INFLUENCE OF ORGANIC MATTER AND MOISTURE ON ADSORPTION OF CHLOROACETANILIDE HERBICIDES IN LATERITE SOIL

By

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THESIS

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DECLARATION

I, hereby declare that the thesis entitled **"Influence of organic matter and moisture on adsorption of chloroacetanilide herbicides in laterite soil"** is a bonafide record of research work done by me during the course of research and that it has not been previously formed the basis for the award to me of any degree, diploma, fellowship or other similar title, of any other University or Society.

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ABBREVIATIONS

AICRP - All India Coordinated Research Programme
Al^{3+} - aluminium ion
@ - at the rate of
CO - carboxylic group
CO_2 - carbon dioxide
CEC - cation exchange capacity
cm - centimetre
CRD - Completely Randomised Design
DAHA - Days After Herbicide Application
DAS - Days After Sowing
$dS\ m^{-1}$ - deci Siemen per metre
^0C - degree Celsius
i.d. - internal diametre
2,4-D - 2,4-dichloro phenoxy acetic acid
DOC - dissolved organic carbon
DOM - dissolved organic matter
DT_{50} - time taken for 50% dissipation of the chemical
EC - Electrical Conductivity
FYM - Farm Yard Manure
Fe^{3+} - ferric ion
Fe_2O_3 - Ferric oxide
Fig. - Figure
g - gram
$g\ g^{-1}$ - gram per gram
h - hour
HA - humic acid
kg - kilogram
$kg\ a.i.\ ha^{-1}$ - kilogram active ingredient per hectare
$kg\ ha^{-1}$ - kilogram per hectare
$kg\ pot^{-1}$ - kilogram per pot
$\mu g\ g^{-1}$ - microgram per gram
$\mu g\ mL^{-1}$ - microgram per millilitre

μm - micrometer
μmol dm^{-3} - micromole per decimetre
μmol kg^{-1} - micromol per kilogram
mg g^{-1} - milligram per gram
mg g^{-1}week^{-1} - milligram per gram per week
mg kg^{-1} - milligram per kilogram
mg L^{-1} - milligram per litre
mL - millilitre
mL min^{-1} - milliliter per minute
mm - millimetre
mPa - milli pascal
viz. - namely
nA - nano Ampere
N - nitrogen
No. - Number
Nos. - Numbers
OC - Organic Carbon
OECD - Organisation for Economic Co-operation and Development
OH - hydroxyl group
% - percentage
rpm - rotations per minute
R_t - Retention time
SOC - Solid Organic Carbon
t ha^{-1} - tonnes per hectare
TOC - total organic carbon
2,4,5-T - 2,4,5-trichloro phenoxy acetic acid
VC - Vermi Compost

Introduction

1. INTRODUCTION

Chloroacetanilide herbicides are a group of chemicals widely used for weed control in rice. They are pre emergence herbicides which control grasses. Butachlor [N-(butoxymethyl)-2-chloro-N-2',6'-diethyl acetanilide] and pretilachlor [2-chloro-2',6'-diethyl-N-(2-propoxyethyl) acetaniliide] are the major pre emergence herbicides used for weed control in rice. In wet sown rice (rice sown broadcast in puddled soil), these chemicals are recommended at the rate of 1.25 kg ha^{-1} and 0.45 kg ha^{-1} respectively at 6-9 days after sowing (KAU, 2007). These herbicides are absorbed primarily by the germinating shoots and secondarily by the roots with translocation throughout the plant giving higher concentration in vegetative parts than in the grains.

Adsorption is one of the important factors determining the fate, biological activity and persistence of herbicides in soil. It reduces leaching loss of the chemical. The term adsorption denotes the attraction and deposition of ions or molecules to the surface of a solid. Adsorption is important particularly for pre emergence herbicides, as they are applied directly to the soil in the early crop season. Due to the little vegetative cover during this period, major quantity of the applied chemical falls on the soil where it is subjected to physical, chemical and biological processes. Some quantity of the chemical is likely to be leached away which may cause contamination of surface and ground water. If the extent of adsorption can be increased by some means, leaching losses can be reduced. It will improve the weed control efficiency also by increasing the persistence of herbicides in soil.

The factors affecting adsorption include soil texture, soil type, pH, total organic carbon (TOC), clay content, sesquioxide content, silt content, cation exchange capacity, anion exchange capacity, bulk density, solution composition, temperature, tillage practices as well as structure and properties of the herbicides.

Dissolved organic carbon content exhibited a significant effect on pesticide adsorption-desorption behaviour (Gao *et al.*, 1998).

In this study, major focus is given to study the effect of organic matter and moisture on adsorption of chloroacetanilide herbicides *viz.*, butachlor and pretilachlor. In laterite soil, leaching loss of herbicides are more because of its low capacity for retaining these chemicals. Therefore, addition of the organic matter is an important measure to improve herbicidal efficiency. Moisture content present in the soil also has significant effect on adsorption of herbicides. Adequate quantity of organic matter and maintenance of appropriate moisture condition are needed to improve the adsorption of herbicides in the laterite soils of Kerala. It has been shown that manure application greatly increases the amount of dissolved organic carbon in solution (Mc Gill *et al.*, 1986) which affect the sorption and leaching of pesticides. There has been only limited work on DOC and the methods of estimation of DOC are laborious. Since rice is grown under different conditions in the laterite soils of Kerala, studies related to these aspects have significance. Experiments on the above aspects have not been conducted in the state so far. Therefore, the present research programme was formulated with the following objectives:

1. To standardize the method for dissolved organic carbon estimation.

2. To study the influence of dissolved organic carbon and total organic carbon on the adsorption of butachlor and pretilachlor.

3. To evaluate the adsorption pattern of butachlor and pretilachlor under different sources of organic matter and moisture levels.

4. To find out the relationship between major characteristics of laterite soil and the adsorption of butachlor and pretilachlor.

Review of Literature

2. REVIEW OF LITERATURE

This review of literature briefly summarises about chloroacetanilide herbicides, their general structure and characteristics, adsorption, factors affecting adsorption and adsorption of individual herbicides.

2.1 Chloroacetanilide herbicides

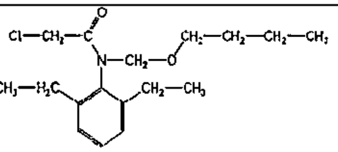
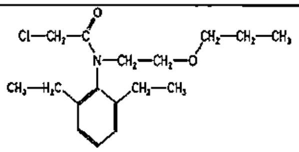
Chloroacetanilide herbicides are effective as pre emergence herbicides. They inhibit early seedling growth by inhibiting synthesis of long chain fatty acids. They can be applied safely in certain susceptible grass crops when applied with antidotes. Major portion of these herbicides are degraded by microbial activity.

The herbicides coming under this group are non ionic in nature. The conjugate carbonyl oxygen and amide nitrogen in the chloroacetanilide structure enables stronger specific interactions with the sorbents leading to lower dissipation compared to the dinitroaniline herbicides (Yang and Holmen, 2007). The major herbicides in this group include butachlor, pretilachlor, alachlor, acetachlor, metolachlor etc. The technical information and toxicity data for the herbicides, butachlor and pretilachlor are furnished in table 1.

Bailey *et al.* (1968) suggested that within a chemical family the magnitude of pesticide adsorption is directly related to and governed by the degree of water solubility. The hydrophobic character of a pesticide will increase by a decrease in its water solubility thereby resulting in stronger adsorption on soil organic matter (Hance, 1965; Leenheer and Ahlrichs, 1971). In general, pesticides of relatively high water solubility would be expected to be more effective in higher organic matter soils than chemicals of low water solubility (Khan, 1989). The adsorption of pesticides involving this mechanism would be independent of pH (Hance, 1965; Walker and Crawford, 1968).

Non polar pesticides or compounds whose molecules often have regions of significant size in proportion to polar regions are likely to be adsorbed onto the hydrophobic regions of soil organic matter. Water molecules present in the system will not compete with non polar molecules for adsorption on hydrophobic surfaces. The potential importance of the hydrophobic fractions of organic matter for the retention of pesticides was cited by Hance (1969). Non polar portions of the humic polymer and hydrophobic molecules trapped within the polymer could provide hydrophobic binding sites for hydrophobic pesticides.

Table 1 Technical information and toxicity data on butachlor and pretilachlor

Common name	Butachlor	Pretilachlor
Chemical Name	N-(butoxy methyl)-2-chloro-N-(2,6-diethyl phenyl)acetamide	2-chloro-N-(2,6-diethyl phenyl)-N-(2-propoxy ethyl)acetamide
Chemical structure		
Molecular weight	311.9	311.9
Physical state, colour, odour	Yellow to purple liquid with a faint, sweet odour	Colourless liquid
Specific gravity	1.076(25^{0}C)	1.076(20^{0}C)
Melting point	-2.8^{0}C to 1.7^{0}C	-
Boiling point	156^{0}C	135^{0}C
Stability	Decomposes $\geq$ 165^{0}C, stable indefinitely $\leq$ 45^{0}C	At 20^{0}C, 50% hydrolysis occurs in 14 days at pH 13
Vapour pressure	0.24 mPa(25^{0}C)	0.133mPa(20^{0}C)

Solubility:		
Water	20 mg L^{-1}(20^{0}C)	50mg L^{-1} (20^{0}C)
Organic Solvents	Soluble in diethyl ether, acetone, benzene, ethanol, ethyl acetate and hexane	Soluble in benzene, hexane, methanol and dichloromethane
Acute toxicity:		
Acute oral LD$_{50}$	2000 mg kg^{-1}(rats)	6099mg L^{-1}(rats)
Acute percutaneousLD$_{50}$	>13000mg kg^{-1}(rabbit)	>3100mg kg^{-1}(rats)
Inhalation LD$_{50}$ (4h) for rats	>3.34mg L^{-1} air	>2.8mg L^{-1} air
Acceptable daily intake	0.01 mg kg^{-1} body weight	0.018 mg kg^{-1} body weight
Environmental fate		
In soil	Degradation is principally by microbial activity. Persistence for 6-10 weeks. Converted to water soluble derivatives, with slow evolution of CO$_2$	Strongly adsorbed to soil, DT$_{50}$(lab) 30days, rapidly degraded
In plant	Rapidly metabolized to water-soluble metabolites, leading eventually to mineralisation	Substitution of chlorine atom to form conjugate. Cleavage of ether bond to yield an ethyl alcohol

		derivative. Hydrolytic and reductive removal of the chlorine atom

(Source: RSC, 1987)

2.2 Adsorption

Adsorption is the accumulation of atoms or molecules on the surface of a material. The term sorption encompasses both processes, that is adsorption and desorption. Adsorption/desorption studies are useful for generating essential information on the mobility of chemicals and their distribution in the soil, water and air compartments of our biosphere (Calvet, 1980).

According to Harper (1994), adsorption is the bonding of chemical to sites on soil mineral or organic surfaces. Adsorption of herbicides can be physical or chemical. Physical adsorption is the result of Van der Waal's forces interacting between neutral molecules and surface of soil colloids. Chemical sorption is the result of coulombic forces interacting between oppositely charged adsorbent and adsorbates.

2.3 Adsorption of herbicides

Sorption-desorption are one of the key processes affecting the fate of agrochemicals in the sediment-water environment. So a thorough understanding of sorption is of paramount importance for the prediction of pesticide movement in soils and aquifers. Pesticides are adsorbed on both organic and inorganic soil constituents and their relative importance depends on the amount distribution and properties of these constituents and the chemical properties of the pesticides (Bailey and White, 1970). The long term fate of herbicides in the environment is strongly influenced by adsorption phenomena operated by soil colloids (clay and humus). Persistence and leachability, bioactivity and biodegradability of herbicides are mainly dependent upon the bonding mechanisms involved in the adsorption process (Senesi and Testini, 1983). In order to improve the efficiency of the soil applied herbicides, with minimum residues, understanding the adsorption process of the applied chemical is important (Sato *et al.*, 1987).

The review paper by Senesi (1992) summarized and discussed the nature of the binding forces involved and the types of mechanisms operating, often simultaneously in the adsorption process of several pesticides onto soil humic substances, humic acids and fulvic acids. These include ionic, hydrogen and covalent bonding, charge transfer or electron donor-acceptor mechanisms, Van der Waal's forces, ligand exchange and hydrophobic bonding or partitioning.

Mechrafi *et al.* (2001) reported that the organic fraction is the most important constituent for adsorption of atrazine in the seven soils they studied. The adsorption isotherm was affected by the reactive fraction of organic matter of soils. No correlation was found between atrazine adsorption and soil properties

Xu *et al.* (2005) showed that the adsorption mainly took place on the CO, phenolic and alcoholic OH groups of Humic Acids (HA). It was also confirmed that the adsorption mechanism was hydrogen bonds formation between the above groups of HA, and butachlor molecules. Under the experimental conditions, the adsorption amount of butachlor on soils was positively correlated with the content of soil organic matter.

2.3.1 Adsorption of butachlor and pretilachlor

Liu *et al.* (2008) reported that total organic carbon content, clay content, amorphous Fe_2O_3 content, silt content, CEC, and pH had a combined effect on the butachlor sorption on soil.

Zhen *et al.* (2010) investigated butachlor sorption by different size organomineral fractions of black soil and found that about 60-70% of butachlor was adsorbed on the clay fraction. For an adsorbent with a very low soil organic matter (SOM) content, mineral colloids could enhance butachlor adsorption because of their high exposed mineral surface. Quan *et al.* (1999) studied adsorption of metolachlor, acetochlor, pretilachlor and butachlor, as a group of acetanilide herbicides on eight soils with various physical and chemical properties. The adsorption isotherm fit the Freundlich equation well. The extent of adsorption increased in the order: metolachlor<acetochlor<pretilachlor<butachlor. The product of Freundlich adsorption constants k_f (1/n), showed good correlation with organic matter content of soils for each of these herbicides.

Adsorption of the chloroacetanilide herbicides acetochlor, alachlor, metolachlor and propachlor was determined on soil and soil components, and their structural differences were used to explain their sorptivity orders. On all soils and soil humic acids, adsorption decreased in the order: metolachlor>acetochlor>propachlor>alachlor (Liu *et al.*, 2000). Rytwo *et al.* (2008) found that adsorption of alachlor on montmorillonite was 30% more than that of difenzoquat and diquat.

2.4 Factors of adsorption

Beckie and Mc Kercher (1990) demonstrated a positive correlation between sorption and soil organic carbon (OC) content and/or a negative correlation with soil pH, indicating that chlorsulfuron sorption is favoured by hydrophobic interaction between the neutral species and organic soil domains.

Reinhardt *et al.* (1990) suggested that persistence of the atrazine herbicide was more closely linked to soil characteristics than to climatic conditions. Kozak *et al.* (1991) found that the four soil characteristics were suitable for the estimation and prediction of the adsorption: clay content, carbon, pH and CEC.

Organic matter played the most important role in the adsorption of all the herbicides they studied. Barriuso and Calvet (1992) reported that the adsorption of herbicides like atrazine, terbutryn and 2,4-D was influenced by chemical structure of herbicides, soil constituents and physico-chemical factors such as pH.

Sahid *et al.* (1997) studied the effects of environmental factors on bioactivity, adsorption and persistence of two herbicides, alachlor and terbuthylazine. Alachlor adsorption by sand-peat mixture increased proportionately with an increase of soil organic matter content and with increasing herbicide concentration. The half life of alachlor decreased from 15.2 to 6.2 days as temperature increased from 25-35 ^{0}C in the Selanger series soil and from 14.5 to 6.2 days in the Serdang series soil. An increase of temperature from 25-35 ^{0}C also reduced the half life of terbuthylazine in both soils. The half-life of alachlor decreased at a moisture level of 70% field capacity in both soils. However, the dissipation rate of terbuthylazine was significantly faster at 50 % field capacity (94 days) in Serdang series than at 70 % (11.4 days).

According to Basham *et al.* (1987), the mobility of herbicides in soil is influenced by soil organic matter and pH. Mon *et al.* (2009) measured the linear adsorption co-efficient (K_d) values for 2, 4-dichlorophenoxy acetic acid (2, 4-D) adsorption on Japanese volcanic ash soils with different amount of soil organic matter in batch experiments under different pH conditions. Strong correlations were found between measured K_d values and pH as well as soil organic matter. The adsorption of 2,4-D increased with decreasing pH and with increasing soil organic matter.

2.4.1 Soil Texture:

Kumar and Philip (2006) reported that adsorption of hydrophobic pesticides was more in clay soil. Barton *et al.* (1994) showed that soil texture and soil parent material had significant effect on sulphate adsorption.

2.4.2 Soil type:

Beestman and Deming (1974) determined degradation of alachlor in different soils. Half life values of alachlor in silt, silty loam, silty clay, clay loam and sandy loam were 4.0, 11, 7.3, 9 and 11-24 days respectively. Stougaard *et al.* (1990) observed that adsorption was greater in silty clay loam and less in sandy loam soils.

2.4.3 Clay content:

Clay content is one of the principal factors influencing persistence of herbicides in soil, because clay and organic matter contents are correlated (Edwards, 1973). Weber and Peter (1982) reported that the adsorption and bioactivity of herbicides were correlated with clay content. Cations such as Al^{3+} and Fe^{3+} can form hydroxide on the clay surface. This results in a greater increase of the adsorption capacity of the clay mineral (Calvet, 1980).

2.4.4 Organic carbon content:

Johnson *et al.* (1997) reported that the application of endogenous or exogenous organic matter to soil increased its organic carbon content, resulting increased pesticide sorption and decreased leaching. Jenks *et al.* (1998) reported that organic matter content was the best single predictor of atrazine adsorption followed by soil pH. According to Mitra and Bhowmik (2001), the soil organic matter content was the best single determining factor of sorption and the net sorption constant was correlated to the organic matter content of the soil. According to the study conducted by Altfelder *et al.* (1999), there was increased adsorption and less desorption in soil due to changes of soil organic matter caused by air-drying. Adsorption-desorption process of fluometuron and soil differed according to the soil organic matter (Rankins *et al.*, 2002). The data presented by Strebe and Talbert (2001) indicated a higher rate of adsorption of flumetsulam in soils with a higher organic matter and Fe-content in the surface and subsurface depths. According to Krutz *et al.* (2004), sorption coefficients of metolachlor were higher in organic carbon rich soil. Studies of Kawakami *et al.* (2007) indicated that hysteresis in the adsorption-desorption phenomena was affected by organic matter especially in case of pretilachlor. Liu *et al.* (2008) reported that the ratio of clay content to total organic carbon content was a useful parameter to predict adsorption of herbicide butachlor in soils.

According to Si *et al.* (2009), adsorption of metolachlor was greater in the high organic matter surface soils than in subsoils. Lower adsorption distribution coefficient (K_{ads}) values with increasing depth indicated less adsorption at lower depths and greater leaching potential of metolachlor after passage through the surface horizon. Desorption of metolachlor showed hysteresis, indicated by the higher adsorption slope ($1/n_{ads}$) compared with the desorption slope ($1/n_{des}$). Soils that adsorbed more metolachlor also desorbed less metolachlor. Metolachlor dissipation rates generally decreased with increasing soil depth. The first order dissipation rate was highest at the 0-50 cm depth (0.140 per week) and lowest at the 350-425 cm depth (0.005 per week).

2.4.5 Dissolved organic carbon:

Suba and Essington (1999) reported that herbicide adsorption process is influenced by both the solid organic carbon and dissolved organic carbon (SOC and DOC) content of soil. The influence of DOC on herbicide adsorption was a function of DOC source and concentration.

Dissolved organic matter (DOM) is defined as "the organic matter that is able to dissolve in the field conditions". According to McDowell and Likens (1988), dissolved organic carbon (DOC) is a leaching product from plants, litter and humus and it is generated by microbial activity. These fractions in solution pass through a 0.45 μm filter. It has high affinity for organic non-ionic hydrocarbons and pesticides, there by affecting their retention and transport in soils. Dissolved organic matter plays an important role in the biogeochemistry of carbon, nitrogen, and phosphorous, in pedogenesis and in the transport of pollutants in soils (Kalbitz *et al.*, 2000). The source of virtually all DOM in soils is photosynthesis; this includes both recent photosynthate (throughfall, leaf litter, root exudates, decaying fine roots) as well as the leaching and decomposition of older, microbialy processed soil organic matter (McDowell, 2003). Dissolved organic matter ranges in age from hours to days, to decades and even up to thousands of years. Sinks of DOM include microbial transformation and immobilization, mineralization (to CO_2, inorganic N, etc.), precipitation, and adsorption on mineral surfaces. Microbial soil communities are the most important agents in DOM formation. Guggenberger *et al.* (1994) studied DOM fraction and structure and demonstrated that microbial metabolites constitute a significant portion of DOM. According to these studies, the carbohydrate fraction of DOM is chemically different from that in plant residues or bulk humus; in that DOM carbohydrates have higher proportion of hexose- and deoxysugars than pentose sugars. Since pentose sugars are rarely found in microbial cells, DOM may be predominantly of microbial origin

Zsolnay (1996) and Tipping (1998) had suggested that the DOM could be partitioned into mobile and immobile fractions according to the pore sizes of the soil matrix. Only the mobile DOM fraction in macro- and mesopores is subjected to convective transport by seepage. DOM in micropores is immobile and interacts with soil depth because DOM was adsorbed along the soil profile. High molecular weight fractions are preferentially adsorbed when compared with low molecular weight components (Gue *et al.*, 1995). The presence of aromatic rings, carboxylic acids, N- and S-containing groups, and amino acid residues in organic molecules increases the adsorption capacity (McKnight *et al.*, 1992). Adsorption involves the free surfaces of colloidal minerals and the presence of organic matter which has already been adsorbed further reduces DOM adsorption (Kalbitz *et al.*, 2000).

Polyvalent and monovalent cation capacity affects the solubility of organic matter (Baham and Sposito, 1994). Chemical reactions between anionic functional groups of organic molecules and solution cations can reduce the surface charge density, alter the structural conformation of the adsorbed species, and consequently reduce solubility. At high concentrations of ions in solution these processes increase and the solubility of organic matter is reduced by flocculation (Tipping and Woof, 1990)

Various environmental factors influence DOM concentrations and fluxes in soils. Temperature is always a factor regulating DOM microbial production (Mulholland *et al.*, 1990). One of the most consistent findings in both field and laboratory studies is that DOM concentrations increased following rewetting after dry periods (Lundquist *et al.*, 1999; Tipping *et al.*, 1999 and Zsolany *et al.*, 1999). It is likely that reduced rates of decomposition in dry soils cause microbial products to accumulate. This together with cell death and lysis, can contribute to high DOM concentrations in the soil leachate after dry periods.

