CHAPTER-1

INTRODUCTION

1.1 Soil

Soil occupies the pedosphere, one of the Earth's spheres and is a complex structure. Soils are natural unconsolidated materials on the Earth's surface and are composed of solid, liquid and gas. It is a complex mixture consisting mainly of weathered mineral materials from rock and partially decomposed organic molecules and a host of living organisms. However, soil has been defined in many ways according to its utility. The farmer, engineer, chemist and geologist bring different viewpoints or perspectives to the concept of soil. To the engineer and geologist, the soil is no more than finely divided rock materials. The hydrologist sees the soil as a storage reservoir affecting the water balance of the catchments, while the ecologist is interested in only those properties of soil that influence the growth of different plant species. The farmer looks upon the soil as a habitat for plants.

For existence of living beings, soil possesses not only a nucleus position but also ensures their future existence. In our society, soil serves many imperative functions, particularly for production of food. It is the medium for plant growth, means of water storage, supply and purification; it is a modifier of Earth's atmosphere and serves as habitat for living organisms; all of which, in turn modify the soil. It is thus of extreme importance to protect this resource and ensure its sustainability. Therefore, an adequate land management is very essential to maintain the quality of soil in both rural and urban areas.

For agricultural production systems, soil forms a fundamental resource base which meets essential human needs. Besides being the main medium for plant growth, soil functions to sustain plant productivity, maintain environmental quality, and provide nutrition for plants, animals and human health.

1.1.1 Composition of soil

Soil contains mainly five major components which are mineral matter, air, water, organic matter and living organisms. However, the quantity of these components in the soil varies with the locality. Excluding microorganisms, an ideal soil contains about 50% solid space and 50% pore space. Mineral matter and organic matter occupy the total solid space of the soil by about 45% and 5% respectively. The total pore space of the soil is occupied by water and air on 50:50 basis that is in this case 25% water and 25% air. The proportion of water will vary under natural conditions depending upon the weather and environment factors. The percentage of each component shown in Figure 1.1 is the percentage of the soil volume, and each is typical of the top 10-20 cm of a soil. (Nath, T.N. 2010).

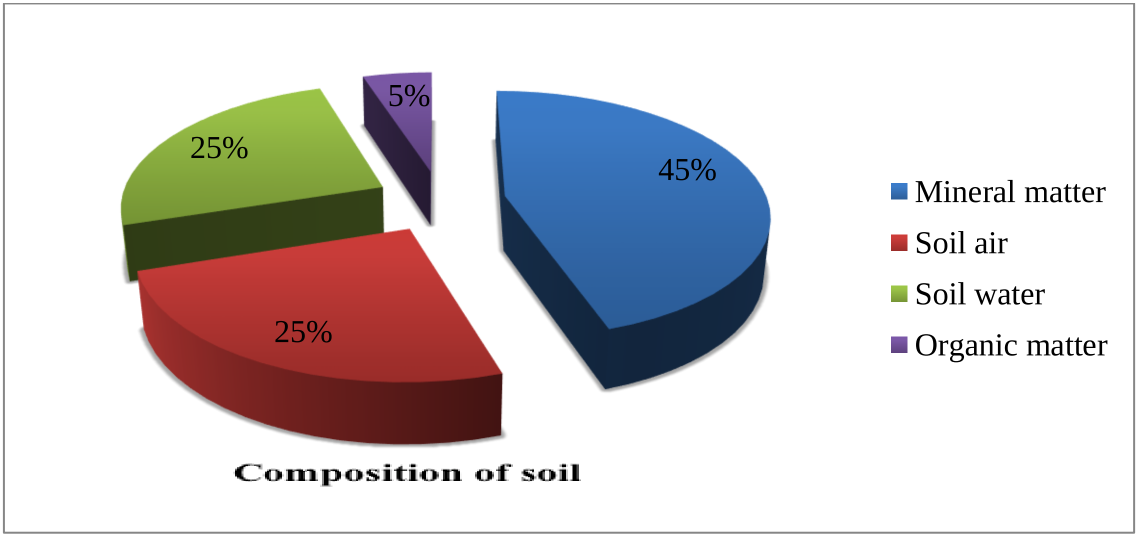


Figure 1.1: Average relative abundances of 4 components of soil

1.1.2 Soil factors for plant growth

Soil is the medium in which crops grow to provide food, cloth and shelter to the world. Soil is the major factor that limits types of vegetation and crops. The basic need of crop production is to maintain soil fertility and soil productivity. Soil fertility is the inherent capacity of soil to provide essential chemical elements for plant growth. Soil fertility in modem day agriculture is a part of a dynamic system. Nutrients are constantly being exported in the form of plant and animal products. Organic matter of plant and soil organisms immobilize, then release, nutrients throughout time. If agriculture production were a closed system, nutrient balance might be relatively stable. Soil productivity is the capacity of soil to produce crops and be expressed in terms of yield. Plant growth depends upon certain external factors such as air, temperature, light, mechanical support, nutrients and water. The plant depends on the soil for all these factors, except light. Each factor directly affects plant growth and is linked to the others.

Essential plant nutrients

The elements required by higher plants for their growth are known as nutrients. Plants need 16 elements for their growth and completion of life cycle. They are: carbon, hydrogen, oxygen, nitrogen, phosphorous, potassium, calcium, magnesium, sulphur, iron, manganese, zinc, copper, boron, molybdenum and chlorine. In addition, four more elements viz., sodium, cobalt, vanadium and silicon have also been established as essential nutrients in some plants. These four nutrients are almost never deficient in soil. On the basis of amount of nutrients present in plants, they can be classified into three groups.

Basic nutrients: The basic nutrients, carbon, hydrogen and oxygen, constitute 96% of the total dry matter of plants. Among them, carbon and oxygen constitute 45% each and hydrogen constitutes nearly 6% of the total tissue. These elements are abundantly present in atmosphere and need not to be applied.

Macronntrients: The nutrients required in large quantities are known as macronutrients. They are N, P, K, Ca, Mg, and S. Among these, N, P and K are called primary nutrients or major nutrients and Ca, Mg and S are known as secondary nutrients. N, P and K are often deficient in soils because of their heavy depletion. The deficiency is corrected by application of fertilizers and manures. Ca, Mg and S are required right from the beginning of the plant growth but in relatively lesser quantity

Micronutrients: The nutrients, which are required in small quantities, i.e. traces are known as micronutrients or trace elements. They are Fe, Zn, Cu, Mn, B, Mo and Cl. Minute quantities of these elements produce optimum effects. In contrast, even a slight deficiency or excess is harmful to the plants. Though micronutrients are required in trace but they are just as important as the major nutrients.

1.1.3 Soil quality

Soil quality describes the soil's ability to perform its crucial functions. The term soil quality has been coined to describe the combination of chemical, physical and biological characteristics that enables soil to perform a wide range of functions. *Soil health* and *soil quality* are terms used interchangeably to describe soils that are not only fertile but also possess adequate physical, chemical and biological properties, within natural or managed ecosystem boundaries, to "sustain plant and animal productivity, maintain or enhance environmental quality and promote plant and animal health” (Doron 1994).

According to the (USDA) Natural Resource Conservation Service, “Soil quality is how well soil does what we want it to do.” Healthy or high quality soil has the following features (Cornell, Soil Health Training Manual, 2009)-

- Good soil tilth
- Sufficient depth
- Sufficient, but not excessive nutrient supply
- Small population of plant pathogens and insect pests
- Good soil drainage
- Large population of beneficial organisms
- Low weed pressure
- No chemicals or toxins that may harm the crops
- Resilience to degradation and unfavorable conditions.

Soil fertility is the only vital component of soil quality. Fertile soils are able to provide the nutrients required for plant growth. It is an utmost necessity to maintain soil fertility as without its maintenance, it is difficult to boost agricultural production for feeding the alarming population. Therefore, to get optimum, sustained and self-sufficient crop production, soil fertility needs to be properly maintained.

Soil health can change over time due to various factors viz. natural events or human induced factors. Good quality soil and congenial climate for productivity are valuable assets for any nation. But, due to urbanization and industrialization, soil is the receptor of many pollutants, including fertilizers, pesticides, manure etc. The inventories of soil productive capacity indicate that human-induced degradation on nearly 40% of the earth's arable land, within the last decade, is basically due to soil erosion, atmospheric pollution, extensive soil cultivation, over-grazing, land clearing, salinization and desertification (Oldeman, 1994). Thus, for optimal soil health, it necessitates balance between soil function for productivity, environmental quality and the overall plant and animal health. However, resistance and resilience to disturbances are characteristics to healthy soil. A soil may not be considered as "healthy" if it not managed sustainably, considering short-term productivity at the expense of future deterioration of soil quality (Doran et al., 1996).

