Persistence of atrazine in soil under fodder sorghum

S. K. NAG AND S. K. DAS

Indian Grassland and Fodder Research Institute,
Jhansi-284 003, Uttar Pradesh

ABSTRACT

Atrazine was applied @ 1.5 kg ai/ha in soil before emergence of fodder sorghum (cv.PC-6) grown during kharif season in two successive years 2006 and 2007 under two different nitrogen sources viz., sole inorganic (T_2) and organic and inorganic in the ratio of 50:50 (T_4) keeping T_1 and T_3 as their respective controls. Samples collected at different intervals from two depths of soil i.e. 0-15 and 15-30 cm were analysed for atrazine residues in both the years. The average initial zero day deposition in 0-15 cm depth soil was 0.4779 and 0.4619mg/kg which dissipated by 62% (0.1823mg/kg) and 65% (0.1619mg/kg) in 15 days in T_2 and T_4 respectively. However, after elapse of 30 days about 86-88% residues disappeared in both the treatments. In samples of 15-30 cm depth the initial zero day deposits were 0.1935 and 0.2005 mg/kg in T_2 and T_4 respectively which dissipated down to 0.066mg/kg in 15 days in both the treatments. Residues were below detectable level in samples collected at 30 days from 15-30 cm depth and at 45 days from 0-15cm depth. In plant foliage collected at harvest we could detect traces of atrazine in few samples only in first year but in the second year's sample it was totally absent, thus the fodder at harvest was absolutely safe for animal feeding. The dissipation pattern followed first order rate kinetics with high correlation coefficients ($r = -0.98$ to -0.99). The statistically calculated half-life values were found to be 10.27, 9.35 days in 0-15 cm and 9.65, 9.38 days in 15-30 cm depth soil in T_2 and T_4 respectively.

Key Words: Atrazine, dissipation, fodder crops, persistence and sorghum

Sorghum or jowar [*Sorghum bicolor* (L.) Moench] is one of the most important fodder crops of the semi arid tropics. It is also grown for grain and dual purpose during summer and kharif season mainly in northern and central India. The crop is preferred as a fodder crop because it can be utilized as green fodder, stover and also for silage making. Atrazine (6-chloro-N^2-ethyl-N^4-isopropyl-1,3,5-triazine-2,4-diamine), a substituted s-triazine, selective herbicide is used for the control of grasses and broad leaved weeds in maize, sorghum, sugarcane, vines, fruit orchards and many others. It is recommended for pre emergent application in fodder sorghum for control of various weeds (Tomar *et al.,* 1999).

Presence of organic matter plays an important role in persistence, adsorption and degradation of herbicides in soil. The difference in adsorption of atrazine between soils has been attributed mainly to organic matter level, type of clay and pH in the immediate vicinity of clay surface (Anderson *et al.*, 1980, Raman *et al.*, 1988, Bhardwaj and Gehlan, 1986). Atrazine is absorbed through roots and foliage with translocation. So, it is important to know about the persistence of the herbicide in soil and its translocation to foliage of fodder crops because green fodders are straight way fed to animals after harvesting from the field having, therefore, very little chance of decontamination. If the fodder is contaminated then the residues present in it may be transferred to animal body from where subsequently it may translocate and contaminate milk in case lactating animals, which is absolutely undesirable. The contaminated fodder, therefore, should either be allowed to decontaminate to lower the residue level below the permissible level or discarded for the sake of safety of human and animal health.

E-mail i.d.: nagsk_67@rediffmail.com

Keeping these points in view, the present investigation was undertaken to observe the residues and difference in persistence pattern of atrazine from soil under fodder sorghum grown with two sources of nitrogen, *i.e.* sole inorganic and combination of organic and inorganic in 50:50 ratio. Another important objective of the experiment was to see the translocation of atrazine residues, if any, to sorghum foliage at the time of harvest.

