant alone. For pesticides that have a Henry's Law constant less than 3×10^{-7} atm-m^3/mole, volatilization from surface water is unimportant. For pesticides that have a Henry's Law constant greater than 1×10^{-5} atm-m^3/mole, volatilization is significant for all waters. Many of the volatile pesticides used as fumigants have Henry's Law constants in the range where volatilization can be a significant process in their environmental behavior. In contrast to this, only a few of the high-use herbicides exhibit any tendency toward volatilization from surface water. The organochlorine pesticides fall between these two extremes and may or may not volatilize from water, depending on the environmental conditions and the relative concentrations of the compound in the water and in the atmosphere. Just as pesticides distribute themselves between the water and particle surfaces in water, they also distribute themselves between the air and particle surfaces in soils. The extent of this vapor sorption (i.e., air-to-solid transfer) is a function of the chemical's properties, the soil particle's properties, and the water content of the soil. **Sitea (2001**) has shown that in dry soils, vapor sorption interactions are stronger between the pesticide and the inorganic surface of the particle (particularly clay surfaces) than with the organic matter on the particle surface. As the water content of the soil increases, the inorganic surface becomes hydrated and the water outcompetes the pesticides for the inorganic sorption sites. The extent of vapor sorption decreases and the interactions with the organic carbon surface coatings become the dominant mechanism.

3.4 Transport of pesticides in surface waters

The transport of a pesticide in surface waters depends on the form in which the compound exists in the water and the hydrodynamics of the system. As discussed in the preceding section, a pesticide molecule can exist either in the dissolved phase or it can be associated with a particle or colloid. In the dissolved phase, transport of the pesticide will be governed essentially by water flow. In the associated phase, transport will be governed by the movement of the particle or colloid. Pesticides in the associated phase can undergo a variety of transport processes, depending on the type of substrate with which it is associated. Transport of pesticides associated with dissolved organic matter or colloids is primarily governed by water flow, similar to that of dissolved pesticides. Pesticides associated with particles (sands to clays), fecal pellets, or coagulations of very fine particles tend to settle out in lakes and reservoirs, and in low-energy sections of streams, such as backwaters and behind large objects. Because of the propensity of hydrophobic organic pesticides to associate with natural organic matter, they tend to accumulate in bed sediments with a relatively high organic matter content (more than 1 percent). These sediment deposition areas can serve as long- or short-term sinks for pesticides until the sediments are disturbed by the hydrodynamics of the system. In streams, high-energy events, such as spring runoff and large storms, can transport bed sediments and their associated pesticides downstream. When particle-associated pesticides are reintroduced into the water column, they may become redistributed between the dissolved and particulate phases in the attempt to reach sorptive equilibrium. The newly dissolved pesticides will be transported with the flow of water, while the pesticides still associated with particles can again return to the bed sediments, once the energy level of the stream subsides to a point where the particles settle out of the water column. Thus, pesticides with low water solubility and a high affinity for surfaces, such as the OCs, tend to remain in the bed sediments of streams for long periods of time and are transported slowly from the system. Pesticides with relatively high water solubility and little affinity for solids, such as triazine and acetanilide herbicides, are transported in a flowing stream at a rate approximating the river's velocity. In slow-moving surface water systems, such as lakes and reservoirs, the hydrodynamic conditions controlling the transport of pesticides are different from those of faster moving systems such as streams, although the sorptive interactions in slow- and fast-moving waters are essentially the same.

4.0 CONCLUSION

Knowledge of the behavior and fate of pesticide in water is useful as all water soluble pesticides end up in water bodies irrespective of the point of application. This is particularly important in fisheries and aquaculture management, and in the water treatment industry.

5.0 SUMMARY

In this unit students have leant that:

- Degradation of pesticide in water occurs through chemical transformation, microbial degradation and photolysis.
- Pesticide degradation in the water is also affected by phase-transfer processes, which include pesticide sorption in water, bioaccumulation, bio-concentration and the Henry’s Law constant.

6.0 TUTOR-MARKED QUESTIONS

1. Explain the various transformation processes of pesticides in water.
2. Discuss the fate transfer processes of pesticides in water.

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UNIT 10 DEGRADATION AND METABOLISM OF PESTICIDES IN PLANTS

CONTENTS

1.0 INTRODUCTION

Understanding pesticide metabolism in plants is necessary for pesticide development, for safe and efficient use, as well as for developing pesticide phytoremediation strategies for contaminated soil and water. Individual reactions of degradation–detoxification pathways in plants include oxidation, reduction, hydrolysis, and conjugation. Metabolic pathway diversity depends on the chemical structure of the xenobiotic compound (pesticide), the plant, environmental conditions, metabolic factors, and the regulating expression of these biochemical pathways. Knowledge of these enzymatic processes, especially concepts related to pesticide mechanism of action, resistance, selectivity, tolerance, and environmental fate, has advanced understanding of pesticide science, and of plant biochemistry and physiology (Van Eerd et al., 2003). In this unit, we shall discuss the fundamental mechanisms of pesticide metabolism in plants.

2.0 OBJECTIVES

By the end of this unit, students should be able to:

1. describe enzymatic transformations of a wide variety of pesticides,
2. present the mechanism, biochemistry, genetics, and regulation of pesticide metabolism in plants,
3. understand the broad aspects of pesticide metabolism in plants, and
4. identify the importance of these biochemical pathways for pesticide development and environmental stewardship.

3.0 MAIN CONTENT

3.1 Pesticide metabolism in Plants

Enzymatic transformation, which is mainly the result of biotic processes mediated by plants and microorganisms, is by far the major route of detoxification. Metabolism of pesticides may involve a three-phase process (Hatzios 1991). In Phase I metabolism, the initial properties of a parent compound are transformed through oxidation, reduction, or hydrolysis to generally produce a more water-soluble and usually a less toxic product than the parent. The second phase involves conjugation of a pesticide or pesticide metabolite to a sugar, amino acid, or glutathione, which increases the water solubility and reduces toxicity compared with the parent pesticide. Generally, Phase II metabolites have little or no phytotoxicity and may be stored in cellular organelles. The third phase involves conversion of Phase II metabolites into secondary conjugates, which are also nontoxic (Hatzios 1991). In leafy spurge (*Euphorbia esula*L.), examples of Phase III metabolism are the conjugation of the *N*-glycoside metabolite of picloram with malonate and the formation of a gentibioside from the picloram glucose ester metabolite.

Although there are fundamental similarities and differences between plant and microbial pesticide metabolism, this unit will emphasize the enzymatic transformations of a wide variety of pesticides in plants, and present the mechanism, biochemistry, genetics, and regulation of these processes in plants.Furthermore, the broad aspects of pesticide metabolism in plants as well as the importance of these biochemical pathways for pesticide development and environmental stewardship will be discussed.

3.1.1 Oxidative Transformations

Oxygenation is the most frequent first step in the biotransformation of pesticides and other organic xenobiotics, and many of these reactions are mediated by oxidative enzymes. Plants therefore produce a wide range of oxidative enzymes. These include cytochrome P450, peroxidases, polyphenoloxidase, laccase, and tyrosinase, and polyphenol oxidases.

3.1.1.1 Reactions by Cytochromes P450

The most extensively studied oxidative enzymes in plants are the P450s, which are the most important enzymes in Phase I pesticide metabolism (Barrett, 2000). Cytochrome P450s are hemethiolate proteins that have been characterized in animals, plants, bacteria, and filamentous fungi. In plants, P450s produce many secondary metabolites including plant growth regulators, isoprenoids, and alkaloids. Cytochrome P450s are encoded by a superfamily of genes designated as *CYP*, which have highly conserved residues around the heme portionof the protein (Barrett 2000). The first plant P450 gene was sequenced in 1990 (Bolwell et al. 1994), and presently, more than 500 P450 plant genes have been described (Barret 2000). P450 genes occur in clusters in the genome. Regulation and expression of P450s are not well understood in plants mainly because of the very low quantities of P450 enzymes usually present in plant cells, particularly if the plant has not been exposed to physiochemical, physiological, or xenobiotic stress. Cytochrome P450s often catalyze monooxygenase reactions, usually resulting in hydroxylation. However, there are many other P450-mediated reactions including dehydration, dimerization, deamination, dehydrogenation, heteroatom dealkylation, epoxidation, reduction, and C–C or C5N cleavage. Among the three classes of P450 found in plants, animals and microorganisms, only class I and class III P450s are found in plants. Class I P450s are flavin adenine dinucleotide (FAD) or flavin mononucleotide (FMN) dependent, and reduced nicotinamide adenine dinucleotide phosphate (NADPH) requiring P450s that are usually microsomal membrane-bound proteins in plants and filamentous fungi. Class III P450s are located in plant plastids and do not require auxillary redox partners.

Agrochemicals can influence cytochrome P450 systems by acting as effectors, thereby modifying pesticide metabolism, or by modulating overall metabolism of an organism. These effects can increase or decrease physiological activities, which may affect growth and development. Direct evidence that xenobiotic metabolism was mediated by P450swas obtained through experimentation with plant microsomal preparations. Using microsomal preparations from several plant species, it was shown that chlortoluron was metabolized to two metabolites by at least two different P450 enzymes. Since that time, a number of P450-mediated phenylurea-metabolizing genes have been characterized. Mougin et al. (2001) demonstrated that the fungicide fenpropimorph was metabolized to an oxygenated metabolite in wheat seedling microsomal preparations. Increased metabolism occurred when seeds were pretreated with naphthalic anhydride, a chemical safener that enhances cytochrome P450 levels. Further, oxidation of fenpropimorph in wheat seedling microsomes was inhibited when the preparations were exposed to carbon monoxide, which binds to the heme portion of the P450 molecule instead of oxygen, thereby blocking enzymatic reactions. These authors suggested that fenpropimorph metabolism is P450-mediated. Other researchers have used microsomes to demonstrate that the mechanism of resistance to several dissimilar herbicide chemistries in blackgrass (*Alopecurusmyosuroides*) and rigid ryegrass (*Loliumrigidum*) was based on enhanced P450-mediated metabolism. Herbicide resistance mediated by P450s mayarise via two scenarios: (1) mutation of an existing P450, allowing increased binding and metabolism of the herbicide or (2) increased activity of existing P450s (Barrett 2000). In the future, researchers will no doubt continue to focus on isolating and characterizing plant P450 genes associated with pesticide metabolism. With a better understanding of P450 genes and their regulation, it may be possible to manipulate the crop plant system to increase herbicide tolerance.

3.1.1.2. Peroxidases, Phenoloxidases, and Related Oxidoreductases

Other than P450s that catalyze the polymerization of various anilines and phenols (Dec and Bollag2001), there are other peroxidase-mediated pesticide transformations in plants that function similar to P450s. These include decarboxylation, sulfur oxidation, *N*-demethylation, ring hydroxylation, and aromatic methyl group oxidations. In plants, peroxidase enzymes often function in Phase III metabolism, e.g., formation of bound residues. Horseradish (*Amorocialapathifolia*Gilib.) roots contain large quantities of peroxidase. Horseradish root tissue has been used to remove 2,4-dichlorophenol from water and was more effective in contaminant removal than the purified peroxidase enzyme (Dec and Bollag 2001). In most instances, polymerization products have reduced toxicity compared with the substrate (Dec and Bollag, 2001).

3.1.2 Hydrolytic Transformations

Hydrolytic enzymes cleave bonds of a substrate by adding H or OH from H_2O to each product. There are many hydrolytic enzymes that are capable of metabolizing a variety of substrates, particularly those containing amide, carbamate, or ester functional groups. These enzymes may be compartmentalized or extracellular, and reactions can occur under aerobic or anaerobic conditions. Like most classes of enzymes, hydrolytic enzymes may have broad substrate specificities, thereby allowing degradation of a variety of pesticides. Pesticide ester hydrolysis in plants has been extensively studied and reviewed (Hoagland and Zablotowicz 2001). Ester hydrolysis is commonly carried out by esterases and to a much lesser extent by lipases and proteases. Often, herbicides such as fenoxaprop-ethyl, diclofop-methyl, and 2,4-DB are esterified to increase absorption and selectivity. In plants, the ester bond is metabolized, forming the acid, which is usually more phytotoxic. Depending on the herbicide, deesterification also can result in immediate herbicide detoxification, as is the case with thifensulfuron-methyl in certain plant species.

Propanil is the most widely studied pesticide with regard to amide hydrolysis. Rice (*Oryza sativa* L.) is tolerant to propanil because of high levels of aryl acylamidase, which cleaves the amide bond and is the basis for crop selectivity Propanil resistance is due to enhanced hydrolysis by aryl acylamidase in resistant barnyard grass and resistant jungle-rice (*Echinochloacolona*) biotypes.

In plants, there is limited literature on the role of phosphatases and sulfatases in pesticide metabolism (Hoagland and Zablotowicz 2001). Nitrile hydrolysis is the main route of metabolism of bromoxynilin wheat and of cyanazine in wheat and potato (*Solanumtuberosum*L.). Hydrolysis of the nitrile group produces an amide moiety that is converted to carboxylic acid, which may be subsequently decarboxylated. In plants, the major metabolic route for the phenylcarbamate pesticides CIPC and IPC is aryl hydroxylation and conjugation, rather than hydrolysis of the carbamate moiety.

3.1.3 Aromatic Nitroreductive Processes

Generally, nitroaromatic compounds are transformed to different products in individual plant species. For example, the major metabolite of trifluralin in peanut (*Arachishypogaea*L.) is *N*-depropylatedtrifluralin, whereas in sweet potato (*Ipomoea batatas*L.), the monoamino-derivativeof trifluralin is predominant. In plants, glutathione conjugation of pentachloronitrobenzene occurs concomitant with the removal of Cl or NO_2. Glutathione-mediated displacement of the nitro group of aromatic compounds has also been described in plants.

It is sometimes difficult to separate biological and chemical xenobiotic reductions because reduction of aromatic nitrogroups, e.g., trifluralin and diphenyl ether herbicides, may be coupled with anaerobic reduction of humic acids or iron reduction. The conversion of the herbicide acifluorfen to aminoacifluorfen is a common example of an aromatic nitroreduction reaction. There is potential to develop transgenic crops that express a bacterial nitroreductase gene to metabolize diphenyl ether herbicides, thereby providing crop tolerance to these herbicides (Zablotowicz *et al.* 2001).

3.1.4 Pesticide Conjugation Reactions

3.1.4.1 Carbohydrate and Amino Acid Conjugation

Hall *et al.* (2001) recently defined pesticide conjugation as the ‘‘metabolic process whereby an exogenous or endogenous natural compound is joined to a pesticide or its metabolite(s) facilitating detoxification, compartmentalization, sequestration, and/or mineralization.’’ Conjugation of pesticides often involves utilization of existing enzymatic machinery and is therefore called a cometabolic process. Glucose conjugation to pesticides occurs primarily in plants, resulting in several metabolites including *O*-, *S*-, and *N*glucosides, glucose ester, gentibioside (e.g., 6-*O*-b-D-glucopyranosyl-D-glucose), and malonyl-glucose conjugates. The most common glucose conjugates are *O*-glucosides because pesticide oxidation reactions form hydoxyl groups, which are suitable sites for glucose conjugation. Differential conjugation of 2,4-D imparts differences of susceptibility in wheat and some broadleaf species. Many susceptible broadleaf weeds produce glucose ester metabolites, which are readily susceptible to hydrolysis, yieldingphytotoxic 2,4-D. Conversely, 2,4-D–tolerant wheat rapidly produces amino acid conjugates and *O*-glucosides, which are stable nonphytotoxic metabolites that are not easily hydrolyzed. Amino acid conjugation occurs primarily in plants and is very common. Most of the research on amino acid conjugation of pesticides has been conducted on 2,4-D and twenty amino acids have been found to conjugate with the herbicide.

Uridine diphosphate–glucosyl (UDPG) transferase, anenzyme involved in cellulose biosynthesis, mediates pesticide–glucose conjugation and pesticide–glucose ester conjugation reactions. As mentioned above, glucose esters of pesticides are cleaved by esterases, often resulting in the release of the pesticide. However, the addition of a second glucose molecule to the glucose ester produces a gentiobiose conjugate, which is not readily hydrolyzed. Other complex sugar conjugates in addition to gentibioside (two glucose molecules) are glycosides (a glucose and one other sugar, such as arabinose). Pesticide–sugar conjugates can undergo further conjugation with malonate via reaction with malonyl CoA, a common reaction in higher plants. In tomato (*Lycopersiconesculentum*L.), the herbicide metribuzin is conjugated to glucose, which is subsequently conjugated to malonate, forming the *N*-malonyl–glucose conjugate. A range of UDPG transferase activity within various tomato cultivars confers differential tolerance of these cultivars to metribuzin (Smith et al. 1989). Furthermore, increased metribuzinphytotoxicity in all the cultivars was noted under low light conditions. It was speculated that under low light conditions less glucose and UDPG were produced, thereby reducing conjugation and elevating herbicide phytotoxicity.

3.1.4.2 Plant Glutathione Conjugation Reactions

Glutathione (g-L-glutamyl-L-cysteinylglycine [GSH]), commonly present in the reduced form, is ubiquitously distributed in most aerobic organisms. Homoglutathione (g-Lglutamyl-L-cystein-b-alanine), a GSH analog, occurs in several legume species. Although GSH concentrations vary during plant development, GSH is found in relatively high concentrations in most plant tissues. Glutathione is phloem mobile and is degraded by carboxypeptidases and transpeptidases in the cytoplasm and vacuoles. Generally, GSH synthesis is limited by availability of cysteine and hence by the concentration of sulfate ions. Nonenzymatic GSH conjugation may be important for the metabolism of several herbicides. For example, increased GSH concentrations protects wheat from fenoxaprop injury, and this reaction is considered nonenzymatic because glutathione *S*-transferase (GST) activity in these plants is low. However, enzymatic conjugation of xenobiotics with GSH via GSTs is more common than nonenzymatic conjugation. Glutathione-*S*-transferases are homo- or heterodimer, multifunctional enzymes located in the cytosol, which catalyze the nucleophilic attack of the sulfur atom of GSH by the electrophilic center of the substrate. More than 50 plant GST gene sequences from 13 plant species have been published. Compared with other plant and bacterial species, corn (*Zea mays* L.) GST gene enzyme systems have been the most extensively studied.

The role of GSTs and GSH in plants encompasses several major functions. The first is the metabolism of secondary products, including cinnamic acid and anthocyanins. A second function is regulation and transport of both endogenous and exogenous compounds, which are often GS-X tagged for compartmentalization in the vacuole or cell wall (Hatzios 2001). This is a particularly important aspect for herbicides, anthocyanins, and indole-3-acetic acid. Protection against oxidative stress from herbicides, air pollutants (Sharma and Davis, 1994), pathogen attack, and heavy metal exposure is a third function. Glutathione conjugates and their terminal metabolites are stored in the vacuole or bound to the cell wall.

3.1.5 Formation of Bound Pesticide Residues

Pesticides (mainly conjugated pesticides) are often bound to plant cell walls. Bound pesticide residues are generally considered as those that cannot be extracted with aqueous and organic solvents. However, a more precise definition has been provided by Skidmore et al. (1998): A bound xenobiotic residue is a residue associated with one or more classes of endogenous macromolecules. It cannot be dissociated from the natural macromolecule using exhaustive extraction or digestion without significantly changing the nature of the associated endogenous macromolecules. When studying bound-pesticide residues using radiolabeled pesticides, it is important to differentiate the bound residue containing the labeled xenobiotic or its metabolite from the ‘‘natural label’’ Natural labeling occurs when $^{14}CO_2$ is released from the mineralized pesticide and is incorporated into the plant cell wall. Natural labeling in plants has been observed with several pesticides. Furthermore, it is important to know the precise position of the label on the pesticide molecule so that the site of pesticide incorporation into the cell wall can be determined (Sandermann *et al*. 2001). Digestive treatment with different enzymes such as cellulase, collagenase, pepsin, amylase, and proteases can aid in identifying the nature of pesticide incorporation.

On the basis of reports in the literature, it appears that xenobiotics are incorporated randomly into different cell wall components (Sandermann et al. 2001); however, little is known about the type of linkages involved in this binding. There is concern about the bioavailability of bound pesticides from plant residues. *Phanerochaetechrysosporium*mineralized bound chloroaniline and 2,4-dichlorophenol, indicating that these compounds may become bioavailable. The ability of animals to release xenobiotics bound to plant residues is unknown. Experimentsusing a ‘‘simulated stomach’’ demonstrated that pesticides were released from plant residues, but only when high concentrations of bound pesticide residues were used. In comparison, only low concentrations of bound pesticide residues are typically present in plant residues (Sandermann et al. 2001). However, the biological relevance of typically low concentrations of bound pesticide residues is not known. Presently, the U.S. Environmental Protection Agency requires no characterization ofbound pesticide residues if concentrations are less than 0.05 ppm of the parent equivalents or 10% of the total pesticide residue. If concentrations exceed these levels, determination of the bioavailability based on ‘‘simulated stomach’’ experiments is required. The toxicological nature and bioavailability of bound xenobiotic residues requires continued research to fully assess its impact on human health and theenvironment (Sandermann *et al*. 2001).

4.0 CONCLUSIONS

The basis for selectivity of plants to pesticides has been extensively studied during the past 40 years and has provided a wealth of information on diverse biological processes and enzymes in plants. Understanding the plant enzymatic systems involved in metabolic processes will provide a basis for developing novel, more effective, and environmentally benign herbicides and safeners. One particular strategy is phytoremediation, a process by which plants and their associated microorganisms collectively degrade, detoxify, and remove pollutants.

5.0 SUMMARY

In this unit students have leant that:

- enzymatic transformation, which is mainly the result of biotic processes mediated by plants and microorganisms, is by far the major route of pesticide transformation in plants,
- the various processes involved in the transformation of pesticide in plants include oxidative transformation, hydrolytic transformation, aromatic nitroreductive processes, pesticide conjugation reactions, and the formation of bound pesticide residues.

6.0 TUTOR-MARKED QUESTIONS

3. Explain the various transformation processes of pesticides in plants.
4. Discuss the three phases involved in pesticides metabolism in plants.
5. List the major oxidative enzymes produced by plants.

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UNIT 11 DEGRADATION OF PESTICIDES IN ANIMALS

CONTENTS

1.0 INTRODUCTION

Elucidation of the metabolism and fate of organic pesticides in animals is prerequisite to the development of these chemicals for use in pest control. From a public health viewpoint, information on the chemical behavior and reactions of insecticides in living systems is essential for the assessment of hazards arising from the use of these compounds. Metabolism studies in large animals, as well as small animals, play an essential role in this hazard evaluation. Identification and establishment of the toxicological properties of the metabolic products formed in animals after exposure to pesticides is indeed mandatory before residual hazards may be assessed. From a more fundamental aspect, metabolism studies are necessary for our understanding of the mode of action of pesticidal chemicals, i.e., the elucidation of the intoxication and detoxication processes that occur in biological systems. Explanations for such important phenomena as pesticide specificity and the development of pesticide resistance are often found in the intoxication and detoxication reactions that occur in the animal.

2.0 OBJECTIVES

By the end of this unit, students should be able to:

1. describe enzymatic transformations of a wide variety of pesticides in animals
2. highlight the significance of metabolism studies in animals
3. Understand the various enzymatic reactions involved in pesticide degradation in animals
4. Understand the peculiarity of pesticide metabolism in ruminant animals

3.0 MAIN CONTENT

3.1 Degradation and metabolism of pesticides in animals

The term ‘metabolism’ generally refers to the chemical transformation of the pesticide resulting from natural processes in the environmental system under investigation. Biological systems have evolved to survive against a wide range of environmental influences. To survive, the system needs to absorb nourishment and to defend itself against threats from chemical or biological entities. To achieve this, it has developed a wide range of enzyme and chemical defence mechanisms, which will assert themselves on any foreign compound entering the system. Therefore, a xenobiotic entering a biological system is likely to suffer a chemical change which will facilitate its utilization or its elimination from the system.

The metabolism of organic pesticides may be divided into two large but distinct categories: (1) activation and (2) detoxication. Activation is defined as the metabolic reaction or reactions that convert an intrinsically inactive compound to an active compound or an active compound to another active compound. In some cases a number of different toxic compounds may be produced. Detoxicationis defined as the reaction or reactions that lead to nontoxic substances. Owing to the vastness of the subject dealing with metabolism of pesticides in animals, we shall generalize for insecticides, fungicides and herbicides rather than dwelling on individual class of pesticides. Specific examples will however be chosen to illustrate the various types of activation and detoxication reactions that take place with these compounds.

The mixed-function oxidases that require NADPH and molecular oxygen are responsible to a large degree for the activation of insecticides and for detoxication. The importance of these enzymes in metabolism will become evident in the following discussion.

3.2 Toxicological Significance of Pesticide Metabolism Studies in Animals

Many studies have been conducted to establish conditions for pesticide use, which will permit the pest control essential for food production and yet insure safety to humans. It is clear that animal metabolism studies assume in the overall evaluation program that each has essential toxicological significance. Without knowledge of the metabolic pathways taken by the pesticide in laboratory animals, oral toxicity testing may not be complete, as it may be difficult to test all the appropriate toxicants. Further, if the metabolic fate of pesticide residues present in the diet of food animals was not known, it would not be possible either to evaluate the toxicity or to quantify the amounts of pesticide residues occurring in animal tissues or products destined for human consumption. The toxicological significance of pesticide metabolism studies in both large and small animals is thus clear for the overall evaluation of safety to humans associated with the use of agricultural pesticides.

3.3 Techniques and procedures used to study the metabolism of pesticides in animals

The experimental equipment, procedures and techniques that may be used to study the metabolism of pesticides in large animals (chickens, sheep, goats, swine, cattle, and horses) include: (1) techniques for administration of pesticides to animals; (2) metabolism stalls and cages for restraining experimental animals; (3) methods and equipment for separate and quantitative collection of excreta, respiratory gases and other volatile products from animals; (4) surgical techniques used to modify animals for metabolic studies (colostomy, cannul at ions, fistulations, etc.); (5) biopsy techniques; and (6) in vitro techniques that may be useful for studying the metabolism of pesticides in large animals.

3.4 Pesticide biotransformation in animals

Pesticide biotransformation is the process by which lipophilic foreign compounds are metabolized through enzymatic catalysis to hydrophilic metabolites that are eliminated directly or after conjugation with endogenous cofactors via renal or biliary excretion. These metabolic enzymes are divided into four groups, Phase I, II, III and IV reactions (Oesch*et al.* 2000).

3.4.1 Phase I Metabolism

Phase I reactions, considered as functionalization reactions, add or uncover functional groups on pesticides with increasing polarity or nucleophilicity that create a suitable substrate for Phase II metabolism. Phase I reactions generally involve oxidation, reduction and hydrolytic reactions as well as other rarer miscellaneous reactions. Primarily the cytochrome P450 family of enzymes mediates these reactions, but other enzymes (e.g. Flavin monooxygenases, peroxidases, amine oxidases, dehydrogenases, xanthine oxidases) also catalyze the oxidation of certain functional groups. In addition to the oxidative reactions, there are different types of hydrolytic reactions catalyzed by enzymes like carboxylesterases and epoxide hydrolases (Hodgson & Goldstein 2001, Parkinson 2001). Phase I products are not usually eliminated rapidly, but undergo a subsequent reaction in which an endogenous substrate such as glucuronic acid, sulfuric acid, acetic acid, or an amino acid combines with the newly established functional group to form a highly polar conjugate to make them more easily excreted.Sulfation, glucuronidation and glutathione conjugation are the most prevalent classes of phase II metabolism, which may occur directly on the parent compounds that contain appropriate structural motifs, or, as is usually the case, on functional groups added or exposed by Phase I oxidation (Zamek-Gliszczynski*et al.* 2006).