Soil's physical, chemical and biological parameters that are sensitive to changes in the soil management systems can be used as indicator to soil quality. As for example, Soil pH, a measure of the acidity or alkalinity of soil, is an important chemical parameter of soil and can serve as an important indicator of soil quality as acidity influences the ability of plants to grow in soil, the availability of nutrients and the functioning of beneficial organisms. Acidification is a natural soil process, however, can be accelerated by various activities like cropping, excessive use of fertilizers and pesticides, leaching and application of acidic wastes. Thus, any particular soil function operates, depending on the state of the soil at any particular time.

1.1.4 Impact of modern agricultural practices on soil quality

Until the industrial revolution of the early to mid-1900's, farming practices were relatively environmental friendly. During that period, the traditional farms were small-scale, crop yields in agricultural systems depended on internal resources, recycling of organic matter, built-in biological control mechanisms and rainfall patterns, used crop rotation to maintain soil nutrients, included buffer zones at field edges, and involved little or no heavy machinery. In such types of farming systems the link between agriculture and ecology was quite strong and there were seldom-evident signs of environmental degradation. But, as modernization of agricultural practices progressed, the linkage between ecology-farming was often broken as ecological principles were ignored and/or overridden. The application of modern farming practices around the 1950's, resulted in extreme increases in food productivity often to the detriment of environmental quality.

Modern agricultural practices, also known as conventional farming involves intensive tillage, application of inorganic/chemical fertilizers, chemical pest control mechanisms, monoculture, irrigation, and plant genome modification to maximize profit and food production (Gliessman, 1998). There was no doubt that adopting such practices greatly increased crop yields, and agricultural production rose steadily after World War II. However extensive rely on these practices have led to soil degradation which is one of the most serious consequences of conventional agriculture.

There is a common believe that soil contamination is a relatively recent issue however, in reality, it has started long time ago, even though only recently mankind has been aware of its dimension and persistence. In fact, even though soil is a valuable resource and is the support of our ecosystem, man, either by ignorance, or for several purposes, mainly for economic reasons, keeps contaminating soil with various organic and inorganic matters, maintaining the fact that it possesses an infinite assimilation capability. However, only in 1972 (European Soil Charter-Council of Europe, 1972) it was probably recognized that appropriate protection measures that must be implemented as quickly as possible, whenever soil integrity face danger.

Agrochemicals (or agrichemicals) are the various chemical products used in agriculture that improves the quality of crops production. In most cases, *agrochemical* refers to the broad range of pesticides, including insecticides, herbicides, and fungicides. It may also include synthetic fertilizers, hormones and other chemical growth agents, and concentrated stores of raw animal manure. Agrochemicals are used in agricultural setting in an effort to ensure an abundant food supply for the growing population demands for food. However, many negative effects are associated with application of agrochemicals. Some of these agrochemicals, more commonly called pesticides, reach many organisms that were not the intended target. Adding any chemicals to the soil can have far-reaching effects due to the fact that producers rely on soil for their growth. Chemicals from agricultural field repeatedly penetrate the soil, sub-soil and aquifer. This may be consequences of normal management practices followed by the workers or by accidents, thereby the resulting chemical residues in the soil create environment and ecosystems degradation.

Amongst common conventional farming practices, inappropriate and improper use of chemical fertilizers and pesticides, can contribute significantly to the soil degradation process. There is evidence that prolonged and excessive use of heavy doses of fertilisers can result in soils becoming more acidic, which may affect soil quality leading to loss of valuable soil nutrients, which has serious implications in terms of long term and sustainable soil productivity. Inappropriate, viz. imbalanced or excessive, use of fertilisers is a major cause of pollution of ground waters or surface water bodies resulting from inefficient use of applied nutrients. Moreover, many of the chemicals used in pesticides are persistent soil contaminants, whose impact may endure for decades and adversely affect soil conservation. Pesticides enter the soil by various means including spray drift during foliage treatment, wash-off from treated foliage, release from granulates or from treated seeds in soil. The presence and bio-availability of pesticides in soil can adversely affect beneficial plants and soil organisms and even have very serious implication to human and animal health. These are detrimental to many living organisms in the soil, vital to soil health and productivity. Pesticides can even move off-site further contaminating water including both, surface and groundwater and possibly causing adverse impacts on aquatic ecosystems.

It is commonly known that extensive farming uses relatively small amounts of labor and capital. It requires more land than intensive farming practices to produce similar yields as it produces a lower yield per unit of land, so it has a larger crop and grazing Footprint. However, intensive farms, with an aim in achieving higher crop yields, apply various external agricultural inputs to agricultural production systems which include mineral fertilisers such as urea, ammonium nitrate, sulfates, and phosphates; organic fertilisers such as animal manures, composts, and biosolids; various other organic products such as humic acids and microbial inoculants, and pesticides including herbicides, insecticides, nematicides, fungicides, veterinary health products, and soil fumigants. All these products are applied with the ultimate goal of maximizing food productivity to meet the growing food demands and economic returns. However, extensive application of external agricultural inputs to agricultural production systems leads to deterioration of soil quality.

Agricultural practices that use high amounts of external-inputs, such as inorganic fertilizers, pesticides, and other such amendments, can overcome specific soil constraints to crop production. These practices have led to considerable increases in overall food production in different parts of the world. However, especially in the most intensively managed systems, this has resulted in continuous environmental degradation, particularly of soil, vegetation and water resources.

Any misuse of high external inputs (pesticides and chemical fertilizers) for crop production has far reaching effects, which include:

- Deterioration of soil quality and reduction in agricultural productivity due to nutrient depletion, organic matter losses, erosion and compaction
- Pollution of soil and water through the over use of fertilizers and the improper use and disposal of animal wastes
- Increased incidence of human and ecosystem health problems due to the indiscriminate use of pesticides and chemical fertilizers
- Loss of biodiversity due to the use of reduced number of species being cultivated for commercial purposes
- Loss of adaptability traits when species that grow under specific local environmental conditions become extinct
- Loss of beneficial crop-associated biodiversity that provides ecosystem services such as pollination, nutrient cycling and regulation of pest and disease outbreaks
- Soil salinisation, depletion of freshwater resources and reduction of water quality due to unsustainable irrigation practices throughout the world
- Disturbance of soil physicochemical and biological processes as a result of intensive tillage and slash and burning.

In fact, several agricultural scientists have arrived at a general consensus that modern agriculture confronts an environmental crisis. Evidence has accumulated showing that whereas the present capital- and technology- intensive farming systems have been extremely productive and competitive; they also bring a variety of economic, environmental and social problems.

1.2 Pesticides

Pesticides are substances or mixture of substances intended for preventing, destroying, repelling or mitigating any pest. Pesticides form a significant input in modern agriculture and are used for management of pests that are deleterious, destructive or troublesome organisms. A pesticide may be a chemical, 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 vectors for disease or cause nuisance. In agriculture, pesticide includes herbicides (weeds), insecticides (insects), fungicides (fungi), nematocides (nematodes) and rodenticides (vertebrate poisons). They are an essential component of an agricultural industry from viewpoint of economic and effective pest control; therefore, their continued use is an utmost necessity. In 2006 and 2008, it has been estimated that approximately 5.2 billion pounds of pesticides are being used worldwide. The use of fungicides, insecticides and herbicides contribute 10%, 17% and 40% respectively of the total world pesticide use (EPA, 2011).

Although the use of chemicals to combat agricultural pests dates antiquity, the comprehensive utilization of chemicals as major components of pests' management systems is a development of twentieth century. However, types of chemicals in use have changed considerably in response to various environmental concerns that have arises since their introduction.

Pesticides are widely used to control the growth and proliferation of undesirable organisms that, if left unchecked, would cause significant damage to forests, crops, stored food products, ornamental and landscape plants, and building structures. The use of pesticides in both agricultural and non-agricultural settings provides important benefits to society, contributing to an abundant supply of food and fiber and to the control of a variety of public health hazards and nuisance pests.

Pesticides have potential to cause undesirable side effects, owing to the fact that they are designed to be biologically active. These include adverse effects on workers, consumers, community health and safety, groundwater, surface waters, and non-target wildlife organisms. In addition, pesticide use also raise concerns about its persistence and accumulation in various environmental matrices and even in food chains, quite distant from the original point of use of the same, and about the responsibility of certain pesticides in causing various health implications including reproductive failure and endocrine system abnormalities in both wildlife and humans and other species that are not their intended target.

