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DISSIPATION OF ATRAZINE IN ALFISOLS AND SWEET CORN

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ABSTRACT

A field experiment was conducted in the College Farm, Rajendranagar, Hyderabad to study the persistence in soils and residual effects of atrazine in sweet corn during rainy season (*Kharif*) 2012 and 2013. Atrazine was applied as pre-emergence and post-emergence spray at two levels (1.0 and 2.0 kg/ha) and persistence was studied in soils (0, 10, 30, 45, 60 days after application, DAA, and harvest), maize grain/stover at harvest. Atrazine residue were determined using GC-NPD. In pre-emergence treatments, atrazine residues persisted in the soil upto 60 DAA at 1.0 and 2.0 kg/ha dose of application during both years. Atrazine residues concentration in the soil was lower in post-emergence treatments and residues persisted upto 45 DAA during two years at 1.0 kg and 2.0 kg/ ha application rates._Residues of atrazine in sweet corn grain and stover were below the detection during two years at two rates of application. Atrazine persistence insoil_followed first order kinetics with half-life varying from 26.45 days to 35.77 days. Atrazine can be safely applied to sweet corn as the grain and stover residues were below the MRL values.

INTRODUCTION

Maize is consumed in various forms like sweet corn, baby corn, pop corn, waxy corn, quality protein maize, high oil corn etc. Sweet corn (Zea mays var. saccharata) is type of maize with high sugar content and evolved due to naturally occurring recessive mutation in genes which control conversion of sugar to starch inside the endosperm of corn kernel (Rajeev kumar *et al.,* 2013). Weed management in sweet corn is an important issue in view of the short duration of the crop. Biotic stress on maize is one of the major constraints to achieve the attainable yield (Sandip *et al.,* 2013). Two year field study has clearly established the detrimental effect of weeds on growth of sweet corn, height, leaf area, aboveground biomass and phenological development which significantly resulted in yield reduction (Martin and John, 2009). Initial 25-30 DAS are considered to most critical period of weed competition in sweet corn.

Cultivation of sweet corn is gaining popularity especially in peri-urban areas and in regions surrounding Hyderabad city in view of the huge consumer demand. Grain corn being a traditional crop, farmers adoptsimilar weed management practices in both grain and sweet corn. Atrazine is the most widely used herbicide by the corn growers.Eventhough usage of atrazine as pre-emergence (PE) herbicide is most common among the maize growers of the state, usage of herbicide as post-emergence (PoE) spray at 20-30 DAS is also being practiced by most farmers in view of the non-availability of selective post-emergence herbicides. General dose adopted incase of post-emergence herbicide is also 1.0 kg a.i./ha. In grain corn, the usual time gap between the post-emergence spray and harvest of the crop is more than 90 days. However in sweet corn most of cultivated varieties/hybrids have a duration of 80 days, which considerably reduces the gap between the post-emergence spray and harvest of the crop. Residues of atrazine persist in the soil up to 45-60 days depending on the dose adopted and residues of atrazine were never detected in maize grain (AICRP, 2010). Data on persistence of atrazine in grain/ stover is important from food-chain entry point of view and residual life in soil is vital for in identifying suitable sequence crop after the harvest of sweet corn as the possible residue carryover of the atrazine in soil, may result in germination failure or poor establishment of the susceptible crop sown in sequence.

Atrazine is also one of the commonly detected compounds in groundwater (Jayachandra *et al.*,1994, Kanwar *et al.*, 1999). Understanding the fate and transport of herbicides within the soil profile and leaching from the bottom of the root zone to the groundwater aquifers help in developing better management options to reduce the contamination potential Baksh *et al.* (2004). Specific data on field level leaching of atrazine and potential for contamination of groundwater is also lacking under the present experimental conditions. With this background current experiment was initiated to study theleaching potential and persistence of atrazine in soil, stover and grain of sweet corn crop.

