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Degradation of oxyfluorfen in sandy clay loam soil

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Abstract

Even though the persistence of oxyfluorfen may be shorter, depends upon the soil, weather and the crop for which it's being applied, may vary in the oxyfluorfen residues in the soil environment. Considering the above facts, an attempt has been made to study the persistence and degradation of Oxyfluorfen in sandy clay loam soils under laboratory conditions. Disappearance parameters for Oxyfluorfen residues were calculated using first order reaction kinetics equation and found that its dissipation fit the first order degradation with the R_2 values of >0.99 and >0.93 at both the doses of 200 and 400 g/ha during 2018-19 and 2019-2020, respectively. Increase in concentration of application increased the half life of oxyfluorfen with DT_{50} values of 6.83 & 8.75 days and 9.55 & 10.65 days, during 2018-19 and 2019-20, respectively, at 200 and 400 g/ha applied treatments. The Oxyfluorfen in soil declined sharply and persisted up to 45 days after herbicide application (DAHA) and became Below Detectable Limit (BDL) at 60DAHA at both the doses.

Keywords: Oxyfluorfen, sandy clay loam, herbicide residues, degradation, persistence

Introduction

Herbicides use is increasing throughout the globe due to increasing labour cost, choice of application of herbicides, quick weed control in crop and non-cropped areas. Globally consumption of herbicides is 44% followed by the insecticides (22%), fungicides (27%) and others (7%). Herbicides have become one of the most important components for efficient weed control and in turn for increasing the agricultural production and to maintain the non-cropped area free from weeds and pests. In India, herbicide use has increased to 30% during the last 10 years in managing weeds in the country (Sondhia, 2014) [7]. As herbicides are chemical in nature and thus excessive and repeated use may pose residue problems, phyto-toxicity to crop plants, residual effect on susceptible inter-crops or succeeding crops or non targets organisms and ultimately health hazards due to accumulation of herbicide residues in the soil. In general, herbicides have been formulated in such a way that they degrade from the environment after completion of their intended job of controlling weeds, but a few of the herbicides persist in the environment and pose a serious hazard to the succeeding crop and also to the soil environment. However, the herbicide should persist long enough to check weeds until the end of critical period of crop weed competition but should not persist beyond the crop harvest, as it would be injurious to the sensitive crops grown in rotation. A herbicide is said to be persistent when it may be found to exist in soil in its original or a closely related but phytotoxic form longer than one crop season after its original application (Sondhia, 2013) [6]. The use of herbicides offers selective and economic control of weeds from the beginning and gives the crop an advantage of a good start and competitive superiority. Even though the persistence of Oxyfluorfen may be shorter, depends upon the soil, weather and the crop for which its applied will vary in the Oxyfluorfen residues.

Active ingredient in oxyfluorfen (23.5% EC) is a 2-Chloro-1-(3-ethoxy-4-nitrophenoxy)-4-(trifluoromethyl) benzene belonging to a diphenyl-ether group of herbicide. Oxyfluorfen is a contact, herbicide and light is required for its herbicidal activity in plants. Oxyfluorfen acts by free radical formation *via* inhibition of protoporphyrinogen oxidase (Protox), which is the enzyme that converts protoporphyrinogen IX to protoporphyrin IX and also induces necrosis in applied plants.

Degradation is defined as a substantive change in the molecular makeup of the given herbicide, with a component of the parent molecule removed by some process to form a metabolite or metabolites. Dissipation is considered to be the sum of all possible outcomes of the parent herbicide. A herbicide molecule can dissipate by the process of chemical or microbial degradation which indicates a chemical change in the parent. The inverse process of dissipation is herbicide persistence. Persistence is often considered to be a negative association, such as herbicide persistence that damages rotational crops or herbicide persistence that causes contamination of rivers and groundwater aquifers (Mueller and Senseman, 2015). On the other hand, herbicide persistence can allow for residual weed control to provide maximum agricultural productivity in managed ecosystems.