MATERIALS AND METHODS

The experiment was conducted during *kharif* season of two successive years, 2006 and 2007, at the experimental central research farm of Indian Grassland and Fodder Research Institute, Jhansi. Fodder sorghum (cv PC-6) was sown in 4 x 3 square meter plots and pre emergence application of atrazine was done as per the following treatment schedule. Each treatment and control was replicated four times and the experiment was laid out in randomized block design. The treatments were :

T_1 = No herbicide and total nitrogen applied through fertilizer (inorganic)

T_2 = Atrazine @ 1.5 Kg ai/ha and total nitrogen applied through fertilizer (inorganic)

T_3 = No herbicide and total nitrogen applied through FYM (organic) and fertilizer (inorganic) in 50:50 ratio

T_4 = Atrazine @1.5 Kg ai/ha and total nitrogen applied through FYM (organic) and fertilizer (inorganic) in 50:50 ratio

Soil samples were collected from two depths *viz.* 0-15 and 15-30 cm from all the replicates at 0, 3, 7, 10, 15, 30 and 45 days after treatment and at harvest time. Sorghum foliage samples were also collected at harvest time which is about 90 days after treatment.

Extraction and clean up

Soil: Soil samples were collected with an auger from two depths 0-15 and 15-30cm. They were dried in air under shade, pulverized and screened through 2 mm sieve and stored at sub zero temperature. A representative of 50 g soil was taken in 150 mL of conical flask and extracted with 100 mL of dichloromethane for 2 hours in a mechanical horizontal shaker. The suspension was filtered through Whatman filter paper No.1 placed on a Buchner filtering funnel connected to an air suction pump to create vacuum. The extraction flask was washed with 2x50 mL dichloromethane which was transferred to same filter paper and filtered. The filtrate collected in the filtering flask was quantitatively transferred to a separating funnel and washed thrice with 3x50 mL distilled water, the aqueous fraction being discarded each time. The organic layer was finally passed through anhydrous sodium sulfate and evaporated to dryness in a rotary vacuum evaporator. The residue was dissolved in hexane and acetone (8:2 v/v) mixture and subjected to gas chromatographic (GC) analysis.

Plants: A representative of 50 g samples of sorghum foliage from each replicate collected at harvest i.e. after about 90 days after treatment were blended in a mixer grinder for two minutes each with 100 mL and 2x50 mL of acetone. The extract was then filtered through Buchner filtering funnel to a filtering flask. The residue on the funnel was washed 2-3 times with acetone and collected in the same flask. The combined acetone extract was placed in a 1 liter separating funnel and mixed with 100 ml. each of petroleum ether and dichloromethane. After partitioning the lower aqueous layer was transferred in a conical flask and upper organic layer was passed through anhydrous sodium sulfate. The aqueous layer was again transferred to the separating funnel and 5% sodium chloride and 100 ml. dichloromethane was added to it. After shaking the separating funnel for 2-3 times the lower organic layer was separated and collected in the same flask after passing through anhydrous sodium sulfate. The same process was repeated twice. The combined dichloromethane fraction was concentrated in rotary vacuum evaporator, the residue was dissolved in hexane and acetone (8:2 v/v) and subjected to column chromatography using silica gel, florisil and anhydrous sodium sulfate as adsorbents. The column was eluted with 100 ml. of hexane and acetone (8:2 v/v) and the eluate was concentrated to 10 mL for GC analysis.

Analysis in GC: The qualitative and quantitative determination was done in gas chromatograph on a Varian 3800 equipment fitted with TSD (Thermionic Specific Detector). The column used was WCOT fused silica chrompack capillary column having a dimension of 10m x 0.53 mm id x 1 μm film thickness and CP-SIL 5CB coating at the temperature programming of 150^{o}C (1min) to 200^{o}C (0 min) at 10^{o}C/min to 240^{o}C (5 min) at 20^{o}C/min. The injector and detector temperatures were kept at 250^{o}C and 300^{o}C respectively. Nitrogen was used as carrier gas with a flow rate of 2 ml/min through column and 30 ml/min as back up. The detector gas flow rates were 4 ml/min for hydrogen and 175 ml/min for air. The identification of peak and quantification of concentration in the samples was done on the basis of known concentration of external standard solution injected intermittently.