MATERIALS AND METHODS

Field Experiment

A field experiment was conducted in the College Farm, Rajendranagar, Hyderabad to study the residual effects of atrazine in sweet corn during rainy season (*Kharif*) 2013 and 2014at different locations in the same field with the following treatments viz., T1:Atrazine at recommended dose (1.0 kg/ha) as pre-emergence (PE), T2:Atrazine at recommended dose (1.0

kg /ha) as Post emergence (Po E), T3:Atrazine at double the recommended dose (2.0 kg /ha) as PE, T4:Atrazine at double the recommended dose (2.0 kg /ha) as PoE, T5:Control (no herbicide spray) T6:Hand weeding at 20 and 40 DAS. These treatments were replicated four times in the field.Pre-emergence treatments of atrazine were applied 24 hours after sowing of the crop and post-emergence sprays were applied at 22 DASduring both years.

Experimental soil was neutral in pH (7.05), non-saline (EC: 0.18 dS/m), medium in organic carbon content (0.56%). Available Nitrogen was 260 kg/ha, available P_2O_5 47 kg/ha and available K_2O (342 kg/ha).

Samples collection and preparation

Soil samples were collected at 0, 10, 30, 60 days after application (DAA) of atrazine and at harvest time from the maize field where atrazine were applied as pre-emergence application. In post-emergence atrazine application treatments, soil samples were collected at 0,10,30 DAA and at harvest (64 DAA). Soil samples were collected fromsurface (0-10 cm) and subsurface layers (10-20, 20-30, 30-60 and 60-90 cm layers)using a screw auger. Soil samples collected from different points for the same depth in a treatment were bulked together and representative sample was drawn from each replication. Soil samples were also collected from control and hand weeding treatments.Soil sampleswere air dried, homogenized, passed through 2 mm sieve and stored in sealed airtight polythene bag and storedin deep freezer (-20ºC) freezer.

Maize grain and stover samples were also collected from each replication at the time of harvest from different locations in the treatment plots. Samples were stored in deep freezer.

Residue analysis of atrazine

Atrazine residue extraction, clean-up and residue estimation was done according tho the procedure outlined by Sankaran*et al.* (1993). Soil sample (50 g) grain (20 g) in triplicate was extracted by shaking with 100 ml of acetone: hexane. The suspension was filtered through whatman No.1 and filtered on a Buchner funnel. The extract was taken in a separating funnel and washed twice with 100 mL of distilled water and the washings were discarded. For column chromatography, 1.5 cm (id) x 50 cm length glass columns were used. Five grams of florosil and 10 g of anhydrous sodium sulphate were used as sorbents. For eluting, acetone: hexane extract was applied on the top of the column and allowed to percolate. The elute was collected in a 250mL conical flask and evaporated to near dryness. The residue was dissolved in n-hexane (5 mL) for final determination. . One micro-liter was injected manually into injector for estimation of residues.

Residue estimation

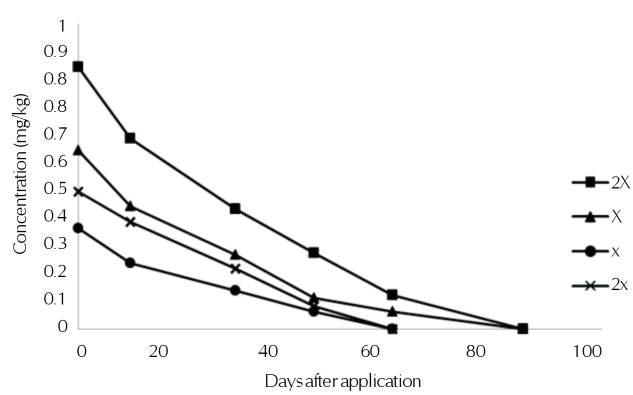
Atrazine residues were determined usinggas chromatograph with FTD (Flame Thermionic Detector) containing a split injector (Shimadzu GC 2010-FTD). Mega-bore capillary column was used in GC for separation of the atrazine (AB-5 Capillary Column, length 30 m,I D 0.53μm, 1.5 μm thick coating of 5% phenyl polysiloxane).Oven, injector and detector were maintained at 240ºC, 250ºC and 270ºC, respectively.Carrier gas used was nitrogen with a flowrate of 3.50 mL/min. Hydrogen and pure air were used to maintain the flame in the FTD. All the gases used in the study were 99.999% pure. Analytical grade atrazine (> 98% purity) was obtained from were purchased from Dr. EhhrenstorfergmbH chemicals, Germany. All solvents and reagents used were of GC grade.