The pervasive use of pesticides for agricultural and non-agricultural purposes has resulted in the presence of their residues in various environmental matrices, such as soil, water and air (Spyros et al., 2003). More than 500 different pesticides formulations are being used in our environment, mostly in agriculture, although the control of biological public health hazards also continues to be an important field of application (Lee et al., 2009). In the last 50 years, pesticides utilization have increased the quantity and improved the quality of food for the growing world population to a great extent. (Lee et al., 2009). It is therefore, crucial to control the use of pesticides, by cautiously weighing the benefits that they confer against any possible adverse effects.

According to the Stockholm Convention on Persistent Organic Pollutants, 9 of the 12 most hazardous and persistent *organic chemicals* are pesticides. However, a number of environmental concerns arise from pesticides use. These include:

1. *Persistence in the environment,*

2. *Toxicity in soil, vegetation and water supplies and*

3. *Impact beyond the target organism including bioaccumulation and its implication for human health.*

1.2.1 Classification of pesticides

Pesticides can be classified in a variety of ways based on target organism, chemical structure and physical state. Pesticides can also be classed as inorganic, synthetic or biologicals (bio pesticides) (American Medical Association, 1997).

The main types of pesticides on the basis of their activity are presented in Table 1.1.

Table- 1.1: Main types of pesticides

TYPE	**ACTIVITY**
Algaecides	Control algae in bodies of water, including swimming pools.
Antimicrobials	Kill microorganisms that produce diseases.
Attractants	Attract specific pests using natural insect chemicals called pheromones that confuse the mating behavior of insects.
Avicides	Control pest birds.
Biopesticides	Naturally occurring substances with pesticidal properties
Defoliants	Cause foliage to drop from a plant.
Desiccants	Aid in the drying process of plants or insects, usually for laboratory purposes.
Fumigants	Produce vapors or gases to control air-borne or soil-borne insects and diseases.
Fungicides	Destroy fungi that infect plants, animals or people.
Herbicides	Control noxious weeds and other vegetation that are growing or competing with a desired species.
Insects Growth Regulators (IGRs)	Accelerate or retard the growth of insects.
Insecticides	Control or eliminate insects that affect plants, animals or people.

Miticides/Acaricides	Kill mites that live on plants, livestock and people.
Molluscicides	Kill snails and slugs.
Nematicides	Kill nematodes, which are microscopic worm like organisms that live in the soil and cause damage to food crops.
Ovicides	Control insect's eggs through the application of low-sulfur petroleum oils to plants and animals.
Piscicides	Control pest fish.
Plant Growth Regulators (PGRs)	Accelerate or retard the growth of a plant.
Predacides	Control vertebrate pests.
Repellents	Repel pests such as mosquitoes, flies, ticks and fleas.
Rodenticides	Control mice, rats and other rodents.

On the basis of ***Chemical structure*** *pesticides can be classified as: -*

Inorganic pesticides*: - eg. Copper sulphate, ferrous sulphate etc. and*

Organic pesticides*: - It includes-*

- **Biologicals** *(botanicals),* **microbial** *(fungi that control certain weeds, subspecies and strains of Bacillus thuringiensis which kill specific insects etc.) pesticides.*
- **Plant derived compounds** *(pyrethroids, rotenoids, nicitinoids etc.) and*

- **Synthetic pesticides**- *It includes:* -
    a) **Organochlorine Insecticides** eg. Aldrin, chlordane, DDT, BHC, dieldrin etc.
    b) **Organophosphate Pesticides** eg. Parathion, malathion, dimethate, quinalphos, etc.
    c) **Carbamate Pesticides** eg. Carbaryl, baygon etc.
    d) **Pyrethroid Pesticides** eg. Allethrin, dimethrin etc.

Prominent insecticide families include organochlorines, organophosphates and carbamates.

- ***Organochlorines*** such as chlorinated pesticides and polychlorinated biphenyls (PCBs) represent important groups of persistent organic pollutants, which have caused worldwide concern as toxic environmental contaminants (Covacia et al., 2005). Organochlorine pesticides (OCPs) are synthetic organochlorines, which are lipophilic and hydrophobic. Their various properties like lipophilicity, hydrophobicity, low vapour pressure, stability to photo-oxidation, and low chemical and biological degradation rates have led to their accumulation in biological tissues succeeding through the food chain and the subsequent magnification of concentrations in organisms (Helberg et al., 2005). They can be recycled through food chains and at the end of the chain produce a significant magnification of the original concentration (Doong et al., 2002). They are even resistant to natural breakdown processes and are tremendously stable and persistent, highly toxic and can also bioaccumulate in the fatty tissues of animals and humans (Forget et al., 2001).

Persistent organic pollutants are ubiquitous contaminants and have been detected far from their sources of origin because of long-range transport stemming from atmospheric exchange, water currents, animal migration and other pathways (Zhang et al., 2007). The Stockholm Convention in 2001, focuses at efforts in minimizing and eventually phasing out POPs globally. Under the Convention, organochlorine pesticides (OCPs), namely aldrin, dieldrin, endrin, chlordane, dichlorodiphenyltrichloroethane (DDT), heptachlor, mirex, toxaphene, hexachlorobenzene (HCB) and industrial chemicals and byproducts, including PCBs, dioxins and furans, constitute the twelve chemical substances and designated as "dirty dozen" and defined.

- ***Organophosphorus*** group, among the various groups of pesticides that are currently being used the world over, forms a major and the most widely used group (Kanekar *et al*., 2004). Schrader in 1930, during World War II, first developed OP pesticides in Germany in the form of tetraethyl pyrophosphate as a by-product of nerve gas development. OPs are acutely toxic and act by inhibiting acetylcholine esterase, an important enzyme in the nervous system (Kanekar *et al*., 2004). On exposure to OPs, the enzyme is unable to function causing accumulation of acetylcholine, which interferes with the transmission of nerve impulses at the nerve endings. Accounting 38 percent of total global pesticide consumption, organophosphorus pesticides forms one of the major groups of pesticides that eventually replace organochlorines to a greater extent against crop loss by pest attack and improving crop yield.

Organophosphorus insecticides, also called organophosphates, are all esters of phosphoric acid which include aliphatic, phenyl and heterocyclic derivatives and have one of the basic building blocks as a part of their complex chemical structure. They are used to control a variety of sucking, chewing and boring insects, spider mites, aphides and pests attacking crops like cotton, vegetables, fruits, sugarcane, peanuts, tobacco, and ornamentals. Some of the main agricultural products are chlorpyriphos, dimethoate, malathion, methyl parathion, monocrotophos, parathion, quinalphos etc.

Several aspects are involved in the fate and behavior of OPs in the environment: effluent irrigation (Muller et al., 2007), photodecomposition mechanisms (Kiss and Virag, 2009), volatilization (Bedos et al., 2009) and finally biodegradation (Singh and Walker, 2006; Muller et al., 2007). Although organophosphates are biodegradable in nature, studies reveal the presence of their residues in various environmental matrices. However, taking into account their toxicity, research on degradation of organophosphates using biological agents is being carried out all over the world.

- ***Carbamates*** group represents a unique class of diverse compounds. The mode of action of these chemicals is similar to the organophosphates and inhibits the acetylcholonesterase. The symptoms of poisoning are cholinergic, salivation, miosis, convulsions and ultimately death. They are reversible inhibitors and are rapidly detoxified and eliminated from animal tissues. Consequently, carbamates do not accumulate in fats and are not excreted in milk. Carbaryl (Sevin), a contact insecticide was first introduced in 1956 (Naidoo and Buckeley, 2003). It is only slightly soluble in water but highly soluble in organic solvents. The compound is mildly phototoxic but toxic to fish (Naidoo and Buckeley, 2003). Bendiocarb, carbofuran, carbaryl, dioxacarb, fenobucarb, fenoxycarb, isoprocarb and methomyl are some of the examples of carbamate insecticides.

- ***Pyrethroids*** pesticides, the chemical compound have been developed to mimic the insecticidal activity of the natural compound pyrethrum. These are non persistent, which is a sodium channel modulators, and are much less acutely toxic in comparison to that of organophosphates and carbamates. Compounds in this group are often applied against household pests. Cypermethrin, cyfluthrin, deltamethrin, etofenprox, fenvalerate, permethrin, phenothrin, prallethrin, resmethrin and tetramethrin are some of the pyrethroids.

