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Field dissipation of pendimethalin and alachlor in sandy clay loam soil and its terminal residues in sunflower (*Helianthus annus L.*)

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Abstract: Field experiments were conducted with sunflower as a test crop during 2010-11 to study the dissipation kinetics and the persistence of pendimethalin and alachlor in sandy clay loam soil and its terminal residues in sunflower. Herbicides were applied at recommended and double the recommended dose along with control and the treatments were replicated thrice in randomized block design. The soil and plant samples collected at periodical intervals for herbicides residue determination using GC equipped with ECD detector. Results shows that the degradation of both the herbicides in soil was faster at higher dose of application than at the lower dose and the concentration decreased with the advancement in crop growth. While pendimethalin persisted in soil for 60 – 90 days, the alachlor persisted in soil for 30 - 45 days depending on the quantity of application. Degradation of both the herbicides in soil followed first order kinetics with the mean half life of 14.6 and 9.8 days respectively for pendimethalin and alachlor. Residues of these herbicides were below 0.001 mg/kg at the time of harvest in soil, sunflower seeds and stalks showed that these herbicides a can be safely used for the control of weeds in sunflower cultivation.

Keywords: Alachlor, Dissipation, Pendimethalin, Persistence, Sunflower

INTRODUCTION

Sunflower *(Helianthus annus* L.) is one of the important oil seeds crop in India and is the preferred edible oil by the consumers' world over and in India too due to health appeal. Sunflower is also a crop of choice for farmers due to its wider adaptability, high yield potential, shorter duration and profitability (Anonymous, 2010). Sunflower has a medium tolerance for weeds because of their lower compe-tition ability. Weed competition is mani-fested by a decrease of sunflower biomass and yield loss and depends on weed density, time of competition and duration, weed spectrum and other factors (Carranza *et al.,* 1995). The yield reduction due to weeds in sunflower is estimated to be as high as 81 per cent (Jaykumar *et al.,* 1988). Due to acute labour shortage and relatively tender nature of the sunflower, adopting the hand weeding or mechanical weeding, circumvented the chemical weed control as the only available option. However the herbicides available for chemical weed control are mostly pre emergence and also are relatively high in selectivity to sunflower. This is because most herbicides were primarily developed for weed control in economically more important crops (Gressel, 2002), and intensive precipitation after application of these herbicides can cause high phytotoxicity to sunflower, especially in sandy soils (Jursik *et al*., 2011). Hence it is essential to study the

field dissipation of pendimethalin and alachlor which are frequently used in Tamil Nadu to have good weed control and achieve higher yield of sunflower.
Alachlor [2-chloro-2-, 6-diethyl-N-(methoximethyl) acetanilide] is a chloro-acetamide herbicide widely used to control grass weeds in corn, soyabean, sugar-cane, and other crops. The primary factors that affect the degradation of acetanilide herbicides in soils are microbial activity and organic matter and clay contents (Weber and Peter, 1982). The dissipation of alachlor in soil was found to follow the first-order kinetics and the half-life in soil varied from 2.6 to 7.8 days (Ramesh and Maheswari, 2004; Shaner, 2012) under different cropped soils. In soil, alachlor degradation was found to increase with time and also increases with increase in soil pH (Sethi and Chopra, 1975). Janaki et al. (2012a) reported that the sorption of alachlor in soil is affected by the organic matter and clay content and was high in soil with high organic matter. Pendimethalin is grouped under dinitroaniline family with the field half lives of 60 and 44 days respectively (Vencill, 2002). Tsiropoulos and Lolas (2003) reported that the half life of pendimethalin varied from 43 and 62 days in the soil grown with cotton under drip and normal irrigated conditions. Degradation of pendimethalin was faster under anaerobic condition than aerobic condition and varies with soil moisture and temperature (Vencill, 2002).

