Madras Agric. J., 99 (7-9): 533-537, September 2012
https://doi.org/10.29321/MAJ.10.100133

Field Persistence of Repeated Use of Atrazine in Sandy Clay Loam Soil under Maize

P. Janaki*, S. Meena, C. Chinnusamy, P. Murali Arthanari and K. Nalini
Department of Agronomy,
Tamil Nadu Agricultural University, Coimbatore - 641 003

Field experiments were conducted with maize as a test crop during 2006-2009 to study the effect of atrazine on its persistence and residue in soil and crop produce as influenced by the quantity of application and seasons. The treatments imposed were control, 0.5 and 1.0 kg ai of atrazine ha^{-1} and were replicated thrice in randomized block design. For residue analysis, the soil samples were collected at periodical intervals from 0 day to harvest and the crop produce were also sampled at post harvest. The atrazine was determined using GC equipped with FID detector. Persistence of atrazine in soil showed a gradual degradation with advancement in crop growth. The application of atrazine at recommended dose left no residue in the soil whereas the application of atrazine at double the recommended dose recorded 0.056 ppm of atrazine residue in the post harvest soil. Pooled data showed that the dissipation of atrazine was biphasic in nature and the degradation was faster at higher dose of application than at the lower dose. Degradation of atrazine in soil followed first order kinetics and the mean half life of atrazine was 21.54 days. Persistence of atrazine was also influenced by the season and years of application.

Key words: Atrazine, persistence, maize, half life, seasonal influence

Atrazine is one of the most widely used herbicides in Indian agriculture since the late 1990s for the pre- and post emergent control of annual grasses and broadleaf weeds in crops such as maize, sorghum, sweet corn, millet and sugarcane. Atrazine is a selective systemic herbicide, absorbed by roots and leaves, translocated acropetally in the xylem and it accumulates in the apical meristems. It is physiologically selective for maize, sorghum species that rapidly decompounds.

Atrazine (2-chloro-4-ethylamino-6-isopropy lamino-1,3,5-triazine), a chlorinated s-triazine group of herbicide, has very high environmental significance due to its extensive use, long half-life and various toxic properties (Ghosh and Philip, 2006). Atrazine is almost non-volatile and its half-life in neutral condition is about 200 days but varies from 4-57 weeks (Mc-Cormick 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). The high mobility of atrazine in soil (Tindall and Vencill, 1995) and its potential contamination of ground waters (Ritter *et al*., 1994) may represent a serious human health hazard because of the potential carcinogenic effects of s-triazines (Biradar and Rayburn, 1995). The maize metabolizes the atrazine into hydroxyl-atrazine and conjugated amino acids (Ostafe, 2006). When sprayed on maize, it is quickly transformed by the plant into its hydroxyl metabolites. The replacement of the chlorine atom by a hydroxyl group results in non phytotoxic metabolites and is the explanation for the tolerance of maize to atrazine (Marcacci, 2004).

Numerous studies on the residue, persistence of atrazine in sugarcane grown soils and crop produce have been studied. However, studies in maize grown soil are lacking. Hence, this study was conducted on the persistence and residue of atrazine in maize grown soils and crop produce.

Materials and Methods

Field Experiments

Field experiments were carried out at Eastern Block Farm of Tamil Nadu Agricultural University, Coimbatore, Tamil Nadu, India during *kharif* and *rabi* seasons' from 2006 to 2009 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 maize crop. Test genotype grown was Co1 during all the seasons except *rabi*, 2006 when COMH 5 was grown as a test crop. Each treatment plot was of 5 x 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. Atrazine was applied as pre

*Corresponding author email: janakibalamurugan@rediffmail.com

emergence at two levels (x- Recommended dose; 2x- Double the recommended dose) along with the Control (no herbicide application). Atrazine was sprayed using Knapsack sprayer with the spray volume of 450 lit of water / ha. Water alone was sprayed in control treatment to maintain the uniformity. Experiment was conducted in same field every season and year. Experimental field soil was sandy clay loam in texture, pH – 7.77, EC – 0.45 dS m^{-1}, organic carbon – 0.33 %, low in available nitrogen (137, 9.0 and 704 kg ha^{-1}), medium in available phosphorus (9.0 kg ha^{-1}) and high in available potassium (704 kg ha^{-1}).

