SORPTION AND MOVEMENT OF FLUPYRADIFURONE IN SANDY LOAM SOILS WITH AND WITHOUT ORGANIC AMENDMENT

by

RESHMA V.

(2017-11-042)

THESIS

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DECLARATION

I, hereby declare that this thesis entitled **"SORPTION AND MOVEMENT OF FLUPYRADIFURONE IN SANDY LOAM SOILS WITH AND WITHOUT ORGANIC AMENDMENT"** is a bonafide record of research work done by me during the course of research and the thesis has not previously formed the basis for the award to me of any degree, diploma, associate ship, fellowship or other similar title, of any other University or Society.

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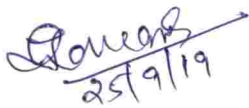
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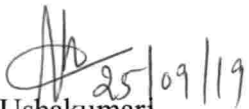
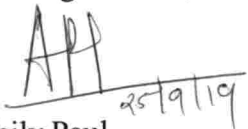AINP on Pesticide Residues

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LIST OF ABBREVIATIONS

@	-	at the rate of
ai	-	active ingredient
AINP	-	All India Network Project
%	-	Per cent
µg	-	microgram
6- CNA	-	6- chloronicotinic acid
AEC	-	Anion Exchange Capacity
Ca	-	Calcium
CD	-	Critical Difference
CEC	-	Cation exchange Capacity
CIB & RC	-	Central Insecticide Bureau and Registration Committee
cm	-	Centimetre
CRD	-	Completely Randomized Design
CRM	-	Certified Reference Material
DCM	-	Dichloro methane
DFA	-	difluro acetic acid
DFEAF	-	Difluro ethyl- amino furanone
dS	-	Desi Siemen
et al	-	And others
Ex. Ca	-	Exchangeable Calcium

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Ex. Mg	-	Exchangeable Magnesium
Fig	-	Figure
FS	-	Flowable concentrate
FYM	-	Farmyard manure
g	-	Gram
GOI	-	Government of India
h	-	Hour
ha	-	Hectare
i.e	-	That is
k	-	Potassium
KAU	-	Kerala Agricultural University
Kg	-	Kilogram
		Laboratory
LC	-	Liquid Chromatography
LD	-	Lethal dosage
LOQ	-	Limit of Quantitation
M	-	Molar
Mg kg^{-1}	-	Megagram per kilogram
Mg m^{-3}	-	Megagram per cubic metre
Mg	-	Magnesium
mg	-	milligram
mL	-	milliliter
N	-	Nitrogen

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O.M	-	Organic matter
P	-	Phosphorus
ppm	-	Parts per million
PRRAL	-	Pesticide Residue Research and analytical
PSA	-	Primary Secondary amine
QuEChERS	-	Quick, Easy, Cheap, Effective, Rugged and Safe
S	-	Sulphur
S.E	-	Standard Error
SL	-	Soluble liquid
WHC	-	Water Holding Capacity

Introduction

1. INTRODUCTION

Plants are the primary producers in the natural ecosystem, supporting all other forms of life on earth. Humans heavily depend on agriculture for their daily requirement of food and nutrition. Increased population growth and vast industrialization resulted in over utilization of resources for human survival as well as industrialization in the agriculture sector. This resulted in large scale production of the food and its availability in affordable prices and was achieved by the use of high yielding varieties, good management practices and use of appropriate inputs like chemical fertilizers and pesticides.

The use of pesticides in agriculture is important as it plays an effective role in plant protection measures since the plant diseases and attack of pests causes a 40 per cent reduction in yield worldwide (Oerke *et al.*, 1994). In India, as on March 2019, 279 pesticides were registered under CIB & RC (www.cibrc.nic.in). The total consumption of pesticides in India is 57000 Metric Tonnes of active ingredient. Among the states in India, Andhra Pradesh is the leading consumer with 24 per cent share of pesticide consumption followed by Maharashtra and Punjab (FICCI, 2015). The consumption of pesticides in Kerala is relatively low, with a rate of 0.41 kg ha^{-1} (GOI, 2017).

The transformation and transfer pathways of applied pesticides are complex and are influenced by site specific conditions and management practices. In the soil environment, fate of applied pesticides depend on various physical and chemical parameters of soil, of which pH, type of clay, extent of organic matter, concentration / amount of pesticide reaching the environment, moisture regime are the most important. The movement of pesticides through soil is dependent on the solubility, polarity, soil texture, clay content, organic matter and the volume of water infiltered. (Scheunert, 2018).

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The continuous and indiscriminate use of pesticide has resulted in increased pesticide resistance and undesirable levels of pesticides in the environment. Among the pesticides, insecticides possess maximum toxicity; all types are involved in polluting of the environment due to their molecular recalcitrance to degradation. But with the development of new generation insecticides, pest control has become effective with least impact on environment. New classes of pesticides with lower dose requirement, low mammalian toxicity were developed and commercialized for efficient crop protection measures and for sustainable yields.

Flupyradifurone (Sivanto 200SL) is a novel broad spectrum systemic insecticide of the class butenolide having similar action as that of neonicotinoids. It is used to control sucking pests like aphids and whiteflies on a variety of vegetable crops, through foliar spray and soil drenching. They act as reversible agonists on insect nicotinic acetyl choline receptors but are structurally different from the known agonists. Laboratory bioassays demonstrated a fast action on a broad range of sucking pests and also showed excellent field efficacy on a number of crops with different application methods such as drip irrigation, foliar, soil and seed treatment. It was also found to be active against resistant pests such as cotton whiteflies. Flupyradifurone is formulated as soluble liquid (SL) and flowable concentrate (FS) for seed treatment. FS formulation is for use as seed treatment only. It can be applied as a foliar treatment to cereals grains (except rice), cole, legume, root, cucurbit vegetables at the rate of 0.1-0.2 kg ai ha^{-1}. It can also be applied to the soil as in citrus fruits, fruiting vegetables and cucurbitaceous vegetables. Flupyradifurone has the label claim in bhindi against jassids and whiteflies. The recommended application rate is 1250 mL per 500 mL for one hectare (CIB & RC, 2019).

It is considered safe as it showed minimal risk to natural enemies and non-target insects making it an ideal component in Integrated Pest Management Programs. The mammalian oral LD$_{50}$ value was >300 mg kg^{-1} in the laboratory under which it can be grouped in moderate toxicity level and the field studies it was found to

degrade at a moderate rate and under aerobic conditions, extensive mineralization occurred to produce CO_2. The two major metabolite 6-CNA and DFA was found to degrade very fast and hence was not found to be accumulated in the environment (Nauen *et al.*, 2015). The solubility of the compound was found to be higher in water *i.e*, 3200 mg L^{-1}. It showed moderate mobility and reported to be moderately degraded with no major metabolites in the aquatic system. Considering the very many advantages associated with the compound, it is likely to be used on a large scale thereby increasing the chance for its entry in the environment especially in soil, from where it will find its way into water owing to its high water solubility. The usage of the pesticide at present was not quantified and reported. The compound will be registered for a wide variety of crops in the near future thereby a more widespread use of the chemical is likely to take place after label expansion. This necessitated studying the dynamics of flupyradifurone in soil and hence the study was undertaken with the following objectives.

- To study the rate of adsorption and desorption of pesticide in both soil and soil amended with 0.5 per cent FYM.
- To study the mobility of flupyradifurone in soil columns of sandy loam soil and 0.5 per cent FYM amended soil.
- To study the persistence of flupyradifurone in the sandy loam soil and also the soil amended with organic matter under air dry, field capacity and saturated soil condition.

Review of Literature

2. REVIEW OF LITERATURE

A pesticide is a substance intended for preventing, destroying, repelling, or mitigating any pest. Based on their biological activity, they could be classified as insecticides, fungicides, herbicides, rodenticides etc. Based on their chemical nature, can be classified as organic i.e. having a carbon structure (e.g. carbofuran, phorate), inorganic (arsenic and fluorine compounds) and botanicals (nicotine, pyrethrum). Various new generation pesticides are developed with unique mode of action specific to insects, with low dose of requirement.

Flupyradifurone, a novel systematic butenolide insecticide is being registered for the use as a foliar application and for seed treatment against the piercing, sucking insects such as aphids and whiteflies. Its mode of action is similar to the neonicotinoid insecticides that act on the central nervous system of target pests as an agonist of the nicotinic acetyl choline receptor (nAChR). Flupyradifurone is characterized as being persistent to very persistent and is moderately mobile to mobile depending on the soil conditions; therefore, it has the potential to reach aquatic environments, including surface and groundwater, after several months or more following application. The data available on the fate of flupyradifurone suggest that it is likely to dissipate from the point of application through various transport mechanisms, including runoff, erosion, and leaching to groundwater. In this context a study was conducted to understand the sorption and movement of flupyradifurone in the sandy loam soils and also with the addition of organic matter.

2.1 PESTICIDE CONSUMPTION IN INDIA

India is the fourth largest global producer of agrochemicals after the US, Japan and China. Per hectare consumption of pesticides in India is amongst the lowest in the world and stands at 0.6 kg ha^{-1} against 5-7 kg ha^{-1} in the UK and

~ 13 kg ha^{-1} in China (FICCI, 2015). Among the states in India, Andhra Pradesh is the leading consumer with 24 per cent share of pesticide consumption followed by Maharashtra and Punjab (FICCI, 2015). Per cent area treated with pesticides was the highest in cotton (66.70%) followed by Arhar (64.74%), jute (53.27%) and paddy (48.62%) and low in maize (25.01%) in 2011-12 (DAC & FW, 2017).

2.1.1 Advantages of Pesticides

Tremendous benefits have been attributed to pesticides in various sectors with special emphasis to the agricultural sector. Pest-induced losses were more than 50 per cent of attainable crop output. Insects caused destruction of 15 per cent of crops, disease pathogens and weeds 13 per cent each, and post-harvest pest infestations another 10 per cent (Oerke et al., 1994).

Usage of pesticides not only prevents the crop loss to pests, it improves the yield and ensures quality of agricultural produce with affordable prices to the consumers. In India, the food grain production was found to have increased four-fold i.e. 50 million tons in 1948-49 to 198 million tons in 1996-97 from an estimated 169 million hectares of permanently cropped land where one of the leading factor was the usage of agrochemicals.

Warren (1997) reported that there had been a tremendous corn crop yield in United States by the usage of the pesticides due to the reduction in the losses from the weeds, diseases and insect pests that can markedly reduce the amount of harvestable produce. Similarly, Webster et al. (1999) quantified the increase in the yield and economic margin after pesticide use with the losses before the usage. Pesticides will also continue to remain as arsenals for maintaining the food security in the future. Also, the applied pesticides undergo photochemical and biological transformation to produce relatively non-toxic metabolites to human beings and environment (Kole and Lehn, 1999) which reduce the risk associated with its application.

2.1.2 Disadvantages of Pesticides

Pesticides are found to pollute air, water and soil and are detrimental to the ecosystem affecting even the non-target pest species. Pesticides diminish the biodiversity, threaten the aquatic habitat, destroy the bird and animal habitats etc. An ideal pesticide property is selectivity to target pests, however absolute selectivity is difficult and they affect the non-target organisms and the environment.

The proportion of pesticides applied reaching the target pest has been found to be less than 0.3 per cent (Pimentel, 1995) and soil act as the sink for 50 per cent of applied pesticides (Shabeer *et al.*, 2011).

An ideal pesticide should be toxic only to the target organism, biodegradable and should not leach into ground water. Unfortunately, this is rarely the case and the widespread use of pesticides in modern agriculture is of concern (Johnsen *et al.*, 2001). It is the indiscriminate use of pesticides that have adversely affected the environment causing pest resurgence, environmental pollution most importantly their residues in food and feed causing serious human health hazards.

During one survey in India, 58 per cent of drinking water samples drawn from hand pumps and wells around Bhopal were contaminated with Organo Chlorine pesticides above the EPA standards (Kole and Bagchi, 1995). Similarly, in a study conducted in US by Kole *et al.* (2001), it was found that one or several pesticide molecules were found in 90 percent of water sample in all streams. Endosulfan was banned in Kerala due to the unprecedented health hazards it created such as the neurological disorders in children (Srivastava, 2013).

Despite the lowest consumption rate of pesticides, India faces the problem of pesticide residue which is due to the non- prescribed, wrong advice and supply of the pesticides to farmers for vested interests, non- observance of the waiting period

prescribed, use of sub- standard pesticides and also because of the lack of awareness among farmers or consumers (Kumar *et al.*, 2016).

2.2 FATE OF PESTICIDES IN SOIL

The transformation and transfer pathways of applied pesticides are complex and are influenced by site specific conditions and management practices. The major loss pathways of pesticides to the environment are volatilization into the atmosphere and aerial drift, runoff to surface water bodies in dissolved and particulate forms, and leaching into groundwater basins. The fate *i.e.* transformation and transport of pesticide in a soil system is mainly influenced by the organic matter content which is a major sorbent of pesticides (Albarran *et al.*, 2004).

2.2.1 Sorption of Pesticides

Adsorption is probably the most important mode of interaction between soil and pesticides and controls the concentration of the latter in the soil-liquid phase (Navarro *et al.*, 2007). It is evaluated by the adsorption coefficient which is dependent on organic carbon status of soil.

Pesticide adsorption- desorption was significantly affected by the organic carbon content and the rate of adsorption- desorption was found to be a function of dissolved organic carbon source and concentration (Suba and Essington, 1999). Also the pesticide sorption is also inversely propotional to the soil particle size fractions (de Jonge *et al.*, 2000). The trend in K_d value (distribution coefficient) is not only attributed to the soil physical and chemical properties but also the chemical nature of the pesticide (Gajbhiye and Gupta, 2001). The K_d values increased with increased organic matter content (Baskaran *et al.*, 2003; Yu *et al.*, 2006). A slightly greater distribution coefficient was found in soil with lower pH for sulfosulfuron and also for sulfonyl urea herbicides (Beyer *et al.*, 1988: Eleftherohorinos *et al.*, 2004). A low K_d indicates that more pesticide is in solution; a higher value indicates that the pesticide

is more strongly sorbed to soil (Kerle *et al.*, 1994). Similarly, Bansal (2010) in his study of three carbamate pesticide sorption had observed that, the addition of organic matter to soil increases soil organic carbon content and electrical conductivity while decreases pH. Adsorption was found to be positively correlated to the soil organic carbon and cation exchange capacity while negatively correlated with the soil pH. Similar trend of correlation between adsorption and soil pH was also observed by Ping and his coworkers, 2010. A higher persistence of a mix of pesticides was found in the Cardamom plantations of the Idukki district. It could be attributed to the higher adsorption due to higher OM content, acidic pH of soil (Nath, 2011). In contrast to this, the partitioning of hydrophobic organic chemicals such as Chlorpyriphos is through physical partitioning to the hydrophobic sites of organic matter, the observation was supported by the little correlation of the K_d values with the soil pH, CEC, clay fraction of soil, which are found to be controlling the pesticide sorption. But the K_d value was found to be positively correlated with the organic carbon fraction (Gebremariam *et al.*, 2012).

The content and quality of soil organic matter along with mineralogical content played an important role in sorption, being highest for humic acids followed by soils of decreasing organic carbon content (Cadkova *et al.*, 2013). Similarly, on a study conducted by Kumar and his coworkers (2015) on the adsorption- desorption of tricyclazole, it was found that the percentage of adsorption was found to be higher in vertisol with clayey texture and higher organic carbon content than ultisol having sandy loam texture. Amendment with farmyard manure was found to increase the adsorption rate. Similarly, the effect of organic matter in adsorption of pesticides has also been reported in literatures by Rai *et al.* (2000); Akma *et al.* (2009); Paterio Moure *et al.* (2009); Hiller *et al.* (2012). Besides that clay mineralogy also plays an important role in adsorption of organic compounds (Yuncong and Gupta, 1994; Fushiwaki *et al.*, 2001; Rytwo *et al.*, 2004; Tristan *et al.*, 2007).

A study on the adsorption- desorption of Pyridalyl on three types of clays., showed that Pyridalyl is highly sorbed in the clays with nano- bentonite and montmorillonite clays exhibiting higher insecticide sorption. Sorption was found to be positively correlated with the CEC while negative correlation was observed with the particle size (Anirban *et al.*, 2013). Also, the Freundlich adsorption coefficient, K_f value was 9.52 for analytical grade and 16.9 for commercial grade formulation in the case of adsorption studies in Tebuconazole (Raunaq *et al.*, 2017).

Particularly the clay and the organic matter in the soil sorb the pesticide molecules, making it unavailable to leaching to the groundwater but may be present in the sediments in the cropland. The compound may be desorbed and pass to the soil solution again, if the soil conditions vary (moisture content, temperature, etc.) with attendant biocide risks, termed as desorption. Some non-desorbable parts remain due to strong bonds termed as bound residues.

The increase in organic matter and clay content resulted in increase in the extent of hysteresis (Krishna and Philip, 2008). The clayey soil showed high adsorption of carpropamid and was found to be strongly bound to soil particles resulting in slow desorption and high hysteresis (Shabeer and Gupta, 2013). Highest desorption rate was observed during the first cycle, progressively reducing in the subsequent cycles and a total of 10-25 per cent of adsorbed hexaconazole was desorbed in five cycles and it was also reported that the rate of desorption decreased with increasing organic matter content (Sharma *et al.*, 2013). Similarly, Tatarkova *et al.* (2014) reported that pretilachlor desorption was controlled by organo- mineral complexes rather than individual soil organic or inorganic components.

Similar results were obtained in the studies related to sorption of azole group of fungicides (Thornsten *et al.*, 2001; Sharma *et al.*, 2013; Zainol *et al.*, 2016).

2.2.2 Mobility of Pesticides

Mobility may result in the redistribution of pesticide within the application site or movement of some amount of pesticide off site. Once a pesticide is applied, it can follow three pathways either it can adhere to the soil particles mainly clay and humic oxides or it could be degraded by organisms or free enzymes and can also be moved along with water in soil column. Pesticides that leach through soil column reach the ground water.

DDT and HCH were reported in ground water of Aligarh District of Uttar Pradesh but concentrations of these pesticides were within the prescribed limits (Bansal and Rachana, 2000). DDT and HCH have been reported on coastal marine environment in Mumbai (Pandit *et al.*, 2006). Pesticide contamination of groundwater is a natural issue because groundwater is used for drinking for 50 percent of population. Concern about pesticides in groundwater is especially acute in rural areas where over 95 per cent of the population relies upon groundwater for drinking (Begum *et al.*, 2009). Akhil and Sujatha (2012) studied the prevalence of organo chlorine pesticide residues in the groundwater of the Kasargod district in Kerala (South India).

The most important chemical variables that contributed in pesticide leaching include sorption coefficient and degradation half-life. Mediating factors include properties of the soil (e.g., organic carbon content, hydraulic conductivity) as well as climatic (e.g., rainfall, groundwater recharge rate) and landscape (e.g., depth to groundwater) variables (Utulu *et al.*, 1986). The amount of pesticides leached below the root zone depends on the chemical properties and the ecological conditions as well. The chemical leached is in the range of 0.1 to 1 per cent and reach up to 4 per cent in the case of worst rainfall conditions (Flury, 1996). The hydrophobic pesticides have higher tendency to leach as they are less adsorbed on to the soil matrix (Wauchope *et al.*, 2002). But the mechanisms and kinetics of the sorption and

desorption of chemicals from the soil particles mainly influence the mobility of pesticides in soil, hence their bioavailability and their transformation to other agricultural commodities (Moorman *et al.*, 2001).

Soil with high organic carbon content has more affinity towards the sorption of organic compound thus limiting its mobility. Sakaliene *et al.* (2007) reported that faster mobility observed in soil with high sand content and low organic matter content. Similar observations were obtained for the study on flubendamide transport through packed columns by Das and Mukherjee (2012). Fresh Cowdung and cereal straw soil amendments used were found to reduce the leaching of fipronil to ground water and was found to convert the pesticides to products having less health hazards (Joshi *et al.*, 2015). A study by Lekshmi and Shah, 2014 on the downward movement of agrochemicals in sandy, clayey and sandy loam soils, it was found that higher depth wise retention was found in clayey followed by sandy and sandy loam soils. Leachate from sandy soil showed the highest residue concentration followed by sandy loam soil. Thus the areas with sandy soil possess high groundwater contamination risk as it has highest leaching potential.

In a study conducted by Meite *et al.* (2018) showed that the export patterns of fungicide Metalaxyl and herbicide S- metachlor were depended on the rainfall characteristics. The maximum residue was recovered from 0-5 cm depth of column under the continuous flow condition. As the volume of water was increased, mobility increased and residues moved to lower depth. In a study conducted Singh *et al.* (2018), on the effect of organic amendment on leaching of pesticide clothianidin in two different Indian soils revealed that organic amendment application reduced the leaching.

2.2.3 Persistence of Pesticides in Soil

The length of time a chemical remains in soil without losing the molecular integrity, physical, chemical and biological characteristics through which it is

transported and distributed is termed as "soil persistence" (Navarro *et al.*, 2007) of that chemical.

Half-life is used to evaluate the persistence. Half-life is the time taken for degrading half of the amount present. The pesticides could be categorized as persistent (>100 days), moderately persistent (30-100 days) and non-persistent (< 30 days) (Kerle *et al.*, 1994). After a single half-life, 50 per cent of chemical remains and 25 per cent and 12 per cent after second and third half-lives (Hanson *et al.*, 2015).

Pesticides vary in their potential to persist. The intrinsic pesticide properties such as vapor pressure, water solubility, resistance to chemical changes and also the extrinsic properties such as the soil organic carbon content, soil microbial activity, soil moisture, temperature affects the fate of the pesticide in the environment (Rao and Davidson, 1980). The butachlor dissipation was faster under higher soil moisture conditions and soil temperature (Mabbayad *et al.*, 1986). Slower dissipation of imidachlorprid was observed as the pH increased (Sarkar *et al.*, 2001).

The degradation of pesticides depends on soil characteristics, nature of the chemical compound, cropping systems, irrigation pattern and the existing climatic conditions (Agnihotri *et al.*, 1994). The degradation can be photo degradation or biochemical degradation. Organic soil amendments like manure, cow dung, and compost applied to soil influence the degradation, sorption and leaching of pesticides along with enhancing productivity (Cox *et al.*, 2000). Pesticides may break down faster inside plastic-covered greenhouses than inside glass greenhouses, since glass filters out much of the ultraviolet light that degrades pesticides. (Navarro *et al.*, 2007). DDT and Endosulfan residues were found in the soils of cardamom plantations of Idukki district even though there has been no application for the past 10 years (Beevi *et al.*, 2007).

Thus soil amendments play an important role in the persistence of pesticides in soil. Increased organic matter addition increase the retention of pesticides thus making it less available in the soil solution for degradation by microbial degradation (Barriusa *et al*., 1997).

However, increased organic matter content enhances the microbial mediated degradation of pesticides (Felsot and Shelton, 1993). And Baskaran *et al*. (1996) reported that application of FYM enhanced the degradation as well as increased adsorption of organic herbicides which reduced the leaching losses.

A study conducted by Das and Mukherjee (2012) on the effect of moisture and organic manure on persistence of flubendamide in soil, it was found that persistence is affected by both these factors. The pesticide persistence was found to be higher in air dry soil than at field capacity and saturated level of soil. The higher persistence under air dry condition could be attributed to lower microbial activity. Higher dissipation occurred in submerged conditions and this may be due to the partial anaerobic conditions and the anaerobic microbes may be more efficient in degrading flubendamide than aerobic microbes. The organic manure amendment enhanced the degradation and reduced the half-life, this may be due to the increased microbial activity due to increase in the organic carbon content and also due to the increased sorption of pesticide and thus available for degradation for soil microbes. The residue content declined slowly with time and 5.3- 29.2 per cent of applied pesticide lost at 10 μg g^{-1} fortification level and at 1 μg g^{-1}, the loss accounted to 4.3- 30.8 per cent. In contrast to it, the dissipation of herbicides butachlor and pretilachlor were lowered in FYM amended soil in comparison with the normal soil and with vermi compost amended soil and the increase in the half- life period, which shows the superiority of organic manure in retaining the pesticide molecules. In this study, the initial residue content was found higher in the soil treated with organic amendments. But after the 30 days after application and during harvest the residual content did not

vary significantly among the treatment due to the enhanced degradation by organic amendment (Devi *et al.*, 2015).

Pesticides in the upper layer of soil usually are adsorbed more than degraded. Upon addition of mulching materials, decomposition of it favours the increase in the microbial biomass which further enhances the pesticide degradation (Aslam *et al.*, 2018). All the amendments were found to be enhancing the dissipation of pesticides but their relative activity was found to differ owing to its interaction with soil properties like pH, organic carbon content and also presence of readily decomposable organic matter (Suyal *et al.*, 2018).

2.3 FLUPYRADIFURONE

Flupyradifurone is the first representative of the novel Butenolidae family of insecticides. It is a systemic pesticide mainly used against broad range of sucking and piercing pests. It is registered in vegetables, fruits, ornamental plants, cereal grains (except rice), alfalfa, clover and berries. Its mode of action is similar to neonicotinoids in the way that they act reversibly as agonists on insect acetylcholine receptors. The different application methods used are foliar, seed, soil treatment and also applied in drip irrigation systems. Its oral LD_{50} value for rats is >300 mg kg^{-1} and has a dermal LD_{50} value of 3000 mg kg^{-1}, which shows the possibility of slight absorption through skin.

