ADSORPTION AND DESORPTION OF METRIBUZIN, TRIFLURALIN AND TRIAZOPHOS ON SANDY LOAM AND CLAY LOAM SOILS

By

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DEDICATED
TO MY
BELOVED PARENTS

CERTIFICATE - I

This is to certify that this thesis entitled, "**Adsorption and desorption of metribuzin, trifluralin and triazophos on sandy loam and clay loam soils**", submitted for the degree of **Master of Science** in the subject of **Chemistry** to the Chaudhary Charan Singh Haryana Agricultural University, Hisar, is a bonafide research work carried out by **Mr. Tavinder Singh** under my supervision and that no part of this thesis has been submitted for any other degree.

The assistance and help received during the course of investigation have been fully acknowledged.

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CERTIFICATE - II

This is to certify that this thesis entitled, "**Adsorption and desorption of metribuzin, trifluralin and triazophos on sandy loam and clay loam soils**", submitted by **Mr. Tavinder Singh** to the Chaudhary Charan Singh Haryana Agricultural University, Hisar, in partial fulfilment of the requirements for the degree of **Master of Science** in the subject of **Chemistry**, has been approved by the Student's Advisory committee after an oral examination on the same.

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1. INTRODUCTION

India is the third largest consumer of pesticides in the world and highest among the South-Asian countries with pesticides consumption of 54135 MT based on 1999-2000 demand (Agnihotri, 2000). Regardless of the method of application, large amount of pesticides ultimately find their way into the soil. Estimate indicates that as high as 50 per cent of the pesticides applied on the foliage fall on the soil depending upon the density of crop and the mode of application (Edward, 1972; Khan 1980). Pimental (1995) reported that less than 0.1 per cent of the pesticides applied for the pest control reach their target pests and more than 99.9 per cent of pesticides move into the environment. Hence,soil serves as a major environmental sink of bulk of pesticides used in agriculture.

Organic pesticides added directly or indirectly to soils undergo a number of transformation processes which includes adsorption onto the soil particles, microbial degradation, volatilization, plant uptake, leaching and surface runoff (Bolan and Baskaran, 1997). It is, therefore, of great interest to gain information concerning the factors that determine the site and duration of pesticides residence.

Among the processes affecting the behaviour of pesticides in soils, adsorption is of paramount importance as it helps in determining the fate and effectiveness of pesticides in soil environment (Ali *et al.*, 2000). Adsorption decreases the concentration of pesticides in soil-solution and thereby, render them less liable for leaching to ground water and microbial degradation (Bolan and Baskaran, 1997). Adsorption also influences the bioavailability of organic compounds (Grover *et al.*, 1979), thereby controlling directly or indirectly the rate of biodegradation, uptake by plants and other biota (Mersie and Foy, 1986).

Among various soil properties like organic matter, pH, clay content, soil temperature etc. organic matter is considered to be the principal component involved in the adsorption of majority of organic pesticides (Bolan and Baskaran, 1997). Since the majority of organic pesticides are non ionic, therefore, it is accepted that the adsorption of non-ionic pesticides by soils in aqueous medium is essentially controlled by organic matter content (Karickhoff, 1981; Chiou, 1989). For the adsorption of ionic/polar pesticides, clay minerals, pH of the soil solution contribute the most (Green and Karickhoff, 1990; Werkheiser and Anderson, 1996; Grey *et al.*, 1997).

The distribution (adsorption-desorption) of the active ingredient of a pesticide in the soil obviously depends on its chemical nature, mode of formulation and size of suspended particles. The concentration (activity of pesticides after sorption on soil) of an organic chemical in the solution phase is determined to a large extent by the solute distribution between solution and organic/inorganic solid phases. Adsorption leads to retardation of solute transport in both liquid and vapour phases, thus influencing the residence in a given zone (e.g. crop root zone), time of arrival at a specified depth (e.g. water table) and the rates of mass loss (volatilization, leaching).

Desorption of pesticides from soil is also an important parameter in determining the pesticide available to the target species, their behaviour in runoff streams, mixing in watershed and in ground water pollution (Cohen *et al.*, 1984). Thus release (desorption) of pesticides from soil is also of importance for the final distribution of pesticides in soil (Farrel *et al.*, 1999). In addition to the adsorption-desorption behaviour of pesticides on soils, the equilibrium studies of adsorption of pesticides on soils are also of importance because plant uptake, bioefficiency and transport of pesticides depends largely on adsorption-desorption equilibrium (Raman *et al.*, 1988).

The chlorinated pesticides usually persist for longer period in soil and thus harmful to successive crops. So these are being replaced by the less persistent pesticides. Among these, metribuzin and trifluralin, both herbicides are widely used for the control of many annual grasses and broadleaved weed species in many useful field crops (Tomlin, 1997). Both the herbicides are relatively less toxic. The acute-oral LD_{50} value of metribuzin is about 2,000 mg/kg body weight for rats and above 500 mg/kg body weight for cats. The acute-oral LD_{50} value of trifluralin is more than 10,000 mg/kg body weight for rats and more than 2,000 mg/kg body weight for dogs (Tomlin, 1997).

Triazophos, an organophosphate insecticide is relatively of recent origin which is being advocated for control of many insects-pests of soils and crops (Tomlin, 1997). However, triazophos is highly toxic insecticide having acute-oral LD_{50} of 57-68 mg/kg body weight for rats and 320 mg/kg body weight for dogs (Tomlin, 1997).

Survey of literature reveals that practically no work has been done on the adsorption equilibrium and sorption (adsorption-desorption) behaviour of metribuzin, trifluralin and triazophos on soils of Indian region. In order to generate information on these aspects, the present studies are planned with the following objectives :

1. Equilibrium studies of adsorption of metribuzin, trifluralin and triazophos on sandy loam and clay loam soils.
2. Adsorption studies of metribuzin, trifluralin and triazophos on sandy loam and clay loam soils.
3. Desorption studies of metribuzin, trifluralin and triazophos on sandy loam and clay loam soils.

2. REVIEW OF LITERATURE

Metribuzin and trifluralin, both herbicides are effective in controlling many important annual grasses and broad leaved weeds in a number of useful field crops whereas, triazophos, an organophosphate insecticide, is widely used for the control of insect-pests of soils and crops. Survey of literature reveals that a lot of work has been done on the adsorption-desorption of herbicides as well as organophosphate insecticides. However, very little information is available on the adsorption-desorption of metribuzin, trifluralin and triazophos on soils of Haryana region. This chapter deals with the analytical techniques employed for adsorption-desorption studies of various herbicides (including metribuzin and trifluralin) and organophosphate compounds (including triazophos) alongwith their adsorption-desorption behaviour on various soils under different agroclimatic conditions. The review has been discussed under the following heads :

2.1 Methods of adsorption studies

2.2 Methods of desorption studies

2.3 Extraction and clean-up

2.4 Estimation

2.5 Adsorption-desorption behaviour

2.6 Equilibrium studies

Information available in each step is recorded as under :

2.1 Methods of adsorption studies

2.1.1 Herbicides

Harvey (1974) studied the adsorption of 12 dinitroaniline herbicides on plano silt loam soils by equilibrating the soils with aqueous solution of herbicides in distilled water for 24 h on a gyrotary shaker at 100 rpm, centrifuged at 5000 g. The adsorption studies of trifluralin on three soils viz. Peat, Gilat and Newe Ya'ar regions was carried out by agitating the aqueous solution of trifluralin in 1M $CaCl_2$ with soils for 24 h in stoppered bottle to avoid volatilization and the suspensions were filtered (Horowitz *et al.*, 1974). Grover *et al.* (1979) carried out the adsorption studies of ^{14}C-diallate, ^{14}C-tri-allate and ^{14}C-trifluralin on five soils viz. Melford loam, Weyburnoxbow sandy loam, Regina clay, Indian head sandy loam and Asquith loamy sand by shaking the soils with aqueous solution of herbicides on an end over end shaker at 32 rpm for 24 h in a cabinet maintained at 25°±1°C followed by centrifuged at 10,000 rpm for 10 minutes. Jacques and Harvey (1979) studied the adsorption of six dinitroaniline herbicides on 10 soils viz. Aldoph, Ferrette, Peebles, Plano etc. by shaking the aqueous solution of pesticides with soils for 16 h at 22±1°C on a rotary shaker at 400 rpm, centrifuged at 1600 rpm for 30 min. The adsorption of metribuzin was studied on eight soils viz. sand + alumina, Quartz sand, sand + Kaolinite etc. by shaking the herbicide solution in 0.01M ethanol with soils on reciprocal shaker at 100 cycles/min (Lafleur, 1979).

The various research workers have studied the adsorption of atrazine on various soils by equilibrating the aqueous solution of herbicides in 0.01 M $CaCl_2$/0.01N $Ca(NO_3)_2$ with soils for 12-24 h at 27±1°C and centrifuged at 2000 rpm. for 15 minutes (Raman *et al.,* 1988; Ma *et al.,* 1993; Seybold *et al.,* 1994; Sonan and Schwab, 1995; Kumaran and Devi, 1996). Adsorption of three herbicides viz. triallate, EPTC and Prometon on Hanford sandy loam and Tujunga loamy sand soils were carried out by equilibrating the soils with aqueous solution of herbicides using end over end electrical shaker at 40 rpm for 24 h, centrifuged in a thermostable high speed centrifuge at 14000 for 10 min. at 25±1°C (Singh *et al.,* 1990). Alvarez-Benedi *et al.* (1998) studied the adsorption of three herbicides on three soils by shaking the soils with herbicide solution taken on magnetic stirrer, centrifuged at 3500 rpm for 10 min. The adsorption of pendimethalin, fluchloralin and oxadiazinon on sandy loam and clayey soils was studied by shaking the soils with herbicide solution in 0.01M $CaCl_2$ solution for 6 h followed by centrifuged at 6000 rpm for 30 min. (Raj *et al.,* 1999; Rai *et al.,* 2000).

2.1.2 Organophosphates

Felsot and Dahm (1979) studied the adsorption of four organophosphate insecticides viz. ^{14}C-phorate, ^{14}C-parathion, ^{14}C-terbufos and chlorpyrifos on five soils viz. Sarpy fine sandy loam, Thurman loamy find sand Clarion, Peat and

Harps of Iowa by shaking the soils with aqueous solution of insecticides in 0.01M $CaCl_2$ solution for 3 h in glass culture tubes and centrifuged at 1580 g rpm for 15 min. The adsorption of methyl parathion on three soils viz. EL-Nanda, Tel EL-Kabeer and Tahreer was studied by shaking the soils with pesticide-solution in acetone water (15% v/v) mixture for 4 h followed by centrifuged at 5000 rpm for 15 min (Kishk *et al.*, 1979).

Sharom *et al.* (1980) studied the adsorption of 12 insecticides viz. chlorpyrifos, parathion, ethion and diazinon etc. on four soils (organic soil, sediment, Beverly sandy loam and Plainfield sand) by tumbling the aqueous solution of pesticides with soils for 4 h (8 h for organic soil) and centrifuged at 16,300 g for 1 h. The adsorption studies of oxamyl and dimecron on three soils viz. red, alluvial and black was done by shaking soils with aqueous solution of oxamyl and dimecron in distilled water for 27 h in polyethylene tubes followed by centrifuged at 15000 g for 15 min (Bansal, 1982). Mishra and Joshi (1983) studied the adsorption of phosphamidon on four soils viz. red, alluvial, black and peat soils by shaking the soils with aqueous solution of pesticide in 0.01M $CaCl_2$ solution followed by centrifuged at 2000 rpm for 15 min. The adsorption studies of fenitrothion was done on five soils of Canada by shaking the soils with pesticide solution in distilled water for 24 h on magnetic stirrer followed by centrifuged at 15000 rpm for 10 min (Baarschers *et al.*, 1983).

Adhikari and Roy (1989) studied the adsorption of methyl parathion on Baruipur soils by shaking the soils with aqueous solution of methyl parathion in distilled water on a mechanical shaker fitted in a thermostat at a particular temperature followed by centrifuged. Adsorption studies of mevinphos on 20 soils of Spain was done by keeping the soils in contact with aqueous solution of mevinphos for 48 h in a thermostat controlled chamber at 20°C with intermittent shaking and centrifuged (Sanchez-Camazano and Sanchez-Martin, 1990).

Adhikari *et al.* (1991) studied the adsorption of sumithion on five soils viz. Burawan, Kakdwip, Mohitnagar, Krishnagar and Purilla by shaking the soils with aqueous solution of sumithion for 12 h at 30, 24 and 10°C in a thermostat followed by centrifuged. The adsorption for organophosphates (methyl parathion, methyl paraoxan, ethyl parathion, ethyl paraoxan) on eight soils (2 Mollic Solonetz, 4 humic combisols and 1 Pellic vertisols) was carried out by keeping the soils in contact with aqueous solution of pesticides in deionized water at 20°C for 24 h in a thermostat controlled chamber with intermittent stirring and centrifuged (Sanchez-Martin and Sanchez-Camazano, 1991).

Rao *et al.* (1991) studied the adsorption of triazophos on black and red soils by equilibrating the soils (by contact) with pesticide solution for 2 h, followed by centrifuged at 1000 rpm for 15 min. The adsorption studies of malathion on two sandy loam soils was done by intermittent shaking of soils with aqueous solution of pesticides in distilled water making use of glass stirrer at 12, 25 and 35±1°C in a constant temperature electrically heated water bath followed by centrifuged at 2,000 rpm for 5 min (Ali *et al.*, 1994).

Mandal and Adhikari (1995, 1997) studied the adsorption of metacid, sumithion, methyl parathion and fenitrothion on five soils viz. Bardhaman, Purulia, Mohitnagar, Kakdwip and Krishnagar by shaking the soils with aqueous solution of pesticides for 12 h in a thermostat at 33, 24 and 10±1°C followed by centrifuged. The adsorption of chlorpyrifos on sandy loam and loamy sand soils was carried out by shaking the chlorpyrifos in 0.01M $CaCl_2$ solution with soils on mechanical shaker for 3 h followed by centrifuged at 2500 rpm for 15 min. (Kumar, 1997).

2.2 Methods of desorption studies

2.2.1 Herbicides

The desorption of chlorsulfuron from four soils viz. Aredale silt loam, Cullen clay loam, Ronanoke sandy loam and Kenans ville loam were carried out by replacing a known quantity of supernatant with herbicide free 0.01N $CaCl_2$ solution, shaken for 24 h followed by centrifuged and the process was repeated for 2 desorption steps (Mersie and Foy, 1986). The desorption studies of atrazine from seven soils of Hyderabad and Devanur, Vijayapura and Arkunte regions was done by replacing the supernatant with 0.01M $CaCl_2$ solution shaken for 24 h and centrifuged at 10,000 g for 15 min. This procedure was repeated for 6 times (Raman et al., 1988; Kumaran and Devi, 1996). Desorption of atrazine from sharkey clay soil was also carried out by replacing the 10 ml supernatant with 0.01N $Ca(NO_3)_2$ solution, shaken for 24 h followed by centrifuged and the process was repeated for 6 consecutive desorption steps (Ma *et al.*, 1993).

The desorption studies of atrazine and its metabolities on Levy silt loam soils was done by replacing the 6.5 ml of supernatant with 0.01M $CaCl_2$ solution shaken at 250 rpm for 24 h and then centrifuged at 2000 g for 30 minutes (Mersie and Seybold, 1996). Shanti *et al.*(1997b) studied the adsorption of isoproturon from eight soils viz. four Alfisols and four Vertisols by replacing 5 ml of supernatant with 0.01M $CaCl_2$ solution incubated for 24 h and then centrifuged. Desorption of pendimethalin from three soils (1 clay and 2 sandy clay loam) was carried out by replacing the 2 ml supernatant with 2 ml of 0.01M $CaCl_2$ solution, shaken for 6 h and centrifuged at 15000 rpm for 15 min. The process was repeated for four times (Prakash and Devi, 1998).

The desorption of pendimethalin, fluracholin and oxadiazinon was carried out from sandy loam and clayey soils by replacing the supernatant with 20 ml of 0.01M $CaCl_2$ solution shaken for 30 min followed by centrifuged at 6000 rpm for 30 min (Raj *et al.*, 1999).

2.2.2 Organophosphates

For studying the desorption of parathion from three soils (Dark rendzina, Meron and Terra rossa) Saltzman *et al.* (1972) discarded the supernatant, replaced with same volume of water, equilibrated for 1 h in centrifuge tubes. The process was repeated for four times. Wahid and Sethunathan (1978) studied the desorption of parathion from 16 soils viz. Pakkali, Kari, Sandy Lateritic and Alluvials soils by replacing 5 ml of supernatant with distilled water, shaken for 2 h and centrifuged. The process was repeated for three times.

Sharom *et al.* (1980) studied the desorption of 12 insecticides viz. ethion, Chlorpyrifos, and diazinon etc. from four soils (organic soil, sandy loam, sediment and Plainfield sand) by replacing 190 ml of supernatant with distilled water, equilibrated by tumbling for 4 h followed by centrifuged and the process was repeated for four times. The desorption studies of methyl parathion from Barapur soil was carried out by immediately replacing 15 ml supernatant with distilled water, shaking on mechanical shaker fitted in water thermostat followed by centrifuged. The process was repeated for three times (Adhikari and Roy, 1989). Adhikari *et al.* (1991) studied the desorption of sumithion from five soils viz. Purulia, Mohitnagar, Kakdwip, Krishnagar and Bardhaman by replacing 10 ml of supernatant with 10 ml of 0.1N KCl solution, shaken for 12 h in a thermostat (33±1°C) followed by centrifuged. The process was repeated for three times.

The desorption of methyl parathion, fenitrothion, metacid and sumithion was carried out from five soils (Bardhaman, Purulia, Mohitnagar, Krishnagar and Kikdwip soils) by replacing the supernatant with equal volume of 0.01M KCl solution, shaken for 12 h in a thermostat followed by centrifuged. The process was repeated for 3 times (Mandal and Adhikari, 1995; Mandal and Adhikari, 1997). Kumar (1997) studied the desorption of chlorpyrifos from sandy loam and loamy sand soils by replacing supernatant with 0.01M $CaCl_2$ solution shaken mechanically for 3 h and centrifuged.

2.2 Extraction and clean up

2.2.1 Herbicides

Harvey (1974) extracted trifluralin from distilled water with benzene whereas nitralin and oxyzalin were extracted by using toluene. n-Hexane was used to extract atrazine, EPTC and tri-allate from aqueous solution (0.01M $CaCl_2$ solution) whereas dichloromethane was used for the extraction of prometon (Singh *et al.*, 1990). Fleming *et al.* (1992) used ethyl acetate to extract alachlor and metribuzin from deionised water.

Sonan and Schwab (1995) extracted alachlor and atrazine from supernatant (0.01M $CaCl_2$ solution) by using ethyl acetate. Mixture of ethyl acetate : n-Hexane (1:1, v/v) was used to extract anilophos from 0.1N $CaCl_2$ solution aqueous solution (Rai *et al.*, 1998). Raj *et al.* (1999) used toluene to extract pendimethalin, fluchloralin and oxadiazinon residues from 0.01M $CaCl_2$ solution. Trifluralin was extracted from water by partitioning it with hexane (Goyal, 2000). Rai *et al.* (2000) extracted pendimethalin from 0.1 N $CaCl_2$ solution with hexane : acetone (1:1, v/v) mixture.

2.3.2 Organophosphates

Leenheer and Ahlrichs (1971) extracted parathion from water by vigorous shaking it with doubly distilled methylene chloride. Chlorpyrifos from 0.01M $CaCl_2$ solution was extracted by partitioning it with benzene thrice (Felsot and Dahm, 1979). Sharom *et al.* (1980) extracted nine insecticides viz. chlorpyrifos. parathion, ethion, mevinphos, diazinon etc. from water by partitioning with hexane : acetone (4:1, v/v) mixture whereas mevinphos was extracted with benzene : acetone (4:1, v/v) mixture. Ethyl acetate was used to extract fenitrothion from water (Baraschers *et al.*, 1983). Misra and Joshi (1983) extracted phosphamidon from 0.01M $CaCl_2$ solution by partitioning thrice with chloroform. Triazophos was extracted from water by partitioning thrice with benzene (Rao *et al.*, 1991). Beltran *et al.* (1995) extracted three organophosphate pesticides viz. dimethoate, fenitrothion and methidathion from water by using dichloromethane. Chlorpyrifos was extracted from 0.01M $CaCl_2$ solution (supernatant) by partitioning thrice with benzene (Kumar, 1997). Rani (1998) extracted triazophos from canal water by partitioning it with hexane, thrice.

2.4 Estimation

Various analytical techniques used for estimation of herbicides and organophosphates includes colorimetric method and chromatographic techniques such as thin layer chromatography (TLC), gas liquid chromatography (GLC) and high performance liquid chromatography (HPLC). Various techniques followed for estimation of residues of herbicides and organophosphates are reviewed as under :

2.4.1 Colorimetric method

Colorimetric method has been widely used for estimation of residues of herbicides and organophosphate insecticides. The estimation of the herbicides viz. chlorsulfuron, metoxuron. atrazine was done by measuring the absorbance in the range of standard curve by the use of spectrophotometer (Shea. 1986;

Raman *et al.*, 1988; Kumaran and Devi, 1996; Shanti *et al.*, 1997a, b). The residues of malathion, parathion. methyl parathion. oxamyl. dimecron. mevinphos, sumithon and metacid were estimated by using the spectrophotometer by various research workers (Bansal, 1982; Adhikari and Roy, 1989; Adhikari *et al.*, 1991; Ali *et al.*, 1994; Mandal and Adhikari, 1995; Mandal and Adhikari, 1997).

2.4.2 Thin layer chromatography

Various research workers used the thin layer chromatography for the estimation of herbicides residues viz. norpropamide 4-(Trifluoromethyl), chlorobenenze, chlorsulfuron and organophosphates viz. phosphomidon, dimethoate. malation, dichlorvos and diazinon by coating the thin layer chromatography plates with soil slurries and using the mixture of suitable organic solvent with water in different ratios as developer (Wu *et al.*, 1975; Cocco and Ferrari, 1982; Misra and Joshi, 1983; Mersie and Foy, 1986; Khan and Khan, 1986; Arienzo *et al.*, 1994).

2.4.3 Gas liquid chromatography

2.4.3.1 Herbicides

Spencer and Cliath (1974) estimated trifluralin residues by using a Beckman GC-5 gas liquid chromatograph fitted with glass column (3m x ·43 cm) and a non-radioactive electron capture detector. Harvey (1974) used gas chromatograph with electron capture detector and stainless steel column (1.52 m x 3.1 mm) packed with 3% SE 30 on 100-120 acid washed, chromosorb W for determination of 9 dinitroaniline herbicides residues. A varian Gas chromatograph Model 2440, equipped with a scandium-tritide detector was used by Duseja and Holmes (1978) for determination of trifluralin residues.

Singh *et al.* (1990) used a varian 3700 gas chromatograph fitted with nitrogen phosphorus and ^{63}Ni electron capture detectors for residues estimation of four herbicides viz. atrazine, EPTC, prometom and triallate. Sonan and Schwab (1995) used gas chromatograph equipped with nitrogen-phosphorous detector for the determination of alachlor and atrazine residues. Rai *et al.* (1998) estimated anilophos residues by using Hewlett Packard 5890A Series II gas chromatograph equipped with ^{63}Ni electron capture detector. Hexazinone and simazine residues were estimated by Garcia-Valcarcel and Tadeo (1999) by using Hewlett Packard Model 5890 gas chromatograph fitted with nitrogen phosphorous detector and fused silica capillary column HP-I (12.5 m x 0.20 mm i.d.) and 0.33 µm film thickness. Raj *et al.* (1999) estimated pendimethalin, fluchloralin and oxadiazinon residues by using chemito gas chromatograph (Model 8510) fitted with different columns [Pyrex 1.5% OV-17 + 1.95 OF-1 (200 cm x 3 mm), GLT-5% OV-17 (200 cm x 3 mm) and capillary BP-10 (25 m x 0.22 mm] and equipped with electron capture detector. Pendimethalin residues were estimated by Rai *et al.* (2000) by using Hewlett Packard Model 5890 A Series-II gas chromatograph equipped with ^{63}Ni electron capture detector.

2.4.3.2 Organophosphates

Lichtenstein and Schulz (1964) used gas chromatograph equipped with tritium electron affinity ionization detector and stainless steel column (1.22 m x 3.00 mm i.d.) packed with 5% DOW-11 silicone grease on chromosorb-W, 60-80 mesh for the detection of residues of parathion and methyl parathion. Chapman and Harris (1980) and Chapman *et al.* (1982a, b) analysed residues of terbufos, terbufos sulfone and phorate on gas chromatograph fitted with rubidium sulphate alkali detctor and glass column measuring 1.80 m x 2 mm i.d. packed with 5% OV-1 (for terbufos and its metabolites) and 5% DC-200 (for phorate) on Carbowax-20M, 100-120 mesh. Talekar *et al.* (1983) estimated triazophos residues by using gas chromatograph equipped with a Melpar flame photometric detector (phosphorus made by 526 m) interference filter. Barcelo *et al.* (1991) used mass spectrometric and gas chromatograph fitted with nitrogen-phosphorus detector for estimation of organophosphate residues. Various research workers have used gas chromatograph with nitrogen phosphorus and flame photometric detector for various organophosphate insecticides including triazophos (Malto *et al.*, 1991: Katagi *et al.*, 1993; Mohapatra *et al.*, 1994). Gajbhiye *et al.* (1995) estimated residues of various organophosphate insecticides using gas chromatograph equipped with megabore column HP-1 (10 m x 0.53 mm x 2.63 μm) and flame ionization detector (phosphorus made). Wylie and Uchiyama (1996) used gas chromatograph equipped with nitrogen phosphorus and mass selective detector with pulsed splitless injection system for the analysis of organophosphate insecticides.

2.4.4 High performance liquid chromatography (HPLC)

2.4.4.1 Herbicides

Clay *et al.* (1988) used Hewlett Packard 1090 HPLC equipped with ODS-Hypersil column with methanol/water (60:40. v/v) as mobile phase for atrazine residues and acetonitrile-water (40:60, v/v) as mobile phase for cyanazine residues estimation. Gamerdinger *et al.* (1991) estimated three-triazine herbicides residues by using Hewlett Packard 1090A HPLC equipped with a diode array model of UV detector with mobile phase [methanol-water (55:45,v/v) buffered to pH of 6.8] for atrazine and cyanazine, (45:55. v/v) for simazine Ma *et al.* (1993) determined atrazine residue by using methanol-water (70:30. v/v) as a mobile phase. Acifluorfen residues were estimated by using varian 5020 instrument equipped with a UV-Visible detector with water acidified to pH 3 plus acetonitrile as mobile phase (30:70, v/v) (Gennari *et al.*. 1994). Ukrainczyk and Ajwa (1996) used a variable wavelength detector with acetonitrile-0.1M acetic acid (70:30, v/v) as mobile phase for primisulfuron residues estimation. Nicosulfuron residues were estimated by using acetonitrile with 0.1% (v/v) phosphoric acid (A) and water with 0.1% (v/v) phosphoric acid (B) as a mobile phase (Ganzalez and Ukrainczyk, 1996). Pusino *et al.* (1997) used a water 501 liquid chromatograph equipped with a multiwavelength waters 490 programmable detector with [acetonitrile + water + methanol (25:70:5 by volume, pH 3)] as mobile phase for imazapyr residues estimation.

