

## EMT 508

### Environmental Aspects of Pesticides and other Toxicant Use

#### Pesticide

**Pesticides** are substances or mixture of substances intended for preventing, destroying, repelling or mitigating any pest. A pesticide may be a chemical substance, biological agent (such as a virus or bacterium), antimicrobial, disinfectant or device used against any pest. Pests include insects, plant pathogens, weeds, molluscs, birds, mammals, fish, nematodes (roundworms), and microbes that destroy property, spread disease or are a vector for disease or cause a nuisance. Although there are benefits to the use of pesticides, there are also drawbacks, such as potential toxicity to humans and other animals. According to the Stockholm Convention on Persistent Organic Pollutants, 9 of the 12 most dangerous and persistent organic chemicals are pesticides.

Humans have used pesticides to protect their crops. Elemental sulphur dusting was the first known pesticide used in ancient Sumer about 4,500 years ago in ancient Mesopotamia. The 15th century saw the application of toxic chemicals such as arsenic, mercury and lead on crops to kill pests. Nicotine sulfate was extracted from tobacco leaves for use as an insecticide in the 17th century. Two more natural pesticides, pyrethrum, derived from chrysanthemums, and rotenone, derived from the roots of tropical vegetables were introduced in the 19th century. Arsenic-based pesticides were dominant until the 1950s. Paul Müller discovered that Dichlorodiphenyltrichloroethane (DDT) was a very effective insecticide. Organochlorines such as DDT were dominant, but because of their persistence in the environment they have been replaced by organophosphates and carbamates. The compounds of pyrethrin became the dominant insecticide in 1957. The use of herbicides became extensive in the 1960s, with "triazine and other nitrogen-based compounds, carboxylic acids such as 2,4-dichlorophenoxyacetic acid, and glyphosate" being the most used. Seventy-five percent of all pesticides in the world are used in developed countries; however pesticide use in developing countries is increasing.

In the 1960s, it was discovered that DDT was preventing many fish-eating birds from reproducing, which was a serious threat to biodiversity. Rachel Carson talked about biological magnification of pesticides in her book "Silent Spring". The agricultural use of DDT is now banned under the Stockholm Convention on Persistent Organic Pollutants, but it is still used in some developing nations to prevent malaria and other tropical diseases by spraying on interior walls to kill or repel mosquitoes.

#### Definition

The Food and Agriculture Organization (FAO) has defined the term of pesticide as any substance or mixture of substances intended for preventing, destroying or controlling any pest, including vectors of human or animal disease, unwanted species of plants or animals causing harm during or otherwise interfering with the production, processing, storage, transport or marketing of food, agricultural commodities, wood and wood products or animal feedstuffs, or substances which may be administered to animals for the control of insects, arachnids or other pests in or on their

bodies. The term includes substances intended for use as a plant growth regulator, defoliant, desiccant or agent for thinning fruit or preventing the premature fall of fruit. Also used as substances applied to crops either before or after harvest to protect the commodity from deterioration during storage and transport.

## **Uses**

Pesticides are used to control organisms considered harmful. For example, they are used to kill mosquitoes that can transmit potentially deadly diseases like west nile virus, yellow fever, and malaria. They can also kill bees, wasps or ants that can cause allergic reactions. Insecticides can protect animals from illnesses that can be caused by parasites such as fleas. Pesticides can prevent sickness in humans that could be caused by moldy food or diseased produce. Herbicides can be used to clear roadside weeds, trees and brush. They can also kill invasive weeds that may cause environmental damage. Herbicides are commonly applied in ponds and lakes to control algae and plants such as water grasses that can interfere with activities like swimming and fishing and cause the water to look or smell unpleasant. Uncontrolled pests such as termites and mould can damage structures such as houses. Pesticides are used in grocery stores and food storage facilities to manage rodents and insects that infest food such as grain. Thus pesticides can save farmers' money by preventing crop losses to insects and other pests

The spraying of DDT on the walls of houses is a method that has been used to fight malaria since the 1950s. Recent policy statements by the World Health Organization have given stronger support to this approach. Dr. Arata Kochi, WHO's malaria chief, said, "One of the best tools we have against malaria is indoor residual house spraying. Of the dozen insecticides WHO has approved as safe for house spraying, the most effective is DDT".

The use of any pesticide carries some associated risk. Proper pesticide use decreases these associated risks to a level deemed acceptable by pesticide regulatory agencies such as the United States Environmental Protection Agency (EPA) and the Pest Management Regulatory Agency (PMRA) of Canada. It was estimated that DDT and other chemicals in the organophosphate class of pesticides have saved 7 million human lives since 1945 by preventing the transmission of diseases such as malaria, bubonic plague, sleeping sickness, and typhus. A 2007 study however revealed some negative effect of pesticide use. For example exposure to DDT prior to puberty has linked breast cancer. Poisoning may also occur due to use of DDT and other chlorinated hydrocarbons by entering the human food chain when animal tissues are affected. Symptoms include nervous excitement, tremors, convulsions or death. Also the use of DDT is not always effective, as resistance to DDT was identified in Africa as early as 1955, and by 1972 nineteen species of mosquito worldwide were resistant to DDT. A study for the World Health Organization in 2000 from Vietnam established that non-DDT malaria controls were significantly more effective than DDT use. The ecological effect of DDT on organisms is an example of bioaccumulation.