Soil Sampling

Soil samples were collected at different intervals from 0 day (2 hr) after herbicide application to harvest of the crop. About 1 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 mixed thoroughly and 250 g was sub sampled for the analysis of atrazine residue. Collected samples were stored at -10^0C, processed and analyzed within seven days.

Analytical Techniques

For atrazine analysis, soil samples were extracted with acetonitrile, filtered and cleaned up through anhydrous sodium sulphate in chromato graphic column and evaporated over water bath. Finally moistened residue was mixed with known quantity of hexane. The extracted sample was injected in gas chromatograph equipped with flame ionization detector.

Recovery and Detection limits

Different known concentrations of atrazine (2.0, 1.0, 0.5, 0.1, 0.01 and 0.001 mg kg^{-1}) were prepared in hexane by diluting the stock solution. Standard solution of 0.5 µl was injected and the peak area was measured. Validation of the method was performed in terms of recovery studies before analysis of unknown sample. The average recovery of atrazine was 91, 88 and 83 per cent for respectively for soil, grain and straw of rice. Limit of detection (LOD) and limit of quantification (LOQ) of atrazine studied in different matrices was 0.01 and 0.06 ppm, respectively.

Dissipation Coefficients

Degradation of herbicide was described using first order kinetics and in this study also the following first order kinetics equation was used to describe the field dissipation.

$dA/dt = Ka' \rightarrow A(t) = A_o \exp(kt)$

Where 'A' is herbicide amount, 't' is time, 'A_o' is the initial amount and 'k' is degradation coefficient. The half life of the herbicide molecules were determined from the equation given below using the highest concentration.

$T_{1/2} = 0.6931 / K$

Results and Discussion

Initial deposition of atrazine in soil

Initial deposition of atrazine in soil (2 hrs after application) differed with the applied quantity and seasons (Figure 1). It was observed that the quantity

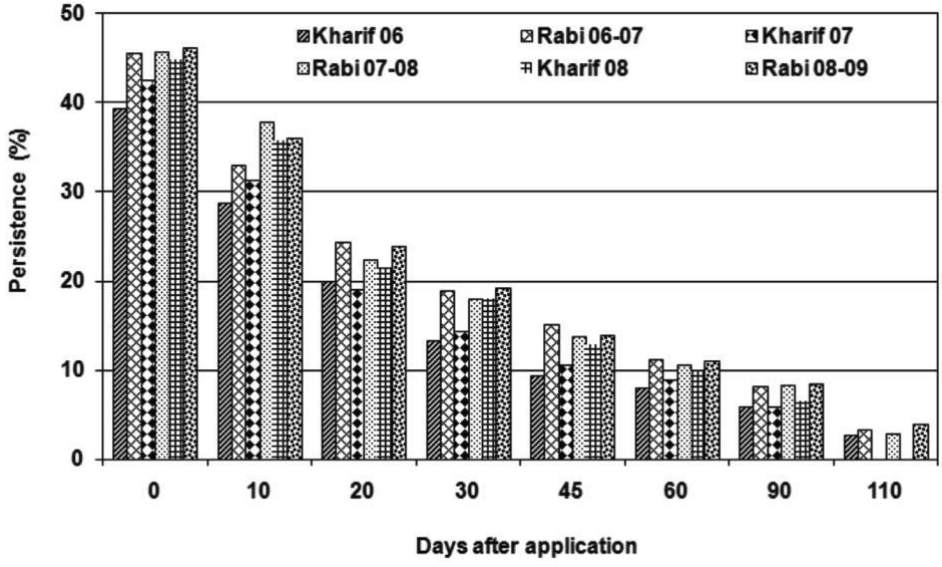

Fig. 1. Variation in persistence of atrazine as influenced by the seasons and years (mean of two doses of applications)

of applied atrazine detected in the soil at 0 day after application (2 hrs after application) was in the range of 39.1 to 47.0 per cent. Rate of atrazine application did not have significant influence on changing the initial quantity deposited in soil; however it increased over the years of application and seasons (Table 1 & Figure 1). It was 39.5 per cent during *kharif* 2006 and 46.22 per cent during *rabi*, 2008-