Janaki *et al*. (2012b) found that the degradation of both alachlor and pendimethalin in soil depends on the intrinsic properties of the herbicides and soil properties with the half life of alachlor and pendimethalin ranged from 4.4 – 5.1 and 13.2 – 16.0 days respectively in sandy clay loam soils. In India, most literatures on these herbicides has been limited to laboratory dissipation studies and other field crops and other oilseeds (Janaki *et al*., 2009; 2012b; Sondhia, 2014) and only under north Indian subtropical humid ecosystem on wheat (Kulshrestha and Yaduraju, 1987), maize-wheat cropping system (Kulshrestha et al., 2000; Sondhia, 2014) and few literatures on microbial degradation (Singh and Kulshretha, 1991). Similar is the case with respect to alachlor behaviuor in soil (Janaki *et al*., 2009; Sondhia, 2014). In view of these facts, and the persistence of herbicide is correlated not only with climatic conditions, but also with management practices and soil physico-chemistry (Sondhia, 2013; Janaki et al., 2015), the behaviour of herbicides in subtropical semi arid agro climatic conditions need to be examined. Hence this study was carried out to scrutinize the field dissipation behavior of pendimethalin and alachlor in sandy clay loam and its terminal residues in sunflower crop.

MATERIALS AND METHODS

Field experiments were carried out at Eastern Block Farm of Tamil Nadu Agricultural University, Coimbatore, Tamil Nadu, India during *Rabi* season 2010-2011 in randomized block design with three replications. Field was prepared to fine tilth as needed for each crop and all agronomic and cultural practices were followed as recommended for each crop. Each treatment plot was of 5×4 m^2 in dimension and all four sides of the plots were protected by soil boundaries raised to a level of 40 cm height and 30 cm width. One meter distance was maintained between plots. Both the herbicides were applied as pre emergence at two levels (x- Recommended dose; 2x- Double the recommended dose) along with the Control (no herbicide application). Herbicides were sprayed using Knapsack sprayer with the spray volume of 500 lit of water ha^{-1}. Water alone was sprayed in control treatment to maintain the uniformity. Experimental fields soil were sandy clay loam (sand 32 %, clay 29 % and silt 24 % per cent) in texture and has the pH – 7.0, EC – 0.08 dSm^{-1}, organic carbon – 0.36 %, low in available nitrogen, medium in available phosphorus and high in available potassium.

Soil samples were collected at different intervals viz., 0, (2 hrs), 5, 10, 20, 30, 45, 60, 90 days after herbicide application and also at the time of crop harvest. About 500 kg of soil sample was collected randomly from each plot using a soil auger up to a depth of 15 cm from the surface. Pebbles and other unwanted materials were removed, the soil sample was homogenized thoroughly and about 250 g was sub sampled for the

analysis of herbicide residues. Collected samples were stored at -10 ^{0}C, processed and analyzed within seven days.

While alachlor was extracted from soil samples using acetonitrile, pendimethalin was extracted with methanol and the extracts were filtered and evaporated at 60°C to about 10 ml. The cleanup of all herbicide residues was done using anhydrous sodium sulphate / NaCl and florisil. Dried residues were re-dissolved in known volume of acetone / hexane to inject in to gas chromatograph (Janaki *et al.,* 2012b). Residues of all herbicides were determined using gas chromatograph equipped with electron capture detector (ECD). Separation of the compound was achieved using mega bore capillary column of 30 m × 0.53 mm, ID-BP1 0.5 µm following the instrumental conditions as suggested by Janaki *et al.* (2012b).

Different known concentrations of both herbicides (2.0, 1.0, 0.5, 0.1, 0.01 and 0.001 mg kg^{-1}) studied were prepared in acetone/ hexane by diluting the stock solution. 0.5 µl of standard solution was injected and the peak area measured. Validation of the method was performed in terms of recovery studies before analysis of unknown sample. The recovery study was conducted for all herbicides in soil. The average recovery and detection limits of all herbicides are shown in table 1. Degradation of herbicide was described using first order kinetics as given by Timme *et al.* (1986).

RESULTS AND DISCUSSION

Efficiency of the extraction methods of both the herbicides were validated through recovery studies and found that the overall recovery of both the herbicides were above 80 per cent and confirms the suitability of the extraction methods for the determination of pendimethalin and alachlor residues in soil and sunflower stalk and seeds. The average recoveries for each herbicide varied from 80-84 and 79-82 percent for pendimethalin and alachlor respectively (Table 1) across different matrices.