2.3.1 Salient Features of Flupyradifurone

Common name: Flupyradifurone

Chemical name: 4-((6-chloro-3-pyridylmethyl) (2,2

                            difluoroethyl) amino)furan- 2(5H)-one

CAS Registry No: 951659-40-8

CIPAC No: 987

Synonyms:	Sivanto 200SL, Sivanto Prime, Aeron
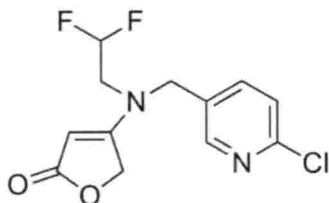
Molecular structure:	
Odour:	No specific odour
Molecular formula:	$C_{12}H_{11}ClF_2N_2O_2$
Molecular weight:	288.68 g mol^{-1}
Vapour pressure:	9.1x 10^{-4} Pa (20°C)
Melting point:	69 °C
Boiling point:	No boiling point at atmospheric pressure
Hydrolysis:	Stable in aqueous solution at pH 4 to 9 for 5 days
Photolysis:	Succinamide and Azabicyclosuccinamide are degrades
Half-life:	79-799 days (aerobic)
Solubility in water:	3.2 g L^{-1} (at 20 °C)
Solubility in solvents:	

Solvent	[g L^{-1}]
n-heptane	0.0005
toluene	3.7
1,2-dichloromethane	> 250
ethyl acetate	> 250
methanol	> 250
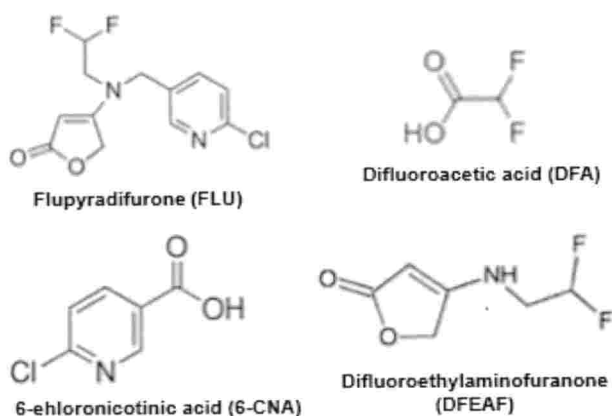
Figure 1. Flupyradifurone and its metabolites

2.3.2 Uses of Flupyradifurone

Flupyradifurone is found to be a very versatile chemical in terms of different application methods to a variety of crops. It exhibits excellent and fast action against a broad spectrum of sucking pests, insects and also demonstrates resistance breaking properties. The basic formulations include the 200SL, used for foliar and drench/drip use and 480FS for seed treatment. It exhibits a very promising safety profile comparing with other insecticides. They are used in variety of crops such as vegetables, grapes, fruits, date palm, and coffee and cocoa as foliar spray or soil drench and in soya bean, it can be used for seed treatment. It is a systemic insecticide, flexible in application mainly intended for sucking pests control such as white flies, hoppers and aphids. But the label claim of flupyradifurone is currently for the crop bhindi for jassids and whiteflies. The application rate is 2.5 mL L^{-1} with a waiting period of three days. It only possesses minimal risk to the natural enemies and predators making it suitable to be included under the IPM strategy.

2.3.3 Behavior of Flupyradifurone in Soil and Water

The field studies with the application of flupyradifurone in the soil, showed that it degrade at a moderate rate and under aerobic conditions, extensive mineralization occurred to produce CO_2 (up to 59 %), and moderate levels of non-

extractable residues were observed (up to 34 %). Through biological process, some of the residues are bound to the solid humic fractions of soil which makes it non-extractable (Nauen *et al.*, 2015). The two major metabolite 6-CNA and DFA was found to degrade very fast and hence was not found to be accumulated in the environment.

The solubility of the compound was found to be higher in water *i.e.* 3200 mg L^{-1}. It showed moderate mobility and reported to be moderately degraded with no major metabolites in the aquatic system.

In a study conducted by Dubey *et al.* (2017) on residues of flupyradifurone on apple fruits and soil, the residues were below detectable level in both soil and fruits at the time of harvest and the half- life were found to be 3.0 and 4.1 days at single and double doses respectively in apple. Only DFA was the metabolite found in the fruit sample and was also below determination level at the 10th day of sampling. From the study it was inferred that an 11 days of waiting period was considered safe in crop protection and environment point of view.
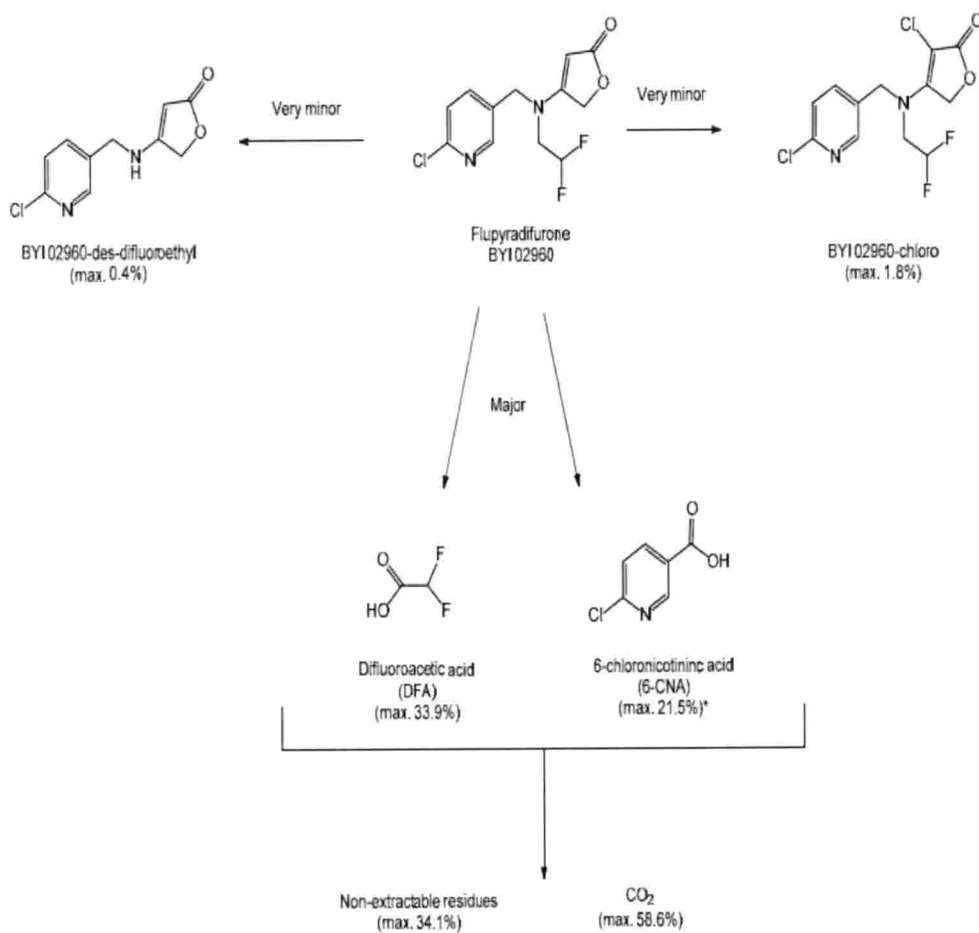
Figure 2. Proposed degradation pathway of flupyradifurone in soil

Materials and Methods

3. MATERIALS AND METHODS

The present study entitled "Sorption and movement of flupyradifurone in sandy loam soils with and without organic amendment" has been carried out to assess the adsorption- desorption characteristics of flupyradifurone, to study its migration tendency in the packed soil columns and its persistence in sandy loam soils with and without the organic amendment under laboratory conditions.

3.1 PHYSICAL AND CHEMICAL ANALYSIS OF SOILS

The study was conducted in sandy loam soil of Kerala. The representative soil sample was collected from various locations near Kazhakoottam, Thiruvananthapuram, Kerala at a depth of 0-15 cm using a spade. Along with this core samples were also taken for physical analysis. The collections were done during October 2018. The collected soil samples were spread and shade dried for one week and the physical and chemical analysis of the soil were carried out as per standard procedures as given in Table 1.

3.2 VALIDATION OF MULTIRESIDUE METHODS FOR PESTICIDE RESIDUE ESTIMATION IN SOIL

Analytical method for the estimation of residues of flupyradifurone and its metabolites in soil were validated by conducting recovery experiment using known concentrations of pure analytical standards and its metabolites. A mixture of the analytical standards of flupyradifurone and its metabolites *viz*., 6-chloronicotinic acid (6-CNA), difluroacetic acid (DFA) and difluro ethyl amino furonone (DFEAF) were fortified in soil at three different levels (0.10, 0.50 and 1 mg kg^{-1}). Extraction and cleanup methods were performed by adopting QuEChERS multi residue estimation method as well as by the traditional acetone extraction followed by partitioning using dichloromethane (Anastassiades *et al*., 2003).

Table 1. Analytical methods followed to test the physical and chemical parameters in soil

Sl.No	Parameter	Method	Reference
1	Texture	International pipette method	Piper (1966)
2	Bulk density	Core method	Gupta and Dakshnamoorthy (1980)
3	Particle density	Pycnometer method	Gupta and Dakshnamoorthy (1980)
4	Water holding capacity (WHC)	Core method	Gupta and Dakshnamoorthy (1980)
5	Field capacity	Pressure plate apparatus	Gupta and Dakshnamoorthy (1980)
6	Hydraulic Conductivity	Constant head method	Gupta and Dakshnamoorthy (1980)
7	pH	pH meter with glass electrode	Jackson (1973)
8	Electrical conductivity (EC)	Conductivity meter	Jackson (1973)
9	Cation exchange capacity (CEC)	Neutral N ammonium acetate method	Jackson (1973)
10	Anion exchange capacity(AEC)	Barium Chloride- Tri ethanol Amine	Jackson (1973)
11	Organic carbon	Walkley and Black method	Jackson (1973)
12	Available nitrogen	Alkaline permanganate method	Jackson (1973)
13	Available phosphorus	Bray No1 extraction and Spectrophotometry	Jackson (1973)
14	Available potassium	Neutral N ammonium acetate extraction & Flame Photometry	Jackson (1973)
15	Exchangeable Ca	Versanate method	Jackson (1973)
16	Exchangeable Mg	Versanate method	Jackson (1973)
17	Available Sulphur	Turbidimetry method	Jackson (1973)

3.2.1 Details of Experiment

Design: CRD

Treatments: 3

Replications: 6

Treatments

T_1- 0.10 mg kg^{-1} analytical standard mixture

T_2- 0.50 mg kg^{-1} analytical standard mixture

T_3- 1.00 mg kg^{-1} analytical standard mixture

3.2.2 Laboratory Glass Ware, Chemical Reagents and Equipments

The glass wares, chemical reagents and equipments used for the study are given in the Table 2. The reference analytical standards of the pesticide and its metabolites were obtained from Bayer Crop Science, USA and stored in deep freezer at a temperature below -20°C, without exposure to light and moisture.

Initially glass wares were washed with tap water and then immersed overnight in 1 per cent laboline and then again washed with tap water. After that, they were dipped in boiling water for 2 hrs and rinsed with acetone and were kept in the oven at 50°C for 3 hrs for drying. The plastic tubes were similarly washed and kept at room temperature for drying. The syringes were thoroughly pre rinsed with acetone and methanol before use.

Table 2. The glass wares, equipments, and reagents used for residue analysis

Laboratory glass wares	Chemical reagents	Equipments
Beakers 100, 250 and 500 mL	Acetone AR grade	Analytical balance
Centrifuge tubes 15 mL and 50 mL	Acetonitrile HPLC grade	Laboratory centrifuge
Class A micropipettes 0.1, 0.5, 1, 2, 10 and 20 mL	Magnesium sulphate (hydrated) AR grade	Mechanical shaker
Conical flasks and standard flasks 250 mL, 500 mL and 1 L	Methanol HPLC grade	Vortex shaker
Graduated test tubes 5 mL and 10 mL	Primary Secondary Amine	Turbo Vap Evaporator
Separating funnels 750 mL and 1 L	Sodium Chloride (AR grade)	Rotary vacuum flash evaporator
PVC pipes (50× 2.5 cm)	Ammonia solution	Liquid chromatograph-Mass Spectrometer
Hypodermic syringe 10 mL and Randisc	Dichloromethane	
	Sodium Sulphate	
	Calcium Chloride (anhydrous)	

3.2.3 Preparation of Mixture of Standard Insecticides

The steps involved in the preparation of standard mixture of flupyradifurone and its metabolites were as follows:

3.2.3.1 Procurement of Certified Reference Material (CRM)

The CRMs of flupyradifurone, 6-chloronicotinic acid (6-CNA), difluroacetic acid (DFA) and difluro ethyl amino furanone (DFEAF) were obtained from Bayer Crop Science, USA. Required quantities of each of the standards were accurately

weighed to prepare 250 mL of the analytical standard solutions of 400 ppm concentration.

Table 3. Details of CRMs used for the preparation of pesticide mixture

SL. No	Compound	Formula	Purity (% w/w)
1	Flupyradifurone	$C_{12}H_{11}ClF_2N_2O_2$	99.4
2	6-chloronicotinic acid	$C_6H_4ClNO_2$	98.9
3	Difluro ethyl amino furanone	$C_6H_7F_2NO_2$	97.3
4	Difluro acetic acid	$C_2H_4F_2O_2$	95.5

3.2.3.2 Preparation of Standard Solution

Standard stock solutions of flupyradifurone and its metabolites (400 mg L^{-1}) were prepared in methanol and stored at -20°C in deep freezer. The amount of CRM required for preparation of the standard solution was calculated using the formula:

$$= \frac{\text{Weight (in milligram)} \times 10^3 \times 100}{25 \times \text{Purity (\%)}}$$

3.2.3.3 Intermediate Stock Solution and Working Standards

Intermediate standards of 100 mg kg^{-1} of flupyradifurone and its metabolites were prepared by diluting the required quantity of stock solution with methanol.

Aliquots of intermediate standards were taken in separate standard flasks in order to prepare working standards of 10 mg kg^{-1} of each compound. From this working standard, a mixture of these compounds were prepared in methanol solvent and stored in refrigerator for further use. From this, working standard serial dilution was done to obtain 1, 0.50, 0.25, 0.10, 0.05, 0.025 and 0.01 mg kg^{-1} concentrations. The individual standards of different insecticides were injected in Liquid

Chromatography- Mass Spectrometer and a calibration curve was prepared by plotting concentration vs. peak area.

3.2.4 Fortification of Soil with Standard Insecticide and its Metabolites

A fixed quantity of 10 g each of air dried (2 mm sieved) soil samples were taken in 18, 50 mL centrifuge tubes and were spiked separately with 0.10, 0.50 and 1 mL each of 10 mg kg^{-1} working standard mixture to get 0.10, 0.50 and 1 mg kg^{-1} levels of concentration respectively. The spiked soil was thoroughly shaken to ensure uniform homogenization.

3.2.5 Recovery Experiment

A recovery experiment was conducted to standardize the procedure for extraction and clean up processes. The experiment was conducted by adding a known quantity of insecticide and it's metabolites to soil and trying the extraction process using different solvent systems. All the chemicals and solvents used in the research were either of analytical grade or HPLC grade.

3.2.5.1 Extraction

The soil samples were extracted using acetonitrile and the efficiency of extraction was assessed. QuEChERS method was adopted for acetonitrile extraction of spiked insecticide from soil. For this purpose, 10 g of air dried, sieved (2 mm) soil was weighed in 50 mL centrifuge tube and spiked with the standard insecticide mixture and evaporated to release the solvent vapors. The soil samples were spiked with 0.10, 0.50 and 1 mL each of 10 mg kg^{-1} solution to get 0.10, 0.50 and 1 mg kg^{-1} levels of each of the spiked compounds. To this, 4 g magnesium sulphate, followed by 1 g sodium chloride and 20 mL acetonitrile were added, shaken for 2 minutes in a vortex shaker and was centrifuged for 4 minutes at 3300 rpm. A 10 mL supernatant was transferred to a 15 mL centrifuge tube using a micropipette and 0.25 g primary secondary amine and 1.50 g magnesium sulphate were added and was shaken for 30

seconds in a vortex followed by centrifugation at 4400 rpm for 10 minutes. After the centrifugation, 4 mL of the cleaned supernatant extract was transferred to a turbo tube and evaporated to dryness at $40^{\circ}C$ using turbo Vap. The dry residue redissolved in methanol and the volume made up to 1mL, filtered through 0.22µm poly vinylidene fluoride (PVDF) syringe filter and passed to a vial which was wrapped with parafilm to avoid evaporation.

Another set of spiked samples were also extracted through a separate procedure. Extraction was done by adding 20 mL acetone in 10g soil taken after addition of 10 mL water. They were shaken and centrifuged for 4 minutes at 3300 rpm. The supernatant was filtered and concentrated which is then transferred to a separating funnel. After the addition of 100 mL water, 25 mL DCM was added, shaken for layer separation and washed out through a funnel with anhydrous Sodium Sulphate for three times and collected in a round bottom flask. It was concentrated and made up to 1mL with methanol in vials.

Proper method for the extraction and estimation of residues in water sample was also done by transferring 10 mL of the samples each spiked at the concentration levels of 1.00, 0.50 and 0.10 mg L^{-1} to a separatory funnel to which 90 mL distilled water was added. Then 20 g sodium chloride and 10 mL DCM were added followed by mechanical shaking for 5 minutes to cause layer separation and the lower layer was collected in the round bottom flask after passing through a funnel containing anhydrous sodium sulphate. The extraction was repeated with 10.6 mL of dichloromethane. n- Hexane 6.60 mL was added and again shaken and the upper layer separated was collected. The collected extracts were concentrated using a flash evaporator and were made up to 1 mL using methanol and the residues were estimated with LC-MS/MS.

3.2.5.2 Estimation

The cleaned extracts were analyzed on ThermoScientific TSQ Quantiva LC-MS/MS (Dionex Ultimate 3000 UHPLC). The samples as well as standards were injected into the equipment.

3.2.5.2.1 LC-MS System

The Thermo Scientific Dionex Ultimate 3000 UHPLC system was used for chromatographic separation using column Accucare aQ C_{18} placed in a column temperature at 30°C. Elution was done using two elutents (solvent mixtures), *viz.,*

A: 0.10 per cent formic acid + 5 mM ammonium formate in water

B: 0.10 per cent formic acid + 5 mM ammonium formate in methanol

The flow rate was maintained at 0.30 mL min^{-1} and 10 minutes run time.

Then the effluent from LC was introduced into Thermo Scientific TSQ Quantiva mass spectrometer. The source parameters were, ion source type is H-ESI (Heated electrospray ionization), Sheath gas, 60.00 (Arbitrary units), Aux gas, 60.00 (Arbitrary units) and Sweep gas, 1.00 (Arbitrary units) with ion transfer tube temperature, 320°C and ion spray voltage source of 3800 V (positive ion) and 2900V (negative ion). The vaporization temperature is 45^{0}C. The residues were quantified in MS/MS system. The other compound dependent parameters used are shown in Table 4.

Table 4. Liquid Chromatography (LC) parameters for flupyradifurone and its metabolites.

Compound	Retention time (min)	Polarity	Precursor (m/z)	Product (m/z)	Collision energy (V)	Quantitative/ Qualitative
Flupyradifurone	4.65	Positive	289.061	89.966	41.800	Qualitative
				125.96	23.850	Quantitative
Difluro ethyl amino furanone	1.34	Positive	164.293	55.058	25.067	Qualitative
				64.986	28.067	Quantitative
6-chloronicotinic acid	4.22	Negative	155.900	112.054	10.250	Qualitative
				121.970	10.250	Quantitative

3.2.5.3 Residue Quantification and Recovery Experiment

Pesticide residues in the sample (mg kg^{-1}) =

$$\frac{\text{Peak area of sample} \times \text{Concentration of standard injected} \times \text{Dilution factor (DF)}}{\text{Peak area of standard}}$$

$$\text{Dilution factor (DF)} = \frac{\text{Volume of solvent added} \times \text{Final volume of the extract}}{\text{Weight of sample} \times \text{Volume of extract taken for concentration}}$$

$$\text{Percentage Recovery (\%)} = \frac{\text{Concentration of pesticide residue obtained} \times 100}{\text{Concentration of pesticide residue added}}$$

$$\text{Relative Standard Deviation (RSD, \%)} = \frac{\text{Standard deviation} \times 100}{\text{Mean Recovery}}$$

A method with recovery percentage in a range of 80-120 and the Relative Standard Deviation (RSD) value < 20 per cent was selected for the study. Limit of quantification (LOQ) was 0.10 mg kg^{-1}. The concentration of flupyradifurone and its metabolites in the samples were derived from the calibration curve and chromatogram of the standards of these compounds. These calibration curves and chromatograms are appended from I- IV.

3.3 SORPTION STUDY OF PESTICIDE

The sorption experiment was conducted by the batch equilibration technique. CaCl$_2$ solution (0.01 mol L^{-1}) was used as an aqueous phase to make phase separation easier and to simulate an ionic strength to soil solution (OECD, 2000).

3.3.1 Estimation of Equilibration Time

The optimum time required for the adsorption of pesticide to the soil is termed as equilibration time. Preliminary kinetic studies were carried out for this purpose. The time was calculated for both sandy loam soil and 0.5 per cent FYM amended soil.

For this, 10 g each of soil samples was taken in 50 mL centrifuge tubes. $0.01\ M$ CaCl$_2$ solutions were prepared. 0.50 ppm aqueous pesticide solution in $0.01M$ CaCl$_2$ solution was prepared. 20 mL of this solution was added to the samples taken. Parallel method of sample analysis was done $i.e.$ number of samples would be same as that of time intervals at which the study to be conducted for adsorption kinetics. One blank with no soil and control was also taken. The samples were shaken and at desired time intervals such as 0th, 1st, 2nd, 4th, 6th and 24th hours after spiking, the mixture was centrifuged to separate the phase and 10 mL of the aqueous phase was extracted and analyzed similar to the study of residues in water samples.

3.3.2 Adsorption Study

The adsorption studies were carried out by transferring 100, 80, 60, 40 and 20 µg of flupyradifurone from the standard solution into 50 mL centrifuge tubes and 20 mL $0.01M$ $CaCl_2$ solution was added. Thus the initial concentration became 1, 2, 3, 4 and 5 mg L^{-1} respectively. Test tubes were shaken to dissolve the residues and after 30 min, 10 g soil was added. The tubes were then shaken for 6 h and 4 h (equilibration time) for normal soil and 0.5 per cent FYM amended soil respectively. After equilibration, they were centrifuged and 10 mL supernatant was drawn for analysis after processing. Control samples without the soil were also analyzed.

3.3.2.1 Details of Experiment

Design: CRD

Treatments: 10

Replications: 3

Treatments

T_1: 100 µg of flupyradifurone in soil

T_2: 80 µg of flupyradifurone in soil

T_3: 60 µg of flupyradifurone in soil

T_4: 40 µg of flupyradifurone in soil

T_5: 20 µg of flupyradifurone in soil

T_6: 100 µg of flupyradifurone in amended soil

T_7: 80 µg of flupyradifurone in amended soil

T_8: 60 µg of flupyradifurone in amended soil

T_9: 40 µg of flupyradifurone in amended soil

T_{10}: 20 µg of flupyradifurone in amended soil

3.3.3 Desorption Study

The de-sorption studies were carried out in the same soil samples in adsorption. After the extraction of supernatant in the adsorption study, the samples were re- suspended with a glass rod and fresh 10 mL $CaCl_2$ solution was added. Again the test tubes were shaken for respective equilibration time, centrifuged and 10 mL supernatant was withdrawn and analyzed. Desorption study was also conducted by spiking the soil sample with 60, 40 and 20 µg of flupyradifurone in 50 mL centrifuge tubes and 20 mL *0.01 M* $CaCl_2$ solution was added. The tubes were then shaken for 6h and 4h (equilibration time) for normal soil and 0.5 per cent FYM amended soil respectively. The sample supernatants (10 mL) were drawn for analysis after centrifugation. Again the samples were suspended and fresh 10 mL *0.01 M* $CaCl_2$ was added and shaken for the equilibration time. After that the samples were centrifuged and supernatant were analyzed in the same way as in adsorption studies. Three desorption cycles were carried out.

3.3.3.1 Details of Experiment

Design: CRD

Treatments: 6

Replications: 3

Treatments

T_1: 60 µg of flupyradifurone in soil

T_2: 40 µg of flupyradifurone in soil

T_3: 20 µg of flupyradifurone in soil

T_4: 60 µg of flupyradifurone in amended soil

T_5: 40 µg of flupyradifurone in amended soil

T_6: 20 µg of flupyradifurone in amended soil

3.3.4 Adsorption- desorption Constants and Isotherms

The amount adsorbed on soil (C_s, mg kg^{-1}) was calculated from the difference between the initial aqueous phase concentration and the equilibrium concentration (C_e, mg L^{-1}). The distribution coefficient (K_d) was calculated as the ratio of the adsorbed concentration in the soil and its equilibrium concentration in the solution. The amount desorbed was calculated from the difference in the amount of flupyradifurone in solution before and after the desorption cycle. The adsorption/ desorption data were fitted into a linearized form of the Freundlich empirical equation:

$$\log C_s = \log K_F + 1/n \log C_e$$

The values of K_F and n were calculated from this regression equation, expressing sorption capacity of soil and sorption affinity/adsorption strength of pesticide, respectively. All the data values were rounded off as per the significance.

