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Factors Affecting Atrazine Fate in North Central U.S. soils

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Factors Affecting Atrazine Fate in North Central U.S. Soils

W.C. Koskinen and S.A. Clay

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I. Introduction

Atrazine (6-chloro-*N*-ethyl-*N'*-(1-methylethyl)-1,3,5-triazine-2,4-diamine) is a herbicide of the triazine family used for controlling broadleaf and some grassy weeds in corn and sorghum. Since its introduction in the late 1950s, atrazine has been a popular herbicide because it is relatively inexpensive and, in most cases, gives good season-long weed control. It can be applied pre- or postemergence and is often tank mixed with grass herbicides, such as alachlor (2-chloro-*N*-(2,6-diethylphenyl)-*N*-(methoxymethyl)acetamide),

Communicated by George W. Ware

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S.A. Clay

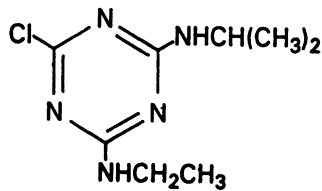
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metolachlor (2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methyl-ethyl)acetamide), butylate (*S*-ethyl bis(2-methylpropyl)carbamothioate), or EPTC (*S*-ethyl dipropylcarbamothioate), or with other broadleaf herbicides, such as dicamba (3,6-dichloro-2-methoxybenzoic acid), to obtain broad-spectrum weed control. Atrazine mixed with nicosulfuron {2-[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]-*N,N*-dimethyl-3-pyridinecarboxamide} or bromoxynil (3,5-dibromo-4-hydroxybenzotrile) is commonly used across the northern Corn Belt; when mixed with cyanazine {2-[[4-chloro-6-(ethylamino)-1,3,5-triazin-2-yl]amino]-2-methylpropanenitrile}, it is commonly used in total weed control programs in southern Iowa, Illinois, Indiana, and Ohio.

From 1987 to 1989, atrazine was the herbicide that had the greatest annual use amounts, 29 million kg active ingredient (a.i.), and was applied to about 84% of the U.S. corn crop (Gianessi and Puffer 1991). About 70 million ha of corn in the Midwest was treated with atrazine in 1990 (Gianessi and Puffer 1991). Recent U.S. Environmental Protection Agency (USEPA) data show atrazine as the most heavily used pesticide in the U.S. — 31–33 million kg a.i. for 1995 (Aspelin 1996). Recommended rates in the North Central states had been 2.2 kg a.i. ha⁻¹ on coarse-textured soils to 3.3 kg a.i. ha⁻¹ on fine-textured soils in the 1960s and 1970s to control both annual grasses and broadleaf weeds. However, the use rate in the 1980s and 1990s ranged from 0.8 to 1.5 kg a.i. ha⁻¹, with about 85% of the atrazine applied in tank-mix applications (Gianessi and Puffer 1991). Tank-mix uses with lower atrazine concentrations increased due to the recognition of triazine-resistant weeds that appeared throughout the United States (Bandein et al. 1982; Ryan 1970) and because of carryover injury to rotational broadleaf crops such as soybean.

Although the majority of the applied atrazine remains in the surface soil, where it can control weeds while it degrades, off-site movement has been well documented. For instance, atrazine has been found in rainwater (Nations and Hallberg 1992; Richards et al. 1987), tile drainage water (Buhler et al. 1993; Jayachandran et al. 1994), and wind-eroded sediments (Glutfelty et al. 1989; DeSutter et al. 1995). Atrazine also has been detected in groundwater more frequently than any other herbicide (Ritter 1990) and has been detected in the groundwater of most Midwestern states. Most of these detections are considerably below (Richards et al. 1996) the USEPA maximum contamination level (MCL) for atrazine in drinking water of 3 µg L⁻¹ (ppb) (USEPA 1995). Transport of atrazine to groundwater depends on combinations of factors, including the chemical properties of atrazine (Fig. 1), the soil chemical and physical properties and conditions, and environmental variables.

Atrazine movement through the root zone, vadose zone, and into groundwater is affected by several soil processes that vary throughout the profile. Transformation and retention (sorption) are two major processes that affect the amount of atrazine present and available for transport through the soil profile. Transformation processes actually reduce or elimi-



Atrazine

C.A. name: 6-chloro-N-ethyl-N'-(1-methylethyl)-1,3,5-triazine-2,4-diamine

CAS RN: 1912-24-9

Molecular weight: 215.7 pKa: 1.7

Melting point: 175.8 °C Vapor pressure: 0.039 mPa (25 °C)

K_{ow} log P: 2.5 (25 °C) Solubility (water): 33 mg L⁻¹

Fig. 1. Selected physical and chemical properties of atrazine (from Tomlin 1994).

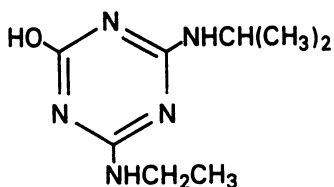
nate the amount of atrazine present and available for transport through soil. Atrazine can be degraded partially or completely to inorganic products by chemical, biochemical, and photochemical means. Plants remove some of the atrazine from soil, and uptake is necessary to control weeds. Tolerant plants and some microbes have the ability to transform atrazine by *N*-dealkylation, hydroxylation, or conjugation with glutathione, all of which reduce atrazine amounts in soil. Atrazine can volatilize and move into the atmosphere, also reducing soil concentrations. On the other hand, the sorption process can retain or retard atrazine movement with water. While retention processes do not affect the total amount of atrazine present in soil, retention can decrease or eliminate the amount available for transport.

This paper reviews the inherent soil factors and processes that impact atrazine movement, with emphasis on groundwater deposition in the North Central U.S. Application and soil management practices that influence the risk of groundwater contamination by atrazine also are discussed. This paper is not a comprehensive literature survey; rather, it focuses on research performed in the North Central U.S.

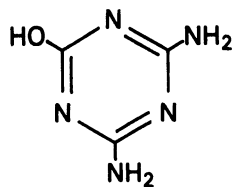
II. Transformation

In soil-water systems, atrazine is transformed by abiotic and biotic processes. Hydrolysis (hydrolytic dechlorination), *N*-dealkylation, deamination, and ring cleavage are the major transformation processes that

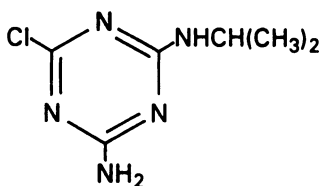
degrade atrazine. The transformation products of these reactions include hydroxyatrazine (HA) (6-hydroxy-*N*-ethyl-*N'*-(1-methylethyl)-1,3,5-triazine-2,4-diamine), deethylatrazine (DEA) (6-chloro-*N*-(1-methylethyl)-1,3,5-triazine-2,4-diamine), deisopropylatrazine (DIA) (6-chloro-*N*-ethyl-1,3,5-triazine-2,4-diamine), and deethyldeisopropylatrazine (DEDIA) (6-chloro-1,3,5-triazine-2,4-diamine) (Fig. 2). Other products, including the hydroxylated



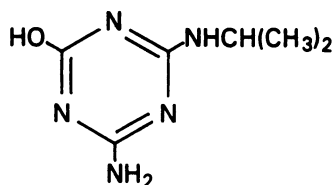
hydroxyatrazine



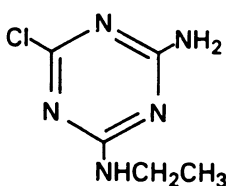
ammeline



deethylatrazine



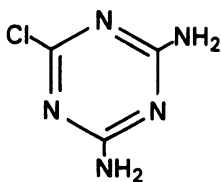
deethylhydroxyatrazine



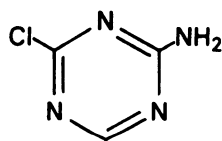
deisopropylatrazine



deisopropylhydroxyatrazine



deethyldeisopropylatrazine



4-amino-2-chloro-1,3,5-triazine

Fig. 2. Structures of selected atrazine metabolites.

analogs of DEA, DIA, and DEDIA, may also be formed. These degradates differ from atrazine in their degradation and soil retention characteristics (Barrett 1996), which ultimately influence their potential to leach through soil.