3.4.1.1 Oxidation

Oxidation reactions are arguably the most important metabolic reactions and are found in both plants and animals. Although the enzymology of oxidative reactions is beyond the scope of this present chapter, it is evident that oxidation can be mediated by a range of enzymes, e.g. cytochrome P450s and peroxidases. The former enzyme has been widely researched and shown to consist of a wide range of different isoforms, the relative proportions and types present being dependent on the species, e.g. chlortoluron undergoes benzylic oxidation in maize and *N*-demethylation in wheat. Oxidation is also an important mechanism in the de-activation and metabolic selectivity of the sulfonylurea herbicides.

3.4.1.2 Hydrolysis

Hydrolysis reactions are limited by the chemistry and so appear to be less common than oxidative processes. They nevertheless have significant importance in the detoxification of many pesticides and can be both chemical- or enzyme-mediated. Ester hydrolysis is particularly important in the case of the arylphenoxypropionic acid herbicides, e.g. fluazifop and fenoxaprop, where the herbicide is formulated and used as the alkyl ester to facilitate foliar absorption. Once in the plant, the ester is rapidly hydrolysed to the free acid, which is the active moiety. Ester hydrolysis is also a key metabolic step in the detoxification of the pyrethroid insecticides. Esterase activity is particularly important in the toxicity of the phosphorothionate insecticides. In an *in vitro* study investigating the relative toxicity of diazinon to mammalian and avian species, it was demonstrated that the oxon metabolites (active moieties) were generated in the liver at essentially an equivalent level. However, studies investigating the stability of the oxon in blood showed that mammalian blood (cow, sheep, pig and rat) readily hydrolysed the ester, whereas avian blood had virtually no hydrolytic activity. This finding is consistent with the observed toxicity which shows that avian species are highly susceptible to diazinon toxicity. It was therefore concluded that the extrahepatic metabolism of diazinon is more toxicologically important than liver metabolism. These data also demonstrate that esterases in the blood are important metabolically and are species-dependent. Hydrolysis reactions resulting in the opening of heterocyclic ring systems have also been reported, e.g. cleavage of the oxazolidone ring in vinclozolin, and the heterocyclic ring in some of the sulfonylurea herbicides. In the poultry metabolism of the fungicide vinclozolin, the major component of the residue in fat, liver and muscle resulted from the hydrolytic cleavage of the oxazolidone ring. Other dicarboximide fungicides, e.g. procymidone and chlozolinate, also readily undergo opening of the heterocyclic ring by hydrolysis, a mechanism for which is described by Villedieu *et al*. (1994).

In the case of the sulfonylurea herbicides containing triazine or pyrimidine as the heterocyclic ring, mechanisms for the hydrolytic ring cleavage have been proposed. In the cases of chlorsulfuron and prosulfuron, the product of the opening of the triazine ring is a triuret, while the pyrimidine ring of bensulfuron-methyl and halosulfuron-methyl hydrolyses to give a guanidine, The classic example of amidase activity is propanil, a rice herbicide, which is rapidly metabolized in rice and animals to dichloroaniline.

3.4.1.3 ReductiveProcesses

Reduction reactions have been reported in all biological systems. It is probable that these reactions are more common, but the reaction products may be subsequently re-oxidized within other compartments of the biological system. Typical reactions include the reduction of nitro groups, aldehydes, ketones and alkenes. In animals, the reactions are characteristically found in the liver and GIT and would be expected to occur in ruminants.

3.4.2 Phase II Metabolism

Phase II or conjugation reactions represent chemical synthesis where the xenobiotic (exocon) is chemically bonded to an endogenous substrate (endocon).

3.4.2.1 Glutathione

Glutathione (GSH) is a tripeptide found in both plants and animals and is important as a source of endogenous thiols, which act as scavengers of free radicals and active electrophiles. The reaction results from nucleophilic attack of the thiolate anion on an electrophilic centre and is catalysed by the enzyme, glutathione-*S*transferase.In animals, the formation of mercapturates facilitates the elimination of the xenobiotic in the urine. The transport of the conjugates between cells and to various organs is complex and has been described as involving the formation of the glutathione conjugate inside the cell which is then released for conversion to the *S*-cysteine conjugate. This must then be reabsorbed into the cell to be *N*-acetylated, and finally the mercapturate is released from the cell and excreted.

3.4.2.2 Sugar Conjugates

Conjugation of xenobiotic chemicals with endogenous sugar units is common in both plants and animals and is most frequently observed with alcohols, amines, mercapto moieties and carboxylic acids. In plants, sugar conjugates are usually in the form of glucosides and in animals as glucuronides, although there are exceptions, e.g. glucuronic acid conjugates of 4-nonylphenol found from wheat suspension cultures and the use of glucose conjugates in mammals to conjugate endogenous steroids and bilirubin (Bounds and Hutson, 2000). In animals, glucuronic acid is an important conjugation partner for foreign and endogenous substances in preparation for excretion, especially phenols and acids which are frequently excreted in urine as glucuronides. An additional complexity of glucuronide conjugation was described by Sidelmann*et al*. (1995) who showed that glucuronide conjugates of 4-fluorobenzoic acid could exist as isomers through internal acyl migration and rotation. The glucuronides rearrange to the 2-, 3- and 4-acyl derivatives, each of which exists in α- and β-forms.

3.4.2.3 Amino Acid Conjugation

Amino acid conjugation has been observed in all species; the nature of the amino acid used in the conjugations appears to be dependent on the nature of the acid rather than on the species (Bounds and Hutson, 2000).One of the best known examples of amino acid conjugation is the reaction of 1,2,4-triazole with serine to give triazolylalanine. It has been generally accepted that triazolylalanine is a unique plant metabolite and can also be detected in rotational crops (e.g. fenbuconazole) but recent reports have shown that it is also found in the goat and hen following dosing with fenbuconazole. Following feeding at 100 mg/kg in the diet, the metabolite was identified in liver, milk, kidney and muscle of the goat and in hen muscle. Triazolylalaninewas not found in the rat following dosing with fenbuconazole.

3.4.2.4 Lipophilic Conjugation

Some conjugation reactions increase the lipophilicity of the xenobiotic with the implication that it will be retained within the system and not be as readily eliminated. Some of the best known examples of these conjugates are found in the metabolism of the pyrethroid insecticides. The metabolism of the miticidecycloprate in the cow resulted in 52–76% of the radio-label becoming associated with triacylglycerols in the milk. These were identified as comprising a mixture of cyclopropyl fatty acids resulting from the metabolism of cycloprate to cyclopropanecarboxylicacid (CPCA) and subsequent chain elongation of the carboxylic acid group in a similar manner to that found in fatty acid biosynthesis. It was particularly interesting that a CPCA conjugate of carnitine was present in milk at a level of 39% of the totalradioactive residue in milk 12 h after dosing. The significance of this finding is related to the entry of fatty acids into the mitochondria where fatty acid synthesis and oxidation take place. In this instance, the carnitine acts as a carrier facilitating the transfer of CPCA across the membrane. Based on the above findings it is likely that other xenobiotic carboxylic acids can be incorporated into triglycerides and can be expected to be present in high-fat commodities such as milk.

3.4.2.5 Sulfate Conjugates

Sulfate conjugates are commonly observed in animals, and are formed from substrates similar to those, which readily form sugar conjugates. Indeed, in many cases, these conjugates are competitive with glucuronidation and it has been shown that sulfate conjugation can be promoted by administration of sulfate precursors, e.g. cysteine. The formation of sulfate conjugates is proposed as being an enzyme-catalysed transfer of sulfate from 3-phosphoadenosine-5-phosphosulfate to the substrate and has been widely reported for phenolic xenobiotics.

3.4.3 Phase III Metabolism

Phase III metabolism refers to pesticide residues that are associated with endogenous materials; they can be either covalently bound, or in some way physically encapsulated within the macromolecular matrix. The significance of these residues is difficult to assess and requires that they are characterized in terms ofbioavailability and differentiated from the natural incorporation of the radio-atom. In animals, the most common endogenous materials to which xenobiotics are bound are protein or nucleic acids. In the case of the triazine herbicide ametryn, 61 and 79% of the liver residue in goat and hen, respectively, were unextracted, but following protease hydrolysis could be solubilized. After a further hydrolysis using conditions typical of those used to degrade proteins, several metabolites containing the intact triazine ring were released. The study concluded that conjugations with protein represented a major pathway in the biotransformationpathway of ametryn.

3.4.4 Phase IV Metabolism

A phase IV residue is essentially an artefact of the metabolism study and results from the incorporation of the radio-label into natural compounds. This incorporation is obviously dependent on the positioning of the radio-label but usually results from the extensive metabolism of the xenobiotic. The products can be widely distributed throughout the biological system and result in a significant challenge for the metabolism chemist. In the metabolism of chlorethoxyfos in the goat, total degradation of the xenobiotic was evident with the formation, and expiration, of 14CO2.

3.5 Pesticide metabolism in livestock animals

Although the metabolism in biological systems is described as similar, some species have a particular diversity, which can add complexity to the metabolism. In all animals, macromolecules in food and feed items are digested into simpler compounds, which can be absorbed into the blood stream through the gastrointestinal tract. This digestion occurs through fermentation, by microorganisms in the gut, by hydrolysis and enzymatic reactions. The ruminant is, however, unique in being highly specialized in terms of fermentation, which takes place in the rumen. The latter acts as a batch fermenter and has been defined as an intact ecosystem comprising bacteria, protozoa and anaerobic fungi. In return for the appropriate conditions for survival, the microbial population assist in the digestion of fibrous feeds which would otherwise be underutilized, which is a classical example of a symbiotic relationship.

The environment in the rumen is reducing (the opposite of oxidizing). The gases above the rumen comprise 65% CO2, 27% methane, 7% nitrogen and 0.6% oxygen, while the fluid has a pH of 6–7 and a negative redox potential (*E*h) of −250 mV. In this environment, microbes have little oxygen and therefore any metabolism is limited; however, reductive processes are abundant, e.g. conversion of CO_2 to CH_4, and unsaturated acids are converted to saturated acids. In the rumen, it is therefore possible that the pesticide may be chemically modified prior to being introduced into the gastric stomach. Although the major organ of metabolism is the liver, the areas of administration of the pesticide also have significant metabolizing ability, i.e. the gastrointestinal tract (GIT) and the skin. In the GIT, the intestinal microflora operate in an oxygen-free environment which can favour reductive processes, e.g. reduction of a nitro moiety to an amine. In contrast to the liver, which forms conjugates to assist elimination, the gut flora hydrolyse conjugates excreted in the bile such as glucuronides and sulfate esters. For dermal applications, reactions include bacterial degradation on the skin surface and enzymatic reactions in the epidermis and dermis. The functions of the enzyme systems in the skin were reported as including all those found in the liver, including conjugating ability. The qualitative and quantitative nature of the metabolism can be influenced by species, gender and dose rate, e.g. when tebufenozide was fed to rats, 4% of the 250 mg/kg single dose was metabolized, while about 46% of the 3 mg/kg dose could be metabolized. In many cases, however, an approximately proportional relationship was found between the dose rate and the level of residues.

4.0 CONCLUSION

In this unit, we have examined the degradation and metabolisms of pesticides in animals. The purpose of livestock metabolism studies is essentially to define the nature of the residues present in tissues, milk and eggs intended for human consumption. Additionally, the studies define the distribution of the residues in tissues and the validation of the efficiency of the extraction techniques used for residue analytical testing. Studies are carried out with typical livestock species used in agricultural commerce and are required whenever a pesticide is applied directly to animals or when treated plant commodities are used for animal feed.

5.0 SUMMARY

In this unit the students have leant:

- the significant and purpose of studying pesticide metabolism in animals
- that pesticide metabolism reactions in animals are in two major phases. Viz Phase I, which involves oxidation, hydrolysis, and reductive processes; and phase II reactions, which involves several conjugation reactions.

6.0 TUTOR MARKED ASSIGNMENT

1. Explain the major reasons why the study of pesticides metabolisms in animals in important in pesticide formulation
2. Write a short note on the various enzymatic reations involved in pesticide metabolism in animals

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UNIT 12 REMEDIATION OF OTHER TOXICANTS (HEAVY METALS) IN SOIL

CONTENTS

1.0 INTRODUCTION

With the development of the global economy, both type and content of heavy metals in the soil caused by human activities have gradually increased in recent years resulting in serious environmental deterioration (Su *et al*., 2014). Fertilizers, pesticides and mulch are important agricultural inputs for agricultural production. However, their long-term cum excessive application has resulted in the heavy metal contamination of soils and groundwater. Heavy metals are the most reported pollutants in fertilizers. Heavy metal content is relatively low in nitrogen and potash fertilizers, while phosphoric fertilizers usually contain considerable toxic heavy metals. Heavy metals in the compound fertilizers are mainly from master materials and manufacturing processes.

2.0 OBJECTIVES

By the end of this unit, students should be able to:

- identify the sources of heavy metals contamination in the environment;
- explain the engineering remediation techniques; and
- outline the various bioremediation techniques used in coping with heavy metals contamination in soil.

3.0 MAIN CONTENTS

3.1 Heavy Metals Contamination in Soil

Sources of soil contamination can occur through industrial wastewater, sewage water used for irrigation, quarrying sites and through hazardous waste disposal on the soil (Ojo, 2017). According to Gebreyesus (2014), low concentration of these metals can interact with the soil to cause nutrient deficiency. These heavy metals can affect soil matrices, and hence metal transport. Heavy metal contamination of urban and agricultural soils can result from mining, manufacturing, and the use of synthetic products (e.g. pesticides, paints, batteries, industrial waste and land application of industrial or domestic sludge (Ojo, 2017). Contaminated soils may occur at fields that had past applications of waste water or municipal sludge, areas in or around mining waste piles and tailings, industrial areas where chemicals may have been dumped on the ground and so on. The presence of toxic metals in soil can severely inhibit the biodegradation of organic contaminants (Maslin and Maier, 2000). Erosion, bush burning and oil spillage which are land degradation forms can affect distribution of heavy metals (Oghenero, 2012). Ayodele *et al.* (2014) reported heavy metals contamination of soil and plant samples taken from an abandoned granite quarry in Ekiti State. Other sources of soil contamination include hazardous waste disposal sites, waste incinerators and ash dumps. The factors affecting the bioavailability and occurrence of metals in soil include soil pH, cation exchange capacity, organic matter content, soil and interaction among the target elements (Jung, 2008).

3.2 Remediation of heavy metal contaminated soils

3.2.1 Engineering remediation

Engineering remediation is the use of physical or chemical methods to control heavy metal contamination of soils.

3.2.1.1 Replacement of contaminated soil, soil removal and soil isolation

Replacement of contaminated soil implies adding large amount of clean soil to cover on the surface of the contaminated soil or to blend with the latter. Soil removal is the removal of contaminated soil and its subsequent renewal with the clean soil, which is necessary for the seriously contaminated soil with little area. Soil isolation means isolating the contaminated soil from the uncontaminated soil, but to completely remedy it still needs other auxiliary engineering measures (Zheng *et al.*, 2002). All of the foregoing methods will cost large amount of manpower and material resources, so they can only be applied to small area of soils (Su *et al.*, 2014).

3.2.1.2 Electrokinetic remediation

Soil electrokinetic remediation is a new economically effective technology in which the DC-voltage is applied to form the electric field gradient on both sides of the electrolytic tank containing the contaminated soil; contaminants in the soil are taken to the processing chamber located at the two polar sides of electrolytic cell, through the way of electro-migration, electric seepage or electrophoresis, and thus reduce the contamination. The method performs well in the soil with low permeability (Hanson *et al.*, 1992).

3.2.1.3 Soil leaching

The principle of soil leaching is to wash the heavy metal contaminated soil with specific reagents and thus remove the heavy metal complex and soluble ions adsorbed on the solid phase particles. By using this method, heavy metals are separated from the soil, and are then recycled from extracting solution (Su *et al.*, 2014).

3.2.1.4 Adsorption

Adsorption method is based on the fact that almost all heavy metal ions can be fixed and adsorbed by clay mineral (bentonite, zeolite, furnace slag, etc (Wang and Zhou, 2004).

3.2.1.5 Other methods

Other engineering methods include washing and compounding, heat treatment, physical solidification, chemical improvers, chemical curing lamp remediation, etc. (Su *et al*., 2014).

3.2.2 Bioremediation.

3.2.2.1 Phytoremediation

This is achieved by growing specific plants in the soil contaminated by heavy metals. These plants have certain hyper-accumulation ability for the contaminants in the soil (accumulated mainly in the root or above the root). When the plants are ripe or reach certain enrichment level of heavy metals, remove heavy metals in the contaminated soil layer thoroughly by harvesting, burning and curing plants. Using plants and their coexisting microbial system to remove heavy metals is a new technology. This method is based on the principle of finding the suitable plants with strong ability for heavy metal accumulation and tolerance. Over 400 species of such plants have been found in the world, and most of them belong to Cruciferae, including the genus Brassica, Alyssums, and Thlaspi (Xin *et al*., 2003).

3.2.2.2 Microbial remediation

Microbial remediation is the use of some microorganisms to perform the absorption, precipitation, oxidation and reduction of heavy metals in the soil. It has been established that fungi could secrete amino acids, organic acids and other metabolites to dissolve heavy metals and the mineral containing heavy metals (Siegel *et al*., 1986). Fred *et al*. (2001) reported that the fungi, *Gomus intraradices*, may improve the tolerance and absorption of sunflower to Cr.

3.2.2.3 Animal remediation

Some animals living in the soil (maggots, earthworms, etc) can take heavy metals in the soil. Wang *et al*. (2007) proved that when the concentration of Cu was low in the soil, the activities and secretion of earthworms could promote the absorption of Cu by ryegrass.

4.0 CONCLUSION

The heavy metals concentration in the environment should be monitored to prevent hazards to human beings and animals. This can be achieved through proper discharge of environmental pollutants to the environment from the industry, through proper examination of soil for heavy metal contamination before planting crops in soil with sewage water for irrigation, or area near industrial waste discharge. There should be involvement of environmental protection agency in proper monitoring of heavy metal contamination in the environment.

5.0 SUMMARY

In this unit the students have learnt that:

i. sources of soil contamination can occur through industrial wastewater, sewage water used for irrigation, quarrying sites and through hazardous waste disposal on the soil;
ii. engineering remediation is the use of physical or chemical methods to control heavy metal contamination of soils;
iii. some specific plants, microorganisms and animals can be used to reduce heavy metals contamination in the soil.

6.0 TUTOR-MARKED ASSIGNMENTS

(i) Outline the various engineering remediation techniques.
(ii) Discuss the basis, principles and applications of bioremediation techniques.

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UNIT 13 REMEDIATION OF OTHER TOXICANTS (HEAVY METALS) IN WATER

CONTENTS

1.0 INTRODUCTION

Heavy metals are found widely in the earth’s crust and are non-biodegradable in nature. They enter into the human body via air, water and food. A small number have an essential role in the metabolism of humans and animals in very trace amounts but their higher concentration may cause toxicity and health hazards. The hazardous nature of heavy metals has been recognized because of their bioaccumulative nature in biotic systems. They can enter into the environment through mining activities, industrial discharge and from household applications, into nearby bodies of water (Gautam *et al.*, 2014). Other sources of environmental contamination by heavy metals include atmospheric deposition, fertilizer, pesticide application and nuclear waste (Ojo, 2017).

2.0 OBJECTIVES

By the end of this unit, students should be able to:

- identify the sources of heavy metals contamination in water;
- understand the common physicochemical treatment processes for metal remediation in water; and
- understand the phytoremediation and microbial remediation processes and their applications.

3.0 MAIN CONTENTS

3.1 Heavy Metals Contamination in Water

Heavy metals from the mining, agricultural runoffs, industrial sources are leached into the underground water , moving along water pathways and eventually depositing in aquifer or are washed away by runoffs into surface water, resulting in water pollution. For example, the sources of heavy metals (such as As, Cd, Hg, Pb, Cr and Zn) contamination in Port Klagn in Malaysia were industrial wastewater and port activities, where water was collected from 21 stations at 3 months intervals and contamination factor (C_f) and contamination degree (C_d) were calculated to estimate the contamination status at the sampling areas (Sany *et al.*, 2013). Wu *et al.* (2015) indicated that there has been contamination of pond water and soil from illegal e-waste recycling activity. The presence of heavy metals such as Pb, Cd, Cu, Mo, Ni and Cr in drinking water in some Great Cairo Cities in Egypt has been linked to the occurrence of certain diseases such as renal failure, liver cirrhosis, hair loss, and chronic anemia (Salem *et al.*, 2000).

3.2 Physicochemical Remediation Processes and Applications

The common physicochemical treatment processes for metal remediation in water include: chemical precipitation, ion exchange and reverse osmosis.

3.2.1 Chemical precipitation

This is a widely practiced technology for the removal of heavy metals from water. It has long been the primary method of treating metal-laden industrial wastewater (Akpor and Muchie, 2010). This process involves the transformation of dissolved contaminants into insoluble solids, thereby facilitating the contaminant's subsequent removal from the liquid phase by physical methods, such as clarification and filtration. In a precipitation process, chemical precipitants (also called coagulants and flocculants) are used to increase particle size through aggregation. The amount of chemical required during treatment depends on pH and alkalinity of the water. As a rule, heavy metals in water are precipitated by adding sodium hydroxide or lime during neutralization. However, the results of this process are far from being satisfactory in many instances as complete hydroxide precipitation does not take place especially in the presence of complexing agents (Xu and Xu, 2008).

A combination of precipitation with other chemical treatment techniques, such as ion exchange has been reported to be effective in heavy metal removal in polluted waters. In South Africa, acid mine water from gold mine has been treated by the precipitation of heavy metals with lime and sulphides, followed by ion exchange. The process was reported to generate very pure water from acid mine water with a great flexibility and an acceptable cost (Akpor and Muchie, 2010).

Chemical precipitation of metals can be justified by their low costs and can be performed by a simple pH adjustment. Other advantages include:

1. It is a well-established technology with ready availability of equipment and chemicals.
2. Being a completely enclosed system, it is convenient, self-operating and requires low maintenance since only replenishment of chemicals is needed with no need for sophisticated operators.

In spite of the above advantages, chemical precipitation of metals in water still has the following disadvantages:

1. The precipitates are in the form of light tiny flocs requiring an extra coagulation/flocculation.

2. Large volumes of sludge are generated, inducing additional waste-disposal costs. The addition of treatment chemicals may increase the waste sludge up to 50% (EPA, 2000).
3. Regulation requirements are not always met using hydroxide and carbonate precipitation alone. Each dissolved metal has its own distinct pH level for maximum hydroxide precipitation.
4. Because metal hydroxides are increasingly soluble above or below their maximum precipitation point, even a slight pH adjustment to precipitate one metal may put another back into solution.
5. It requires working with corrosive chemicals, thereby increasing safety concerns (EPA, 2000).

3.2.2 Ion exchange

Ion exchange is a reversible chemical reaction wherein an ion from water or wastewater solution is exchanged for a similarly charged ion attached to an immobile solid particle. These solid ion exchange particles are either naturally inorganic zeolites or synthetically produced organic resins. It is a process that is very similar to biosorption whereby the latter is known to actually function predominantly on the basis of ion exchange. Ion exchange employs mainly hydrocarbon-derived polymeric resins (Volesky *et al.*, 2003). This technique has been successfully used in the removal of heavy metals from water.

3.2.3 Reverse osmosis

Reverse osmosis is a membrane process acting as a molecular filter to remove over 99% of all dissolved minerals. In this process, water passes through the membrane while the dissolved and particulate matter is left behind. The process is very effective for removal of ionic species from solution. The resulting concentrated by-product solutions make eventual recovery of metals more feasible.

In spite of the effectiveness, the membranes are relatively costly to procure and operate. The use of elevated pressures makes this technique expensive and sensitive to operating conditions. A significant advantage of reverse osmosis over other traditional water treatment technologies is the ability to reduce the concentration of other ionic contaminants, as well as dissolved organic compounds (Volesky *et al.*, 2003; Pawlak *et* *al*., 2005). Reverse osmosis had been applied in heavy metal removal both in small and large scales.

3.3 Phytoremediation Processes and Applications

Phytoremediation is a remediation process that entails the use of plants to partially or substantially remediate selected substances in contaminated soil, sludge, sediment, groundwater, surface water and wastewater. It is also called green remediation, botano-remediation, agro-remediation or vegetative remediation. Based on the type of contaminant and underlying process, phytoremediation is broadly categorized into the following main areas: phytodegradation/phytotransformation, phytoaccumulation, phytoextraction, phytostimulation/rhizostimulation, phytovolatilization, rhizofiltration and phytostabilization. The removal of metal contaminants from water through Phytoremediation occurs by any of three mechanisms: phytoextraction, rhizofiltration and phytostabilization (Lasat, 2000; UNEP, 2010).

3.3.1 Phytodegradation

Phytodegradation is the breakdown of organic contaminants by internal and external metabolic processes driven by the plant. Its involves the use of plants to absorb, store and degrade contaminants within their tissues. In the process, plants actually metabolize and destroy contaminants within their tissues. Some contaminants can be absorbed by the plant and are then broken down by enzymes (Newman and Reynolds, 2004). During phytodegradation, the plants are able to take-up metal contaminants directly from soil water or release exudates that help to degrade pollutants through cometabolism in the rhizosphere. For environmental application, it is important that the metabolites that accumulate in vegetation are non-toxic or at least significantly less toxic than the parent compound.

3.3.2 Phytoextraction

Phytoextraction is a phytoremediation process wherein plant roots take-up, translocate and store contaminants along with other nutrients and water. This method is used primarily for wastes containing metals. Because different plants have varying abilities to absorb and withstand high levels of pollutants, many different plants may be used. Metal compounds that have been successfully phytoextracted include zinc, copper, and nickel, but there is promising research on the verge of completion on lead and chromium absorbing plants (Lasat, 2000; UNEP, 2010).

3.3.3 Phytostimulation

In this process, plants release natural substances through their roots, thereby supplying nutrients to microorganisms, which in turn enhance biological degradation. It is a symbiotic relationship between plants and microorganisms for the degradation of contaminants (Lasat, 2000). During phytostimulation, there is the release of organic substances and oxygen by plant roots, which stimulates microbial activity in the rhizosphere compared to bulk soils. This results in increased microbial activity, which in turn results in a stimulation of natural degradation of organic contaminants (Meers and Tack, 2004).

3.3.4 Rhizofiltration

This process is similar to phytofiltration, but the only difference is that the plants for remediation are raised in greenhouses with their roots in water. It is the breakdown of organic contaminants in water through enhanced microbial activity in the plant root zone or rhizosphere. The process is concerned with the remediation of contaminated groundwater rather than the remediation of polluted soils. The contaminants are either adsorbed onto the root surface or are absorbed by the plant roots. Plants used for this are not planted directly in situ but are first acclimated to the pollutant (Lasat, 2000). A suitable plant for rhizofiltration applications can remove toxic metals from solution over an extended period with its rapid-growth root system. A variety of plant species have been found to be effective in removing toxic metals, such as Cu^{2+}, Cd^{2+}, Cr^{6+}, Ni^{2+}, Pb^{2+} and Zn^{2+} from aqueous solutions.

3.3.5 Phytovolatilization

This process makes use of the ability of the plant to absorb contaminants from the growth matrix and subsequently transform and volatilize them into the atmosphere through its leaves. The contaminant may become modified along the way, as the water travels along the plant’s vascular system from the roots to the leaves, whereby the contaminants evaporate or volatilize into the air surrounding the plant. Some of these contaminants can pass through the plants to the leaves and volatilize into the atmosphere at comparatively low concentrations. The process of phytovolatilization depends heavily on the physical characteristics of the contaminant itself. Io order to get into the plant, the contaminant must have the proper chemistry to pass through the root membrane. Once inside the plant it can then be phytovolatilized into the atmosphere through the stomata.

3.3.6 Phytostabilization

Phytostabilization, also referred to as in-place inactivation, is primarily used for the remediation of soil, sediment, and sludges. It is the use of plant roots to limit contaminant mobility and bioavailabilty in the soil. During the process, contaminants are absorbed onto the roots, or precipitated in the rhizosphere. When this happens, there is the prevention of mobility of the contaminants, hence reducing their availability in the food chain (Lasat, 2000). The process of phytostabilization depends on the tolerance ability of a plant to a contaminant. Even if the plant physically remove little or no contaminant, they are useful as phytostabilization agents as long as they tolerate and grow under the contaminated conditions.