Table 1. Persistence of atrazine (%) in soil under maize crop

Treatment	Days after application							
	0	10	20	30	45	60	90	Harvest
Kharif 06	39.35	28.70	20.00	13.40	9.40	8.00	5.95	2.80
Rabi 06-07	45.55	33.00	24.45	18.95	15.10	11.25	8.15	3.30
Kharif 07	42.50	31.30	19.1	14.40	10.55	8.90	5.85	0.00
Rabi 07-08	45.80	37.85	22.35	18.10	13.75	10.55	8.40	2.95
Kharif 08	44.80	35.70	21.45	18.05	12.90	9.85	6.45	0.00
Rabi 08-09	46.22	36.01	23.97	19.24	13.99	11.03	8.547	4.01

9. Continuous cropping of this area with maize has increased the soil organic matter and carbon which might have increased the atrazine concentration in the soil during 2008 when compared to 2006. The difference in initial deposition could also be attributed to the physico-chemical properties of the soil (Savoca *et al.,* 2000) and environment factors such as rainfall, topography and climate (Lin *et al*., 1999) besides the genotype of the crop grown. Gasic *et al*. (2002) stated that the atrazine residues in the soil depends on the soil composition, temperature, pH and soil humidity and applied atrazine is subjected to sorption and to several chemical and biological degradation mechanisms which promote the reduction of the atrazine concentration in the soil.

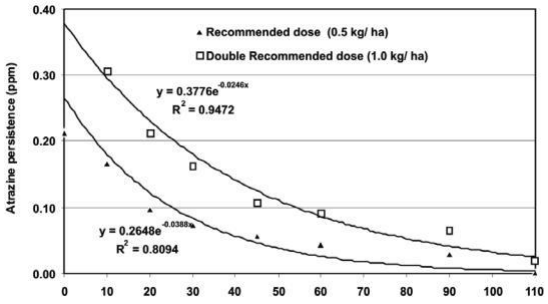

Fig. 2. Persistence of atrazine in maize grown soil during *kharif* season (mean of three year experiments)

Persistence of atrazine in soil

Persistence data of atrazine in maize grown soil during different seasons is given in figure 2, 3 and Table 1. Degradation of atrazine showed first order kinetics (Figure 4) that the persistence of atrazine in soil showed gradual degradation with advancement in crop growth irrespective of dose of application.

The pattern of atrazine dissipation in soil grown with maize crop during *kharif* and *rabi* season was similar. Irrespective of dose of application, the atrazine concentration was below detectable level in both soils and plant produce at harvest during *kharif* seasons however it persisted in soil upto harvest during *rabi* seasons. The mean concentration of atrazine varied from 0.418 to 0.028 and 0.448 to 0.012 ppm during *kharif* and *rabi* seasons across different doses and years. This might be attributed to the enhanced and faster microbial degradation of atrazine in the soil due to optimum temperature and moisture during *kharif* seasons (data not given). Walker and Zimdahl (1981) reported that the degradation of atrazine was greater in moist soil than in dry soil. Vencill (2002) also reported that the persistence of atrazine is increased by soil pH as well as by cool and dry soil conditions. The present experimental field received atrazine repeatedly over three years which might enhance the atrazine degradation through increased microbial population. This is in line with the findings of Krutz *et al.* (2008) that soils with a long history of using particular herbicides have the ability to break down related herbicides more rapidly. Application of atrazine at recommended dose left no residue in the soil whereas application of atrazine at double recommended dose (1.0 kg /ha) had 0.056 ppm of atrazine residue in the post harvest soil (Table 1).

