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Leaching behavior of metribuzin and pretilachlor

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Abstract
A lab experiment was conducted for two years (2012 and 2013) in red and black soils to study leaching behavior of pretilachlor and metribuzin with soil columns (PVC tubes of 10 cm diameter and 65 cm length). Soils were collected horizon wise and were filled into the column and pre-conditioned. Pretilachlor and metribuzin were applied to the column surface at recommended (X dose-500 g/ha and 350 g/ha, respectively) and double doses (2X) equated to surface area of the column and water was added to the column surface. After 7 days, soil samples were collected from each 5 cm blocks and analyzed for herbicide residues. Herbicide residues were determined using GC-ECD. Pretilachlor recovery varied from 89.2 to 96.4% in soil with LOQ of 0.025 mg/kg. Recovery of metribuzin in the soil varied from 92.4 to 94.8% and with LOQ of 0.015 mg/kg.
In red soils, pretilachlor leached up to 10-15 cm in both X and 2X doses. Depth wise distribution showed that, 46.2% and 50.6% of the total herbicide was detected in the top 0-5 cm layer in X and 2X doses. In 5-10 cm layer, 32.6% and in 10-15 cm layer 14.1% of residues were detected. In 2X dose, herbicide detection was 50.6% in 0-5 cm layer, 36.5% in 5-10 cm layer and 12.9% in 10-15 cm layers. In black soils, pretilachlor leached up to 10 cm and 15 cm depth in X and 2X doses, respectively. In X-dose, 72.55% was detected in the top 0-5 cm layer and 27.44 in the 5-10 cm layer. At 2X dose, 73.35%, 19.90% and 6.74% the herbicide detected in the top 0-5 cm, 5-10 and 10-15 cm soil layers, respectively.
Metribuzin could be detected upto 15-20 cm and 20-25 cm layer in X and 2X doses respectively in red soils,. Highest concentration of the herbicide could be detected in 05-10 cm layer in both doses (38.25% 32.59% in X and 2X doses respectively). In black soils, highest concentration of the leached herbicide could be detected in the 05-10 cm layer in both X and 2X doses (39.05% and 37.53%). Leaching of metribuzin was restricted upto 15-20 cm layer in both doses in black soils.

Keywords: Leaching, Metribuzin, Pretilachlor, Red soils, Black soils

Introduction
Leaching is the downward movement of a substance dissolved in water through soil. Leaching may determine herbicide effectiveness, may explain selectivity or crop injury, or may account for a herbicide's removal from the soil. A leaching chemical can move downward in one of two pathways. Matrix flow is a slow movement through the small pore spaces in the bulk soil. The water and the herbicide interact with the small pores on the way down the profile. In contrast, preferential flow is a rapid movement of water in the large channels and flow paths. The solubility of a herbicide in water helps determine its leaching potential. Leaching occurs when a herbicide is dissolved in water and moves down through the soil profile. Herbicides that readily leach may be carried away from crop and weed germination zones.
Herbicide leaching is determined by other factors as well. These include herbicide-soil binding properties, soil physical characteristics, rainfall frequency and intensity, herbicide concentration, and time of herbicide application. In general, herbicides that are less soluble in water and strongly attracted to soil particles are less likely to leach, particularly in dry years. Chemicals are more likely to leach down when they are weakly adsorbed to soil. The movement especially leaching has a direct implication on ground water contamination and on pollution in aquatic environment and these soil column leaching studies are simple and reliable methods.
Pretilachlor and metribuzin are two important herbicides used by the farmers. Pretilachlor is the highest used rice herbicide by the rice famers especially in transplanted rice and metribuzin is commonly used as pre and post-emergence herbicide in sugarcane and vegetable (tomato, carrot, potato). Information pertaining to the leaching behavior of the herbicides in soils of Andhra Pradesh and Telangana is lacking. Hence the present study is proposed to study the herbicide leaching behavior of pretilachlor and metribuzin.