Land use changes, such as afforestation, liming, and fertilization, converting forests into arable sites, and other management activities influence DOM dynamics by 1) changing input of organic matter, 2) changing substrate quality and 3) altering rates, extent, and pathways of microbial degradation and the synthesis of organic matter (Cronan *et al.*, 1992). Li *et al.* (2010) found that the dissolved organic matter contents in soils were significantly affected by fertility levels and land use patterns. Dissolved organic carbon and dissolved organic nitrogen contents in soil increased with crop improvement and soil fertility.

The understanding of the dynamics and fluxes of DOM in soils is important in limiting the loss of organic matter from the soil, improving agronomic practices, and reducing the environmental impact of substances on the DOM, such as agrochemicals. The major problem of evaluating the functionality of DOM in the soil environment is its complex and heterogenous composition. The hydrophobic fraction of DOM consists of lignin-derived, partly aromatic molecules (Guuggenberger *et al.*, 1994 and Kaiser *et al.*, 2001). It comprises traditional humic and fulvic acids and is of brownish colour due to aromatic structures (Thurman, 1985). The incubation of pesticides with dissolved organic matter increases the apparent solubility of these chemicals and there by results in an increase in the mobility of the chemicals in soil (Chiou *et al.*, 1986). Neff and Asner (2001) found that physical factors most notably, sorption dynamics and hydrology play the dominant role in regulating dissolved organic carbon losses from terrestrial ecosystems.

Davidson *et al.* (1987) found a strong correlation between dissolved organic carbon concentration and soil organic carbon mineralization in a variety of soil types. Dissolved organic carbon has a well established role in soil formation (Ugolini and Dahlgren, 1987). An increase in pH and/or decrease in ionic strength lead to an increase in the leaching of dissolved organic carbon (Evans *et al.*, 1988). Dissolved organic carbon involved in nutrient and heavy metal transport (Qualls and Haines, 1991). Cook and Allan (1992) reported that there was no obvious relationship between dissolved organic carbon and instantaneous rates of soil organic carbon mineralization over a long incubation period. Guggenberger and Zech (1993) found that dissolved organic carbon concentrations in soil solutions are often elevated during summer when microbial activity is high. Anderson and Nilsson (2001) reported that the pH and temperature have significant influence in solubility and production of dissolved organic carbon.

Christ and David (1996) reported that in wetter samples (moisture content from 1.8 to 5 mg g^{-1}), dissolved organic carbon production increased by approximately 0.1 mg $g^{-1}week^{-1}$ for every g g^{-1} increase in moisture content. The production of dissolved organic carbon increased exponentially with temperature. The composition of the dissolved organic carbon extracted from the driest samples suggested disruption of microbial biomass. Wetter incubation conditions increased the proportion of hydrophobic acids, where as warmer incubation conditions increased the proportion of hydrophilic acids.

Dissolved organic carbon (DOC) plays an important role in various soil processes. These include solubilisation, complexation or sorption of metals and hydrophobic organic compounds (Zsolnay, 1997). Dissolved organic carbon (DOC) plays an important role in transport, mineralization, and stabilization of C in soil (Kalbitz *et al.*, 2000).

According to Spark and Swift (2002), the major factor governing the sorption of pesticides such as atrazine, isoproturon and paraquat was the solid state organic fraction with the clay mineral content. The dissolved organic carbon fraction of the total organic carbon in the soil and ionic strength of the soil solution had little or no effect on the sorption/transport characteristics of these pesticides over the range of concentrations studied.

The study done by Fernadez-Bayo *et al.* (2009) revealed that addition of vermicompost enhanced the sorption capacity by two to four folds. Exogenous organic carbon composition influenced herbicide sorption. Vermicompost which had largest organic carbon and lignin content recorded the largest sorption increment. Vermicompost which had the greatest dissolved organic carbon content and high degree of humification made the smallest contribution to sorption.

Celis *et al.* (1998) reported that addition of insoluble and soluble organic carbon to soil through management practices, such as sewage sludge application, may greatly alter pesticide sorption-desorption in soil.

2.4.5.1 Role of dissolved organic carbon on herbicides

Barriuso *et al.* (1992) showed the importance of endogenous as well as exogenous DOC on the sorption of herbicides by soil. Sorption and movement of two ionic herbicides (2,4-D and atrazine) by three soil materials which were amended with different levels of exogenous carbon materials were examined by Baskaran *et al.* (1996) using ^{14}C- labeled compounds. The difference in the effect of C sources on the sorption of herbicides was related to the difference in the amount of DOC and the pH. The addition of DOC to solutions of herbicides prior to sorption measurements decreased the sorption of herbicides, whereas the addition of DOC to soil increased the sorption of herbicides. Column studies, have shown that DOC enhanced the movement of herbicides in soils. The effect of DOC on the movement of herbicides varied between the soil materials and may be related to the difference in the sorption of both the herbicides and the DOC.

2.4.6 pH

According to Boivin *et al.* (2005), the adsorption/desorption is influenced by soil pH. Renner *et al.* (1988) reported that adsorption of imazaquin and imazethapyr to soil increased as the soil pH decreased from 8 to 3 in laboratory studies. Stougaard *et al.* (1990) found that the herbicides, imazaquin and imazethapyr were more strongly adsorbed and less mobile at lower pH. Barriuso *et al.* (1992) reported that adsorption intensity of herbicides is greatly influenced by pH.

2.4.7 Soil moisture

According to Merkle *et al.* (1966) rainfall was an important factor in determining the movement and persistence of pesticides. Dao and Lavy (1978) found that a decrease in water: soil ratio and in soil moisture content led to an increased adsorption of the herbicide. Gaillardon and Dur (1995) reported that adsorption of herbicides was favoured by low soil moisture initially, but was enhanced by higher soil moistures at sorption times greater than 30 minutes.

2.5 Assessment of strength of adsorption of herbicides using distribution coefficient (K_d) and organic carbon partition coefficient (K_{oc})

Mobility of herbicide in soil environment is controlled to a large extent by its sorptive interaction with soil constituents. Earlier studies have indicated that soil organic matter is the principal adsorbent for the sorption of non ionic organic compounds on soil (Bailey and White, 1970; Chiou *et al.*, 1985; Hamaker and Thompson, 1972). The partition coefficient (K_d) and soil organic carbon partition coefficient (K_{oc}) could be used for assessing the strength of soil sorption (Hamaker and Thompson, 1972). Chiou *et al.* (1983) suggested that the sorption of non ionic organic compounds by organic matter is essentially a partitioning process. According to Reddy and Locke (1994), the soil organic carbon partition coefficient (K_{oc}) is the ratio of concentration of a chemical sorbed by the soil to its concentration in the soil water normalized to soil organic carbon. Jaw *et al.* (2007) reported that if the adsorption of chemicals on soils is by partitioning into soil organic matter surrounding the soil mineral particles, the adsorption constant (K_d) of a chemical in soil-water system could be stated as the distribution coefficient (or partition constant, K_{oc}) of the chemical in the two adjunct immiscible phases-water and soil organic matter. According to Vogue *et al.* (1994), the sorption coefficient (K_{oc}) describes the tendency of a pesticide to bind to soil particles. Sorption retards movement and may also increase persistence because the pesticide is protected from degradation. The higher the K_{oc}, the greater the sorption potential. Kibe *et al.* (2000) used K_d and K_{oc} for expressing the adsorption equilibrium of five principal herbicides, esprocarb, mefenacet, pretilachlor, simetryn and thiobencarb on five kinds of paddy soil in Japan. Kim and Kim (1990) reported that the soil adsorption coefficient (K_{oc}) of butachlor was 543. So this value means that butachlor is tightly bound to organic matter in soil and is considered immobile. Moon and Kim (2000) reported that the adsorption distribution coefficient (K_d) of butachlor and pretilachlor were 1.34 and 2.86 respectively.

Materials and Methods

3. MATERIALS AND METHODS

The research work consisted of an incubation experiment to study the influence of moisture and organic matter on adsorption of butachlor and pretilachlor in laterite soil and a pot culture experiment to estimate the adsorption of butachlor and pretilachlor under different sources of organic matter. Incubation experiment, pot culture experiment and all the analytical works related to these experiments were conducted at the Herbicide Residue Laboratory of All India Coordinated Research Programme on Weed Control, Thrissur centre and Department of Soil Science and Agricultural Chemistry, College of Horticulture, Vellanikkara.

3.1 Collection and preparation of soil sample

The soil samples for incubation and pot culture experiments were collected from rice fields of College of Horticulture, Vellanikkara. The sample collection was done on 20th October 2010, just after the harvest of the rice crop. Approximately 200 kg of soil sample was collected in sacks. These samples were air dried, ground and sieved through 2mm sieve and kept for pot culture and incubation experiments and also for further laboratory analysis.

3.2 Physicochemical properties of soil

Major physicochemical properties of the soil *viz.*, soil moisture, soil texture, pH, CEC and organic carbon content were analysed before starting the experiments and the methods adopted for the analysis are given in table 2.

3.3 Dissolved organic carbon

The analytical procedure for dissolved organic carbon suggested by Barriuso *et al.* (1992) was modified in the present study. The method involves

Table 2 Methods employed for soil analysis

Properties	Method	Reference
Texture	International pipette method	Robinson (1922)
Moisture	Gravimetric method	Chopra and Kanwar (1976)
pH	pH meter	Jackson (1958)
Electrical Conductivity	Electrical conductivity meter	Jackson (1958)
Cation Exchange Capacity	extraction and estimation by sodium acetate	Bower *et al.* (1952)
Organic carbon	Walkley-Black	Walkley (1947)

water extraction followed by estimation of organic carbon in the filtrate using Walkley-Black method (Walkley, 1947).

3.3.1 Standardization of procedure for estimation of dissolved organic carbon

Standardization procedure involved selection of shaking time, centrifugation speed and time and filtering technique. Air dried (0.5 mm sieved) soil samples of 25g were taken in 250 mL conical flasks, added 75 mL of distilled water and shaken in an orbital incubation shaker at 20 ^{0}C at 500 rpm. In order to standardize the shaking time, two and four hours were tested. Then the supernatant was filtered. Standardization of filtering technique was done by using Whatman No. 42 and Whatman No. 1 filter paper. The filtrate was centrifuged using Rotek laboratory centrifuge. The centrifugation speed and time were standardized by testing three combinations, 3000 rpm for 15 minutes, 3000 rpm for 30 minutes and 4500 rpm for 30 minutes. After centrifugation, the supernatant was filtered through cellulose acetate membrane filter of pore size 0.45 µm. The membrane filtration apparatus is given in plate 1. From the filtrate, 10 mL was pipetted out into a 500 mL conical flask and the dissolved organic carbon in the solution was estimated by Walkley-Black wet digestion method.

3.4 Forms of butachlor and pretilachlor used for the study

Details of forms of butachlor and pretilachlor used for gas chromatograph analysis in incubation and pot culture experiment are given in table 3.

3.5 Estimation of herbicide adsorption by the soil samples

The quantities of butachlor and pretilachlor adsorbed by the soil samples were estimated by direct method suggested by Organization for Economic Co-operation and Development (OECD, 2000) using gas chromatography following the common protocol developed at AICRP on weed control, College of Horticulture (KAU, 2008) which is detailed below.

Table 3 Technical information on the forms of reference standard and formulation

Name of the chemical	Molecular weight	Physical appearance	Purity (%) or a.i.content	Source
1. For gas chromatograph analysis				
Butachlor	311.9	Colourless liquid	97	Dr. Ehrenstorfer GmbH, D-86199Augsburg, Germany
Pretilachlor	311.9	Colourless liquid	97	Dr. Ehrenstorfer GmbH, D-86199Augsburg, Germany
2. For incubation and pot culture experiments				
Butachlor	311.9	Light violet coloured liquid	50%EC	Machete(TN) Aristo and life science Pvt. Ltd.
Pretilachlor	311.9	Light brown coloured liquid	50%EC	Rifit (TN) Syngenta India Pvt. Ltd.

The soil sample collected from the adsorption experiments were kept for air drying (12 hours) and sieved through 2 mm sieve . The sieved sample (15g) was thoroughly mixed with 10g of anhydrous sodium sulphate, 2g of florisil (60-100 mesh size) and 0.3g of activated charcoal. A glass column of 30 cm length and 2 cm internal diameter was taken. Anhydrous sodium sulphate of 3 cm layer was put on the non adsorbent cotton kept at the lower end of the column. Then the soil sample mixture (prepared as above) was added to the column and another layer of anhydrous sodium sulphate of 1 cm was put over this layer. The herbicide was extracted with 100 mL of hexanes: acetone mixture (9:1) and excess solvent was evaporated under vacuum to one mL. The evaporated sample was made upto 5 mL with n-hexane and one microlitre was injected into gas chromatograph. Herbicide content was estimated from the peak area.

Gas chromatographic conditions:

Instrument: Shimadzu GC-2010
Detector: Electron capture detector
Column: BPX5
Temperature conditions:
Capillary injector: 250 °C
Column: 220 °C
ECD: 280 °C
Current: 0.1 nA
Make up flow: 30 mL min^{-1}
Column flow: 1.24 mL min^{-1}

Plate 1 Membrane filtration apparatus

3.6 Incubation experiment

Incubation experiment was done to understand the effect of both moisture and organic matter on adsorption of herbicides in soil. General view of incubation experiment shown in plate 2.

Treatments:

a. Herbicides : 2
    1) Butachlor @1.25 kg ha^{-1}
    2) Pretilachlor @ 0.45 kg ha^{-1}
b. Organic matter sources: 3
    1) Soil alone (no org. matter added)
    2) Soil + FYM @ 5 t ha^{-1}
    3) Soil + vermicompost @ 5 t ha^{-1}
c. Moisture levels: 2
    1) Air dried
    2) Field capacity

No. of treatments: 12
Design: CRD
Replications: 3

Methodology:

Air dried (2 mm sieved) soil sample of 100g was taken in a 250 mL conical flask. For the treatments under field capacity, 25 mL distilled water was added to the flask. The required quantity of organic manures were added to the respective treatments and mixed thoroughly. Conical flasks were capped with aluminium foils and incubated for one week under normal laboratory conditions. After one week of incubation, 10 g of soil samples were taken from each treatment and 50 mL of 0.4 µg mL^{-1} of butachlor and 0.12 µg mL^{-1} of pretilachlor standard solutions (made in distilled water) were added to this according to the treatment. The contents were shaken in an orbital incubator shaker for 2 hours at 20 ^{0}C. This shaking time was chosen based on the assumption that major portion of the herbicides applied to the soil is adsorbed within 2 h. The soil sample was filtered, and the amount of the herbicide adsorbed (direct method suggested by OECD, 2000) was determined by analysis of soil using the common protocol (single step extraction and clean up). The direct method was used due to the fact that the analytical procedure in the aqueous phase is more tedious involving step wise extraction and clean up.

3.6.1 Observations

The quantity of herbicides retained in soil in the different treatment was estimated by gas chromatography. From this data, the distribution pattern (partitioning between soil and solution phases) of herbicides under different sources of organic matter and moisture levels was compared using distribution coefficient (K_d). The distribution coefficient (K_d) was worked out using the formula:

$$K_d = \text{Sorbed concentration } (\mu\text{mol kg}^{-1}) \; / \; \text{Equilibrium concentration } (\mu\text{mol dm}^{-3})$$

Dissolved organic carbon, total organic carbon, pH and electrical conductivity of the soil samples taken from the treatments were also estimated simultaneously.

3.7 Pot culture experiment

The study was conducted to quantify the adsorption of herbicides in soil when the organic manures like FYM and vermicompost are added to the soil. General view of pot culture experiment is given in plate 3.

Plate 2 General view of incubation experiment

Plate 3 General view of pot culture experiment

Treatments :

a. Herbicides : 2

  1) Butachlor @ 1.25 kg ha^{-1} (6-9 DAS)
  2) Pretilachlor @ 0.45 kg ha^{-1}(6-9 DAS)

b. Organic matter sources : 3

  1) Control (soil alone)
  2) FYM @ 5 t ha^{-1}
  3) Vermicompost @ 5 t ha^{-1}

No. of treatments: 6

Design: CRD

Replications: 3

3.7.1 Sowing

Mud pots of 30 cm diameter and 25 cm depth were taken for the study. The pots were filled with soil upto ¾ th of its depth (6.5 kg pot $^{-1}$). The soil was kept under submerged condition by maintaining 3 cm water above the soil surface and the water level was maintained throughout the rice growing period. The short duration rice variety, Hraswa (75-80 days) was used for the study. Pre germinated seeds were sown in pots. Nine plants were maintained in each pot.

3.7.2 Manures and Fertilizers

Organic manures, FYM/ vermicompost were mixed with soil as per treatments. The quantity of manures and fertilizers applied was according to the Package of Practices Recommendations of Kerala Agricultural University for wetland direct seeded rice crop (KAU, 2007).

3.7.3 Herbicide application

Butachlor @1.25 kg ha^{-1} and pretilachlor @ 0.45 kg ha^{-1} were applied seven days after sowing. Quantity of herbicide formulations (Machete® 50% EC for butachlor and Rifit® 50% EC for pretilachlor) required for each pot was measured, mixed with water and sprayed using hand sprayer, using a spray volume of 500 L ha^{-1}(14 mL per pot).

3.7.4 Plant protection

According to the requirement, plant protection measures were carried out as per the Package of Practices Recommendations (KAU, 2007)

3.7.5 Harvesting

Harvesting was done at 90 days after sowing. The crop harvested from each pot was threshed and weight was recorded for the separated grains and straw. Yield was worked out on per pot basis.

3.7.6 Observations

The soil samples were taken at one day, one week, two weeks and four weeks after herbicide application and after harvest. Two samples were taken from a pot, pooled and the following analysis were carried out using samples taken at 5 cm depth from surface (Plate 4).

a) Herbicide adsorption and dissipation in soil at one day, one week, two week, and four week after herbicide application and after harvest. Quantity of herbicide remained in the pooled sample was determined by Gas chromatography using the method standardized at AICRP on Weed Control, College of Horticulture, Kerala Agricultural University

(KAU, 2008) as given in section 3.5. The half lives of herbicides under different treatments were worked out from the linear regression equation of the form $y= -ax+b$

b) Changes in chemical properties of soil *viz*., pH, EC, organic carbon, dissolved organic carbon and herbicide content in soil at one day, one week, two week and four week after herbicide application.

The following observations on the plants grown in the pots were taken periodically

a) Phytotoxicity shown by rice plants in each treatment and the period of recovery at one week, two week, three week and four week after herbicide application. Phytotoxicity was measured by calculating the percentage of plants showing phytotoxicity out of the total plants in the pot.

c) Observations on plant height, productive tillers, grain and straw yield were taken at the time of harvest. Grain and straw yield were recorded as gram per pot.

3.8 Statistical analysis

The data on herbicide retention in soil, dissolved organic carbon, organic carbon, pH and EC in various treatments at different sampling periods were satistically analysed by applying the analysis of variance. The relationship between herbicide adsorption and the DOC as well as other chemical characteristics of soil samples were determined by working out their correlation (Cochran and Cox, 1992).

late 4 Experimental set up showing points of soil sample collection (holes represent the location)

Results

4. RESULTS

The results pertaining to the study 'Influences of organic matter and moisture on adsorption of chloroacetanilide herbicides in laterite soil' is presented in this section.

4.1 Physicochemical characteristics of the soil

The major physicochemical characteristics of soil *viz.*, soil texture, pH, cation exchange capacity (CEC), electrical conductivity (EC) and organic carbon content of the soil sample taken from the rice field before conducting experiment are presented in table 4.

Table 4 Physicochemical characteristics of the soil

Characters	Value
Sand	73.13 %
Silt	16.88 %
Clay	10.00 %
Texture	Sandy loam
Moisture	3.56 %
pH	4.7
EC	0.05 dS m^{-1}
CEC	4.67 C mol(+) kg^{-1}
Organic carbon	0.61 %

Based on the sand, silt and clay content of the soil samples, the soil could be classified as sandy loam texture. The samples registered sand, silt and clay content of 73.13%, 16.88% and 10.00% respectively. Moisture content of the soil sample was 3.56 percent. The soil was acidic in nature with a pH of 4.7. Electrical conductivity of the sample was 0.05 dS m^{-1} which is with in the safe limits. The samples recorded cation exchange capacity of 4.67 C mol (+) kg^{-1}. The soil sample had medium range of organic carbon *i.e.* 0.61%.

4.2 Important characters of the manures under study

The manure samples recorded a pH of 6.6 and 5.7 for FYM and vermicompost respectively. They differ widely in moisture content (11.56% for FYM and 127.01% for vermicompost) and hence their organic carbon and dissolved organic carbon was estimated on air dry as well as oven dry basis and the values are given in table 5. On oven dry basis vermicompost had high organic carbon content (20.02%) than farmyard manure (10.17%). However, air dried manure samples registered comparable values. Organic carbon content of the air dried manure samples were 9.38 and 8.00% for FYM and vermicompost respectively. Only the air dried manures were used for conducting experiments because FYM and vermicompost are usually applied to the rice crop in the air dry form.

4.2 Standardization of dissolved organic carbon estimation

The methodology of estimation of dissolved organic carbon (DOC) was designed by standardizing the soil shaking time, filtration technique, centrifugation speed and time. Among the two shaking intervals *viz.*, two (101.87 $\mu g\ g^{-1}$) and four (67.91 $\mu g\ g^{-1}$) hours, two hours was better in terms of DOC recovery. Two filtration techniques were employed *i.e.* filtration through Whatman No.1 (67.20 $\mu g\ g^{-1}$) and Whatman No. 42 (66.94 $\mu g\ g^{-1}$). Among them, filtration through Whatman No. 1 was the best for quick recovery. Among the three methods of centrifuging, *viz.*, 3000 rpm for 15 minutes (33.34 $\mu g\ g^{-1}$), 3000 rpm for 30 minutes(64.18 $\mu g\ g^{-1}$) and 4500 rpm for 30 minutes (65.70 $\mu g\ g^{-1}$), 4500 rpm for 30 minutes gave maximum recovery of DOC. The standardized

Table.5 Important physico-chemical characteristics of manures under the study

Organic manure	Physico-chemical characteristics					
	pH	Moisture content (%)	Organic carbon (%)		Dissolved organic carbon ($\mu g\ g^{-1}$)	
			Oven dry	Air dry	Oven dry	Air dry
Farmyard manure	6.6	11.56	10.17	9.38	737.51	425.23
Vermicompost	5.7	127.01	20.02	8.00	2636.45	525.57

procedure for DOC estimation is as follows, 25 g of air dried soil sample were taken, added 75 mL of distilled water and shaken for 2 hours at 20 ^{0}C in 500 rpm. Then it was filtered through Whatman No. 1 filter paper, centrifuged at 4500 rpm for 30 minutes, the supernatant was fitered through cellulose acetate membrane filter of pore size 0.45 µm. From the filtrate, 10 mL was pipetted out into a 500 mL conical flask and the dissolved organic carbon in the solution was estimated by Walkley-Black wet digestion method.

