



Leaching behaviour of four herbicides in two soils of Kerala

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ABSTRACT

The present study was conducted to find out the extent of leaching of butachlor, pretilachlor, 2,4-D and oxyfluorfen in two soil types, viz. Type I [coarse textured low organic matter soil (Mannuthy–Ultisol)] and Type II [fine textured high organic matter soil (Alappad-Inceptisol)]. Intact soil columns were collected from the paddy fields after the harvest of second crop. Butachlor, pretilachlor, 2,4-D and oxyfluorfen were applied in moist soil columns at the recommended rate of application. Soil samples from different depths up to 10 cm (top 5 segments of 2 cm each) and the leachate at 30 and 60 cm depths were analyzed for herbicide residues using gas chromatography. Among the four herbicides tested, 2,4-D registered highest level of residue in the leachate (0.20 ppm at 60 cm depth). Pretilachlor and butachlor followed the same trend in the pattern of movement of residue through the soil columns. However, the leachate of pretilachlor registered much lower quantity of residue (0.006 ppm). Fine textured organic matter rich soil recorded lower residue levels compared to the soil with coarse texture and poor organic matter. It could be attributed to the high adsorptive power of the soil, especially at the top layers with high organic matter content. Oxyfluorfen residues could not be detected in the leachate, because of its poor water solubility.

Key words: 2,4-D, Butachlor, Leaching, Oxyfluorfen, Pretilachlor

Among the different pre-emergence herbicides in rice, butachlor, pretilachlor and oxyfluorfen are more popular in the paddy fields of Kerala. Sodium salt of 2, 4-D is the most common post-emergence herbicide in the major rice bowls of the state, viz. Kole and Kuttanad. Herbicide movement in soils is of major concern in tropical soils with heavy rainfall. Since these herbicides are applied to the soil surface without incorporation, heavy rainfall soon after application may cause excessive leaching of the herbicide from the surface zone, resulting in poor weed control. In the case of herbicides with high soil mobility, leaching may lead to injury of deeper-rooted desirable species. In addition, herbicide leaching may result in contamination of ground and surface water (Anderson 1983). Movement of herbicide within the soil profile is influenced by many factors such as chemical nature of herbicide, the adsorptive capacity of soil and the amount of water available for downward movement through the soil. Butachlor, pretilachlor, oxyfluorfen and 2,4-D differ much in their water solubility (RSC 1987). Considering these factors, studies on leaching pattern of three pre-emergence herbicides and one post-emergence herbicide were conducted in two soil types of Kerala, under All India Coordinated Research Programme on Weed Control during the period from 2007-08 to 2010-11.

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MATERIALS AND METHODS

Intact soil columns were collected from two soil types, viz. Type I (sandy loam low organic matter soil of Ultisol order at Rice field of Agricultural Research station, Mannuthy) and Type II (high organic matter clayey soil of Inceptisol order, Kole Lands, Alappad) after the harvest of second crop. Long PVC tubes (60 cm) of 16 cm diameter were taken for Type I soil. Tubes of only 30 cm and 16 cm diameter were taken for Type II soil because the area is below mean sea level and hence collection of intact soil columns below 30 cm was not possible. The tubes were cut vertically and the two halves were pressed onto the lateral sides of the soil pit of 60 cm deep, dug in the rice field. The soil corresponding to the different depths were transferred as such to the two halves of the PVC column and they were joined together using adhesive tape. The tube was kept on an iron stand after tying the lower end with a muslin cloth. After adding water continuously to attain constant percolation rate, the herbicides were added at the recommended rate of application, viz. 1.25, 0.75, 1.0 and 0.2 kg/ha for butachlor (Machete®), pretilachlor (Rifit®), 2,4-D (Fernozone®) and oxyfluorfen (Goal®), respectively using a spray volume of 500 L/ha. The quantity of solution required for spraying was calculated based on the surface area.

Water was added frequently to the top of the column at one day after spraying. A total of 1000 mL water was added through the column (200 mL x 5 times) so as to simulate the normal rainfall receiving in the area. Methods were standardized for estimation residues in soil and water samples using the gas chromatograph. Soil samples from different layers (top 5 segments of 2 cm each) leachate were analysed for herbicide residues. Average values of residues from three replications were worked out for comparison of data.