Oxyfluorfen degrade in soil mainly by photolysis and to some extent by evaporation in moist soil surfaces (WSSA, 1994)^[11]. The dissipation of oxyfluorfen was usually moderate with the average field half life of 35 days (Wauchope *et al.*, 1992)^[10] and typically ranges from 30-40 days. While, the results indicated that the persistence of oxyfluorfen residues in the rhizosphere soil of rice up to 60 days after application (Das *et al.*, 2003). Oxyfluorfen residues present in the soil and rice grain up to harvest (100 days) and suggested, there is a chance for the bioaccumulation of residues if it is used at higher dose and also continuously (Sondhia, 2009)^[5]. Oxyfluorfen is classified as a highly toxic and persistent herbicide, which persist in soil and accumulates in terrestrial plants and certain aquatic environments through runoff (USEPA, 1992)^[8].

Recently, oxyfluorfen has been registered in India as a pre-emergence herbicide for crops and is used widely for annual crops. Many field experiments revealed the bio-efficacy of this herbicide and its persistence in soil grown with rice crop; however, information is seldom available on the persistence of Oxyfluorfen herbicide in soils grown with various vegetable crops under Indian tropical conditions. Therefore, laboratory experiments were undertaken to investigate persistence and degradation of Oxyfluorfen in sandy clay loam soils.

Materials and Methods

Laboratory experiments have been conducted under All India Coordinated Research Programme on Weed Management, Department of Agronomy, TNAU, Coimbatore during 2018-19 and 2019-20. The surface (0-15 cm) soil samples collected from pesticide free zone was used for studying the degradation of Oxyfluorfen with X (200 g / ha) and 2X (400 g / ha) doses. The soil was sandy clay loam in texture and had pH of 8.01 and 8.21, EC of 0.46 and 0.41 dS/m and OC of

0.37 and 0.34 per cent during 2018-19 and 2019-20, respectively. The study was conducted under controlled condition by imposing the treatments following the standard OECD guidelines for degradation of pesticides in soil.

Fifty grams of soil was taken in a 100 ml centrifuge tube and it was added with oxyfluorfen at X (200 g/ha) and 2X (400 g/ha) doses with 3 replications. The soil samples were collected at periodical interval (0,3,7,10,15,30,45 and 60 DAHA) and analyzed for oxyfluorfen residues to study the dissipation pattern in sandy clay loam soil. The soil sample was extracted with 100 ml methanol as extracting solution after shaking in orbital shaker for 1 hr. The suspension was filtered through whatman no.42 filter paper and the extract was evaporated in water bath till the suspension reduced to 10 ml. The concentrated extract was transferred to separating funnel and the Oxyfluorfen residue was portioned with 30 ml of 1% NaCl and 50 ml of hexane. The upper organic layer was collected separately. The lower aqueous layer was re-extracted twice with 25 ml hexane each time. The organic layer was pooled and filtered through whatman no. 42 filter paper containing a pinch (2 gm) of anhydrous sodium sulphate. The filtered residue extract was concentrated to dryness using rotary vacuum evaporator. The dried residues of oxyfluorfen compounds were dissolved in 2 ml acetonitrile HPLC grade solvent for HPLC determination. The data were subjected to statistical analysis using the kinetics equation to calculate half life and degradation constant.

Instrumentation

Oxyfluorfen residues were determined by HPLC (1200 series) with Diode Array Detector (DAD), binary pump and autosampler with Rheodyne injection system. The Oxyfluorfen compound was separated using Agilent Eclipse XDB – C18, 5 μ m, 4.6x150mm column maintained at 30°C. The instrument was connected to a computer, which converts the signal response in to peak area using EZChrom software (USA). Acetonitrile / water 75/25, v/v) was the mobile phase used for the determination. The injection volume of the sample was 20 μ L with the flow rate of 0.6mL min⁻¹ and detection at 275nm. The retention time was 4.36 minutes (Fig.1). The stock solution of Oxyfluorfen and its working concentrations were prepared in acetonitrile by diluting the stock solution as described by Janaki *et al.* 2013^[3] for oxyfluorfen. Then 20 μ l of each working standards were injected in to HPLC and the peak area was measured for linearity check study. Calibration curve was prepared by plotting the concentrations and peak area in x and y axis respectively.

