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Study of Dimensions of Soil Pollution by Pesticides in Crop fields of Saran, Chapra, Bihar

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Chapter-I

INTRODUCTION

The worldwide impel for sustainable agriculture systems involve optimizing agriculture resources to gratify human needs and simultaneously maintaining the quality of the environment and uphold natural resources. India being a developing country is facing constraints in agriculture such as land area and immense use of expensive chemical fertilizers & pesticides, such constraints diminish crop yield that is unbearable for the low-income farmers. Due to all these factors the production of crop is inadequate to stay pace with increasing population (Hafeez *et al.*, 2002).

Pesticide application is still the most effective and accepted means for the protection of plants from pest (Bolognesi, 2003). But the extensive use of pesticides over the past four decades has resulted in tribulations caused by the interaction with natural biological system (Ayansina & Oso, 2006). Pesticide seed treatment is frequently used to improve early plant emergence and to control the early attack by the pests. This strategy is familiar as useful in reducing fatalities from seed borne pathogens and seedling damping off agents (Phipps, 1984; Sinclair & Backman, 1989). These Pesticides may harmfully effect the non-target soil microflora (Ayansina & Oso, 2006).

Repeated long term application of pesticides to the soil may cause the chemical to accumulate to the point that it may have deleterious effects on soil microbiological and biochemical activities thereby creating an unhealthy soil having a lasting impact on soil fertility. At present, little is known of such effects and those recorded are restricted to few pesticides and involves changes in single microbial activities or populations, which are regarded as having no importance in terms of overall activity. Recently, the impact of pesticides on microbial populations and their activities as well as on other parameters such as respiration, soil enzymes and other soil biochemical processes, has been studied by several workers. However, most of these studies were undertaken following single applications of pesticides for a short period, which does not represent a real situation in the field. Investigations of the effects of different pesticides would help to understand what might happen in practical situations at local level.

Pesticides are biologically active compounds, formulated to affect target species. They are designed and used for the control of weeds, plant pathogens and animal pests. These products can have different biologically active origins, for example:

1. Natural compounds, such as sulphur;
2. Plant extracts, such as that derived from a daisy flower;
3. Microbes, like virus, bacteria etc;
4. Synthetic chemical compounds, like those used in the pesticides.

Nearly all forms of agriculture, including both organic and conventional farming, require pest control, and pesticides are the most widely used and recognised tool for this job. Organic farming relies on naturally occurring inorganic molecules such as copper or microorganisms like bacteria and viruses; conventional farming uses in addition, synthetic compounds, which are formulated to be efficient and targeted in their action.

There are key factors that determine the effectiveness of a product; the intrinsic properties of its active ingredient formulation, the characteristics of the target organism(s), and the mode of product application. Environmental variables such as local temperature and weather conditions also have influence over the effectiveness of pesticides.

Pesticides contain biologically active compounds and can therefore have direct or indirect unwanted effects on biodiversity. For example, the effective use of herbicides to remove weeds can have the secondary effect of reducing forage for pollinators.

In recent years, research attention has been focused increasingly on environmental pollution and its effects on humans and other creatures. The soil is a primary recipient, intended or otherwise, of many of these waste products and chemicals. Furthermore, once these materials enter the soil, they become part of a cycle that affects all forms of life. At least a general understanding of the pesticides themselves, their reactions in soils, and available means of managing, destroying, or inactivating them is essential.

Now there are thousands of *pesticide* preparations, most of which are used for agricultural purposes and all of which reach the soil. Second is a group of *inorganic pollutants*, such as mercury, cadmium, and lead, which have been discovered in toxic quantities as they move along the food chain. Until now the use of pesticides have proved to be the only means to protect crops on a large scale. However, the effects of pesticides usage must be seen also in the context of soil pollution and sustainability of the agroecosystem. The soil burden resulting from the repeated applications of pesticide chemicals necessary for protection of rice plant is of special concern. Such treatments may suppress soil microflora and hence affect soil properties. Pesticides may have potential to bind to soil, the extent of which depends greatly on the nature of the chemical used. A proportion of the pesticide applied eventually becomes incorporated into the soil. Dispersion of pesticides and their transformation products within the soil environment, or from the soil to other environments, is influenced not only by the properties of pesticides and soil but also the prevailing local climatic conditions. The physico-chemical nature of the soil is important for the persistence, metabolism and binding of pesticides in soil.

Crop losses due to pests, pathogens and weed competition exceeded 40% worldwide. To try to contain these losses, farmers and growers use chemical pesticides. Although pesticides are credited with success in increasing food production and helping to protect man and animals against disease vectors, there are concerns that they have the potential to harm human and environmental health and even compromise the sustainability of agricultural systems.

Part of a pesticide application usually reaches the soil, even if sprayed on the growing crop, and so may have an effect on organisms living in the soil. Therefore, it is important to study the possible effects of specific practices on soil properties. Such possibilities are of particular concern where pesticides are applied at high rates, as occurs in crops such as paddy which often receive applications of several pesticides during a single growing season.

Soil is a dynamic living system with a variety of micro-and macro-flora and fauna including bacteria, actinomycetes, fungi, nematodes, arthropods, crustaceans and earthworms. They play a primary role in the degradation of plant and animal residues and other organic matter in the environment as well as in nitrogen fixation, nitrification and the release of nutrients from soil minerals. Anything that affects their activities might affect the function of soils not only in crop production, but also in the global carbon and nitrogen cycles and in the removal of a range of environmental pollutants.

This requirement has lead to considerable research on the impact of pesticides on soil and their fate and degradation following single applications for short periods.

Soil is one of the major input mechanisms for harmful anthropogenic substances into the atmosphere of different regions. Pesticides are the major components of these toxic substances in soils of agricultural regions. This research examined the occurrence of herbicides in soil and in crop grains from various experimental paddy crop fields of Chapra (Saran, Bihar).

Anthropogenic organic matter including herbicides are now firmly established as major carbonaceous components in the ecosphere. Their occurrence is related to human activities mainly in rural and remote regions (AI-Mutlaq *et al.,* 2002; Beak *et al.,* 1991; Buehler *et al.,* 2001; Cox *et al.,* 1982; Fraser *et al.,* 1997; Menichini, 1992; Rogge *et al.,* 1996; Simoneit, 1989; Simoneit and Mazurek, 1989; Simoneit *et al.,* 1993). Herbicides, consisting of a great variety of synthetic organic compounds, have received attention because some can cause health effects (Beak *et al.,* 1991; Menichini, 1992). Much of the research to date on these compounds have been guided by the mutagenic and genotoxic potential of related compounds found in soil, water and food (e.g.. polycyclic aromatic hydrocarbon (PAH), oxygenated PAH (oxy-PAH), and nitroarenes) (Alsberg *et al.,* 1985; Choudhury, 1982; Schuetzle and Daisey, 1990; Schuetzie *et al.,* 1985; Stenberg *et al.,* 1983; Westerholm *et al.,* 1991). Some pesticide compounds may be relatively stable molecules and could be used to trace and quantify their presence in different environmental spheres.

Since the purpose of pesticides are to kill organisms, it is not surprising that some of them are toxic to specific soil organisms. At the same time, the diversity of the soil organism population is so great that most pesticides do not kill a broad spectrum of soil organisms. It is perhaps surprising that the extensive use of pesticides have not provided more extensive evidence of damage to soil organism numbers. Even so, there is evidence that some commonly used pesticides adversely affect specific groups of organisms, some of which carry out important processes in the soil.

Microbial Metabolism

Biochemical degradation by soil organisms is perhaps the single most important method by which pesticides are removed from soils. Apparently the presence of certain polar groups on the pesticide molecules provides points of attack for the organisms. These groups include -OH, $-COO^-$, $-NH_2$, and $-N0_2$. Chlorinated hydrocarbons (such as aldrin, dieldrin, and heptachlor) are subject to only slow “partial decomposition” since organisms have not adapted themselves to the rapid destruction of such compounds. This helps account for the marked persistence of these compounds in soils and elsewhere. The organophosphate insecticides are degraded quite rapidly in soils, apparently by a variety of organisms. Likewise, the most widely used herbicides, such as 2,4-D, and the carbamates, are readily attacked by a host of organisms.

Persistence in Soils

The persistence of pesticides in soil is a summation of all the reactions, movements, and degradations affecting these chemicals. Marked differences in persistence are the rule. For example, organophosphate insecticides may last only a few days in soil; the most widely used herbicide, 2,4-D, persists in soil for only two to four weeks; chlorinated hydrocarbons may persist from three to fifteen years or longer. The persistence time of hundreds of other pesticides, are between the extremes cited. The majority of pesticides degrade rapidly enough to prevent buildup in soil. Those that do not do so have potential for environmental damage.

Continued use of the same pesticide on the same land can result in the rapid microbial breakdown of the chemical. For example, certain thiocarbamate herbicides that may be used year after year for continuous corn are degraded rapidly in same soils (Fox, 1983). While there is an advantage in relation to environmental quality, the breakdown is so rapid that the herbicide's effectiveness is greatly reduced.

Among the practices suggested to reduce pesticide levels in soils is the addition of easily decomposed organic matter. The growth of high-nitrogen cover crops or the additions of large quantities of animal manures should be helpful. Apparently degradation of even the most resistant pesticides is encouraged by conditions favouring overall microbial action. Other practices suggested to reduce pesticide levels are cropping to plants that accumulate the pesticide, and leaching the soil. Unfortunately, some of these procedures merely transfer the chemical from the soil to some other part of the environment, a process of dubious value.

This introductory review of the behavior of pesticides in soils reemphasizes the complexity of the changes that take place. Pesticides are commonly applied to plant foliage or on the soil surface or are incorporated into the soil. In any case, a high proportion of the chemicals eventually moves into the soil, a fact that adds significance to studies of the fate of these chemicals in soil.

Pesticides Entry Into Crop

Once a pesticide is applied, its entry into the plant is facilitated by absorption through the root, shoot, and stem. Absorption is influenced by morphological characteristics of the plant and chemical and electrical properties of the plant surface. The rate of absorption and the amount of chemical which entered the plant vary with plant species and stage of plant growth. This differential absorption from one plant species to the other determines herbicide activity and selectivity. Once a pesticide enters the plant, it must be transported to the site of action for it to disrupt the metabolic activities of the plant. The translocated pesticide moves from the site of entry to the site of action via the phloem or xylem. But contact pesticide moves very little or not at all from the point of entry. Under certain conditions, contact pesticides are also subjected to limited movement. Many factors like plant species, age of plants, stage of plant development, environmental and soil conditions affecting plant growth, biophysical and biochemical processes within the plant, and inherent properties of the chemicals cause differential movement of pesticide to the sites of action. This determines the activity and selectivity of a pesticide.

Once a pesticide is absorbed into the plant system, it moves either apoplastically or symplastically. The term apoplast is referred to the system of the nonliving interconnecting cell walls, intercellular spaces, and the water-filled and air-filled xylem elements. Thus, apoplastic movement takes place predominantly through the xylem and intercellular spaces. The word symplast is referred to the system of interconnected protoplasm that is connected from cell to cell by means of plasmodesmata, excluding the vacuoles. The sieve tubes are the highly specialized components of the symplast. Generally, the symplast includes the pholem transportation mechanism and the apoplast includes the xylem stream. The cuticle which is a part of the apoplast and the plasma membrane which covers all surfaces of the symplast including the plasmodesmata are the two main barriers that a chemical must penetrate to enter the symplast (Weaver, 1972).

Pesticide that enter the symplast migrate to the phloem and translocate in the lumina of the sieve tubes in the assimilate stream (Crafts and Crisp, 1971). Crafts and Yamaguchi (1964) reported that compounds like 2,4-D are subject to export and accumulation in the living cells during migration across the mesophyll along the sieve-tube conduits.

Once the pesticide has penetrated the cuticle, it moves inside the plant both apoplastically and symplastically. During the symplastic transport, the chief pathway of translocation of the chemical moves with the stream of assimilates from source, i.e. the photosynthesizing leaves, to sink, i.e. the sites of active growth in roots, shoots, flowers, and fruits.

Soil Temperature

Increase in temperature has a beneficial effect on the absorption of phenoxy pesticide due to disorganization of the lipid materials on the cuticle and consequent increased membrane permeability. Similar beneficial effect is also obtained at high humidity which helps in the opening of stomata.

Addition of organic matter to soils of low organic matter content increases the activity of pesticide. Warren (1973) reported that on a soil with 0.7% organic matter propachlor leached out rapidly. However, it performed well on a soil of 3% organic matter, indicating that organic matter enhanced the adsorptive capacity of the soil and hence reduced the leaching losses.

Soil pH

Soil pH affects the detoxification of pesticide by affecting the ionic or molecular character of the chemical, the ionic character and the cation exchange capacity of soil colloids, and the inherent capacity of soil micro-organisms to react with the pesticide. The term soil pH refers to the pH of the soil solution, the water, and other elements that exist in a free state around soil particles. Basically, the pH number is related to the number of hydrogen (H^+) ions in the soil water solution; the more the hydrogen ions, the more acidic the solution becomes. As hydrogen ions decrease, hodroxyl (OH^-) ions increase, making the solution more basic. A pH value of 7 has equal number of hydrogen and hodroxyl ions and it is considered neutral.

Many pesticide are ionic which enables them, when in soil solution, to give off or attract hydrogen ions depending on the pH of the soil solution. For example, 2,4-D, MCPA, etc. which are acidic in character, can release hydrogen ions in a neutral or basic solution, while other pesticide which are chemically basic in nature can accept hydrogen ions in an acidic solution. Another group of pesticide are nonionic in character, and they do not react with water and do not carry an electrical charge. These include metolachlor, etc. Even though they are not ionic, many of them are polar and can be affected by soil pH, but the effect is generally smaller than with the ionic pesticide.

Differences in the pH of the soil affect its ability to adsorb and retain the pesticide molecules. Harris and Warren (1964) found that soil pH influenced pesticide adsorption and that different pesticide responded differently to changes in soil pH. They also observed that as pH was lowered more hydrogen ions were associated with pesticide molecules to give them more cationic characteristics which would lead to more adsorption. Soil pH enhanced adsorption through its effect on the number of soil anion exchange sites and sites for polyvalent cation bridging and hydrogen bonding.

Soil pH also influence the phytotoxicity of pesticide by affecting their adsorption by soil and availability for plant uptakes. Grover, (1968) and Corbin *et al*., (1971) who found an increase in phytotoxicity as the soil pH increased and reached a maximum of 6.5 for the weak aromatic acids like 2,4-D and for the weak bases. They also found an increase in phytotoxicity as soil pH decreased and reached a maximum of 4.3. They observed that soil pH levels between 4.3 and 4.5 had no effect on the phytotoxicity of the weak nonionic pesticide. A change in one pH unit decreased the phytotoxicity of 2,4-D, by a factor of two to four depending on the herbicide and the pH values considered.

In studies Best et al. (1975) found that liming an acid silt loam soil from pH 5.5 to 7.5 increased the phytotoxicity of atrazine and Harrison *et al.,* (1976) reported that phytotoxicity of atrazine was pH-dependent. Best and Weber (1974) found more rapid hydrolysis of atrazine to hydroxyatrazine in soil at pH 5.5 than at pH 7.5.

Soil Moisture

The moisture content of soil system has considerable effect on both the degree of adsorption and the phytotoxicity of pesticide present in the aqueous phase. When a pesticide is applied to the soil it is partitioned into adsorption and solution phases.

Green and Obien (1969) found that the effect of a change in soil water content on pesticide concentration in solution was dependent on the magnitude of adsorption. Their results suggested that pesticide phytotoxicity should increase with increasing soil water content under most circumstances. Baumann and Merkle (1979) found a positive correlation between pesticide phytotoxicity and soil moisture.

Most of the pesticide have lower phytotoxicity at lower soil moisture contents. Bailey and White (1964) attributed this to the degree of competition of the organic compound for the adsorption sites at different moisture levels. Hance (1981, personal communication) observed that competition is important only when not enough water molecules are present to cover all colloidal surfaces. If there is enough water in the system for the plants to take it up, all surfaces will be covered with water, and so the competition phenomenon will not be observed.

Adams *et al.*, (1970) and Rust *et al.*, (1972) reported that the major determinant expressing atrazine injury to oats and soybeans was rainfall occurring during the seedling establishment period. They found that for each inch of rainfall above the minimum level where no injury occurred yields were reduced by 17% for a constant amount of *herbicide* or the amount of atrazine required to reduce yields by a constant amount decreased by 17%.

Of the many chemical characteristics of *herbicides*, molecular structure, charge characteristics, and water solubility have greater influence on *herbicide* adsorption by the soil. The charge on a pesticide molecule may be strong resulting in dissociation, or weak arising from an unequal distribution of electrons producing polarity in the molecule (Adams, 1973). Generally, soil and organic matter particles have negative electrical charges. Pesticide that have strong positive charges are attracted and bound to them. During this process, they either displace the positively charged ions of the soil and organic matter particles or react directly with the hydrogen ions.

Most organic molecules ionize only under certain pH conditions. The pH of ionization may range from -0.5 to 11.2 depending on the functional group in question (Adams, 1973). Compounds that ionize at these extremes would be unlikely to occur as ions in soils. Within the normal pH range of soils, 4.0 to 9.0, dissociation usually takes the form of H^+ loss by acids and H^+ gain by bases. Soil pH affects vapourization of pesticide from soils by influencing their adsorption and through differential ionization properties of the compounds. The degree of dissociation of a pesticide in the soil solution may determine its rate of vapourization. A decrease in pH favours the undissociated form of anionic pesticide such as 2,4-D and increases their potential for vapour loss.

Pesticides reaching the soil become dissipated or removed in the following ways:

(1) Uptake and metabolism by plants, (2) Volatilization, (3) Photo-decomposition, (4) Adsorption, (5) Leaching, (6) Degradation by soil microorganisms, and (7) Chemical degradation.

Pesticides are absorbed and metabolized by plants. They return to the soil, either in the original form or as metabolites, through crop and weed residues.

In the case of postemergence pesticides, in practice only a relatively small percentage (0.1 to 1.0%) of the applied pesticide reaches the crop plants, mostly through spray drift, and the remainder falling onto the weeds or soil. At 1 % level (under directed spraying conditions), the crop plant material at harvest accumulates herbicide residues of 1 ppm. All the pesticide absorbed by the crop, except that retained in the edible parts would eventually return to the soil through plant residues. Residues of pesticides in harvested produce would normally range from undetectable to below 1 ppm (Fryer and Evans, 1968).

The pesticide transport and transformation processes in soil column under transient flow condition are complex. Several complicating factors which control transport of different types of pesticides include: a) pore water velocity, b) evaporation and transformation fluxes, c) concentration gradient and d) seasonal rise and fall of the water table. In general, contamination of soil by pesticides are the result of mass flow and concentration gradient. Physical, chemical and microbial factors affect the process. Selenium transport and transformation in soil column contamination was studied with other researchers (Mirbagheri, 1995; Mirbagheri and Kazemi, 2008; Mirhagheri *et al.,* 2008). Some researches provided a model for predicting the fate of nonvolatile pesticides (Wagenet and Huston, 1987; Wagenet *et al.*. 1989). In many cases, they considered a distribution coefficient (Deeley *et al.,* 1991). Developing models with molecular diffusion and other important factors have been done by other researchers (Jury *et al*., 1983; Kalita *et al.,* 1998).

Leaching pesticides from biological wastes modeled by others (Taube *et al.*. 2002; Vorkamp *et al.,* 1999). DBCP and 2,4-D effects in soil column in unsaturated zone and in groundwater were studied comparing with experimental works (Loague *et al.,* 1998). Models for long-term fate of pesticides in soils is considered in recent years (Schoitz and Bidleman. 2007). Also a study was carried out on the sorption of the sparingly water-soluble pesticide in various types of soil with different levels of organic matter by Zbytniewski and Buszewsk; (2002). Also USDA, forest service, forest health protection (2006) performed experimental works on 2,4-D transport in soil column.

Degradation or Breakdown Processes

Degradation is the process of pesticide breakdown after application. Pesticides are broken down by microbes, chemical reactions, and light or photodegradation. This process may take anywhere from hours or days to years, depending on environmental conditions and the chemical characteristics of the pesticide. 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.

1. **Microbial breakdown** is the breakdown of chemicals by microorganisms such as fungi and bacteria. Microbial breakdown tends to increase when:
    - I. temperatures are warm
    - II. soil pH is favourable
    - III. soil moisture and oxygen are adequate

IV. soil fertility is good

2. **Chemical breakdown** is the breakdown of pesticides by chemical reactions in the soil. The rate and type of chemical reactions that occur are influenced by:

   I. the binding of pesticides to the soil

   II. soil temperatures

   III. pH levels - Many pesticides, break down more rapidly in alkaline soils or in spray tank water with a high pH level.

   IV. moisture

3. **Photodegradation** is the breakdown of pesticides by sunlight. All pesticides are susceptible to photodegradation 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. Pesticides may break down faster inside plastic-covered greenhouses than inside glass greenhouses, since glass filters out much of the ultra-violet light that degrades pesticides.

Chemical and microbial degradation is one of the major pathways by which pesticides are dissipated in soils. Some pesticides have low persistence and thus are either dissipated quickly or are transformed to their daughter products or metabolites. Depending on the chemical structure and environmental conditions, the biodegradation of pesticides, however, is not fully understood, it is known that the availability of soil moisture is required for enhanced biomass activity. The rate of pesticide degradation under saturated soil conditions is also known to be very slow (Goswami and Green, 1971). It is possible that the biodegradation of pesticides may be occurring at a higher rate on farms under sub irrigation since the soil moisture content in the profile is maintained at a higher level.

Although work under other projects resulted in survey and identification of weed flora and in the development of some pest control recommendations, its overall impact on Indian agriculture was only marginal. Many institutions and universities in India like Indian Agricultural Research institute, Punjab Agricultural University, Haryana Agricultural University, G.B. Pant University of Agriculture & Technology, Andhra Pradesh Agricultural University, Vikram University, University of Jodhpur, Calcutta University, Gorakhpur University, have advanced pesticides research programmes manned by full time top or intermediate level weed scientists. Many more universities and research institutions are attempting to initiate pesticide evaluation research programmes. But in most universities and research institutions, weed research is generally limited to herbicide screening and selection, with very little or inadequate attention to the other areas like herbicide residues in soil, integrated weed management, weed biology and competition, etc. (Rao, 1979).

Weed control management should include careful herbicide selection, use of active agent mixtures, alteration of herbicides with different mode of action, and adoption to the cultivated crop, selectivity and persistency. So, if the pesticides are applied at higher rates, they endanger to the safety of environment and the toxicological justification of application, which lead to a limitation of their use. In view of this, the present study has been undertaken to evaluate the dimensions of soil pollution by different herbicides in crop fields of Saran (Chapra), Bihar.

In this context, it is observed that uptill now the impact of pesticides on soil and crops of Saran (Chapra) is not well undertaken and analysed. In this situation it is decided to conduct "study of dimensions of soil pollution by pesticides in crop fields of Chapra (Bihar)”. The findings and suggestions obtained during this research will enhance the economic and health status of rural people of this locality. The facts and findings of this research will also be beneficial for students, teachers, research scholars and other professionals involved in the field of Botany and crop sciences.

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Chapter-II

REVIEW OF LITERATURE

The application of pesticides, to soil can result in the reduction of soil microbial biomass, diversity and activity (Crecchio *et al.,* 2006). Many studies have demonstrated that microorganism communities in soil are significantly affected by the addition of pesticides (Demanou *et al.,* 2006; Gopal *et al.*, 2006; Niemi *et al.*, 2008; Eisenhauer *et al.*, 2009; Lupwayi *et al.,* 2009; Zhang *et al.,* 2009a). Pesticides affect non target soil microorganisms such as non-pathogenic fungi and microbes that are beneficial to the productivity of crops (Bjorlund *et al.*, 1999; Chen and Edwards, 2001; Bending, Rodriguez-Cruz and Lincoln, 2007; Niemi *et al.*, 2008). For example, high application rates of captan and chlorothalonil have been shown to cause shifts in soil nitrogen dynamics and destroy microorganism communities leading to a loss of soil fertility (Chen, Edwards and Subler, 2001). Wakelin *et al.* (2007b) showed that application of the pesticide tolclofosmethyl to maize seeds reduces the number of microorganisms competing with *Fusarium oxysporum* Schltdl. and *F.*

verticillioides Nirenberg thus increasing the possibility of disease. Ferreira *et al.,* (2009) observed that application of the pesticides tebuconazole and mancozeb to crop plants, significantly affected the community structure of soil microorganisms.

Pesticides which target insects and arthropods that exist within and above soil may also alter non-target soil microorganisms. The application of pesticides such as λ-Cyhalothrin (Lupwayi *et al.,* 2009), azadirachtin (Gopal *et al.,* 2006) and nemacur (Abramovich and Steinberger, 2006) cause changes to bacterial community structures in soil at a functional level that leads to a decline in soil fertility. Applications of organophosphate and chlorinated hydrocarbon based pesticides are found to directly kill non-target organisms in soil (Das and Mukherjee, 1999). This leads to increases of available N and P in soil. The increase in N and P following insecticide addition can lead to shifts in fungal diversity due to the increased food source (Das and Mukherjee, 1999; Vig *et al.,* 2008). Biodegradable residues which remain in soil can serve as a food source for certain microorganisms (Robertson *et al.,* 1998; Gomez *et al.,* 1999; Cycori, Wojcik and Piotrowska-Seget, 2009) which favours certain microorganisms that can lead to a change in the microorganism community.

Pesticides such as 2,4-dicholorophenoxy-acetic acid (2,4-D) can lead to an increase in microorganisms which degrade the pesticide; a phenomenon that can significantly affect microorganism community structure in soil (Chinalia and Killham, 2006; Zhang *et al,* 2009b). Glyphosate has been reported to either increase or decrease populations of soil microorganisms (Araujo, Monteiro and Abarkeli, 2003; Lupwayi *et al.*, 2008; Mijangos *et al.,* 2009). Direct toxic effects of pesticides on soil microorganisms have also been observed immediately after application. Glyphosate, 2,4-D and metsulfuron methyl are found to have direct toxic effects on microorganisms (Zabaloy, Garland and Gomez, 2008). Exposure to low concentrations of pesticide over a long period of time can also influence microbial communities in soil. The *in situ* application of phenoxy acid pesticides over 216 days stresses microorganisms and thus changes their functional diversity (de Lipthay *et al.,* 2002). Pesticide induced effects on soil microorganisms can also result in changes to N and P activity in the soil (Perucci *et al.,*1999).

