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Degradation and movement of atrazine and deisopropylatrazine in soil

Ellen Louise Kruger
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Degradation and movement of atrazine
and deisopropylatrazine in soil

by

Ellen Louise Kruger

A Thesis Submitted to the
Graduate Faculty in Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

Department: Entomology
Interdepartmental Major: Toxicology

Approved:

Signatures have been redacted for privacy

Iowa State University
Ames, Iowa
1992
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This research was supported by grants from the Leopold Center for Sustainable Agriculture, and USDA’s Management System Evaluation Area Program and North Central Region Pesticide Impact Assessment Program. Ciba-Geigy Corporation provided analytical standards and radiolabeled chemicals. I thank Mike Wallendorf for assistance with statistical analysis and also Dr. H.M. Stahr for sharing his expertise in TLC techniques.

I would like to express my love and appreciation to my son, Adam, for his support and understanding. I would also like to extend my sincere gratitude to family members who gave their love and support, especially my parents Bernice and Bazil Wenzel who also showed me the value of hard work. And last but not least I want to express a special heartfelt thanks to Marie Rogge, my grandma, who gave me unending encouragement.
As pesticides are a vital part of intensive agriculture, much research has been done on their environmental fate. A significant portion of the applied pesticides ultimately reach the soil matrix. Pesticides undergo complex interactions within the soil and can be degraded physically, chemically and biologically. Parent compounds as well as their degradation products have potential to move in the environment and be further transformed until they are no longer detectable (Weber, 1991).

With advances in analytical techniques increasing the sensitivity of detection, it is now possible to monitor the dissipation of pesticides and their degradation products to the picogram level. Dissipation of a chemical in the environment includes degradation, sorption to soil, absorption, exudation and retention by organisms, movement in runoff, volatilization, and movement downward in the soil profile through leaching (Weber, 1991). As pesticides move through the soil profile they are exposed to a changing environment. Moisture, aeration, chemical properties of soil, and composition of microbial populations which change with depth (Alexander, 1961; Paul and Clark, 1989) can effect the fate of pesticides.

Transport processes are affected by a chemical’s tendency to partition in a particular way between soil, water and air (McCall et al., 1980). Adsorption of pesticides to soil can directly and indirectly influence their fate, movement in the soil, and leaching to groundwater (Clay and Koskinen, 1990).

Undegraded parent pesticides and/or their degradation products can become tightly bound to the soil (Weber, 1991). Bound residues can be a result of chemical binding, adsorption to the external soil surface, or entrapment in the internal voids of the molecular sieve-like structure of the soil (Khan, 1991). Pesticides can also be enzymatically bound to soil organic matter (Bollag, 1991). These residues are unextractable by conventional extraction procedures used in pesticide residue analysis. The exact mechanism of formation, ultimate fate and toxicological significance of bound residues are not understood for most pesticides (Sethunathan et al., 1991). There is a question in the literature as to whether or not bound residues will remain bound, or if there will there be a subsequent release of these residues during further microbial or chemical degradation (Bollag, 1991).

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine) is one of the most widely used pesticides in the United States with an estimated annual usage of 36 million kg (Rostad et al., 1989). This s-triazine herbicide is used to control broadleaf weeds and some grasses in corn and other crops. Since atrazine first became available commercially in 1958, much research has been conducted to determine the processes involved in its dissipation in the environment.

The relative persistence of atrazine not only provides the advantage of extended
control, but also increases the chance of its leaching to the groundwater. Groundwater monitoring programs have detected significant levels of atrazine (Hallberg, 1989; Rostad et al., 1989; Spalding et al., 1989). The occurrence of atrazine in groundwater is attributed to its heavy usage, moderate persistence and mobility (Spalding et al., 1989).

Atrazine has been found more frequently in water supplies than other commonly used agricultural pesticides in Iowa (Hartzler and Jost, 1990). During a 1987 water quality monitoring study in Iowa, the most commonly detected herbicide was atrazine with the majority of detections below 1 ppb (Stoltenberg et al., 1990). Two degradation products of atrazine, deethylatrazine (2-chloro-4-amino-6-isopropylamino-s-triazine) and deisopropylatrazine (2-chloro-4-ethylamino-6-amino-s-triazine), have also been detected in groundwater (Rostad et al., 1989).

The U.S. Environmental Protection Agency (USEPA) has developed guidelines for risk assessment of pesticides in the environment. This process involves evaluating the full data base of a pesticide in order to determine if the pesticide presents an environmental or human health hazard (USEPA, 1987). Because of potential health concerns, the USEPA has issued a lifetime health advisory level of 3 ppb for atrazine (Stoltenberg et al., 1990). However, this takes into consideration only the parent compound. It is important to note that regulatory limits can be exceeded by total atrazine residues (atrazine and its degradation products) even though the atrazine level alone may not exceed them (Belluck et al., 1991).

Degradation products are an important consideration in monitoring our environment for contamination, especially since a recent USEPA national survey of drinking water
wells revealed that the most frequently detected pesticide product was tetrachloroterephthalic acid, a metabolite of DCPA (USEPA, 1990). Inadequate regulatory policies regarding transformation products presently exist primarily due to the lack of scientific data to support the development of new policies (Somasundaram and Coats, 1991).

The persistence and degradation of atrazine is influenced by such factors as soil pH, moisture, temperature, and microbiological activity. As pesticides move through the soil profile they can be influenced by changes in these conditions (Goswami and Green, 1971).

Atrazine can be degraded chemically and biologically in soil. It can be difficult to distinguish between the biological and chemical origin of atrazine degradation. For example, hydroxyatrazine can result from either chemical hydrolysis (Armstrong et al., 1967) or from metabolism by some soil fungi (Couch et al., 1965). Although N-dealkylation can occur as a result of chemical degradation (Esser et al., 1975), it is also an important mechanism of biological degradation and can be brought about by fungi and bacteria present in the soil (Behki and Khan, 1986; Kaufman and Blake 1970). It has been found that some microorganisms remove the ethyl side chain preferentially (Skipper and Volk, 1972; Schiavon, 1988), while others preferentially remove the isopropyl side chain (Behki and Khan, 1986).

The sorption and mobility of atrazine and its degradation products have been studied. Brouwer et al. (1990) measured the soil-water partitioning coefficients ($K_d$) and distribution coefficients of organic matter to water ($K_{om}$) for atrazine and its breakdown
products. They found that movement of atrazine, deisopropylatrazine, and deethylatrazine to groundwater can be explained by their low $K_{OM}$ values. Hydroxyatrazine with a high $K_{OM}$ would be considered much less mobile than atrazine. Their study suggested that hydroxyatrazine found at depths of 40 cm in soil may be the result of degradation of the parent compound after reaching this depth.

Clay and Koskinen (1990) found adsorption of atrazine and hydroxyatrazine to be pH dependent with higher adsorption in low pH soils. The sorption of metribuzin, an asymmetrical triazine, was strongly correlated with pH and clay in soil samples taken in sections down to 175 cm depth (Harper, 1988). Helling (1971) found soil pH to be an important factor in influencing the movement of acidic compounds but did not find a strong correlation between pH and atrazine movement.

Organic carbon content has been shown to be a very important soil property influencing sorption of neutral organic compounds. McCall et al. (1980) suggested that the $K_{OC}$ value provides a reliable estimate of a chemical's mobility in soil. Atrazine has a $K_{OC}$ value of 170 which indicates that it is moderately mobile.

Degradation of pesticides usually results in products that are more soluble than the parent compound. Differences in molecular symmetry, and therefore polarity, can account for higher solubilities of structurally modified atrazine (Esser et al., 1975). With the use of soil thin-layer chromatography, Somasundaram et al. (1991) found that both the octanol/water partition coefficient ($K_{ow}$) and water solubility significantly correlated with the mobility of atrazine and hydroxyatrazine.

In a study using radiolabeled atrazine under field conditions, bound residues of
atrazine and its degradation products were found in the soil 9 years after application (Capriel et al., 1985). Khan and Saidak (1981) stated that the degradation products of atrazine, especially the hydroxylated analogs, persisted in soil one year after cessation of a long-term application with atrazine. There is no clear agreement as to the nature of atrazine derived bound residues. Erickson and Lee (1989) reported that hydroxyatrazine, the hydrolysis product of atrazine, is strongly bound to soil, while Schiavon (1988) indicated that hydroxyatrazine formed practically no soil-bound residues.

By conducting laboratory studies under controlled conditions, it is possible to get a better understanding of the comparative fate of atrazine and its degradation products in soil. In using ¹⁴C-radiolabeled atrazine, the ultimate fate of the parent pesticide can be assessed. Radiotracers such as carbon-14 provide a very sensitive means for monitoring organic chemicals since carbon is a universal component of organic pesticides.

Studies have traditionally focused on parent compounds. Previously, a lack of suitable analytical techniques has prevented detection of trace amounts of pesticide metabolites. With the availability of radiolabeled pesticides, an efficient means exists for quantitatively and qualitatively documenting the behavior of these compounds under varying conditions (Somasundaram & Coats, 1991).

Dissertation objectives

The overall objective of the proposed research is to investigate the persistence and degradation of atrazine and deisopropylatrazine at different depths in a soil using radiolabeled compounds. Specific objectives are:
1. To determine the persistence and degradation of atrazine and deisopropylatrazine in soils collected at 4 depths down to 120 cm, under saturated and unsaturated soil moisture conditions.

