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Degradation Pattern and Residues of Atrazine in Maize under Long Term Conservation Agriculture

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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ABSTRACT

Field experiment was conducted at Eastern block farm, Tamil Nadu Agricultural University 11°29"N latitude and 77° 08"E longitude with an altitude of 426.7M above MSL with maize to study the degradation, persistence and residues of atrazine under long term conservation agriculture system. The treatments constituted atrazine 1.0 kg ha^{-1} on 3 DAS and atrazine 1.0 kg ha^{-1} on 3DAS +Hand weeding on 45^{th} day under different conservation tillage practices. Degradation, persistence and residue analysis were carried out for atrazine using HPLC. Residues of atrazine was analyzed at different periods *viz*., 0,15,30,45,60,75 and 90 days after herbicide application and at harvest and the results revealed that degradation of atrazine was found to follow first order reaction kinetics (R^2>

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0.94) with the half life of 13.7–16.2 days irrespective of tillage practices and weed management methods. The recommended rate of atrazine @1.0 kgha^{-1} recorded terminal residues below detectable limit of <0.01 mg kg^{-1} in soil and plant parts of maize.

Keywords: Maize; conservation tillage; atrazine; degradation; persistence; residue.

1. INTRODUCTION

Maize (*Zea mays* L.) is one of the most important cereal crops in the world agricultural economy used both as a food and fodder crop. It is a miracle crop with very high yield potential. The productivity of maize largely is dependent upon its weed and nutrient management. It is very susceptible to the weed infestation. Atrazine is in a group of human-made systemic herbicides called triazines. It is used for broadleaf weeds both before and after they sprout. It is also used on some grassy weeds. Atrazine interferes with photosynthesis in some broadleaf plants and grasses. Atrazine is almost non-volatile and its half-life in neutral condition is about 200 days but varies from 4-57 weeks (McCormick and Hiltbold, 1966) depending on various environmental factors like pH, moisture content, temperature and microbial activity (Armstrong, et al., 1967; Frank and Sirons, 1985; Nair et al., 1993). "In agricultural environments, the pathways of atrazine presence and removal include plant absorption, soil absorption, microbial degradation, and chemical hydrolysis, However, a portion of atrazine persists and diffuses into the surrounding environment, potentially contaminating soils, sediments, plantations, pastures, water reservoirs, and groundwater. atrazine undergoes a series of environmental behaviors after entering the environment, including hydrolysis, volatilization, sorption-desorption, transformation, degradation, leaching, runoff and bioaccumulation"(Deng et al., 2024). Shrinivas et al. (2014) reported that "combined application of atrazine (50 %) + pendimethalin (50%), showed best control of all the grasses, sedges and broad leaved weeds for long time without any phytotoxic effect. It was well observed from the data that, application of herbicides showed lower weeds than hand weeding twice and farmers practice indicating the efficiency of the herbicides in controlling weeds". Channabasavanna et al. (2015) reported that "tank mix application of atrazine 50 WP @ 625 g a.i. ha^{-1} + pendimethalin 30 EC @ 750 g a.i ha^{-1} resulted in effective control of grass, broad leaved and sedge weeds".

"Conservation agriculture is a sustainable farming that reduces soil disturbance, keeps the soil covered, and uses different crop rotations" (Hobbs et al., 2008). "It helps to improve soil health and crop productivity and reduces environmental impacts. Weed management is crucial for obtaining profitable yields in reduced tillage system and achieving satisfactory weed control requires intensive management. Tillage practices were found to modify significantly pesticide degradation in soil, but in contrasted ways according to studies. For example, in no-tillage, vetch residues accelerated the degradation of metolachlor from 1.5 to 3 times, but had no effect on the degradation of atrazine" (Teasdale et al., 2003). "The nature and decomposition degree of crop residues both influence interception and retention of pesticides. In combination with other weed management practices, residues mulching prevents germination of weed seeds by blocking the light required for weed seeds germination or inhibits weeds growth due to its allelopathic effect" (Teasdale and Mohler, 2000).

Once the herbicides are added to the soil, besides decomposition and physical removal, a portion of them may be taken up by the plant and accumulated in the edible parts. The residue accumulation should not exceed the maximum residue limit (MRL) prescribed by the National and International standards. The information on the degradation of atrazine in maize under conservation agriculture is limited. Hence, the present study on the degradation and residues of atrazine in maize was carried out.