Validity,sensitivity, repeatability, reproducibility and recoveryof the method was confirmed by applying the standard addition technique.In this method, several different concentrations of the standard solution of atrazine(0.05, 0.1, 0.25, 0.5, 1.0 mg/kgto soil and 0.025, 0.05 and 0.1 mg/kgfor corn grain and stover) were added to thesample in triplicate and the above-mentioned procedure was used for extraction, clean-up and estimation. Limit of quantification(LOQ) for atrazine was 0.025 mg kg^{-1} for grain, plant and soil.Mean recoveries were 86.3-89.2 percent and 91.2-94.6 percent from fortified grain / plant and soil for atrazine, respectively. Retention time for atrazine was 9.58 min.

RESULTS AND DISCUSSION

Pre-emergence application (Table 1 a and b)

In recommended dose treatments, after 2 hours of application of herbicide, the soil sample contained 0.652 and 0.524 mg/ kg atrazine residues in surface soil samples during 2012 and 2013 years respectively.Atrazine residues persisted in the soil upto 60 DAA during both the years in the surface samples. These findings are in concurrence with the persistence reported by Amabile *et al.,* 2006 and AICRP, 2009). At 0 DAA, leaching of herbicide into deeper layers was not observed. However, at 10 DAA residues could be detected in 10-20 and 20-30 cm layers, which indicated relative mobility of atrazine in soil (Fashola and Oyedunmade, 2007). Atrazine residues could be detected in 10-20 cm layer at 30 DAA during 2012 and even in 20-30 cm layer during 2013. Residues could not be detected in layers beyond 20-30 cm during both



Dissipation trends of the atrazine at different doses of application at different times of crop was as following.

Pre-emergence- Double dose (2.0 kg/ha) $y = -0.009x + 0.753$ $R^2 = 0.942$ ......(1)

Pre-emergence- recommended dose (1.0 kg/ha) $y = -0.006x + 0.491$ $R^2 = 0.895$ ......(2)

Post-emergence- Double dose (2.0 kg/ha) $y = -0.007x + 0.436$ $R^2 = 0.992$ ......(3)

Post-emergence- recommended dose (1.0 kg/ha) $y = -0.005x + 0.298$ $R^2 = 0.964$ ......(4)

Figure 1: Dissipation trend of atrazine

Table 1a: Residue (mg/kg) of Atrazine in Soil samples collected at different depths at different days after Pre-emergence application

Days after application	2012					2013				
	Depth of samples (cm)									
	0-10	10-20	20-30	30-60	60-90	0-10	10-20	20-30	30-60	60-90
0	0.652	BDL	BDL	BDL	BDL	0.524	BDL	BDL	BDL	BDL
10	0.411	0.091	0.055	BDL	BDL	0.395	0.078	0.049	BDL	BDL
30	0.264	0.054	BDL	BDL	BDL	0.221	0.042	0.027	BDL	BDL
45	0.112	BDL	BDL	BDL	BDL	0.091	BDL	BDL	BDL	BDL
60	0.071	BDL	BDL	BDL	BDL	0.046	BDL	BDL	BDL	BDL
Harvest (86)	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL

(BDL : Below Detection Limit)

Table 1b: Double the recommended dose [2X dose 2.0 kg/ha)]

Days after application	2012					2013				
	Depth of samples (cm)									
	0-10	10-20	20-30	30-60	60-90	0-10	10-20	20-30	30-60	60-90
0	0.912	BDL	BDL	BDL	BDL	0.811	BDL	BDL	BDL	BDL
10	0.648	0.153	0.051	BDL	BDL	0.601	0.134	0.051	BDL	BDL
30	0.402	0.082	0.061	BDL	BDL	0.386	0.067	0.061	BDL	BDL
45	0.275	0.052	BDL	BDL	BDL	0.224	0.031	BDL	BDL	BDL
60	0.112	BDL	BDL	BDL	BDL	0.110	BDL	BDL	BDL	BDL
Harvest (86)	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL

(BDL : Below Detection Limit)

Table 2a: Residue (mg/kg) of Atrazine in Soil samples collected at different depths at different days after Post-emergence application