A handful of recent studies have examined pesticide effects on rice. Wang (1994) reported rice seed toxicity exposed to paraquat, 2,4-D, glyphosate, and bromacil. A comparison of herbicidal activity effects on germination and seedling growth of rice and hemp sesbania was conducted by Hirase and Molin (2002). Other studies have examined specific pesticide and other organic contaminant effects on rice (Su and Zhu 2007; TenBrook and Tjeerdema 2006).

Su *et al.*, (2005) reported on the uptake of atrazine by rice seedlings, determining that both atrazine and cadmium were toxic to seedlings. Later studies (Su and Zhu, 2007) determined a decrease in rice seedling transpiration as atrazine concentrations increased, emphasizing the necessity to account for different transport pathways of organic compounds in plant roots. The metolachlor/atrazine mixture in the study resulted in significantly decreased coleoptile growth when compared with controls. This is not completely unexpected, since metolachlor's mode of action is as a seedling shoot growth inhibitor. It is important to keep in mind, however, that referenced studies continued to examine rice at later growth stages.

Very little work was reported on the microbial degradation of amide herbicides. Propachlor undergoes dehalogenation to form two major metabolites, 2-hydroxy-*N*-isopropylacetanilide and bis (*N*-isopropylanilino-*N*-carboxymethylene)oxide, with the former being predominant in the soil. $C0_2$ is liberated from the soil during propachlor breakdown. Beestman and

Deming (1974) observed that the major avenue of dissipation of alachlor, butachlor, and propachlor from soil is by microbial decomposition. Chou and Tiedje (1973) reported that soil fungi degrade alachlor, and release chloride ion. They identified four metabolites in cultures of *Chaetomium globosum.* They were: 2-chloro-2',6'-diethylacetanilide, 2,6-diethyl-*N*-(methoxymethyl)aniline, 2,6-diethylaniline, and 1-chloro-acetyl-2,3-dihydro-7-ethylindole. Incubation of *C. globosum* with the first and second metabolites mentioned above demonstrated further degradation of these products. Fisher (1974) showed that 13% of pronamide was degraded in nonsterilized soils to CO_2 after 33 days indicating that the process was microbially mediated. After 33 days, pronamide accounted for 45% of the extractable residues.

Propanil is rapidly hydrolyzed by *Pencillium piscardium* to yield 3,4-dichloroaniline, and *Geotrichum candidum* converted this to 3,4', 4,4'-tetrachloroazobenzene and other products (Bordeleau and Bartha, 1971). They also isolated two other products, 6-amino-l-ethyl-2-methyl-7-nitro-5-(trifluoro)-ra-benzimidazole, and 6-amino-2-methyl-7-nitro-5-(trifluoromethyl)benzimidazole.

Bromoxynil and ioxynil are extremely effective inhibitors of nitrification in soils. However, soil microorganisms are believed to have an ability to adapt to these pesticides and degrade them. They degrade bromoxynil and ioxynil to the respective benzamide and benzoic acid derivatives. Phenoxy acids are metabolized by various organisms in the soil. Many phenoxyacetic acids are degraded completely or almost completely, with the loss of their aromatic structure and release of their chlorine as chloride ion. The most important pathway of degradation of phenoxy acids, particularly 2,4-D and MCPA, is the removal of the acetic acid side chain by *Arthrobacterium* and *Pseudomonas* to yield the corresponding phenol which is hydroxylated at the *ortho* position to produce a catechol. Catechols are subjected to ortho cleavage of the aromatic ring and converted to muconic acid.

Another pathway of 2,4-D and MCPA break down are dehalogenation by *Pseudonomas* at the 4-position on the aromatic ring and replacement by OH to yield 2-chloro-4-hydroxyphenoxyacetic acid (Fig.-2).

In another pathway, the side chain of 2,4-D and MCPA is removed by *Arthrobacterium* bacteria as a glyoxalate (CHO-COOH), yielding 2,4-dichlorophenol. The released glyoxalate undergoes condensation with decarboxylation and simultaneous incorporation of ammonia to form alanine.

Fungi also degrade phenoxyacetic acid compounds. For example, *Aspergillus niger* hydroxylates 2,4-D at the 2-, *4*- or 2- and 4-positions to yield the corresponding hydroxyphenoxyacetic acids. It is also metabolized by 4-hydroxylation followed by a shift in chlorine position to form 2,5-dichloro-4-hydroxyphenoxyacetic acid. 2,4,5-T is more persistent in soils than 2,4-D, though both of them are structurally related. Alexander (1965) suggested that the resistance of some of the phenoxy acids is related to (a) the type of linkage of the aliphatic acid to the ring and (b) the position or the number of chlorines. His data indicated that the position and not the number of chlorines determined persistence. The results of his study also demonstrated that the two series of substances containing a chlorine in the *meta* position were not metabolized to a significant extent.

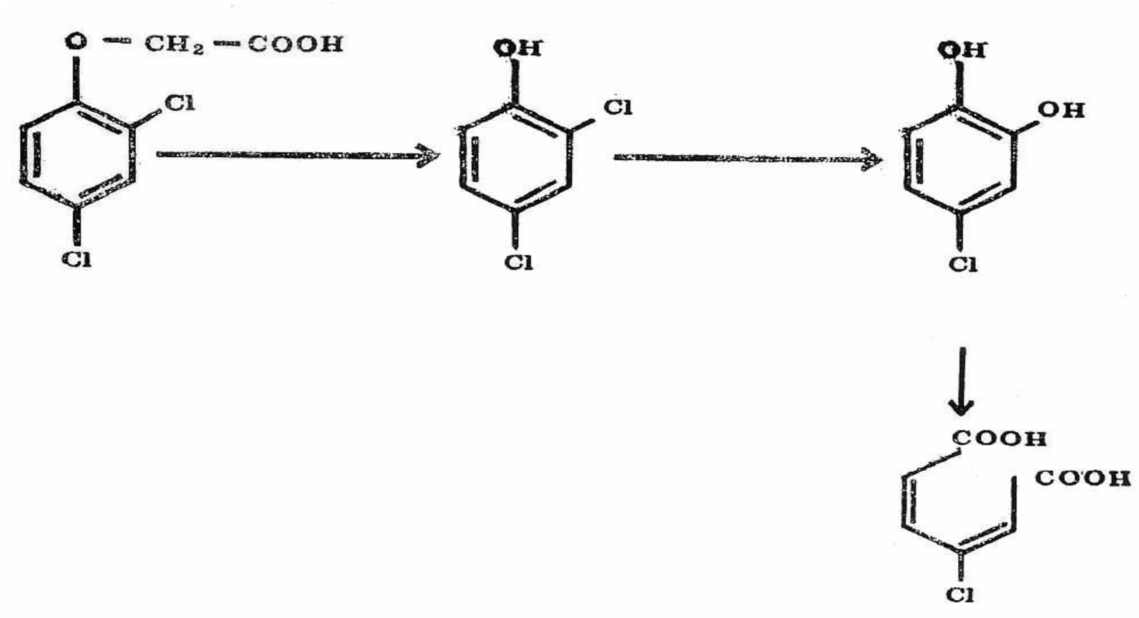

Figure.-1 Pathway of 2,4-D degradation by *Arthrobacterium* and *Pseudomonas* resulting in a phenol, catechol and muconate.

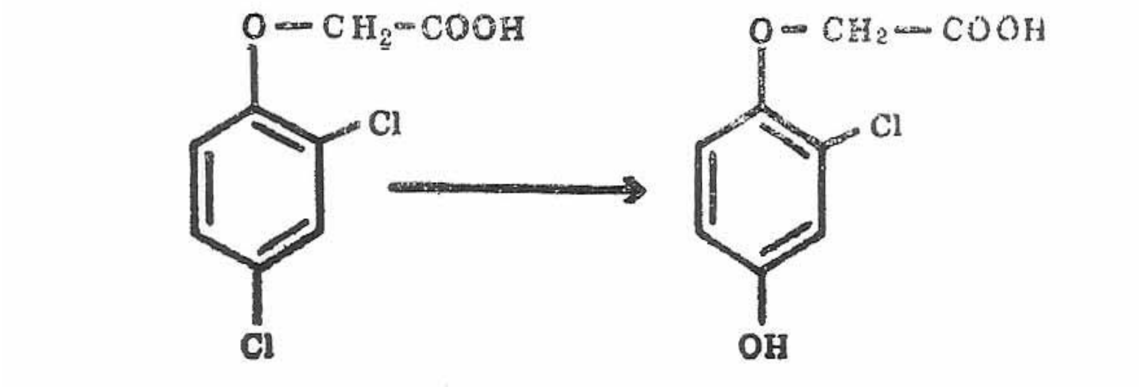

Figure.-2 Degradation of 2,4-D by Pseudomonas through the dehalogenation pathway.

DB is metabolized by *Flavobacterium* by cleavage at the ether linkage to yield 2,4-dichlorophenol, 4-chlorocatechol, butyric acid, and crotonic acid. A fungus *Aspergillus niger* degrades 2,4-DB through *β*-oxidation to form 4-hydroxyphenoxyacetic acid with small amounts of 2-hydroxyphenoxyacetic acid.

For bentazon the results of a study in Brazil show that on average of three years, there was a decreasing of up to 64% of the herbicide concentration on the first seven days of the herbicide application. The average half-life of this herbicide was 2.1 days, with persistence of 20 days, being similar to the values reported by Crosby (1987), which mentioned that the concentration in paddy water fell to 22 p,g Lr^1 in 6 days and was undetectable within 12 days.

In the conducted dissipation study at Brazil, residues of bispyribac-sodium were found up to 60 days after application and the concentration at this time was of 0.3 μg L^{-1}. The average half-life of this herbicide was 5.6 days, with values between 2.0 and 12.4. These results corroborate Sanchez & Tarazona (2006) who reported that the dissipation of bispyribac-sodium in soil is rapid, with half-life of 2 to 7.6 days, while the dissipation in water is highly variable, with half-life of 7.7 to 56 days. Bispyribac-sodium belongs to the toxicological class II, considered very toxic. Clomazone is a quite persistent pesticide being detected in Brazil average up to 30 days, in concordance with the results obtained by Cumming et al. (2002). Clomazone was also the most frequently found pesticide in irrigation water in other studies (Quayle, 2003). The characteristic of this pesticide results in the maintenance of high concentration of clomazone in the rice field enhancing the possibility of environmental pollution. This is very important, since studies conducted with fishes had demonstrated short-term effects of exposure to environmentally relevant concentrations of clomazone on AChE activity in brain and muscle tissue (Crestani *et al.,* 2007; Miron *et al.,* 2005).

For the pesticide imazapic, the persistence in paddy water/ranged from 14 to 39 days, with an average value of 23 days. The average half-life of this pesticide was 10.6, with values between 3.9 and 16.1 days. The higher values were observed when the pesticide was applied in pre- and also in post-emergence.

Related to the herbicide imazethapyr, it presented a middle persistence in paddy water, with detectable residues from 13 to 28 days and an average persistence of 20.3 days. The half-life ranged from 1.6 to 7.1, with average value of 4.4 days. The difference can be related to the application form of the commercial pesticide, which can be in pre- and postemergence, or only pre- or post-emergence. Similar results were reported by Marcolin et al. (2003), which found detectable concentrations of imazethapyr in water up to 30 days after application. Application in pre- and post-emergence had the highest half-life between the different application forms. For imazethapyr, photolysis is a major mechanism for its dissipation in anaerobic conditions, since the microbial degradation of the pesticide in these conditions is almost negligible (Senseman, 2007). Avila (2005) also states that, when applied in pre-emergence, the pesticide has more time for absorption to the soil, reducing its availability in the soil solution. This can affect the photodecomposition of imazethapyr applied. Study presented by Santos *et al.*, (2008) shows that imazethapyr half-life in paddy water varied between 1.6 days, for application at the recommended dose in pre-emergence, and 6.2 days, for application in post-emergence.

Silva *et al.*, (2009) conducted a monitoring study in surface water of rice production areas in seven regions of southern Brazil associated with the rice cropping and stated that imazethapyr, carbofuran and fipronil were detected in all regions studied.

Penoxsulam presented half-life of 12.4 days with relatively high remained concentration for several weeks. Detectable herbicide concentration was observed up to 60 days after the application of the recommended dose in post-emergence. The characteristic of this compound results in the maintenance of high concentration of penoxsulam in the rice field enhancing the possibility of environmental pollution. The penoxsulam is rapidly adsorbed by the soil, except at pH above 8.0 (Senseman, 2007). In flooded soil, the penoxsulam occurs almost exclusively in the dissociated anionic form, but is somewhat persistent in water (Senseman, 2007). The dissipation of penoxsulam is rapid (Jabusch & Tjeerdema, 2006) and occurs mainly by microbial degradation or photolysis (Senseman, 2007).

The herbicide propanil show the shortest persistence, with detectable residues up to the tenth day after application and half-life of 0.8 days. The rapid reduction of the concentration of propanil from 3600 to 0.1 $\mu g\ L^{-1}$ is due to its fast hydrolysis (Barcelo *et al.,* 1998). However, propanil and its metabolite 3,4-dichloroaniline (3,4-DCA) can constitute a risk for surface waters and for human health (Pereira & Hostettler, 1992; Pastorelli *et al.,* 1998). Monitoring studies of surface water carried out in the USA showed that 3% of the 1560 analyzed samples contained propanil in a concentration of up to 2 μg L^{-1} and 3,4-DCA was detected in 50% of the samples with concentration of up to 8,9 μg L^{-4} (EPA, 2006). Studies on the persistence of propanil in irrigated rice conditions conducted by Deul *et al.,* (1977) showed that its dissipation occurs within 24 hours and that the amount of dissipated propanil corresponds to the concentration of 3,4-dichloroaniline (DCA), indicating biological degradation of propanil to DCA.

Crosby (1987) published that in USA, under field conditions, quinclorac dissipated to undetectable levels in 31 days. Vencill (2002) reported that quinclorac present variable mobility depending on soil type and organic matter and it can persist in the soil for one year affecting susceptible crops in rotation programs.

For the herbicide 2,4-D, the persistence in paddy water was 12 days, varying the concentration from 2 to 50 μg L^{-1} at the end of the first week. The average half-life of this herbicide was 1.4 days. In water, the speed of 2,4-D degradation is fast depending on: concentration of nutrients, sediments, dissolved organic carbon and water oxygenation (Sanches-Brunete *et al.*, 1991). Under simulated conditions, studies showed that light is also an important element on 2,4-D degradation, showing that this pesticide under light degradated faster than quinclorac (Lavy *et al.*, 1998).

The situation is often aggravated when discontinuous irrigation cannot maintain a permanent and weed-suppressive flood. This allows weeds to emerge in successive flushes, prompting farmers to use herbicides two times during the growing season. Thus, with rice grown almost all year round, and a large number of chemicals available, the herbicide load on rice soils and waterways must be large. A more recent problem resulting from the repeated use of herbicides has been the development of herbicide resistance in populations of relevant weeds of rice. Propanil [*N*-(3',4'-dichlorophenyl) propionamide]-resistant biotypes of jungle rice abound in rice areas of Colombia and Costa Rica (Fischer *et al.,* 1993; Valverde, 1996). Increasingly frequent and complex pesticide use to control pesticide-resistant weed biotypes has led to the development of multiple resistance (Valverde, 1996). Herbicides, although a much-needed tool, cost Latin American farmers $218 million (U.S. dollars) yearly. Early weed control is almost invariably required to manage the generalized weed infestations resulting from the heavy seed rain in most tropical rice fields. The need for herbicide applications beyond 30 d after rice emergence (DAE) must be clearly justified. Thus, objective decisions on pesticide use, based on cost-benefit analysis, are needed to address high production costs, herbicide resistance, and other possible effects of herbicide overuse on soil microflora. Such analysis requires an objective method for predicting yield losses based upon early assessments of the weed population and other parameters (Kropff, 1988).

Advisory systems based on short and long-term economic analysis have been developed for various crops to assist in the selection of weed control alternatives (Coble and Mortensen, 1992; Lybecker *et al.,* 1991: Wilkerson *et al.*, 1991; Kwon *et al.*, 1995). Such advisory packages must rely on accurate equations to predict crop losses from weed competition. These simple empirical functions can be more widely adopted than more complex ecophysiological competition models. Such mechanistic models are helpful in scientific research, because yield losses can be predicted for different weed and crop growing scenarios (Kropff, 1993), but their parameters can be difficult to estimate, leading to inaccuracies in the final predictions (Kropff and Spitters, 1991).

GENERAL EFFECTIVITY OF PESTICIDES :

Pesticides which are used for preventing or destroying pest is having more negative impact on our ecological system when compared to its desired action. Pesticides are carried by wind to other areas and make them contaminate. Pesticides are also causing water pollution and some pesticides are persistent organic pollutants which contribute to soil contamination. (Rockets & Rusty, 2007).

The amount of pesticide from the intended application area is influenced by the particular chemical's properties: its propensity for binding to soil, its vapor pressure, its water solubility, and its resistance to being broken down over time (Tashkent, 1998)

1. Water:

Pesticides were found to pollute every source of water including wells (Gilliom *et al.*,2007). Pesticide residues have also been found in rain and groundwater (Kellogg *et al.*,2000).Pesticide impacts on aquatic systems are often studied using a hydrology transport model to study movement and fate of chemicals in rivers and streams. Studies by the UK government showed that pesticide concentrations exceeded those allowable for drinking water in some samples of river water and groundwater. (Bingham,2007).

The main routes through which pesticides reach the water are:

i. It may drift outside of the intended area when it is sprayed.

ii. It may percolate, or leach, in the crop soil.

iii. It may be carried to the water as runoff to other crop fields.

iv. It may be spilled accidentally or through neglect during Paddy Cultivation (States of Jersey, 2007).

They may also be carried to water by eroding soil (Papendick *et al.*, 1986). Factors that affect a pesticide's ability to contaminate crop field water include its water solubility, the distance from an application site, weather, soil type, presence of a growing crop, and the method used to apply the chemical.

2. Soil:

Many of the chemicals used in pesticides are persistent soil contaminants, whose impact may endure for decades and adversely affect soil conservation (U.S. Environmental Protection Agency, 2007).The use of pesticides decreases the general biodiversity in the soil. Not using the chemicals results in higher soil quality verified needed, (Johnston, 1986) with the additional effect that more organic matter in the soil allows for higher water retention (Kellogg *et al.,* 2000). This helps increase yields for farms in drought years, when organic farms have had yields 20-40% higher than their conventional counterparts. (Lotter *et al.,* 2003) A smaller content of organic matter in the soil increases the amount of pesticide that will leave the area of application, because organic matter binds to and helps break down pesticides.(Kellogg *et al.*, 2000).

3. Air :

Pesticides can contribute to air pollution . Pesticide drift occurs when pesticides suspended in the air as particles are carried by wind to other areas, potentially contaminating them. (Kellogg *et al.,* 2000). Volatile pesticides applied to crops will volatilize and are blown by winds to nearby areas posing a threat to wildlife (Reynolds, 1997). Sprayed pesticides or particles from pesticides applied as dusts may travel on the wind to other areas, or pesticides may adhere to particles that blow in the wind, such as dust particles (National Park Service, 2006). Compared to aerial spraying ground spraying produces less pesticide drift (U.S. Environmental Protection Agency, PR, 2007). Farmers can employ a buffer zone around their crop, consisting of empty land or non-crop plants such as evergreen trees to serve as windbreaks and absorb the pesticides, preventing drift into other areas.

4. Plants :

Nitrogen fixation, which is required for the growth of higher plants, is hindered by pesticides in soil. The insecticides DDT, methyl parathion, and especially pentachlorophenol have been shown to interfere with legume-rhizobium chemical signaling. Reduction of this symbiotic chemical signaling results in reduced nitrogen fixation and thus reduces crop yields (Rockets & Rusty, 2007). Root nodule formation in these plants saves the world economy $10 billion in synthetic nitrogen fertilizer every year (Fox *et al.*, 2007).

Pesticides can kill bees and are strongly implicated in pollinator decline, the loss of species that pollinate plants, including through the mechanism of Colony Collapse Disorder (Wells, 2007) in which worker bees from a beehive or Western honey bee colony abruptly disappear. Application of pesticides to crops that are in bloom can kill honeybees, (Cornell University, 2007) which act as pollinators. The USDA and USFWS estimate that US farmers lose at least $200 million a year from reduced crop pollination because pesticides applied to fields eliminate about a fifth of honeybee colonies in the US and harm an additional 15%.(Rockets & Rusty, 2007),

5. Animals :

Pesticides inflict extremely widespread damage to biota, and many countries have acted to discourage pesticide usage through their Biodiversity Action Plans. Animals may be poisoned by pesticide residues that remain on food after spraying, for example when wild animals enter sprayed fields or nearby areas shortly after spraying (Palmer *et al.,* 2007).

6. Microbes :

Soil fungi and bacteria are vitally important for nutrient cycling in soil, but may either cause plant diseases or alternatively, protecting plants against pathogens (Liu, Glenn and Buckley, 2008). An important benefit of microbial diversity in soil is that it provides crops with increased resistance to environmental stress and other external abiotic disturbances (Bucher and Lanyon, 2004; Bin-Ru *et al.,* 2005; Brussaard *et al.*, 2007). Microorganisms in soil are often used as bio-indicators of soil quality since they are extremely sensitive to agricultural management practices and are thus widely used in assessing soil health (Bossio *et al.,* 2005; Epelde *et al.,* 2008). Monitoring of bacterial and fungal populations or communities in soil provides a more reliable assay than single parameter analyses such as enzymatic or chemical activity (Avidano *et al.*, 2005).

Soil bacteria are the most metabolic significant group of microorganisms in soil. They are the primary decomposers of organic material and supply the nutrients necessary to enhance plant growth (Bin-Ru *et al,* 2005). They are also responsible for the transformation of NO_3 and NO_2, which are unavailable to plants, into nitrogen which plants can absorb (Gunapala and Scow, 1997). They are also responsible for more specific transformations of nutrients in the soil: the mineralization and solubilization of phosphorus, the oxidation, the reduction and the precipitation of iron and the transformation of inorganic sulphur within soil (Beare *et al,* 1996). Bacteria may also benefit plants directly by forming symbiotic relationships with the roots of plants, e.g. the relationship between nitrogen-fixing bacteria and legumes (Kahindi *et al*, 1996).

Bacteria are found to be most abundant just below the soil surface of crop fields, since nutrients and plant compounds are most abundant in the rhizosphere (Xu *et al,* 2008). Their numbers increase rapidly below this layer of soil to approximately 50 mm deep and then slowly decline as organic carbon decreases. Rhizosphere bacteria provide numerous benefits in terms of buffering plants against pathogen attacks, the solubilization of inorganic nutrients and the production of metabolites promoting plant growth (Hoflich, Wiehe and Hecht- Buchholz, 1995; Kozdroj, Trevors and van Elsas, 2004). They also produce various toxic compounds which can control the activity of plant pathogens. For example, resveratrol has been shown to successfully suppress the appearance of grey mould on grapevines (Paul *et al*, 1998). The phytotoxic substances produced by some soil bacteria can be also used to suppress plant growth and can therefore be used to control weeds (Harris and Stahlman, 1995). The ability of bacteria to reproduce exponentially can also be used to suppress plant pathogens by competing with them for nutrient sources and living space (Kobayashi, Guglielmoni and Clarke, 1995).

Microbes are a vital component of soil due to the crucial role they play in nutrient cycling, toxin removal, decomposition and soil structure (Zhong *et al.,* 2009; Blagodatsky *et al.,* 2010; Yao and Shi, 2010; Garcia-Pausas and Paterson, 2011). Due to their sensitivity towards changes in the environment, microbial organisms are often used as an indicator of soil quality and fertility (Bending *et al.,* 2004; Epelde *et al.,* 2008). Changes in the microbial biomass, functional diversity and structure of soil microbial organisms often serve as parameters indicating changes in structure, fertility, quality and microbial metabolism of soil (Bending *et al.*, 2004; Zhang and Wang, 2006).

In the past, studies concerning the effects of management practices on soil biological properties mainly focused on specific soil organisms, microbial biomass and activity. Recently, more attention has been devoted to investigating microbial diversity over a broader range. Agricultural management practices influence the physical, chemical and biological properties of soil, which impact directly on the habitat of soil microbes. Various tillage practices for example have a significant impact on microbial populations by changing the physical structure of soil. Jin *et al.* (2009) investigated in the effect of different tillage practices on the enzyme activity in soil and demonstrated an increase in microbial biomass and yield in soils with no-tillage and mulching compared to conventional tillage and reduced tillage. Microbial diversity is also affected by tillage practices. Diosma *et al.* (2005) compared the effect of conventional tillage and reduced tillage on microbial diversity and found higher microbial diversity in soil undergoing reduced tillage. Soil compaction is an almost unavoidable factor that effects the physical structure of soil due to the wide use of mechanized farming equipments in conventional agriculture systems. Soil compaction influences soil porosity, water content and respiration, which reduces microbial activity in soil.

Pesticidal non-target effects are reported for the pesticides, glyphosate and 2,4-D, where changes in both microbial activity and community structure were found in herbicide treated soil compared to no pesticide treatment (Zabaloy, Garland and Gomez, 2008; Mijangos *et al.,* 2009).

Soilborne pathogens increase in population size under monoculture cropping and cause between 40-80% yield losses if not controlled (Choi *et al.,* 2006). Grain crops suffer great losses each year due to soilborne pathogens. Several of these soilborne pathogens are found in the Genus *Fusarium,* which can cause severe root rot symptoms on grain crops (Idris, Labuschagne and Korsten, 2006). Traditional control methods for soilborne pathogens are mainly via solarisation and fumigation, but since the worldwide ban on methyl bromide in 2005, alternative control methods had to be found (Horinouchi *et al.,* 2007). Although direct methods such as solarization, biological control agents and applications of fungicides have all shown promising effects in controlling soilborne pathogens (Pavlou and

Vakalounakis, 2004; Choi *et al.*, 2006; Horinouchi *et al.*, 2007), there has been less focus on the use of microbes to control soilborne pathogens.

