

Research Article

Leaching Behavior of Oxyfluorfen and Oxdiargyl in Red and Black Soils

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Abstract

Leaching studies of herbicides in soil columns are simple and reliable methods to assess their environmental fate and contamination potential. Pretilachlor and metribuzin are popular herbicides used in transplanted rice and vegetables crops (tomato, carrot, potato) respectively. A lab experiment was conducted for two years (2012 and 2013) in red and black soils to study leaching behavior of oxyfluorfen and oxdiargyl with soil columns (PVC tubes of 10 cm diameter and 65 cm length). Retention time of oxdiargyl was 6.95 min. Recovery of in the soil varied from 86.8 to 90.2 %. LOD was 0.005 mg/kg and LOQ was 0.015 mg/kg. Retention time of oxyfluorfen was 9.17 min. recovery of oxyfluorfen in the soil varied from 90.2 to 94.8 %. LOD was 0.005 mg/kg and LOQ was 0.025 mg/kg. Oxdiargyl 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. At double the recommended rates of application oxyfluorfen and oxdiargyl leached up to 10-15 cm depth in red soils. In black soils the leaching was restricted to top 10 cm layer in double dose also.

Keywords: Leaching, oxdiargyl, oxyfluorfen, red soils, black soils

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Introduction

Leaching is one of the major transportation processes responsible for ground water contamination. The movement of pesticides through soil is an important process that determines their fate in both soil and aquatic environment and the mobility of herbicides in soil influences their persistence and ultimate dissipation. 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. Leaching of soil applied pesticides is considered to be the main source on non-point contamination of ground water.

Oxyfluorfen and oxdiargyl belong to chemical family PPO inhibitors (protoporphyrinogen oxidase enzyme inhibitors). Protoporphyrinogen oxidase enzyme (PROTOX) is a protein located in the chloroplast, where it is involved in chlorophyll and heme synthesis, and in mitochondria, where it is involved in non plastidic heme synthesis. The singlet oxygen (produced due to reaction of protopyrinogen with oxygen and light in the absence of PPO oxidase) rapidly reacts with lipids in cell membranes, causing lipid peroxidation and membrane disruption, and this leads to plant death.

Oxyfluorfen (2-chloro-1-(3-ethoxy-4-nitrophenoxy)-4-(trifluoromethyl)benzene) is a dark red-brown to yellow semisolid (**Figure 1**) with a vapor pressure of 2×10^{-6} mm Hg at 25°C, a very low water solubility of 0.1 mg/l at 25°C, and an oral LD₅₀ (rat) of >500 mg/kg [1, 2]. Oxyfluorfen is formulated as an emulsifiable concentrate, which has utility as a postemergence or a preemergence treatment for control of broadleaf weeds in many crops.

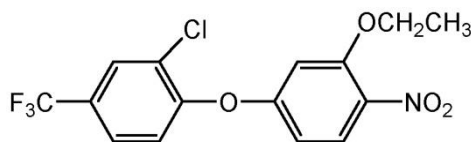


Figure 1 Oxyfluorfen

Oxdiargyl [5-tert-butyl-3-[2,4-dichloro-5-(prop-2-ynxyloxy)phenyl]-1,3,4-oxadiazol-2(3H)-one] has a molecular weight of 341.2, white to beige powder (**Figure 2**) with no characteristic odour, density 1.484 (20°C), melting point 131°C, vapour pressure 2.5×10^{-3} m Pa, water solubility of 0.37 mg/l coefficient (n-octanol-water) log P = 3.95. Acute oral LD₅₀ for rats is >5000 mg/L. Oxdiargyl is available in Indian markets in two formulations viz,

wettable powder and emulsifiable concentrate. Wettable powder (80 % WP) formulation is sold under several brand names and is recommended as emergence application in transplanted and direct seeded (puddle) rice crop. Emulsifiable concentrate (6%) is sold under brand name "Raft" and is recommended for pre-emergence application for vegetable crops. So far many studies have examined the bioefficacy of oxadiargyl against different crops [3, 4].