Organochlorine pesticides are known to resist biodegradation and therefore they can be recycled through food chains, accumulating in living tissues and even produce a significant magnification of the original concentration at the end of the chain. Recently, organochlorines are largely replaced by organophosphate and carbamates. Both operate through same means, thereby inhibiting the enzyme acetylcholinesterase, allowing acetylcholine to transfer nerve impulses indefinitely and causing a variety of symptoms such as weakness or paralysis (Kamrin, 1997).

Organophosphorus pesticides (OPPs) are a group of very effective compounds widely used in agriculture and residence as insecticides and herbicides (Jauregui et al., 2003). OPPs are regarded as less persistent in the environment than organochlorine pesticides (OCPs) (Ferrando et al., 1992), and this family of chemicals is one of the substitutes for OCPs, which was banned for use in the 1970s (Vonderheide et al., 2003). Organophosphates are quite toxic to vertebrates and have in some cases been replaced by less toxic carbamates.

The WHO Recommended Classification of Pesticides by Hazard was approved by the 28th World Health Assembly in 1975 and has since gained wide acceptance. The classification distinguishes between the more and the less hazardous forms of each pesticide in that it is based on the toxicity of the technical compound and on its formulations. In particular, allowance is made for the lesser hazards from solids as compared with liquids.

On the basis of their acute toxicity, pesticides are classified as (classified by WHO).

a) Extremely hazardous, demarcated in red triangle.

b) Highly hazardous, symbolized by a yellow triangle.

c) Moderately hazardous, marked by a blue triangle.

d) Slightly hazardous.

1.2.2. Pesticide used for the present study

The current study involves use of two most widely used pesticides by the farmers in the study area, namely **malathion** and **quinalphos.**

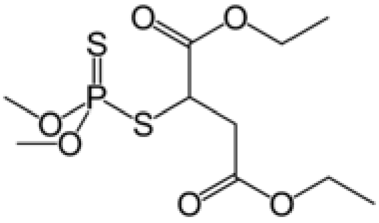
Malathion:

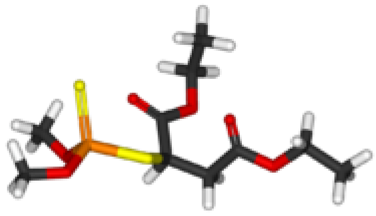
Malathion is an organophosphate parasympathomimetic which binds irreversibly to cholinesterase. Malathion is an insecticide of relatively low human toxicity. Malathion is used for control of household and agricultural pests. High levels of malathion contaminates soil, water and aquatic ecosystems. Organophosphorous group, among the various groups of pesticides that are being used the world over, currently forms a major and most widely used group accounting for more than 36% of the total world market. Malathion is primarily released to soils through direct deposition of spray droplets, which reach the soil surface following aerial spraying, ground spraying, and fogging applications. These releases to soil may occur following applications that are either made directly to soil (public health use in residential areas) or to crops. Releases to soil may also occur as a result of wet deposition of malathion.

Malathion itself is of low toxicity, it mainly concentrates in peel and may not readily removed by washing in water alone but easily enter the body through ingestion, inhalation and absorption through the skin results in its metabolism to malaoxon which is substantially more toxic. Long-term exposure to oral ingestion of malaoxon in rats, showed 61 times more toxic than malathion. It is cleared from the body quickly, in three to five days. Bacteria in soil may break down malathion and sunlight can breakdown malathion in air. It can also combine with water and move quickly through soil. The time it takes to break down to half of the original amount in soil is about 17 days, depending on soil type.

Malathion degradation products include dimethyl phosphate, dimethyldithiophosphate, dimethylthiophosphate, isomalathion, malaoxon and due to cutinase, carboxylesterase, phosphatase enzymatic activity, malathion is degraded into malathion mono and dicarboxylic acid. Malathion kills insects and other animals, including humans, by inhibiting the acetylcholinesterases (AChE) that breaks down acetylcholine a chemical essential in transmitting nerve impulses across junctions between nerves, thus prolonging action potential in nerves, causing spasma, incoordination, convulsions, paralysis and ultimately death.

Malathion





<u>IUPAC name</u>

Diethyl 2-[(dimethoxyphosphorothioyl) sulfanyl] butanedioate

<u>Other names</u>

2-(dimethoxyphosphinothioylthio) butanedioic acid diethyl ester

Malathion, Carbofos, Maldison, Mercaptothion, Orthomalathion

Figure 1.2: Structure of malathion

Physical / Chemical properties:

- Malathion is a colorless to amber liquid with a skunk- or garlic-like odour.
- Chemical formula: $C_{10}H_{19}O_6PS_2$
- Boiling point at 0.093kPa: 156-157°C
- Melting point: 3°C
- Relative density (water = 1): 1.2
- Solubility in water, mg/l: 145
- Vapor pressure: at 30°C: negligible
- Octanol-Water partition co-efficient (log K_{ow}): 2.75, 2.36-2.89
- Molecular weight: 330.4 g/mol
- pH: Mildly acidic
- Solubility (water): 145 mg/L
- Soil Sorption Coefficient (K_{oc}): 30, 93-1800 depending on soil type and environmental conditions.

Toxicity:

- EPA Toxicity- Class III (slightly toxic compound).

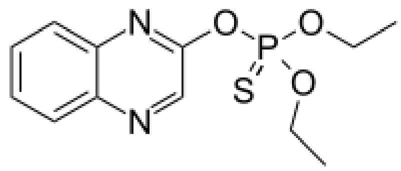
The World Health Organization estimates that 500,000 pesticides poisoning cases occur annually in the world and that 1% are fatal (5000 death/year) (Rosenstock, et al.).

According to the Ministry of Commerce, Government of India, malathion residues were found exceeding the MRL (5 ppb).

Quinalphos:

Quinalphos is an organothiophosphate chemical chiefly used as a pesticide. It is a reddish brown liquid. The chemical formula is $C_{12}H_{15}N_2O_3PS$, and IUPAC name *O*, *O*-diethyl *O*-quinoxalin-2-yl phosphorothioate. Ranked 'moderately hazardous' in *World Health Organization's* (WHO) acute hazard ranking, use of quinalphos is either banned or restricted in most nations. Quinalphos, which is classified as a *yellow label*(highly toxic) pesticide in India, is widely used in the following crops: wheat, rice, coffee, sugarcane, and cotton.

Quinalphos



IUPAC name

O,*O*-Diethyl *O*-2-quinoxalinyl phosphorothioate

Other names

O,*O*-diethyl *O*-quinoxalin-2-yl

phosphorothioateDiethquinalphion;

Diethquinalphione

Figure 1.3: Structure of quinalphos

Quinalphos is a broad-spectrum organophosphorus insecticide and acaricide with good penetrative properties. Because of its broad spectrum application in tea plantation there has been growing concern among the regulation agencies, researcher and environmentalists to know its fate in tea and the surrounding environment. Quinalphos, being an inhibitor of acetylcholinesterase is a very effective, widely accepted broad-spectrum organophosphate pesticide applied as spray and used actively against the pests of cotton, vegetables, rice, groundnut and tea.

Some of its degradation products are stronger inhibitor of AchE than the parent compound. Studies revealed that quinalphos is susceptible to hydrolysis and its degradation is influence by the soil type. It degrades rapidly in soil under aerobic condition with a half-life of 2 weeks (Babu. et al., 1998). Quinalphos in soil is first degraded to form the metabolite Quinoxolin-2-ol followed by complete mineralization to CO_2 and H_2O.

Physical / Chemical properties:

- Appearance: Reddish brown clear liquid.
- Quinalphos content by GLC: 70% (w/w) minimum.
- Boiling point: 142 °C
- Melting point:31 °C (88 °F; 304 K)
- Solubility in water: 17.8 mg/L at 22 °C
- Volatility: volatile.
- Molecular weight: 298.3g/mol.
- Acidity (as H2SO4): 0.4% (w/w) maximum.
- Moisture Content by Karl Fischer method: 0.1% (w/w) maximum.

- Specific gravity at 25OC: 1.04 minimum.
- Material insoluble in acetone: 0.1% (w/w) maximum.

Toxicity:

a) Mammalian toxicity: WHO classification: Class II "moderately hazardous"

b) Environmental toxicity: Quinalphos is highly toxic to fish and birds.