Metribuzin [4-amino-6-(1,1- dimethylethyl)-3-(methylthio)-1,2,4-triazin- 5(4H)-one], a triazine, (Fig:1) is widely used as a selective herbicides for pre and postemergence control of annual grasses (Papadakis and Mourkidou, 2002; Worthing, 1987) [5, 8] and numerous broadleaf weeds in the field and vegetable crops, turf grass, and on fallow lands by inhibiting photosynthesis of susceptible plant species (WSSA, 1994) [9]. Metribuzin is a white crystalline solid compound with a molar mass of 214.3 g/mol and solubility of about 1.22 g/L in water. It is highly soluble in most organic solvents including acetone (820 g/L) and ethanol (450 g/L) (Kidd and James, 1991) [2].

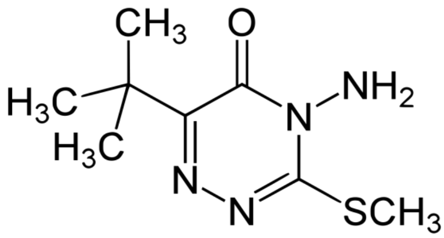


Fig 1: Metribuzin

Pretilachlor, 2- chloro-2, 6- diethyl – N-(2-propoxyethyl) (Fig: 2) acetanilide belongs chloracetamide group of herbicides with a molecular weight of 311.85 g/mol, water solubility of 500 mg/L at 20 ^{0}C vapour pressure of 0.133 m Pa at 25 ^{0}C. Acute oral LD50 is 6099 mg/kg body weight (UOH, 2017)

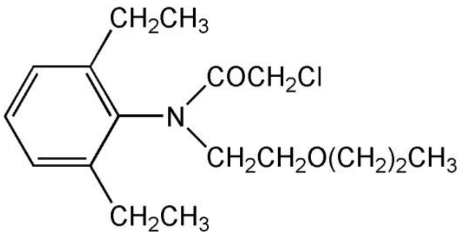


Fig 2: Pretilachlor

Methodology

This experiment was conducted under laboratory conditions with PVC columns in red and black soils PVC tubes (diameter 10 cm and 65 cm length) were cut vertically into two and joined together with a wide tape. The joint was made leak proof. Fine cloth was tied to one end of the column to prevent of loss of soil. Soil collected horizon wise was filled into the column by gently tapping the columns. Water was added to the surface for pre-conditioning the column. Pretilachlor and metribuzin were applied to the surface portions of the column diluted with 5.0 ml of water. Quantity of herbicide added was the recommended (X dose-500 g/ha and 350 g/ha, respectively) and double the recommended doses (2X dose-1000 g/ha and 700 g/ha, respectively) equated to surface area of the column. Water was added to the surface of the column equal to the rainfall of the period. Long term average of the area was taken into consideration for determining the quantity of the water. Blank columns without herbicide were maintained for comparison. After 7 days adhesive tape was removed, PVC tubes were separated carefully without disturbing the soil and soil columns were cut into 5 cm blocks up to 30 cm depth and thereafter 10 cm blocks up to 60 cm. The soil samples were properly labeled and stored in freezer for analysis. At the time of analysis the soil samples were removed from the freezer and brought to the room temperature and analyzed according to the procedure outlined below.

Analysis of pretilachlor

A stock solution (1.0 mg/ ml) was prepared for pretilachlor in Hexane. A 100 microgram per ml fortification standard was prepared by taking a 5 ml aliquot in 50 ml volumetric flask with acetone. Further dilutions were made to make a 10 and 1 microgram per ml solution. Fortification trials were conducted with 1.0 and 2.0 mg/kg solutions and all stock, fortification and internal standard solutions were stored at – 20 ^{0}C in the deep freezer until analysis.

Method and level of fortification

The reference standard of pretilachlor was used for quantification, recovery and determination of retention time of the herbicide. The soil and grain samples were collected from fields where no herbicide was applied. The samples were sieved/ground and the required quantity of the technical grade pretilachlor was added to 50 g soil/ 20 g grain sample. All samples were replicated twice. The soil and grain samples were fortified with 1 mg/kg and 2 mg/kg solutions. Control as well as blank samples were maintained to check for the contamination and interferences.

Extraction

A representative 10 g sieved soil /5 g grain was extracted with 150 ml of acetone: hexane. The samples were kept overnight and filtered through Buchner funnel and again the samples were rinsed with another fifty ml of acetone: hexane and the extract was evaporated. Mixed with 0.3 g activated charcoal, 0.3 g florosil, 10 g anhydrous sodium sulphate and packed in the glass column. Column was eluted with 100 ml of mixture of acetone: hexane (1:9), elute was evaporated to dryness in a rotary evaporator at 45 °C and residue is re-dissolved in 5 ml of n-hexane.