## **Classification of Pesticides**

Pesticides can be classified based on target organism, chemical structure, and physical state. Pesticides can also be classed as inorganic, synthetic, or biologicals (biopesticides), although the

distinction may sometimes not be distinct. Biopesticides include microbial pesticides and biochemical pesticides. Plant-derived pesticides, or "botanicals", have been developing quickly. These include the pyrethroids, rotenoids, nicotinoids, and a fourth group that includes strychnine and scilliroside. Many pesticides can be grouped into chemical families.

Prominent insecticide families include organochlorines, organophosphates, and carbamates. Organochlorine hydrocarbons (e.g. DDT) could be separated into dichlorodiphenylethanes, cyclodiene compounds, and other related compounds. Their toxicities vary greatly, but they have been phased out because of their persistence and potential to bioaccumulate.

Pesticides classified based on target organism include algicides or algaecides, avicides, bactericides, fungicides, insecticides, miticides or acaricides, molluscicides, nematocides, rodenticides, virucides. Other subclasses of pesticides include: herbicides, insecticides, fungicides, rodenticides, pediculicides, and biocides.

Pesticides can be classified based upon their biological mechanism function or application method. Most pesticides work by poisoning pests. A systemic pesticide moves inside a plant following absorption by the plant. With insecticides and most fungicides, this movement is usually upward (through the xylem) and outward. Increased efficiency may be a result. Systemic insecticides, which poison pollen and nectar in the flowers, may kill bees and other needed pollinators.

The development of a new class of fungicides called paldoxins was announced in 2009. These work by taking advantage of natural defense chemicals released by plants called phytoalexins, which fungi then detoxify using enzymes. The paldoxins inhibit the fungi's detoxification enzymes. They are believed to be safer and greener.

### **Estimate of Pesticide Usage**

Approximately 5.2 billion pounds of pesticides was used worldwide in 2006 and 2008 with herbicides constituting the majority pesticide accounting for about 40%, followed by insecticides and fungicides with totals of 17% and 10% respectively. In the years 2006 and 2007, the U.S. consumed approximately 1.1 billion pounds of pesticides which account for 22% of the world total. In the U.S., conventional pesticides used in the agricultural sector, industry, commercial, governmental and the home & garden sectors, amount to a total of about 857 million pounds, with the agricultural sector accounting for 80% of the total pesticide use. Detailed and accurate measure about pesticide consumption in Nigeria is conflicting, although the Canadian sponsored African Stockpile Programme aimed at eliminating obsolete pesticides has details and provisional estimates. There are more than 1,055 active ingredients registered as pesticides, which are put together to produce over 16,000 pesticide products that are being marketed in the United States.

### **Fumigant pesticides action and systematic activities**

Fumigants pesticides may affect organisms in variety of ways depending on the organism type, physiology and metabolic activities. They may operate by disrupting the sodium/potassium

balance of the nerve fiber, forcing the nerve to transmit continuously. Organophosphate and carbamates operate through inhibiting the enzyme acetylcholinesterase, allowing acetylcholine to transfer nerve impulses indefinitely and causing a variety of symptoms such as weakness or paralysis. Organophosphates are quite toxic to vertebrates, but they have in some cases been replaced by less toxic carbamates. Prominent herbicides include phenoxy and benzoic acid. Phenoxy compounds tend to selectively kill broadleaved weeds rather than grasses. The phenoxy and benzoic acid herbicides function similar to plant growth hormones, and grow cells without normal cell division, crushing the plants nutrient transport system. Triazines interfere with photosynthesis.

The newly developed class of fungicides called paldoxins works by taking advantage of natural defense chemicals released by plants called phytoalexins, which fungi then detoxify using enzymes. Thus paldoxins will inhibit fungi's detoxification enzymes. The mode of systematic action of phytoalexins is believed to be safer and greener.

### **Benefits of Pesticides Use**

There are two levels of benefits for pesticide use, primary and secondary. Primary benefits are direct gains from the use of pesticides and secondary benefits are effects that are more long-term, while the third benefit is that of economic advantages.

#### **Primary benefits include:**

##### 1. Controlling pests and plant disease vectors

- Improved crop/livestock yields
- Improved crop/livestock quality
- Invasive species controlled

##### 2. Controlling human/livestock disease vectors and nuisance organisms

- Human lives saved and suffering reduced
- Animal lives saved and suffering reduced
- Diseases contained geographically

##### 3. Prevent of control organisms that harm other human activities and structures

- Drivers view unobstructed
- Tree/brush/leaf hazards prevented
- Wooden structures protected

#### **Secondary benefits include:**

##### 1. Community benefits

- Farm and agribusiness revenues

- Nutrition and health improved
- Food safety and security

## 2. National benefits

- Workforce productivity increased
- Increased export revenues
- National agriculture economy

## 3. Global benefits

- Assured safe and diverse food supply
- Less greenhouse gas
- Reduced civil unrest

### **The third benefit is that of economic advantage i.e. monetary**

Generally speaking, farmers benefit from having an increase crop yield and from being able to grow a variety of crops throughout the year. Consumers of agricultural products also benefit from being able to afford the vast quantities of produce available year round. The general public also benefits from the use of pesticides for the control of insect-borne diseases and illnesses, such as malaria. The use of pesticides creates a large job market, which provides jobs for all of the people who work within the industry. It was estimated in the US that, for every dollar spent on pesticides to enhance crops yield, about four dollars in crops saved. This means that, for every \$1 spent on pesticides, there is an additional \$4 savings on crop that would have been lost to damage by insects and weeds per year.