1.2.3. Fate of pesticides in the environment

Several hundred pesticides of different chemical nature are currently used for agricultural purposes all over the world. Because of their widespread use, they are detected in various environmental matrices, such as soil, water and air. Pesticides behave in a variety of ways in the environment following application. In general, the environmental processes that govern the behaviour and fate of a pesticide in soil as well as surface and ground water can be classified into three types (Kerle et al., 1996; Nowell et al., 1999; Logan, 1999).

- ***Transport processes***, which move it away from its initial point of introduction to the environment and throughout the surface-water system;
- ***Transfer processes,*** which control its movement among environmental compartments, such as water, biota, suspended sediment, bed sediment, and the atmosphere; transfer refers to the way in which a pesticide is distributed between solids and liquids (e.g., between soil and soil water), or between solids and gases (as between soil and the air it contains);
- ***Transformation processes*** refer to biological and chemical processes that change the structure of a pesticide or completely degrade it. In general, the short-term behavior

and long-term fate of a pesticide in surface-water systems are controlled by the physical, chemical, and biological properties of the pesticide (which in turn are determined by its chemical structure) and by the environmental conditions in the hydrologic system.

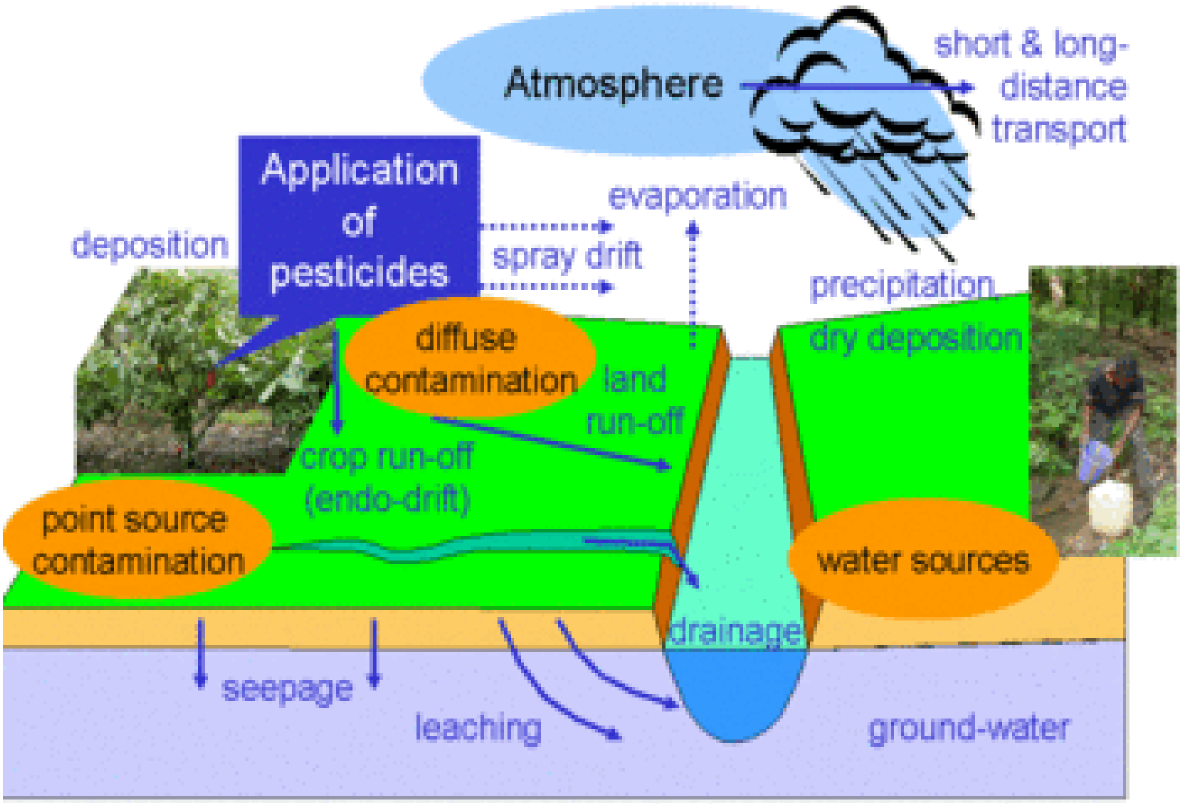


Figure 1.4: Pesticide Pathways (Source: Internet)

1.2.3.1 Transport of pesticides

Pesticides have the potential to move three-dimensionally in many environmental media. The nature of the pesticide and what kind of medium it is transported in will determine the area it will move, the manner it will collect, how fast this will occur, and how long it will reside in the environment. Pesticides can be present anywhere in soil, water, air, and the tissues of organisms (plants, birds, fish, and humans).

- ***Transport of pesticides in air***

Pesticides, regardless of the medium that they are applied in, all have the potential to be transported by air. The releasing process of pesticides into the air from agricultural fields, i.e. pesticide emission occurs from plant canopy or soil surface to the atmosphere. Airborne pesticides can move very long distances and can occur in several ways. They can be carried in the wind during application. Also, they can be transported on small particulates such as soil or on larger objects like leaves that are caught up by wind, and they can volatilize off of any surface that they are applied to.

- ***Transport of pesticides in water***

Water transport of pesticides can occur through wet deposition, run-off from surfaces, infiltration of water through the ground, ditches, storm sewers, tile lines, drains, rivers, and open water currents. Water can behave much like air in terms of transporting pesticides. Pesticides can be relatively mobile when suspended in stream or river flow. Transport down- stream and dispersion within the reservoirs of the hydrologic cycle result in the potential to affect both human and environmental health over a relatively wide area. Pesticides in open water systems may float on the water, diffuse into the water, or deposit onto the sediments at the bottom of the water body. Pesticides that move from the ground surface through the soil may reach shallow ground water or deeper aquifers. Pesticide leaching leads to contamination of subsurface water systems.

- ***Transport of pesticides in soils***

Once a pesticide is in the soil it will most likely follow one of three pathways: (Evangelou, 1998)

- moving through the soil with water,
- attaching to soil particles,
- being metabolized by organisms and/or free enzymes in the soil.

Soil texture (percent sand, silt, and clay) and structure plays a great role in the transport processes of pesticides.

- ***Transport of pesticides in organisms***

Generally, pesticides can accumulate in the tissues of organisms. This process (the so-called bioaccumulation) leads to higher concentrations of pesticide (Evangelou, 1998).Pesticides that bioaccumulate in organisms are often very persistent in the environment. They do not break down easily and retain their form even when ingested and stored in the body. Pesticide-organism interactions are involved in the metabolism, accumulation, and elimination of pesticides by the organism as well as in biodegradation and biological magnification (Fishel et al., 2005). The movement of a pesticide from the place where it entered an organism to its site of action involves the mobility of the pesticide molecule and the efficiency of the transporting mechanism of the plant or animal. The extent of penetration depends on the permeability of the organism to the specific pesticide. This permeability differs significantly among plants and insects and even among different tissues of the same organism. Among animals, tissues of the respiratory and digestive system are usually much more permeable than the skin (Fishel et al., 2005).

1.2.3.2 Transfer of pesticides

Transfer of a pesticide is equivalent to its mobility, being essential for pest control. 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 adsorption/desorption, volatilization, spray drift, runoff, leaching, and uptake. (B.E. Logan, Environmental Transport Processes, John Wiley & Sons, New York 1999).

- ***Adsorption*** is the binding of pesticides to soil particles. Adsorption on soil is an important physicochemical characteristic governing the fate of pesticides in the environment (Kan et al., 1994). The adsorption of pesticides occurs as a result of interactions between a chemical and soil particle. The tendency of a pesticide to leach also depends on how strongly it adsorbs to soil. The amount a pesticide is adsorbed to 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.

As a rule, adsorption decreases with increasing pH and temperature. A pesticide's tendency to be adsorbed by soil is expressed by its adsorption coefficient, as given below:

$$K_{OC} = K_d \times \%\ \textit{Organic carbon in soil}$$

First term is expressed as adsorption coefficient (K_d) and can be calculated by mixing soil, pesticide, and water, then measuring the concentration of pesticide in solution after equilibrium is reached.

$$K_d = \frac{Concentration\ of\ chemical\ adsorbed}{Concentration\ of\ chemical\ dissolved}$$

High Koc values indicate a tendency for the chemical to be adsorbed by soil particles rather than remain in the soil solution. Adsorption coefficients less than 500 indicate a considerable potential for losses through leaching.

Most soil-bound pesticides are less likely to give off vapors 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.

- ***Volatilization*** is the process of solids or liquids converting into a gas, which can move away from the initial application site. This movement is called vapour drift. Vapour drift from some herbicides can damage nearby crops.