Recovery experiments were also conducted to test the efficiency of extraction, clean up and estimation procedure by spiking the untreated soil and sorghum foliage samples with known concentrations of atrazine. The average recovery in soil was between 92-95% while that in foliage samples was between 85-90%. The limit of determination was 0.015 mg/kg.

RESULTS AND DISCUSSION

Soils of the experimental plots were clayey in texture and neutral in reaction (pH around 7) and the electrical conductivity was low (Table-1). The organic carbon status was in the medium range. The data on residues and dissipation of atrazine in soil under fodder sorghum presented in Tables 1 and 2 are the average of two consecutive years study. The concentration and percent dissipation values reveal a slow but steady disappearance of the residues. In samples of 0-15 cm depth soil the initial deposits were around 0.48 and 0.46 mg/kg in treatments T_2 and T_4 which dissipated by 11-13% to 0.42 and 0.40 mg/kg, respectively, in initial three days. After 7 days the dissipation of residues was 23-26% while after 10 days about 36-38% of initial deposits were lost. Atrazine residue at a concentration of 0.23 mg/kg was detected at 4 days after treatment in soil samples of a maize field in Saldana, Tolima, Colombia after application of the herbicide @ 2.4 kg *a.i.*/ha (Fuentes *et al.*, 2003).

The residue after 15 days of application was around 0.18 and 0.16 mg/kg in T_2 and T_4 respectively, thus measuring a dissipation of 62-65%. After elapse of 30 days the concentraton of atrazine went below 0.1 mg/kg level and measured at 0.068 in T_2 and 0.054 mg/kg in T_4. The samples of 45 days had no detectable residues at all. The above data revealed that the dissipation of atrazine in soil was slow but steady and on almost uniform rate. There was not much variation in rate of dissipation during initial or later days which might be due to the fact that there was not much rainfall (~500 mm) during the study period as the area suffered from draught in both the years. So, the degradation and dissipation of residues occurred due to usual microbial activity in the soil.

In soils of 15-30 cm depth, initial atrazine concentration was around 0.2 mg/kg which dissipated by about 66-67% in 15 days to the level of 0.066 mg/kg in both the treatments T_2 and T_4 and in samples collected after 30 days no residues could be detected. The dissipation pattern of atrazine in soil followed first order kinetics as high coefficient of determination (R^2) as observed from the semi logarithmic plot between mean residue level and days after application (Fig.1 and 2). This corroborate well with the reports of Sheets (1970) and Wood et al (2005). In the 0-15 cm layer soil the statistically calculated half-life values were 10.27 days in T_2 and 9.35 days T_4 while the corresponding figures in 15-30 cm layer soil were 9.65 and 9.38 days respectively. Atrazine dissipation at all soil depths under study with a residual half-life of 15-28 days was also observed by Wood *et al.* (2005). But these half-life values were quite low as compared to reported value of 37-138 days (Erickson and Lee, 1989) or a half-life value of 23.8-39.4 days at 25^{o}C reported by Xiongwu Qiao *et al.*, 1996) in certain acidic and alkaline soils. Warm and moist climate promote disappearance of atrazine herbicides from soils (Dowler *et al.*, 1968, Harrris *et al.*, 1969) and persistence is more prolonged in cold, dry climate (Adams, 1968, Burnside *et al.*, 1969).

It is also reported that atrazine decomposition in soil increased with temperature between 10-35^{o}C (Burnside, 1965; Roeth *et al.*, 1969). Buchanon and Rogers (1963) reported that inactivation of simazine, ipazine, atrazine and atratone proceeded more rapidly at 45^{o}C than at 25, 30 or 35^{o}C. The prevailing hot and humid condition during *kharif* season and due to possible enhanced mineralization of atrazine in the rhizospheric and nearby lower zone under fodder sorghum helped in degrading and dissipating atrazine at a comparatively higher rate thus residual half lives becoming shorter than the reported values in other areas. Atrazine mineralization was the main dissipation mechanism in the superficial horizon of the Argiustoll because of microbial adaptation after repeated applications.