### **Environmental and Human Health Impact of Pesticide Use**

The environmental and health impact of pesticide use could be detrimental and difficult to salvage, especially if expressed in humans. Thus there can be an economic implication for damage to the environment and human health, as well as budgetary appropriation for the research and development of new pesticides.

### **Health Impact in Human**

Pesticides may cause acute and delayed health effects in those who are exposed to it. Pesticide exposure can cause a variety of adverse health effects. These effects can range from simple irritation of the skin and eyes to more severe effects such as affecting the nervous system, mimicking hormones causing reproductive problems, and also causing cancer. A 2007 systematic review found that "most studies on non-Hodgkin lymphoma and leukemia showed positive associations with pesticide exposure" and thus concluded that cosmetic use of pesticides should be decreased. Strong evidence also exists for other negative outcomes from pesticide exposure including neurological, birth defects, fetal death, and neuro-developmental disorder. The American Medical Association recommends limiting exposure to pesticides and the use of safe alternatives because uncertainty exists regarding the long-term effects of low-dose to

pesticide exposures. This is because current surveillance systems are inadequate to characterize potential exposure problems related either to pesticide usage or pesticide-related illnesses. In considering these data gaps, it is prudent to limit pesticide exposures and to use the least toxic chemical pesticide or non-chemical alternative.

The World Health Organization and the UN Environment Programme estimate that each year, 3 million workers in agriculture in the developing world experience severe poisoning from pesticides, about 18,000 of whom die. According to another study, as many as 25 million workers in developing countries may suffer mild pesticide poisoning yearly. One study report found pesticide self-poisoning as the method of choice in one third cases of suicides worldwide, and recommended among other things, more restrictions on the types of pesticides that are most harmful to humans.

### **Environmental effect**

The use of pesticide raises a number of environmental concerns. Over 98% of sprayed insecticides and 95% of herbicides reach a destination other than their target species, including non-target species, air, water and soil. Pesticide drift occurs when pesticides suspended in the air as particles are carried by wind to other areas, potentially contaminating them. Pesticides are one of the causes of water pollution, and some pesticides are persistent organic pollutants and contribute to soil contamination.

In addition, pesticide use reduces biodiversity, reduces nitrogen fixation, contributes to pollinator decline, destroys habitat (especially for birds), and threatens endangered species. Pests can develop a resistance to the pesticide (pesticide resistance), necessitating a new pesticide. Alternatively a greater dose of the pesticide can be used to counteract the resistance, although this will cause a worsening of the ambient pollution problem. Economic losses are associated with virtually all impacts arising from pesticide use. For instance in the US, the annual economic loss is estimated for various pesticides impacts vis-a-vis public health, pesticide resistance in pest, crop losses caused by pesticides, birds losses due to pesticides, ground water contamination, and other exigencies cost that may arise. Thus the financial implications associated with pesticide impart on environmental and human health may be high.

### **Minimizing Pesticide Impact**

Pesticides have the potential to cause harm to the environment if they are not used safely. The potential for environmental damage can be minimized by following label directions, storing pesticides safely, and using them properly. This helps to keep the environment (soil, groundwater and other compartment) free of contaminants, safeguard livestock and human health, and ensure clean healthy environment. Some of the suggested practices are:

### **Integrated Pest Management**

Integrated pest management (IPM) does not rely solely on chemicals for pest control. Biological control, cultural practices, and timely chemical applications are used to obtain the necessary level of control. Pesticides are the last line of defense and are used only when pest levels are

causing sufficient damage to offset the expense of the application. IPM also requires the combination of two or more of the following actions: i). Monitor crops regularly to check the levels of pest populations and their damage, ii). Implement the available non-chemical control practices, including mechanical, cultural and biological controls, sanitation, and plant resistance. For example, use crop rotation to manage corn rootworms and cut alfalfa early to manage weevils (cultural controls); select resistant varieties (plant resistance); thoroughly clean combines between fields to reduce weed seed introductions (sanitation); and use cultivation to control weeds (mechanical control), iii). Maximize the benefits of naturally occurring biological controls by using pesticides only when necessary and selecting pesticides which are the least harmful to beneficial. For example, some insecticides and fungicides kill predatory mites, which can cause mite outbreaks.

### **Prevent back-siphoning and spills**

The hose used for filling a spray tank should never be allowed to extend below the level of the water in the tank. All spills should be contained as quickly as possible and handle according to label directions (the Material Safety Data Sheet (MSDS) information is a useful tool in this regards). Anti-siphon devices should be used in the water line; they are inexpensive and effective.

### **Consideration of weather and irrigation plans**

The application of pesticides just before rainfall or irrigation may result in reduced efficacy if the pesticide is washed off the target crop, resulting in the need to reapply the pesticide. Heavy rainfall may also cause pesticide-contaminated runoff at the application site.

### **Pesticide use and storage**

Always read and follow the label directions on the pesticide container. Use pesticides only when economic thresholds are reached and buy only what you need. Use appropriate protective equipment and clothing according to label instructions. Avoid mixing pesticides near wells or other sources of water. Store all pesticides safely, and according to legal requirements.

### **Safe disposal of pesticide and chemical wastes**

Dispose of excess chemical and pesticide containers in accordance with label directions. Triple-rinse empty pesticide containers (use this water in the spray tank), punch holes in containers, and dispose of them at approved waste disposal sites.

