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Chapter 12

Fate of Atrazine and Atrazine Degradates in Soils of Iowa

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Several studies have been conducted to investigate the fate of atrazine (ATR, 2-chloro-4[ethylamino]-6[isopropylamino]-s-triazine) and major degradation products of ATR in soils of Iowa by using laboratory radiotracer studies, field lysimeters, and a field-scale approach. Complete metabolism studies of uniformly ring-labeled $^{14}$C-chemicals revealed some major trends. Persistence of ATR, deethylatrazine (DEA, 2-chloro-4[amino]-6[isopropylamino]-s-triazine), and deisopropylatrazine (DIA, 2-chloro-4[ethylamino]-6[amino]-s-triazine) was greater in subsurface soils than in surface soils. In surface soil of Ames, DEA and didealkylatrazine (DDA, 2-chloro-4,6-[diamino]-s-triazine) were predominant degradates of ATR after 60 d, and hydroxyatrazine (HYA, 2-hydroxy-4[ethylamino]-6[isopropylamino]-s-triazine) was the predominant degrade of ATR after 180 d. The persistence of ATR, DEA, and DIA was significantly reduced under saturated soil moisture conditions than in soils held at a moisture near field capacity. Relative mobilities of ATR and degradates in five Iowa soils (surface and subsurface), determined by soil thin-layer chromatography, indicate that DEA is more mobile than ATR. The relative mobilities of DIA, DDA, and ATR were similar. Also, laboratory studies with undisturbed soil columns are supportive of greater mobility of DEA than ATR. In a field-scale study investigating the mobility of ATR and its degradates, it was indicated that ATR degradation products by themselves, or in combination with the parent compound can exceed the maximum contaminant level (MCL) of 3 μg/L currently set for ATR alone. In ATR-applied field plots, DEA and DIA were detected along with ATR in tile drain water samples, with concentrations of DEA exceeding DIA. In Extrazine®- (a herbicide mixture of 67% cyanazine [CYA; 2-chloro-4-ethylamino-6-(1-cyano-1 methylethylamino)-s-triazine] and 21% ATR) - applied field lysimeters, the concentrations of DIA exceeded those of DEA.

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Detection of pesticide degradates in surface and groundwater has prompted increased interest in the fate of these compounds in soil. Controlled laboratory studies using radiotracers can provide important information about the behavior of pesticides and their breakdown products under various conditions. Numerous studies have been conducted using radiolabeled compounds. Results are greatly influenced by many factors including experimental design, temperature, moisture content, soil type, and analytical techniques. Direct comparisons to literature data are difficult to make due to these factors.

Laboratory studies using radiotracers provide a very sensitive means for determining degradation, mobility, and persistence. In our laboratory, several approaches have been used to study environmental fate of ATR and ATR degradates. Degradation pathways have been presented in the literature [1,2]. We have conducted soil microcosm studies to investigate the degradation of s-triazine herbicides as influenced by soil characteristics, soil moisture, and soil pesticide history. We have also been involved in mobility studies using large undisturbed soil columns, field box lysimeters, and field-scale tile drain systems. It is the intent of this chapter to summarize the studies conducted in this laboratory (and in collaboration with other laboratories) and to make comparisons of the fate of ATR and major degradation products of ATR in Iowa soils.

Fate of $^{14}$C-ATR and Degradates in Soil Microcosm Studies

Soils from five locations in Iowa were used for studies conducted in this laboratory. Pertinent soil characteristics are shown in Table 1; the five locations represent a wide range in soils. All $^{14}$C-compounds used in these studies were uniformly-ring labeled, and labeled chemicals were supplied by Ciba Crop Protection (Greensboro, NC).

Comparative Fates of ATR, DEA, DIA, and HYA in Ames Soils. Two independent radiotracer studies conducted in our laboratory looked at the fate of ATR, DEA, DIA, HYA in some or all of the soils listed in Table 1 [2,3]. The comparative fates of these four compounds can only be made for the Ames surface (0 to 30 cm) and subsurface (65 to 90 cm) soils, as these were the soils common in both studies. Soils were treated with $^{14}$C-ATR, DEA, DIA, or HYA. Soil moisture tensions were adjusted to near field capacity (-33 kPa soil moisture tension) and incubated for 60 d in the dark at 24°C. During the incubations, $^{14}$CO$_2$ was trapped in NaOH (1 N). Soils were extracted and analyzed using thin-layer chromatography, autoradiography, soil combustion, and liquid scintillation techniques [2,3].