The procedure was validated by analyzing more number of samples and working out relative standard deviation (RSD) of the data for dissolved organic carbon content (oven dry) in soil (8 No.), vermicompost (12 No.) and farmyard manure (12 No.). The DOC content of soil, farmyard manure and vermicompost were in the range of 223.16-654.95 µg g^{-1}, 300.00-1133.71 µg g^{-1}, and 2181.89-3151.62 µg g^{-1} respectively. The RSD of soil, farmyard manure and vermicompost DOC were 40.77, 38.77 and 13.17% respectively (Table 6). All these values were below 50% and hence the method was found suitable for estimation of DOC of soil as well as manures.

As in the case of organic carbon, the mean dissolved organic carbon content of oven dry samples was also more in vermicompost than farmyard manure. Vermicompost contained 2636.45 µg g^{-1} dissolved organic carbon and farmyard manure contained 737.51 µg g^{-1} dissolved organic carbon on oven dry basis. On air dry basis the values were 525.57 and 425.23 µg g^{-1} for vermicompost and FYM respectively.

4.3 Adsorption of herbicides

The adsorption pattern of two chloroacetanilide herbicides *viz.*, butachlor and pretilachlor was assessed by conducting incubation and pot culture experiment.

Table 6 Validity of dissolved organic carbon estimation

Materials	Mean DOC content ($\mu g\ g^{-1}$)				Relative standard deviation(RSD) (%)
	Oven dry		Air dry		
	Range	Mean	Range	Mean	
Soil	223.16-654.95	378.56	215.49-632.43	365.55	40.77
Vermicompost	2181.89-3151.62	2636.45	969.73-1400.72	525.57	13.17
FYM	300.00-1133.71	737.51	269.37-1045.86	425.23	38.77

Table 7 Retention of butachlor and pretilachlor under different sources of organic carbon and moisture conditions

Herbicide	Moisture level	Herbicide retention ($\mu g\ g^{-1}$)		
		Sources of organic carbon		
		Soil alone	Farmyard manure	Vermicompost
Butachlor	Air dry	0.40	0.45	0.43
	Field capacity	0.43	0.47	0.40
Pretilachlor	Air dry	0.24	0.28	0.24
	Field capacity	0.20	0.26	0.24

CD $_{(0.05)}$ =0.053

a) Incubation experiment:

Incubation experiment was conducted with two organic carbon sources *viz.*, FYM and vermicompost and one control (soil alone) under two moisture levels *viz.*, air dry and field capacity. Adsorption of herbicides, butachlor and pretilachlor by the soil matrix was estimated by gas chromatographic technique. Gas chromatographic analysis reports showing chromatogram, retention time (R_t), peak area and method (GC conditions) of the reference standard solution of butachlor and pretilachlor (1 µg mL^{-1}) are given separately. Application of organic matter resulted in a significant increase in the adsorption of herbicides by soil. The adsorption of herbicides was highest in FYM treated soil samples (Table 7) which has high organic carbon content (Table 13) both under air dry and field capacity moisture conditions. Butachlor concentration in the FYM added soil under air dry condition was 0.45 µg g^{-1}, while that under field capacity condition was 0.47 µg g^{-1}. Corresponding values for pretilachlor were 0.28 and 0.26 µg g^{-1} respectively. Herbicide retention in soil alone and vermicompost treatment did not show a definite trend under the moisture levels tested. Chromatograms obtained for both butachlor and pretilachlor under air dry and field capacity conditions presented in fig. 1 and fig. 2 respectively.

When herbicides are applied to the soil, it will be distributed between solid and solution phases. The distribution pattern of herbicides was compared using distribution coefficient (K_d). The distribution coefficient (K_d) was worked out using the formula:

$$K_d = \text{Sorbed concentration } (\mu\text{mol kg}^{-1}) \ / \ \text{Equilibrium concentration } (\mu\text{mol dm}^{-3})$$

If the distribution coefficient is more than one, it means that the herbicides are strictly adsorbed to the soil particles, if it is less than one; it means that the

Butachlor

Air dry

Field capacity

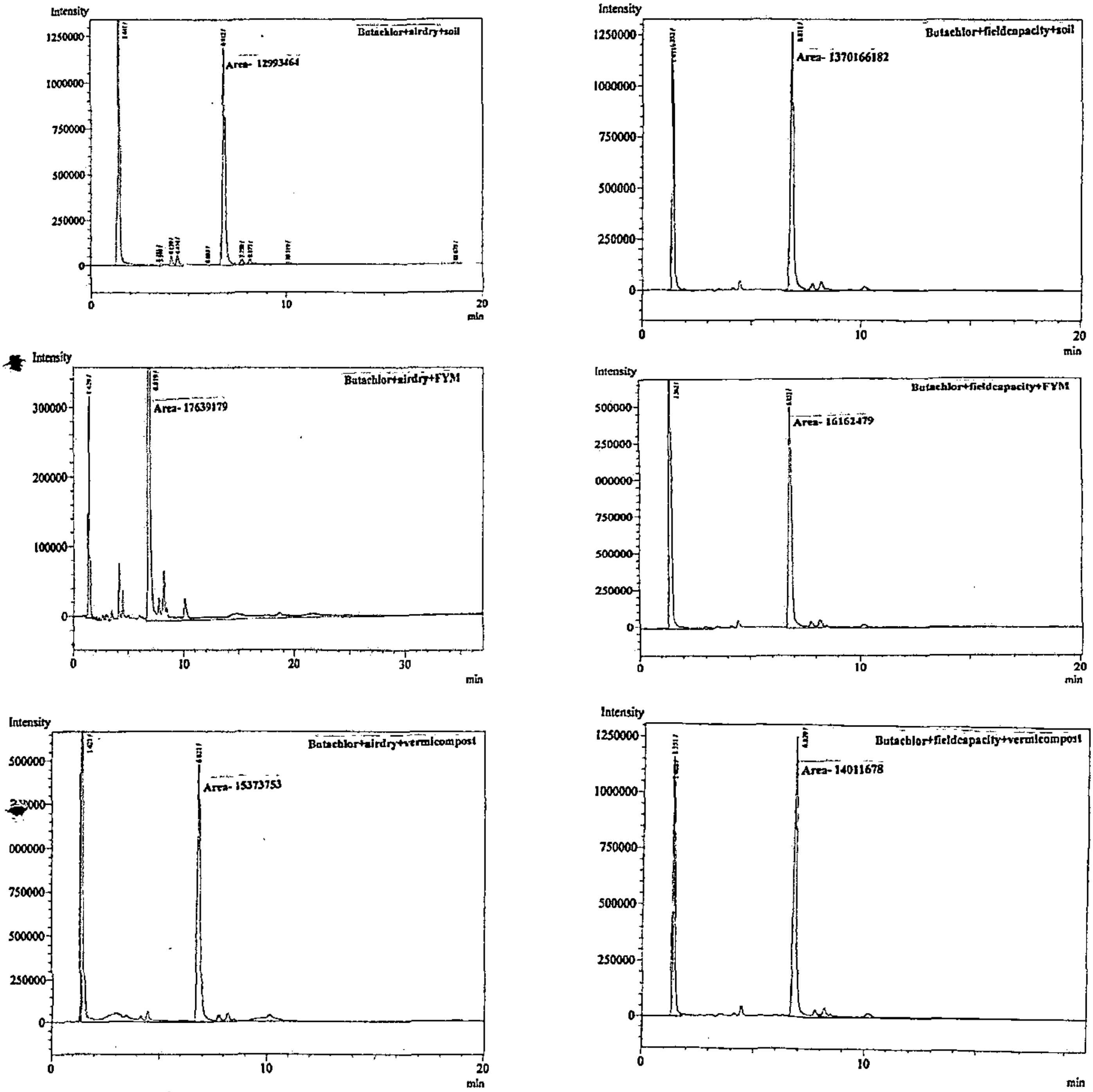
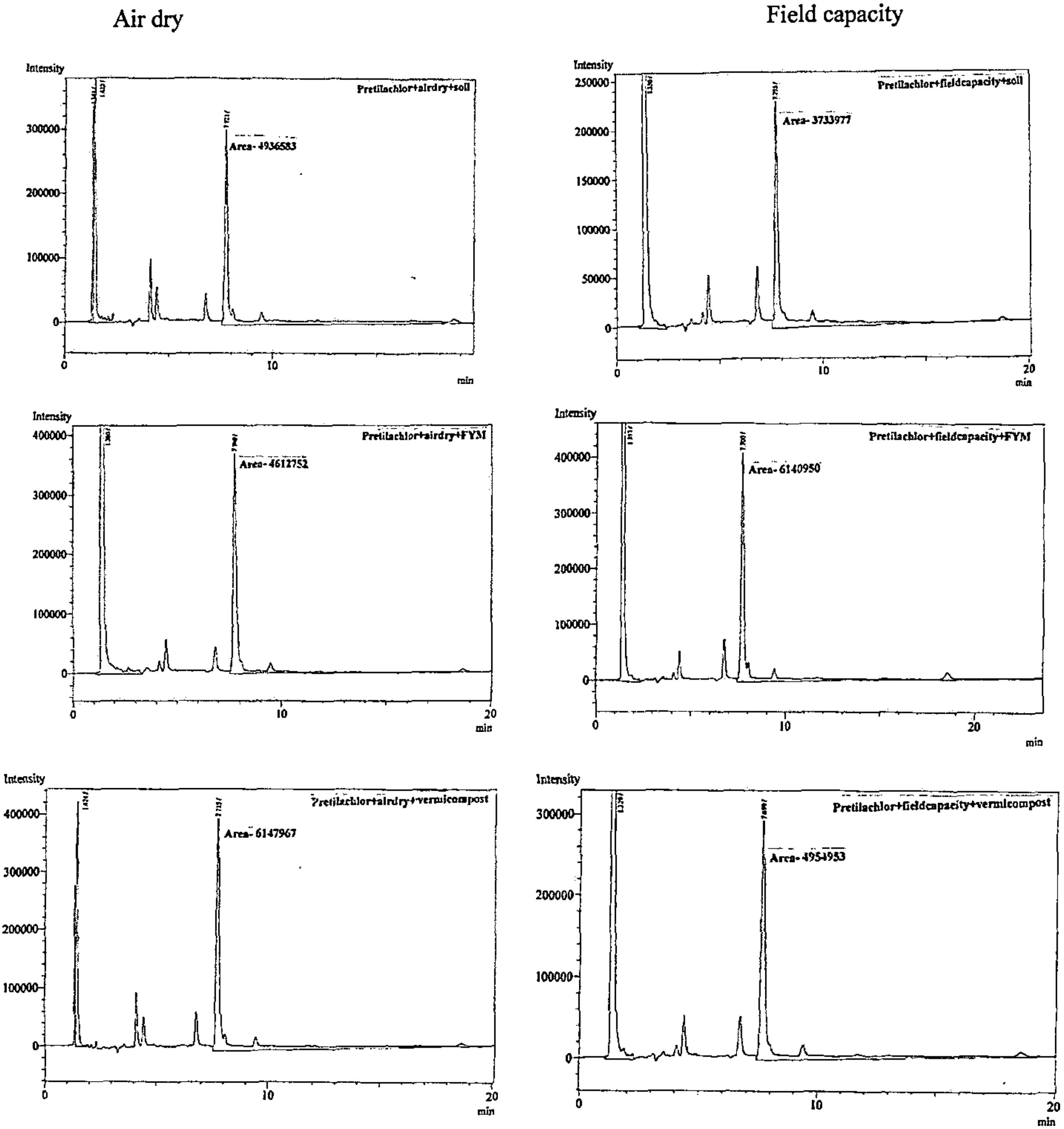


Fig.1 Chromatograms (R_t=6.8) showing butachlor adsorption in soil under different moisture conditions

Pretilachlor



Air dry

Field capacity

Fig.2 Chromatograms (R_t =7.8) showing pretilachlor adsorption in soil under different moisture conditions

Table 8 Distribution coefficient (K_d) of butachlor and pretilachlor under different organic carbon sources and moisture conditions

Herbicide	Moisture level	Distribution coefficient (K_d)		
		Organic matter source		
		Soil alone	Farmyard manure	Vermicompost
Butachlor	Air dry	0.99	1.13	1.08
	Field capacity	1.08	1.17	0.99
Pretilachlor	Air dry	1.97	2.33	1.97
	Field capacity	1.64	2.14	1.97

CD $_{(0.05)}$ = 0.38

herbicides are more in solution phase. The distribution coefficient (K_d) of butachlor and pretilachlor in each treatment is given in table 8. The K_d value is more for pretilachlor compared to butachlor. Among the organic matter sources, K_d value is highest for farmyard manure both for butachlor (1.13 in air dry and 1.17 in field capacity conditions) and pretilachlor (2.33 in air dry and 2.14 in field capacity conditions). The soil alone treatment recorded comparatively lower K_d values (0.99 for butachlor and 1.97 for pretilachlor under air dry condition). At field capacity also soil alone treatment gave lower values (1.08 for butachlor and 1.64 for pretilachlor) compared to farmyard manure.

b) Pot culture experiment:

The adsorption of butachlor and pretilachlor (concentration of herbicides in soil at one day after application) was more in the vermicompost treatment. The data are presented in table 9. The concentration was 8.21 μg g^{-1} for butachlor and 2.19 μg g^{-1} for pretilachlor. The adsorption on farmyard manure treated soil was 5.14 μg g^{-1} and 1.30 μg g^{-1} for butachlor and pretilachlor respectively. The soil without any organic matter addition had lowest adsorption, 4.58 μg g^{-1} in case of butachlor. For pretilachlor the adsorption for the same treatment was 1.45 μg g^{-1}which was more than that of farmyard manure treatment. In the case of butachlor, there was significant difference between the treatments, while it was not so for pretilachlor. At one week, the concentration of butachlor as well as pretilachlor drastically reduced to 3.15 μg g^{-1} and 0.51 μg g^{-1} respectively in the vermicompost treatment. The extent of reduction was less in farmyard manure, the concentration being 4.86 μg g^{-1} for butachlor and 1.14 μg g^{-1} for pretilachlor. Farmyard manure retained the herbicides to a higher degree than vermicompost. At two weeks also the concentration of butachlor and pretilachlor was more in farmyard manure treated samples, the quantities being 2.38 μg g^{-1} and 0.70 μg g^{-1} for butachlor and pretilachlor respectively. At four weeks, the herbicide concentration was more in vermicompost treatment in case of butachlor (1.50 μg g^{-1}) and in farmyard manure treatment in case of pretilachlor (0.32 μg g^{-1}). The

Butachlor

One day after herbicide application

After harvest

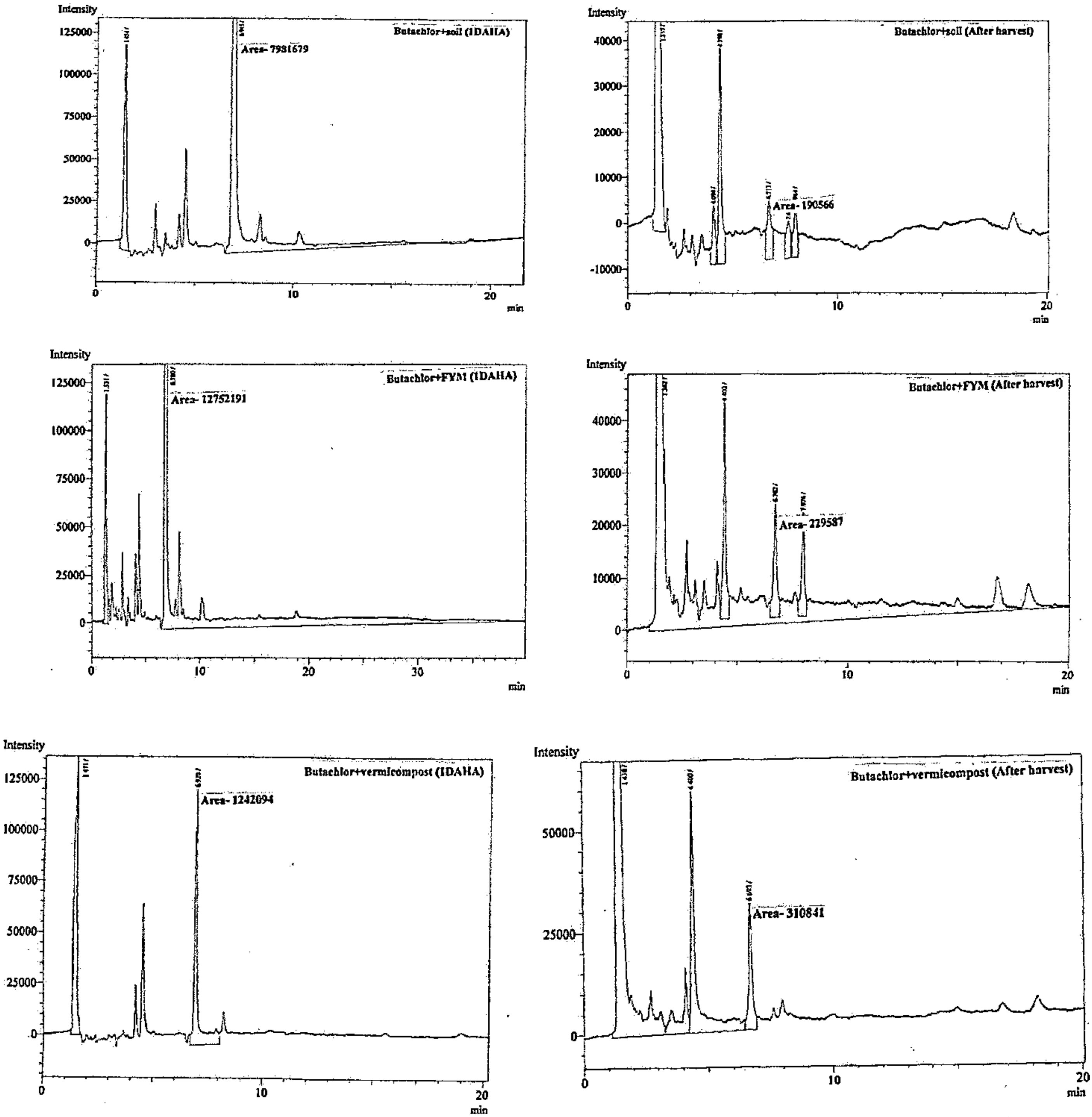
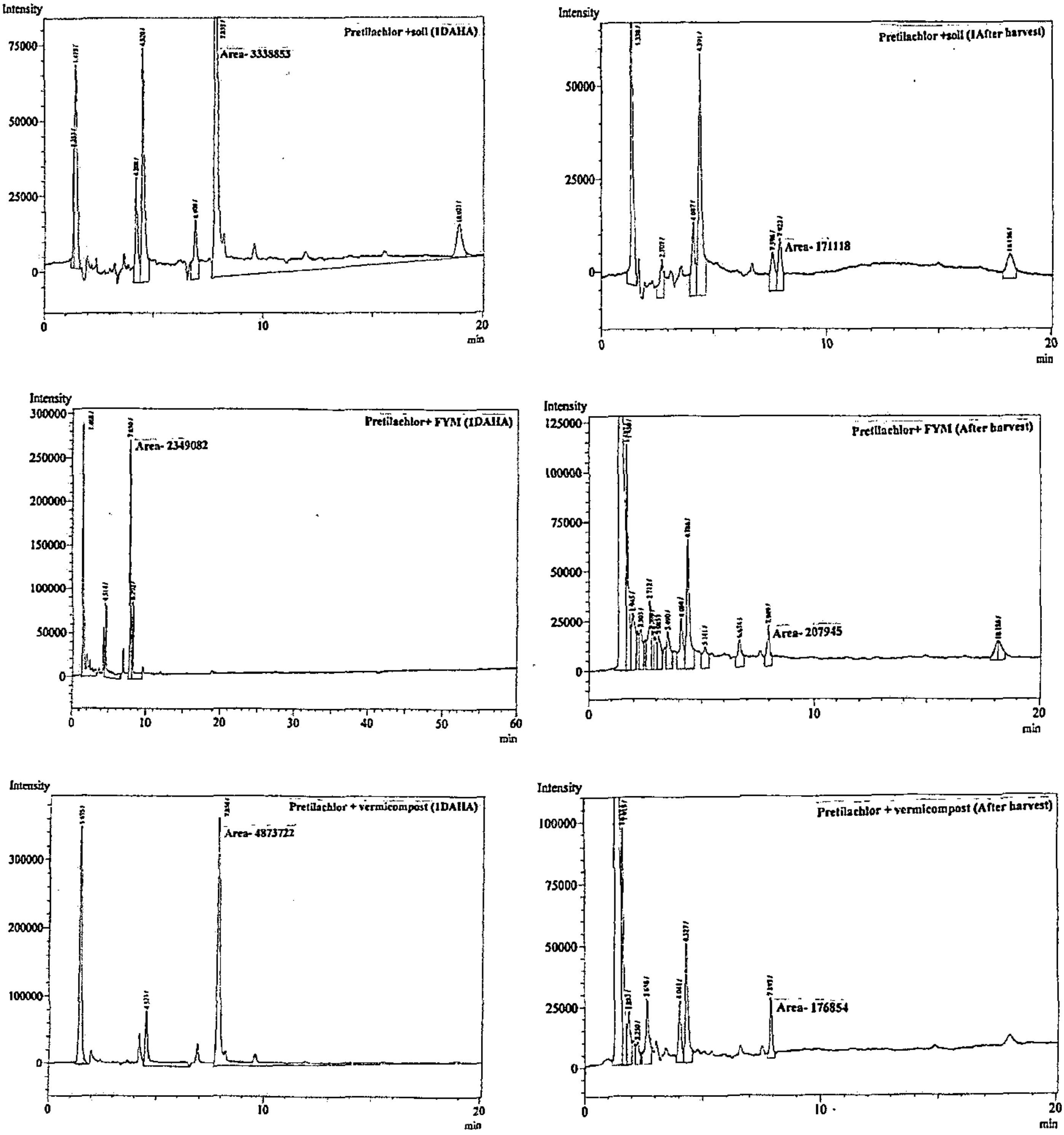


Fig.3 Chromatograms (R_t=6.8) showing changes in concentration of butachlor during the crop period



Pretilachlor

One day after herbicide application

After harvest

Fig.4 Chromatograms(R_t =7.8) showing changes in concentration of pretilachlor during the crop period

Table 9 Herbicide retention at different days after herbicide application (DAHA) in the pot culture experiment

Treatments	Retention of butachlor and pretilachlor (µg g^{-1})				
	1 DAHA	7 DAHA	14 DAHA	28 DAHA	100 DAHA
Butachlor + soil	4.58	3.61	2.20	0.68	0.18
Butachlor+FYM	5.14	4.86	2.38	0.78	0.17
Butachlor+vermicompost	8.21	3.15	2.15	1.50	0.19
Pretilachlor +soil	1.45	0.59	0.24	0.18	0.17
Pretilachlor +FYM	1.30	1.14	0.70	0.32	0.26
Pretilachlor+vermicompost	2.19	0.51	0.35	0.27	0.21
CD $_{(0.05)}$	2.17	1.04	0.59	0.52	0.11

Table 10 Phytotoxicity at different days after herbicide application (DAHA) in the pot culture experiment

Treatments	Phytotoxicity (%)			
	7DAHA	14 DAHA	21DAHA	28DAHA
Butachlor+soil	15.27	47.22	52.91	0
Butachlor+FYM	22.20	55.56	47.68	0
Butachlor+vermicompost	33.30	42.96	66.67	0
Pretilachlor+soil	3.30	35.55	42.59	0
Pretilachlor+FYM	18.50	48.15	38.49	0
Pretilachlor+vermicompost	27.77	48.15	61.90	0
$CD_{(0.05)}$	NS	NS	NS	NS

same trend was noted after the harvest of rice crop. However, at this stage, no significant difference was observed between the organic carbon sources. Chromatograms obtained for butachlor and pretilachlor at one day after herbicide application and after harvest of the crop are given in fig. 3 and fig. 4 respectively.