Extraction and estimation of 2,4-D residues

Water samples were filtered out of any particulate matter. A 50 mL portion of the sample was taken and saturated with sodium chloride. The pH was adjusted to <2 with HCl. It was then extracted with (5 x 25 mL) portions of acetonitrile. The pooled extract was then concentrated to 15 mL. Fifteen mL 10% NaOH was added and the pH was adjusted to > 13. The organic phase was evaporated off in presence of the alkali. The aqueous alkaline solution was refluxed for 20 min. It was then cooled and extracted with equal volume of hexane (x3). The hexane fraction was discarded and the aqueous portion was acidified with HCl to pH<2. It was then extracted with equal volumes of diethyl ether (x3)

Twenty five gram of wet soil sample after draining excess water by spreading over a filter paper was shaken on a shaker with 80 mL extracting mixture (acetonitrile: water: glacial acetic acid in the ratio 80:20:25) for a period of 30 minutes at 220 rpm and filtered through Whatman No.1 filter paper. The filtrate was acidified with concentrated HCl (15 mL) and separated by extracting thrice each with 50 mL diethyl ether.

From the combined diethyl ether extract, the organic phase was evaporated off and the residue was dissolved in 3 mL of methanol. Added a 3ml portion of boron tri fluoride methanol reagent and refluxed for 10 minutes on a water bath. After reaction, excess alcohol was evaporated off and 20mL water was added, shaken vigorously for 5 min. and extracted with hexane (3x10mL). The hexane portions were combined, the organic phase evaporated off and the residue was concentrated

A 5 cm bed of activated silica gel Pyrex glass column packed at the two ends each with 1g of anhydrous sodium sulfate was used. The column was washed with 25 mL hexane. The extract obtained after derivatisation as given in step II was placed on the column. The residue in the column was washed with 100 mL solvent system containing (70% hexane/

30% dichloromethane). It was then eluted with 100 mL of (70% dichloromethane/30% hexane) solvent mixture. First 20 mL was discarded and next 80 mL was collected. The solvent was then evaporated off and the residue was dissolved in 1 mL n-hexane.

One micro litre of n- hexane extract was injected in to the GC 2010 fitted with a ⁶³Ni electron capture detector, a DB-17 capillary column and a split injector. The temperature of the injector, column and detector were 180, 210 and 300°C, respectively with a split ratio of 3:1. The residue content was calculated from the standard curve obtained with the reference standard.

Air dried soil sample (15 g, 2 mm sieved) was thoroughly mixed with 10g of anhydrous sodium sulphate, 2 g of florisol (60-100 mesh size) and 0.3g of activated charcoal. A glass column of 30 cm length and 2 cm internal diameter was taken. Anhydrous sodium sulphate of 3 cm layer was put on the non adsorbent cotton kept at the lower end of the column. Then the soil sample mixture (prepared as above) was added to the column and another layer of anhydrous sodium sulphate of 1 cm was put over this layer. The herbicide was extracted with 100 mL of hexanes: acetone mixture (9:1) and excess solvent was evaporated under vacuum to one mL. The evaporated sample was made up to 5 mL with n-hexane. One micro litre portion of the n- hexane extract was injected in to the GC 2010 fitted with a ⁶³ Ni electron capture detector, a BPX-5 capillary column and a split injector. The temperature conditions for butachlor and petilachlor were the same (250, 220 and 300°C for injector, column and the detector were respectively). For oxyfluorfen, optimum temperature conditions were 220, 210 and 240°C for injector, column and the detector respectively). The residue content was calculated from the standard curve obtained with the reference material (97% pure reference standards obtained from Dr. Ehrenstorfer, GmbH, Germany)

Gas chromatographic technique (KAU 2008) was used for estimation of butachlor, pretilachlor and oxyfluorfen residues in the leachate.

RESULTS AND DISCUSSION

Physicochemical characteristics of the soil

The major physico-chemical characteristics of soil, viz. soil texture, pH, cation exchange capacity (CEC), anion exchange capacity (AEC) and organic carbon content of the soil sample taken from the rice field before conducting experiment are presented in (Table 1).

Table 1. Major physico chemical characteristics of the soil columns collected for the study

Characteristics	Soil type (average values)	
	Type I (Mannuthy) coarse textured low organic matter soil sandy loam- ultisol	Type II (Alappad) fine textured high organic matter soil- clay- inceptisol
Clay %	26.0	64.0
Organic carbon, %	0.90	1.87
pH	5.09	5.1
C.E.C, C mol(+)/kg	9.25	15.7
A.E.C, C mol(-)/kg	12.4	9.38
Sesquioxide, %	4.6	3.0

The soils showed wide differences in their textural characteristics. The mean clay content varied from 25.98% (Type I) to 64.00% (Type II). The organic carbon content of Type I soil (Mannuthy) was 0.90% and that of Type II (Alappad) was 1.87%. The soils were uniformly acidic in nature (5.1). Cation and anion exchange capacities showed variations between the soil types (9.25 to 15.75. mol

(+)/kg and 9.38 to 12.4 C mol (-)/kg respectively). Sesquioxide content varied from 3.0 to 4.60 per cent between the soil types.

Herbicide residues at different soil depths

All the herbicides registered maximum quantity of residue in the upper 2 cm of the soil column.