A. Abiotic Processes

Abiotic decomposition to HA (Fig. 3) occurs via sorption-catalyzed chemical hydrolysis (Armstrong and Chesters 1968; Armstrong et al. 1967; Skipper et al. 1967). The importance of abiotic transformation of atrazine varies

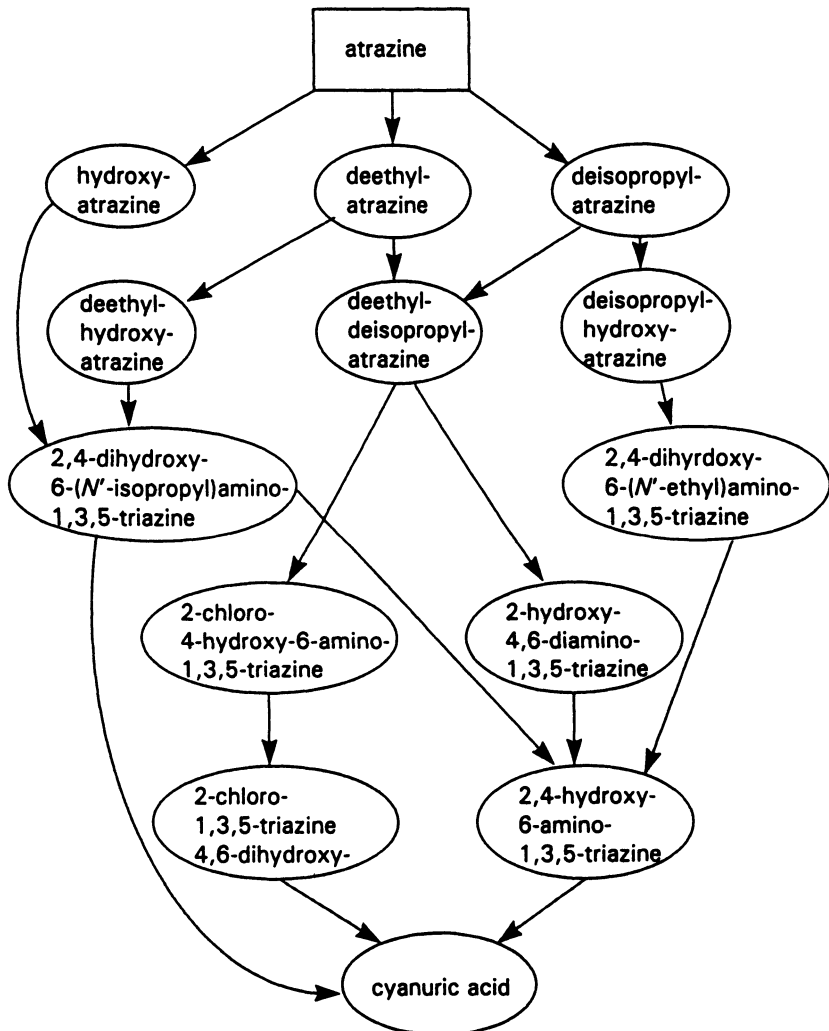


Fig. 3. Atrazine degradation pathway.

with the system conditions and is dependent on several factors such as pH, concentration of dissolved organic carbon, and temperature. For instance, pH of the soil or water system has the greatest effect on hydrolysis, with acidic pH levels promoting atrazine hydrolysis to HA; at pH > 7, first-order rate coefficients in water are more than 10^3 times slower than those reported at pH 2 (Widmer et al. 1993). The kinetics of atrazine hydrolysis in water also increase when concentrations of dissolved organic carbon present in the system and temperature increase. Atrazine can also be chemically decomposed by free radicals in solution (Koskinen et al. 1994).

B. Biotic Processes

In soil, atrazine is primarily degraded biologically (Kaufman and Blake 1970; Wolf and Martin 1975) to a variety of products (Fig. 3). The complete biodegradation pathway is available on the Internet (Ellis 1996). *N*-dealkylation of atrazine, which has been shown to be microbially mediated, results in the formation of DEA, DIA, DEDIA, or a combination of these metabolites (Behki and Khan 1986, 1994; Behki et al. 1993; Giardi et al. 1985; Giardina et al. 1980, 1982; Hickey et al. 1994; Masaphy et al. 1993; Mougín et al. 1994; Nagy et al. 1995). Although many microorganisms do not further metabolize the dealkylated metabolites, additional degradation of metabolites can occur (Behki and Khan 1994; Behki et al. 1993; Hickey et al. 1994; Masaphy et al. 1993; Mougín et al. 1994; Nagy et al. 1995). For instance, DEA can be further degraded to DEDIA (Kruger et al. 1993a). Formation of 4-amino-2-chloro-1,3,5-triazine indicates that deamination can also occur as well as dealkylation (Giardina et al. 1980).

Atrazine hydrolysis to HA had been attributed solely to abiotic processes. However, hydrolysis of atrazine has been reported to occur in soil bacteria (Mandelbaum et al. 1993a). Genes encoding hydrolysis reactions are widespread in nature and contribute to the formation of HA in soil (de Souza et al. 1995). Deethylhydroxyatrazine (DEHA) and deisopropylhydroxyatrazine (DIHA) are formed by hydroxylation of DEA or DIA, respectively, or by *N*-dealkylation of HA (Behki and Khan 1986; Giardi et al. 1985; Khan and Marriage 1977).

There are only isolated reports of bacterial pure cultures that metabolize atrazine to CO_2 (e.g., Radosevich et al. 1995), yet complete degradation of atrazine to CO_2 has been observed (Mandelbaum et al. 1993b). Previously, however, mineralization of the triazine ring of atrazine was thought to be relatively slow, with less than 20% of applied atrazine mineralized after 180 d (Skipper and Volk 1972; Winkelmann and Klaine 1991). More recently, Assaf and Turco (1994) found 39% of applied ring- ^{14}C -atrazine was mineralized to $^{14}\text{CO}_2$ in 326 d compared to 60% in 28 d (Stolpe and Shea 1995) in silt loam soils. In a clay loam soil, after a 5-wk lag phase, ring- ^{14}C -atrazine mineralized to $^{14}\text{CO}_2$ rapidly over the next 15–20 wk; at soil concentrations from 5 to 500 mg kg^{-1} , an average 64% was mineralized at 20 wk (Gan et

al. 1996). Dealkylated metabolites can also be mineralized to CO₂. After 180 d, evolution of ¹⁴CO₂ from radiolabeled DEA and DIA increased to 25% and 16%, respectively, of the total ¹⁴C added (Winkelman and Klaine 1991).

Biochemical alterations by plant and conjugation reactions also represent important mechanisms of atrazine transformation. Several metabolic reactions occur in plants, including dechlorination of atrazine to HA and conjugation of atrazine with glutathione, a tripeptide, via glutathione-*s*-transferase (Lamoureux et al. 1972).

C. Factors Affecting Biodegradation

Atrazine biodegradation in soil is dependent on a number of factors, most importantly the presence and activity of atrazine-degrading microorganisms. Therefore, soil and environmental factors that affect soil microbial populations often influence atrazine degradation. Soil temperature, oxygen and water status, previous soil management and crop practices, and their interactions are factors that affect rates of atrazine biodegradation (Table 1). Generally, as soil temperature increases, as oxygen content increases, and as water content nears field capacity, atrazine degradation conditions are optimized.

Oxygen appears to be essential for biodegradation to occur as atrazine was not degraded under anaerobic or denitrifying conditions (Topp et al. 1995). In a laboratory experiment with three Iowa soils, mineralization of ring and methylethyl carbons was proportional to soil oxygen and organic matter content of the soils (Nair and Schnoor 1994).

Soil water and temperature also influence atrazine degradation. Ring-carbon mineralization increased with soil water content in three Iowa soils (Nair and Schnoor 1994). In a laboratory study with a clay soil, atrazine half-life averaged about 62 d at 20 °C when soil water ranged from 20% to

Table 1. Factors affecting atrazine biodegradation.

Factor	References
Oxygen status	Nair and Schnoor 1994; Topp et al. 1995
Water content	Nair and Schnoor 1994; Smith and Walker 1989
Soil type, depth	Konopka and Turco 1991; Lavy et al. 1973; Stolpe and Shea 1995; Topp et al. 1994, 1995; Widmer and Spalding 1995
Temperature	Radosevich et al. 1995; Smith and Walker 1989
Atrazine concentration	Gan et al. 1996
Crop and soil management	Anderson et al. 1994; Levanon et al. 1994; Shelton et al. 1995; Stolpe and Shea 1995

40%; however, at 8%, the half-life increased to 338 d (Smith and Walker 1989). Decreasing temperature from 30 ° to 5 °C (34% moisture) increased the half-life from 44 to 206 d.

Soil type, as well as atrazine concentration by soil type interactions, has been reported to influence its degradation. Half-lives varied from 32 d (loam soil) and 30 d (sandy loam soil) to 16 d in clay loam soil (Topp et al. 1995). In a Webster clay loam, atrazine concentration from 5 to 5000 mg kg⁻¹ did not influence the degradation rate ($t_{1/2} < 8$ wk) (Gan et al. 1996). However, in an Estherville sandy loam, the degradation rate decreased with increased concentration from 5 ($t_{1/2} = 8$ wk) to 5000 mg kg⁻¹ ($t_{1/2} = 13$ wk).

Atrazine degradation has usually been found to be slower in subsurface horizons. Rates of degradation decreased with increasing soil depths in a silty clay loam (Lavy et al. 1973). Topp et al. (1995) observed rapid degradation in concentrated suspended particulates and surface sediments but not in subsurface sediments. Konopka and Turco (1991) reported that some Indiana subsurface horizons, to a depth of 25 m, had high numbers of microorganisms and microbial activity, although both were lower than in surface horizons. In spite of the microbial populations and activity, no atrazine degradation was observed during a 128-d incubation of atrazine-amended subsurface materials. Stolpe and Shea (1995) concurred with the Indiana study and reported that degradation was most rapid in a Hord silt loam surface soil taken from three locations in a field in Nebraska and was slowest in subsurface materials at all sites.