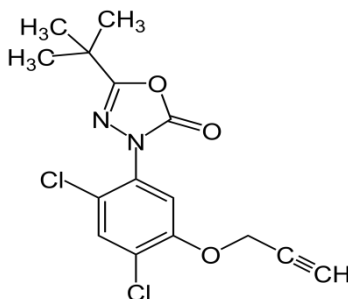


Figure 2 Oxadiargyl

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 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. Oxyfluorfen (23.5 %EC) and oxadiargyl (80% WP) were applied to the surface portions of the column diluted with 5.0 ml of water. Quantity of herbicide added was the recommended (100 g and 125 g a.i./ha respectively for oxadiargyl and oxyfluorfen) and double the recommended doses (200g and 250 g a.i./ha) equated to surface area of the column. Water was added (equivalent to the area of the column) to the surface equal to the rainfall of the period. 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 labeled and stored in freezer (-20⁰C) for analysis. At the time of analysis the soil samples were removed from the freezer and brought to the room temperature and analyzed.

Residues of oxadiargyl in soil were analyzed according to the procedure outlined by [5]. Oxyfluorfen residues were determined according to the protocol given by [6, 7].

Oxadiargyl residues in soil

Extraction, cleanup was done by modified QuEChERS method [3]. Sieved soil sample (10 g) was transferred into a 50 ml centrifuge tube, followed by the addition of 4 g Mg SO₄, 1.0 g Na Cl and 15 ml of acetonitrile. The sample tube is vigorously shaken for one min. and the mixture is centrifuged at 2000 rpm for 5 min. Five ml of supernatant was transferred to a flask through a layer of anhydrous sodium sulphate. The extract in the flask was concentrated to near dryness in rotary vacuum evaporator. The residue was dissolved in ethyl acetate and estimated on GC.

Mega-bore capillary column was used in GC (Shimadzu 2010) for separation of the atrazine (AB-5 Capillary Column, length 30 m, ID 0.53 μm, 1.5 μm thick coating of 5% phenyl polysiloxane). Carrier gas was nitrogen at 15 psi pressure constantly. The makeup gas flow was 50 ml/min. the oven temperature was 60°C (held for 0.5 min) to 150°C at 30°C/min, then at 230°C (held for 2 min) at the rate of 10°C/min. The injector temperature was 250°C. The injected volume was 1 micro-liter. The detector temperature was maintained at 280⁰C.

Oxyfluorfen residues in soil

Analysis for the residues of oxyfluorfen in the soil samples was carried out employing the procedure described by [6].

Extraction

A representative 10 g sieved soil was extracted with 150 ml of acetone: hexane(9:1). The samples were kept overnight and filtered through buchner funnel and again the samples were rinsed with another 50 ml of acetone: hexane and the extract was evaporated.

Clean up

To a chromatographic column (2 cm i.d.) fitted below with cotton, 4 g of florisil followed by 10 g of anhydrous sodium sulphate was added. The concentrated extract was diluted to 10 ml with 10% acetone in hexane. Then the solution was transferred to florisil column. Container was rinsed with hexane and transferred to column. The column was eluted with about 5 ml min⁻¹. Florisil elute is concentrated to 1 ml. The extract is used for the determination of herbicide residues by GLC on ECD. The prepared solutions were injected to GC by using following requirements: Gas Chromatograph (Shimadzu GC 2010) equipped with Electron capture detector with Ni 63 (ECD), AB-5, 30 m length ID 0.53 mm, film thickness 1.50 um column was used for determination of residues. The following parameters were maintained for analysis. Carrier gas: Nitrogen; Carrier gas flow rate: 53.6 ml/minute. Injector temperature: 240; Injector split ratio: 1: 10; Detector temperature: 260 and make up gas flow: 60 ml/minute.

Results***Oxyfluorfen***

Retention time of oxyfluorfen was 9.17 min. recovery of oxyfluorfen in the soil varied from 92.6 to 94.8 %. LOD was 0.005 mg/kg and LOQ was 0.025 mg/kg. Results of the leaching studies indicated that, in red soils oxyfluorfen applied to surface of the soil @ 125 g/ha) leached up to 5-10 cm and 10-15 cm (**Table 1**) in both recommended and double the recommended doses, respectively. In X dose, depth wise distribution showed that 57.53 % of the total herbicide detected in the top 0-5 cm layer of soil. Herbicide detected in the 5-10 cm layer was 42.46 %. When the oxyfluorfen was applied at double the recommended dose, the herbicide detected in the top 0-5 cm layer was 47.61 % 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 32.53 % and 19.84 % 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 oxyfluorfen. The stronger adsorption of the herbicide in the top layers of the soil indicated adsorption of the herbicide strongly on the soil particles.