4.4 Phytotoxicity

Phytotoxicity was observed after one week of herbicide application. The typical symptom of phytotoxicity (curling of emerging leaf) is shown in plate 5. The average phytotoxicity observed at different intervals for all treatments are presented in table 10. Initially phytotoxicity was more in the pots where vermicompost was applied (33.30% and 27.77% for butachlor and pretilachlor respectively). This was followed by farmyard manure treated pots (22.20% and 18.50% for butachlor and pretilachlor respectively).

Phytotoxicity gradually increased in vermicompost and control treatments, while it showed increasing and decreasing pattern in the farmyard manure treatment from 14 days to 21 days after herbicide application. After 21 days, phytotoxicity was least in farmyard manure treatment (47.68% and 38.49% for butachlor and pretilachlor respectively). After 28 days of application, no symptom of phytotoxicity was observed in rice plants (Plate 6).

4.5 Effect of organic carbon sources and moisture levels on dissolved organic carbon content

a) Incubation experiment:

The dissolved organic carbon content in soil under air dry and field capacity moisture levels are shown in table 11. Varying trends were observed under the two moisture levels taken for the study. Farmyard manure treatment recorded higher dissolved organic carbon in the air dry soil (173.16 $\mu g\ g^{-1}$) taken

Plate 5 Typical symptom of phytotoxicity

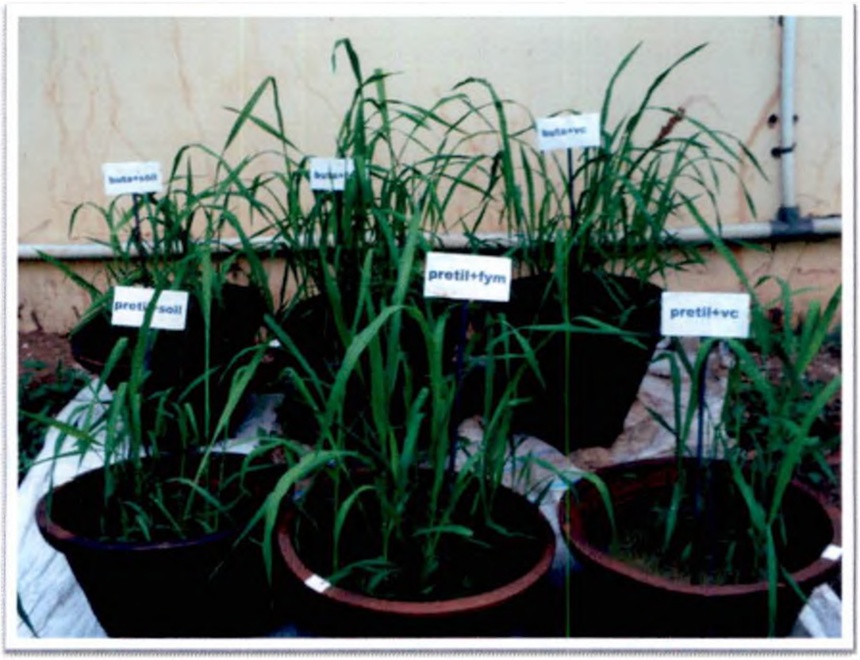


Plate 6 Plants recovered at 28 days after herbicide application

Table 11 Dissolved organic carbon content in soil under different organic carbon sources and moisture levels in incubation experiment

Herbicides	Moisture levels	Dissolved organic carbon ($\mu g\ g^{-1}$)		
		Sources of organic carbon		
		Soil alone	Farmyard manure	Vermicompost
Butachlor	Air dry	107.63	173.16	116.16
	Field capacity	104.12	157.56	450.97
Pretilachlor	Air dry	80.72	79.56	176.80
	Field capacity	53.82	173.16	115.30

CD $_{(0.05)}$ = 77.43

Table 12 Dissolved organic carbon (DOC) content at different days after herbicide application (DAHA) in the pot culture experiment

Treatments	Dissolved organic carbon ($\mu g\ g^{-1}$)			
	1 DAHA	7 DAHA	14 DAHA	28 DAHA
Butachlor+soil	1437.54	489.76	206.35	536.09
Butachlor+FYM	2875.08	376.74	281.39	351.23
Butachlor+vermicompost	2231.97	565.11	243.87	388.21
Pretilachlor +soil	907.92	320.23	243.87	425.18
Pretilachlor +FYM	1170.71	659.30	243.87	462.15
Pretilachlor+vermicompost	1017.20	433.25	225.11	443.67
$CD_{(0.05)}$	563.22	230.98	155.32	262.09

for butachlor application. However, the reverse trend was observed for soil taken for pretilachlor application (DOC values 79.56 µg $g^{-1}$and 173.16 µg g^{-1} for air dry and field capacity respectively). In case of soil alone treatment (without any organic matter), high DOC was registered (107.63 µg g^{-1} and 80.72 µg g^{-1} for soil samples taken for butachlor and pretilachlor applications respectively) under air dry condition both for butachlor and pretilachlor.

b) Pot culture experiment:

The changes in dissolved organic carbon content from one day to four week are given in table 12. At one day, farmyard manure treatment had highest DOC content of 2875.08 µg g^{-1} for butachlor and 1170.71 µg g^{-1} for pretilachlor. The DOC content of vermicompost treatment was 2231.97 µg g^{-1} and 1017.20 µg g^{-1} for butachlor and pretilachlor respectively. The least concentration was in control, 1437.54 µg g^{-1} and 907.92 µg g^{-1} for butachlor and pretilachlor respectively. Farmyard manure treatment differed significantly from other treatments in case of butachlor. But the same was not observed in the case of pretilachlor. At one week, DOC content was highest in vermicompost treatment (565.11 µg g^{-1}) for butachlor and in farmyard manure treatment (659.30 µg g^{-1}) for pretilachlor. Farmyard manure treatment was on par with vermicompost treatment and control under butachlor and was on par with vermicompost treatment under pretilachlor application. At two weeks, DOC content was almost stabilized, there was no significant difference between the organic manure treatments. The highest DOC content was in farmyard manure treatment (281.39 µg g^{-1}) in case of butachlor. In case of pretilachlor, the control and farmyard manure treatments had highest DOC values (243.87 µg g^{-1}). At four weeks after herbicide application, DOC content was more in soil alone treatment (536.09 µg g^{-1}) for butachlor and in Farmyard manure (462.15 µg g^{-1}) for pretilachlor. However, the treatments were found to be on par statistically.

4.6 Effect of organic carbon sources and moisture levels on organic carbon content

a) Incubation experiment:

The percentage organic carbon content at two moisture levels for all the treatments are presented in the table 13. The percentage organic carbon content was high in farmyard manure treatment when compared to other treatments for both air dry and field capacity conditions. The air dry soil samples had organic carbon content of 1.88 % and 1.80 % under butachlor and pretilachlor treatments respectively. The soil samples under field capacity contained 1.53 % and 1.84 % organic carbon content in case of farmyard manure treatment. The results indicated that moisture conditions had not much impact on the organic carbon content of soil.

b) Pot culture experiment:

The changes in organic carbon content from one day to one week after application of herbicides are given in table 14. At one day after application, farmyard manure treated pot, recorded higher organic carbon content, 2.19% and 1.48% for butachlor and pretilachlor respectively. At one week, there was reduction in the organic carbon content in all treatments under butachlor and increased in case of pretilachlor. However, the organic carbon content was uniformly high in farmyard manure treatment (1.79 % and 1.75 % for both butachlor and pretilachlor respectively) irrespective of the kind of herbicide used. At two weeks after herbicide application, there was an increase in organic carbon content for all treatments except for control in case of pretilachlor. The organic carbon content showed an increase for control, FYM and vermicompost in this period in case of butachlor, the values being 1.14 %, 1.98 % and 1.41 % and for pretilachlor, it was 1.01%, 1.87% and 1.37% respectively. At four week, there was

Table 13 Effect of organic carbon sources and moisture levels on organic carbon content in soil in incubation experiment

Herbicide	Moisture level	Organic carbon (%)		
		Sources of organic carbon		
		Soil alone	Farmyard manure	Vermicompost
Butachlor	Air dry	0.55	1.88	1.06
	Field capacity	0.70	1.53	1.25
Pretilachlor	Air dry	0.76	1.80	1.25
	Field capacity	0.63	1.84	1.16

CD $_{(0.05)}$ =0.282

Table 14 Organic carbon content at different days after herbicide application (DAHA) in the pot culture experiment

Treatments	Organic carbon (%)			
	1 DAHA	7 DAHA	14 DAHA	28 DAHA
Butachlor+soil	1.18	0.96	1.14	1.07
Butachlor+FYM	2.19	1.79	1.98	2.06
Butachlor+vermicompost	1.34	1.13	1.41	1.88
Pretilachlor+soil	1.06	1.17	1.01	0.94
Pretilachlor+FYM	1.48	1.75	1.87	1.72
Pretilachlor+vermicompost	0.93	1.26	1.37	1.82
$CD_{(0.05)}$	0.61	0.42	0.39	0.50

significant increase in organic carbon content in vermicompost treatment in case of both butachlor and pretilachlor herbicides. In the other treatments organic carbon content did not vary significantly. In general, an increasing trend was noticed in organic carbon content in farmyard manure and vermicompost treatment for both butachlor and pretilachlor application. The organic carbon content in control (soil alone) did not show significant change. The highest values of organic carbon content were recorded in farmyard manure treatment for both butachlor and pretilachlor at almost all the time intervals.

4.7 Effect of organic carbon sources and moisture levels on pH

a) Incubation experiment:

The effect of moisture and organic carbon sources on the pH of soil samples are presented in table 15. The organic carbon sources had more influence on soil pH as compared to moisture levels. The pH was high for farmyard manure treated soil for both air dry and field capacity condition. Air dry soil samples recorded pH of 5.6 (butachlor) and 5.9 (pretilachlor) and field capacity soil samples had pH of 5.8 (butachlor) and 5.9 (pretilachlor) for farmyard manure treatment. Lowest pH was recorded by the soil alone treatment (5.1-5.3). Vermicompost application resulted in intermediary pH values (5.2-5.7).

b) Pot culture experiment:

There was significant difference in pH between the treatments at different time intervals of crop period. The results are given in table 16. The soil alone treatment recorded significantly lower values at all the time intervals studied. In case of butachlor+soil treatment, the pH remained almost same from one day to fourth week after herbicide application. In pretilachlor +soil treatment, there was a drastic increase of pH from 5.3 to 5.7 after one week. At two week after application, there was a decrease in pH to 5.5 and after four week of application,

Table 15 pH in soil samples under different organic carbon sources and moisture levels in incubation experiment

Herbicide	Moisture level	pH		
		Sources of organic carbon		
		Soil alone	Farmyard manure	Vermicompost
Butachlor	Air dry	5.1	5.6	5.2
	Field capacity	5.0	5.8	5.7
Pretilachlor	Air dry	5.3	5.9	5.4
	Field capacity	5.0	5.9	5.7

CD $_{(0.05)}$ = 0.26

Table 16 pH at different days after herbicide application (DAHA) in the pot culture experiment

Treatments	pH			
	1 DAHA	7 DAHA	14 DAHA	28 DAHA
Butachlor +soil	5.4	5.4	5.4	5.3
Butachlor+fym	5.8	6.0	5.9	5.9
Butachlor+vermicompost	5.9	5.9	5.8	5.6
Pretilachlor+soil	5.3	5.7	5.5	5.2
Pretilachlor+fym	5.8	5.9	5.8	5.9
Pretilachlor+vermicompost	5.5	5.8	5.7	5.8
$CD_{(0.05)}$	0.23	0.17	0.20	0.17

the pH again decreased to 5.2. In farmyard manure treatment, there was no significant change in pH in case of both butachlor and pretilachlor application. The pH was in a range of 5.8 to 6.0 in all time intervals. In case of vermicompost treatment, the pH remained stable upto one week (5.9), and then decreased to 5.6 after four week for butachlor. For pretilachlor, an increase in pH (5.8) was noticed after one week which decreased to 5.7 after two week and again increased to 5.8 after four week. The highest pH was recorded in farmyard manure treatment for butachlor and pretilachlor application at all the time intervals, except at one day after application for the treatment butachlor+vermicompost.

4.8 Effect of organic carbon sources and moisture levels on Electrical conductivity

a) Incubation experiment:

The influence of moisture levels and organic carbon sources on the electrical conductivity is shown in the table 17. Farmyard manure treated soil recorded higher EC and the values were more under field capacity as compared to air dry conditions. The lowest values were recorded by soil alone treatment. However, the effect of moisture on EC was the same as that of FYM treatment. In the case of vermicompost treatment, the samples shown higher values under air dry condition and the trend was different from that of soil alone and FYM treatment. In case of soil alone, EC for air dry soil was 0.03 dS m^{-1} (butachlor) and 0.02 dS m^{-1} (pretilachlor) and for field capacity soil, it was 0.07 dS m^{-1} (butachlor) and 0.08 dS m^{-1} (pretilachlor). In case of farmyard manure treatment, EC for air dry soil was 0.38 dS m^{-1} and 0.37 dS m^{-1} for soils taken for butachlor and pretilachlor applications respectively and for field capacity soil; it was 0.42 dS m^{-1} (butachlor) and 0.47 dS m^{-1} (pretilachlor). In the case of vermicompost, the EC was 0.41 dS m^{-1} and 0.37 dS m^{-1} for air dry soil and 0.20 dS m^{-1} and 0.27 dS m^{-1} for field capacity in case of soil samples taken for butachlor and pretilachlor applications respectively.

Table 17 Electrical conductivity in soil samples under different organic carbon sources and moisture levels in incubation experiment

Herbicide	Moisture level	Electrical conductivity (dS m^{-1})		
		Sources of organic carbon		
		Soil alone	Farmyard manure	Vermicompost
Butachlor	Air dry	0.03	0.38	0.41
	Field capacity	0.07	0.42	0.20
Pretilachlor	Air dry	0.02	0.37	0.37
	Field capacity	0.08^{d}	0.47	0.27

CD $_{(0.05)}$ =0.08

Table 18 Electrical conductivity at different days after herbicide application (DAHA) in the pot culture experiment

Treatments	Electrical conductivity (dS m^{-1})			
	1 DAHA	7 DAHA	14 DAHA	28 DAHA
Butachlor + soil	0.32	0.19	0.14	0.10
Butachlor + FYM	0.60	0.16	0.12	0.10
Butachlor + vermicompost	0.17	0.08	0.10	0.08
Pretilachlor + soil	0.16	0.13	0.08	0.07
Pretilachlor + FYM	0.25	0.13	0.13	0.07
Pretilachlor + vermicompost	0.29	0.07	0.18	0.08
$CD_{(0.05)}$	0.16	0.06	0.08	NS

b) Pot culture experiment:

The changes in electrical conductivity at different intervals were recorded and the results are given in table 18. At one day, electrical conductivity was very low in butachlor + vermicompost (0.17 dS m^{-1}) and pretilachlor+soil (0.16 dSm^{-1}) treatments. Electrical conductivity was high in butachlor+ farmyard manure treatment (0.60 dS m^{-1}). In case of pretilachlor, electrical conductivity was highest for vermicompost treatment (0.29 dS m^{-1}) and lowest for control (soil alone) (0.16 dS m^{-1}). At one week, the data on electrical conductivity showed lower values in all the treatments. There was a reduction of electrical conductivity in farmyard manure applied soil for butachlor (0.16 dS m^{-1}) and vermicompost applied soil for pretilachlor (0.07 dS m^{-1}). Electrical conductivity was more in soil alone (0.19 dS m^{-1}) for butachlor and it was high in soil alone as well as farmyard manure (0.13 dS m^{-1}) for pretilachlor treatment. Electrical conductivity values were low in vermicompost applied soil, 0.08 dS m^{-1} and 0.07 dS m^{-1} respectively for butachlor and pretilachlor herbicides. After two weeks, the electrical conductivity again decreased in all treatments except for the two vermicompost treatments. Electrical conductivity recorded high value for soil alone in case of butachlor (0.14 dS m^{-1}) and was highest for vermicompost in case of pretilachlor (0.18 dS m^{-1}). After four weeks, the electrical conductivity data showed a decreasing trend in all the treatments and the difference between treatments was not significant. The electrical conductivity of soil alone was 0.10 dS m^{-1} and 0.07 dS m^{-1} respectively for butachlor and pretilachlor. The electrical conductivity of farmyard manure applied soils was 0.10 dS m^{-1} and 0.07 dS m^{-1}. The electrical conductivity of vermicompost applied soils were 0.08 dS m^{-1} for both butachlor and pretilachlor herbicides.

4.9 Biometric observations

Biometric observations such as plant height, number of plants, productive tillers, grain yield and straw yield were recorded and are given in table 19. The plant height did not differ significantly between the treatments. The highest plant height was recorded for farmyard manure treatment and the lowest plant height recorded for soil alone. Productive tillers were more in farmyard manure treatment (21 No.). The straw yield and grain yield per pot were more for farmyard manure treatment. In this treatment, the straw yield was 26.94g for butachlor and 26.04 g for pretilachlor and the grain yield was 17.16 g for butachlor and 22.38 g for pretilachlor. The lowest grain yield was recorded by butachlor+vermicompost treatment and the same was a consequence of higher pest incidence (stem borer) in this particular treatment.

Table 19 Biometric observations from pot culture experiment

Treatments	Biometric characters			
	Plant height(cm)	Productive tillers (No.)	Grain yield/pot(g)	Straw yield/pot(g)
Butachlor+soil	98.33	17.00	15.52	17.76
Butachlor+FYM	104.33	21.00	17.16	26.94
Butachlor+vermicompost	99.00	15.00	9.12	21.68
Pretilachlor+soil	94.67	18.00	15.95	15.45
Pretilachlor+FYM	99.67	18.00	22.38	26.04
Pretilachlor+vermicompost	100.33	12.00	22.35	22.60
$CD_{(0.05)}$	20.22	13.10	19.25	13.73

Discussion

5. DISCUSSION

The findings of each experiment are discussed in sections 5.3 to 5.8. Discussion on the physicochemical characters of the soil under study and the standardization procedure for estimation of dissolved organic carbon is given in sections 5.1 and 5.2

5.1 Physicochemical characteristics of soil

The soil sample collected for the study was characterized by high sand content and hence classified under sandy loam texture. The soil comes under the Ultisol order, the major characteristics of which are low pH and low CEC (4.7 and 4.67 C mol (+) kg^{-1} respectively). Organic carbon content was in the medium range (0.61 %) only and hence the addition of organic matter to the soil would have a profound influence on the adsorption of chloroacetanilide herbicides.

5.2 Dissolved organic carbon content in soil and manure samples used for the study

The mean dissolved organic carbon content on oven dry basis was more in vermicompost than farmyard manure. Vermicompost contained 2636.45 $\mu g\ g^{-1}$ dissolved organic carbon and farmyard manure contained 737.51 $\mu g\ g^{-1}$ dissolved organic carbon. Wide variation in the DOC between vermicompost and FYM samples was due to the difference in their moisture content. Moisture content of vermicompost was 127.01% and that of FYM was 11.56%. Air dried samples recorded DOC values of 525.57 $\mu g\ g^{-1}$ and 425.23 $\mu g\ g^{-1}$ for vermicompost and FYM respectively. In the experiments conducted, only the air dried manure samples were taken.

Dissolved organic carbon constituted 6.00 % (oven dry) / 5.98 % (air dry) of the soil organic carbon, 0.73 % (oven dry) / 0.45 % (air dry) of FYM and 1.30 % (oven dry) / 0.66 % (air dry) of vermicompost.

5.3 Adsorption of herbicides

The degree of adsorption of herbicides under the influence of different organic carbon sources was evaluated in the incubation as well as pot culture study.

a) Incubation study:

In the incubation experiment, the degree of adsorption of butachlor and pretilachlor was evaluated using the K_d (distribution coefficient) values. The K_d values followed the order of organic carbon content of soils. Several studies had shown the importance of organic carbon on pesticide sorption in soils (Hamaker and Thompson, 1972; Karickhoff *et al.*, 1979). The K_d values were higher for pretilachlor with the order being FYM (2.33 % at air dry and 2.14 % at field capacity conditions) > vermicompost (1.97 % at air dry and field capacity conditions) > soil (1.97 % at air dry and 1.64 % at field capacity conditions). Only slight variations were observed between air dry and field capacity levels. For butachlor also higher K_d values were recorded in the FYM treatment (1.13 % at air dry and 1.17 % at field capacity conditions) which was followed by soil (0.99 % at air dry and 1.08 % at field capacity conditions) and vermicompost (1.08 % at air dry and 0.99 % at field capacity conditions) treatments. The lower K_d values for butachlor compared to pretilachlor had been reported earlier (Moon and Kim, 2000).

The efficiency of exogenous and endogenous soil organic carbon to adsorb butachlor and pretilachlor could be compared by normalizing the K_d adsorption coefficient for the organic carbon content (K_{oc}) and the values are given in table

20. Although the K_d values of herbicides increased with increasing carbon, the K_{oc} values decreased with increasing carbon addition. Higher K_{oc} values for butachlor and pretilachlor in the soil alone treatment suggested the higher efficiency of endogenous organic carbon to adsorb the herbicide. It has been reported that the increase in sorption of chemicals per unit carbon addition, increased with a decrease in the endogenous carbon content of the soil materials (Baskaran *et al.*, 1996). The results indicated that the percentage increase in sorption per unit carbon addition decreased with increasing rate of exogenous carbon addition. As in the case of K_d, K_{oc} values were also higher for pretilachlor indicating the higher degree of adsorption to the soil organic matter.