2. To determine the degradation and movement of atrazine in undisturbed soil columns.

Explanation of thesis format

This thesis is composed of two papers, each of which has been submitted to an appropriate scientific journal. A general introduction precedes Paper I. Paper I addresses the persistence and degradation of atrazine and deisopropylatrazine at different depths in saturated and unsaturated soils and has been submitted to Environmental Toxicology and Chemistry. Paper II addresses the movement and degradation of atrazine in undisturbed soil columns and has also been submitted to Environmental Toxicology and Chemistry. Reference sections are included at the end of each paper. There is a general summary of both papers following Paper II. An additional reference section at the end of the thesis lists sources used in the GENERAL INTRODUCTION and SUMMARY sections.
PAPER I. PERSISTENCE AND DEGRADATION OF ATRAZINE AND DEISOPROPYLATRAZINE AS AFFECTED BY SOIL DEPTH AND SATURATED/UNSATURATED MOISTURE CONDITIONS
Complete metabolism studies using radiotracers were performed in the laboratory to determine the fate of atrazine (ATR) and deisopropylatrazine (DIA) in soil as affected by depth and saturated/unsaturated conditions. Soil samples taken from four depths (0-30 cm, 30-65 cm, 65-90 cm, and 90-120 cm) were treated with either $^{14}$C-ATR or $^{14}$C-DIA and incubated under unsaturated conditions for 60 or 180 d. Additional soil from the 90-120 cm depth was treated similarly but incubated under saturated conditions for 60 or 120 d. A mass balance was determined for all treatments.

Major degradation products identified were deethylatrazine (DEA) in $^{14}$C-ATR treated soils and didealkylatrazine (DAA) in $^{14}$C-DIA treated soils for both saturated and unsaturated conditions. Minor degradation products detected in this study were hydroxyatrazine (HYA), deethylhydroxyatrazine (DEHYA), and deisopropylhydroxyatrazine (DIHYA).

In the unsaturated study, ATR and DIA were least persistent in the 0-30 cm soil and their persistence increased with increase in depth. The amount of ATR remaining after 180 d ranged from 4 to 58% for the different depths studied while the amount of DIA remaining after 180 d ranged from 2 to 48%. DIA was more susceptible to mineralization (2 to 19% at 180 d) than ATR (<1% at 180 d). The amount of mineralization decreased with increase in depth. Soil-bound residues were formed to a greater extent in surface soils (58% of $^{14}$C-ATR and 70% of $^{14}$C-DIA after 180 d).

Saturated conditions had minimal effect on ATR degradation. DIA was less
persistent in saturated soil than in unsaturated soil. More soil-bound residues were formed in $^{14}$C-DIA treated saturated soil (32%) than in unsaturated soil (14%) and the amount of bound residues formed increased over time under saturated conditions.

The increased degradability of DIA as compared to ATR and the decreased persistence of DIA under saturated soil conditions might explain its low concentrations in groundwater as compared to ATR.
INTRODUCTION

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine) is a herbicide that is used widely in the U.S. The relative persistence of this compound increases its potential to leach to the groundwater (Stoltenberg et al., 1990). Atrazine and two of its major degradation products, deethylatrazine (2-chloro-4-amino-6-isopropylamino-s-triazine) and deisopropylatrazine (2-chloro-4-ethylamino-6-amino-s-triazine) have been detected in the groundwater (Hallberg, 1989; Rostad et al., 1989; Spalding et al., 1989; Jayachandran et al., 1992).

Pesticides that are transported down through the soil profile are exposed to increased soil moistures that create conditions much different from those of aerated soils (Goswami and Green, 1971). Factors such as soil pH, moisture, temperature and microbial activity can influence the persistence and degradation of atrazine (Walker, 1987, Weber, 1991). Throughout the soil profile these may parameters change (Paul and Clark, 1988; Alexander, 1961). Atrazine can be chemically or biologically degraded in soil. Degradation pathways of atrazine are shown in Figure 1.

Research has, for the most part, focussed on the parent compound. By studying the effects of depth and moisture content on the persistence and degradation of ATR and DIA, a better understanding may be obtained about their behavior in the soil profile.
Figure 1. Degradation of atrazine in soil
MATERIALS AND METHODS

Chemicals

The following radiolabeled chemicals were obtained from Ciba-Geigy Co., Greensboro, NC: [U-ring-14C]atrazine (98.2% pure); [U-ring-14C]deethylatrazine (94.8% pure); [U-ring-14C]deisopropylatrazine (92.9% pure); [U-ring-14C]didealkylatrazine (98.8% pure); [U-ring-14C]hydroxyatrazine (97.5% pure).

The following analytical standards were also obtained: atrazine (98.7% pure), deethylatrazine (99% pure), deisopropylatrazine (98% pure), didealkylatrazine (97% pure) and hydroxyatrazine (97% pure).

Soil sampling

Soil samples were taken from a field with no previous pesticide history at the Till Hydrology Site, Iowa State University Agronomy and Agricultural Engineering farm near Ames, IA. Samples were taken from four depths (0-30 cm, 30-65 cm, 65-90 cm, and 90-120 cm) using a Back Saver Model N3 soil probe (Clements Associates Inc., Newton, IA). Soils were passed through an 8-mm sieve and stored at 4°C for 90 days or less prior to treatment. Soil samples were sent to A & L Mid West Laboratories (Omaha, NE) for analysis to determine pertinent soil characteristics (Table 1). Soils for this study were classified as Nicollett Webster. The organic matter content ranged from 2.7% in the 0-30 cm soil to 1.6% in the 90-120 cm soil.
Table 1. Characteristics of Ames soil

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>Texture</th>
<th>Sand</th>
<th>Silt</th>
<th>Clay</th>
<th>O.M.</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-30</td>
<td>Sandy Clay Loam</td>
<td>52</td>
<td>26</td>
<td>22</td>
<td>2.7</td>
<td>5.7</td>
</tr>
<tr>
<td>30-65</td>
<td>Loam</td>
<td>40</td>
<td>34</td>
<td>26</td>
<td>2.7</td>
<td>6.2</td>
</tr>
<tr>
<td>65-90</td>
<td>Sandy Clay Loam</td>
<td>46</td>
<td>26</td>
<td>28</td>
<td>1.7</td>
<td>6.2</td>
</tr>
<tr>
<td>90-120</td>
<td>Sandy Clay Loam</td>
<td>46</td>
<td>28</td>
<td>26</td>
<td>1.6</td>
<td>6.2</td>
</tr>
</tbody>
</table>
Treatments and soil incubation

Laboratory studies were performed on two replicates. Six soil cores were collected from the field, and three adjacent cores were composited by depth for each replicate. Length of incubation periods were randomly assigned to subsamples from each depth. An analysis of variance was performed on this split-plot design.

**Unsaturated study**  
$^{14}$C-ATR was applied at a concentration of 5 ppm and $^{14}$C-DIA was applied at a concentration of 1 ppm to soils from all four depths. These rates were chosen to represent the relative concentration that these compounds might actually occur in the field. Radiolabeled compounds were dissolved in methanol which had to be evaporated from the soil before adjusting the soil moisture in order to prevent harmful effects on microbes. One 50-g (dry weight) aliquot was extracted three times with 150 ml of methanol:water (9:1) to quantify the actual amount of $^{14}$C-pesticide applied. The extraction efficiency was 99%. Two other 50-g (dry weight) aliquots were each placed in French square bottles, and soil moisture was adjusted to one-third bar. A vial containing 10 ml 0.1 N NaOH was enclosed inside each bottle to trap $^{14}$CO$_2$ that would evolve from mineralization of the compounds (Figure 2). The vials were changed weekly and counted using a liquid scintillation technique. Soils were incubated for 60 or 180 d at 25°C.

**Saturated study**  
Soils from the 90-120 cm depth were treated as stated above. One 50-g aliquot was extracted immediately and two other 50-g aliquots were each placed in jars. Soil moisture was adjusted to 30% above one-third bar. This provided a uniform layer of water approximately 2-mm deep above the soil of and insured the full saturation of the soil. The headspace of these jars was filled with ultrapure nitrogen to
Figure 2. Soil incubation setup for unsaturated soil study
provide an anaerobic atmosphere above the soil. A nitrogen flow-through system was used to trap $^{14}$C$_2$O$_2$ in 0.1 N NaOH and $^{14}$C-volatile organics, such as methane, in Ultima Gold™ scintillation cocktail (Packard Instrument Co., Downers Grove, IL) each week (Figure 3). After incubation, soils were centrifuged, and the supernatant was removed with a pipet. After decreasing the pH of the supernatant to one with 1 M HCl, the supernatant was partitioned three times with 50 ml of dichloromethane. Each time, a saturated solution of sodium chloride was added in order to expel polar metabolites from the aqueous phase into the dichloromethane. Soils were extracted and partitioned as stated above. Thin-layer chromatography was carried out on the organic fraction of the supernatant and soil extract.