### **Leave buffer zones around sensitive areas**

Read the pesticide label for guidance on required buffer zones around water, buildings, wetlands, wildlife habitats and other sensitive areas.

## **Reduce off-target drift**

Pesticides should not be applied when wind or temperature favours pesticide drift to off target locations and areas. The selection and use of appropriate spray pressure and nozzle will help to minimize drift.

## **Application equipment**

All pesticides and chemicals application equipment should be maintained and kept in good working order. Regular equipment calibration should also be carried out often.

In summary: practicing Integrated Pest Management (IPM), using pesticides that are labeled for the intended crop and pest, consideration of application site characteristics (soil texture, slope, organic matter), consideration of the location of wells, ponds and other water bodies, accurate measurement, maintenance of application equipment and accurate calibration, mixing and loading carefully, preventing back-siphoning and spills, consideration of the impact of weather and irrigation, safe and secure storage of pesticides, safe disposal of wastes, leaving buffer zones around sensitive areas, and reduction in off-target drift, minimizes environmental impact of pesticides use.

## **Alternatives to Pesticides use**

Alternatives to pesticides are available which include methods of cultivation, use of biological pest controls (such as pheromones and microbial pesticides), genetic engineering, and methods of interfering with insect breeding. Application of composted yard waste has also been used as a way of controlling pests. These methods are becoming increasingly popular and often are safer than traditional chemical pesticides. In addition, the US EPA is registering reduced-risk conventional pesticides in increasing numbers.

Cultivation practices include poly-culture (growing multiple types of plants), crop rotation, planting crops in areas where the pests that damage them do not live, timing planting according to when pests will be least problematic, and use of trap crops that attract pests away from the real crop. In the U.S., farmers have had success controlling insects by spraying with hot water at a cost that is about the same as pesticide spraying.

Release of other organisms that fight the pest is another example of an alternative to pesticide use. These organisms can include natural predators or parasites of the pests. Biological pesticides based on entomopathogenic fungi, bacteria and viruses cause disease in the pest species can also be used.

Interfering with insects' reproduction can be accomplished by sterilizing males of the target species and releasing them, so that they mate with females but do not produce offspring. This technique was first used on the screwworm fly in 1958 and has since been used with the medfly, the tsetse fly, and the gypsy moth. However, this can be a costly, time consuming approach that only works on some types of insects.



Another alternative to pesticides is the thermal treatment of soil through steam. Soil steaming kills pest and increases soil health.

### **Push pull strategy**

The term "push-pull" was established in 1987 as an approach for integrated pest management (IPM). This strategy uses a mixture of behavior-modifying stimuli to manipulate the distribution and abundance of insects. "Push" means the insects are repelled or deterred away from whatever resource that is being protected. "Pull" means that certain stimuli (semiochemical stimuli, pheromones, food additives, visual stimuli, genetically altered plants, etc.) are used to attract pests to trap crops where they will be killed. There are numerous different components involved in order to implement a Push-Pull Strategy in IPM.

Many case studies testing the effectiveness of the push-pull approach have been done across the world. The most successful push-pull strategy was developed in Africa for subsistence farming. Another successful case study was performed on the control of *Helicoverpa* in cotton crops in Australia. In Europe, the Middle East, and the United States, push-pull strategies were successfully used in the controlling of *Sitona lineatus* in bean fields. Plus many more cases where this strategy was more beneficial than simply using pesticides on their crops.

Some advantages of using the push-pull method are less use of chemical or biological materials and better protection against insect habituation to this control method. Some disadvantages of the push-pull strategy is that, if there is a lack of appropriate knowledge of behavioral and chemical ecology of the host-pest interactions then this method becomes unreliable. Furthermore, because the push-pull method is not a very popular method of IPM operational and registration costs are higher.

### **Effectiveness**

Evidence showed that alternatives to pesticides can be equally effective as the use of chemicals. In Sweden for example, pesticides use has been halved with hardly any reduction in crops yield. Indonesia farmers have reduced pesticide use on rice fields by 65% and experienced a 15% crop increase. In northern Florida, a study of Maize yields found that the application of composted yard waste with high carbon to nitrogen ratio to agricultural fields was highly effective at reducing the population of plant-parasitic nematodes and increasing crop yield, with yield increases ranging from 10% to 212%; the observed effects were long-term, often not appearing until the third season of the study.

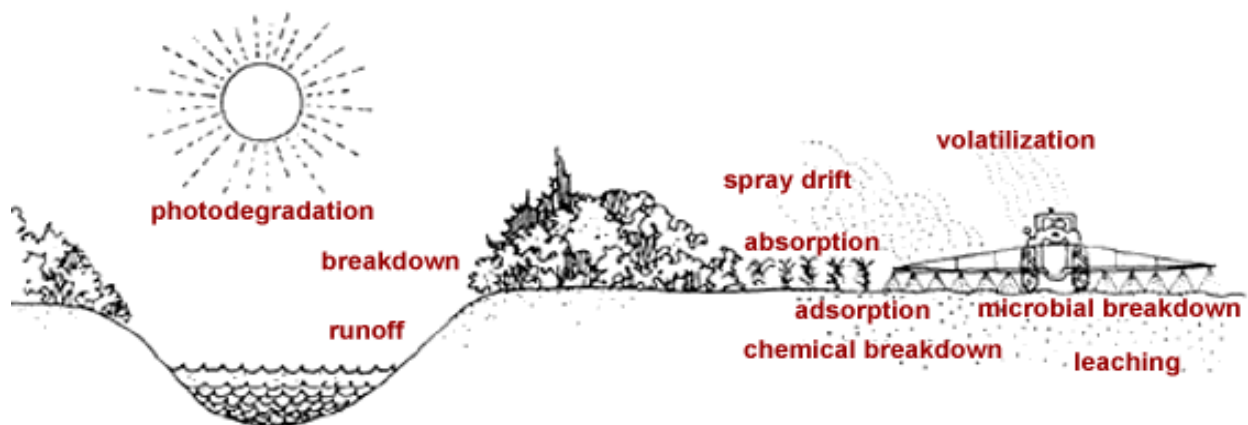
Pesticide resistance is however increasing. In the 1940s, U.S. farmers lost only 7% of their crops to pests. Since the 1980s, loss has increased to 13%, even though more pesticides are being used. Between 500 and 1,000 insect and weed species have developed pesticide resistance since 1945.