Clean up

To a chromatographic column (2 mm i.d.) 4 g of florosil was added followed by 10 g of anhydrous sodium sulphate. The concentrated extract was diluted to 10 ml with 10% acetone in hexane. Then the solution was transferred to florosil column. Container was rinsed with hexane and transferred to column. The column was eluted with about 5 ml/min. Florisil elute is concentrated 1 ml. The extract is used for the determination of pretilachlor residues by GLC on ECD.

Extraction and clean up soil residues of metribuzin

The soil samples were extracted with 50 ml mixture of acteonitrile and water in a horizontal mechanical shaker for one hour, filtered and partitioned with methylene chloride (50 ml). The soil samples were filtered through anhydrous sodium sulphate for dehydration and concentration to 2.0 on a water bath. This residue was transferred to a silica gel column for cleanup and it was eluted with 50 ml of dichloromethane. The collected elute was concentrated a water-bath to 10 ml and analyzed on GC-ECD for residues.

Results

Pretilachlor

Recovery of pretilachlor in the soil varied from 89.2 to 96.4%. LOD was 0.005 mg/kg and LOQ was 0.025 mg/kg.

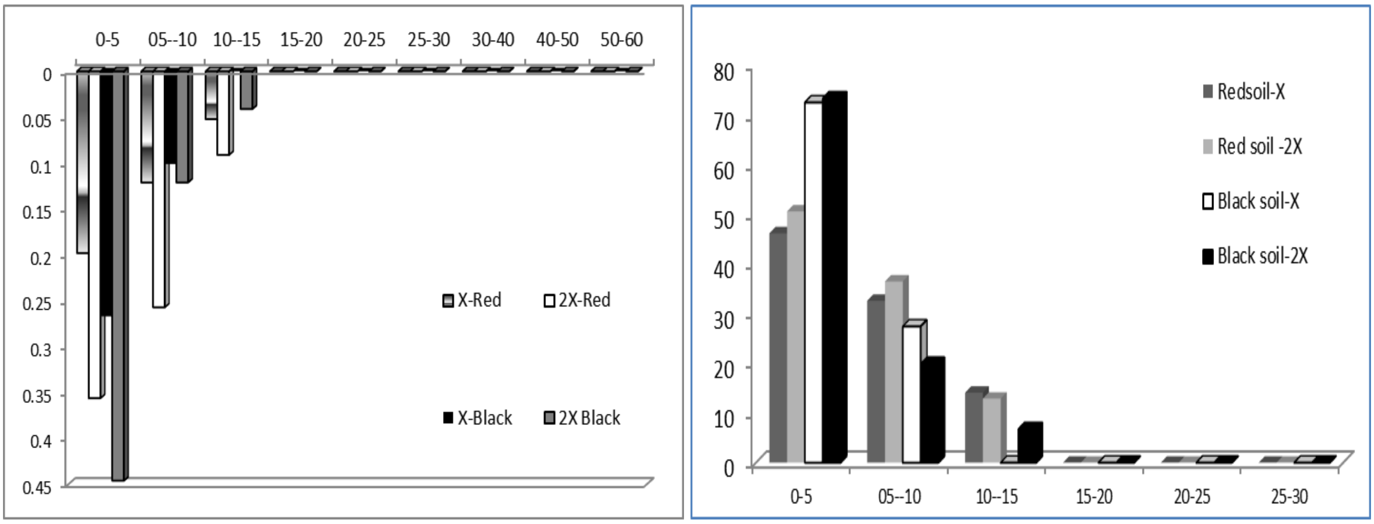
In red soils pretilachlor applied to surface of the soil @ 500 g/ha) leached up to 10-15 cm in (Table 1 and Fig 3) both recommended and double the recommended dose. In X dose depth wise distribution showed that 46.2% of the total herbicide detected in the top 0-5 cm layer of soil. Herbicide detected in the 5-10 and 10-15 and15-20 layers were 32.6%