2. MATERIALS AND METHODS

Maize - sunflower cropping system was followed from 2016 as a long term experiment to study the herbicidal weed management in conservation tillage practices. In this study a field experiment was conducted with maize during kharif 2019 at field no.37 Eastern Block farm of Tamil Nadu Agricultural Uuniversity, Coimbatore at 11°29"N latitude and 77° 08"E longitude with an altitude of 426.7 M above MSL The experimental soil is sandy clay loam with a pH of 7.81 and EC 1.48 dSm^{-1}. The experiment was conducted in a split plot design with 3 replications. The treatments were as follows.

2.1 Treatment Details

	Rabi 2018 (sunflower) Previous crop	Kharif 2019 (Maize)
T_1	Conventional tillage	Conventional tillage
T_2	Conventional tillage	Zero tillage
T_3	Zero tillage + Residue	Zero tillage
T_4	Zero tillage	Zero tillage + Residue
T_5	Zero tillage + Residue	Zero tillage + Residue

Sub plot (Weed management practices)	
W_1	Recommended PE Atrazine 1.0 kg/ha
W_2	PE Atrazine 1.0 kg/ha + HW on 45 DAS
W_3	Unweeded check

During Kharif 2019, maize (COHM6) was grown as test crop which received atrazine as pre emergence herbicide to control weeds. Soil and plant samples were collected from the herbicide applied and hand weeding plots on 0,15,30,45,60,75 days after herbicide application and subjected to atrazine residue analysis to find out the persistence of herbicides in soil and to study the terminal residues as influenced by the tillage practices, soil, maize grain and straw at harvest.

2.2 Residue Extraction

"The 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 atrazine residue was portioned with 30 ml of 1% NaCl and 50 ml of hexane. The upper organic layer (hexane fraction) 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 atrazine compounds were dissolved in 2 ml acetonitrile HPLC grade solvent for HPLC determination with the injection volume of 20 µl using autosampler" (Bharathi et al. 2020).

2.3 HPLC Parameters for Atrazine Detection

i)	Column	:	Agilent Eclipse C18, 4.6 x 150 mm, 5 µm
ii)	Mobile phase	:	Acetonitrile:MilliQ-Water (80:20 % v/v)
iii)	Flow rate	:	0.8mL min^{-1}
iv)	Detector	:	Photo Diode Array Detector
	Parameters		
v)	Wavelength (λ_{max})	:	221 nm
vii)	Injection volume	:	20 µl
viii)	Retention time	:	3.29 ± 0.2 min
ix)	LOD	:	0.01 mg /kg
x)	LOQ	:	0.05 mg/kg

2.4 Calculation

The amount of atrazine in the sample was calculated as given below (Janaki et al.,2012):

$$Residue\ in\ ppm\ (mg/kg) = \frac{A_1\ x\ C\ x\ V_1}{A_2\ x\ W}\ x\ R_f$$

Where,

A_1 = Area of compound from sample, in chromatogram
A_2 = Area of compound from standard, in chromatogram
V_1 = Total volume of sample in ml
C = Concentration of analytical standard (96.55%) in ppm
W = Weight of the sample in g
R_f = Recovery factor

Analytical standard of different concentration was used to study the linearity of atrazine. In this study a calibration curve was prepared by taking the areas corresponding to different concentrations of analytical standard (0.01 to1.0 mg L^{-1}). Before analysing the unknown samples, recovery studies were carried out to establish the reliability of the analytical method employed for the present study. The blank soil and plant samples were fortified with known concentrations of atrazine standard that ranged from 0.05 to 0.5mgL^{-1} and fortified matrices were subjected to extraction and determination.

3. RESULTS AND DISCUSSION

The instrumental conditions presented above were followed for the determination of atrazine from different matrices. The LOD of atrazine molecule was found to be 0.05 mg/kg and resolved at 3.29 min under the optimized HPLC conditions.

3.1 Standard Calibration of Atrazine

The chromatogram of atrazine standard as determined by HPLC-DAD was sketched in Fig. 1. By plotting peak areas and concentration on X and Y-axis respectively, the equation of calibration graph for atrazine was represented in (Fig. 2) within range of 0.05 to 0.5 mg L^{-1}.