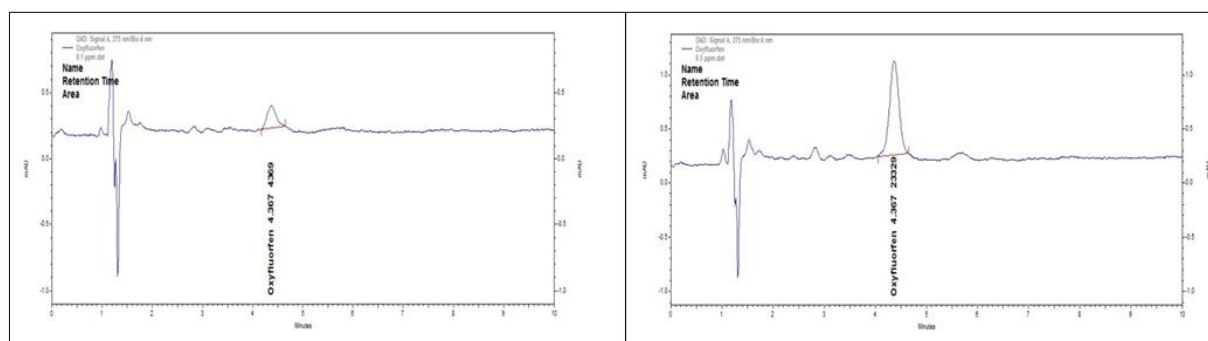


Fig 1: Chromatograms of Oxyfluorfen standards (0.1 and 0.5 mg/Lit)

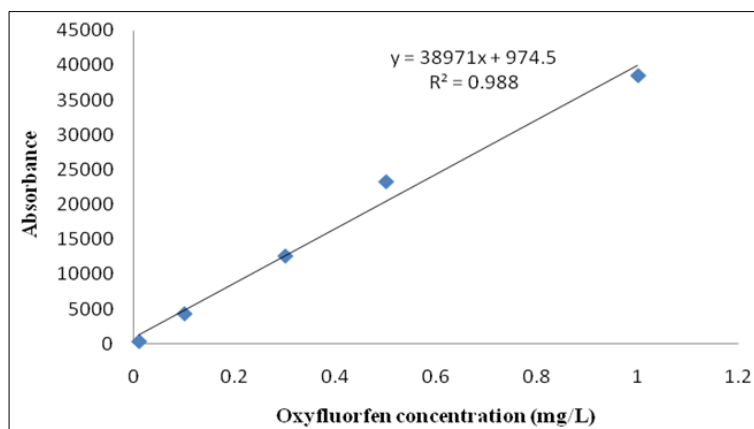


Fig 2: Calibration curve of Oxyfluorfen analytical standards

Results and Discussions

After the application of Oxyfluorfen, the residues were found to vary with the applied concentration (Table 1) from 0.320 to 0.527 and 0.011 to 0.024 mg/kg in soil and 0.308 to 0.525 and 0.013 to 0.028 mg/kg in soil for 200 and 400 g/ha at 0 and 45 DAHA of Oxyfluorfen, during 2018-19 and 2019-20, respectively. The Oxyfluorfen in soil declined sharply and persisted up to 45 days after application and became BDL at 60 DAHA. Oxyfluorfen was applied to the soil at two rates (200 and 400 g a.i./ha). Herbicide residues were monitored from 0 (2 hrs) days after herbicide application (DAHA) and up to 60 DAHA. On day 45, more than 90% of the applied oxyfluorfen dissipated from soil at both the rates of application and at 60 DAHA it was observed that the residue of oxyfluorfen was below detectable limit