**Extraction and analyses**

After the incubation periods, soils were extracted three times with 150 ml of 9:1 methanol/water. The extract was concentrated with a rotary evaporator and acidified with 1 M HCl to a pH of one. The extract was partitioned into an aqueous and organic phase three times with 50 ml of dichloromethane. A saturated solution of sodium chloride was used at each partitioning step to expel polar metabolites from the aqueous phase into dichloromethane. The organic fraction was concentrated and rediluted to 10 ml.

Thin-layer chromatography was performed using a concentrated portion of the organic fraction from each soil sample. Normal phase silica gel plates were used and developed in a solvent system of chloroform: methanol: formic acid: water (100:20:4:2) (Ciba-Geigy, Greensboro, NC). Autoradiography was performed using X-Omat™ Kodak
Figure 3. Nitrogen flow-through system for collecting 14C-organic volatiles during incubation of saturated soils.
diagnostic film (Eastman Kodak Co., Rochester, NY). A film was placed in contact with each plate for 3 to 5 wk and then developed. The distribution of ATR and degradation products in the organic fraction was determined through this process and \( R_f \) values are shown in Table 2.

Soil-bound residues were determined by combusting pellets made up of 0.5 g soil and 0.1 g hydrolyzed starch in a Packard Sample Oxidizer (Packard Instrument Co, Downers Grove, IL). \(^{14}\text{CO}_2\) was trapped in Carbo-Sorb\textsuperscript{E} and Permafluor\textsuperscript{V} (Packard Instrument Co., Downers Grove, IL). Trapping efficiency was determined using SpecChec\textsuperscript{TM}. \(^{14}\text{C}\) standard (9.12 x 10\(^5\) dpm/ml) and Spec-Chec\textsuperscript{TM} nonactive standard. Three pellets were burned per replicate and radioactivity was determined by using a RackBeta model 1217 liquid scintillation counter (Pharmacia LKB Biotechnology, Inc., Gaithersburg, MD).
Table 2. $R_f$ values of atrazine and its degradation products using a solvent system of chloroform: methanol: formic acid: water (100:20:4:2)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$R_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atrazine</td>
<td>0.90</td>
</tr>
<tr>
<td>Deethylatrazine</td>
<td>0.79</td>
</tr>
<tr>
<td>Deisopropylatrazine</td>
<td>0.73</td>
</tr>
<tr>
<td>Didealkylatrazine</td>
<td>0.50</td>
</tr>
<tr>
<td>Hydroxyatrazine</td>
<td>0.40</td>
</tr>
<tr>
<td>Deethylhydroxyatrazine</td>
<td>0.16</td>
</tr>
<tr>
<td>Deisopropylhydroxyatrazine</td>
<td>0.13</td>
</tr>
</tbody>
</table>
RESULTS AND DISCUSSION

ATR degradation in unsaturated soil

The mass balance data for $^{14}$C-ATR treated soils incubated for 60 and 180 d are shown in Tables 2 and 3, respectively. ATR was significantly more persistent in the 90-120 cm soil with 77% and 58% of the applied $^{14}$C recovered, respectively, for the 60-d and 180-d incubations. Harris et al. (1969) reported that a relatively higher percent of ATR was recovered from subsurface soils than from surface soils. The organic matter content of the 90-120 cm layer (1.6%) was less than that of the upper depths (Table 1). Less biological degradation might be occurring at this depth since microorganisms are less active in soils with lower organic matter content (Alexander, 1961; Roeth et al., 1969; Kaufman and Kearney, 1970; Nicholls, 1988).

Persistence of ATR was shorter in the upper soil layers, with no significant differences seen among the soils from the 0-30, 30-60, or 60-90 cm depths. As little as 4% of the applied $^{14}$C remained as ATR in the 0-30 cm depth after 180 d (Table 3). Winkelmann and Klaine (1991a) found 40% of the ATR remaining in surface soil brought to 80% field capacity. In the current study, soil moisture was brought to 100% field capacity. Soil moisture promotes microbial growth, and the rate of pesticide degradation increases with increased soil moisture to the point of maximum field capacity (Wolf et al., 1989). Wagner and Chahal (1966) recovered only 10% of applied ATR after 180 d. Best et al. (1975) recovered 34% of applied ATR from soils with a pH of 7.5, as compared to 10% in soils with a pH of 5.5. The range of pH for the four depths used in
Table 2. Effect of depth on the degradation of $^{14}$C-atrazine under unsaturated conditions (60-day incubation)

(Mass Balance Reported as % of Applied $^{14}$C)

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>0-30</th>
<th>30-65</th>
<th>65-90</th>
<th>90-120</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atrazine</td>
<td>33.08&lt;sup&gt;a&lt;/sup&gt;</td>
<td>47.56&lt;sup&gt;a&lt;/sup&gt;</td>
<td>39.51&lt;sup&gt;a&lt;/sup&gt;</td>
<td>76.83&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Deethylatrazine</td>
<td>2.40&lt;sup&gt;a&lt;/sup&gt;</td>
<td>3.73&lt;sup&gt;b&lt;/sup&gt;</td>
<td>2.46&lt;sup&gt;ab&lt;/sup&gt;</td>
<td>2.27&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Deisopropylatrazine</td>
<td>0.73&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.72&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.83&lt;sup&gt;ab&lt;/sup&gt;</td>
<td>1.26&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Didealkyatrazine</td>
<td>4.12&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.72&lt;sup&gt;ab&lt;/sup&gt;</td>
<td>0.68&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.11&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Hydroxyatrazine</td>
<td>0.15&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.18&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.18&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.17&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Deethylhydroxyatrazine</td>
<td>0.04&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.20&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.05&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.02&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Deisopropylhydroxyatrazine</td>
<td>0.10&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.01&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.01&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.00&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Polar metabolites</td>
<td>9.20&lt;sup&gt;a&lt;/sup&gt;</td>
<td>8.37&lt;sup&gt;a&lt;/sup&gt;</td>
<td>6.07&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.86&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>CO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.34&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.27&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.10&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.01&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Soil bound</td>
<td>44.72&lt;sup&gt;a&lt;/sup&gt;</td>
<td>30.81&lt;sup&gt;ab&lt;/sup&gt;</td>
<td>25.75&lt;sup&gt;b&lt;/sup&gt;</td>
<td>12.62&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Others&lt;sup&gt;d&lt;/sup&gt;</td>
<td>0.50&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.14&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.26&lt;sup&gt;ab&lt;/sup&gt;</td>
<td>0.45&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Total</td>
<td>95.29&lt;sup&gt;a&lt;/sup&gt;</td>
<td>93.53&lt;sup&gt;a&lt;/sup&gt;</td>
<td>75.90&lt;sup&gt;a&lt;/sup&gt;</td>
<td>95.60&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a-c</sup>Means in each row followed by the same letter are not significantly different (p=0.05).
<sup>d</sup>Others include unidentifiable minor degradation products observed in the TLC system.
Table 3. Effect of depth on the degradation of $^{14}$C-atrazine under unsaturated conditions (180-day incubation)

(Mass Balance Reported as % of Applied $^{14}$C)

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>0-30</th>
<th>30-65</th>
<th>65-90</th>
<th>90-120</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atrazine</td>
<td>4.28&lt;sup&gt;a&lt;/sup&gt;</td>
<td>15.00&lt;sup&gt;a&lt;/sup&gt;</td>
<td>14.04&lt;sup&gt;a&lt;/sup&gt;</td>
<td>58.33&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Deethylatrazine</td>
<td>0.36&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.62&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.53&lt;sup&gt;a&lt;/sup&gt;</td>
<td>3.13&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Deisopropylatrazine</td>
<td>0.21&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.47&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.48&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.14&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Didealkylatrazine</td>
<td>0.10&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.10&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.14&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.93&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Hydroxyatrazine</td>
<td>1.78&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.99&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.95&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.36&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Deethylhydroxyatrazine</td>
<td>0.04&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.01&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.04&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.05&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Deisopropylhydroxyatrazine</td>
<td>0.00&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.00&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.01&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.01&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Polar metabolites</td>
<td>13.79&lt;sup&gt;a&lt;/sup&gt;</td>
<td>17.51&lt;sup&gt;a&lt;/sup&gt;</td>
<td>13.85&lt;sup&gt;a&lt;/sup&gt;</td>
<td>4.50&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>CO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.82&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.57&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.69&lt;sup&gt;ab&lt;/sup&gt;</td>
<td>0.01&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Soil bound</td>
<td>58.24&lt;sup&gt;a&lt;/sup&gt;</td>
<td>41.03&lt;sup&gt;a&lt;/sup&gt;</td>
<td>53.31&lt;sup&gt;a&lt;/sup&gt;</td>
<td>19.79&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Others&lt;sup&gt;d&lt;/sup&gt;</td>
<td>0.16&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.20&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.19&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.00&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Total</td>
<td>79.78&lt;sup&gt;a&lt;/sup&gt;</td>
<td>77.50&lt;sup&gt;a&lt;/sup&gt;</td>
<td>85.23&lt;sup&gt;a&lt;/sup&gt;</td>
<td>88.25&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup>Means in each row followed by the same letter are not significantly different (p=0.05).

<sup>d</sup>Others include unidentifiable minor degradation products observed in the TLC system.
the current study was between 5.7 to 6.2. A simple regression showed no specific correlation of ATR persistence with pH.