A positive correlation between rate of degradation and aqueous-phase concentration in incubation experiments at 25 °C suggests that atrazine sorption influences mineralization rates (Radosevich et al. 1995). They concluded that sorption can limit degradation of weakly sorbed solutes at high solid-to-solution ratios and at ambient temperatures if an active degrading population is present. The sorption effect was greatly diminished at 10 °C; however, under vadose zone and subsurface conditions, low temperature and the lack of degrading organisms are likely to be primary factors limiting atrazine degradation.

Once atrazine reaches an aquifer, degradation is relatively slow. When a shallow sand and gravel aquifer was monitored for 3 mon after injection of atrazine, DEA and DIA showed no detectable loss of the three chemicals (Widmer and Spalding 1995). Once in groundwater, estimated atrazine and DEA degradation half-lives are >3400 and >2700 d, respectively (Levy and Chesters 1995). Atrazine also was not degraded in aquifer sediments from the Big Sioux aquifer (South Dakota) at 5 µg L⁻¹, with or without C or C+N added to the sediment, after a 112-d incubation at 5 °C (S.A. Clay, unpublished data).

Crop and soil management also influences atrazine degradation rates. Degradation was faster in soil from the two sites that had been in continuous corn and treated with atrazine for a number of years ($t_{1/2} = 12$ d) than

in soil from a site planted with alfalfa for 4 yr with no recent application ($t_{1/2} = 27$ d) (Stolpe and Shea 1995). The corn sites had three to four times more atrazine-degrading microorganisms than alfalfa sites. Enhanced degradation was probably caused by microbial adaption to atrazine. Rapid rates of biodegradation were observed in cornstalk-amended soils shortly after rewetting, whereas degradation was not observed in unamended soil (Shelton et al. 1995). Higher microbial populations and activity in no-tillage than in a plow-based tillage system were associated with higher atrazine mineralization rates in the no-tillage soils (Levanon et al. 1994). Enhanced degradation was also observed in rhizosphere soils after 14-d incubations (Anderson et al. 1994). Microorganisms in the bulk soil also showed the ability to degrade atrazine, but not to the extent of the rhizosphere soil.

Factors that affect atrazine degradation also affect metabolite degradation. For instance, greater DEA degradation was observed in surface soils compared to subsurface soils (Baluch et al. 1993). Major degradation products from DEA included CO_2 and polar metabolites; DEHA and DEDIA were only detected in minor amounts. HA degraded more slowly than DEA in the same soils, and some DEA, DIHA, and ammeline (4,6-diamino-*s*-triazine-2-ol) were observed in the soils. Under saturated conditions, DIA was less persistent in the top 30 cm, and persistence increased with increase in depth. DEA was less persistent in saturated soil than in unsaturated soil at the 90- to 120-cm depth (Kruger et al. 1993a).

III. Retention

Unlike the transformation processes that reduce the total amount of atrazine present in soil, retention only decreases the amount available for weed control and microbial transformations (Anderson et al. 1980) or that may be potentially moved in soil. The amount retained or sorbed by soil can range from 0 to 100% of the amount applied, but typically sorption on silt loam, loam, or clay loam surface soils ranges from 50% to 80% under slurry conditions. Atrazine retention in soil is influenced by several major factors, e.g., organic carbon content, soil clay content and type, and soil pH. Other factors influencing retention include the amount of atrazine applied, the amount of dissolved organic carbon (DOC) in soil solution, and atrazine-soil contact time (aging).

A. Effect of Soil Properties

Organic Carbon. As organic carbon content increases, sorption of many pesticides increases (Calvet 1980; Clay et al. 1988b; Guo et al. 1991b; Hamaker and Thompson 1972; Koskinen and Harper 1990; Patrick 1989). For many years, atrazine sorption has arguably been most correlated to organic carbon content in typical agricultural soils. For instance, atrazine sorption was correlated to organic carbon ($r = 0.82$) in 25 Missouri agricultural

soils (Talbert and Fletchall 1965), 9 surface and subsurface soils (Stolpe and Shea 1995), and in 5 Wisconsin surface soils (Seybold et al. 1994). Sorption was greater on the earthworm burrow linings, which are enriched in organic carbon and soluble organic carbon relative to bulk soil, than on bulk soil (Stehouwer et al. 1993, 1994). Through hydrogen bonds, atrazine can form complexes with amide and carboxylic acid functional groups of soil organic matter (Welhouse and Blear 1993a,b) and possibly with phenol- and quinone-like functional groups.

However, a simple correlation between organic carbon content and atrazine sorption does not wholly describe the sorption process. In a literature review of data from 1964 to 1984 that included 343 K_d (partition coefficient between soil and solution) values from 148 soils, it was shown that atrazine $K_d = 4.0 \pm 4.0$ and was not correlated to organic carbon (Koskinen and Moorman 1985). Sorption on soils with less than 10% organic carbon was less strongly correlated to soil organic carbon; $r^2 = 0.64$ for single variable regression (Fig. 4). Correcting the soil K_d for organic carbon actually increased variability: $K_{oc} = 190 \pm 279$. More recently, no correlation was found between atrazine sorption and organic carbon in 15 soil samples from surface and subsurface horizons (Sonon and Schwab 1995).

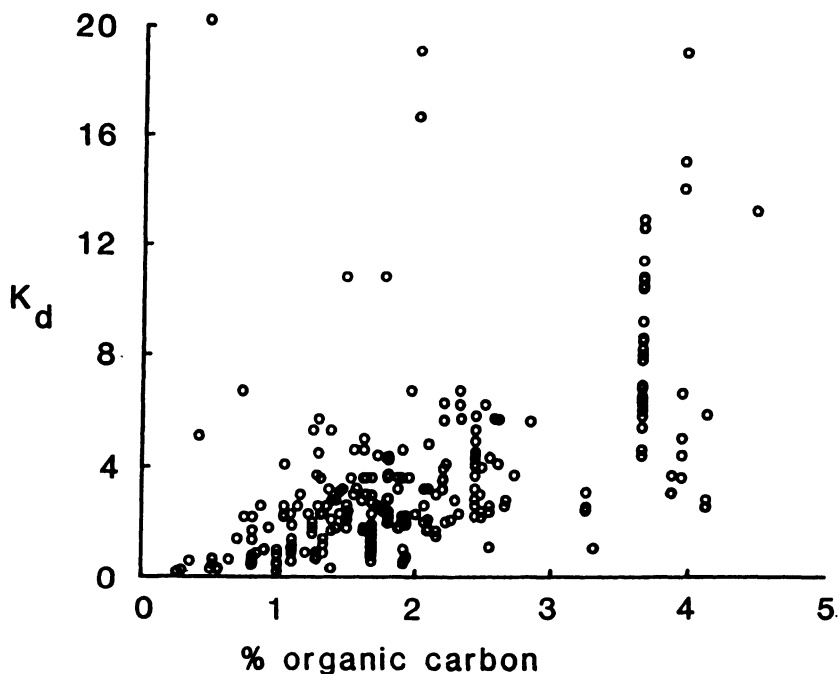


Fig. 4. Atrazine sorption on soil as a function of soil organic carbon.

Clay. Correlation of atrazine sorption to soil organic carbon is problematic because of its sorption on clay. Although organic and inorganic components comprise 11% and 89% of a clay-sized soil fraction, they contributed 68% and 32% of the affinity of the soil clay for atrazine, respectively (Laird et al. 1994). Clay-sized fractions have more surface area and exchange sites than either the silt- or sand-sized particles.

The type of clay present in the clay fraction influences atrazine sorption (Brown and White 1969). For instance, smectites have a large potential for influencing atrazine sorption because they contribute much of the inorganic surface area of soils. However, atrazine sorption to smectites is variable. For example, sorption of atrazine on 13 clay samples, of which smectite was the dominant mineral, ranged from 0 to 100% and was inversely correlated to the surface charge density of the smectite (Laird et al. 1992) (Fig. 5).

Desorption from 12 smectites was greater than desorption from bulk soil, suggesting that atrazine is bound to smectite surfaces by relatively weak forces (Barriuso et al. 1994), such as a combination of hydrophobic bonding between the alkyl side chains and hydrophobic microsites on the smectite surface, and water bridging between electronegative moieties on the atrazine molecule and interlayer cations (Laird 1996).