Increase in doses of oxyfluorfen herbicide progressively increased the residue content in soil as observed by Sathya Priya *et al.* (2017)^[4]. An average field half life of oxyfluorfen

was 35 days (WSSA, 1994)^[11] and in the present study, lower half life of oxyfluorfen might be due to the enhanced photolysis of Oxyfluorfen. As the soil photolysis is the significant route of oxyfluorfen degradation as it proceeds via cleavage of the either bridge (Janaki *et al.*, 2012)^[1, 2] the formation of photodegradates is unlikely. The low solubility of oxyfluorfen in water (0.116 mgL⁻¹ at 20 °C) might have got retained it in soil surface and could have augmented the faster photochemical decomposition from soil. These results are in accordance with the findings of Janaki and Chinnusamy (2012)^[1, 2]. Soil organic matter and clay content might have also influenced the dissipation of Oxyfluorfen from soil. Solubility of oxyfluorfen in water and mobility in sandy clay loam soil was low and adsorption of oxyfluorfen to the soil was highly influenced by the soil organic carbon (Janaki *et al.*, 2013)^[1, 2]. At 60 DAHA, no oxyfluorfen residues could be detected in soil samples with higher doses of oxyfluorfen at 200 and 400 g a.i./ha.

Table 1(A): Persistence, half- lives and statistical parameters for oxyfluorfen dissipation in soil 2018-19

Dose	Days after oxyfluorfen application (mg/kg)								k	R ²	DT ₅₀ (days)
	0	3	7	10	15	30	45	60			
200 g /ha	0.320	0.243	0.162	0.074	0.033	0.018	0.011	BDL	0.102	0.903	6.83
400 g/ ha	0.527	0.414	0.268	0.154	0.092	0.039	0.024	BDL	0.089	0.957	8.75

Table 1(B): 2019-20

Doses	Days after oxyfluorfen application (mg/kg)								k	R ²	DT ₅₀ (days)
	0	3	7	10	15	30	45	60			
200 g /ha	0.308	0.265	0.178	0.080	0.047	0.022	0.013	BDL	0.081	0.912	9.55
400 g/ ha	0.525	0.410	0.314	0.248	0.124	0.065	0.028	BDL	0.064	0.977	10.65