The pooled data of the six experiments showed that the atrazine content decreased with the advancement in crop growth (Table 1) at both the rate of application. The degradation (Figure 4) of atrazine in maize soils occurred in two distinct phases. The degradation was straight and faster upto 20 DAHA (days after herbicide application) thereafter its dissipation from soil becomes slow. This could be attributed to an equilibrium that was reached with these herbicides where soil adsorption

Table 2. Variation in half life of atrazine applied at two concentrations during different seasons and years

Seasons	Dose of atrazine applied	
	0.5 kg ha^{-1}	1.0 kg ha^{-1}
Kharif 06	17.90	20.80
Rabi 06-07	21.42	23.34
Kharif 07	18.28	20.18
Rabi 07-08	20.47	24.58
Kharif 08	20.98	22.10
Rabi 08-09	22.54	25.66
Mean	20.31	22.76

had occurred, and then desorption of the parent was observed over time (Patakioutas and Albanis, 2002). This biphasic degradation was more evidenced in the plots which received the atrazine quantity of 0.5 kg ha^{-1}. At lower dose the atrazine persisted in soil upto 90 days while it persisted up to harvest under double dose of application. This showed that doubling the concentration slows down the degradation during later period of degradation. This decrease in degradation rate might be result of sudden decrease in microbial population caused

by the higher dose of atrazine (Weber and Weed, 1974).

The persistence of atrazine was influenced by the seasons and years (Figure 2 and 3). In general higher per cent of atrazine persists in soil during *kharif* 2006 and it increased to *kharif* 2008 and similar result was also observed during *rabi* seasons. Because of continuous use of atrazine and other triazines in this area, these substances might have probably been present for a number of years such that the current values include possible residue accumulations from past uses, when larger amounts were applied (Du Preez *et al*., 2005). These results show that the weather variables should be taken into account while studying the dissipation of herbicides from soils.

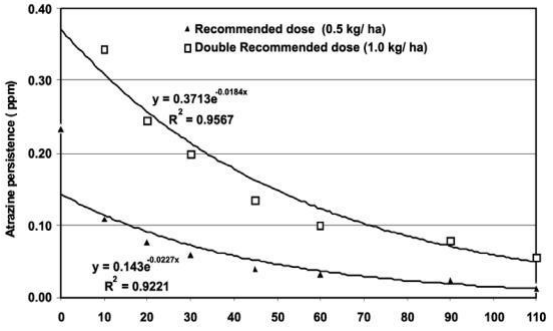

Fig. 3. Persistence of atrazine in maize grown soil during *rabi* season (mean of three year experiments)

Half life of atrazine

The mean half life of atrazine calculated from the pooled experimental data is 21.54 days. Such a shorter half life in cropped soil has also been reported by Popov *et al*. (2005) where as Wauchope *et al*. (1992) reported atrazine half-lives ranged from 12 to 120 days. Shorter half life of atrazine in the present study when compared to the literatures available might be attributed to the rapid leaching of atrazine through macropores (Baer *et al.,* 1992 and Graham *et al.,* 1992). The half life varied with the concentration of atrazine applied and season and year of application (Table 2). Increased concentration of atrazine application increased the half life from 21 days to 24 days. Though rainfall received during *rabi* season was high, half life was high during *rabi* than *kharif* season and showed that the soil temperature and distribution of rainfall (Sadeghi and Isensee, 1992) plays a key role on the degradation of atrazine in soil. Heydel *et al*. (1999) reported that the atrazine residues were identified even after several months of its application because of the migration of atrazine through the microporous structure and by adsorption/desorption on soil particles. Slow leaching has also been observed by Buhler *et al*. (1993). Popov et al. (2005) reported that the relatively rapid (~2 to 7 days) atrazine degradation in cropped soils with a history of atrazine application was associated with a consortia of bacteria known to be responsible for accelerated degradation. Atrazine in cropped soils may provide an additional source of N and C to microbial population that can degrade the herbicide (Boundy-Mills *et al.* 1997; Sims and Cupples, 1999). The highest rates of atrazine inactivation are generally found under those conditions that are favorable for microbial growth, such as warm temperatures, high moisture, and high soil organic matter content (WSSA, 1994). The application of atrazine @ 0.5 kg /ha and 1 kg /ha did not record any residue in grain and straw samples.