In contrast, little atrazine mineralization was found in the Haplustoll profile, and it decreased with depth as observed by Hang *et al.* (2005) in their investigation of atrazine behavior in the different pedological horizons from profiles of two non-tilled soils in Argentina. Atrazine residues in the range of 0.02-0.10 mg/kg in 0-15 cm and up 0.05 mg/kg in 15-30 cm soil depending on soil type was reported from temperate country Serbia as a result of five year investigation of pollution of soil during 1995-1999 (Gasic *et al.*, 2002). On the other hand soil samples, collected from 20 locations at four depths (0-15, 15-30, 30-45 and 45-60 cm) from sugarcane growing areas of Nizamabad district of Andhra Pradesh where atrazine application was a regular practice for over 20 years, had no detectable residues (< 0.01 mg/kg) (Sannappa *et al.*, 1997).

A comparison of the percent dissipation of atrazine and the residual half-life values obtained in the experiment shows a slightly higher rate of dissipation in treatment T_4 than in T_2 which might be due to the presence of higher organic matter in the former since organic matter plays an active role in degradation of pesticides in soil. Another reason may be the increased formation of bound residues which can not be extracted by normal extraction procedure. Hang *et al.* (2005) reported that atrazine-bound residues depended on the soil organic matter content and the size of the fraction. Organic matter in the largest size fractions had a higher capacity to form atrazine-bound residues.

Sorghum plants harvested around 90 days after sowing were also analyzed to detect any residues of atrazine if translocated and still persisting in foliage. Although in the first year we could detect traces of atrazine in few plant samples but in the second year nothing could be detected in any sample. In the succeeding berseem fodder crop taken in rotation in following rabi season there was no carry over of atrazine residues or any initial phytotoxicty observed by us. Thus the fodder at harvest was absolutely safe for animal feeding as far as atrazine residue was concerned in sorghum as well as succeeding berseem crop.

ACKNOWLEDGEMENT

The authors are highly thankful to the Heads of CP and PAR Division, and the Director, IGFRI, Jhansi for providing the facilities and encouraging support.

Table 1: Soil characteristics before and after the experiment

Soil parameter	Initial	Final
pH	7.19	7.20
EC (dS/m)	0.14	0.10
Texture	Clay	Clay
Organic carbon (%)	0.52	0.61
Total nitrogen (%)	0.08	-
Available nitrogen (Kg/ha)	133	236
Available phosphorus (Kg/ha)	12.7	17.5
Available potassium (Kg/ha)	272	311

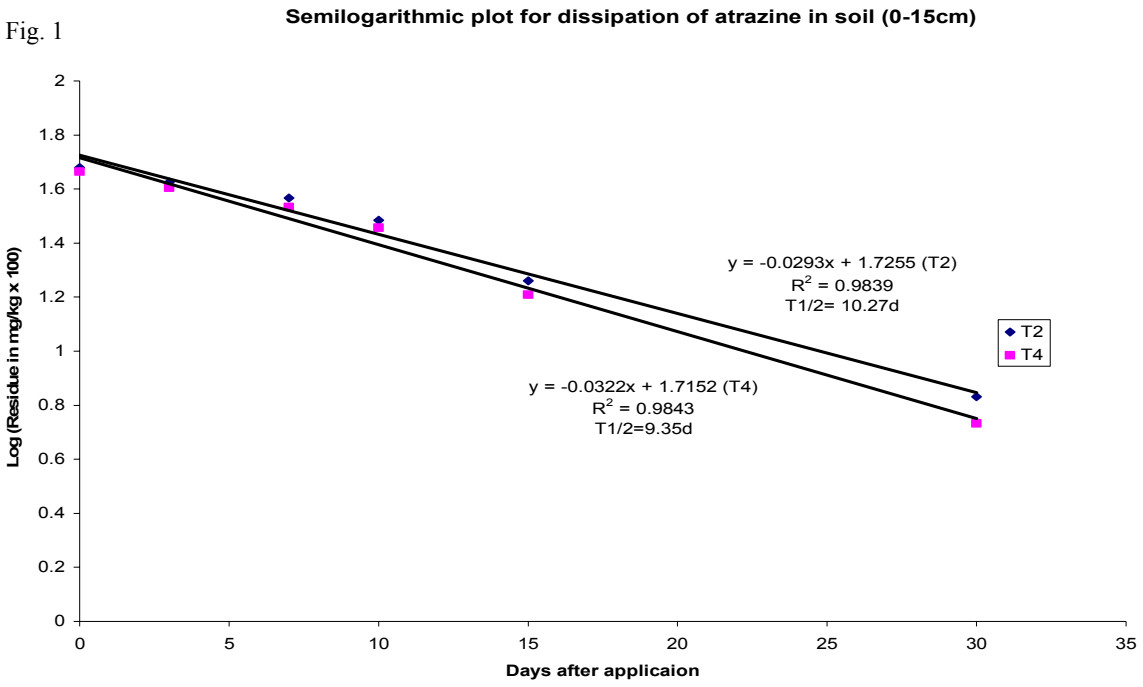
Table 2: Dissipation of atrazine residues in soil (0-15cm) after its pre emergence application @ 1.5 kg ai/ha.