Dealkylated degradation products were detected in extracts of $^{14}$C-ATR treated soils and included DEA, DIA and DAA. DEA was the predominant degradation product as has been the case in other studies (Sirons et al., 1973; Adams and Thurman, 1991). DEA was also detected in higher concentrations than DIA in the four soil depths studied here. Others have found the same relationship between these two degradation products (Sirons et al., 1973; Muir and Baker, 1978; Schiavon, 1988; Jayachandran et al., 1992).

Skipper and Volk (1972) indicated that microbial removal of the ethyl side chain is eight to twelve times more rapid than for the isopropyl side chain. The concentration of DEA increased over time in the 90-120 cm soil and was significantly more abundant in this layer than in the upper layers after the 180-d incubation (Table 3). Frank et al. (1991) also found that the percentage of the total residue present as DEA increased in the soil profile with time and depth and DEA was the predominant degradation product below 30 cm. DAA was detected in all four soil depths for both incubation lengths, ranging in concentration from 0.1% to 4%. In a similar study, Winkelmann and Klaine (1991a) did not detect this degradation product.

Only a small portion of the applied $^{14}$C was accounted for as HYA with no significant differences seen among soils from the four depths. Others have found HYA to be a principal degradation product (Skipper et al., 1967; Muir and Baker, 1978; Khan and Saidak, 1981; Jones et al, 1982; Winkelmann and Klaine, 1991a). Soils used in at least one of these studies (Winkelmann and Klaine, 1991a) were more acidic than soils in
the current study. ATR hydrolysis is generally favored by extreme pH conditions (Armstrong et al., 1967) but not in the range used in this study. This could be the reason for the low amount of HYA obtained in the current study.

DEHYA and DIHYA were detected in very low amounts at all depths. Khan and Saidak (1981) detected monodealkylated hydroxy analogs in soil samples with 20 consecutive years of atrazine application.

Polar metabolites were those which could not be extracted from the aqueous phase in partitioning, and the amount formed increased over time for the four depths. Dao et al. (1979) also detected an increase in polar metabolites over time. No significant differences were seen in the amount of polar metabolites formed in the upper three layers for both incubation periods, however, significantly smaller quantities of polar metabolites were formed (4.5%) in the 90-120 cm soil after 180 d.

The amount of soil-bound residues formed was highest in the 0-30 cm soil (45% after 60 d and 58% after 180 d), and the amount decreased with increasing depth. Previous studies have detected high amounts of soil-bound residues in surface soils (Wagner and Chahal, 1966; Capriel et al., 1985). Soil-bound residues were formed to a significantly lesser extent in the 90-120 cm soil (13% after 60 d and 20% after 180 d). The amount of soil-bound residues formed increased over time for all four soil depths. A similar trend in surface soil has been noted by others (Dao et al., 1979; Winkelmann and Klaine, 1991a and 1991b).

The composition of soil-bound residues in this study was not determined. It has been discussed that HYA and other hydroxy analogs are likely to make up the soil-bound
fraction (Khan and Saidak, 1981; Erickson et al., 1989). There is some disagreement with this, however. Schiavon (1988) indicated that HYA formed practically no bound residues and suggested that DAA is the product most likely to form bound residues. Baluch (1992) found no evidence of HYA forming significant amounts of bound residues.

ATR underwent only minimal mineralization, with less than 1% of the applied $^{14}$C recovered as $^{14}$CO$_2$ for all depths and both incubation periods. This is consistent with the findings of others (Wagner and Chahal, 1966; Skipper et al., 1967; Dao et al., 1979). Skipper et al. (1967) stated that microorganisms were unable to degrade the atrazine ring. Winkelmann and Klaine (1991a) detected as much as 28% of the applied $^{14}$C-ATR applied to intact soil microcosms as $^{14}$CO$_2$. In their study, a flow through system was used to trap carbon dioxide in a trapping solution of phenethylamine. Not only would aeration be increased by this method, but also the trapping solution is likely to capture carbon dioxide and any organic volatiles that may arise from the degradation of ATR. The radioactivity reported in their study might actually represent more than just $^{14}$CO$_2$. The current study used an enclosed system containing a vial of NaOH which was replaced weekly. The amount of $^{14}$CO$_2$ evolved was significantly less in the 90-120 cm soil. As was stated earlier, less microbial activity would be expected at this depth (Alexander, 1961; Nicholls, 1988).

Degradation of DIA in unsaturated soils

The mass balance data for the 60-d and 180-d incubation of DIA under unsaturated soil moisture conditions are provided in Tables 4 and 5, respectively. The persistence of DIA increased with increasing depth in soils incubated for 60 d and ranged from 14% in
Table 4. Effect of depth on the degradation of ¹⁴C-deisopropylatrazine under unsaturated conditions (60-day incubation)

(Mass Balance Reported as % of Applied ¹⁴C)

<table>
<thead>
<tr>
<th></th>
<th>0-30</th>
<th>30-65</th>
<th>65-90</th>
<th>90-120</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deisopropylatrazine</td>
<td>13.50a</td>
<td>39.25b</td>
<td>31.90b</td>
<td>65.65c</td>
</tr>
<tr>
<td>Didealkylatrazine</td>
<td>0.31a</td>
<td>3.53a</td>
<td>0.61a</td>
<td>2.01a</td>
</tr>
<tr>
<td>Deisopropylhydroxyatrazine</td>
<td>0.01a</td>
<td>0.05b</td>
<td>0.03ab</td>
<td>0.02a</td>
</tr>
<tr>
<td>Polar metabolites</td>
<td>5.80a</td>
<td>5.05a</td>
<td>6.95a</td>
<td>3.85a</td>
</tr>
<tr>
<td>Soil bound residues</td>
<td>60.70a</td>
<td>37.56b</td>
<td>34.28b</td>
<td>14.17c</td>
</tr>
<tr>
<td>CO₂</td>
<td>7.40a</td>
<td>7.92a</td>
<td>4.48ab</td>
<td>0.62b</td>
</tr>
<tr>
<td>Others d</td>
<td>2.56a</td>
<td>0.65a</td>
<td>0.88a</td>
<td>0.94a</td>
</tr>
<tr>
<td>Total</td>
<td>90.28ab</td>
<td>94.01a</td>
<td>79.13b</td>
<td>87.26ab</td>
</tr>
</tbody>
</table>

*Means in each row followed by the same letter are not significantly different (p=0.05).

*Others include unidentifiable minor degradation products observed in the TLC system.
Table 5. Effect of depth on the degradation of 14C-deisopropylatrazine under unsaturated conditions (180-day incubation)

(Mass Balance Reported as % of Applied 14C)

<table>
<thead>
<tr>
<th></th>
<th>Depth (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0-30</td>
</tr>
<tr>
<td>Deisopropylatrazine</td>
<td>1.58a</td>
</tr>
<tr>
<td>Didealkylatrazine</td>
<td>0.01a</td>
</tr>
<tr>
<td>Deisopropylhydroxyatrazine</td>
<td>0.01a</td>
</tr>
<tr>
<td>Polar metabolites</td>
<td>2.65a</td>
</tr>
<tr>
<td>Soil bound residues</td>
<td>70.11a</td>
</tr>
<tr>
<td>CO2</td>
<td>19.18a</td>
</tr>
<tr>
<td>Othersd</td>
<td>0.13a</td>
</tr>
<tr>
<td>Total</td>
<td>93.67a</td>
</tr>
</tbody>
</table>

**Means in each row followed by the same letter are not significantly different (p=0.05).**

**dOthers include unidentifiable minor degradation products observed in the TLC system.**
the 0-30 cm soil to 66% in the 90-120 cm soil (Table 4). After 180 d, 48% of the applied $^{14}$C remained as DIA in the 90-120 cm soil which was significantly more than that found in the upper layers (Table 5). Microbial degradation would presumably be less in the subsurface soil due to less microbial activity in that environment (Alexander, 1961; Kaufman and Kearney, 1970; Nicholls, 1988; Paul and Clark, 1989).

The persistence of DIA in surface soil in the current study is lower that reported by Winkelmann and Klaine (1991b). As was the case with ATR degradation, DIA degradation appears to be favored by increased moisture (Wolf et al., 1989).

DAA was the most prominent degradation product characterized with a maximum concentration of 3.5% in the 30-65 cm soil after 60 d incubation. No statistical differences were seen in the amount formed for the four depths and both incubation periods. Small quantities of DIHYA were detected at all depths and ranged from 0.1 to 0.5% of the applied $^{14}$C. Polar metabolites increased over time in soils from the lower three depths.

The amount of bound residues formed was highest in the 0-30 cm soil (61% after 60 d and 70% after 180 d), and its proportion decreased in soils with increase in depth. No significant differences were seen in amounts of bound residues formed in soils from the two intermediate depths.