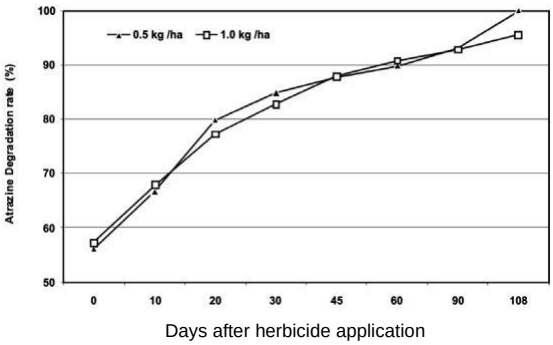

Fig. 4. Degradation rate of atrazine in sandy clay loam soil under maize crop (pooled data of six experiments)

Conclusion

Persistence of atrazine in soil showed a gradual degradation with advancement in crop growth. Atrazine residue was detected up to harvest only at double the recommended dose received soil and also during *rabi* season in all years. The dissipation of atrazine followed biphasic pattern and it was faster at higher dose of application than at the lower dose. Thus, it can be concluded from the results that the longer persistence of atrazine can be expected at higher dose of application and also during *rabi* season. In addition to this, the bioaccumulation of atrazine in soil was significant in terms of continuous application which requires further extensive study.

References

Armstrong, D.E., Chesters, G. and Harris R.F. 1967. Atrazine hydrolysis in soil, *Soil Sci. Soc. Am. Proc.*,**31:** 61-66.

Baer, J.U., Powers, W.L., Shea, P.J. and Stuefer-Powell, C.L. 1992. Pore size distribution index as an indicator of atrazine movement in a crete silt loam soil. *Soil Sci.,* **154:** 377–386

Biradar D.P. and Rayburn, A.L. 1995. Chromosomal damage induced by herbicide contamination at concentration observed in public water supplies, *J. Environ. Qual.*, **24:** 1232-1235

Boundy-Mills, K.L., de Souza, M.L., Mandelbaum, R.T., Wackett, L.P. and Sadowsky, M.J. 1997. The atzB gene of Pseudomonas sp. strain ADP encodes the second enzyme of a novel atrazine degradation pathway. *Appl. Environ. Microbiol.,* **63**: 916-923.

Buhler, D.D., Randall, G.W., Koskinen, W.C. and Wyse, D.L. 1993. Atrazine and alachlor losses from subsurface tile drainage of a clay loam soil. *J. Environ. Quality* **22**: 583-588.

Du Preez, L.H., Jansen van Rensburg, P.J., Jooste, A.M., Carr, J.A., Giesy, J.P., Gross,T.S., Kendall, R.J., Smith, E.E., Van Der Kraak,G. and Solomon, K.R. 2005. Seasonal exposures to triazine and other pesticides in surface waters in the western Highveld corn-production region in South Africa, *Environ. Poll.,* **135**: 131–141

Frank, R. and Sirons, G. 1985. Dissipation of atrazine residues from soil, *Bull. Environ. Contam. Toxicol.***, 34:** 541-548.

Gasic, S., Budimir, M., Brkic, D. and Neskovic, N. 2002. Residues of atrazine in agricultural areas of Serbia. *J.Serb.Chem.Soc.* **67***:* 887-892.

Ghosh, P.K. and Philip, L. 2006. Environmental significance of atrazine in aqueous systems and its removal by biological processes: an overview. *Global NEST Journal,* **8**:159-178.

Graham, R.C., Ulery, A.L., Neal, R.H. and Teso, R.R. 1992. Herbicide residue distributions in relation to soil morphology in two California vertisols. *Soil Sci.,* **153**: 115–121

Heydel, L., Benoit, M. and Schiavon, M. 1999. Reducing atrazine leaching by integrating reduced herbicide use with mechanical weeding in corn (*Zea mays*). *European J. Agron* ., **11:** 217–225

Krutz, L.J., Burke, I.C., Reddy, K.N. and Zablotowicz, R.M. 2008. Evidence for cross-adaptation between *s*-triazine herbicides resulting in reduced efficacy under field conditions. *Pest Management Sci.,* **64**: 1024-30.