Because of the low clay and organic matter content of materials below the root zone and aquifer sediments, little sorption would be expected. For instance, the atrazine K_f in the Bw (silt loam texture) and 2C (sandy loam

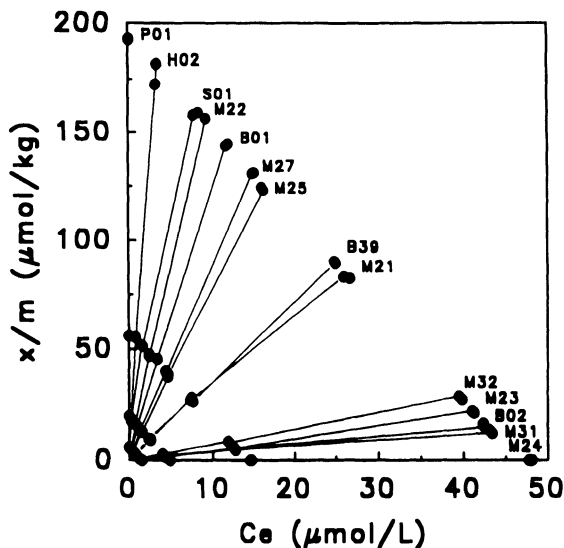


Fig. 5. Freundlich isotherms for adsorption of atrazine on reference and soil smectitic clay samples (from Laird et al. 1992, with permission of the Soil Science Society of America).

texture) horizons of a Brandt soil were 1.0 and 0.2, respectively, whereas the Ap horizon (silty clay loam texture) had a $K_f = 5.4$; other soils showed similar results (Table 2) (Clay, unpublished data). Monitoring a plume of atrazine, DEA, and DIA injected into a shallow sand and gravel aquifer for a 3-mon period showed little retention of the three chemicals (Widmer and Spalding 1995).

pH. Numerous reports have shown that soil pH affects atrazine sorption to soil. Atrazine is a weakly basic molecule with a pK_a of 1.7 and is easily protonated at low pH. At soil pH in the range of 4 to 6, more atrazine is sorbed to soil compared to the amount sorbed at soil pH 7 or greater (Clay and Koskinen 1990b; Clay et al. 1988b; Goetz et al. 1988; Liu et al. 1995b; McGlamery and Slife 1966). At low soil pH, cation exchange may be the dominant binding mechanism, while at high pH hydrogen bonding (Welhouse and Bleam 1993a,b) and hydrophobic attraction increase in importance (Koskinen and Harper 1990). On smectite surfaces, surface acidity, which arises principally from enhanced ionization of water solvated on sorbed cations, catalyzes atrazine protonation and hydrolysis (Laird 1996).

Increasing soil pH with ammonia-based fertilizer decreased sorption by 50% and increased atrazine desorption from soil (Liu et al. 1995b). It is unclear if the effects were due only to changes in pH. Increasing the pH with ammonia also increased the DOC from 60 to 700 ppm in the soil solution, which may have affected the atrazine sorption-desorption characteristics. Changing the base from ammonia to KOH or NaOH also influenced DOC content and affected atrazine sorption (Clay et al. 1996). Very high solution pH also promotes the formation of HA, which may influence atrazine sorption.

Atrazine/Soil Aging. The incubation time or aging of atrazine in soil influences its retention (Barriuso et al. 1992; Capriel et al. 1985; Pignatello and Huang 1991). The longer the aging process, the more atrazine is retained in soil. Early in the aging process, a portion of the atrazine retained during aging can be removed from soil relatively easily. With time, however, larger portions of the amount applied become very slowly desorbable, nondesorbable, or bound to soil (Khan 1982; Pignatello and Huang 1991; Rao and Davidson 1980; Schiavon 1988a,b; Smith 1981; Winkelmann and Klaine 1991). For instance, Pignatello and Huang (1991) found that soils collected from a field with a previous atrazine history contain a large fraction of atrazine in a slowly reversible sorbed state and that this fraction increases with time. The ratio of apparent K_d from aged samples to K_d from "fresh" samples varied from 2.3 to 42 and was directly related to the "age" of the residue. Also, in column elution studies, freshly injected atrazine was more mobile than aged residues (Pignatello et al. 1993).

In many soils, even freshly added atrazine is not readily desorbed; that is, the desorption equilibrium does not match the sorption equilibrium.

Table 2. Atrazine sorption in subsurface soils.

Soil	Horizon	Silt (%)	Clay (%)	pH	OC (%)	K_r	$1/n$
Clarno loam	A	41	29	6.5	1.5	2.8	0.85
	Bw	38	30	7.0	1.1	1.6	0.91
	Bk	38	25	7.8	0.5	—	—
	2C	38	25	7.9	0.05	0.6	0.92
Moody silty clay loam	A	57	35	6.4	2.5	3.2	0.93
	Bw	54	25	7.1	0.6	0.9	0.94
	Bk	56	17	7.9	0.3	0.6	0.87
	2C	75	18	8.2	0.04	0.6	0.96
Nora silty clay loam	A	61	30	7.2	2.0	2.2	0.90
	Bw	62	27	7.4	0.5	0.7	0.94
	Bk	65	25	7.7	0.3	0.8	0.86
	2C	70	19	8.0	0.2	—	—
Brandt silty clay loam	A	56	29	5.5	4.5	5.4	0.82
	Bw	53	30	6.2	1.0	1.0	0.87
	2C	0	0	7.9	0.2	0.2	0.95

OC, organic carbon.

This phenomenon, known as hysteresis ($1/n$ -sorption \neq $1/n$ -desorption), has been observed for atrazine in several studies (Clay and Koskinen 1990a,b; Clay et al. 1988a). Several explanations of hysteresis have been proposed. Physical and chemical changes in soil solution may influence atrazine retention (Clay and Koskinen 1990a; Clay et al. 1988b; Gamberinger et al. 1991). It may become incorporated into organic matter complexes (Wang et al. 1991, 1992) or become chemically or microbially degraded (Cook and Hutter 1981; Gamble and Khan 1990; Sirons et al. 1973), with the metabolites differentially bound to soil (Capriel et al. 1985; Dao et al. 1979; Clay and Koskinen 1990a). Freundlich desorption coefficients can be dependent on the sorbed atrazine concentration, with low concentrations being retained to a greater extent and more difficult to desorb than higher concentrations (Barriuso et al. 1992). Also, in aged field residues, desorption K_f values increased slightly with aging (Barriuso et al. 1992).

It appears that atrazine binds to soil by several binding mechanisms and that the mechanisms or binding strengths change with time (Koskinen et al. 1995). For example, supercritical fluid (SF)-CO₂ extracted 48% of that present after 35 d in the field, but only 31% of that present after 138 d. Extraction efficiency using SF-CO₂/5% methanol was 66% of the atrazine present in the field after 35 d compared to 50% at 138 d (Koskinen et al. 1995). These data indicate that either binding mechanism(s) become stronger with time or that there are multiple binding sites with different binding energies. In the latter case, atrazine on labile sites may have desorbed and been degraded, leaving only that bound to high-energy sites.

The most stable bound residues are associated with humified organic matter, especially in the clay size fraction (0.2–2 μm). The largest proportion of total bound atrazine residues in the whole soil was in the clay size (0.2–2 μm) fraction, which also contained 50% of the total soil organic carbon (Barriuso and Koskinen 1996). The ratio of bound residues to OC content decreased with the particle size and was highest in the fraction of particles greater than 50 μm , which is rich in nonhumified matter.

Bound atrazine residues are very resistant to decomposition. Nine years after application of ¹⁴C-atrazine to soil, ~50% of the ¹⁴C was still present in the bound form in humic materials (Capriel et al. 1985). Of this ¹⁴C, atrazine, HA, DEHA, and DIHA could be detected in measurable quantities. However, it appears that some soil microorganisms can release bound ¹⁴C residues from soil treated with ¹⁴C-atrazine. The bound ¹⁴C residues released from soil by *Pseudomonas* species were identified as atrazine, HA, DEA, DIA, DEHA, and DIHA (Khan and Behki 1990). Therefore, while bound atrazine residues are difficult or impossible to extract by laboratory methods, some of these bound residues are still bioavailable to plants and soil microorganisms.

B. Effect of Solution Composition

Dissolved Organic Carbon. Dissolved organic carbon present in soil solution has been shown to increase, decrease, or have little or no measurable effect on the initial binding of atrazine to soil. However, DOC content appears to influence atrazine release from soil (Clay and Koskinen 1990a; Liu et al. 1995b), with more released in the presence of DOC. Fulvic acid in solution may form a complex with atrazine (Gamble et al. 1986; Haniff et al. 1985) or cause its hydrolysis to the hydroxy species (Gamble and Khan 1985; Khan 1978). Wang et al. (1990) reported that small molecular weight fractions of the fulvic acid complex compete with atrazine for binding sites on larger molecules.

Atrazine Concentration. The amount of atrazine applied also has been shown to influence retention to soil. In most cases, the percentage sorbed to soil decreases as atrazine concentration increases (Brouwer et al. 1990; Clay and Koskinen 1990a,b; Clay et al. 1988a; Gaber et al. 1995; Liu et al. 1995b; Pignatello and Huang 1991; Rochette and Koskinen 1996; Sonon and Schwab 1995; Stehouwer et al. 1993; Stolpe and Shea 1995), as indicated by slopes of Freundlich isotherms ($1/n$) < 1.0. The average value for $1/n$ for 43 soils from references cited in this section was 0.85. In contrast, atrazine sorption has been shown to be concentration independent in a number of soils (Gamerding et al. 1991; Guo et al. 1991b; Roy and Krapac 1994; Sonon and Schwab 1995).