Microbes can inhibit the development of plant pathogens by means of direct or indirect interactions with host plants and with the pathogen themselves. Direct interference can result from the production of antibiotics and enzymes as well as predatory effects (Wehner *et al.*, 2009; Garcia *et al.*, 2010). Indirect interference can result from competitive interactions with pathogens due to the utilization of common C/N resources (Wehner *et al.*, 2009). Microbes are easily affected by the changes in physical and chemical structure of soil (Lupwayi *et al.*, 2009) and many agricultural amendments have been shown to affect organic matter, moisture, oxygen content and pH in the soil (Chinalia and Killham, 2006; Bending, Rodriguez-Craz, and Lincoln, 2007; Kong *et al.*, 2008; Li *et al*, 2008). These physical and chemical changes can thus enhance or reduce the ability of soil microbes to suppress soilborne pathogens.

Certain agricultural practices may improve the biological properties of soil and suppress plant pathogens. For example, an increase in soil organic matter resulting from the application of animal manure composts, inorganic fertilizers and cover crop residues can provide an abundant food source for soil microbes. This will lead to an increase in total soil microbial biomass and changes in the function and structure of the microbial community (de Lipthay *et al.*, 2002; Forge, Bittman and, Kowalenko, 2004; Chinalia and Killham, 2006; Ratcliff, Busse and Shestak, 2006; Tejada *et al.*, 2007; Gu *et al.*, 2009). The application of liming agents reduces soil acidification and changes the bacterial/fungal ratio in soil, which in turn increases microbial biomass and activity in soil that suppresses soil pathogens (Blagodatskaya and Anderson, 1998; Fuentes *et al.*, 2005). Numerous antagonistic organisms present inside composts have also successfully been used to suppress soilborne pathogens in both laboratory and field experiments (Perez-Piqueres *et al.*, 2005; Choi *et al.*, 2006).

In contrast to the positive effects discussed above, negative effects of agricultural soil amendments that decrease microbial diversity and activity in soil and lead to an increase in disease incidence, have been shown in numerous studies (Smith, Hartnett and Rice, 1999; Chen, Edwards and Subler, 2001; Zabaloy, Garland and Gomez, 2008). For example, the sole application of N rich fertilizers, without supplementary organic matter, decreases soil C content, which in turn decreases microbial biomass and activity (Marschner, Kandeler and Marschner, 2002). Non-target effects of pesticides have been shown to not only decrease total microbial biomass in soil but, also result in changes to the functional diversity of soil microbes (Sigler and Turco, 2002; Ferreira *et al.*, 2009).

Soil microorganisms are significantly influenced by soil pH (Yao, Bowman and Shi, 2006). Wakelin *et al.* (2007a) showed that changes in pH affect microbial diversity in agricultural soil ecosystems as well as microbial enzyme activities. The latter are affected more by a change in pH than changes in organic material (Acosta-Martinez *et al.* 2007). Changes in pH can also affect the community structure of the soil microbial community. Pietri and Brookes (2008) showed that a change in soil pH within a single soil type has significant effects on soil microbial biomass and activity (Bucher and Lanyon, 2004; Kjoller and Clemmensen, 2009) and other amendments which alter soil pH (Yuan and Li, 2007).

The application of liming agents and other pH altering amendments significantly impacts microbial diversity, activity, biomass as well as microbial community structure in soil (Chagnon *et al*, 2000). Comparisons between the effects of pH, pesticides, organic matter and fertilizers, showed that pH plays a more important role in influencing the community composition of microbial organisms (Blagodatskaya and Anderson, 1998;

Fernandez-Calvino *et al.*, 2010). The application of liming agents significantly changes the community composition of microbial organisms. Changes in pH apparently cause shifts in the fungal/bacterial ratio and gram-positive: gram negative ratio in soil (Pietri and Brookes, 2008).

The use of soil microcosms to investigate the effects of soil amendments on soil ecological processes has recently replaced traditional single organism tests (Bogomolov *et al*, 1996). Advantages of using soil microcosms are, an easily controllable environment, low costs and the easily reproducible results they offer. Microcosms are thus a far better method for studying soil microbes than using field trials (Chen and Edwards, 2001). Several ecological studies investigating the effects of herbicide amendments on microbial organisms in soil by using microcosms have provided conclusive proof of changes in microbial activity, biomass and diversity (Burrows and Edwards 2001; Chen, Edwards and Subler, 2001).

The removal of the competitive effect of weeds by pesticide application led to an increase in the participation of the yield components of rice crops and as a result the grain production also increases. Chin *et al.* (2000) reported a significant increase in rice yield after the application of herbicides in comparison with untreated controls. Herbicide treatments for the control of barnyardgrass doubled rice yields in Italian experiments (Tabacchi & Romani 2002). In experiments in Greece, the control of barnyardgrass led to a fourfold increase in rice yields (Ntanos *et al*. 2001). Talbert and Burgos (2007) found that penoxsulam did not injure rice and improved rice yields compared with standard propanil-based programs. Rice treated with penoxsulam (POST) yielded 3110 and 2730 kg/ha with and without the addition of clomazone PRE, respectively, in comparison with 1140 kg/ha in untreated plots (Griffin, 2006).

There is growing concern that potentially toxic chemicals added to the soils may be absorbed by plants in sufficient quantities which are ultimately harmful to human being. In recent past, research attention has been increasingly focused on environmental pollution and its effect on human and other creatures on earth. The soil is a primary recipient, intended or otherwise, of many waste products and chemicals. Furthermore, once these materials enter the soil, they become part of many bio-geo-chemical cycles, that adversely affects all forms of life. A major source of soil pollution especially of crop fields are several pesticides used for agricultural purposes. But as little as one percent of the pesticides applied in crop-field may contact the target organism, much of the remainder moves into the soil. Soil flora may be adversely affected and this problem is compounded by the tendency of these chemicals to build up in organisms as they move through the food chain.

Damage to soil flora of polluted soil, now sounding the warning cry that we must know more about the ecological effects of pesticides if their use is to be continued. Regional field trials are essential for determination of the economic relevance of different herbicides in direction of food safety and food- security in our country.

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Chapter-III

MATERIALS AND METHODS

Pesticides play a very important role in modern agriculture. The use of pesticides has increased rapidly in recent years. Although toxicological data of most pesticides have been documented before pesticides are being marketed, toxic effects are always modified or enhanced depending on the application, methods in various agricultural systems. The side-effects of pesticides therefore have to be considered based on their use and on the regional agricultural system to which a particular pesticide is applied.

General emphasis in this research was placed on the acute toxicity of pesticides, residues on food crops, potential to pollute the environment, effect on the growth of non-target crops, and on the soil microorganisms.

Yield Trials

Yield trials are conducted to determine: (a) the direct effect of the pesticide on the crop (through toxicity), and (b) the indirect effect of the pesticide through weed control. While recording crop yield, data were also collected on toxicity symptoms.

Yield trials are essential for economic evaluation of a particular pesticide or weed control treatment in comparison with the standard recommended pesticide or treatment. Hence, they include only those treatments which are absolutely essential and after thorough testing at screening stage. Thus grain yield of Paddy Crop in our experimental fields were recorded.

Residue Trials

Residue trials, conducted in the field, are useful to determine the duration of pesticide activity, and effects on the following crops in rotation and weed species infesting later. They need to be conducted under different environmental and soil conditions to bring out residual toxicity problems, if any. Five pesticides were tested to establish the full range of residual effects.

Soil and plant samples collected from residue trials were used for quantitative determination of pesticide residues and for understanding the transformation or degradation mechanisms of the pesticide under study. Thus residual pesticides were determined in soil as well as in grains of crop.

Soil factors directly affect the movement of soil-applied pesticides absorbed by roots and shoots. They have an indirect effect on the foliage-applied herbicides through the vigour and growth of the plant.

Soil Water Stress and Temperature

Transport of a pesticide along its pathway is a function of soil water stress and oil temperature because of their effects on transport coefficients and pesticide solubility. Soil water stress and temperature affect the permeability of roots to water and pesticide solution. Under water stress and high temperatures, the rate of penetration of pesticide molecules will be considerably reduced.

Soil water potential affects transpiration, photosynthesis, and root permeability which in turn influence herbicide uptake, translocation, and eventually phytotoxicity. Schreiber *et al.,* (1975) observed that a reduction in soil water potential from -0.35 to -2.50 bars reduced the uptake of bromacil by roots of wheat seedlings, and at this reduced water potential more of the pesticide absorbed remained in the roots rather than being translocated to shoots. Their study suggested that the rate of uptake was controlled by the effect of soil water potential on the apoplastic movement of water and solutes in the root cells.

Water stress may also lead to an increased thickness of the cuticle which results in reduced entry and translocation of foliage-applied herbicides. So, soil moisture and soil temperature of experimental fields were record.

Soil pH

Soil pH has profound effects on the uptake of pesticides by roots. Changes in soil pH affect the cation exchange capacity of soils.

The ionic nature of certain pesticides is a function of pH. Many acid herbicides have values lower than the pH of the soil to which they are applied and they exist primarily in ionic form in the soil environment. Generally, pesticides exist in the ionic form in the soil between pH 4.3 and 7.5, with an increase in ionic concentration being proportional to an increase in pH. The negatively charged functional groups in the soil predominate at pH above 5.3 and they repel the anionic form herbicides like 2,4-D anionic. Thus soil pH of our experimental fields were also recorded periodically.

Soil organic matter and the type of clay predominant in the soil which influence movement, availability, and absorption of herbicides in the soil, also affect their uptake and transport.

Materials:

Penetration of translocated pesticides has relationship with their concentration. At supraoptimal concentrations, pesticides may cause physiological injury more rapidly, thus precluding the normal rate of absorption and translocation. In this situation recommended doses of pesticides were used during our this research work.

PESTICIDE DESCRIPTION:

Molecular structure may affect absorption of a pesticide by the plant tissue. Pesticide vary in their lipid solubility. A modification of molecular structure may increase lipid solubility, resulting in greater penetration of pesticides. Thus pesticides of different chemical groups were used during present research work. Descriptions of these pesticides were detailed below:-

1. 2,4-D-Phenoxyaliphatic acids and their derivatives are a major group of organic pesticides because of their selectivity and outstanding ability to be translocated within plants. The chlorophenoxy pesticides are of historical

importance because of discovery of 2,4-D in the 1940's and the impetus given for the search of a host of organic pesticides. They have hormonal activity at low rates and bring about growth responses in - regions distant from the point of application. At higher rates, they exhibit herbicidal properties. They show a fine degree of selectivity between the susceptible broadleaf weeds and the tolerant grasses, thus facilitating their use in many cereals including Paddy Crop.

2,4-D: 2,4-dichlorophenoxy acetic acid

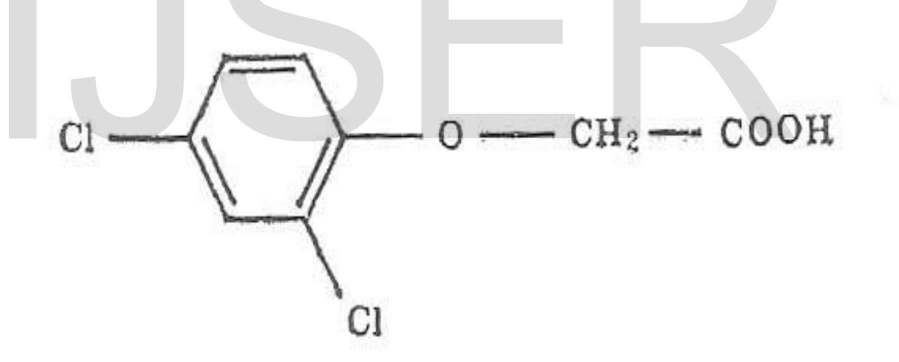

Fig:- Molecular Structure

2,4-D is a selective systemic postemergence herbicide used for control of many annual broadleaf weeds in cereal crops, It is also effective when applied at preemergence to soil for adsorption by emerging weed seedlings.

The transformations of phenoxy acids have been known since 1950 when Holley *et al.*, (1950) and Weintrub *et al.*, (1952) reported the metabolism of 2,4-D by *Phaseolus vulgaris*. These early studies and subsequent investigations suggested that phenoxyacetic acids are metabolized by plants by three mechanisms, namely, degradation of the acetic acid side chain, hydroxylation of the aromatic ring, and conjugation with a plant constituent.

During degradation of side chain, CO_2 was released from 2,4-D. Side chain degradation was slow and hence this pathway was not considered to be of any significance in pesticide metabolism. This degradation took place by oxidation at carboxyl and methylene carbons of the side chain (Weintraub *et al.*, 1952; Luckwill and Lloyd-Jones, 1960). The resistant species were able to metabolize 2,4-D via oxidation and decarboxylation pathways than the susceptible species (Luckwill and Lloyd-Jones, 1980).

When the side chain was lost from a phenoxyacetic acid without further metabolic changes to the molecule it may result in the formation of corresponding phenol. Luckwill and Lloyd-Jones (1960) reported formation of 2,4-dichlorophenol from 2,4-D metabolism. The side chain was subjected to a step-wise degradation resulting in the formation of an intermediate containing only one carbon from the original side chain. It was suggested that the intermediate might be a bound form of 2,4-dichloroanisole which would be formed by the decarboxylation of 2,4-D (Luckwill and Lloyd-Jones, 1960) .

Bach (1961) reported that the degradation of 2,4-D molecule would involve hydroxylation of the ring and oxidation of the hydroxyls to carboxyls with a split in the ring. 2,4-D also undergoes β-oxidation followed by ring hydroxylation (Wilcox *et al.*, 1963) forming 4-hydroxyphenoxyacetic acid, and this hydroxylation pathway was considered to be the mechanism of detoxification in resistant species. The hydroxylated-2,4-D might conjugate with glucose to form the 4-O-β-D-glucosides.

The higher phenoxyalkanoic acids with even numbered carbons in the side chain might alsobe first β-oxidized to phenoxyacetic acid which was then hydroxylated to form 4-hydroxyphenoxyacetic acid which in turn may conjugate with glucose to form 4-O-β-D-glucosides. Phenoxy acids form complexes with plant components notably proteins and amino acids, particularly aspartic acid. The phenoxy acids with no hydroxy group also conjugate with glucose during esterification to form glucose ester of 2,4-D. Butts and Fang (1956) reported that when the 2,4-D-protein complex was injected into the stems of beans, 2,4-D was decarboxylated three times faster than when free 2,4-D was injected, suggesting that the 2,4-D- protein complex was a product of a detoxification process and probably an intermediate in the metabolism of 2,4-D. The protein complexes of 2,4-D on hydrolysis were found to contain at least 12 amino acids. Feung *et al.,* (1977) found that the amino acid conjugates of 2,4-D possessed herbicidal properties. The most active compounds were the less polar amino acid conjugates of leucine, isoleucine, valine, alanine, and methionine. In general, the aromatic and polar amino acid conjugates exhibited poor herbicidal properties.

The degree of sensitivity to phenoxyacetic acid herbicides was influenced by the ability of the plant to degrade them. The rapid detoxification of 2,4-D side chain forms the basis of selectivity of certain plant species to the herbicide. Linscott *et al.,* (1968) observed that the mechanism of resistance of alfalfa to 2,4-D might result from the synthesis of pesticidally inactive chlorophenoxy compounds having longer side chains than the parent herbicide. They further noted that alfalfa prevented the production of 2,4-D in lethal quantity by β-oxidation of 2,4-D and subsequent translocation to the sites of action.

Hydroxylation might also serve as a detoxification mechanism. The resistance of graminaceous species to phenoxyacetic acids is apparently due to their ability to hydroxylate these compounds. Similarly, conjugation also appears to be another detoxification mechanism, and the resistance was perhaps determined by the rate of conjugate formation. Butts and Fang (1956) reported that graminaceous species formed 2,4-D conjugate much more rapidly than 2,4-D-susceptible species like beans, tomatoes, and cotton. The conjugates did not have growth regulating activity.

Mineralization and volatilization were the two major methods for dissipation of pesticides from soil. Mineralization was the process by which pesticides are completely degraded into inorganic substances that dissipate into the environment. Volatilization, however might not be a desirable process, since, even though the pesticide was released from the soil, it still remained present in the air in undegraded form and might be harmful to susceptible species elsewhere. Low volatilization was particularly desirable for pesticides since high volatility might not only cause injury to susceptible crops nearby, but might also reduce the efficacy of the pesticide in the soil.

2. Isoproturon:- Isoproturon was a phenyl urea pesticide. Isoproturon (3,4 isopropyl phenyl 1, 1-dimethyl urea) was an odourless white crystalline powder. It was very stable to light, acids and alkalies, but was hydrolyically cleared by strong alkalies on heating. It was an effective herbicide for control of crop field weeds. It had been estimated that more than three quarters of the total herbicide load of the efficient of the rural waste water. Isoproturon acted as passive absorption by the roots by penetrating the membranes of cortical cells in and forward movement into the stele and upwards in the transpiration stream. The absorption spectrum was similar to chlorophyll which results in chlorophyll degeneration and chloroplast disorganization leading to progressive chlorosis and retardation of growth.

Isoproturon→ N,N-Dimethyl-N[4-(1-methyl ethyl) phenyl] urea.

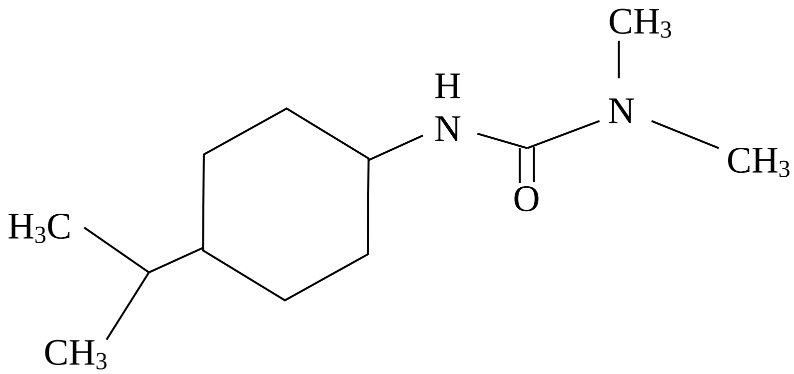

Fig:- Molecular Structure

Although ureas were primarily suggested for industrial weed control, their potential as selective pesticides in agriculture was recognized later. Today, the urea pesticides constitute one of the most important families of pesticides used for weed control in agriculture. Chemical degradation was relatively of lower importance as compared to microbial degradation. Urea were very persistent in soil. Their persistence was dependent on organic matter content, clay content and cation exchange capacity of the soil. Dawson *et al.*, (1968) found that most residue of this group pesticides were located near the soil surface of the total residue present in the surface, 62 to 89 % was located in the upper 5 cm of soil and 86 to 100 % in the upper 10 cm. The removal of the second group would make the pesticide non-phytotoxic. Urea pesticides also did conjugation with proteins. Urea pesticides were apparently not metabolized by the hydrolytic pathway.

3. Metolachlor:- 2-chloro-N-(2-ethyl-6-methyiphenyl)-N-(2-methoxy-l-methylethyl) acetamide.

Metolachlor was applied at preemergence in crops like Rice, Maize, etc. for control of annual grasses and perennial grasses including *Echinochloa crusgalli*, *Cyperus esculentus*, etc. It was also incorporated before planting the crop.

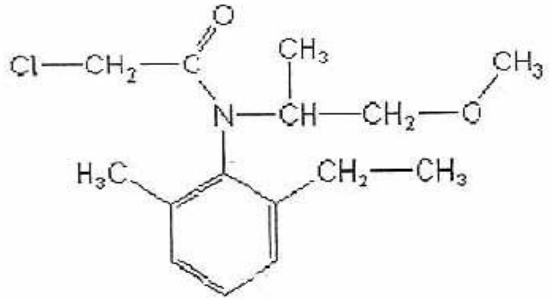

Fig:- Molecular Structure

Metolachlor which was structurally similar to alachlor, inhibited seed germination- and early seedling growth. It affected root growth by inhibiting protein synthesis (Davis *et al.,* 1979). Deal and Hess (1980) observed that metolachlor inhibited both cell division and cell enlargement. Deal (1980) found that metolachlor inhibited protein synthesis without showing any effect on the rates of polypeptide elongation or on the synthesis of specific polypeptide.

Truelove *et al.,* (1979) reported that metolachlor inhibited incorporation of choline into phosphatidylcholine during germination of cotton seeds. It had no effect on any other phospholipid. Pillai and Davis (1975) found that metolachlor inhibited photosynthesis in Chlorella and respiration in *Chlorella* and *Phaseolus vulgaris.* However, they did not consider that these effects on photosynthesis and respiration were sufficient to explain the phytotoxicity of metolachlor. On the basis of evidence presented here, it could be said protein synthesis was the primary mechanism of metolachlor action in susceptible species.

4. MCPA: [(4-chloro-O-toly)oxy]acetic acid

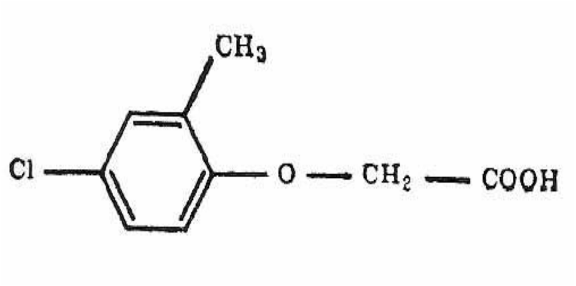

Fig:- Molecular Structure

MCPA is an analogue of 2,4-D, used for selective postemergence herbicide against broadleaf weeds. It is more selective than 2,4-D at equal rates. It is widely used in cereals, legumes, and aquatic areas. It was discovered in 1945.

5. *Bromoxynil*

Studies by Davies *et al.,* (1968) showed that ioxynil was rapidly degraded by resistant barley after foliar treatment. Four days after treatment, unchanged ioxynil, traces of the benzamide and the benzoic acid derivatives, and at least two other unknown compounds were identified in resistant barley. Schafer and Chilcote (1970) found degradation of bromoxynil, resistant in winter wheat (*Triticum aestivum* L.). Degradation to CO_2 was also observed in both the susceptible and resistant species. Frear (1975) suggested that the unhindered nitrile groups of bromoxynil are slowly hydrolyzed in the plant to the corresponding benzamide and benzoic acid derivatives with possible further degradation through decarboxylation, dehalogenation or conjugation of the benzyl moiety or the aromatic ring. Decarboxylation and/or possible conjugation reactions may be much faster than hydrolysis. This suggestion is supported by the detection of trace amounts of hydrolysis products (Davies *et al.,* 1968; Schafer and Chilcote, 1970) and the rapid accumulation of insoluble residues (Schafer and Chilcote, 1970) with (cyano-^{14}C) ioxynil and (cyano-^{14}C) bromoxynil. The expected benzamide and benzoic acid analogues may be only transitory intermediates. Additional data are needed to determine the role of each of the degradation reactions to further elucidate the degradation pathway of bromoxynil.

Bromoxynil is postemergence contact herbicides. Soon after application it burns the foliage which is followed by necrosis and extensive destruction of the leaf tissue.

Bromoxynil affect a number of essential physiological and biochemical processes in higher plants. Wain (1964) reported that ioxynil inhibited the Hill reaction and uncoupled oxidative phosphorylation. Its toxicity was greater in the light than in the dark. Paton and Smith (1965) found ioxynil inhibiting electron transport, noncyclic photophosphorylation, and CO_2 fixation in leaf chloroplasts. Kerr and Wain (1964) observed that ioxynil may depress the uptake of inorganic phosphate (Pi) and oxygen eventually resulting in a low P/O ratio; the effect of ioxynil far exceeded that of DNP and was comparable to that of dinitro-ortho-cresol. Smith *et al.*, (1966) reported that ioxynil inhibited the uptake of CO_2. They also reported that the inhibition of the Hill reaction by ioxynil was far more efficient than that caused by 2,4,5-T and chlorpropham, and the effect was comparable with that of diuron. They concluded that since electron transport is essential for photosynthesis, a blockage of this transport by ioxynil could lead to cessation of ATP synthesis and an eventual death of the plant. They considered that the actual site of action to be near plastoquinone which is an essential component of the electron transport system, in the photosynthesis of higher plants.

Nitrile herbicides also inhibited proteolytic and amylolytic enzyme activities (Penner and Ashton, 1968; Tsay and Ashton, 1971), RNA biosynthesis (Moreland *et al.,* 1969; Gruenhagen and Moreland, 1971), and lipid biosynthesis (Mann and Pu, 1968). Gruenhagen and Moreland (1971) suggested that a marked reduction in ATP levels and associated reduction of NADPH levels in photosynthetic systems may significantly affect a number of energy-requiring processes including RNA, protein and lipid biosynthesis, and hormonal regulation of proteolytic and amylolytic enzyme activities.

The evidence presented here suggests that the most sensitive site of action of bromoxynil is uncoupling of the oxidative and photosynthetic phosphorylation. Their effects on electron transport, hormonal regulation, and biosynthesis of RNA, protein and lipid are apparently less sensitive and hence they can be considered as secondary sites of action.

Bromoxynil applied at postemergence, are absorbed by the foliage. They move apoplastically but very slowly. Davies *et al.,* (1968) found that the movement down to the base of the petiole of the treated leaf was detected in 5 hours, and with an increase in time ioxynil followed up the stem and accumulated in young leaves at the apex bypassing the mature leaves. This suggested symplastic movement in sieve tubes. When ioxynil was applied to the roots, there was only slight apoplastic movement to the foliage. Bromoxynil have localized contact activity.

Nitrile herbicides were introduced in 1958 when dichlobenil showed herbicidal properties. In I960, ioxynil was discovered followed by bromoxynil. Bromoxynil: 3,5-dibromo-4-hydroxybenzonitrile

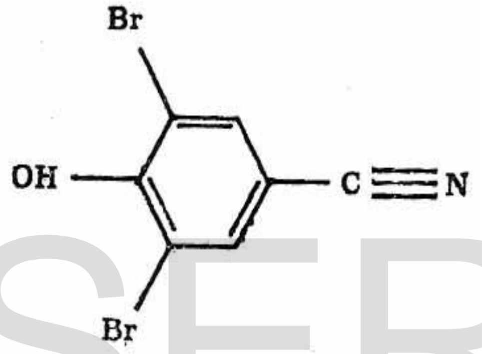

Fig:- Molecular Structure

Bromoxynil is applied at postemergence for weed control in cereal crops, etc. It is similar to ioxynil but less active. It. is effective against certain broadleaf weeds like *Chorispora tenella, Chenopodium album*, *Solatium* spp., *Polygonum convolvulus, Brassica kaber,* etc. It is also used for weed control on industrial sites, roadsides, railroad sides, and other noncrop areas. It is applied on weeds at an early growth stage, i.e. 3 to 4-leaf stage.