## Environmental Fate of Pesticides

The characteristics of pesticides are important factors in determining the fate of the chemicals in the environment. These characteristics include: pesticide solubility in water (water solubility), tendency to adsorb to the soil (soil adsorption), and pesticide persistence in the environment (half-life). Pesticides with high water solubility, low tendency to adsorb to soil particles and long persistence or half-life have the highest potential to move into water. These three factors, soil adsorption, water solubility, and persistence are used to determine pesticides behavior and their potential to leach or move with surface runoff after application. It is the interaction of these factors and their interaction with the particular soil type and environmental conditions that determines pesticide behavior in the field.

The fate of pesticide in the environment is dependent on the type, amount released and its persistence. Thus, when pesticides are released into the environment many things happen to it. Sometimes what happens is beneficial. For example, the leaching of some herbicides into the root zone can give you better weed control. The release of pesticides into the environment can be harmful, because not all the applied chemical reaches the target site. For example, runoff can move herbicides away from target weeds thereby wasting chemicals, and resulting in reduced weed control. This may facilitate more chance of damaging other plants and polluting soil and water. Or some of the pesticide may drift downwind and outside of the intended application site.

Many processes affect what happens to pesticides in the environment. These processes include adsorption, transfer, breakdown and degradation. Transfer includes processes that move the pesticide away from the target site. These include volatilization, spray drift, runoff, leaching, absorption and crop removal, illustrated in the diagram below



## Movement and Absorption of Pesticides in soil: Soil Transfer Processes

**Adsorption and Desorption:** Movement of pesticides in soil is largely controlled by adsorption and desorption mechanism. Adsorption is the binding of pesticides to soil particles, while **desorption** is the release of pesticides from soil particles. The amount a pesticide is adsorbed to or /desorbed from the soil varies with the type of pesticide, soil, moisture, soil pH, and soil

texture. Pesticides are strongly adsorbed to soils that are high in clay or organic matter. They are not as strongly adsorbed to sandy soils. Soil characteristics are important to pesticide movement. Clay soils have a high capacity to adsorb many chemicals including pesticides and soil nutrients. Sandy soils have a much lower capacity to adsorb pesticides. Organic matter in the soil also can adsorb pesticides. Soil structure influences the movement of water and pesticides. Coarse textured sandy soils with large air spaces allow more rapid movement of water than fine textured or compacted soils with fewer air spaces. Other characteristics of the site, such as depth to groundwater, or distance to surface water, are important. Finally, the pattern of water falling on the soil through irrigation or rainfall is significant. Small volumes of water at infrequent intervals are less likely to move pesticides than large volumes of water at more frequent intervals.

Most soil-bound pesticides are less likely to give off vapours or leach through the soil. They are also less easily taken up by plants. For this reason you may require the higher rate listed on the pesticide label for soils high in clay or organic matter.

**Runoff:** This is the movement of pesticides in water over a sloping surface. The pesticides are either mixed in the water or bound to eroding soil. Runoff can also occur when water is added to a field faster than it can be absorbed into the soil. Pesticides may move with runoff as compounds dissolved in the water or attached to soil particles. The amount of pesticide runoff depends on: land topography (slope), texture of the soil, soil moisture content, amount and timing of a rain-event (irrigation or rainfall) and the type of pesticide used

Runoff from areas treated with pesticides can pollute streams, ponds, lakes, and wells. Pesticide residues in surface water can harm plants and animals and contaminate groundwater. Water contamination can affect livestock and crops downstream. Pesticide runoff can be reduced by using minimum tillage techniques to reduce soil erosion, grading surface to reduce slopes, diking to contain runoff, leaving border vegetation and plant cover to contain runoff

Pesticide losses from runoff are greatest when it rains heavily right after you spray. Reduce the chances of runoff by watching the weather forecast. If heavy rain is expected, delay spraying may minimize runoff. If farm is to be irrigated, it should be irrigate according to instructions.

Similar factors influence pesticide movement in surface runoff, except that pesticides with low water solubility may move with surface runoff if they are strongly adsorbed to soil particles and have some degree of persistence.

**Leaching:** This is the movement of pesticides in water through the soil. Leaching occurs downward, upward, or sideways. The factors influencing whether pesticides will be leached into groundwater include characteristics of the soil and pesticide, and their interaction with water from a rain-event such as irrigation or rainfall. Leaching of pesticide depends on pesticide solubility in water, soil textural class especially if the soil is sandy, rainfall or soil wetting/spraying and if the pesticide is not strongly adsorbed to the soil. Leaching can lead to groundwater contamination if pesticides leach from treated fields, mixing sites, washing sites, or waste disposal areas is washed down into groundwater.