The initial concentration of both the herbicides in soil (2 hrs after their application) was varied with the quantity of application (Table 2). Generally higher rate of deposition was recorded under double the recommended rate of application and varied with the herbicides (Kulshrestha and Yaduraju, 1987). Initial deposition of different herbicides in soil was in the order of pendimethalin > alachlor and could be attributed to the rate of application (Janaki *et al*., 2012b). Further the difference in initial deposition could be attributed to the physical and chemical properties of the herbicides such as organic-carbon and mineral-surface sorption coefficients, aqueous solubility, soil dissipation half-life etc., and environment factors such as application rate, herbicide persistence and mobility, rainfall, topography, and climate (Lin *et al*., 1999, Shaner, 2012).

Table 1. Gas chromatographic conditions and recovery of herbicides from soil.

Herbicide molecules	Temperature conditions (^{0}C) Oven / Injection / Detector	Retention time (minutes)	Limit of detection (μg/g)	Average Recovery in soil (%)	Average Recovery in sunflower seeds (%)	Average Recovery in sunflower stalks (%)
Pendimethalin	185 - 220 /240/260	3.47	0.001	84	82	80
Alachlor	240/220/260	2.49	0.001	82	79	81

**Table 2**. Persistence (mg/kg) of herbicides in soil under sunflower.

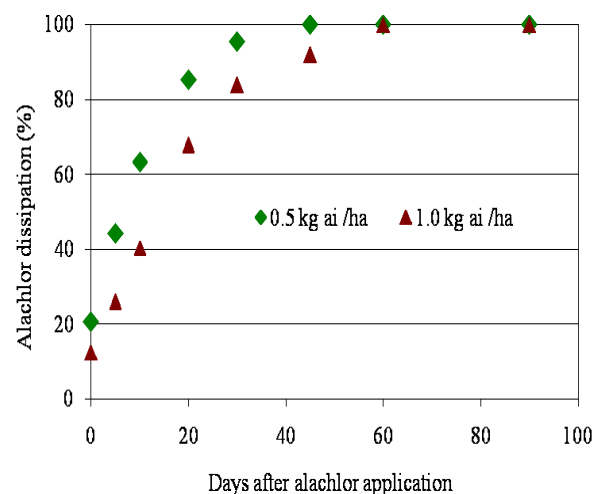| Days after herbicide application	Pendimethalin		Alachlor	
	1 kg /ha	2 kg /ha	0.5 kg /ha	1.0 kg /ha
0	0.924	2.200	0.397	0.876
5	0.718	1.870	0.279	0.741
10	0.572	1.541	0.184	0.597
20	0.328	0.866	0.074	0.323
30	0.208	0.568	0.023	0.161
45	0.126	0.282	BDL	0.081
60	0.078	0.145	BDL	BDL
90	BDL	0.042	BDL	BDL
At harvest	BDL	BDL	BDL	BDL

Table 3. Optimized first order field dissipation curves of herbicides under sunflower cropping as influenced by quantity of application.

Herbicides*	DT$_{50}$	Predicted equation	Goodness of fit
Pendimethalin @1 kg /ha	13.9	y = -0.009x + 0.677	R² = 0.772
Pendimethalin @ 2 kg /ha	15.4	y = -0.023x + 1.715	R² = 0.790
Alachlor @ 0.5 kg /ha	7.3	y = -0.006x + 0.285	R² = 0.753
Alachlor @ 1.0 kg /ha	12.3	y = -0.014x + 0.753	R² = 0.891

* x- Recommended dose; 2x – double the recommended dose
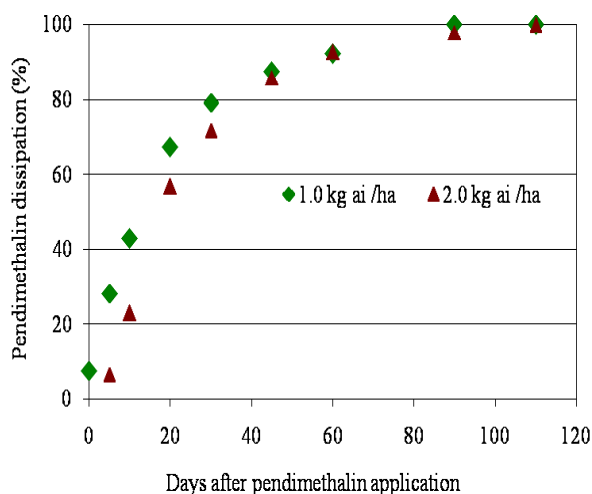
Fig. 1. *Field dissipation of pendimethalin in sandy clay loam soil under sunflower.*