3.4 MOBILITY OF FLUPYRADIFURONE IN SOIL

The mobility of flupyradifurone in the sandy loam soil and FYM amended soil column were assessed by analyzing the residues at different depths after loading 3 levels of concentration of flupyradifurone- 17.09 per cent w/w SL (Sivanto Prime) and the subsequent elution with different levels of water as detailed below. The extent of migration of the pesticide as affected by differential volume of water as well as with addition of farmyard manure was studied using soil column percolation method.

3.4.1 Details of Experiment

Design: CRD

Treatment: 18 (3 levels of pesticides, 3 levels of water in soil and amended soil)

Replication: 3

Treatments

T_1- 25 µg level of formulation in sandy loam soil + 40 mL water

T_2- 25 µg level of formulation in sandy loam soil + 80 mL water

T_3- 25 µg level of formulation in sandy loam soil + 160 mL water

T_4- 50 µg level of formulation in sandy loam soil + 40 mL water

T_5- 50 µg level of formulation in sandy loam soil + 80 mL water

T_6- 50 µg level of formulation in sandy loam soil + 160 mL water

T_7- 75 µg level of formulation in sandy loam soil + 40 mL water

T_8- 75 µg level of formulation in sandy loam soil + 80 mL water

T_9- 75 µg level of formulation in sandy loam soil + 160 mL water

T_{10}- 25 µg level of formulation in FYM amended sandy loam soil + 40 mL water

T_{11}- 25 µg level of formulation in FYM amended sandy loam soil + 80 mL water

T_{12}- 25 µg level of formulation in FYM amended sandy loam soil + 160 mL water

T_{13}- 50 µg level of formulation in FYM amended sandy loam soil + 40 mL water

T_{14}- 50 µg level of formulation in FYM amended sandy loam soil + 80 mL water

T_{15}- 50 µg level of formulation in FYM amended sandy loam soil + 160 mL water

T_{16}- 75 µg level of formulation in FYM amended sandy loam soil + 40 mL water

T_{17}- 75 µg level of formulation in FYM amended sandy loam soil + 80 mL water

T_{18}- 75 µg level of formulation in FYM amended sandy loam soil + 160 mL water

3.4.1.1 Column Preparation and Leaching

Studies on the mobility of flupyradifurone was done by using packed soil column method by loading the given formulation so as to give 25, 50 and 75 µg on top of the preloaded column, followed by leaching with measured amount of water.

Soil sample of 200 g were packed in the PVC columns of height 50 cm and 2.50 cm inner diameter to a height of 25 cm maintaining the bulk density, simulating the field compaction level and were fixed firmly to burette stands. The lower end of the columns was firmly fastened by using a muslin cloth so as to retain the soil as per the desired bulk density. The lower end of the soil column was immersed to a conical flask containing water for 12 h for saturation. On the next day, the saturated soil column was top loaded with 5 g soil to which required quantity of pesticide was added to get 25, 50 and 75 µg level and kept immersed in dry conical flask for collecting the leachate. The columns were eluted by controlled addition of water at 40, 80 and 160 mL, respectively using drip system at a steady flow in accordance with the hydraulic conductivity of the soils $viz.$, 0.4 mL min^{-1} obtained from the analysis. The water used for elution corresponds to 100, 200 and 400 mm rainfall in field condition and is used for the prediction of relative mobility along with water under field condition. The leachates obtained were collected in the conical flasks kept under the soil column. After the leaching was completed, the leachates as well as the soil were analyzed for residues. For the soil sample analysis, the pipe were opened and the soil core was cut into 5 portions of 5 cm each viz., 0-5 cm, 5-10 cm, 10-15 cm, 15-20 cm and 20-25 cm and the residues present in each of the vertical soil fractions were extracted and quantified.

3.4.2 Monitoring of Pesticide Residues in Leachate

The leachates were separately collected and from each sample a 10 mL subsample was transferred to a separatory funnel to which 90 mL distilled water was added. Then 20g sodium chloride and 10 mL dichloro methane were added followed by mechanical shaking for 5 minutes to cause layer separation and the lower layer was collected in the round bottom flask after passing through a funnel containing anhydrous sodium sulphate. The extraction was repeated with 10.60 mL of dichloromethane again. n- Hexane 6.60 mL was added and again shaken and the upper layer separated was collected. The collected extracts were concentrated using a

Plate 1: Elution of soil column after treatment

Plate 2: Collection of leachate after elution

Plate 3: Cut pieces of soil column for residue analysis

flash evaporator and were made up to 1 mL using methanol and the residues were estimated with LC-MS/MS.

3.5 STUDIES ON THE PERSISTENCE OF FLUPYRADIFURONE IN SOIL

Studies on the persistence of flupyradifurone in sandy loam soils were done in air dry, field capacity and saturated soil condition at three levels of spiking (1, 2 and 4 mg kg^{-1}) in the laboratory condition and also in the soil sample amended with dry farmyard manure at 0.5 per cent level. The commercial formulation of flupyradifurone (Sivanto Prime) was used for the study. The experiment was planned as per the following statistical design.

3.5.1 Details of Experiment

Design: CRD

Treatments: 18

Replication: 3

Treatments

T_1: Fortification of air dry soil with 1 mg kg^{-1} formulation

T_2: Fortification of air dry soil with 2 mg kg^{-1} formulation

T_3: Fortification of air dry soil with 4 mg kg^{-1} formulation

T_4: Fortification of FYM amended air dry soil with 1 mg kg^{-1} formulation

T_5: Fortification of FYM amended air dry soil with 2 mg kg^{-1} formulation

T_6: Fortification of FYM amended air dry soil with 4 mg kg^{-1} formulation

T_7: Fortification of soil at field capacity with 1 mg kg^{-1} formulation

T_8: Fortification of soil at field capacity with 2 mg kg^{-1} formulation

T_9: Fortification of soil at field capacity with 4 mg kg^{-1} formulation

T_{10}: Fortification of FYM amended soil at field capacity with 1 mg kg^{-1} formulation

T_{11}: Fortification of FYM amended soil at field capacity with 2 mg kg^{-1} formulation

T_{12}: Fortification of FYM amended soil at field capacity with 4 mg kg^{-1} formulation

T_{13}: Fortification of soil at saturated level with 1 mg kg^{-1} formulation

T_{14}: Fortification of soil at saturated level with 2 mg kg^{-1} formulation

T_{15}: Fortification of soil at saturated level with 4 mg kg^{-1} formulation

T_{16}: Fortification of FYM amended soil at saturated level with 1 mg kg^{-1} formulation

T_{17}: Fortification of FYM amended soil at saturated level with 2 mg kg^{-1} formulation

T_{18}: Fortification of FYM amended soil at saturated level with 4 mg kg^{-1} formulation

For conducting the laboratory study, one kg each soil and FYM amended soil in the air dry condition, at the field capacity level (90 mL kg^{-1} of sandy loam) and in saturated condition were taken in conical flask and spiked separately at 1, 2 and 4 mg kg^{-1} levels of flupyradifurone, homogenized and kept aside for 2 hours (0th day). A 10 g soil was taken from the conical flask in triplicate and analyzed for residue estimation. Likewise samples were drawn on 1st, 3rd, 5th, 7th, 10th, 15th, 20th and 30th day for analysis of residues and to identify the metabolites formed. The levels of flupyradifurone persisting at different time intervals were recorded from which the half-life was calculated.

3.5.2 Calculation of Half Life

Theoretically, the pesticide residue should decrease logarithmically with time since amount lost per unit time should be proportional to the total present at any time because all were exposed equally to weathering and degradation (Hoskins, 1981). A graph should be plotted with time (t) against log of residue parameters (log D), 'D' indicates residue in ppm. The graph shows a linear trend which indicate that log D can be represented as a linear function of 't' (in days or weeks). The model is, D= k_1E+log k_2, that means D = k_2 where k_2 represents initial deposits. The time required to reduce D to D/2 is defined as half- life so it is calculated as $t_{1/2}$=log 2/ k_1.

Plate 4: Persistence study under laboratory condition – soil at air dry condition

Plate 5: Persistence study under laboratory condition – soil at field capacity condition

Plate ☐ Persistence study under laboratory condition – soil at saturated condition

Results

4. RESULTS

The results of the study entitled "Sorption and movement of flupyradifurone in sandy loam soils with and without organic amendment" are presented under the following headings.

4.1 PHYSICAL AND CHEMICAL ANALYSIS OF SOILS

The physical and chemical characteristics of the soil used for the study were analyzed as per the standardized procedure and the results obtained are presented in Table 5.

4.1.1 Physical and chemical Properties of Sandy loam soil

The soil was sandy loam in texture with 68.70 per cent sand, 20.50 per cent silt and 10.80 per cent clay content. The bulk density and particle density of the soil were found to be 1.63 and 2.60 Mg m^{-3}. The porosity was found to be 37.3 per cent with field moisture of 8.50 per cent and water holding capacity of 17.01 per cent. The soil was found to be strongly acidic with a pH of 5.35 and electrical conductivity value of 0.30 dSm^{-1}.

The cation exchange capacity of the soil was found to be 4.3 cmol (+) kg^{-1} whereas the anion exchange capacity was found to be 1.21 cmol (-) kg^{-1}. The organic carbon content of the soil was 0.84 per cent. The availability of major primary and secondary nutrients in the soil were 178.89 kg ha^{-1} of available nitrogen, 60.03 kg ha^{-1} of available phosphorous, 150.6 kg ha^{-1} of available potassium. The secondary nutrients such as calcium, magnesium and sulphur were found to be 180, 57, 3.0 mg kg^{-1}.

Table 5. Physical and chemical properties of soil

Sl. No.	Parameters	Results
1	Texture	Sandy loam
2	Sand (%)	68.70
3	Silt (%)	20.50
4	Clay (%)	10.80
5	Bulk density (Mg m^{-3})	1.63
6	Particle density (Mg m^{-3})	2.60
7	Porosity (%)	37.30
8	Field Moisture (%)	8.50
9	Water Holding Capacity (WHC, %)	17.01
10	Hydraulic conductivity (mL min^{-1})	0.4
11	pH	5.35
12	Electrical Conductivity (EC, dS m^{-1})	0.30
13	Cation Exchange Capacity (CEC, cmol (+) kg^{-1})	4.30
14	Anion Exchange Capacity (AEC, cmol (-)kg^{-1})	1.21
15	Organic Matter (OM, %)	0.84
16	Available Nitrogen (kg ha^{-1})	178.89
17	Available Phosphorus (kg ha^{-1})	60.03
18	Available Potassium (kg ha^{-1})	150.60
19	Exchangeable Calcium (kg ha^{-1})	180.00
20	Exchangeable Magnesium (kg ha^{-1})	57.00
21	Exchangeable Sulphur (kg ha^{-1})	3.00

4.2 MULTIRESIDUE METHOD VALIDATION IN SOIL

The method for the extraction and estimation of residues of flupyradifurone and its metabolites were standardized by conducting recovery experiment by spiking with known amount of pure analytical standards. The method validation for extraction of flupyradifurone and its metabolites from soil and water were done by spiking with the respective standards so as to obtain concentration of 0.10, 0.50 and 1 mg kg^{-1} followed by extraction using acetonitrile and the residue estimation at different concentrations. The results are given in the Tables 6 & 7.

4.2.1 Mean Recovery of Flupyradifurone and its Metabolites in Sandy loam Soil and Water

The mean recovery percentage at 0.1 mg kg^{-1} level of fortification for flupyradifurone and its metabolites in sandy loam soil ranged from 80.74- 83.43. The highest recovery percentage was obtained for flupyradifurone (83.43 %). The RSD values obtained ranged from 0.85- 3.75 per cent. At the same concentration level, recovery was done in water sample, it ranged from 81.00 – 70.74 per cent with RSD values in range 3.95-1.65 per cent. The recovery percentage obtained were within the satisfactory range (80-120 %) and the RSD values obtained were also in the satisfactory range (< 20 %) for the spiked compounds and the method was found suitable at 0.10 mg kg^{-1}.

The mean recovery percentage at 0.50 mg kg^{-1} level of fortification of the compounds in the soil ranged from 84.00- 93.62 per cent. Flupyradifurone had the highest recovery per cent which is 93.62 per cent. The RSD calculated ranged from 1.50-3.80 per cent. For water samples at the same level of spiking, the recovery percentages were in the range of 77.61-84.00 per cent with RSD values in the range of 2.50-4.80 per cent. Since all the parameters obtained for this level of fortification were within the satisfactory range, the method was found suitable in the adoption of studies.

Table 6. Mean recovery of flupyradifurone and its metabolites spiked in sandy loam soil

Compounds/ Levels of spiking (mg kg^{-1})	Recovery Percentage			Relative Standard Deviation (RSD, %)		
	0.10	0.50	1	0.10	0.50	1
Flupyradifurone	83.43	93.62	91.11	3.75	1.50	3.42
DFEAF	80.74	87.91	83.74	6.25	2.19	6.10
6- CNA	82.00	84.00	83.00	0.85	3.80	6.70

Table 7. Mean recovery of flupyradifurone and its metabolites in water

Compounds/ Levels of spiking (mg kg^{-1})	Recovery Percentage			Relative Standard Deviation (RSD, %)		
	0.10	0.50	1	0.10	0.50	1
Flupyradifurone	81.30	83.42	81.11	3.95	2.50	4.42
DFEAF	70.74	77.61	74.94	5.25	3.29	5.10
6- CNA	81.00	84.00	85.00	1.65	4.80	5.70

The mean recovery percentage of various compounds spiked at 1 mg kg^{-1} level of fortification in soil ranged from 83.00 -91.11. Flupyradifurone obtained the highest recovery percentage. The RSD values ranged from 3.42-6.70 per cent. For water samples, the recovery percentages were 74.92-85.00 and RSD values were in the range of 4.42- 5.70 per cent. Since all the parameters obtained for this level of fortification was within the satisfactory range, the method is suitable in the adoption of studies. One of the major metabolite difluro acetic acid (DFA) was not recovered in the method validation.

4.3 SORPTION STUDY BY BATCH EQUILIBRIUM TECHNIQUE

4.3.1 Estimation of Equilibration Time

The optimum time for the maximum adsorption of flupyradifurone in normal soil and also the 0.5 per cent FYM amended soil were worked out. The aqueous phase supernatants in the soil samples spiked with 0.5 mg kg^{-1} after shaking and centrifugation were drawn at time intervals of 0th, 1st, 2nd, 4th, 6th and 24th hours after spiking and analyzed. The results obtained are given in Table 8.

The equilibration time for the amended soil was taken as 4 hours and for sandy loam soil as 6 hours.

Table 8. Estimation of equilibration time at 0.5 mg kg^{-1} level

Time intervals (HAS)	*Average concentration adsorbed (mg kg^{-1})	
	Soil	Amended soil
0th	0.21	0.29
1st	0.24	0.28
2nd	0.25	0.34
4th	0.28	0.35
6th	0.29	0.35
24th	0.29	0.35

*Mean of three replications, HAS- Hours after spiking

4.3.2 Adsorption Studies in Soil and Soil Amended with 0.5 per cent FYM

Adsorption –desorption studies were carried out at five concentration levels of 20, 40, 60, 80 and 100 µg levels of flupyradifurone. The adsorption data of both soil and amended soil are presented in Tables 9- 10.

The amount of flupyradifurone adsorbed on to the soil was calculated from the difference between the amount in the soil solution and the initial amount added. The mean K_d values were 2.41 and 2.58 for soil and amended soil respectively. The K_d value decreased with the increase in the concentration of the applied pesticide that is, the value decreased from 2.77 to 1.89 and 2.93 to 2.58 at conceentration from 20 to 100 µg for both soil and amended soil respectively. Adsorption data fitted into linearized form of the Freundlich equation, $\log (C_s) = 1/n \log (C_e) + \log K_f$ with the R^2 values were 0.979 and 0.980 respectively, for soil and amended soil. The K_f values were found to be 2.46 for soil and 2.57 for the amended soil and n_{ads} values of 1.27 and 1.23. Also the K_d value for amended soil with 0.5% FYM (2.58) was found greater than the value for the soil ($K_d = 2.41$).

4.3.3 Desorption Studies in Soil and Soil Amended with 0.5 per cent FYM

Desorption studies were carried out in the same soil used for the adsorption study, at five different concentrations (20, 40, 60, 80 and 100 µg) of flupyradifurone. Three desorption cycles were carried out in triplicates for each concentration. The desorption data in terms of the amount of flupyradifurone adsorbed to the soil and equilibrium concentration is presented in Table 11 & 12 for soil and amended soils, respectively. About 15.68- 27.77 per cent of the adsorbed flupyradifurone desorbed in three desorption cycles for different concentrations for soil. Desorption in various desorption cycles varied in the range 5.94- 3.89, 7.92- 3.65, 10.16- 4.47, 11.35- 5.41 and 12.73- 6.48 per cent for 1, 2, 3, 4 and 5 mg L^{-1} of initial concentration of flupyradifurone, respectively.

Table 9. Adsorption of flupyradifurone in sandy loam soil at 26± 2 °C

Amount added, I (µg)	Initial concentration (mg kg⁻¹)	Equilibrium concentration (mg kg⁻¹) C_e	Amount adsorbed, C_s		$K_d = C_s/C_e$
			*µg	mg kg⁻¹	
20	1	0.42	11.62	1.16	2.77
40	2	0.85	23.00	2.30	2.71
60	3	1.29	34.24	3.42	2.66
80	4	1.98	40.36	4.04	2.04
100	5	2.57	48.56	4.86	1.89
				Mean	2.41

*I - $C_e \times 20$, K_d- distribution coefficient

Freundlich equation and constants:

Linearized equation: log (C_s) = 0.788 log (C_e) +0.391; R^2= 0.979

Capacity factor (K_f) = 2.46

Intensity factor (n $_{ads}$) = 1.27

Table 10. Adsorption of flupyradifurone in sandy loam soil amended with 0.5 per cent FYM at 26± 2°C

Amount added, I (µg)	Initial concentration (mg kg⁻¹)	Equilibrium concentration (mg kg⁻¹) C_e	Amount adsorbed, C_s		$K_d = C_s/C_e$
			*µg	mg kg⁻¹	
20	1	0.41	11.88	1.19	2.93
40	2	0.82	23.68	2.37	2.90
60	3	1.28	34.38	3.44	2.68
80	4	1.90	42.10	4.21	2.22
100	5	2.39	52.18	5.22	2.18
		Mean			2.58

*I - $C_e \times 20$, K_d- distribution coefficient

Freundlich equation and constants:

Linearized equation: log (C_s) = 0.814 log (C_e) + 0.410; R^2= 0.980

Capacity factor (K_f) = 2.57

Intensity factor (n $_{ads}$) = 1.2

Table 11. Desorption of flupyradifurone in sandy loam soil at different concentrations at 26± 2°C

Desorption cycles	Equilibrium concentration (mg L^{-1}) C_e	Amount desorbed (µg)	Concentration remaining adsorbed (µg) C_s	Desorption percentage (%)
Initial concentration: 1 mg L^{-1}	0.42		11.62	
I	0.24	0.69	10.93	5.94
II	0.15	0.64	10.29	5.86
III	0.09	0.40	9.89	3.89
Total				15.68
Initial concentration: 2 mg L^{-1}	0.85		23.00	
I	0.52	1.82	21.18	7.92
II	0.32	1.18	20.00	5.57
III	0.20	0.73	19.27	3.65
Total				17.14
Initial concentration: 3 mg L^{-1}	1.29		34.24	
I	0.82	3.48	30.76	10.16
II	0.50	1.88	28.88	6.11
III	0.32	1.29	27.59	4.47
Total				20.74
Initial concentration: 4 mg L^{-1}	1.98		40.36	
I	1.22	4.58	35.78	11.35
II	0.73	2.48	33.30	6.93
III	0.46	1.80	31.50	5.41
Total				23.69
Initial concentration: 5 mg L^{-1}	2.57		48.56	
I	1.60	6.18	42.38	12.73
II	0.98	3.63	38.75	8.57
III	0.62	2.51	36.24	6.48
Total				27.77

Desorption carried out in the amended soil revealed that about 14.39- 26.00 per cent of the adsorbed flupyradifurone desorbed in three desorption cycles for different concentrations . Desorption in various desorption cycles varied in the range 5.83- 3.27 , 7.52- 3.32 , 9.51- 4.06 , 11.76- 4.60 and 12.02- 6.03 per cent for 1, 2, 3, 4 and 5 mg L^{-1} of initial concentrtion respectively. The amount of flupyradifurone desorbed increased, as the initial concentration of flupyradifurone increased from 20 to 100 µg levels.

In all the concentrations, both for soil and amended soil, rate of desorption was slower than adsorption. The adsorption- desorption data also fitted well into freundlich isotherm. The regression equation and fruendlich constant values are given in Tables 13 & 14. The hysteresis coefficient (ratio of $1/n_{ads}$ and $1/n_{des}$) varied from 6.90-3.80 for soil and 7.6-4.0 for FYM amended soil.

4.3.4 Adsorption- desorption Studies by Direct Spiking in Soil and Amended Soil

Adsorption studies by direct spiking of flupyradifurone were carried out in three different concentrations of 20, 40 and 60 µg levels of concentration in soil and soil amended with 0.5 per cent FYM. The data obtained are presented in Tables 15 & 16. The amount of flupyradifurone adsorbed to the soil was calculated from the difference between the amount in the soil solution and the initial amount added. The calculated k_d values ranged from 2.90-2.78 and 3.27-2.91 for soil and amended soil respectively. The k_d values showed high adsorption in case of direct spiking. The k_d values decreased gradually with the increase in the concentration applied.

Table 12. Desorption of flupyradifurone in sandy loam soil amended with 0.5 per cent FYM at different concentrations at 26± 2°C

Desorption cycles	Equilibrium concentration (mg L^{-1}) C$_e$	Amount desorbed (µg)	Concentration remaining adsorbed (µg) C$_s$	Desorption percentage (%)
Initial concentration: 1 mg L^{-1}	0.41		12.02	
I	0.24	0.70	11.32	5.83
II	0.15	0.60	10.72	5.30
III	0.09	0.35	10.40	3.27
Total				14.39
Initial concentration: 2 mg L^{-1}	0.82		23.74	
I	0.50	1.78	21.91	7.52
II	0.31	1.13	20.77	5.16
III	0.19	0.69	20.10	3.32
Total				15.99
Initial concentration: 3 mg L^{-1}	1.28		34.41	
I	0.80	3.27	31.11	9.51
II	0.49	1.78	29.33	5.72
III	0.31	1.19	28.14	4.06
Total				19.29
Initial concentration: 4 mg L^{-1}	1.90		42.10	
I	1.20	4.95	37.15	11.76
II	0.72	2.37	34.78	6.38
III	0.44	1.60	33.18	4.60
Total				22.74
Initial concentration: 5 mg L^{-1}	2.39		52.18	
I	1.51	6.27	45.91	12.02
II	0.94	3.65	42.26	7.95
III	0.60	2.55	39.71	6.03
Total				26.00

Table 13. Linearized form of Freundlich equation and constants for desorption in sandy loam soil

Initial concentration ($mg\ L^{-1}$)	Regression equation $\log (C_s) = \log K_F + 1/n\ \log (C_e)$	r	K_F	n_{des}	H (n_{des}/n_{ads})
1	$\log (C_s) = 0.109 + 0.112 \log (C_e)$	0.994	1.29	8.9	6.9
2	$\log (C_s) = 0.364 + 0.120 \log (C_e)$	0.971	2.31	8.3	6.5
3	$\log (C_s) = 0.512 + 0.159 \log (C_e)$	0.957	3.20	6.3	4.9
4	$\log (C_s) = 0.548 + 0.161 \log (C_e)$	0.965	3.53	6.2	4.8
5	$\log (C_s) = 0.593 + 0.205 \log (C_e)$	0.979	3.90	4.8	3.8

C_s- Concentration adsorbed, K_F- capacity factor, n_{des}- intensity factor,

C_e – equilibrium concentration, H- Hysteresis coefficient, r- correlation coefficient

Table 14. Linearized form of Freund lich equation and constants for desorption in sandy loam soil amended with 0.5 per cent FYM

Initial concentration ($mg\ L^{-1}$)	Regression equation $\log (C_s) = \log K_F + 1/n\ \log (C_e)$	r	K_F	n_{des}	H (n_{des}/n_{ads})
1	$\log (C_s) = 0.116 + 0.102 \log (C_e)$	0.985	1.3	9.8	7.6
2	$\log (C_s) = 0.374 + 0.116 \log (C_e)$	0.962	2.3	8.6	6.7
3	$\log (C_s) = 0.513 + 0.133 \log (C_e)$	0.953	3.3	7.5	5.9
4	$\log (C_s) = 0.569 + 0.153 \log (C_e)$	0.943	3.7	6.5	5.1
5	$\log (C_s) = 0.632 + 0.193 \log (C_e)$	0.970	4.3	5.2	4.0

C_s- Concentration adsorbed, K_F- capacity factor, n_{des}- intensity factor,

C_e – equilibrium concentration, H- Hysteresis coefficient, r- correlation coefficient

Adsorption isotherm was obtained by plotting equilibrium concentration against adsorbed concentration was L- shaped adsorption isotherm with the R^2 values were 0.99 for both soil and amended soil respectively.