Atrazine and MCPA residues were also estimated by using diode array detector with acetonitrile-water (60:40, v/v) and acetonitrile-water (0.02% H_3PO_4) as mobile phases, respectively (Socias-Viciana *et al.*, 1999). Harberhaver *et al.* (2000) estimated phenoxyalkanoic herbicides by using UV detector with methanol-water mixture (ratio 65:35) with 0.5% acetic acid (isocralic elution) as mobile phase.

2.4.1.2 Organophosphates

Skelly *et al.* (1981) used a method utilizing Zorbex® ODS column with acetonitrile-water-acetic acid (82:17.5:0.5, v/v) as mobile phase and UV detector for the estimation of chlorpyrifos residues. Dickinson *et al.* (1988) used HPLC method for the determination of temephos residue in water. The method was found to be reliable for measuring concentration of 0.005-5.00 ppm. The detection limit was 1 ng at 254 nm. Rodriguez *et al.* (1991) estimated the residues of acephate from aqueous extracts of agriculture soils by using a C_{18} reverse phase column, a mobile phase of 5% (v/v) methanol-water and UV detection at 215 nm. Racke *et al.* (1996) estimated chlorpyrifos residues from 37 different soils by using μ Bandapak C_{18} column (10 cm x 0.8 cm) with 100% solvent A [water : acetonitrile : glacial acetic acid (90:10:0.5, v/v)] to 100% solvent B [acetonitrile : water : glacial acetic acid (90:10:0.5, v/v)].

2.4.5 ELISA Technique

To screen water samples collected from the Cameron Highlands, Malaysia for the estimation of fenitrothion and chlorpyrifos residues, Nazni *et al.* (1995) used an ELISA technique (Envirogard Kits). Oubina *et al.* (1996) used a magnetic particle based ELISA technique for the determination of chlorpyrifos ethyl from soil samples and reported that substantial saving time was achieved when compared to conventional methods which require a clean up step prior to chromatographic determination.

2.5 Adsorption-desorption behaviour

2.5.1 Herbicides

2.5.1.1 Metribuzin

Several batch-type laboratory studies have been reported high and strong adsorption of herbicides on soil organic matter using variety of soils. Telbert *et al.* (1974) reported that among 21 out of 27 soil properties, including total C, CEC and coarse clay content, there was a high correlation between I_{50} (50% inhibition of fresh weight of cucumber biassay) and metribuzin adsorption for a number of soils. Sharon (1974) observed that the distribution co-efficient (Kd=0.562 to 31.667) for the adsorption of metribuzin on eight Ontario soils were significantly correlated with the soil organic matter content and almost all the adsorbed metribuzin was desorbed from mineral soils after six aqueous extractions; however, substantial amount of metribuzin remained adsorbed on the muck soils after 10 aqueous extractions. Soil organic matter and clay contents were correlated significantly with K values (0.25 to 2.2) as observed from the adsorption studies of ^{14}C-metribuzin on 16 soils of lower alluvial flood plain of Mississippi river (Savage, 1974).

The distribution coefficient for the adsorption of metribuzin on eight Ontario soils varied from 0.56 for the least adsorptive Fox sandy loam soil to 31.67 for the most highly adsorptive Leaming much soil and most of the adsorbed metribuzin was desorbed from mineral soils after 6 aqueous extractions; however, substantial amounts of metribuzin remained adsorbed on the muck soils after 10 aqueous extractions (Sharom and Stephenson, 1976). Savage (1976) reported that metribuzin adsorption was significantly associated with clay content organic matter and water content. The adsorption of ^{14}C-metribuzin on soils increased gradually as soil pH decreased towards the pK$_a$ values of metribuzin for a number of soils (Ladlie *et al.*, 1976).

Metribuzin adsorption on various soil types was reported to be influenced more by organic matter content than by clay (Pestemer and Mass. 1977). Filep *et al.* (1979) reported the degree of adsorption of metribuzin on three soils viz. chernozem, alluvial meadow and brown forest with clay illuviation soils, was influenced mainly by the quantity of the organic and mineral colloids because there was no great differences between the colloid content and pH values of the investigated soils.

The adsorption of four triazines herbicides including metribuzin on various soils of China were found to be decreased with increasing soil pH

(Chang, 1980). The metrabuzin adsorption on Dundee silty clay loam surface and subsurface soils was correlated more to clay content of the soils. The combination of two variables most related to adsorption was clay and pH and metribuzin was easily desorbed in all the soils with <5% of the originally applied metribuzin remaining after three desorption treatment (Harper. 1988). Peek and Appleby (1989) reported that the adsorption of metribuzin and ethyl metribuzin on sandy loam soil decreased as pH increased. Organic matter was shown to influence the adsorption of four herbicides including metribuzin on various soils of Prauge (Kozak and Lopuchin, 1989). Garcia-Valcarcel *et al.* (1997) reported that there was no correlation between metribuzin adsorption with organic matter content for eight Spanish soils.

2.5.1.2 Trifluralin

Jacques and Harvey (1979) reported that adsorption of trifluralin on 10 Wisconsin soils (mean K_{oc}= 810) increased with increasing soil organic matter content. Neither pH nor clay content made any significant correlation with the adsorption of trifluralin on five soils viz. Melfort loam. Weyburn oxbow sandy loam, Regina clay, Indian head sandy loam and Asquith loamy sand whereas adsorption of trifluralin on these soils increased with increasing soil organic matter (Grover *et al.*, 1979). Similar correlation for adsorption of trifluralin with soil organic matter was reported by Moyer (1979) for 11 North Carolina soils (K_{oc} = 10,945). This trend was also reflected in the loss of phytotoxicity. Phytotoxicity of trifluralin was less in higher organic matter content soils than in lower organic matter content of soils (Grover *et al.*, 1979). Kenaga (1980) and Briggs (1981) used mean K_{oc} values of 13,700 for trifluralin in soils for calculation of its bioaccumulation factor. McCall *et al.* (1980) and Rao *et al.* (1985) used mean K_{oc} values of trifluralin in soils for mobility classification and modeling, respectively. The increase in adsorption of trifluralin with organic matter was reported by Peter and Weber (1985) for nine North Carolina soils (mean K_{oc} = 4,563), and by Saunders and Powers (1988) for four soils (mean K_{oc} = 9,543) obtained from various locations of U.S.

Saunders and Powers (1988) reported that the mean slopes of initial isotherms of adsorption were linear with 1/n values equal to or near 1.0. The desorption isotherms, however, were non linear with means of slopes ranging from 0.3 to 0.6 depending on the soil type. These data indicate strong resistance to desorption or possibly hysteresis. Jolly *et al.* (1990) reported that organic matter has been shown to affect trifluralin persistence by increasing the adsorption of trifluralin to soil and thus decreasing its degradation. The adsorption of trifluralin was significantly affected by the content of organic matter in soils (Zheng and Wang, 1993). Moura Pries-N-de *et al.* (1997) also reported that trifluralin adsorbed on clay soils, rich in organic matter than sandy loam soils. Trifluralin adsorption increases with the increase in soil organic matter content. The higher K_{oc} values and low desorption from organic constitutents indicates that trifluralin is relatively immobile in soil (Grover *et al.*, 1997).

2.5.1.3 Other herbicides

Hirai and Kawamura (1975) reported that soil organic matter acted as an adsorbent for oxadiazinon adsorption on 29 type of paddy soils whereas Carringer *et al.* (1975) observed that the adsorption of 10 herbicides viz. butralin. profluralin. norflurazon, dicamba etc. on soil organic matter was inversely correlated (proportional to) with their water solubilities. Jacques (1977) reported that the adsorption of six dinitroaniline herbicides on Wisconin soils was more closely related to soil organic matter than to other physical and chemical properties of soils. The adsorption of three dinitroaniline herbicides viz. dinitromine, fluchloralin and profluralin was directly proportional to organic matter content and the length of aniline side chain whereas desorption was inversely proportional to soil's organic matter content (Akins, 1977). Smit *et al.* (1980) reported that adsorption of atrazine was found to be decreased with increase in pH for three soils of South-Africa. The adsorption of atrazine and simazine on three soils (red, black and alluvial) of Karnataka was depended mainly on the quantity and nature of organic fraction in the soils (Rajanna and Devi, 1987). Seybold *et al.* (1994) correlated the adsorption of atrazine on the five soil viz. Sparta, Plainfield, Tarr, Shawano and Rousseau soils with the organic carbon content (Kd = 0.025 to 4.680). The extent of hysteresis during adsorption and desorption of atrazine was a function of incubation time for a sharkey soil (Ma *et al.*, 1993).

Sonan and Schwab (1995) reported that atrazine and alachlor adsorption on five soils viz. Kansas, Pratt, Kahala, Smolan, Eudora and Naron regions was not related to organic carbon or clay but there was a correlation between sand and silt (K_{oc} = 50 to 2950 for atrazine and 37 to 457 for alachlor) whereas Kumaran and Devi (1996) reported that adsorption of atrazine increased with organic matter addition in three soils and it was favoured by acidic pH in Vijayapura soil, whereas the type of clay and native organic matter, contributed more towards adsorption in Devanur soil. The adsorption and desorption of pendimethalin on six soils viz. Ferralsol, Regosal, Andosol, Fluvisol and 2 Vertisol was correlated with the physico-chemical properties of herbicides (water solubilities and octanol/water partition coefficient) (Zheng and Copper, 1996). They also reported that clay and sand (CEC) of soils play important role in the adsorption-desorption of the pendimethalin on soils.

Jenks *et al.* (1998) reported that atrazine adsorption was highly correlated with organic matter content and soil pH ($K_{f,oc}$ = 169 to 371). Prakash and Devi (1998) also reported that organic carbon content was the most influential parameter for pendimethalin adsorption on three soils viz. 1 clay and 2 sandy loam soils (K_{oc} = 5842 to 6726) and addition of farm yard manure (FYM) increases pendimethalin adsorption by soils (K_{oc} = 4548 to 6195) (Prakash and Devi, 1998). Socias-Viciana *et al.* (1999) observed that adsorption of atrazine and MCPA on four soil types from Almeria region (South-Eastern Spain) increased with increase in organic matter (Mean K_{oc} = 239.8 for atrazine and

70.41 kg^{-1} for MCPA). Raj *et al.* (1999) also reported that the adsorption of pendimethalin, fluchloralin and oxadiazinon on clayey and sandy loam soils was better correlated with organic matter content of the soils than clay content, as organic matter gave high K_{oc} values for both the soils.

Sanchez-Camazano *et al.* (2000) observed that adsorption of linuron on 39 soils was significantly correlated with organic matter content and with clay and silt contents for soils having organic matter less than 2 per cent. Rai *et al.* (2000) reported that the adsorption of pendimethalin on six soils viz. Affsol, Aridisol, Inceptisol, Vertisol and Mollisol regions was correlated with the organic matter content of soils (K_{oc} = 1926 to 5041). They also reported that in the organic matter free soils, clay content played important role in the adsorption of pendimethalin which is further controlled by pH and types of clay.

2.5.2 Organophosphates

Felsot and Dham (1979) correlated the adsorption of four organophosphate insecticides on five soils viz. clarion, Peat and Harsps regions were correlated with the organic matter content (mean K_{om} = 250-2645). They also reported that destruction of organic matter resulted decrease in adsorption. Kishk *et al.* (1979) reported that adsorption of methyl parathion on three soils viz. El-Nanda, Tel El-Kobeer and Tahreer regions was correlated with the organic matter content in the soils. The adsorption of phosphomidon on four soils viz. alluvial, black and red soils was correlated not only with the organic matter but also with high exchangeable bases and high clay content of the soils (Misra and Joshi, 1983). Baarschers *et al.* (1983) reported that fenitrothion adsorption increased or mobility decreased with increase in percentage organic matter in five soil of Canada (K_f=15.5 to 354.8). Reddy and Gambrell (1987) also reported that organic matter was the most important single factor affecting adsorption of methyl parathion. Valverde-Garcia *et al.* (1988) observed that adsorption of thiram and dimethoate on Andalucian soils seems to be conditioned by soil organic matter content, specific surface area and CEC of soils, respectively (K_f= 1.06 to 13.73). The most important parameter in the adsorption of mevinphos by soil was the clay content, adsorption being facilitated by the clay-organic matter complex (Sanchez-Camazano and Sanchez-Martin, 1990). Singh *et al.* (1990) also reported that the organic matter content of the soils was the most important factor which determined the rate of adsorption-desorption of methyl parathion and fenitrothion on four soils. Adhikari *et al.* (1991) observed that correlation between adsorption and organic matter was positive and significant (K=5.00±0.37 to 44.60±3.40). They also reported that increase in temperature resulted decrease in adsorption of sumithion on four soils viz. Bardwan. Mohitnagar, Krishnagar and Kakdwip regions and negative value of enthalphy indicates physical nature of adsorption. Rao *et al.* (1991) reported that the adsorption of triazophos on black soil was higher than red soil which may be possibly due to higher CEC, organic matter content, higher surface area and higher exchangeable Ca^{++} content of black soil (K_0 = 43.1 to 70.4, respectively) and adsorption of triazophos is minimum at neutral pH, possibly due to direct association of the chemical with the cation over adsorbing surface, thus favouring the maximum adsorption. The amount of phosphomidon adsorbed on soils (loam and black silty clay loam) was lower in Tarai loam soil than black silt clay loam soil and was related to organic matter content, clay content, $CaCO_3$ content, surface area and CEC of the soils. It was also found that phosphomidon adsorption was slightly better correlated with clay content than organic matter content (Kumari and Singh, 1994). Ali *et al.* (1994) reported that adsorption of malathion on two sandy loam soils was dependent on temperature, pH, organic matter, exchangeable cations and clay contents of the soils.

Mandal and Adhikari (1995, 1997) reported that adsorption of metacid, sevin, sumithion was largely controlled by organic matter content whereas in case of organic matter free soils (after treatment with H_2O_2), clay minerals, Al_2O_3, Fe_2O_3 and specific surface area accounts for major variation of the adsorption of these pesticides on five soils viz. Kakdwip, Bradhaman, Purulia, Mohitnagar and Krishnagar regions. Bolan and Baskaran (1997) reported that the adsorption of ^{14}C-phorate on soils of Egmont and Tokomaru regions was correlated with the organic matter of the soils.

2.6 Equilibrium studies

2.6.1 Herbicides

Wu *et al.* (1975) observed that adsorption equilibrium for four pesticides on five soils viz. cobb sand, cobb sand + 1% organic matter, cobb sand + 2% organic matter, silty clay loam and sandy loam was achieved within 8 h. The adsorption equilibrium for metribuzin on eight agronomic and model soils approached before 10^5 min (<70 day) by keeping the soil in contact with metribuzin solution (Lafleur. 1979). Winkel (1980) reported that adsorption equilibrium for atrazine and alachlor was approached in 12 h for silty clay loam soil and in 24 h for loam soil by keeping the pesticide solution in contact with soils. Adsorption equilibrium for ^{14}C-2,4,5-T on Palouse and Glendale regions soils was approached within 24 h and same time was found to be sufficient for desorption equilibrium (Koskinen *et al.*, 1979). Gamerdinger *et al.* (1991) reported that adsorption equilibrium for three 2-chloro s-triazine herbicides on soils of Voloisand and Rainbecks regions was approached in 48 h. Adsorption equilibrium of acifluorfen on five soils viz. Entisol, Inceptisol, Andosol regions was complete in 16 h and for desorption equilibrium 2 h was found to be sufficient (Gennari *et al.*, 1994). Sensi *et al.* (1997) reported that adsorption equilibrium of imazethapyr on four soils of Trani and Andria regions was approached within 20 h by magnetic stirring. The adsorption equilibrium for imazethapyr on six soils (clay loam, loamy sand and sandy loam) was reached within 20 h (Pusino *et al.*, 1997). Jenks *et al.* (1998) reported that adsorption equilibrium of atrazine on Hastling silty clay loam soils of depth upto 30 cm was approached in 48 h while the adsorption equilibrium for soils of depth more than 30 cm was completed in 4 h. No significant change was found in pendimethalin adsorption on three soils (clay, sandy loam) after 6 h of shaking on wrist action shaker (Prakash and Devi, 1998). Bresnahan *et al.* (2000) observed that the adsorption equilibrium for three pesticides was almost completed within 1 h of mechanical shaking.

2.6.2 Organophosphates

Leenheer and Ahlriches (1971) reported that adsorption equilibrium of parathion on three soils (Zensville silt loam, Rommey silty clay loam and Carlisle muck) was approached after 24 h of mechanical shaking. Adsorption equilibrium of parathion on three soils viz. Dark rendzina, Meron and Terra rossa reached within 1 h by keeping the soils in contact with pesticide solution. Felsot and Dahm (1979) reported that adsorption equilibrium for four organophosphates insecticides on five soils (Clarion, Peat, Sharpy fine sandy loam, Thurman loamy sand and Harps of Iowa) was approached within 2 h of mechanical shaking. The adsorption equilibrium of oxamyl and dimecron on three soils (red, black and alluvial) was approached within 27 h of shaking (Bansal, 1982). Adhikari *et al.* (1991) reported that 12 h was sufficient for attainment of sumithion adsorption equilibrium on five soils viz. Kakdwip, Mohitnagar, Krishnagar, Purulia and Burdwan regions. Adsorption equilibrium for four organophosphate insecticides (methyl parathion, methyl paraoxon, ethyl parathion, ethyl paraoxan) on eight soils (Mollic solonetz, Humic combisol and Pellic vertisols) was attained within 24 h by keeping the soils in contact with pesticide solution and intermittent stirring (Sanchez-Martin and Sanchez-Camazano, 1991). Rao *et al.* (1991) reported that adsorption equilibrium of triazophos on black and red soils was attained by keeping the soils in contact with aqueous solution of triazophos for

1.5 h. The adsorption equilibrium for the adsorption of ^{14}C-diazinon on 25 soils of Marismas and Solamanca regions was approached within 24 h (Arienzo *et al.*, 1994). Mandal and Adhikari (1997) reported that the adsorption equilibrium of metacid and sumithion on five soils viz. Kakdwip, Mohitnagar, Purulia, Krishnagar and Burdwan regions was approached within 12 h of magnetic stirring.

3. MATERIALS AND METHODS

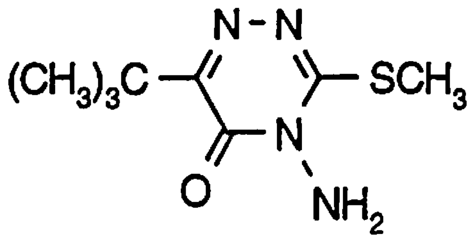
Testing of promising insecticides for the control of insect-pests of cultivated crops, vegetables, fruits, fodders etc. is the main research activity of Pesticide Residue Laboratory of the Department of Entomology, CCS Haryana Agricultural University, Hisar from point of view of their efficacy, residual toxicity and safety to the consumers. In present studies, adsorption equilibrium and adsorption-desorption behaviour of three pesticides viz. metribuzin, trifluralin and triazophos on two types of soils viz. sandy loam and clay loam have been studied from the point of view of determination of amounts of pesticide adsorbed on soil and thereafter its desorption from soil. This chapter provides information regarding the materials used and techniques employed to achieve the objectives of the proposed studies. Experimental details have been provided under the following heads :

3.1 Physico-chemical and toxicological characteristics of pesticides

3.1.1 Metribuzin

Common name	:	Metribuzin
Chemical name	:	4-amino-6-(1,1-dimethyl ethyl)-3-(methylthio)-1,2,4-triazin-5(4H)-one

Structure:



Molecular weight : 241.3

Molecular formula : $C_8H_{14}N_4OS$

Chemical family : Triazine

Trade name : Sencor

Physical state : White crystal with weak characteristic odour

Melting point : 126.2°C

Vapour pressure (mPa at 20°C) : 0.058

Source of analytical grade : M/s Bayer (India) Ltd.
New Delhi

Formulation used : 70% W.P.

Solubility (g substance in 1000 ml solvent at 20°C)

Water : 1.05
Dimethyl formamide : 1780
Acetone : 820
Dichloromethane : 340
Hexane : 1

Mode of action : Selective systemic herbicide. Translocation acropetally in the xylem

Toxicity (acute-oral LD_{50}) :
Rats : 2000 mg/kg
Mice : 700 mg/kg
Cats : >500 mg/kg

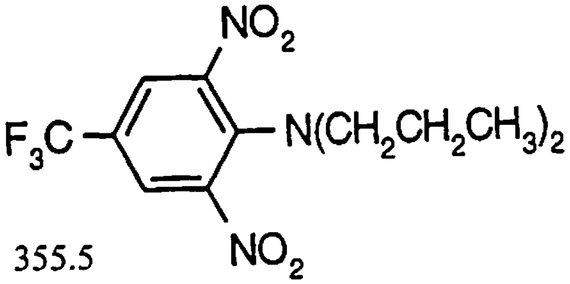
Ref. The Pesticide Manual (Tomlin, C.D.S., 1997)

3.1.2 Trifluralin

Common name : Trifluralin

Chemical name : α,α,α-trifluoro-2,6-dinitro-N.N-dipropyl-p-toluidine

Structure :



Molecular weight : 355.5

Molecular formula : $C_{13}H_{16}F_3N_3O_4$

Chemical family : Dinitroaniline

Trade name : Treflan

Physical state : Yellow orange crystals

Melting point : 48.5-49°C (technical ≥95%)
42°C (Pure)

Vapour pressure (mPA at 25°C) : 13.7

Source of analytical grade : De-Nocil Crop Production Ltd., Mumbai

Formulation used : 48% EC

Solubility (g substance in 1000 ml of solvent at 27°C)

Water : 0.001
Acetone : >1000
Hexane : 50-67

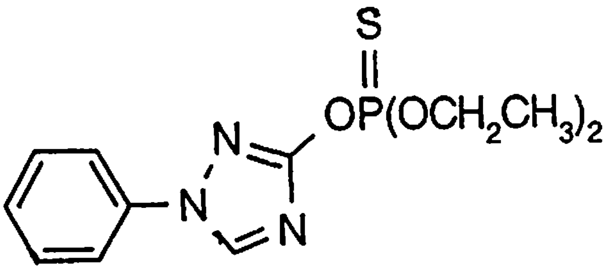
Mode of action : Acts by entering in the hypocotyl region and disturbing cell division, also inhibit root development

Toxicity (acute-oral LD_{50})

Rats	:	>10,000 mg/kg
Mice	:	500 mg/kg
Dogs	:	>2000 mg/kg

Ref. The Pesticide Manual (Tomlin, C.D.S., 1997)

3.1.3 Triazophos

Common name	:	Triazophos
Chemical name	:	3-(O,O-Diethyl)-1-Phenyl thiophos phoryl 1,2,4-triazole
Structure	:	
Molecular weight	:	313.3
Molecular formula	:	$C_{12}H_{16}N_3O_3PS$
Chemical family	:	Organophosphate triazole
Trade name	:	Hostathion
Physical state	:	Pale-yellowish liquid
Melting point (°C)	:	2-5
Vapour pressure (mPa at 55°C)	:	13
Source of analytical grade	:	M/s Hoechst Schering Agr Evo Ltd.. Germany
Formulation used	:	40% EC

Solubility (g substance in
1000 ml of solvent at 20°C) :

Water	:	0.003-0.039
Acetone and ethyl acetate	:	>500
n-Hexane	:	11.1

Mode of action : Cholinesterase inhibitor

Toxicity (acute-oral LD_{50}) :

Rats	:	57-68 mg/kg
Dogs	:	>320 mg/kg

Ref. The Pesticide Manual (Tomlin, C.D.S., 1997)

3.2 Preparation of solutions

3.2.1 Preparation of standard solutions

The standard solutions for the GLC assay were prepared from the analytical grade of metribuzin. trifluralin and triazophos. The details of solutions are given below :

3.2.1.1 Preparation of standard solutions of metribuzin

The standard solutions of metribuzin were prepared by using methanol as solvent.

Stock solution 'A' (100 ppm) was prepared by dissolving precalculated (10 mg) amount of pure (99.9%) analytical grade of metribuzin in 100 ml of methanol.

Stock solution 'B' was also prepared by using methanol as a solvent. Ten ml of 'A' and 90 ml of methanol = 10 ppm (10 µg of of metribuzin/ml of solution).

Ten ml of 'B' + 90 ml of n-Hexane = 1 ppm (1 μg of metribuzin/ml of solution) (stock solution 'C').

Five ml of 'C' + 20 ml of n-Hexane = 0.2 ppm (200 ng of metribuzin/ml of solution) (Stock solution 'D').

3.2.1.2 Preparation of standard solutions of trifluralin

The standard solutions of trifluralin were prepared by using n-Hexane : acetane (9:1) mixture as solvent.

Stock solution 'A' (100 ppm) was prepared by dissolving 10 mg of pure (99.9%) analytical grade of trifluralin in 100 ml of n-Hexane-acetone mixture (9:1, v/v) as solvent.

Ten ml of 'A' + 90 ml of n-hexane : acetone = 10 ppm (10 μg of trifluralin/ml of solution) (Stock solution 'B').

Ten ml of 'B' + 90 ml of n-Hexane = 1 ppm (1 μg of trifluralin/ml of solution) (Stock solution 'C').

Five ml of 'C' + 20 ml of n-hexane = 0.2 ppm (200 ng of trifluralin/ml of solution) (Stock solution 'D').

3.2.1.3 Preparation of standard solutions of triazophos

The standard solutions of triazophos were prepared by using acetone and ethyl acetate as solvent.

Stock solution 'A' (100 ppm) was prepared by dissolving the precalculated amount of analytical grade (purity 40.7%) of triazophos in 100 ml of acetone.

Ten ml of 'A' + 90 ml of ethyl acetate = 10 ppm (10 μg of triazophos/ml of solution) (Stock solution 'B').

Ten ml of 'B' + 90 ml of ethyl acetate = 1 ppm (1 μg of triazophos/ml of solution) (Stock solution 'C').

Five ml of 'C' + 20 ml of ethyl acetate = 0.2 ppm (200 ng of triazophos/ml of solution) (Stock solution 'D').

3.2.2 Preparation of calibration curve of pesticides

1, 10, 20, 30, 40, 50 and 100 pg of standard metribuzin, trifluralin and triazophos were injected into the gas chromatograph operated under condition given under section 3.6. A calibration curve for each individual pesticide was obtained by plotting the amount of pesticide injected (pg) along X-axis and detector response (area) along Y-axis (Fig. 1 to3).

3.2.3 Preparation of formulation solutions

The formulation solutions of metribuzin, trifluralin and triazophos were prepared for adsorption equilibrium and adsorption-desorption studies of these pesticides on soils.

3.2.3.1 Preparation of formulation solutions of metribuzin

The metribuzin formulation solutions were prepared from 70% WP by using methanol as solvent.

Metribuzin 70% WP i.e. 100 mg represent 70 mg a.i. of metribuzin. For stock solution 'A' (700 ppm) 100 mg of 70% WP metribuzin was dissolved in 100 ml (700 μg/ml of solution) of methanol.

14.3 ml of 'A' – 85.7 ml of methanol = 100 ppm (100 µg/ml of solution) (Stock solution 'B').

Ten ml of 'B' – 90 ml of methanol = 10 ppm (10 µg/ml of solution) (Stock solution 'C').

Ten ml of 'C' – 90 ml of n-Hexane = 1 ppm (1 µg/ml of solution) (Stock solution 'D').