  Volatilization as the process of conversion of solid and liquid pesticide into a gas determines its movement with air currents away from the treated surface (Whitford et al., 1995). 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*** 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

- Distance between nozzle and target plant or ground - the greater the distance, the more the wind can affect the spray.

➢ ***Runoff*** determines the movement of water over a sloping surface that occurs when water is applied faster than it enters the soil. Pesticides carried by surface runoff from agricultural areas are a significant portion of the pesticide pollutant loading rates to surface water bodies.

The runoff of pesticides depends on: - (Cohen et al., 1995).

- The slope of the area,
- Soil texture, moisture and erodibility,
- The amount and timing of rainfall and irrigation,
- The presence of vegetation on crop residue,
- Physicochemical properties of the pesticide.

Pesticide runoff can lead to groundwater contamination and can cause injury to crops, livestock or humans if contaminated water is used downstream.

➢ ***Leaching*** is the movement of pesticides through the soil rather than over surface. Leaching of pesticides through soil is an environmental concern because of the possibility that they will reach the water table and contaminate the ground water. However, whether a pesticide will reach the ground- water will depend not only upon its movement through the soil, but also upon its disappearance from the soil.

The most important factors in determining whether a pesticide will leach are its degradation (persistence) capabilities, its sorption characteristics, and its preference to release rapidly into soil solution once it is sorbed. Pesticides that are weakly sorbed by soil and resist degradation are more likely to be leached to ground water than are those that remain bound to soil.

- ***Uptake*** is the movement of pesticides into plants and animals.

  Pesticide uptake depends on:

  - Environmental conditions,
  - Physicochemical properties of pesticide,
  - Physicochemical properties of soil.

The most important factors of influence are the plant species, growth stage, and intended use (Finlayson et al., 1973). Soil characteristics such as the pH, temperature, clay fraction, moisture content, and particularly organic matter content also influence the uptake of pesticides by plants (Kaufman, 1983; Finlayson et al., 1973). In addition, the type of pesticide, the pesticide formulation, the method of application, and the mode of action affect uptake (Kaufman, 1983).

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 absorb pesticides. Organic matter in the soil canal so absorb 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.

Therefore, the disappearance and fate of a pesticide in soil is dependent upon many factors. These may be summarized as follows:

- ***Type of soil:*** composition (clay, silt, sand), structure (bulk density, surface area) and prior treatment (chemical and agricultural);
- ***Type of the chemical:*** physical properties such as solubility, vapor pressure, stability, sensitivity to light, etc., and chemical properties (such as those which affect the ad- sorption and absorption to organic and inorganic com- pounds);
- ***Climatic conditions:*** rainfall, temperature, sunlight, humidity, etc.;
- ***Biological populations:*** type, nutrient requirements, etc.;
- ***Method of application:*** granular, solution, suspension, powder, in organic solvents, as wettable powders, etc.

1.2.3.3 Pesticides degradation or transformation

Pesticide transformation or degradation is the major process of loss for most pesticides after their application. Pesticide degradation refers to the breakdown of pesticides within the environment. A pesticide is susceptible to photo- chemical, chemical, and microbial decomposition (Kuhard et al., 2004; Chen et al., 2005; Ward and Singh, 2004).

Pesticide degradation or breakdown changes most pesticide residues in the environment into harmless non- toxic compounds. Most are degraded or detoxified by physical, chemical and biological treatments before they are released into the environment.

Degradation is detrimental when a pesticide is destroyed before the pest was controlled. Pesticide degradation occurs by different processes (Foght et al., 2001; Leeson et al., 2001; Whitford et al., 1995; Evangelou, 1998; Edgehill and Fin., 1983).

- Microbial degradation,
- Chemical degradation,
- Photodegradation.

➢ ***Microbial degradation:***

Microbial degradation (biodegradation) is the result of microbial metabolism of pesticides, and is often the main source of pesticide degradation in soils. (Waldman and Shevah, 1993; Edgehill and Fin, 1983; Haque and Freed, 1974). It occurs when fungi, bacteria, and other microorganisms in the soil use pesticides as a source of carbon and energy, or consume the pesticides along with other sources of food or energy.

Recent studies have revealed that microorganism consortia often are involved in the degradation phenomenon (Whitford et al., 1995; Van Hamme, 2004; Dua et al., 2002).

A pesticide in soil solution has to move to these microbial colonies and cross the microbial cell membrane into the cell to metabolize. Some microbes produce enzymes, which are exported from the cell to predigest pesticides that are poorly transported. Once inside an organism, a pesticide can metabolize via internal enzyme systems. The ability of microorganisms to degrade or modify compounds depends on the ability to produce requisite enzymes and ideal environmental conditions for the reactions to occur. In addition, sufficient biomass and communication between the pollutant and the enzymes (intracellular or extracellular) is necessary.

The biodegradation rate is dependent on an important group of factors such as:

- Soil conditions - Soil organic matter content, moisture, temperature, aeration, and pH all affect microbial degradation. Microbial activity is high in warm, moist soils with neutral pH.
- Frequency of pesticide application (alternating between different classes, groups or formulations of pesticide can minimize the potential for microbial degradation problems as well as pest resistance).

➢ ***Chemical degradation:***

Chemical degradation or abiotic degradation occurs by different reactions (including hydrolysis, oxidation-reduction, and ionization that usually happen through the presence of acidity or alkalinity) and is, therefore, related to the pH value. (Whitford et al., 1995; Evangelou, 1998).

- **Hydrolysis**

Hydrolysis is the breaking of bonds in a molecule due to reaction with water. Typically a compound is altered in a hydrolytic reaction by the replacement of some chemical groups of a compound with a hydroxyl group. The hydrolysis reactions are commonly catalyzed by the presence of hydrogen or hydroxide ions, and hence the reaction rate is strongly dependent on the pH of the system. Hydrolytic reactions alter the structure of the reacting compound and may change its properties. Depending on the specific reaction, the new compound is usually less toxic than the original compound.

- **Oxidation-Reduction (Redox)**

Oxidation-reduction (redox) reactions involve the transfer of electrons from the reduced species to the oxidized species. The oxidation-reduction potential is an important indicator as it allows the oxidation numbers of the metals present in solution to be controlled and the oxidation state and structure of organics to be changed. (US EPA, OPPTS, 1995).

The redox conditions strongly influence the electron acceptor for microbial activities and thus the biotransformation or biodegradation of chemicals.

- **Ionization**

The fate of toxic organics that are either acids or bases can be strongly affected by the concentration of hydrogen ions in a water body. To the same extent, organic chemicals that partition among the gaseous, solid, and solution compartments could be determined from acid-base interactions between the chemical and the aqueous or soil/sediment components of the environment. Since many toxic organics seem to exist in very low concentrations and are at best only weak acids or weak bases, they will have little influence, if any, on the pH values of the water. The hydrogen ion concentration of the water will, however, determine whether acids or bases exist in neutral or ionic forms (Mills et al., 1985).

➢ ***Photodegradation:***

Photodegradation is the breakdown of pesticides by light (sunlight) and can occur on foliage, on the surface of the soil, and in the air. Photochemical degradation (photolysis) occurs whereby radiant energy in the form of photons breaks the chemical bonds of a molecule (US EPA, 1987).

- Direct photolysis involves direct absorption of photons by the molecule.
- Indirect photolysis involves the absorption of energy by a molecule from another molecule that has absorbed the photons. In indirect photolysis, the two steps are usually combined and the photochemical reaction is characterized by first-order kinetics.

All pesticides are susceptible to photodegradation to some degree. Factors affecting pesticide photodegradation are:

- Intensity of sunlight,
- Time of exposure,
- Properties of the site,
- Method of application,
- Properties of the pesticide.

Pesticides that are applied to foliage or to the soil surface are more susceptible to photodegradation than pesticides that are incorporated into the soil.

1.2.4 Soil persistency of pesticides

Many factors govern the soil persistency of pesticides and its potential for groundwater or surface water contamination. These factors include: properties of the soil, properties of the pesticides, hydraulic loading on the soil and crop management practices. Out of all these factors, properties of pesticides that affect their fate in the environment and the environmental and site conditions that influence these properties are of major significance. The possible fate of a pesticide can be grouped into those that affect **persistence**, including photodegradation, chemical degradation and microbial degradation, and those that affect mobility, including sorption, volatilization, plant uptake, wind erosion, leaching and runoff. Pesticides behave in fairly predictable ways in the environment. To predict environmental fate of pesticides, some of its most important properties that can be used include half-life, water solubility, soil sorption coefficient, and vapour pressure. Other functional parameters for predicting environmental fate include the Groundwater Ubiquity Score, or GUS, which is a number derived from the half-life and the sorption coefficient, and the Henry's law constant, which is a number derived from the water solubility and the vapour pressure.