Adsorption data fitted into linearized form of the Freundlich equation, $\log (C_s) = 1/n \log (C_e) + \log K_f$. The values of constant K_f were 2.79 and 2.95 respectively for soil and amended soil. The n_{ads} values were 1.03 and 1.01.

Desorption studies were carried out in three initial concentrations (1, 2 and 3 mg L^{-1}). Three desorption cycles were carried out in triplicates for each concentration. The desorption data in terms of the amount of flupyradifurone adsorbed on soil and equilibrium concentration in soil and amended soil are presented in Tables 17 & 19. About 14.86- 20.86 per cent of the adsorbed flupyradifurone desorbed in three desorption cycles for the different concentrations. Desorption in various desorption cycles varied in the ranges 6.59- 2.96, 7.24- 4.22 and 10.52- 4.42 per cent for 1, 2 and 3 mg L^{-1} respectively.

In amended soil, about 13.91- 20.25 per cent of the adsorbed flupyradifurone desorbed in three desorption cycles. For 1, 2 and 3 mg L^{-1}, the desorption percentages varied in the ranges of 5.56-3.23, 8.08-3.24 and 10.71-3.97 per cent, respectively. The desorption increased as the added initial concentrations increased.

The adsorption- desorption data also fitted well into Freundlich isotherm. The regression equation and the Freundlich constants values are given in Tables 18 & 20.

The hysteresis coefficient (ratio of $1/n_{ads}$ and $1/n_{des}$) varied from 8.90-6.40 for soil and 9.00-6.10 for FYM amended soil.

Table 15. Adsorption of flupyradifurone in sandy loam soil at 26± 2 °C by direct spiking

Amount added, I (μg)	Initial concentration (mg kg^{-1})	Equilibrium concentration (mg kg^{-1}) C_e	Amount adsorbed C_s		$K_d=$ C_s/C_e
			*μg	mg kg^{-1}	
20	1	0.41	11.84	1.18	2.90
40	2	0.83	23.34	2.33	2.80
60	3	1.26	34.90	3.49	2.78
				Mean	2.83

*I - $C_e \times 20$, K_d- distribution coefficient

Freundlich equation and constants:

Linearized equation: $\log (C_s) = 0.968 \log (C_e) +0.446$; $R^2= 0.999$

Capacity factor (K_f) = 2.79

Intensity factor (n_{ads}) = 1.03

Table 16. Adsorption of flupyradifurone in sandy loam soil amended with 0.5 per cent FYM at 26± 2°C by direct spiking

Amount added, I (μg)	Initial concentration (mg kg^{-1})	Equilibrium concentration (mg kg^{-1}) C_e	Amount adsorbed C_s		$K_d= C_s/C_e$
			*μg	mg kg^{-1}	
20	1	0.38	12.42	1.24	3.27
40	2	0.78	24.38	2.44	3.12
60	3	1.22	35.58	3.56	2.91
				Mean	3.10

*I - $C_e \times 20$, K_d- distribution coefficient

Freundlich equation and constants:

Linearized equation: $\log (C_s) = 0.908 \log (C_e) + 0.471$; $R^2= 0.999$

Capacity factor (K_f) = 2.95

Intensity factor (n_{ads}) = 1.01

Table 17. Desorption of flupyradifurone in directly spiked sandy loam soil at different concentrations at 26± 2°C

Desorption cycles	Equilibrium concentration (mg L⁻¹) C_e	Amount desorbed (µg)	Concentration remaining adsorbed (µg) C_s	Desorption percentage (%)
Initial concentration: 1 mg L⁻¹	0.41		11.84	
I	0.24	0.78	11.06	6.59
II	0.15	0.59	10.47	5.33
III	0.09	0.31	10.16	2.96
			Total	14.88
Initial concentration: 2 mg L⁻¹	0.83		23.34	
I	0.50	1.69	21.65	7.24
II	0.30	1.01	20.64	4.67
III	0.19	0.87	19.77	4.22
			Total	16.13
Initial concentration: 3 mg L⁻¹	1.26		34.90	
I	0.81	3.67	31.23	10.52
II	0.50	1.85	29.38	5.92
III	0.31	1.30	28.08	4.42
			Total	20.86

Table 18. Linearized form of Freund lich equation and constants for desorption in sandy loam soil by direct spiking

Initial concentration (mg L⁻¹)	Regression equation $\log (C_s) = \log K_F + 1/n \ \log (C_e)$	r	K_F	n_{des}	H (n_{des}/n_{ads})
1	$\log (C_s) = 0.109 + 0.102 \log (C_e)$	0.976	1.29	9.17	8.9
2	$\log (C_s) = 0.377 + 0.110 \log (C_e)$	0.981	2.38	9.09	8.8
3	$\log (C_s) = 0.519 + 0.150 \log (C_e)$	0.954	3.3	6.60	6.4

C_s- Concentration adsorbed, K_F- capacity factor, n_{des}- intensity factor,

C_e – equilibrium concentration, H- Hysteresis coefficient, r- correlation coefficient

Table 19. Desorption of flupyradifurone in directly spiked amended sandy loam soil at different concentrations at 26± 2°C

Desorption cycles	Equilibrium concentration (mg L^{-1}) C_e	Amount desorbed (µg)	Concentration remaining adsorbed (µg) C_s	Desorption percentage (%)
Initial concentration: 1 mg L^{-1}	0.38		12.42	
I	0.22	0.69	11.73	5.56
II	0.14	0.60	11.13	5.12
III	0.09	0.36	10.77	3.23
			Total	13.91
Initial concentration: 2 mg L^{-1}	0.78		24.38	
I	0.49	1.97	22.41	8.08
II	0.30	1.13	21.28	5.04
III	0.19	0.69	20.59	3.24
			Total	16.36
Initial concentration: 3 mg L^{-1}	1.22		35.58	
I	0.80	3.81	31.77	10.71
II	0.49	1.77	30.00	5.57
III	0.30	1.19	28.81	3.97
			Total	20.25

Table 20. Linearized form of Freundlich equation and constants for desorption in amended sandy loam soil by direct spiking

Initial concentration (mg L^{-1})	Regression equation $\log (C_s) = \log K_F + 1/n \ \log (C_e)$	r	K_F	n_{des}	H (n_{des}/n_{ads})
1	$\log (C_s) = 0.138 + 0.101 \log (C_e)$	0.994	1.37	9.9	9.0
2	$\log (C_s) = 0.392 + 0.110 \log (C_e)$	0.953	2.4	9.1	8.27
3	$\log (C_s) = 0.522 + 0.148 \log (C_e)$	0.930	3.3	6.7	6.1

C_s- Concentration adsorbed, K_F- capacity factor, n_{des}- intensity factor,

C_e – equilibrium concentration, H- Hysteresis coefficient, r- correlation coefficient

4.4 MOBILITY OF FLUPYRADIFURONE IN SOIL

The mobility of flupyradifurone was determined by analyzing the residue found at different depths of the soil columns through which definite concentration of pesticide (25, 50, 75 µg) was allowed to elute by application of definite volume of water (40, 80, 160 mL) to the column. The results obtained are given in the Tables 21- 26.

4.4.1 Mobility of Flupyradifurone in Sandy loam Soil

Data on the downward migration of flupyradifurone by application at 25 µg level in sandy loam soil when eluted with 40, 80, 160 mL of water are presented in the Table 21. The data revealed that, when 40 mL water was added, flupyradifurone moved up to 10 cm depth and majority of the residues (14.24 µg) were confined to the top 0-5 cm layer of soil. When the water used for elution increased to 80 mL, the migration was detected up to 15 cm and the quantity of flupyradifurone in the top layer was reduced (10.32 µg). When the water for elution was 160 mL, more migration was noticed and a further decrease in concentration of flupyradifurone was noticed at to 0-5 cm, indicating a more migration of flupyradifurone with increase in volume of water for elution.

Data regarding the downward movement of flupyradifurone with the application at 50 µg level in sandy loam soil when eluted with 40, 80, 160 mL of water are presented in the Table 22. The data revealed that, when 40 mL water was added, flupyradifurone moved up to 10 cm depth and majority of the residues (26.38 µg) were confined to the top 0-5 cm layer of soil. When the water used for elution increased to 80 mL, the migration was detected up to 15 cm and the quantity of flupyradifurone in the top layer was reduced (23.88 µg). When the water for elution was 160 mL, more migration was noticed up to 20 cm and a further decrease in concentration was noticed at top 0-5 cm, indicates more migration of flupyradifurone with increased volume of water for elution.

Data regarding the downward migration of flupyradifurone with the application at 75 µg level in sandy loam soil when eluted with 40, 80, 160 mL of water are presented in the Table 23. The data revealed that, when 40 mL water was added, flupyradifurone was moved up to 15 cm depth and majority of residues (34.30 µg) were confined to the top 0-5 cm layer of soil. When the water used for elution increased to 80 mL, the migration was detected up to 20 cm and the quantity of flupyradifurone in the top layer was reduced (27.83 µg). When the water for elution was 160 mL, more migration was noticed up to 25 cm and a further decrease in concentration was noticed at top 0-5 cm. The leachate also had the residues of flupyradifurone, but was found below the limit of quantitation level, indicating more migration of flupyradifurone with increased volume of water for elution.

4.4.2 Mobility of Flupyradifurone in Sandy loam Soil Amended with 0.5 per cent FYM

Data on the downward migration of flupyradifurone by application at 25 µg level in sandy loam soil amended with 0.5 per cent FYM when eluted with 40, 80, 160 mL of water are presented in the Table 24. The data revealed that, when 40 mL water was added, flupyradifurone moved up to 10 cm depth and majority of the residues (15.48 µg) were confined to the top 0-5 cm layer of soil. When the water used for elution increased to 80 mL, the migration was detected up to 15 cm and the quantity of flupyradifurone in the top layer was reduced (12.28 µg). When the water for elution was 160 mL, a further decrease in concentration of flupyradifurone was noticed at to 0-5 cm.

Data regarding the downward movement of flupyradifurone with the application at 50 µg level in sandy loam soil with 0.5 per cent FYM amended when eluted with 40, 80, 160 mL of water are presented in the Table 25. The data revealed that, when 40 mL water was added, flupyradifurone moved up to 10 cm depth and majority of the residues (34.96 µg) were confined to the top 0-5 cm layer of soil.

When the water used for elution increased to 80 mL, the migration was detected only up to 10 cm and the quantity of flupyradifurone in the top layer was reduced (27.36 µg). When the water for elution was 160 mL, more migration was noticed up to 15 cm and a further decrease in concentration was noticed at top 0-5 cm. The depth of migration of residues was considerably decreased by the farm yard manure amendment in the soil.

Data regarding the downward migration of flupyradifurone with the application at 75 µg level in sandy loam soil amended with 0.5 per cent FYM when eluted with 40, 80, 160 mL of water are presented in the Table 26. The data revealed that, when 40 mL water was added, flupyradifurone only moved up to 10 cm depth and majority of residues (36.62 µg) were confined to the top 0-5 cm layer of soil. When the water used for elution increased to 80 mL, the migration was detected up to 15 cm and the quantity of flupyradifurone in the top layer was reduced (34.45 µg). When the water for elution was 160 mL, migration was noticed only up to 15 cm and a further decrease in concentration was noticed at top 0-5 cm.

Table 21. Migration of flupyradifurone in sandy loam soil column when loaded with 25 µg level

Depth of soil column (cm) / leachate	*Residues (µg) at different depths		
	40 mL	80 mL	160 mL
0-5	14.24	10.32	9.56
5-10	3.74	4.55	4.15
10-15	< LOQ	2.26	1.21
15-20	< LOQ	< LOQ	0.33
20-25	< LOQ	< LOQ	< LOQ
Leachate	< LOQ	< LOQ	< LOQ

*Mean of three replications

Table 22. Migration of flupyradifurone in sandy loam soil column when loaded with 50 µg level

Depth of soil column (cm) / leachate	*Residues (µg) at different depths		
	40 mL	80 mL	160 mL
0-5	26.38	23.88	19.08
5-10	5.20	4.60	4.48
10-15	< LOQ	2.28	1.73
15-20	< LOQ	< LOQ	0.44
20-25	< LOQ	< LOQ	< LOQ
Leachate	< LOQ	< LOQ	< LOQ

*Mean of three replications

Table 23. Migration of flupyradifurone in sandy loam soil column when loaded with 75 µg level

Depth of soil column (cm) / leachate	*Residues (µg) at different depths		
	40 mL	80 mL	160 mL
0-5	34.30	27.83	23.17
5-10	9.02	8.45	7.24
10-15	6.28	7.20	7.00
15-20	< LOQ	4.00	4.20
20-25	< LOQ	< LOQ	< LOQ
Leachate	< LOQ	< LOQ	< LOQ

*Mean of three replications

Table 24. Migration of flupyradifurone in 0.5 per cent FYM amended sandy loam soil column when loaded with 25 µg level

Depth of soil column (cm)/ leachate	*Residues (µg) at different depths		
	40 mL	80 mL	160 mL
0-5	15.48	12.28	11.79
5-10	4.48	7.12	4.47
10-15	< LOQ	0.44	2.04
15-20	< LOQ	< LOQ	< LOQ
20-25	< LOQ	< LOQ	< LOQ
Leachate	< LOQ	< LOQ	< LOQ

*Mean of three replications

Table 25. Migration of flupyradifurone in 0.5 per cent FYM amended sandy loam soil column when loaded with 50 µg level

Depth of soil column (cm)/ leachate	*Residues (µg) at different depths		
	40 mL	80 mL	160 mL
0-5	34.96	27.56	22.00
5-10	3.44	6.16	4.96
10-15	< LOQ	< LOQ	4.08
15-20	< LOQ	< LOQ	< LOQ
20-25	< LOQ	< LOQ	< LOQ
Leachate	< LOQ	< LOQ	< LOQ

*Mean of three replications

Table 26. Migration of flupyradifurone in 0.5 per cent FYM amended sandy loam soil column when loaded with 75 µg level

Depth of soil column (cm)/ leachate	*Residues (µg) at different depths		
	40 mL	80 mL	160 mL
0-5	36.62	34.45	29.78
5-10	11.52	5.54	4.56
10-15	< LOQ	3.88	3.48
15-20	< LOQ	< LOQ	< LOQ
20-25	< LOQ	< LOQ	< LOQ
Leachate	< LOQ	< LOQ	< LOQ

*Mean of three replications

4.5 PERSISTENCE OF FLUPYRADIFURONE IN SOIL

The persistence of flupyradifurone in sandy loam soil as well as the amended soil with 0.5 per cent FYM was studied at three levels of flupyradifurone *viz.*, 1, 2 and 4 mg kg^{-1} at three soil conditions of air dry, soil at field capacity level and saturated soil. The half-life of the compounds at different treatment levels and soil conditions were also found out after quantifying the residue level in the soil on the 0th, 1st, 3rd, 5th, 7th, 10th, 15th, 20th and 30th day. The results obtained are given in the Tables 27- 29.

4.5.1 Dissipation of Flupyradifurone in Sandy loam Soil and the Soil Amended with 0.5 per cent FYM in Air dry Soil Condition

The data on the persistence of flupyradifurone in sandy loam soil and the soil amended with 0.5 per cent FYM in air dry soil condition are presented in Table 27. The data revealed that the mean residue content of flupyradifurone considerably decreased with time. The half- life of the flupyradifurone increased with the increase in the concentration applied i.e. lower period of half-life was for the concentration applied at the rate of 1 mg kg^{-1}, while a higher half- life period for higher concentration of 4 mg kg^{-1} level of fortification of flupyradifurone. The half- life periods were found to be increased in the soils amended with 0.5 per cent FYM. At 1 mg kg^{-1} applied concentration of flupyradifurone the half -life was 19.38 days whereas it was 20.41 days in the amended soil. The similar was the condition at both 2 and 4 mg kg^{-1}. At the 0th day of application of flupyradifurone at the rate of 1 mg kg^{-1}, the amounts of residues were 0.64 mg kg^{-1} initially and finally reduced to an amount of 0.25 mg kg^{-1}. At an application rate of 2 mg kg^{-1} in soil, the initial residue content was 1.68 mg kg^{-1} which was reduced further to 0.61 mg kg^{-1} at the 30th day of observation taken. The corresponding half-life was found to be 20.87 days. The half-life period of 22.47days was obtained when the application rate was increased to 4 mg kg^{-1} level of flupyradifurone.

When the soil was amended with 0.5 per cent FYM, the residue amount retained increased and also the half-life period. At 2 mg kg^{-1} level, a half-life period of 21.79 days was obtained and the residue at the 30th day of observation was 0.73 mg kg^{-1} which was higher than that remained in the soil at the same level of spiking. The half- life period increased to 22.94 at the application rate of 4 mg kg^{-1} level.

4.5.2 Dissipation of Flupyradifurone in Sandy loam Soil and the Soil Amended with 0.5 per cent FYM at Field Capacity Level

The data regarding the dissipation of flupyradifurone in sandy loam soil and the soil amended with 0.5 per cent FYM at field capacity level are presented in Table 28. It is seen that the half- life period were lower than that under air dry soil condition.

The residue content decreased from the day of application to the 30th day of observation taken. At 1 mg kg^{-1} level, the residue content reduced to half by the fifth day in the soil whereas it took 7 days in the soil amended with FYM with the respective half- lives of 11.14 and 9.51 days. The half –life was found lowered in the amended soil condition.

At 2 and 4 mg kg^{-1} level of concentration, the half-life was 13.08 and 13.21 days respectively. This shows that with the increase in concentration the half- life also increases. In the amended soil, the half- life at these concentrations was found increased to 14.59 and 15.71 days. The 30th day residue amount account for 0.73 mg kg^{-1} in the soil under field capacity condition whereas it was found to be 0.93 mg kg^{-1} in the amended soil at 4 mg kg^{-1} level of fortification.

4.5.3 Dissipation of Flupyradifurone in Sandy loam Soil and the Soil Amended with 0.5 per cent FYM at Saturated Soil Condition

The data regarding the dissipation of flupyradifurone in sandy loam soil and the soil amended with 0.5 per cent FYM at saturated soil condition are presented in

Table 29. It is seen that the half- life period were lower than that under air dry soil condition and field capacity condition.

The residue content reduced from the initial day to the 30th day of observation taken. At 1 mg kg^{-1} level of spiking in soil under the saturated condition, the half- life was found to be 9.08 days which increased in the amended soil condition (10.02 days) at the same level of fortification. As the initial level of concentration spiked to the soil increased, the half-life was also found to be increasing. At 2 mg kg^{-1}, it was 9.12 days and at 4 mg kg^{-1}, it was 9.85 days. In the amended soil, the half- life was 10.12 and 10.28 days respectively, for 2 mg kg^{-1} and 4 mg kg^{-1} levels of fortification.

4.5.4 Comparison of Half- life Values of Flupyradifurone as Influenced by the Treatment Levels, Soil Amendment and Soil Conditions

The half-life of chemical at different concentrations and soil conditions were statistically analyzed (Table 30) and the results showed that the three soil conditions i.e., air dry condition, field capacity and saturated condition significantly influenced the half-life of the chemical and the highest half-life was found in air dry soil condition. Dissipation was found fastest at saturated condition followed by field capacity and dry moisture regimes. Comparison of the treatment levels revealed that the treatment T_1 and treatment T_4, were found statistically on par with the other treatments.

4.5.5 Metabolism of Flupyradifurone in Laboratory Condition

The data on the metabolism of flupyradifurone under laboratory condition revealed that no major metabolites were detected in the soil in the experiment conducted for assessing the persistence of flupyradifurone.

Table 27. Dissipation of flupyradifurone in sandy loam soil and the soil amended with 0.5 per cent FYM in air dry soil condition

Treatment	*Mean Residues of Flupyradifurone (mg kg^{-1})									$t_{1/2}$ (days)
	Days after treatment									
	0	1	3	5	7	10	15	20	30	
T1(1 mg kg^{-1} in soil)	0.64	0.63	0.62	0.61	0.59	0.59	0.33	0.31	0.25	19.38
T2(2 mg kg^{-1} in soil)	1.68	1.64	1.59	1.55	1.46	1.06	1.03	0.99	0.61	20.87
T3(4 mg kg^{-1} in soil)	3.34	2.94	2.80	2.50	2.50	1.84	1.71	1.43	1.38	22.47
T4(1 mg kg^{-1} in amended soil)	0.94	0.93	0.86	0.84	0.83	0.75	0.51	0.49	0.36	20.41
T5(2 mg kg^{-1} in amended soil)	1.83	1.69	1.60	1.56	1.48	1.39	1.18	0.84	0.73	21.79
T6(4 mg kg^{-1} in amended soil)	3.58	3.38	3.15	3.13	2.96	2.78	1.90	1.70	1.60	22.94

*Mean of three replications

Table 28. Dissipation of flupyradifurone in sandy loam soil and the soil amended with 0.5 per cent FYM at field capacity level

Treatment	*Mean Residues of Flupyradifurone (mg kg^{-1}) Days after treatment									$t_{1/2}$ (day)
	0	1	3	5	7	10	15	20	30	
T1(1 mg kg^{-1} in soil)	0.40	0.26	0.20	0.20	0.17	0.15	0.13	0.10	<LOQ	11.14
T2(2 mg kg^{-1} in soil)	1.48	1.43	1.42	1.38	1.34	1.24	1.08	0.70	0.27	13.21
T3(4 mg kg^{-1} in soil)	3.95	3.63	2.70	2.63	2.55	2.54	1.56	1.37	0.73	13.08
T4(1 mg kg^{-1} in amended soil)	0.41	0.31	0.25	0.23	0.22	0.19	0.16	0.11	<LOQ	9.51
T5(2 mg kg^{-1} in amended soil)	1.78	1.56	1.48	1.37	1.25	1.16	1.10	0.66	0.39	14.59
T6(4 mg kg^{-1} in amended soil)	3.23	3.25	2.89	2.86	2.67	2.57	1.57	1.40	0.93	15.74

*Mean of three replications, LOQ- 0.1 mg kg^{-1}

Table 29. Dissipation of flupyradifurone in sandy loam soil and the soil amended with 0.5 per cent FYM at saturated soil condition

| Treatment | *Mean Residues of Flupyradifurone (mg kg^{-1}) | | | | | | | | | $t_{1/2}$ (days) |
| | Days after treatment | | | | | | | | | |
	0	1	3	5	7	10	15	20	30	
T1(1 mg kg^{-1} in soil)	0.918	0.815	0.795	0.721	0.688	0.406	0.177	0.147	0.135	9.08
T2(2 mg kg^{-1} in soil)	1.895	1.874	1.447	1.240	0.527	0.417	0.382	0.342	0.213	9.12
T3(4 mg kg^{-1} in soil)	3.420	3.395	2.885	2.635	1.058	0.982	0.852	0.760	0.454	9.85
T4(1 mg kg^{-1} in amended soil)	0.929	0.864	0.781	0.667	0.414	0.342	0.280	0.173	0.136	10.02
T5(2 mg kg^{-1} in amended soil)	1.773	1.331	1.309	1.167	0.583	0.419	0.407	0.348	0.223	10.12
T6(4 mg kg^{-1} in amended soil)	3.719	3.616	3.435	2.939	1.861	1.574	1.161	0.974	0.538	10.28

*Mean of three replications

Table 30. Comparison of half- life values of flupyradifurone as influenced by the treatment levels, soil amendment and soil conditions

Treatments/ soil conditions	Air dry soil	Soil at Field Capacity	Saturated soil	CD (0.05)
T1(1 mg kg^{-1} in soil)	19.38	11.14	9.08	
T2(2 mg kg^{-1} in soil)	20.87	13.21	9.12	
T3(4 mg kg^{-1} in soil)	22.47	13.08	9.85	
T4(1 mg kg^{-1} in amended soil)	20.41	9.51	10.02	2.12
T5(2 mg kg^{-1} in amended soil)	21.79	14.59	10.12	
T6(4 mg kg^{-1} in amended soil)	22.94	15.74	10.28	
CD (0.05)	1.49			
SE (m±) = 1.29				

Discussion

5. DISCUSSION

Flupyradifurone is a novel broad spectrum systemic insecticide belonging to the new class of butenolidae. Its action is similar to the neonicotinoid group of insecticides *i.e.* they act as reversible agonists on insect nicotinic acetyl choline receptors but are structurally different from the known agonists. It is used to control sucking pests like aphids and whiteflies on a variety of vegetable crops. Laboratory bioassays demonstrated a fast action on a broad range of sucking pests and also showed excellent field efficacy on a number of crops with different application methods such as drip irrigation, foliar, soil and seed treatment. It was also found to be active against resistant pests such as cotton whiteflies. The solubility of the compound was found to be higher in water *i.e.* 3200 mg L^{-1}. It showed moderate mobility and found to be moderately degraded with no major metabolites in the aquatic system.