Phytoremediation has several advantages and disadvantages when compared to conventional remediation processes. Its advantages include:

1. Economical and low cost technology.
2. Less disruptive to the environment and does not involve waiting for new plant communities to decolonize the site.
3. No need for disposal sites, hence reducing risk of spread of contaminants.
4. More aesthetically pleasing than traditional methods.
5. Potential to treat sites polluted with more than one type of pollutant.

Its disadvantages include:

1. Dependent on the growing conditions (climate, geology, altitude, temperature) required by the plant, hence success depends on tolerance of the plant to the pollutant.
2. Requires access to agricultural equipment and knowledge to operate at large scale.

3. Risk of release of contaminants collected in senescing tissues being released back into the environment.
4. Contaminants may be collected in woody tissues used as fuel
5. Since it is dependent on plant growth, when compared to other technologies, remediation time is long.
6. Possibility for environmental damage due to leaching of soluble contaminants.
7. Because of shallowness of plant roots, there is the problem of depth limitation, hence effectiveness can only be achieved within zone of influence of plant roots.

3.4 Microbial Remediation Processes and Applications

Microbial bioremediation is defined as the process by which microorganisms are stimulated to rapidly degrade hazardous organic contaminants to environmentally safe levels in soils, subsurface materials, water, sludge and residues. Microbes deal with poisonous chemicals by applying enzymes to convert one chemical into another form and taking energy or utilizable matter from this process. The chemical transformations generally involve breaking of large molecules into several small molecules in simpler form. Given the interest in water and wastewater treatment, the response of microorganisms towards toxix heavy metals is of importance. In some cases the by-products of microbial remediation are not only harmless but may prove useful.

Microbial activity is considered to play a key role in the detoxification of metals in water. For example, wastewater treatment systems are known to rely on microbes to perform the function of the breakdown of sewage influent. The microbes live in the sludge of the treatment plants, digest the solids and breakdown various compounds. Being living organisms, microbes require certain nutrients and environments to survive, multiply and perform. In any wastewater treatment system there is a vast array of microbes present, that is aerobic, anaerobic and facultative, each performing specific functions in their respective parts of the system. Each of these microbial species has tolerance of ecological minimums and maximums with respect to various conditions, such as pH, temperature, dissolved oxygen levels and nutrient levels.

Microbial metal uptake can either occur actively (bioaccumulation) and/or passively (biosorption). Studies conducted in large-scale systems have shown that biosorptive processes are more applicable the the bioaccumulative processes. This is because living systems (active uptake) often require the addition of nutrients and hence increase biological oxygen demand or chemical oxygen demand in the effluent. On the contrary, biosorption is reported to be quite effective for the removal of metal ions from contaminated solution in low cost and environmental friendly manner.

Microbial remediation has several advantages and disadvantages. Its advantages include:

1. It uses relatively low-cost, low-technology techniques, hence requires moderate capital investment. It is fairly inexpensive when compared to other remediation processes.
2. It is environmentally safe since it is a natural process usually perceived by the public as an acceptable treatment process.
3. It does not generate waste, hence less wasted groundwater.
4. It is self-sustaining since the microbes able to degrade the contaminant increase in numbers when the contaminant is present; and decreases when the contaminant is degraded.
5. The residues for the treatment are usually harmless products and include carbon dioxide, water, and cell biomass.
6. It can be used alongside other technologies; and
7. It can be conducted on site, often without causing a major disruption of normal activities.

Some of the disadvantages are:

1. It is not always suitable, however, as the range of contaminants on which it is effective is limited, the time scales involved are relatively long, and the residual contaminant levels achievable may not always be appropriate.
2. Bioremediation is limited to those compounds that are biodegradable. Not all compounds are susceptible to rapid and complete degradation.
3. There are some concerns that the products of biodegradation may be more persistent or toxic than the parent compound.
4. Biological processes are often highly specific, since success is dependent on the presence of metabolically capable microbial populations, suitable environmental growth conditions, and appropriate levels of nutrients and contaminants.

5. It is difficult to extrapolate from bench and pilot-scale studies to full-scale field operations, for research is needed to develop and engineer bioremediation technologies that are appropriate for sites with complex mixtures of contaminants that are not evenly dispersed in the environment.
6. Although the methodologies employed are not technically complex, considerable experience and expertise may be required to design and implement a successful bioremediation program because of the need to thoroughly assess a site for suitability and to optimize conditions to achieve a satisfactory result (Akpor and Muchie, 2010).

4.0 CONCLUSION

Heavy metal contamination of distributed water and discharged wastewater is a constant area of concern. There is the challenge to remediate hazardous metal-containing water and wastewater worldwide. The removal of heavy metals from domestic and industrial waters has become an important application in water and wastewater treatment systems. This is because legislations and guidelines have created strict distribution and discharge limits, which has compelled plants to add or upgrade metal removal processes. Currently, there is no single technology for heavy metal remediation (chemical remediation, phytoremediation or microbial remediation) that is devoid of some form of merits and demerits. Consequently, there is a need for the implementation of an integrated remediation technology capable of having great potential.

5.0 SUMMARY

In this unit the students have learnt that:

i. the common physicochemical treatment processes for metal remediation in water include: chemical precipitation, ion exchange and reverse osmosis;
ii. phytoremediation is a remediation process entailing the use of plants to partially or substantially remediate selected substances in contaminated soil, sludge, sediment, groundwater, surface water and wastewater;

iii. phytoremediation is broadly categorized into the following main areas: phytodegradation/phytotransformation, phytoaccumulation, phytoextraction, phytostimulation/rhizostimulation, phytovolatilization, rhizofiltration and phytostabilization; and
iv. microbial bioremediation is a process by which microorganisms are stimulated to rapidly degrade hazardous organic contaminants to environmentally safe levels in soils, subsurface materials, water, sludge and residues.

6.0 TUTOR-MARKED ASSIGNMENTS

i. Write short notes on chemical remediation, ion exchange and reverse osmosis.
ii List the advantages and disadvantages of microbial remediation..
iii. Differentiate between phytovolatilization and phytostabilization.

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UNIT 14 PESTICIDE RESIDUES IN THE FOOD CHAIN: PESTICIDE RESIDUES IN CEREALS AND PULSES

CONTENTS

1.0 INTRODUCTION

The growing demand for food and feed due to consistent increase in the world population has led to increase in the use of chemical pesticides in order to obtain more yield and protection of crop from pests and diseases. These have made crop protection to increase by about 100%, while the cropping area has increased marginally by about 20%. The indiscriminate usage of pesticide leads to accumulation of pesticide residues in food chain, aquatic system and soil (Jayashree and Vasudevan, 2007). The non-degradability of pesticide residues causes resistance of pests to the chemicals indicating 50-70% of contamination with insecticide residues. Public concern towards pesticide residues has risen over decades to a point where it has become a significant food safety issue. The determination of pesticide residues in food has therefore become an essential requirement for consumer, producers and authorities responsible for food quality control (Aguilear*et al.*, 2003).

2.0 OBJECTIVES

By the end of this study, students should be able to:

- Define pesticide residues;
- Identify the possible ways pesticide residues get into cereals and pulses;
- Explain the human health hazards associated with pesticides residues;
- Outline measures to reduce pesticide residues in cereals and legumes

3.0 MAIN CONTENT

3.1 Public concerns about pesticide residues

Pesticides applied to food crops in the field can leave potentially harmful residues; and organochlorines in particular are persistent in foodstuffs for longer periods. If crops are sprayed on to harvest without an appropriate waiting period, even organophosphorus insecticides can persist in food. Pesticide residues in foods are a growing source of concern for the general population. A substantial body of research and epidemiological evidence suggests that certain pesticides are associated with carcinogenesis, immunotoxicity, neurotoxicity, behavioural impairment, reproductive dysfunction, endocrine disruption, developmental disabilities and respiratory diseases, such as asthama (Solomon *et al.*, 2000).

3.2 Cereals and Pulses

Cereals and pulses form a large proportion of the global diet, and control of pests during storage is a bigger problem with these classes of crop. Storage pests can be controlled by the use of insecticides as residual protectants. This grain treatment method can be easily adaptable to all types and sizes of storage with minimum expense. This post harvest application of pesticides leads to the persistence of pesticides in food grains and may cause health hazards. The short as well as long term impacts of the use of pesticides on biological systems are being evaluated continuously in an effort to minimize the hazards. A wide spread use of pesticides and their toxic residues have been reported in various environmental matrices by researchers (Singh *et a*l.,2004). The presence of pesticide residues in rice, wheat and pulses can be a significant route to human exposure and most of organochlorine pesticides have been banned because they are highly persistent insecticides, and their residues still appear as pollutants in food and environment.

3.2.1 Pesticide residues in cereals and pulses

The Food and Agriculture Organization and World Health Organization have recommended residue limits for bioresmethrin, bromophos, Carbaryl, chlorpyrifos-methyl, deltamethrin, dichlorvos, etrimfos, fenitrothion, fenvalerate, malathion, methacrifos, permethrin, phenothrin, irimiphosmethyl and pyrethins used for the protection of grains (Amenze*et al*., 2014). A study in Poland revealed that out of 380 samples of the cereal grains, 34% were found to contain pesticide residues (Neme and Satheesh, 2016). According to their investigation out of the analyzed cereals, the smallest amount of plant protection products residues was in mixed cereal grains (below 10%) and Avena grains (below 15%) whereasHordeum and Triticum grains contained the highest content of pesticide residues (over 50%).

A study in Nigeria on organochlorine pesticide residues in cereal grains showed the presence of aldrin, dichloran, dieldrin, endrin, endosulfan, heptachlor epoxide, dichlorodiphenyltrichloroethane lindane, methoxychlor, and mirex. A study in Pakistan on pesticide residue of cereals showed that wheat contained the highest concentration of tested pesticides than maizeand rice and maize contained a much higher concentration of pesticides than rice. The accumulation of pesticide residues depends on the physiochemical properties of the pesticide molecules as well as food (Bajwa, and Sandhu, 2014).

3.3 Regulation of pesticide residues in cereals and pulses

3.3.1 Setting maximum residue limits through regulations

As part of its health risk assessment process before a pesticide is registered, Government regulatory agencies determine whether eating residues that are likely to remain in or on food at the time of harvest is acceptable and unlikely to cause a health concern to any group of people, including infants, children, and pregnant women. This maximum amount of expected residue is then legally established as a Maximum Residue Limit (MRL), following public (national and international) consultation. Maximum residue level is the highest level of a pesticide residue that is legally tolerated in or on food or feed when pesticides are applied correctly. International parties such as the European Union, Codex Alimentarius Commission, and North American Free Trade Agreement have attempted to harmonize pesticide legislation by providing maximum residue limits, but globally these limits remain variable. In Nigeria, the National Food and Drug Law Enforcement Agency (NAFDAC) sets the maximum resdue limits for pesticides in crops, foods, vegetables and fruits.

MRLs ensure that exposure to the pesticide residue presents no concerns for human health. Each MRL is set for a specific pesticide and food type combination, taking into consideration the nation’s unique climate, geography, topography and water systems. MRLs apply to food types that include, but are not limited to, fruits, vegetables, meat, dairy products, grains and some processed foods. The MRLs set by the regulating body are assessed using modern scientific methodology and are consistent with those of other major Organisation for Economic Co-operation and Development (OECD) countries.

MRLs are set at levels far below the amount of pesticide residue that could present a health concern. MRLs are set for all food commodities sold in open markets, whether imported or produced locally. Pesticide residues in or on imported foods are measured at the point of entry into the country to make sure that imported foods meet Government stringent MRL pesticide residue standard before they are distributed in open markets.

Under the guidance of international organizations like the OECD and the United Nations, the government participates with other countries in developing the standards and processes used worldwide for determining acceptable pesticide residue levels.

3.3.2 Sustainable and integrated pest management

Sustainable pest management happens when pest management strategies are integrated: that is, when all possible effective techniques, including both chemical and non-chemical methods, have been considered to get rid of pests economically, in an environmentally sound manner, and in a way that protects human health. Government encourages citizens , including growers, to reduce their reliance on and minimize their exposure to pesticides. Through different programs at the Pest Management Regulatory Agency, who works with partners like Farmers congres, and with Nigerian pesticide users, to achieve sustainable pest management. Government also works with the stateses and industry associations on research projects to identify and promote different methods to effectively control pests and prevent infestations, and to identify and provide access to newer, reduced risk pesticides.

3.4 Choice of pesticides for cereals and pulses

The application of pesticide is widely used for grains before harvest and after harvest to protect the grains from damage or loss. Cultivation and storage of grains often require an intensive use of pesticides, which may then be found in grains and in foods prepared from them (Vela *et al*., 2007). Cereal grains are treated with degradable pesticides, including organophosphates, carbamate, synthetic pyrethroids and insect growth regulators, both in storages and prior to shipment in order to prevent insect infestation (Collin, 2006).

4.0 CONCLUSION

The unit concluded that while pesticides help protect our food supply, many people are concerned about pesticides on the food they eat. Small amounts of pesticide residues may stay in or on our food after it is applied, but pesticides ‘break down’ over time, meaning very little residue is left by the time we eat the food.

The rate of ‘break down’ depends on the type of pesticide used, the application conditions, and the type of food treated. So, the amount and nature of pesticide residue can be different from one pesticide or food type to another. Government regulatory agencies are responsible for approving pesticide uses and conditions of use, and for setting Maximum Residue Limits (MRLs) for pesticides.

Food safety is a shared priority between growers, industry, statess and federal organizations. While government agencies work to enforce food regulatory laws, food producers help keep food safe by using and improving on good agricultural and pest management practices. One key practice is to follow pesticide label directions, because they give instructions for the safe and proper use of pesticides. This helps keep residues within the limits, helping ensure a safe food supply. Government agencies should engage food producers to participate in a variety of on-farm programs to help put in place effective food safety procedures in their day-to-day operations.

5.0 SUMMARY

In this unit students have leant that:

i. pesticide residues get into cereals and pulses either through pesticide application to control pest on the field or in storage;
ii. the extent of pesticide residues problems in grains depends on the type of pesticide applied, application environment, and the type of crop
iii. minimum residue limit (MRL) can be achieved in cereals and pulse if the growers abide by standards set by regulatory agencies.

6.0 TUTOR MARKED ASSIGNMENTS

- Define pesticide residues;
- Identify the possible ways pesticide residues get into cereals and pulses;
- Outline measures to reduce pesticide residues in cereals and legumes

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UNIT 15 PESTICIDE RESIDUES IN THE FOOD CHAIN: PESTICIDE RESIDUES IN FRUITS AND VEGETABLES

CONTENTS

1.0 INTRODUCTION

Pesticide residue refers to the pesticides or metabolic products of the pesticides that may remain in food grains, vegetables and fruits after they are applied to crops. Many of these chemical residues, especially derivatives of chlorinated pesticides, exhibit bioaccumulation, which could build up to harmful levels in the body as well as in the environment (Sachs *et al*., 2010). Persistent chemicals can be magnified through the food chain and have been detected in products ranging from meat, poultry, and fish, to vegetable oils, nuts, and various fruits and vegetables (Crinnion, 2009). Insects and pests can cause a loss in the quality and quantity of grains and their products.

2.0 OBJECTIVES

By the end of this study, students should be able to:

- Make a list of the pesticides that are likely to be found in fruits and vegetables
- Identify the possible ways pesticide residues get into cereals and pulses;
- Outline measures to reduce pesticide residues in cereals and legumes

3.0 MAIN CONTENT

3.1 Pesticide residues in fruits and vegetables

The most consumed pesticides for vegetables and fruits include sulphur, endosulfan, mancozeb, phorate, methyl parathion, monocrotophos, cypermethrin, isoproturon, chlorpyrifos, malathion, carbendazim, butachlor, quinalphos, copper oxychloride, and dichlorvos. The use of pesticides during production often leads to the presence of pesticide residues in fruits and vegetables after harvest. Most farmers and commercial producers treat vegetables and fruit with pesticides on several occasions during growing because pesticides decrease toxins produced by food infecting organisms, increase productivity and are less labor intensive.

3.1.1 Pesticide residues in vegetables

According to a study, the cucumber was the crop with the highest number of pesticide residues with the predominant presence of methomyl, metalaxyl, and imidacloprid. Methomyl is a carbamate insecticide with restricted use because of its high toxicity to humans. The other pesticide residues found in cucumber samples were boscalid, chlorpyrifos, cyprodinil, fenhexamid, imidacloprid, metalaxyl and tebuconazole (Kostik*et al.*, 2014). The commodities with the highest level of pesticide residues found in China were cabbage, legumes and leaf mustard (Chem*et al.*, 2011). High level of pesticide residues was also determined in imported bitter melon, peas, beans, eggplant, spinach and other vegetables. A study on analysis of pesticide residue concentration in vegetables revealed that the risk to consumers varies with the season and it was reported that the winter season has the highest pesticide concentration in vegetables (Bhanti, and Taneja, 2007).

3.1.2 Pesticide residues in fruits

Sudy revealed that many fruits contained more than one residue per product, up to 9 residues in grapes and tea were determined, up to 5 - 9 residues in citrus fruits like orange, mandarins, lemons, peaches, pears and up 3 - 5 residues in pomegranates, plums, cucumbers, tomatoes, strawberries. The most frequently detected pesticide residues were imazalil, thiabendazole, chlorpyrifos, maneb group, procymidone, methidathion, lambda-cyhalothrin, carbendazim, iprodione, orthophenylphenol, vinclozolin, endosulfan, pyrimethanil, fenhexamid, prochloraz, cyprodinil, boscalid. Apples, papayas, sweet peppers and strawberries were among products with the highest percentage of samples with residues above the maximum residue limit found in the Brazilian pesticide residues monitoring program. High level of pesticide residues in pears, grapes, citrus fruit, peppers, cucumbers, tomatoes, carrots were obtained in Lithuania (Petraitis*et al.*, 2013). A study in Belgium revealed that pesticide residues were detected in 72% of the samples and standards were exceeded for 6% of the samples. Imported blackberries, strawberries and other berries as well as mangoes, papaya and pepinos also contained high levels of pesticide residues. The insecticide residues reported in market samples of grapes were acephate, methamidophos, chlorpyriphos, monocrotophos and quinalphos.

3.1.3 Pesticide residues in processed fruits and vegetables

A study on the levels of pesticides in soft drinks available in Indian market indicates pesticide residues 24 times higher than Bureau of Indian Standards (BIS) norms. The levels of pesticide residue in lindane exceeded the BIS standards by 140 times in some samples. Heptachlor, which was banned in India, was found in 71 per cent of the samples, at levels four times higher than BIS standards. Chlorpyrifoswas found 200 times more than the BIS standard in a sample manufactured in Thane. The average amount of pesticide residues found in all the samples was

24 times higher than the BIS standards for total pesticides in soft drinks (Source: The Hindu). Organochlorine pesticides, mainly isomers of hexachlorohexane, dichloro-diphenyl-trichloroethane, endosulphan, endrin, aldrin, dieldrin, and heptachlore, were identified from potable water samples collected from all over India (Agarwal *et al.*, 2015). The residues of lambda-cyhalothrin in acid lime were persisted for 20 days and in juice samples maximum residues were observed for 10 days.

3.2 Preventive measures to reduce pesticide residues in vegetables, and fruits

Different types of pesticides are used in different countries for different types of crops to prevent pests, insects, and weeds. Because of the expansion of worldwide trade, more foods, which are treated by pesticide are being imported into different countries. These worldwide trades increase the expansion of pesticide residues in different areas of the world and it is the issue of public health concern. There are a number of strategies, which can be used to minimize pest and disease problems and reduce pesticide residues in food grains, vegetables and fruits.

3.2.1 Organic farming

One of the methods used to reduce the effect of pesticide residue in food is to eat organic foods than non-organic ones. According to standard meta-analyses the frequency of occurrence of detectable pesticide residues was four times higher in non-organic crops than organic crops (Baranski*et al.*, 2014). There is evidence that indicated organic food consumption can reduce exposure to pesticide residues in food. Organic crops, on average, have higher concentrations of antioxidants and a lower incidence of pesticide residues than the non-organic foods across regions and production seasons. It is advisable to consume foods rich in antioxidant to reduce effects of the chronic disease by suppressing oxidative activity. An increased dietary intake of antioxidant rich foods protect against chronic diseases, including cardio vascular diseases, certain cancers (e.g. prostate cancer) and neurodegenerative diseases.

3.2.1 Washing food products:

The second methods reported to reduce pesticide residue in food is washing. Washing may reduce pesticide residue in food commodities.

Washing with water and various chemical solutions for domestic and commercial applications is necessary to decrease the pesticide residues. The efficiency of the washing treatments on pesticide removal depends on the washing solution, the chemical properties of the pesticide, the surface area, the nature of the food, the length of time the pesticide is in contact with the food, and the formulation and application method of the pesticide. Usually, the pesticide is lodged in the outer wax-like layers and then moves to the inside, making washing and removal of the pesticides less effective (Al-Taher *et al*., 2013).

3.2.3 Processing food products:

An important factor leading to a reduction of any residues left on crops at harvest are processing treatments such as washing, peeling, canning or cooking that the majority of foods receive prior to consumption. Pesticide residue levels in fruit and vegetables may change due to processing, such as peeling, boiling, frying, fermentation, grinding. Cooking also reduces pesticide residues in food; boiling may remove 35 - 60% of organophosphate residues and 20 - 25% of organo chlorines. Husking and immersing of fruit and vegetables are reported to reduce pesticide residues especially organophosphates.

3.2.4 Rational use of pesticides:

Rational use of pesticides involves selection of correct pesticides, dosage rates, dilutions, timing, and frequency of application, treatment intervals, and method of application, precautions, and limitations. Rational use of pesticides can be useful to reduce pesticide residues in food products. In many cases, there may not be any need of a pesticide, particularly where cultural or biological methods are effective.

3.2.5 Use of natural pesticides and biopesticides:

Bio-pesticides are biodegradable so no harmful residues are produced and are eco-friendly. Bio-pesticides encompasses a broad array of microbial pesticides, biochemical’s derived from micro-organisms and other natural sources that confer protection against pest damage. Some insect repellents can also be used for the prevention of pesticide residues accumulation in the food grains, vegetables and fruits (Gupta and Dikshit,, 2010). Natural pesticides such as extracts and compounds from neem tree are also very useful for the prevention of pesticide residues accumulation in the food products.

3.2.6 Implementation and amendment of pesticide-related laws:

In India, the agriculture ministry regulates the manufacture, sale, transport, distribution, export, import and use of pesticides under the Insecticides Act, 1968. Still awaiting Parliamentary approval is the Pesticide Management Bill of 2008, which is meant to replace the Insecticides Act, 1968. The pesticide-related laws should be implemented strictly and amended so as to reduce the cases of pesticide residues in food grains.

4.0 CONCLUSION

The excess consumption of pesticides contributes in the accumulation of pesticide residues in food grains and vegetables associated with variety of human health hazards, including damage to central and peripheral nervous systems, cancer, allergies and hypersensitivities, reproductive disorders, and disruption of the immune system. The impact of pesticide residues can be minimized by preventive measures such as rational use of pesticides, washing and proper processing of food products, practicing organic farming, use of natural pesticides and bio-pesticides, and strict implementation and amendment of pesticide-related laws.

5.0 SUMMARY

In this unit students have leant that:

i. pesticide residues get into fruits and vegetables either through direct pesticide application to control pest and diseases on the field;
ii. the extent of pesticide residues problems is aggravated by the fact that many fruit and vegetables are consumed directly with little or no processing.
iii associated pesticide residues vary from crop to crop depending on the type of pesticide sprayed to enhance their quality.
iv. preventive measures in place to prevent health problems associated with pesticide residues in food includes organic farming, washing food products, processing food products,

rational use of pesticides, use of natural pesticides and biopesticides, etc.

6.0 TUTOR-MARKED ASSIGNMENTS

- Make a list of the pesticides that are likely to be found in fruits and vegetables
- Identify the possible ways pesticide residues get into cereals and pulses;
- Outline measures to reduce pesticide residues in cereals and legumes

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UNIT 16 PESTICIDE RESIDUES IN THE FOOD CHAIN: PESTICIDE RESIDUES IN MEAT AND DAIRY PRODUCTS

CONTENTS

1.0 INTRODUCTION

The problem of satisfying the dietary requirements of a growing world population is becoming increasingly acute. Drugs that improve the rate of weight gain, improve feed efficiency, or prevent and treat diseases in food-producing animals are critically needed to meet the challenge of providing adequate amounts of food for that population. However, the benefit of improved production from the use of animal drugs in food producing species is not without risk. The use of these vaccines has been implicated for leaving harmful residues in animal meats and other products. In addition, as discuss previously, the use of pesticides to enhance crop quality and yield is also prone to the attendant risk of leaving pesticide residues in the plant products. The plant materials when fed to animal have the tendency to in turn deposit these residues in the animal body. The concentration of the residues tend to increase as they are transferred from plant materials to the animal body in a process known as biomagnification or bioamplification. It is therefore necessary to collect data on residues and their safety as a basis for establishing safe residue concentrations and withdrawal periods for food animal drugs. Moreover, it is equally important that slaughtered animals be monitored for possible unsafe residues.

2.0 OBJECTIVES

By the end of this unit, students should be able to:

1. understand how pesticide residues enter into animal products;
2. explain the effects of pesticide residues on animal health; and
3. explain the various ways these residues can be managed to acceptable limits

3.0 MAIN CONTENTS

3.1 Sources of pesticide residue contamination of meat and dairy products

Animal products intended for food may become contaminated with pesticide chemicals in a number of ways.

1. Residues of pesticides sprayed during the early stage of growth are retain even till harvest in fodder maize.
2. Concentrates are important sources of pesticide residue intake by animals.
3. Apart from pesticides used for crop production, their indiscriminate usage during storage also play a role in the case of oil cakes, grains and milling products.
4. Contamination of the soil and water sources used for drinking purpose of animals also forms another source of pesticide residue in animals.
5. Direct contact of the animals with pesticides during control of external parasites on animals and insects and fly control in cattle yards and sheep sheds also form other source of pesticide residues in animal body.
6. The monitoring studies conducted at AICRP on Pesticide Residues, Hyderabad indicated the contamination of animal

products, feed and fodder samples collected from different parts of the state.

DDT and other chlorinated materials are used to control insects on such forage crops as alfalfa, clover, and grass and on peas, beans, corn, and similar crops, of which a part is used as animal feed. Some pest killers, used at recommended dosages and in accordance with good agricultural practices, leave enough residue on forage crops so that some is stored in the animal or excreted in milk if the forage is fed to livestock. Pastures or grain that have had pesticide treatments also may be a source of contamination of animal products.DDT—the common name for the commercial product dichloro-diphenyltrichloroethanehas been found in milk samples from cows stabled in barns sprayed with it, even though the cows were outside when the spraying was done. Enough DDT was picked up from feed troughs, water fountains, and other sources to cause excretion in the milk. Some other pesticides, sprayed directly on the animals, have been excreted in the milk. Some of the pesticides used in spraying and dipping cattle, sheep, goats, and swine are stored in the animals' bodies. Some materials have caused serious disturbances and even fatalities. Others have little apparent effect. Most of the pesticides used for insect control are soluble in the fat and are stored in the fatty tissues of the animal. Three to four months may be required before some of the chemicals are eliminated.

3.2 Effects of pesticide residues on livestock animals

Mannivannan (2001) reported that pesticide affect the quality of dairy products by inhibiting the metabolic activities of starter bacteria. Effects on animal are determined by the chemical structure of the pesticides, its action on metabolism and fate of the chemical within the animal. Not all animals react to all pesticides in the same manner and response can be species or individual specific. The system of one animal may metabolize a pesticide to a nontoxic metabolite, whereas that of another species may not (species –specific response) and individual animals of a species also can respond differently (Individual-specific response).