Maximum value was registered by butachlor treatment (2.43 µg/g) in Type II soil and oxyfluorfen registered lowest value in both the soil types (0.55 and 0.61µg/g for Type I and Type II, respectively). This could be attributed to the differences in the levels of application of herbicides to the columns. The recommended level of application of butachlor was 1.25 kg/ha and that of oxyfluorfen was 0.20 kg/ha (KAU 2011). Higher proportion of applied pretilachlor compared to butachlor observed in the upper layer of soil column could be attributed to higher K_d (distribution coefficient) values for pretilachlor as reported by Hasna (2011).

There was considerable decrease in the residue with increasing depth of the soil. Fine textured organic matter rich soil recorded lower residue levels

Table 2. Leaching pattern of butachlor, pretilachlor oxyfluorfen and 2,4-D, in different soil types

Herbicide and level of application (kg/ha)	Depth of soil (cm)	Concentration of herbicide (µg/g or µg/ mL)	
		Coarse textured low organic matter soil	Fine textured high organic matter soil
Butachlor (1.25)	0-2	1.47 (35.28)	2.43 (58.32)
	2-4	0.25 (6.0)	0.77 (18.48)
	4-6	0.15 (3.6)	0.14 (3.36)
	6-8	0.05 (1.2)	0.02 (0.48)
	8-10	0.05 (1.2)	0.02 (0.48)
	Leachate	0.16 (3.84) (>60 cm depth)	0.04 (0.96) (>30 cm depth)
	Pretilachlor (0.75)	0-2	1.56 (62.4)
2-4		0.19 (7.6)	0.21 (8.4)
4-6		0.09 (3.6)	0.09 (3.6)
6-8		0.06 (2.4)	0.03 (1.2)
8-10		0.03 (1.2)	0.01 (0.4)
Leachate		0.006 (0.24) (>60 cm depth)	0.004 (0.16) (>30 cm depth)
Oxyfluorfen (0.20)		0-2	0.55 (82.5)
	2-4	0.005 (0.75)	0.004 (0.6)
	4-6	0.005(0.75)	0.002 (0.3)
	6-8	0.003 (0.45)	BDL
	8-10	0.003(0.45)	BDL
	Leachate	BDL(>60 cm depth)	BDL(>30 cm depth)
	2,4-D (1.0)	0-2	1.44 (43.2)
2-4		0.17(5.1)	0.19 (5.7)
4-6		0.10 (3.0)	0.16(4.8)
6-8		0.08 (2.4)	0.10 (3.0)
8-10		0.05(1.5)	0.09(2.7)
Leachate		0.20 (6.0) (>60 cm depth)	0.05 (1.5) (>30 cm depth)

Percentage of the applied herbicide remaining at different depths is given in parentheses; BDL: Below detectable level

compared to the soil with coarse texture and poor organic matter. It could be attributed to the high adsorptive power of the soil, especially at the top layers with high organic matter content.

Based on the quantity sprayed over the soil column, percentage of applied herbicide remaining in each layer of soil was calculated (Table 2). It could be noticed that oxyfluorfen is more strongly adsorbed in the first soil layer of 0-2 cm (82.5% and 91.5% of the applied herbicide in Type I and Type II soil, respectively) followed by pretilachlor (62.4 and 74.0%, respectively), 2,4-D (43.2% in Type I soil) and butachlor (35.28% in Type I soil). In Type II soil, butachlor (58.32%) adsorption was higher than that of 2,4-D (54.9%). As reported by Hasna (2011), higher quantity of organic matter resulted in considerable increase in the adsorption of butachlor in the lateritic soil of Kerala.

Herbicide residues in the leachate

Among the four herbicides tested, 2,4-D residue was the maximum in the leachate (Table 2) followed by butachlor, pretilachlor and oxyfluorfen. The leachate collected at 30 cm depth in Type II soil registered 2,4-D residues to an extent of 0.05 µg/mL (1.50% of the applied herbicide). In the case of Type I soil 2,4 D residues registered in the leachate at 60 cm depth was 0.2 µg/mL (6.0%). Oxyfluorfen residues in the leachate collected from both the soil types were below the detectable level. The results indicated that the mobility of oxyfluorfen was very

low in both the soil types and may not contaminate groundwater under recommended rate of application of the herbicide. Similar findings were reported by Yen *et al.* (2003) after evaluating the possible contamination of oxyfluorfen using the behavior assessment model and the groundwater pollution-potential (GWP) model. The present study also revealed that the solubility of herbicide in water is the major factor determining the movement of herbicides in the soils of Kerala. The extent of leaching followed the order: 2,4-D (620 mg/L) >butachlor (50 mg/L) > pretilachlor(20 mg/L) > oxyfluorfen (0.114mg/L).

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