In this context a study was conducted to assess the adsorption- desorption of flupyradifurone in sandy loam soils and also in the soil amended with 0.5 per cent FYM. Along with that, the persistence and the mobility of the applied pesticide in the soil environment were also studied. The results obtained from the study are discussed under the following headings.

5.1 PHYSICAL AND CHEMICAL PROPERTIES OF THE SOIL

The physical and chemical properties of soil were estimated as per standard procedures and the results obtained are presented in Table 5. The soil was found to be sandy loam in texture with 80.70 per cent sand, 8.50 per cent silt and 10.80 per cent clay. The soil was found to be strongly acidic with pH 5.8. The bulk density, particle density and the porosity of the soil are 1.63 Mg m^{-3}, 2.60 Mg m^{-3} and 37.30 per cent, respectively. The organic carbon content of the soil was found in medium range (0.84%). The soil contained low nitrogen and potassium content and higher phosphorus content. The exchangeable calcium, magnesium and sulphur were found

to be deficient in soil. The cation exchange capacity was 4.3 cmol (+) kg^{-1} and anion exchange capacity was cmol (-) kg^{-1}. The results of soil analysis done were in accordance with the work of Dhanya (2016).

5.2 STANDARDIZATION OF ANALYTICAL PROCEDURE FOR MULTIRESIDUE METHOD VALIDATION

The result of the recovery experiment for standardizing the analytical procedure for estimation of flupyradifurone and its metabolites (Table 6) in the soil revealed that, extraction of the residues using acetonitrile followed by MgSO$_4$ and Primary secondary amine (PSA) sorbent clean up and centrifugation to collect supernatant was found to be satisfactory and suitable at 0.1, 0.5 and 1 mg kg^{-1}. The mean recovery percentages ranged from 70.74- 93.62 per cent and RSD values ranged from 0.85- 6.70 per cent. Since the values of recovery percentage and relative standard deviation (RSD) fall in acceptable range of 70-110 per cent and < 20 per cent respectively, and also considering the less time, less solvent requirement and economics of operation, the QuEChERS method was adopted for the further analysis of flupyradifurone in soil. The advantages of the QuEChERS method were also reported by Anastassiades *et al*. (2003).

Similarly, recovery experiment for standardizing the analytical procedure for estimation of flupyradifurone and its metabolites (Table 7) in the water samples revealed that, extraction of residues using partitioning with dichloromethane and n-Hexane and two three times washing with sodium sulphate followed by concentration and final make up to 1 mL using methanol was found to be satisfactory and suitable at 0.1, 0.5 and 1 mg L^{-1} level of spiking. The mean recovery percentages ranged from 70.74- 85 per cent and RSD values ranged from 1.65- 5.70 per cent. Since the values of recovery percentage and relative standard deviation (RSD) fall in acceptable range of 70-110 per cent and < 20 per cent respectively, the method was adopted for the further analysis of flupyradifurone in aqueous samples.

5.3 SORPTION STUDY BY BATCH EQUILIBRIUM TECHNIQUE

The adsorption- desorption studies were carried out in sandy loam soil and soil amended with 0.5 per cent FYM at five different concentrations of 20, 40, 60, 80 and 100 μg levels. Desorption studies were also carried out under direct spiking of soil samples at three concentration levels of 20, 40 and 60 μg levels in both soil and FYM amended soil.

5.3.1 Estimation of Equilibration Time

Equilibration time is the time required for maximum adsorption of pesticide. A large number of vacant sites were available for adsorption during the initial stages, but later a repulsive force between the solute molecule of solid and bulk phase comes into play once the vacant sites get occupied thus hindering further adsorption. Finally, the adsorbed amount by soil remains steady. The time was standardized to 6h for sandy loam soil and 4h for soil amended with FYM based on the study since there was no increase in the adsorption of pesticides into soil after 6h and 4h of shaking. The pattern of adsorption of flupyradifurone with time is depicted in Fig. 3.

5.3.2 Adsorption Studies in Soil and Amended Soil

Adsorption studies were conducted in soil and FYM amended soil at five different concentrations of 20, 40, 60, 80 and 100 μg levels of concentration and the data were presented in Tables 9 & 10.

The amount of flupyradifurone adsorbed on to the soil was calculated from the difference between the amount in the soil solution and the initial amount added. It was found that as the level of concentration of applied flupyradifurone increases, the k_d value was found to be decreasing which is the ratio of the quantity of the adsorbate adsorbed per mass of solid to the amount of the adsorbate remaining in solution at equilibrium. The mean K_d values were 2.41 and 2.58 for soil and amended

soil respectively, indicating greater affinity of the pesticide molecule for soil particles than for soil solution. Also the K_d value for amended soil with 0.5 per cent FYM (2.58) was found greater than the value for the soil ($K_d = 2.41$), which may be due to the increased adsorption followed by the addition of organic matter. Low K_d value indicates soil has low retention capacity. K_d values were found decreasing by 26.7- 28 per cent when the organic matter from the soil was removed (Akma *et al.*, 2009).

Adsorption isotherm obtained by plotting equilibrium concentration against adsorbed concentration for both soil and amended soil are shown in Fig 4 & 5. The adsorption data fitted well into the Freundlich isotherm equation in both normal and amended soil as the R^2 value was 0.979 and 0.980 respectively (Fig. 4 & 5). The K_f values which denote the adsorption capacity of the sorbent were found to be 2.46 for soil and 2.57 for the amended soil indicating a high adsorption capacity and increase in the adsorption with addition of organic amendment. It was reported that the K_f values increased with the increase in the organic matter content (Patakioutas *et al.*, 2002; Singh, N, 2002; Kawakami *et al.*, 2007). Similar results were obtained in the adsorption study of alachlor in soil which concluded that adsorption of alachlor in soil, FYM and charcoal is a function of organic matter content (Jaya *et al.*, 2009). The study by Bansal, 2010 also showed that adsorption increased with the increase in organic manure and the adsorption capacity was positively correlated with soil organic carbon and CEC. The results are strongly supported by the findings of Hiller *et al.* (2012) where the sorption of MCPA decreased by 37- 100 per cent after the removal of organic matter from the soil. Organic amendment may have increased the organic carbon content which has led to the increased sorption capacity which was reported in study of triazine adsorption on organic amended soil (Fenoll *et al.*, 2014).

Thus organic matter and clay content played an important role in pesticide adsorption not only that, the nature of organic matter also influenced the adsorption properties (Krishna and Philip, 2008).
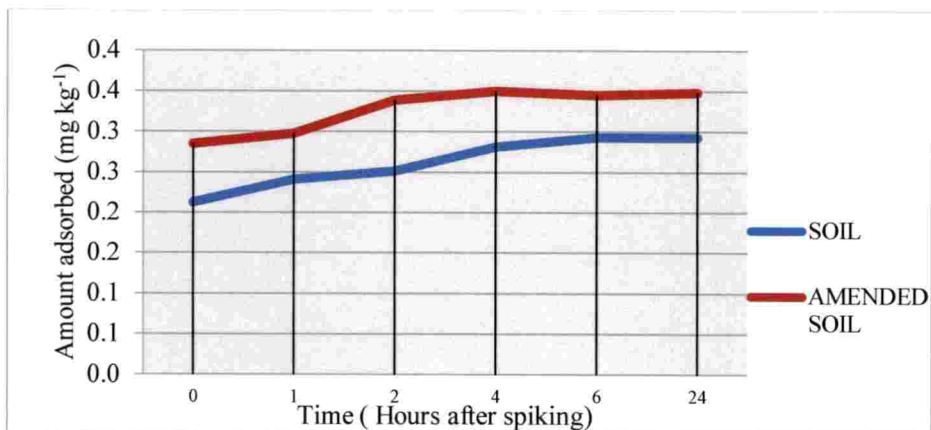
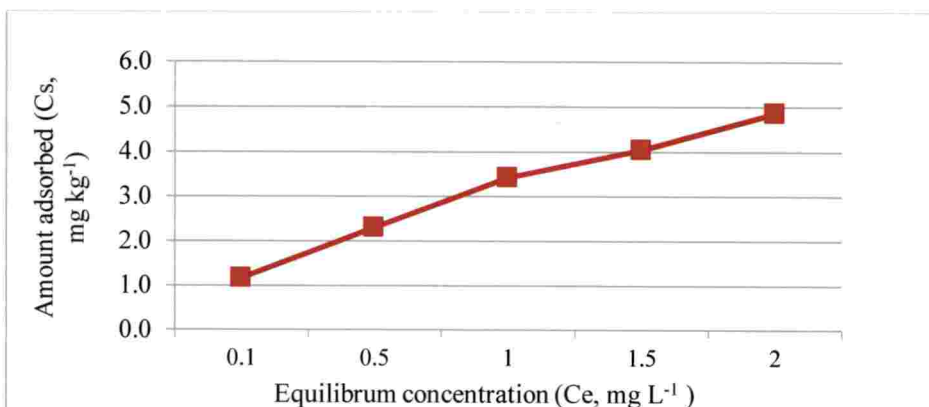Figure 3. Equilibrium time of soil and amended soil

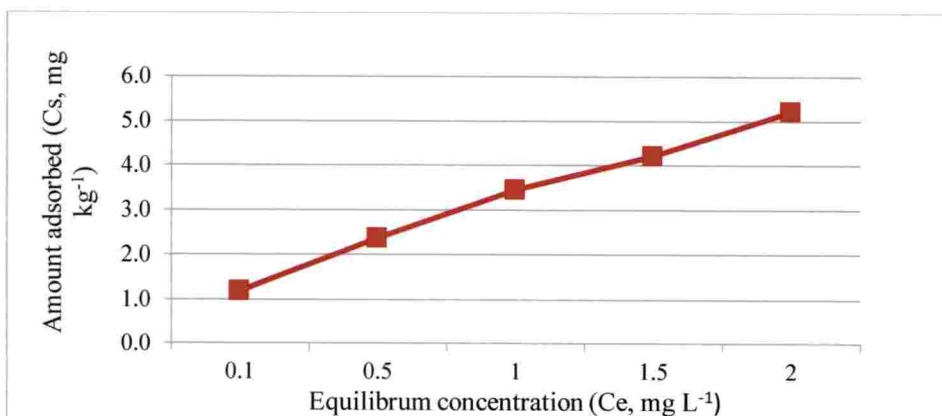Figure 4. Adsorption isotherm of flupyradifurone in soil

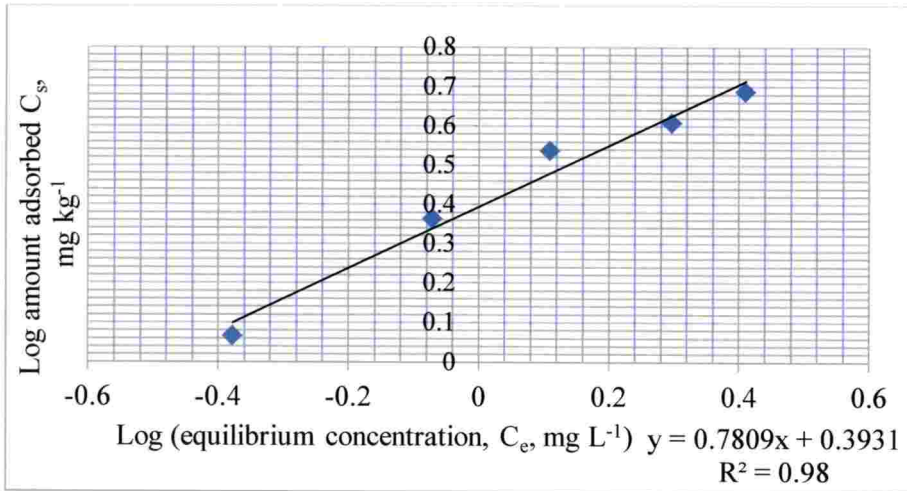Figure 5. Adsorption isotherm of flupyradifurone in 0.5 per cent FYM amended soil

Figure 6. Freundlich adsorption isotherm of soil

Freundlich equation and constants:

- Linearized equation: $\log(C_s) = 0.788 \log(C_e) + 0.391$; $R^2 = 0.98$
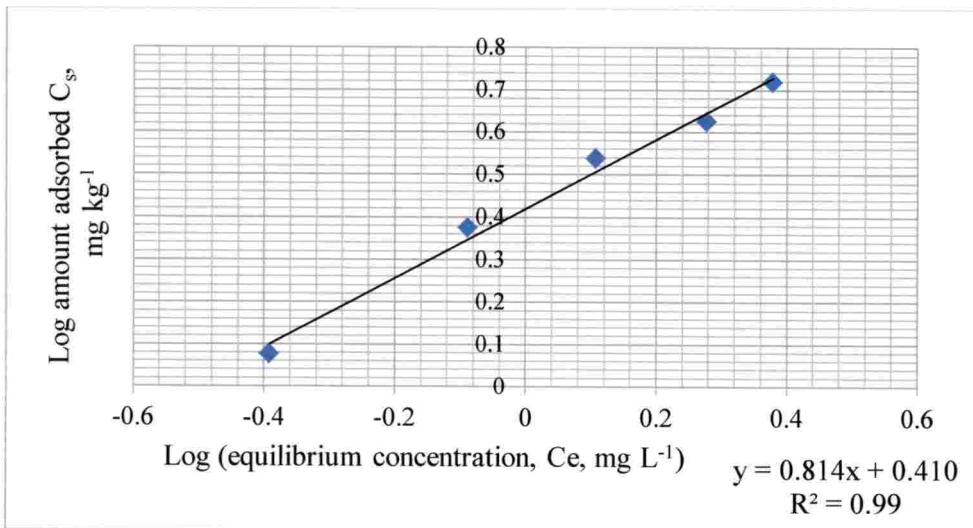- Capacity factor $(K_f) = 2.41$, Intensity factor $(n_{ads}) = 1.27$

Figure 7. Freundlich adsorption isotherm in amended soil

Freundlich equation and constants:

- Linearized equation: $\log(C_s) = 0.814 \log(C_e) + 0.410$; $R^2 = 0.99$
- Capacity factor $(K_f) = 2.57$, Intensity factor $(n_{ads}) = 1.23$

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1/n is an important coefficient of description of isotherm (Weiping *et al.*, 2001). The n_{ads} values of 1.27 and 1.23 indicates convex, L- shaped adsorption isotherm. Similar findings of L- shaped non- linear isotherms were reported by Weiping *et al.* (2001) and Kawakami *et al.* (2007). The downward nature of adsorption isotherm is characterized by a strong interaction of pesticide molecules with soil surface rather than with solvent molecules. This suggests that adsorption decreases as aqueous concentration of pesticide increase in the solution phase (Jaya *et al.*, 2009: Raunaq *et al.*, 2017).

Also this type of isotherm shows that adsorbent and adsorbate has a strong interaction (Giles *et al.*, 1960). The slope of the isotherm decreases with the rise in solute concentration because vacant sites become less accessible with the progressive covering of surface (Rhodes *et al.*, 1970). Also, Cox *et al.* (1997) studied the sorption of imidachlorprid in soil and the results revealed that as the concentration of the imidachlorprid decreased, the sorption to soil particles increased.

5.3.3 Desorption Studies in Soil and Amended Soil

Desorption studies were carried out in the same soil used for adsorption studies. The datas were presented in Tables 11 & 12. From the data, it was found that the desorption increased slightly as the concentration of spiking increased. The data also fitted well into Freundlich equation. Similarly adsorption- desorption isotherms followed Freundlich equation in the study of adsorption desorption of Atrazine in various Indian soils (Raman *et al.*, 1988).

For both the soils, the desorption values (k_{des}) were found higher than the adsorption constants (k_{ads}) and an opposite trend was observed for desorption coefficient ($1/n_{des} < 1/n_{ads}$) of non- linearity. k_{des} value were found higher for FYM amended soil. A higher k_{des} indicates stronger affinity for pesticides. Low desorption was observed in sorptive soils which could be attributed to the irreversible bonding of pesticide molecules and soil colloides especially, the organic matter surfaces (Cox *et*

al., 1997). Thus desorption in soil was inversely related to the organic carbon content when compared with the adsorption, which was reported in penconazole (Jiang *et al.,* 2016). These results obtained were in support of the findings of Raunaq *et al.* 2017 where least desorption was found in Almora soils when compared with the IARI and Jhargram soils under study due to the high organic carbon content and bound residue that resisted desorption in Almora soils.

Desorption carried out in three cycles, the results showed that highest release was observed in the first cycle and decreasing in each consequent cycles. The desorption also decreased with the increase in the organic matter in the soil. Similiar results have been reported in many works (Inoue *et al.,* 2006; Kumar and Philip, 2006; Burns *et al.,* 2008; Bansal, 2010; Sharma *et al.,* 2013; Maznah *et al.,* 2016).

$1/n_{des}$ was found less than $1/n_{ads}$ indicating rate of desorption was slower than the rate of adsorption. The ratio of these Freundlich constants indicates the hysteresis (H) that measures the extent of hysteresis in desorption. Singh *et al.* 1990 studied the desorption of linuron after the removal of organic matter by hydrogen peroxide treatment and in the absence of organic matter no hysteresis was observed which suggests that organic matter fraction of the soil is responsible for the hysteresis effect.

If the value of hysteresis coefficient is 1, it indicates faster desorption than adsorption and no occurrence of hysteresis. A value of H< 1 indicates rate of desorption slower than rate of adsorption and negative hysteresis occurs. But when the value > 1, greater desorption or negative hysteresis or reversible adsorption takes place (Pusino *et al.,* 2004). The hysteresis value obtained were >1 in the study. Similar findings were also observed in the study by Raunaq and his coworkers (2017) in the study of adsorption- desorption of tebuconazole in three types of soils. A positive value of hysteresis was obtained (H= 2.24) depicting rate of desorption was more compared to adsorption.

5.4 MOBILITY OF FLUPYRADIFURONE IN SOIL

The mobility of flupyradifurone was determined by analyzing the residue found at different depths of the soil columns through which definite concentration of pesticide (25, 50, 75 µg) was allowed to elute by application of definite volume of water (40, 80, 160 mL), as per standard procedure which was considered equivalent to 100, 200 and 400 mm rainfall in the field condition.

5.4.1 Mobility of Flupyradifurone in Sandy loam Soil

Data on the downward migration of flupyradifurone applied at the rate of 25, 50 and 75 µg in sandy loam soil when eluted with 40, 80, 160 mL of water were presented in the Tables 21- 23 and the depth wise proliferation of residues are depicted in Fig. 8-10.

The mobility of fllupyradifurone in sandy loam soil when loaded with 25 µg of flupyradifurone is depicted in Fig.8. When leached with 40mL water, the residues were detected up to 10 cm only and 72 per cent of the residues were confined to the surface layers alone. When the volume of the water increased to 160 mL, the residues moved further down and were detected up to 20 cm and most of the residues were detected in the 0-5 cm layer. It can be inferred from the above observations that flupyradifurone possess higher water solubility, due to which it moved down with the percolating water and at the same time possess a high adsorption to soil which adsorbed the molecule on the upper layer and when thoroughly eluted, it moved further, till a balance between the two is achieved. Thus the application of 40 mL water (T1) equivalent to 100 mm rainfall confined the flupyradifurone residues at the top layers while the application of 80 and 160 mL equivalent to 200 and 400 mm rainfall respectively resulted the residues to leach down to deeper layers.

At 50 µg level application of flupyradifurone, its downward mobility when eluted with different volumes of water is depicted in Fig.9. The data revealed that,

upon 40 mL water addition, the residues were detected up to 10 cm and the concentration of flupyradifurone markedly increased in each layer than 25 µg level of application. With increasing volume of water used for leaching purpose, the residues further moved down and were detected up to 20 cm depth but in very low concentrations.

At 75 µg level application of flupyradifurone, downward mobility when eluted with different volumes of water is depicted in Fig.10. The data revealed that at 40 mL water addition the residues were detected up to 15 cm and a further increase in the residue concentration was noticed than 50 µg level application. With the increase in volume of water used for elution, the residues further moved down to 20 cm and in the leachate the residues found were below the limit of quantitation level.

Aktar *et al.* (2009) reported that pendimethalin residue in column studies were confined to upper soil because of the strong adsorption of pesticides to soil particle fractions. Similar findings were observed by Chopra *et al.* (2010) where the maximum concentration of herbicide pendimethalin was found in the top 10 cm layer of soil but continuous rainfall can lead to further leaching and ground water contamination. The results of leaching study are in accordance with the findings of Das and Mukherjee (2012) in which flubendamide transport through packed columns were studied. When 20 mL water was used for elution, the residues were confined to 0-5 cm depth and with 40-80 mL water, the residues were detected up to 10-15 cm depth but~85 per cent were confined to the top 0-5 cm layer.

5.4.2 Mobility of Flupyradifurone in 0.5 per cent FYM Amended Sandy loam Soil

Data on the downward migration of flupyradifurone by application at the rate of 25, 50 and 75 µg in 0.5 per cent FYM amended sandy loam soil and when eluted with 40, 80, 160 mL of water were presented in the Tables 24-26 and the depth wise proliferation of residues are depicted in Fig.11-13.
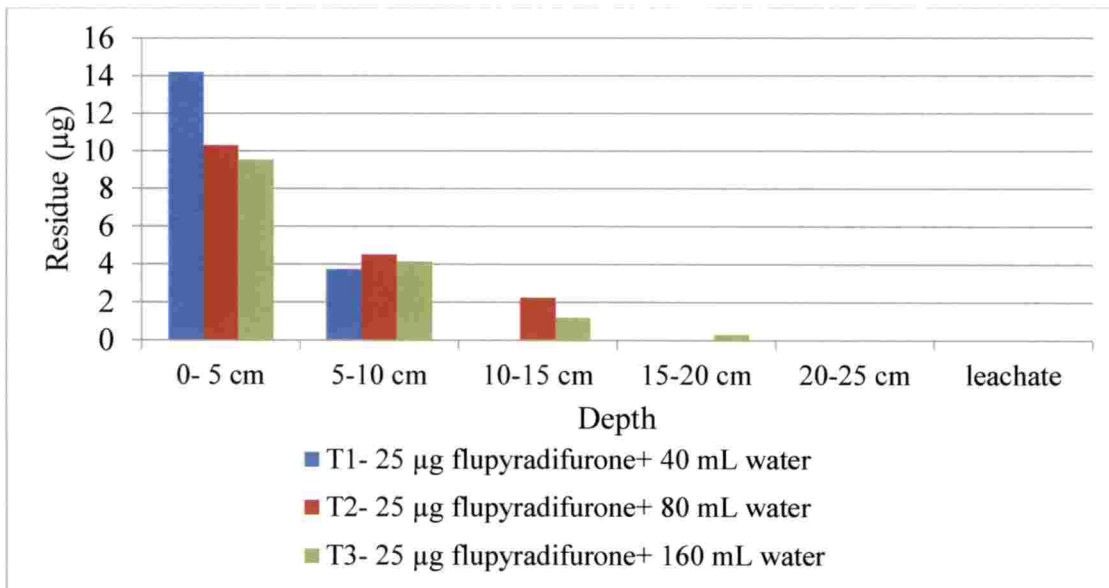
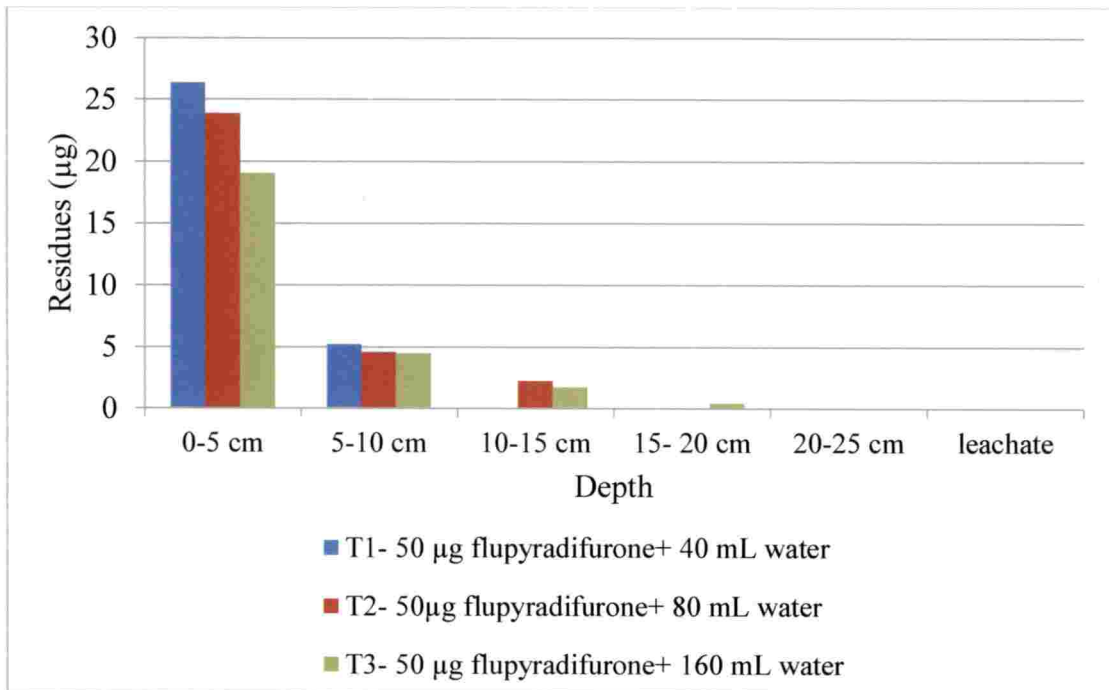Figure 8. Migration of flupyradifurone in sandy loam soil column when loaded at 25 µg level

Figure 9. Migration of flupyradifurone in sandy loam soil column when loaded at 50 µg level

The mobility of fllupyradifurone in FYM amended sandy loam soil when loaded with 25 μg of flupyradifurone is depicted in Fig.11. When leached with 40 mL water, the residues were detected up to 10 cm only. When the volume of water increased to 160 mL, further downward movement of the residues was obtained and was up to 15 cm and most of the residues were confined to the top 0-5 cm layer. As the amount of water used for elution increased, depth of the soil column up to which residues detected increased due to the movement of flupyradifurone along with the percolating water due to its higher water solubility.