**Volatilization:** This is the process of solids or liquids converting into a gas, thus moving away from the initial application site. This movement is called vapour drift. Vapour drift from some herbicides can damage nearby crops. Pesticides volatilize most readily from sandy and wet soils. Hot, dry, or windy weather and small spray drops increase volatilization. Where recommended, incorporating the pesticide into the soil can help reduce volatilization.

**Spray Drift:** This is the airborne movement of spray droplets away from a treatment site during application. Spray drift is affected by spray droplet size - the smaller the droplets, the more likely they will drift; wind speed - the stronger the wind, the more pesticide spray will drift; and distance between nozzle and target plant or ground - the greater the distance, the more the wind can affect the spray

Drift can damage nearby sensitive crops or can contaminate crops ready to harvest. Drift may also be a hazard to people, domestic animals, or pollinating insects. Drift can contaminate water in ponds, streams, and ditches and harm fish or other aquatic plants and animals. Excessive drift also reduces the pesticide applied to the target and can reduce the effectiveness of a treatment.

**Absorption** is the uptake of pesticides and other chemicals into plants or microorganisms. Most pesticides break down once they are absorbed. Pesticide residues may be broken down or remain inside the plant or animal and be released back into the environment when the animal dies or as the plant decays. Some pesticides stay in the soil long enough to be absorbed by plants grown in a field years later. They may damage or leave residues in future crops.

**Crop Removal** through harvest or grazing may remove pesticide residues.

### **Pesticide Degradation or Breakdown Processes**

Pesticides reaching the soil have direct effect on soil microbiological aspects, which in turn influence plant growth. Some of the most important effects caused by pesticides are: alterations in ecological balance of the soil microflora; changes in the soil microflora; adverse effect on soil fertility and crop productivity; inhibition of nitrogen fixing soil microorganisms such as *Rhizobium*, *Azotobacter*, *Azospirillum* etc. and cellulolytic and phosphate solubilizing microorganisms; suppression of nitrifying bacteria, *Nitrosomonas* and *Nitrobacter* by soil fumigants ethylene bromide, Telone, and vapam; alterations in nitrogen balance of the soil; interference with ammonification in soil; adverse effect on mycorrhizal symbioses in plants and nodulation in legumes; and alterations in the rhizosphere microflora, both quantitatively and qualitatively.

Pesticide degradation is the breaking down of toxic pesticides after application into a nontoxic compounds and, in some cases, down to the original elements from which they were derived. They are broken down by microbes, chemical reactions, and light or photo-degradation. The most common type of degradation is carried out in the soil by microorganisms, especially the fungi and bacteria. This process can occur within hours or days to years, depending on environmental conditions and the chemical characteristics of the pesticide. Pesticides which are rapidly degraded are called non-persistent while those which resist degradation are termed

persistent. Pesticides that break down quickly generally do not persist in the environment or on the crop. However pesticides that break down too rapidly may only provide short-term control.

**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 the soil. Soil conditions such as moisture, temperature, aeration, pH, and the amount of organic matter affect the rate of microbial degradation because of their direct influence on microbial growth and activity. The frequency of pesticide applications can also influence microbial degradation. 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 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. Microbial breakdown tends to increase when: temperatures are warm, soil pH is favourable, soil moisture and oxygen are adequate and soil fertility is good. Microbial degradation of pesticides can however be achieved via enzymes and non enzyme catalysis.

## **Enzymatic and Non-enzymatic degradation and conversion of pesticides**

### **Enzymatic Decontamination**

An appropriate mixture of enzymes and other natural products offers considerable advantages over other decontaminants. The enzymes being catalytic are highly efficient and can detoxify many times their own weight of agent in seconds or minutes. Since their first discovery during World War II, a variety of enzymes with activity against nerve agents and numerous organophosphorus pesticides has been identified. Some of the primary enzymes currently under investigation and intended for use are:

### **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  $Zn^{2+}$  ions per sub-unit. The  $Co^{2+}$  substituted enzyme has greater activity on nerve agents and substrates with P-F and P-S bonds.

### **Organophosphorus Acid Anhydrolase**

Organophosphorus Acid Anhydrolase (OPAA) is another Nerve Agent Detoxifying Enzymes which enhances activity of the Bacteria *Alteromonas* sp. in degradation of phosphorus 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  $\text{Ca}^{2+}$  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.

### **Phenoloxidas**es (peroxidases and laccases)

Phenoloxidas

es 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 phenoloxidas

es (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 phenoloxidas

es 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 phenoloxidas

es, while higher nitrogen levels can enhance growth but inhibit the production of enzymes. Therefore, addition of nitrogen to biomixtures is not recommended.

### **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. fenoxyp

rop is more toxic to grassy weeds than fenoxyp

rop-ethyl).

