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

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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-isopropylamino-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 (McCormick and Hilbold, 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 m² 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
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°C, 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 chromatographic 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.

\[
\frac{dA}{dt} = Ka \rightarrow A(t) = A_o \exp (kt)
\]

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.

\[ T_{1/2} = \frac{0.6931}{K} \]

**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 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-
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.

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

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Days after application</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>Kharif 06</td>
<td>39.35</td>
</tr>
<tr>
<td>Rabi 06-07</td>
<td>45.55</td>
</tr>
<tr>
<td>Kharif 07</td>
<td>42.50</td>
</tr>
<tr>
<td>Rabi 07-08</td>
<td>45.80</td>
</tr>
<tr>
<td>Kharif 08</td>
<td>44.80</td>
</tr>
<tr>
<td>Rabi 08-09</td>
<td>46.22</td>
</tr>
</tbody>
</table>

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

Persistence of atrazine in soil

Persistense 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 up to 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

<table>
<thead>
<tr>
<th>Seasons</th>
<th>Dose of atrazine applied</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.5 kg ha⁻¹</td>
</tr>
<tr>
<td>Kharif 06</td>
<td>17.90</td>
</tr>
<tr>
<td>Rabi 06-07</td>
<td>21.42</td>
</tr>
<tr>
<td>Kharif 07</td>
<td>18.28</td>
</tr>
<tr>
<td>Rabi 07-08</td>
<td>20.47</td>
</tr>
<tr>
<td>Kharif 08</td>
<td>20.98</td>
</tr>
<tr>
<td>Rabi 08-09</td>
<td>22.54</td>
</tr>
<tr>
<td>Mean</td>
<td>20.31</td>
</tr>
</tbody>
</table>

had occurred, and then desorption of the parent was observed over time (Patakiioutas and Albanis, 2002). This biphasic degradation was more evidentied 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


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