3.2 Recovery Studies of Atrazine

The recovery studies of atrazine carried out in blank soil, maize grain and straw. The range of atrazine fortified were between 0.05 and 1.0 mg kg^{-1}. The average numerical value of recovery percentage of soil was 90.9% among different concentrations (Table 1). Atrazine recovery detected from maize plant parts and mean recovery from maize grain and straw were 85.7 and 87.8 per cent at spiked concentrations from 0.05 to 0.50 mg kg^{-1}.

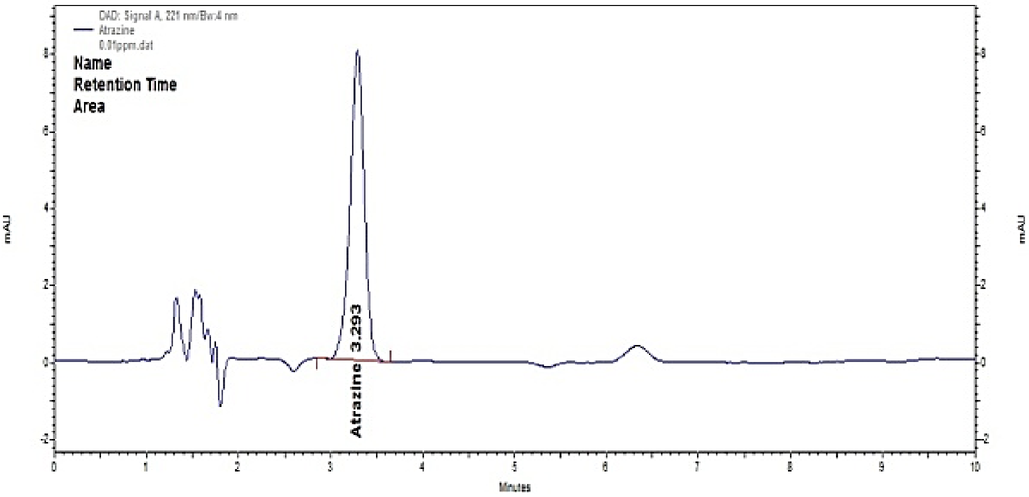

Fig. 1. Chromatograms of atrazine (0.01mg/Lit) standards

Table 1. Recovery of atrazine in field soil and plant parts

Matrix	Concentration (ppm)	Amount recovered	Recovery percentage	Average
Field soil	0.05	0.046	92.0	
	0.10	0.089	89.0	
	0.50	0.458	91.6	90.9
Grain	0.05	0.040	80.0	
	0.10	0.085	85.0	
	0.50	0.461	92.2	85.7
Straw	0.05	0.042	84.0	
	0.10	0.091	91.0	
	0.50	0.442	88.4	87.8

Average of three replicates

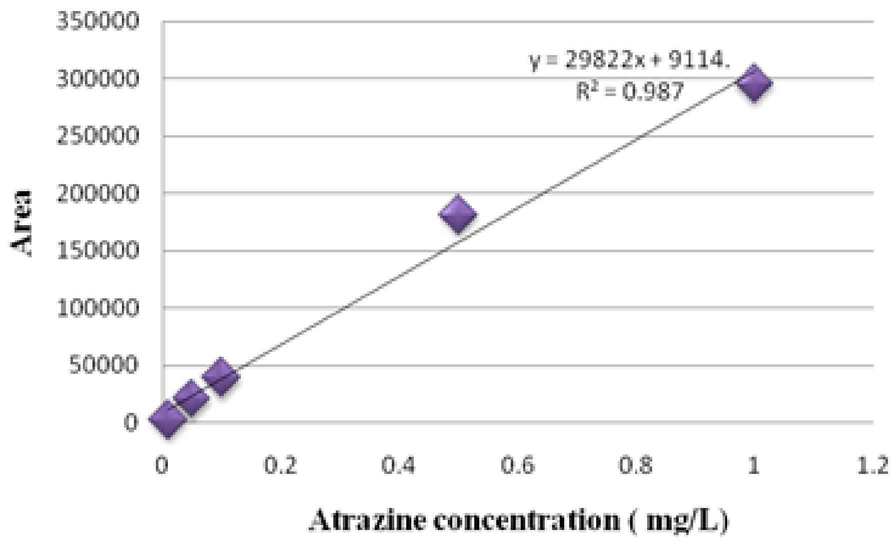

Fig. 2. Standard graph of atrazine determined by HPLC

Table 2. Influence of conservation tillage and weed management practices on residues of atrazine (mg/kg) in soil with maize (kharif'19) in maize –sunflower system