MATERIALS: Rice Crop

In this research rice-crop was selected due to its unparallel importance in the area of our research. Rice is the staple food of more than 60 per cent of the world's population. It is the staple food of most of the people of South-Eastern Asia. About 90 per cent of all rice grown in the world is produced and consumed in the Asian region. In India, rice is the most important and extensively grown food crop, occupying about 40 million hectares of land. Rice is the vital food for more than two billion people in Asia (IRRI, 2006).

Rice is primarily a high-energy or high calorie food. It contains less protein than wheat. The protein content of milled rice is usually 6 to 7 per cent. Rice, however, compares favourably with other cereals in amino acids content. The biological value of its protein is high. The fat content of rice is low (2.0 to 2.5 per cent) and much of the fat is lost during milling. Rice contains a low percentage of calcium. Rice grain contains as much B group vitamins as wheat. Milled rice loses valuable proteins, vitamins and minerals in the milling process during which the embryo and the aleurone layer are removed. Much of the loss of nutrients can be avoided through parboiling, process.

The by-products of rice milling are used for a variety of purposes. Rice bran is used as cattle and poultry feed.. Rice hulls can be used in manufacture of insulation materials, cement and cardboard and are also used as litter in poultry keeping. Rice straw can be used as cattle feed as well as litter during winter.

Classification of Rice

Rice belongs to genus *Oryza* of Poaceae *(Graminae)* family. The genus *Oryza* includes 24 species, of which 22 are wild and two namely *Oryza sativa* and *Oryza glaberrima* are cultivated. All the varieties found in Asia, America and Europe belong to *O. sativa* and varieties found in West Africa belong to species *O. glaberrima.*

Oryza sativa. is a diploid species having 24 chromosomes. The sativa rice varieties of the world are commonly grouped into three subspecies namely *indica, japonica* and *javanica.*

There are some abiotic and biotic factors contributing to the low yield. Weeds are the most serious biotic constraint to higher yields (Dr. Datta & Bernasor 1973; Subhas & Jitendra 2001; Mandal *et al* 2002). In rice crops worldwide, losses due to competitive effects of weeds are estimated at 10%

to 15% of potential production (Smith 1983; Zoschke 1990; Baltazar & Dr. Datta 1992). Madrid *et al.* (1972) reported that loses in rice yields due to weeds ranged from 41 % to 100%.

Successful weed control is essential for economic rice production (Ishaya *et al.*, 2007). Weed can reduce rice yield by competing for moisture, nutrients and light during the growing season. Weed infestation can also interfere with combine operations at harvest and significantly increase harvesting and drying costs. Weed seeds contamination of rice grain lower grain quality and may lower the cash value of the crop. Weed infestation is one the causes of serious yield reduction in rice production worldwide. Losses caused by weeds vary from one country to another, depending on the predominant weed flora and on the control methods practiced by farmers (Ferrero 2003).

Weed management in rice is a combination of cultural and chemical tools (Baltazar & DeData 1992). Chemical control is proved as the most commonly used and reliable method for controlling weeds in rice. The importance of their control was emphasised in the past by various authors (DeData & Baltazar, 1996; Larrada, 1996; Ze - Pu Zhang 1996). Chemical method of weed control in our study area of Chapra has increased significantly over the last ten years This is due to labour shortages and economic factors.

Taking into consideration the necessity of chemical weed control for stable rice production, the objective of this study was to investigate the effectiveness of five pesticides for controlling weeds in rice crop, and, at the same time to estimate the influence of these pesticide on rice yield.

Weeds are one of the primary factors limiting rice yield in Bihar. Hoe weeding is the commonest method adopted in controlling weeds in the study area (Chapra). The practice is however expensive, labour intensive and the availability of labour is often not reliable particularly at the peak of the season. Rice being a closely spaced crop, yield losses could even be caused by hoe weeding through crop injury and stand losses, while some grass weeds which have close resemblance to the rice crop may escape hand weeding. This necessitates the evaluation of an alternative weed control method that may be more effective.

MORPHOLOGY OF RICE PLANT

The rice plant is a semi-aquatic, free tillering annual grass with a cylindrical jointed stem (culm), about 50-150 cm tall, but may go up. The internodes are shortest at the base, becoming progressively longer. Above each node, there is a pronounced thickening 'pulvinus' with an intercalary meristem. Rice has a shallow root system, its extent being controlled by the nature of the soil and the water supply. The first leaf at the base of the main culm and each tiller is rudimentary, consisting of a bladeless 'prophyllum'. The leaves are borne alternately on the stem in two ranks - one at each node, each consisting of leaf sheath, leaf blade, ligule and auricles, the former encircling the whole or part of the internode. At the junction of the leaf sheath and leaf blade, there is a triangular membranous, usually colourless ligule that tends to split with age and is flanked on either side by a small sickle-like appendage, fringed with long hairs (auricles) . The leaf blade is long, narrow, 30-50 cm or more in length and 1-2 cm broad and somewhat pubescent having spiny hairs on the margins. The lamina of the uppermost leaf below the panicle ('flag' or 'boot') is wider and shorter than the others.

The spikelets are usually borne singly, but clustered forms with two to seven spikelets together are known. Each spikelet is laterally compressed and one flowered, borne on a short pedicel and is subtended by two diminutive sterile glumes that are lanceolate, leathery, shiny structures. The flower is self pollinated and is surrounded by a lemma and palea that make up the hull or husk and remains attached to the grains in threshing. The lemma is tough, papery while the palea is somewhat smaller, sometimes awned. Enclosed within the lemma and palea are two broad, thick, fleshy lodicules, six stamens in two alternating whorls, and a pistil with two plumose stigmas on two styles.

The mature rice grain is a caryopsis. Rice invested in the hull is called ‘rough rice’ or ‘paddy’, while that with the hull removed is known as ‘brown’, ‘husked’ or ‘cleaned’ rice. Rough rice consists of about 20 per cent hull. The grain coat is often pigmented and is differentiated into epicarp, mesocarp, cross cells, tube cells and spermoderm or integument. The remnants of the nucellar tissue are present just underneath the integument. The endosperm consists of a single aleurone layer of polygonal cells with a central mass of thin walled parenchymatous tissue containing mostly starch.

The embryo is located near the base towards the lemma or ventral side of the grain and consists of strongly differentiated scutellum, plumule and radicle. The plumule is ensheathed by the coleoptile and the radicle by the coleorhiza.

The pericarp, nucellus, aleurone layer and the embryo constitute the 'bran' which is quite rich in oils, proteins, mineral salts and vitamins; but most of the nutritional parts are lost during the milling operations.

CLIMATIC AND SOIL REQUIREMENTS

The rice crop is grown over an extremely wide range of climatic conditions extending from 49 °N (in Czechoslovakia) to 40 °S latitude, and from sea level or even below, to 3000 m in the Himalayas. For the satisfactory production of rice the following prerequisites must be satisfied: 1. a relatively high temperature during the growing season; 2. an abundant and dependable source of water for irrigation; 3. a close textured or relatively impervious subsoil to prevent excessive loss of water by seepage and 4. provision for steady surface drainage to allow the land to dry out sufficiently for harvesting.

The cultivated varieties differ a great deal from each other in their season of growth, maturation period, suitability to varying conditions of soils, temperature, rainfall, altitude and adaptability to such special environments such as flooded land, alkalinity and acidity of soil and depth of standing water. Rice can be grown on many types of soil from sandy loams and shallow lateritic soils to heavy clay, but heavy alluvial soils of river valleys and deltas are preferable. The crop is able to tolerate a wide range of soil reactions, but it does have a preference for acidic soils.

Rice is essentially a crop of swampy soils where the land remains submerged under water for 60-90 days during the growing season. Compared with water supply, soils are relatively unimportant. Upland varieties need a minimum of 60-120 cm of rainfall; while lowland types demand 180-240 cm. If the rainfall is not sufficient, the deficit must be made up by artificial irrigation.

It is very important to take advantage of the substantial processing capacity available in the country by boosting paddy rice production. Efficient rice production will create employment, increases incomes and reduce poverty.

METHODS:

The experiment entitled "Study of dimensions of soil pollution by pesticides in crop field of Saran (Chapra), Bihar" was conducted at Chapra during the Kharif Season 2012-2013 using the Parmal variety of rice. Crop was sown on August, 2012. The experiment was laid out in a RCBD design with four replications. In each replication, there were six treatments each with size of 5m x 1.8m. Row to row distance was kept at 30 cm. All the pesticides applied as post emergence as detailed in Table-1.

Table-1.

Treatments used in the experiment

Herbicides common names	Rate (kg/hectare)
1. 2,4-D	0.02
2. Isoproturon	1.00
3. Metolachlor	0.75
4. MCPA	0.45
5. Bromaxaynil	0.04

To spray the pesticides successfully all the precautionary measures were adopted so as to avoid any misuse of the pesticides. The yield related data were recorded on maturity of crop on thousand grains weight (g), biological yield (kg ha^{-1}) and grain yield (kg ha^{-1}).

Soil Sampling:-

In each sampling, 20 g of soil was removed from each collection bag. About 5 g of this soil was placed in the oven at 105^o C for 24 hours to determine the soil moisture content. The remaining soil was put in a flatbottomed Flask to which 100 ml of methanol was added, and the mixture was shaken for one hour. The mixture was transferred to a Buchner flask and was filtered under partial suction. The collected organic phase was evaporated in a rotary evaporator for about 15 minutes, and the dried residues were dissolved in 10 ml of hexane. The extracts were stored in 15 ml glass vials in the refrigerator.

Samples from the plough layer (upper 15-cm zone) of the different experimental fields were used for assessment of soil bioactivity. A minimum of 5 bags per plot were collected, pooled and mixed thoroughly before use. Sieved soil (5 mm mesh) samples, from experimental and control plots, were adjusted to about 55% maximum water holding capacity and kept, till use in a dessicator in a temperature regulated chamber at 24 °C. Soil samples were not stored more than two weeks.

To determine changes in microbial population, soil samples were subjected to a soil dilution plate method, using sodium albuminate agar for bacteria, Jenson's medium agar for actinomycetes and rose bengal streptomycin agar for fungi.

The rhizosphere is well recognized as the hot spot for microbial abundance and diversify, and metabolic activities intimately related to the successful production of crops and sustenance of soil fertility. However, the rhizosphere of crop plants is a relatively unexplored frontier in terms of cyanobaeterial abundance, diversity and the general belief that cyanobacteria are obligate phototrophs has been perhaps the major reason for the dearth of information on these organisms in this niche. Most of the published work on Bio-biofertilizers has been carried out in relation to rice crop, with few reports on their effects on vegetables, wheat or other horticultural crops (Venkataraman 1981).

Microbiological methods

Aseptic techniques were used for all subsequent procedures involving the soil samples. To decrease sampling errors, relatively large samples were used; 12 g moist soil (10 g dry weight) was resuspended in 100 ml sodium hexametaphosphate (2%), shaken for 30 min, diluted in sterile water and 100 μl aliquots spread. Five replicate plates were inoculated at each dilution, and incubated at 21 °C for 4-5 d before observation, which precluded slower-growing microorganisms such as actinomycetes. Bacterial fluorescence was examined by illuminating colonies on PSA agar under u.v. light at 260 nm.

Agar media were prepared according to the protocol, sterilized in autoclave at 1.05 kg cm^2 and 120°C for 30 min and cooled to a pouring temperature of about 37°C. Serial soil dilutions were prepared according to the microorganisms to be studied. One mL of the required dilution was spread evenly on an agar-media petriplate to determine population per gram soil. Thornton's medium was used for estimation of Bacteria. Jensen's medium was used for estimation of azotobacter. Knight's medium was used for estimation of actinomycetes and Martin's streptomycin — Rose Bengal medium was used for estimation of fungi. Fogg's medium was used for algal estimation.

1. Experimental layout

i. Plots

a) Control soil without any pesticide treatment.

b) Test soil with pesticide treatment.

c) Minimum size of each field plot: $500m^2$

2. Soil sampling

- sampling depth: 0-15 cm (plough layer) and 15-30 cm

- sample size: minimum 10 cores (diameter 2-5 cm) per field
- minimum amount of collected soil: 1 kg per soil depth.
- dates of sampling: 1st (Zero) sample = before any application of pesticides

  2nd sample = 2 days after the first pesticide application

  3rd sample = immediately before the following pesticide application

  4th sample = 2 days after second application and so on

  x. sample at harvest

  y. samples during crop rotation

Time of sampling, weather at sampling time, last soil treatment, last fertilizer application, soil moisture content, growth stage of plants.

3. Transport

Samples should be transported:-

- Without loss of soil humidity but with free gas transfer (e.g. in polyethy lene bags)

4. Handling after sampling

- Determination of soil water content, max. water holding capacity, pH etc.
- Each soil sample was divided into subsamples
- IMMEDIATELY with a sieved, “fresh” soil sub sample in triplicates was used to determine dehydrogenase activity.

5. Soil preparation prior to experiments

Soils stored at 4°C were brought to 40-60% of Water Holding Capacity and incubated in the dark for 3d in flask. Soils frozen for pesticide analysis were thawed at 4°C and the moisture content determined prior to analysis.

6. Yield Data

Yield data were collected after maturation of rice-crop in all treated and control plots.

7. Presentation of results

- All measurements and observations were made at least in triplicate.

- All results were presented on the basis of pesticide used.

Therefore, timely weed control is imperative for realizing desired level of productivity. Accordingly, an efficient and economic weed management program is necessary to control different types of weeds throughout the cropping period. Hand weeding is expensive, time consuming, difficult and often limited by scarcity of laborers in time. On the other hand, pesticides offer economic and efficient weed control if applied at proper dose and stage (Kumar and Sharma 2005). However, the continuous use of single pesticide or pesticides having the same mode of action may lead to the resistance problem in weeds. Hence it is necessary to test some high efficacy pesticides and sequential application of pesticides to control mixed weed flora and microflora in transplanted rice. Keeping these points in view, a field experiment was carried out to evaluate the performance of five pesticides in transplanted Parmal rice.

In the concluding part of this chapter, we summarised the materials and methods of this research work as follows:-

1. The objective of this study was to establish an appropriate herbicides selectivity, their effects on soil and on grain would be evaluated. The

experiments would be conducted at crop-fields of Chapra. The proposed research study would use a combination of research approaches, including secondary literature review, in depth study by use of quantitative and qualitative tools involving methods and analyses of secondary and primary data.

2. The initial assessment would be done at different intervals assessments would be conducted separately for different herbicidal treatments in separate rice crop fields. The data obtained after observations for following parameters will be individually and comparatively analysed to reach a prefect conclusion:-

   a) Biological yield of crop (kg/ha).
   b) Grain yield of crop (kg/ha).
   c) Thousand grain weight of crop (gm).
   d) Pesticide residue in crop Grains.
   e) Pesticide residue in soil.
   f) Amount of decomposed organic matter of soil.
   g) Microbial population density of soil.

h) Moisture content of soil.
i) pH of soil.
j) Temperature of soil.

3. The finding of this study would be a milestone in direction of better institutional policy and incentive framework within which pesticides could be effectively used for agriculture with minimal environmental and health impacts. Hence, the proposed research could provide key insights helping to respond to the needs of the communities more effectively.

4. Dimensions of Soil pollution by pesticides like 2,4-D; Isopoturon, Metalachlor, MCPA and Bromoxynil were analysed during this research. Periodic measurement of moisture content, pH, and temperature of the soil of experimental crop fields were conducted. Yield of crops of experimental fields were also accounted. Microscopic observations were conducted for study of microbial population. Moisture content, amount of pesticide residue in soil, amount of decomposed organic matter of soil and pesticide residue in crop grains.

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Chapter-IV

OBSERVATIONS

Pesticides (fungicides, insecticides and herbicides) improve crop yields by controlling specific pests, weeds and pathogens, but they are also known for their inhibitory effects on non-target organisms in the agroecosystem. The removal of non-target microbial organisms may impact negatively on the microbial mediated functional cycles in soil, ultimately influencing soil quality and fertility (Ferreira *et al.*, 2009). Post-emergence pesticides such as glyphosate and 2,4-dichlorophenoxyacetic acid (2,4-D) and others may remain in soil and become a food source for certain microbial organisms thus causing changes in the microbial community structure which can impact negatively on soil fertility (Zabaloy, Garland and Gomez, 2008). A change in vegetation due to pesticide application can sometimes lead to changes in rhizosphere exudates which can also ultimately impact on microbial activity and enzyme activity in soil (Turk and Tawaha, 2002).

The introduction of bordeaux mixture in 1896 stimulated interest in chemical method of weed control. This led to the discovery of copper salts for selective control of broadleaf weeds in cereals. The period between 1896 and 1910 was important for chemical weed control as many chemicals like sulphuric acid, iron sulphate, copper nitrate, ammonium and potassium salts, sodium nitrate, etc. were discovered for weed control. After this initial interest, research on chemical control of weeds languished for about 30 years largely due to lack of adequate spraying equipment and the frequent failure of herbicides because of low humidity. During this period, particularly in the 1930's chemicals like sodium chlorate, carbon bisulphide, sodium arsenite, and dinitrophenols have been used only occasionally and on limited scale in USA and Europe. The concept of systemic control of weeds through absorption by roots and translocation in the plant body and the use of organic chemicals for weed control took pace with the introduction of nitrophenols as selective herbicides in 1935. The discovery of 2,4-D in the early 1940's has, however, revolutionized the chemical method of weed control.

The global importance of rice as a food source is evident; however, it is also a valuable tool in assessing potential phytotoxicity of different types of Pesticides. Phytotoxicity is defined as the impact or damage that a

Pesticide compound causes on certain plant characteristics. Rice has been recommended by the Organisation for Economic Co-operation and Development (OECD) for use in standardized phytotoxicity assessments for over decades (OECD 1984). Additionally, several studies have demonstrated rice’s increased sensitivity to complex effluents (Wang 1990, 1991; Wang and Keturi 1990) as compared with other commonly used seed species. In this context, the phyto-toxicity effect of herbicides on crop-plant was also assessed during this experiment.

Bihar is an agro-based state of India. Food security of Bihar depends on rice agriculture. Rice (*Oryza sativa* L.) is the staple food of Bihar where it's production has increased more than two times during the last 3 decades. But till to-day, required potential of rice productivity in the state faced the problem of less rice production as per unit area of fields.

Among the various factors responsible for low rice production, weeds are considered to be as one of the major limiting factors due to manifold harmful effects (Kalyanasundaram *et al.*, 2006). Weeds are the most competitors in their early growth stages than the later and hence the growth of crops slows down and grain yield decreases (Jacob and Syriac, 2005).

The prevailing climatic and edaphic factors of Chapra district are highly favourable for numerous species of weeds that strongly compete with the rice crop. For centuries, manual and mechanical methods are the only methods available for farmers to control weed from crop-fields in the area under study. As a result, labour has been extensively used for weed control. With the rapid development of pesticides in the past years, there has been widespread concern in India over the replacement of labour by pesticides and its consequences on employment of agricultural labour in villages. In fact, this has been one of the reasons for slow acceptance and growth of pesticides technology in this country. The following facts, however, prove that the advantages due to pesticides technology, are far too many to ignore it any longer, and the contention that it leads to unemployment of agricultural labour is a myth and is not borne out by facts.

Pesticides enable the farmer to use labour more efficiently. Effective weed management involves the integration of many practices. Pesticides are undeniably the most effective, reliable technology available today for weed control in rice (Marwat *et al.,* 2004).

In Chapra (Bihar), traditional methods of weed control practices include preparatory land tillage, hand weeding by hoe and hand pulling. Usually two or three hand weeding are normally done for growing a rice crop depending upon the density of weeds and, their intensity of infestation. Weed control in transplant Parmal variety of Rice by mechanical and cultural methods is expensive. Especially at periods of labour crisis late weeding can cause drastic losses in grain yield. In contrast, chemical weed control is sufficient. Nowadays the use of Pesticides is gaining popularity in rice culture due to their rapid effects and lower costs compared to traditional methods. The available pesticides in controlling weeds in rice field are of overseas origin. Our country depends on foreign multinational companies for the supply of pesticides and the companies do not supply the same brand of pesticides for long time. So, continuous evaluation is necessary for the benefit of the farmers of this country.

Therefore, the study was undertaken to observe the performance of different pesticides in Parmal rice crop-fields of Chapra (Bihar).

Presently, pesticides are more extensively used in developed countries. Their use in developing countries like India is growing rapidly and the trend will continue. The study was undertaken to observe the performance of different pesticides on controlling weeds in Parmal Rice for different parameters.

One could argue that when this knowledge is available from the work done elsewhere, why should it be repeated here in Chapra. The point that should be remembered here is that variations in weed species, crop varieties, soil types, agroclimatic conditions, etc. could result in differential modes of action and degradative patterns, and it will be essential to understand these mechanisms for better knowledge on selectivity, placement, dosage, application time, and more effective use of herbicides.

Another area of great importance in basic pesticide research is that related to pesticide persistence, residues, and residual effects. Detection and measuring of residues was done by using simple bioassay techniques as well as by calorimetrie.

Observation for different parameters undertaken under this research study are detailed as follows:-

Table-1

Biological Yield

Grain Yield + Straw Yield

Sl. No.	**Treatments**	**Biological Yield of Rice crop (t ha^{-1})**
T_0	Control	6.67
T_1	2,4-D	8.83
T_2	Isoproturon	8.53
T_3	Metolachlor	7.37
T_4	MCPA	7.94
T_5	Bromoxynil	9.12

The highest biological yield (9.12 t/ha) was produced by rice-crop of Bromoxynil treated experimental plots. 2,4-D and Isoproturon treated crop plants produced higher biological yield (as summed together Grain Yield + Straw Yield) as 8.83 t/ha and 8.53 t/ha respectively. Here again application of only one pre-emergence herbicide as Bromoxynil or 2,4-D supports more productivity of Biomas in per unit area of herbicidal treatments having plots.

Table-2

Grain Yield of Rice

Sl. No.	**Treatments**	**Grain Yield (t ha^{-1})**
T_0	Control	2.39
T_1	2,4-D	3.27

T_2	Isoproturon	3.27
T_3	Metolachlor	2.93
T_4	MCPA	2.96
T_5	Bromoxynil	3.61

Grain yield of rice crop plants as calculated as t/ha. was significantly differed and highest grain yield (3.60 t/ha) was obtained from Bromoxynil treated plots. The lowest yield was obtained from Metachlor and MCPA treated crops produced low-yield as 2.93 t/ha and 2.96 t/ha respectively.

Table-3

1000 grain weight (gm)

Sl. No.	Treatments	1000-grain wt. (g)
T_0	Control	21.45
T_1	2,4-D	21.90
T_2	Isoproturon	21.87
T_3	Metolachlor	22.03
T_4	MCPA	22.01

T_5	Bromoxynil	23.37

1000 grain weight found significantly increased in the crop plants of Bromoxynil, Metolachlor and MCPA treated experimental plots. In other treated plots and control plot crop plants'1000-grain weight remain as more or less similar as between 21.45 gram and 21.90 grain.

Table-4A

Toxicity Symptoms and Toxicity level of rice crop

Sl. No	Treatments	Toxicity	Toxicity Symptoms
T_0	Control	0	No toxicity
T_1	2,4-D	0	No Yellowing of leaves
T_2	Isoproturon	3	Slight yellowing of leaves
T_3	Metolachlor	1	Very sight yellowing of leaves
T_4	MCPA	3	Slight yellowing of leave
T_5	Bromoxynil	1	Very Slight yellowing of leave

The Phyto-toxicity level of the herbicide to rice plants was determined by visual observations. The degree of toxicity on rice plants was measured by the following scale used by IRRI (1965):-

1. No toxicity
2. Very slightly toxicity
3. Slight/moderate toxicity
4. Severe toxicity
5. Toxic (Plant Kill)

The rating was done on 7th day after application of pesticidal treatments on crop plants. Isoproturon treatments on crop plants showed more toxicity level (3) as compared to Bromoxynil and Metolachlor pesticidal treatments. 2,4-D treated crop fields showed toxicity level as zero, mean that there is no toxicity effect of 2,4-D on rice crop.

Table-4B

Crop Injury

Sl. No	Treatments	Cropland	Crop Injury
T_0	Control	100	0
T_1	2,4-D	100	3
T_2	Isoproturon	100	10
T_3	Metolachlor	100	5

T_4	MCPA	100	9
T_5	Bromoxynil	100	5

Crop injury was observed visually and calculated on 0-100 scale. We observed no crop injury in control plot. Maximum crop injury was found in Isoproturon treated plots (10), followed by MCPA Metolachlor (5), and 2,4-D (3) treated plots respectively. So, it became evident that the Isoproturon caused highest crop injury.

Table-4C

Crop Vigour

Sl. No.	Treatments	Crop Vigour
T_0	Control	7
T_1	2,4-D	8
T_2	Isoproturon	7
T_3	Metolachlor	8
T_4	MCPA	9
T_5	Bromoxynil	8

Crop vigour score was observed by visual observation on a scale of 0-10, where 0 represents complete crop kill and 10 represents fully grown healtly crop.

Table above shows the effect of different pesticides on crop vigour. Crop vigour of the rice-crops of all pesticidal treatments having plots observed between (7) and (9). But there was only a slight increase in crop vigour of pesticidal treatment having crops than the control. The best crop vigour was observed in MCPA treated plots as (9).

Table-5

Pesticide residue in crop

Sl. No	Treatments	Pesticide residue	
		In Straw (ppm)	In unpolished rice (ppm)
T_0	Control	___	___
T_1	2,4-D	0.0039	0.1530
T_2	Isoproturon	0.0195	0.8230
T_3	Metolachlor	0.0011	0.0455
T_4	MCPA	0.0522	0.0173
T_5	Bromoxynil	0.1270	0.0113

Pesticide residue level was observed by spectrophotometer in the straw and unpolished rice-grains after harvest of the crop for all replicates of treated crop-fields. Maximum concentration of Isoproturon pesticide was observed as 0.8230 ppm in crop-grain but maximum concentration of Bromoxynil was observed in straw as 0.1270 ppm among all treated plots. 2,4-D and Metolachlor proved as less toxic because their presence were very less as 0.0039 and 0.0011 ppm in straw but MCPA and Bromoxynil residue in crop grain remained less as 0.0173 and 0.0113 respectively.