Some major trends were seen in the persistence and degradation of these chemicals in the Ames soils. Persistence of ATR, DEA, and DIA was greater in subsurface soil than in surface soil (Figure 1) [2, 3]. HYA was equally persistent in surface and subsurface soils. Degradation studies were not carried out in the 90-to 120-cm depth for DEA and HYA.

Significantly greater amounts of DIA and ATR were mineralized in the surface (0 to 30 cm) soil than in subsurface soil (90 to 120 cm) from Ames (Figure 2), as
Table 1. Characteristics of Iowa soils with no previous pesticide history

<table>
<thead>
<tr>
<th>Site</th>
<th>Depth (cm)</th>
<th>Texture</th>
<th>Sand %</th>
<th>Silt %</th>
<th>Clay %</th>
<th>O.M. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ames</td>
<td>0-30</td>
<td>Sandy Loam</td>
<td>64</td>
<td>22</td>
<td>14</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>65-90</td>
<td>Sandy Clay Loam</td>
<td>54</td>
<td>22</td>
<td>24</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>90-120</td>
<td>Sandy Clay Loam</td>
<td>46</td>
<td>28</td>
<td>26</td>
<td>1.6</td>
</tr>
<tr>
<td>Treynor</td>
<td>0-30</td>
<td>Silty Clay Loam</td>
<td>14</td>
<td>58</td>
<td>28</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td>65-90</td>
<td>Silty Clay Loam</td>
<td>10</td>
<td>54</td>
<td>36</td>
<td>0.8</td>
</tr>
<tr>
<td>Chariton</td>
<td>0-30</td>
<td>Clay Loam</td>
<td>26</td>
<td>40</td>
<td>34</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>65-90</td>
<td>Clay</td>
<td>2</td>
<td>34</td>
<td>64</td>
<td>0.4</td>
</tr>
<tr>
<td>Fruitland</td>
<td>0-30</td>
<td>Sand</td>
<td>90</td>
<td>4</td>
<td>6</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>65-90</td>
<td>Sand</td>
<td>90</td>
<td>4</td>
<td>6</td>
<td>0.4</td>
</tr>
<tr>
<td>Nashua</td>
<td>0-30</td>
<td>Loam</td>
<td>42</td>
<td>34</td>
<td>24</td>
<td>3.6</td>
</tr>
<tr>
<td></td>
<td>65-90</td>
<td>Sandy Clay Loam</td>
<td>46</td>
<td>26</td>
<td>28</td>
<td>0.4</td>
</tr>
</tbody>
</table>

* Organic matter content of soil

Figure 1. The percent of extractable 14C remaining as the applied compounds in Ames soil treated with either 14C-ATR, -DEA, -DIA, or -HYA after a 60-d incubation. Degradation studies for DEA and HYA were not carried out in the 90- to 120-cm depth. Bars (with standard deviations) represent the mean of two replicates.
determined by the amount of $^{14}$CO$_2$ in NaOH traps for the 60-d incubation period. Baluch et al. [3] did not find significant differences in mineralization of DEA and HYA in Ames soils among depths from 0 to 90 cm (Figure 2). DIA was the degrade most readily mineralized, with approximately 7.5% of the applied $^{14}$C-DIA recovered as $^{14}$CO$_2$ in surface soils after 60 d. This is consistent with research by Skipper and Volk [4], which indicated that the ethyl side chain is more readily removed from ATR compared to the isopropyl side chain. Minimal mineralization of ATR occurred in soil from either depth (< 1% of applied $^{14}$C).

The major degradates of ATR after a 60-d incubation in surface soil of Ames, held at a soil moisture near field capacity, were DEA (2.4% of the applied $^{14}$C) and DDA (4%) [2]. After 120 d, however, the quantity of HYA exceeded that of DEA, DIA, and DDA in ATR-treated surface soil. The greater persistence of HYA compared with ATR, DEA, and DIA may explain why HYA is sometimes reported to be the major degrade of ATR.