At 50 μg level of spiking of flupyradifurone, downward mobility when eluted with different volumes of water is depicted in Fig.12. Here, the data revealed that when 40 mL water was used for elution, the detection of residues were up to 10 cm only with~ 77 per cent residues were detected in top layer of soil column. With the increase in the water used for elution, the residues moved up to 10 cm and 15 cm with 80 mL and 160 mL of water used. The amount of residues obtained from the top 0-5 cm layer of soil column was found reduced when amount of eluted water increased but the depth of migration increased.

At 75 μg level of spiking of flupyradifurone, downward mobility when eluted with different volumes of water is depicted in Fig.12. The residues were detected only up to 10 cm when eluted water was 40 mL and it was increased to 15 cm when the eluted water increased to 160 mL. An increase in the residue amount was noticed at 75 μg level of spiking when compared to 50 and 25 μg level.

The amount of the residues detected in each of the soil layer column was increased in the FYM amended soil when compared with the soil without amendment at each level of spiking. This could be attributed to the increase in the adsorption sites for the pesticide molecule followed by the addition of organic matter resulting in increased residue content and reduced leaching of the pesticide. It was also reported that the removal of organic matter increased the movement of pyrethroids in soil
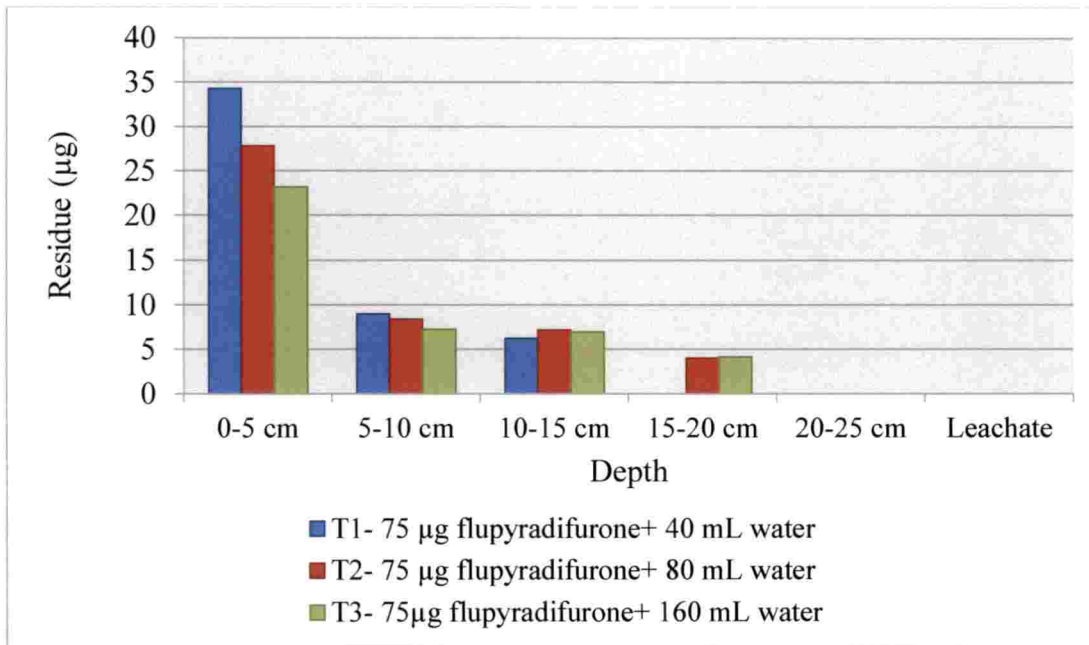
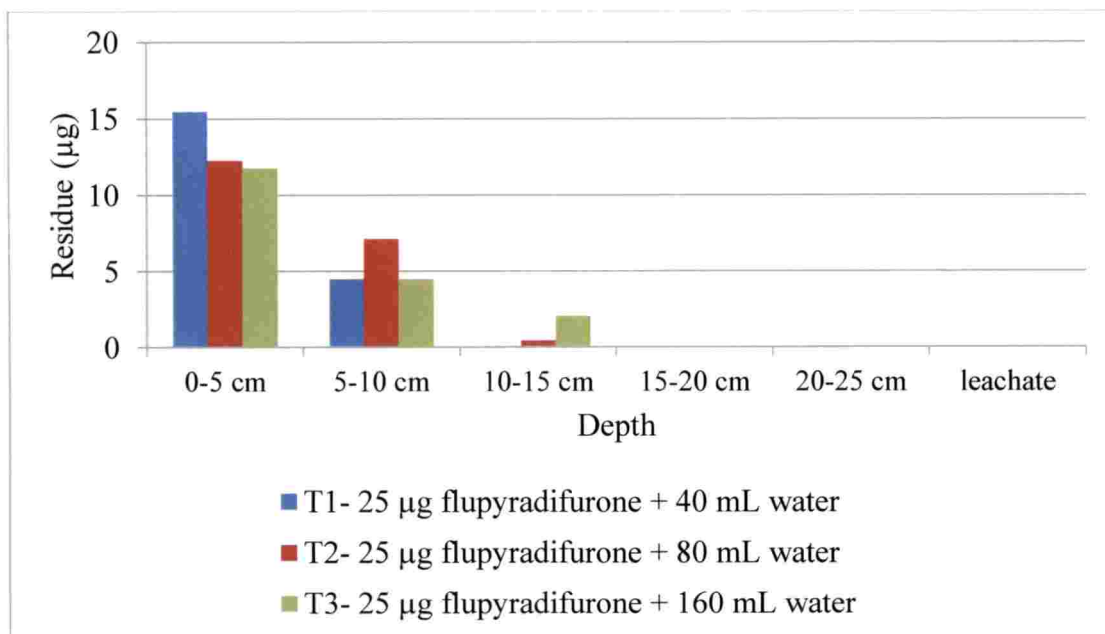Figure 10. Migration of flupyradifurone in sandy loam soil column when loaded at 75 µg level

Figure 11. Migration of flupyradifurone in 0.5 per cent FYM amended sandy loam soil column when loaded at 25 µg level
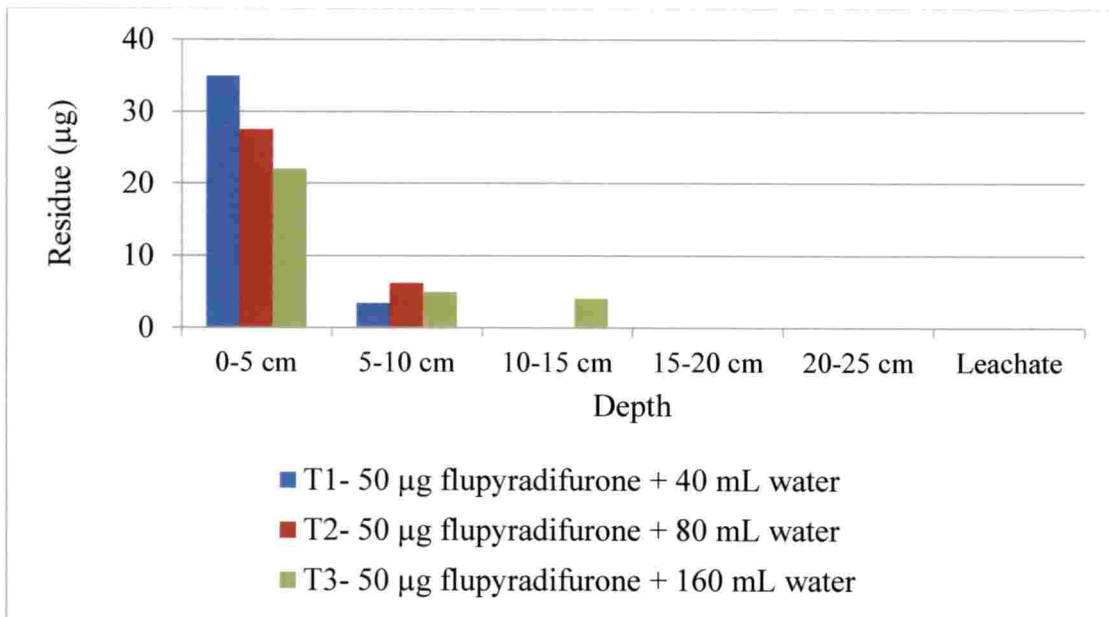
Figure 12. Migration of flupyradifurone in 0.5 per cent FYM amended sandy loam soil column when loaded at 50 µg level
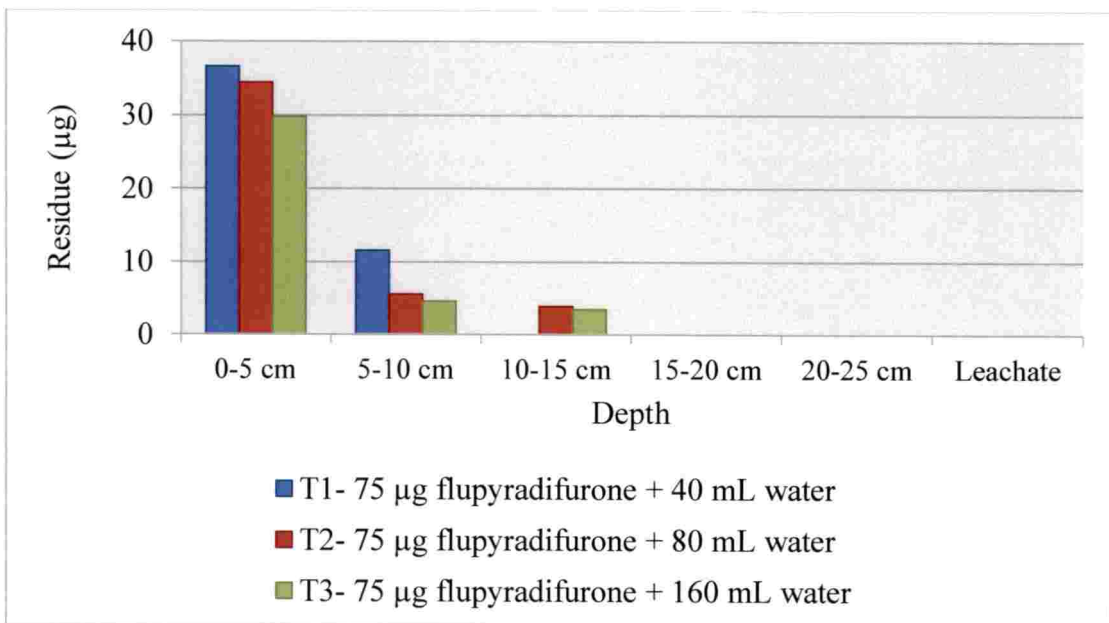

Figure 13. Migration of flupyradifurone in 0.5 per cent FYM amended sandy loam soil column when loaded at 75 µg level

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(Singh and Kumar, 1998). Ismail *et al.* (2009) has reported the importance of organic matter in reducing the mobility. Similarly, Fenoll *et al.* (2011) also concluded that pollution of ground water by pesticide drainage can be reduced by organic amendment. The results are similar to the findings of Singh *et al.* (2013) where leaching of lindane was reduced in soils with high clay and organic matter content. Thus low cost FYM can be an effective option to reduce the leaching (Singh *et al.*, 2018).

Lekshmi and Shah (2014) also concluded that the depth wise residue retention was high in clayey soils followed by sandy loam and sandy soils. Thus the leaching and downward movement of pesticide in soils depends on physical and chemical properties of pesticides and also soils.

5.5 PERSISTENCE OF FLUPYRADIFURONE IN SOIL

The persistence of flupyradifurone under different levels of fortification were studied in three different soil conditions such as air dry, at field capacity level and also in saturated soil.

5.5.1 Dissipation of Flupyradifurone in Air Dry Condition

The dissipation of flupyradaifurone in sandy loam soil and soil amended with organic matter at three different levels of application rate at air dry condition is presented in Fig 14. The result showed that T_6 has the highest half- life (22.94 days) i.e., 4 mg kg^{-1} level of flupyradifurone in 0.5 per cent FYM amended sandy loam soil. The smallest half- life is for T_1 where 1 mg kg^{-1} flupyradifurone was applied in soil. The half-life for T_4, T_5 and T_6 (1, 2 and 4 mg kg^{-1} in 0.5 per cent FYM amended soil) were higher compared to T_1, T_2 and T_3 (1, 2 and 4 mg kg^{-1} in soil respectively). Thus the result showed that, in the soil amended with 0.5 per cent FYM flupyradifurone dissipated at a slower rate than the non-amended soil. This could be due to the soil amendment with farmyard manure which increased the retention of the residue due to

the higher adsorption due to presence of high organic matter content.

These results are in accordance with the earlier findings of study of persistence of chlorpyriphos by George et al. (2007) where higher organic matter application increased the persistence and also persistence was found increasing with the increase in concentration of applied chemical. In contrast to this, Das and Mukherjee (2012) reported that organic manure application enhanced flubendamide degradation. This may be due to the increased organic carbon content and microbial activity followed by the addition of organic manure. The increased retention of pesticide by the organic matter reduced its amount in soil solution and thus making it available for microbial degradation.

5.5.2 Dissipation of Flupyradifurone in Soil at Field Capacity Condition

The dissipation of flupyradaifurone in sandy loam soil and soil amended with organic matter at three different levels of application rate at field capacity condition is presented in Fig. 15. The results revealed that, in all the treatments the half- life was reduced comparing with the air dry soil condition. This can be due to the reduced microbial activity in air dry soil which resulted in lower dissipation. Similar findings were also observed by Gupta et al. (2008) where the effect of moisture was prominent and longer persistence was observed under dry conditions followed by field capacity moisture and submerged condition. Similar results were reported by Miles et al. (1984) and Das and Mukherjee (2012) where slower dissipation of chlorfenvinphos in dry soil when compared with moist soil and flubendamide was found to persist longer under dry condition than in the field capacity condition respectively. The dissipation was found to be higher in the soil without amendment compared to the soil amended with FYM. This could be attributed to the increase in the residue retention due to increased organic matter content in the soil.

5.5.3 Dissipation of Flupyradifurone in Soil at Submerged Condition

The dissipation of flupyradaifurone in sandy loam soil and soil amended with organic matter at three different levels of application rate at submerged condition is presented in Fig.16. The results showed that faster dissipation occurred in saturated soil condition, may be due to the anaerobic condition. Pendimethalin also dissipated faster under submerged condition (Kulshretha and Singh, 1992). Similarly, Smith *et al.* (1995) also reported faster dissipation of cyfluthrin under anaerobic soil conditions and George *et al.* (2007) reported faster degradation in flooded condition. The amended soil with 0.5 per cent organic matter showed an increase in the half-life at various concentration levels. Similarly, a higher half- life of fipronil was obtained in organic matter rich soils than in sandy loam soils (Mohapatra *et al.*, 2010).

Statistical analysis of the data on dissipation of flupyradifurone showed that the soil moisture regimes do have an influence on the persistence in the soil and also for the soil amended with farmyard manure. The farm yard manure amendment had a statistically significant effect on the persistence of flupyradifurone. Similar findings have been reported by Suyal and his coworkers (2018). The treatments T_1 (1 mg kg^{-1} fortification in soil) and T_4 (1 mg kg^{-1} fortification in amended soil) were found significantly on par with other treatments which could be attributed to the increased degradation due to the lower concentration of applied flupyradifurone.

5.5.4 Metabolism of Flupyradifurone in Soil

As part of the persistence study of flupyradifurone in soil, attempts were made to identify and quantify the metabolites formed (if any) *viz*: 6- CNA, DFA, and DFEAF from soil samples. None of the major metabolites of flupyradifurone were detected in the persistence study. This could presumably be due to the faster degradation and disappearance of these transformation products resulting in their no accumulation or detection. They may also have under gone extensive mineralization by microbial metabolism to produce CO_2 and H_2O or some of the residues may be
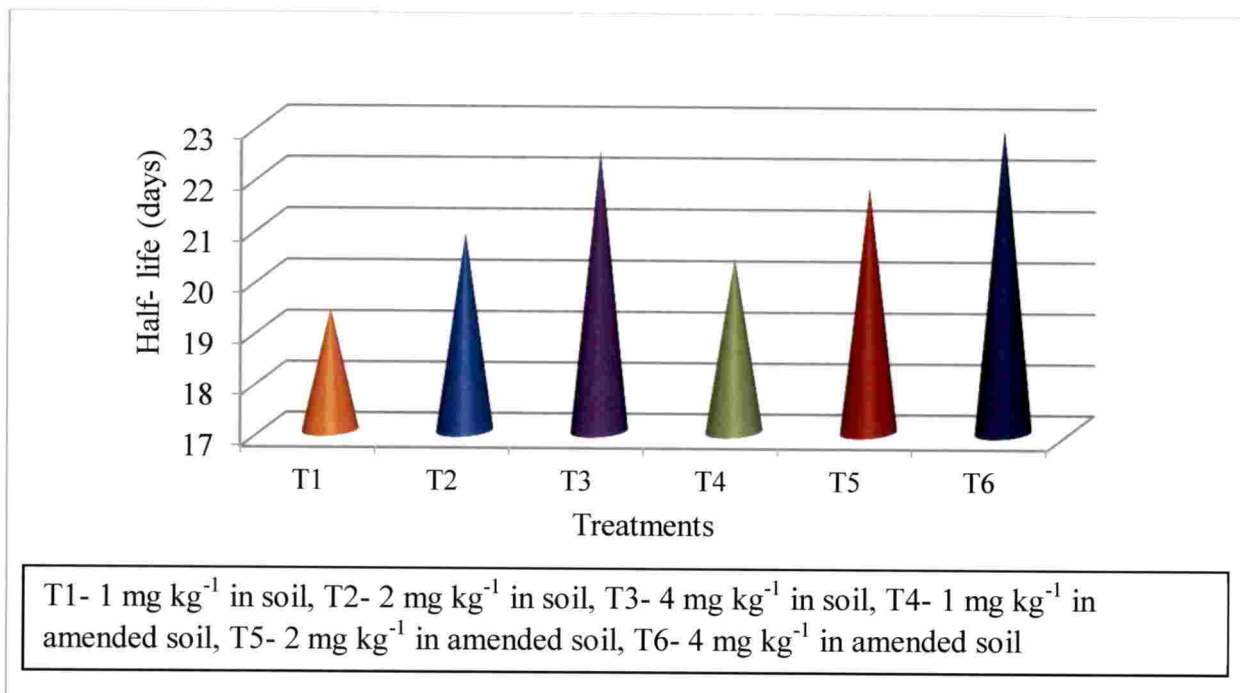
T1- 1 mg kg^{-1} in soil, T2- 2 mg kg^{-1} in soil, T3- 4 mg kg^{-1} in soil, T4- 1 mg kg^{-1} in amended soil, T5- 2 mg kg^{-1} in amended soil, T6- 4 mg kg^{-1} in amended soil

Figure 14. Half-life of flupyradifurone in sandy loam soil and 0.5 per cent FYM amended soil at air dry soil condition

T1- 1 mg kg^{-1} in soil, T2- 2 mg kg^{-1} in soil, T3- 4 mg kg^{-1} in soil, T4- 1 mg kg^{-1} in amended soil, T5- 2 mg kg^{-1} in amended soil, T6- 4 mg kg^{-1} in amended soil
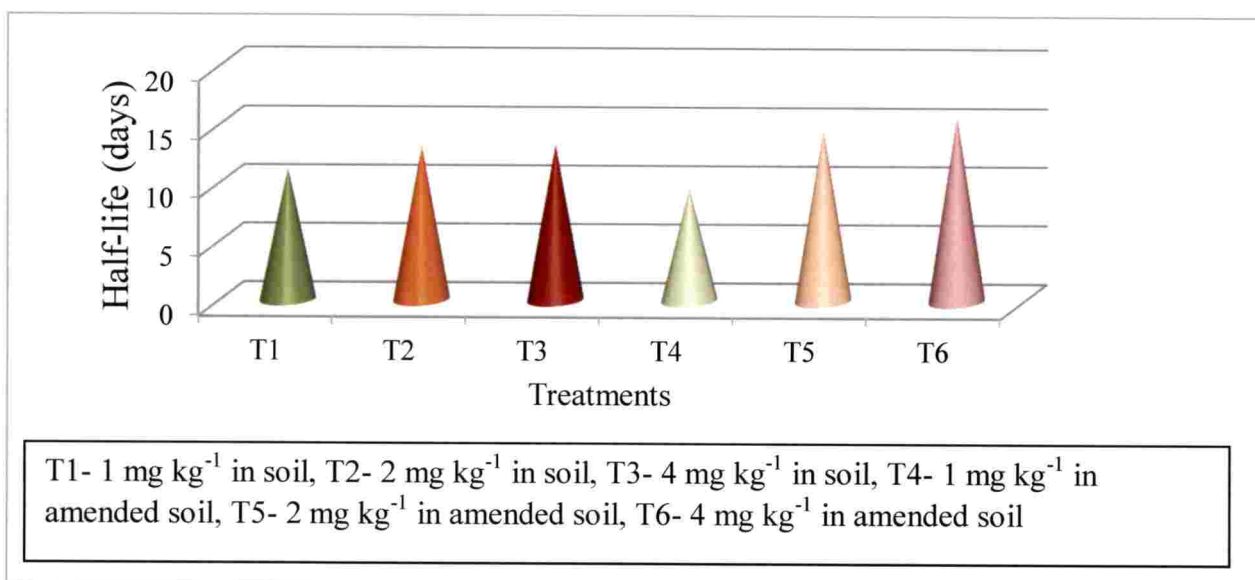
Figure 15. Half-life of flupyradifurone in sandy loam soil and 0.5 per cent FYM amended soil at field capacity condition
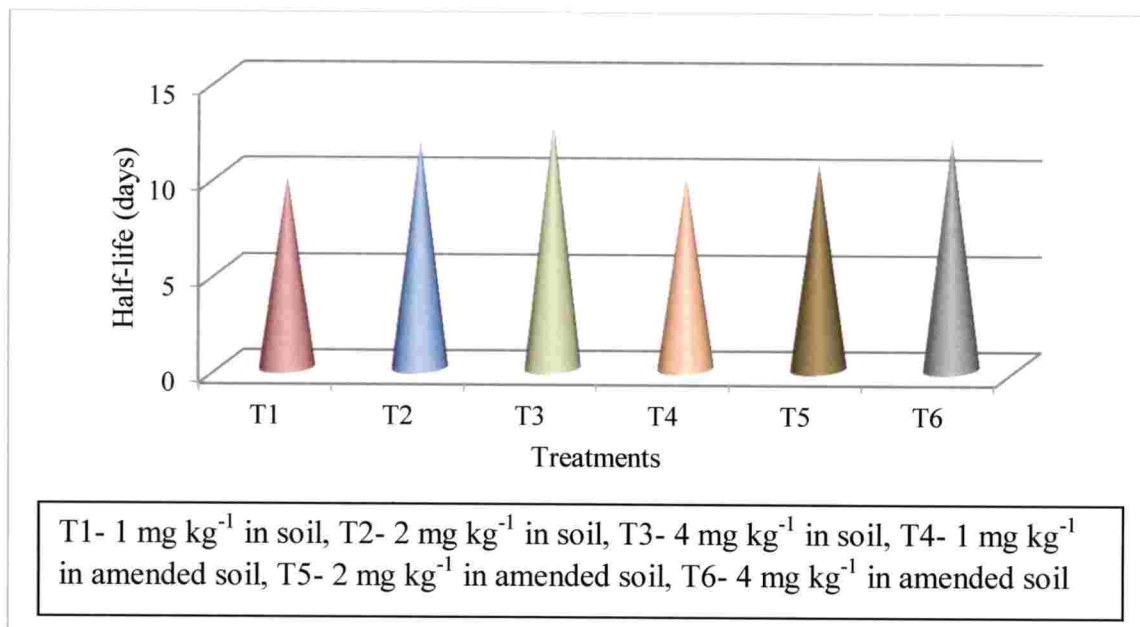
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Figure 16. Half-life of flupyradifurone in sandy loam soil and 0.5 per cent FYM amended soil under saturated soil condition
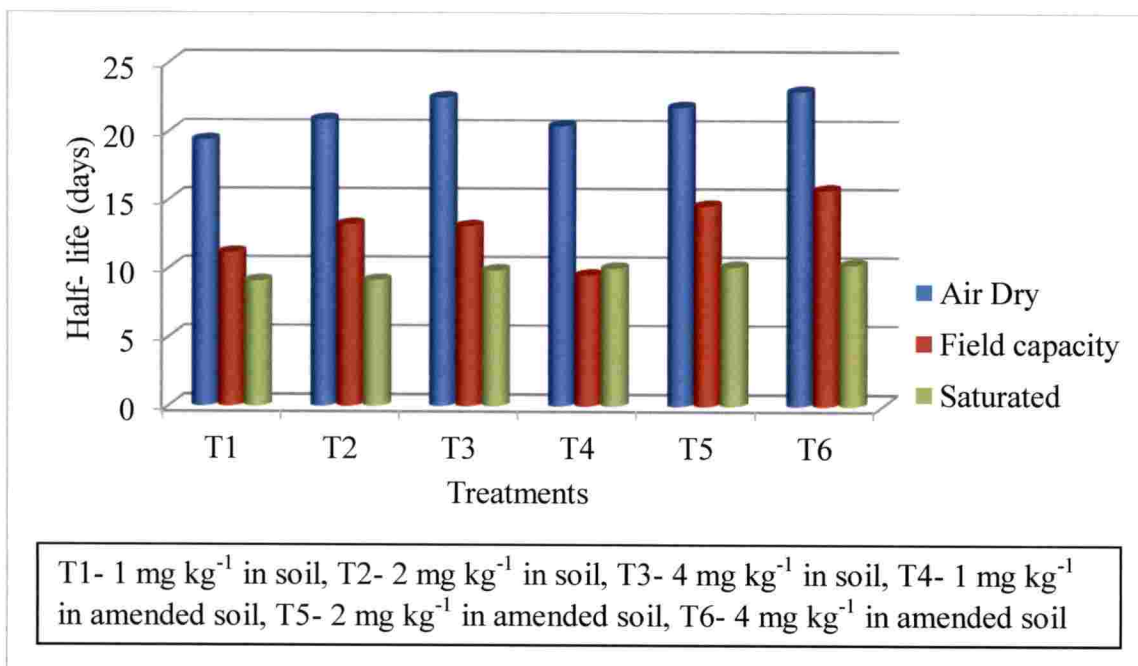

Figure 17. Effect of different moisture regimes on dissipation of flupyradifurone

found to bind on the solid humic fractions of the soil which made it non- extractable (Nauen *et al.*, 2015).