3.3 Pesticide residues in animal feeds

Poultry feed samples (maize grains, soyabean, groundnut cake, sunflower cake, concentrate feed mixture) were contaminated with

HCH, DDT, Aldrin, Carbendazine and Thiram. Thiram residues were as high as (1.25mg/kg) inconcentrate feed mixture and 2.25 mg/kg in maize grain in comparison to other pesticides. Contamination with HCH, DDT, Aldrin and Endosulphan was evident in the samples of feed and fodder.

3.4 Pesticides residues in livestock meats

Dressed chicken samples were found contaminated with HCH, DDT and Endosulphan and the pesticides residues are retained in the fat of the animal whether they are by direct contact or by indirect contamination of soil, water, feed and fodder. The rate of accumulation in the body and excretion depends on nature and amount of pesticide ingested and duration of exposure. Long-term oral intake of pesticides at low levels had been found to result in higher accumulation than short-term intake at higher doses.

3.5 Pesticide residues in milk

Organophosphorous pesticides used to control external parasites in cattle and sheep are absorbed largely, deposited in fatty tissues, and excreted in milk. Pesticide excretion may continue upto five days following dipping and spraying. 17 and 12 mg of Lindane per kg in buffalo and cow milk were respectively recorded in India. Higher levels of DDT and the presence of aldrin and dieldrinwere also found in cow milk. Milk samples however showed decreasing trend in level of pesticide residue when compared to tissues such as kidney, liver and adipose of cattle, sheep and goat which contain noticeable levels of DDT and HCH. Surendranath*et al* (2002) reported milk samples from areas where DDT was used to eradicate mosquitoes and found to contain 25% higher levels. Ramesh and Vijayalaxhmi (2002) reported that endosulfan residues could not be detected in milk samples in areas where aerial spraying carried out 3 months prior to sample collection.

3.6 Measures to manage pesticide residues in livestock

3.6.1 Epidemiology

(a) *Origin*

The great majority of residues found in edible tissues of animals have their source at the farm of origin. Most are fairly transient residues derived from recent treatment with pesticides or drugs. Some, however, are derived from inadvertentcontamination of soil or buildings with persistent chemicals used in past years. By far the most common cause of residues is the failure to observe the proper withholding period following treatment. Occasional residues will be acquired during transport, in saleyards, in holding paddocks at abattoirs, or during processing at the abattoir. Care must be taken to avoid confusion by false positives which can arise from post-sampling contamination or from sample switching. In addition, laboratories must take care to ensure that their standards are accurate and that their calculations are correct.

(b) *Distribution*

Logically, the potential for exposure is greatest and the likelihood of residues highest in those areas where farming is more intensive and where chemicals are used more freely. It can therefore be anticipated that lot-fed animals would be more vulnerable than range-fed animals, that pigs and poultry would be more vulnerable than sheep and cattle, and that dairy cattle would be more vulnerable than beef cattle. In general, it is found that animals from the tropics are more likely to haveresidues than animals from temperate regions.

(c) *Animal pathology*

At ante mortem inspection any animal showing a diseased condition or showing signs of a recent disease condition should be regarded with suspicion. There is every likelihood that such animals have been recently treated. There is a particular needfor caution in emergency slaughter. In the normal course of events, there may be little evidence of recent injections but inspectors should nevertheless be watchful. In the great majority of cases there will be no visual evidence to suggest the presence of residues and laboratory analysis of appropriate samples will be the only means of their recognition.

3.6.2 Technology

(a) *Control of the environment*

The animal environment will be kept free from contamination if farmers use pesticides in strict accordance with directions on registered labels. This includes compliance with any withholding periods for grazing on treated pastures and crops.There is little that can be done to overcome contamination resulting from past use of persistent organochlorine pesticides other than to wait for the passage of a sufficient number of years. Present day evaluation procedures should ensure that contamination of the environment is minimal from this time on.

(b) *Control of chemicals*

Good regulatory control of pesticides and veterinary drugs is the first line of defense against the occurrence of undesirable residues in agricultural commodities. Control procedures should be designed to ensure that each new product is suitablefor its intended purpose and that it will not give rise to unacceptable residues in food or feed if used in accordance with the directions on the registered label. There should be legislation to make it an offense to sell or offer for sale any unregistered product. In this way it can be arranged that farmers have access only to approved and properly labeled products. Any residues found in food or feed can then be taken as evidence of misuse. It does not take many inspectors to maintainsurveillance over products on shelves in retail outlets. Effective policing of use on the farm is a far more difficult matter and for this reason many authorities are not convinced of the value of legislation providing power to control use. Good regulatory control necessitates sound evaluation of data submitted by chemical manufacturers or sponsors. This evaluation can only be performed by knowledgeable persons with sound judgment. The aim should be to provide the maximum protection for consumers and operators, consistent with keeping producers supplied with the chemical tools they need to remain competitive. At the same time regulatory authorities must bring forward new products as quickly as possibleand avoid putting unnecessary obstacles in the path of manufacturers, who, after all, need some encouragement if they are to keep putting new chemicals into the developmental pipeline. The system will undoubtedly grind to a halt if regulatoryauthorities ask for unreasonable safeguards and safety factors.

(c) *Standards for residues*

Residues cannot be controlled legally unless legal limits are established. These are called maximum residue limits (MRLs) or tolerances. Food and drug legislation then makes it an offense to sell food in which these limits are exceeded. It has become accepted procedure that an MRL is set just high enough to cover residues which are difficult to avoid when the particular chemical is used in accordance with good agriculture practice. This approach derives from the philosophythat notwithstanding the apparent harmlessness of a residue, it is prudent to keep human consumption to the absolute minimum. This implies that in nearly all cases the MRL is merely a legal limit. Violations are not likely to be a health hazard unless flagrantly excessive. In any case, the acceptable daily intake (ADI) on which MRLs are based, is estimated as the quantity which would be without observable effect if ingested every day for the whole of a lifetime. Occasional consumption of food containing levels in excess of the MRL, or even in excess of the ADI, is therefore unlikely to be hazardous.

(d) The second line of defense is surveillance over the occurrence of residues in agricultural commodities. This entails submission of samples for laboratory analysis. Samples may be collected at random to provide an overall estimate ofthe occurrence of residues, or taken selectively from areas where use of the particular chemical is greatest, to provide an estimate of residue occurrence in the worst possible situation. The selective approach is often used in order to makethe best possible use of scarce analytical resources. It always seems a little pointless to search for residues in areas where there is little or no likelihood of their occurrence. Statisticians often criticize analytical programs on the grounds that insufficient numbers of samples are tested. It is noted that 300 consecutive samples must be tested and found compliant in order to be 95% confident that the true violation rate in the population does not exceed 1%. However, resources do not always permit this luxury and it is often necessary to be satisfied with less.

(e) ***The corrective role***

Wherever possible, violative or near violative residues found in a residue survey should be traced back to the farm of origin where suitable corrective action can be taken to ensure there is no recurrence. Corrective action may vary from advice byextension authorities to quarantine in extreme cases. Quarantine is normally used only in the case of persistent residues. The effectiveness of traceback depends on identification of the sample. In the case of meat, it depends on animal identificationand samples are therefore best taken from the killing floor of an abattoir rather than from a retail meat outlet.

(f) ***Preparation of food***

Where a residue is removed during normal preparation by peeling or skinning, or if it is destroyed by cooking in a food which is normally cooked, due allowance can be made for this in evaluation of the residue hazard.

(g) Regulatory authorities must watch closely for changes or new trends in agricultural management and practice. Such changes can cause large alterations in the pattern of residues.

3.6.3 Economy

Importance of technological progress

Farmers must stay abreast of contemporary technology if their product is to be competitive on world markets.In order that a country's farmers may have access to new products suited to their unique requirements, it is necessary that the country demonstrate a standard of regulatory control which inspires confidence in their overseas trade partners. In the absence of an adequate standard of control, considerable caution must be exercised and the approval and adoption of new technology is delayed.

4.0 CONCLUSION

The presence of pesticide residues in feed and animal products is in the focus at the present in the view of WTO. The residues not only affect the public health but also cause economic losses to the livestock industry.

These not only affect the health of livestock and human beings but also affect the quality of animal products. Pesticide residues accumulate in the animals either by direct contact with pesticide or by indirect contactwith environment. Pesticides are used in crops for pest control and they leave the residues in the feed and fodder consumed by animals. The source of contamination of feed and fodder may be by direct spraying or by drift from other crops, contamination of soil and water used for fodder production. Pesticide use regulations should therefore be emphasized and embraced in order to maintain the minimum residue limits (MRL) in all countries.

5.0 SUMMARY

In this unit the students has leant:

i. the different ways by which pesticide residues reduces the quality and economic value of livestock products;
ii. the various was by which pesticide residues gain entry into animal products; and
iii. the various ways residues can be managed to keep pesticide residues in the minimum residues limits.

6.0 TUTOR-MARKED ASSIGNMENTS

(iii) Explain the various ways pesticide residues can find their ways into the animals body and its products
(iv) Discuss in general, the management of pesticide residues in animals and their products.

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UNIT 17 PESTICIDE RESIDUES IN THE FOOD CHAIN: PESTICIDE RESIDUES IN HUMAN BODY

CONTENTS

1.0 INTRODUCTION

Pesticides are widely used in agriculture mainly to increase crop yields to cater for the huge supply of food products for increasing world population as well as to protect crops from pests and control insect-borne diseases. Increased use of pesticides results in contamination of the environment and the excess accumulation of pesticide residues in food products, which has always been a matter of serious concern. Pesticide residues in food and crops are directly related to the irrational application of pesticides to the growing crops. Accumulated pesticide residues in food products have been associated with a broad variety of human health hazards, ranging from short-term effects to longterm toxic effects.

2.0 OBJECTIVES

By the end of this unit, students should be able to:

1. Understand the various routes of entry of pesticide into the human body;
2. understand the harm pesticide residues do to the human body and health; and
3. understand the fate of pesticide in the human body.

3.0 MAIN CONTENTS

3.1 Routes of exposure to pesticides

There are four routes by which a substance can enter the body: inhalation, skin (or eye) absorption, ingestion, and injection.

- **Inhalation**: For most chemicals in the form of vapors, gases, mists, or particulates, inhalation is the major route of entry. Once inhaled, chemicals are either exhaled or deposited in the respiratory tract. If deposited, damage can occur through direct contact with tissue or the chemical may diffuse into the blood through the lung-blood interface. Upon contact with tissue in the upper respiratory tract or lungs, chemicals may cause health effects ranging from simple irritation to severe tissue destruction. Substances absorbed into the blood are circulated and distributed to organs that have an affinity for that particular chemical. Health effects can then occur in the organs, which are sensitive to the toxicant.

- **Skin (or eye) absorption**: Skin (dermal) contact can cause effects that are relatively innocuous such as redness or mild dermatitis; more severe effects include destruction of skin tissue or other debilitating conditions.

Many chemicals can also cross the skin barrier and be absorbed into the blood system. Once absorbed, they may produce systemic damage to internal organs. The eyes are particularly sensitive to chemicals. Even a short exposure can cause severe effects to the eyes or the substance can be absorbed through the eyes and be transported to other parts of the body causing harmful effects.

- **Ingestion**: Chemicals that inadvertently get into the mouth and are swallowed do not generally harm the gastrointestinal tract itself unless they are irritating or corrosive. Chemicals that are insoluble in the fluids of the gastrointestinal tract (stomach, small, and large intestines) are generally excreted. Others that are soluble are absorbed through the lining of the gastrointestinal tract. They are then transported by the blood to internal organs where they can cause damage.

- **Injection**: Substances may enter the body if the skin is penetrated or punctured by contaminated objects. Effects can then occur as the substance is circulated in the blood and deposited in the target organs.

3.2 The Dose-Response Relationship

In general, a given amount of a toxic agent will elicit a given type and intensity of response. The dose-response relationship is a fundamental concept in toxicology and the basis for measurement of the relative harmfulness of a chemical. A dose-response relationship is defined as a consistent mathematical and biologically plausible correlation between the number of individuals responding and a given dose over an exposure period.

3.3 Dose Terms.

In toxicology, studies of the dose given to test organisms is expressed in terms of the quantity administered:

- **Quantity per unit mass (or weight)**. Usually expressed as milligram per kilogram of body weight (mg/kg).

- **Quantity per unit area of skin surface**. Usually expressed as milligram per square Centimeter (mg/cm2).

• **Volume of substance in air per unit volume of air**. Usually given as microliters of vapor or gas per liter of air by volume (ppm). Particulates and gases are also given as milligrams of material per cubic meter of air (mg/m3). The period of time over which a dose has been administered is generally specified. For example, 5 mg/kg/3 D is 5 milligrams of chemical per kilogram of the subject's body weight administered over a period of three days. For dose to be meaningful, it must be related to the effect it causes. For example, 50 mg/kg of chemical "X" administered orally to female rats has no relevancy unless the effect of the dose, say sterility in all test subjects, was reported.

3.4 Human health risk assessment of pesticide as representative xenobiotic

Protecting public health is the primary reason why risk assessment of xenobiotics, be they pharmaceuticals, agrochemicals, or industrial chemicals, is of utmost importance. Exposure to pesticides is a global challenge to risk assessment (Maroni *et al.* 2006). Chronic exposure to low levels of pesticides can cause mutations and/ or carcinogenicity (Bull *et al.* 2006). On a worldwide basis, acute pesticide poisoning is an important cause of morbidity and mortality. In an extrapolation, WHO/UNEP estimated that more than 3 million people were hospitalized for pesticide poisoning every year and that 220 000 died; it particularly noted that two-thirds of hospitalizations and the majority of deaths were attributable to intentional self-poisoning rather than to occupational or accidental poisoning. Humans are inevitably exposed to pesticides in a variety of ways: at different dose levels and for varying periods of time (Boobis*et al.* 2008). This is why pesticides are used as representative xenobiotics in this research program.

3.5 General considerations in health risk assessment of pesticides

In the health risk assessment of chemicals, the determination of a NOAEL (No Observed Adverse Effect Level) is often based on data only from animal experiments. The safety or uncertainty factor 100 is used to convert NOAEL from an animal toxicity study to an ADI (Acceptable Daily Intake) value for human intake, ADI = NOAEL/100. Historically, the assessment factor of 100 intended to cover the interspecies (animal-to-human) and interindividual (human-to-human) variations has often been used as a default. Based on factor 100, Renwick (Renwick 1991, Renwick 1993) has attempted to provide a scientific basis for the default values of 10 for interspecies and 10 for interindividual variability. Renwick also proposed a division of each of these factors into subfactors to allow for separate evaluations of differences in toxicokinetic and toxicodynamic based on the relative magnitude of toxicokinetics and toxicodynamics variation between and within species. He proposed that the 10-fold factors for inter- and intraspecies variation should be subdivided into factors of 4 for toxicokinetics and 2.5 for toxicodynamics. WHO/IPCS has adapted the Renwick approach with one deviation. While the uncertainty factor (UF) for interspecies extrapolation should be divided into default values of 4 for toxicokinetics and 2.5 toxicodynamics, the UF for interindividual variation should be divided into 3.16- fold for both toxicokinetics and toxicodynamics. The reason for this deviation from Renwick's proposal was that the WHO/IPCS considered the slightly greater variability in the kinetics in humans compared with dynamics was not sufficient to warrant an unequal subdivision of the 10-fold factor into a toxicokinetic factor of 4 and a toxicodynamic factor of 2.5

3.6 Toxic effects of pesticide residues on human health

Many pesticides achieve their intended use of killing pests by disrupting the nervous system. Due to similarities in brain biochemistry among many different organisms, there is much assumption that these chemicals can have a negative impact on humans as well. There are epidemiological studies that show positive correlations between exposures to pesticides through occupational hazard, which tends to be significantly higher than that ingested by the general population through food, and the occurrence of certain cancers (Damalas and Eleftherohorinos, 2011). Although most of the general population may not expose to a large portion of pesticides, many of the pesticide residues that are attached tend to be lipophilic and can bio-accumulate in the body (Crinnionm, 2009)

Toxic effects of pesticides depend upon their toxicological properties, the level of residues and degree of exposure of human beings to residues. The presence of pesticide residues in grains does not necessarily mean that it is hazardous. To be toxic, the residues have to be present in quantities large enough to be considered unsafe (Selvaraj*et al.*, 2014). The organophosphate, organochlorine and related pesticides act by binding to the enzyme acetylcholinesterase, disrupting nerve function, resulting in paralysis and may cause death. They may produce acute effects manifesting as meiosis, urination, diarrhea, diaphoresis, lacrimation, excitation of central nervous system and salivation. The chronic exposure involves neurotic and behavioral effects. Specific effects of pesticides can include damage to the central and peripheral nervous systems, cancer, allergies and hypersensitivities, reproductive disorders and disruption of the immune system (Mishra *et al*,., 2014).

3.6.1 Neuronal damage due to cholinergic neuronal excitotoxicity and dysfunction:

1. Following exposure to organophosphates, accumulation of acetylcholine at synapses results in rapid and profound excitotoxicity and dysfunction of cholinergic neurons in the brain.
2. Overstimulation of muscarinic acetylcholine receptors may also disrupt the balance of excitatory and inhibitory mechanisms to cause neuronal excitotoxic lesions leading to seizures and respiratory depression.
3. Seizures may result from over release of glutamate from glutamatergic neurons, triggering excessive calcium release in post-synaptic neuronal cells.
4. Seizures caused by cholinergic neuronal excitotoxic lesion in the brain may play a synergistic role in development of irreversible brain damage and long-term neurological and behavioural disorders.
5. Irreversible neural injury and neuronal cell death caused by organophosphate poisoning.
6. Serious neuropsychiatric impairments, including memory loss, inability to concentrate, speech problems, motor and sensory deficits, and behaviouralproblems.
7. In the first few hours after organophosphate poisoning, as the result of the cholinergic neuronal excitotoxicity, extensive intracellular edema, cerebral hemorrhages, intracellular calcium overload, oxidative stress and increased neuro inflammatory responses were generally observed in the affected brain regions.
8. The altered calcium influx activates lipases, proteases, kinases, phosphatases, and endonucleases in potentially harmful metabolic cascades, thus arresting protein synthesis and depriving cells of enzymes or trophic factors essential to their survival.

9. Many studies have demonstrated that obvious neuronal cell death, neural loss, and axonal degeneration were observed in different species of animals exposed to organophosphates.

3.6.2 Long-term neuropsychiatric and neurological disorders:

Exposure to organophosphates involve damage to cholinergic neurons of basal forebrain and the limbic system, which may cause memory, cognitive, mental, emotional, motor and sensory deficits by disrupting this putative sensory-limbic gating mechanism.

3.6.3 Persistent memory and cognitive deficits:

1. Memory and cognitive deficits are one of the most common and persistent behavioral sequelae in victims exposed to organophosphates.
2. Exposure to organophosphates sarin and cyclosarin at Khamisiyah resulted in long-term cognitive and memory impairments in the Gulf War-deployed veterans in 1991.
3. Chronic memory and cognitive impairments were also observed in the victims of the Tokyo subway sarin attack. 7 years after the Tokyo subway sarin attack, a chronic decline of memory function still existed in 23 subway workers exposed to sarin. The exposed subway workers performed less well in the memory function tests, and their digit number of the backward digit span test was significantly smaller.
4. Loss of cholinergic neurons in the basal forebrain with aging results in a decline in cognitive capacity.

3.6.4 Psychomotor performance deficits and somatic complaints:

Clinical study has demonstrated that the Gulf War-deployed veterans exposed to sarin and cyclosarin at Khamisiyah suffered impaired fine psychomotor dexterity, reduced visuospatial abilities and deficits in motor function and coordination. After the Tokyo subway sarin attack, a chronic decline of psychomotor function existed in 23 subway workers exposed to sarin for 7 years. The high-exposure subway workers had a significantly slower performance of the finger tapping tests of both the dominant and non-dominant hands than control group. In another clinical study, most of the victims of the Tokyo subway sarin attack were found to have long-lasting somatic complaints (such as gastrointestinal problems, constipation, heartburn, nausea, vomiting, colitis, migraines, headaches, backaches, and skin disorders) at 5 - 6 years after poisoning. The long lasting somatic complaints and decreased psychomotor function of the victims exposed to organophosphates may be associated with neuronal damage in the cortex and thalamus.

3.6.5 Oxidative stress:

In sub chronic or chronic organophosphate exposition induction of oxidative stress has been reported as the main mechanism of organophosphate toxicity. Oxidative stress is induced in both acute and chronic intoxication with organophosphate compounds in humans and experimental animals. Hyperglycaemia is one of the mechanism of oxidative stress in organophosphate intoxication. Studies on chronic exposure to carbamate insecticides and case reports of long-term exposure give equivocal results. An extensive survey of the toxicology of the common insecticide, carbaryl, reports a variety of reversible neurobehavioral and neurotoxic effects in vertebrates, all associated with acute poisoning symptoms. The carbamate, carbofuran, has been observed to accentuate oxidative stress in rat brain by inducing lipid peroxidation and diminishing the antioxidant defense.

3.6.6 Development of cancer:

The studies on cancer analyze the risks associated with the consumption of specific products which have some pesticide residues. These consumption products include fish, water, seafood, and milk or other dairy products. In general, these studies find a small but statistically significant association between cancer risks and some specific pesticide residues, such as dichlorodiphenyltrichloroethane and dichlorodiphenyltrichloroethane. Specifically polychlorinated biphenyls present a higher risk for consumers. Organochlorine pesticide residue levelswere reported significantly higher in the cancer patients (Moon *et al.*, 2009).

3.6.7 Reproductive disorders:

Results indicated that increase of insecticides in blood level in vertebrates causes reproductive dysfunction and suggested that for human beings food like fish, chick and goat containing beyond permissible limit of insecticides must be avoided. Consumption of high pesticide residue fruits and vegetables was associated with lower total sperm count, ejaculate volume and percentage of morphologically normal sperm among men attending a fertility clinic (Chiu *et al.*, 2015). Pesticides exposure may lead to reduced fertility, early and late pregnancy loss, prolonged time-to-pregnancy, spontaneous abortion, and premature birth in female and genetic alterations in sperm, reduced sperm count, damage to germinal epithelium and altered hormone function in male.

3.7 Pesticide metabolism in the human body

Risk assessment needs reliable scientific information and one source of information is the characterization of the metabolic fate and toxicokinetics of compounds. Toxicokinetics refers to the movement of a xenobiotic into, through, and out of the body and is divided into several processes including absorption, distribution, metabolism, and excretion, ADME. Metabolism is one of the most important factors that can affect the overall toxic profile of a pesticide. During metabolism, the chemical is first biotransformed by phase I enzymes, usually by the cytochrome P450 (CYP) enzyme system, and then conjugated to a more soluble and excretable form by phase II conjugating enzyme systems. In general, these enzymatic reactions are beneficial in that they help eliminate foreign compounds. Sometimes, however, these enzymes transform an otherwise harmless substance into a reactive form – a phenomenon known as metabolic activation.

3.7.1 Cytochrome P450 (CYPs) – the human xenobiotic-metabolizing enzymes

The P450 enzymes are hemoproteins with approximate molecular weights of 50,000 Da. These enzymes catalyze the monooxidation of a wide variety of CYP oxidation reactions involve a complex series of steps. The initial step involves the binding of a substrate to oxidized CYP, followed by a one-electron reduction catalyzed by NADPH cytochrome P450 reductase to form a reduced cytochrome-substrate complex. The next several steps involve interaction with molecular oxygen, the acceptance of the second electron from NADPHcytochrome P450 reductase, followed by subsequent release of water and the oxygenated product of the reaction. This reaction sequence results in the addition of one oxygen atom to the substrate, while the other atom is reduced to water (Parkinson 2001, Rose & Hodgson 2004). CYPs are found in high concentrations in the liver, but are present in a variety of other tissues, including lung, kidney, the gastrointestinal tract, nasal mucosa, skin and brain. P450 enzymes are categorized into families and subfamilies by their sequence similarities. Humans have 18 families of cytochrome P450 genes and 44 subfamilies. The enzymes are thus identified by a number denoting the family, a letter denoting the subfamily and a number identifying the specific member of the subfamily.

4.0 CONCLUSION

Public concern about the adverse environmental and human health impacts of pesticides led to strict regulations on their use in many countries. Nevertheless, many pesticides are still being used for agricultural and public health programmes. Consequently, consumers are exposed to greater dietary levels of these pesticides. The available information regarding pesticide residues in meat, poultry and fish, milk and crop products in developing countries is very limited. Therefore, the design and implementation of appropriate epidemiological studies and their integration with monitoring of samples from foods of plant and animal origins as well as environmental samples would be a major step in assessing the risk of pesticide residues in food items and controlling or eliminating them. With the continued globalization of trade in plant and animal food products and the concomitant risk that the food contamination through point-source pollution may be widely distributed, identification of sources and their control should be matters of international concern, research and action.

5.0 SUMMARY

In this unit the students has leant that:

i. The four routes by which a substance can enter the body are inhalation, skin (or eye) absorption, ingestion, and injection.
ii. Pesticide residues have potentials to cause disorder in the human body system performance following chronic exposure to even low concentrations.ii.econoclimate is very important in

management decisions involving use and non-use of atmospheric resources;

iii. The magnitude of the harm they cause also cut across all areas of human health.iv.applicability of econoclimatic model is not restricted to agricultural planning.

iv. Toxicokinetics refers to the movement of a xenobiotic into, through, and out of the body and is divided into several processes including absorption, distribution, metabolism, and excretion, ADME.

6.0 TUTOR-MARKED ASSIGNMENTS

i. Outline the various routes of entry of pesticides into the human body

ii. Discuss some of the effects of pesticide residues on human's health

7.0 REFERENCES AND OTHER RESOURCES

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UNIT 18 DETECTION/DETERMINATION OF TOXIC WASTES IN THE ENVIRONMENT

CONTENTS

1.0 INTRODUCTION

When it comes to matters of environmental pollution, the words “toxic” and “hazardous” are used interchangeably. The word “toxic” simply means “poisonous”, and by implication, poisons are harmful to life and health and anything that is harmful is said to be hazardous. In most developed countries, businesses and institutions are required by federal and state laws to determine if the waste materials they generate are toxic waste. Accurate waste determinations are the first step in ensuring safe management of toxic wastes. Failure to properly identify a toxic waste may result in damage to human and environmental health, while accurate waste determinations have the potential to reduce management and disposal costs. Based on regulatory requirements, records of all waste determinations conducted on solid wastes must be maintained, regardless of whether the outcome of the determination is positive or negative. The records associated with the waste determinations must be maintained and available during compliance inspections. However, there are solid waste streams that do not require a waste determination and they include wastes not having the potential to be a toxic waste. Examples include food waste and office-generated paper wastes.

2.0 OBJECTIVES

By the end of this unit, students should be able to:

- understand the principal steps involved in the waste determination process.
- understand the waste determination methods; and
- understand the differences between listed and characteristic hazardous wastes.

3.0 MAIN CONTENTS

3.1 Waste Determination Process

There are five principal steps in the waste determination process:

1. Identify the waste streams: Make a list of all facility waste streams and include how the waste is generated.
2. Determine whether the waste stream is a solid waste: Check to see if each waste meets the definition of "solid waste".
3. Determine if the solid waste is excluded from regulation.
4. Determine whether the solid waste is a hazardous waste.
5. Document the information in steps 1-4: Compile the information used to make the waste determination, including a statement on whether the waste is a hazardous waste. If it is hazardous waste, list the applicable waste codes and what the generation rate of this waste is per month. Knowing your waste generation rates will help in determining the correct generator status and applicable regulations for your facility.

Written documentation is a required step in the hazardous waste determination process. These documents must be kept as part of your recordkeeping requirements.

In the United States, small quantity generators (SQGs), large quantity generators (LQGs), storage and disposal (TSD) facilities are required to document and retain their hazardous waste determinations. The Department of Natural Resources (DNR) and U.S. Environmental Protection Agency (EPA) strongly recommend that very small quantity generators (VSQGs) also retain these documents. However, if no documentation is available during a facility inspection, both the DNR and the EPA can require a generator to perform a waste determination to support the facility findings that a waste of concern is not a hazardous waste.