## Degradation of pesticides by actinomycetes

Actinomycetes have considerable potential for the biotransformation and biodegradation of pesticides. Members of this group of Gram-positive bacteria have been found to degrade pesticides with widely different chemical structures, including organochlorines, s-triazines, triazinones, carbamates, organophosphates, organophosphonates, acetanilides, and sulfonylureas. A limited number of these xenobiotic pesticides can be mineralized by single isolates, but often consortia of bacteria are required for complete degradation. Cometabolism of pesticides is frequently observed within this group of bacteria. When compared with pesticide degradation by Gram-negative bacteria, much less information about molecular mechanisms involved in biotransformations of pesticides by actinomycetes is available. Progress in this area has been seriously hampered by a lack of suitable molecular genetic tools for most representatives of this major group of soil bacteria. Overcoming this constraint would enable a better exploitation of the biodegradation and biotransformation abilities of actinomycetes for applications such as bioremediation and construction of transgenic herbicide-resistant crops.

## Hydrolysis of Cyano Groups Pesticides

The cyano group ( $C\equiv N$ ) of herbicides such as cyanazine and bromoxynil can be metabolized via hydrolysis as well. The nitrile group is hydrolyzed to an amide and then to a carboxylic acid. The gene for the bacterial enzyme, nitrilase, has been moved from *Klebsiella* to crop plants to provide bromoxynil tolerance (e.g. cotton).

## Hydrolysis of Amide group pesticides

Amide hydrolysis is probably most important for the acylanilide group of herbicides. The major mechanism of selectivity for barnyardgrass control in rice using propanil, is that rice hydrolyzes propanil using the enzyme, acyl arylamidase. Barnyardgrass has about sixty-fold less acyl arylamidase in its tissue than rice does. Interestingly, some insecticides (carbamates and organic phosphates) act as synergists, by binding to the enzyme and inhibiting propanil hydrolysis resulting in more rice injury.

## Benzoxazinone-Mediated Hydrolysis of Chloro-S-triazines

In roots of atrazine-tolerant corn, the natural product, DIMBOA with water, performs a nucleophilic substitution at the Cl in position 2 of the triazine ring. This non-enzymatic reaction replaces the Cl with an OH at the same position resulting in hydroxyl-atrazine, a Phase I product with much less toxicity and which is now predisposed to Phase II reactions of conjugation.

Note that unlike most chemical catalysts, enzymes with different properties and specificities can be mixed together in a single formulation. This takes advantage of their different activities and properties to provide as broad coverage as possible when in use. For example, if one enzyme is inhibited by a certain metal, other enzymes in the formulation with activity on the same substrate may be either stimulated or unaffected by it. This will ensure that no matter the type or quality of water used, enough of the various enzymes will be functioning to provide the necessary coverage. In addition, since most enzymes function best at pH values near neutrality, there are

few, if any, compatibility or corrosion concerns as long as the material being decontaminated can tolerate water.

**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 the pesticide, determine which chemical reactions take place and how quickly they occur. Because of lack of light, heat, and oxygen in the water-saturated layers of the soil profile below the surface, chemical breakdown is generally much slower than at the surface. Seasonal changes influence groundwater temperatures from 5-10 feet below the ground surface, varying from 39 degrees F to 41 degrees F during the coldest part of the winter to 59 degrees F to 61 degrees F during the hottest part of the summer. Groundwater below 10 to 15 feet maintains a constant temperature of 50 degrees F to 53 degrees F. These low temperatures greatly reduce the rate of chemical breakdown. One of the most common pesticide degradation reactions is hydrolysis a breakdown process where the pesticide reacts with water. Depending on the pesticide, this may occur in both acid and alkaline conditions. 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. The rate and type of chemical reactions that occur are influenced by: the binding of pesticides to the soil, soil temperatures, pH levels - many pesticides, especially the organophosphate insecticides, break down more rapidly in alkaline soils or in spray tank water with a high pH level; and moisture

### **Alkaline Degradation of Pesticides**

Some pesticides are chemically denatured by mixing with alkaline water, or in alkaline soil. As an example, the label of Azatin XL mentions that dilute solutions should be maintained at a pH between 3 and 7, and applied soon after preparation. It states that the diluted solution must not be stored for later use. In order to use this product effectively, you will have to correct the pH of your water before mixing. Azatin is not the only pesticide that degrades rapidly in alkaline water (pH greater than 7). The carbamates and organophosphates are generally more susceptible than chlorinated hydrocarbons or pyrethroids.

The first step in preventing alkaline hydrolysis is to determine the pH of the water used for measuring chemicals. Because of the seasonal variability, it is important to measure the pH several times over the course of the growing season. Samples should be collected in a clean, non-reactive container, such as a glass bottle or jar. The water should be representative of the water used for spraying, so let the water run long enough to flush out the water that was standing in the hose and pipes. The pH should be determined soon after collection, because it can change if it is stored too long.

Buffering agents are available to add to the tank water if the spray chemical is subject to alkaline degradation. Chemical breakdown can take place quickly, before the tank is emptied. If you are using a tank mix, it is important to know that susceptible materials should not be mixed with anything that raises the pH of the solution, such as lime sulfur and liquid ammonia. Also, fixed copper fungicides such as Bordeaux mixture should not be acidified. Copper is more soluble under acid conditions, and so if acidified, more copper will dissolve and could be phytotoxic.



**Stability of Pesticides:** Diazinon is most stable in pH 7 water, with a half life of 10 weeks; at pH 5, it is 2 weeks; Chlorpyrifos (Dursban) at pH 8.0 has a half life of 1.5 days; Malathion is stable at pH 5.0-7.0 but rapidly hydrolyzes in more acidic or alkaline conditions; Carbaryl (Sevin) has a half-life of 24 days at pH 7.0, but only 1 day at pH 9; Bendiocarb (Dycarb) can be less effective if alkaline spray water is used; Azadirachtin (Azatin XL) should be maintained at pH 3-7, and applied soon after mixing; Iprodione (Chipco 26019) rapidly hydrolyzes at pH above 8.0; Mancozeb (Dithane) is most stable at pH 5.5-6.0 and Maneb may be sensitive to alkaline hydrolysis.