The cause of the concentration dependence is not known. Using the data from 62 isotherms from the references just cited, there was no correlation of $1/n$ to organic carbon content, clay content, or pH. It appears that the heterogeneity of the soils results in a continuum of sorption sites with differing amounts of low- and high-energy sites in different soils.

Water Content. Methods commonly used to obtain sorption coefficients require that the soils be above field capacity moisture so that the aqueous phase containing the test pesticide can be separated from the soil. Rochette and Koskinen (1996) have developed a system using supercritical CO₂ that can remove the pesticide from a soil solution of unsaturated soil without first requiring the separation of the solution from soil. Sorption coefficients increased with increasing soil organic carbon and clay contents for three field-moist soils (Koskinen and Rochette 1996). Moreover, sorption significantly increased in a sand as gravimetric moisture content increased from 4.0% to 16% and in a silt loam as moisture increased from 9.6% to 27% (Table 3).

Isosteric heats of sorption, ranging from -10 to -12 kcal mol⁻¹, were easily determined with the supercritical fluid system and were correlated to organic carbon and clay contents (Koskinen and Rochette 1996). Sorption

Table 3. Effect of water content and potential on atrazine sorption-desorption.

Soil	Water content (%)	Water potential (bars)	K_d (L kg ⁻¹)
Zimmerman	16	0.025	7.67 ± 0.08
	9.6	0.15	5.82 ± 0.07
	5.6	0.95	2.92 ± 0.03
	4.0	2.94	1.21 ± 0.04
Verndale	9.6	0.95	12.4 ± 1.1
Waukegan	26.7	0.95	53.3 ± 1.4
	9.6	3600	20.6 ± 1.9

From Rochette and Koskinen (1996) and Koskinen and Rochette (1996).

coefficients in field-moist soils were much greater than are typically obtained with the batch slurry system, while heats of sorption were much more negative, indicating greater sorption at low moisture contents.

C. Sorption-Desorption of Metabolites

Each of the atrazine metabolites (i.e., HA, DEA, DIA, and *S*-glutathione-atrazine) have different properties known to influence their strength of retention to soil. DIA and DEA are less sorbed to soil than atrazine; DEA is the metabolite least retained by soil (Bowman 1990; Brouwer et al. 1990). DEA had a lower affinity than atrazine for low organic carbon sands and sediments, and sorption did not correlate to organic carbon, clay content, or pH (Roy and Krapac 1994). Unlike atrazine sorption, DEA sorption was reversible.

HA and *S*-glutathione-atrazine are sorbed to soil to a greater extent than atrazine (Brouwer et al. 1990; Clay and Koskinen 1990b; Clay et al. 1996). Soil pH of two silt loam soils influenced sorption, with more of the *S*-glutathione- and hydroxy metabolites sorbed at pH 4.0–4.5 than at pH 6.1 (Clay and Koskinen 1990b). HA also was more strongly sorbed to soil amended with ammonia than to unamended soil (Clay et al. 1996). HA and *S*-glutathione-atrazine are strongly retained by soil, with little if any desorption occurring over a 6-d period (Clay and Koskinen 1990b).

Soil thin-layer chromatography (TLC) was developed to evaluate pesticide mobility by using soil as the sorbent in a TLC system (Helling, 1968; Helling and Turner 1968). The ratio of the distance that the pesticide moves to the distance that the solvent (water) moves (R_f) is inversely proportional to sorption on the soil. Based on R_f values, Kruger et al. (1996b) identified three mobility groups for atrazine and selected metabolites in five Iowa soils: most mobile, DEA; intermediate mobility, atrazine, DIA, and DEDIA; nearly immobile, HA and ammeline.

IV. Transport

Although the downward transport of atrazine by water is of ultimate concern in evaluating the potential of groundwater contamination, other modes of transport should also be taken into consideration. These include upward transport to the soil surface by water, volatilization from the soil surface, spray drift during application, movement on wind-eroded particles, plant uptake, and transport in surface runoff water and sediment.

A. Movement to Atmosphere

Volatilization involves two stages: upward movement to the soil surface and escape from the soil surface. Volatilization is affected by vapor pressure of atrazine, Henry's constant, concentration in soil solution, soil water content, sorption to soil, diffusion rate in soil, air and soil temperature, and air movement. Although atrazine has a relatively low vapor pressure of 0.039 mPa (Tomlin 1994), it does volatilize. Whang et al. (1993) measured volatilization of 1%–2% of applied atrazine over a 26-d period. Atrazine can also enter the atmosphere by spray drift during and immediately after application. Another potential mechanism of atmospheric loading is thought to be atrazine retention on suspended sediments that are removed from treated fields during wind events (DeSutter et al. 1995; Glotfelty et al. 1989).

Once in the atmosphere, atrazine can be deposited off-site in dust or rainfall (Ciba-Geigy 1993; Richards et al. 1987). For instance, 39% of 325 rainwater samples collected in Iowa contained atrazine in concentrations ranging from 0.10 to 40 $\mu\text{g L}^{-1}$ with a detection mean of 0.91 $\mu\text{g L}^{-1}$ and median of 0.34 $\mu\text{g L}^{-1}$ (Nations and Hallberg 1992). In a later Iowa study, Hatfield et al. (1996) reported that 28% of rainfall samples contained atrazine with a detection mean of 0.7 $\mu\text{g L}^{-1}$ and maximum concentration of 154 $\mu\text{g L}^{-1}$. Both of these studies had the greatest number of detects in the first 3 mon directly following normal spring application periods, possibly because of volatilization of atrazine (Nations and Hallberg 1992) or deposition of spray drift directly into the atmosphere (Hatfield et al. 1996). Highest concentrations were also observed during the start of the rainfall event.

More than 50% of wind-eroded sediments collected from ditch areas of eastern South Dakota in early spring prior to atrazine application contained atrazine, DEA, DIA, or all three compounds (DeSutter et al. 1995) One day after application, soil aggregates < 1.0 mm (those most subject to wind erosion) had concentrations ranging from 51 to 76 $\mu\text{g g}^{-1}$, whereas sediments greater than 1 mm had concentrations from 29 to 38 $\mu\text{g g}^{-1}$.

B. Movement to Surface Water

Many studies have shown atrazine movement from the point of application in runoff water (see Nelson and Jones 1994, and references cited therein) (Table 4). Amounts detected for surface runoff studies range from <0.1%

Table 4. Surface runoff of atrazine.

Site	Soil	Slope (%)	Tillage	Time (yr)	Amount ($\text{g ha}^{-1} \text{yr}^{-1}$)	Reference
Wisconsin	Silt loam	6	Conventional	2	10; 130	Sauer and Daniel 1987
			Chisel plow	2	8; 92	
			Ridge-plant	2	11; 254	
			No-tillage	2	11; 214	
Ohio	-	8-22	No-tillage	2	0; 0	Triplett et al. 1978
			No-tillage	2	21; 0.5	
			No-tillage	2	41; 0.1	
			No-till (corn)	4	0.4; 7.4; 2.4; 1.8	
Pennsylvania	Silty clay loam	3-4 3-5	No-till (soybean)	4	0.2; 0.1; 0.4; 9.8	Logan et al. 1994
			Moldboard (corn)	4	1.3; 4.2; 3.3; 2.3	
			Moldboard (soybean)	4	0.1; 0.1; 0.1; 1.2	
			Moldboard	4	6.1; 5.7; 0.4; 0.05	
Kentucky	Silt loam	9	No-tillage	4	-; 0.1; <0.01; <0.01	Hall et al. 1991
			No-tillage	2	831; 14,900	
			Chisel plow	2	211; 4,710	
			Moldboard	2	945; 16,600	

Maryland	—	5.4	—	1	17	Wu 1980
Canada	Clay loam	?	Ridge-tillage	4	18; 1; 51; 13 ^a	Gaynor et al. 1995
			Zero-tillage Moldboard	1	19	Gaynor and van Wessen- beek 1995
	Clay loam	0.5	Moldboard, 25-cm band	1	25	Gaynor et al. 1992
			Moldboard, 50-cm band	1	25	Frank et al. 1991
	Clay loam	0.2	Conservation	4	0.2; 0.1; <0.1; 0.1	
			Conventional	3	14; 14; 98 ^a	
			Zero tillage Ridge-till	3		

^aRunoff averaged over the three tillages.

to 7.2% of applied atrazine (Gaynor et al. 1992, 1995). Atrazine is carried on sediments and as free molecules in surface runoff (Gaynor et al. 1992; Hall et al. 1991; Kolpin and Kalkhoff 1993; Pantone et al. 1992; Sauer and Daniel 1987; Triplett et al. 1978; Wu 1980; Wu et al. 1983) to nontarget areas, such as surface waters and riparian zones (Paterson and Schnoor 1992).