Moisture levels had no significant influence on the K_d or K_{oc} values. This could be explained by hydrophobic character of the herbicides under study, the molecules of which have non polar regions and they are likely to adsorb on to the hydrophobic regions of soil organic matter. Water molecules present in the system will not compete with non polar molecules for adsorption on hydrophobic surfaces. This also explains the relative independence of pesticide adsorption on moisture in soils with good amount of organic carbon (Pierce *et al.*, 1971).

Significant differences in the degree of adsorption between the two herbicides tested were attributed to the differences in their rate of application (2.00 $\mu g\ g^{-1}$ for butachlor and 0.60 $\mu g\ g^{-1}$ for pretilachlor).

Relationship between adsorption and selected soil properties:

No significant relationship was observed between the herbicide adsorption and soil parameters like DOC, organic carbon, pH and EC (Table 21). However, significant positive relationship was observed between pH and organic carbon. This could be attributed to the high pH of FYM and vermicompost used for the study. It may also be partly explained by proton exchange between the soil and added FYM which contains some phenolic, humic-like material (Tang *et al.*,

Table 20 Soil organic carbon partition coefficient (K_{oc}) of butachlor and pretilachlor under different organic carbon sources and moisture levels

Herbicides	Moisture levels	K_{oc} (%)		
		Sources of organic carbon		
		Soil alone	FYM	Vermicompost
Butachlor	Air dry	181.81	60.11	101.89
	Field capacity	154.29	77.12	80.00
Pretilachlor	Air dry	263.16	129.44	160.00
	Field capacity	265.08	84.79	172.41

Table 21 Correlation between quantity of herbicide adsorbed, DOC, organic carbon, pH and EC in incubation experiment

Parameters	Karl Pearson coefficient				
	Quantity of herbicide adsorbed	DOC	Organic carbon	pH	EC
Quantity of herbicide adsorbed	1.00	0.28	0.07	-0.08	0.15
DOC	0.28	1.00	0.26	0.33	0.16
Organic carbon	0.07	0.26	1.00	0.79**	0.77**
pH	-0.08	0.33	0.79**	1.00	0.66**
EC	0.15	0.16	0.77**	0.66**	1.00

** Correlation is significant at the 0.01 level

2007). Another mechanism that has been proposed to explain the increase in pH by such materials as FYM is the specific adsorption of humic material and /or organic acids (the products of decomposition of organic materials) onto hydrous surfaces of Al and Fe oxides by ligand exchange with corresponding release of OH^- as suggested by Hue *et al.* (1986).

The increase in the pH of the soil due to the organic carbon addition which followed the order: FYM (6.6) > vermicompost (5.7) > soil (4.7). The electrical conductivity in the soil was also high in proportion to the organic carbon content in the order: FYM > vermicompost > soil. The major reason for the higher EC in the FYM and vermicompost would be the release of various soluble forms of ions from these materials during the incubation period.

The incubation study made it clear that butachlor and pretilachlor are strongly adsorbed to laterite soil containing good amount of organic carbon.

b) Pot culture experiment:

In this experiment, the adsorption as well as dissipation pattern of butachlor and pretilachlor were evaluated under different organic carbon sources *viz.*, FYM, vermicompost and soil.

Results indicated that there was variation in the quantity of herbicides adsorbed by soil in the different treatments. Significant differences were observed between the herbicides as well as the organic matter sources. The major reason for the higher concentration of butachlor compared to pretilachlor in the soil at one day after application is the differences in their rate of application (butachlor @ 1.25 kg ha^{-1} and pretilachlor @ 0.45 kg ha^{-1}).

Adsorption of butachlor as well as pretilachlor was highest in vermicompost (Fig.5.). Pretilachlor with farmyard manure treatment recorded

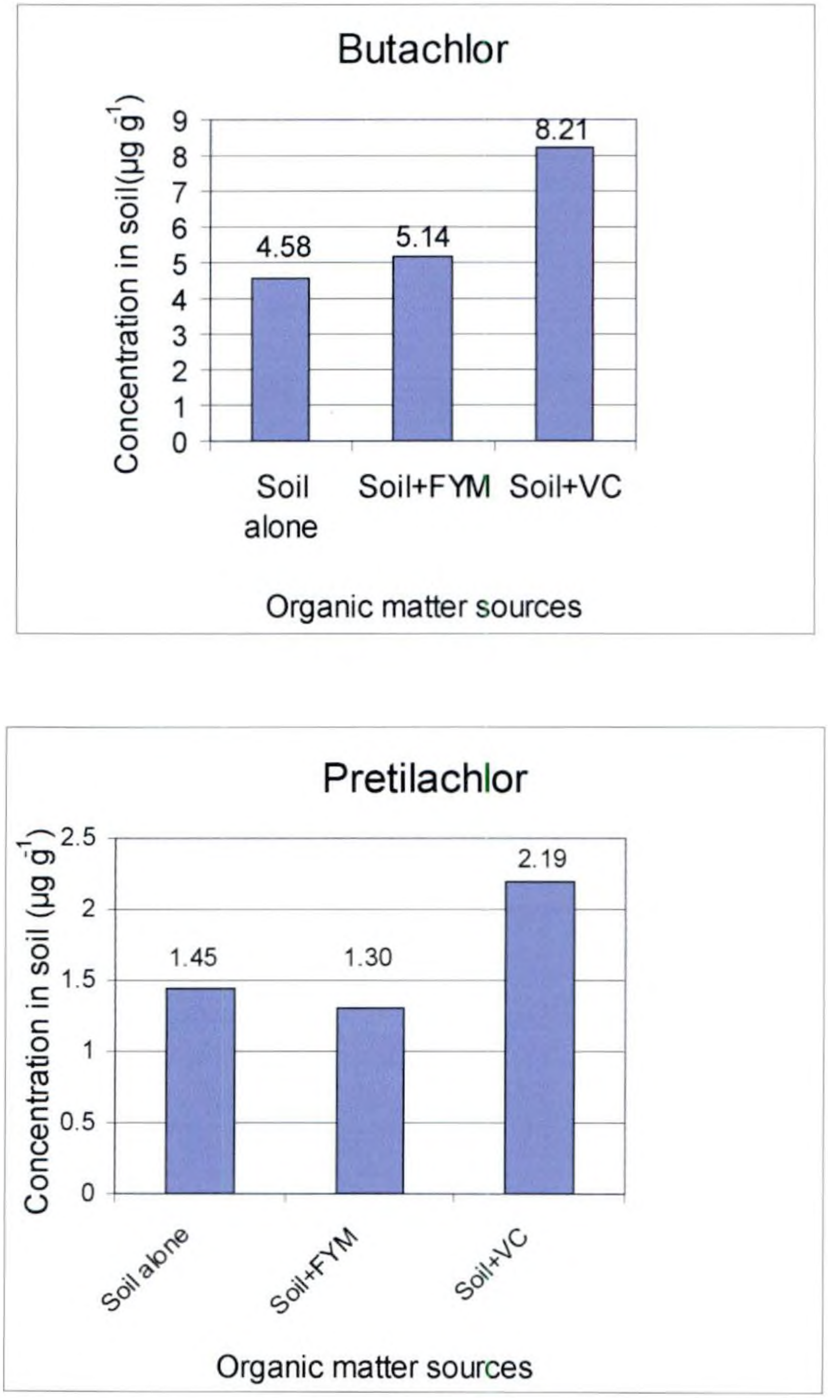
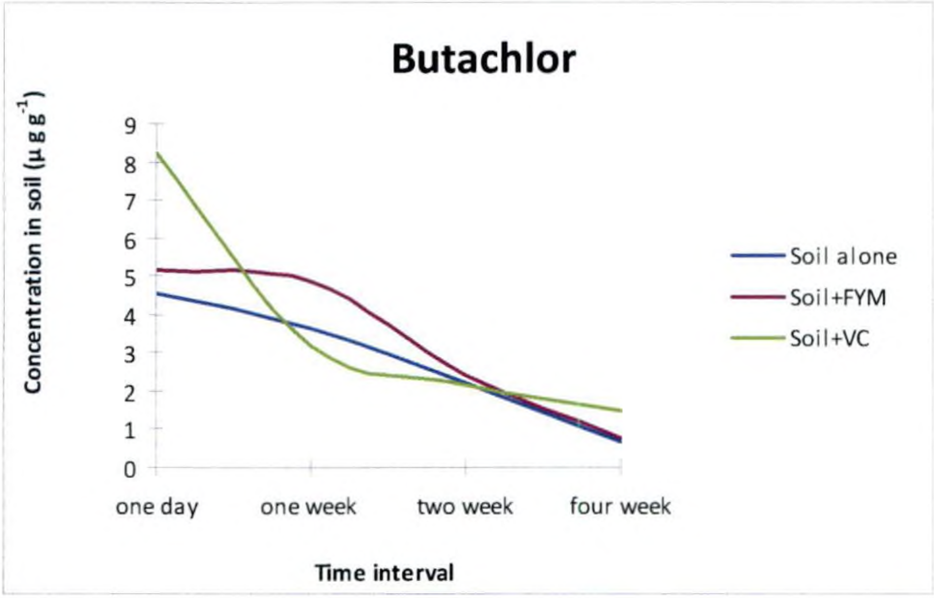


Fig. 5 Concentration of butachlor and pretilachlor by the soil at one day after herbicide application

lower herbicide content in the soil samples compared to that of soil alone treatment which could be explained by comparatively higher DOC in this treatment. A number of investigators (Lee and Farmer, 1989; Kan and Tomson, 1990; Logan *et al.*, 1992; Liu and Amy, 1993) have found that the interaction of pesticides with DOC increases the apparent solubility of these chemicals and thereby results in an increase in the mobility of the chemicals in soils. Butachlor + FYM treatment also recorded higher DOC than that of vermicompost which resulted in lesser adsorption of the chemical onto the soil matrix than that in the vermicompost treatment. Since FYM is in the early stage of mineralization compared to vermicompost and soil material, it had released more DOC to the soil solution which would have increased the apparent solubility of this chemical and thereby resulted in an increase in the movement of chemical in soil. Water solubility (20 and 50 mg L^{-1} for butachlor and pretilachlor respectively) of pretilachlor is higher than that of butachlor which would have resulted in the increased mobility and downward movement of this chemical along with DOC. This effect was not noticed in the incubation study, which may be due to the narrow moisture levels used for the study (Gupta and Gajbhiye, 2004). The soil was under submergence in the pot culture study which would have given a chance for movement of herbicide along with DOC.

Percentage dissipation of butachlor and pretilachlor by day one, seven, fourteen and twenty eight as well as immediately after harvest in the different treatments was investigated. Butachlor as well as pretilachlor with FYM treatment dissipated slowly compared to the soil alone and vermicompost (percent dissipation being 5.45 and 11.77 % between one day and one week for butachlor and pretilachlor respectively and 52.91 and 45.81% between one day and two week for butachlor and pretilachlor respectively). The percentage dissipation of herbicide at different time intervals is given in table 22. The differences in the percent dissipation of butachlor and pretilachlor in the different treatments at four weeks after application was not significant (Fig.6). However, it was noticed that



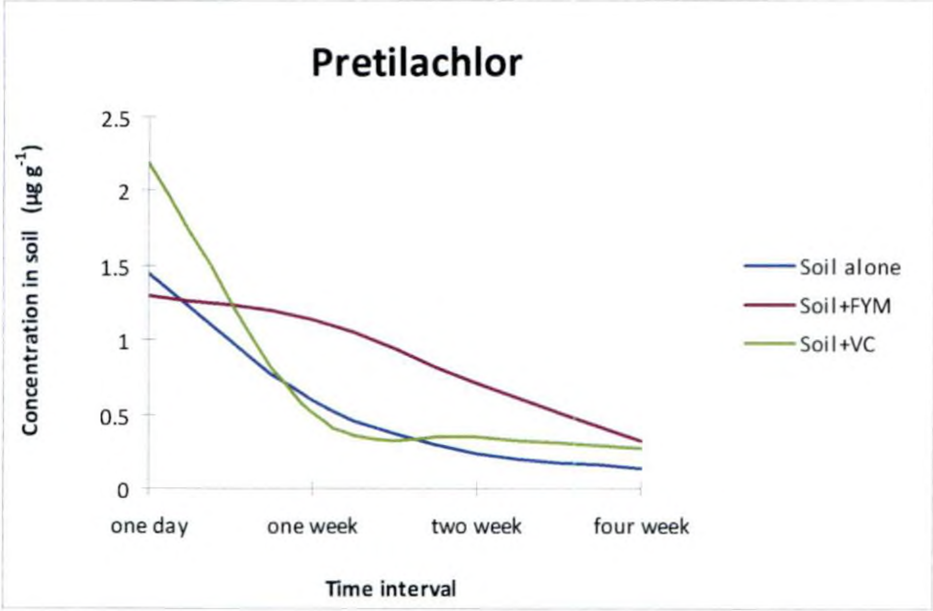


Fig.6 Concentration of butachlor and pretilachlor in soil, soil + FYM, soil + vermicompost at different periods after herbicide application

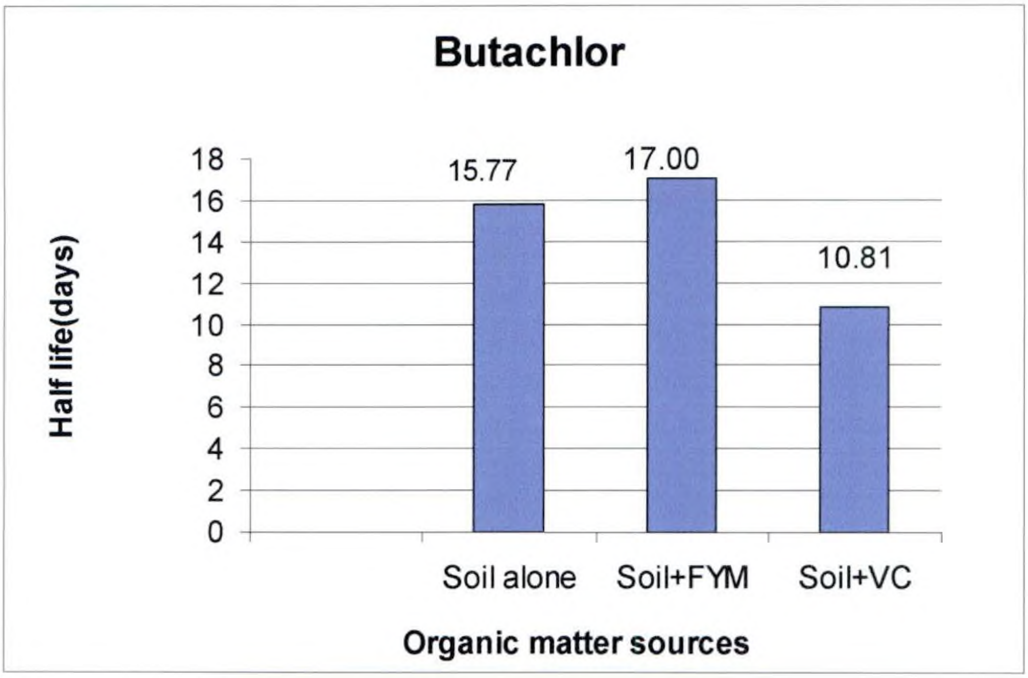
Table 22 Dissipation of the herbicides at different periods after application

Treatments	Percent dissipation of herbicides (with respect to one day after herbicide application)			
	7 DAHA	14 DAHA	28 DAHA	100 DAHA
Butachlor +soil	21.24	65.47	83.15	96.07
Butachlor +FYM	5.45	52.91	83.32	96.69
Butachlor+vermicompost	61.61	73.13	81.72	97.69
Pretilachlor+soil	54.90	80.58	89.48	88.28
Pretilachlor+FYM	11.77	45.81	75.25	79.23
Pretilachlor+vermicompost	76.65	83.99	87.78	90.41
$CD_{(0.05)}$	10.30	23.71	22.41	15.06

pretilachlor dissipation was faster compared to butachlor at all sampling intervals except in 4th week after herbicide application.

Dissipation data for butachlor and pretilachlor under different organic matter treatments upto four weeks after herbicide application fitted well to linear regression equations of the form –ax+b (Table 23). The dissipation data obtained at the time of harvest was not considered for the study, because of its wide interval and the data did not follow linear regression equation.

The half lives of herbicides under different treatments were worked out from the linear regression equations. Persistence of butachlor and pretilachlor in terms of half life was highest under FYM treatment (Fig.7). It indicated the superiority of FYM in the retention of herbicide molecules. Significant variation in the DOC content between the organic manure treatments was seen only at one day after application of herbicides and particularly for butachlor. However, total organic carbon content upto four weeks after application varied between treatments as FYM recorded higher value compared to vermicompost and soil. This would have facilitated improved persistence of the chemical. It has been reported that continuous mineralization of soluble organic compounds in the FYM leads to repolymerisation and condensation which results in the synthesis of humic like substances that have a lower solubility in water. At this stage, the concentration of carbon in the hydrophobic fraction (HODOM) will be equal to or greater than hydrophilic fraction (HIDOM). For non polar herbicides like butachlor and pretilachlor, organic matter is the most important sorbent surface in soil and hence hydrophobic interactions are the driving force (Hamaker and Thompson, 1972).



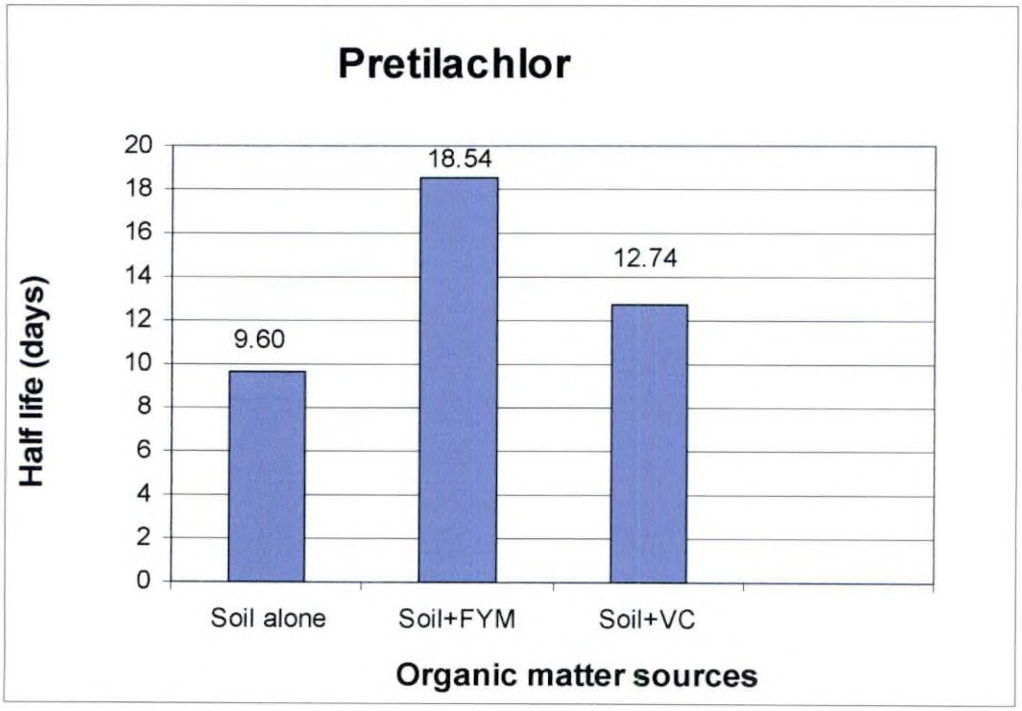
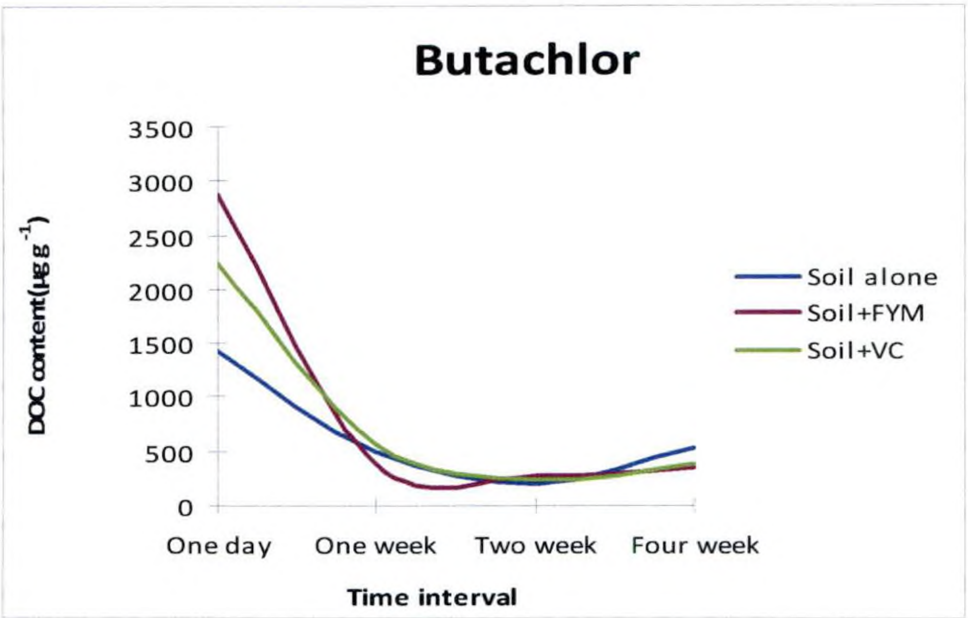