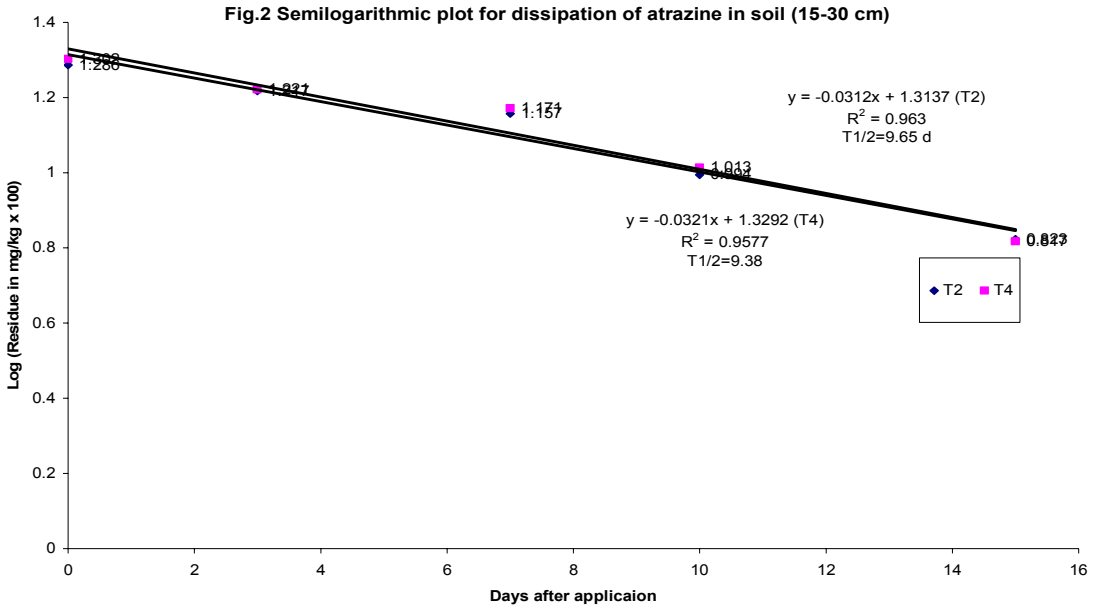
Days after application	T_2		T_4	
	Residue in mg/kg (mean+s.d.)	Dissipation (%)	Residue in mg/kg (mean+s.d)	Dissipation (%)
0	0.4779±0.042	-	0.4619±0.066	-
3	0.4218±0.104	11.74	0.4029±0.103	12.77
7	0.3692±0.063	22.75	0.3414±0.089	26.08
10	0.3060±0.048	35.97	0.2869±0.052	37.88
15	0.1823±0.033	61.85	0.1619±0.020	64.95
30	0.068 ±0.022	85.77	0.054 ±0.015	88.31
45	ND		ND	

Table 3: Dissipation of atrazine residues in soil (15-30cm) after its pre emergence application @ 1.5 kg ai/ha.