In monitoring studies ranging from small streams to large agricultural river systems covering the entire Midwest, atrazine concentrations up to $10 \mu\text{g kg}^{-1}$ have been reported (Ciba-Geigy 1992a,b; Frank et al. 1990b; Goolsby and Battaglia 1995; Kolpin and Kalkhoff 1993; Schottler et al. 1994; Thurman et al. 1991, 1992), but most detections are below the MCL of $3.0 \mu\text{g L}^{-1}$. However, the cumulative effects of many small runoff events (see Table 4) can result in a large absolute amount of atrazine entering a surface water body. For instance, total annual loading of atrazine into the Minnesota River was 1–2 t (Schottler et al. 1994).

The highest atrazine concentrations in surface water have been detected in the first 2 months after application, in early summer, with decreasing concentrations during the fall and winter months (Frank et al. 1990b; Thurman et al. 1991, 1992). High residue levels also have been observed after fall applications that are generally applied in September (a practice now prohibited by the atrazine label) (Frank et al. 1990b).

Atrazine metabolites also have been found in surface runoff and surface waters. Mills and Thurman (1994) found more DEA than DIA in shallow unsaturated surface water runoff from Eudora silt loam soil. Dissolved atrazine, DEA, and DIA concentrations in water samples from two closely spaced lakes indicated large differences in input from watershed nonpoint sources. Levels of these chemicals increased in response to spring and early summer runoff events (Spalding et al. 1994). DEA was found in all surface runoff samples that contained atrazine (Gaynor et al. 1992, 1995). HA, DEHA, and DIHA have also been identified in surface water (Lerch et al. 1995).

C. Movement to Groundwater

Atrazine can move through soil and has been found in groundwater in numerous areas of the Midwest through monitoring studies. For instance, in a 1970s study of water in the Central Platte region of Nebraska, all 14 locations sampled contained atrazine (Spalding et al. 1980). Concentrations ranged from 0.06 to $3.1 \mu\text{g L}^{-1}$ and were correlated to NO_3^- concentrations. In a Wisconsin survey of 2177 rural well water samples, approximately 27% gave an immunoassay response of ≥ 0.10 ppb atrazine equivalents; however, only 0.6% had levels greater than $3.0 \mu\text{g L}^{-1}$ MCL (Brady et al. 1995). In a survey of more than 12,000 wells in five Midwestern states, triazines were detected in 4.9%, while the atrazine MCL was exceeded in 0.1% of samples (Richards et al. 1996). In a monitoring study across the

Midwest, atrazine was detected ($>0.05 \mu\text{g L}^{-1}$) in 22%, and atrazine, DEA, or DIA was detected in 26% of 303 wells sampled; the median detectable atrazine concentration was almost half that of the total residue (atrazine plus two metabolites) detected (Kolpin et al. 1996).

Results from groundwater monitoring studies in eastern Canada are similar to those for the Midwest. Atrazine, DEA, and DIA were also found in groundwater under two agricultural soils in eastern Canada over a 3-yr monitoring period (Masse et al. 1994). Frequency of detections decreased with depth in the alluvial aquifer (Kalkhoff et al. 1992). For instance, atrazine was detected in 18% of the samples from the upper 1.6 m of the alluvial aquifer and was not detected in samples taken below 3.4 m.

The results of Wehtje et al. (1984) support direct downward leaching as the major source for low-level atrazine contamination detected in groundwater throughout the irrigated corn production areas of the Platte River valley of central Nebraska. Current contamination levels probably reflect a steady-state situation between the yearly amount that enters into the aquifer and the partial degradation that occurs within it (Wehtje et al. 1983). However, contamination of groundwater is probably the result of both point and nonpoint-source pollution. Of wells on 172 farms, 24 were contaminated with atrazine, 14 from spills from mixing or loading and 10 from leaching or runoff (Frank et al. 1987, 1990a).

Water Movement. Downward movement of atrazine may occur from percolating water carrying it to lower soil depths. Well-structured soils have been reported to have more chemical movement to deeper depths when compared to nonstructured soil as the result of water flow through macropores in structured soils. Increased permeability, percolation, and solute movement can result from increased porosity, especially in no-tillage systems where there is pore connectivity at the soil surface (Barley 1954; Quisenberry and Phillips 1976; Thomas and Phillips 1979).

Plant roots are important in the creation and stabilization of soil macropores (Barley 1954). Preferential flow through root-mediated soil pores has been demonstrated for chloride, nitrate, and other ions, which are not sorbed onto soil organic matter and clays. Although atrazine is sorbed on soil organic carbon and clay, its movement through soil columns has been shown to be influenced by roots. The greatest difference in distribution of atrazine in 100-cm soil columns was at the 15- to 30-cm depth. More was present at these depths in columns with roots than without roots, presumably due to greater movement through channels created as roots decayed (Zins et al. 1991).

Earthworm burrows can function as preferential flow conduits. However, it is unclear if earthworm burrows actually increase the atrazine leaching because many factors influence these potential routes. First, the total organic carbon in the burrow lining is two to three times greater than in bulk soil. This increase in organic carbon has been attributed to result in

increased atrazine sorption to the burrow lining (Stehouwer et al. 1993, 1994). In fact, water and atrazine mixtures poured through earthworm burrows showed that these linings greatly reduced the concentration of atrazine (Edwards et al. 1992b).

A second important consideration in determining whether these macropores contribute to atrazine movement is that movement depends on rainfall amount, intensity, and antecedent soil water content with percolate volume dominating the movement mechanism (Edwards et al. 1992a). For instance, high-intensity rains on relatively dry no-till soils shortly after atrazine application produced the greatest amounts of preferential flow and movement (Edwards et al. 1993). However, leaching was reduced if rainfall was delayed or if low-intensity rains occurred prior to high-percolate-producing events (Edwards et al. 1993). After the first rainfall, surface-applied atrazine leached less in subsequent high-percolate high-volume storms, regardless of intensity or volume of percolate produced by the first storm. Shipitalo et al. (1990) reported that the first storm after application moved atrazine into the soil matrix, thereby reducing the potential for transport in macropores during subsequent rainfalls.

Along with movement through earthworm and root macropores, atrazine can also be vertically transported via irrigation return flows. Junk et al. (1980) reported a significant correlation between atrazine and $\text{NO}_3\text{-N}$ concentrations in wells down gradient from irrigated croplands with the occurrence of peak atrazine levels in the fall immediately after the irrigation season.

Movement of atrazine through the plant root zone of soil is a function of water availability. Crop canopy plays a significant role in asymmetrical distribution of incoming precipitation that reaches the soil surface, causing a potential differential movement of atrazine. For instance, the least throughfall of precipitation occurs within 20 cm of the row in corn and soybean (Dowdy et al. 1995). Atrazine movement was reduced by applying it as a band over the row and using corn foliage as a shelter from incoming precipitation. Essentially all atrazine remained in the top 7 cm of a loamy sand soil during the first 22 d after application with very little lateral movement into the interrow beyond the spray band. Dowdy et al. also found that some moved from the soil surface into the top 30 cm of soil but not deeper.

Column Leaching Studies. Differences in atrazine leaching between soils have been attributed to differences in physical and chemical properties of the soils, which affect retention and transformation processes, leaching volumes and velocities, presence of macropores, and field management including crop residues, fertilizer, and herbicide practices. To illustrate the influence of these variables on atrazine movement through the profile, numerous studies have been conducted using disturbed and undisturbed soil columns of different sizes in the laboratory, greenhouse, and field (Table 5).

Table 5. Atrazine leaching in large^a soil columns.

Soil	Soil column		Time (wk)	Water	Atrazine movement		Reference	
	Soil profile	Length (cm)			Depth (cm)	Amount (% of applied)		Atrazine in leachate (% of applied)
Sand	Repacked by horizon	104	35	Rain	60-100	3.3	0.1	Alhajjar et al. 1990
Silt loam	Repacked by horizon	104	35	Rain	60-100	3.6	0.1	Alhajjar et al. 1990
Sand	Uniformly packed	70	21	Rain Rain + ^b	20-30 70	Trace Trace	0 <0.8	Bowman 1989
Sand	Uniformly packed	70	21	Rain Rain +	20 30-40	Trace Trace	0 0	Bowman 1990
Silt loam	0-15 cm 15-70 cm	70	21	Rain Rain +	40 50	- -	Occasionally Occasionally	Bowman 1990
Sand	Uniformly packed	70	21	Rain +	30	<0.1	Occasionally	Bowman 1993
Sand	Repacked by horizon	75	-	Unsaturated flow	60	0.6	62	Guo et al. 1991b

(continued)

Table 5. (Continued)

Soil	Soil column			Atrazine movement			Reference	
	Soil profile	Length (cm)	Time (wk)	Water	Depth (cm)	Amount (% of applied)		Atrazine in leachate (% of applied)
Sandy clay loam	Intact	60	12	Weekly irrigation	60	0.3	1.2	Kruger et al. 1993b
Sandy clay loam	Intact	60	13	Weekly irrigation	60	0.3	3.6	Kruger et al. 1996a
Loamy sand	Intact	95	13	Rain	80	0.1 (¹⁴ C)	—	Lee and Weber 1993
Sandy loam	Intact	120	78	Rain +	40	0.3	0	Sorenson et al. 1993
Clay loam	Intact	90	78	Rain +	80	0.1	0.04	Sorenson et al. 1994
Silt loam	Intact	90	78	Rain +	80	0.1	<0.01	Sorenson et al. 1995
Sand	Intact	80	22	Rain +	40-80	9	8	Wieterson et al. 1993b
Sand	Intact	90	22	Rain +	40-80	3	0	Wieterson et al. 1993a
Silt loam	Packed	60	—	Saturated flow	50	<1	9	Zins et al. 1991

^aminimum size is 10 × 60 cm.