DIA was more susceptible to mineralization than was ATR. Nineteen percent of $^{14}$C-DIA was evolved as $^{14}$CO$_2$ (Table 5) in the 0-30 cm soil after 180 d as compared with less than 1% for atrazine (Table 3). Comparable DIA mineralization has been reported by Winkelmann and Klaine (1991b) who detected 16% of applied $^{14}$C as $^{14}$CO$_2$ after 180
d. In the current study, significantly less mineralization occurred with increased depth with a minimum amount evolved from the 90-120 cm soil (2% of applied $^{14}$C) after 180 days. Facultative aerobic microorganisms responsible for dealkylation and cleavage of the triazine ring would likely not occur in submerged soils (Goswami and Green, 1971). Also, decreased organic matter along with decreased microbial activity in soils of increased depth would result in slower degradation (Nicholls, 1988)

**Saturated versus unsaturated soils**

**Atrazine** Saturation of soil had only minimal effect on the degradation of ATR at the 90-120 cm depth (Table 6). High variation between the two replications under saturated conditions did not allow for statistical differences between the two treatments. Jones *et al.* (1982) noted more rapid degradation of ATR to HYA in estuarine sediment, which is 40% water by weight, than in terrestrial soil systems. Agundis *et al.* (1966) reported that the disappearance of atrazine was more rapid in soils exposed to nitrogen atmospheres and higher soil moisture content at high temperatures.

DEA and DIA were formed to a lesser extent under saturated conditions. Wolf and Martin (1975) found less degradation under saturated conditions and suggested that removal of ethyl and isopropyl side chains may be an aerobic process. Virtually no mineralization of atrazine occurred under saturated or unsaturated conditions at the 90-120 cm depth. Others have also found little or no mineralization of atrazine under anaerobic and/or saturated conditions (Goswami and Green, 1971; Wolf and Martin, 1975).
Table 6. Degradation of $^{14}$C- atrazine under unsaturated and saturated conditions at 90-120 cm depth (60-day incubation)

<table>
<thead>
<tr>
<th></th>
<th>Unsaturated</th>
<th>Saturated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atrazine</td>
<td>76.83$^a$</td>
<td>66.64$^a$</td>
</tr>
<tr>
<td>Deethylatrazine</td>
<td>2.27$^a$</td>
<td>1.58$^b$</td>
</tr>
<tr>
<td>Deisopropylatrazine</td>
<td>1.26$^a$</td>
<td>0.58$^b$</td>
</tr>
<tr>
<td>Didealkylatrazine</td>
<td>0.11$^a$</td>
<td>0.18$^a$</td>
</tr>
<tr>
<td>Hydroxyatrazine</td>
<td>0.17$^a$</td>
<td>0.21$^a$</td>
</tr>
<tr>
<td>Deethylhydroxyatrazine</td>
<td>0.02$^a$</td>
<td>0.04$^a$</td>
</tr>
<tr>
<td>Deisopropylhydroxyatrazine</td>
<td>0.00$^a$</td>
<td>0.01$^a$</td>
</tr>
<tr>
<td>Polar metabolites</td>
<td>1.86$^a$</td>
<td>6.14$^a$</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>0.01$^a$</td>
<td>0.00$^a$</td>
</tr>
<tr>
<td>Soil bound</td>
<td>12.62$^a$</td>
<td>23.42$^a$</td>
</tr>
<tr>
<td>Others$^d$</td>
<td>0.45$^a$</td>
<td>0.41$^a$</td>
</tr>
<tr>
<td>Total</td>
<td>95.60$^a$</td>
<td>99.21$^a$</td>
</tr>
</tbody>
</table>

$^a$$^c$Means in each row followed by the same letter are not significantly different (p=0.05).

$^d$Others include unidentifiable minor degradation products observed in the TLC system.
Deisopropylatrazine  DIA was less persistent in saturated soils (Table 7). The increased degradation of DIA under saturated conditions is contrary to the assumption made by Goswami and Green (1971) that the degradation of chloro-s-triazines would be slower in submerged soils. A significantly greater quantity of polar metabolites was formed under saturated conditions (18%) than unsaturated conditions (4%). DAA and DIHYA were formed in low concentrations (< 1%) under saturated conditions. Bound residues were formed to a greater extent in the saturated soil (32%) as compared with 14% in unsaturated soil. Soil under flooded conditions can change from an aerobic and oxidative environment to an anaerobic and reductive environment (Sethunathan, 1973). Thus, differences in the fate of ATR and DIA would be expected under saturated and unsaturated conditions. Mineralization was not affected by saturated conditions. Less than 1% of the $^{14}$C-DIA applied was mineralized to $^{14}$CO$_2$ in both treatments.

Effect of incubation length under saturated conditions

No significant differences were seen in the mass balance of $^{14}$C-ATR treated soils incubated for 60 d or 120 d (Table 8). However, with the $^{14}$C-DIA treated soils, significantly larger quantities of polar metabolites and bound residues were formed upon extended incubation (Table 9).

Degradation rates and half-lives

In order to make quantitative comparisons of degradation rates among treatments, a rate constant was determined by plotting the natural log of the percent of applied $^{14}$C-ATR or -DIA remaining versus time. A linear regression was performed to produce a line with a slope proportional to the degradation rate constant, $k$ (Walker, 1987). Typical
Table 7. Degradation of $^{14}$C-deisopropylatrazine under unsaturated and saturated conditions at the 90-120 cm depth (60-day incubation)

(Mass Balance Reported as % of Applied $^{14}$C)

<table>
<thead>
<tr>
<th></th>
<th>Unsaturated</th>
<th>Saturated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deisopropylatrazine</td>
<td>65.65$^a$</td>
<td>44.65$^b$</td>
</tr>
<tr>
<td>Didealkylatrazine</td>
<td>2.01$^a$</td>
<td>0.51$^a$</td>
</tr>
<tr>
<td>Deisopropylhydroxyatrazine</td>
<td>0.02$^a$</td>
<td>0.06$^b$</td>
</tr>
<tr>
<td>Polar metabolites</td>
<td>3.85$^a$</td>
<td>17.93$^b$</td>
</tr>
<tr>
<td>Soil bound residues</td>
<td>14.17$^a$</td>
<td>32.13$^b$</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>0.62$^a$</td>
<td>0.52$^a$</td>
</tr>
<tr>
<td>Others$^d$</td>
<td>0.94$^a$</td>
<td>0.99$^a$</td>
</tr>
<tr>
<td>Total</td>
<td>87.26$^a$</td>
<td>96.79$^a$</td>
</tr>
</tbody>
</table>

$^a$-$^c$: Means in each row followed by the same letter are not significantly different (p=0.05).

$^d$: Others include unidentifiable minor degradation products observed in the TLC system.
Table 8. Effect of incubation length on the degradation of \(^{14}\text{C}\)-atrazine under saturated conditions (90-120 cm depth)

(Mass Balance Reported as \% of Applied \(^{14}\text{C}\))

<table>
<thead>
<tr>
<th>Incubation Length</th>
<th>60 Days</th>
<th>120 Days</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atrazine</td>
<td>66.64*</td>
<td>42.64*</td>
</tr>
<tr>
<td>Deethylatrazine</td>
<td>1.58*</td>
<td>1.40*</td>
</tr>
<tr>
<td>Deisopropylatrazine</td>
<td>0.58*</td>
<td>0.61*</td>
</tr>
<tr>
<td>Didealkylatrazine</td>
<td>0.18*</td>
<td>0.11*</td>
</tr>
<tr>
<td>Hydroxyatrazine</td>
<td>0.21*</td>
<td>0.05*</td>
</tr>
<tr>
<td>Deethylhydroxyatrazine</td>
<td>0.04*</td>
<td>0.01*</td>
</tr>
<tr>
<td>Deisopropylhydroxyatrazine</td>
<td>0.01*</td>
<td>0.01*</td>
</tr>
<tr>
<td>Polar metabolites</td>
<td>6.14*</td>
<td>13.72*</td>
</tr>
<tr>
<td>Soil bound</td>
<td>23.42*</td>
<td>37.13*</td>
</tr>
<tr>
<td>Others(^d)</td>
<td>0.41*</td>
<td>0.27*</td>
</tr>
<tr>
<td>Total</td>
<td>99.21*</td>
<td>95.95*</td>
</tr>
</tbody>
</table>

*Means in each row followed by the same letter are not significantly different (p=0.05).
\(^d\)Others include unidentifiable minor degradation products observed in the TLC system.
Table 9. Effect of incubation length on the degradation of $^{14}$C-deisopropylatrazine under saturated conditions (90-120 cm depth)

(Mass Balance Reported as % of Applied $^{14}$C)

<table>
<thead>
<tr>
<th>Incubation Length</th>
<th>60 Days</th>
<th>120 Days</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deisopropylatrazine</td>
<td>44.65$^a$</td>
<td>30.94$^a$</td>
</tr>
<tr>
<td>Didealkylatrazine</td>
<td>0.51$^a$</td>
<td>0.34$^a$</td>
</tr>
<tr>
<td>Deisopropylhydroxyatrazine</td>
<td>0.06$^a$</td>
<td>0.02$^b$</td>
</tr>
<tr>
<td>Polar metabolites</td>
<td>14.18$^a$</td>
<td>21.11$^b$</td>
</tr>
<tr>
<td>Soil bound residues</td>
<td>32.13$^a$</td>
<td>40.06$^b$</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>0.52$^a$</td>
<td>1.19$^a$</td>
</tr>
<tr>
<td>Others$^d$</td>
<td>0.99$^a$</td>
<td>0.49$^a$</td>
</tr>
<tr>
<td>Total</td>
<td>93.03$^a$</td>
<td>94.17$^a$</td>
</tr>
</tbody>
</table>

$^a$Means in each row followed by the same letter are not significantly different (p=0.05).