A study was conducted by Dubey *et al.* 2017 on residues of flupyradifurone in apple and soil in four orchards in Jammu and Kashmir. Flupyradifurone was sprayed twice at 20 d interval @ 400 (single dose) and 800 (double dose) g ai ha^{-1}. Combined residual concentrations of flupyradifurone and its metabolite difluoroacetic acid (DFA) were considered as flupyradifurone. Among metabolites, only difluroacetic acid was detected during analysis. The soil and fruit samples analyzed at the time of harvest revealed that the residues found were below determination levels.

Summary

6. SUMMARY

Food security is threatened by the growing population, climatic changes and the risks of unpredictable pest and disease attack. Thus to meet the ever increasing food demand, the loss of crops due to pest and disease attack should be reduced and pesticides act as tools for their management. Flupyradifurone (Sivanto Prime) is a novel broad spectrum systemic insecticide of the class butenolide having similar action as that of neonicotinoids. It is used to control sucking pests like aphids and whiteflies on a variety of vegetable crops, it could be used as foliar spray and can be soil drenched. They act as reversible agonists on insect nicotinic acetyl choline receptors but are structurally different from the known agonists. The label claim flupyradifurone is for the crop bhindi against the jassids and whiteflies. For the practical conditions it was considered safe as it showed minimal risk to natural enemies and non-target insects making it an ideal component in Integrated Pest Management Programs. Considering these advantages, a study was conducted to understand the adsorption- desorption characteristics, the mobility and persistent nature of the pesticide in the sandy loam soil and also the effect of organic manure amendment for the above.

The sandy loam soil was collected from the Kazhakoottam sandy loam belts and the farmyard manure was procured locally. Their physical and chemical properties were analyzed; a proper method was validated for the single step estimation of flupyradifurone and its metabolites from soil and water by the QuEChERS method.

The sorption experiment was conducted by the batch equilibrium technique using $CaCl_2$ at 20, 40, 60, 80 and 100 µg level of flupyradifurone in soil and amended soil after the estimation of equilibration time. The mobility of flupyradifurone was studied by packed soil column method using 25, 50 and 75 µg level of pesticide and elution with 40, 80 and 160 mL of water equivalent to 100, 200 and 400 mm rainfall

in the field condition both in soil and 0.5 per cent FYM amended soil. The persistence study was conducted by application of formulation of flupyradifurone at a concentration of 1, 2 and 4 mg kg^{-1} level in laboratory condition in soil and FYM amended soil at air-dry, field capacity and saturated soil condition. The residues were estimated and quantified by using LC-MS/MS method. The data were analyzed and the results are summarized below:

1. The physical and chemical analysis of the soil indicated that it was sandy loam in texture and with bulk density and particle density of the soil to be 1.63 and 2.60 Mg m^{-3}. The soil was found to be strongly acidic with a pH of 5.35. The cation exchange capacity of the soil was found to be 4.3 cmol (+) kg^{-1} whereas the anion exchange capacity was found to be 1.21 cmol (-)kg^{-1}. The organic matter content of the soil was 0.84 per cent. The availability of major primary in the soil was 178.89 kg ha^{-1} of available nitrogen, 60.03 kg ha^{-1} of available phosphorous, 150.6 kg ha^{-1} of available potassium. The secondary nutrients such as calcium, magnesium and sulphur were found to be 180, 57, 3.0 mg kg^{-1}, respectively. Thus the soil was found to be low in available nitrogen and potassium and high in available phosphorus. Exchangeable calcium, magnesium and sulphur were found to be deficient in soil.

2. The efficiency of extraction of flupyradifurone and its metabolites from soil and water was standardized through the recovery experiment. The QuChERS method with extraction using acetonitrile followed by dispersive solid phase cleanup was found to be suitable. The analytical procedures gave good recovery for the residues ranging from 80.74 – 93.62 and 70.74 – 85.00 per cent and relative standard deviation values of 0.85- 6.70 and 1.65- 5.70 per cent for soil and water, respectively.

3. In the adsorption- desorption studies, the equilibration time was analyzed to be 6h and 4h for soil and soil amended with 0.5 per cent FYM. Also a slighter

higher adsorption and reduced desorption was noticed in soil amended with organic matter. This shows that the addition of organic matter increased the organic carbon content which has increased the sorption capacity of the soil.

4. The adsorption was found decreasing as the aqueous concentration of pesticide increase in the solution phase which resulted in the L- type adsorption isotherm. The slope of the isotherm decreased with the rise in the concentration due to the less availability of vacant sites for adsorption.

5. The desorption process carried out in three cycles revealed that the highest desorption was observed in the first cycle subsequently decreasing in each cycles and the rate of the desorption was slower than the rate of adsorption.

6. The mobility study showed that, with an increase in the volume of water used for leaching, more migration occurred to the lower layers. The residues of flupyradifurone were found to be below detectable level. The amount of residues retained in each of the soil column depth was found higher in the column of the soil amended with farmyard manure.

7. The mobility study revealed that, the importance of organic matter in reducing the mobility due to the increased adsorption sites followed by the addition of organic matter content.

8. The increased concentration of flupyradifurone along with the more volume of water used for elution significantly increased the migration tendency of the flupyradifurone.

9. The half- life of flupyradifurone in the soil when applied at 1,2 and 4 mg kg^{-1} levels were 19.38, 20.87 and 22.47 days respectively, whereas in the FYM amended soil it was 20.41, 21.79 and 22.94 days respectively under the air-dry soil condition.

10. When the soil was brought to field- capacity condition, the half- life were 11.17, 13.08 and 13.21 at 1, 2 and 4 mg kg^{-1} level of flupyradifurone application in the sandy loam soil, respectively and in the soil amended with 0.5 per cent FYM, the half–life were 9.51, 14.59 and 15.74 days, respectively.

The half-life of the compound at different concentration reduced at the soil at the field capacity level compared to the soil at air dry condition.

11. Under the saturated soil condition, when flupyradifurone was applied at 1, 2 and 4 mg kg^{-1}, the half- life were 9.08, 9.12 and 9.85 days, respectively, whereas it was 10.02, 10.12 and 10.28 days in the soil amended with farmyard manure.

12. The half- life of the compound was found reducing when the moisture content has increased that is highest half- life was obtained for the soil under air- dry condition and the lowest under the saturated soil condition. Faster dissipation in saturated condition may be due to the activity of anaerobic microorganisms. Slower dissipation in air dry condition may be due to the reduced microbial activity.

13. The results showed that the half- life increased with the increase in the concentration of the flupyradifurone that is applied to the soil.

14. The persistence data also revealed that the half-life was found slightly increased in the soil amended with farmyard manure in all the three soil conditions. Thus the dissipation was lowered in the amended soil which could be attributed to the increased residue retention due to the addition of organic matter to the soil.

The study concluded that the soil was found acidic with pH of 5.8 and organic matter content of soil was medium (0.84%). The soil contained low nitrogen and potassium content and higher phosphorus content. The exchangeable calcium, magnesium and sulphur were found to be deficient in soil. The adsorption- desorption studies revealed that the organic matter addition could increase the sorption capacity of the soil. An L- type adsorption isotherm was obtained which revealed that the adsorbate and adsorbent has strong interaction. Desorption was inversely related to the organic carbon content and the rate of desorption was higher during the first cycle and decreasing in the subsequent cycles. Flupyradifurone was found to be moderately

mobile in the soil and as the amount of water used for elution increased, the depth of migration of flupyradifurone also increased. A higher dose of application and subsequent elution with higher amount of water resulted in deeper migration. In the soil column amended with farmyard manure, more amounts of residues were extracted in each depth of soil column. The persistence study revealed that the half-life of flupyradifurone was found higher in the soil amended with farmyard manure due to higher retention of residues in all the three soil conditions. Dissipation was found fastest at saturated condition followed by field capacity and dry moisture regimes. Metabolites, 6- chloronicotinic acid (6-CNA) and difluro-ethyl amino furanone (DFEAF) were found below limit of quantitation (LOQ). The metabolite difluro acetic acid (DFA) was not detected at the recovery stages.

FUTURE LINE OF WORK

❖ Proper method to be validated to estimate one of the major metabolite of flupyradifurone, difluroacetic acid (DFA).

❖ The possibility of groundwater contamination by the pesticide in different soils can be studied.

❖ Impact of the applied pesticide on soil organisms and the biochemical mechanisms for the promotion or decline in population can be studied.

❖ Distribution and fate of the pesticide applied in soil, leachate and crop can be studied.

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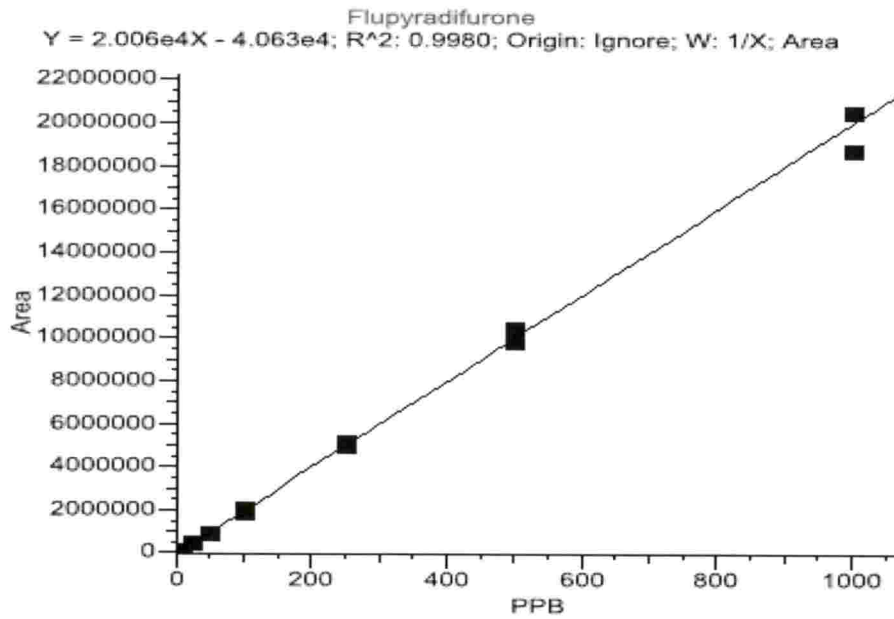
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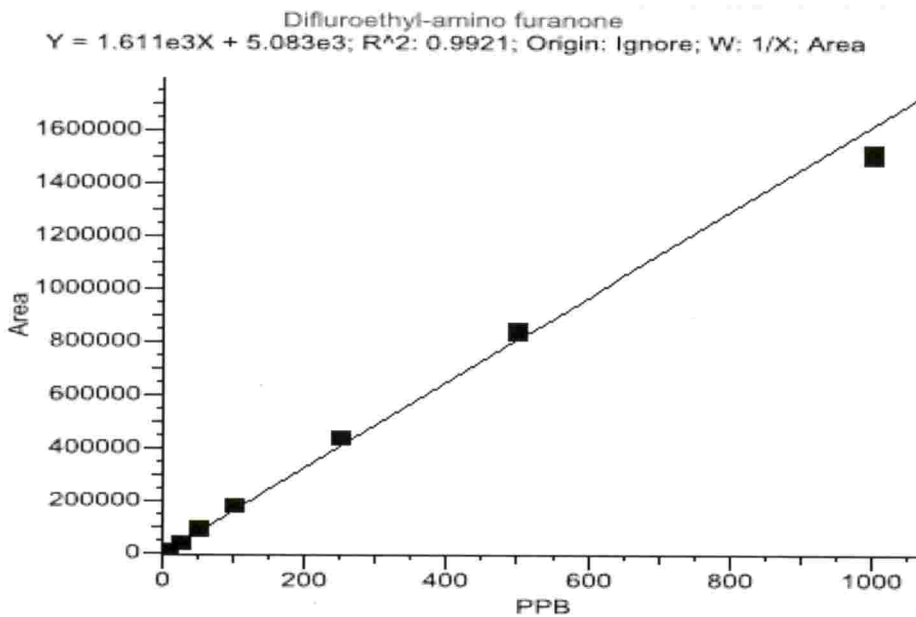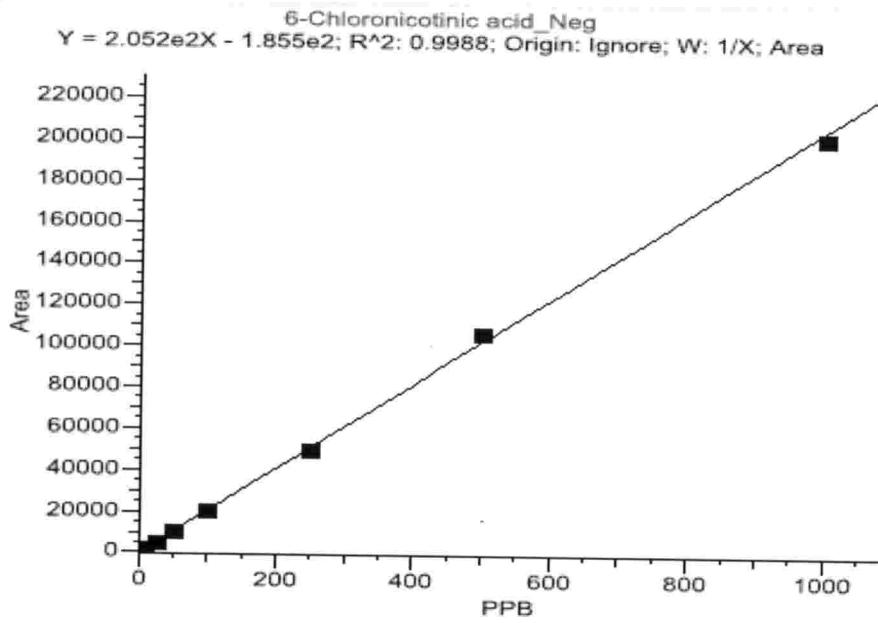
Appendices

APPENDIX I

Calibration Curve of Standard Flupyradifurone and its Metabolites

Flupyradifurone
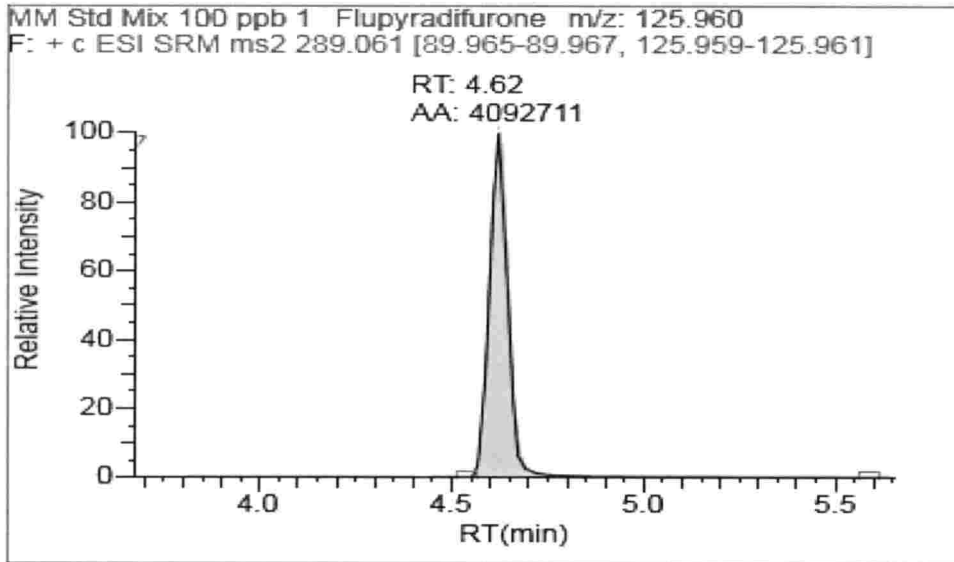Y = 2.006e4X - 4.063e4; R^2: 0.9980; Origin: Ignore; W: 1/X; Area

Calibration curve of Flupyradifurone

Difluroethyl-amino furanone
Y = 1.611e3X + 5.083e3; R^2: 0.9921; Origin: Ignore; W: 1/X; Area

Calibration curve of Difluroethyl-amino furanone

131

Calibration curve of 6-chloronicotinic acid

132

APPENDIX II

Chromatogram of Standard of flupyradifurone and its Metabolites at 0.1mg kg^{-1}

MM Std Mix 100 ppb 1   Flupyradifurone   m/z: 125.960
F: + c ESI SRM ms2 289.061 [89.965-89.967, 125.959-125.961]

RT: 4.62
AA: 4092711

Chromatogram of flupyradifurone at 0.1 mg kg^{-1} in sandy loam soil

MM Std Mix 100 ppb 1   Difluroethyl-amino furanone   m/z: 55.058
F: + c ESI SRM ms2 164.293 [55.057-55.059, 64.985-64.987]

RT: 1.36
MA: 204870
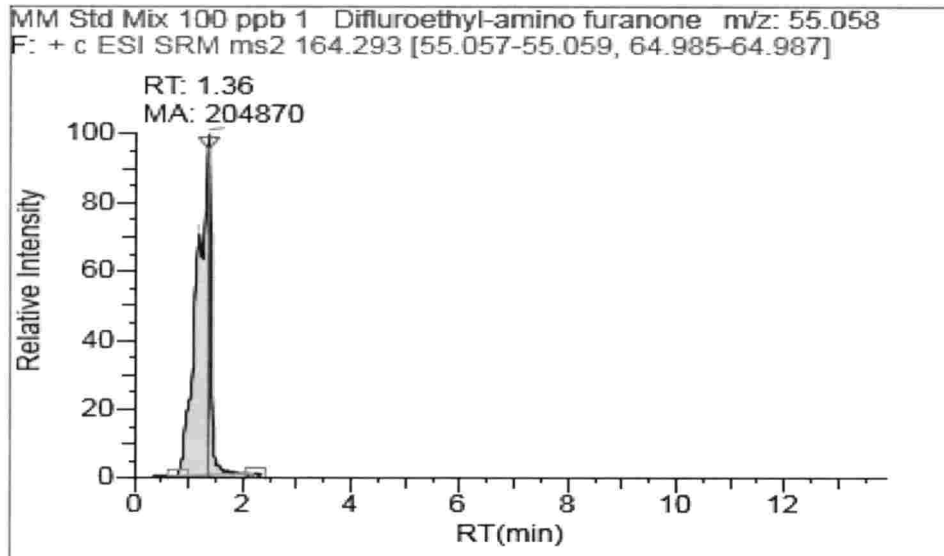
Chromatogram of DFEAF at 0.1 mg kg^{-1} in sandy loam soil

133
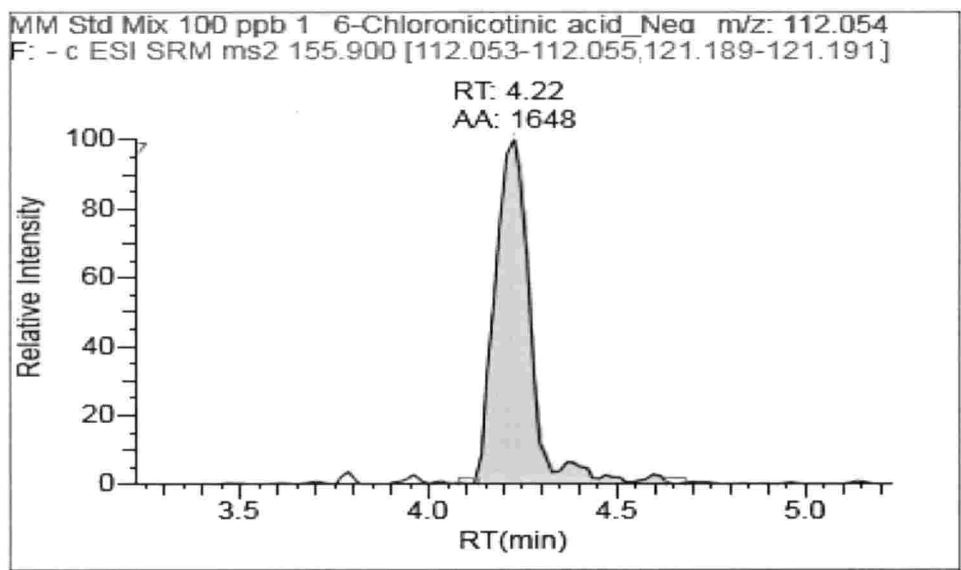
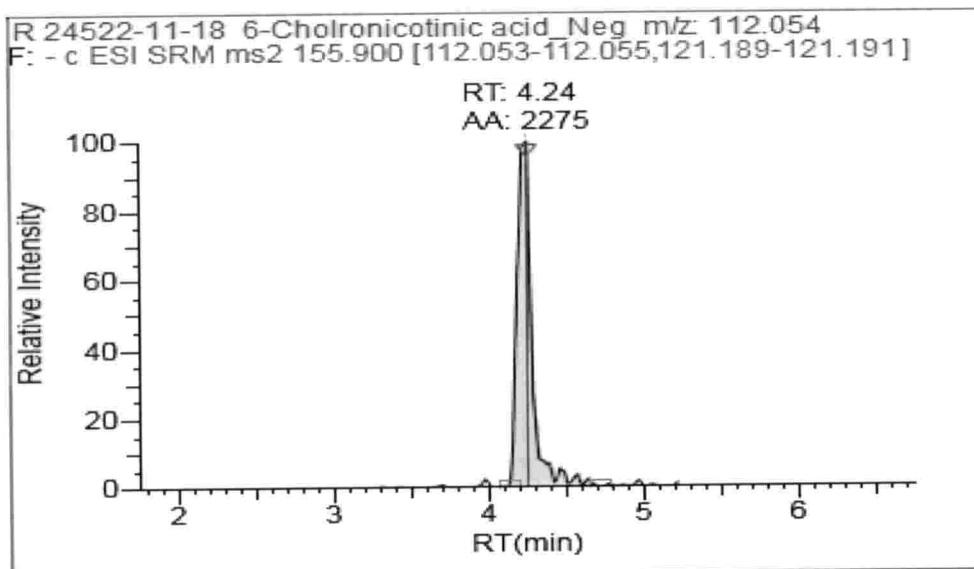Chromatogram of 6- CNA at 0.1 mg kg^{-1} in sandy loam soil