Every chemical leaves residues in the environment. Various studies conducted in USA, where pesticides are used more widely than in any country in the world, showed very minute quantities of pesticides residues in the soil. For example, if one kilogram of active ingredient of a chemical is applied and mixed thoroughly in the soil of 30 cm depth weighing 4 million kilograms, the pesticide concentration would be 0.25 ppm. If it is mixed in the top 15 cm of soil, the concentration would be 0.50 ppm. Most of the pesticide dosages range between 0.5 and 2 kg/ha, and hence the concentrations in the top 30 cm soil would be between 0.125 ppm and 0.5 ppm, much below the international pesticide residue limits. Herbicides are generally not long-lived in the environment. Many of them are rapidly degraded into innocuous and harmless products. The 1967-68 Market Basket Survey (diet for a 17-year old boy) conducted in U.S.A. revealed a total pesticide intake of 0.00006 milligrams per kilogram of body weight per day and it would take 670 years for a 68-kilogram person to consume 1 gram of pesticide from his food (McGlamery and Knake, 1971).

Table-6

Pesticide residue in soil

Sl. No	Name of Pesticides	Pesticide residue as	Mineralization	Residues in soil
T_1	2,4-D	Aryloxyalkonoic	42.1% (90d)	33.2% (90d)
T_2	Isoproturon	Urea	10-22% (90d)	56-68% (90d)
T_3	Metolachlor	Chloroacetamide	15.3% (90d)	4.6% (90d)
T_4	MCPA	Aryloxyalkanoic acid	54% (90d)	34.4% (90d)
T_5	Bromoxynil	Hydroxybenzonitrile	27.3-33.6% (90d)	72.9-74.2% (90d)

On the basis of the observational detailed in above mentioned table, it was clear that MCPA and 2,4-D underwent fast mineralization under rice crop-field’s soil and Metolachlor and Isoproturon underwent slow mineralization. But the amount of residue in soil was found highest in Bromoxynil treated plots after 90 days of application as 72.9 to 42.2 percent. Lowest pesticidal residue was observed in Metolachlor treated plots. The remaining amount of applied pesticides drifted from the crop-fields soil by evaporation, percolation, absorption by crop plant and exit as runoff water.

The average pesticide persistence in soil, in decreasing order remained as Bromoxynil (74.2) Isoproturon (68). MCPA (34.4), 2,4-D (33.2) and Metolachlor (4.6). These informations obtained with the field experiments allowed a better understanding of the behaviour of the different pesticides in the soil of rice-crop fields. Since bromoxynil is mineralized to CO_2 and since its residues are bound in soil in an unextractable form to a large extent, its availability for uptake by plants as well as for leaching is low. However, attention should be paid to the formation of conversion products whose chemical identity is not yet known and which might have unfavourable properties. Therefore, research into this pesticide should be continued. Results for the persistence of the different applied pesticides in soils are presented in Table-6. Shows that amount of 2,4-D varied being higher some while after its application, but decreasing onwards. Metolachlor was only detectable in samplings just after its application, but Bromoxynil was always detected, although in decreasing amounts as time passed.

Table-7

Amount of decomposed organic matter of soil

Sl. No	Treatments having crop fields	Amount of decomposed organic matter in soil		
		15 days	30 days	45 days
T_0	Control	10%	14%	18%
T_1	2,4-D	12%	15%	19%
T_2	Isoproturon	11%	13%	17%
T_3	Metolachlor	12%	14%	20%
T_4	MCPA	11%	14%	19%
T_5	Bromoxynil	11%	16%	20%

Decomposed organic matter of soil as compost; used in experimental crop fields were observed in the top soil below to 10 cm at different periodic intervals as 15 days, 30 days and 45 days after the transplant of the crop. Our experimental crop fields showed as rich for decomposed organic matter. When observed after 15 days of transplant of crop remain in between 10-12, after 30 days as 13-16 and after 45 days as 17-20 % in all experimental fields. This trend indicates that the crop-debries residue, dead weed biomass and dead biomass of other micro-organisms contributes to increase the amount of decomposed organic matter in control and also in all treated experimental fields.

Soil biota were significantly influenced by their abiotic environment. Agricultural practices that included the application of pesticides which affected the physical, biological and chemical properties of the soil (Magdoff and Vanes 2000) could have major ecological implications (Avidano *et al.*, 2005; Eisenhauer *et al*, 2009). The addition of biological agents might also lead to the inhibition of beneficial microorganisms

Pesticides also alter non-target soil microorganisms. The application of pesticides such as λ-Cyhalothrin (Lupwayi *et al.*, 2009). Azadirachtin (Gopal *et al.*, 2006) and nemacur (Abramovich and Steinberger, 2006) caused changes to bacterial community structures in soil at a functional level that led to a decline in soil fertility. Applications of organophosphate and chlorinated hydrocarbon based insecticides were found to directly kill non-target organisms in soil (Das and Mukheijee, 1999). This led to increase of available N and P in soil. Fungi were generally more resistant to insecticides. The increase in N and P following insecticide addition could lead to shifts in fungal diversity due to the increased food source (Das and Mukherjee, 1999; Vig *et al.,* 2008). Biodegradable residues of pesticides which remained in soil could serve as a food source for certain microorganisms (Robertson *et al.,* 1998; Gomez *et al.,* 1999; Cycori, Wojcik and Piotrowska-Seget, 2009) which favoured certain microorganisms that could led to a change in the microorganism community.

Pesticides such as 2,4-dicholorophenoxy-acetic acid (2,4-D) could led to an increase in microorganisms which degraded the herbicide; a phenomenon that could significantly affect microorganism community structure in soil (Chinalia and Killham, 2006; Zhang *et al.,* 2009). This co-relates our observations also. Glyphosate had been reported to either increase or decrease of the populations of soil microorganisms (Araujo, Monteiro and Abarkeli, 2003; Lupwayi *et al.,* 2008; Mijangos *et al.,* 2009). Direct toxic effects of pesticides on soil microorganisms had also been observed immediately after application. Glyphosate, 2,4-D and metsulfuron methyl were found to have direct toxic effects on microorganisms (Zabaloy, Garland and Gomez, 2008).

In our observations here also application of only 2,4-D enhanced baterial population in crop fields except this all other pesticides applied in experimental crop-fields showed decreased baterial population in soil as compared to control.

Table-8

EFFECT OF PESTICIDES ON BACTERIAL POPULATION (OF OVEN DRY SOIL X 10^4)

Sl. No	Treatments	Bacterial population (at the rate of pergram of soil)	
		At Tillering	At flowering
T_0	Control	298.41	310.60
T_1	2,4-D	302.63	309.16
T_2	Isoproturon	284.16	304.70
T_3	Metolachlor	285.60	304.96
T_4	MCPA	282.09	302.27
T_5	Bromoxynil	283.83	302.42

The bacterial population at maximum tillering stage was significantly influenced by weed control treatments. At maximum tillering stage, the population of bacteria was significantly reduced by pesticide application except 2,4-D when compared with that of unweeded control. All bacterial and fungal population determination were done after harvest of crop in all experimental fields.

Table-9

Effect of Pesticides on Microbial Population (G^{-1} OF OVEN DRY SOIL X 10^4)

Sl. No	Treatments	*Fungi*		Actinomycetes	
		At Tillering	At Flowering	At Tillering	At Flowering
T_0	Control	2.52	2.63	71.46	76.90
T_1	2,4-D	2.49	2.61	70.04	75.24
T_2	Isoproturon	2.40	2.55	68.15	73.54
T_3	Metolachlor	2.41	2.59	68.25	73.90
T_4	MCPA	2.36	2.49	67.56	71.28
T_5	Bromoxynil	2.32	2.50	67.93	71.70

The numbers of bacteria occurring in soils are usually higher than those of the other groups; however, because of their small size in relation to the large cell size and extensive filaments of the other groups, bacteria account for less than half of the total microbial biomass in soil. The pesticide treatment schedule used in the present investigation did not cause any adverse effect on bacterial numbers. An increase in bacterial number from was observed in the pesticide treated field with 2,4-D. A temporary adverse effect with a little decrease in numbers was noticed with Isoproturon, Metolachlor, MCPA and Bromoxynil treatments.

Although numerically much less abundant than bacteria, fungi are the major contributors to soil biomass. Most soil fungi are opportunistic. They grow and conduct their activities when environmental conditions (e.g., nutrients, moisture, temperature, aeration) are favourable. The acidic side of pH is generally more favorable for fungi. Fungi were quite resistant to the pesticides used in the present investigation as no noticeable adverse effect on fungal numbers was observed after pesticides treatments. However, a little decrease in fungal numbers was observed in the treated fields which showed that the population in concerned field could not recover either due to treatment or due to some synergistic effect. But all treated crop-fields soil both at tilling stage and flowering stage showed decreased fungal population as compared to control.

Actinomycetes are more abundant in surface soil. They are more abundant in soils with high pH. Pesticides had no major adverse effect on actinomycetes population in all treatments but slightly reduce their number.

Actinomycetes number tend to remain significantly less immediately after treatment, however recovery was observed in another ten days and at the end of the experimental period actinomycetes numbers were more-or-less similar in both treated and untreated fields again indicating that the pesticides used had only temporary effects. Stimulatory effects of insecticides on actinomycetes have been confirmed by same authors whereas significant and lasting reductions were reported by others and no effect of insecticides on actinomycetes were also reported.

Table-10

Moisture content of soil (Relateive Humidity)

Sl. No	Treatments	During crop season	After harvest
T_0	Control (Hand weeded)	80-85	30-40
T_1	2,4-D	78-88	25-35
T_2	Isoproturon	82-90	28-40
T_3	Metolachlor	80-90	26-40
T_4	MCPA	82-90	22-34
T_5	Bromoxynil	81-86	24-36

Moisture content of soil measured as relative humidity for different periodic observations during crop-season remained in between 78-90 in all treated crop-fields and control. Rice crop-soil remained as submerged in water for a longer period of cultivation, thus moisture content remained maximum as compared to other crops. The relative humidity of experimental crop-field's soil after harvest of crop remained in between 22-40. Thus it was clear that sufficient water availability in rice-crop field provided suitable medium for dissolution, percolation and absorption of used pesticides.

Table-11

pH of soil

Sl. No	Treatments	pH of soil		
		15 days	30 days	45 days
T_0	Control (Hand weeded)	5.5	5.8	6.0
T_1	2,4-D	6.0	6.5	6.5
T_2	Isoproturon	5.6	6.1	6.2
T_3	Metolachlor	5.8	6.2	6.4
T_4	MCPA	5.8	6.4	6.6
T_5	Bromoxynil	5.5	6.0	6.5

pH of the experimental crop fields were measured at different intervals as after 15 days, 30 days and 45 days after transplantation of crop. Overall pH for all experimental crop field's soil remained in between 5.5 and 6.6. But in all experimental crop fields an increasing trend of pH value were noticed by increasing days after transplant. This might be due to increase in organic content of the soil progressively.

Table-12

Temperature of soil

Sl. No	Treatments	Temp. of soil (At maturity of Crop)
T_0	Control	19 °C
T_1	2,4-D	20 °C
T_2	Isoproturon	19 °C
T_3	Metolachlor	22 °C
T_4	MCPA	21 °C
T_5	Bromoxynil	21 °C

Temperature of the experimental crop field soil were measured for each treatments and control at the maturity of the crop and it remained in between 19-22 ^{o}C. But during entire crop-season the temperature of soil remained lower.

Weeds compete aggressively with rice resulting in severe yield reduction at harvesting. The success of rice production is fundamentally dependent on weed control with herbicides (Day, 1974) because the use of herbicides ensures effective weed control during periods of labour shortage when weeding coincides with other farm work and the critical period of weed competition. Maximum yields can only be obtained if weeds are controlled early because most damage is done when crop plants and weeds are small. The photographs of experimental crop fields were taken periodically at 15 days, 30 days, 45 days after treatment of pesticides and at the time of maturity of the crop and are arranged as description given. The photographs self explains the status of soil, weeds and crop of the respective crop fields.

PLATE-1

Status of experimental crop-fields at 15 days after treatment

T_0 ——— Untreated-Control

T_1 ——— Treated with 2,4-D

T_2 ——— Treated with Isoprotoron

T_3 ——— Treated with Metolachlor

T_4 ——— Treated with MCPA

T_5 ——— Treated with Bromoxynil

PLATE-2

Status of experimental crop-fields at 30 days after treatment

T_0 ——— Untreated-Control

T_1 ——— Treated with 2,4-D

T_2 ——— Treated with Isoproturon

T_3 ——— Treated with Metolachlor

T_4 ——— Treated with MCPA

T_5 ——— Treated with Bromoxynil

PLATE-3

Status of experimental crop-fields at 45 days after treatment

T_0 ——— Untreated-Control

T_1 ——— Treated with 2,4-D

T_2 ——— Treated with Isoproturon

T_3 ——— Treated with Metolachlor

T_4 ——— Treated with MCPA

T_5 ——— Treated with Bromoxynil

PLATE-4

Status of Yield Components of Rice Crop at the time of maturity

T_0 ——— Untreated-Control

T_1 ——— Treated with 2,4-D

T_2 ——— Treated with Isoproturon

T_3 ——— Treated with Metolachlor

T_4 ——— Treated with MCPA

T_5 ——— Treated with Bromoxynil

The study was undertaken to observe the performance of different Pesticides compared with control and selection of suitable pesticide in controlling weeds of transplanting Parmal rice in agro-climatic region of Chapra to increase the crop yield and to lessen negative impact on health of microflora and other constituents of the soil.

In India rice is grown under widely varying conditions of altitude and climate. Rice crop needs a hot and humid climate. It is best suited to regions which have high humidity, prolonged sunshine and an assured supply of water. The average temperature required throughout the life period of the crop ranges from 21 to 37 ^{o}C. Temp, in Chapra district during rice crop season temperature varies between 20 ^{o}C to 35 ^{o}C. At the time of tillering, the crop requires a higher temperature than for growth. Temperature during blooming period was in the range of 26.5 to 29.5°C. At the time of ripening the temperature was between 20-25°C. Photo periodically, rice is a short-day plant so, Chapra district's winter temperatures remained fairly low and only one crop of rice is taken during *Kharif* season.

In India rice is grown under so diverse soil conditions that it can be said that there is hardly any type of soil in which it can not be grown, including alkaline and acidic soils. Soil having good water retention capacity with good amount of clay and organic matter like soil of Chapra district is ideal for rice cultivation. Clay or clay loams are most suited for rice cultivation. Such soils are capable of holding water for long and sustain crop. Rice being a semi-aquatic crop, grows best under submerged conditions. A major part of rice crop in Chapra district is grown under low land conditions. Rice plant is able to tolerate a wide range of soil reaction, but it does have a preference for acidic soils. It grows well in soils of Chapra having a pH range between 5.5 and *6.6.*

Parmal Rice is grown by direct transplanted method in the fields of our Study area. All above detailed observations for different parametrs related with our research study were analysed and discussed in details, in the next chapter of this thesis in the light of better productivity of crop and lesser harm on soil.

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Chapter-V

RESULTS AND DISCUSSION

The potential of a high yielding crop variety bred into it by the plant breeder cannot be maintained if nutrition, water supply or light becomes limiting due to competition of weeds growing along with crop plants. The yield potential of a crop at seeding time is 100% and to maintain this potential weed control must be imposed before any of the above limiting factors for growth becomes operating (Hay, 1974). Similarly, the potential of a soil to support a crop of 2000 or 4000 kg/ha per season cannot be maintained if weeds are a limiting factor. Thus, the gains accrued by weed control have a remarkable effect in permitting a crop variety or a soil or even a production practice achieve its production potential.

Hay (1974) identified the stages in the evolution of weed control practices and they are as follows: (i) 10,000 B.C.—removing weeds by hand, (ii) 6,000 B.C.—the use of primitive hand tools to till the land and destroy weeds, (iii) 1,000 B.C.—animal-powered implements like harrows, (iv)

1920 A.D.—mechanically-powered implements and improved animal-powered implements like cultivators, blades, harrows, linger weeders, rotary hoes, rod-weeders, etc., (v) 1930 A.D.—biological weed control, and (vi) 1947 A.D.—chemical weed control, with the commercial development of organic herbicides like 2,4-D and MCPA.

Thus, through the advances made in weed control since 10,000 B.C. man has succeeded in preventing weed competition and raising crop yield levels to feed not only himself and his family, and others as well. Holm (1971) observed "Crop weed control is the most complex, but also the most important dimension of weed control activity, for it is from our immediate efforts here that we may have more food. Quite unseen and with the dreary stubborn patience of evil, the weeds in crops suck night and day at the soil and moisture to deprive our plants of the vigour and dry matter needed to feed the world."

Commenting on the discovery of the selective action of copper sulphate as a herbicide in 1890, Bolley (1908) observed "when the farming public has accepted this method of attacking weeds as a regular farm operation, the gains to the country at large will be greater in monetary consideration than that which has been afforded by any single piece of investigation applied to field work in agriculture" This prophecy came true some 36 years later when 2,4-D was discovered, which revolutionized agriculture so much that food shortage plagueing North America and Europe at the conclusion of World War II disappeared within a few years. Freed (1980) observed that without pesticides the world would have been lacking a good many tons of grain, and also that the same varieties of wheat under the same climatic conditions yielded 600 to 900 kg/ha more simply due to control of weeds. He further observed that wheat could not be produced in the large acreages in eastern Oregon in USA that were heavily infested with bindweed (*Convolvulus arvensis*). Within a year or two of the availability of 2,4-D, these acreages were released for wheat production, something that had been achieved in almost 15 years of cultivation using cultural-mechanical practices. Thus pesticides made a significant contribution to the agriculture.

Rice Crop Yield Parameters

Generally, weeds have higher content of nutrients than the crop plants and they grow faster and absorb nutrients earlier with the result that there may be a lack of nutrients for the crop plants. Further, the weeds are capable of absorbing just as much or even bigger amounts of nutrients than crop.

In long term trials conducted by Kolbe (1977), it was found that for every 1% increase in yield, weed infestation should be eliminated to the extent of 3% in winter barley, 2% in winter wheat, 0.5% in maize, 1% in potatoes, 3% in tomatoes, and 8% in apples. This shows that crops differ appreciably in competitive ability with weeds. In a review on yield losses due to weed competition, Mani *et al.,* (1968) reported that yield reduction in wheat ranged from 6.3% to 34.8%, in rice from 9.1% to 51.4%, in corn from 29.5% to 74%, in millets from 6.2% to 81.9%, in peas from 25.3% to 35.5%, in carrot 70.2% to 78%, in groundnut 29.7% to 32.9%, in linseed 30.9% to 39.1%, in sugarcane 14.1% to 71.7%, and in cotton 20.7% to 61.0%.

Maintenance of crop yield potential is dependent on the degree of weed control. Complete weed control is rarely achieved by manual or mechanical methods alone. However, pesticides either alone or in combination with mechanical or manual methods provide best weed control and maximum realization of yield potential of a crop. In Colombia, Lange *et al.* (1973) found increased yields resulting from herbicide use over a hand weeded check averaged 17%, the increases in individual crops being 15.6% in barley, 24.1% in beans, 21.3% in corn, 12.8% in cotton, 20.1% and 24.4% in rice.

1. Biological yield (kg ha^{-1})

Analysis of the data, exhibited that pesticides affected the biological yield of crop significantly. Table-1 shows the effect of different pesticides on the biological yield of rice crop. The data indicated that maximum biological yield of 9.12 t ha^{-1} was recorded in Bromoxynil and minimum 6.6 was recorded in weedy control. These results are in conformity with those reported by Salarzai *et al.* (1999).

2. Grain yield (kg ha^{-1})

Analysis of the data exhibited that pesticides had significant effect on the grain yield. The data regarding the effect of different pesticides on the grain yield in Table-2 showed that the maximum grain yield of 3.616 t ha^{-1} was observed in Bromoxynil treated plots. This was followed by 2,4-D and Isoproturon as 3.2 t ha^{-1}. Minimum grain yield of 2.34 t ha^{-1} was obtained in weedy control plots.

The highest grain yield obtained in Bromoxynil treatment was perhaps due to its best control of weeds, while the lowest grain yield obtained in weedy control was probably due to more weed competition. These results are in conformity with those reported by Hassan *et al.* (2003). They reported that herbicidal treatments significantly increased grain yield in wheat.

3. Thousand grain weight (g)

Pesticides use affected 1000 grain weight significantly. Data regarding the effect of different herbicides on 1000 grain weight are given in Table-3. Thousand grain weight was highest (23,374) in plots treated with Bromoxynil followed by MCPA (22.01 g) and Metolachlor (22.03 g). Lowest 1000 grain weight was recorded (21.45 g) from the weedy control. Similar results were reported by Hassan *et al.* (2003) who found that herbicides increased the 1000 grain weight significantly when compared with the weedy check.

Among the yield contributing characters Biological yield of Crop, Grain Yield of Crop and thousand grain weight of Crop were significantly influenced by different herbicide treatments (Table-1). Among the treatments it was visually observed that all pesticidal plots produced the tallest plants where the lowest plant height was observed from control plot (weedy check). The pesticidal treatment gave the efficient weed control in the treated experimental plots.However, 1000 grain weight was remained changed due to different treatment (Table-3). These results corresponds with the results Antigua *et al.* (1988).

The ultimate reflection of Bromoxynil treatment was appeared as highest grain yield (3.61 t ha^{-1}) of transplanted Parmal rice in this experiment (Table-2). It might be the resultant effects of higher tillers hill^{-1} and grains panicle^{-1}. Straw yield also significantly affected by different treatments (Table-1). In this study, the highest straw yield was obtained, from the treatment of Bromoxynil which was followed by other treatments. Both of the grain yield and straw yield was observed from the treatment plots as Biological yield. It was also clear that maximum weed infestation in control plot suppressed the growth of rice plant. These result corroborated with the results of Ahmed *et al.* (2005) and Smith and Moody (1979).

Weed management treatments significantly promoted rice grain yield components as compared to the control (Table-2). The highest number of productive tillers was visually observed in experimental plots in which bromoxynil, 2,4-D and Isoproturon were applied, while the lowest was found in the control plots. Improvement in grain yield and related traits as compared to the control in the present study could be attributed to reduced weed-crop competition, thereby attaining a higher number of productive tillers. Weeds usually emerge just after the transplantation of rice and outcompete young rice seedlings due to their aggressive growth characteristics. The yield of Parmal Rice particularly remain at risk due to weeds that establish in the field. Delaying weeding beyond 20 days after transplant substantially reduces yield (Adigun *et al.,* 2005). Moody (1991) reported that weeds accomplish 20-30% of their growth as compared with 2-3% for the rice crop. Most of the weed flora encountered in the present study was comprised of highly competitive C_4 weed species as also found by (Caton *et al.,* 2004). The level of yield reduction in control plot under season-long weed infestation corroborates previous work done by Moody (1992). Be effectively used to control broadleaf weeds and thin leaves and more grain yield in direct seed rice, once hand weeding in 45 days after planting and Pendimethalin application (750 g/ha) was used as the preemergence pesticide (Riaz *et al,* 2007).

The removal of the competitive effect of weeds led to an increase in the growth of the yield components of rice crops and as a result the grain production also increased. The lowest grain yield was recorded in untreated control plots (2.39 t/ha)while the highest grain yield (3.61 t/ha) was recorded in plots treated with Bromoxynil. Chin *et al.,* (2000) also reported a significant increase in rice yield after the application of herbicides in comparison with untreated controls. Herbicide treatments for the control of weeds doubled rice yields in Italian experiments (Tabachhi & Romani 2002). In experiments in Greece, the control of barnyardgrass led to a fourfold increase in rice yields (Ntanos *et al.,* 2001). Talbert and Burgos(2007) found that penoxsulam did not injure rice and improved rice yields compared with standard propanil-based programs. Our results corresponds with the outcome of above discussed authors.

TOXICITY:-

Pesticides are phytotoxic by design, and any selectivity achieved depends upon several factors (environment, dose, stage & timing and method of application of pesticides). Thus, phytotoxicity of the herbicide to crop itself is not uncommon due to the selectivity achieved under field conditions under various climatic conditions. Nevertheless, even if a pesticide molecule is phytotoxic on crop, its potential for weed management will still depend on relative benefits compared with other methods of weed control. Present study concludes that 2,4-D, Metolachlor and Bromoxynil were relatively less harmful to rice and were still effective against weeds. Positive effect of weed control associated with these may be considerable and outweigh toxic effects on rice seedling, and possibly on yield, if any.

Metolachlor, Isoproturon and MCPA are mostly active as surface active pesticides interfering with the synthesis of protein, nucleic acid and long-chain fatty acids as their primary mode of action. They are taken up primarily by germinating shoot and secondly through root passing through continuous layer of soil. Although Isoproturon and MCPA are quite effective against grasses in wet-seeded rice, its efficacy is lowered in dry-seeded rice presumably due to low soil moisture of dry seeded rice fields (Bindra *el al*, 2002; Saha *et al.*, 2003; Yadav *et al.*, 2008). They also revealed its phytotoxicity, which is also reported elsewhere (Koger *et al*, 2006). Penoxsulam seizures root growth by inhibiting translocation of photosynthates from source (leaves) to roots. Pesticides has the enzyme acetolactate synthase as target site. The inhibition of this enzyme retards the synthesis of branch chain of amino acids like valine, leucine and isoleucine, thereby hampering growth due to rapid cessation. All the plants whether susceptible or not posses this enzyme; selectivity, however, arises due to metabolic detoxification because some of the plants convert it into inactive form. In our study 2,4-D was found most suitable because it's toxicity level on crop remained as zero.

Pesticide residue in crop grains and soil

All used pesticides showed less residue in crop grain and straw during this research study. But accumulation of pesticides were observed in significant amount in the grains obtained from the treated crop-field with Isoproturon as 0.8230 ppm.

The degradation of applied pesticides or their conversion into other products does not; necessarily mean the loss of biological activity, and many times, this conversion can result in even more toxic products. The study of the persistence of pesticides in crop fields is of great importance in order to evaluate the risks of, environmental pollution. Due to the new model of agriculture adopted in recent years pesticides usage has become intensive.