In black soils, oxyfluorfen applied to surface of the soil leached up to 10 cm depth (Table 1) in recommended and double the recommended dose treatments. Layer-wise distribution at recommended dose of application showed that 69.73 % of the total herbicide detected in the top 0-5 cm layer of soil. Herbicide detected in the 5-10 cm layer was 30.26 %. At 2X dose, the herbicide detected in the top 0-5 cm layer was 68.06 % of the total herbicide detected in the soil column. Further, 31.93 % of the herbicide was detected in 5-10 cm soil layer. At both the doses of herbicide application, the residues could not be detected beyond 15 cm depth, which indicated limited leaching potential of oxyfluorfen. 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 soil surface horizon. The herbicide retained in the top layer was higher in the black soil compared to the red soil which could be due to higher active clays in the black soils (smectitic) and higher clay content in the surface soils compared to the red soils. Similar leaching behavior of oxyfluorfen in different soils was earlier reported [8, 9].

Table 1 Leaching of oxyfluorfen to different soil layers (mg/kg)

Depth	Red soils				Black soils			
	125 g/ha	% distribution	250 g/ha	% Distribution	125 g/ha	% distribution	250 g/ha	% Distribution
0-5	0.042	57.53	0.060	47.61	0.053	69.73	0.081	68.06
5-10	0.031	42.46	0.041	32.53	0.023	30.26	0.038	31.93
10-15	BDL	0	0.025	19.84	BDL	0	BDL	0
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

Oxadiargyl

Retention time of oxadiargyl was 6.95 min. Recovery in the soil varied from 94.2 to 98.8 %. LOD was 0.005 mg/kg and LOQ was 0.015 mg/kg. In red soils (**Table 2**) oxadiargyl applied to surface of the soil @ 125 g/ha leached up to 5-10 cm and 10-15 cm in recommended and double the recommended doses, respectively. In X dose, depth wise distribution showed that 61.19 % of the total herbicide detected in the top 0-5 cm layer of soil. Herbicide detected in the 5-10 cm layer was 38.80 %. When the oxadiargyl was applied at double the recommended dose, the herbicide detected in the top 0-5 cm layer was 51.4 % 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 31.77 % and 16.82 % 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 oxadiargyl. The stronger adsorption of the herbicide in the top layers of the soil indicated adsorption of the herbicide strongly on the soil particles.

Table 2 Leaching of oxadiargyl to different soil layers (mg/kg)

Depth	Red soils				Black soils			
	100 g/ha	% distribution	200 g/ha	% Distribution	100 g/ha	% distribution	200 g/ha	% Distribution
0-5	0.041	61.19	0.055	51.4	0.049	70.00	0.078	71.55
5-10	0.026	38.8	0.034	31.77	0.021	30.00	0.031	28.44
10-15	BDL	0	0.018	16.82	BDL	0	BDL	0
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

In Black soils, oxadiargyl applied to surface of the soil leached up to 10 cm depth in recommended and double the recommended dose treatments (Table 2). Layer wise distribution at recommended dose of application showed that 70.00 % of the total herbicide detected in the top 0-5 cm layer of soil. Herbicide detected in the 5-10 cm layer was 30.00 %. At 2X dose, the herbicide detected in the top 0-5 cm layer was 71.55 % of the total herbicide detected in the soil column. Further, 28.44 % of the herbicide was detected in 5-10 cm soil layer. At both the doses of herbicide application, the residues could not be detected beyond 15 cm depth, which indicated limited leaching potential of oxadiargyl. 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 soil surface horizon. The herbicide retained in the top layer was higher in the black soil compared to the red soil which could be due to higher active clays in the black soils (smectitic) and higher clay content in the surface soils compared to the red soils. Similar leaching behaviour of oxadiargyl was earlier reported [10, 11].

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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