3.2.3.2 Preparation of formulation solutions of trifluralin

The formulation solutions of trifluralin were prepared from 48% EC by using Hexane : acetone (80 : 20, v/v) as a solvent.

Trifluralin 48% EC i.e. 1 ml (1 g) represent 0.48 g or 480 mg a.i. of trifluralin. Stock solution 'A' (4800 ppm) was prepared by dissolving 1 ml of 48% EC trifluralin in 100 ml of hexane : acetone (80:20, v/v) solution.

1.04 ml of 'A' 98.86 ml of n-hexane = 50 ppm (50 µg ml of solution) (Stock solution 'B').

Five ml of 'B' + 20 ml of acetone = 10 ppm (10 µg/ml of solution) (Stock solution 'C').

Ten ml of 'C' + 90 ml of n-Hexane = 1 ppm (1 µg/ml of solution) (Stock solution 'D').

3.2.3.3 Preparation of formulation solutions of triazophos

The formulation solutions of triazophos were prepared from 40% EC triazophos by using acetone : n-hexane (50:50, v/v) as solvent.

Triazophos 40% EC i.e. 1 ml (1 g) represent 0.4 g or 400 mg a.i. of triazophos.

Stock solution 'A' (4000 ppm) of triazophos was prepared by dissolving 1 ml (1 g) of 40% EC triazophos in 100 ml of hexane : acetone (50:50, v/v).

2.5 ml of 'A' ÷ 97.5 ml of ethyl acetate = 100 ppm (100 µg/ml of solution) (Stock solution 'B').

Ten ml of 'B' ÷ 90 ml of acetone = 10 ppm (10 µg/ml of solution) (Stock solution 'C').

Ten ml of 'C' + 90 ml of ethyl acetate = 1 ppm (1 µg/ml of solution) (Solution solution 'D').

3.2.3.4 Active ingredient checking of metribuzin, trifluralin and triazophos formulations

The active ingredient of formulation of each pesticide (Sencor 70% WP. Treflan 48% EC and Hostathion 40% EC) was checked by injecting the stock solution 'D' of the formulation in Gas Chromatograph and the data obtained was compared by injecting stock solution 'D' of the standard in Gas Chromatograph.

3.2.4 Preparation of calcium chloride solution

Preparation of 0.1M calcium chloride solution

11.1 g of anhydrous calcium chloride was dissolved in one litre distilled water.

For preparing 0.01M $CaCl_2$ solution, 100 ml of 0.1M $CaCl_2$ solution was diluted (with distilled water) to 1000 ml.

3.3 Reagents

- Metribuzin analytical grade
- Trifluralin analytical grade
- Triazophos analytical grade
- Acetone (AR)
- Hexane (AR)
- Dichloromethane (AR)
- Ethyl acetate (AR)
- Methanol (AR)
- Sodium chloride
- Anhydrous sodium sulphate (AR)
- Mineral oil (paraffin)
- Calcium chloride

Equipments

- Digital analytical balance
- Centrifuge (Remi R-22)
- Centrifuge tubes
- Rotary vacuum flash evaporator
- Glass manifold air evaporator
- Gas liquid chromatograph (Hewlett Packard Model-5890A)

Others

- Cotton
- Filter papers

3.4 Recovery experiments

In order to test the efficiency and accuracy of the analytical methods of residues estimations of metribuzin, trifluralin and triazophos, recovery experiments were conducted by fortifying the 0.01M $CaCl_2$ solution (at 0.25 and 0.5 ppm fortification levels) with standard solutions of metribuzin. trifluralin and triazophos. In 500 ml beaker, 100 ml of 0.01 M $CaCl_2$ solution sample was taken. The calcium chloride solution was spiked with metribuzin at 0.25 and 0.5 ppm levels by adding 25 and 50 µg of metribuzin from standard solution. The samples were replicated thrice and one control was taken with no pesticide in it. The spiked samples were kept for four hours and processed as per details given under section 3.5.

For conducting the recovery experiments of trifluralin and triazophos. each set of 0.01M calcium chloride solution was spiked (0.25 and 0.5 ppm level) with standard solutions of trifluralin and triazophos separately, as stated above and processed as per details given under section 3.5.

3.5 Processing of samples

3.5.1 Extraction and clean-up

The extraction and clean up of metribuzin. trifluralin and triazophos from 0.01 M calcium chloride solution containing these pesticides was done as given below :

3.5.1.1 Metribuzin

1. 100 ml of 0.01M calcium chloride solution containing metribuzin was taken in 500 ml separatory funnel and 2 g sodium chloride was added.
2. Calcium chloride solution was partitioned with dichloromethane : ethylacetate (9:1, v/v) mixture thrice (40,25,20ml) and the dichloromethane : ethyl acetate layer was collected through anhydrous calcium chloride. Rinsing was done with 10 ml dichloromethane : ethyl acetate mixture.
3. The dichloromethane : ethyl acetate extract was concentrated to near dryness on rotary vacuum flash evaporator by putting one drop of mineral oil followed by manifold evaporator and the process was repeated three times after rinsing with hexane to eliminate the traces of dichloromethane.
4. The final volume (2 ml) was made in n-hexane for GLC injection.

3.5.1.2 Trifluralin

1. 100 ml of 0.01 M calcium chloride solution containing trifluralin was taken in 500 ml separatory funnel and 1.6 ml of conc. HCl was added.
2. Calcium chloride solution was partitioned with hexane thrice (30, 20, 20 ml) and the hexane layer was collected through anhydrous sodium sulphate. Rinsing was done with 10 ml hexane.

3. The hexane extract was concentrated to near dryness on rotary flash evaporator by putting one drop of mineral oil followed by manifold evaporator.
4. The final volume (2 ml) was made in n-hexane for GLC injection.

3.5.1.3 Triazophos

1. 100 ml of 0.01M calcium chloride solution containing triazophos was taken in 500 ml separatory funnel and 2 g of sodium chloride was added.
2. Calcium chloride solution was partitioned with hexane thrice (30, 20. 20 ml) and hexane layer was collected through anhydrous sodium sulphate. Rinsing was done with 10 ml hexane.
3. The hexane extract was concentrated to near dryness on rotary flash evaporator by putting one drop of mineral oil followed by manifold evaporator.
4. The final volume (2 ml) was made in ethyl acetate for GLC injection.

3.5.2 Calculations of recovery experiment

Per cent recovery was calculated as :

$$\text{Amount recovered } (\mu\text{g}) = \frac{\text{Amount of standard injected (pg)} \times \text{Area of sample injected} \times \text{Final volume of sample (ml)}}{\text{Area of standard injected} \times \text{Volume of sample injected } (\mu\text{l})}$$

$$\text{Per cent recovery} = \frac{\text{Amount recovered } (\mu\text{g})}{\text{Amount added } (\mu\text{g})} \times 100$$

3.6 GLC parameters

3.6.1 Metribuzin

i) Model : Hewlett Packard Model-5890 A

ii) Detector : Electron Capture

iii) Column : SPB-5 Fused Silica Capillary Column

30m x 0.32 mm i.d. with 0.25 µm film thickness of

poly (5% diphenyl-95% dimethyl) siloxane

iv) Temperature (°C)

Oven : 215

Injection port : 250

Detector : 300

v) Gas flow (ml/min)

Nitrogen

Through column : 2

Through vent : 18

Make up : 65

vi) Attenuation : 6

vii) Range : Zero

viii) Capillary split ratio: 1:10

Ref. Smith and Hayden (1982)

3.6.2 Trifluralin

i) Model : Hewlett Packard Model-5890 A

ii) Detector : Electron Capture

iii) Column : SPB-5

Fused Silica Capillary Column 30 m x 0.32 mm i.d.-with 0.25 µm film thickness of poly (5% diphenyl-95% dimethyl) Siloxane

iv) Temperature (°C)

Oven : 180

Injection port : 250

Detector : 250

v) Gas flows (ml/min)

Nitrogen

Through Column : 2

Through vent : 18

Make up : 65

vi) Attenuation : 6

vii) Range : Zero

viii) Capillary split ratio : 1:10

Ref. Anonymous (1998)

3.6.3 Triazophos

i) Model : Hewlett Packard Model-5890 A

ii) Detector : Nitrogen Phosphorus

iii) Column : HP-1, Fused Silica Column, 10 m x 0.53 mm i.d. x 2.65 μm film thickness of methyl silicon gum

iv) Temperature (°C)

Oven : 205

Injection port : 225

Detector : 250

v) Gas flow (ml min^{-1})

Nitrogen : 23.0±1.0

Hydrogen : 2.80±0.10

Zero Air : 110.0±10.0

vi) Attenuation : 5

vii) Range : 2

Ref. Singh *et al.* (1996)

3.7 Equilibrium studies of adsorption of metribuzin, trifluralin and triazophos on sandy loam and clay loam soils

The studies were conducted under laboratory conditions and the details of experiments are as follows :

3.7.1 Procurement of soils

Sandy loam soil was collected from Research Farm of CCS Haryana Agricultural University, Hisar and clay loam soil was collected from Regional Research Station, CCS Haryana Agricultural University, Kaul.

3.7.2 Preparation of soils

The soils were dried, crushed and sieved through 2 mm sieve before use to remove the plant debris and other extraneous particles.

3.7.3 Physico-chemical characteristics of soils

The sandy loam and clay loam soils of experiment were got analysed from the Soil Testing Laboratory, Department of Soil Sciences, CCS Haryana Agricultural University, Hisar. Soil characteristics are given in Table 1.

Table 1. Physico-chemical characteristics of the soils

Soil property	Sandy loam soil	Clay loam soil
Sand (%)	73.9	29.8
Silt (%)	9.0	25.2
Clay (%)	16.0	45.0
Texture	Loam	Loam
pH	7.70	7.20
EC (dSm^{-1})	0.56	0.32
O.C. (%)	0.65	0.78
P_2O_5 (kg ha^{-1})	30	53
K_2O (kg ha^{-1})	427	307

3.7.4 Adsorption equilibrium studies

These studies were conducted to determine the time required to establish adsorption equilibrium of metribuzin, trifluralin and triazophos on two types of soils viz. sandy loam and clay loam soils. The details of experiment are as under:

1. Adsorption equilibrium of metribuzin was achieved by taking 20 g (air dried) of each soil in eight conical flasks of 250 ml.
2. 100 ml of 0.01M $CaCl_2$ solution was added in each flask.

3. 25 µg of metribuzin from stock solution 'C' of formulation was added in each flask.
4. Two blanks (with no soil) in 250 ml conical flasks containing 100 ml of 0.01M $CaCl_2$ solution alongwith 25 µg of metribuzin were also taken.
5. All the 10 flasks were shaken on a mechanical shaker.
6. After 1 h of mechanical shaking, two flasks were taken out and soil mixture was centrifuged at 3500 rpm for 10 min. Similarly every sample (in duplicate) was shaken for 2, 3 and 4 h and soil mixture was centrifuged at 3500 rpm for 10 min. The blanks were also shaken for 4 h.
7. The volume of each supernatant was noted.
8. Supernatant and blank samples (with no soil) were partitioned with dichloromethane : ethyl acetate (9:1, v/v) mixture as per details given earlier under section 3.5.

For adsorption equilibrium of trifluralin and triazophos 25 µg of trifluralin and triazophos (from stock solution 'C' of formulation), respectively was added as per the above Sr. No. 3. The respective blanks as per the above Sr. No. 4 were also taken. The supernatant and blank samples (with no soil) were partitioned with hexane as per details given earlier under section 3.5.

3.8 Adsorption and desorption studies of metribuzin, trifluralin and triazophos on sandy loam and clay loam soils

For conducting the adsorption and desorption studies of pesticides (i.e. metribuzin, trifluralin and triazophos) on two soils viz. sandy loam and clay loam, the soil-pesticide contact was established by using batch method (Raj *et al.*, 1999) as under :

3.8.1 Adsorption studies

1. Adsorption behaviour of metribuzin was studied by taking 20 g (air dried) of each soil in eight conical flasks of 250 ml.
2. 100 ml of 0.01M calcium chloride was added in each flask.
3. 10, 20, 30 and 40 μg of metribuzin from stock solution 'C' of formulation was added in every sample (in duplicate).
4. Two blanks (with no soil) in 250 ml conical flasks containing 100 ml of 0.01 M $CaCl_2$ solution alongwith 25 μg of metribuzin were also taken.
5. All the 10 flasks were shaken on a mechanical shaker for 3 h (as per the equilibrium studies) for adsorption of metribuzin on soil.
6. After required shaking, each soil mixture was centrifuged at 3500 rpm for 10 min.
7. The volume of each supernatant was noted.
8. Supernatant and blank samples (with no soil) were partitioned with dichloromethane : ethyl acetate (9:1, v/v) mixture as per details given earlier under section 3.5.

For adsorption studies of trifluralin and triazophos 10, 20, 30 and 40 μg of trifluralin and triazophos from stock solution 'C' of formulation, respectively was added in each set as per the above Sr. No. 3. The respective blanks as per the above Sr. No. 4 were also taken. The supernatant and blank samples were partitioned with hexane as per details given earlier under section 3.5.

3.8.2 Desorption studies

After careful decantation of the supernatant, as described under the section 3.8.1, the soil left in the centrifuge tube was used for desorption studies. The soil from each centrifuge tubes was taken in 250 ml conical flasks and 100 ml of 0.01M calcium chloride solution was added. The mixture was shaken for 3 h on a mechanical shaker, followed by centrifugation at 3500 rpm for 10 minutes. The supernatant was decanted and 50 ml of supernatant was partitioned with dichloromethane : ethyl acetate (9:1, v/v) mixture for meterbuzin and with hexane for trifluralin and triazophos as per the details given earlier under section 3.5.

3.9 Calculations

3.9.1 Calculations for the determination of residues in the supernatant (i.e. 0.01M $CaCl_2$ solution)

Residues in the supernatant after adsorption equilibrium studies (Section 3.7) and after adsorption-desorption studies (Section 3.8) were calculated as under :

$$\text{Residues of pesticides } (\mu g/ml) \text{ in supernatant} = \frac{\text{Amount of standard injected (pg)} \times \text{Area of sample injected} \times \text{Final volume (ml)} \times 100}{\text{Area of standard injected} \times \text{Volume of sample injected } (\mu l) \times 1000 \times \text{volume of sample (ml)} \times \text{Per cent mean recovery}}$$

3.9.2 Calculations of C_e and x/m (Ads) and x/m (Des)

i) Residues data obtained in $\mu g\ ml^{-1}$ from supernatant i.e. 0.01M $CaCl_2$ solution is called C_e (equilibrium concentration of pesticides i, e. metribuzin/trifluralin/triazophos per ml of solution).

ii) For calculation of residues of pesticides (metribuzin/trifluralin/triazophos) in soil after adsorption, C_e was multiplied by 100 for calculating the residues in 100 ml of 0.01M $CaCl_2$ solution. This gives the amount of residues remains in 100 ml of 0.01M $CaCl_2$ solution.

This amount is substracted from initially added pesticides (metribuzin/trifluralin/triazophos) i.e. 10, 20, 30 or 40 µg. It gives the amount of residues of pesticides (metribuzin/trifluralin/triazophos) remains in soil i.e. adsorbed by 20 g soil.

iii) The data obtained at (ii) above was divided by weight of soil (20 g). This amount is called x/m (Ads) (concentration of pesticides i, e. metribuzin/trifluralin/triazophos per g of soil).

iv) For calculation of residues of pesticides (metribuzin/trifluralin/triazophos) in soils after desorption, substracted the residues obtained in 100 ml of supernatant after desorption of pesticides (metribuzin/trifluralin/triazophos) from pesticides adsorbed by soil. It will give the amount of pesticides still remained in 20 g of soil after desorption. This amount is divided by weight of soil (i.e. 20 g) for calculation of x/m (Des) (concentration of pesticides (metribuzin/trifluralin/triazophos) per g of soil after desorption).

3.9.3 Calculation of Kd (distribution co-efficient), K_{OC} (distribution co-efficient normalized to organic carbon of soils) and K_C (distribution co-efficient normalized to clay content of soils)

The distribution coefficient Kd for each soil was calculated from adsorption-desorption data using the following equation :

$$Kd = \frac{\Sigma(x/m.C_e)}{\Sigma(C_e)^2}$$

Where,

Σ indicates the summation of the values $[(C_e)^2$ and $(x/m.C_e)]$

It is evident from literature that among different soil constitutents, organic matter and clay play a major role in the adsorption and desorption of organic chemicals. Therefore, distribution co-efficients (Kd) were also expressed in terms of the soil organic carbon and clay contents using the following equations :

$$K_{OC} = \frac{(Kd \times 100)}{\%\ \text{organic carbon}}$$

$$K_C = \frac{Kd \times 100}{\%\ \text{clay}}$$

Where, K_{OC} and K_C are the distribution co-efficients based on soil organic carbon and clay contents, respectively.

3.9.4 Calculations of Freundlich's constants

Freundlich constants for the pesticides (metribuzin, trifluralin and triazophos) were calculated by using Freundlich equation given below :

$$x/m = K_f C_e^{1/n}$$

Taking log on both sides

$$\log x/m = \log K_f + 1/n \log C_e$$

Where,

x/m, is the concentration of adsorbate (pesticide) per unit adsorbent i.e. soil ($\mu g\ g^{-1}$).

C_e, is the aqueous phase concentration of pesticide in $\mu g\ ml^{-1}$.

K_f and 1/n are freundlich constants.

K_f is the measure of strength of adsorption and desorption whereas 1/n indicates the degree of linearity between solution equilibrium concentration and adsorption/desorption. The constant K_f and 1/n were determined from intercept and slope, respectively of linear regression equations.

4. RESULTS

The results obtained from the present investigations have been presented under the following headings :

4.1 Standardization of analytical techniques for estimation of metribuzin, trifluralin and triazophos residues

4.2 Recovery tests for metribuzin, trifluralin and triazophos in 0.01M calcium chloride solution

4.3 Equilibrium studies for the adsorption of metribuzin, trifluralin and triazophos on sandy loam and clay loam soils

4.4 Adsorption and desorption studies of metribuzin on sandy loam and clay loam soils

4.5 Adsorption and desorption studies of trifluralin on sandy loam and clay loam soils

4.6 Adsorption and desorption studies of triazophos on sandy loam and clay loam soils

4.1 Standardization of analytical techniques for estimation of metribuzin, trifluralin and triazophos residues

The analytical techniques recommended for estimation of microquantities of metribuzin, trifluralin and triazophos were standardized under laboratory conditions before adoption for residues estimation. Details about the techniques employed for residues estimation in 0.01M calcium chloride solution have been discussed earlier under Section 3.5 of 'Material and Methods'. The experimental data obtained for the perfection of techniques are given here as under :

4.1.1 Preparation of calibration curves

4.1.1.1 Metribuzin

Per cent full scale deflection recorded against different known amounts of metribuzin are given in Table 2 and standard calibration curve is given in Fig. 1. Linear relationship between concentration and area was observed for 1 to 100 pg. Retention time (R_t) obtained for metribuzin was 3.11 min as shown in Fig. 2.

4.1.1.2 Trifluralin

Per cent full scale deflection recorded against different known amounts of trifluralin are given in Table 3 and standard calibration curve is given in Fig. 3. Linear relationship between concentration and area was observed for 1 to 100 pg. Retention time (R_t) observed for trifluralin was 3.06 min as shown in Fig. 4.

4.1.1.3 Triazophos

Per cent full scale deflection recorded against different known amounts of triazophos are given in Table 4 and standard calibration curve is given in Fig. 5.

Table 2. Standard curve data of metribuzin

Sr.No.	Retention time (min.)	Amount of metribuzin injected (pg)	Peak area			Average peak area
			R_1	R_2	R_3	
1.	3.12	1	18	18	19	18±0.45
2.	3.11	10	185	180	182	182±2.06
3.	3.12	20	370	365	360	365±4.08
4.	3.13	30	545	538	547	543±3.86
5.	3.11	40	737	725	720	727±7.18
6.	3.12	50	903	907	897	902±4.11
7.	3.12	100	1834	1829	1838	1834±3.68

Table 3. Standard curve data of trifluralin

Sr.No.	Retention time (min.)	Amount of trifluralin injected (pg)	Peak area			Average peak area
			R_1	R_2	R_3	
1.	3.08	1	19	20	22	20±1.25
2.	3.06	10	198	203	199	200±2.16
3	3.06	20	400	392	407	400±6.13
4.	3.08	30	604	597	603	601±3.09
5.	3.07	40	797	802	805	801±3.30
6.	3.06	50	1005	1004	998	1002±3.09
7.	3.07	100	2003	1996	2010	2003±7.00

Table 4. Standard curve data of triazophos

Sr.No.	Retention time (min.)	Amount of triazophos injected (pg)	Peak area			Average peak area
			R_1	R_2	R_3	
1.	4.24	10	29	25	27	27±1.63
2.	4.25	20	58	59	63	60±2.16
3.	4.26	30	89	85	92	89±2.87
4.	4.24	40	118	125	116	120±3.86
5.	4.24	50	145	147	143	145±1.63
6.	4.25	100	285	289	286	287±1.70

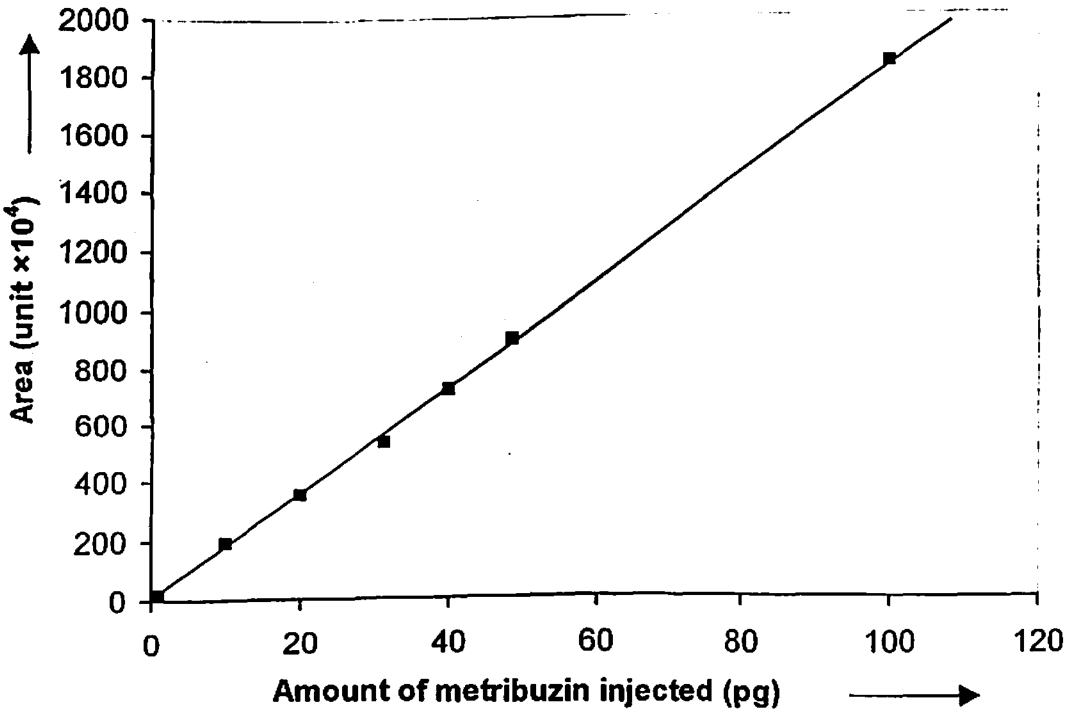
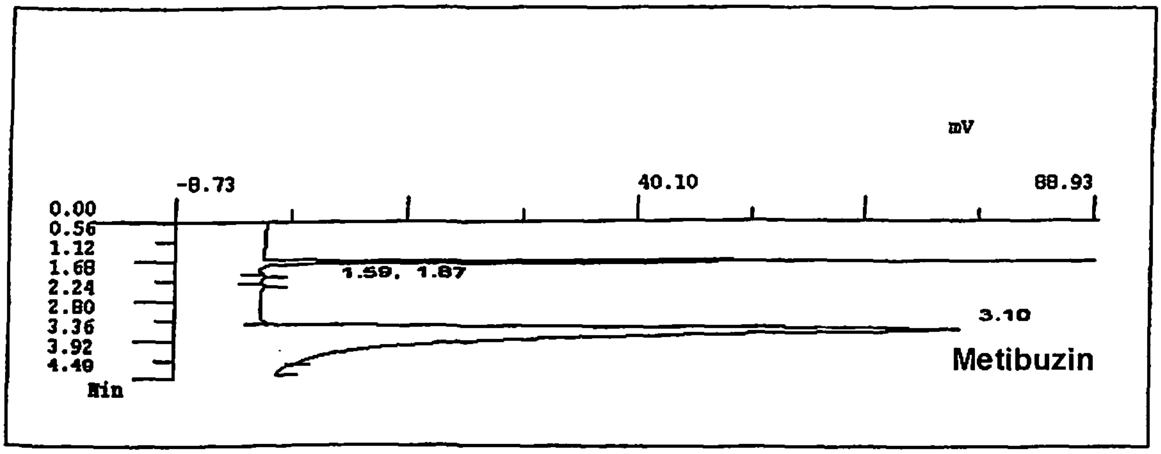


Fig. 1 : Calibration curve for metribuzin

Sample Name: Metribuzi100 pg Data File: ...R1\TWMETR19.DAT
Method File: C:\NETWIN~1\USER1\TWMETR.MET
Detector: ECD System: GC
Date: 01 Dec 2000 Time: 13:28:36
Run: ch1: 1
Type of Analysis : Percent On Area

Pk.Wdth	Peak Thrsh.	Area Rej.	Ht.Rej.
4	150	5	4



Retn. Time	Area	Area %	Pk Ty	Component Name
1.59	7938	0.0420	BB	
1.87	21255	0.1125	BB	
3.10	18871569	99.8455	BB	Metibuzin
	18900762			