^bRain plus supplemental irrigation.

In most of these studies, the bulk of atrazine remained near the soil surface as a result of sorption processes. In intact soil cores containing a silt loam soil, its leaching was primarily influenced by sorption-related nonequilibrium at low pore water velocities and by a combination of both transport-related and sorption-related nonequilibrium at high pore water velocities (Gaber et al. 1995). However, a portion does leach; the depth and amount depends on soil type, amount of water, soil horizons, crop residues, and fertilizer placement. For instance, small amounts (approximately 3% of applied) of ^{14}C from ^{14}C -atrazine leached to the 60- to 100-cm-depth increment within 35 wk in sand and silt loam columns, with most remaining in the top 15 cm (Alhajjar et al. 1990). Wietersen et al. (1993a) determined ^{14}C -atrazine movement using intact soil columns of two sandy Wisconsin soils. Its mobility in a Sparta sand was greater than in a Plainfield sand as the result of higher hydraulic conductivity, smaller water-holding capacity, and less sorption from lower organic carbon and clay contents.

In lysimeters packed with Plainfield sand, the maximum movement of atrazine after 21 wk under natural rainfall was 30 cm, compared to 70 cm when supplemental irrigation was supplied (Bowman 1989, 1991). The length of time for half of the atrazine to dissipate (DT_{50}) was 2.5 wk under rainfall and 3.5 wk under supplementary watering. The difference in DT_{50} between the two treatments was attributed to greater movement away from the surface soil, where most degradation would have occurred.

Kruger et al. (1993b) found that approximately 1.2% of the ^{14}C -atrazine was recovered in leachate during a 12-wk period from a 60-cm-long column of an Iowa soil that was taken from a field with no previous pesticide history. However, by the end of the experiment, 77% of the ^{14}C applied remained in the upper 10 cm, of which bound residue was the primary component. Degradation products found in the surface 10 cm of soil were $\text{DIA} > \text{HA} > \text{DEDIA} > \text{DEHA} > \text{DIHA}$.

Metabolites of atrazine may leach from upper layers or be formed at lower soil depths. Metabolites most likely to leach are DEA and DIA because their retention by soil is lower (Barriuso et al. 1992; Bowman 1990; Muir and Baker 1978; Schiavon 1988a,b). For instance, in a study by Kruger et al. (1993b), atrazine, DEA, and DIA were found at all depths, whereas other metabolites leached to a lesser extent. In a 13-wk leaching study with 60-cm intact soil columns, the percentage of ^{14}C -DEA recovered was greatest in the first leaching event (1.3% of applied ^{14}C), suggesting preferential flow (Kruger et al. 1996a). The total DEA loss from leaching was 3.6% of applied ^{14}C -DEA.

More DEA also has been found in soil water at deeper depths than atrazine or DIA (Adams and Thurman 1991). HA does not readily leach through soil (Schiavon 1988a,b) because it is tightly bound (see previous section). Therefore, HA detected deep in the profile is the result of degradation or hydrolysis at depths (Sorensen et al. 1993, 1994, 1995). Relative mobilities in a Honeywood silt loam were $\text{DEA} > \text{atrazine}$, but relative

mobilities were about the same in Plainfield sand (Bowman 1990). Maximum movement of DEA and atrazine in the sand occurred at about 40 cm after 8 wk. In field lysimeters receiving supplemental water, DEA was more mobile than atrazine. DT_{50} for both chemicals in both soils was about 4 wk. The difference in persistence in the two Plainfield sand experiments was attributed to spatial variability of texture and organic carbon in the Plainfield sand. DT_{50} of 4.3–4.9 wk has also been reported for this soil (Bowman 1991). In another leaching study with the Plainfield sand, no detectable atrazine leached through a 70-cm lysimeter (Bowman 1993).

The influence of crop residues on atrazine leaching is unclear. In one study using undisturbed soil columns, greater amounts were recovered with the first 5 cm of leachate in 100% surface residue columns than from zero-residue columns with high and medium saturated hydraulic conductivities (Green et al. 1995). Also, the time to peak atrazine concentration in leachate decreased as residue levels increased for columns with high saturated conductivities. In contrast, covering soil cores with 200 or 2000 kg ha⁻¹ of crop residue reduced leaching by 26% and 37%, respectively, compared to soil cores without crop residue (Sigua et al. 1993). Sigua et al. (1993) also reported that the age of the residue may influence its movement; soil cores covered with recently harvested vegetation reduced leaching by 39% compared with cores covered with aged residue.

In undisturbed soil columns, higher atrazine concentrations occurred in the leachates of the plow-tillage columns than in the no-tillage columns (Levanon et al. 1993). However, more atrazine has been reported to leach through untilled cores than tilled cores, and increasing the number of earthworms in soil cores increased the amount leached through both untilled cores and tilled cores (Sigua et al. 1995).

Changing soil surface pH with fertilizer also may influence atrazine's leaching potential. For instance, application of NH₄OH increased surface soil and leachate pH and resulted in increased amounts in leachates from columns containing silty clay loam and clay loam soils (Liu et al. 1995a).

Field Leaching Studies. There are numerous reports that atrazine leaches into the vadose zone (Adams and Thurman 1991; Clay et al. 1994; Helling et al. 1988; Wehtje et al. 1984), into tile drains (Buhler et al. 1993; Kladivko et al. 1991; Muir and Baker 1976), or into groundwater (Frank et al. 1991; Isensee et al. 1988, 1990; Pionke and Glotfelty 1990; Starr and Glotfelty 1990; Verstraeten et al. 1995). Most of the field leaching studies are limited to depths <2 m. In most studies, the majority is bound and degraded in the surface 50 cm, similar to what has been observed in column leaching studies. However, small amounts of atrazine or atrazine degradates are consistently found at lower depths in the soil profile. For example, an estimated minimum of 3.2%–6.5% leached below 15 cm and was detected to a depth of 60 cm (Frank et al. 1991). Atrazine applied at 2.2 and 4.5 kg ha⁻¹ was detected in a silty clay loam and a clay loam to a depth of 76 cm approxi-

mately 2 mon after application; however, most remained in the surface 30 cm of soil (Hall and Hartwig 1978). Hall et al. (1989) detected atrazine at all soil depths down to 122 cm. Differences in the yearly extent and magnitude of leaching losses were strongly correlated to rainfall distribution and number of leaching events proximal to application.

Two months after application of ^{14}C -atrazine to a sandy loam soil, ^{14}C was detected at the 30- to 40-cm depth but was not found deeper (Sorenson et al. 1993). At 30- to 40-cm depth, ^{14}C was identified as ^{14}C -labeled atrazine, DEA, DIA, and HA. Twelve months after application of ^{14}C -atrazine to a silt loam soil, ^{14}C had leached to the 70- to 80-cm depth (Sorenson et al. 1995) and was identified as ^{14}C -labeled atrazine, DEA, DIA, and HA. Only one month after application of ^{14}C -atrazine to a clay loam soil, ^{14}C was detected at the 70- to 80-cm depth (Sorenson et al. 1994) and was identified as ^{14}C -labeled atrazine and HA. DEA was not observed at this depth until 16 mon after application, while DIA was never detected.

In a loam soil, atrazine levels in conventional and no-till treatments were similar for a given depth and sampling time after application. Most was present in the upper 5 cm of the profile, and only a trace was found at the 40-cm depth (Ghadiri et al. 1984). Distribution patterns through field soil under plow-tilled and conservation-tilled corn were quite similar. The bulk was in the surface soil, but some was found at the deepest sampling depth (90 cm) (Starr and Glotfelty 1990). Atrazine appeared to move by both one-dimensional movement through the soil matrix and by rapid downward movement through macropores, bypassing most of the soil matrix. However, Gish et al. (1995b) obtained slightly different results when water samples (rather than soil samples) were analyzed. Movement was less under no-till than under tilled conditions. Under no-tillage, it was detected in <28% of the water samples obtained from suction lysimeters at 1.5- and 1.8-m depths, with <13% exceeding the MCL of $3 \mu\text{g L}^{-1}$ (Gish et al. 1995b). In contrast, under tilled conditions, atrazine was detected in 53% of the water samples obtained from suction lysimeters at 1.5- and 1.8-m depths, with 35% exceeding $3 \mu\text{g L}^{-1}$.

Tile drains, placed between 1 and 2 m below the soil surface to help drain wet areas, are effective tools to determine leaching in the field. Monitoring the drainage outflow for atrazine can determine timing of fluxes and cumulative atrazine loss through leaching over a large area (Table 6). Water discharge from tiles into surface waters normally occurs in spring and early summer, both before and after spring applications. Because atrazine is mobile and tiles are near the surface, it is not surprising that numerous studies have reported atrazine detected in subsurface tile drainage water.