By use of pesticides, now-a-days, many related environmental problems are occurring (Steckert *et al*, 2009). The characteristics of rice fields, the climate conditions and the use of pesticides contribute to the enhanced risk of surface water pollution, justifying the need to quantify their degree of occurrence and to implement measures to prevent it. In our observation it was found that after 90 days of application 2,4-D persisted in rice-crop field soil as 33.2%, Isoproturon upto 68%, Bromoxynil upto 74.2%, MCPA upto 34.4% and Metolachlor upto 4.6% only. Thus it is evident that Metolachlor and 2,4-D mineralises fast and persists for comparatively lesser period. The cultivation of irrigated rice can generates a great impact to the environment so much in amount as in the quality of the surrounding water because it is a submerged crop and also demands intense agrochemical use, mainly herbicides, and fertilizers (Noldin *et al.*, 2001). In Indian conditions, the contribution of agriculture to water pollution is not well quantified, but in United States, 50 to 61% of the pollution load that affects lakes and rivers come from agriculture (Gburek & Sharpley, 1997) being the superficial runoff the main mechanism of pesticides transport. Although agriculture is just one of the countless nonpoint-sources of pollution, it is generally targeted as the largest source among all pollutant categories.

In most of the rice crop field farms, the pesticide applications and on the occurrence of rain after pesticide application, there is a risk that part of the applied compounds will be carried out of the area, contaminating water sources (Jury *et al.,* 1990; Squillace & Thurman, 1992; Solomon *et al.* 1996; Primel *et al.,* 2005). Irrigated farming for food production is the agricultural practice that most contributes to the deviation of water from its natural courses. Scarcity of water resources, which is occurring on a world-wide level, as well as the use of a large quantity of water, which is partially returned to its natural sources, makes irrigated rice farming a serious concern in terms of possible consequences for the environment, both in quantity and quality of the water sources (Kurz *et al,* 2009).

Rice productivity levels raised high during recent years. However this high productivity is associated with the intense use of pesticides and chemical fertilizers (Baird & Cann, 2005). Pesticides are potential contaminants of environmental water because they are directly applied. Thus, they can be leached to the surface water and transported into the groundwater (Hatrik & Tekel, 1996; Zanella *et al.,* 2002). According to specialized literature (Barcelo & Hennion, 1997; Primel *et al.;* 2005; Cabrera *et al.,* 2008), a pesticide can pollute the aquatic environmental water. But it was observed during our study that herbicides used during this study did not persists for long time in soil. So, check of the outflow of water from treated plots, especially during rains would check pollution of water bodies.

In the pre-germinated system of irrigated rice cultivation frequently employed drainage from the area after sowing can set off serious environmental problems, as well as cause the loss of nutrients and/or pesticides that are in suspension in the irrigation water that is released. This has been evidenced in studies carried out by Primel (2003) and Machado (2003), where the occurrence of some pesticides, mainly those that present high persistence, was confirmed in river and irrigation waters. Some studies has been done until now to investigate the behavior and destination of pesticides in the systems related to the rice paddy fields in an attempt to evaluate the risk to the environment. Bortoluzzi *et al.* 2007; Grutzmacher *et al.* 2008; Caldas *et al.* 2009; Silva *et al.*, 2009; Caldas *et al.* 2010: Demoliner *et al.* 2010; Marchesan *et al.* 2010; Reimche, 2010).

The difference in the soil sorption process of pesticides might be explained by several factors. The extent of adsorption depends on the amount of the pesticide and properties both of the soil and the pesticide. 2,4-D and MCPA were more strongly and extensively adsorbed in the soil, than Metolachlor, Isoproturon and Bromoxynil. A magnitude higher absorption capacity of pesticides might be explained in part by their water solubilities and hydrophobicities. The strong adsorption and low desorption characteristics of 2,4-D and MCPA suggested that for the soil, migration to the groundwater would be lower than for the other chemicals examined. Isoproturon acted by passive absorption by the roots by penetrating the membranes of cortical cells in and forward movement into the stele and upwards in the transpiration stream. The absorption spectrum was similar to chlorophyll and acted by blocking oxygen evolution which resulted in chlorophyll degeneration and chloroplast disorganization leading to progressive chlorosis, retardation of growth and death of the plant.

Thus it became clear that the generation of pesticide waste was an inevitable by-product of every aspect of pesticide technology. In the end, the important matter was not so much how the residue was defined, but the question of its biological availability (Calderbank, 1989; Gevao *et al.*, 2003). In the absence of information on the nature and on the degree of reversibility of the stabilised residues, it seemed necessary to consider this aspect in a broader context of pollution. The idea was to propose the definition of different pesticide pollution levels according to specific "variable" thresholds in relation to the target or to the methods used. The "biocidal pollution" could be defined by a concentration threshold for which a toxic action was observable. This pollution level was directly related to the pesticide bioavailability, in relation to the concentration of pesticides in the soil water. It was the most perceptible pollution level as it results for instance in fish mortality, crop phytotoxicity or the inhibition of soil microbial activity. The "chemical pollution" corresponded to the presence of xenobiotic organic molecules in soils. The concentration threshold was related to the extraction yield and the sensibility of the analytical methods used for their quantification. The "ecological pollution" is defined in relation to any manifestation of pesticides or of their degradation products in the short or long term. This pollution level included biocidal and chemical pollution, and had a concentration threshold lower than the two others.

Decomposed organic matter in soil

Several studies had shown that, the soil properties, particularly the content and nature of organic matter in the soil played a key role in the performance of applied pesticides (Hamaker and Thomson. 1972; Stevenson. 1972). The soil organic matter have a polydisperse nature with polyelectrolytic character, surface activity properties and various chemically reactive functional groups, hydrophilic and hydrophobic sites, which influence the soil-organic pesticide adsorptive interaction. The natures of the binding forces were determined by the type of mechanisms that operated often simultaneously. These included ionic, hydrogen and covalent bonding, charge transfer and electron donor-acceptor mechanisms. In our observations it became evident that amount of decomposed organic matter in all experimental fields increased gradually over span of time. This trend facilitated the process of mineralization of used pesticides & reduced possibility of persistence in soil for long time.

The dependence of pesticide behaviour in soils with soil organic matter is related to more or less specific interactions or reactivities (Ahmad *et al.,* 2001; Martin-Neto *et al.,* 2001). Physical interactions are responsible for sorption and colloidal entrapment, chemical interactions imply establishment of covalent bonds, and biological interactions concern pesticide transformation and incorporation into the soil microbial biomass. All these interactions are space and time dependent. Spatially, sorption and degradation depend on the accessibility of sorption sites and degrading microorganisms (Alexander, 2000), respectively. Pesticide availability in soils was time dependent, and decreased with increasing pesticide residence time because of the evolution of the initial interactions between the pesticide and the soil constituents. The initial physico-chemical interactions responsible for sorption were reversible, but they could become less or non reversible with time, leading to the stabilization of the pesticide residues under less available and less biodegradable forms (Khan, 1982). Various hypotheses have been proposed to explain residue formation: chemical binding to soil organic matter constituents, oxidative coupling with phenolic soil constituents and incorporation into phenolic co-polymers, bioincorporation in cellular structures through metabolic activity of soil microorganisms, blocking of internal voids of soil organic constituents and soil microorganisms (Mathur & Morley, 1975; Bollag & Myers, 1992). All of these hypotheses point out the fundamental role of soil organic matter and soil microorganisms. However, White (1976) indicated early that some interactions with soil mineral constituents (clays) could contribute to residue. This type of interactions could be determinant in the deeper soil horizons where the organic matter contents were low. The interactions leading to residue formation could be classified into two categories: those implying the establishment of the chemical bonding (corresponding to a "chemical stabilisation") and those implying a sequestration or physical trapping into the organic constituents. In addition, soil microbial biomass was an additional soil compartment to be considered because it could directly stock pesticide residues under non extractable forms.

This was explained by the creation of anaerobic microenvironments for the microbial degradation which normally contributed to the reductive dechlorination. Other information on anaerobic degradation or on the effect of flooded soil conditions on pesticide degradation for acetochlor (Loor-Vela *et al.,* 2003), atrazine (Weaver *et al.,* 2004), carbaryl (Murthy & Raghu, 1991), carbofuran (Kale *et al.,* 2001), dimethenamid (Crawford *et al.,* 2002), fluometuron (Weaver *et al.,* 2004), metolachlor (Rice *et al.,* 2002) and nitrofen (Kale *et al.,* 1997). Soil organic matter was the most significant factor affecting adsorption, and hence herbicide behaviour in soils. Organic matter increased the adsorptive capacity of the soils through humic acids which were responsible for stable bonding during adsorption. Senesi and Testini (1980) reported that adsorption involved H-bonding, van der Waal's forces, and ionic bonds in triazines. Upchurch and Mason (1962) examined

12 different herbicides including CIPC, 2,4-D, EPTC, CD A A, simazine, dalapon, DNBP, sesone, diuron, etc., and found that the activity of all of them were highly correlated with organic matter content. Their results also indicated that organic matter adsorbed the herbicides and this greatly affected their toxicity. Upchurch et al. (1966) found no consistency in the effect of organic matter on the phytotoxicity of five herbicides among three crop species. Organic matter reduced the phytotoxicity of simazine to grass weeds more than to cotton, of diuron to cotton more than grass weeds, and of CIPC (chlorpropham) about equally to cotton and grass weeds but more than to soybean. Organic matter had little effect on the phytotoxicity of CDAA. These studies indicated that the influence of organic matter on the phytotoxicity of herbicides in soil may vary according to crop species.

Generally, an increase in organic matter content results in reduced herbicidal activity and this warrants an increase in the rate of application. Parochetti (1973) found that an increase in organic matter content of the soil resulted in an increase in the GR_{50} values (rate of herbicide required for 50% growth reduction) for propachlor, alachlor, prynachlor, CDAA, and atrazine. Rahman and Matthews (1979) observed similar correlation between organic matter and 13 triazine herbicides.

Larger microbial communities develop in soils that have been treated with composts, mulches, manures, compared to those that have been supplemented with mineral nutrients (Gunapala and Scow, 1997). Different types of cover crops for example soybean, maize, legumes, have a positive effect on enhancing soil microbial functions and enhancing soil microbial biomass (Han *et al.,* 2007). Phytotoxic substances produced by certain cover crops can also have inhibitory effects on seed germination and growth of other plants, a phenomenon referred to as allelopathy. For example, extracts from black mustard have shown a reduction in germination and seedling weight of wild oats (Turk and Tawaha, 2002). The amount of organic matter in soil directly influences soil microorganisms by affecting their biological activity (Rotenberg *et al.*, 2007). One of the major factors in agriculturally induced soil degradation is mineralization of organic matter (Crecchio *et al.*, 2006) which influences the physical, chemical and biological properties of the soil. Organic amendments are well known for their ability to improve soil conditions and this serves as a source of carbon and nutrients, favouring microbial diversity (Gomez *et al.,* 2005). Organic amendments indirectly stimulate the biogeochemical cycles in soil and increase certain minerals that are essential for the growth of plants (Ros *et al.*, 2006). Organic amendments also increase organic matter within the soil, change the structure of the soil and alter several physical, chemical and biological properties (Odlare, Pell and Svensson, 2007). They alter the functional diversity of microorganism communities in soil. Microorganisms which utilize applied organic amendments will out-compete other soil biota; this alters not only the microorganism communities but also soil fertility as a whole (Geisseler *et al.,* 2010).

Compost is well known for its ability to enhance plant growth, improve soil quality, enhance microorganism activity and suppress plant pathogens (Abawi and Widmer, 2000; Ros *et al.,* 2006). Significant changes in microorganism community structure have been demonstrated following the application of different kinds of composts (Carrera *et al.,* 2007); animal manure (Gomez *et al.,* 2005); and other organic amendments (Tejada *et al.,* 2007). Diosma *et al.* (2005) showed that a substantial increase in organic N in soil leads to an increase in microorganisms which metabolize carboxylic acids. These microorganisms out-compete others due to high N availability thereby altering the functional diversity of other microorganisms and ultimately soil fertility. The long term application of compost in rice paddies significantly increased carbon utilizing soil microorganisms judging by a concomitant increase in enzymatic activity (Nayak *et al.,* 2007). Comparisons between the application of long term organic and inorganic fertilizers showed clear differences in terms of community diversity of the associated microorganisms (Nayak *et al.,* 2007).

Microbial Population in Soil

Organic and inorganic mulches play an important role in the management of several anaerobics (Jensen *et al.,* 1996). In severe cases of soil compaction, the functional ability and enzyme activities mediated by microbial organisms can be greatly decreased (Jordan, Ponder and Hubbard, 2002). Variation in crop species because of crop rotation, intercropping and cover crops can also alter the physical and chemical properties of soil. This in turn will lead to changes in the functional diversity of microbial communities under different cropping systems (Wang *et al.,* 2006). Gil *et al.* (2010) showed that bacterial and fungal diversity increases in soil undergoing crop rotation compared to soil undergoing tillage treatments. Increases in microbial and enzyme activity also has been observed in multi-cropping and crop rotation systems compared to monocropping systems.

Agricultural soil amendments have been shown to severely affect soil microbial organisms within an agroecosystem. Applications of organic manures changes the nutrient and pH status in soil, which in turn influences the functional diversity and biomass of microbial organisms. While organic fertilizers are known to increase microbial biomass due to N and C input into soil, they impact directly on microbial diversity.. Wang *et al.* (2008) found no significant changes in microbial diversity with the application of organic manure, but a decrease when chemical fertilizers were applied. The non-target effect of fungicides, herbicides and pesticides on microbial organisms has always been a topic of interest (Lupwayi *et al.*, 2009). Long-term fungicide and herbicide inputs may result in a reduction of soil processes mediated by microbial organisms. For example the application of fungicides, results in a decrease in nutrient cycling, nitrogen dynamics and enzyme activities in soil due to the direct toxic effect of these chemicals on microbes (Wang, Zhou and Cang, 2009). In our observation the population of bacteria and fungi showed initial inhibition after the application of pesticides (Tables-8 and 9), which is in accordance with the above mentioned studies.

Respiration is considered as an indicator of biological activity in soil. Application of pesticides appears to have had an inhibitory effect on soil respiration. It was also observed during our study that the microbial mass of pesticide treated soil was in general less than the untreated soil.

Climatic factors (Moisture Content, pH and Temperature of Soil)

Persistence is a measure of the adaptive potential of pesticide and enables it to remain present in any environment. In an agricultural situation, the cropping system with its associated habitat management practices, determines the persistence of applied pesticides.

Climatic Factors. The important climatic factors of the environment that affect persistence of pesticide were as follows:-

(i) Light intensity, quality, and duration were important in influencing the growth, reproduction, and distribution of weeds and also to persistence of pesticides. Our experimental fields got good light intensity and duration.

(ii) Temperature of atmosphere and soil affects the distribution of weeds and also persistence of pesticides. Soil temperature affects seed germination and dormancy which is a major survival mechanism of weeds. Temperature of soil at the time of maturity of crop was found as 20 ^{o}C during our environmental study.

(iii) Rainfall and water have a significant effect on weed persistence and from those of aquatic environments. The pattern of rain is a determining factor in utilization of water supply by the plant, since water shortages at critical stages of growth was often responsible for reproduction and survival of weeds in experimental rice crop fields.

(iv) Average relative humidity of soil ranged between 80 to 90 percent during crop season and between 22 to 40 after harvest of crop during experimental period.

(v) Soil Factor: Soil factors which influence pesticide persistence are soil water aeration, temperature & pH. pH of the soil of our experimental fields ranged between 5.5 and 6.6.

Selectivity of an applied pesticide is also influenced by the environmental factors under which the plant grows. The response of a plant to an applied chemical depends upon the environmental stresses to which it has been subjected following treatment. The various environmental factors that affect plant growth and hence pesticide activity and selectivity are temperature, rainfall (water), humidity, light, and wind. They largely influence absorption and translocation of pesticide by the plant. The environment before, during, and after the pesticide application, has considerable effect on the growth and development of the plant. This eventually affects the absorption and translocation of pesticide. It is difficult to isolate the effect of one environmental factor from the other.

Plant species and varieties vary greatly in their requirement of optimum temperature and humidity. Temperature and humidity have significant effect on transpiration, respiration, and evaporation. High temperature causes injury to plants by altering the balance between water absorbed by roots and that lost through transpiration. When air temperature rises the rate of transpiration increases, resulting in possible adverse effects on the metabolic and physiological activities of the plant which may have a critical effect on pesticide absorption and translocation. Respiration remains low at lower temperatures and it increases with an increase in temperature. High temperature causes rapid evaporation of water, causing water stress on the plants.

Humidity has considerable influence on the development of cuticle, transpiration, and water stress. Relative humidity is more important than absolute humidity. Aqueous solutions enter the hydrated cuticle more easily. At high relative humidity, water content of the leaf is high and this facilitates free movement of the pesticide in the apoplast and the symplast. High turgor pressure in the protoplasm at high humidity leads to more active protoplasmic streaming and more rapid translocation in the pholem sieve tubes. This explains the rapid absorption and translocation of foliage-applied pesticides under high humidity conditions. Throughout our experimental period the crop field soil remained as highly humid.

An increase in temperature enhances absorption and translocation. Pallas (1960) found that at the temperatures 20°C, 25°C, and 35°C, less 2,4-D and benzoic acid was absorbed and translocated at lower humidities (34 to 48%) than at higher humidities. The increased absorption and translocation at higher humidity was correlated with the degree of stomatal opening. Such an increase in absorption and translocation at higher humidity is due to increased phloem transport. McWhorter and Wills (1978) reported that at a constant level of 40 to 100% relative humidity, an increase in air temperature from 22°C to 32°C resulted in a two- or three-fold increase in absorption and a four- to-eightfold increase in translocation of mefluidide in soybeans. Similarly, at a constant temperature of either 22°C or

32°C an increase in relative humidity from 40% to 100% resulted in less than two-fold increase in absorption and translocation of mefluidide.

The volatilization of a pesticide from soil or foliar surfaces depends mainly on the vapour pressure of the compound, its concentration, its adsorption to soil, and its solubility in water. It is also affected by air temperature, wind velocity above the soil surface, relative humidity, soil temperature, and soil moisture. Drift during spraying also provides an opportunity for volatilization. It is also influenced by the chemical nature of the compound. Some pesticides are metabolized or degraded relatively rapidly to more polar products which may be strongly absorbed to soil. Volatility can be a factor in reducing the effectiveness of a pesticide. In such cases, incorporation in soil or improved formulation reduces the loss by volatilization.

Codistillation with water is sometimes explained to cause substantial loss of some pesticide from soil surfaces. Codistillation with water involves physical or chemical reaction between water and the chemical, with the product being more volatile than the parent chemical itself. However, codistillation is generally referred to as the creation by water of an interface at which the chemical is concentrated and/or at which the chemical is held with reduced energy. If the net result of the presence of water increases partition into the air phase it is commonly said that the volatility of the chemical has been enhanced by codistillation with water.

Many volatile pesticide show a direct relationship between volatilization and soil moisture. These include carbamate, dinitroaniline, and thiocarbamate pesticide. Their vapour loss is greater in moist soil than in dry soil. At low soil moisture, the vapour of the herbicide is considerably reduced and it is adsorbed to the soil although the binding energy is weak. In high soil moisture situation, water competes with pesticide for sites of adsorption resulting in decreased pesticide adsorption and hence greater volatilization. Gray and Weierich (1965) found that during the first 15 minutes after spraying on the soil surface, 20% of the applied EPTC was lost by volatilization from dry soil, 27% from the moist soil, and 44% from the wet soil. After one day, the losses were 23%, 49%, and 69% from dry, moist, and wet soils respectively. They also found that increasing the air temperature from 32 to 60 °F (0 to 15.5 °C) increased the rate of EPTC vaporization from moist soil than from dry soil. Parochetti and Hein (1973) showed increased vapour losses of dinitroaniline pesticide trifiuralin and benefin, with an increase in temperature from 30 to 50 °C and soil moisture from air dryness to field capacity, but failed to increase at moisture level above field capacity at temperatures 40 or 50 °C. Harper *et al.*, (1976) reported that under field conditions trifluralin flux increased during the day when soil surface water content was low even though air turbulence, soil temperature, and evaporative demand were high. During the night when evaporative demand subsided and soil surface water content increased, the trifluralin flux also increased. They also reported that trifluralin adsorption to soil particles upon drying is apparently a reversible process since efflux of the herbicide was rapid when the soil was rewetted by dew or rainfall to above the equivalent of three molecular layers of adsorbed soil water. Hollingworth (1980) found trifluralin vapours accumulating rapidly during a period in which several centimetres of rain fall, but with continued precipitation the vapour density declined. The influence of rainfall and resultant soil moisture upon vaporization became less apparent as the soil concentration of the herbicides declined.

The vapours of herbicides emitted during volatilization could be phytotoxic. Swann and Behrens (1972) observed severe shoot growth inhibition from trifluralin (vapour pressure 1.99×10^{-4} mm Hg at 30

°C) vapours emitting even 16 to 22 days after application to soil. Jaques and Harvey (1979) found that all the 8 dinitroaniline herbicides except oryzalin inhibited primary root growth of oats through vapour activity. Dinitra- mine vapours were most inhibitory. The inhibition due to herbicide vapours increased with increasing temperature. Benefin which has a vapour pressure of 3.89 X 10“^{5} mm Hg at 30 °’C caused severe injury to tobacco seedlings through its vapours (Yamasue and Worsham, 1980). Gray and Weierich (1965) recommended soil incorporation to a depth of 2 to 3 inches (5 to 7.5 cm) to prevent large vapour losses of EPTC, with a follow up of light rain or sprinkler irrigation.

Adsorption of herbicides to soil reduces volatilization. Vapour loss has direct relationship with the percentage of sand and inverse relationship with the percentage of clay and organic matter. Volatile feticides that are strongly adsorbed may remain on the surface of clay soils or soils containing large amounts of organic matter. Bardsley *et al.,* (1967) found that increasing organic matter from 1.5 to 6.0% resulted in proportionally greater retention of active trifluralin in the soil. They suggested that the increased adsorotive capacity of the organic materials was instrumental in retaining herbicides vapours.

Sprankle *et al.,* (1975) found that glyphosate was inactivated rapidly by clay, loam and muck soil. In the case of urea pesticides, adsorption was greater on bentonite than on montmorillonite clay largely because the lattice charge in the former originated from tetrahedral and octahedral layers, whereas in the latter only from octahedral layers (Van Bladel and Moreale, 1974). The persistence of EPTC in dry soils is due to the ability of soil particles to adsorb this chemical. Mortland and Meggitt (1966) proposed three mechanisms of adsorption of EPTC to montmorillonite: (a) coordination to exchangeable metal cations through the carboxyl group, (b) coordination to metal cations through the nitrogen, and (c) hydrogen bonding to methylene hydrogens through surface oxygen atoms on the clay surface.

Smith (1970) found that triallate was adsorbed almost completely by four soils while diallate was adsorbed to a lesser extent. Hence, soil volatility losses and leaching losses of triallate were negligible as compared to those of diallate. As a result, persistence of triallate is greater than of diallate.

The weak base pesticides like atrazines are less effective in soils of low pH. They adsorb hydrogen ions in an acidic solution and become cationic. Hams and Warren (1964) found that more atrazine was adsorbed by a muck soil at pH 3.2 than at 5.3 as little atrazine (pKa 1.85) would exist as cation at pH 5.3. Adsorption is generally more pronounced when the pH of the soil is near the pKa (ionization constant) of the herbicide. In high pH soils, triazines are desorbed into the soil solution which would result in greater availability of the chemical for uptake by plant and possible risk of injury even at rates considered safe. The strongly basic herbicides like paraquat and diquat are so rapidly and tightly bound to montmorillonite clay and organic matter particles that they are virtually inactivated as soon as they come in contact with the soil. A strongly acidic herbicide like glyphosate is adsorbed more at low pH. Sprankle *et al.*, (1975) reported that Fe^{+++-} axid Al^{+++-} saturated clays and organic matter adsorbed more glyphosate than Na^{+}- or Ca^{+}- saturated clays and organic matter. Glyphosate was readily bound to kaolinite, illite and bentonite clays, and to charcoal and muck. The strongly acidic herbicides like benzoic acids, phenols, aliphatics, and nitriles possess carboxyl, phenolic or phosphonic functional groups and they ionize in soil solution to become anions. The weakly acidic pesticides like 2,4-D, dicamba, and dinoseb are less active at a soil pH 5.0 or below (Corbin *et al.*, 1971). They tend to be repelled by, rather than attracted to, the negatively charged soil and organic matter surfaces. As the percentage of negatively charged herbicide molecules decreases at low pH, adsorption increases, and hence their low activity at pH below 5.0. In general, acidic herbicides are adsorbed more strongly by charcoal, organic matter, and anion-exchange resins, and the basic herbicides are adsorbed more strongly by cation-exchange resins and soils. pH of our experimental fields ranged between 5.5 and 6.6, which favours above stated references.

The nonionic pesticides like urea herbicides, and trifluralin and other dinitroanilines which do not ionize significantly in soil solution can also be affected by soil pH,, but to a much smaller degree than the basic and acidic herbicides. These nonionic pesticides are adsorbed through physical adsorption forces (Weber, 1973). Hance (1965) reported the following order of increasing adsorption tendency among urea pesticides: fenuron, neburon, phenylurea, monuron, monolinuron, diuron, linuron, and chloroxuron. He found that *N*-alkyl and *N*-aryl substituents played a part in the adsorption of substituted ureas by soils. Increasing chain length in the alkyl substituents, and chloro- and chlorophenoxy- substitution in the aryl substituents increased adsorption. Bailey and White (1964) observed that the presence and amount of such functional groups as the carboxyl, amino, phenolic hydroxyl, and alcoholic hydroxyl would have a great effect on the cation and anion adsorption of pesticides.

Water solubility of a pesticide is expected to affect adsorption by the soil. However, the results found in the literature did not always support this contention. Bailey *et al.,* (1968) reported that there was a relationship between water solubility and extent of adsorption. Several workers (Hilton and Yuen, 1963) found an inverse relationship between solubility of pesticides including urea pesticides, and adsorption, while Bailey *et al.*, (1968) reported a direct correlation between solubility and adsorption of urea pesticides. Hance (1967), however, found no relationship between solubility and absorption of the ureas. These conflicting reports suggest some disagreement on the influence of water solubility of a pesticide and its adsorption and availability in the soil. Thus our observations for different parameters showed that the climatic conditions of our crop fields showed as best suitable for mineralization of pesticides and finally removal from soil.