Days after application	T_2		T_4	
	Residue in mg/kg (mean+s.d.)	Dissipation (%)	Residue in mg/kg (mean+s.d	Dissipation (%)
0	0.1935±0.044	-	0.2000±0.038	-
3	0.165±0.082	14.73	0.1664±0.049	16.8
7	0.1438±0.051	25.68	0.1485±0.032	25.75
10	0.0987±0.034	48.99	0.1031±0.052	48.45
15	0.066±0.022	65.89	0.0657±0.010	67.15
30	ND		ND	

Fig. 1





REFERENCES

Adams, R.S. Jr. 1968. Soil factors contributing to atrazine carry over. *Minnesota Sci.* **25**: 9.

Anderson, G.R. Stephensor, G. R. and Corka, C.T. 1980. Atrazine and cyanazine activity in Ontario Manitoba soils. *Canadian J. Soil Sci.* **60**: 773-81.

Bhardwaj, S.S. and Gehlan, M.S. 1986. Adsorption of atrazine by some soils and clay minerals. *J. Res. Punjab Agril. Univ.* **23**: 82-90.

Buchanon, G.A. and Rogers, E.G. 1963. Role of temperature in the activation of some s-traizine herbicides. *Proc. Weed Conf.* **16**: 393.

Burnside, O.C. 1965. Longevity of amiben, atrazine, and 2,3,6-TBA in incubated soils. *Weeds* **13**: 274.

Burnside, O.C., Fenster, C.R. Wicks, G.A. and Drew, J.V. 1969. Effect of soil and climate on herbicide dissipation. *Weed Sci.* **17**: 241.

Dowler, C. C., Forestier, W. and Tschirley, F. H. 1968. Effects and persistence of herbicides applied to soil in Puerto Rican forests. *Weed Sci.* **16**: 45.

Erickson, L. E. and Lee, K. H. 1989. Degradation of atrazine and related s-triazines. *Critical Rev. Env. Control* **19**: 1-13.

Fuentes, C.L., Lozano-de-Yunda, A, Guerrero-Dallos, J.A., Perez, L.E, Olarte, I. and Acevedo, B. 2003. Environmental behavior of atrazine in soils: detection of environmental concentrations using HPLC and 14C under controlled and field conditions at Saldana-Tolima, Colombia. *Agronomia Colombiana.* **21:**29-48.

Gasic, S., Budimir, M., Brkic, D. and Neskovic, N. 2002. Residues of atrazine in agricultural areas of Serbia. *J. Serbian Chem.Soc.***67**: 11.

Hang,S, Barriuso, E. and Houot, S. 2005. Atrazine behaviour in the different pedological horizons of two Argentinean non-till soil profiles. *Weed Res. Oxford*. **45**: 130-39.

Harris , C.I., Woolson, E.A. and Hummer, B.E. 1969. Dissipation of herbicides at three soil depths. *Weed Sci.* **17**: 27.

Raman, S, Krishna, M. and Chandrasekhara Rao, R. 1988. Adsorption desorption of atrazine on four soils of Hyderabad. *Water Air Soil Pollution* **40**: 177-84.

Roeth, F.W., Lavy, T.L. and Burnside, O.C. 1969. Atrazine degradation in two soil profiles. *Weed Sci.***17**: 202.

Sannappa, H., Rajesh, V.N., Kumar, Y. and Mithyantha, M.S. 1997. Atrazine residues in soils and groundwater from intensive sugarcane growing tract of Andhra Pradesh. *Pestology* **21**: 8-15.

Sheets, T. J. 1970. Persistence of triazine herbicides in soils. *Residue Rev.* **32**: 287-310.

Tomar, P. S. 1999. In: *Forage Production Technology*, IGFRI, Jhansi, pp.1-2.

Wood, B.P., Gums, F. and Headley, J. V. 2005. Dissipation of atrazine and two N-dealkylated metabolites in soils of sugarcane plantations under field conditions in Barbados. *Soil Sci. Pl. Analysis* **36:**783-94.

Xiongwu Qiao, Liping Ma and Hummel, H.F. 1996. Persistence of atrazine and occurrence of its primary metabolites in three soils. *J. Agri. Food Chem.***44**: 2846-48.