3.2 What Is a Solid Waste?

Generally, if a material can longer be used for its intended purpose, and the waste is being discarded, abandoned, recycled or deemed inherently waste-like, the material would be classified as a solid waste. The term “solid waste” does not refer to the physical state of the waste. Solid wastes can be *solid*, *liquid*, or *containerized gas*.

Certain solid wastes that are recycled are excluded from the definition of a solid waste. If a material is not a solid waste, it cannot be considered a hazardous waste. Materials that are excluded from being a solid waste when recycled are listed in the appropriate documentation. It is important to document the reasoning behind any exclusions used in the waste determination process.

3.3 What Is a Hazardous Waste?

Hazardous waste is a waste with properties that make it dangerous or harmful to human health or the environment. The universe of hazardous wastes is large and diverse. Hazardous wastes can be liquids, solids, or containerized gases. They can be the by-products of manufacturing processes, discarded used materials, or discarded unused commercial products, such as cleaning fluids (solvents) or pesticides. In regulatory terms, a hazardous waste is a waste that appears on one of the four hazardous wastes lists (the F-list, K-list, P-list, or U-list) or that exhibits one of the four characteristics of a hazardous waste- ignitability, corrosivity, reactivity, or toxicity. However, materials can be hazardous wastes even if they are not specifically listed or do not exhibit any characteristic of a hazardous waste.

3.4 Listed or Characteristic Hazardous Wastes

Hazardous wastes can be process wastes, chemicals or compounds designated as “listed wastes” and/or they can exhibit hazardous characteristics (ignitability, corrosivity, reactivity or toxicity). A hazardous waste may be listed, characteristic, or both. The waste codes outlined below are used to identify and track the wastes on shipping manifests from generation and transportation through treatment and disposal or recycling.

Listed Wastes

F-list wastes: These waste types (F001-F039) typically include certain spent solvents, paint thinners, brake and carburetor cleaners, vapour degreasing and dry cleaning solvents, electroplating wastes, and manufacturing and process wastes.

K-list wastes: These waste types (K001-K178) typically come from specific sources such as industrial processes like wood preserving, manufacturing pesticides, organic chemicals and veterinary drugs.

P-list wastes: These wastes are identified as acute hazardous wastes (P001-P205) and include discarded commercial chemical products; off-specification species; container and spill residues including unused chemicals such as cyanides, arsenic compounds and several pesticides. These wastes are extremely dangerous to human health and the environment in very small doses or short-term exposure.

U-list wastes: These wastes are identified as toxic wastes (U001-U411) and include discarded commercial chemical products, off-specification species, container residues, and spill residues including used chemicals that pose health risks due to their persistence in the environment or their potential for migrating through the environment. These wastes are dangerous to humans and the environment in small doses, but are not as toxic as “P-listed” wastes.

Characteristic Wastes

Waste Code D001: Ignitability represents the ability of the waste to burn. Liquid wastes are ignitable if their flash point is less than 140 degrees F. Some non-liquids, flammable gases and certain oxidizers also have this characteristic.

Liquid wastes w/flash point <140F	Gasoline, xylene, toluene, acetone, benzene, methanol, isopropyl alcohol
Non-liquids	Sulfer, oily rag containing drying oils (linseed oil, soya bean oil, tung oil, wetted titanium powder, aluminum powder, magnesium powder, alkali metals.
Flammable gases	Propane, acetylene, butane, hydrogen, methane
Oxidizers	Chlorates, permanganates, inorganic peroxides, organic peroxides, nitric acid in concentrations from 65 to 70%

Source: Publication WA1152-Waste Determinations and Recordkeeping, Wisconsin Department of Natural Resources (Revised February 2017, formerly titled "Is Your Waste Hazardous?")

Waste Code D002: Corrosivity represents the ability of the waste to destroy or deteriorate materials, chemically burn skin, enhance movement of toxic chemicals in the environment, react dangerously with other wastes, or harm fish and other aquatic life. Aqueous wastes (>50% water) are corrosive if their pH is less than or equal to 2 or greater than or equal to 12.5 (e.g. rust remover, descalling products). Liquid wastes (e.g. ferric chloride) are corrosive if they corrode steel by more than one-quarter inch per year.

Waste Code D003: Reactivity is the waste's tendency to react violently or explode. Wastes are reactive if they are unstable either alone or in the presence of water. These wastes can form explosive mixtures with water and produce dangerous quantities of toxic gases, vapours or fumes when mixed or when exposed to mild acids or bases. They can detonate, react or decompose explosively (hydrogen sulfide, cyanide or sulfide-bearing wastes, lithium-sulfur batteries, nitroglycerin formulations, ethylene oxide, sodium azide, and phosphorous.

Waste Code D004-D043: Toxicity is the ability of hazardous constituents to leach out of the waste. Wastes are toxic if they release or leach any of 39 specified heavy metals, pesticides or other organic chemicals above their regulatory level concentration (e.g. benzene, carbon tetrachloride, chromium, chlordane, endrin, lead, mercury).

3.5 Waste Determination Methods

In order to make a waste determination, the generator can use either laboratory analysis results and/or apply knowledge of the waste based on the materials and processes used to generate the waste. While representative sampling and analysis of the waste might be considered as convenient as relying solely on applying knowledge, it provides advantages. An accurate waste determination is a critical factor in demonstrating compliance with hazardous waste regulations and reducing disposal costs by avoiding the over-classification of hazardous wastes.

3.5.1 Laboratory analysis

A generator of wastes is required to use a DNR-certified laboratory to analyze waste samples for making waste determinations. Before collecting the representative waste sample, select a lab and discuss the following: sample volumes, required containers, sample collection methods, and correct analytical test methods.

3.5.2 Representative sampling

The methods and equipment used for sampling waste materials will vary based on the form and consistency of the waste. A representative sample of each waste stream must be collected and analyzed in order to provide sufficient data to make the waste determination. The sample collected should reflect an unbiased representation of the waste, exhibit the average properties of the waste stream (or universe, such as a waste pile or lagoon) and reflect potential process variations. According to EPA guidelines, for a sample to be representative, it needs to be collected and handled in a way that preserves its original physical form and chemical composition and prevents contamination. For a sample to provide meaningful data, it is important that it reflect the properties of the waste from which it was obtained, that its physical and chemical integrity be maintained, and that it be analyzed within a dedicated quality assurance program.

3.5.3 Acceptable knowledge

Use of knowledge to determine whether a waste material is hazardous waste or non-hazardous waste may be acceptable, but it must be supported with documentation. Examples of supporting documentation include: Safety Data Sheets (SDSs), published information, process flow diagrams, chemical reaction diagrams, identified breakdown products,and other process reactions or chemical information. Typically, none of these documents are acceptable as stand-alone information for a waste determination as most do not state conclusively whether or not the waste is hazardous or non-hazardous. Consequently, multiple document sources may be needed to support a knowledge-based determination.

3.5.3.1 Safety data sheets

SDSs can provide useful information regarding ignitability (flash point), corrosivity (pH), or reactivity of the material going into the process. However, they tend to be less useful when it comes to identifying the toxic characteristics of waste generated from that process. The SDS only lists ingredients that make up greater than 1% of the total constituents (0.1% if they are carcinogens). Ingredients that are less than 1% by mass can equal up to 10,000 parts per million (ppm). This means that a material used in a process may contain a toxic constituent that is not listed on the SDS, but which contributes to the generation of a hazardous waste. Additionally, the process itself may chemically or physically change the properties of the materials such that the generated waste is hazardous.

3.5.3.2 Waste profiles

A documented “waste profile” is typically generated by Treatment, Storage or Disposal (TSD) facilities as a means for them to standardize and categorize information regarding wastes they intend to accept. The information outlined in the waste profiles regarding waste characterization needs to be supported by either laboratory analysis or acceptable knowledge. Waste profiles are not standardized forms and may not adequately characterize the waste. The generator will likely have a better understanding of the waste materials they generate and should work with the TSD to ensure adequate characterization.

3.6 Recordkeeping

Adequate written documentation (records) should include a statement regarding the waste determination for each waste stream. It should state whether the waste is hazardous or non-hazardous waste and include copies of all information used to support the determination. Written documentation includes, but is not limited to:

- A description of each identified waste stream and process.
- Analytical sampling results including a description of how each representative sample was collected and managed, why the specific test method was chosen, and evidence that the laboratory was certified for the test method used.
- Records that justify and support knowledge-based determinations such as SDSa, published information, process flow diagrams, chemical reaction diagrams, identified breakdown products, and other process reactions or chemical information.

During a hazardous waste generator inspection, waste determination records will be requested by the inspector to verify compliance with hazardous waste regulations, and it is recommended that this information be kept organized and readily accessible.

Re-evaluation of waste determinations should occur following process or material changes, or if the waste is highly variable, to verify that the original waste determination remains valid. Additionally, the DNR recommends a re-characterization of each waste stream be conducted every one to three years. It is the responsibility of the generator to make a correct waste determination and retain the supporting documentation.

4.0 CONCLUSION

From the foregoing, it can be concluded that hazardous wastes being generated from diverse businesses and institution still constitute a significant threat to human and environmental health. Accurate waste determinations have the potential to reduce the danger of indiscriminate dumping of hazardous wastes in the environment.

5.0 SUMMARY

In this unit the students have learnt that:

i. there are five principal steps involved in the waste determination process;
ii. hazardous wastes can be process wastes, chemicals or compounds designated as “listed wastes” and/or they can exhibit hazardous characteristics (ignitability, corrosivity, reactivity or toxicity);
iii. the generator can use either laboratory analysis results and/or apply knowledge of the waste based on the materials and processes used to generate the waste.; and
iv. adequate written documentation (records) should include a statement regarding the waste determination for each waste stream.

6.0 TUTOR-MARKED ASSIGNMENTS

(i) What is hazardous waste and how can it be determined in the environment?
(ii) List the five steps involved in the waste determination process.
(iii) Highlight the importance of recordkeeping in the waste determination process.

7.0 RESOURCES

EPA (2005). Introduction to Hazardous Waste Identification (40 CFR Parts 261). Solid Waste and Emergency Response (5305W). EPA530-K-05-012.

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Publication WA1152-Waste Determinations and Recordkeeping, Wisconsin Department of Natural Resources (Revised February 2017, formerly titled “Is Your Waste Hazardous?”).

UNIT 19 MANAGEMENT OF TOXIC WASTES IN THE ENVIRONMENT

CONTENTS

1.0 INTRODUCTION

Hazardous wastes are materials which are discarded after use from e-products, vehicles, clinical and medical products, fuel products (e.g. oil), gas exploration and extraction. Scientific research indicates that these include materials such as industrial solvents, waste oils, industrial sludges and chemical wastes. Household, small businesses, farms, and the healthcare and construction sectors also generate quantities of hazardous waste including batteries, electrical equipment, healthcare risk waste, solvent based paint and varnish waste, sheep dip, and fluorescent lamps (Bauer and Herrmann, 1997). Hazardous waste not only poses risks to the surrounding air, water, and soil, but also do harm to the ecological environment and human health through diversified channels (Li *et al*., 2015). This unit focuses on the best processes for the management of hazardous waste in the environment.

2.0 OBJECTIVES

By the end of this unit, students should be able to:

- identify the various categories of hazardous wastes and their sources;
- name the equipment used for collection of hazardous wastes;
- explain the techniques of hazardous waste management.

3.0 MAIN CONTENTS

3.1 Hazardous Waste Management

Hazardous waste management consists of several functional elements, which are discussed below.

3.1.1 Generation

Hazardous wastes are generated in limited amounts in a community and information on the quantities of hazardous waste generated within a community and in various industries is often scanty. Hazardous waste generation outside the industry is irregular and very less in amount, rendering the waste generation parameter meaningless. The only practical means to overcome these limitations is to conduct a detailed inventory and measurement studies at each potential source in a community. As a first step in developing a community inventory, potential sources of hazardous waste are to be identified. The total annual quantity of hazardous waste at any given source in a community must be established through data inventory completed during onsite visits. The list of hazardous waste generation sources is presented in the table below.

Waste Categories and their Sources

Waste Categories	**Sources**
Radioactive substances	Biomedical research facilities, colleges and university laboratories, offices, hospitals, nuclear power plants, etc.
Toxic chemicals	Agricultural chemical companies, battery shops, college and university laboratories, construction companies, electric utilities, hospitals and clinics, industrial cooling towers, newspaper and photographic solutions, nuclear power plants, pest control agencies, photographic processing facilities, plating shops, service stations, etc.
Biological wastes	Biomedical research facilities, drug companies, hospitals, medical clinics, etc.
Flammable wastes	Dry cleaners, petroleum reclamation plants, petroleum refining and processing facilities, service stations, tanker truck cleaning stations, etc.
Explosives	Construction companies, dry cleaners, ammunition production facilities, etc.

Source: Tchobanoglous *et al*. (1977 and 1993)

The spillage of containerized hazardous waste must also be considered an important source in addition to the sources listed. The quantities of hazardous wastes that are involved in spillage are usually not known. The occurrence of spillage cannot be predicted and hence, the potential threat to human health and environment is greater than that from routinely generated hazardous waste.

3.1.2 Storage and collection

Onsite storage practices are a function of the types and amounts of hazardous wastes generated and the period over which generation occurs. Usually, when large quantities are generated, special facilities are used that have sufficient capacity to hold wastes accumulated over a period of several days. If only a small amount is generated, the waste can be containerized, and limited quantity may be stored. Containers and facilities used in hazardous waste storage and handling are selected on the basis of waste characteristics. For example, corrosive acids or caustic solutions are stored in fibreglass or glass-lined containers to prevent deterioration of metals in the container. Great care must be exercised to avoid storing incompatible wastes in the same container or location.

The waste generator, or a specialized hauler, generally collects the hazardous waste for delivery to a treatment or disposal site. The loading of collection vehicles is completed in either of the following ways:

1. Wastes stored in large-capacity tanks are either drained or pumped into collection vehicles;
2. Wastes stored in sealed drums or sealed containers are loaded by hand or by mechanical equipment onto flatbed trucks.

The stored containers are transported unopened to the treatment and disposal facility. In order to avoid accidents and the possible loss of life, two collectors should be assigned when hazardous wastes are to be collected. The equipment used for collection varies with the waste characteristics, and the typical collection equipment are listed in the table below:

Equipment for Collection of Hazardous Waste

Waste Category	Collection equipment and accessories
Radioactive substances	Various types of trucks and railroad equipment depending on characteristics of wastes; special marking to show safety hazard; heavy loading equipment to handle concrete-encased lead containers.
Toxic chemicals	Flatbed trucks for wastes stored in drums; tractor-trailer tank truck combination for large volumes of wastes; railroad tank cars; special interior linings such as glass, fiberglass or rubber.
Biological wastes	Standard packers' collection truck with some special precautions to prevent contact between wastes and the collector; flatbed trucks for wastes stored in drums.
Flammable wastes	Same as those for toxic chemicals, with special colourings and safety warning printed on vehicles.
Explosives	Same as those for toxic chemicals with some restriction on transport routes, especially residential areas.

Source: Tchobanoglous *et al*. (1977 and 1993)

It should be noted that for short-haul distances, drum storage and collection with a flatbed truck is often used. The larger tank trucks, trailers and railroad tank cars are as hauling distances increase.

3.1.3 Transfer and transport

Typically, hazardous wastes are not compacted (i.e., mechanical volume reduction) or delivered by numerous community residents. Instead, liquid hazardous wastes are generally pumped from collection vehicles and sludge or solids are reloaded without removal from the collection containers for transport to processing and disposal facilities.

It is unusual to find a hazardous waste transfer facility, where wastes are simply transferred to larger transport vehicles. Some processing and storage facilities are often part of the material handling sequence at a transfer station. For example, neutralization of corrosive wastes might result in the use of a lower-cost holding tank on transport vehicles. However, great care must be exercised to avoid the danger of mixing incompatible wastes.

3.1.4 Processing

Processing of hazardous waste is done for purposes of recovering useful materials and preparing the wastes for disposal.

Processing can be accomplished on-site or off-site. The variables affecting the selection of processing site include the characteristics of wastes, the quantity of wastes, the technical, economical and environmental aspects of available on-site treatment processes and the availability of the nearest off-site treatment facility (e.g., haul distance, fees, and exclusions). The treatment of hazardous waste can be accomplished by physical, chemical, thermal or biological means.

3.1.5 Disposal

Irrespective of their form (i.e., solid, liquid, or gas), most hazardous waste is disposed off either near the surface or by deep burial. The various hazardous waste disposal methods are given in the table below:

Hazardous Wastes Disposal and Storage Methods

Operation/Process	Functions performed	Types of wastes	Forms of waste
Deep well injection	Di	1,2,3,4,5,6,7	L
Detonation	Di	6,8	S,L,G
Engineered storage	St	1,2,3,4,5,6,7,8	S,L,G
Land burial	Di	1,2,3,4,5,6,7,8	S,L
Ocean dumping	Di	1,2,3,4,7,8	S,L,G

Source: Tchobanoglous *et al*. (1977 and 1993)

***$** Functions: Di=disposal; St=storage; *Waste types: 1=inorganic chemical without heavy metals; 2=inorganic chemical with heavy metal; 3=organic chemical without heavy metal; 4=organic chemical with heavy metal; 5=radiological; 6=biological; 7=flammable and 8=explosive. # Waste form: S=solid; L=liquid and G=gas*

Although controlled landfill methods have been proved adequate for disposing of municipal solid waste and limited amounts of hazardous waste, they are not suitable enough for the disposal of a large quantity of hazardous waste because of the following reasons:

- possible percolation of toxic liquid waste to the groundwater;
- dissolution of solids followed by leaching and percolation to the groundwater;
- dissolution of solid hazardous wastes by acid leachate from solid, followed by leaching and percolation to the groundwater;
- potential for undesirable reactions in the landfill that may lead to the development of explosive or toxic gases;
- volatilization of hazardous waste leading to the release of toxic or explosive vapours to the atmosphere; and
- corrosion of containers with hazardous wastes.

In general, disposal sites for hazardous wastes should be separate from those for municipal solid wastes. As hazardous wastes can exist in the form of liquids, sludges, solids and dusts, a correct approach for co-disposal for each of the hazardous wastes should be determined. To preclude the co-disposal of incompatible wastes, separate storage areas within the total landfill site should be designated for various classes of compatible wastes (Phelps *et al.*, 1995).

Liquid wastes are usually stored in a tank near the site and can be introduced into the landfill by means of trenches or lagoons, injection or irrigation. During disposal of lightweight wastes, the disposal area must be kept wet to prevent dust emissions. Hazardous solid waste characterized by a high degree of impermeability as such must not be disposed of over large areas. When containerized wastes are to be disposed of, precautions must be taken to avoid the rupture of containers during the unloading operation and the placement of incompatible waste in the same location. To avoid rupturing, the containers are unloaded and placed in position individually. The covering of the containers with earth should be monitored and controlled carefully to ensure that a soil layer exists between each container and the equipment placing the soil does not crush or deform the container.

While designing a landfill site for hazardous waste, provision should be made to prevent any leachate escaping from landfill site. This requires a clay liner, and in some cases, both clay and impermeable membrane liners are used. A layer of limestone is placed at the bottom of the landfill to neutralize the pH of leachate. A final soil cover of 25 cm or more should be placed over the liner. The completed site should be monitored continuously, both visually and with sample wells.

4.0 CONCLUSION

From the foregoing, it can be concluded that for effective hazardous waste management, the total annual quantity of hazardous waste at any given source in a community must be established through data inventory completed during onsite visits. Great care must be exercised to avoid storing incompatible wastes in the same container or location. As hazardous wastes can exist in the form of liquids, sludges, solids and dusts, a correct approach for co-disposal for each of the hazardous wastes should be determined. It is imperative to use the appropriate materials to prevent leachate escaping from landfill site during its design.

5.0 SUMMARY

In this unit the students have learnt that:

i. management of hazardous wastes follows the functional elements of solid waste, viz., generation, storage and collection, transfer and transport, processing and disposal;
ii. processing can be accomplished either on-site or off-site to recover useful materials and to prepare the wastes for disposal;
iii. regardless of their forms, most hazardous wastes are disposed of either near the surface or by deep burial; and
iv. controlled landfill methods used for disposing of municipal solid waste are not suitable for the disposal of a large quantity of hazardous waste.

6.0 TUTOR-MARKED ASSIGNMENTS

(i) Write short notes on the storage and collection, transfer and transport, of hazardous wastes.
(ii) Suggest ways and means of properly managing hazardous wastes.

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UNIT 20 SANITARY FUNDAMENTALS OF PESTICIDE APPLICATION

CONTENTS

1.0 INTRODUCTION

Pesticides are biologically active compounds that act not only on their targets, but also constitute a potential hazard for human health and the environment. All pesticides are poisonous, some more so than others. Their toxic effects on target organisms are manifested not only during the period of application, but also after application and may be chronic. Some pesticides accumulate on objects of the environment, gradually concentrating in the food and fodder and becoming a real hazard to beneficial animals and humans. Extensive areas of agricultural lands and hundreds of thousands of tons of products are treated with pesticides, and hence they continue to circulate in human habitat. Pesticide residues are detected in the air, water, soil, plants and animals including human body. Consequently, use of pesticides must be regulated and monitored from a general sanitary viewpoint in terms of their fate and behaviour in the environment and the human body (Gruzdyev *et al*, 1983).

2.0 OBJECTIVES

By the end of this unit, students should be able to:

- understand the safety rules for pesticide application;
- understand the basis for sanitary classification of pesticides; and
- understand the precautionary measures that should be taken by pesticide applicators during spraying and mixing of pesticides.

3.0 MAIN CONTENTS

3.1 Sanitary Fundamentals of Pesticide Application

Pesticides or their metabolites may poison humans and animals. Pesticide poisoning may be occupational when it occurs among workers engaged in routine preparation of working formulations of pesticides or those spraying orchards or agricultural fields or those applying seed treatments. To prevent occupational hazard, it is necessary to comply strictly with the sanitary rules for applying, storing, and transporting pesticides. It is also necessary to observe the pre-harvest intervals after pesticide application and use the recommended personal protection equipment. The action of a pesticide on warm-blooded animals and animals depends on a multiplicity of factors, including the nature of its active ingredient, its dose, longevity of action, and the general well-being of the organism. Pesticides entering an organism spread rapidly in it, becoming selectively accumulated in separate parts or organs. Proteins bind some pesticides, while others are metabolized and excreted from the organism.

3.1.1 Sanitary classification of pesticides

A sanitary classification allows for comparative characterization of various pesticides and determination of what pathological effect is of the greatest danger when applying a given pesticide. The relative toxicity of pesticides, and hence the danger they pose to warm-blooded animals, is expressed in a measure known as LD_{50}, which stands for lethal dose, 50 percent. The LD_{50} is the amount of a pesticide that resulted in the death of 50 percent of a test animal population. It is based on milligrams (mg) of active ingredient per kilogram (kg) of body weight. Thus, the lower LD_{50}, the more toxic a pesticide is to people as indicated in the table overleaf.

For simplicity's sake, a pesticide label contains one of three "signal words" to indicate the product's relative toxicity to humans:

- DANGER applies to those pesticides with an LD_{50} of less than 50 mg. These highly toxic pesticides require special certification to buy and use.
- WARNING refers to pesticides that are only moderately toxic. The LD_{50} range for these pesticides is between 50 and 500.
- CAUTION is applied to pesticides with low to very low human toxicity. The LD_{50} for this group is 500 or more. Most of the pesticides available to the homeowner contain the signal word CAUTION on their labels.

Interpreting toxicity categories and signal words on pesticide labels

Toxicity category	**Oral** LD_{50} (mg/kg)	**Signal word**	**Approximate adult lethal dose (oral)**
I	0-50	DANGER/POISON	Few drops to 1 teaspoon
II	50-500	WARNING	1 teaspoon to 1 ounce
III	500-5,000	CAUTION	1 ounce to 1 pint or pound
IV	5,000 or more	CAUTION	More than 1 pint or pound

Regardless of the signal word on a pesticide label, remember that every pesticide is toxic and has the potential to poison. Therefore, always read the label and follow all of the directions on the label each time you use a pesticide. It is always better to be safe than sorry. Read the product label, and be prepared to use the product in a responsible way. When children, pets or wildlife could be present, take special precautions (Kroening and Fishel, 2016).

3.1.2 Safe use of pesticides

Pesticides are toxic to both pests and humans, but they need not be hazardous to humans and non-target animal species if appropriate precautions are taken. Most pesticides will cause adverse effects if intentionally or accidentally ingested or if they are in contact with the skin for a long time. Pesticides particles may be inhaled with the air while they are being sprayed. An additional risk is the contamination of drinking-water, food or soil.

3.1.3 Precautions

Special precautions must be taken during transport, storage and handling of pesticides. Spray equipment should be regularly cleaned and maintained to prevent leaks. People working with pesticides should receive proper training in their safe use.

3.1.3.1 The label

Pesticides should be packed and labeled according to World Health Organization (WHO) specifications. The label should be in English and in the local language, and should indicate the contents, safety instructions (warnings) and possible measures in the event of swallowing or contamination. Always keep pesticides in their original containers; take safety measures and put on protective clothing as recommended.

3.1.3.2 Storage and transport

Pesticides should be stored in a place that can be locked and is not accessible to unauthorized people or children; they should never be kept in a place where they might be mistaken for food or drink as some beverages may have the same colour with some pesticides. Keep them dry but away from fires and out of direct sunlight. Do not carry them in a vehicle that is also used to transport food.

3.1.3.3 Disposal

Leftover insecticide suspension can be disposed of safely by pouring it into a specially dug hole in the ground or a pit latrine. It should not be disposed of where it may enter water used for drinking or washing, fishponds or rivers. Some insecticides, such as the pyrethroids, are very toxic to fish. Dig a hole at least 100 metres away from the streams, wells and houses. In a hilly area the hole should be on the lower side of such areas. Pour run-off water from hand washings into the hole, and bury containers, boxes and bottles used for pesticides in it. Close the hole as soon as possible. Cardboard, paper and cleaned plastic containers can be burned, where this is allowed, far away from houses and sources of drinking water. Pyrethroid suspensions can be poured on to dry ground where they are quickly absorbed and degraded and do not cause any environmental problems.

3.1.3.4 General hygiene

Do not eat, drink or smoke while using insecticide. Keep food in tightly closed boxes. Use suitable equipment for measuring out, mixing and transferring insecticides. Do not stir liquids or scoop pesticides with bare hands. Use the pressure-release valve of the pump or a soft probe to clear blockages in the nozzle. Wash the hands and face with soap and water each time the pump has been refilled. Eat and drink only after washing the hands and face. Take a shower or bath at the end of the day.

3.1.3.5 Protective clothing

Pesticides can enter the body in several ways: ingestion, inhalation or contact with the skin. Surveys indicate that most exposure victims contact pesticides through their skin. Consequently, personal protection equipment must be used when spraying and mixing pesticides, or during impregnation of fabrics with pesticides.

3.1.3.5.1 Spraying indoors

Pesticide applicators should wear overalls or shirts with long sleeves and trousers, a broad-brimmed hat, a turban or other headgear and sturdy shoes or boots. Sandals are unacceptable. The mouth and nose should be covered with a simple device such as a disposable paper mask, a surgical-type disposable or washable mask, or any clean piece of cotton.

The cotton should be changed if it becomes wet. The clothing should be of cotton for ease of washing and drying. It should cover the body without leaving any openings. In hot and humid climates the wearing of additional protective clothing may be uncomfortable, and any pesticides should therefore be applied during the cooler hours of the day.

3.1.3.5.2 Mixing

In addition to the use of protective clothing, it is recommended for people who mix and pack insecticides in bags that gloves, an apron and eye protection such as a face shield or goggles be worn. Face shields provide protection for the whole face and are cooler to wear. The mouth and nose should be covered as recommended for indoor spraying. Care should be taken not to touch any part of the body with gloves while handling pesticides.

3.1.3.5.3 Impregnation of fabrics

Long rubber gloves should be worn when treating mosquito nets, clothes, screening or tsetse traps with insecticides. Under certain circumstances extra protection may be required, e.g. from vapour, dust or spray of hazardous products. Such additional protective items should be indicated on the product label and may include aprons, boots, face masks, overalls and hats.