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Chapter-VI

CONCLUSION AND SUGGESTIONS

Rice is considered the most important staple food in the world as it supplies the major food requirement for more than one half of the world's population. This crop has become an important staple food whose demand is always on the increase. As a staple food, rice has also provided more calories per hectare than other cereal crops.

In spite of its diversified uses and high acceptability both as food and cash crop, the production of rice is constrained by a number of factors. These include problems of insect pests, diseases and weeds. Of all the constraints limiting the production of this crop, weeds, appear to have the most deleterious effect causing reduction in potential paddy rice yield. Inadequate land preparation, use of short-stature early maturing cultivars and increased fertilizer use have resulted in severe weed problems in rice.

Traditional manual weeding is the most popular method of weed control in India and also in Chapra (Bihar). This is however, time consuming, labour-intensive and generally expensive. It is estimated that about 40-60% of production cost is spent on manual weeding. Rice being a closely sown crop also makes mechanical weeding difficult and some degree of crop damage is unavoidably involved in manual weeding. In addition hand weeding allows weeds with similar morphological characteristics to rice to escape detection. Besides, weeding cannot be done at a time when labour is available but this may not coincide with the optimum weeding time for minimizing weed competition. Medium and large scale farmers are particularly affected by lack of labour for hand weeding which to be effective, must take place early in the crop life cycle.

Hence in large scale rice production in India, chemical weed control represents a practical and economical alternative to hand weeding because the use of pesticides ensures effective weed control during the period of labour shortage when weeding coincides with other farm work.

Successful weed control is essential for economic rice production. Weed can reduce rice yield by competing for moisture, nutrients and light during the growing season. Weed infestation can also interfere with combine operations at harvest and significantly increase harvesting and drying costs. Weed seeds contamination of rice grain lower grain quality and may lower the cash value of the crop. Weed infestation is one the causes of serious yield reduction in rice production worldwide.

Every farmer knows that pesticides cost money. But there are other costs the farmer may not consider when he buys pesticides. There is the cost to the health of the farmer and other people affected by pesticides. There is the cost of polluted water and soil. And there is the cost to the environment, fish, animals, and other microflora of soil. Soil organisms eat, drink and breathe toxic chemicals in the environment just like people do. When large animals such as owls, hawks, and humans eat smaller animal's containing small amounts of pesticides, all of those pesticides collect in their bodies and poison them. This is one way that toxic chemicals spread from one place to another.

Farmers know that soil is not just dead material. Healthy soil is full of life. Insects, worms, fungi and bacteria keep the soil alive and create nutrients that make plants grow healthy. When pesticides kill these creatures, the soil becomes less able to support growing plants. Plants that grow in this soil do not have the natural ability to protect themselves from pests. Farmers then use even more pesticides. This makes the problem worse. Over time, the soil dies and healthy plants will not grow in it at all.

Pesticides are considered almost synonymous with modern weed science technology as they gave a new direction to the farmer to realize the maximum yield potential of the crop at lower production costs which has never been possible. At the same time, weed science became an intriguing and a fascinating technology that it never was. The weed scientists saw enormous scope for research to unravel the mysteries of their science in the field. Today, after the commercial development of 2,4-D, MCPA and other pesticides, weed scientists made phenomenal progress in understanding the selective action of over 250 pesticides by studying their absorption and translocation patterns, mechanisms of their action in plants, degradative and detoxification mechanisms in plant and soil, interactions with other pesticides and chemicals, etc. All this helped in making more effective, economical, and safe recommendations for control of numerous weeds in different crops.

During this process the scope of weed science has widened to areas outside of agronomy and botany, like soil science, plant physiology, biochemistry, organic chemistry, ecology, toxicology, etc. to evolve into a distinct discipline of its own. It now strongly identifies itself as a major discipline of plant protection as manual, mechanical, biological, and chemical methods effectively protect the crop from the ravages of weeds.

In spite of the dominating influence of herbicides on modern weed control technology, the need for cultivation, hand weeding, hoeing, and other manual, mechanical, and cultural methods has not disappeared from agriculture nor will it. However, in certain regions of India and other developing countries where farmers are progressive and have greater managerial ability, where labour is scarce and expensive, and where modern agricultural practices have been successful, pesticide technology has made deeper inroads and met with an instant success.

The one major factor that could retard the acceptance of modern weed science technology in India is the limited supply of weed scientists to explore new avenues in weed science research, to train future weed scientists, and to help implement the technology in the farmers’ field. Excessive, and often irrational regulation of pesticides in the country may also become another factor that could retard the beneficial effects that modern weed science technology offers to the farmer. Immediate steps need to be taken by governments to create departments solely devoted to weed science in universities and research institutions in the country and intensify research, teaching, and extension activities so that the potential of modern weed control technology will not be left unharnessed and unrealized.

The greater contribution of anthropogenic versus natural organic components is significant and requires further studies to determine the fraction of each source of organic components to soil in crop fields. Additional detailed studies are also needed to identify the reason(s) for the occurrence and distribution of these pesticides and herbicides in certain locations and not in others. The characterization, identification and quantification of organic compounds in soil, sand and atmospheric particulate matter of remote versus rural areas are also crucial and important in order to facilitate the processes of environmental assessment aid prediction of the impact of these compounds on human health.

Damage Caused by Weeds:

(1) Reduction in Crop Yield

Weeds compete with crop plants for nutrients, soil moisture, and sunlight. The intensity of weed competition depends upon: (a) type of weed species, (b) severity of infestation, (c) duration of weed infestation, (d) competing ability of crop plants, (e) climatic conditions which affect weed and crop growth, and (f) chemical weed control measures.

Reduction in crop yield has a direct correlation with weed competition. Generally, an increase in one kilogram of weed growth corresponds to reduction in one kilogram of crop growth. Weeds remove plant nutrients more efficiently than crop plants. In drought situation they thrive better than crop plants. When left uncontrolled, some weeds can grow taller than crop plants and inhibit tillering and branching. They curtail sunlight and adversely affect photosynthesis and plant productivity of crop plant. Crop yield loss from weeds is highest in the tropics. For example, a study conducted in five Asian countries showed that proper weed control increases the yield of rice by 45%. In extreme weed situations, weed control may triple the yield of rice. In our experiment 2,4-D and Bromoxynil herbicide treatment increased yield of Parmal rice.

(2) Reduction in Land Value

Heavy infestation by perennial weeds could make the land unsuitable, or less suitable for cultivation resulting in reduction of land value.

Thousands of hectares of cultivable area in the rice growing regions of India have been abandoned or are not being regularly cultivated due to severe infestation of nutgrass *(Cyperus rotundus)* and other perennial grasses.

(3) Loss of Quality of Crop Produce

Wild rice, may impair the quality of rice produce. Contamination of other noxious weed seeds greatly reduces the value of crop seeds and grains, and sometimes even renders them unsaleable. Presence of weeds and weed debris in grains and other farm products reduces their market value and causes spoilage in storage.

(4) Problems Through Aquatic Weeds

Aquatic weeds reduce markedly the flow of water in irrigation and drainage channels. Weeds are no strangers to man. They have been there ever since he started to cultivate crops about 10,000 B.C**.** and were undoubtedly recognized as a problem from the beginning. When man first started to grow crops for food, he soon learned that yields were higher when weeds were removed to allow only crop plants.

Since the water requirement of rice is higher than that of any other crop of a similar duration, assured and timely supply of irrigation water has a great influence on the yield of the crop. In the life cycle of rice plant there are certain critical stages when water requirement is high. The water requirement is high during the initial seedling period covering about 10 days. Tillering to flowering is the most critical stage when rice crop should not be subjected to any moisture stress. Ensure of enough water is necessary from panicle initiation stage to flowering. Flooding is not necessary if weeds can be controlled economically through chemical means or by manual weeding before the plants become vegetatively strong. Application of small quantities of water at short intervals to keep the soil saturated is more effective and economical than flooding at long intervals. Flooding is not necessary if the soil is saturated with water and bio-fertilisers have not been used. However, flooding suppresses the weed growth. It increases the availability of many nutrients, particularly phosphorus, potassium, calcium, iron and silica. Until the transplanted seedlings are well established, water should be allowed to stand in the field at a depth of two to five centimeter. Thereafter about five centimeter of water maintained up to the dough stage of the crop.

Interactions among herbicides and chemicals also affect their persistence and residues in soil. Reduced degradation, and hence increased persistence of pesticide, is desirable if the residual activity of the pesticide needs to be improved for obtaining long term weed control. The interactions could also result in decreased persistence. The soil microorganisms which adapt to metabolizing one herbicide develop the ability to degrade another herbicide of the same chemical family. Such interactions may have ecological significance in reducing residual accumulation of agricultural chemicals.

Although the agricultural activity is only one of the several sources of water pollution, it is thought to be an important cause on reducing the water quality through pollution by agrochemicals, in special pesticides. Environmental water pollution by pesticides is a topic of current international concern with widespread ecological consequences. The selective use of pesticides to control pests (insects, weeds and diseases) and vectors of plant diseases can aims at the increase of production of food crops.

In agricultural production, pesticides are often used to efficiently control of weeds, however there is widespread concern over the effects of these synthetic chemicals on native fauna and flora. The risks of pesticides use to kill or otherwise manage certain species of plants considered to be pests need to be balanced against the benefits to the production. Weeds compete with desired crop plants for light, water, nutrients and space. To reduce the intensity of the negative effects of weeds on the productivity of desired agricultural crops, fields may be sprayed with an herbicide that is toxic to the weeds, but not to the crop species. Consequently, the pest plants are selectively eliminated, while maintaining the growth of the desired plant species. In our experimental study, it became evident that 2,4-D and Bromoxynil proved as safest and suitable pesticide for rice cultivation, because they persisted for less time, less toxic on crop and also for microflora of soil.

Weed control by pesticides played a significant role in revolutionizing agriculture in several developed countries of the world. The impact of chemical weed control on agriculture in the developing countries is only marginal, apparently due to availability of plenty of agriculture labour for manual weed control. However, due to rapid industrialization, increased literacy, and mass migration of people to urban areas in India, labour availability in villages for agriculture is fast becoming scarce and even if available, the wages are high in relation to agricultural income. Hand weeding is a tedious and unrewarding social activity. Pesticides do replace a sizeable portion of farm labour and this is the main hurdle for their wider usage in the developing countries. But little is realized that there are peaks for labour demand in the cropping season and all the available labour cannot meet this demand. The farmers cannot afford to lose time on the time-consuming manual weed control under intensive and multiple cropping of the interactions of factors of climate and soil.

From the results from our field experiments it could be concluded that the application of 2,4-D and Bromoxynil pesticides as applied enhanced rice yield appreciably. Their application therefore considered as the best pesticides combination in rice among the evaluated pesticides in the study area. There is however the need for continuous evaluation to prevent pesticide resistant over time. The results of this study confirms earlier reports by Akobundu (1981) and Imeokparia (1989) about the possibility of controlling weeds in rice with pesticides without adverse effect on the crop. Pesticide treatments showing great promise for weed control in rice in these trials.

Pesticides are safe when used correctly:-

(1) Pesticides are strictly regulated to protect the safety of people and the

environment.

(2) They help produce an abundance of food which is safe to eat.

(3) The use of pesticides ensures that we get the quantity and quality of fresh food we need at affordable prices.

(4) The positive benefits of eating fresh fruit and vegetables as part of a healthy, balanced diet, far outweigh any concern about pesticide residues.

(5) Pesticides are vital to sustainable development in many countries in the developing world.

Although pesticides have proven extremely useful in solving many weed problems particularly in the developed countries, they have not become very popular in the developing countries like India where small scale subsistence farmers predominate agriculture. This can be ascribed to the following factors.

1. Ignorance of losses caused by weeds and a fatalistic acceptance of weeds, ironically, because of their almost universal presence as against awareness regarding losses caused by insects and diseases.

2. Poor economic resources of the farmer and his inability to invest on pesticide inputs.
3. Illiteracy or inadequate literacy of the farmer.
4. Smaller land holdings, with majority being less than 1.5 ha in size.
5. Lack of trained weed scientists to generate appropriate weed control technology and disseminate it to the farmers.
6. Lack of adequate choice of pesticides for multitude of weed problems in different agroclimatic and soil conditions across the country.
7. Imposition of import duty and taxes to the extent of 75% on all imports of pesticides and technical materials, thus making chemical weed control more expensive to the small farmer.
8. Nonexistence of adequate pesticides manufacturing facility within the country.

The success story of pesticides in India is at present confined only to areas where farmers are enterprising enough to realize the potential losses due to weeds, where size of farm holding varied from medium to large, where there was shortage of labour and even if available it was expensive, where intensive production technology was followed, where the farmers were literate and had greater managerial ability, where the pesticide were made available, sometimes at subsidized prices, and where weed scientists were able to transfer weed control technology to the farmer more effectively. The pesticides are yet to reach the small farmer and to the dryland areas which constitute two-thirds of the total area under agriculture.

SUGGESTIONS

Best results on weed control with pesticides will be obtained when they are used in conjunction with tillage and other agronomic practices. The choice of the best specific treatment varies with local and regional agronomic, ecological, and economic factors. Pesticides are profitable not only in situations where labour is scarce and expensive, but also where labour is plentiful and cheap. But some weeds of rice crop fields of our experiment persists also after pesticidal treatment. In the prevailing situation following suggestions are recommended:-

1. Pesticides can be applied for weed control in crop field soil, to lessen phytotoxic effects on crop plant.
2. Pesticides provide early-season weed control. This is very beneficial

as weed competition during early stages of crop growth is maximum than at later stages. So, these should be applied just after transplantation of crop.

3. Manual methods of weed control may also be applied. A hand weeding after treatment of herbicide will eliminate nearly all of the weeds from crop field. In our study, no hand weeding was applied. Due to this, weed of many species persists till the maturity of rice-crop even in less population, in this situation a hand weeding after herbicide treatment is recommended to have good crop and yield from the rice crop fields.
4. On the basis of facts and findings of our research, 2,4-D and Bromoxynil herbicides are recommended as best for control of weeds of rice crop field of Chapra district. This also lead to high productivity of the rice-crop with less negative effect on soil and less persistence in crop grains.

Apart from the fungal and plant pathogens weeds are also a great menace to agricultural crops. Botanically speaking, weeds are undesirable plants that compete with economically valuable plants for space, water, sunlight and soil nutrients and, if their growth is not checked, cause serious loss in crop production. Weeds are also indirectly responsible for crop losses as they act as hosts for other plant pests such as, viruses, fungi and insects. They are a perpetual nuisance. They often clog irrigation ways, making rice cultivation nearly impossible. The control of weeds is a matter of great concern. Before the discovery of pesticides, the pulling or grubbing of weeds was the simplest and most ancient form of weed control. Various other practices such as hoeing, cutting, mulching, pasturing, flaming and crop rotation were widely used.

Thus integrated approach involving the minimal use of chemicals with proper use of other cultural weed control and management techniques such as good land preparation and/or use of weed suppressive varieties will reduce the farmer's dependence on a heavy application of pesticides and thus offers the best hope for increasing food production.

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REFERENCES

1. Abramovich T.K. and Y. Steinberger, 2006, Soil microbial functional diversity response following nematocide and biocide amendments in a desert ecosystem, *Soil Biology & Biochemistry*, 38 : 1966-1976.

2. Acosta-Martinez V., Acosta-Mercado D., Sotomayor-Ramirez D., and Cruz-Rodriguez L., 2007, Microbial communities and enzymatic activities under different management in semiarid soils, *Applied Soil Ecology,* 38 : 249-260.

3. Adams R.S. Jr., 1973, Factors influencing soil adsorption and bioactivity of herbicides, In : F.A. Gunther (ed.) *Residue review*, Springer-Verlag, New York, P.-198.

4. Adams R.S. Jr., Baker D.G. and Nelson S.E., 1970, Atrazine herbicides interactions in Soybeans, *Meeting of Weed Sci.Soc.Amer.*, Abst. No.-38.

5. Alexander M., 1965, Persistence and biological reactions of pesticides in soil, *Proc.Soil Sci.Soc.Amer*, 29 : 1-7.

6. Al-Mutlaq K., Rushdi A.I. and Simoneit B.R.T., 2002, Characteristics and sources of organic matter in desert sand, *Arab Gulf Journal of Scientific Research*, 20 : 141-155.

7. Araujo A.S.F., Monteiro R.T.R. and R.B. Abarkeli, 2003, Effect of glyphosate on the microbial activity of two Brazilian soil, *Chemosphere*, 52 : 799-804.

8. Avidano L., Gamalero E., Cossa G.P. and Carraro E., 2005, Characterization of soil health in an Italian polluted site by using microorganisms as bioindicators, *Applied Soil Ecology*, 30 : 21-33.

9. Ayansina A.D.V. and B.A. Oso, 2006, Effect of two commonly used herbicides on soil micro flora at two different concentrations, *African J. Biotech.* 5(2) : 139-132.

10. Bach M.K., 1961, Metabolites of 2,4-D from bean stems, *Plant Physiol.*, 36 : 558-565.

11. Bailey G.W. and J.L. White, 1964, Review of adsorption and desorption of organic pesticides by soil colloids with implications concerning pesticides bioactivity, *J.Agr. Food Chem.*, 12 : 324-332.

12. Baltazar A.M. and De Datta S.K., 1992, Weed Management in rice, *Weed Abstracts,* 41 : 495-507.

13. Baumann P.A. and M.G. Merkle, 1979, The effects of soil moisture on the phytotoxicity of diuron, fluridone and triffuralin, *Proc. Meeting Sou. Weed Sci.Soc.,* USA, P.-315.

14. Beak S.O., Field R.A., Goldstone M.E., Kirk P.W., Lester J.N. and Perry R., 1991, A review of polycyclic aromatic hydrocarbons; *Water, Air, Soil Pollution,* 60 : 279-300.

15. Beare M.H., Reddy M.V., Tian G. and Srivastava S.C., 1996, Agricultural intensification, soil biodiversity and agroecosystem function in the tropics : the role of decomposer biota, *Applied Soil Ecology,* 6 : 87-108.

16. Beestman G.B. and J.M. Deming, 1974, Dissipation of acetanilide herbicides from soils, *Agron.J.,* 66 : 308-311.

17. Bending G.D., Rodriguez-Cruz M.S. and S.D. Lincolin, 2007, Fungicide impact on microbial communities in soil with contrasting management histories, *Chemosphere*, 69 : 82-88.

18. Best J.A. and J.B. Weber, 1974, Disappearance of S-triazines as affected by soil pH using a balance-sheet approach, *Weed Sci.*, 22 : 364-373.

19. Best J.A., Webr J.B. and Monaco T.J., 1975, Influence of soil pH on S-triazine availability of plants, *Weed Sci.*, 23 : 378-382.

20. Bingham S., 2007, Pesticides in rivers and groundwater, Environment Agency, U.K.

21. Bin-Ru L., Guo-Mei J. Jian C. and Gang W., 2005, A review of methods for studing microbial diversity in soil, *Pedosphere*, 16 : 18-24.

22. Bjorlund L., Ekelund F., Christensen S., Jacobsen C.S., Krogh P.H. and Johnsen K., 1999, Interactions between saprophytic fungi, bacteria and protozoa on decomposing wheat roots in soil influenced by the fungicide, *Soil Biology & Biochemistry*, 32 : 967-975.

23. Blagodatskaya E.V. and T.H. Anderson, 1998, Interactive effects of pH and substrate quality on the fungal-to-bacterial ratio and Q CO_2 of microbial communities in forest soil, *Soil Biology and Biochemistry*, 30 : 1267-1274.

24. Blagodatsky S., Blagodatskaya E., Yuyukina T. and Kuzyakov Y., 2010, Model of apparent and real priming effects : microbial activity with soil organic matter decomposition, *Soil Biology and Biochemistry,* 42 : 1275-1283.

25. Bogomolov D.M., Chen S.K., Parmelee R.W., Subler S. and Edwards C.A., 1996, An ecosystem approach to soil toxicity testing : a study of copper contamination in laboratory soil microcosms, *Applied Soil Ecology,* 4 : 95-105.

26. Bolognesi C.,2003, Genotoxicity of pesticides : A review of human biomonitoring studies, *Mutation Res.,* 543 : 251-271.

27. Bordeleau L.M. and R. Bartha, 1971, *Soil Biol. Biochem.,* 3 : 218.

28. Brussaard L., de Ruiter P.C. and Brown G.G., 2007, Soil Biodiversity for agricultural sustainability; *Agriculture, Ecosystems and Environment,* 121 : 233-244.

29. Bossio D.A., Girvan M.S., Verchot L., Bullimore J., Borelli T., Albrecht A., Scow K.M., Ball A.S., Pretty J.N. and obsborn A.M., 2005, Soil Microbiol community response to land use change in an agricultural land scape of Western Kenya, *Microbial Ecology,* 49 : 50-62

30. Bucher A.E. and Lanyon L.E., 2004. Evaluating Soil management with microbial-community-level physiological profiles, *Applied Soil Ecology*, 29 : 59-71.

31. Buchler S., Bsua I. and Hites R.A., 2001, A comparison of PAH, PCB and pesticide concentrations, *Environmental Science and Technology,* 35 : 2417-2422.

32. Burrows L.A. and C.A. Edwards, 2001, The use of integrated soil microcosms to predict effects of pesticides on soil ecosystems, *European Journal of Soil Biology,* 38 : 145-249.

33. Butts J.S. and S.C. Fang, 1956, In A conference on Radioactive Isotopes in Agriculture, A.E.C. Rep.No. TID-7512, P.-209-214.

34. Chagnon M., Pare D., Hebert C. and Camire C., 2000, Effect of experimental liming on Collembalan communities and soil microbial biomass in a southern Quebec Sugar maple stand, *Applied Soil Ecology*, 17 : 81-90.

35. Chen S.K. and C.A. Edwards, 2001, A microcosm approach to assess the effects of fungicides on soil ecological processes and plant growth : comparisons of two soil types., *Soil*

Biology & Biochemistry, 33 : 1981-1991.

36. Chen S.K., C.A. Edwards and S. Subler, 2001, Effects of the fungicides benomyl, captan and chlorothalonil on soil microbial activity an nitrogen dynamics in laboratory incubations, *Soil Biology & Biochemistry*, 33 : 1971-1980.

37. Chen S.K., Edwards C.A. and S. Subler, 2001, A microcosm approach for evaluating the effects of the fungicides benomyl and captan on soil ecological processes and plant growth, *Applied Soil Ecology*, 28 : 69-82.

38. Chinalia F.A. and K.S. Killham, 2006; 2,4-D biodegradation in river sediments of North east-Scotland and its effect on the microbial communities, *Chemosphere*, 64 : 1675-1683.

39. Chin D.V., Hach C.V., Thanh N.C. and Tai N.T. 2000, Weedy Rice Situation in Vietnam, In : *FAO Report of Global Workshop on Red Rice Control*, Information Division, Food and Agricultural Organisation of UN, Rome, P.-67-74.

40. Choi H.W., Chung I.M., Sin M.H., Kim Y.S., Sim J.B., Kim J.B., Kim K.D. and Chun S.C., 2006, The effect of calcium

Cyanamid on cactus, *Crop Protection*, 26 : 162-168.

41. Chou S.F. and J.M. Tiedje, 1973, Alachlor degradation in soils, Michigan State Univ., *J.Agr.Food.Chem.*, 23 : 77-81.

42. Coats R.J., 1991, Pesticide degration mechanisms and environmental action, In: Pesticide Transformation products, *ACS symposium series*, 459, American Chemical Society, Washington.

43. Corbin F.T., Upchurch R.P. and Selmen F.L., 1971, Influence of pH on the phytotoxicity of herbicides in soil, *Weed Sci.*, 19 : 233-239.

44. Cornell University, 2007, Pesticides in the environment. Pesticide fact sheets and tutorial, module 6, *Pesticide Safety Education Programme.*

45. Cox R.E., Mazurek M.A. and Simoneit B.R.T., 1982, Lipids in Harmattan Soil of Nigeria, Nature, 296 : 848-849.

46. Craft A.S. and S. Yamaguchi, 1964, The autoradiography of plant materials, *Agr. Extension Serv Mannual*, 35, University of California, Berkeley, P.-143.

47. Craft A.S. and C.E. Crisp, 1971, *Phloem Transport in Plants*,

Freeman and Co., San Francisco, P.-481.

48. Crecchio C., Curci M., Pellegrino A., Ricciuti P., Tursi N. and Ruggiero P., 2006, Soil microbial dynamics and genetic diversity in soil under monoculture wheat grown in different long term management systems, *Soil Biology & Biochemistry*, 39 : 1391-1400.

49. Cycon M., Wojcik M. and Z. Piotrowska-Seget, 2009, Biodegradation of the organophosphorus insecticide diazinon by *Serratia* sp. and *Pseudomonas* sp. and their use in bioremedian of contaminated soil, *Chemosphere;* 76 : 494-501.

50. Das A.C. and D. Mukherjee, 1999, Soil application of insecticides influences on microorganisms and plant nutrient, *Applied Soil Ecology*, 14 : 55-62.

51. DeDatta S.K. and P.C. Bernasor, 1973, Chemical weed control in broadcast-seeded flooded tropical rice, *Weed Research,* 13 : 351-354.

52. Davis D.E., Pillai P. and Truelove B., 1979, Selectivity and mode of metalachlor, *Abstr. Weed Sci. Soc.Amer.*, P.-99.

53. Davis P.J., Drennan D.S.H., Fryer J.D. and Holly K., 1968, *Weed Res*., 8 : 241-248.

54. De Datta S.K. and A. Baltazar, 1996, Weed control technology as a component of rice production systems In : *Auid B. and Kim K.U. (ed.) : Weed Management in Rice*, FAO Plant Production and Protection Paper No.-139 : 25-52.

55. de lipthay J.R., Tuxen N., Johnsen K., Hansen L.H., Albrechtsen H.J., Bjerg P.L. and Aamand J., 2002, In situ exposure to low herbicide concentrations affects microbial population composition, *Applied and Environmental Microbilogy*, 69 : 461-467.

56. Deal L.M. and F.D. Hess, 1980, An analysis of the growth inhibitory characteristics of alachlor and metalachlor, *Weed Sci.,* 28 : 168-175.