SUMMARY

TOTAL PEAKS	3
MUL. FACTOR	1.0000
SAMPLEAMT.	100.0000
DILUTION .	1.0000

Fig. 2 : A gas liquid chramatograph of standard metibuzin

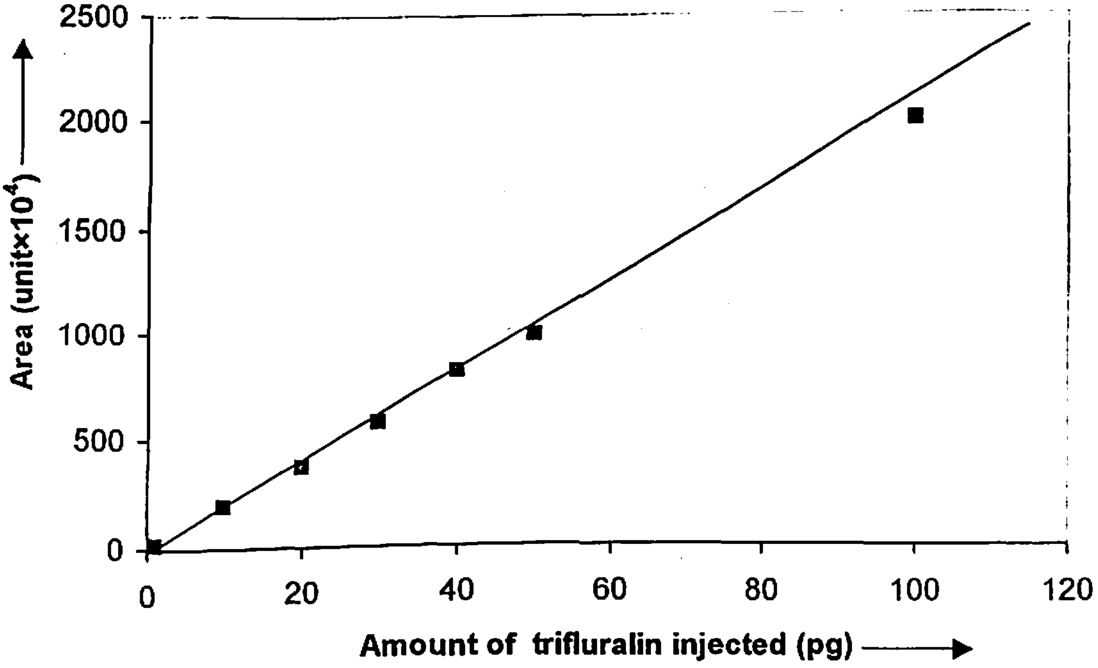
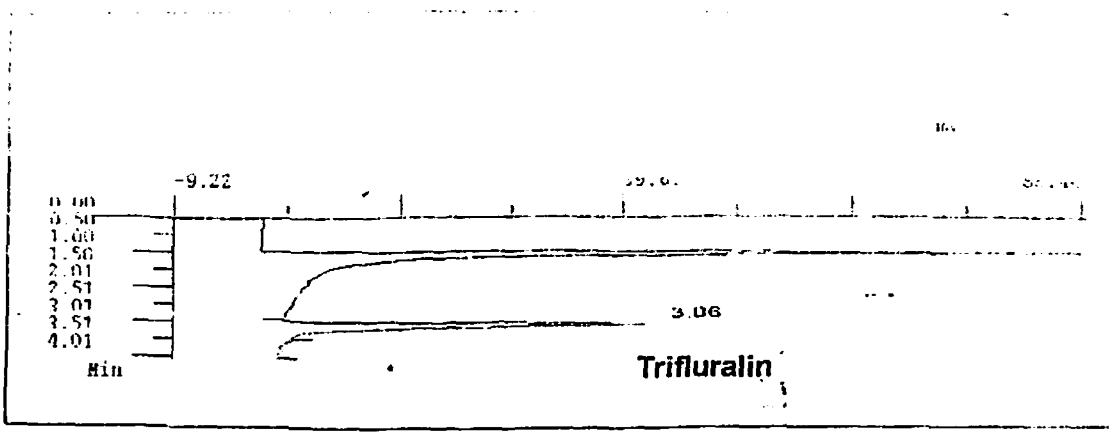


Fig. 3 : Calibration curve for trifluralin

Sample Name: Trifluralin20pg   Data File: ...R1\TWTRIR63.DAT
Method File: C:\NETWIN~1\USER1\VISHAL.MET
Detector: ECD   System: GC.
Date: 15 Sep 2000   Time 16:45:50
Run ch1 24
Type of Analysis : Percent On Area

Pk.Wdth	Peak Thrsh	Area Rej	Ht.Rej
4	160	8	4



Retn. Time	Area	Area %	Pk Ty	Component Name
3.06	4788297	100.0000	BB	Trifluralin
	4788297			

SUMMARY

TOTAL PEAKS	1
MUL. FACTOR	1.0000
SAMPLE AMT.	100.0000
DILUTION	1.0000

Fig. 4 : A gas liquid chramatograph of standard trifluralin

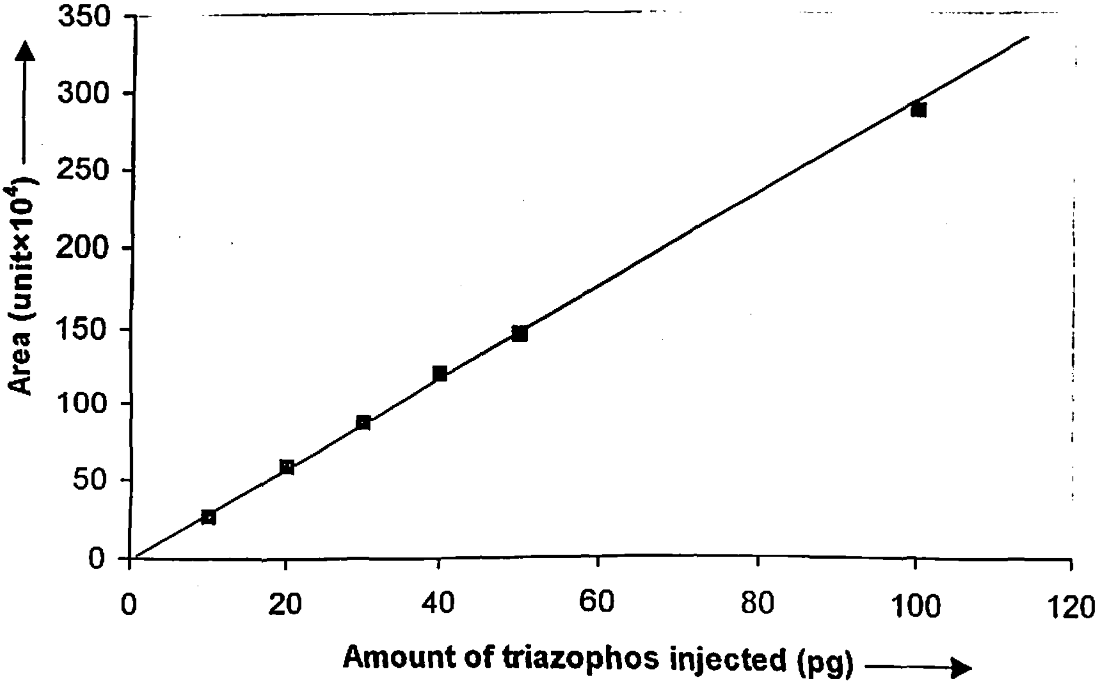


Fig. 5 : Calibration curve for triazophos

Linear relationship between concentration and area was obtained for 10 to 100 pg. Retention time (R_t) observed for triazophos was 4.26 min as shown in Fig. 6.

4.2 Recovery test for metribuzin, trifluralin and triazophos in 0.01M calcium chloride solution system

Untreated samples of 0.01M calcium chloride solution were fortified with metribuzin, trifluralin and triazophos separately. The fortification levels of each pesticide were 0.25 and 0.50 ppm. The fortified samples were extracted, cleaned and analysed as per details given in 'Materials and Methods'. The recovery data obtained is presented in Table 5-7.

4.2.1 Recovery tests for metribuzin in 0.01M calcium chloride solution system

Recoveries (Table 5) of metribuzin varied from 76.08 to 86.46 per cent (Av. 81.55±4.26) at 0.25 ppm level and 87.44 to 89.02 per cent (Av. 88.37±0.68) at 0.50 ppm level. The overall recovery was calculated to be 84.96±3.41 per cent. A correction factor of 1.18 (100/84.96=1.18) was used during calculation of metribuzin residues.

4.2.2 Recovery tests for trifluralin in 0.01M calcium chloride solution system

Recoveries (Table 6) of trifluralin varied from 75.44 to 89.08 per cent (Av. 82.11±5.57) at 0.25 ppm level and 86.64 to 88.62 per cent (Av. 87.49±1.02) at 0.50 ppm level. The overall recovery was calculated to be 84.80±2.20 per cent. A correction factor of 1.18 (100/84.80=1.18) was used during calculation of trifluralin residues.

Table 5. **Per cent recovery of metribuzin from 0.01M $CaCl_2$ solution fortified at 0.25 and 0.50 ppm levels**

Sr.No.	Replicate	Fortification level (ppm)	Volume of 0.01M $CaCl_2$ solution (ml)	Amount of pesticide added (µg)	Amount recovered (µg)	Recovery (%)	Average recovery (%)
1.	R_1	0.25	100	25	21.17	86.46	81.55±4.26
	R_2	0.25	100	25	19.02	76.08	
	R_3	0.25	100	25	20.53	82.12	
2.	R_1	0.50	100	50	44.51	89.02	88.37±0.68
	R_2	0.50	100	50	43.72	87.44	
	R_3	0.50	100	50	44.33	88.66	

Overall average recovery = 84.96±3.41.

Correction factor = 1.18 (100/84.96=1.18).

Table 6. **Per cent recovery of trifluralin from 0.01M $CaCl_2$ solution fortified at 0.25 and 0.50 ppm levels**

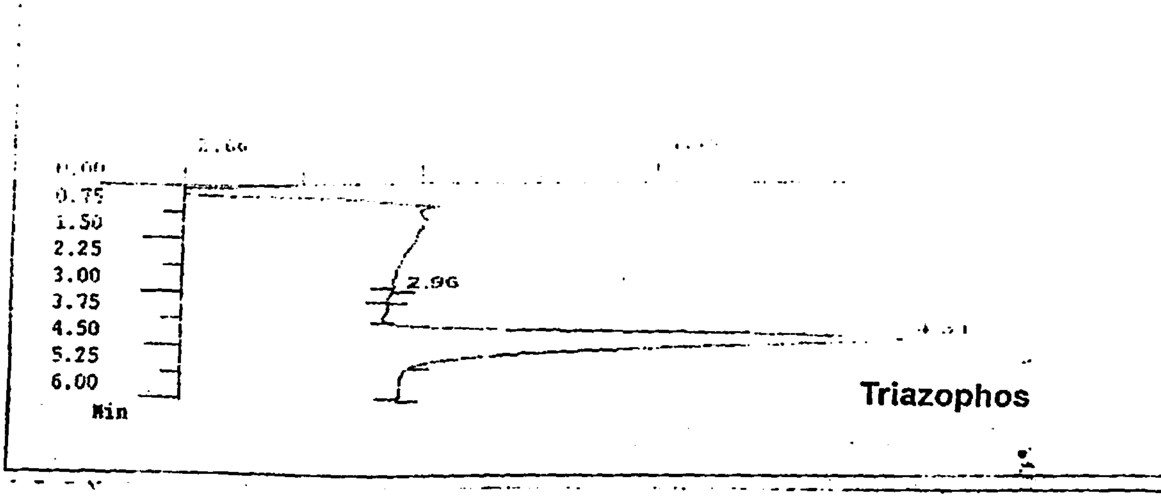
Sr.No.	Replicate	Fortification level (ppm)	Volume of 0.01M $CaCl_2$ solution (ml)	Amount of pesticide added (µg)	Amount recovered (µg)	Recovery (%)	Average recovery (%)
1.	R_1	0.25	100	25	22.27	89.98	82.11±5.57
	R_2	0.25	100	25	18.86	75.44	
	R_3	0.25	100	25	20.45	81.80	
2.	R_1	0.50	100	50	43.32	86.64	87.49±1.02
	R_2	0.50	100	50	44.81	88.62	
	R_3	0.50	100	50	43.62	87.22	

Overall average recovery = 84.80±2.20.

Correction factor = 1.18 (100/84.80=1.18).

```
Sample  Name: Triazophos1000pg                 Data   File:    ...R1\TTRIAZ05.DAT
Method  File:    C:\NETWIN~1\USER1\TWTRI.MET
Detector:     NPD.                             System:    GC
Date:    04  Nov  2000                         Time:    10:52:32
Run:  ch1:     6
Type  of  Analysis     :  Percent   On    Area

PK.Wdth         Peak  Thrsh.      Area   Rej       Ht.Rej
   4             150                8                4
```



```
Retn.            Area               Area        Pk          Component
 Time                                 %         Ty            Name

 2.96                 0            0.0000       BB
 4.31           8935873          100.0000       BB        Triazophos

                3935873

SUMMARY

TOTAL PEAKS                    2
MUL  FACTOR               1.0000
SAMPLEAMT               [illegible]
DILUTION                  1.0000
```

Fig. 6 : A gas liquid chramatograph of standard triazophos

4.2.3 Recovery tests for triazophos in 0.01M calcium chloride solution system

Recoveries (Table 7) of triazophos varied from 91.52 to 105.36 per cent (Av. 99.01±5.71) at 0.25 ppm level and 93.96 to 112.04 per cent (Av. 102.08±7.50) at 0.50 ppm level. The overall recovery was calculated to be 100.55±1.54 per cent. Since the recoveries were 100 per cent, therefore, no correction factor was used for calculation of triazophos residues.

4.3 Equilibrium studies for the adsorption of metribuzin, trifluralin and triazophos on sandy loam and clay loam soils

The equilibrium studies for adsorption of metribuzin, trifluralin and triazophos on soils viz. sandy loam and clay loam were conducted by following the batch method. The results of these studies are presented in Tables 8 to 13.

4.3.1 Equilibrium studies of metribuzin

4.3.1.1 Sandy loam soil

The initial concentration level of metribuzin (0.25 µg/ml^{-1}) in 0.01M calcium chloride solution reached to 0.151, 0.148, 0.141 and 0.140 µg ml^{-1} (Table 8) after 1, 2, 3 and 4 h of mechanical shaking with sandy loam soil (20 g). Thus, the amount of metribuzin adsorbed on soil reached to 0.495, 0.510, 0.545 and 0.548 µg g^{-1} after 1, 2, 3 and 4 h of sandy loam soil-metribuzin contact, respectively. The per cent adsorption of metribuzin on soil was 39.64, 40.77, 43.64 and 43.82, respectively. During this period, the distribution coefficient (Kd) was calculated to be3.28 (1 h), 3.45 (2 h), 3.87 (3 h) and 3.91 (4 h).

Table 7. **Per cent recovery of trizophos from 0.01M $CaCl_2$ solution fortified at 0.25 and 0.50 ppm levels**

Sr.No.	Replicate	Fortification level (ppm)	Volume of 0.01M $CaCl_2$ solution (ml)	Amount of pesticide added (µg)	Amount recovered (µg)	Recovery (%)	Average recovery (%)
1.	R_1	0.25	100	25	22.88	91.52	99.01±5.71
	R_2	0.25	100	25	28.09	105.36	
	R_3	0.25	100	25	25.04	100.16	
2.	R_1	0.50	100	50	50.12	100.24	102.08±7.50
	R_2	0.50	100	50	46.98	93.96	
	R_3	0.50	100	50	56.02	112.04	

Overall average recovery = 100.55±1.54.

Correction factor = Nil.

Table 8. **Equilibrium study of adsorption of metribuzin on sandy loam soil**

Concentration level (ppm)	Mechanical shaking/ Shaking period (h)	Weight of dry soil (g)	Volume of 0.01M $CaCl_2$ solution (ml)	Pesticide added (µg)	Residue/ 100 ml of 0.01M $CaCl_2$ solution (µg)	Residue/ 20 g of soil (µg)	C_e (Residue/ ml of 0.01M $CaCl_2$ solution) (µg)	x/m (Residue/g of soil) (µg)	$Kd= \frac{\Sigma C_e.x/m}{\Sigma C_e^2}$
0.25	1	20	100	25	15.091	9.909	0.151	0.495	3.28
0.25	2	20	100	25	14.808	10.192	0.148	0.510	3.45
0.25	3	20	100	25	14.091	10.909	0.141	0.545	3.87
0.25	4	20	100	25	14.046	10.954	0.140	0.548	3.91

4.3.1.2 Clay loam soil

The initial concentration of metribuzin (0.25 μg ml^{-1}) in 0.01M calcium chloride solution reached to 0.167, 0.152, 0.122 and 0.122 μg ml^{-1} (Table 9) after 1, 2, 3 and 4 h of mechanical shaking with clay loam soil. Thus, the amount of metribuzin adsorbed on soil reached to 0.413, 0.490, 0.638 and 0.638 μg g^{-1} after 1, 2, 3 and 4 h of clay loam soil-metribuzin contact, respectively. The per cent adsorption of metribuzin on soil was 33.04, 39.19, 51.05 and 51.06, respectively. During this period, the distribution coefficient (Kd) was calculated to be 2.47 (1 h), 3.22 (2 h), 5.23 (3 h) and 5.23 (4 h).

4.3.2 Equilibrium studies of trifluralin

4.3.2.1 Sandy loam soil

The initial concentration level of trifluralin (0.25 μg ml^{-1}) in 0.01M calcium chloride solution reached to 0.184, 0.155, 0.148 and 0.148 μg ml^{-1} (Table 10) after 1, 2, 3 and 4 h of mechanical shaking with sandy loam soil (20 g). Thus, the amount of trifluralin adsorbed on soil reached to 1.158, 1.172, 1.176 and 1.176 μg g^{-1} after 1, 2, 3 and 4 h of sandy loam soil-trifluralin contact, respectively. The per cent adsorption of trifluralin on soil was 92.64, 93.78, 94.08 and 94.10, respectively. During this period the distribution coefficient (Kd) was calculated to be 6.29 (1 h), 7.56 (2 h), 7.95 (3 h) and 7.95 (4 h).

4.3.2.2 Clay loam soil

The initial concentration of trifluralin (0.25 μg ml^{-1}) in 0.01M calcium chloride solution reached to 0.192, 0.163, 0.135 and 0.134 μg ml^{-1} (Table 11)

Table 9. Equilibrium study of adsorption of metribuzin on clay loam soil

Concentration level (ppm)	Mechanical shaking/ Shaking period (h)	Weight of dry soil (g)	Volume of 0.01M $CaCl_2$ solution (ml)	Pesticide added (µg)	Residue/ 100 ml of 0.01M $CaCl_2$ solution (µg)	Residue/ 20 g of soil (µg)	C_e (Residue/ ml of 0.01 M $CaCl_2$ solution) (µg)	x/m (Residue/g of soil) (µg)	Kd= $\frac{\Sigma C_e.x/m}{\Sigma C_e^2}$
0.25	1	20	100	25	16.741	8.259	0.167	0.413	2.47
0.25	1	20	100	25	15.203	9.797	0.152	0.490	3.22
0.25	3	20	100	25	12.237	12.763	0.122	0.638	5.23
0.25	4	20	100	25	12.236	12.764	0.122	0.638	5.23

Table 10. Equilibrium study of adsorption of trifluralin on sandy loam soil

Concentration level (ppm)	Mechanical shaking/ Shaking period (h)	Weight of dry soil (g)	Volume of 0.01M $CaCl_2$ solution (ml)	Pesticide added (µg)	Residue/ 100 ml of 0.01M $CaCl_2$ solution (µg)	Residue/ 20 g of soil (µg)	C_e (Residue/ ml of 0.01M $CaCl_2$ solution) (µg)	x/m (Residue/g of soil) (µg)	$Kd= \frac{\Sigma C_e . x/m}{\Sigma C_e^2}$
0.25	1	20	100	25	1.840	23.160	0.184	1.158	6.29
0.25	2	20	100	25	1.554	23.446	0.155	1.172	7.56
0.25	3	20	100	25	1.480	23.520	0.148	1.176	7.95
0.25	4	20	100	25	1.475	23.525	0.148	1.176	7.95

Table 11. Equilibrium study of adsorption of trifluralin on clay loam soil

Concentration level (ppm)	Mechanical shaking/ Shaking period (h)	Weight of dry soil (g)	Volume of 0.01M $CaCl_2$ solution (ml)	Pesticide added (µg)	Residue/ 100 ml of 0.01M $CaCl_2$ solution (µg)	Residue/ 20 g of soil (µg)	C_e (Residue/ ml of 0.01M $CaCl_2$ solution) (µg)	x/m (Residue/g of soil) (µg)	Kd= $\frac{\Sigma C_e.x/m}{\Sigma C_e^2}$
0.25	1	20	100	25	1.920	23.080	0.192	1.154	6.01
0.25	2	20	100	25	1.626	23.374	0.163	1.169	7.17
0.25	3	20	100	25	1.345	23.655	0.135	1.183	8.76
0.25	4	20	100	25	1.340	23.660	0.134	1.183	8.83

after 1, 2, 3 and 4 h of mechanical shaking with clay loam soil. Thus, the amount of trifluralin adsorbed on soil reached to 1.154, 1.169, 1.183 and 1.183 µg g^{-1} after 1, 2, 3 and 4 h of clay loam soil-trifluralin contact, respectively. The per cent adsorption of trifluralin on soil was 92.32, 93.39, 94.62 and 94.64, respectively. During this period, the distribution coefficient (Kd) was calculated to be 6.01 (1 h), 7.17 (2 h), 8.76 (3 h) and 8.83 (4 h).

4.3.3 Equilibrium studies of triazophos

4.3.3.1 Sandy loam soil

The initial concentration level of triazophos (0.25 µg ml^{-1}) in 0.01 M calcium chloride solution reached to 0.189, 0.129, 0.126 and 0.126 µg ml^{-1} (Table 12) after 1, 2, 3 and 4 h of mechanical shaking with sandy loam soil (20 g). Thus, the amount of triazophos adsorbed on soil reached to 0.305, 0.603, 0.620 and 0.622 µg g^{-1} after 1, 2, 3 and 4 h of sandy loam soil-triazophos contact, respectively. The per cent adsorption of triazophos on soil was 24.42, 48.25, 49.60 and 49.73, respectively. During this period the distribution coefficient (Kd) was calculated to 1.61 (1 h), 4.67 (2 h), 4.92 (3 h) and 4.94 (4 h).

4.3.3.2 Clay loam soil

The initial concentration of triazophos (0.25 µg ml^{-1}) in 0.01M calcium chloride solution reached to 0.164, 0.115, 0.105 and 0.104 µg ml^{-1} (Table13) after 1, 2, 3 and 4 h of mechanical shaking with clay loam soil. Thus, the amount of triazophos adsorbed on soil reached to 0.429, 0.674, 0.726 and 0.730 µg g^{-1} after 1, 2, 3 and 4 h of clay loam soil-triazophos contact, respectively. The per cent

Table 12. **Equilibrium study of adsorption of triazophos on sandy loam soil**

Concentration level (ppm)	Mechanical shaking/ Shaking period (h)	Weight of dry soil (g)	Volume of 0.01M $CaCl_2$ solution (ml)	Pesticide added (µg)	Residue/ 100 ml of 0.01M $CaCl_2$ solution (µg)	Residue/ 20 g of soil (µg)	C_e (Residue/ ml of 0.01M $CaCl_2$ solution) (µg)	x/m (Residue/g of soil) (µg)	Kd= $\frac{\Sigma C_e.x/m}{\Sigma C_e^2}$
0.25	1	20	100	25	18.894	6.106	0.189	0.305	1.61
0.25	2	20	100	25	12.937	12.063	0.129	0.603	4.67
0.25	3	20	100	25	12.600	12.400	0.126	0.620	4.92
0.25	4	20	100	25	12.568	12.432	0.126	0.622	4.94

Table 13. Equilibrium study of adsorption of triazophos on clay loam soil

Concentration level (ppm)	Mechanical shaking/ Shaking period (h)	Weight of dry soil (g)	Volume of 0.01M $CaCl_2$ solution (ml)	Pesticide added (µg)	Residue/ 100 ml of 0.01M $CaCl_2$ solution (µg)	Residue/ 20 g of soil (µg)	C_e (Residue/ ml of 0.01M $CaCl_2$ solution) (µg)	x/m (Residue/g of soil) (µg)	Kd= $\frac{\Sigma C_e.x/m}{\Sigma C_e^2}$
0.25	1	20	100	25	16.425	8.575	0.164	0.429	2.61
0.25	2	20	100	25	11.520	13.480	0.115	0.674	5.86
0.25	3	20	100	25	10.487	14.513	0.105	0.726	6.91
0.25	4	20	100	25	10.391	14.609	0.104	0.730	7.02

adsorption of triazophos on soil was 34.30, 53.92, 58.05 and 58.44, respectively. During this period, the distribution coefficient (Kd) was calculated to be 2.61 (1 h), 5.86 (2 h), 6.91 (3 h) and 7.02 (4 h).

4.4 Adsorption and desorption studies of metribuzin on sandy loam and clay loam soils

The sorption i.e. adsorption and desorption studies of metribuzin on two types of soils viz. sandy loam and clay loam were conducted by following the batch equilibrium method (Tables 14-17). The results are presented below :

4.4.1 Sandy loam soil

4.4.1.1 Adsorption

At four concentration levels i.e. 0.10, 0.20, 0.30 and 0.40 μg ml^{-1} of metribuzin solution (100 ml), the amount of metribuzin adsorbed on sandy loam soil (20 g) was 0.162, 0.309, 0.494 and 0.696 μg g^{-1}, respectively (Table 16). Thus, about 30.9 to 34.8 per cent of metribuzin present in solution got adsorbed on sandy loam soil. Concentration of metribuzin solutions after adsorption were 0.067, 0.138, 0.201 and 0.261 μg ml^{-1}, respectively.

4.4.1.2 Desorption

After desorption 0.085, 0.189, 0.331 and 0.496 μg g^{-1} of metribuzin (Table 16) still remained adsorbed on sandy loam soil at the above said levels and 0.016, 0.024, 0.033 and 0.040 μg ml^{-1} of metribuzin got desorbed after one desorption cycle at the corresponding levels. The range of desorption was 28.7 to 47.9 per cent.

Table 14. Adsorption and desorption of metribuzin on sandy loam soil

Adsorption/ Desorption	Ionic strength/ Concentration level (ppm)	Replicate	Weight of dry soil (g)	Volume of 0.01M $CaCl_2$ solution (ml)	Pesticide added (µg)	Volume of 0.01M $CaCl_2$ solution recovered after centri-fugation (ml)	Volume of 0.01M $CaCl_2$ solution taken for extraction (ml)	Volume of dichloromethane:ethyl acetate (9:1, v/v) after partitioning (ml)	Residue in 0.01M $CaCl_2$ solution (µg/ml)	Average residue in 0.01M $CaCl_2$ solution (µg/ml)
Adsorption	0.1	R_1	20	100	10	92	50	78.0	0.063	0.067
		R_2	20	100	10	92	50	85.0	0.071	
	0.2	R_1	20	100	20	91	50	75.0	0.130	0.138
		R_2	20	100	20	92	50	81.5	0.146	
	0.3	R_1	20	100	30	92	50	78.0	0.187	0.201
		R_2	20	100	30	91	50	81.0	0.215	
	0.4	R_1	20	100	40	92	50	78.0	0.231	0.261
		R_2	20	100	40	91	50	79.0	0.291	
Desorption	0.1	R_1	20	100	-	97	50	80.0	0.015	0.016
		R_2	20	100	-	99	50	80.0	0.016	
	0.2	R_1	20	100	-	96	50	79.0	0.024	0.024
		R_2	20	100	-	99	50	80.0	0.024	
	0.3	R_1	20	100	-	98	50	82.0	0.031	0.033
		R_2	20	100	-	96	50	83.5	0.034	
	0.4	R_1	20	100	-	97	50	75.0	0.040	0.040
		R_2	20	100	-	95	50	81.0	0.040	

Table 15. Adsorption and desorption of metribuzin on clay loam soil

Adsorption/ Desorption	Ionic strength/ Concentration level (ppm)	Replicate	Weight of dry soil (g)	Volume of 0.01M $CaCl_2$ solution (ml)	Pesticide added (µg)	Volume of 0.01M $CaCl_2$ solution recovered after centri-fugation (ml)	Volume of 0.01M $CaCl_2$ solution taken for extraction (ml)	Volume of dichloromethane:ethyl acetate (9:1, v/v) after partitioning (ml)	Residue in 0.01M $CaCl_2$ solution (µg/ml)	Average residue in 0.01M $CaCl_2$ solution (µg/ml)
Adsorption	0.1	R_1	20	100	10	91	50	78.0	0.062	0.065
		R_2	20	100	10	90	50	65.0	0.068	
	0.2	R_1	20	100	20	91	50	68.0	0.120	0.127
		R_2	20	100	20	91	50	82.0	0.133	
	0.3	R_1	20	100	30	91	50	81.0	0.182	0.185
		R_2	20	100	30	92	50	78.0	0.189	
	0.4	R_1	20	100	40	91	50	81.0	0.246	0.254
		R_2	20	100	40	91	50	81.0	0.262	
Desorption	0.1	R_1	20	100	-	95	50	82.5	0.014	0.011
		R_2	20	100	-	97	50	79.0	0.008	
	0.2	R_1	20	100	-	98	50	79.0	0.023	0.020
		R_2	20	100	-	99	50	79.0	0.017	
	0.3	R_1	20	100	-	95	50	79.5	0.036	0.035
		R_2	20	100	-	97	50	81.0	0.033	
	0.4	R_1	20	100	-	98	50	84.0	0.053	0.047
		R_2	20	100	-	99	50	78.0	0.040	

Table 16. Concentration[5] of metribuzin in soil and 0.01M $CaCl_2$ solution following the adsorption and desorption (ppm)

Soil	Initial concentration of metribuzin (µg ml^{-1})			
	0.10	0.20	0.30	0.40
Sandy loam				
C_e (Ads)[1]	0.067	0.138	0.201	0.261
x/m (Ads)[2]	0.162	0.309	0.494	0.696
C_e (Des)[3]	0.016	0.024	0.033	0.040
x/m (Des)[4]	0.085	0.189	0.331	0.496
Clay loam				
C_e (Ads)	0.065	0.127	0.185	0.245
X/m (Ads)	0.173	0.367	0.574	0.732
C_e (Des)	0.011	0.020	0.034	0.046
x/m (Des)	0.117	0.266	0.403	0.501

1. Concentration (µg ml^{-1}) of metribuzin in solution following adsorption.
2. Concentration (µg g^{-1}) of metribuzin in soil following adsorption.
3. Concentration (µg ml^{-1}) of metribuzin in solution following desorption.
4. Concentration (µg g^{-1}) of metribuzin in soil following desorption.
5. Values are average of two replicates.