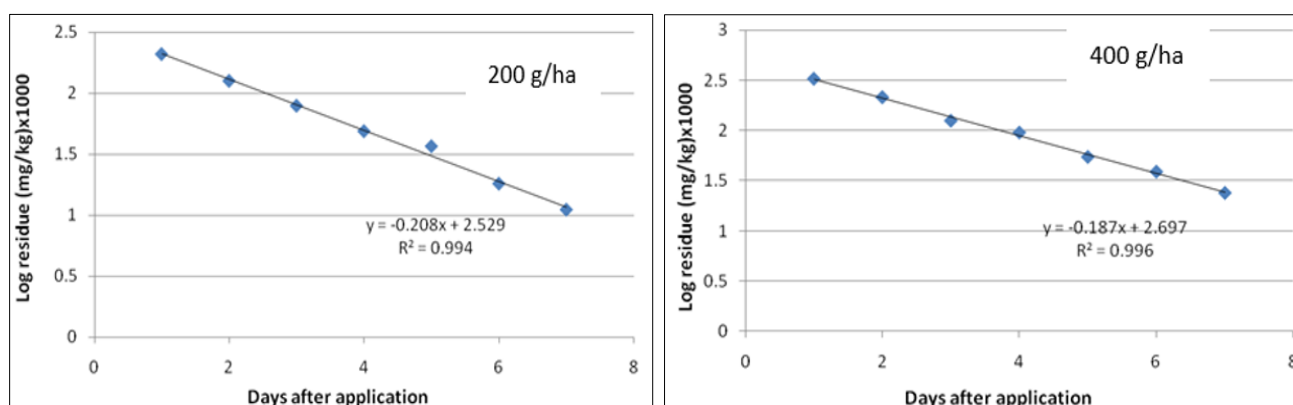


Fig 3: Dissipation kinetics of Oxyfluorfen in soil during 2018-19

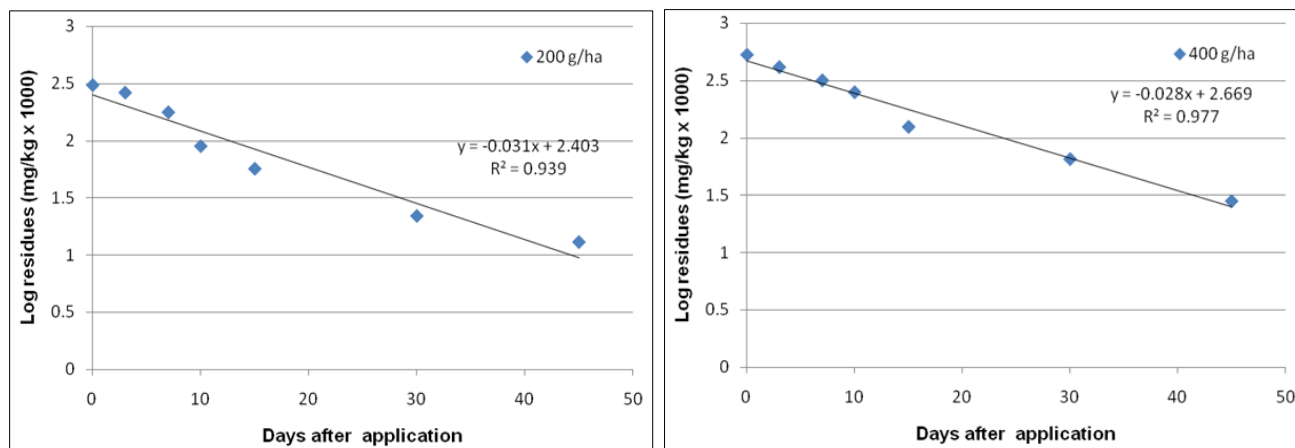


Fig 4: Dissipation kinetics of Oxyfluorfen in soil during 2019-20

The disappearance parameters for oxyfluorfen residues were calculated using first order reaction kinetics equation and found that its dissipation fit the first order degradation with the R^2 values of >0.93 at both the doses of 200 and 400 g/ha during 2018-19 and 2019-20, respectively (Fig3 and 4). Increase in concentration of application increased the half life of oxyfluorfen with DT_{50} values of 6.83 & 8.75 days and 9.55 & 10.65 days, at 200 and 400 g/ha applied treatments during 2018-19 and 2019-20, respectively (Fig 3 and 4). Similarly on the day of 50, more than 90% of the applied oxyfluorfen dissipated from soil at both the rates of application and at 70 DAHA it was observed that the residue of oxyfluorfen was below detectable limit (Janaki *et al.*, 2013) [3]. Further they observed that the rate of disappearance of Oxyfluorfen in soil followed first-order kinetics with the R^2 values of 0.98. The half-life values of oxyfluorfen calculated from the regression equation ranged between 8.9 to 12.5 days at the four rates of application.

Conclusion

Persistence and degradation of oxyfluorfen under laboratory study clearly showed that the residues of oxyfluorfen herbicide dissipated faster in soil. Oxyfluorfen residues dissipated with a half-life of 6.83 & 8.75 and 9.55 & 10.65 days in soil with 200 and 400 g/ha, during 2018-19 and 2019-20 respectively. It became BDL at 60 DAHA. Hence it is clear that the recommended dose of 200 g/ha can be followed for field application so as to have residue free environment.

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