3.1.3.5.4 Maintenance

Clothing should be kept in a good state of repair and should be inspected regularly for tears or worn areas through which skin contamination might occur. Protective clothing and equipment should be washed daily with soap, separately from other clothing. Gloves need special attention and should be replaced when here is any sign of wear and tear. After use, gloves should be rinsed with water before they are taken off. At the end of each working day they should be washed inside and outside.

3.1.3.6 Safe techniques

The great variety of pesticides used in agricultural production system worldwide presents varying degrees of hazard. These products are synthesized to alter life cycles of living pest organisms, and many of these products are dangerous to people if not handled properly.

3.1.3.6.1 Spraying

The discharge from the sprayer should be directed away from the body. Leaking equipment should be repaired and the skin should be washed after any accidental contamination. Persons and domestic animals must not remain indoors during spraying. Rooms must not be sprayed if someone, e.g. a sick person, cannot be moved out. Cooking utensils, food and drinking-water containers should be put outdoors before spraying. Alternatively, they can be placed in the centre of a room and covered with a plastic sheet. Hammocks, paintings and pictures must not be sprayed. If furniture has to be sprayed on the lower side and the side next to a wall, care should be taken that other surfaces are not left unsprayed. Floors should be swept clean or washed after spraying. Inhabitants should avoid contact with the walls. Clothes and equipment should be washed daily.

Organophosphorus and carbamate compounds should not be applied for more than 5-6 hours a day and the hands should be washed after every pump charge. Blood cholinesterase activity of spray personnel should be checked weekly if fenitrothion or old stocks of malathion are used.

3.1.3.6.2 Impregnation of fabrics

Gloves should be worn when handling the insecticide concentrate and preparing the insecticide mixture. Care should be exercised to avoid splashing insecticide into the eyes. A wide, shallow bowl should be used, and the room should be well-ventilated to avoid fumes being inhaled.

3.1.4 Emergency measures

Many pesticides can cause poisoning after being swallowed, inhaled, or absorbed through the skin. Symptoms may include eye tearing, coughing, heart problems, and breeding difficulties. The diagnosis is based on symptoms, blood tests, and a description of events surrounding the poisoning. Several drugs are effective in treating serious insecticide poisonings.

3.1.4.1 Signs and symptoms of poisoning

Poisonings due to pesticides are usually acute and result from extensive skin contact or ingestion. Signs and symptoms vary with the type of pesticide and can sometimes be confused with those of other illnesses.

Indications of pesticide poisoning

General : extreme weakness and fatigue
Skin: irritation, burning sensation, excessive sweating, staining.
Eyes: itching, burning sensation, watering, difficult or blurred vision, narrowed or widened pupils.
Digestive system: burning sensation in mouth and throat, excessive salivation, nausea, vomiting, abdominal pain, diarrhea.
Nervous system: headaches, dizziness, confusion, restlessness, muscle twitching, staggering gait, slurred speech, fits, unconsciousness.
Respiratory system: cough, chest pain and tightness, difficulty with breathing, wheezing.

It is important to gather additional information:

- Has the patient been working with a pesticide?
- Did contamination occur?
- Precisely which product was used?
- How much was ingested?
- How long ago?

An effort should be made to obtain evidence from pesticide containers or spray equipment; the labels on containers should be read and retained.

If pesticide poisoning is suspected, first aid must be given immediately and medical advice and assistance must be sought immediately. If possible, the patient should be taken to the nearest medical facility.

3.1.4.2 First-aid treatment

If breathing has stopped: Give artificial respiration. If no insecticide has been swallowed, mouth-to-mouth resuscitation may be given. Pull the patient’s chin up and tilt the head back with one hand to keep the airway clear. Place the other hand on the patient’s forehead, with the thumb and index finger toward the nose. Pinch together the patient’s nostrils with the thumb and index finger to prevent air from escaping. Take a deep breath, then form a tight seal with your mouth over and around the patient’s mouth. Blow four quick, full breaths in first without allowing the lungs to deflate fully. Watch the patient’s chest while inflating the lungs. If adequate respiration is taking place, the chest should rise and fall. Remove your and allow the patient to breathe out. Take another deep breath, form a tight seal around the patient’s mouth, and blow into the mouth again. This procedure has to be repeated 10-12 times a minute (once every five seconds). Artificial respiration should be continued for as long as possible if there is still a pulse. If insecticide has been swallowed, another form of artificial ventilation should be used.

If there is insecticide on the skin or in the eyes: Rinse the eyes with large quantities of clean water for at least five minutes. Remove contaminated clothing from the patient and remove the patient from the contaminated area. Wash the body completely for at least 10 minutes, using soap if possible. If no water is available, wipe the skin gently with cloths or paper to soak up the pesticide. Avoid harsh rubbing or scrubbing.

3.1.4.2.1 Vomiting

Do not induce vomiting unless the patient has swallowed pesticide that is known to be highly toxic, and medical help is not expected soon. Never induce vomiting if the patient has swallowed oil spray or products diluted in diesel or kerosene, because of the possibility of inhalation of the vomited material, which would be more dangerous than the intestinal poisoning. The product label should indicate whether the pesticide is highly toxic (skull-and-crossbones signs). Vomiting should be induced if the patient is conscious. If necessary, sit or stand the person up and tickle the back of the throat with a finger. Whether vomiting occurs or not, give the patient a drink comprising three tablespoonfuls of activity charcoal in half a glass of water. Repeat until medical help arrives.

3.1.4.2.2 Caring for the patient

The patient should be made to lie down and rest because poisoning with organophosphorus and carbamate compounds is made by movement. Place the patient on her or his side with the head lower than the body. If the patient is unconscious, pull the chin forward and the head back to ensure a clear airway. Cover the patient with a blanket if he or she feels cold, and cool the patient by sponging with cold water if excessive sweating occurs. If the patient vomits spontaneously, ensure that he or she does not inhale the vomit. In the event of convulsions, put padded material between the teeth to avoid injury. Do not allow patients to smoke or drink alcohol. Do not give milk. Water can be given.

4.0 CONCLUSION

The great variety of pesticides used in agricultural production system worldwide presents varying degrees of hazard. Consequently, personal protection equipment must be used when spraying and mixing pesticides, or during impregnation of fabrics with pesticides. If pesticide poisoning is suspected, first aid must be given immediately and medical advice and assistance must be sought immediately. If possible, the patient should be taken to the nearest medical facility.

5.0 SUMMARY

In this unit the students have learnt that:

i. pesticides or their metabolites may poison humans and animals;
ii. the relative toxicity of pesticides, and hence the danger they pose to warm-blooded animals, is expressed in a measure known as LD_{50}, which stands for lethal dose, 50 percent.;
iii. personal protection equipment must be used when spraying and mixing pesticides, or during impregnation of fabrics with pesticides; and
iv. poisonings due to pesticides are usually acute and result from extensive skin contact or ingestion.

6.0 TUTOR-MARKED ASSIGNMENTS

(i) What is pesticide poisoning and how can it be prevented in the home and farmer’s field?
(ii) Explain the first-aid treatment that should be given to a patient whose breathing has stopped.
(iii) Describe the signs and symptoms of pesticide poisoning.

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UNIT 21 SAFETY MEASURES IN STORAGE AND DISPENSING OF PESTICIDES

CONTENTS

1.0 INTRODUCTION

Correct and safe storage of crop protection products is essential to protect human health, protect the environment as well as to maintain product integrity and effectiveness. Most product labels require that the product is stored within a locked facility while some are required to be separated from other products. Handlers of pesticides are therefore required to follow the storage instructions on the label because secured storage protects the products integrity and reduces the risk of theft. They are also require to always understand the storage hazard warning on the label. Pesticide injuries are most likely to occur while the chemicals are being dispensed and mixed than in storage. Pesticide containers are opened during mixing, and pesticide formulations are usually concentrated since the pesticide is yet to be diluted. People who work with pesticides should therefore be more safety conscious when dispensing.

2.0 OBJECTIVES

By the end of this unit, students should be able to:

i understand the necessary safety measures in the design and construction of a pesticide storage facility;
ii understand the safety precautions to be taken for secure storage of pesticides and
iii understand how to dispense pesticides while keeping the handlers and the environment safe.

3.0 MAIN CONTENTS

3.1 Safety measures in the storage of pesticides

It is essential that pesticides are stored safely as the concentrated formulations pose the most risk to human health and the environment. Equipment is best stored separately away from chemicals. In most advanced nations, commercial pesticide stores are inspected annually to ensure that the building is soundly constructed with fire-resistant materials, is well-lit and ventilated on a suitable site with adequate capacity and segregation of products. Pesticides must never be stored in places where flooding is possible, or where they might spill or leak into wells, drains, groundwater or surface water. Pesticide stores should be bunded and have a sump to prevent spillages reaching watercourses. This is also important if a fire occurs and water is used to quench the flames. The building must be dry and frost-free, with appropriate warning signs and secure against theft and vandalism. Suitable access and exits must also be provided with provision to contain any spillage or leakages. Staff must be trained.

The following guidelines also need to be followed where pesticides are stored on farms:

1. Avoid excessive quantities in stock by having only the amount needed in the near future.
2. Keep all pesticides in a locked, ideally separate store or cabinet in a well-ventilated utility area, barn or garden shed, and ensure that any spillages do not seep into the ground or enter watercourses. Where small quantities are involved, the locked cabinet must be high enough to be out of reach of children.
3. Never store pesticides in the same area as food, animal feed or medical supplies. In some countries, where pesticides were in the same general stores, legislation now insists that pesticides are sold from separate shops.
4. Pesticides must be stored in their original containers, with the label listing ingredients, directions for use, and first aid steps in case of accidental poisoning. Follow all storage instructions on the pesticide label. *Never* transfer pesticides to soft drink bottles or other containers. Children or others may mistake them for something to eat or drink.
5. In domestic use, always use containers that are child-resistant and close the container tightly after using the product. However, ‘child-resistant’ does not mean ‘child-proof’, so extra care is needed to store the container properly in a locked cabinet as described above.
6. If the contents of the container cannot be identified, or how old the contents are, follow advice on safe disposal.

3.1.1 Store types and sizes

The type and size of store will be dependent on the amount of product to store and any local legislation relating to that storage. Stores may be:

1. Purpose built chemical store
2. Locked building
3. Locked box

Keys and access to any product store must be controlled by someone who has been trained. Where possible, reduce the need, and volume, of crop protection products to be stored. Buy products as required.

3.1.2 Store location

Stores should be situated in a location away from houses, schools, hospitals etc

1. Locate stores away from water courses and wells.
2. Do not locate stores in areas that are prone to flooding and/or fire.
3. The site chosen should have easy access for both the reception and distribution of products as well as for emergency services in the event of an accident.
4. Locate lockable, box stores outside of any dwelling, away from direct sunlight and protected from rain. If in a cool climate, protect the box from frost.

3.1.3 Construction of a pesticide store

The aim is to provide a store that is resistant to fire, capable of retaining leakage/spillage (eg if containers were to melt in a fire), dry, frost-free, adequately ventilated and secure against unauthorised access. The following factors should be taken into account:

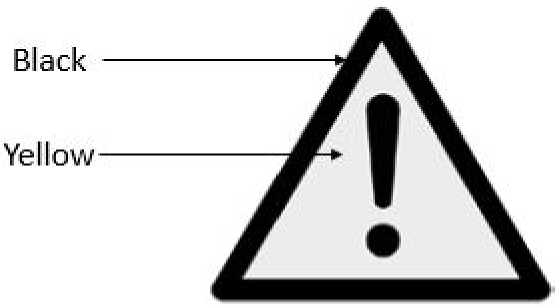
3.1.4 General principles applying to all stores

1. The store, including any doors but not the roof should be made of materials which will resist fire for 30 minutes or longer.
2. The store, or the area in which the store is located, should be able to retain leakage or spillage to a volume of 110% of the total quantity of products likely to be stored (185% if you are in an ‘environmentally sensitive area’). Bunding is the most usual way of achieving this.
3. The bund should be soundly constructed of non-fragile materials resistant to permeation by liquids, eg metal (not foil), concrete, bricks, stone slabs and concrete products. Rendering or sealing the building materials may be necessary, especially at joints.
4. The bund should comprise, or extend around, the whole periphery of the store, and should not be compromised by, for example, entrances and exits, or apertures where services enter the store.
5. Bunding may be achieved by standing your pesticides within a metal container of sufficient capacity, eg a redundant water tank. Before converting any storage tank to form a store or bund, make sure that it is suitable and not contaminated and that flammable

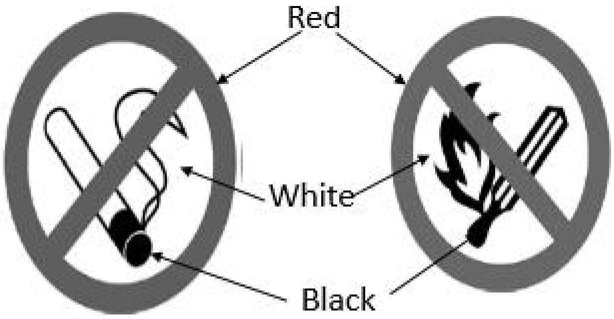
liquids/gases are purged.Make sure doors/lids and windows provide adequate security and are kept locked or otherwise secure when not in use.

3.1.5 Organizing a pesticide store

1. Mark the exterior of the store (and where it is located within a larger building, the exterior of the building) with the general danger warning sign (see diagram).



2. Put 'No Smoking' or 'Smoking and Naked Flames Forbidden' prohibitory signs (see diagrams) on the exterior door of the store.



3. Provide adequate shelving so that products can be seen by staff.
4. Store powders above liquids (liquids can leak if containers are damaged).
5. Provide adequate lighting so that you can read the labels.
6. Protect stocks against frost – oil or gas heaters or electrical equipment with exposed elements are not suitable.
7. Avoid storing plastic containers in direct sunlight – shade windows if necessary.

8. If pallets are used to keep stocks off the floor, make sure they do not present a tripping hazard and that the bunding capacity remains adequate.
9. Lag water pipes.
10. Provide a brush, shovel, absorbent granules/sand and an impermeable container to deal with any spillages or leaking drums/packages.
11. Practice good store management by ensuring that waste cardboard packaging is removed, old stocks are used up, damaged or deteriorating containers are properly disposed of and an up-to-date stock record is kept (away from the store).
12. Keep an accurate stock record available as well as useful telephone numbers, including your local fire service.

3.1.6 Product Storage: smaller product volumes

Where legislation permits a dedicated storage area within a building, a chest or box may be adequate for smaller amounts of crop protection products. These facilities must:

1. Have adequate space to enable products to be stored tidely and safely.
2. Be labeled to identify the store with appropriate hazard warnings
3. Be located away from children and animals.
4. Be located outside of any dwelling area
5. Be kept locked at all times to avoid unauthorised access when unsupervised the store.
6. Be able to store products on trays –or within secondary containers -that would retain the contents in the event of a leak.
7. Keep products off the floor.

3.2 Additional precautions for special classes of pesticides

Guidance in this section deals only with amounts that can be safely stored in cabinets, chests and bins. The hazardous chemical properties of certain pesticides mean that extra measures have to be taken to store them safely. Check to see if you store any of the following:

3.2.1 Moisture-activated gassing compounds

People have died as a result of poor storage of these compounds at fixed stores and in transit. In particular, using water to fight a fire can present a significant danger to the emergency services. In your fixed store, provide a separate storage cabinet, which should be:

1. made of metal or fire-resistant materials;
2. located above the level of the store bunding and away from direct sunlight and sources of heat;
3. provided with adequate stability, eg by bolting it to the wall; and
4. marked ‘Gassing Compound – Do Not Use Water’.
   During transport, reduce the risk of exposure if an accident happens by:
5. storing gassing compounds in a separate vapour-proof container within the load space;
6. providing some means of securing the container in the load space, eg a frame bolted to the structure in which the container can be strapped.

3.2.2 Pesticides marked ‘Oxidising Agent’ – such as sodium chlorate

When heated, oxidising agents give off large amounts of oxygen which can rapidly increase the spread of fire. Large quantities need a completely separate store. However, up to 10 kg may be kept in your store if it is kept in a fire-resistant, dry container away from heat sources and other pesticides.

3.3 Safety measures in dispensing of pesticides

When mixing or dispensing liquid formulations, the user is particularly at risk of absorbing the pesticide through the skin. Some liquid formulations, the emulsifiable concentrates contain solvents. These solvents make pesticides readily absorbable through the skin. Some liquid formulations are irritants that can cause rashes and cracking of the skin, further increasing the chance of the pesticide's being absorbed into the body. It is advisable to use personal protective equipment when dispensing liquid formulations, especially when mixing them.

Again, the pesticide label should be read carefully to determine what personal protective equipment (PPE) is needed. And keep in mind that once dry formulations have been mixed with water, their active ingredients can readily be absorbed through the skin. ***Before dispensing*** Before dispensing pesticides, and after reading and understanding the label directions, the applicator should take the following precautions:

- Have detergent or soap and an adequate supply of water available.
- Learn the early symptoms of poisoning for the pesticide you're using.
- Learn the first aid procedures for the pesticide you're using, and make certain that the right first aid supplies are close by.
- Be certain that spill cleanup materials are on hand.
- Make certain that all the equipment you're working with are functioning properly. It's a good idea to do a quick daily inspection. Develop and run through a written or at least mental inspection list of equipment.
- Do not work alone. Be sure that help is available nearby in case you get into trouble.
- Use all recommended protective clothing and equipment. Double-check that your respirator fits properly and that the kind of canister cartridge recommended on the product label is attached to it.
- When working with pesticides, never eat, drink, smoke or go the bathroom without first washing your hands.
- Never mix or transfer pesticides near a well or other water source. If you're mixing pesticide in the field, do so at various locations. Over time, small quantities of pesticide spilled in one area, else pesticide spill may accumulate and cause serious contamination.

3.3.1 Guidelines for safely mixing and loading pesticides

- Only authorized pesticide handlers or supervisors should be in the mixing and loading area. All handlers should be wearing proper personal protective equipment (PPE). No other persons, and no animals, should be present.
- To prevent spills, place pesticide containers in a secure position when you're opening and handling them.

- Read and follow label directions. Pay special attention to warnings and precautions.
- Work only in a well-ventilated, well-lighted area.
- Never stir pesticides with your hands. Use a stir-stick.
- Use a catch basin--a container within a container--to prevent inadvertent spills. For example, a measuring jar can be placed inside a plastic tub. If the measuring jar happened to tip over, the spill would be conned to the tub.
- *Never pour pesticides at eye level.* In fact, never lift any open pesticide container higher than your chest. Mix and pour concentrated pesticides no higher than waist level. A spill or splash could be disastrous.
- If pesticides are spilled or splashed on you, remove your clothing immediately and wash yourself thoroughly within two minutes. Then wash your clothing.
- Protect your eyes with splash-proof goggles.
- Stand with your back to the wind so any fumes or dusts are blown away from you.
- *Never* pour pesticide directly into a spray tank. *Always* mix and dilute the pesticide in a small container.
- Pour the pesticide into water. *Never* pour water into the pesticide.
- When pouring, keep your head well above and to one side of the spray tank opening. This will reduce the chance of your being splashed in the face.
- Mix and load on a concrete slab where spills can be contained, or, if no slab is available, use a catch basin.
- Avoid mixing or loading near surface water or a well head.
- Do not leave a pesticide tank you're filling unattended.
- Never allow a spray tank to overflow. The cleanup could be a costly and dangerous all-day, all-night task.

4.0 CONCLUSION

Although pesticides can be useful, they also can be dangerous if used carelessly or are not stored properly. The first step to the safe handling of pesticides is to always read the label and follow the directions to the letter, including all precautions and restrictions. Pesticide handlers must be educated on the safety regulations guiding the design, construction of a pesticide store, as well as maintenance practices in the store. Extra precaution should be taken when dispensing pesticides because of the risk of exposure to the pesticide.

5.0 SUMMARY

In this unit the students has leant:

i. the the necessary safety measured in the design and construction of a pesticide storage facility;
ii. the safety precautions to be taken for secure storage of pesticides and
iii. how to dispense pesticides while keeping the handlers and the environment safe.

6.0 TUTOR-MARKED ASSIGNMENTS

i Explain the safety measures to be followed in the design, construction and operation of a pesticide store
ii Discuss why more attention should be paid to safety guideline during pesticide dispensing than in storage.
iii. What is the first step to take when handling pesticides?

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UNIT 22 SAFETY MEASURES IN TRANSPORTATION AND USE OF PESTICIDES

CONTENTS

1.0 INTRODUCTION

A good understanding of the safety measures to follow in the transport and use of pesticides will ensure that the risk of any adverse impact following their use can be greatly minimized. Pesticides when carefully applied, used only when needed, can contribute to higher productivity and allow us to feed and protect the growing human population while leaving the environment and human lives relatively safe. This requires much better education and practical training with certification so that pesticides are indeed applied more accurately and with greater safety than in the past.

2.0 OBJECTIVES

By the end of this unit, students should be able to:

i. understand the safety measures to be considered in transporting pesticides from one location to another;
ii. understand the measures to adopt in the use of pesticides; and
iii. understand the various ways pesticide users are exposed to hazardous effects of pesticide both during transportation and during use.

3.0 MAIN CONTENTS

3.1 Transportation of pesticides

This refers to the movement of pesticides from one location to another. This guidance may apply to storage, normally for less than 24-hour periods, in vehicles, bowsers and sprayers stocked from a fixed store.

3.2 Safety measures in the transportation of pesticides

1. Be aware of any local legislation regarding the transport of products.
2. Be prepared for any accidental spillage or emergency situation.
3. Transport seperately products or spraying equipment from foodstuff, livestock or humans.
4. Ensure crop protection products are in their original containers and that the seals are still OK and tightened to avoid the possibility of leaks and spills.
5. When transporting spraying equipment ensure it is washed and clean before leaving the field.
6. Clean up any spillages using absorbant material such as sand or soil.
7. If transporting heavy containers ensure that there is equipment available to enable safe on and off loading.
8. When transporting products from the farmstead to the field only take what is required for the job, always transport in the original containers, do not decant.

3.2.1 Safety measures on transporting vehicles

You should ensure all pesticides are safely transported to the application site and remain safely stored at the site.

Never carry pesticides in the cabs of tractors, self-propelled sprayers or other vehicles, and consider the following key points before you carry concentrated pesticides to an application site:

1. Use a vehicle with a floor-to-ceiling bulkhead between the iver/passenger compartment and the load compartment.
2. Where the vehicle has no bulkhead, fit secure chemical containers or provide a secure cabinet mounted on the exterior of the vehicle or on a trailer.
3. Check that the load-carrying area is free of projections, which might damage containers.
4. Mark the load-carrying area with the general danger and warning sign.
5. When away from your fixed store, pesticides should always be secure against unauthorized access:
6. Park your mobile store away from any location where water pollution could occur.
7. Try to work within sight of your mobile store – especially in areas where the public may have access.
8. Lock the cabinet or vehicle when it is unattended.

At the end of the job:

9. Check that lids/caps on any part-used products are secure before the journey back to the fixed store;
10. Make sure you take all empty containers, packaging and other equipment back to your empties store;
11. Return unused pesticides to your fixed store.

In the event of any leakage –

1. Keep people away from any spillage.
2. Contain the spillage by placing soil or sand around the spill.
3. Carefully add more soil or sand to absorb spill.
4. Sweep or shovel up the absorbed spill and place in strong bag.
5. Label bag and seek help from product supplier for best disposal options.

6. If the spillage involves a significant volume notify to local emergency services.

3.3 Safety measure in the use of pesticides

Most exposure to crop protection products by operators is when:

- Mixing and weighing out
- Working with a leaking sprayer

3.3.1 Mixing and preparing undiluted products

1. Always maintain high standards of hygiene when working with crop protection products.
2. Work in an area away from children and animals.
3. Avoid any risk of polluting water courses
4. Ensure you understand the product label information: especially product dose rate and safety requirements when mixing and preparing the product.
5. Only use dedicated equipment for measuring and weighing products: Do not use food containers or cutlery
6. Wash all equipment and empty containers after the spraying job is completed.
7. Store equipment safely away from animals and children.

Before starting any spraying activity always:-

1. Read and understand the product label
2. Check the sprayer for leaks
3. Ensure you have the correct PPE
4. If you feel unwell then do not work with pesticides

Never mix products or fill sprayers close to water courses, wells or where products could get into ground water.
Never decant products into other containers.
Always dispose of empty packaging and other contaminated waste following best practice.

3.4 Operator's exposure

Decisions on operator exposure are based on a comparison of the No Observed Adverse Effect Level (NOAEL) and an estimate of human exposure. The Acceptable Operator Exposure Level (AOEL) is derived from the NOAEL by dividing it by an assessment factor (usually by a factor of 100, which is essentially made up of two ×10 uncertainty factors (Anon, 1999a; Renwick, 1991) to allow for inter- and intra-species variation, as discussed in previous units. In some countries, such as the USA, the margin of exposure (MOE) or margin of safety are derived in a similar manner. As it would be impossible to measure the exposure in all situations, there is considerable reliance on experimental data obtained from particular usage situations that have been incorporated into generic models such as the European Predictive Operator Exposure Model (EUROPOEM; Gilbert, 1995), which is still being developed.

The impact of exposure will also be affected by the frequency of exposure. In Holland, the use of insecticides and fungicides was more frequent than the use of herbicides as they were used ten to twenty times a year on the most intensively treated crops, but single pesticide products were not used more than seven times a year (van Droogee*et al.*, 2001). In that study, ornamental crops such as chrysanthemums were treated more than arable crops. Some spray operators, such as those employed by contractors will be exposed for more days per year than individuals on small farms.

3.4.1 Potential dermal exposure

Thisis the total amount of pesticide landing on the body, including clothing, but the actual exposure of the skin will depend on the amount deposited directly on the skin plus any that penetrates clothing and is therefore available on the skin for absorption into the body. Operator exposure is significantly reduced by wearing protective clothing. The basic requirement is good overalls of closely woven fabric. In temperate climates, impermeable materials are suitable and in many cases operators use disposable overalls made from a polypropylene material. Although this eliminates the need for laundering, such overalls are generally considered to be too hot to wear in tropical climates, and do not always provide as much protection as those made from cotton (Moreira *et al*., 1999).

Various special finishes to cotton fabrics have also been tried for use in tropical countries. Laundering of garments does not always remove the entire pesticide residue in a garment. Nelson *et al*. (1992) reported that the percentage not removed could vary from 1% to over 40%. However, in the tropics some degradation will occur when the garments are exposed to sunlight (Shaw *et al*.,1997). The washing of used protective clothing may also cross-contaminate other garments. Wearing an apron of impermeable plastic, especially when opening pesticide containers, will protect the overalls from splashing during preparation of sprays and can be readily removed while spraying. Similarly, a face shield is also recommended during mixing to protect the face, and especially the eyes. Some countries prefer to recommend goggles but these do not protect the face. When suitable overalls are not available or are too expensive for small-scale farmers, the area of exposed skin should be minimized by wearing long trousers and a long-sleeved shirt. These need to be removed and washed separately from domestic laundry as soon as possible after a spray application has been completed.

3.4.2 Exposure of hands

The hands, inevitably, are the part of the body most exposed to pesticides, due to handling of containers and when operating equipment. Data from PHED indicates that a person mixing and loading pesticide in the USA can be exposed to 6300 μg/kg ai when not wearing gloves compared to only51.1 μg/kg ai when wearing gloves (Fenske and Day, 2005). The type of exposure will depend on many factors, but in the worst case the whole hand could be coated with liquid. Substances can be removed from the surface of the skin (especially the hands) by using swabs or towels, moistened with a solvent, such as 95% ethanol. The technique does not indicate what could have been absorbed before the skin was washed.

To protect hands, the wearing of impermeable gloves is recommended, but these vary in their thickness and suitability, especially when adjusting small parts such as nozzles.

Gloves with a cuff long enough to be covered by the end of the coverall sleeve are advised so that any liquid, or granule, that is on the arm does not pass down inside the glove.