Persistence of pesticide is often expressed in terms of half-life. This is the length of time required for one-half of the original quantity to break down. Pesticides can be divided into three categories based on half-lives:

- ***Nonpersistent*** pesticides having a typical soil half-life of less than 30 days,
- ***Moderately persistent*** pesticides having a typical soil half-life of 30 to 100 days, or
- ***Persistent*** pesticides having a typical soil half- life of more than 100 days.

Ultimately, the degradation products of any organic chemical will be water, carbon dioxide, and minerals. However, intermediate degradation products of some pesticides are of concern for health or environmental reasons. In these cases, half-life values should be determined for the intermediate products. In general, pesticide residues on canopy foliage or ground cover tend to be less persistent than soil residues.

Pesticides being highly stable organic pollutants are extensively recognized as a problem, besides whatever may be the mechanism of their persistence. Pesticides have been classified according to their volatilization, mobility and persistence characteristic and groundwater pollution potential. Pesticides can be classified in three categories based on their volatilization behaviour, as given in the **Table 1.2**.

Table 1.2: Three categories of pesticides based on volatilization behaviour

Pesticide Category	**Volatilization Behaviour**
Category-1	High Volatile
Category-2	Medium Volatile
Category-3	Low Volatile

On the basis of persistence, pesticides have been classified into five groups as given in the **Table 1.3**. The soil persistency (half-life) of some commonly used pesticides is mentioned in the **Table 1.4**.

Table 1.3: Classification of pesticides with regard to their persistence

Pesticides	**Persistency**	**Classification**
Group 1	$T_{1/2}$ >100days	Very high persistence
Group 2	31days<$T_{1/2}$ <100days	High persistence
Group 3	16days<$T_{1/2}$ <30days	Normal persistence
Group 4	6 days < $T_{1/2}$ < 15 days	Low persistence
Group 5	$T_{1/2}$ < 5 days	Very low persistence

Source: Commission of the European Communities, 1999

Table 1.4: Soil persistency (half-life) of some commonly used pesticides

Sl. No.	Pesticides	Half-life in soil (Days)
1	Endosulfan	60 - 800
2	Chlorpyrifos	60 - 120
3	Imidacloprid	997
4	Monocrotophos	14 - 21
5	Carbofuran	30 - 120
6	Parathion	< 30
7	Methyl parathion	10 - 60
8	Malathion	1 - 25
9	Profenofos	2 - 7
10	Aldicarb	45 - 408
11	Propanil	1 - 3
12	Methomyl	14
13	Mancozeb	1 - 7
14	Quinalphos	13 - 21
15	Cypermethrin	4 - 56

Source: *Compiled from different research papers & EPA's Pesticide FSD*

1.2.5 Impact of pesticides used on soil quality

The quality and health of soil determine agriculture sustainability, environmental quality and, as a consequence of both, it influence plant, animal and human health.

Intensive farming extensively relies on application of chemical pesticides for pest's control. However, extensive application of external agricultural inputs to agricultural production systems leads to deterioration of soil quality. Pesticides are also among the organic (carbon-based) pollutants that impact soil quality. Pesticides, which are very persistent in soil, slowly break down and result in source of contamination (Stephenson and Solomon, 1993).

The presence of man-made chemicals or other alterations in the natural soil environment results in soil contamination or soil pollution. It is typically causes by agricultural chemicals, various industrial activity or improper disposal of wastes.

In this century great efforts have been made to techniques involving extensive mechanization, advanced agricultural practices and the selection of more appropriate plant varieties. The extensive use of pesticides also played an important role in the increase of the world food production. Environmental pollution by pesticides has been identified as one of the major environmental impacts from agriculture (Skinner et al., 1997). Parent compounds as well as metabolites of pesticides have been identified in various environmental components like air (Rudel, 1997), water (Boonyatumanond et al., 1997) and soil (Redondo et al, 1997).

Soil acts as filter, buffer and degradation potentials with respect to storage of pollutant with the help of soil organic carbon (Burauel and Bassmann, 2005), but it is recognized that the soil is a potential pathway of pesticide transport to contaminate water, air, plants, food and ultimately to human via, runoff and sub-surface drainage; interflow and leaching; and the transfer of mineral nutrients and pesticides from soil into the plants and animals that constitute the human food chain (Abrahams,2002).

Once a pesticide gets into the soil, it will most probably follow one of three pathways- *move through the soil with water, attach to soil particles, get metabolized by organisms and/or free enzymes in the soil (Evangelou, 1998).*The ability of the soil to filter, buffer, degrade, immobilize, and detoxify pesticides is an important function of soil. Soil quality also encompasses the impacts that soil use and management can impose on air and water quality, and on animal and human health. The presence and bio-availability of pesticides residue in soil can have unfavourable implications on animal and human health, and beneficial plants and soil organisms. Pesticides can even move off-site, thereby contaminating surface and groundwater and probably causing undesirable impacts on aquatic ecosystems.

In the present world, more than any other environmental contaminants, pesticides in soils continue to be studied, as they are continuously used in present modern agriculture. Though beneficial, many adverse consequences are associated with their application, as they continue to contaminate soil eco-system and also affect the balance equilibrium that exist among various microbial groups and components in the soil. There is also increasing interest in their transformation products (TPs), because they can be present at higher levels in soil than the parent pesticide itself. Most of the pesticides, insecticides etc applied on the crops in due course end as accumulation in the soil. There are a number of ways in which an insecticide reaches the soil and may be more risky in the soil as because, result of their residues which may be comprises of many substances including any specified derivatives such as degradation products, metabolites and congeners might be more hazardous.

The application of pesticides greatly reduces the biodiversity of the soil. The microorganisms of soil are more ruined by soil disturbance by application of various chemicals from different sources than any other parameters. Due to overuse of pesticides, the communities of beneficial microorganisms in soil have declined, which has a negative impact on the available nutrients like nitrogen, phosphorus and potassium (NPK) amount essential for proper plant growth in soil (Sardar and Kole, 2005), thereby degrading the soil quality. Various groups of organisms and the balanced equilibrium existing among them in the soil influence many important processes like mineralization, nitrification and phosphorus recycling. However, excessive pesticidal usage disturbs the presence of soil enzymes, which are essential for the above mentioned processes and for matter turnover. Several studies have been done to analyze the contaminated soil in which various kinds of pesticides residues have been detected (Nawab et al., 2003, Zhang et al., 2006).

With the exception of those chemicals that are deposited at the bottom of oceans, those that were once released into air or water will end up in soils. Among various organic pollutants some referred to as 'POPs,' (persistent organic pollutants), persist for a longer period in the environment, as, they do not break down quickly and thereby result to a range of hazardous consequence. Incessant and excessive use of pesticidal compounds has led to the contamination of several ecosystems with its residues in different parts of the world.

Environmental risk due to soil contamination is of particular concern for agricultural areas, as extensive reliance on agrochemicals for agricultural productions has immensely resulted in the accumulation of various heavy metals in the soil leading to serious consequences. Thus soil contamination with heavy metals poses a threat to a country's food production. Some fertilizers and pesticides are known to contain various levels of heavy metals, including Cd and Cu (Kabata-Pendias and Pendias, 1992). In conventional agriculture, several common pesticides which are fairly extensively used contain substantial concentration of metal which may result their accumulation in soil. Therefore, continuous and heavy application of these agrochemicals and other soil amendments can potentially exacerbate the accumulation of heavy metals in agricultural soils over time (Siamwalla, 1996; Chen et al. 2007).

1.3 Statement of the problem

Environmental pollution is one of the serious predicaments of the modern world. During the last two decades, worldwide usage of pesticides has increased considerably coinciding with changes in farming practices and the increasingly intensive agriculture. Pesticides, particularly insecticides and herbicides form an integral part of modern agricultural practices. The presence of pesticide residues is one of the main problems usually associated with application of pesticides to the soil leading to several adverse consequences. A hundreds of pesticides of different chemical moieties are widely used for agricultural purpose. Soil receives large amounts of pesticides even from bulk handling, direct application at fields or accidental release which result to occasional contamination of a wide range of environmental ecosystems, both water and terrestrial ecosystems, and accumulation of these compounds are associated with many health hazards (Singh *et al*., 2004). Several factors like the resurgence of pests, development of resistance, contamination of soil, water and air, destruction of predators, parasites and other non-targeted organisms including wildlife, brought about the realization that these chemicals are not solely performing the job they are intended to do but also are associated with many adverse effects on ecological systems with which human welfare is inseparably bound. Pesticides contamination of soil has been well documented and scales.