Table 17. Freundlich constants, correlation coefficients and distribution coefficients (Kd, K_{oc}, K_c) for metribuzin following adsorption and desorption

Freundlich constants, correlation coefficients and distribution coefficients	Sorption data	
	Sandy loam	Clay loam
	Adosrption data	
$K_{f, Ads}$ (ml g^{-1})	2.76	3.37
1/n	1.06	1.08
r	0.99	0.99
Kd (ml g^{-1})	2.52	2.94
K_{oc} (ml g^{-1})	387.69	376.92
K_c (ml g^{-1})	15.75	6.53
	Desorption data	
$K_{f, Des}$ (ml g^{-1})	227.92	11.25
1/n	1.91	0.99
r	0.99	0.98
Kd (ml g^{-1})	10.17	11.84
K_{oc} (ml g^{-1})	1564.62	1517.95
K_c (ml g^{-1})	63.56	26.31

4.4.1.3 Sorption isotherms

All replicates (for adsorption and desorption) were averaged. The data were fitted by linear regression to the log form of empirical equation :

$$\log x/m = \log K_f + 1/n \log C_e$$

Where,

K_f and 1/n are Freundlich constants and

x = amount (µg) of pesticide adsorbed by soil (20 g).

m = weight of soil (20 g)

C_e = equilibrium concentration of the solution (µg ml^{-1})

The various regression equations for adsorption and desorption isotherms of metribuzin, trifluralin and triazophos are given in Table 26. Values of K_f and 1/n were obtained from calculated regression equation of a straight line as the intercept and slope, respectively.

The values of Freundlich constants K_f (Ads), 1/n, distribution coefficients Kd, K_{oc}, K_c and co efficient of correlation (r) for adsorption of metribuzin on sandy loam soil were 2.76 ml g^{-1}, 1.06, 2.52 ml g^{-1}, 387.69 ml g^{-1}, 15.75 ml g^{-1} and 0.99, respectively (Table 17). Desorption isotherms represents the amount of metribuzin still remains adsorbed on per gram of soil as a function of equilibrium concentration of solution after one desorption cycle (Fig. 7). The values of K_f (Des), 1/n, Kd, K_{oc}, K_c and r for desorption of metribuzin from sandy loam soil were calculated to be 227.92 ml g^{-1}, 1.91, 10.17 ml g^{-1}, 1564.62 ml g^{-1}, 63.56 ml

g^{-1} and 0.99, respectively (Table 17). The adsorption and desorption isotherms are shown in Fig. 7.

4.4.2 Clay loam soil

4.4.2.1 Adsorption

At four concentration levels as used in case of sandy loam soil i.e. 0.1, 0.2, 0.3 and 0.4 μg ml^{-1} of metribuzin solution (100 ml), the amount of metribuzin adsorbed on clay loam soil (20 g) was 0.173, 0.367, 0.574 and 0.732 μg g^{-1}, respectively (Table 16). Thus about 34.5 to 38.2 per cent of metribuzin present in solution got adsorbed on clay loam soil. Concentration of metribuzin solutions after adsorption were 0.065, 0.127, 0.185 and 0.245 μg ml^{-1}, respectively (Table 16).

4.4.2.2 Desorption

After desorption 0.117, 0.266, 0.403, 0.501 μg g^{-1} of metribuzin (Table 16) still remained adsorbed on clay loam soil at the above said levels and 0.011, 0.020, 0.034 and 0.046 μg ml^{-1} got desorbed after one desorption cycle at the corresponding levels. The range of desorption was 27.6 to 32.0 per cent.

4.4.2.3 Sorption isotherms

The values of Freundlich constants K_f (Ads), 1/n, distribution coefficients Kd, K_{oc}, K_c and r for adsorption of metribuzin on clay loam soil were 3.37 ml g^{-1}, 1.08, 2.94 ml g^{-1}, 376.92 ml g^{-1}, 6.53 ml g^{-1} and 0.99, respectively (Table 17). The corresponding figures for desorption of metribuzin from clay loam soil were 11.25 ml g^{-1}, 0.99, 11.84 ml g^{-1}, 1517.95 ml g^{-1}, 26.31 ml g^{-1} and 0.98,

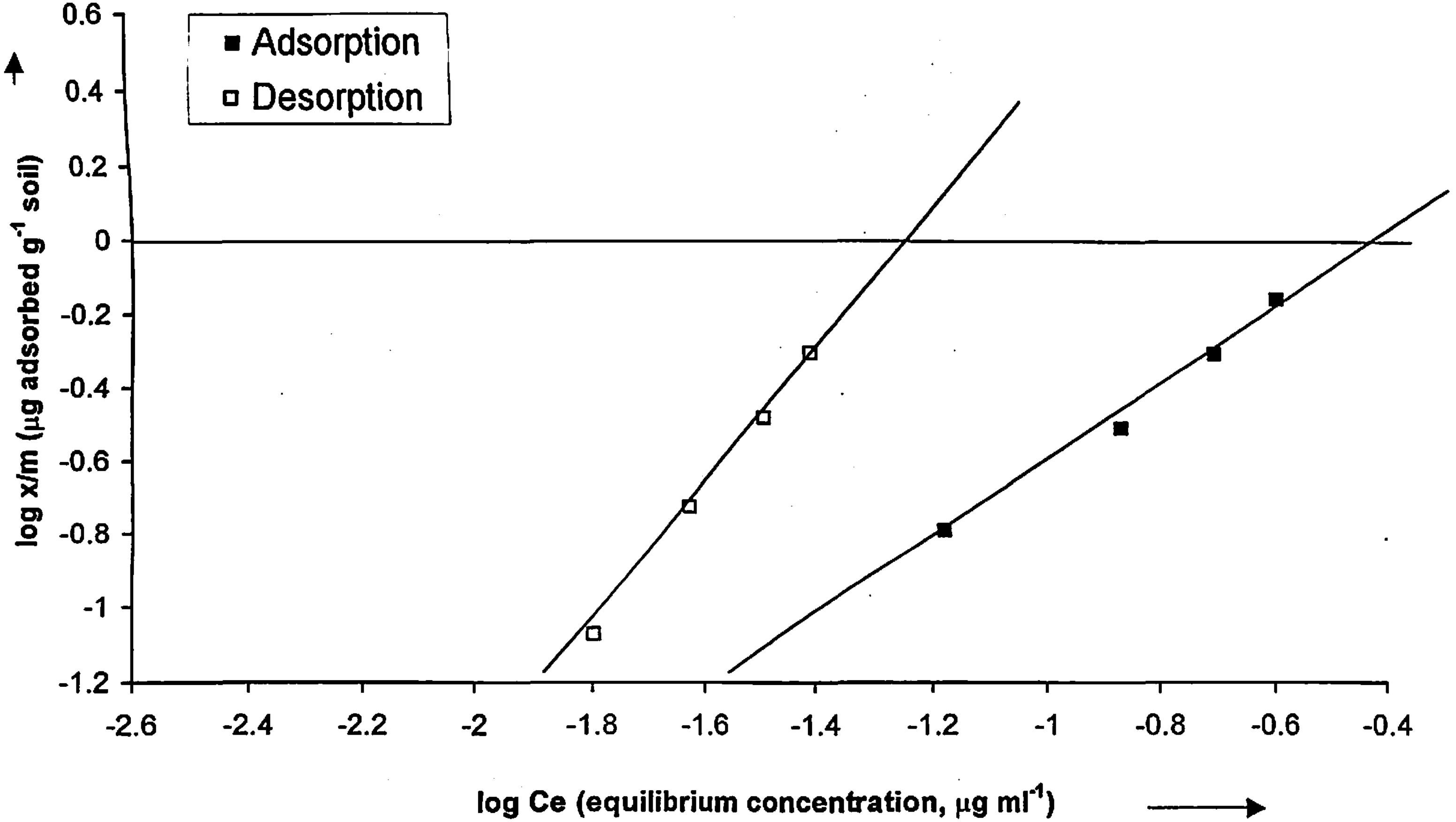


Fig. 7 : Freundlich isotherms for metribuzin sorption on sandy loam soil

respectively (Table 17). The adsorption and desorption isotherms are shown in Fig 8.

4.5 Adsorption and desorption studies of trifluralin on sandy loam and clay loam soil

The sorption i.e. adsorption and desorption studies of trifluralin on two types of soils viz. sandy loam and clay loam were conducted by following the batch equilibrium method (Tables 18-21). The results are presented below :

4.5.1 Sandy loam soil

4.5.1.1 Adsorption

At four concentration levels i.e. 0.10, 0.20, 0.30 and 0.40 μg ml^{-1} of trifluralin solution (100 ml), the amount of trifluralin adsorbed on sandy loam soil (20 g) was 0.464, 0.939, 1.422 and 1.900 μg g^{-1}, respectively (Table 20). Thus, about 91.9 to 95.0 per cent of trifluralin present in solution got adsorbed on sandy loam soil. Concentration of trifluralin solutions after adsorption were 0.008, 0.012, 0.016 and 0.020 μg ml^{-1}, respectively (Table 20).

4.5.1.2 Desorption

After desorption 0.442, 0.906, 1.379 and 1.883 μg g^{-1} of trifluralin (Table 20) still remained adsorbed on sandy loam soil, at the above said levels and 0.005, 0.007, 0.008 and 0.013 μg ml^{-1} of trifluralin got desorbed after one desorption cycle at the corresponding levels. The range of desorption was 3.0 to 5.2 per cent.

Table 18. Adsorption and desorption of trifluralin *on sandy loam soil*

Adsorption/ Desorption	Ionic strength/ Concentration level (ppm)	Replicate	Weight of dry soil (g)	Volume of 0.01M $CaCl_2$ solution (ml)	Pesticide added (µg)	Volume of 0.01M $CaCl_2$ solution recovered after centri-fugation (ml)	Volume of 0.01M $CaCl_2$ solution taken for extraction (ml)	Volume of hexane after partitioning (ml)	Residue in 0.01M $CaCl_2$ solution (µg/ml)	Average residue in 0.01M $CaCl_2$ solution (µg/ml)
Adsorption	0.1	R_1	20	100	10	91	50	68.0	0.009	0.008
		R_2	20	100	10	91	50	65.0	0.007	
	0.2	R_1	20	100	20	86	50	63.0	0.013	0.012
		R_2	20	100	20	91	50	60.0	0.011	
	0.3	R_1	20	100	30	93	50	62.0	0.018	0.016
		R_2	20	100	30	92	50	57.0	0.014	
	0.4	R_1	20	100	40	93	50	61.0	0.022	0.020
		R_2	20	100	40	93	50	57.5	0.018	
Desorption	0.1	R_1	20	100	-	98	50	66.0	0.005	0.005
		R_2	20	100	-	99	50	57.0	0.005	
	0.2	R_1	20	100	-	97	50	63.0	0.007	0.007
		R_2	20	100	-	98	50	63.5	0.006	
	0.3	R_1	20	100	-	96	50	63.0	0.008	0.008
		R_2	20	100	-	98	50	60.0	0.008	
	0.4	R_1	20	100	-	99	50	65.5	0.013	0.013
		R_2	20	100	-	98	50	61.0	0.013	

Table 19. Adsorption and *desorption of trifluralin* on clay loam soil

Adsorption/ Desorption	Ionic strength/ Concentration level (ppm)	Replicate	Weight of dry soil (g)	Volume of 0.01M $CaCl_2$ solution (ml)	Pesticide added (μg)	Volume of 0.01M $CaCl_2$ solution recovered after centri-fugation (ml)	Volume of 0.01M $CaCl_2$ solution taken for extraction (ml)	Volume of hexane after partitioning (ml)	Residue in 0.01M $CaCl_2$ solution (μg/ml)	Average residue in 0.01M $CaCl_2$ solution (μg/ml)
Adsorption	0.1	R_1	20	100	10	90	50	60.0	0.008	0.006
		R_2	20	100	10	89	50	61.0	0.006	
	0.2	R_1	20	100	20	90	50	60.0	0.011	0.011
		R_2	20	100	20	90	50	61.0	0.011	
	0.3	R_1	20	100	30	91	50	66.0	0.016	0.016
		R_2	20	100	30	91	50	66.0	0.016	
	0.4	R_1	20	100	40	91	50	63.0	0.021	0.020
		R_2	20	100	40	91	50	61.0	0.019	
Desorption	0.1	R_1	20	100	-	97	50	60.5	0.005	0.004
		R_2	20	100	-	96	50	68.0	0.003	
	0.2	R_1	20	100	-	97	50	63.0	0.008	0.008
		R_2	20	100	-	97	50	60.0	0.007	
	0.3	R_1	20	100	-	96	50	61.5	0.009	0.009
		R_2	20	100	-	98	50	67.0	0.008	
	0.4	R_1	20	100	-	98	50	59.0	0.013	0.012
		R_2	20	100	-	99	50	72.0	0.011	

Table 20. **Concentration[5] of trifluralin in soil and 0.01M $CaCl_2$ solution following the adsorption and desorption (ppm)**

Soil	Initial concentration of trifluralin (µg ml^{-1})			
	0.10	0.20	0.30	0.40
Sandy loam				
C_e (Ads)[1]	0.008	0.012	0.016	0.020
x/m (Ads)[2]	0.464	0.939	1.422	1.900
C_e (Des)[3]	0.005	0.007	0.008	0.013
x/m (Des)[4]	0.442	0.906	1.379	1.833
Clay loam				
C_e (Ads)	0.007	0.011	0.016	0.020
x/m (Ads)	0.464	0.945	1.421	1.898
C_e (Des)	0.004	0.008	0.009	0.012
x/m (Des)	0.444	0.900	1.377	1.838

1. Concentration (µg ml^{-1}) of trifluralin in solution following adsorption.
2. Concentration (µg gl^{-1}) of trifluralin in soil following adsorption.
3. Concentration (µg ml^{-1}) of trifluralin in solution following desorption.
4. Concentration (µg g^{-1}) of trifluralin in soil following desorption.
5. Values are average of two replicates.

Table 21. **Freundlich constants, correlation coefficients and distribution coefficients (Kd, K_{oc}, K_c) for *trifluralin following adsorption and desorption***

Freundlich constants, correlation coefficients and distribution coefficients	Sorption data	
	Sandy loam	Clay loam
	Adosrption data	
$K_{f,\,Ads}$ (ml g^{-1})	966.05	418.11
1/n	1.58	1.37
r	0.99	0.99
Kd (ml g^{-1})	87.37	89.86
K_{oc} (ml g^{-1})	14091.94	11520.51
K_c (ml g^{-1})	546.06	199.69
	Desorption data	
$K_{f,\,Des}$ (ml g^{-1})	845.17	242.77
1/n	1.39	1.13
r	0.94	0.97
Kd (ml g^{-1})	138.13	143.37
K_{oc} (ml g^{-1})	21250.77	18844.87
K_c (ml g^{-1})	863.31	319.71

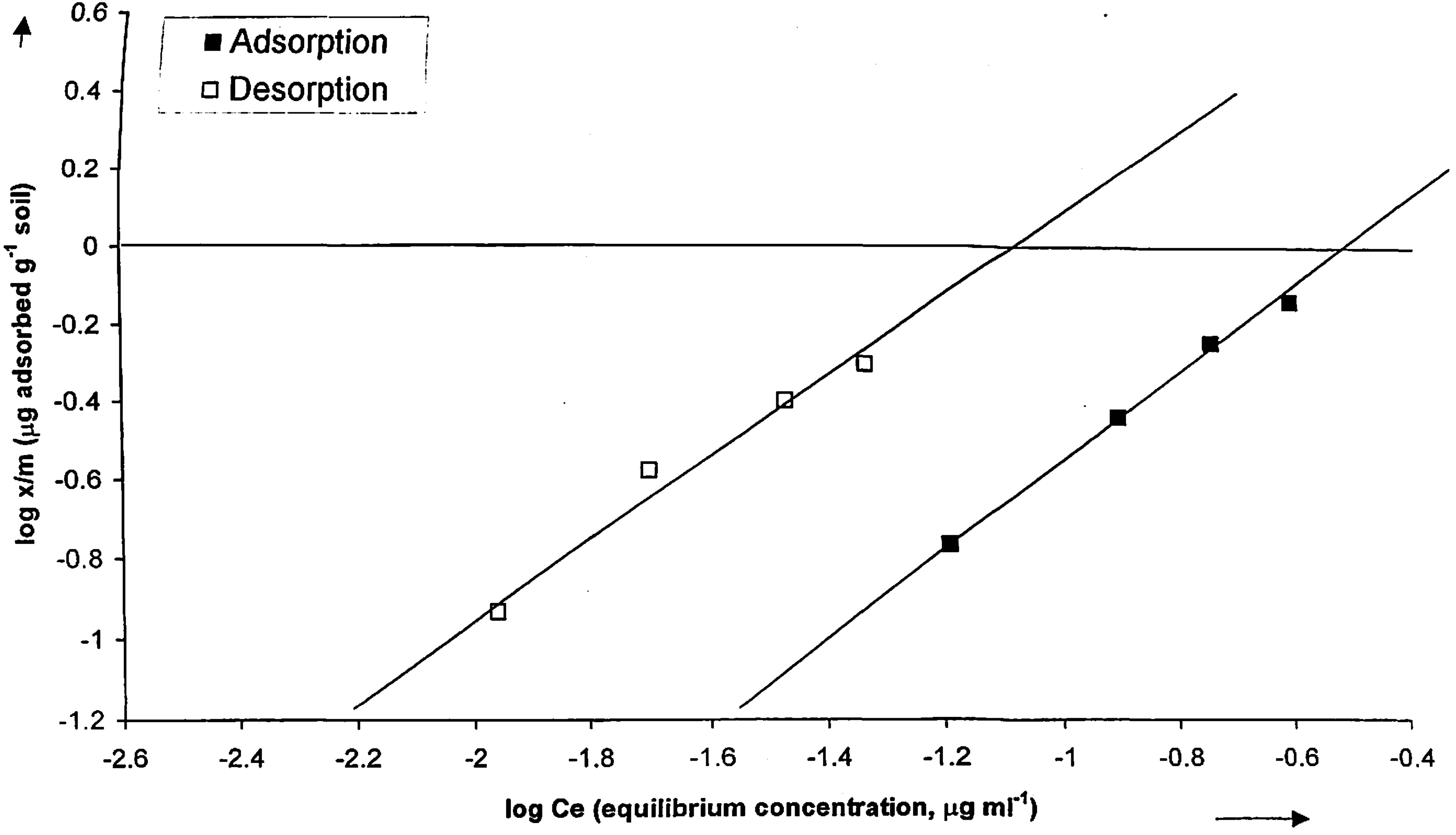


Fig. 8 : Freundlich isotherms for metribuzin sorption on clay loam soil

4.5.1.3 Sorption isotherms

The values of Freundlich constants K_f(Ads), 1/n, distribution coefficients Kd, K_{oc}, K_c and coefficient of correlation r for adsorption of trifluralin on sandy loam soil were 966.05 ml g^{-1}, 1.58, 87.37 ml g^{-1}, 14091.94 ml g^{-1}, 546.06 ml g^{-1} and 0.99, respectively (Table 21). The values for K_f (Des), 1/n, Kd, K_{oc}, Kc and r for desorption of trifluralin from sandy loam soil were calculated to be 845.17 ml g^{-1}, 1.39, 138.13 ml g^{-1}, 21250.77 ml g^{-1}, 863.31 ml g^{-1} and 0.94; respectively. The adsorption and desorption isotherms are shown in Fig 9.

4.5.2 Clay loam soil

4.5.2.1 Adsorption

At the four concentration levels as used in the case of sandy loam soil i.e. 0.10, 0.20, 0.30 and 0.40 μg ml^{-1} of trifluralin solution (100 ml), the amount of trifluralin adsorbed on clay loam soil was 0.464, 0.945, 1.421 and 1.898 μg g^{-1}, respectively (Table 20). Thus about 92.8 to 94.9 per cent of trifluralin present in solution got adsorbed on clay loam soil. Concentration of trifluralin solution after adsorption were 0.007, 0.011, 0.016, 0.020 μg ml^{-1}, respectively.

4.5.2.2 Desorption

After desorption 0.444, 0.900, 1.377 and 1.838 μg g^{-1} of trifluralin (Table 20) still remained adsorbed on clay loam soil, at the above said levels and 0.004, 0.008, 0.009 and 0.012 μg ml^{-1} got desorbed after one desorption cycle at the corresponding levels. The range of desorption was 3.1 to 4.3 per cent.

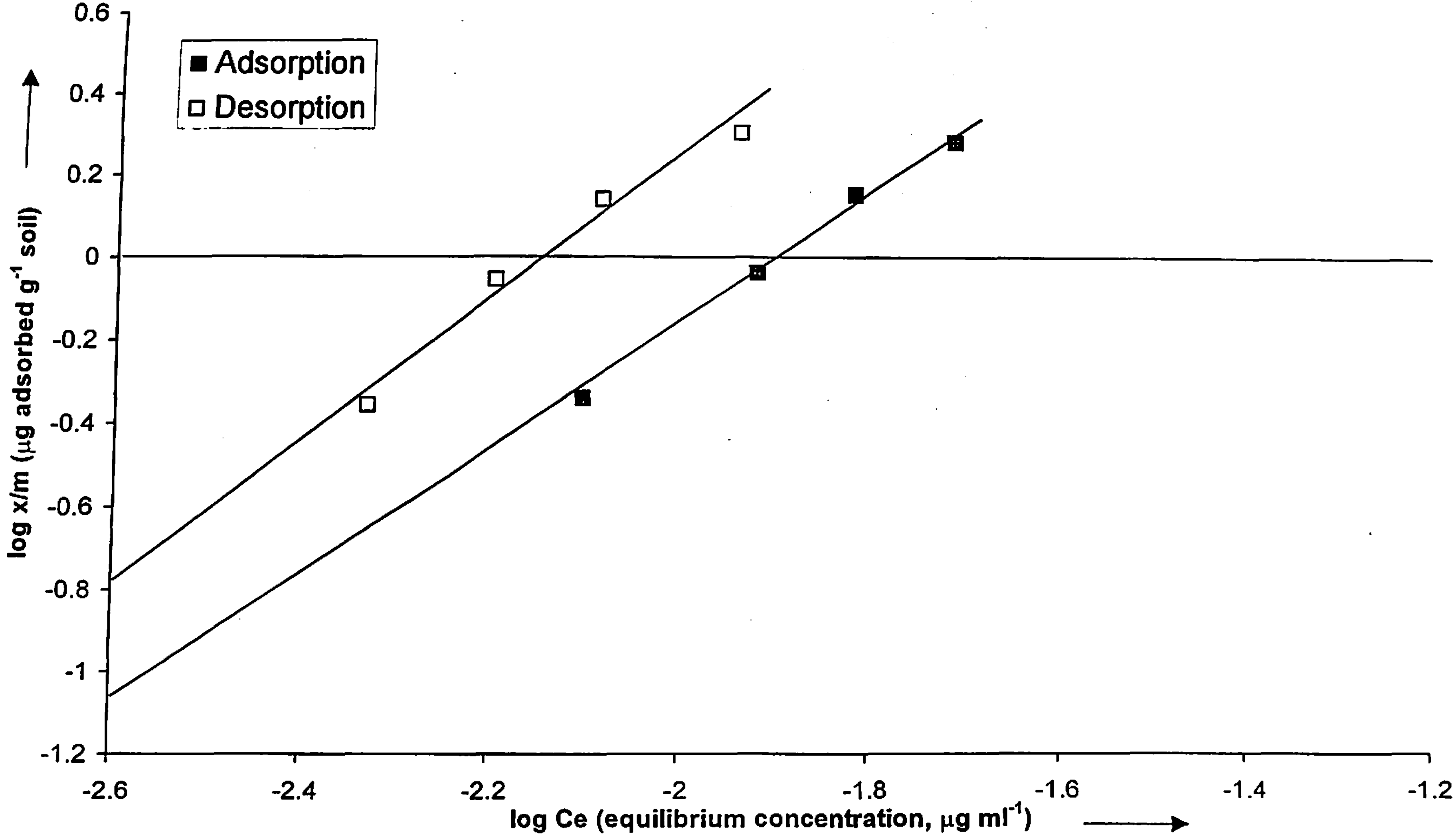


Fig. 9 : Freundlich isotherms for trifluralin sorption on Sandy loam soil

4.5.2.3 Sorption isotherms

The values of Freundlich constants K_f (Ads), 1/n, distribution coefficients Kd, K_{oc}, K_c and coefficient correlation r for adsorption of trifluralin on clay loam soil were 418.11 ml g^{-1}, 1.37, 89.86 ml g^{-1} 11520.51 ml g^{-1}, 199.69 ml g^{-1}, respectively (Table 21). The corresponding figures for desorption of trifluralin from clay loam soil were 242.77 ml g^{-1}, 1.13, 143.37 ml g^{-1}, 18444.87 ml g^{-1}, 319.71 ml g^{-1} and 0.97, respectively (Table 21). The adsorption and desorption isotherms are shown in Fig. 10.