Fig. 2. *Field dissipation of alachlor in sandy clay loam soil under sunflower.*

Persistence characteristics of both the herbicides are shown in table 2 and residues of them decreased consistently with the advancement of time. Application of pendimethalin at 1 kg ha^{-1} persisted in soil up to 60 days while up to 90 days at 2 kg ha^{-1} application rate (Table 2). This is in line with the findings of Arora and Tomar (2008) and Janaki *et al.* (2009) that the application of pendimethalin at 1.0 kg ha^{-1} to different rabi crops

persisted in soil up to 75 days after sowing and afterwards degraded completely leaving no toxic residue in post harvest soil. The residues of alachlor persisted in soil up to 30 and 45 days after application (Table 2) under 0.5 and 1.0 kg/ha applied plots respectively. Thereafter the residue concentration went down below detectable level. The dissipation of herbicides in soil followed first order kinetics and the corresponding

data fitting first order kinetics are given in table 3, Figs. 1 and 2. The correlation coefficient (r^2) derived from the regression lines lies between 0.753 and 0.891 and the best fit was observed for alachlor at the application of double the recommended dose. Pendimethalin dissipation followed biphasic pattern of degradation i.e. initial faster dissipation up to 20 days thereafter their dissipation becomes slow. This could be attributed to an equilibrium that was reached with this herbicide where soil adsorption had occurred and then desorption of the parent molecule over time (Patakioutas and Albanis, 2002). Similar biphasic pattern of pendimethalin degradation in soil under sunflower cropped field ie., initial rapid loss between 3 to 5 d after application and then a slower rate was reported by Shaner (2012) in Colorado. Faster dissipation of pendimethalin at later stages could be ascribed to the enhanced microbial degradation due to increased population after an initial lag phase (Singh and Kulashretha, (1991).

Half life of the herbicides increased with the increase in its applied concentration. The mean half life of initial concentration of herbicides studied in sandy clay loam was 14.6 and 9.8 days for pendimethalin and alachlor respectively (Table 2). Similar half-life 23-30 days for pendimethalin under field conditions was reported by Lee *et al.* (2000) and also found that its half life was not affected by the dose and rainfall treatment. Higher half life of pendimethalin when compared to alachlor could be attributed to the bounding of pendimethalin to soil organic matter and slow loss from soil rich in clay or organic matter (Kulshrestha and Yaduraju, 1987) besides it's immobility in soil (Vencill, 2002). Further the degradation of these herbicides in soil initially depends on the intrinsic properties of the herbicides, secondly on the soil properties and climatic conditions (Janaki *et al.,* 2012b; Shohba, 2014). Alachlor dissipated at a faster rate than pendimethalin which might be due to the faster microbial degradation of this herbicide in soil. It was found that the residues of these herbicides in the seeds and stalks of sunflower were below the detectable limit of 0.001 mg/kg.

The maximum residue limits (MRLs) of alachlor and pendimethalin on sunflower crop have not been established yet by EPA/FSSAI, whereas the MRL was set as 0.05 mg/kg on oilseeds by EFSA (2014 and 2015) and for soybean by FSSAI (2011). Under the present experimental conditions, the residues in crop produce at harvest were below the MRL's set by both FSSAI and EFSA for some oilseeds; consequently, the alachlor and pendimethalin at the present recommended application rates could be considered safe to food and environment.

Conclusion

It was concluded that the initial deposition of herbicides was influenced by the quantity of application and showed that the persistence decreased with the progression of crop growth and with the mean half life of 14.6 and 9.8 days respectively for pendimethalin and alachlor. However, the pendimethalin degradation followed biphasic pattern of degradation and persistence of both the herbicides followed first order reaction kinetics. These herbicides may be safely applied for the weed control in sunflower at recommended level, since the residues in soil, seeds and stalk were well below the MRL's besides establishing its safety to the succeeding crops.

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