The study area Dimoria Tribal Development Block lies in Kamrup District of Assam. In this region the people practice different land use systems like food agriculture, bamboo plantation, tea plantation, horticulture, agro-forestry, natural forest, shifting cultivation, etc. Dimoria tribal belt area is rich in natural resources. Regarding cropping pattern, it has been found that most of the total cropped area was occupied by the food grains, among food grains, rice cultivation was predominant. The crops, which come next to rice in order of rank, are fruits, vegetables, wheat and maize. The cropping pattern of Dimoria remains traditional without much diversification. Food grains dominate the agricultural economy of the area. The tribal people of the area heavily depend on forest for shifting cultivation, food gathering, building materials and employment. On the other hand, water resource i.e. fishery, ponds, beels, river and swamps provide considerable income to the people. But the resources have not been utilized properly. The tribal communities of Dimoria are traditionally agriculturists. As such their economy, which is at subsistence level, is dependent on land. But due to some historical and socio-cultural reasons these communities have remained very poor in possession of agricultural land. The landholding pattern of the communities is uneven and the level of education is also low among the farmers.

In the recent times, people in the area use a range of pesticides and fertilizers to boost the production of the crops like paddy, vegetables and tea, etc. Soil quality and productivity studies have not been done with emphasis on the application of pesticides. Many farmers are not aware of the environmental as well as health effects of such agrochemicals. Safety guidelines w.r.t pesticides application is not often understood by the people, even if so, the guidelines are not properly followed. Moreover, the fate of these chemicals on the environment has not been documented so far. Therefore, the study on environmental-cum-health risk assessment studies may be regarded as an aid towards a better understanding of the problem. The importance of education and training of workers as a major vehicle to ensure a safe use of pesticides and sustainable agricultural practices is being increasingly recognized. Sound health and wealth of the farmers is the need of the hour.

1.4 Purpose of the study

General agricultural use of pesticides are associated with it potential hazards to man either directly by exposure to toxic residues in food through food chain or indirectly contaminating the environment. Due to the widespread use of pesticides for agricultural and non-agricultural purposes, presence of their residues has been resulted in various environmental matrices, such as soil, water and air (Spyros et al., 2003). The ability of the soil to filter, degrade, buffer, immobilize, and detoxify pesticides is a function or quality of the soil.

Soil fertility or quality assessment is relatively new in Assam and the most of the studies have been confined to urban areas. In Assam, particularly in the study area Dimoria Tribal Development Block, there is an almost dearth of reliable and quantitative data on soil properties (and variations in time and space). Database need to be established to assess the effects of various forms of environmental hazards including pesticides application, and to derive meaningful measures of soil quality in relation to human activities. Accurate soil tests can be an excellent management tool also. The real value of soil testing lies in finding out the information about the available nutrients present in the soil. Scientific assessment of soil quality is essential to monitor the sustainability of agricultural systems. Soil's physical and chemical properties can be used as indicators for assessing soil-quality and for determining the sustainability of farming systems.

In relation with the increasing application of pesticide and insecticides for agricultural purposes and their possible consequences on the environment, it is necessary to study and understand the effect of pesticide and insecticide on various factors including soil quality, microflora and the pesticide utilizing ability of microorganisms. Hence the degradation process of pesticides in different ecosystems universally takes a large space of interest. Although organophosphates are biodegradable in nature, the presence of their residues is found in various environmental matrices. Since organophosphorus pesticides and some of their metabolites are toxic, their degradation in contaminated soil is necessary. Isolating indigenous bacteria capable of metabolizing OP compounds has received substantial attention as these bacterial isolates can provide an environmental friendly means of in situ detoxification of toxic pesticides residues.

1.5 Objectives of the study

The main objective of this research was to assess the contamination levels of organophosphates in the soil to assess the soil quality. Therefore, an attempt was made to analyse the organophosphorus pesticide residues in soil of different land-use of Dimoria Tribal Development Block and to assess the soil quality in terms of its nutrient status along with heavy metal accumulation of the same and also to isolate and characterize bacterial strains capable of degrading pesticide residues with a view of bioremediation of contaminated sites.

Baseline survey: To assess the different types of agrochemicals used and the level of awareness of the cultivator with respect to pesticides used, and possible impacts associated with the handling and disposal of pesticides, in some of the selected landuse systems of Dimoria Tribal Development Block. (Questionnarie method)

The main objectives were –

1. To assess the soil quality of the selected landuse systems of Dimoria Tribal Development Block in terms of its physico-chemical parameters.
2. To analyse the impact of agrochemicals used on heavy metal (Cd, Cu, Cr, Ni, Pb, and Zn) accumulation.
3. To compare the soil quality of the selected conventionally managed systems with that of some selected organically managed systems, in terms of the nutrient status (basically available NPK) to access the impact of agrochemicals on soil quality.
4. To analyse the presence of pesticide residues (malathion and quinalphos) in soil of some pesticides used landuse systems of Dimoria Block.

5. To isolate and characterize the pesticide (malathion and quinalphos) degrading bacteria.
6. To study the effect of temperature, pH, carbon and nitrogen sources on the growth of pesticide degrading bacterial isolates.

1.6 Significance of the study

The research will provide various information regarding various pesticides used in the study area and farmer's level of awareness on key issues like potential impact of pesticides on environment and human health resulting due to improper handling and disposal practices, their presence in the soil.

Soil properties, comprising the physical, chemical and biological parameters that are sensitive to changes in the management can be used as indicator to soil quality. Soil testing is the only way to accurately determine fertility status of a specific field. The present work has been undertaken with a specific view to further strengthen the database on soil quality of the area under study, as analyzing the physico-chemical properties and heavy metals concentrations of the soils of different pesticides used landuse systems will further determine the soil quality, predicting the fertility status of the same. Besides these, the comparative study of the soil quality of conventionally and organically managed system, taking natural forest as a control sample can provide a fruitful result on the impact of agrochemicals application on soil quality. The significance of the present study, therefore, lies in scientific assessment of soil quality to access the impact of pesticides on soil quality, which is essential to monitor the sustainability of agricultural systems. The findings will therefore provide the logistic and basic information regarding sustainable agricultural planning in the study area.

Moreover, bioremediation has been proven a suitable technique for reducing pesticide poisoning. In this context, isolation of various microbial strains can immensely help degrading various pesticide residues and can help in bioremediation of the contaminated sites. When few or no indigenous degradative microorganisms exist in a contaminated area and practically does not allow time for the natural enrichment of suitable population, inoculation may be a convenient option.

1.7 Limitations of the study

Soil is a multidimensional function, and the present study couldn't cover all the aspects. Only representative land use systems were taken into account and the top (0-15 cm) soil was taken to test the fertility and presence of pesticides; sub-soil, was not taken into consideration to estimate its presence. Moreover, soil sampling was done only for two years; replicate samples over years can give an idea about the fate of these chemicals on the environment.

In the present study, a survey of the study area was carried out to assess the extent of widely used pesticides and the farmers' level of awareness on the key issues like on the impacts of pesticide, toxicity of pesticides, handling practices, disposal practices through a well-structured questionnaire and were also ranked accordingly before sample collection and analysis. Random samples of only 20 farmers were chosen to assess their awareness on health and ecosystem. More trials could have been made to understand the problem. Toxicity cases were difficult to determine due to lack of people knowledge and non-diagnosis of the diseases.

On the basis of the survey conducted before sampling, the people of the study area were found to use many pesticides of different classes in their land use systems which includes organophosphorus insecticides like malathion, dimethoate, quinalphos, fungicides like indofil M-45, bavistin, antracol, pyrethroid like decis etc. However, only two pesticides of organophosphorus class namely, malathion and quinalphos were selected for the present study.

Moreover, to assess the impact of pesticides used on soil quality, only physico-chemical parameters and heavy metals concentration of soil were taken into account, focusing mainly on the nutrient status. The biological indicators of soil quality that are commonly measured include respiration, microbial biomass (total, bacterial, fungal, or all of these), microbial biomass carbon and nitrogen, and mineralizable nitrogen was not taken into account due to time constraints. Additionally, there were limitations of GC analysis and instrumentation facility at the right time.