APPENDIX III

Chromatogram of Recovery of Flupyradifurone and its Metabolites from Soil
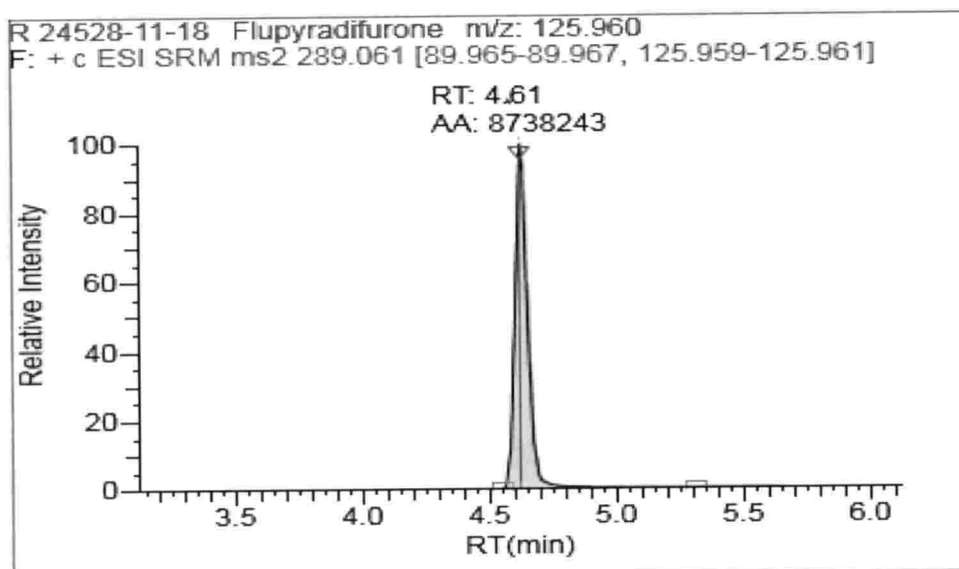
R 24522-11-18 Flupyradifurone m/z: 125.960
F: + c ESI SRM ms2 289.061 [89.965-89.967, 125.959-125.961]

RT: 4.63
AA: 2254056

Recovery of flupyradifurone at 0.1 mg kg^{-1} in soil

R 24522-11-18 Difluroethyl-amino furanone m/z: 55.058
F: + c ESI SRM ms2 164.293 [55.057-55.059, 64.985-64.987]

RT: 1.36
AA: 110748
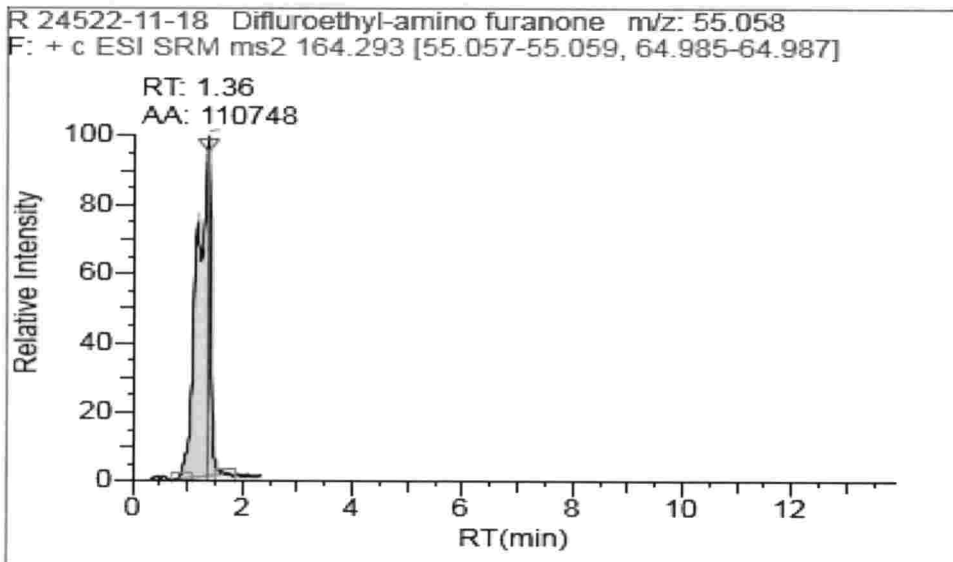
Recovery of DFEAF at 0.1 mg kg^{-1} in soil

R 24522-11-18 6-Cholronicotinic acid_Neg m/z: 112.054
F: - c ESI SRM ms2 155.900 [112.053-112.055,121.189-121.191]

RT: 4.24
AA: 2275

Recovery of 6- CNA at 0.1 mg kg^{-1} in soil

R 24528-11-18 Flupyradifurone m/z: 125.960
F: + c ESI SRM ms2 289.061 [89.965-89.967, 125.959-125.961]

RT: 4.61
AA: 8738243

Recovery of flupyradifurone at 0.5 mg kg^{-1} in soil

136
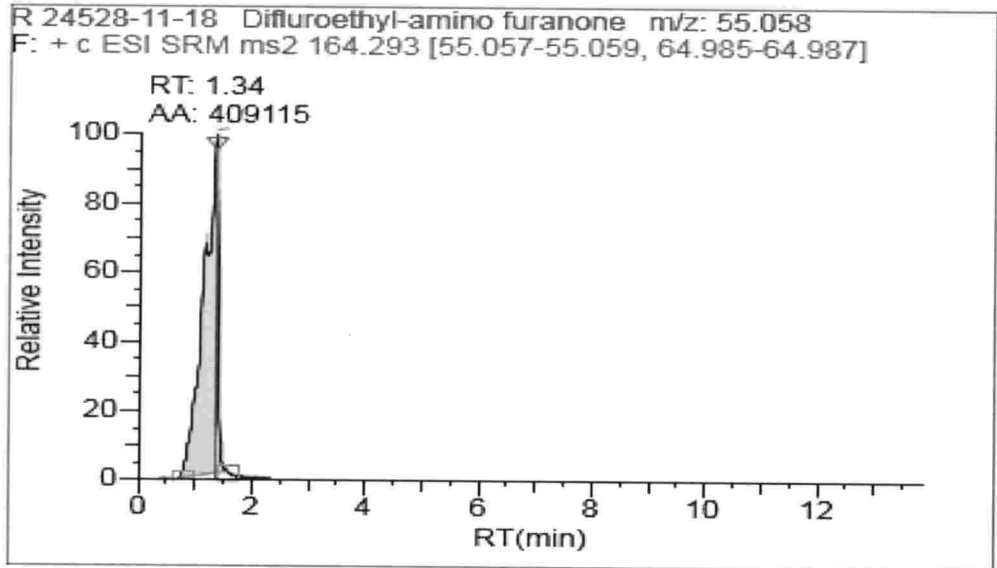
Recovery of DFEAF at 0.5 mg kg^{-1} in soil
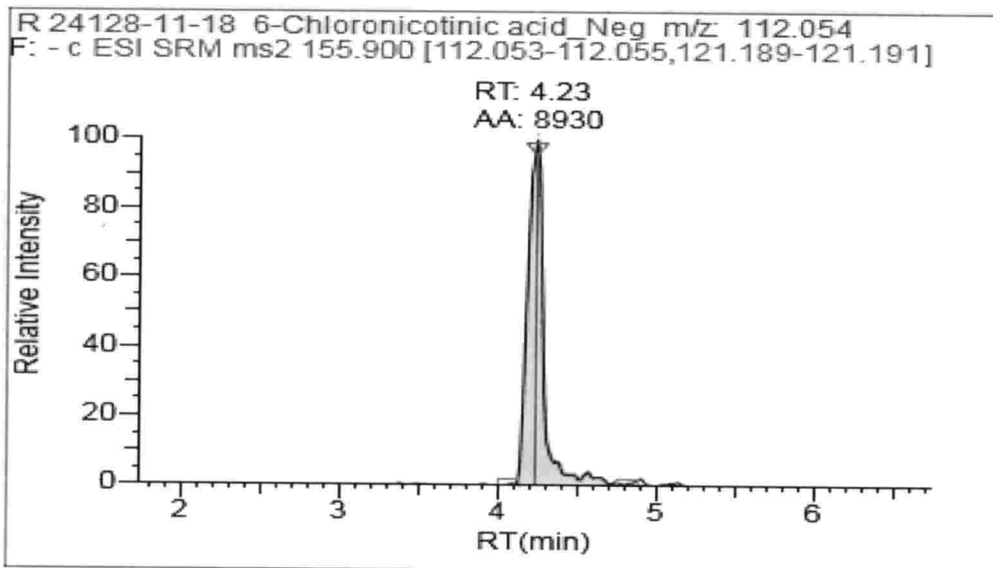

Recovery of 6- CNA at 0.5 mg kg^{-1} in soil

R 24535-11-18 Flupyradifurone m/z: 125.960
F: + c ESI SRM ms2 289.061 [89.965-89.967, 125.959-125.961]

RT: 4.61
AA: 18142088
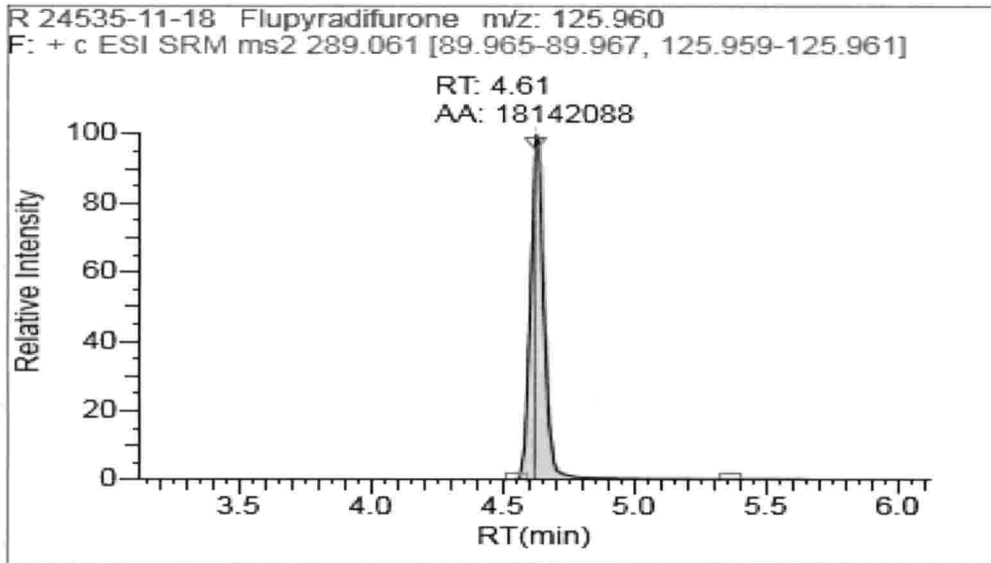
Recovery of flupyradifurone at 1 mg kg^{-1} in soil

R 24535-11-18 Difluroethyl-amino furanone m/z: 55.058
F: + c ESI SRM ms2 164.293 [55.057-55.059, 64.985-64.987]
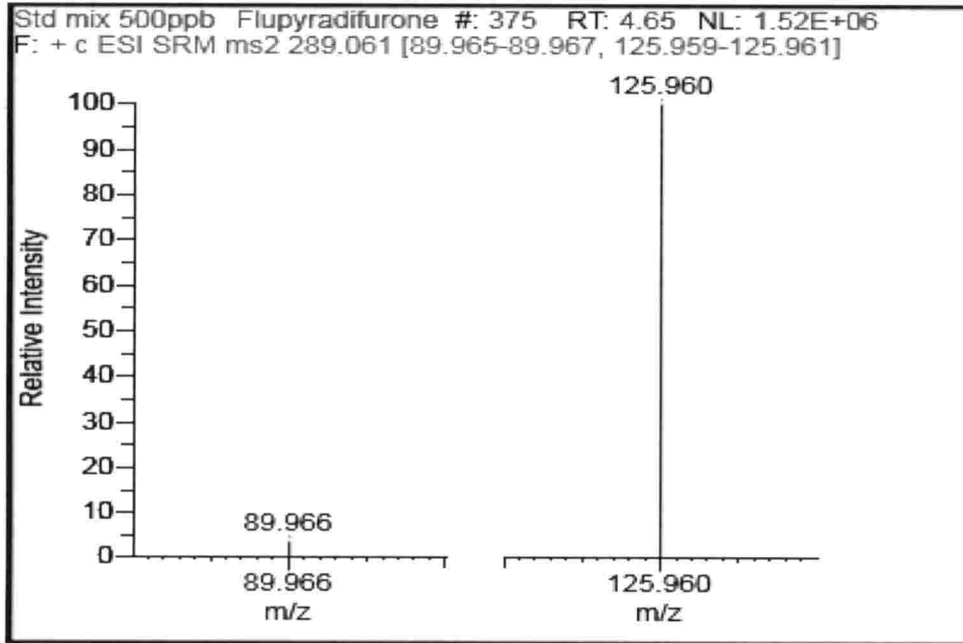
RT: 1.36
AA: 824038
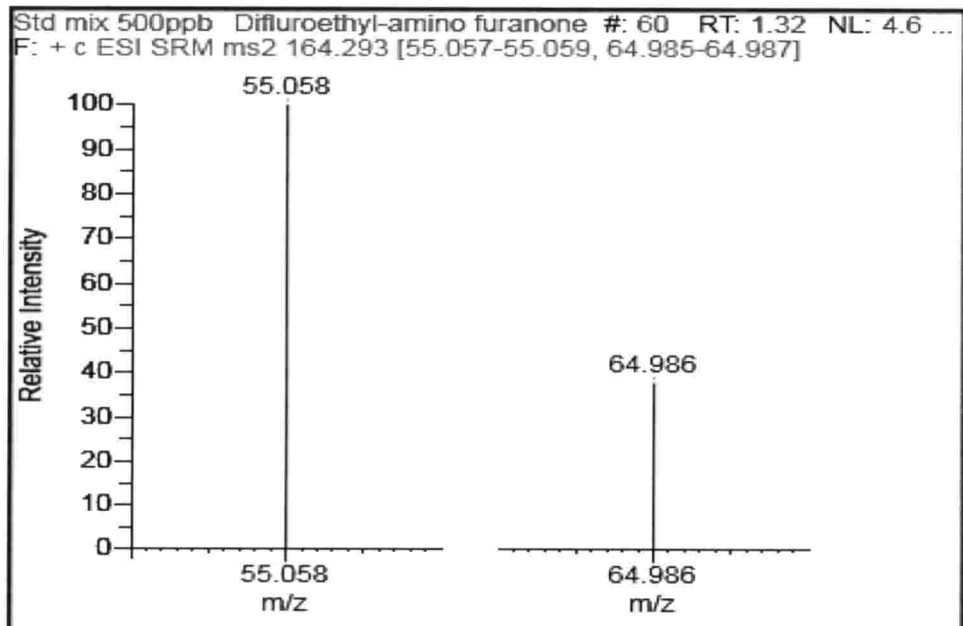
Recovery of DFEAF at 0.5 mg kg^{-1} in soil

138
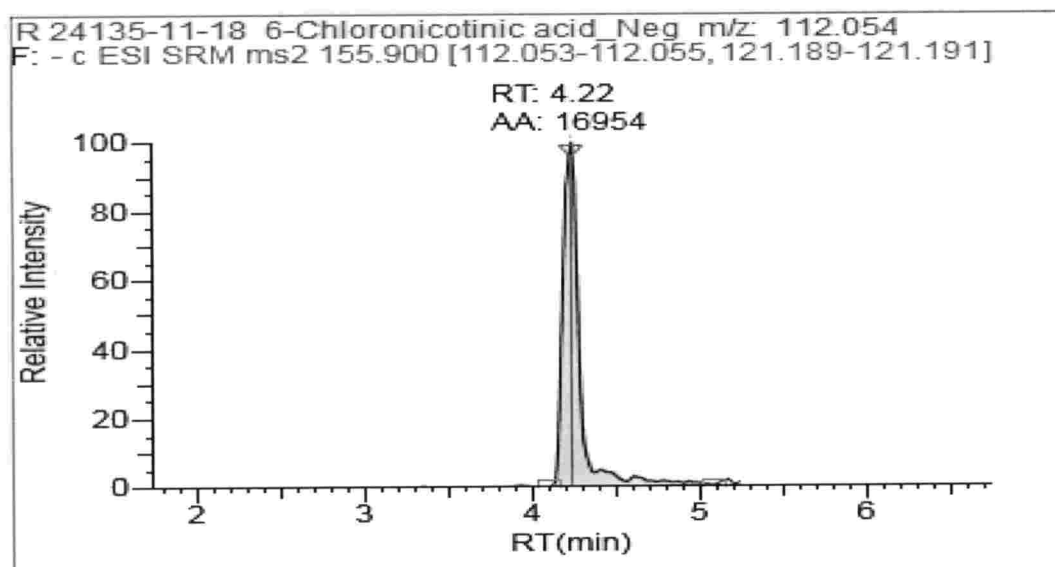
Recovery of 6- CNA at 1 mg kg^{-1} in soil

APPENDIX IV

Mass Spectra of Flupyradifurone and its Metabolites

Std mix 500ppb   Flupyradifurone   #: 375   RT: 4.65   NL: 1.52E+06
F: + c ESI SRM ms2 289.061 [89.965-89.967, 125.959-125.961]

Mass spectrum of flupyradifurone

Std mix 500ppb   Difluroethyl-amino furanone   #: 60   RT: 1.32   NL: 4.6 ...
F: + c ESI SRM ms2 164.293 [55.057-55.059, 64.985-64.987]

Mass spectrum of Difluroethyl-amino furanone

140

Std mix 500ppb 6-Chloronicotinic acid_Neg #: 326 RT: 4.22 NL: 364
F: - c ESI SRM ms2 155.900 [112.053-112.055,121.189-121.191]
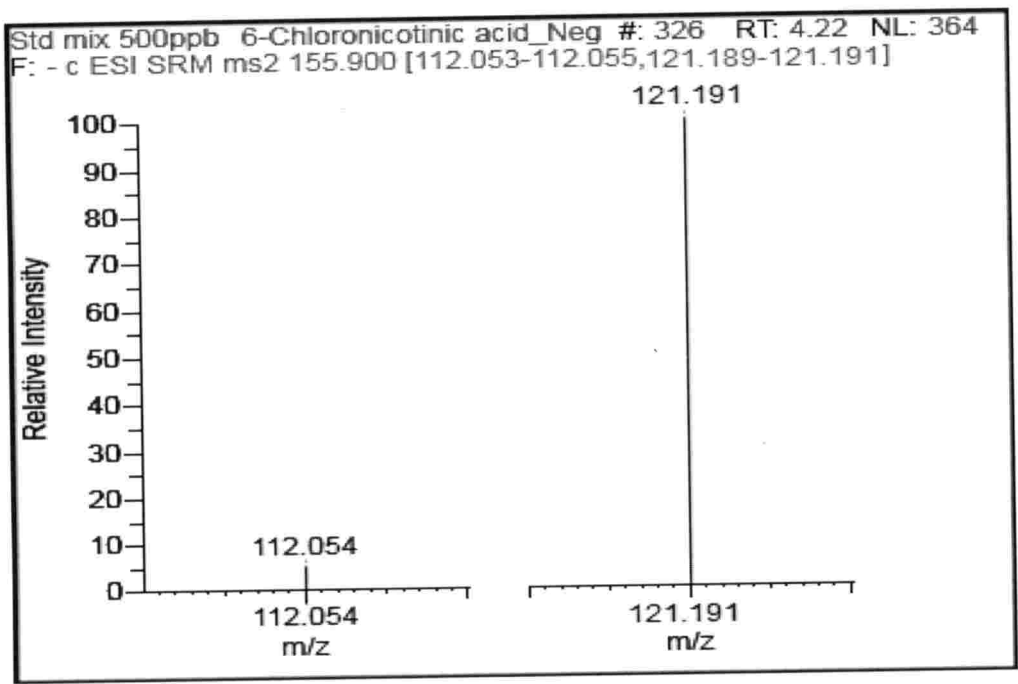
Mass spectrum of 6-chloronicotinic acid

SORPTION AND MOVEMENT OF FLUPYRADIFURONE IN SANDY LOAM SOILS WITH AND WITHOUT ORGANIC AMENDMENT

by

RESHMA V.
(2017-11-042)

ABSTRACT

Submitted in partial fulfillment of the
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MASTER OF SCIENCE IN AGRICULTURE

Faculty of Agriculture

Kerala Agricultural University

DEPARTMENT OF SOIL SCIENCE AND AGRICULTURAL CHEMISTRY

COLLEGE OF AGRICULTURE

VELLAYANI, THIRUVANANTHAPURAM - 695 522

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ABSTRACT

The study entitled "Sorption and movement of flupyradifurone in sandy loam soils with and without organic amendment" was conducted in Department of Soil Science and Agricultural Chemistry and the laboratory attached to the All India Network Project (AINP) on Pesticide Residues, College of Agriculture, Vellayani, Thiruvananthapuram, Kerala during 2017-19. The main objectives of the experiment were to study the adsorption, desorption, persistence and leaching of flupyradifurone in sandy loam soils with and without addition of organic amendment at the rate of 0.5 per cent farmyard manure. The soil was collected from the sandy belts of Kazhakkoottam, Thiruvananthapuram. The physical and chemical analysis of the soil revealed that the soil was acidic with 0.84 per cent organic matter content. Among the major nutrients, phosphorus content was found to be high; potassium was medium while other nutrients were low. The method for estimation of flupyradifurone residues from the soil was validated at 0.1, 0.5 and 1 $\mu g\ g^{-1}$ level of flupyradifurone. Modified QuEChERS method with acetonitrile as the extracting solvent and Primary Secondary Amine (PSA) sorbent for cleanup was found to be suitable for the estimation of flupyradifurone and its metabolites from the soil. The method validation for estimation of flupyradifurone residues from water was done by liquid- liquid partitioning using dichloromethane, concentrated and made up in HPLC grade methanol for LC- MS/ MS analysis.

The adsorption- desorption studies were carried out at 5 concentrations of 20, 40, 60, 80 and 100 μg levels each both in soil and 0.5 per cent FYM amended soil in completely randomized design (ten treatments and three replications) . The study was also conducted under direct spiking of flupyradifurone at 3 levels *viz.*, 20, 40 and 60 μg in 10g soil. The adsorption and desorption data fitted well in isotherms. The distribution coefficient K_d (mean value) was found high in the soil amended with FYM (2.58) than soil without amendment (2.41) which indicated increased sorption in both systems at all levels. The k_f values (adsorption coefficient) were 2.57 and 2.46

for amended and soil without amendment respectively, indicating a high sorption capacity for the amended soil. The desorption was carried out in three cycles, the percentage desorption decreasing in each consecutive cycle. The desorption percentages were found in the range of 15.68, 17.14 , 20.74 , 23.69 and 27.77 per cent for the initial concentrations of 20, 40, 60, 80 and 100 µg, respectively and was found reduced in FYM amended soil $viz.$, 14.39, 15.99, 19.29 , 22.74 and 26 percent for each of the concentrations. In all levels of concentration, hysteresis effect (n_{des}/n_{ads}) was noticed indicating desorption was slower than adsorption. In the soil samples directly spiked with flupyradifurone done in completely randomized design with six treatments and three replications, the desorption percentages were found lower and a still higher hysteresis was observed.

Mobility of flupyradifurone was assessed in completely randomized design with eighteen treatments and three replications $i.e$ by loading 3 levels $viz.$, 25, 50 and 75 µg formulation of flupyradifurone, separately on top of 200g soil columns loaded in PVC pipes and followed by eluting with 40, 80 and 160 mL of water @ 0.4ml min^{-1}. In the sandy loam soil without amendment, flupyradifurone moved down the soil column which resulted in residue levels ranging from 13.84-9.56, 26.38- 19.08 and 34.30- 23.17 µg at 25, 50 and 75 µg levels, respectively when eluted with different volumes of water. In the soil amended with 0.5 per cent FYM, the corresponding residues ranged from 15.48- 11.79, 34.96- 22.00 and 36.62- 29.78 µg at 25, 50 and 75 µg levels indicating a higher retention in soil. The residue present in the leachate was found below detectable level for both amended soil and soil without amendment.

The persistence of flupyradifurone in sandy loam soil and 0.5 per cent FYM amended soil under three soil moisture conditions was studied using the formulation of flupyradifurone added at the rate of 1, 2 and 4 mg kg^{-1} in completely randomized design with eighteen treatments and three replications. The half- life of flupyradifurone in air dry soil when applied 1, 2 and 4 mg kg^{-1} levels were 19.38, 20.87, 22.47 days respectively and they were 20.41, 21.79 and 22.94 days,

respectively in amended soil. For the soil at the field capacity level, application at 1, 2 and 4 mg kg^{-1} levels resulted in half- life of 11.14, 13.08 and 13.21 days for normal soil and 9.51, 14.59 and 15.74 days for amended soil, respectively. Under saturated soil conditions, the half- life were 9.08, 9.12 and 9.85 days in soil without amendment and 10.02, 10.12 and 10.28 days for the amended soil at 1, 2 and 4 mg kg^{-1} levels of application respectively. In the persistence study, no metabolites of flupyradifurone were detected.

Soil under the study was acidic, low in organic matter with 10.80 per cent clay, 20.50 per cent silt and 68.70 per cent sand. Extraction using acetonitrile followed by dispersive solid phase clean up using $MgSO_4$-PSA was ideal for extraction of flupyradifurone. The estimation was done using LC-MS/ MS with retention time for flupyradifurone, 6-chloronicotinic acid and difluro ethyl amino furanone as 4.65, 4.22 and 1.34 respectively.

The study concluded that the adsorption coefficient was higher in FYM amended soil indicating stronger adsorption than soil without amendment and the desorption percentages were reduced in the same. Hysteresis effect was noticed in all the treatments indicating slower desorption than adsorption. The mobility of flupyradifurone was found to be slightly higher in soil without amendment compared to the 0.5 per cent FYM amended soil. The dissipation was found to be the fastest under submerged condition followed by field capacity and dry moisture conditions.