Neoprene and nitrile gloves provide protection to a range of solvents and oils, and are suitable when using emulsifiable concentrate and similar liquid formulations. Nevertheless, users should wash off any pesticide as soon as possible as some chemicals can penetrate a glove.

Care is needed when washing gloves, as the rinsate subsequently acts as a source of exposure for other workers or family members, water courses, etc. Often, contamination of the gloves occurs when the operator removes the gloves using a clean hand to remove a dirty glove. Washing the gloves before removal is advised, but care is still needed when removing the glove. In some situations, especially in the tropics, an impermeable glove causes the hand to sweat and this may increase the risk of absorption. Spray operators not using gloves should only apply the less hazardous pesticides and have a bucket of water readily available so that a bare hand that has been exposed to spray can be washed immediately.

3.4.3 Inhalation exposure

In the open air, the risk of inhaling spray droplets is extremely low. Most sprays contain only a small fraction of the volume in droplets smaller than 100 µm. While these small droplets can shrink, especially on hot days and with low humidity, the smallest droplets in the range of 1–10 µm that could be inhaled are readily carried downwind and away from the spray operator. Any larger droplets close to the nose may be deposited on the face or filtered within the nose, and would not reach the lungs. The situation is different when applying pesticides inside buildings, stores and glasshouses where small droplets can remain airborne close to the operator.

The main concern with inhalation exposure is when pesticides are applied as fogs, where a high proportion of the droplets are below 25 µm. It is essential to wear the correct respiratory protection equipment (RPE) when fogging, especially inside buildings.

The main item is a respirator, which has a filter to remove the very small particles of pesticide in a fog. The correct filter, depending on the chemical being applied, must be fitted and replaced according to instructions.

Inexpensive disposable masks are not respirators and often merely reduce the impaction of spray droplets directly on the skin around the nose and mouth.

Some more expensive protectors which cover the operator’s head may not be true respirators but have a pump to draw air through the filter and blow the filtered air over the face.

The *feet* should always be well protected by wearing ‘rubber’ boots or equivalent, with the bottom of the trouser legs placed over the boot so that liquid or granules do not fall into the boot. In some areas spray operators fail to wear shoes, but if they do so the shoes are often of very poor quality and made from absorbent materials.

The *ears* should always be protected when the noise of the operating spraying equipment exceeds 85 decibels. This applies especially to manually carriedmotorised equipment fitted with a two-stroke engine, and when pulsejet fogging equipment is used.

3.5 First aid

If a spray operator becomes ill, while working, the doctor must be informed of the name of the active ingredient and given as much information as possible by being shown a leaflet or label about the chemical being used. Treatment by a doctor will depend very much on the type of poisoning. When using an OP or a carbamate (anticholinesterase), an injection of atropine is useful, but suitable antidotes for organochlorine poisoning are not available. A person who has ingested liquid that contained paraquat can be treated by their ingesting large quantities of Fuller’s earth, which adsorbs the herbicide. Morphine should not be given to patients affected by pesticide poisoning.

A first-aid kit and a supply of clean water for drinking and washing any contaminated areas of the body should be readily available. On large-scale spraying programmes first-aid kits should be carried in vehicles and aircraft. People regularly involved in applying OP pesticides should undergo routine medical examinations in order to check cholinesterase levels in their blood plasma.

4.0 CONCLUSION

It is obvious from the foregoing, that adequate knowledge of, as well as strict adherence to the safety measures suggested will go a long way to minimize the attendant risks accrued to pesticide transport and use. Legislative bodies should therefore make it a point of duty to provide adequate education to the handlers of plant and animal protection chemicals relating to the safety of human and the environment. These bodies should also ensure/enforce compliance to the safety measure by users of pesticides. This will not only ensure access to healthy food but will also guaranty a near safe environment.

5.0 SUMMARY

In this unit the students have learnt:

i. the safety measures to accompany transportation of pesticide from one location to the other;
ii. the things to do and not to do while using any of the past control chemicals available for use in crop and animal protection;
iii. the various ways a pesticide applicator may be exposed to pesticides, the degree of expossure; and
iv. how to protect the various body parts through which pesticides can gain entry into the body.

6.0 TUTOR-MARKED ASSIGNMENTS

i. What do you understand by pesticide transportation, ad what are the precuations to take to prevent accidents when transporting pesticides?
ii. Discuss the different areas of exposure to pesticides, and how these parts of the body can be adequately protected against exposure to pesticides.

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UNIT 23 DISPOSAL OF PESTICIDE CONTAINERS AND WASTES: ECOLOGICAL AND ENVIRONMENTAL HEALTH EFFECTS

CONTENTS

1.0 INTRODUCTION

Proper pesticide waste and container disposal is an important part of responsible pesticide use. Improper disposal can lead to contamination of soil, groundwater, and surface water, causing serious liability problems for the pesticide user, as well as a poor public image. In the United States, several federal and state laws, including the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) regulate the disposal of pesticide waste and empty pesticide containers. Improper disposal can result in fines for the pesticide applicator. Everyone who handles pesticides must know how to dispose of these wastes legally, responsibly, and economically (Nesheim and Fishel, 2017).

2.0 OBJECTIVES

By the end of this unit, students should be able to:

- understand the importance of proper pesticide waste disposal;
- understand how the amount of pesticide waste can be reduced.;

- understand the disposal mechanisms for different categories of pesticide waste; and
- explain the procedures for disposing of waste pesticide containers and other pesticide waste materials.

3.0 MAIN CONTENTS

3.1 How to Reduce the Amount of waste you produce

If you reduce your use of pesticides, you will also reduce the amount of waste pesticide and empty containers you produce, and you will save money. You should consider the following questions:

- Do you need to use the pesticide and, if you do, can you reduce its use?
- Do you have suitable pesticides currently in stock and can you order less new stock?
- Have you chosen the most suitable pack sizes?
- Can you manage and control the use of pesticides any better?
- Can you use any of the following methods to reduce packaging waste and reduce the washings produced?

    - Soluble packs
    - Returnable containers
    - Flushing systems for low-volume sprayers
    - Direct-injection systems
    - Rounding down your calculations of the amount of pesticide needed when filling your sprayer to allow you to dispose of the washings on an under-dosed area (or using a suitable electronic sprayer controller to achieve the same result).

- Will your contractor or distributor take back properly cleaned (using a pressure rinsing device or manually rinsed at least three times) empty containers?

3.2 Disposal of Unwanted Pesticide Concentrates and Ready-to-Use Formulations

Whenever possible, use up pesticides in the approved way. When a product's approval has been withdrawn or amended (for commercial, safety or other reasons), a 'wind-down' period is given (except when there are major safety concerns) to allow remaining stocks of the product to be used up. The website at www.pesticides.gov.uk gives details of the approval status of individual products and details of reviews which may affect a range of products. By checking this information, or asking your supplier, the manufacturer or an adviser, you should be able to avoid having to dispose of unapproved products.

Similarly, by managing your chemical store properly, you should be able to avoid having to dispose of pesticides because they have deteriorated or because products are out of date.

Avoid storing an unwanted pesticide because it is illegal to do so if the approval for storing and using it has been withdrawn.

If a container (or other packaging) is damaged, but the product is still approved for use, you may be able to carefully transfer the product to the equipment used to apply it, leaving only the container to be disposed of.

Despite good management, you may have some concentrates or ready-to-use pesticides that you need to dispose of. You should never dilute an unwanted concentrate in order to dispose of it as dilute pesticide waste. You should consider the following points:

- Firstly, ask your supplier if they will take back any unwanted unused pesticides that are packaged, labeled and of good quality;
- Pesticide concentrates are likely to be 'hazardous waste' and may present a significant risk to the environment or to humans. Handling and disposing of this type of waste is tightly controlled and you will need to use a registered carrier (registered with the Environment Agency) and a licensed waste-disposal contractor .
- You must store unwanted concentrates and ready-to-use formulation in your chemical store to ensure that they are secure and that any spills will be contained;

- You (or the carrier if you use one), must fill in a ‘consignment note’ and pay a fee to the Environment Agency if you are moving or disposing of ‘hazardous waste’. You (as the waste producer) and the people transporting and receiving the waste must keep copies of the consignment notes for at least three years. Also, you must not move ‘hazardous waste’ until the appropriate period for notice has passed;
- When you have filled in the necessary consignment notes, you should pass the unwanted concentrates to a waste-disposal contractor;
- As the producer of the waste, you must make sure that the person who takes your waste is registered to take it and can transport it safely, and that it will be safely disposed of or recycled;
- You must also fill in a ‘waste transfer note’ and provide a written description of the waste. Both you and the waste-disposal contractor must keep copies of the transfer note and written description for two years. If the waste is ‘hazardous’ and you have filled in a ‘consignment note’, you do not also need to fill in a ‘waste transfer note’;
- If you can transport your own unwanted pesticides safely and legally, you can take these to a licensed treatment or disposal site, after checking whether the site will accept your waste.

3.3 Disposal of Dilute Pesticide Waste

If you are spraying a pesticide, you should be able to do so with no, or very little, spray solution left over. Planning this will reduce your waste disposal problems and will save you money. However, in other situations (such as when you are applying a pesticide as a before planting or after harvesting dipping treatment) you may not always be able to avoid having dilute pesticide left over at the end of the treatment.

When you are treating several sites, one after another, using the same pesticide and the same equipment, you may be able to use left over spray from one site to treat another, if you can transport the pesticide safely and legally.

You must dispose of all dilute pesticide waste (including any leftover pesticides and all sprayer washings) safely and legally to protect humans, wildlife and the environment, especially groundwater and surface water.

When you have finished applying the pesticide, clean both the inside and the outside of all equipment you have used. By thoroughly cleaning your application equipment, in line with the manufacturer’s instructions, you will help to:

- reduce any risk from handling contaminated surfaces;
- prevent damage to crops and areas which will be treated later using the same equipment; and
- reduce the risk of blockages.

Before cleaning your equipment, you should read and follow the label instructions on:

- using appropriate personal protective equipment when handling contaminated surfaces; and
- carrying out any decontamination procedures relating to the particular product (for example, some herbicides need to be de-activated with ammonia-based cleaning agents).

If possible, you should clean the equipment you have used (inside and out) at the site of the treatment, rather than having a single, dedicated site for cleaning. You should use any built-in rinsing systems that are fitted to clean the inside of the equipment quickly and effectively while using the minimum volume of rinse water. Similarly, a hose and brush attachment (which is available on some sprayers and can be fitted to others) will help you to clean the outside of the equipment more effectively than a high pressure spray gun, and will use less water. Repeated tank washing, each using a small amount of water, will achieve better results than a single rinse using a large amount of water and will also produce less washings. As well as cleaning the tank, you will also need to make sure that all pipes, hoses, filters, valves, nozzles and induction systems are thoroughly cleaned. All facilities for washing equipment should be designed to make sure that the pesticide solution cannot get into your washing water under any circumstances.

Possible options for disposing of dilute pesticide waste include the following:

- You can apply the contaminated water to the treated or untreated crop or area within the terms of the product approval, but make sure not to exceed the maximum dose;
- You can store the contaminated water in a suitable container until a licensed waste-disposal contractor can collect it;
- When using pesticides in agriculture, you can only dispose of the dilute waste onto soil or grass (either directly or fed by the drainage from a hard surface) under the terms of an authorization under the Groundwater Regulations issued by the Environment Agency. To keep to the Landfill Regulations, you must not use a single site in this way more often than once a year. The land of choice for this purpose must:

  a. be able to absorb the volume of liquid to be disposed of onto it without run-off or leaving puddles;
  b. result in the smallest possible risk to wildlife and watercourses;
  c. protect groundwater (by not allowing the pesticide to reach the water table);
  d. present the smallest possible risk to septic tanks, field drains or sewage systems; and
  e. where necessary, be signposted and fenced to keep people and livestock out.

- If you have suitable equipment (such as your own effluent treatment plant designed for treating liquid waste containing pesticides(, you can process the dilute waste yourself, as long as:

  − You (or the person using the equipment) have an appropriate waste-management licence (or have registered an exemption) under the Waste Management Licensing Regulations; and
  − the treated effluent is collected and either disposed of as stated in the waste- management licence or, if registered as exempt, reused (for example, as irrigation water or for preparing a spray solution).
- You can dispose of the dilute waste to a lined biobed as long as:

  - you have an appropriate waste-management licence (o have registered an exemption) under the Waste Management Licensing Regulations; and
  - the water flowing out from the base of the biobed is collected and either disposed of as stated in the waste-management licence or, if registered as exempt, reused (for example, as irrigation water or preparing a spray solution).
- You can dispose of the dilute waste into a sewer under a ‘trade effluent consent’ issued (in rare circumstances) by the local company which manages the sewage treatment works the sewer is connected to. Waste that contains substances classified as ‘special category effluent’ also need approval from the Environment Agency before a ‘trade effluent consent’ can be issued.

3.4 Disposal of Waste Pesticide Containers

Do not reuse an empty pesticide container for any purpose unless:

- it is specifically designed to be returned and refilled and you are doing so in line with the label instructions; or
- you are filling it with an identical pesticide product transferred from a damaged container.

The product label will state whether you should rinse the container after emptying it.

Before disposing of a non-returnable container, make sure it is completely empty.

If you can, containers for products which are concentrates and are applied as a solution should be thoroughly rinsed before being disposed of.

Containers for ready-to-use formulations or products not applied as a solution are normally not rinsed after emptying.

Containers for hydrogen cyanide gassing powders or aluminium, magnesium or zinc phosphides must never be rinsed or cleaned.

Before disposing of rigid, non-returnable containers, you should always thoroughly rinse them in line with the label instructions.

If there are no instructions, you should:

- use purpose-made container-rinsing equipment in line with the manufacturer's instructions (for example, pressure rinsing devices forming part of many sprayer induction bowls; the pressure-rinse procedure punctures the container).; or
- triple-rinse the container by emptying the pesticide concentrate into your spray tank and draining the container in a vertical position for 30 seconds. Refill the container about 1/4-1/5 full with water and rinse thoroughly. Add this rinse water to your tank, unless the product is to be applied without dilution. Be sure to let the pesticide container drain for a few seconds. Repeat rinsing and draining two more times. After triple-rinsing, punch holes in the containers to prevent re-use. Properly rinsed containers may then be buried in a sanitary landfill, if the operator and local regulations allow.

You may also be able to rinse some types of flexible packaging designed for solid pesticides which are applied as a solution, depending on the material and designs of these packs. You should always rinse containers immediately after emptying them, once you have allowed the product to drain fully into the equipment that is applying it. You should also rinse contaminated closures (caps and seals) and any contamination on the outside of containers. All rinsings should be added to the spray solution.

If, for any reason, you have container rinsings which you cannot add to the application equipment (for example, if you are not applying the pesticide as a spray solution or dipping solution), you should collect the contaminated rinsings in a suitable, labeled container, and store it in a safe place. You should then dispose of the rinsings in line with the guidance for disposal of dilute pesticide waste.

Containers which are not suitable for rinsing (for example, paper sacks and cardboard cartons) and those containing products which are either ready-to-use or not applied as a solution, are normally emptied completely but not rinsed. These will have the phrase 'Empty container completely and dispose of safely' on the label. You should handle and store these empty containers as if they still contained the pesticide, and you should dispose of them through a licensed waste-disposal contractor.

You must not rinse or clean empty containers which hydrogen cyanide gassing powders or aluminum, magnesium or zinc phosphides have been supplied in or kept in because of the dangerous gases they give off when they come into contact with moisture. You should handle and store these empty containers as if they still contained the pesticide and you should dispose of them through a licensed waste-disposal contractor.

Firmly replace caps on containers immediately after rinsing and draining them into the equipment used for applying pesticide. Put the rinsed foil seal inside the container. Store the rinsed and drained containers upright in a secure, weatherproof area away from stored pesticides (either in a separate store or a separate part of your chemical store), until you can dispose of them.

You can dispose of rinsed pesticide containers in the following ways:

- Pass them on to a licensed waste-disposal contractor;
- Take them to licensed waste-disposal or waste-recovery site, after checking whether the site will accept rinsed containers;
- Burn them only in an incinerator licensed by your local authority or the Environment Agency.

Containers that have been thoroughly rinsed and drained will generally be accepted at licensed waste-disposal sites as long as the conditions of the site operator's licence allow this. The local Environment Agency can give you details of these sites.

Do not use empty pesticide containers or contaminated pallets for transporting food or animal feed.

3.5 Disposal of Other Pesticide Waste Materials

You should arrange to dispose of contaminated packaging, equipment, unwanted protective clothing and waste from dealing with spills and leaks through a licensed waste-disposal contractor. Some of this waste may need to be dealt with as 'hazardous waste'.

You should dispose of used vertebrate control agents, other pesticide baits and dead bodies in line with guidance on the product label. If no advice is given on the label, arrange to dispose of this waste through a licensed waste-disposal contractor, making sure that you follow the correct procedure.

You should dispose of used compost, soil and so on which have been treated with pesticides in line with the guidance on the product label. If no advice is given on the label, get guidance from your local Environment Agency office. You can also get information on the PSD website www.pesticides.gov.uk.

You should arrange to dispose of other materials, such as treated seed, other treated plant material and used crop covers which are contaminated with pesticides through a licensed waste-disposal contractor.

4.0 CONCLUSION

The indiscriminate disposal of pesticide waste and pesticide containers constitutes an environmental hazard and can threaten human health and safety. Pesticide wastes and containers that are improperly disposed can result in a number of problems. It can cause contamination of soil, groundwater and surface water. However, these problems can be avoided by using appropriate pesticide waste management techniques.

5.0 SUMMARY

In this unit the students have learnt:

i. how the amount of pesticide waste generated can be minimized;
ii. how to dispose of unwanted pesticide concentrates and ready-to-use formulations;
iii. how to dispose of dilute pesticide waste; and
iv. how to dispose of waste pesticide containers and other pesticide waste materials.

6.0 TUTOR-MARKED ASSIGNMENTS

(i) Why are pesticide wastes and pesticide containers considered an environmental health hazard?
(ii) Briefly describe the procedure for disposing of waste pesticide containers.

7.0 REFERENCE AND OTHER RESOURCES

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UNIT 24 ENVIRONMENTAL CRITERIA STANDARDS AND REGULATIONS ON PESTICIDE USE

CONTENTS

1.0 INTRODUCTION

The impact of pesticide residues on human health is a worldwide problem, as human exposure to pesticides can occur through ingestion, inhalation, and dermal contact. Regulatory jurisdictions have promulgated the standard values for pesticides in residential soil, air, drinking water, and agricultural commodity for years. Until now, more than 19,400 pesticide soil regulatory guidance values (RGVs) and 5400 pesticide drinking water maximum concentration levels (MCLs) have been regulated by 54 and 102 nations, respectively. Over 90 nations have provided pesticide agricultural commodity maximum residue limits (MRLs) for at least one of the 12 most commonly consumed agricultural foods. A total of 22 pesticides have been regulated with more than 100 soil RGVs, and 25 pesticides have more than 100 drinking water MCLs. All of these were with the aim of making food production with pesticide sustainable as well as protecting human health and the environment. International and national legal frameworks governing pesticide management have however undergone significant changes over the past 25 years. The International Code of Conduct on the Distribution and Use of Pesticides was adopted by FAO in 1985. It was subsequently amended in 1989 to include the prior informed consent (PIC) procedure and revised in 2002. In 2013, it was updated to include public health pesticides and its title was changed to The International Code of Conduct on Pesticide Management (Code of Conduct). In 2014, the WHO also adopted the Code of Conduct as its reference framework for international guidance on pesticide management.

2.0 OBJECTIVES

By the end of this unit, students should be able to:

i. understand some legislative basis for pesticide regulation;
ii. understand the level of compliance to pesticide regulations by developed nations and developing nations; and
iii. understand the best approach to pesticide and pesticide use regulation use in developing countries.

3.0 MAIN CONTENTS

3.1 Legislative basis for pesticide regulation

In the United States, the EPA regulates pesticide registration, manufacture and distribution under the authority of the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA). In addition, the Federal Food, Drug and Cosmetic Act has authorized the EPA to establish tolerable levels for pesticide residues in foods. The FIFRA requires that all pesticides distributed and sold in the United States be registered by the EPA after pesticide approval, which is granted upon determination that the substance “will not generally cause unreasonable adverse effects on the environment”. The FIFRA defines “unreasonable adverse effects on the environment” as “(i) any unreasonable risk to man or the environment, taking into account the economic, social, and environmental costs and benefits of the use of any pesticide, or (ii) a human dietary risk from residues that result from a use of a pesticide in or on any food inconsistent with the standard under section 408 of the Federal Food, Drug, and Cosmetic Act" (WHO, 2017)

Regulation of pesticides is not backed by any law in many developing country, and where there are legislations, such laws are weakly enforced.

3.1.1 Pesticide registration

In the United States, a registrant must submit data on a given pesticide to the EPA for registration, as required by the FIFRA. The EPA decides whether to register the pesticide based on the results of a risk–benefit evaluation, which weighs the pesticide's potential adverse effects against the benefits of its use (NIST, 2014) Registration of the pesticide is not approved unless the pesticide meets: (i) the efficiency and labelling requirements of the FIFRA; and (ii) has been shown to not generally cause "unreasonable adverse effects on the environment" (Global MRL, 2014). Under the FIFRA, the EPA administrators also take into account the economic, social and environmental costs and benefits of the pesticide.

The EPA dictates what procedures and data are required to evaluate the risk–benefit ratio of a pesticide and provides guidance in determining whether a pesticide causes unreasonable adverse effects. The results of these risk–benefit analyses are then published together with the EPA's proposed regulatory decision, followed by the comments of stakeholders. If the pesticide is classified as destined for cancellation or restricted use, the US Department of Agriculture and the EPA's Scientific Advisory Panel are requested to review the risk–benefit analyses before the final regulatory decision.

After registration of a pesticide, the registrant is still required to inform the EPA of any "additional factual information regarding unreasonable adverse effects on the environment". The information that a registrant must submit consists of: toxicological and epidemiological studies, data on pesticide residues in foods and/or the environment, reports of adverse effects and other information of interest in assessing the desirability of continued registration. The registrants will be convicted of a violation if they do not report the required information.

3.1.2 Suspension and cancellation

The EPA may reconsider the registration of a particular pesticide if new evidence of potential adverse effects emerges. The EPA has authority to restrict, suspend or cancel a pesticide's registration. A decision to cancel or suspend a pesticide also depends on the results of cost–benefit analyses focusing particularly on the impact of the cancellation on the production and price of agricultural commodities, retail food prices and other economic factors. Before deciding to cancel or suspend a pesticide's registration, an administrator must consider restricting its use. If restriction is deemed unfeasible, the EPA will cancel the pesticide and provide a full justification for its action.

3.1.3 Pesticide labelling

In the United States, the labelling and use of pesticides are also subject to EPA regulation under the FIFRA. Accordingly, the sale and distribution of any mislabelled pesticide is an illegal action. In addition to directions for use, a pesticide's label must contain a statement to the effect that it is safe for human health and the environment. Altering a label or using a pesticide that fails to comply with labelling requirements is prohibited.

3.1.4 Worker protection

The Worker Protection Standard (WPS), which is the United States federal regulation issued to protect people from occupational exposure to agricultural pesticides, contains regulations on pesticide safety training, notification of pesticide application, use of personal protective equipment, field re-entry time restrictions following pesticide application and emergency medical assistance (FERA, 2014). The EPA is authorized to work closely with state-level pesticide regulatory agencies in conducting inspections to ensure that the regulation is implemented and enforced in agricultural communities.

In the United States, a pesticide is considered suitable for general use if it has no unreasonable adverse effects on the environment when used as indicated on the label. A pesticide is for restricted use if it "may generally cause, without additional regulatory restriction, unreasonable adverse effects on the environment". Under the WPS, only a certified applicator or someone supervised by a certified applicator can apply pesticides whose use is restricted, whereas anyone can use non-restricted pesticides. The EPA is authorized to issue certification standards for pesticide applicators to ensure that they are competent in the safe and effective use of pesticides. In Viet Nam, no equivalent WPS has been designed, and despite the fact that MARD regularly issues a list of pesticides for restricted use, Viet Nam has established no similar requirements for the training or certification of pesticide applicators.

3.1.5 Pesticide storage and disposal

In the United States the EPA regulates pesticide storage and disposal for four categories of pesticide users: household consumers, farmers, retailers and commercial applicators. For each of these groups it provides detailed instructions,but the corresponding state and local laws are often stricter than the federal regulations. For example, most states have developed programmes whereby farmers can "collect and dispose of pesticides in a safe and simple way at little or no cost".

3.1.6 Pesticide import and export policy

In the United States the EPA regulates both the import and export of pesticides under the FIFRA (Section 17). However, the FIFRA has been criticized for authorizing the EPA to comprehensively regulate the domestic use of pesticides while neglecting regulation on pesticide exportation. Although the EPA issued the new export policy for pesticides "to protect public health and the environment from unreasonable adverse effects of pesticides, both domestically and internationally", the agency still allows companies to export pesticides not registered for use in the United States as long as they fulfil certain labelling and warning requirements. Moreover, despite a domestic requirement that product package labels be multilingual, exporters are only required to print multilingual labels for shipping containers but not for attachment to the product packages.Therefore, applicators in foreign countries may not have an opportunity to review warning information.

3.2 The Conditions of work in developing nations

Most studies on pesticide health impacts and most pesticide risk analyses have been performed with reference to the conditions of highly industrial countries. In many cases, agricultural labor is performed in these countries by migrant workers, immigrants, ethnic minorities and the poor. National laws and regulations that govern the conditions of work and that restrict how pesticides are used are often inadequately enforced. Nonetheless, the conditions and circumstances in the developing world are generally quite different, and the likelihood of exposure to hazardous pesticides is often much greater:

Pesticide containers are frequently unlabeled or are labeled with information that farmers or agricultural workers cannot read (because they are not in local languages or because of insufficient literacy).

National pesticide regulatory regimes are often very weak and inefficient. They sometimes lack meaningful controls on even the most hazardous pesticides and they frequently lack effective surveillance systems and enforcement mechanisms.

Pesticides are frequently used inappropriately or in the wrong concentrations.

Agricultural workers and small farmers frequently lack training and have little access to necessary information. And even when agricultural workers do know that they are using pesticides inappropriately or unsafely, they often fear the consequences of refusing unsafe work practices or even reporting them. In many cases, especially where casual labor is being used, agricultural workers may have few if any rights that they can exercise.

Necessary protective equipment may not be available, may be poorly maintained, and/or may be inappropriate for climatic conditions, especially in regions that are hot and humid. And even where protective equipment is available, many small farmers may be too poor to purchase them.

In highly industrial countries, reported rates of acute pesticide poisoning in agricultural workers may be more than 18 cases per year for each 100,000 full time workers.In many developing countries, because of the frequently different conditions and circumstances, the rates of acute pesticide poisoning are almost certainly much higher. The number of workers employed in agriculture in most developing countries is also much higher. The combination of higher pesticide poisoning rates and larger percentages of the population engaged in agriculture makes pesticide poisoning a much greater health problem in the developing world than in highly industrial countries. However, because public health priorities often tend to emphasize the health problems and concerns of the industrial world, the problem of health injuries caused by pesticide exposure often receives less attention from the public health community than it should.

Additionally, approaches to the regulation of pesticides often assume that conditions of work and regulatory capabilities in developing countries are similar to those in highly industrial countries, but this frequently is not the case.

3.2.1 Pesticide regulation and administration in developing nations

In many developing countries, once a “Highly hazardous pesticide” (HHP) is imported, it is usually difficult or impossible for the national authorities to effectively enforce laws and regulations that would ensure the pesticide will be used only in accordance with the regulatory guidelines. In such countries, the responsible regulatory approach should be to prohibit the import and use of such pesticides, and to help farmers identify effective, less-hazardous alternatives.