Fig.7 Half life of butachlor and pretilachlor in different treatments



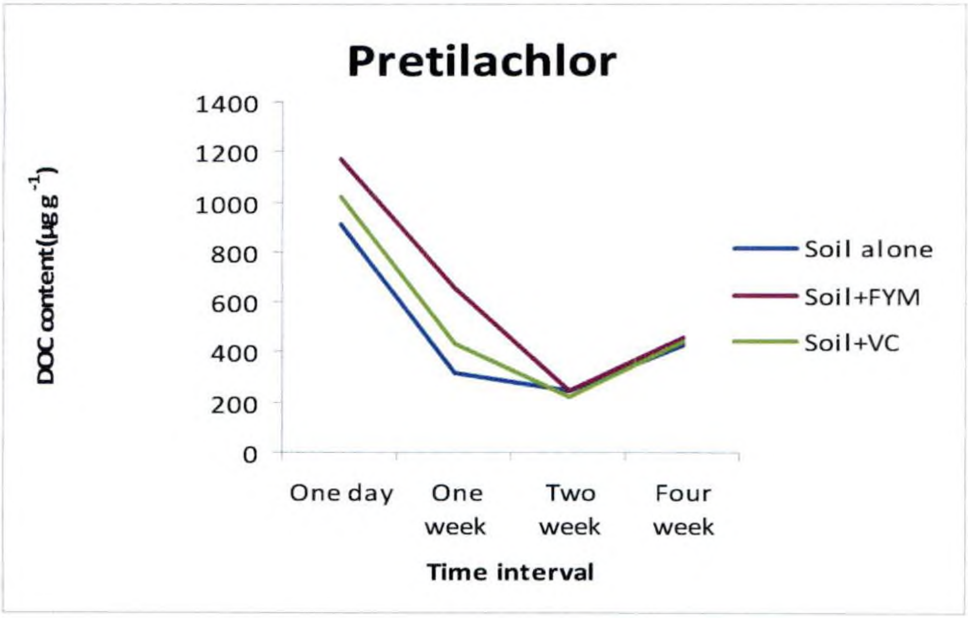
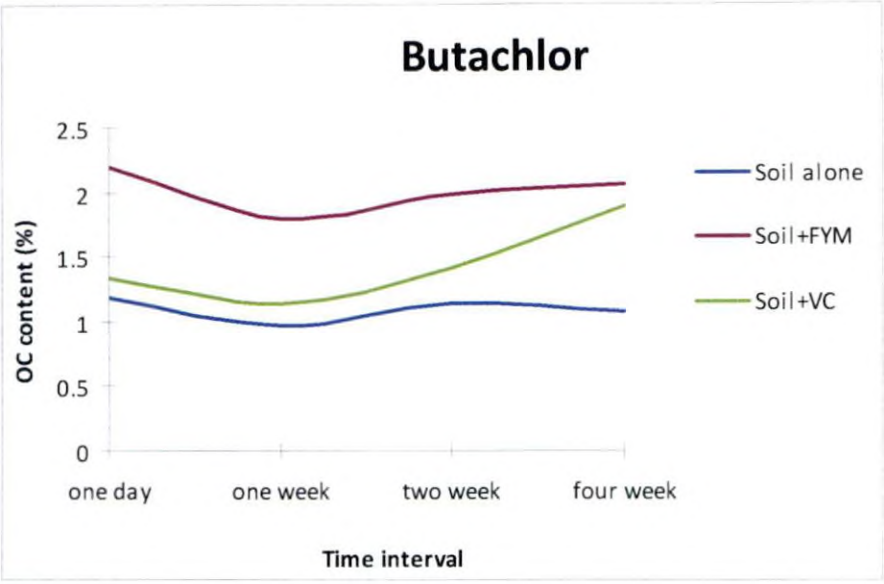


Fig.8 Changes in dissolved organic carbon content in soil at different intervals after herbicide application



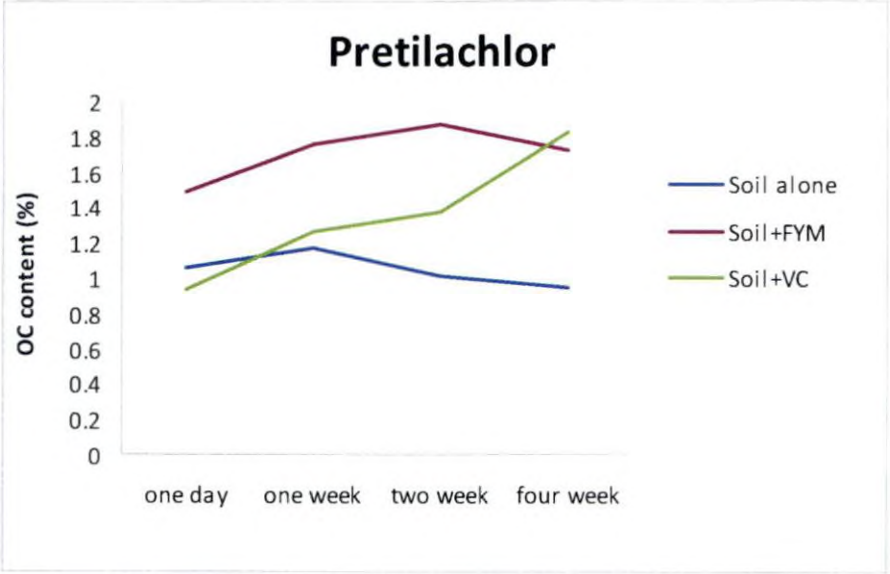


Fig.9 Changes in organic carbon content in soil at different intervals after herbicide application

Table 23 Linear regression equation and half life of butachlor and pretilachlor in different treatments

Treatments	R square	Linear equation	Half life
Butachlor +soil	0.99	2.29=4.577-0.145d	15.77
Butachlor+FYM	0.844	2.57=5.426-0.168d	17.00
Butachlor+vermicompost	0.559	4.11=6.381-0.210d	10.81
Pretilachlor+soil	0.471	0.73=1.143-.043d	9.60
Pretilachlor+FYM	0.551	0.65=1.336-0.037d	19.00
Pretilachlor +vermicompost	0.374	1.10=1.543-0.057d	12.74

5.4 Changes in the dissolved organic carbon and organic carbon content at different intervals

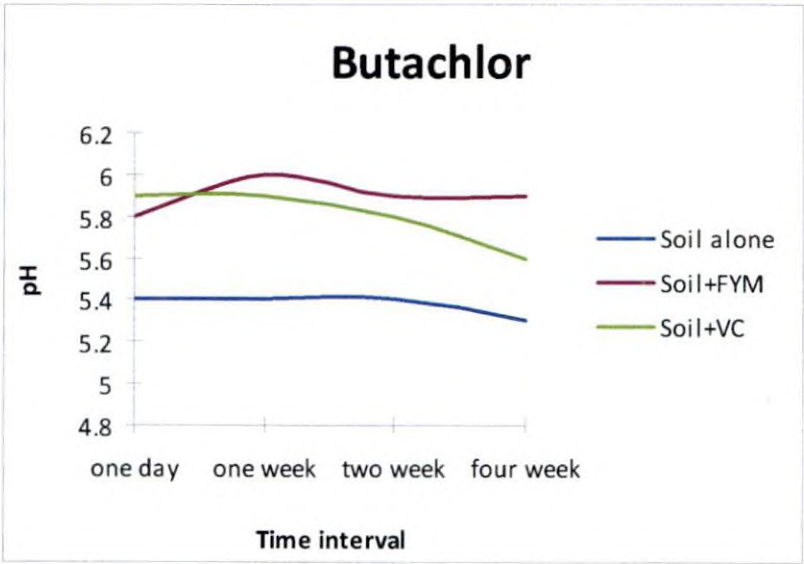
Variations in the DOC and OC content between treatments and between time intervals are depicted in fig.8 and fig.9

The DOC content was more in FYM at one day after application of herbicides. The percentage change in DOC during 1-7 days period vary significantly between treatments. Though the percentage change was more in the FYM treatment. The percentage change of DOC with respect to one day after herbicide application (Table 24) was more in the FYM treatment, but treatment differences were not noticed after two weeks. This is because of initial mineralization of complex molecules of FYM and release of DOC. It means that after two week (3 weeks after application of manures), mineralization would have been completed and resulted in no significant differences in DOC between treatments.

The organic carbon content in soil was comparatively low in vermicompost added treatments than that of FYM, mainly because of the lower organic carbon content of the vermicompost taken for experiments. The percentage change in organic carbon content (45.39 and 136.76 % for butachlor and pretilachlor respectively) between one day and four week was more in vermicompost compared to other treatments (Table 25).

5.5 pH and electrical conductivity changes at different time intervals

The effect of organic manure sources *viz.*, FYM and vermicompost on the pH and EC of the soil samples under different treatments were studied over the period from one day to fourth week after herbicide application.



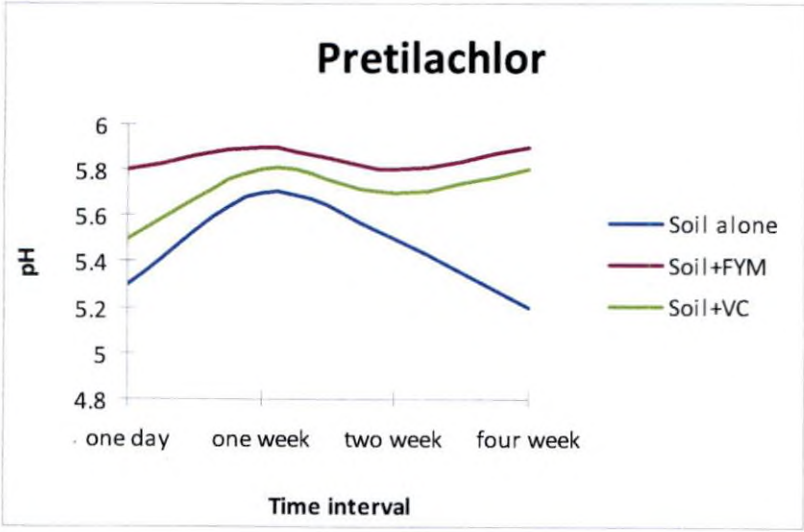


Fig.10 Changes in pH of soil at different intervals after herbicide application

Table 24 Percentage change in dissolved organic carbon content with respect to one day after application

Treatments	Change in dissolved organic carbon content (%)		
	7 DAHA	14 DAHA	28 DAHA
Butachlor +soil	-65.95	-85.70	-63.40
Butachlor +FYM	-86.69	-91.20	-87.01
Butachlor+vermicompost	-74.72	-89.14	-82.43
Pretilachlor+soil	-63.51	-75.68	-51.17
Pretilachlor+FYM	-41.35	-78.82	-59.83
Pretilachlor+vermicompost	-57.55	-79.68	-56.13
$CD_{(0.05)}$	24.67	42.58	26.55

Table 25 Percentage change in organic carbon content with respect to one day after application

Treatments	Change in organic carbon content (%)		
	7 DAHA	14 DAHA	28 DAHA
Butachlor +soil	-17.72	-3.04	-8.05
Butachlor +FYM	-17.57	-8.97	5.52
Butachlor+vermicompost	-11.85	16.48	45.39
Pretilachlor+soil	9.45	23.86	-6.4
Pretilachlor+FYM	5.16	28.54	18.32
Pretilachlor+vermicompost	71.76	78.15	136.76
$CD_{(0.05)}$	87.70	49.25	35.03

Addition of FYM and vermicompost had significant effect on soil pH. Butachlor and pretilachlor application with FYM gave highest soil pH (Fig.10) and the trend was maintained at all the sampling intervals studied. The observed increase in pH due to the application of manures was consistent with the results obtained in the incubation experiment, the reasons of which are detailed in section 5.3.

In the pot culture study significant correlations were obtained between pH and organic carbon at one week, two weeks, as well as four weeks after application of herbicides. However, significant effect of DOC on pH was obtained only at one day after application of herbicides. No significant correlation was obtained between the herbicide content and pH, mainly because of the non-ionic nature of herbicides under study. Butachlor and pretilachlor do not ionize significantly in aqueous or soil system and hence pH of the system may not be an important factor in their adsorption.

Electrical conductivity also had no significant effect on adsorption. The electrical conductivity of organic manure treated pots were higher when compared to soil alone treatment. This may be due to more water soluble salts present in organic manures.

5.6 Effect of moisture

The effect of moisture on DOC content was also not significant except for butachlor+vermicompost treatment. It has been reported that 22-67 fold increase in moisture content resulted in 6-19 fold decrease in the DOM concentration. The variation in the DOM concentration with moisture content can be caused by either dilution if DOM behaves as a soluble non sorbing organic substance or by desorption if the DOM is adsorbed on the surface of soil particles (Ponizovsky *et al.*, 2006). In the present study the difference in the moisture content between air dry and field capacity condition was only 8.3 fold. Lack of correlation between moisture content and DOC was due to the narrow range of moisture variations taken for the study.

Dissolved organic carbon (DOC) is a highly variable parameter. It depends on many factors because FYM and vermicompost contain more of non resistant fraction of organic matter where as soil contain humus which is the resistant fraction.

In general, moisture had no significant effect on organic carbon content. Farmyard manure, both in air dry and field capacity level recorded high organic carbon compared to other treatments. It is shown in fig.11.

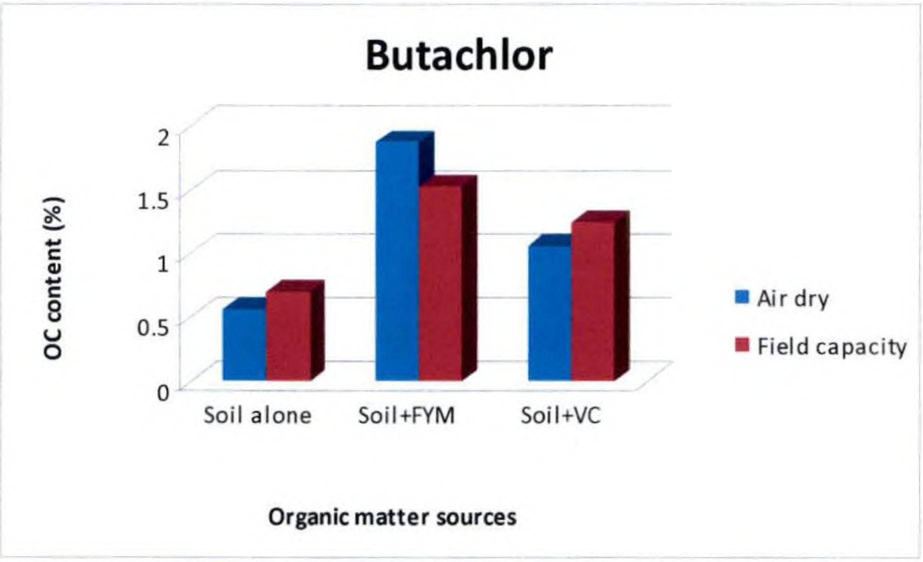
Moisture had significant impact on pH (Fig.12) and EC (Fig. 13) particularly in vermicompost treatments. The EC of vermicompost treatment at field capacity level was lower than that of air dry soil. The higher values of EC registered by organic manure added soil was due to high content of soluble substances in FYM and vermicompost.

5.7 Relationship between soil characteristics and extent of adsorption

The correlation coefficients(r) between herbicide content, DOC, OC and pH are given in table 26.

At one day, significant correlation was found between herbicide concentrations and dissolved organic carbon content, organic carbon and dissolved organic carbon, dissolved organic carbon and pH. At four weeks, only one relationship was found significant *i.e.* between organic carbon and herbicide adsorption, which indicated that persistence is determined by total organic carbon where as initial adsorption is mainly influenced by dissolved organic carbon.

At one week, two weeks and four weeks intervals, significant inter correlation was found between organic carbon and pH. This kind of relationship



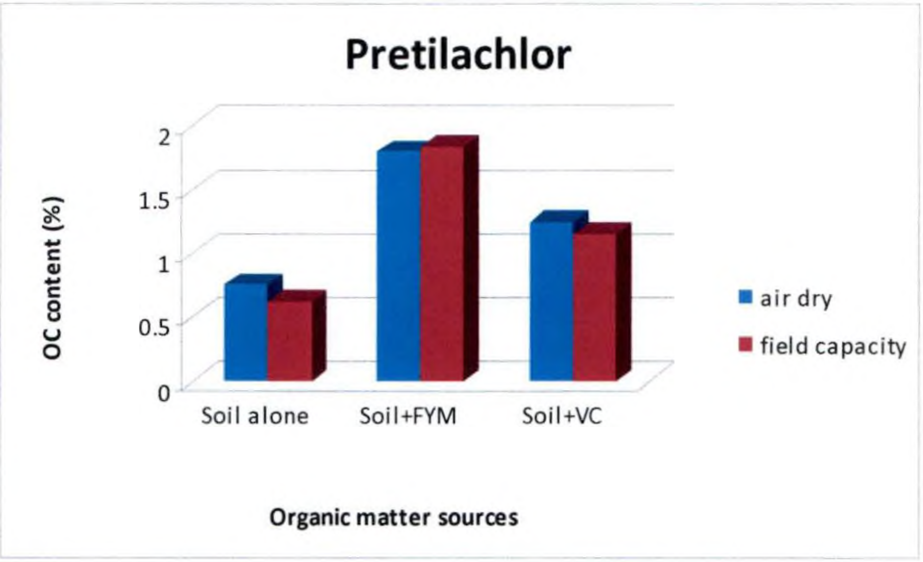
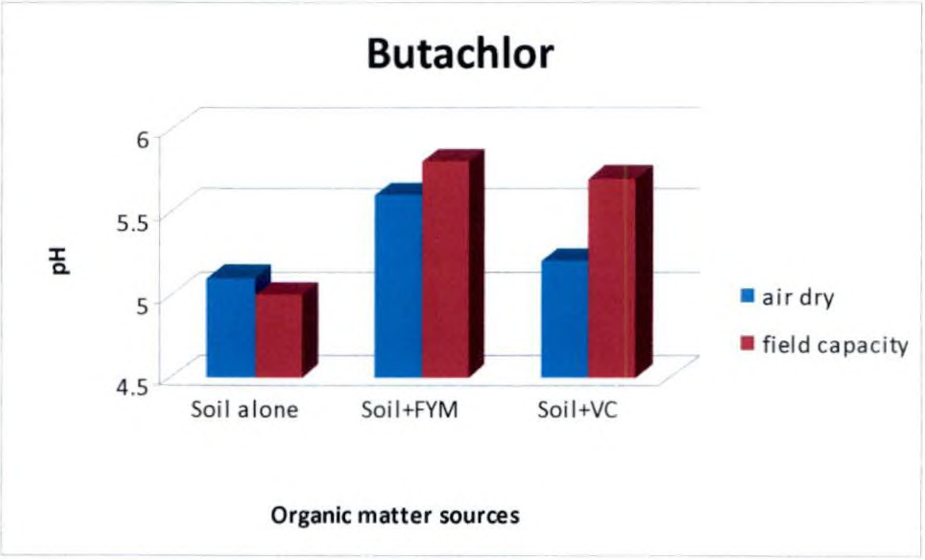


Fig.11 Effect of soil moisture and organic carbon sources on organic carbon content in soil



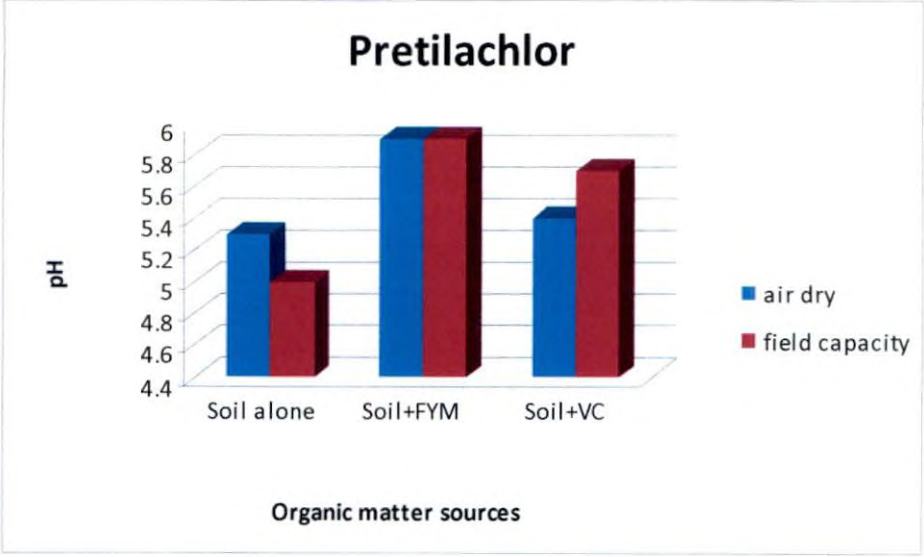


Fig.12 Effect of soil moisture and organic carbon sources on pH of soil

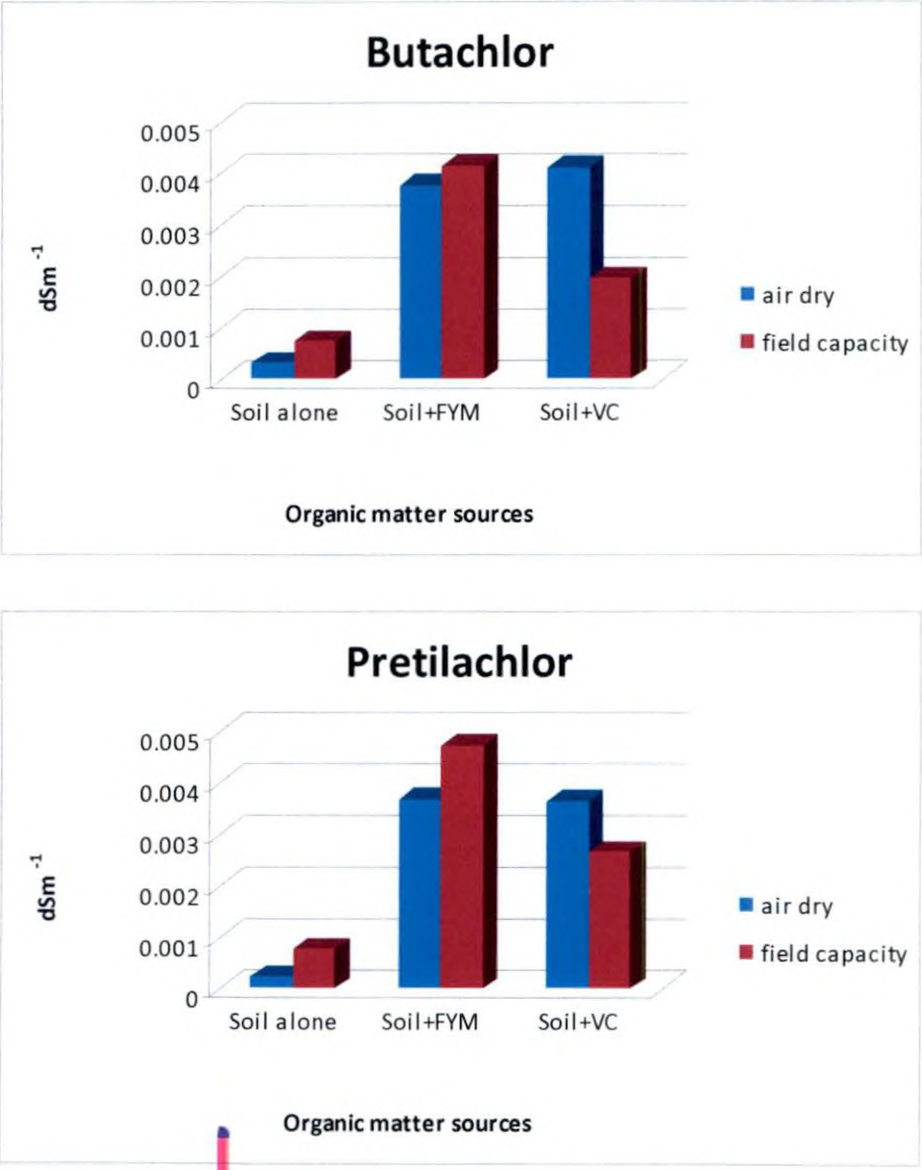


Fig.13 Effect of soil moisture and organic matter sources on electrical conductivity of soil

Table 26 Correlation coefficients(r) between herbicide adsorption, DOC, OC and pH

Parameters	Correlation coefficient			
	7 DAHA	14 DAHA	28 DAHA	100 DAHA
Adsorption and DOC	0.688**	0.019	0.169	-0.196
Adsorption and OC	0.262	0.156	0.255	0.558*
DOC and OC	0.666**	0.242	0.193	-0.326
DOC and pH	0.512*	0.002	0.092	-0.128
OC and pH	0.414	0.638**	0.640**	0.813**

** Correlation significant at the 0.01 level
* Correlation significant at the 0.05 level

was observed by many scientists (Whalen *et al.*, 2000 and Narambuye and Hayens, 2006)

5.8 Phytotoxicity

The extent of toxicity due to herbicide application was almost same with butachlor and pretilachlor. However, the magnitude of phytotoxicity was increased with organic manure application in the order, vermicompost>FYM>soil alone. The symptoms were seen even upto 21 days after herbicide application. In FYM treatment, plants started recovery by three weeks after herbicide application. Slightly higher percentage of phytotoxicity in the vermicompost treatment could be easily explained by the higher initial adsorption of herbicides in this treatment (Table 10).