4.6 Adsorption and desorption studies of triazophos on sandy loam and clay loam soils

The sorption i.e. adsorption and desorption studies of triazophos on two types of soils viz. sandy loam and clay loam were conducted by following the batch equilibrium method (Tables 22-25). The results are presented below :

4.6.1 Sandy loam soil

4.6.1.1 Adsorption

At four concentration levels i.e. 0.1, 0.2, 0.3 and 0.4 μg ml^{-1} of triazophos solution (100 ml), the amount of triazophos adsorbed on sandy loam soil (20 g), was 0.302, 0.531, 0.781 and 0.969 μg g^{-1}, respectively (Table 24). Thus, about 48.5 to 60.4 per cent of triazophos present in solution got adsorbed on sandy loam soil. Concentration of triazophos solution after adsorption were 0.040, 0.094, 0.144 and 0.206 μg ml^{-1}, respectively.

Table 22. Adsorption and desorption of triazophos on sandy loam soil

Adsorption/ Desorption	Ionic strength/ Concentration level (ppm)	Replicate	Weight of dry soil (g)	Volume of 0.01M $CaCl_2$ solution (ml)	Pesticide added (µg)	Volume of 0.01M $CaCl_2$ solution recovered after centri-fugation (ml)	Volume of 0.01M $CaCl_2$ solution taken for extraction (ml)	Volume of hexane after partitioning (ml)	Residue in 0.01M $CaCl_2$ solution (µg/ml)	Average residue in 0.01M $CaCl_2$ solution (µg/ml)
Adsorption	0.1	R_1	20	100	10	92	50	54.0	0.034	0.040
		R_2	20	100	10	91	50	59.0	0.045	
	0.2	R_1	20	100	20	92	50	55.0	0.083	0.094
		R_2	20	100	20	91	50	56.0	0.104	
	0.3	R_1	20	100	30	92	50	59.5	0.137	0.141
		R_2	20	100	30	92	50	55.0	0.151	
	0.4	R_1	20	100	40	91	50	48.0	0.191	0.206
		R_2	20	100	40	91	50	58.0	0.221	
Desorption	0.1	R_1	20	100	-	96	50	68.0	0.015	0.016
		R_2	20	100	-	98	50	56.0	0.017	
	0.2	R_1	20	100	-	97	50	70.0	0.030	0.031
		R_2	20	100	-	99	50	60.0	0.032	
	0.3	R_1	20	100	-	97	50	68.0	0.040	0.044
		R_2	20	100	-	98	50	58.0	0.048	
	0.4	R_1	20	100	-	97	50	70.0	0.059	0.060
		R_2	20	100	-	98	50	60.0	0.061	

Table 23. Adsorption and desorption of triazophos on clay loam soil

Adsorption/ Desorption	Ionic strength/ Concentration level (ppm)	Replicate	Weight of dry soil (g)	Volume of 0.01M $CaCl_2$ solution (ml)	Pesticide added (µg)	Volume of 0.01M $CaCl_2$ solution recovered after centri-fugation (ml)	Volume of 0.01M $CaCl_2$ solution taken for extraction (ml)	Volume of hexane after partitioning (ml)	Residue in 0.01M $CaCl_2$ solution (µg/ml)	Average residue in 0.01M $CaCl_2$ solution (µg/ml)
Adsorption	0.1	R_1	20	100	10	90	50	60.0	0.030	0.033
		R_2	20	100	10	90	50	55.0	0.035	
	0.2	R_1	20	100	20	90	50	64.0	0.067	0.078
		R_2	20	100	20	91	50	59.0	0.089	
	0.3	R_1	20	100	30	91	50	65.0	0.114	0.128
		R_2	20	100	30	90	50	55.5	0.142	
	0.4	R_1	20	100	40	90	50	68.0	0.164	0.181
		R_2	20	100	40	91	50	56.0	0.198	
Desorption	0.1	R_1	20	100	-	96	50	65.0	0.016	0.017
		R_2	20	100	-	98	50	69.0	0.018	
	0.2	R_1	20	100	-	97	50	66.0	0.032	0.033
		R_2	20	100	-	95	50	63.5	0.034	
	0.3	R_1	20	100	-	98	50	66.0	0.049	0.053
		R_2	20	100	-	97	50	67.0	0.056	
	0.4	R_1	20	100	-	96	50	69.0	0.065	0.067
		R_2	20	100	-	98	50	66.0	0.069	

Table 24. Concentration[5] of triazophos in soil and 0.01M $CaCl_2$ solution following the adsorption and desorption (ppm)

Soil	Initial concentration of triazophos (μg ml^{-1})			
	0.10	0.20	0.30	0.40
Sandy loam				
C_e (Ads)[1]	0.040	0.094	0.144	0.206
x/m (Ads)[2]	0.302	0.531	0.781	0.969
C_e (Des)[3]	0.016	0.031	0.044	0.060
x/m (Des)[4]	0.223	0.374	0.559	0.669
Clay loam				
C_e (Ads)	0.033	0.078	0.128	0.181
x/m (Ads)	0.336	0.608	0.859	1.093
C_e (Des)	0.017	0.033	0.053	0.067
x/m (Des)	0.250	0.443	0.595	0.758

0 Concentration (μg ml^{-1}) of triazophos in solution following adsorption.
1 Concentration (μg g^{-1}) of triazophos in soil following adsorption.
2 Concentration (μg ml^{-1}) of triazophos in solution following desorption.
3 Concentration (μg g^{-1}) of triazophos in soil following desorption.
4 Values are average of two replicates.

Table 25. **Freundlich constants, correlation coefficients and distribution coefficients (Kd, K_{oc}, K_c) for triazophos following adsorption and desorption**

Freundlich constants, correlation coefficients and distribution coefficients	Sorption data	
	Sandy loam	Clay loam
	Adosrption data	
$K_{f, Ads}$ (ml g^{-1})	3.03	3.54
1/n	0.72	0.69
r	0.99	0.99
Kd (ml g^{-1})	5.09	5.87
K_{oc} (ml g^{-1})	783.05	752.59
K_c (ml g^{-1})	31.81	13.04
	Desorption data	
$K_{f, Des}$ (ml g^{-1})	7.38	6.30
1/n	0.84	0.79
r	0.99	0.99
Kd (ml g^{-1})	11.75	11.24
K_{oc} (ml g^{-1})	1807.69	1441.28
K_c (ml g^{-1})	73.44	24.98

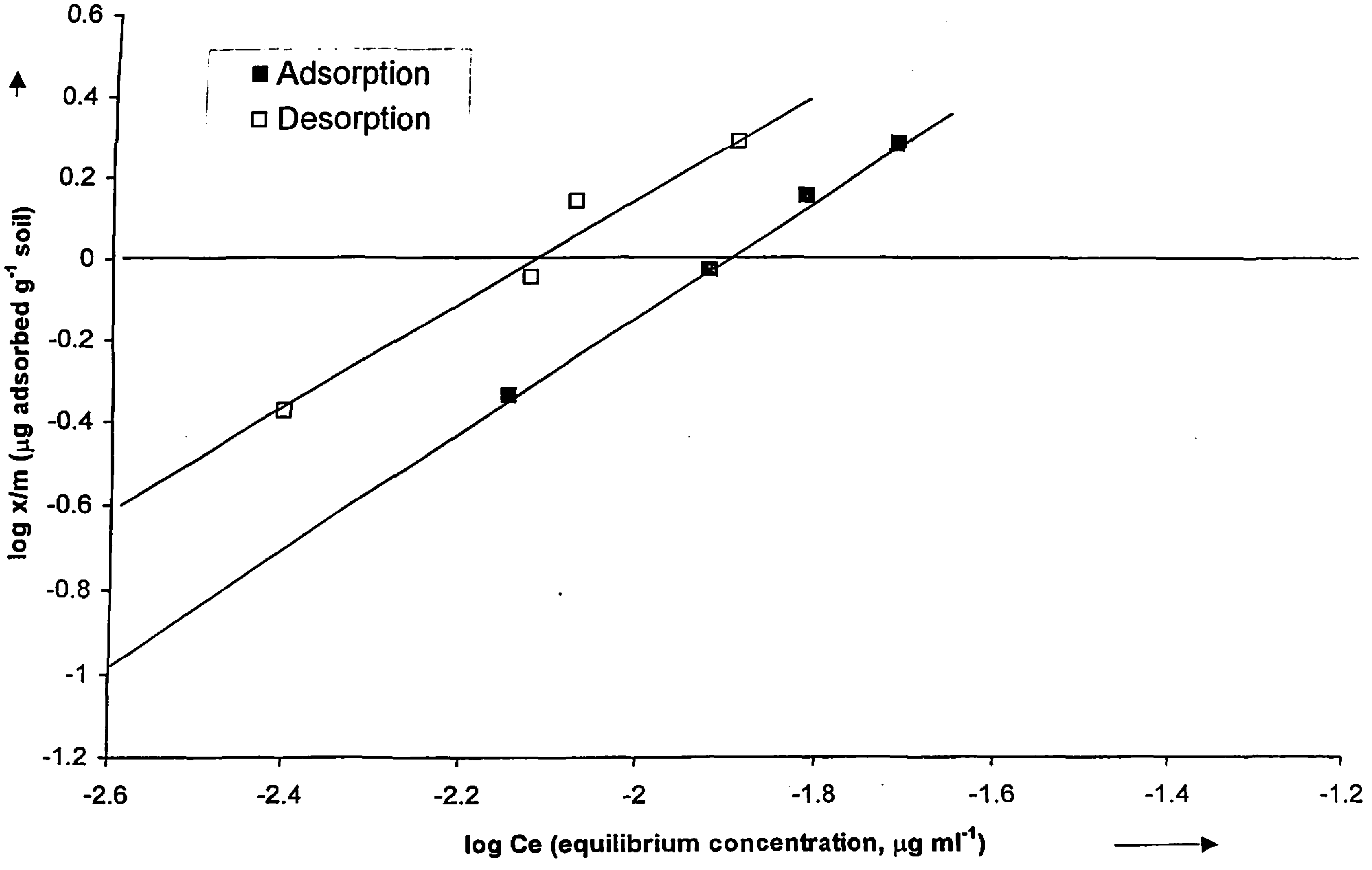


Fig. 10 : Freundlich isotherms for trifluralin sorption on clay loam soil

4.6.1.2 Desorption

After desorption 0.223, 0.374, 0.559 and 0.669 μg g^{-1}, of triazophos (Table 24) still remained adsorbed on sandy loam soil, at the above said levels and 0.016, 0.031, 0.044 and 0.060 μg ml^{-1} of triazophos got desorbed after one desorption cycle at the corresponding levels. The range of desorption was about 26.2 to 31.0 per cent.

4.6.1.3 Sorption isotherms

The values of Freundlich constants K_f (Ads), 1/n, distribution coefficients Kd, K_{oc}, K_c and coefficient of correlation r for adsorption of triazophos on sandy loam soil were 3.03 ml g^{-1}, 0.72, 5.09 ml g^{-1}, 783.05 ml g^{-1}, 31.81 ml g^{-1} and 0.99, respectively (Table 25). The values for K_f (Des), 1/n Kd, K_{oc}, K_c and r of desorption of triazophos from sandy loam soil were 7.38 ml g^{-1}, 0.84, 11.75 ml g^{-1}, 1807.69 ml g^{-1}, 73.44 ml g^{-1} and 0.99, respectively (Table 25). The adsorption and desorption isotherms are shown in Fig. 11.

4.6.2 Clay loam soil

4.6.2.1 Adsorption

At the four concentration levels as used in case of sandy loam soil i.e. 0.1, 0.2, 0.3 and 0.4 μg ml^{-1} of triazophos solution (100 ml), the amount of triazophos adsorbed on clay loam soil (20 g) was 0.336, 0.608, 0.859 and 1.093 μg g^{-1}, respectively. Thus, about 54.7 to 67.3 per cent of triazophos present in solution got adsorbed on clay loam soil. Concentration of triazophos solution after adsorption were 0.033, 0.078, 0.128 and 0.181 μg ml^{-1}, respectively (Table 24).

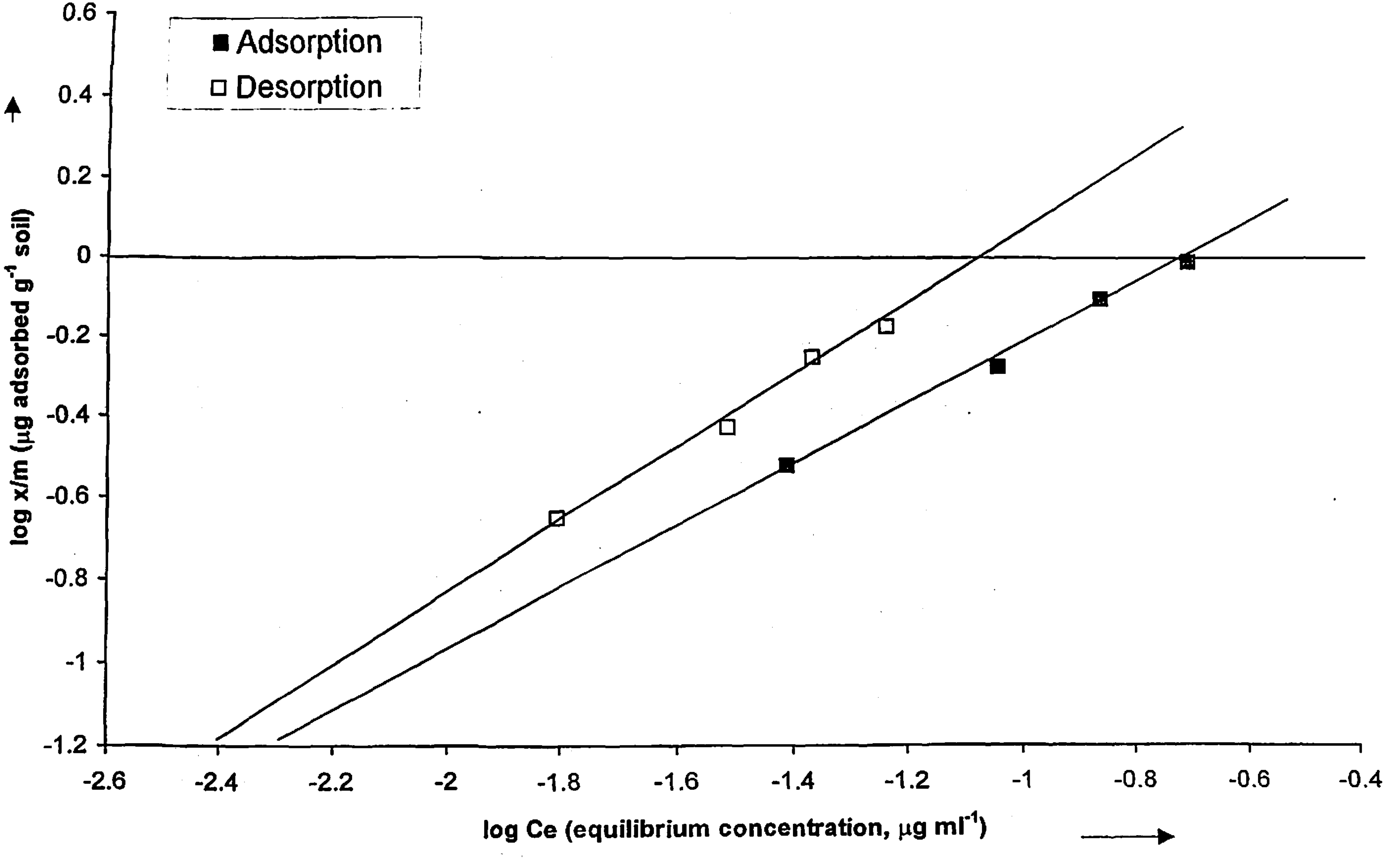


Fig. 11 : Freundlich isotherms for triazophos sorption on sandy loam soil

4.6.2.2 Desorption

After desorption 0.250, 0.443, 0.595 and 0.758 μg g^{-1} of triazophos still remained adsorbed on clay loam soil at the above said levels and 0.017, 0.033, 0.053 and 0.067 μg ml^{-1} of triazophos got desorbed after one desorption cycle (Table 24) at the corresponding levels. The range of desorption was 25.7 to 30.7 per cent.

4.6.2.3 Sorption isotherms

The values of Freundlich constants K_f (ads), 1/n, distribution coefficients Kd, K_{oc}, K_c and coefficient of correlation r for adsorption of triazophos on clay loam soil were 3.54 ml g^{-1}, 0.69, 5.87 ml g^{-1}, 752.59 ml g^{-1}, 13.04 ml g^{-1} and 0.99, respectively (Table 25). The corresponding values of these constants for desorption of triazophos from clay loam soil were 6.30 ml g^{-1}, 0.79, 11.24 ml g^{-1}, 1441.28 ml g^{-1}, 24.98 ml g^{-1} and 0.99, respectively (Table 25). The adsorption and desorption isotherms are shown in Fig. 12.

4.7 Summary of results

The various regression equations for adsorption and desorption isotherms of metribuzin, trifluralin and triazophos on sandy loam and clay loam soils are given in Table 26. From the values of intercept and slope, the values of Frendlich constants K_f and 1/n, respectively for adsorption and desorption were calculated which are given in Table 17, 21 & 25.

The summary of per cent adsorption and desorption of metribuzin, trifluralin and triazophos on sandy loam and clay loam soils are given in Table

Table 26. Regression equations for adsorption and desorption of pesticides on soils

Soil	Pesticides	Regression equations	
		Adsorption	Desorption
Sandy loam	Metribuzin	$Y = 0.440 + 1.062 X$ ($r = 0.99$)	$Y = 2.357 + 1.908 X$ ($r = 0.99$)
	Trifluralin	$Y = 2.985 + 1.580 X$ ($r = 0.99$)	$Y = 2.927 + 1.386 X$ ($r = 0.94$)
	Triazophos	$Y = 0.482 + 0.718 X$ ($r = 0.99$)	$Y = 0.868 + 0.846 X$ ($r = 0.99$)
Clay loam	Metribuzin	$Y = 0.527 + 1.080 X$ ($r = 0.99$)	$Y = 1.051 + 0.993 X$ ($r = 0.99$)
	Trifluralin	$Y = 2.621 + 1.378 X$ ($r = 0.99$)	$Y = 2.385 + 1.134 X$ ($r = 0.97$)
	Triazophos	$Y = 0.549 + 0.689 X$ ($r = 0.99$)	$Y = 0.799 + 0.789 X$ ($r = 0.99$)

In the equation $Y = a + b X$
Where
$Y = \log x/m$, $X = \log Ce$, $a = \log K_f$, $b = 1/n$

Table 27. **Summary table for per cent adsorption and desorption of pesticides on soils**

Soil	Concentration level/ionic strength (ppm)	Pesticide added (µg)	Metribuzin		Trifluralin		Triazophos	
			Per cent adsorption w.r.t pesticide added	Per cent desorption w.r.t. pesticide adsorbed on soil	Per cent adsorption w.r.t pesticide added	Per cent desorption w.r.t. pesticide adsorbed on soil	Per cent adsorption wr.t. pesticide added	Per cent desorption w.r.t. pesticide adsorbed on soil
Sandy loam	0.1	10	32.5	47.5	91.9	5.2	60.4	26.2
	0.2	20	30.9	39.0	93.9	3.5	53.1	29.4
	0.3	30	32.9	33.1	94.8	3.0	52.1	28.4
	0.4	40	34.8	28.7	95.0	3.6	48.5	31.0
Average	-	-	33.5	37.1	93.9	3.8	53.5	28.8
Clay loam	0.1	10	34.5	32.0	92.8	4.3	67.3	25.7
	0.2	20	36.7	27.6	93.9	4.1	60.8	27.1
	0.3	30	38.2	29.8	94.7	3.1	57.2	30.7
	0.4	40	36.6	31.6	94.9	3.2	54.7	30.7
Average	-	-	36.5	30.3	94.1	3.7	59.5	28.6
Overall average	-	-	35.0	33.7	94.0	3.8	56.5	28.7

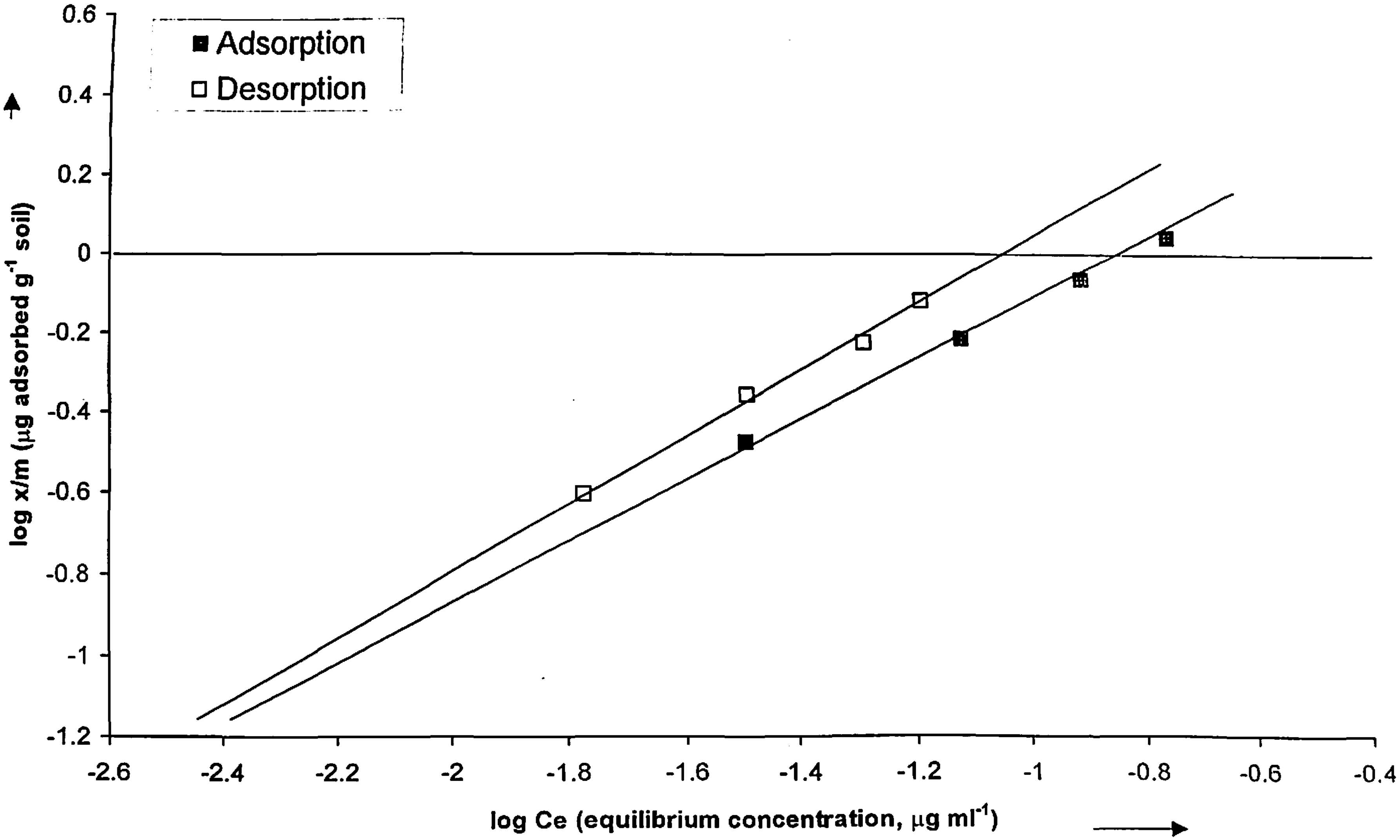


Fig. 12 : Freundlich isotherms for triazophos sorption on clay loam soil

27. The overall average of per cent adsorption of pesticides on both soils was highest in trifluralin (94%) followed by triazophos (56.5%) and metribuzin (35%). The average of per cent desorption from both soils was minimal in trifluralin (3.8%) followed by triazophos (28.7%) and metribuzin (33.7%).

5. DISCUSSION

The results presented in the chapter 4 have been discussed under the following heads :

5.1 Standardization of analytical techniques and its adoption for estimation of metribuzin, trifluralin and triazophos residues in 0.01M $CaCl_2$ solution

5.2 Recovery tests for metribuzin, trifluralin and triazophos from fortified 0.01M $CaCl_2$ solution

5.3 Adsorption equilibrium studies

5.4 Adsorption-desorption studies

5.1 Standardization of analytical techniques for estimation of residues of metribuzin, trifluralin and triazophos

5.1.1 Metribuzin

The analytical data obtained by processing known amount of standard metribuzin has been presented in Table 2. Calibration curve given in Fig.1 indicates a linear relationship between peak area and amount injected from 1 to 100 pg. Retention time (R_t) of metribuzin peak was 3.11 min. Hyzak and Zimdahl (1974) reported the retention time of metribuzin 3.00 min using GC-tritium foil ECD with glass column (122 cm x 2 mm) packed with 80-100 mesh chromosorb Gaschrom Q coated with 5% OV-101. Smith and Hayden (1982) reported the retention time for metribuzin 3.35 min using Hewlett Packard 5713A gas chromatograph equipped with a ^{63}Ni detector and glass column (1.5 m. x 4 mm.) packed with 100-120 mesh ultra-bond 20m. Zimdahl *et al.* (1994) reported the retention time of metribuzin 3.00 min using GC-ECD equipped with glass column (122 cm x 2 mm) packed with 5% OV-101 on 80-100 mesh packing. Thus, the retention time of 3.11 min in our studies was found to be correct. Keeping in view the repeatability of responses, sharp and well resolved peaks of metribuzin, the GC technique was considered satisfactory for the adoption in the present investigations.

5.1.2 Trifluralin

The analytical data obtained by processing known amounts of standard trifluralin has been presented in Table 3. Calibration curve given in Fig. 3 indicates a linear relationship between peak area and amount injected from 1 to 100 pg. Retention time (R_t) of trifluralin peak was 3.06 min. Smith (1979) reported the retention time of trifluralin 2.00 min using GC-ECD (Hewlett Packard 5713) equipped with packed glass column (1.5 m x 4 mm) with 100-120 mesh ultra-bond 20m. The probable reason of slightly more R_t in our studies may be attributed to capillary column measuring 30 m and relatively low flow rate (2 ml/min) of nitrogen through capillary column as compared to 40 ml/min flow rate of argon containing 5% of methane through glass column of 1.5 m length by Smith (1979). Keeping in view the repeatability of responses, sharp and well resolved peaks of trifluralin, the GC technique was considered satisfactory for the adoption in the present investigations.

5.1.3 Triazophos

The analytical data obtained by processing known amounts of standard triazophos has been presented in Table 4. Calibration curve given in Fig. 5 indicates linear relationship between peak area and amount injected from 10 to 100 pg. Retention time of triazophos peak was 4.26 min. Singh *et al.* (1996) reported the retention time of triazophos 1.76 min using GC-NPD equipped with a packerd glass column having stationary phase 3% OV-17 coated on chromosorb W (HP, 100-160 mesh). The retention time of 3.76 min for triazophos was reported by Rani (1998) using GC-NPD equipped with megabore column. Vijayalakshmi *et al.* (2000) reported the retention time of triazophos 4.58 min by using a chemito 8610 HT GC-fitted with thermoionsation detector; using megabore capillary column (30 m length). Thus the retention time of 4.26 min in our studies was found to be correct. Keeping in view the repeatability of responses, sharp and well resolved peaks of triazophos, the GC technique was considered satisfactory.