57. Deeley G.M., Reinhard M. and Stearns S.M., 1991, Transformation and absorption of 1,2-dibromo-3-chloropropane in subsurface samples, J.Environ.Qual., 20(3) : 547-556.

58. Demanou J., Sharma S., Dorfler U., Schroll R., Monkiedje A., Munch J.C. and Schloter M., 2006, Structural and functional diversity of soil microbial communities as a result

of combined applications of copper and meferioxam, *Soil Biology & Biochemistry*, 38 : 2381-2389.

59. Diosma G., Aulicino M., Chidichimo H. and Balatti P.A., 2005, Effect of tillage and N fertilization on microbial physiological profile of soils cultivated with wheat, *Soil and Tillage Research*, 91 : 236-243.

60. Eisenhauer N., Klier M., Partsch S., Sabais A.C.W., Scherber C., Wiesser W.W. and Scheu S., 2009, No interactive effects of Pesticides and plant diversity on soil microbial biomas and respiration, *Applied Soil Ecology*, 42 : 31-36.

61. Epelde L., Mijangos I., Becerril J.M. and Garbisu C., 2008, Soil microbial community as bioindicator of the recovery of soil functioning derived from metal phytoextraction with Sorghum, *Soil Biology and Biochemistry*, 41 : 1788-1794.

62. Fernandez-Calvino D., Martin A., Arias-Estevez M., Baath and E. Diaz-Ravina M., 2010 Microbial community structure of vineyard soils with different pH and copper content, *Applied Soil Ecology*, 46 : 276-282.

63. Ferreira E.P., de B., Dusi A.N., Costa J.R., Xavier G.R. and Rumjanek N.G., 2009, Assesing insecticide and fungicide effects on the culturable soil bacterial community by analysis of variance, *Europe an Journal of Soil Biology*, 45 : 1-7.

64. IRRI, 2006, World Rice Statistics, Intl. Rice Res. Inst. Manila.

65. Ferrero A., 2003, Weedy rice, biological features and control. In : Labraoa R. (ed.) : *Weed Management for developing countries*, Addendum-1, FAO Plant Production and Protection Paper No. 120 : 89-107.

66. Feung C.S., Hamilton R.H. and Mumma R.O., 1977, Metabolism of 2,4-D. II. Herbicidal properties of amino acid conjugates, *J.Agr.Food Chem.*, 25 : 898-900.

67. Fisher J.D., 1974, Metabolism of the herbicide pronamide in soil, *J.Agr.Food Chem.*, 22 : 606-608.

68. Forge T.A., Bittman S. and Kowalenko C.G., 2004, Response of grassland soil nematodes and protozoa to applications of fertilizer, *Soil Biology & Biochemistry*, 37 : 1751-1762.

69. Fox J.E.,Gulledge J., Engelhaupt E., Burrow M.E. and McLachlan

J.A., 2007, Pesticides reduce symbiotic efficiency of nitrogen fixing rhizobia and host plants, *Proceedings of the National Academy of Science of the USA.*

70. Frazer M.P., Cass G.R., Simoneit B.R.T. and Rasmussen R.A., 1997, Quality model evaluation data for organics, *Environmental Science and Technology*, 31 : 2356.

71. Frear D.S., 1975, The benzoic acid herbicides, In : P.C. Kearney and D.D. Kaufman (ed.), *Herbicides : Chemistry, degradation and mode of action*, Marcel Dekker, New York., P.-541-311.

72. Fryer J.D. and S.A. Evans, 1968, ed., Weed control handbook, *The British Crop Protection Council,* Blackwell Sci.Publi., Oxford, P.-494.

73. Fuentes J.P., Bezdicek D.F., Fury M., Albrecht S. and Smith J.L., 2005, Microbial activity affected by lime in a long-term no-till soil, *Soil & Tillage Research*, 88 : 123-131.

74. Garcia-Pausas J. and E. Paterson, 2011, Microbial Community abundance and structure are determinants of soil organic matter mineralization in the presence of labile carbon, *Soil*

Biology and Biochemistry, 43 : 1705-1713.

75. Gilliom R.J., Barbash J.E., Crawford G.G., Hamilton P.A., Martin J.C., Stackelberg P.E., Thelin G.P. and Wolock D.M., 2007, *Pesticides in the nations streams and groundwater,* 1992-2001, U.S. Geological Survey p.-4.

76. Gomez F., Martinez-Toledo M.V., Salmeron V. Rodelas B. and Gonzalez-Lopez J., 1999, Influence of the insecticides profenophos and diazinon on the microbial activities, *Chemosphere,* 39 : 945-957.

77. Gopal M., Gupta A., Arunachalam V. and Magu S.P., 2009, Impact of azadirachtin, an insecticidal allelochemical from neem on soil microflora, enzyme and respiratory activities, *Bioresource Technology,* 98 : 3154-3158.

78. Green R.E. and S.R. Obien, 1969, Herbicides equilibrium in relation to soil water content, *Weed Sci.,* 18 : 514-519.

79. Griffin R.M., 2006, *Echinochloa polystachya* management in Louisiana Rice, Louisiana State University.

80. Grover R., 1968, Influence of soil properties on the phytotoxicity of 4-amino-3,5,6-trichloro picolinic acid, *Weed Res.*, 8 : 226-232.

81. Gruenhagen R.D. and D.E. Moreland, 1971, Effect of herbicides on ATP levels in excised soybean hypocotyls, *Weed Sci.,* 19 : 319-323.

82. Gu Y., Zhang X., Tu S. and Lindstrom K., 2009; Soil microbial biomass, crop yields and bacterial community structure as affected by long-term fertilizer treatments under wheat-rice cropping, *European Journal of Soil Biology*, 45 : 1-8.

83. Gunapla N. and K.M. Scow, 1997, Dynamics of soil microbial biomass and activity in conventional and organic farming systems, *Soil Biology and Biochemistry*, 30 : 805-815.

84. Hance R.J., 1967, The speed of attainment of sorption equilibria in some systems involving herbicides, *Weed Res.*, 7 : 29-33.

85. Harris C.I. and G.F. Warren, 1964, Adsorption and desorption of herbicides by soil, *Weeds;* 12 : 120-126.

86. Harris P.A. and P.W. Stahlman, 1995, Soil bacteria as selective biological control agents of winter annual grass weeds in winter

wheat, *Applied Soil Ecology,* 3 : 275-281.

87. Harrison G.W., Weber J.B. and Baird J.W., 1976, Herbicides phytotoxicity as affected by selected properties of North Carolina Soils, *Weed Sci.,* 24 : 120-126.

88. Hoflich G., Wiche W. and C. Hecht-Buchholz, 1995, Rhizosphere colonization of different crops with growth promoting *Pseudomonas* and *Rhizobium* bacteria, *Microbiological Research,* 150 : 139-147.

89. Holley R.W., Boyle F.P. and Hand D.B., 1950, *Arch.Biochem.Biophys.,* 27 : 143-146.

90. Hussain A., 1994, Studies of the effects of temperatures and solar radiation on volatilization, mineralization and binding of DDT in soil under laboratory conditions, *J.Environ.Sci* Health, B29 : 141-151.

91. Idris H.A., Labuschagne N. and L. Korsten, 2006, Screening rhizobacteria for biological control of *Fusarium, Biological Control,* 40 : 97-106.

92. Jin K., Sleutel S., Buchan D., De Neve S., Cai D.X., Gabriels D. and

Jin J.Y., 2009, Changes of soil enzymes activities in the Chinese Loess Plateau, *Soil and Tillage Research*.

93. Johnston A.E., 1986, Soil organic matter, effects on soil and crops, *Soil use management*, 2 : 97-105.

94. Julfiquare A.W., Haque M.M., Enamul Haque and Rashid M.A., 1998, Current Status of hybrid rice research and future programme in Bangladesh, *BARC*, 18-19. May.

95. Jury W.A., Spencer W.F. and Farmer W.J., 1983, Behavior assessment model for trace organics in soil, *J.Environ.Qual.*, 12(4) : 558-564.

96. Kahindi J.H.P., Woomer P., George T., de Souza Moreira F.M., Karanja N.K. and Giller K.E., 1996; Agricultural intensification, Soil biodiversity and ecosystem function in the tropics : the role of nitrogen-fixing bacteria, *Applied Soil Ecology*, 6 : 55-76.

97. Kalita P.K., Ward A.D., Kanwar R.S. and McCoo D.K., 1998, Simulation of Pesticide concentrations in Agriculture Drainage and Pesticide transport model, *Agr. Water Manage*, 36(1) : 23-44.

98. Kellogg R.L., Nehring R., Grube A., Goss D.W. and Plot Kin S., 2000, Environmental indicators of pesticides leaching and runoff from farm field. United States Department of Agriculture Natural Resources Conservation Service.

99. Kerr M.W. and R.L. Wain, 1964, The uncoupling of oxidative phosphorylation in pea shoot mitochondria by ioxynil and related compounds, *Ann.Appl.Biol.*, 54 : 441-446.

100. Kjoller R. and K.E. Clemmensen, 2009, Belowground ectomycorrhizal fungal communities respond to liming in three southern Swedish coniferous forest stands, *Forest Ecology and Management*, 257 : 2217-2225.

101. Kobayashi D.Y., Guglielmoni M. and and B.B. Clarke, 1995, Isolation of the Chitinolytic bacteria *Xanthomonas maltophilia* and *Serratia marcescens* as biological control agents for summer patch disease of turfgrass, *Soil Biology and Biochemistry,* 27 : 1479-1987.

102. Kong W.D., Zhu Y.G., Fu B.J., Han X.Z., Zhang L. and He. J.Z., 2008, Effect of long term application of chemical fertilizers on microbial biomass and functional diversity of a black soil,

Pedosphere, 18 : 801-808.

103. Kozdroj J., Trevors J.T. and J.D. Van Elsas, 2004, Influence of introduced potential biocontrol agents on maize seedling growth and bacterial community structure in the rhizosphere, *Soil Biology and Biochemistry*, 36 : 1775-1784.

104. Kumar M. and G. Sharma, 2005, Effect of herbicides alone and in combination on direct seeded rice, *Indian Journal of Weed Sciences*, 37(3-4) : 197-201.

105. Labrada R., 1996, Weed Control in Rice, In : Auid B. and Kim K.U. (ed.) : *Weed Management in Rice*, FAO Plant Production and Protection, Paper No. 139 : 3-5.

106. Li. J., Zhao B., Li X., Jiang R. and So H.B., 2008, Effects of long term combined application of organic and mineral fertilizers on microbial biomass, soil enzyme activities and soil fertility, *Agricultural Science in China*, 7 : 336-343.

107. Linscott D.L., Hagin R.D. and Dawson J.E., 1968, Conversion of 4-(2,4-D) butyric acid to homologs by alfalfa. Mechanism of resistance to this herbicide, *J.Agr. Food Chem.*, 16 : 844-848.

108. Liu B., Glenn D. and K. Buckley, 2008, *Trichoderma* Communities in soil from organic, sustainable and conventional farm, *Soil Biology and Biochemistry,* 40 : 1124-1136.

109. Loague K., Lloyd D., Nguyen A., Davis S.N. Abrams R.H., 1998, A case study simulation of groundwater contamination, *J. Contam.Hydrol.,* 29(1) : 109-136.

110. Lotter D.W., Seidel R. and Liebhardt W., 2003, The performance of organic and conventional cropping systems in an extreme climate year, *American Journal of Alternative Agriculture,* 18 : 146-154.

111. Luckwill L.C. and C.P. Lloyd-Jones, 1960, Metabolism of plant growth regulators-I., 2-4-D in leaves of red and black currant, *Ann.Appl.Biol.,* 48 : 613-625.

112. Lupwayi N.Z., Harker K.N., Clayton G.W., O'Donovan J.T. and Blackshaw R.E., 2008, Soil microbial response to herbicides applied to glyphosate-resistant Canola; *Agriculture, Ecosystems and Environment,* 129 : 171-176.

113. Lupwayi N.Z., Harker K.N., Dosdall L.M., Turkington T.K., Black Shaw R.E. O'Donovan J.T., Carcamo H.A., Otani J.K., and Clayton

G.W., 2009, Changes in functional structure of soil bacterial communities due to fungicide and insecticide applications in canola; *Agr. Eco. and Env.*, 130 : 109-114.

114. Madrid M.T., Punzalan F.L. and Lubigan R.T., 1972, Some common weeds and their control, *Weed Science Society of the Philippines*, Languna.

115. Mandal B., De P. and De G.C., 2002, Efficiency of herbal leaves on weed management of transplanted Kharif rice, *Journal of Interacademicia*, 6 : 109-112.

116. Mann J.D. and M. Pu, 1968, Inhibition of lipid synthesis by certain herbicides, *Weed Sci.*, 16 : 197-198.

117. Marschner P., Kandeler E. and B. Marschner, 2002, Structure and function of soil microbial community in a long-term fertilizer treatment, *Soil Biology & Biochemistry*, 35 : 453-461.

118. Martin J.H., Leonard W.H. and Stamp D.L., 1976, *Principles of field crop production*, Macmillan, New York.

119. Mijangos I., Becerril J.M., Albizu I., Epelde L. and Garbisu C.,

2009, Effects of glyphosate on rhizosphere soil microbial communities, *Soil Biology & Biochemistry,* 41 : 505-513.

120. Mirbagheri S.A. and E.H.R. Kazemi, 2008, Finite element modeling of leaching from a municipal landfill, *J.Appl.Sci.,* 8(4) : 629-635.

121. Mirbagheri S.A., 1995, Modeling contaminant transport in soil column and groundwater pollution control. *Proceeding of regional conference on water resource management,* Isfahan University of Technology, August, P.-279-293.

122. Mirbagheri S.A., Tanji K.K. and Rajaee T., 2008, Selenium transport and transformation modeling in soil columns, *Hydrol.Proc.,* 22(14) : 2475-2483.

123. Moreland D.E., Malhotra S.S., Gruenhagen R.D. and Shokrahii, 1969, Effects of herbicides on RNA and protein synthesis, *Weed Sci.,* 17 : 556-563.

124. Niemi R.M., Heiskanen I., Ahtianen J.H., Rahkonen A., Mantykoski K., Welling L., Laitinen P. and Ruttunen P., 2008, Microbial toxicity and impacts on soil enzyme activities of pesticides used in potato cultivation, *Applied Soil Ecology,* 41 : 293-304.

125. Ntanos D.A., Koutroubas S. and Mavrotas D.C., 2000, Barnyardgrass control in water-seeded rice with cyhalofop-butyl., *Weed Technology*, 14 : 383-388.

126. Papendick R.I., Elliott L.F. and Dahlgren R.B., 1986, Environmental consequences of modern production agriculture, *American Journal of Alternative Agriculture,* 1(1) : 3-10.

127. Paton D. and J.E. Smith, 1965, The effect of 4-hydroxy-3,5-iodobenzonitrile on CO_2 fixation, ATP formation and NADP reduction in chloroplasts of *Vicia faba* L., *Weed Res.*, 5 : 75-77.

128. Paul B., Chereyathmanjiyil A., Masih I., Chapuis L. and Benoit A., 1998, Biological control of *Botrytis Cinerea* causing grey mould disease of grapevine and elicitation of stilbene phytoalexin by a soil bacterium, *FEMS Microbiology Letters*, 165 : 65-70.

129. Penner D. and F.M. Ashton, 1968, Influence of dichlobenil, endothall and bromoxynil on kinin control of proteolytic activity, Weed Sci., 16 : 323-326.

130. Perez-Piqueres E., Edel-Hermann V., Alabouvette C. and Steinberg C., 2005, Response of soil microbial communities to compost

amendments, *Soil Biology & Biochemistry*, 38 : 460-470.

131. Perucci P., Dumontet S., Bufo S.A., Mazzatura A. and Casucci C., 1999, Effects of organic amendment and herbicide treatment on soil microbial biomass, *Biology and Fertility of soils*, 32 : 17-23.

132. Pietri J.C.A. and P.C. Brookes, 2008, Relationships between soil pH and microbial properties in a UK arable soil, *Soil Biology & Biochemistry*, 40 : 1856-1861.

133. Pillai C.G.P. and D.E. Davis, 1975, Mode of action of CGA-18762, CGA-17020 and CGA-24705, *Weed Sci.Soc.*, 28 : 308-313.

134. R.L., 1964, Ioxynil-some considerations on its mode of action, Proc.7th.Brit.Weed Control Conf., 1 : 306-311.

135. Rao V.S., 1979, Report on the current status of weed research in India, Presented at *Indian Soc. Weed Sci. Conf.*, Parbhani, Maharastra.

136. Ratcliff A.W., Busse M.D. and C.J. Shestak, 2006, Changes in microbial community structure following herbicide (glyphosate) addition to forest soils, *Applied Soil Ecology*, 34 : 114-124.

137. Reynolds J.D., 1997, International pesticide trade, *Florida State University Journal of Land Use & Environmental Law,* Volume – 131.

138. Robertson L.N., Chandler K.J., Stickely B.D.A., Cocco R.F. and Ahmetagic M., 1998, Enhanced microbial degradation from the controlled release formulation suscon Blue in Soil, *Soil Protection*, 17 : 29-33.

139. Rust R.H., Adams R.S. Jr. and Martin W.P., 1972, Towards developing a soil quality index, *In : indicators of environmental quality*, Plenum Press, Washington.

140. Sahu S.K., 1990, Degradation of alpha and gamma isomers of hexachlorocyclohexane by rhizosphere soil suspension from sugarcane, *Proc.Indian Acad.Sci. Plant-Sci.*, 100 : 165-172.

141. Sahu S.K., 1995, Mineralization of alpha, Beta and gamma isomers of hexachlorocyclohexane by a soil bacterium under aerobic conditions, *J.Agric.Food Chem.,* 43 : 833-837.

142. Schafer D.E. and D.O. Chilcote, 1970, *Weed Sci.,* 88 : 725-730.

143. Scholtz M.T. and T.F. Bidleman, 2007, Modeling of the longterm fate of pesticide residues in agricultural soil, *Sci.Total Environ.*, 377(1) : 61-80.

144. Sethunathan N., 1983, Mircobiology of rice soils, CRC, *Critical Rev. Microbiology*, 10 : 125-172.

145. Sigler W.V. and R.F. Turco, 2002, The impact of chlorothalonil application on soil bacterial and fungal populations as assessed by denaturing gradient gel electrophoresis, *Applied Soil Ecology*, 21 : 107-118.

146. Smith A.E. and Aubin A.J., 1991, Metabolites of 2-4D in Saskatchewan soils, *J.Agric.Food Chem.*, 39 : 2019-2021.

147. Smith J.E., Paton D. and Robertson M.M., 1966, Herbicides and electron transport, *Proc. 8th British Weed Control Conf.*, 1 : 279-282.

148. Smith Jr., R.J. 1983, Weeds of major economic importance in rice and yeild losses due to weed competition. *In weed control in rice*, International Rice Research Institute, Los Banos, Laguna, Philippins, p., 19-36.

149. Smith M.D., Harnett D.C. and C.W. Rice, 1999, Effects of long-term fungicide applications on microbial properties in tallgrass prairie soil, *Soil Biology & Biochemistry,* 32 : 935-946.

150. Straube G., 1991, Microbial transformation of hexachlorocyclohexane, *Zentralbl Mikrobioll.* 146 : 327-338.

151. Subhas C. and P. Jitendra, 2001, Effect of rice (*Oryza Sativa* L.) culture, nitrogen and weed control on nitrogen competition between scented rice and weeds, *Indian Journal of Agronomy*, 46 : 68-74.

152. Tabacchi M. and M. Romani, 2002, *Eichnochloa* spp. control with new herbicides in water and dry-seeded rice in Italy, In : *Proceedings of the 2nd. Temperate Rice Conference,* International Rice Research Institute, Los Banas, Philippines.

153. Talbert R.E. and N.R. Burgos, 2007, History and management of herbicide-resistnt barnyardgrass in Arkansas rice, *Weed Technology;* 21 : 324-331.

154. Tashkent, 1998, Conditions and provisions for developing a national strategy for biodiversity conservation, U.N.D.P.

155. Taube J., Vorkamp K., Forster M. and Herrmann R., 2002, Pesticide residues in biological waste, *Chemosphere,* 49(10) : 1357-1365.

156. Tejada M., Gonzalez J.L., Garcia-Martinez A.M. and Parrdo J., 2007, Effect of different green manures on soil biological properties and maize yield, *Bioresource Technology*, 99 : 1758-1767.

157. Truelove B., Dinner A.M., Davis D.E. and Weete J.D., 1979; Metalachlor, membranes and permeability, *Abst.Meeting Weed Sci.Soc.Amer;* P.-99-100.

158. Tsay R. and F.M. Ashton, 1971, Effect on several herbicides on dipeptidase activity of squash cotyledons, *Weed Sci.*, 19 : 682-684.

159. Tu C.M., 1995, Effect of five insecticides on microbial and enzymatic activities in Sandy Soil, *J. Environ. Sci Health,* B30 : 289-306.

160. US Environmental Protection Agency Report 2007, Sources of Common Contaminants and their effects.

161. USDA, 2006; 2,4-D human health and ecological risk assessment, United States Department of Agriculture.

162. Vig K., Singh D.K., Agarwal H.C., Dhawan A.K. and Dureja P., 2008, Soil microorganism in cotton fields sequentially treated with insecticides, *Ecotoxicology and Environmental Safety,* 69 : 263-276.

163. Vorkamp K., Taube J., Forster M., Kellner E. and Hermann R., 1999, Pesticides as an unknown component of biological waste and its products, *XI international symposium on pesticide chemistry, Italy.*

164. Wagenet R.J. and J.L. Huston, 1987, Leaching estimation and chemistry model, continuum vol.-2 Water Resources Institute, Cornell University, New York.

165. Wagenet R.J., Huston J.L. and Biggar J.W., 1989, Simulating the fate of a volatile pesticide in unsaturated soil, J. Environ., Qual., 18(1) : 74-84.

166. Wakelin S.A., Macdonald L.M., Rogers S.L., Gregg A.L., Bolger T.P. and Baldock J.A., 2007, Habitat selective factors influencing the structural composition and functional capacity of microbial communities in agricultural soils, *Soil Biology & Biochemistry,* 40 : 803-813.

167. Wakelin S.A., Warren R.A., Kong L. and Harvey P.R., 2007, Management factors affecting size and structure of soil Fusarium communities under irrigated maize in Australia, *Applied Soil Ecology*, 39 : 201-209.

168. Warren G.F., 1973, Action of herbicides in soil, *Weeds Today*, 4(2) : 10-11.

169. Weaver R.J., 1972, Plant growth substances in agriculture, Freeman and Co., San Francisco, USA.

170. Weintrub R.L., Brown J.W., Fields M. and Rohan J., 1952, Metabolism of 2,4-D, I, CO_2 production by bean plants treated with labeled 2,4-dichlorophenoxyacetic acid, *Plant Physiol.*, 27 : 293-301.

171. Wells M., 2007, Vanishing bees threaten US Crops, *BBC News*, March, 11.

172. Wilcox M., Moreland D.E. and Klingman G.C., 1963, Aryl hydroxylation of phenoxy aliphatic acids by excised roots, *Physiol.Plant*, 16 : 565-571.

173. Xu Y., Wang G., Jin J., Liu J., Zhang Q. and Liu X., 2008, Bacterial communities in soybean rhizosphere in response to soil type, soybean genotype and their growth stage, *Soil Biology & Biochemistry*, 41 : 919-925.

174. Yao H. and W. Shi, 2010, Soil organic matter stabilization in turf grass ecosystems : Importance of microbial processing, *Soil Biology and Biochemistry,* 42 : 642-648.

175. Yao H., Bowman D. and W. Shi, 2006, Soil microbial community structure and diversity in a turfgrass chronosequence Land-use change versus turfgrass management, *Applied Soil Ecology*, 34 : 209-218.

176. Yuan B.C. and Li Z.Z., 2007, Microbial biomass and activity in alkalized magnesic soils under arid conditions, *Soil Biology & Biochemistry*, 39 : 3004-3013.

177. Wain R.L., 1964, Ioxynil-some considerations on its mode of actions, *Proc.7thBrit.Weed Control Conf.,* 1:306-311.

178. Zabaloy M.C., Garland J.L. and M.A. Gomez, 2008, An integrated approach to evaluate the impacts of the herbicides

glyphosate 2,4-D and metasulfuron-methyl on soil microbial communities in the Pampas region, Argentina; *Applied Soil Ecology*, 40 : 1-12.

179. Zayed S.M.A.D., 1994, Degradation and fate of DDT and DDE in Egyptian Soil, *J. Environ.Sci.Health,* B-29 : 47-56.

180. Zbaloy M.C., Garland J.L., and M.A. Gomez, 2008, An integrated approach to evaluate the impacts of the herbicides glyphosate; 2,4-D and metasulfuron-methyl on soil microbial communities in the Pampas region, Argentina, *Applied Soil Ecology,* 40 : 1-12.

181. Zbytniewski R. and B. Buszewski, 2002, Sorption of pesticides in soil and compost, *Pol.J.Environ.Stud.,* 11(2) : 179-184.

182. Ze-Pu Zhang, 1996, Weed Management in transplanted rice, In : Auid B. and Kim K.U. (ed.) : *Weed Management in Rice,* FAO Plant Production and Protection, Paper No. 139 : 75-86.

183. Zhang B., Baiz, Hoefel D., Tang L., Wang X., Li B., Liz. and Zhuang G., 2009, The impacts of Cypermethrin pesticide application on non-target microbial community of the pepper plant phyllosphere, *Science of the total Environment,* 407 : 1915-1922.

184. Zhang C., Liu X., Dong F., Xu J., Zheng Y. and Li J., 2009, Soil microbial communities response to herbicide 2,4-D butyl ester, *European Journal of Soil Biology*, 1-6.

185. Zhang Q. and G. Wang, 2006, Effect of different fertilization treatments on ecological characteristics of microorganism in paddy soil, *SCIENCE*, A7 : 376-380.

186. Zhong W., Gu T., Wei W., Zhang B., Lin X, Huang Q. and Shen W., 2009, The effect of mineral fertilizer and organic manure on soil microbial community and diversity, *Plant Soil*, 326 : 511-322.

187. Zoschke A., 1990, Yeild loss in tropical rice as influenced by the competition of weed Flora and the timing of its elimination, In : Grayson B.T., Green M.B. and Copping L.G. (ed.); *Pest Management in Rice, Elsevier Science, London* : 301-313.

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