Lin, Yaw-Jian, Makesh Karuppiah, Anugrah Shaw, and Gian Gupta. 1999. Effect of simulated sunlight on atrazine and metolachlor toxicity of surface waters. *Ecotoxicol. Environ. Safety,* **43**: 35-37.

Marcacci, S. 2004. A phytoremediation approach to remove pesticides (atrazine and lindane) from contaminated environment, Thesis, *Ecole Politechnique de Lausanne.*

Mc-Cormick L.L. and Hiltbold, A.E. 1966. Microbiological decomposition of atrazine and diuron in soil, *Weeds*, **14:** 77-82.

Nair, D.R., Burken, J.G., Licht, L.A. and Schnoor, J.L. 1993. Mineralization and uptake of triazine pesticide in soil-plant systems, *J. Env. Engrg., ASCE*, **119:** 842-854.

Ostafe, V. 2006. The degradation of triazine herbicides, *Seria de Monografii de Biochimie Cuanticã ºi Interacþii Specifice*, **8:** 1-97

Patakioutas G. and Albanis, T.A. 2002. Adsorption–desorption studies of alachlor, metolachlor, EPTC, chlorothalonil and pirimiphos-methyl in contrasting soils. *Pest Management Science,* **58**: 352-362

Popov, V.H., Cornish, P.S., Sultana, K. and Morris, E.C. 2005. Atrazine degradation in soils: the role of microbial communities, atrazine application history and soil carbon. *Australian J. Soil Res.,* **43** : 861-871

Ritter, W.F., Scarborough, R.W. and Chirnside, A.E.M. 1994. Contamination of ground water by triazines, metolachlor, and alachlor, *J. Contam. Hydrol.,* **15:** 73-92.

Sadeghi, A.M. and Isensee, A.R. 1992. Effect of tillage systems and rainfall patterns on atrazine distribution in soil. *J. Environ. Qual*. **21**: 464–469.

Savoca Mark, E., Eric, M., Sadorf, S., Mike Linhart, Kymm and Akers, K.B. 2000. Effects of land use and hydrogeology on the water quality of alluvial aquifers in Eastern Iowa and Southern Minnesota, 1997. *U.S. Geological Survey, Water-Resources Investigations Report,* 2000, pp. 99-4246. Iowa City, IA.

Sims,G.K. and Cupples, A.M. 1999. Factors controlling degradation of pesticides in soil. *Pesticide Science,* **55**: 598-601.

Tindall, J.A. and Vencill, W.K. 1995. Transport of atrazine, 2,4-D and dicamba through preferential flowpaths in an unsaturated clayen soil near Centralia Missouri, *J. Hydrol.*, **166:** 37-59.

Vencill, W.K. 2002. Herbicide Handbook.8th edition, *Weed Science Society of America*, Lawrence, KS, U.S.A. pp 1-440.

Walker, A. and Zimdahl, R.L. 1981. Simulation of the persistence of atrazine, linuron and metolachlor in soil at different sites in the USA. *Weed Res*., **21**: 255-265.

Wauchope, R.D., Buttler, T.M., Hornsby, A.G., Augustijn-Beckers, P.W.M. and Burt, J.P. 1992. The SCS/ARS/ CES pesticide database for environmental decision making. *Rev. Environ. Contam. Toxicol.,* **123**: 1-155.

Weber, J.B. and Weed, S.B. 1974. Effects of soil on the biological activity of pesticides. In: Guenzi WD. (ed). Pesticides in Soil and Water. *Soil Science Society of America,* Madison, p.223-226.

WSSA. 1994. Herbicide Handbook of the Weed Science Society of America, 7th ed. W.F. Humphrey Press. Genevea, NY.

Received: February 12, 2012; Revised: April 10, 2012; Accepted: June 18, 2012