**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.

### **Pesticide in food chain**

The transfer of pesticides within a food chain is generally from lower heterotroph to higher heterotroph. The transfer route process is often a cyclic one although straight transfer routes do exist. The movement is often insidious with effect and levels ranging from symptomatic to sub-lethal concentration which does not preclude lethality. A dosing experiment on wood frogs and leopard frogs with very small concentrations of the popular pesticide malathion, showed that the chemical did not kill the frogs directly instead, they died from the indirect effects of the pesticide on tiny zooplankton and the entire food chain. Thus there is need to further investigate the indirect effects of these chemicals on ecosystems.

Direct toxicological impacts on components of food chain populations are hard to decipher. Most toxicity tests study had been on species in isolation from their ecosystems with the aim to determine lethal effects of pesticides on a single species. Regulatory agencies, such as the U.S. EPA, rely on such studies to assess the risks posed by pesticides. These studies use concentrations higher than those found in the environment. In addition, they use single-exposure scenarios, which are unrealistic because ecosystems are continuously exposed to these chemicals through rain and wind. However, most toxicological studies looked at concentrations that have lethal effects on species, without looking at impacts in the medium of exposure.

### **Regulation to Pesticides Use**

#### **International**

In Europe, recent EU legislation has been approved banning the use of highly toxic pesticides including those that are carcinogenic, mutagenic or toxic to reproduction, those that are endocrine-disrupting, and those that are persistent, bio-accumulative and toxic (PBT) or very

persistent and very bio-accumulative. Measures were approved to improve the general safety of pesticides across all EU member states.

Though pesticide regulations differ from country to country, pesticides and products on which they were used are traded across international borders. To deal with inconsistencies in regulations among countries, delegates to a conference of the United Nations Food and Agriculture Organization adopted an International Code of Conduct on the Distribution and Use of Pesticides in 1985 to create voluntary standards of pesticide regulation for different countries. The Code was updated in 1998 and 2002. The FAO claims that the code has raised awareness about pesticide hazards and decreased the number of countries without restrictions on pesticide use.

Three other efforts to improve regulation of international pesticide trade are the United Nations London Guidelines for the Exchange of Information on Chemicals in International Trade and the United Nations Codex Alimentarius Commission. The former seeks to implement procedures for ensuring that prior informed consent exists between countries buying and selling pesticides, while the latter seeks to create uniform standards for maximum levels of pesticide residues among participating countries. Both initiatives operate on a voluntary basis.

Pesticide safety education and pesticide applicator regulation are designed to protect the public from pesticide misuse, but do not eliminate all misuse. Reducing the use of pesticides and choosing less toxic pesticides may reduce risks placed on society and the environment from pesticide use. Integrated pest management, the use of multiple approaches to control pests, is becoming widespread and has been used with success in countries such as Indonesia, China, Bangladesh, the U.S., Australia, and Mexico. IPM attempts to recognize the more widespread impacts of an action on an ecosystem, so that natural balances are not upset. New pesticides are being developed, including biological and botanical derivatives and alternatives that are thought to reduce health and environmental risks. In addition, applicators are being encouraged to consider alternative controls and adopt methods that reduce the use of chemical pesticides.

Pesticides can be created that are targeted to a specific pest's life cycle, which can be environmentally friendlier. For example, potato cyst nematodes emerge from their protective cysts in response to a chemical excreted by potatoes; they feed on the potatoes and damage the crop. A similar chemical can be applied to fields early, before the potatoes are planted, causing the nematodes to emerge early and starve in the absence of potatoes.

### **Pesticide regulation in the United States**

In most countries, pesticides must be approved for sale and use by a government agency. In the United States, the Environmental Protection Agency (EPA) is responsible for regulating pesticides under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) and the Food Quality Protection Act (FQPA). Complex and costly studies must be conducted to indicate whether the material is safe to use and effective against the intended pest. The EPA regulates pesticides to ensure that these products do not pose adverse effects to humans or the environment. Pesticides produced before November 1984 continue to be reassessed in order to meet the current scientific and regulatory standards. All registered pesticides are reviewed every

15 years to ensure they meet the proper standards. During the registration process, a label is created. The label contains directions for proper use of the material. Based on acute toxicity, pesticides are assigned to a Toxicity Class.

Some pesticides are considered too hazardous for sale to the general public and are designated restricted use pesticides. Only certified applicators, who have passed an exam, may purchase or supervise the application of restricted use pesticides. Records of sales and use are required to be maintained and may be audited by government agencies charged with the enforcement of pesticide regulations.

The EPA regulates pesticides under two under main acts, both of which were amended by the Food Quality Protection Act of 1996. In addition to the EPA, the United States Department of Agriculture (USDA) and the United States Food and Drug Administration (FDA) set standards for the level of pesticide residue that is allowed on or in crops. The EPA looks at what the potential human health and environmental effects might be associated with the use of the pesticide.

Additionally, the U.S. EPA uses the National Research Council's four-step process for human health risk assessment: (1) Hazard Identification, (2) Dose-Response Assessment, (3) Exposure Assessment, and (4) Risk Characterization.