$^d$Others include unidentifiable minor degradation products observed in the TLC system.
soil kinetic studies require rigorous control of all experimental variables, conditions and measurements. Although this study was not initially designed to determine the kinetics of degradation, the coefficients of determination ranged from 0.85 to 1.00 (Table 10) indicating an excellent fit of the experimental data to the kinetic model employed.

The rate of degradation decreased with increasing depth for both ATR and DIA. DIA was degraded more rapidly than ATR. Rate constants under saturated soil moisture conditions for both ATR and DIA were slightly higher, possibly indicating hydrolysis as an important process in the degradation of ATR and DIA. Hydrolysis of DIA has been observed under anaerobic conditions (Cook and Hutter, 1986).

Half-lives (t_{1/2}) (time for 50% of the chemical to degrade) were calculated using the formula \( t_{1/2} = \frac{0.693}{k} \) (Walker, 1987). The half-life of ATR under unsaturated soil moisture conditions ranged from 41 d in the 0-30 cm soil to 231 d in the 90-120 cm soil. This is consistent with varying degrees of microbial activity with depth in the soil profile (Alexander, 1961; Kaufman and Kearney, 1970; Paul and Clark, 1989). Under saturated soil moisture conditions in the 90-120 cm depth, the half-life of ATR was 116 d. DIA had a shorter half-life than ATR for all treatments, and under unsaturated soil moisture conditions the half-life of DIA ranged from 32 d in the topsoil to 173 d in the 90-120 cm soil. In the 90-120 cm depth under saturated conditions, the half-life of DIA was reduced to 139 d.

Decreased persistence of ATR and DIA under saturated soil conditions may be due to the compounds being less sorbed to soil under high moisture conditions, making them more available for degradation microbially and/or chemically. No attempt was made to
Table 10. First-order degradation rate constants (k) and half-lives (t_{1/2}) of ATR and DIA in soils

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Depth (cm)</th>
<th>Moisture*</th>
<th>k**</th>
<th>r^2</th>
<th>T_{1/2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>ATR</td>
<td>0-30</td>
<td>U</td>
<td>-0.017</td>
<td>1.00</td>
<td>41 d</td>
</tr>
<tr>
<td>ATR</td>
<td>30-65</td>
<td>U</td>
<td>-0.010</td>
<td>1.00</td>
<td>69 d</td>
</tr>
<tr>
<td>ATR</td>
<td>65-90</td>
<td>U</td>
<td>-0.010</td>
<td>0.99</td>
<td>69 d</td>
</tr>
<tr>
<td>ATR</td>
<td>90-120</td>
<td>U</td>
<td>-0.003</td>
<td>0.96</td>
<td>231 d</td>
</tr>
<tr>
<td>ATR</td>
<td>90-120</td>
<td>S</td>
<td>-0.006</td>
<td>0.85</td>
<td>116 d</td>
</tr>
<tr>
<td>DIA</td>
<td>0-30</td>
<td>U</td>
<td>-0.022</td>
<td>0.97</td>
<td>32 d</td>
</tr>
<tr>
<td>DIA</td>
<td>30-65</td>
<td>U</td>
<td>-0.015</td>
<td>0.99</td>
<td>46 d</td>
</tr>
<tr>
<td>DIA</td>
<td>65-90</td>
<td>U</td>
<td>-0.013</td>
<td>0.98</td>
<td>53 d</td>
</tr>
<tr>
<td>DIA</td>
<td>90-120</td>
<td>U</td>
<td>-0.004</td>
<td>0.92</td>
<td>173 d</td>
</tr>
<tr>
<td>DIA</td>
<td>90-120</td>
<td>S</td>
<td>-0.005</td>
<td>0.97</td>
<td>139 d</td>
</tr>
</tbody>
</table>

*Moistures reported as U=unsaturated and S=saturated.

**Coefficients of determination
differentiate between the microbial and chemical influences of degradation in this study.

Major trends

The fate of ATR and DIA were significantly affected by soil depth. Although DIA was more susceptible to degradation than ATR in the top soil, the persistence of both compounds increased at greater depths. A significantly slower rate of degradation occurred in the deepest soil layer studied. The degradation of DIA was more rapid under saturated soil moisture conditions; however, for ATR this was not the case. The microbial degradation of ATR to DIA is less favored than to DEA (Skipper and Volk, 1972). The degradability of DIA as compared with ATR, and the decreased persistence of DIA under saturated soil conditions might also explain the very low concentrations of DIA detected in groundwater as compared with ATR and DEA.

Percent recoveries were not uniform in all of the mass balances calculations. In each case, one of the two replicates had a lower percent recovery, up to 20% lower. Organic volatiles that might have been produced from degradation of ATR and DIA could have escaped. Winkelmann and Klaine (1991) recovered a higher percentage of applied $^{14}$C when using a trapping solution containing phenethylamine.
REFERENCES


PAPER II. MOVEMENT AND DEGRADATION OF ATRAZINE IN UNDISTURBED SOIL COLUMNS
ABSTRACT

The movement and degradation of $^{14}$C-atrazine (ATR) was studied in undisturbed soil columns that were taken manually from a field with no previous pesticide history. Three weeks after the application of $^{14}$C-ATR (2.2 kg a.i./ha) to the surface of soil columns, the columns were leached at weekly intervals for 12 weeks. Approximately 1.2% of the applied $^{14}$C was recovered in the leachate over the 12-week period. This corresponds to an ATR plus degradation products concentration of 7.1 ppb.

On completion of the last leaching event, the columns were cut into 10-cm increments and analyzed. Seventy-seven percent of the $^{14}$C applied to soil columns remained in the upper 10 cm and included ATR (9%) and soil-bound residues (57%). Deethylatrazine (DEA) was the predominant degradation product in the top 10 cm (3.6%). Other degradation products were found in the top 10 cm at the following relative concentrations: deisopropylatrazine (DIA) > hydroxyatrazine (HYA) > dealkylatrazine (DAA) > deethylhydroxyatrazine (DEHYA) > deisopropylhydroxyatrazine (DIHYA). Uncharacterized polar metabolites in the top 10 cm accounted for 6% of the applied $^{14}$C. ATR, DEA and DIA were found at all depths. Additionally, DAA was detected to the 50-cm depth, HYA to the 30-cm depth, and DEHYA to the 20-cm depth.
INTRODUCTION

In recent years there has been a growing concern about pesticide contamination of our groundwater (Hallberg, 1986). It is estimated that 40-50% of our drinking water needs are supplied by groundwater (Jury, 1982). Numerous groundwater monitoring programs in the U.S. have detected the presence of pesticides (Hallberg, 1989; Rostad et al., 1989; Spalding et al., 1989). One of the most commonly detected compounds is ATR (2-chloro-4-ethylamino-6-isopropylamino-s-triazine), a widely used preemergent herbicide (Hallberg, 1989; Spalding et al., 1989; Hartzler and Jost, 1990; USEPA, 1990; Taylor, 1992). In Iowa, approximately 7.4 million pounds of atrazine were applied during 1991 (USDA, 1991). Frequent detections of ATR in groundwater are assumed to be due not only to its heavy usage, but also to its moderate persistence and mobility (Spalding et al., 1989).

For the most part, surface water and groundwater monitoring programs analyze only for parent compounds. However there is increasing concern over the presence of degradation products since, from an exposure standpoint, they can also be toxic (Hallberg, 1989). Currently, a lifetime health advisory level, only taking into consideration the parent compound, has been set for ATR at 3 ppb (Stoltenberg et al., 1990). It is important to note that ATR residues (ATR and its degradation products) may exceed legal regulatory limits even though ATR, by itself, does not (Belluck et al., 1991). Two degradation products of ATR, DEA (2-chloro-4-amino-6-isopropylamino-s-triazine) and DIA (2-chloro-4-ethylamino-6-amino-s-triazine), have also been detected in
groundwater (Muir and Baker, 1976; Rostad et al., 1989; Jayachandran et al., 1992).

Muir and Baker (1976) noted that DEA occurred even in the absence of the parent compound.

Many factors influence the movement of pesticides down through the soil profile and these factors include precipitation, soil temperature, soil characteristics, pesticide characteristics, transformation processes and management practices (Helling and Gish, 1986; Fermanich et al., 1991). Parent compounds and degradation products can move in two ways under field conditions: 1) dispersion through the soil matrix; and 2) accelerated movement through soil macropores (preferential flow) (Starr & Glotfelty, 1990).

Various approaches have been used to assess the dissipation and movement of pesticides in soil. One approach is the development of models to predict the behavior of pesticides in the environment. Often times, however, these modelling systems do not incorporate the idea of preferential flow paths which play an important role in transport of chemicals to groundwater (Everts and Kanwar, 1990). In order to simulate the movement of pesticides under field conditions, many studies have been conducted using soil columns (Weber and Whitacre, 1982; Weber et al., 1986; Gamerdinger et al., 1990; Fermanich et al., 1991; Fermanich and Daniel, 1991; Loffredo et al., 1991). Nearly as many soil column techniques exist and range from mechanically taken undisturbed soil cores (Vepraskas et al., 1990) to cylinders packed uniformly with soils of different textures and bulk densities (Yaron et al., 1965).