Summary

6. SUMMARY

Investigations were carried out at College of Horticulture, Vellanikkara during 2010, to determine the effect of organic matter and soil moisture on the adsorption of chloroacetanilide herbicides *viz.*, butachlor and pretilachlor in laterite soil. The studies consisted of an incubation experiment and a pot culture with different sources of carbon *viz.*, farm yard manure (FYM), vermicompost and the soil as control. In the incubation experiment, influence of organic matter on the adsorption of herbicides was studied under two moisture levels *viz.*, air dry and field capacity. The magnitude of adsorption as well as dissipation pattern of herbicides in laterite soil under the influence of different organic matter sources were estimated in the pot culture experiment. Significance of dissolved organic carbon derived from the added organic matter on the adsorption of butachlor and pretilachlor was also examined. The salient findings are summarized below.

1) Butachlor and pretilachlor are strongly adsorbed onto laterite soil.

2) The addition of organic manures resulted in an increase in the adsorption of herbicides by the soil matrix. This is represented by the higher K_d values (distribution coefficient) of butachlor and pretilachlor in the manure added treatments compared with soil alone treatment.

3) The magnitude of adsorption varied with organic carbon content of applied manures. The highest value of organic carbon was obtained in the FYM treatment followed by vermicompost and soil alone. The pattern of adsorption also followed the same trend, FYM > vermicompost > soil.

4) Persistence of butachlor and pretilchlor expressed in terms of half life was also significantly higher in the FYM treatment (17.0 and 19.0 days for butachlor and pretilachlor respectively).

5) There was strong inverse relationship between the initial adsorption of the herbicides under study and DOC content of manures. However, total organic carbon was largely responsible for enhancing the period of retention of herbicides by soil which ultimately leads to improved bio-efficacy of pre emergence herbicides.

6) Though initial adsorption of the herbicides under study was higher in the manure added treatments, herbicide residue concentration in the soil at the time of harvest did not differ significantly. This could be attributed to the enhanced degradation of herbicides in the presence of organic matter.

7) On comparing the extent of adsorption of butachlor and pretilachlor it was found that pretilachlor was more tightly adsorbed by the soil organic matter. This was evidenced by the significantly higher K_d values for pretilachlor obtained in the incubation experiment. Percentage decline in the herbicide concentration observed in the pot culture study with respect to one day after herbicide application was also less for pretilachlor than for butachlor.

8) Moisture had no significant influence on the adsorption of butachlor and pretilachlor in the laterite soil, may be because of the non ionic character of the herbicides under study.

9) Dissolved organic carbon content did not differ significantly under the two moisture levels *viz.*, air dry and field capacity, may be because of the narrow range of moisture levels selected for study.

10) Results of the study provided an insight into the utility of manures for improving the bio-efficacy of pre emergence herbicides and for the removal of toxic residues.

References

7. REFERENCES

Altfelder, S., Streck, T. and Richter, J. 1999. Effect of air-drying on sorption kinetics of the herbicide chlortoluron in soil. *J. Environ. Qual.* 28(4): 1154-1161

Anderson, S. and Nilsson, S.T. 2001. Influence of pH and temperature on microbial activity, substrate availability of soil-solution bacteria and leaching of dissolved organic carbon in a mor humus. *Soil Biol. Biochem.* 33: 1181-1191

Baham, J. and Sposito, G. 1994. Adsorption of dissolved carbon extracted from sewage sludge on montmorillonite and kaolinite in the presence of metal ions. *J. Environ. Qual.* 23(1): 147-153

Bailey, G.W., White, J.L. and Rothberg, T. 1968. Adsorption of organic herbicides by montmorillonite: Role of pH and chemical character of adsorbate. *Soil Sci. Soc. Am. Proc.* 32: 222-234

Bailey, G.W. and White, J.L. 1970. Factors influencing adsorption, desorption and movement of pesticides in soil. *Residue Rev.* 32: 29-92

Barriuso, E. and Calvet, R. 1992. Soil type and herbicide adsorption. *Int. J. Environ. Analyt. Chem.* 46(1-3): 117-128

Barriuso, E., Baer, U. and Calvet, R. 1992. Dissolved organic matter and adsorption-desorption of dimefuron, atrazine and carbetamide by soils. *J. Environ. Qual.* 21: 359-367

Barton, D., Hope, D., Billet, M. F. and Cresser, M. S. 1994. Sulphate adsorption capacity and pH of upland podzolic soils in Scotland: Effects of parent material, texture and precipitation chemistry. *Appl. Geochem.* 9(2): 127-139.

Basham,G.W., Lavy, T.L., Oliver, L.R. and Scott, H.D. 1987. Imazaquin persistence and mobility in three Arkansas soils. *Weed Sci.* 35: 576-582

Baskaran, S., Bolan, N.S., Rahman, A. and Tillman, R.W. 1996. Effect of exogenous carbon on the sorption and movement of atrazine and 2,4-D by soils. *Aust. J. Soil Res.* 34: 609-622

Beckie, H.J. and McKercher, R.B. 1990. Mobility of two sulfonylurea herbicides in soil. *J. Agric. Food. Chem.* 38: 310-315

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

Boivin, A., Amellal, S., Schiavon, M. and Genuchten, M.T. 2005. 2,4-Dichlorophenoxyacetic acid (2,4-D) sorption and degradation dynamics in three agricultural soils. *Environ. Pollut.* 138(1): 92-99

Bower, C.A., Reitemeir, R.F. and Fireman, M. 1952. Exchangeable cation analysis of saline and alkali soils. *Soil Sci.* 73: 251-261

Calvet, R. 1980. Adsorption-desorption phenomena. In: Hance R.J. (ed.) *Interactions between Herbicides and Soil.* Academic Press, London, pp.83-122

Celis, R., Barriuso, E. and Houot, S. 1998. Sorption and desorption of atrazine by sludge amended soil: Dissolved organic matter effects. *J. Environ. Qual.* 27(6): 1348-1356

Chiou, C.T., Porter, P.E. and Schmedding, D.W. 1983. Partition equilibria of non ionic organic compounds between soil organic matter and water. *Environ. Sci. Technol.* 17: 227-231

Chiou, C.T., Shoup, T.D. and Porter, P.E. 1985. Mechanistic roles of soil humus and minerals in the sorption of non ionic organic compounds from aqueous and organic solutions. *Org. Geochem.* 8: 9-14

Chiou, C.T., Malcom, R.L., Brinton, T.I. and Kile, D.E. 1986. Water solubility enhancement of some organic pollutants and pesticides by dissolved humic and fulvic acids. *Environ. Sci. Technol.* 20: 502-508

Chopra, S.L. and Kanwar, J.S. 1976. *Analytical Agricultural Chemistry*. Kalyani Publishers, New Delhi, 518p.

Christ, M.J. and David, M.B. 1996. Temperature and moisture effects on the production of dissolved organic carbon in a spodosol. *Soil Biol. Biochem.* 28(9): 1191-1199

Cochran, G.W. and Cox, G.M. 1992. *Experimental Designs*, (2nd Ed.), John Wiley and Sons(ASIA) (P) Ltd., Singapore, 611p.

Cook, B.D. and Allan, D. L. 1992. Dissolved organic carbon in old field soils: Compositional changes during the biodegradation of soil organic matter. *Soil Biol. Biochem.* 36: 2097-2100.

Cronan, C.S., Lakshman, S. and Patterson, H.H. 1992. Effects of disturbance and soil amendments on dissolved organic carbon and organic acidity in red pine forest floors. *J. Environ. Qual.* 21(3): 457-463

Davidson, E.A., Galloway, L.F. and Strand, M.K. 1987. Assessing available carbon: comparison of techniques across selected forest soils. *Commun. Soil Sci. Plant Anal.* 18: 45-64

Dao,T.H. and Lavy, T.L. 1978. Atrazine adsorption on soil as influenced by temperature, moisture content and electrolyte concentration. *Weed Sci.* 26(3): 303-308. Available: http://www.jstor.org/pss/4042722 (23Feb2011)

Edwards, C.A. 1973. Pesticides residues in soil and water. In: *Environmental Pollution by Pesticides* (ed. Edward, C.A.). Plenum press, London, pp. 409-458

Erti, T., Marton, A. and Foldenyi, R. 2004. Effect of pH and the role of organic matter in the adsorption of isoproturon on soils. *Chemosphere* 57(8): 771-779

Evans, A. Jr., Zelazny, L.W. and Zepper, C.E. 1988. Solution parameters influencing dissolved organic carbon levels in three forest soils. *Soil Sci. Soc. Am. J.* 52: 1789-1792

Fernandez-Bayo, J. D., Nogales, R. and Romero, E. 2009. Assessment of three vermicomposts as organic amendments used to enhance diuron sorption in soils with low organic carbon content. *Eur. J. Soil Sci.* 60(6): 935-944

Gaillardon, P. and Dur, J.C. 1995. Influence of soil moisture on short-term adsorption of diuron and isoproturon by soil. *Pestic. Sci.* 45(4): 297-303

Gao, J.P., Maghun, J., Spitzauer, P. and Ketrup, A. 1998. Sorption of pesticides in the sediment of the Teufelsweicher pond (Southern Germany) 11: competitive adsorption, desorption of aged residues and effect of dissolved organic carbon. *Water Res.* 32(7): 2089-2094

Gue, B., Schmitt, J., Chen, Z., Liang, L. and McCarthy, J.F. 1995. Adsorption and desorption of different organic matter fractions on iron oxide. *Geochimica and Cosmochimica Acta*, 59: 219-229

Guggenberger, G. and Zech, W. 1993. Dissolved organic carbon control in acid forest soils of the Fichtelgebirge (Germany) as revealed by distribution patterns and structural composition analysis. *Geoderma* 59: 109-129

Guggenberger, G. and Zech, W., 1994. Composition and dynamics of dissolved carbohydrates and lignin-degradation products in two coniferous forests, N.E. Bavaria, Germany. *Soil Biol. Biochem.* 26: 19-27

Guggenberger, G., Zech, W. and Schulten, H.R. 1994. Formation and mobilization pathways of dissolved organic matter: evidence from chemical structural studies of organic matter fractions in acid forest floor solutions. *Org. Geochem.* 21: 51-66

Gupta, S. and Gajbhiye, V.T. 2004. Adsorption-desorption, persistence and leaching behaviour of thifluzamide in alluvial soil. *Chemosphere* 57 (6): 471-480

Hamaker, J.W. and Thompson, J.M. 1972. Adsorption In: Goring, J.W. and Hamaker, J.W. (eds.) *Organic Chemical in the Soil Environment, Volume 1.* Marcel Dekker Inc., New York, pp.727-734

Hance, R.J. 1965. Observations on the relationship between the adsorption of diuron and the nature of the adsorbent. *Weed Res.* 5: 108-114

Hance, R.J. 1969. The adsorption of linuron, atrazine and EPTC by model aliphatic adsorbents and soil organic preparations. *Weed Res.* 9(2): 108-113

Harper, S. S. 1994. Sorption-desorption and herbicide behaviour in soil In: Duke, S.O. (ed.) *Rev. Weed Sci. Soc. Am.* 6 Champaing, I.H. pp.207-225

Hue, N.V., Craddock, G.R. and Adams, F. 1986. Effect of organic acids on aluminium toxicity in subsoils. *Soil Sci. Soc. Am. J.* 50: 28-34

Jackson, M.L. 1958. *Soil Chemical Analysis*. (Indian reprint, 1967). Prentice-Hall of India Pvt. Ltd., New Delhi, 498p.

Jaw, C.G., Lin, K.H., Yen, J.H. and Wang, Y.S. 2007. Correlation between experimental and predicted equilibrium distribution coefficient of chlorobenzene and chlorophenol compounds in soil-water systems using partial solubility parameters. *J. Environ. Sci. Health B*. 42(1): 97-105

Jenks, B.M., Roeth, F.W., Martin, A.R. and Mc Callister, D.L. 1998. Influence of surface and subsurface soil properties on atrazine sorption and degradation. *Weed Sci*. 46(1): 132-138

Johnson, A., Worral, F., White, C., Walker, A., Besieu, T.J. and Williams, R.J. 1997. The potential of incorporated organic matter to reduce pesticide leaching. *Toxicol. Environ. Chem*. 58: 47-61

Kaiser, K., Guggenberger, G., Haumaier, L. and Zech, W., 2001. Seasonal variations in the chemical composition of dissolved organic matter in organic forest floor layer leachates of old growth Scots pine (*Pinus sylvestris* L.) and European beech (*Fagus sylvatica* L.) stands in northeastern Bavaria, Germany. *Biogeochemistry* 55: 103-143

Kalbitz., K., Solinger, S., Park, J.H., Michalzik, B. and Matzner, E. 2000. Controls on the dynamics of dissolved organic matter in soils: a review. *Soil Sci.* 165: 277-304

Kan, A.T. and Tomson, M.B. 1990. Ground water transport of hydrophobic compounds in the presence of dissolved organic matter. *Environ. Toxicol. Chem.* 9: 253-263

Karickhoff, S.W., Brown, O.S. and Scott, T.A. 1979. Sorption of hydrophobic pollutants on natural sediments and soils. *Water Res.* 13: 241-248

KAU [Kerala Agricultural University] 2007. Package of Practices Recommendations: Crops, (13th Ed.) Kerala Agricultural University, Thrissur, 20p.

KAU [Kerala Agricultural University] 2008. *Annual report 2007.* All India Coordinated Research Programme on Weed Control. Kerala Agricultural University, Kerala, India, 80p.

Kawakami, T., Eun, H., Ishizaka, M., Endo, S., Tamura, K. and Higashi, T. 2007. Adsorption and desorption characteristics of several herbicides on sediment. *J Environ. Sci. Health, Part B.* 42(1): 1-8

Khan, S.U. 1989. The interaction of organic matter with pesticides. In: Schinitzer, M, and Khan, S.U. (eds.), *Soil organic matter* (4th Ed.) Elsevier Science Publishers, Netherlands, pp.137-172.

Kibe, K., Takahashi, M., Kameya, T. and Urano, K. 2000. Adsorption equilibriums of principal herbicides on paddy soils in Japan. *Sci. Total Environ.* 263(1-3): 115-125

Kim, K. and Kim, Y.H. 1990. Adsorption of butachlor on soils. *Korean J. Environ. Agric.* 9(2): 105-106

Kozak, J.,Valla, M., Prokopec, O. and Vacek, O. 1991. Prediction of the role of soil organic matter and some other soil characteristics in herbicide adsorption. In: Kubat, J. (ed.), *Humus, Its Structure and Role in Agriculture and Environment.* Proceedings of the tenth symposium humus et planta, Prague, Czechoslovakia, pp. 165-169

Krutz, L.J., Senseman, S.A., McInnes, K.J., Hoffman, D.W. and Tierney, D.P. 2004. Adsorption and desorption of metolachlor and metolachlor metabolites in vegetated filter strip and cultivated soil. *J. Environ. Qual.* 33: 939-945.

Kumar, M. and Philip, L. 2006. Adsorption and desorption characteristics of hydrophobic pesticide endosulfan in four Indian soils. *Chemosphere* 62: 1064-1077.

Lee, D.Y. and Farmer, W.J. 1989. Dissolved organic matter interaction with napropamide and four other nonionic pesticides. *J. Environ. Qual.* 18: 468-474.

Leenheer, J.A. and Ahlrichs, J.L. 1971. A kinetic and equilibrium study of the adsorption of carbaryl and parathion upon soil organic matter surfaces. *Soil Sci. Soc. Am. Proc.* 35: 700-705

Li, Z.P., Han, C.W. and Han, F.X. 2010. Organic C and N mineralization as affected by organic matter in paddy soils of subtropical China. *Geoderma* 157: 206-213

Liu, H. and Amy, G. 1993. Modelling partitioning and transport interactions between natural organic matter and polynuclear aromatic hydrocarbons in groundwater. *Environ. Sci. Technol.* 27: 1553-1562

Liu,W., Gan, J., Papiernik, S.K. and Yates, S.R. 2000. Structural influences in relative sorptivity of chloroacetanilide herbicides on soil. *J. Agric. Food Chem.* 48(9): 4320-4325.

Liu, Z., He, Y., Xu, J., Huang, P. and Jilani, G. 2008. The ratio of clay content to total organic carbon content is a useful parameter to predict adsorption of the herbicide butachlor in soils. *Environ. Pollut.* 152(1): 163-171

Logan, L.R.J., Robert, E.B. and Stephen, J.K. 1992. Partitioning behaviour and the mobility of chlordane in groundwater. *Environ. Sci. Technol.* 26: 2234-2239

Lundquist, E.J., Jackson, L.E. and Scow, K.M. 1999. Wet-dry cycles affect dissolved organic carbon in two California agricultural soils. *Soil Biol. Biochem.* 31(7): 1031-1038

Mc Dowell, W.H. and Likens, G.E. 1988. Origin, composition and flux of dissolved organic carbon in the Hubbard Brook Valley. *Ecol. Monogr.* 58: 177-195

Mc Dowell, W.H. 2003. Dissolved organic matter in soils-future directions and unanswered questions. *Geoderma* 113: 179-186

Mc Gill, W.B., Cannon, K.R., Robertson, J.A. and Cook, F.D. 1986. Dynamics of soil microbial biomass and water-soluble organic C in Breton L after fifty years of cropping to two rotations. *Can. J. Soil Sci.* 66: 1-19

Mc Knight, D.M., Bencala, K.E., Zellweger, G.W., Aiken, G.R., Feder, G.L. and Thorn, K.A. 1992. Sorption of dissolved organic carbon by hydrous aluminium and iron oxides occurring at the confluence of Deer Creek with the Snake river, Summit country, Colorado. *Environ. Sci. Tech.* 26(7): 1388-1396

Mechrafi, E., Elazzouzi, M. Bouhaouss, A., Dahchour, A., Perrin-Ganier, C. and Schiavon, M. 2001. Adsorption studies of ^{14}C labeled atrazine on Moroccan soils with different organic matter contents. *Fresenius Environ. Bull.* 10(9): 722-726

Merkle, M.G., Bovey, R.W. and Hall, R. 1966. The determination of picloram residues in soil using gas chromatography. *Weeds* 14(2): 161-164

Mitra, S. and Bhowmik, P.C. 2001. Physical and chemical properties of soil influence the sorption of the diketonitrile metabolite of RPA 201772. *Weed Sci.* 49: 423-430

Moon, Y.H. and Kim, Y.S. 2000. Dissipation in surface water and adsorption in soil of butachlor, oxadiazone, pretilachlor and thiobencarb. *Korean J. Weed Sci.* 20(1): 32-38

Mon, E.E., Hirata, T., Kawamoto, K., Hiradate, S., Komatsu, T. and Moldrup, P. 2009. Adsorption of 2, 4-Dichlorophenoxyaceticacid onto volcanic ash soils: Effects of pH and soil organic matter. *Environ. Asia* 2(1): 1-9

Mulholland, P.J., Dahm, C.N., David, M.B., Di Toro, D.M., Fisher, T.R., Kogel-Knabner, I., Meybeck, M.H., Meyer, J.L. and Sedell, J.R. 1990. What are the temporal and spatial variations of organic acids at the ecosystem level? In: Perdue, E.M. and Gjessing, E.T. (eds.), *Organic Acids in Aquatic Ecosystems.* Life Sciences Research Report 48, John Wiley and Sons, pp.315-329.

Narambuye, F.X. and Haynes, R.J. 2006. Effect of organic amendments on soil pH and Al solubility and use of laboratory indices to predict their liming effect. *Soil Sci.* 171(10): 754-763

Neff, J.C. and Asner, G.P. 2001. Dissolved organic carbon in terrestrial ecosystems: synthesis and a model. *Ecosystems* 4: 29-48.

OECD [Organisation for Economic Co-operation and Development] 2000. Test No. 106: Adsorption-Desorption using a batch equilibrium method, OECD guidelines for testing of chemicals, section1: Physical-chemical properties, OECD publishing. Available: http://www.oecd-ilibrary.org/environment/test-no-106-adsorption-desorption-using-a-batch-equilibrium-method_9789264069602-en. [30 Mar 2011].

Pierce, R.H. Jr., Olney, C.E. and Felbeck, G.T. Jr. 1971. Pesticide adsorption in soils and sediments. *Environ. Lett.* 1(2): 157-172

Ponizovsky, A.A., Metzler, D.M., Allen, H.E. and Ackerman, A.J. 2006. The effect of moisture content on the release of organic matter and copper to soil solutions. *Geoderma* 135: 204-215

Qualls, R.G. and Haines, B.L. 1991. Geochemistry of dissolved organic nutrients in water percolating through a forest ecosystem. *Soil Sci. Soc. Am. J.* 55: 1112-1123.