and 14.1% respectively of the total detected herbicide in the soil column. When the pretilachlor was applied at double the recommended dose, the herbicide detected in the top 0-5 cm layer was 50.6% (0.365 mg/kg) of the total herbicide detected in the soil column. However, the herbicide content in the deeper layers decreased with increasing depth of the soil as indicated by the 36.5% and 12.9% in the 5-10 and 10-15 cm soil layers. At both the doses of herbicide application, the residues could not be detected beyond 15 cm depth, which indicated limited leaching potential of pretilachlor. The stronger adsorption of the herbicide in the top layers of the soil indicated adsorption of the herbicide strongly on the soil particles. Studies on mobility of pretilachlor in rice soils of Thailand studied by Runsit and Ubonwan (1990) [6] showed similar results.

In Black soils, pretilachlor applied to surface of the soil leached up to 10 cm in recommended. In double the recommended dose, pretilachlor leached upto 5 cm depth. Layer wise distribution at recommended dose of application showed that 72.55% (0.267 mg/kg) of the total herbicide detected in the top 0-5 cm layer of soil. Herbicide detected in the 5-10cm layer was 27.44% of the total detected herbicide in the soil column. At 2X dose, the herbicide detected in the top 0-5 cm layer was 73.35% (0.445 mg/kg) of the total herbicide detected in the soil column. Further, 19.90% and 6.7% of the herbicide (0.121 and 0.041mg/kg, respectively) were detected in 5-10and 10-15 cm soil layers. At both the doses of herbicide application, the residues could not be detected beyond 15 cm depth, which indicated limited leaching potential of pretilachlor. Higher concentration of the herbicide in the top 5 cm layer of the soil indicated strong affinity of the herbicide molecules with the clay/ organic matter in the surface horizon. The herbicide retained in the top layer was higher in the black soil compared to the black soil which could be due to higher active clays in the black soils and higher clay content in the surface soils compared to the black soils. Analiza and Enrique (2002) [1] reported similar findings in clayey soils.

Table 1: Leaching of pretilachlor to different soil layers in the red soil column experiment (mg/kg)

Depth	Pretilachlor (mg/kg)							
	Red soils				Black soils			
	X dose	% distribution	2 X dose	% Distribution	X dose	% distribution	2 X dose	% Distribution
0-5	0.198	46.2	0.356	50.6	0.267	72.55	0.446	73.35
5-10	0.121	32.6	0.257	36.5	0.101	27.44	0.121	19.90
10-15	0.052	14.1	0.091	12.9	BDL	0	0.041	6.74
15-20	BDL	0	BDL	0	BDL	0	BDL	0
20-25	BDL	0	BDL	0	BDL	0	BDL	0
25-30	BDL	0	BDL	0	BDL	0	BDL	0
30-40	BDL	0	BDL	0	BDL	0	BDL	0
40-50	BDL	0	BDL	0	BDL	0	BDL	0
50-60	BDL	0	BDL	0	BDL	0	BDL	0



Concentration Vs Depth

Distribution Vs Depth

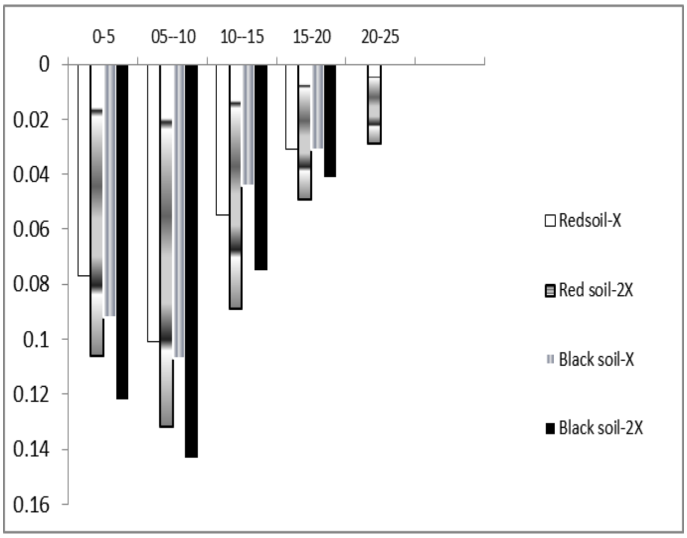
Fig 3: Pretilachlor leaching in red and black soils