The importance of looking at the fate of pesticides through undisturbed soil cores is becoming more evident. Czarap et al. (1992) found that some herbicides were not
detected in leachate of soil columns without continuous macropores, but were detected in those with artificial macropores and suggested that studies using packed columns could significantly underestimate herbicide movement. Singh and Kanwar (1991) found that a higher degree of preferential flow occurred in soil columns from no-till plots as compared to conventional till plots. However, studies comparing movement of pesticides through tilled and no-tilled soils have found that pesticides leach more readily through soil under conventional tillage as compared to soil with no-tillage (Ritter et al., 1991; Fermanich and Daniel, 1991).

Some studies have investigated the mobility of ATR in packed soil columns (Bowman 1989; Alhajjar et al., 1990). These types of studies do not take into consideration the effect of macropores and preferential flow. Few studies have looked at the fate of ATR and its degradation products through the soil profile in undisturbed soil columns (Schiavon, 1988a, 1988b). In studies using soil columns under field conditions, Schiavon (1988a and 1988b) examined the leaching potential of 14C-ATR and its degradation products and also the dispersion of radioactivity as a function of depth. No attempt was made to identify the make up of such activity. In the current study, large undisturbed soil cores were used to assess the degradation, movement and leaching potential of ATR and its degradation products in the laboratory under controlled conditions.
MATERIALS AND METHODS

Chemicals

The following radiolabeled chemicals were obtained from Ciba-Geigy Co.,
Greensboro, NC: [U-ring-^{14}C]atrazine (98.2% pure); [U-ring-^{14}C]deethylatrazine (94.8%
pure); [U-ring-^{14}C]deisopropylatrazine (92.9% pure); [U-ring-^{14}C]didealkylatrazine
(98.8% pure); [U-ring-^{14}C]hydroxyatrazine (97.5% pure).

The following analytical standards were also obtained: atrazine (98.7% pure),
deethylatrazine (99% pure), deisopropylatrazine (98% pure), didealkylatrazine (97%
pure) and hydroxyatrazine (97% pure).

Soil columns

Large undisturbed soil columns (15 cm diameter x 60 cm depth) were taken from a
field with no previous pesticide history at the Till Hydrology Site, Iowa State University
Agronomy and Agricultural Engineering farm near Ames, IA. Soil columns were taken
from the field as described by Singh and Kanwar (1991). A circular trench
approximately 150 x 150 cm at a depth of 70 cm was dug using shovels. An undisturbed
pedestal of soil (50 cm x 50 cm) was left in the center of the circular trench.

A furnace pipe (15 cm x 60 cm) was placed in the center of the undisturbed soil. A
metal plate was placed over the top of the pipe in order to gently press the pipe into the
top few centimeters of soil. Prior to pushing the columns further into the soil, the soil
pedestal was shaved cylindrically to fit the furnace pipe in 15-cm increments. Each time
the pipe was pressed gently downward so that compaction could be prevented. When the
desired 60-cm depth was reached, the top of the column was covered securely with a styrofoam block and taped. After cutting through the soil well below the bottom of the column, it was inverted and trimmed evenly with the end of the pipe. Styrofoam and tape were used to secure the end of the column. The entire column was placed in a large polyethylene bag and sealed to ensure no loss of soil moisture. The columns were stored at 4°C until their use in laboratory experiments. Soil samples were collected as a function of depth while collecting each soil column and soil characteristics were determined for these samples (Table 1). Soils were largely sandy clay loam with a loam soil at the 15-cm depth. The pH of soils ranged from 5.3 at the surface to 6.3 at the 60-cm depth. Organic matter content varied among the depths with the least amount found at 60 cm.

**Laboratory preparation**

Two soil columns were prepared for laboratory experiments (Figure 1). The furnace pipe was opened carefully and removed to expose the soil column. Plasti-Dip® spray (P.D.I., Inc., Circle Pines, MN) was used to provide a coating over the outer surfaces of the soil columns. A polyvinyl chloride pipe (20 cm diameter x 60 cm tall) was centered around the soil column and the gap between the soil column and plastic pipe was filled with molten paraffin wax to prevent boundary flow (Weber et al., 1986). A wire screen was placed at the bottom of the soil column in direct contact with the soil. A perforated plexiglass plate was mounted on the bottom of the pvc pipe 0.1 cm below the screen with spacers between the two surfaces. This was done to prevent air locks and insure continuous flow of leachate during leaching study.
Table 1. Soil characteristics at four depths in soil columns

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>Texture</th>
<th>Sand</th>
<th>Silt</th>
<th>Clay</th>
<th>O.M.</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Sandy Clay Loam</td>
<td>52</td>
<td>26</td>
<td>22</td>
<td>2.3</td>
<td>5.3</td>
</tr>
<tr>
<td>15</td>
<td>Loam</td>
<td>54</td>
<td>24</td>
<td>22</td>
<td>3.0</td>
<td>5.5</td>
</tr>
<tr>
<td>45</td>
<td>Sandy Clay Loam</td>
<td>42</td>
<td>34</td>
<td>24</td>
<td>2.5</td>
<td>5.9</td>
</tr>
<tr>
<td>60</td>
<td>Sandy Clay Loam</td>
<td>44</td>
<td>30</td>
<td>26</td>
<td>1.8</td>
<td>6.3</td>
</tr>
</tbody>
</table>
Figure 1. Soil column preparation for laboratory experiments
Soil columns were saturated with 0.005 M CaCl₂ by placing the columns in a tall garbage can and dripping the solution slowly into the bottom of the container over a 48-h period. This slow saturation allowed for the solution to diffuse slowly upward and prevented any air from being trapped in the column. Once the columns were fully saturated, they were mounted in stands and allowed to drain to field capacity before being treated with ¹⁴C-ATR. Soil columns were maintained in a temperature-controlled room at 25°C. A chloride tracer was applied to the columns to verify their performance (Weber et al., 1986). Chloride ion breakthrough was determined by adding silver nitrate dropwise to the leachate. A comparison was made with controls in order to ensure the amount of chloride in the leachate was above that found normally in soil.

Soil treatment and leaching

AATREX® Nine-0® was mixed with ¹⁴C-ATR to produce a concentration for application of 2.24 kg a.i./ha with an activity of 15 μCi. This mixture was dissolved in 5 ml of deionized water and applied to the surface of two soil columns. Incorporation into the top 2 cm was achieved with the use of a spatula. Soil columns were loosely fitted with foil to minimize evaporation and were allowed to incubate for three weeks at 25°C. After incubation, soil columns were leached once weekly with deionized water at a rate of 3.8 cm of rainfall. Six-hundred and seventy-five ml of water was added to a surface area of 177 cm² for each leaching event and approximately 80% of the volume was recovered as leachate. Leachate was collected at the bottom of columns in 100-ml aliquots. Each aliquot was analyzed for radioactivity by liquid scintillation technique.
Extracts and analyses

Soil columns were cut into 10-cm increments and frozen until the time of extraction. Soil was removed from the center of each section with care so as not to include wax or Plasti-Dip®. Soil from individual sections was mixed well and soil moisture was determined. Two 50-g dry weight subsamples were extracted three times with 150 ml of methanol:water (9:1). The pH of the concentrated extract was brought to one with 1 M HCl. The extract was then partitioned three times into 50 ml of dichloromethane. Each time, polar metabolites were expelled from the aqueous layer with saturated sodium chloride solution. Polar metabolites remaining were quantified by measuring the radioactivity in the aqueous fraction. The organic fraction was further characterized by thin-layer chromatography (TLC) and autoradiography techniques. A solvent system of chloroform: methanol: formic acid: water (100:20:4:2) (Ciba Geigy, Greensboro, NC) was used for TLC. X-Omat™ Kodak diagnostic film (Eastman Kodak Co., Rochester, NY) was used in autoradiography.

Soil-bound residues were determined by combusting soil pellets made up of 0.5 g soil and 0.1 g hydrolyzed starch in a Packard Sample Oxidizer. 14CO₂ was trapped in Carbo-Sorb® E and Permafluor® V (Packard Instrument Co., Downers Grove, IL). Trapping efficiency was determined using Spec-Chec™ 14C standard (9.12 x 10³ dpm/ml) and Spec-Chec™ nonactive standard (Packard Instrument Co., Downers Grove, IL). Three pellets were burned per replicate, and radioactivity was determined by liquid scintillation technique using a RackBeta model 1217 liquid scintillation counter (Pharmacia LKB Biotechnology, Inc, Gaithersburg, MD). The mass balance for soils at
each depth was extrapolated by considering the total dry weight per section.
RESULTS AND DISCUSSION

One percent of the $^{14}$C applied to the soil columns was recovered in the leachate over a 12-week leaching period (Figure 2). This corresponds to 7 ppb of ATR plus degradation products equivalent, a concentration which would exceed the current health advisory level of 3 ppb for atrazine. The leaching potential of pesticides through soil can be affected by the type of tillage practice used (Fermanich and Daniel, 1991; Ritter et al., 1991). Soil columns for this study came from a conventionally tilled field plot thus macropores were not continuous with the surface. Preferential flow was evident during the leaching study since $^{14}$C was detected in the first 100 ml recovered during the first leaching event. Alhajjar et al. (1990) recovered 4.9% of applied $^{14}$C-ATR in leachate from the 60 cm depth of packed soil columns after 23 weeks. Bowman (1989) noted that a leaching event within 24 h after application eluted higher quantities of ATR than an leaching event occurring after one week.