Quan, Q. W., Chun, Y.W. and Ping, L.W. 1999. Adsorption of acetanilide herbicides on soils and its correlation with soil properties. *Pestic. Sci.* 55(11): 1103-1108

Rankins, A., Shaw, D.R. and Kingery, W.L. 2002. Comparison of fluometuron sorption to soil from a filterstrip and cropped field. *Weed Sci.* 50: 820-823

Reddy, K.N. and Locke, M.A. 1994. Prediction of soil sorption (K_{oc}) of herbicides using semiempirical molecular properties. *Weed Sci.* 42(3): 453-461

Reinhardt, C.F., Ehlers, J.G. and Nel, P.C. 1990. Persistence of atrazine as affected by selected soil properties. *S. Afr. J. Pl. Soil* 7(3): 182-187

Renner, K.A., Meggitt, W.F. and Penner, D 1988. Effect of soil pH on imazaquin and imazethapyr adsorption to soil and phytotoxicity to corn (*Zea mays*). *Weed Sci.* 36(1): 78-83

Robinson, G.W. 1992. A new method for the mechanical analysis of soils and other dispersions. *J. Agric. Sci.* 12: 306-321.

RSC [Royal Society of Chemistry] 1987. *Agro Chemical Hand book*, 2nd edition (Hartley, D., ed.). The Royal Society of Chemistry, Notingham, UK, pp.111-936

Rytwo, G., Gonen, Y. and Afuta, S. 2008. Preparation of berberine-montmorillonite formulations from hydrophobic/hydrophilic mixtures. *Appl. Clay Sci.* 41(1-2): 47-60

Sahid, I.B., Kalithasan, K. and Rahman, A. 1997. Bioactivity, adsorption and persistence of two herbicides in tropical soils. *Plant Prot. Q.* 12(3): 128-132

Sato, T., Kohnosu, S. and Hartwig, J.F. 1987. Adsorption of butachlor to soil. *J. Agric. Food Chem.* 35(3): 394-402.

Senesi, N. and Testini, C. 1983. The environmental fate of herbicides: the role of humic substances. In: Hallberg, R. (ed.), *Environmental Biogeochemistry.* Ecological Bulletin (Stock holm) 35: 477-490.

Senesi, N. 1992. Binding mechanisms of pesticides to soil humic substances. *Sci. Total Environ.* 123-124: 63-76

Si, Y., Takagi, K., Iwasaki, A. and Zhou, D. 2009. Adsorption, desorption and dissipation of metolachlor in surface and subsurface soils. *Pest Manag. Sci.* 65(9): 956-962

Spark, K. M. and Swift, R. S. 2002. Effect of soil composition and dissolved organic matter on pesticide sorption. *Sci. Total Environ.* 298(1-3): 147-161.

Stougaard, R.N., Shea, P.J. and Martin, A.R. 1990. Effect of soil type and pH on adsorption, mobility and efficacy of imazaquin and imazethapyr. *Weed Sci.* 38: 67-73

Strebe, T.A. and Talbert, R.E. 2001. Sorption and mobility of flumetsulam in several soils. *Weed Sci.* 49: 806-813

Suba, J.D. and Essington, M.E. 1999. Adsorption of flumeturon and norflurazone: Effect of tillage and dissolved organic carbon. *Soil Sci.* 164(3): 145-155.

Tang, Y., Zhang, H., Schroder, J.L., Payton, M.E. and Zhou, D. 2007. Animal manure reduces aluminum toxicity in an acid soil. *Sci. Soc. Am. J.* 71: 1699-1707.

Thurman, E.M. 1985. *Organic geochemistry of natural waters*. Springer Science and Buisiness, 497p.

Tipping, E. and Woof, C. 1990. Humic substances in acid organic soils: Modelling their release to the soil solution in terms of humic charge. *J. Soil Sci.* 141(4): 573-586

Tipping, E. 1998. Modelling of the properties and behaviour of dissolved organic matter in soils. *Mitteilungen Deutshe Bodenkundliche Gesellschaft* 87: 237-252

Tipping, E., Woof, C., Rigg, E., Harrison, A.F., Inneson, P., Taylor, K., Benham, D., Poskitt, J., Rowland, A.P., Bol, R. and Harkenss, D.D. 1999. Climatic influences on the leaching of dissolved organic matter from upland UK moorland soils, investigated by a field manipulation experiment. *Environ. Int.* 25(1): 83-95

Ugolini, F.C. and Dahlgren, R.A. 1987. The mechanisms of podzolization as revealed by soil solution studies. In: Righi, D. and Chauvel, A. (eds.), *Podzols and Podzolization*. Association Francaise pour L'Etude du Sol, INRA, Paris. pp.185-203

Vogue, P.A., Kerle, E.A. and Jenkins, J.J. 1994. OSU Extension Pesticide Properties data base [online]. National Pesticide Information Centre. Available at: http:// www.npic@ace.orst.edu (14 July 2011)

Walker, A. and Crawford, D. V. 1968. The role of organic matter in adsorption of the triazine herbicides by soils. In: International Atomic Energy Agency (ed.), *Isotopes and radiation in soil organic matter studies.* Proceedings of Second Symposium of International Atomic Energy Agency, Vienna. pp. 91-108

Walkley, A. 1947. A critical examination of a rapid method for determining organic carbon in soils: Effect of variations in digestion conditions an d of inorganic soil constituents. *Soil Sci.* 63: 251-263

Weber, J.B. and Peter, C.J. 1982. Adsorption, bioactivity and evaluation of soil test for alachlor, acetachlor and metolachlor. *Weed Sci.* 30:14-20

Whalen, J.K., Chang, C., Clayton, G.W. and Carefoot, J.P. 2000. Cattle manure amendments can increase the pH of acid soils. *Soil Sci. Soc. Am. J.* 64: 962-966

Xu, D., Xu, Z., Zhu, S., Cao, Y. Wang, Y., Du, X., Gu, Q. and Li, F. 2005. Adsorption behaviour of herbicide butachlor on typical soils in China and humic acid from the soil samples. *J. Colloid Interface Sci.* 285(1): 27-32

Yang, W. and Holmen, B.A. 2007. Effects of relative humidity on chloroacetanilide and dinitroaniline herbicide desorption from agricultural $PM_{2.5}$ on quartz fiber filters. *Environ. Sci. Tech.* 41(11): 3843-3849

Zhen, L.Z., Na, D., Hayat, T., Yan, H., Ming, X.J. and Zhen, W.H. 2010. Butachlor sorption in organically rich soil particles. *Soil Sci. Soc. Am. J.* 74(6): 2032-2038

Zsolany, A. 1996. Dissolved humus in soil waters. In: Piccolo, A. (ed.), *Humic Substances in Terrestrial Ecosystem*. Elsevier Publishers, Netherlands, pp.171-223.

Zsolnay, A. 1997. The development of tests to quantify the potential ecological relevance of the water soluble humus. In: Drozd, J., Gonet, S.S., Senesi, N. and Weber, J. (eds.), *The Role of Humic Substances in the Ecosystems and in Environmental Protection*. Polish Society of Humic Substances, Wroclaw, pp. 251-256.

Zsolany, A., Baigar, E., Jimenez, M., Steinweg, B. and Saccomandi, F. 1999. Differentiating with fluorescence spectroscopy the sources of dissolved organic matter in soils subjected to drying. *Chemosphere* 38(1): 45-50

INFLUENCE OF ORGANIC MATTER AND MOISTURE ON ADSORPTION OF CHLOROACETANILIDE HERBICIDES IN LATERITE SOIL

By

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ABSTRACT OF THE THESIS

Submitted in partial fulfillment of the requirement
for the degree of

Master of Science in Agriculture

Faculty of Agriculture
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ABSTRACT

Experiments were carried out to study the influence of organic matter and soil moisture on the adsorption of chloroacetanilide herbicides, *viz.*, butachlor and pretilachlor, in laterite soil. The technical programme consisted of an incubation experiment and a pot culture study. In the incubation experiment, two moisture levels *viz.*, air dry and field capacity were included along with two herbicides, butachlor and pretilachlor, and three organic matter sources, FYM, vermicompost and soil. The pot culture experiment consisted of six treatments with two herbicides and three organic matter sources. The herbicides, butachlor and pretilachlor were applied @ 1.25 kg ha^{-1} and 0.45 kg ha^{-1} respectively and the manures were applied @ 5.0 t ha $^{-1}$.

The soil sample collected for the study belongs to Ultisol order, the major characteristics of which are low pH, low CEC (4.7 and 4.67 C mol (+) kg^{-1} respectively) and high sand content (73.13 % sand, 16.88 % silt and 10.00 % clay). Organic carbon content was in the medium range (0.61 %).

Dissolved organic carbon (DOC) is the most active fraction of organic matter and hence the procedure for DOC estimation in soil, FYM and vermicompost was standardized. Quantity of herbicides adsorbed by soil was determined by gas chromatography using standard protocols developed at AICRP on Weed Control, College of Horticulture, Vellanikkara.

In the incubation experiment, the degree of adsorption of butachlor and pretilachlor was evaluated using the K_d (distribution coefficient) values. The K_d values followed the order of organic carbon content in the soil samples taken from the treatments. The K_d values were higher for pretilachlor with the order being FYM > vermicompost > soil. Only slight variations were observed between air dry and field capacity levels indicating that moisture levels had no significant

influence on the K_d values. This could be explained by hydrophobic character of the herbicides under study.

The pot culture study showed that adsorption as well as dissipation of herbicides were more in vermicompost treatment. The results also indicated that initial adsorption of herbicides was lessened by dissolved organic carbon released from the farmyard manure. However, the half life of herbicides was more in FYM treatment when compared to vermicompost and control (soil alone). The half life of butachlor was 17.00 days and that of pretilachlor was 19.00 days in FYM treatment. The results indicated the superiority of FYM in retaining the herbicides for the desired period of weed control in rice.

Phytotoxicity due to herbicide application was more with vermicompost treatment than that of FYM and soil alone treatments. This was due to the higher initial adsorption of herbicides by the soil matrix. Biometric observations on plant height, productive tillers, yield of grain and straw showed that FYM is superior to vermicompost in improving the growth and yield of rice.

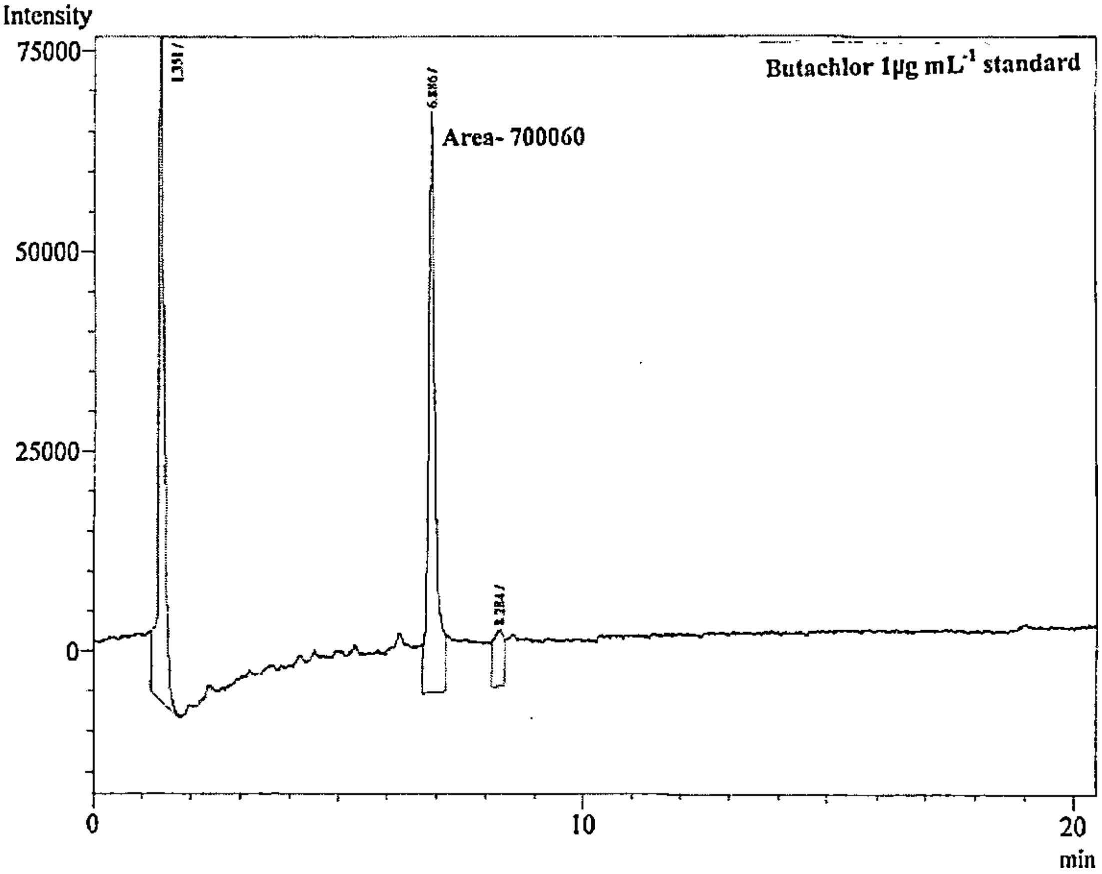
From the above study, it could be concluded that butachlor and pretilachlor are strongly adsorbed on soil organic matter and their adsorption onto soils is affected by the presence of soluble organic matter. Presence of high levels of dissolved organic carbon in the FYM treatment at the time of application of herbicides resulted in a reduction in the magnitude of adsorption. On comparing two organic matter sources, it was noticed that total as well as dissolved organic carbon were higher in the FYM applied soil. The dissolved organic carbon would have facilitated movement of chemicals while the particulate organic carbon improved their retention. Therefore, it is essential to consider both these factors when pre - emergence herbicides are applied to rice.

Annexure

GC analysis report of reference standard butachlor (1μg mL^{-1})

Analysis Date & Time : 2/4/2011 11:23:50 AM
User Name : Admin
Vial# : 1
Sample Name : butastd1ppm4-2-2011
Sample ID : butastd1ppm4-2-2011
Sample Type : Unknown
Injection Volume :
ISTD Amount :

Data Name : D:\sept09.gcd\butastd1ppm4-2-2011.gcd
Method Name : D:\sept09.gcd\Untitled.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark
1	1.351	735628	118559	0.000		V
2	6.886	700060	72495	0.000		V
3	8.284	103378	7151	0.000		V
Total		1539066	198205			

Method

```
<Analytical Line 1>

[Injection Port SPL1]
 Injection Mode              : Split
 Temperature                 : 250.0 C
 Carrier Gas                 : N2/Air
 Flow Control Mode           : Pressure
 Pressure                    : 160.8 kPa
 Total Flow                  : 5.6 mL/min
 Column Flow                 : 1.28 mL/min
 Linear Velocity             : 38.0 cm/sec
 Purge Flow                  : 3.0 mL/min
 Split Ratio                 : 1.0
 High Pressure Injection     : OFF
 Carrier Gas Saver           : OFF
 Splitter Hold               : OFF

[Column Oven]
 Initial Temperature         : 220.0 C
 Equilibration Time          : 3.0 min

[Column Information]
 Column Name                 : BPX5
 Serial Number               :
 Film Thickness              : 0.50 um
 Column Length               : 30.0 m
 Inner Diameter              : 0.25 mm ID
 Column Max Temp             : 300 C
 Installation Date           : 2009/07/04

[Detector Channel 1 ECD1]
 Temperature                 : 280.0 C
 Signal Acquire              : Yes
 Sampling Rate               : 40 msec
 Stop Time                   : 60.00 min
 Delay Time                  : 0.00 min
 Subtract Detector           : None
 Current                     : 0.10 nA
 Makeup Gas                  : N2/Air
 Makeup Flow                 : 30.0 mL/min

[General]
 < Ready Check Heat Unit >
    Column Oven        : Yes
    SPL1               : Yes
    ECD1               : Yes
 < Ready Check Detector (FTD) >
 < Ready Check Baseline Drift >
    ECD1               : No
 < Ready Check Injection Flow >
    SPL1 Carrier       : Yes
    SPL1 Purge         : Yes
 < Ready Check Add. Flow >
 < Ready Check Detector APC Flow >
    ECD1 Makeup        : Yes
 External Wait         : No
 Auto Flame On         : No
 Auto Flame Off        : Yes
 Reignite              : No
 Auto Zero After Ready                        : Yes

[Peak Integration Parameters - Channel 1]
```

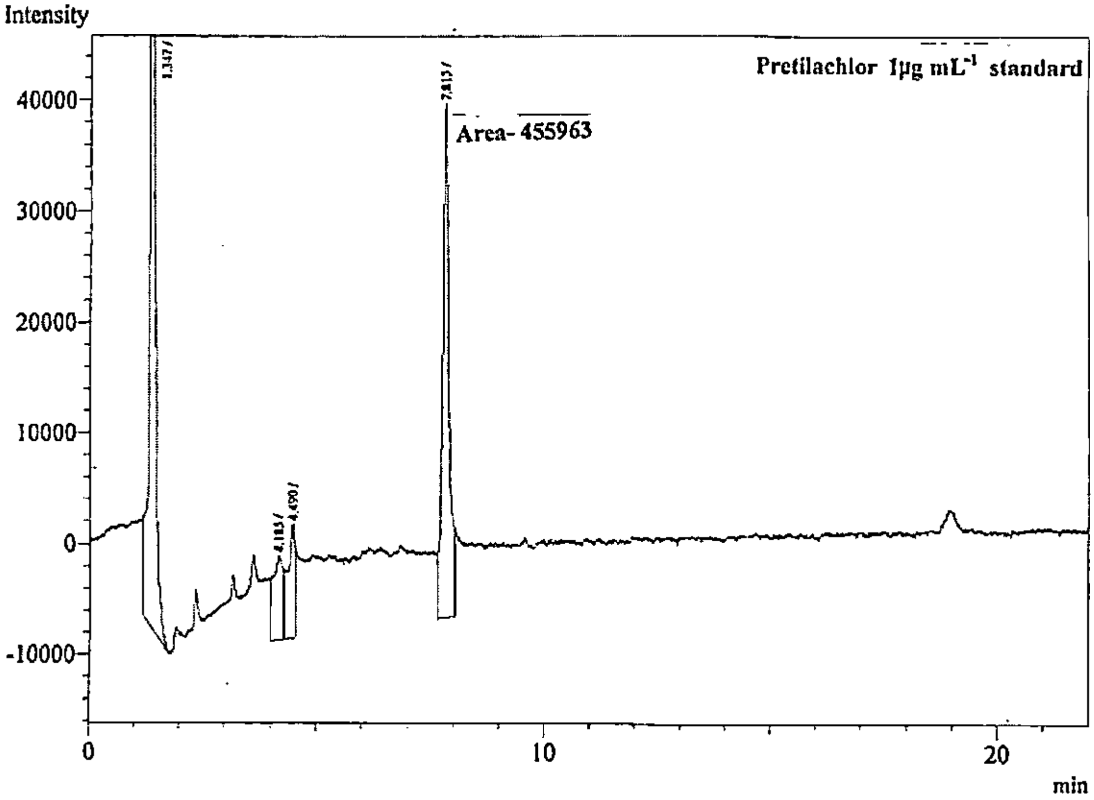
```
  Width                   : 3   sec                   Slope                    : 1000 uV/m
  Drift                   : 0   uV/min                T.DBL                    : 1000 min
  Min.Area/Height         : 100000 counts

[Quantitative Parameters - Channel 1]
=Quantitative Parameters=
  Quantitative Method     : External Standard
  Calculated by           : Area                      Calibration Level#       : 1
  Calibration Curve       : Linear                    Through Origin           : Not throug
  Weight Regression       : None                      Unit                     : ppm
=Identification Parameters=
  Window/Band             : Window                    Window                   : 5 %
  Default Band Time       : ---                       Identification Method    : Absolute
  Peak Select             : All Peaks                 Grouping                 : None
  Correction RT           : No Change
```

GC analysis report of reference standard pretilachlor (1μg mL^{-1})

Analysis Date & Time : 2/4/2011 2:18:53 PM
User Name : Admin
Vial# : 1
Sample Name : pretilstd1ppm4-2-2011
Sample ID : pretilstd1ppm4-2-2011
Sample Type : Unknown
Injection Volume :
ISTD Amount :

Data Name : D:\sept09.gcd\pretilstd1ppm4-2-2011.gcd
Method Name : D:\sept09.gcd\Untitled.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark
1	1.347	658653	90865	0.000		V
2	4.185	104864	7569	0.000		V
3	4.490	104425	10220	0.000		V
4	7.813	455963	46286	0.000		V
Total		1323905	154940			

```
                         Method

<Analytical Line 1>

[Injection Port SPL1]
 Injection Mode              : Split
 Temperature                 : 250.0 C
 Carrier Gas                 : N2/Air
 Flow Control Mode           : Pressure
 Pressure                    : 160.8 kPa
 Total Flow                  : 5.6 mL/min
 Column Flow                 : 1.28 mL/min
 Linear Velocity             : 38.0 cm/sec
 Purge Flow                  : 3.0 mL/min
 Split Ratio                 : 1.0
 High Pressure Injection     : OFF
 Carrier Gas Saver           : OFF
 Splitter Hold               : OFF

[Column Oven]
 Initial Temperature         : 220.0 C
 Equilibration Time          : 3.0 min

[Column Information]
 Column Name                 : BPX5
 Serial Number               :
 Film Thickness              : 0.50 um
 Column Length               : 30.0 m
 Inner Diameter              : 0.25 mm ID
 Column Max Temp             : 300 C
 Installation Date           : 2009/07/04

[Detector Channel 1 ECD1]
 Temperature                 : 280.0 C
 Signal Acquire              : Yes
 Sampling Rate               : 40 msec
 Stop Time                   : 60.00 min
 Delay Time                  : 0.00 min
 Subtract Detector           : None
 Current                     : 0.10 nA
 Makeup Gas                  : N2/Air
 Makeup Flow                 : 30.0 mL/min

[General]
 < Ready Check Heat Unit >
     Column Oven       : Yes
     SPL1              : Yes
     ECD1              : Yes
 < Ready Check Detector (FTD) >
 < Ready Check Baseline Drift >
     ECD1              : No
 < Ready Check Injection Flow >
     SPL1 Carrier      : Yes
     SPL1 Purge        : Yes
 < Ready Check Add. Flow >
 < Ready Check Detector APC Flow >
     ECD1 Makeup       : Yes
 External Wait         : No
 Auto Flame On         : No
 Auto Flame Off        : Yes
 Reignite              : No
 Auto Zero After Ready                      : Yes

[Peak Integration Parameters - Channel 1]
```

```
 Width                   : 3   sec              Slope                   : 1000 uV/n
 Drift                   : 0   uV/min           T.DBL                   : 1000 min
 Min.Area/Height         : 100000 counts

[Quantitative Parameters - Channel 1]
=Quantitative Parameters=
 Quantitative Method     : External Standard
 Calculated by           : Area                 Calibration Level#      : 1
 Calibration Curve       : Linear               Through Origin          : Not throu
 Weight Regression       : None                 Unit                    : ppm
=Identification Parameters=
 Window/Band             : Window               Window                  : 5 %
 Default Band Time       : —                    Identification Method   : Absolute
 Peak Select             : All Peaks            Grouping                : None
 Correction RT           : No Change
```