Soil-bound residues, as determined by combusting subsamples of extracted soil by using a Packard Sample Oxidizer (Packard Instrument Co.), were formed to a greater extent in surface soils than in subsurface soils, with the exception of HYA-treated soils (Figure 3) [2, 3]. Sixty-one percent of the applied $^{14}$C-DIA was bound after 60 d in surface soils, significantly greater than in soil from the 90 to 120-cm depth. Forty-five percent of the applied ATR and 46% of the applied DEA were bound in surface soil after 60 d.

**Influence of Soil Moisture on Degradation of ATR, DEA, and DIA in Ames Soils.** Soil moisture influenced the fate of ATR, DIA, and DEA. Soils were treated with either $^{14}$C-ATR, -DEA, or -DIA, and soil moistures were adjusted to either saturated or a specific unsaturated soil moisture condition. Unsaturated soils were those which had a soil moisture tension of -33 kPa (near field capacity). Saturated soils had a layer of water over the surface of the soil, with a soil moisture content of 30% (gravimetric soil moisture) greater than the soil moisture tension at -33 kPa [2, 5]. Soils were incubated in the dark at 24 °C for 60 d. $^{14}$CO$_2$ was trapped during the incubation period, and soils were extracted and analyzed at the end of the 60-d period as discussed previously.

These studies indicated more rapid degradation of ATR, DEA, and DIA under saturated soil moisture conditions than in unsaturated soils. After a 60-d incubation in Ames soils, 45% of the applied $^{14}$C-DIA remained in saturated subsurface soil (from the 90- to 120-cm depth), significantly less than that remaining in subsurface soils (66%) held at near field capacity [2]. Additionally, ATR and DEA were significantly less persistent in saturated surface soil (0 to 30 cm) than in unsaturated surface soil [5]. A comparison of ATR and DEA fate in sterile and nonsterile soil indicated that this decreased persistence was due to biological degradation (Figure 4).

**Influence of Pesticide History on the Degradation of DEA in Nashua Soils.** The pesticide history of soil can influence the fate of chemicals subsequently applied to
Figure 2. Evolution of $^{14}$C$\text{CO}_2$ from Ames soils treated with either $^{14}$C-ATR, -DEA, -DIA, or -HYA after a 60-d incubation. Degradation studies for DEA and HYA were not carried out in the 90- to 120-cm depth. Bars (with standard deviations) represent the means of two replicates.

Figure 3. Soil-bound residues formed in soil treated with either $^{14}$C-ATR, -DEA, -DIA, or -HYA after a 60-d incubation. Degradation studies for DEA and HYA were not carried out in the 90- to 120-cm depth. Bars (with standard deviations) represent the means of two replicates.
it. Enhanced degradation can result from microbial adaptation, which leads to more rapid degradation of the chemical [6]. Upon repeated exposure to a chemical, adapted microbes may degrade the chemical more rapidly, using it for a source of carbon and/or nitrogen. Although this phenomenon has not been documented for ATR, a study in our laboratory indicated that this does occur with DEA. Soils were compared from adjacent plots which had two different ATR histories. Soils from the plot that had received 15 consecutive years ATR application was designated ATR-history soil, while soil from the plot that had not received ATR application for 15 years were called no-history soils. Soils from the surface (0 to 30 cm) and subsurface (65 to 90 cm) were treated with uniformly ring-labeled $^{14}$C-DEA. Soil moistures were adjusted to and incubated in the dark at 24 °C for 60 d. $^{14}$CO$_2$ was trapped during the incubation period, and soils were extracted and analyzed as stated previously [2-3,5].

DEA was more rapidly degraded in ATR-history soil compared with no-history soil [7]. After a 60-d incubation, 25% of the applied DEA remained in ATR-history soils compared with 35% in no-history soils (ANOVA; p < 0.05). The amount of $^{14}$CO$_2$ evolved from complete mineralization of DEA was significantly greater in the ATR-history surface soil than in the no-history surface soil (ANOVA; p < 0.05), with 34% and 17% mineralization, respectively [7].