Days after application	2012					2013				
	Depth of samples (cm)									
	0-10	10-20	20-30	30-60	60-90	0-10	10-20	20-30	30-60	60-90
0 (22 DAS)	0.347	BDL	BDL	BDL	BDL	0.316	BDL	BDL	BDL	BDL
10 (32 DAS)	0.213	0.062	BDL	BDL	BDL	0.221	0.048	BDL	BDL	BDL
30 (52 DAS)	0.123	0.054	BDL	BDL	BDL	0.128	0.049	BDL	BDL	BDL
45 (67 DAS)	0.058	BDL	BDL	BDL	BDL	0.058	BDL	BDL	BDL	BDL
Harvest (86DAS)	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL

(BDL : Below Detection Limit)

Table 2b: Double the recommended dose [2X dose 2.0 kg/ha)]

Days after application	2012					2013				
	Depth of samples (cm)									
	0-10	10-20	20-30	30-60	60-90	0-10	10-20	20-30	30-60	60-90
0 (22 DAS)	0.481	BDL	BDL	BDL	BDL	0.422	BDL	BDL	BDL	BDL
10 (32 DAS)	0.348	0.062	BDL	BDL	BDL	0.358	0.062	BDL	BDL	BDL
30 (52 DAS)	0.213	0.051	BDL	BDL	BDL	0.187	0.048	BDL	BDL	BDL
45 (67 DAS)	0.087	BDL	BDL	BDL	BDL	0.067	BDL	BDL	BDL	BDL
Harvest (86DAS)	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL

(BDL : Below Detection Limit)

years. Similar results were reported by Anna *et al.* (2008) in sandy clay loam soils.

Atrazine residues persisted in the soil upto 60 DAA in 2X (Double the recommended dose) treatments also during both the years (AICRP, 2010). With increase in dose of application the soil residue concentration in the surface and sub-surface layers increased during both years. Leaching atrazine could be detected upto 20-30 cm layer during two years and the leached herbicide could be detected even upto 45DAA in 20-30 cm layer.No residues of atrazine could be detected in soil at the time of harvest in X and 2X doses during both the years. During both the years atrazine residues could not be detected in the soils, grain and plant samples at the time of harvest of the sweet corn crop.

Post-emergence application (Table 2 a and b)

In post-emergence treatments of atrazine the residue levels observed in the surface soil samples were lower than the pre-emergence treatments owing to the foliar interception of the weeds and crop plants. In the recommended dose treatments, the 0 day residues were 0.347and 0.316 mg/kg during 2012 and 2013 respectively and the residue persisted in the soil up 45 DAA during both years. Leaching of residues could be observed upto 10-20 cm depth. Similar persistence of atrazine was also reported by Syamsuddin *et al.* (2014).

With the application of double the recommended rate of application atrazine, the initial residues in top 10 cm layer of the soil were higher than those observed in X dose. In this case also herbicide persistence in the soil could be detected upto 45 DAA and leached residues could be detected in 10-30 cm layer of the soil.

At harvest stage of the crop (85 DAS) the residues recorded in soil samples, plant samples and grain samples in both the doses applied in the surface as well as deeper layers of soil were below the detection limit.

Dissipation trends of atrazine in soil

Dissipation of the herbicide in soil when the herbicide was applied at different doses were applied is presented in figure. Different curves of fit were tested to predict the dissipation behavior of the herbicide. Among the models tested (Linear, polynomial, logarithmic and exponential) the linear model was found to give better fit for field dissipation of the atrazine in the recommended and double the recommended levels of application.

Using the above exponential equations (1 to 4) the half- life (DT_{50} *i.e.* time taken, in days, for 50 % dissipation of the initial detected amount) were calculated for different levels of atrazine applied at different times.The DT_{50} for pre-emergence application was 35.77 days and 32.83 days in X and 2X levels of atrazine application. Where as in post-emergence application the atrazine half-life was 30.03 and 26.45 days, respectively.Similar half life of atrazine was reported by Swarcewicz and Gregorczyk (2013). The progressive reduction in half life with lowering levels initial residues of atrazine in soil indicate the substrate driven dissipation in soil which classified as first order reaction.

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