3.3 The international code of conduct on the distribution and use of pesticides

As late as the mid-1980s, a large number of developing country governments, possibly most, still lacked any national pesticide control legislation or regulations. Also at that time, pesticide use, including especially the use of highly toxic pesticide formulations, was increasing in the developing world. This resulted in rising health injuries from toxic pesticide exposure and led to international concern. In response, the governing body of the Food and Agriculture Organization of the United Nations (FAO) adopted the *International Code of Conduct on the Distribution and Use of Pesticides* (International Code), an attempt to begin addressing this problem by creating universal standards of conduct for everyone involved in pesticide use and regulation, especially national governments and the pesticide industry.

The International Code has already had a positive impact and has twice been updated to reflect changing circumstances: in 1989 and again in

1992. Since the Code was first adopted in 1985, many additional governments have established legislation to regulate the distribution and use of pesticides; awareness of the problems associated with pesticide use has grown; and many new and successful Integrated Pest Management (IPM) programs that decrease dependence on pesticides are being implemented. Nonetheless, problems remain, especially in many developing countries. The preface to the most recent, 1992 version of the International Code states:

Even where national pesticide legislation has been adopted, it is often not widely enforced due to lack of technical expertise and resources
Highly hazardous or sub-standard pesticide formulations are still widely sold
End-users are often insufficiently trained and protected to ensure pesticides are handled with minimum risk3 The International Code is not perfect. Compliance is purely voluntary and in 1992 when the most recent version of the Code was approved, FAO was not as clear as it is today about its organizational role in promoting national bans on the importation and use of those hazardous pesticides whose proper management and safe use cannot be consistently ensured under prevailing national conditions. Nonetheless, the International Code is a very important and positive document that NGOs should be familiar with, especially NGOs in developing countries and countries with economies in transition whose missions include support for public health and/or environmental objectives. After reviewing the International Code, NGOs may wish to take actions such as:
Promoting the full and effective national implementation of the Code and its guidelines
Undertaking national advocacy campaigners to press for national reforms addressing problem areas where national policy or practice falls short of what is called for in the guidelines
Contributing to training in IPM and safe occupational practices in support of improved implementation of the Code
NGOs have additionally been invited to monitor the implementation of the code in their own country and to report their findings to the FAO Director- General in Rome.

3.4 Regulations on the general use of pesticides

To avoid creating a menace of contamination of the environment and accumulation of pesticide residues, preference must always be given to pesticides that are less persistent, less volatile, and have a lower toxicity when making pesticide recommendation in agriculture. If there are no sufficient substitutes for stable and volatile substances, the use of the latter and the conditions of working with them are strictly regulated. The atmospheric air and water basins may become contaminated as a result of the drifting of pesticide particles in dusting, spraying, and using aerosols, as a result of violation of the rules for fumigation, and of the storage and transportation of pesticides in damaged containers, upon treatments in windy weather, and when soil particles are carried off treated fields.

To avoid the drifting of toxicant particles, aerial dusting, fine-drop spraying, and aerosol treatments are prohibited within a radius of 1,000 m around populated localities, farmsteads, and within a radius of 2,000 m from the shores of fish-farming basins.

Pesticides must not be allowed to enter into the atmosphere air of populated localities in concentrations exceeding the maximum acceptable limits.

It is prohibited to perform spraying, dusting, seed treatment, or bait preparation outdoors if the wind speed exceeds 3 m/s. Aerial dusting is prohibited if the speed of the wind exceeds2 m/s, fine-drop spraying if it exceeds 3 m/s, and large-drop spraying if it exceeds 4 m/s. to reduce the drift of pesticides in aerial treatments, new formulations of pesticides such as inverted emulsions are being developed.

The aerial treatment with chemicals of areas closer than 1 km to populated localities is prohibited. Aerosls may be used only in a calm weather or with a slight wind (up to 2 m/s). Fumigation is not permitted if the wind’s speed exceeds 7 m/s.

Soil, owing to its high biological activity and certain agrochemical properties (acidity, obsorptivity, etc) is characterized by an inactivating ability. But upon the frequent use and large rates of consumption of persistent toxicants, they may accumulate in the soil in considerable amounts. A limited use of persistent pesticides, a strict observance of the rates of use, and the alteration of pesticides of different groups prevent the accumulation of their residues in the soil. Normalization of the maximum permissible residues of pesticides in the soil makes it possible to control and regulate the circulation of pesticides in nature.

It is strictly prohibited to bury and plough into the soil large amounts of pesticides with the aim of destroying them.

It is prohibited to erect pesticide storage facilities near livestock barns and water basins.

Parks and green planting within the confines os populated localities are treated only with pesticides of a moderate and low toxicity having no unpleasant odour, using surface vehicles and machines.

No pesticides may be used for treatment on the territory of hospitals, schools, kindergarden, or sports grounds.

The entire local population is to be informed about the places, times, and the nature of the chemical treatments in good time prior to the commencement of the operation. This is done in order to allow the inhabitants to take relevant safety measures (stop the grazing of cattle, the flight of bees, and field work, to cover wells, etc)

Warning signs are set up on the treated areas and the zones around them at least 300 m wide. It is prohibited to graze cattle during the time indicated in the instruction for the use of the relevant substance.
It is prohibited to feed fodder contaminated with pesticides to agricultural animals.

4.0 CONCLUSION

Measure for public safety are aimed at preventing the contamination of the atmosphere, soil, water sources and food products by toxicants. The strict observant of the rules for working with pesticides exclude the accidental contact with poisonous chemicals, ensure the protection of human, beneficial animals, birds and beneficial insects from the actions of pesticides.

5.0 SUMMARY

In this unit the students has leant:

i. some legislative basis for pesticide regulation;
ii. the level of compliance to pesticide regulations by developed nations and developing nations; and
iii the best approach to pesticide and pesticide use regulation use in developing countries.
applicability of econoclimatic model is not restricted to agricultural planning.

6.0 TUTOR-MARKED ASSIGNMENTS

i. Explain some legislative basis for pesticide regulation
iv. Differentiate the approach to pesticide use regulation in developed and developing nations.

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UNIT 25 CASE STUDIES OF GLOBAL DISASTERS OF MISUSE AND ABUSE OF PESTICIDES

CONTENTS

1.0 INTRODUCTION

Trade in hazardous technology and hazardous products between developed and less developed countries (LDCs) has caused increasing national and international concern for human health and the environment. Pesticide related issues have been increasingly and extensively highlighted in the media including research journals and have attracted sharp focus among the world policy makers. Indiscriminate and excessive use of toxic synthetic pesticides damage not only the environment and agriculture but have also entered into the food chain thereby affecting all living beings. (WHO, 1986), estimated that millions of people were being poisoned annually with about 20,000 cases resulting in death. Much of the problem came from the toxicity of the pesticides used on large plantations as well as by many small-scale farmers, without adequate knowledge and failing to adequately protect themselves during pesticide applications. Pesticide application has caused serious health problems but blames are usually laid on pesticides without considering the way the pesticides are applied.

2.0 OBJECTIVES

By the end of this unit, students should be able to:

i. Understand how legislation contributes to pesticide abuse;
i. understand the various ways pesticides are abused both in developed and less developed nations;
ii. understand the different factors contributing to pesticide abuse especially in less developed nations; and
iii. understand the environmental and health challenges associated with pesticide abuse

3.0 Main Contents

3.1 Concerns about hazardous pesticides and weak regulations

International and private efforts have been thwarted by similar complexities. International and private efforts are often in the form of non-enforceable policy statements regarding standards and guidelines for hazardous trade. This often creates a major impediment to meaningful changes in current chemical trade practices. As a result, international and private efforts are effective only to the extent that each participating party cooperates and enforces the established policies.

3.1.1 The Tris Scandal

Inthe United States this concern was first aroused in 1977 by the scandal surrounding Tris, a flame retardant chemical used in treating clothing. The Consumer Product Safety Commission (CPSC) discovered that Tris was a carcinogen and banned its use in the U.S. market in 1977. After the U.S. market ban, however, sleepwear manufacturers exported Tris-treated garments for use abroad. Much to the dismay of Congress and the public, the Government Operations Committee found that existing law did not regulate or prohibit the manufacture and trade of hazardous products produced solely for export. The Tris scandal prompted a national debate over the means of enhancing governmental control over U.S. exports of hazardous products. As a result of this debate, Congress passed laws requiring federal agencies to track hazardous exports by U.S. manufacturers. The new laws further require U.S. manufacturers to inform importing countries of the nature of the exported hazardous substances. There have also been international efforts to create uniform standards and procedures for hazardous technology trade. These regulatory reforms, however, have regulated hazardous chemical trade insufficiently and have failed to protect foreign and domestic consumers from chemically tainted products, particularly in trade between developed countries and LDCs.

3.1.2 The Alar and Chilean grape crises

This insufficiency was most recently demonstrated in the Alar and Chilean grape crises in 1989. These incidents, discussed below, illustrate for different reasons how vulnerable domestic and imported foods are to chemical contamination. Alar is a trade name for a chemical chiefly used in treating red eating apples.Although the Environmental Protection Agency (EPA) suspected Alar to be a cancer-causing chemical as early as the mid 1970s, it failed to take decisive action.The chemical manufacturer voluntarily withdrew Alar's use only after tremendous public outcry.

The Chilean grape incident did not involve the sanctioned use of chemical additives, but it illustrates how inept the current regulatory procedures are in protecting consumers from tainted foods. The Food and Drug Administration (FDA) acted upon an anonymous tip and

detected two Chilean grapes which had been contaminated with cyanide.The FDA warned consumers not to eat imported Chilean foods while it conducted an investigation.When it detected no further traces of cyanide poisoning, the FDA continued its normal inspection practice whereby only one percent of all imported food shipments are examined.
The current domestic regulatory scheme is complicated by three factors:

1. the involvement of several different regulatory agencies, whose agendas, policies, and goals often conflict;
2. the legal and diplomatic questions regarding U.S. jurisdiction over corporate activity abroad;
3. a strong industrial lobby which effectively resists increased regulations.

3.2 Pesticide abuse in less developed countries

3.2.1 Reasons for Increasing Pesticide Use and Abuse in LDCs

1. Use of Increasingly Sophisticated Technology in LDCs

Numerous international organizations and governments are engaged in efforts to encourage industrialization in the Third World. Both multinational development banks (MDBs) and governmental programs such as the U.S. Agency for International Development (USAID) have funded numerous Third World development projects, particularly in agriculture, which accounts for approximately twenty-five percent of all loans awarded by the World Bank. Intense agricultural development aimed at equipping LDCs with resources to produce foods for domestic consumption and export use is commonly referred to as the green revolution.The green revolution has provided many incentives to multinational corporations (MNCs) involved in agribusiness to locate manufacturing facilities in LDCs and to target sales of their agricultural productsto the developing countries. Generally, MNCs have successfully influenced government policy in LDCs, advocating agricultural programs that have provided considerable windfalls.

2. Agricultural Goals of LDCs

The ever-increasing technological sophistication of agriculture and the developed countries' encouragement of Third World development have drastically expanded the type and amount of pesticides used throughout the world, particularly in the LDCs. Agriculture programs in LDCs emphasize the production of cash crops for export in order to help alleviate LDC national debt.As a result of the marketing influences of agricultural chemical companies, farmers in LDCs introduced foreign high-yielding hybrid seeds, which lacked natural resistance to indigenous pests.The Food and Agriculture Organization estimates that by the year 2000 sixty-seven percent of the seeds distributed for use in Third World agriculture will be foreign hybrid varieties.In addition, cash crop marketing influences are creating plant monocultures-uniform plantings of one plant variety-in the Third World.Plant monocultures present a further problem because nondiverse plant populations are more vulnerable to pest infestation. Pests can destroy entire monoculture crops and cause the loss of an entire growing season. Thus, the agricultural goals of LDCs and the introduction of new hybrid seed varieties create an increasing need and dependency on greater volumes of more toxic pesticides for adequate pest control.

3. The Pesticide Treadmill

The phenomenon of continually replacing a prior pesticide with a new, more toxic pesticide is often referred to as the pesticide treadmill.Part of the problem of pesticide use in the control of pestsis that it both promotes the development of pesticide-resistant insect strains and disturbs the natural system of checks and balances on pest populations. Certain pests, particularly insects, have exhibited an extraordinary ability to become resistant to pesticides.Insects multiply frequently and in great numbers. This multiplication allows for extensive genetic restructuring and potential adaptation to any given poison through natural selection processes. Moreover, the imposition of artificial control on pest populations disturbs the existing, time-evolved methods of natural pest control, Pesticides that are specifically applied to a given pest type may result in the pest's competitor or prey reproducing more prolifically, hence further disrupting the agricultural plants in need of protection. Proliferation of pest populations, caused by a resistance to a given pesticide or a specific targeting of one pest, result in the use of increasingly toxic pesticides that have broader impact upon the environment and the level of exposure to people and food in LDCs.

4. Lack of Standards and Guidelines for Chemical Use in LDCs

As discussed above, the U.S., which stringently restricts the domestic use of pesticide chemicalsand whose industries account for more than one-third of the pesticides produced in the world, has very little regulatory control over pesticides produced solely for export.In addition, in LDCs there is little or no regulation of pesticide imports. One source estimates that forty percent of Third World countries have no regulations governing imports, and those countries which have such regulations have insufficient funds to enforce them adequately. As a result, LDCs are the dumping grounds for the most toxic pesticides available.Even where LDCs have some facility to regulate pesticide use, conflicting priorities and a lack of sufficient regulatory control disrupt pesticide programs.Furthermore, some MNCs that have a stake in the sale of pesticides have proven quite effective at influencing government policies and advocating pesticide use.

5. Physical and Cultural Disparity in LDCs

The physical and cultural environment determine how safely and effectively a given pesticide can be used in LDCs. Pesticides that are promoted for use in LDCs often are not matched accurately to the specific environment in which they will be used.Unforeseen reactions with plant and animal species as well as the physical environment, such as climate, can make otherwise safe chemicals dangerous or ineffective.

3.2.2 Effects of Pesticide Abuse in LDCs

Pesticide use is estimated to result in 500 thousand cases of human poisoning every year. Approximately five thousand of these poisonings result in fatalities.Because pesticides are largely unregulated in LDCs and conditions for farm workers are grossly unsafe, the occurrence of human poisonings is thirteen times the number of poisonings in the U.S., and the percentage of deaths resulting from pesticide poisoning is greater than the worldwide average.Moreover, statistics regarding i~ury and death from pesticides in LDCs underestimate the actual number of cases. Many pesticide-related illnesses go undetected or misdiagnosed because of inadequate medical resources, or because certain pesticide-related illnesses only develop many years after the initial pesticide poisoning.

3.3 Cases of Pesticide Abuse in LDCs

3.3.1 Documented threats of pesticide use in urban agriculture in Ghana.

It is estimated that, about 87% of Ghanaian farmers use chemicals to control insect pests and diseases on vegetables (Dinham, 2003). In a survey by farmers cited the presence of pests as a major indicator for pesticide application. The excessive use of pesticides by farmers, who in most cases misuse the chemicals, has brought about many adverse effects of pesticide application. Literature is therefore replete with the deleterious effects of pesticide use in rural-urban agriculture in Ghana on both human health and the environment. Ntow*et al*. (2006) in their study of farmer perceptions and pesticide use practices in vegetable production in Ghana found body weakness, headache and dizziness as the most frequently reported possible pesticide poisoning symptoms among farmers surveyed. Studies conducted by Mensah *et al.* (2004) found that, in Akomadan and Afrancho, where farmers intensively use pesticides, about 56% of farmers had experienced sneezing , skin irritation (65.9%), headaches (48.2%), dizziness (40.0%), abdominal pains (20.0%) and cough (57.6%) after spraying. About 30% of the farmers were also found to have low red blood cells while 38% had low white blood cells. Other health problems farmers face due to the improper handling and application and in most cases over-application of pesticide ranges from nausea/vomiting, blurred vision to death (including children) (Mensah *et al.*, 2001).

3.3.2 Pesticide misuse and abuse in Nigeria

There is abundant evidence of poor pesticide education leading to extensive misuse in Nigeria(Asogwa and Dongo, 2009). For instance, cases of over-dosage, for one reason or the other, have been reported as common. Even among government-trained, or agency-trained and assisted small-scale farmers, far more quantity of pesticides than prescribed is applied with the general expectation that it would affect more rapid killing of crop pests. Other unfortunate but common misuse of pesticides happening in Nigeria include:

1) Pouring pesticides (particularly old stock of Gammalin – Lindane) into rivers to kill fish which is then sold for human consumption.

2) Spraying Gamalin 20 on drying cocoa beans to prevent moulds and maggot development.

3) Mixing of different classes of pesticides (eg fungicides and insecticides) together so as to reduce the workload of spraying each differently. Apart from affecting effectiveness, such a practice could also dramatically worsen the potential health hazards.[Asogwa and Dongo 2009].

4) Wrong use of nozzles for spraying equipment, making it difficult for desired quantity of pesticides to be administered. Both over-dispensing and underdispensing could have significant adverseimpacts on the environment and on human health.

5) Lack of knowledge on the time needed for degradation of pesticides

6) Use of wrong formulations and doses, and wrong timing of application (all borne out partly due to inability to properly distinguish one pest from the other)

7) Counterfeiting, faking, and recycling of old stocks, manufacturing of empty plastic containers to market adulterated agrochemicals, which are sold at reduced prices.

8). Careless disposal of expired pesticides into the environment as regular waste, due to lack of proper disposal facilities or protocols.

Factors for aggravated health hazards from pesticide use in Nigeria

Some of the major factors leading to a preponderance of adverse health impacts associated with pesticide use in developing countries such as Nigeria, despite relatively lower volume used compared with developed countries, include the following:

i. **Highly toxic pesticides are used in Nigeria:** It is the most-deadly chemicals that are used here due to their being cheaper than newer safer pesticides (Erhunmwunse*et al*, 2012).

ii. **Poor legislation and Lack of Enforcement of Available Legislation**: In Nigeria, the regulations governing use of chemicals are encapsulated in the ECOWAS Regulations on Pesticides which covers all activities involving experiments on, as well as authorization, marketing, use and control of pesticides in the West Africa subregion; and the National Environmental (Hazardous Chemicals and Pesticides) Regulations, 2013 which deals with import, export, storage, usage, and marketing of hazardous chemicals and pesticides including other agrochemicals. The NAFDAC regularly issues permits, valid for five years, for specific brands of pesticide formulations that can be used in the country. These laws are however weakly enforced.

iii. **Issues With Correct, Effective, and Safe Applications of Pesticides:** Too frequently, people get unnecessary serious exposure to pesticides while applying them. This is due mostly to a combination of economic reasons and plain ignorance, many fail to put on required personal protective equipment such as gloves, overcoats, and masks [Asogwa and Dongo, 2009;

.iv. **Lack of Adequate Information, Knowledge, and Awareness of the Inherent Dangers of Pesticides:** There is low level of information, knowledge, and awareness among Nigerians, on the dangers associated with the use of pesticides.

v. **Lack of Training on Correct Handling of Pesticides at Home:** A major issue is the improper disposal of empty pesticide containers. Few people take time to thoroughly wash their hands with soap after the use of pesticides. In a similar vein, some use domestic utensils for measuring and dispensing pesticides while several others store pesticides in family bedrooms and unlocked cabinets that can easily be accessed by children (Asogwa and Dongo, 2009).

vi. Absence of Monitoring for Pesticide Residues on Locally-consumed Products,
Unlike the Situation for Products for Export

vii. Inadequacies in Medical Recognition and Responses to Pesticide Poisoning

3.3.3 Pesticide abuse in Cameroun

According to the Food and Agricultural Organisation, 2004, in a report titled “pest control in cut flowers" many problems related to pesticide usage including environmental, air, water, soil and health.

A survey of pesticide application in Cameroon raises growing concern about various reports of illnesses associated with pesticide users. In 1993, Mamat*et al.* expressed concern about the design of a lever-operated sprayer and listed specific features, which increase the risk of direct physical harm as well as the health hazards due to exposure to the pesticide sprays. The following factors needed serious attention: leakages, design of the spray lance, tank weight, and sharp edges on the size of filler opening due to worn-out, sprayer tank, and narrow straps of unsuitable material. During the preparation of the spray and also by holding the trigger valve on the lance, the hands are particularly exposed to the spray. The average use of pesticides by arable land is estimated at $10/ha. Farmers also fight against diseases affecting crops by using multiple products indiscriminately to the extent without sufficiently being aware and trained on the correct choice of pesticides use. This is the case in Njombe where growers are particularly obliged to use pesticides to protect their crops. This could eventually have an impact on health if they remain ignorant of its risk and adequate measures are not taken to prevent or limit contamination. Meijden, 1998, conducted a study on pesticide applications in cocoa farms and found out that “generally, farmers do not wear any protective materials at all, no matter what pesticide is being applied. Farmers scarcely follow precautionary measures as they are found eating, smoking or drinking in-between spraying activities. The left over pesticides and empty containers are not properly disposed as the containers are sometimes washed and used for domestic purposes”.

3.3.4 Pesticide Poisoning and Associated Health Problem in Sri Lanka

Sri Lanka is one of the few developing countries where basic data are available and these show that the majority of poisoning cases are self-inflicted, by mainly young adults living in rural agricultural areas where agrochemicals are easily available. In several agricultural districts it precedes all other causes of death in government hospitals.

i. Studies in Mahaweli H: In Mahaweli System H a very high incidence of serious pesticide poisoning was observed with 68 percent due to intentional ingestion of liquid pesticides. It is argued that the easy availability and widespread use of highly hazardous pesticides is the most important reason for this high number of poisoning cases. The frequent application of hazardous pesticides in high concentrations was often irrational and posed serious health and financial risks for the farmers. Sales promotion activities and credit facilities promoted this excessive pesticide use, while not being counteracted by an agricultural extension service. Hazardous practices when spraying pesticides were due to the impossibility of applying recommended protective measures under the local conditions, more than to lack of knowledge.

ii. Studies in Uda Walawe: Although it is now well established that the majority of poisoning cases in Sri Lanka are suicide attempts, there is no consensus whether this is completely determined by social and cultural factors or whether it is mainly caused by the easy availability of hazardous agrochemicals. Others say that the prevalence of mental illness is underestimated and accounts for many of the intentional poisoning cases. So far there have been no studies that looked into the risk factors of acute pesticide poisoning and that have tried to establish the relative importance of the different determinants. However, such information is essential to plan effective preventive and control strategies. In fact, it can be stated that the public health community has by and large ignored the subject, despite its importance in terms of morbidity and mortality.

3.3.5 Pesticide abuse in India

Another case of indiscriminate pesticide dumping by a state owned department resulted in serious environment and economic revelations in the highly literate state of Kerala (Rajendran, 2002). Way back in the

1970s, the Plantation Corporation of Kerala (PCK) began aerial spraying of pesticides on its 2,200 ha cashew gardens in Padre village in Kasargod district mainly to check pests during fleshing, flowering and fruit setting seasons. Continuous and indiscriminate application of synthetic pesticides affected the flora and fauna, and local people became victims of severe health problems like cancer (Table 6). Records of disorders in Padre village indicate that in each household at least one person has been found to toil and from 1990 to 2001, 156 cases of disorders from 123 households were noted. In the beginning PCK sprayed endrin and later changed to endosulphan, an organochlorine, effective in a number of field crops. This pesticide has now been either banned or its use restricted in many parts of the world and for little economic gains for cashew production, the state itself contributes to damaging the environment.

3.4 Operation Ranch Hand

Agent Orange was a powerful herbicide used by U.S. military forces during the Vietnam War from 1961 to 1971,to eliminate forest cover and crops for North Vietnamese and Viet Cong troops. The U.S. program, codenamed Operation Ranch Hand, sprayed more than 20 million gallons of various herbicides over Vietnam, Cambodia and Laos from 1961 to 1971. Agent Orange, which contained the deadly chemical dioxin, was the most commonly used herbicide. In all, American forces used more than 20 million gallons of herbicides in Vietnam, Laos and Cambodia during the years of Operation Ranch Hand. Herbicides were also sprayed from trucks and hand-sprayers around U.S. military bases. It was later proven to cause serious health issues—including cancer, birth defects, rashes and severe psychological and neurological problems—among the Vietnamese people as well as among returning U.S. servicemen and their families.

3.4.1 Agent Orange The various herbicides used during Operation Ranch Hand were referred to by the colored marks on the 55-gallon drums in which the chemicals were shipped and stored. In addition to Agent Orange, the U.S. military used herbicides named Agent Pink, Agent Green, Agent Purple, Agent White and Agent Blue. Each of these—manufactured by Monsanto, Dow Chemical and other companies—had different chemical additives in varying strengths. Agent Orange was the most widely used herbicide in Vietnam, and the most potent. It was available in slightly different mixtures, sometimes referred to as Agent Orange I, Agent Orange II, Agent Orange III and "Super Orange." More than 13 million gallons of Agent Orange was used in Vietnam, or almost two-thirds of the total amount of herbicides used during the entire Vietnam War.

3.4.2 Dioxin in Agent Orange In addition to Agent Orange's active ingredients, which caused plants to "defoliate" or lose their leaves, Agent Orange contained significant amounts of 2,3,7,8-tetrachlorodibenzo-p-dioxin, often called TCDD, a type of dioxin. Dioxin was not intentionally added to Agent Orange; rather, dioxin is a byproduct that's produced during the manufacturing of herbicides. It was found in varying concentrations in all the different herbicides used in Vietnam. Dioxins are also created from trash incineration; burning gas, oil and coal; cigarette smoking and in different manufacturing processes such as bleaching. The TCDD found in Agent Orange is the most dangerous of all dioxins.

3.4.3 Effects of Agent Orange: Because Agent Orange (and other Vietnam-era herbicides) contained dioxin in the form of TCDD, it had immediate and long-term effects. Dioxin is a highly persistent chemical compound that lasts for many years in the environment, particularly in soil, lake and river sediments and in the food chain. Dioxin accumulates in fatty tissue in the bodies of fish, birds and other animals. Most human exposure is through foods such as meats, poultry, dairy products, eggs, shellfish and fish. Studies done on laboratory animals have proven that dioxin is highly toxic even in minute doses. It is universally known to be a carcinogen (a cancer-causing agent). Short-term exposure to dioxin can cause darkening of the skin, liver problems and a severe acne-like skin disease called chloracne. Additionally, dioxin is linked to type 2 diabetes, immune system dysfunction, nerve disorders, muscular dysfunction, hormone disruption and heart disease. Developing fetuses are particularly sensitive to dioxin, which is also linked to miscarriages, spina bifida and other problems with fetal brain and nervous system development. Questions regarding Agent Orange arose in the United States after an increasing number of returning Vietnam veterans and their families began to report a range of afflictions, including rashes and other skin irritations, miscarriages, psychological symptoms, type 2 diabetes, birth defects in children and cancers such as Hodgkin's disease, prostate cancer and leukemia.

3.4.4 Legacy of Agent Orange in Vietnam: The controversy over Agent Orange and its effects has persisted for more than four decades. In addition to the massive environmental devastation of the U.S. defoliation program in Vietnam, that nation has reported that some 400,000 people were killed or maimed as a result of exposure to herbicides like Agent Orange. In addition, Vietnam claims half a million children have been born with serious birth defects, while as many 2 million people are suffering from cancer or other illness caused by Agent Orange.

4.0 CONCLUSION

Pesticides are among the most extensively used chemicals in the world today and they are also among the most hazardous compounds to human. Despite the numerous benefits of pesticide in ensuring food security, indiscriminate use of pesticides may become unsafe and can cause both short term and long term damage to human and the environment. Government attention should therefore be focused on the causes of indiscriminate use and abuse of pesticide, and appropriate action should be taken to reduce them.

5.0 SUMMARY

In this unit the students has leant:

i. how weak legislations contribute to pesticide abuse;
iv. the various ways pesticides are abused both in developed and less developed nations;
v. the different factors contributing to pesticide abuse especially in less developed nations; and
vi. the environmental and human health challenges associated with pesticide abuse

6.0 TUTOR-MARKED ASSIGNMENTS

i. Briefly explain various ways pesticides are being abused
ii. Outline some factors contributing to pesticide abuse in the less developed nations of the world.
iii. Explain some of the consequences of pesticide abuse.

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