**Mobilities of ATR and ATR Degradates**

**Mobilities of ATR and DEA in Large Undisturbed Soil Columns from Ames.** The mobilities of ATR and DEA were investigated in our laboratory by using large undisturbed soil columns. Large intact soil columns (15 cm in diameter by 60 cm long) were removed from a field with no pesticide history. Soil columns were brought back to the laboratory and prepared for experimentation as previously described by Kruger et al. [8]. A modification to the top of the soil column allowed for monitoring of $^{14}$CO$_2$, $^{14}$C-organic volatiles, and aerobicity of the headspace [9]. Soil columns were treated with either $^{14}$C-ATR or $^{14}$C-DEA (2 replications each) and then leached weekly with 3.8 cm of simulated rainfall [8,9]. Leachate was collected at the bottom of the soil columns, and the amount of radioactivity recovered in the leachate was determined using liquid scintillation techniques.

For ATR-treated columns, the quantity of radioactivity recovered in the leachate was not sufficient enough to be characterized as parent and degradation products; thus, only the total percentage of $^{14}$C in the leachate could be reported. For DEA-applied soil columns, the level of radioactivity was increased so that the radioactivity recovered in the leachate could be characterized as DEA or degradation products. The leachate from DEA-applied soil columns was extracted by using solid-phase extraction techniques [9]. Liquid scintillation techniques were used to quantify radioactivity in the eluant. Thin-layer chromatography and autoradiography were used to characterize the components in the eluant (DEA or degradates).

In these studies, DEA was more mobile than ATR. Total $^{14}$C-residues leached from soil columns for the 12-wk study are shown in Figure 5. From the DEA-applied
Figure 4. Persistence of ATR and DEA in Ames soils under unsaturated (-33 kPa soil moisture tension) and saturated soil moisture (30% above -33 kPa) conditions (60-d incubation). Pairwise comparisons (by ANOVA; $p < 0.05$) made among moisture conditions for each chemical. Means with the same letter are not statistically different. Bars (with standard deviations) represent the means of two replicates.

Figure 5. Percentage of applied $^{14}$C in leachate of soil columns (representing total $^{14}$C-residues) applied with either $^{14}$C-ATR or -DEA. Soils were leached with 3.8 cm simulated rainfall weekly for 12 weeks. Bars (with standard deviations) represent the means of two soil columns.
soil columns, 6% of the applied $^{14}$C was leached after 12 wk (cumulatively), while only 1% of the applied $^{14}$C from ATR-treated columns had leached after that period of time. From DEA-applied columns, 3.6% of the total radioactivity recovered in the leachate was characterized as DEA. Less than 0.2% of the applied $^{14}$C was characterized as DDA and deethylhydroxyatrazine (DEHYA, 2-hydroxy-4[amino]-6[isopropylamino]-s-triazine), whereas 3.8% was leached as unidentified polar dégradâtes, as determined by the amount of radioactivity in the eluate after solid-phase extraction [9].

Relative Mobilities of ATR and ATR Dégradâtes in Soil Thin-Layer Chromatography (STLC) Experiments with Five Iowa Soils. Relative mobilities of ATR, DEA, DIA, DDA, and HYA were also assessed in our laboratory by using STLC [10]. Surface and subsurface soils from the five locations in Iowa mentioned previously (Table 1) were used in this study. Soil slurry columns were made by using ultrapure soils and ultrapure water. Slurries were poured onto glass plates (20 cm by 20 cm) which had two opposing edges wrapped with masking tape to a thickness of 1 mm. A glass rod was used to roll the slurries evenly across the plates at a depth of 1 mm by using the masking tape as a resting place for both ends of the glass rod. Plates were dried, and approximately 0.5 μCi of $^{14}$C-ATR, -DEA, -DIA, -DDA, and -HYA were spotted individually 3 cm from the bottom of the STLC plates. Ascending chromatography was carried out by placing the plates in developing chambers containing 2 cm ultrapure water. After the water had travelled to within 3 cm of the top of the STLC plates, the plates were removed and allowed to dry. Autoradiography was used to visualize the movement of the $^{14}$C-triazines. The movement of the solvent front and the chemical fronts were determined and used to calculate the $R_f$ values (relative frontal movement which equals the distance travelled by the front of the radioactive spot divided by the distance travelled by the water).