Treatments	W_1 (Atrazine @ 0.5 kg/ha)						
	0 day	**15 day**	**30 day**	**45 day**	**60 day**	**75 day**	**90 day**
T_1	0.280	0.156	0.090	0.022	0.018	0.010	BDL
T_2	0.294	0.163	0.095	0.024	0.020	0.014	BDL
T_3	0.245	0.134	0.072	0.022	0.017	0.012	BDL
T_4	0.259	0.112	0.061	0.019	0.014	0.012	BDL
T_5	0.266	0.108	0.053	0.020	0.012	0.011	BDL
W_2 (Atrazine 0.5 kg/ha + HW on 45 DAS)							
T_1	0.272	0.162	0.075	0.024	0.018	0.012	BDL
T_2	0.283	0.177	0.091	0.028	0.019	0.010	BDL
T_3	0.259	0.132	0.065	0.027	0.015	0.013	BDL
T_4	0.281	0.112	0.038	0.021	0.011	0.011	BDL
T_5	0.278	0.109	0.049	0.029	0.018	0.011	BDL

BDL-Below detectable limit (0.01 mg/kg)

"Degradation of atrazine were analyzed at different periods *viz*., 0,15,30,45,60,75 and 90 days after herbicide application and the results are given in Table 2. The atrazine persisted up to 75 days after herbicide application. The dissipation of atrazine was found to follow first order reaction kinetics (R^2>0.94) irrespective of tillage practices under both the weed control methods with the half life of 13.7–16.2 days. Irrespective of tillage practices and weed management methods, >80 % of atrazine dissipated in 45 days. Similar results were reported by Ram Prakash and Madhavi (2014) who found initial concentration of atrazine in soil was 0.541-0.602 mg kg^{-1} which reduced to 80-88.7% at 45 days" (Bharathi et al. 2020). Similarly, degradation of pendimethalin and metolachlor in sunflower and soybean followed first order reaction kinetics (Janaki et al., 2015).

Residue analyses showed that the terminal residues of atrazine in soil, maize grain and straw from different plots were below 0.01 mg/kg irrespective of the tillage management practices followed for weed control. The findings are in accordance with the results of Tandon et al. (2015) who reported that, "when atrazine was sprayed before emergence, the atrazine in corn kernels, soil and straw during harvest was less than 0.005 mg kg^{-1}". Cao *et.al*. (2023) studied a method for simultaneous determination of atrazine in fresh corn, corn kernels, and corn straw was established based on modified QuEChERS pre-treatment and high-performance liquid chromatography–tandem mass spectrometry (HPLC–MS/MS) and the results revealed that the terminal residues of atrazine in corn kernels, and atrazine was below the LOQ

(0.01 mg kg^{-1}) and 0.05 mg kg^{-1} in maize grain and straw (Janaki et al., 2012). Babu et al (2015) also reported oxyfluorfen and Imazethapyr residues in groundnut kernel were BDL (0.005 mg kg^{-1}). Conversely, atrazine pollution detrimentally affects soil ecosystems, resulting in reduced microbial activity and disrupted nutrient cycling (Hu et al., 2023; Gonçalves et al. (2024). Furthermore, it has the potential to accumulate in plants, posing risks to crop productivity. Janaki *et.al*. (2012) concluded from the results that “the longer persistence of atrazine can be expected at higher dose of application. In addition to this, the bioaccumulation of atrazine in soil was significant in terms of continuous application, which needs remediation”. “Among various remediation technologies, the combination of microbial remediation and phytoremediation for atrazine-contaminated soil and sediment has wide application prospects” (Chang et al., 2022).

4. CONCLUSION

To conclude, persistence studies of atrazine showed that persistence of atrazine in soil was up to 75 days after herbicide application with a half-life that ranged between 13.7 – 16.2 days. The degradation followed 1^{st}order kinetics for atrazine. Recommended rate of atrazine@1.0 kg ha^{-1} recorded terminal residues below detectable limit of <0.01 mg kg $^{-1}$ in soil and maize plant parts of grain and straw.

DISCLAIMER (ARTIFICIAL INTELLIGENCE)

Author(s) hereby declare that NO generative AI technologies such as Large Language Models (ChatGPT, COPILOT, etc) and text-to-image generators have been used during writing or editing of this manuscript.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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