Metribuzin

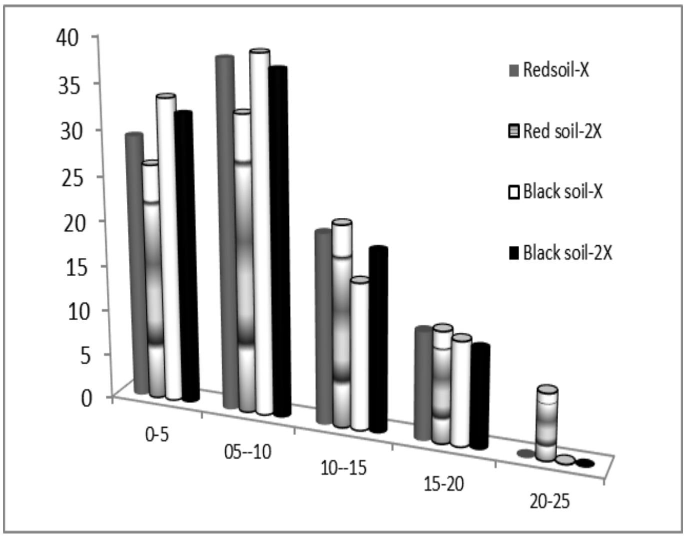
Recovery of in the soil varied from 92.4 to 94.8%. LOD was 0.002 mg/kg and LOQ was 0.015 mg/kg. In red soils, metribuzin applied at the surface could be detected upto 25-30 cm in both the X and 2X doses (Table: 2 and Fig: 4). Depth wise distribution of the detected amount of herbicide amount indicated that most of the applied herbicide could be detected in the top 15 cm layer of the soil (88.24% in X dose and 80.73% in 2x dose). However, highest concentration of the herbicide could be detected in 05-10 cm layer in both doses (38.25% in x dose and 32.59% in 2X dose). In 2X dose herbicide residue leached beyond 20 cm depth and 0.029 mg/kg of metribuzin could be detected in 20-25 cm layer. Beyond 20 cm herbicide reached BDL hence could not detected with the LOQ of 0.015 mg/kg. Similar leaching behavior of metribuzin in sandy loam soils and sandy clay loam soils was reported by Kim and Feagley (2002).

Table 2: Leaching of metribuzin to different soil layers in the column experiment (mg/kg)

Depth	Metribuzin (mg/kg)							
	Red soil				Black soil			
	X	% distribution	2 X	% distribution	X	% distribution	2 X	% distribution
0-5	0.077	29.16	0.106	26.17	0.092	33.57	0.122	32.02
5-10	0.101	38.25	0.132	32.59	0.107	39.05	0.143	37.53
10-15	0.055	20.83	0.089	21.97	0.044	16.05	0.075	19.68
15-20	0.031	11.74	0.049	12.09	0.031	11.31	0.041	10.76
20-25	BDL	0	0.029	7.16	BDL	0	BDL	0
25-30	BDL	0	BDL	0	BDL	0	BDL	0
30-40	BDL	0	BDL	0	BDL	0	BDL	0
40-50	BDL	0	BDL	0	BDL	0	BDL	0
50-60	BDL	0	BDL	0	BDL	0	BDL	0



Concentration Vs Depth



Distribution Vs Depth

Fig 4: Metribuzin leaching in red and black soils

In black soils, highest concentration of the leached herbicide could be detected in the 05-10 cm layer in both X and 2X doses (39.0% and 37.53%). Leaching of metribuzin was restricted upto 15-20 cm layer in both doses. Unlike the red soils, the herbicide concentration in the top 5 cm layer was higher in black soils, which indicated higher active clay adsorption in the black soils. In the top 10 cm layer, relatively higher retention was noticed in black soils. Celia *et al* 2008 studied the leaching behavior of metribuzin clayey soils and reported similar results

Conclusion

Oxadiargyl and oxyfluorfen leached only up 5-10 cm layer in red and black soils at the recommended rates of application (100 g and 125 g a.i./ha). Hence, these herbicides did not present any threat of contaminating the ground water when used at recommended rates.

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