5.2 Recovery tests

Prior to taking up analysis of the test samples of 0.01M $CaCl_2$ solution (supernatant) for quantification of their residue contents, recovery tests were performed for validation of analytical methodology to be adopted. The recovery data obtained in two levels of fortification in respect of 0.01M $CaCl_2$ solution has been discussed below :

5.2.1 Metribuzin

0.01M $CaCl_2$ solution fortified at 0.25 and 0.50 ppm levels with metribuzin, gave average recoveries of 81.55±4.26 and 88.37±0.68 per cent, respectively (Table 5). The recovery of metribuzin from water was about 98 per cent as reported by Fleming *et al.* (1992). Southwick *et al.* (1995) reported 95 per cent recovery of metribuzin from water samples. The recoveries obtained in present studies are comparable with the recoveries reported by other authors. Hence, the recoveries in the present investigations were considered satisfactory and the techniques adopted for residual analysis of metribuzin in 0.01M $CaCl_2$ solution.

5.2.2 Trifluralin

0.01M $CaCl_2$ solution samples fortified at 0.25 and 0.50 ppm level with trifluralin gave average recoveries 82.11±5.57 and 87.49±1.02 per cent, respectively (Table 6). Lee and Chau (1983) reported that average recovery of seven herbicide including trifluralin from distilled water and natural water were between 82 to 104 per cent at two fortification levels. The average recovery of trifluralin from water was found to be more than 80 per cent fortified at 0.1 ppm level by Goyal (2000). The recoveries obtained in present studies are comparable with the recoveries reported by other authors. Hence, the recoveries in the present investigations were considered satisfactory and the techniques adopted for residual analysis of trifluralin in 0.01M $CaCl_2$ solution.

5.2.3 Triazophos

0.01M $CaCl_2$ solution samples fortified at 0.25 and 0.50 ppm levels with triazophos gave average recoveries 99.01±5.71 and 102.08±7.50 per cent, respectively. Malto *et al.* (1991) reported average recoveries of 10 organophosphorous insecticides including triazophos more than 85 per cent form natural water. Rani (1998) reported that the average recoveries of triazophos was 88 per cent at 0.25 to 0.50 ppm levels, respectively. Rao (2000) reported 85 per cent recovery of triazophos from coconut water fortified at 1 ppm level. The recoveries obtained in present studies are comparable with the recoveries reported by other authors. Hence, the recoveries in the present investigations were considered satisfactory and the techniques adopted for residual analysis of triazophos in 0.01M $CaCl_2$ solution.

5.3 Adsorption equilibrium studies

5.3.1 Metribuzin

The amount of metribuzin adsorbed on sandy loam soil in 1 h was 0.495 $\mu g\ g^{-1}$ which reached to 0.548 $\mu g\ g^{-1}$, in 4 h (Table 8). However, in case of clay loam soil the corresponding amounts were 0.413 $\mu g\ g^{-1}$ in 1 h and 0.638 $\mu g\ g^{-1}$ in 4 h (Table 9). This clearly indicates that rate of adsorption of metribuzin was faster in clay loam soil than sandy loam soil. The values of distribution coefficient Kd for both soils was found to be constant after 3 h of soil-metribuzin solution contact. This shows that the adsorption equilibrium of metribuzin on both types of soil reached almost in equal time (3 h).

5.3.2 Trifluralin

The amount of trifluralin adsorbed on sandy loam soil in 1 h was 1.158 μg g^{-1} which reached to 1.176 μg g^{-1} in 4 h (Table 10). However, in case of clay loam soil the corresponding amounts were 1.154 μg g^{-1} in 1 h and 1.183 μg g^{-1} in 4 h (Table 11). This indicates that rate of adsorption of trifluralin was almost same in clay loam and sandy loam soil. The values of distribution coefficient Kd for both soils was constant after 3 h of soil-trifluralin solution contact. This shows that adsorption equilibrium of trifluralin on both types of soil reached almost in equal time (3 h).

The literature on adsorption equilibrium of metribuzin and trifluralin is not available. However, various research workers have reported different times for adsorption equilibrium of various herbicides. Since, metribuzin and trifluralin belongs to triazine and dinitroaniline groups, therefore, some of the adsorption equilibrium studies of herbicides belonging to these groups have been discussed. Prakash and Devi (1998) reported that no significant change was found in the adsorption of pendimethalin on three soils (1 clay, 2 sandy loam soils) after 6 h of shaking on wrist action shaker. The adsorption equilibrium of atrazine on silty clay loam soil of upto 30 cms depth reached in 48 h while adsorption equilibrium on subsurface soil i.e. soil of below 30 cms depth was completed in 4 h (Jenks *et al.* 1998). Wrinkle (1980) reported that the adsorption equilibrium for atrazine was completed after 12 h for a silty clay loam and after 24 h for loam soil. The adsorption equilibrium for three 2-chloro-triazine herbicides on soils of Valois and Rainbecks region approached within 48 h as reported by Gamerdinger *et al.* (1991).

5.3.3 Triazophos

The amount of triazophos adsorbed on sandy loam soil in 1 h was 0.305 $\mu g\ g^{-1}$ which reached to 0.622 $\mu g\ g^{-1}$ in 4 h (Table 12). However, in case of clay loam soil the corresponding amounts were 0.429 $\mu g\ g^{-1}$ in 1 h and 0.730 $\mu g\ g^{-1}$ in 4 h (Table 13). This clearly indicates that rate of adsorption of triazophos was faster in clay loam soil than sandy loam soil. The values of distribution coefficient Kd for both soils was constant after 3 h of soil-triazophos solution contact. This shows that the adsorption equilibrium of triazophos on both types of soil reached almost in equal time. Rao *et al.* (1991) reported that the adsorption equilibrium of triazophos on black and red soils was attained in 1.5 h by keeping the soils in contact with aqueous solution of triazophos.

The various research workers have reported the adsorption equilibrium time from 1 to 24 h for various organophosphates on soils of different agroclimate regions. However, some of them have been reported here.

Saltzman *et al.* (1972) reported that the adsorption equilibrium for adsorption of parathion on three soils viz. Dark rendiza, Meron and Terra rosa was approached within 1 h by keeping the soils in contact with pesticide solution. The adsorption equilibrium for chlorpyrifos on five soils viz. Clarian, Sarpy fine sandy loam, Thurman loamy fine sand, Peat and Harps of Iowa was approached in 2 h (Felsot and Dahm, 1979). Sanchez-Martin and Sanchez-Camazano (1991) reported that adsorption equilibrium for methyl parathion and ethyl parathion on eight soils (Mollic solonetz, Humic combisol, Pellic vertisols) was attained within 24 h by keeping the soils in contact with pesticide solution and intermittent stirring. Leenheer and Ahriches (1971) observed that adsorption equilibrium of parathion on three soils viz. Zensville silt loam, Rommey silty clay loam and Carlisle much was approached after 24 h of mechanical shaking.

5.4 Adsorption-desorption studies

5.4.1 Metribuzin

The per cent adsorption of metribuzin on sandy loam soil ranges from 30.9 to 34.8 (Av. 33.5) as compared to 34.5 to 38.2 (Av. 36.5) in case of clay loam soil (Table 27). However, the per cent desorption from sandy loam soil was 28.7 to 47.5 (Av. 37.1) as compared to 27.6 to 32.0 (Av. 33.7) from clay loam soil. The data clearly show that adsorption of metribuzin on clay loam soil was higher as compared to sandy loam soil. On the other hand, per cent desorption from clay loam soil was lower than sandy loam soil which clearly indicates that herbicide i.e. metribuzin bind with clay loam soil more firmly than sandy loam soil. This may be probably due to more adsorption capacity of clay loam soil as compared to sandy loam soil due to its large surface area, higher cation exchange capacity, organic matter and clay content.

Savage (1976) reported that the metribuzin adsorption was significantly associated with clay content, organic matter and water content. Metribuzin adsorption on various soil types was reported to be influenced more by organic matter content than clay (Pestemer and Mass, 1977). Filep *et al.* (1979) reported that the degree of adsorption of metribuzin on three soils viz. Chernozem, Alluvial meadow and Brown forest illuviation soils was mainly influenced by organic matter. Kazak and Lopuchin (1989) reported that organic matter was shown to influence the adsorption of four herbicides including metribuzin on various soils of Prauge region.

5.4.2 Trifluralin

The per cent adsorption of trifluralin on sandy loam soil ranges from 91.9 to 95.0 (Av. 93.9) as compared to 92.8 to 94.9 (Av. 94.1) in case of clay loam soil (Table 27). However, the per cent desorption from sandy loam soil was 3.0 to 5.2 (Av. 3.8) as compared to 3.1 to 4.3 (Av. 3.7) from clay loam soil. Unlike metribuzin, the per cent adsorption and desorption of trifluralin from sandy loam soil as well as clay loam soil was almost identical.

Grover *et al.* (1979) reported more than 90 per cent adsorption of three herbicides viz. di-allate, tri-allate and trifluralin in all the five soils viz. Melford loam, Weyburanoxbow sandy loam, Asquith loamy sand, Indian clay loam. They also reported that due to high per cent of adsorption, the transport of these herbicides, especially triallate and trifluralin as a result of water flow would be minimal under field conditions.

5.4.3 Triazophos

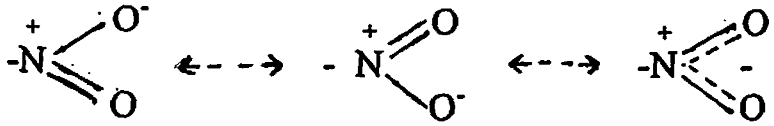
The per cent adsorption of triazophos on sandy loam soil ranges from 48.5 to 60.4 (Av.53.5) as compared to 54.7 to 67.3 (Av. 59.5) in case of clay loam soil

(Table 27). However, the per cent desorption from sandy loam soil was 26.2 to 31.0 (Av. 28.8) as compared to 25.7 to 30.7 (Av. 28.7) from clay from soil. The data show that adsorption of triazophos on clay loam soil was higher as compared to sandy loam soil while the per cent desorption was almost identical from both soils. The data revealed that like metriburin, triazophos also bind with clay loam soil more firmly than sandy loam soil which may be probably due to more adsorption capacity of clay loam soil as compared to sandy loam soil due to its large surface area, higher cation exchange capacity, organic matter and clay content. The effect of two different soils on per cent adsorption of triazophos was discussed by Rao *et al.* (1991) who reported that the adsorption of triazophos on black soil was higher than red soil which may be possibly due to higher CEC, organic matter content, higher surface area and higher exchangeable Ca^{++} content.

Among the pesticides viz. metribuzin, trifluralin and triazophos, the average values of adsorption on both soils viz. sandy loam and clay loam at four concentration levels were 94 per cent for trifluralin followed by 56.5 per cent for triazophos and 35 per cent for metribuzin. However, desorption was 33.7 per cent for metribuzin followed by 28.7 per cent for triazophos and 3.8 per cent for trifluralin. The results indicate that trifluralin got strongly adsorbed by both types of soil followed by triazophos and metribuzin. The decrease in per cent adsorption in the order trifluralin > triazophos > metribuzin may be possibly due to increase in their water solubility in the order trifluralin (<0.001 g/lt) <

triazophos (0.039 g/lt) < metribuzin (1.2 g/lt). Thus we can say that per cent adsorption of pesticides on soil is inversely correlated with their water solubility. Raj *et al.* (1999) also reported that the adsorption of three herbicides viz. pendimethalin, fluchloralin and oxadiazinon on sandy loam and clayey soils was inversely proportional to their water solubilities. The adsorption of 12 insecticides viz. leptophos, ethion, chlorpyrifos, carbofuran, lindane etc. on four soils viz. organic soil, Big Creek sediment, Beverly sandy loam and Plainfield sand was inversely related to their water solubilities (Sharom *et al.*, 1980).

Strong adsorptive nature of trifluralin may be possibly due to presence of two polar NO_2 groups having following resonance structures



thus increasing the bonding sites for adsorption whereas this kind of polar groups are not present in metribuzin and triazophos.

5.4.4 Freundlich isotherms

The adsorption-desorption isotherms of metribuzin, trifluralin and triazophos on sandy loam and clay loam soils are shown in Figs. 7-12.

The adsorption of these pesticides on both soils were found to be linear and in close agreement with the Freundlich equation i.e. :

$$x/m = K_f C_e^{1/n}$$

Where K_f and $1/n$ are empirical adsorption constants specific to each soil-pesticide interaction being considered, x/m is the adsorbed pesticide on soil (µg

g^{-1}) and C_e is the pesticide concentration (µg ml^{-1}) in solution phase. A linear relation was obtained when log x/m (on Y-axis) is *plotted against log C_e (on X*-axis) for each pesticide-soil system, where slope and intercept provides values of 1/n and K, respectively (Table 17, 21, 25). The magnitude of K_f express the adsorption capacity for adsorbate for the system having comparable 1/n values. The values of 1/n provides an idea of intensity of adsorption with nature of adsorbate for a given adsorbent.

The values of Freundlich constants K_f (Ads) for adsorption of these pesticides viz. metribuzin, trifluralin and triazophos were in the range from 3.37 to 418.11 for clay loam soils and 2.76 to 966.05 for sandy loam soil. The values of 1/n were in the range 0.69 to 1.37 for adsorption of pesticides on clay loam soil and 0.72 to 1.58 for sandy loam soil. The values of Freundlich constants K_f (Des) for desorption of these pesticides viz. metribuzin, trifluralin and triazophos were in the range from 6.30 to 242.77 for clay loam soil and 7.38 to 845.17 for sandy loam soil. The values of 1/n were in the range 0.79 to 1.13 for clay loam soil and 0.84 to 1.91 for sandy loam soils. The difference in values of adsorption constants for two soils can be attributed due to difference in organic matter contents. Felsot and Dahm (1979) observed a positive correlation between K_f and organic matter content & cation exchange capacity of four soils for different insecticides.

Within three pesticides of our study, the highest K_f values (highest adsorption) of trifluralin showed that trifluralin has probably very low potential to migrate through the soil profile (leaching) or over the soil surface (runoff) with moving water whereas the low K_f values (lower adsorption) of metribuzin indicate that it may leach to lower surfaces. Various research workers have reported different values of Freundlich constants (K_f, 1/n) for metribuzin, trifluralin and triazophos adsorption on different soils. Savage (1974) reported that values of K_f varies between 0.25 to 2.20 for adsorption of metribuzin on 16 soils of lower alluvial flood plain of Massissipi River and correlated the K_f values with clay content and organic matter content. The Freundlich constant K_f varies between 0.562 for the least adsorptive soil (Fox sandy loam) to 31.667 for the most highly adsorptive soil depending on the organic matter present in the soil (Sharon, 1974). Grover *et al.* (1979) reported the Freundlich K_f values from 96-315 for adsorption of trifluralin on five soils viz. Melford loam, Weyburnoxbow sandy loam Regina clay, Indian head sandy loam, Asquith loamy sand. The Freundlich K_f value for adsorption of triazophos was higher for black soil (13.71) as compared to Red soil (6.86). This may possibly be due to difference in organic matter content in black soil (1.65%) and Red soil (1.24%) [Rao *et al.* 1991].

In our studies of adsorption-desorption of trifluralin and metribuzin on sandy loam and clay loam soils, the values of 1/n are slightly more than unity which are consistent with those reported for adsorption-desorption studies of pendimethalin, fluchloralin and oxadiazinon on sandy loam and clayey soils (Raj *et al.*, 2000) and for adsorption of trifluralin on Plano silt loam soil (Jacques and

Harvey, 1979). However, the values of 1/n obtained in our study for adsorption-desorption of triazophos on sandy loam and clay loam soils are less than unity which are consistent with as reported by Prakash and Devi (1998) in their study of adsorption and desorption of pendimethalin on clay and two sandy clay loam soils. Felsot and Dahm (1979) also reported that 1/n values for adsorption of four organophosphates on five soils of Iowa were less than unity.

The values of Freundlich constant K_f (Des) obtained during desorption of metribuzin, trifluralin and triazophos are higher than their respective adsorption values. This is because of large amount of pesticide still retained after desorption. Similar observations were also reported by Felsot and Dahm (1979), Adhikari *et al.* (1991) for adsorption-desorption behaviour of chlorpyrifos, ethion, phorate etc. for various soils.

5.4.5 Distribution co-efficients

The values of Kd for adsorption of these pesticides were in the range from 2.94 to 89.86 for clay loam soil. The respective values for sandy loam soils were 2.52 to 87.37. The values of K_{oc} for adsorption were in the range from 376.92 to 11520.51 for clay loam soil as compared to 387.69 to 14091.94 for sandy loam soil. The values of K_c for adsorption were in the range from 6.53 to 199.69 for clay loam soil as compared to 15.75 to 546.06 for sandy loam soil. Similar to our results, the various research workers have also reported the higher values of Kd and lower values of K_{oc} and K_c for clay loam soil (soil having high organic carbon) as compared to sandy loam soil (soil having low organic carbon). Raj *et al.* (1999) reported that Kd values for adsorption of three herbicides viz. pendimethalin, fluchloralin and oxadiazinon was higher for clayey soil than sandy loam soil. They also reported that K_{oc}, K_c values for adsorption of the herbicides are more in sandy loam soil than clayey soil. The values of Kd for desorption of pesticides were in the range from 11.24 to 143.87 for clay loam soil and 10.17 to 138.13 for sandy loam soil. The values of K_{oc} for desorption were in the range from 1441.28 to 18444.87 for clay loam soil and 1564.62 to 21250.77 for sandy loam soil. The values of K_c for desorption were in the range from 24.98 to 319.71 for clay loam soil as compared to 63.56 to 863.31 for sandy loam soil. Similar to our results, Raj *et al.* (1999) reported that Kd values for desorption of three herbicides were higher for clayey soil (having more organic carbon) than sandy loam soil (having low organic carbon). They also reported that K_{oc} and K_c values for desorption were higher for sandy soil than clayey soil.

Among the three pesticides viz. metribuzin, trifluralin and triazophos, the values of Kd, K_{oc} and K_c were highest for trifluralin followed by triazophos and metribuzin which also indicate that trifluralin has strong adsorptive nature followed by triazophos and metribuzin.

6. SUMMARY AND CONCLUSIONS

Research studies were carried out under laboratory conditions to study the adsorption equilibrium and adsorption-desorption behaviour of metribuzin, trifluralin and triazophos on sandy loam and clay loam soils.

During these studies, adsorption equilibrium of all the three *pesticides viz.* metribuzin, trifluralin and triazophos on two soils viz. sandy loam and clay loam soils were studied at 0.25 μg ml^{-1} concentration level of pesticide taken in 0.01M $CaCl_2$ solution (100 ml). The soil pesticide solutions were shaken for 1, 2, 3 and 4 h for studying the time required to reach the adsorption equilibrium. The adsorption studies were conducted at four concentration levels i.e. 0.1, 0.2, 0.3 and 0.4 μg ml^{-1} of pesticides taken in 0.01M $CaCl_2$ solution. The soil-pesticide solutions were shaken on mechanical shaker for 3 h as per the equilibrium studies. The soil-pesticide solution (20 g soil, 100 ml $CaCl_2$ solution) were centrifuged at 3500 rpm for 10 min. The supernatant were separated out. The supernatant were processed as per the methods given in "Materials and Methods" for the estimation of residues of metribuzin, trifluralin and triazophos by Gas Chromatograph. From the amount of residues remained in 0.01 $CaCl_2$ solution, the amount of pesticides adsorbed on soils was calculated. For desorption studies of pesticides from soils, the soil left after centrifugation in adsorption studies, was shaken on mechanical shaker with fresh 0.01M $CaCl_2$ solution (100 ml). From the amount of residues obtained in 0.01M $CaCl_2$ solution, per cent desorption of each pesticide in both soils was calculated.

Retention times (R_t) observed for metribuzin, trifluralin and triazophos were 3.11, 3.06 and 4.26 min, respectively. The average recovery of pesticides in 0.01M $CaCl_2$ solution at 0.25 and 0.50 ppm fortification levels was about 85 per cent for metribuzin, 85 per cent for trifluralin and 100 per cent for triazophos (Table 5-7). The finding of investigations are summerised below :

6.1 Adsorption equilibrium studies

1. The adsorption of metribuzin, trifluralin and triazophos on sandy loam and clay loam soils was completed in 3 to 4 h (Table 8-13).
2. Rate of adsorption for metribuzin, trifluralin and triazophos was more in clay loam soil as compared to sandy loam soil.

6.2 *Adsorption-desorption studies*

1. Per cent adsorption of metribuzin was more on clay loam soil as compared to sandy loam soil. However, per cent desorption of metribuzin was less from clay loam soil as compared to sandy loam soil (Table 27).
2. Per cent adsorption and desorption of trifluralin on both types of soils viz. sandy loam and clay loam soils was almost identical (Table 27).

3. Like metribuzin, per cent adsorption of triazophos was more on clay loam soil as compared to sandy loam soil. However, the per cent desorption from clay loam soil was almost same as compared to sandy loam soil (Table 27).

4. The order of adsorption and desorption of all the three pesticides on two soils viz. sandy loam and clay loam soils was as follow :

Adsorption	Trifluralin (94%) > triazophos (57%) > metribuzin (35%)
Desorption	Trifluralin (4%) < triazophos (29%) < metribuzin (34%)

5. Graphs plotted between log C_e (concentration of pesticide in solution) Vs log x/m (concentration of pesticides in soil) taken on X and Y axis, respectively were found to be linear ($r=0.94-0.99$). This indicates that Freundlich equation was best fitted for adsorption and desorption of metribuzin, trifluralin and triazophos on both types of soils (sandy loam and clay loam).

The values of distribution co-efficients Kd for adsorption and desorption of these pesticides were higher for clay loam soil than sandy loam soil. Among the three pesticides, the values of Kd were highest for trifluralin followed by triazophos and metribuzin.

Conclusions

The adsorption of trifluralin was highest (94%) in both types of soils followed by triazophos (57%) and metribuzin (35%) whereas desorption of trifluralin was minimal (4%) followed by triazophos (29%) and metribuzin (34%). Due to strong adsorptive nature of trifluralin, it has probably low potential to migrate through the soil profile (leaching) or over the soil surface (run-off) with the moving water. However, metribuzin due to low adsorptive nature may leach to lower surfaces.

Arienzo, M.; Crisanto, T.; Sanchez-Martin, M.J. and Sanchez-Camazano, M. (1994). *Effect of soil characteristics* on adsorption and mobility of (^{14}C-) diazinon. *J. Agric. Food Chem.*, **42**: 1803-1808.

Baarschers, W.H.; Elvish, J. and Ryan, S.P. (1983). Adsorption of fenitrothion and 3-methyl-4-nitrophenol on soils and sediment. *Bull. Environ. Contam. Toxicol.*, **30**: 621-627.

Bansal, O.P. (1982). Adsorption and interaction of oxamyl and dimecron with some soils of India. *J. Indian Soc. Soil Sci.*, **30**(4): 459-467.

Barcelo, D.; Sole, M.; Durand, G. and Albaiges, J. (1991). Analysis and behaviour of organophosphorous pesticides in rice crop field. *Fresenius' J. Ana. Chem.*, **339**(9): 676-683.

Beltran, J.; Hernandez, F.; Lopez, F.J. and Morell, I. (1995). Study of sorption processes of selected pesticides on soils and ceramic porous cups used for soil solution sampling. In: Proceedings of the 4th Workshop on Chemistry and fate of modern pesticides Prague, Czech, Republic, 8-10 September, 1993 (ed. Albaiges, J.) *International J. Analytical Chem.*, **58**(1/4): 287-303.

Bolan, N.S. and Baskaran, S. (1997). Sorption and degradation of phorate as influenced by soil depth. *Aust. J. Soil Res.*, **35**: 763-775.

Bresnahan, G.A.; Koskinen, W.C.; Dexter, A.G. and Lueschen, W.E. (2000). Influence of soil pH sorption interactions on imazethapyr carry-over. *J. Agric. Chem.*, **48**: 1929-1934.

Briggs, C.G. (1981). Theoretical and experimental relationships between soil-adsorption, octanol-water partition coefficients, water solubilities, bioconcentration factors, and the parachor. *J. Agric. Food Chem.*, **29**: 1050-1059.

BIBLIOGRAPHY

Adhikari, M. and Roy, A. (1989). Sorption of pesticides on soil and soil components. *Indian Agric.*, **33**(1): 23-29.

Adhikari, M.; Mandal, A.K. and Ray, A. (1991). Sorption of sumithion by soil. *J. Indian Soc. Soil Sci.*, **39**: 680-684.

Agnihotri, N.P. (2000). Pesticide consumption in Agriculture in India-an Update. *Pesticide Res. J.,* **12**(1): 150-155.

Akins, M.B. (1977). The adsorption, desorption and the volatility of three dintroaniline herbicide in soil. *Diss. Abst. Int., B.* **38**(2): 443-444.

Ali *et al.* (2000). Studies on adsorption of carbaryl as influenced by soil organic matter (SOM) and other soil characteristics. *J. Indian Chem. Soc.*, **77**: 17-19.

Ali, I.; Rathore, H.S. and Singh, K.K. (1994). Studies on adsorption and persistence of malathion in two sandy loam soils. *Pesticide Res. J.*, **6**(2): 139-145.

Alvarez-Benedi, J.; Carton, A. and Fernandez, J.C. (1998). Sorption of tribenuron, chlorsulfuron and imazamethabenzmethyl by soils. *J. Agric. Food Chem.*, **46**: 2840-2844.

Anonymous (1998). Analysis report of soil, straw and wheat grain samples for trifluralin (Treflan) Residue Content Progress Report, 1997-98 AICRP Pesticide Residues, Gujrat Agricultural University.

Arienzo, M.; Crisanto, T.; Sanchez-Martin, M.J. and Sanchez-Camazano, M. (1994). Effect of soil characteristics on adsorption and mobility of (^{14}C-) diazinon. *J. Agric. Food Chem.*, **42**: 1803-1808.

Baarschers, W.H.; Elvish, J. and Ryan, S.P. (1983). Adsorption of fenitrothion and 3-methyl-4-nitrophenol on soils and sediment. *Bull. Environ. Contam. Toxicol.*, **30**: 621-627.

Bansal, O.P. (1982). Adsorption and interaction of oxamyl and dimecron with some soils of India. *J. Indian Soc. Soil Sci.*, **30**(4): 459-467.

Barcelo, D.; Sole, M.; Durand, G. and Albaiges, J. (1991). Analysis and behaviour of organophosphorous pesticides in rice crop field. *Fresenius' J. Ana. Chem.*, **339**(9): 676-683.

Beltran, J.; Hernandez, F.; Lopez, F.J. and Morell, I. (1995). Study of sorption processes of selected pesticides on soils and ceramic porous cups used for soil solution sampling. In: Proceedings of the 4th Workshop on Chemistry and fate of modern pesticides Prague, Czech, Republic, 8-10 September, 1993 (ed. Albaiges, J.) *International J. Analytical Chem.*, **58**(1/4): 287-303.

Bolan, N.S. and Baskaran, S. (1997). Sorption and degradation of phorate as influenced by soil depth. *Aust. J. Soil Res.*, **35**: 763-775.

Bresnahan, G.A.; Koskinen, W.C.; Dexter, A.G. and Lueschen, W.E. (2000). Influence of soil pH sorption interactions on imazethapyr carry-over. *J. Agric. Chem.*, **48**: 1929-1934.