A major portion (77%) of the $^{14}$C applied to soil columns remained in the top 10 cm 15 weeks after application (Table 2). Helling et al. (1988) also found the majority of atrazine residues in the top 10 cm of field plots. In packed soil columns, Alhajjar et al. (1990) recovered 85% of the applied $^{14}$C-atrazine in the top 15 cm.

DEA was the most predominant degradation product formed in the top 10 cm. The relative proportion of DEA to ATR throughout all depths of the soil columns were similar and ranged from 0.3 to 0.4.

DIA was the second most prominent degradation product formed in the 0-10 cm
Figure 2. Radioactivity (% of applied $^{14}$C) recovered in leachate from undisturbed soil columns over a 12-week leaching study.
Table 2. Degradation of $^{14}$C- atrazine in undisturbed soil columns

(Mass Balance Reported as % of Applied $^{14}$C)

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>0-10</th>
<th>10-20</th>
<th>20-30</th>
<th>30-40</th>
<th>40-50</th>
<th>50-60</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atrazine</td>
<td>9.31a</td>
<td>0.84b</td>
<td>0.39b</td>
<td>0.27b</td>
<td>0.27b</td>
<td>0.23b</td>
</tr>
<tr>
<td>Deethylatrazine</td>
<td>3.63a</td>
<td>0.17b</td>
<td>0.10b</td>
<td>0.10b</td>
<td>0.09b</td>
<td>0.07b</td>
</tr>
<tr>
<td>Deisopropylatrazine</td>
<td>0.83a</td>
<td>0.20b</td>
<td>0.08b</td>
<td>0.04b</td>
<td>0.04b</td>
<td>0.03b</td>
</tr>
<tr>
<td>Didealkylatrazine</td>
<td>0.08a</td>
<td>0.04ab</td>
<td>Trabc*</td>
<td>Trabc*</td>
<td>Trabc*</td>
<td>0.00c</td>
</tr>
<tr>
<td>Hydroxyatrazine</td>
<td>0.38a</td>
<td>0.02b</td>
<td>0.01b</td>
<td>0.00b</td>
<td>0.00b</td>
<td>0.00b</td>
</tr>
<tr>
<td>Deethylhydroxyatrazine</td>
<td>0.02a</td>
<td>Trabc*</td>
<td>0.00b</td>
<td>0.00b</td>
<td>0.00b</td>
<td>0.00b</td>
</tr>
<tr>
<td>Deisopropylhydroxyatrazine</td>
<td>Trabc*</td>
<td>0.00a</td>
<td>0.00a</td>
<td>0.00a</td>
<td>0.00a</td>
<td>0.00a</td>
</tr>
<tr>
<td>Polar metabolites</td>
<td>6.12a</td>
<td>0.31b</td>
<td>0.11b</td>
<td>0.01b</td>
<td>0.02b</td>
<td>0.04b</td>
</tr>
<tr>
<td>Soil bound</td>
<td>56.61a</td>
<td>2.48b</td>
<td>1.11b</td>
<td>0.46b</td>
<td>0.29b</td>
<td>0.20b</td>
</tr>
<tr>
<td>Othersd</td>
<td>0.15a</td>
<td>0.01b</td>
<td>0.01b</td>
<td>Trabc*</td>
<td>Trabc*</td>
<td>0.00b</td>
</tr>
<tr>
<td>Totalc</td>
<td>77.13a</td>
<td>4.07b</td>
<td>1.81b</td>
<td>0.89b</td>
<td>0.72b</td>
<td>0.57b</td>
</tr>
</tbody>
</table>

* Means in each row followed by the same letter are not statistically different (p=0.05).
* Tr = trace amounts > 0.00% and < 0.01%
* Others include unidentifiable minor degradation products observed in the TLC system.
* Total recovery (mean of 2 soil columns) = 85.19%.
depth. Numerous studies have observed a higher relative concentration of DEA to DIA (Sirons et al., 1973; Muir and Baker, 1978; Schiavon, 1988a, 1988b) and this could be attributed to the relative susceptibility of the ethyl side chain to microbial degradation (Skipper and Volk, 1972). It has also been noted, in the first chapter of this thesis, that degradation of DIA was significantly increased under saturated conditions. During the leaching of soil columns, the moisture level was above field capacity which could increase the degradation of DIA.

Other degradation products were found at relatively low concentrations in the top 10 cm and included HYA, DAA, DEHYA, and DIHYA. Uncharacterized polar metabolites made up 6% of the applied ¹⁴C at this depth. DAA was detected down to the 50-cm depth, HYA and DEHYA were detected to the 30-cm and 20-cm depth, respectively, and DIHYA was only detected in the top 10 cm.

The major component of the ¹⁴C remained as soil-bound residues with 57% in the top 10 cm. In a similar study under field conditions, Schiavon (1988b) detected 49 to 67% of applied radioactivity as soil bound residues in the surface soil. No statistical differences were noted in the amount of soil-bound residues formed at depths below 10 cm.

ATR, DEA and DIA exhibited the highest mobility with no significant differences in their concentrations among depths below the top 10 cm. This equal distribution is expected for mobile compounds in structured soils (Nicholls, 1988). These three compounds were the only ones detected in the 50- to 60-cm depth, and they were the likely components of radioactivity recovered in the leachate. ATR, DEA and DIA have
been detected in numerous water monitoring programs and leaching studies (Muir and Baker, 1976; Schiavon, 1988a; Hallberg, 1989; Rostad et al., 1989; Spalding et al., 1989; Adams and Thurman, 1991; Jayachandran et al., 1992; Taylor, 1992). In a field study, Ritter et al. (1991) reported that 15 days after application, ATR was detected at a depth of 150 cm.

The relative proportions of DEA to ATR remained fairly constant throughout the soil profile and ranged from 0.3 to 0.4. In field plots applied with ATR (3.4 kg/ha), Adams and Thurman (1988) found that the concentration of ATR was four times that of DEA in soil core extracts, but that the concentration of DEA was greater than ATR in the soil water. They suggest that a DEA-to-ATR ratio (DAR) in groundwater of less than one might suggest point source contamination. In the current study, the amount of radioactivity recovered in the leachate was not high enough to allow extractions measurable by TLC, thus the DAR was not determined.
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54:1192-1194.

South. Weed Sci. Soc., Champaign, IL.


SUMMARY

In a study to determine the effect of soil depth and saturated/unsaturated soil moisture conditions on the fate of ATR and DIA, radiolabeled ATR and DIA were applied to a soil collected at different depths and incubated for 60 d, 120 d or 180 d prior to being extracted and analyzed. Both compounds were least persistent in the upper layer (0-30 cm), and their persistence increased with depth. The amount of soil-bound residues formed were highest in the upper layer and the amount formed decreased with increased depth. The persistence of ATR was not affected by saturated or unsaturated soil moisture conditions, however, DIA was less persistent under saturated conditions as compared with unsaturated conditions. The amount of soil-bound residues and polar metabolites increased over time.

The major degradation product of ATR was DEA for all soils studied. Other minor degradation products of ATR were detected and included DIA, DAA, HYA, DEHYA, DIHYA. DAA was a major degradation product of DIA while deisopropylhydroxyatrazine (DIHYA) was a minor degradation product.

The concentration of ATR decreased over time for all the four depths studied. The concentrations of DEA and DIA, in 14C-ATR treated soils, decreased over time in the top three layers but increased in the deepest layer.

Degradation rates decreased with increase in soil depth for both ATR and DIA. The rate of degradation of DIA was faster than that of ATR for all depths studied. Under saturated conditions, the rate of degradation for both ATR and DIA increased as
compared with degradation rates under unsaturated conditions.

In a study investigating the degradation and movement of ATR in undisturbed soil columns, radiolabeled ATR was applied to the surface of columns which were then leached weekly for 12 weeks before being cut into 10-cm increments for soil analyses. An ATR/degradation products concentration of 7 ppb was leached from soil columns over a 12-week period. There was evidence of preferential flow since radioactivity was found in the first 100 ml recovered from the soil columns during the first leaching event. A uniform amount of radioactivity was recovered from the soil columns each week.

ATR, DEA and DIA were the most mobile compounds in the soil columns. An even distribution of ATR, DEA, and DIA was seen among depths lower than 10 cm, and these three compounds were the only ones detected in the 50-60 cm soil. Therefore, although the radioactivity in the leachate was not characterized, ATR, DEA and DIA are the likely components. The ratio of DEA to ATR ranged between 0.3 and 0.4 for all depths in the soil columns. A major portion of the radioactivity applied to soil columns remained in the top 10 cm as bound residues. HYA was detected in low concentrations to the 30-cm depth. Trace amounts of DEHYA and DAA were detected down to the 20- and 50-cm depth, respectively.

Not only is the microbial degradation of ATR to DIA less favored than to DEA (Skipper and Volk, 1972), but this study also indicates that the increased degradability of DIA (compared to ATR) and the decreased persistence of DIA under saturated soil conditions might also explain its very low concentrations in the groundwater as compared to ATR and DEA.
REFERENCES