The mobilities of each chemical tested increased in soil from the subsurface (65 to 90 cm) compared with the surface soil (0 to 30 cm). DEA exhibited the greatest mobility, compared with those of ATR, DIA, DDA, and HYA (Figure 6). HYA was nearly immobile in all soils ($R_f$ values < 0.25). ATR, DIA, and DDA were equally mobile in most soils studied (ANOVA; $p < 0.05$).

Mobilities of ATR and ATR Dégradâtes in a Field Plot Study. To further study the mobility of ATR and dégradâtes under field conditions, tile drains were sampled from ATR-applied fields plots [11]. Water samples were collected from tile drains which were separate for each field plot. Solid-phase extraction techniques were used to isolate ATR, DEA & DIA. Samples were analyzed by liquid chromatography. The general trend of concentrations of ATR and dégradâtes in tile drains was ATR > DEA > DIA. It was also noted that the degradation products, by themselves or in combination with ATR, could exceed the maximum contaminant level set for ATR (3 μg L$^{-1}$).

Mobilities of ATR, DEA, and DIA in Field Box Lysimeters Treated with Extrazine®. Additionally, field box lysimeters were used to study the movement of
constituents of Extrazine® II, a herbicide that is a combination of 67% CYA and 21% ATR [12]. Each lysimeter was 229 cm long, 91 cm wide, and 152 cm deep. Each lysimeter was equipped with a porous drainage tile at the 152-cm depth which was connected to a drainage-tile sump apparatus. After each rainfall event, tile drain water was removed, and a subsample was extracted by using solid-phase extraction techniques. Samples were analyzed by gas chromatography and mass spectrometry (GCMS).
From tile drain of lysimeters applied with Extrazine® at a rate of 3.4 kg ha⁻¹, concentrations of DIA exceeded those of DEA during the 1993 growing season (Kruger et al., unpublished). For the first 30 rain events of 1993, the mean concentrations of DEA and DIA in tile drain samples were 0.09 and 0.3 μg/L, respectively. For the last 13 rain events the mean concentrations of DEA and DIA were 0.11 and 1.2 μg/L, respectively. From ATR degradation, it has been reported that DEA concentrations exceed those of DIA [2, 4, 8, 13, 14]. Since CYA can also be degraded to DIA [14], it seems that the contribution of CYA to the DIA concentrations in the tile drain of these lysimeters was very significant.

Summary

In general, degradation is more rapid in surface soils and under saturated soil moisture conditions. Mobility of DEA is greater than that of the parent compound. DIA and DDA mobilities are similar to the mobility of ATR. Levels of DIA were less than DEA in the soil profile of ATR-applied soil columns. Also, DEA was detected in higher concentrations than DIA in the tile drains of ATR-applied field plots. DIA concentrations exceeded those of DEA in tile drains of field lysimeters applied with CYA and ATR. Thus, CYA may contribute to concentrations of DIA in ground water.

Risk assessment of ATR and degradates necessarily depends on their environmental fate, and their environmental fate is a function of several factors, including mobility, persistence, and degradation products formed as well as their degradability. For example, DEA is more mobile than ATR, but it is also more rapidly degraded. Any potential importance of DEA residues must, of course, be balanced by the probabilities and concentrations of its occurrence. Most of the transformation products of ATR are more degradable than the parent under most environmental conditions, but their relative mobilities vary considerably. It is clear that the fate and significance of herbicides and their degradates in the environment depend on multiple factors and require extensive investigation to understand the complete picture.

Conclusions

1. Persistence of ATR, DEA, and DIA was greater in subsurface soils than in surface soils.
2. Mineralization of ATR and DIA was greater in surface soil compared with subsurface soil.
3. DIA was most susceptible to mineralization, compared with ATR, DEA, and HYA.
4. ATR, DEA, and DIA were less persistent in saturated soils than in unsaturated soils.
5. DEA degradation was enhanced in an ATR-history soil compared with a no-history soil.
6. DEA was more mobile than ATR in studies using soil thin-layer chromatography and undisturbed soil columns.
7. ATR, DIA, and DDA were equally mobile in soil thin-layer chromatography experiments.
8. Concentrations of DEA exceeded those of DIA in tile drains from ATR-applied field plots.
9. Concentrations of DIA exceeded those of DEA in tile drains from field box lysimeters treated with Extrazine® (67% CYA and 21% ATR).

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