Briggs, C.G. (1981). Theoretical and experimental relationships between soil-adsorption, octanol-water partition coefficients, water solubilities, bioconcentration factors, and the parachor. *J. Agric. Food Chem.*, **29**: 1050-1059.

Cacco, G. and Ferrari, G. (1982). Adsorption and translocation of 4-(Trifluoromethyl) chlorobenzene in soil and crops. *J. Agric. Food Chem.*, **30**(1): 186-187.

Carringer, R.D.; Wefer, J.B. and Manaco, T.J. (1975). Adsorption-desorption of selected pesticides by organic matter and man.tmorillonite. *J. Agric. Food Chem.* **23**: 568-572.

Chang, S.S. (1980). The influence of soil pH on adsorption and phytotoxicity of triazine herbicides. *J. Agric. Assoc. China,* **109**: 17-29.

Chapman, R.A. and Harris, C.R. (1980). Insecticidal activity and persistence of terbufos, terbufos sulfoxide and terbufos sulfone in soil. *J. Econ. Ent.,* **73**: 536-543.

Chapman, R.A.; Tu, C.M.; Harris, C.R. and Dubois, D. (1982a). Biochemical and chemical transformations of terbufos, terbufos sufoxide and terbufos sulfone in natural and sterile, mineral and organic soil. *J. Econ. Ent.,* **75**: 955-960.

Chapman, R.A.; Tu, C.M.; Harris, C.R. and Harris Carol, R. (1982b). Biochemical and chemical transformations of phorate, phorate sulfoxide and phorate sulfone in natural and sterile mineral and organic soil. *J. Eco. Ent.,* **75**: 112-117.

Chio, C.T. (1989). Theoretical considerations of the partition uptake of non-ionic organic compounds by soil organic matter. In: *Reaction and movement of organic chemicals in soils.* B.L. Sawhney and K. Brown (eds.) SSA Esp. Publ. 22. Madison, WL, pp. 1-29.

Clay, S.A.; Allmaras, R.R.; Koskinen, W.C. and Wyse, D.L. (1988). Desorption of atrazine and cyanazine from soil. *J. Environ. Qual.,* **17**(4): 719-723.

Cohen, S.Z.; Creegers, S.M.; Carsel, R.F. and Enfield, C.G. (1984). In: R.F. Kruenger and J.N. Seiber (eds.), *Treatment and Disposal of Pesticide Wastes*, ACS, Symp. Series, Vol. 259, P. 297.

Dickinson, C.M.; Sullivan, J.J. and Allen, C.R. (1988). A liquid chromatographic study of the effect of adsorption on concentration of aqueous temephos solutions. *J. Liquid Chromatogr.* **11**(16): 3435-3446.

Duseja, D.R. and Holmes. E.E. (1978). Field persistence and movement of trifluralin in two soil types. *Soil Sci.,* **125**(1): 41-47.

Edward, C.A. (1972). Insecticides. In *organic chemicals in the soil environment* Ed. Goring, C.A.I. and Hamakar, J.W.; Marcel Dekker Inc. New York, pp 513-568.

Farrel, J.; Grasslan, D. and Johnes, M. (1999). Investigation of mechanisms contributing to slow desorption of hydrophobic organic compounds from mineral solids. *Environ. Sci. Technol.,* **33**: 1237-1243.

Felsot, A. and Dahm. P.A. (1979). Sorption of organophosphorus and carbamate insecticides by soil. *J. Agric. Food Chem.* **27**(3): 557-563.

Filep, G.; Konya, J. and Kaposztassy, A. (1979). An evaluation of herbicide adsorption in soil. *Agrokemica es Talajtan.,* **28**(1/2): 181-194.

Fleming, G.F.; Wax, L.M.; Simmons, W.S. and Felsot, A.S. (1992). Movement of Alachlor and metribuzin from controlled release formulations in sandy soil. *Weed Sci.,* **40**: 606-613.

Gajbhiye, V.T.; Agnihotri, N.P. and Gupta, R.K. (1995). Effect of formulation on the dissipation of quinalphos from soil and water. *J. Ent. Res.,* **19**(4): 295-300.

Gamerdinger, A.P.; Lemley, A.T. and Wagenet, R.J. *(1991). Nonequilibrium* sorption and degradation of three-2-chloro-s-triazine herbicides in soil water systems. *J. Environ. Qual.,* **20**: 815-822.

Garcia-Valcarcel, A.I.; Matienzo, M.T.; Sanchez-Brunete, C. and Tadeo, J.L. (1997). Atrazine and metribuzin sorption in soil and their relationship with organic matter content. In: *Proc. of the 1997 Congress of the Spanish Weed Sci. Soc., Valencia, Spain,* 24-26.

Garcia-Volcarcel, A.I. and Tadeo, J.L. (1999). Influence of soil moisture on the sorption and degradation of Hexazinone and Simazine in soil. *J. Agric. Food Chem.* **47**: 3895-3900.

Gennari, M.; Negre, M. and Raimondo, E. (1994). Effect of soil properties on adsorption and desorption of acifluorfen. *J. Agric. Food Chem.,* **42**: 2329-2332.

Gonzalez, J.M. and Ukrainczyk, L. (1996). Adsorption and desorption of nicosulfuron in soils. *J. Environ. Qual.,* **25**: 1186-1192.

Goyal, V. (2000). Adsorption and movement of trifluralin in soils and its interaction with zinc. M.Sc. thesis, CCS Haryana Agricultural University, Hisar.

Green, R.E. and Karickhoff, S.W. (1990). Sorption estimates for modeling. In *Pesticides in the Soil Environment : Processes. Impacts and Modeling : Soil Science Society of America* : Madison, W.I. pp 80-99.

Grey, T.I.; Walker, R.H.; Wehtje, G.R. and Hancock, H.G. (1997). Sulfentrazone adsorption and mobility as affected by soil and pH. *Weed Sci.,* **45**: 733-738.

Grover, R.; Banting, J.D. and Morse, P.M. (1979). Adsorption and bioactivity of di-allate, triallate and trifluralin. *Weed Res.,* **19**: 363-369.

Grover, R.; Wolt, J.D.; Cessna, A.J. and Schiefer, H.B. (1997). Environmental fate of trifluralin. *Rev. Environ. Contam. Toxicol.*, **153**: 1-64.

Haberhauer, G.; Pfeiffer, L. and Gerzabek, M.H. (2000). Influence of molecular structure on sorption of phenoxyalkanoic herbicides on soil and its particle size fraction. *J. Agric. Food Chem.*, **48**: 3722-3727.

Harper, S.S. (1988). Sorption of metribuzin in surface and subsurface soils of the Mississippi delta region. *Weed Sci.*, **36**(1): 84-89.

Harvey, R.G. (1974). Soil adsorption and volatility of dinitroaniline herbicides. *Weed Sci.*, **22**(2): 120-124.

Hirai, K. and Kawamura, Y. (1975). Studies on a new herbicide, oxidiazon (G-315, RP 17623).4. Influence of soil properties on the herbicidal activity of oxidiazon under flooded conditions of paddy field. *Weed Res.*, **20**(2): 13-18.

Horowitz, M.; Hulin, N. and Blumenfeld, T. (1974). Behaviour and persistence of trifluralin in soil. *Weed Res.*, **14**: 213-220.

Hyzak, D.L. and Zimdahl, R.L. (1974). Rate of degradation of metribuzin and two analogs in soil. *Weed Sci.*, **22**(1): 75-79.

Jacques, G.L. (1977). Factor influencing the herbicidal activity of dinitroaneline herbicides. *Diss. Abst. Int., B.*, **37**(7): 3192.

Jacques, G.L. and Harvey, R.G. (1979). Adsorption and diffusion of dinitroaniline herbicides in soils. *Weed Sci.*, **27**(4): 450-455.

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

Jolly, A.V.I.; Johnstone, P.K. and Bos, J.A. (1990). Factor influencing trifluralin persistencein soil. *A. review. Proc. 9th Aust. Weed Conf.* 294-298.

Karickhoff, S.W. (1981). Semi empirical estimation of sorption of hydrophobic pollutants on natural sediments and soils. *Chemosphere,* **10**: 833-845.

Katagi, M., Tsuchihshi, H., Hanada, S.; Jimori, H. and Otsuki, K. (1993). Determination of dichlorvos, trichlorfon and their metabilities and degradation products in environment water, drinks and human urine. *Japanese J. Toxicol. Environ. Health,* 39(5): 459-468.

Kenaga, E.E. (1980). Predicted bioconcentration factor and soil sorption co-efficients of pesticides and other chemicals. *Ecotoxicol Environ. Saf.,* 4: 26-38.

Khan, S. and Khan, N.N. (1986). The mobility of some organophosphorous pesticides in soil as affected by some soil parameters. *Soil Sci.,* 142(4): 214-221.

Khan, S.U. (1980). Pesticides in the soil environment. Elsevier Scientific Publishing Co., Amsterdam, Oxford and New York. Pp 240.

Kishk, F.M.; Abu-Shara, T.M.; Bakry, N. and Abou-Donia, M.B. (1979). Adsorption of methyl parathion by soils. *Bull. Environ. Contam. Toxicol.,* 22(6): 733-738.

Koskinen, W.C.; O'Connor, G.A. and Cheng, H.H. (1979). Characterization of hysteresis in the desorption of 2,4,5 T from soils. *Soil Sci. Soc. Am.Proc.,* 43: 871-874.

Kozak, J. and Lopuchin, O.V. (1989). Sorption of selected herbicides by soils and main soil components. *Sbornik Vysoke Skoly Zemedelske v Praze Fakulta Agronomicka Rada A, Rostlinna Vyroba,* **51**: 85-102.

Kumar, R. (1997). Dissipation and persistence studies of isoproturon, dodine and chlorpyrifos. Ph.D. Thesis, CCS Haryana Agricultural University, Hisar.

Kumaran, K. and Devi, S. (1996). Adsorption desorption of atrazine in some selected soils of Karnataka. *Pesticide Res. J.*, **8**(2): 146-151.

Kumari, K. and Singh, R.P. (1994). Influence of different factors on the adsorption of phosphamidon on soils. *Toxicol. Environ. Chem.*, **42**(3/4): 183-190.

Ladlie, J.S.; Meggitt, W.F. and Penner, D. (1976). Effect of soil pH on microbial degradation, adsorption and mobility of metribuzin. *Weed Sci.*, **24**(5): 477-481.

Lafleur, K.S. (1979). Sorption of metribuzin by model soils and agronomic soils. Rates and Equilibria. *Soil Sci.*, **127**(1): 51-55.

Lee, H. and Chau, A.S.Y. (1983). Determination of trifluralin, diallate, triallate, atrazin, barban, dichlorfop-methyl and benzoylprop-ethyl in natural waters at parts per trillion levels. *J. Assoc. Off. Anal. Chem.*, **66**(3): 651-659.

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

Lichtenstein, E.P. and Schulz, K.R. (1964). The effect of moisture and microorganisms on the persistence and metabolism of some organophosphorous insecticides in soils with special emphasis on parathion. *J. Econ. Ent.*, **57**(5): 618-627.

Ma, L.; Southwick, L.M.; Willis, G.H. and Selim, H.M. (1993). Hysteretic characteristics of atrazine adsorption-desorption by a Sharkey soil. *Weed Sci.*, **41**: 627-633.

Malto, J.C.; Pico, Y.; Font, G. and Manes, J. (1991). Determination of triazines and organophosphorous pesticides in water samples using solid phase extraction. *J. Chromatogr.*, **555**(1-2): 137-145.

Mandal, A.K. and Adhikari, M. (1995). Role of organic matter and sesquioxides in the adsorption of pesticides on soils. *J. Indian Soc. Soil Sci.,* **43**(4): 561-567.

Mandal, A.K. and Adhikari, M. (1997). Influence of soil properties on the interactions of pesticides with soils. *J. Indian Chem. Soc., 74*: 114-118.

McCall, P.J.; Swann, R.L.; Lakowski, D.A.; Unger, S.M.; Vrona, S.A. and Dishburger, H.J. (1980). Estimation of chemical mobility in soil from liquid charamatographic retention times. *Bull. Environ. Contam. Toxicol.,* **24**: 190-195.

Mersie, W. and Foy, C.L. (1986). Adsorption, desorption and mobility of chlorsulfuron in soils. *J. Agric. Food Chem.,* **34**: 89-92.

Mersie, W. and Seybold, C. (1996). Adsorption and desorption and desorption of atrazine, dethylatrazine, deisopropyl atrazine, and hydroxyatrazine on Levy wetland soil. *J. Agric. Food Chem.,* **44**: 1925-1929.

Misra, S.G. and Joshi, H.C. (1983). Adsorption, persistence and movement of phosphomidon in soils. *Pesticides.* **17**(10): 15-18.

Mohapatra. S.P.; Gajbhiye. V.T. and Agnihotri. N.P. (1994). Organophosphorous insecticide residues in the aquatic environmental of a rural area. *Pesticide Res. J.,* 6(2): 157-160.

Moura-Pries-N-de; Shiva-J, F. da; Shiva, J.B. da; Ferreira, L.R., Cardosa, A.A. (1997). Trifluralin and imazaquin adsorption and leaching in different soils. *Revista-Ceres.* 44: 300-314.

Moyer, J.R. (1979). Soil organic matter, moisture and temperature effect on wild oats control with trifluralin. *Can. J. Plant Sci.,* **59**: 763-768.

Nazni, W.A.; Lee, H.L. and Abdullah, A.G. (1995). Detection of pesticide residues in water by immunoassay. *Trop. Biomedicine,* **12**(2): 153-157.

Oubina, A.; Gascon, J.; Ferrer, I. And Barcelo, D. (1996). Evaluation of a magnetic particle-based ELISA for determination of chlorpyrifos-ethyl in natural waters and soil samples. *Environ. Sci. Tech.*, 30(2): 509-512.

Peek, D. and Appleby, A.P. (1989). Effect of pH on phytotoxicity of metribuzin and ethyl metribuzin. *Weed Tech.*, 3(4): 636-639.

Pestemer, W. and Mass, G. (1977). Behaviour of Patoran, Sencor and Velsicol in Soils of various sorptive capacity and in potatoes. *Paper at 41 Deutsche Pflanzenschutz-Tagung, Munster,* **178**: 232-233.

Peter, C.J. and Weber, J.B. (1985). Adsorption and efficacy of trifluralin and butralin as influenced by soil properties. *Weed Sci.*, **33**(6): 861-867.

Pimental, D. (1995). Amounts of pesticides reaching target-pests : environmental inputs and ethics. *J. Agric. Environ. Ethics,* **8**(1): 17-29.

Prakash, N.B. and Devi, L.S. (1998). Effect of organic matter on adsorption-desorption of Pendimethalin in soils. *Pesticide Res. J.,* **10**(2): 202-208.

Pusino, A.; Petretto, S. and Gessa, C. (1997). Adsorption and desorption of imazapyr by soil. *J. Agric. Food Chem.*, **45**: 1012-1016.

Racke, K.D.; Stelle, K.P.; Yoder, R.N.; Dick, W.A. and Avidov, E. (1996). Factors affecting the hydrolytic degradation of chlorpyrifos in soil. *J. Agric. Food Chem.*, **44**: 1582-1592.

Rai, A.K.; Chhonkar, P.K. and Agnihotri, N.P. (1998). Adsorption-desorption of anilofos on six diverse soils. *Pesticide Res. J.,* **10**(2): 172-177.

Rai, A.K.; Chhonkar, P.K. and Agnohotri, N.P. (2000). Adosrption-desorption of pendimethalin in six soils of India. *J. Indian Soc. Soil Sci.*, **48**(1): 52-56.

Raj, M.F.; Patel, B.K. and Shah, P.G. (1999). Adsorption and desorption of pendimethalin, fluchloralin and oxadiazon on soils. *Pesticide Res. J.*, **11**(2): 162-167.

Rajanna, K.B. and Devi, L.S. (1987). Adsorption of triazine herbicides in Karnataka soils. *Mysore J. Agric. Sci.*, **21**(4): 440-445.

Raman, S.; Krishna, M. and Rao, C. (1988). Adsorption-desorption of atrazine on four soils of Hyderabad. *Water, Air Soil Polln.*, **40**: 177-184.

Rani, S. (1998). Persistence behaviour of triazophos in soil and water systems. M.Sc. Thesis, CCS Haryana Agricultural University, Hisar, India.

Rao, B.N. (2000). Residues of triazophos in coconut water and kernel when administrated through roots. *Pestology,* **24**(1): 2-4.

Rao, G.S.; Sarkar, D.K. and Pillai, R.N. (1991). Adsorption of triazophos in soils. *Indian J. Agric. Sci.*, **61**(9): 674-676.

Rao, P.S.C.; Hornsby, A.G. and Jessup, R.E. (1985). Indices for ranking the potential for pesticide contamination of ground water. *Soil Crop Sci. Soc. FL Proc.*, **44**: 1-8.

Reddy, K.S. and Gambrell, R.P. (1987). Factor affecting the adsorption of 2,4-D and methyl parathion in sols and sediments. *Agric. Ecosystem Environ.*, **18**(3): 231-241.

Rodriguez, G.E.; Sanchez, M.M. and Sanchez, C.M. (1991). Determination of acephate by liquid chromatography in the presence of aqueous soil extracts. *J. Chromatogr.*, **585**(2): 324-328.

Saltzman, S.; Kliger, L. and Yaron, B. (1972). Adsorption-desorption of parathion as affected by soil organic matter. *J. Agric. Food Chem.*, **20**(6): 1224-1226.

Sanchez-Camazano, M. and Sanchez-Martin, J. (1990). Effect of colloidal soil components on the adsorption of Mevinphos. *Bull. Environ. Contam. Toxicol.*, **44**: 106-113.

Sanchez-Camazano, M.; Sanchez-Martin, M.J. and Delgado-Pascual, R. (2000). Adsorption and mobility of linuron in soils as influenced by soil properties, organic amendments and surfactants. *J. Agric. Food Chem.*, **48**: 3018-3026.

Sanchez-Martin, M.J. and Sanchez-Camazano, M. (1991). Relationship between the structure of organophosphorus pesticides and adsorption by soil components. *Soil Sci.*, **152**(4): 283-288.

Saunders, D.G. and Powers, F.L. (1988). Mobility of trifluralin in soil. DG8 8807, Lilly Research Laboratories, Greenfield, IN.

Savage, K.E. (1974). Adsorption and mobility of metribuzin in soil : In *Abstracts Weed Sci. Soc. America*: 120.

Savage, K.E. (1976). Adsorption and mobility of metribuzin in soil. *Weed Sci.*, **24**(5): 525-528.

Senesi, N.; Cava, P.L. and Miano, T.M. (1997). Adsorption of imazethapyr to amended and non-amended soils and humic acid. *J. Environ. Qual.*, **26**: 1264-1270.

Seybold, C.A.; McSweeney, K. and Lowery, B. (1994). Atrazine adsorption in sandy soils of Wisconsin. *J. Environ. Qual.*, **23**: 1291-1297.

Shanti, G.; Rao, P.C. and Raman, S. (1997a). Adsorption of metoxuron on soil particle size separates of four Alfisols and four Vertisols from Hyderabad. *J. Indian Soc. Soil Sci.*, **45**(1): 73-76.

Shanti, G.; Rao, P.C. and Raman, S. (1997b). Adsorption-desorption of isoproturon on eight soils of Hyderabad, Andhra Pradesh. *J. Indian Soc. Soil Sci.*, 45(3); 494-498.

Sharom, M.S. and Stephenson, G.R. (1976). Behaviour and fate of metribuzin in eight Ontario soils. *Weed Sci.*, 24(2): 153-160.

Sharom, M.S.; Miles, J.R.W.; Harris, C.R. and McEwen, F.L. (1980). Behaviour of 12 insecticides in soil and aqueous suspensions of soil and sediment. *Water Res.*, **14**: 1095-1100.

Sharon, M.S. (1974) (Abstract). The behavior and fate of metribuzin in eight Ontario soils. *In Minutes of the 28th Meeting, Canada Weed Committee, Eastern Section*: 22.

Shea, P.J. (1986). Chlorsulfuron dissociation and adsorption on selected adsorbents and soils. *Weed Sci.*, **34**: 474-478.

Singh, G.; Spencer, W.F.; Cliath, M.M. and Genuchten, M.T. (1990). Sorption behaviour of s-triazine and thiocarbomate herbicides on soils. *J. Environ. Qual.*, **19**: 520-525.

Singh, N.; Wahid, P.A.; Murty, M.V.R. and Sethunathan, N. (1990). Sorption-desorption of methyl parathion, fenitrothion and carbofuran in soils. *J. Environ. Sci. Health.* Part B *Pesticides, Food Contaminants and Agricultural Wastes*: **25**(6): 713-728.

Singh, R.; Kathpal, T.S. and Kushwahahe, K.S. (1996). Harvest time residues of butachlor, quinalphos and triazophos on paddy and endosulfan on maize (*Zea mays* Linn.). *J. Pesticide Res. J.*, **8**(2): 176-181.

Skelly, N.E.: Jensen, D.J. and Aderson, P.K. (1981). High-pressure liquid chromatographic analysis of chlorpyrifos containing insecticide formulations : Collaborative study. *J. Assoc. Off. Anal. Chem.*, 64: 628-634.

Smit, N.S.H.; Nel, P.C. and Folscher, W.J. (1980). Factor affecting the sorption and degradation of atrazine in soil. *Crop Prod.*, 9: 135-139.

Smith, A.E. (1979). Soil persistence experiments with [^{14}C]2,4-D-in a herbicidal mixture, and field persistence studies of tri-allate and trifluralin both singly and combined. *Weed Res.*, 19: 165-170.

Smith, A.E. and Hayden, B.J. (1982). Comparison of the persistence of EPTC, metribuzin and propanil in Saskatchewan field soils. *Bull. Environ. Contam. Toxicol.*, 29: 243-247.

Socias-Viciana, M.M.; Fernandez-Perez, M.; Villafranca-Sanchez, M.; Gonzalez-Pradas, E. and Flores-Cespedes, F. (1999). Sorption and leaching of atrazine and MCPA in natural and peat-amended calcareous soils from Spain. *J. Agric. Food Chem.*, 47: 1236-1241.

Sonan, L.S. and Schwab, A.P. (1995). Adsorption characteristics of atrazine and alachlor in Kansas soils. *Weed Sci.*, 43: 461-466.

Southwick, L.M.; Willis, G.H.; Johnson, D.C. and Selim, H.M. (1995). Leaching of nitrate, atrazine and metribuzin from sugarcane in Southern Louislana. *J. Environ. Qual.*, 24: 684-690.

Spencer, W.F. and Cliath, M.M. (1974). Factor affecting vapour loss of trifluralin from soil. *J. Agric. Food Chem.*, 22(6): 987-991.

Talekar, N.S.; Kao, H.T. and Chen, J.S. (1983). Persistence of selected insecticides in subtropical soil after repeated biweekly applications over two years. *J. Econ. Ent.*, 76: 711-716.

Telbert, R.E.; Howell, S.L. and Rutledge, E.M. (1974). Influence of soil properties on the adsorption and activity of metribuzin (Abstract). In *Proc. 27th Ann. Meeting Southern Weed Sci. Soc.*: 378.

Tomling, C.D.S. ed. (1997). The Pesticide Manual Publ. The British Cr tion of Protection Council. pp. 1606

Ukrainczyk, L. and Ajwa, H.A. (1996). Primisulfuron sorption on minerals and soils. *Soil Sci. Sco. Am. J.,* **60**: 460-467.

Valverde-Garcia, A.; Ganzalez-Pradas, E.; Villafranca-Sanchez, M.; Rey-Buerno, F. Del; Garcia-Rodriguez, A. (1988). Adsorption of thiram and dimethoate on Almeria soils. *Soil Sci. Soc. Am. J.* **52**(6): 1571-1574.

Vijayalakshmi, K.; Jaya Kumar, R. and Kuttalam, S. (2000). Dissipation of triazophos in/on Bhendi. *Pestology,* **24**(8): 32-34.

Wahid, P.A. and Sethunathan, N. (1978). Sorption-desorption of parathion in soils. *J. Agric. Food Chem.,* **26**(10: 101-105.

Werkheiser, W.O. and Anderson, S.J. (1996). Effect of soil properties and surfactant on primsulfuron sorption. *J. Environ. Qual.* **25**: 809-814.

Winkle, M.B. (1980). Effect of weed density, herbicide antidoses, and soil adsorption on herbcide, bioactivity. *Diss. Abst. Int., B.* **41**(2): 433.

Wu, C.; Buehring, N.; Davidson, J.M. and Santelmann, P.W. (1975). Napropamide adsorption, desorption and movement in soils. *Weed Sci.,* **23**(6): 454-457.

Wylic, P.L. and Uchiyama, K. (1996). Improved gas chromatographic analysis of organophosphorous pesticides with pulsed splitless injection. *J. Assoc. Off. Anal. Chem. Int.,* **79**(2): 571-577.

Zheng, L. and Wang, F.J. (1993). The mobility and degradation of ^{14}C-trifluralin in soils. *Acta Agriculture Nucleatae Sinica,* 7(1): 37-44.

Zheng, S.Q. and Copper, J.F. (1996). Adsorption, desorption and degradation of three pesticides in different soils. *Archives Environ. Contam. Toxicol.*, 30(1): 15-20.

Zimdahl, R.L.; Cranmer, B.K. and Stroup, W.W. (1994). Use of empirical equations to describe dissipation of metribuzin and pendimethalin. *Weed Sci.*, 42: 241-248.

ABSTRACT

a) Title of thesis : Adsorption and desorption of metribuzin, trifluralin and triazophos on sandy loam and clay loam soils

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Laboratory studies were conducted for the adsorption equilibrium of three pesticides viz. metribuzin, trifluralin and triazophos on two soils viz. sandy loam and clay loam soils at 0.25 $\mu g\ ml^{-1}$ concentration level. The adsorption and desorption studies were conducted at four concentration levels viz. 0.1, 0.2, 0.3 and 0.4 $\mu g\ ml^{-1}$ of pesticides taken in 0.01M $CaCl_2$ solution. Retention times (R_t) observed for metribuzin, trifluralin and triazophos were 3.11, 3.06 and 4.26 min, respectively. The average recoveries of pesticides in 0.01M $CaCl_2$ solution at 0.25 and 0.50 ppm fortification levels were about 85 per cent for metribuzin, 85 per cent for trifluralin and 100 per cent for triazophos. Rate of adsorption of these pesticides was more in clay loam soil as compared to sandy loam soil. However, the adsorption equilibrium of these pesticides on both types of soils was completed in 3 to 4 h. The per cent adsorption of metribuzin and triazophos was more on clay loam soil as compared to sandy loam soil. Wheres, adsorption of trifluralin on both types of soils was almost same. Per cent desorption of metribuzin was less from clay loam soil as compared to sandy loam soil. However, per cent desorption of trifluralin and triazophos from both types of soils was almost identical. Among three pesticides, trifluralin adsorbed strongly on both soils followed by triazophos and metribuzin. The order of average per cent adsorption was trifluralin (94%) > triazophos (57%) > metribuzin (36%). The average per cent desorption was in the order trifluralin (4%) < triazophos (29%) < metribuzin (34%). Due to strong adsorptive nature of trifluralin, it has probably low potential to migrate through the soil profile (leaching) or over the soil surface (run-off) with the moving water. However, metribuzin due to low adsorptve nature may leach to lower surfaces.

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