Amounts detected in tile drainage water are typically low, but atrazine can be detected over long time periods. For instance, about 0.15% of that applied was found in tile drains either as atrazine or as DEA. DEA was detected in concentration equal to or greater than atrazine (Muir and Baker 1976). In Ontario, atrazine and DEA were found in all samples of tile

Table 6. Atrazine movement to subsurface tile drains.

Site	Soil	Tile depth (m)	Tillage	Time period (yr)	Atrazine in Tile Drainage			Reference
					Maximum concentration ($\mu\text{g L}^{-1}$)	Total loss (g ha^{-1})		
Iowa	Loam	1.2	No-tillage	2	8.2	9.8	Jayachandran et al. 1994	
	Loam	1.2	Moldboard, no-tillage	3	—	<0.4%	Weed et al. 1995	
Indiana	Silt loam	0.7	Moldboard	3	10	<1	Kladivko et al. 1991	
Minnesota	Clay loam	1.2	Moldboard, no-tillage	5	1.5	>4	Buhler et al. 1993	
Ohio	Silty clay	1.0	Moldboard, no-tillage	4	59	31	Logan et al. 1994	
Canada	Clay loam	1.0	Moldboard	4	7.8	26-120	Frank et al. 1991	
	Sandy loam	1.2-1.6	—	2	11	2	Muir and Baker 1976	

drainage water collected from a 1-m depth, with about 1.9% lost in tile drainage following a fall application and as much as 0.2% following spring application (Frank et al. 1991). In Indiana, small amounts were detected in subsurface tile flow within 3 wk of application after less than 2 cm net tile flow from a poorly structured silt loam soil with low organic matter (Kladivko et al. 1991). The rapid appearance of atrazine indicated the possibility of preferential flow. Atrazine, DEA, and DIA were also found in subsurface drainage water in Iowa. The order of concentration was atrazine > DEA > DIA (Jayachandran et al. 1994). Levels in tile drains ranged from 0.1 to 29 $\mu\text{g L}^{-1}$, with concentrations declining after application (Milburn et al. 1995). A spill on one of these plots, followed by 71 mm of rainfall within a few days, resulted in tile drain concentrations of 150 $\mu\text{g L}^{-1}$, which decreased to less than the MCL, 3.0 $\mu\text{g L}^{-1}$, within 6 d of the initiation of tile flow.

Atrazine has also been found in subsurface tile drainage years after the last application. The average concentration in tile water, 24–30 mon after the last application, was 0.4 $\mu\text{g L}^{-1}$, and dropped to 0.3 $\mu\text{g L}^{-1}$ 9 mon later (Buhler et al. 1993).

V. Persistence

Atrazine persistence is usually characterized by assuming first-order dissipation kinetics and calculating a half-life ($t_{1/2}$) or time for 50% dissipation (DT_{50}). Half-life values range from 14 to 109 d (Table 7). However, in reality, its persistence in the field appears to be biphasic. When applied in spring, initial rapid degradation occurs during the first 2 mon after application, followed by slower degradation in the dry summer and cold fall and winter of the Midwestern states. For example, in one experiment the $t_{1/2}$ is 55 d if only growing season data are used in the calculation, compared to 134 d if all data for the year are used (Weed et al. 1995).

While the degradation pattern can be generalized, soil type, initial and seasonal water content, and other variables have been shown to influence the rate of both the rapid and slow degradation phases. For example, 2 mon after application only 32% of the applied atrazine remained in a silt loam (Sorenson et al. 1995), whereas 45% remained in a clay loam (Sorenson et al. 1994) and 35% remained in a sandy loam (Sorenson et al. 1993). However, degradation then slowed down, with 16% still remaining in the silt loam 16 mon after application (Sorenson et al. 1995) compared to 20% in the clay loam (Sorenson et al. 1994) and 22% in the sandy loam (Sorenson et al. 1993). In a 2-yr study on the same soils a year later, dissipation was initially much slower. Averaged over both years, at 21 d after application 93%, 56%, and 85% of applied atrazine still remained in the sandy loam, silt loam, and clay loam soils, respectively, with >95% of the amount present still in the surface soil (Koskinen et al. 1993).

Dissipation half-life in surface soil after spring application at a number

Table 7. Field persistence of atrazine.

Site	Soil	Depth (cm)	Rate (kg ha ⁻¹)	Variable	t _{1/2} day	Reference
Iowa	Loam	100	2.8	—	55	Weed et al. 1995
	—	—	1.3-5.0	—	16	Paterson and Schnoor 1992
Nebraska	Loam	10	1.1-1.7	Conventional till	42	Ghadiri et al. 1984
	Sandy loam	15	2.2-3.4	No-till	50	Brejda et al. 1988
Maryland	Sandy loam	20	1.7	SE formulation	110	Gish et al. 1994
	Sandy loam	20	1.7	EC formulation	36	
	Silt loam	30	2.8	—	60	Helling et al. 1988
	Silt loam	10	1.3	Conventional till	26-35	Isensee and Sadeghi 1994
Canada	Sandy clay loam	20	2.2	No-till	26-35	
				Year	14	Muir and Baker 1978
	Sand	30	2.2	Year	33	
				Year	40	
			Rain	18	Bowman 1989	
			Supplemental water	25		

Sand	30	2.2	Rain	28	Bowman 1989
			Supplemental water	28	
Sand	30	2.2	Rain	30	Bowman 1991
			Supplemental water	34	
Sand	30	2.2	EC formulation	26	Bowman 1993
			25G formulation	28	
Clay loam	15	2.0-3.2	Year	37	Frank et al. 1991
			Year	64	
Clay loam	10	1.8	Conventional till	64	Gaynor et al. 1992
			Zero-till	67	
			Ridge top	80	
			Ridge valley	51	
Clay loam	15	1.1-3.3	Rate: 1.1 kg ha ⁻¹	109	Frank and Sirons 1985
			Rate: 2.2 kg ha ⁻¹	91	
			Rate: 3.3 kg ha ⁻¹	106	

of sites in Ontario, Canada, ranged from 2.4 to 3.0 mon, with rapid breakdown the first 5 mon after application compared to slow dissipation during fall, winter, and early spring (Frank and Sirons 1985). Dissipation half-life was 37 d if calculated over the growing season but 125 d if winter months were included (Frank et al. 1991). When applied in fall, dissipation half-life was 198 d.

In a 2-yr field study in Ohio, atrazine did not move out of the 0- to 15-cm soil depth, and calculated dissipation half-life was 35 d in both years (Workman et al. 1995). Atrazine half-life in the 0- to 15-cm depth was 46 d in a Nebraska sandy loam soil (Brejda et al. 1988). At 30 d after application of 1.1 kg a.i. ha⁻¹ to a sandy loam soil in Minnesota, the majority of the remaining atrazine, 161 µg kg⁻¹, was in the top 15 cm of soil. About 2 µg kg⁻¹ had leached to the 45- to 60-cm depth. By 60 d after application, only 5 µg kg⁻¹ remained in the surface 15 cm (Buhler et al. 1994). Levels in a loam soil in Nebraska decreased to 75% of the application level in both conventional and no-till tillage plots by 61 d after application (Ghadiri et al. 1984). In a similar study the next year, only trace amounts remained 80 d after application.

It is difficult to generalize the effects of tillage on atrazine persistence because tillage influences so many soil characteristics. In general, tillage does not appear to strongly influence its persistence. By the end of the growing season, any initial effects due to tillage on persistence during the first months after application (see Section VI.A) become insignificant. For example, at the end of the growing season <2% of the spring applied atrazine still remained in a clay loam soil under ridge, conventional, and zero-tillage systems (Gaynor et al. 1987). While tillage may not influence atrazine persistence, the initial application rate has been shown to affect persistence, with higher rates having slower dissipation. By the end of the growing season, 3%–21% of atrazine applied at rates of 2.2 and 4.5 kg ha⁻¹ to a silty clay loam and a clay loam still remained (Hall and Hartwig 1978). Climatic conditions may or may not influence atrazine persistence. Residues in a number of Michigan soils after a severe drought during a growing season were similar to those following a more normal growing season (Leavitt et al. 1991).

Atrazine persistence has been shown to be affected by concentration. Persistence increased significantly at high concentrations compared to normal concentrations (Davidson et al. 1980). In clay loam and sandy loam soils, persistence (based on percentage of applied) was greater in high-rate than normal-rate treatments during the first 6 mon in the field (Gan et al. 1996). On an absolute basis, however, the amount dissipated from the high-rate was greater than the low-rate treatment. Atrazine can also persist for long periods after application at low levels (Buhler et al. 1993). It was applied to a clay loam soil for 3 yr, and 4 yr after the final application atrazine (16 µg kg⁻¹), DEA (3.7 µg kg⁻¹), DIA (0.7 µg kg⁻¹), and HA (5.4 µg kg⁻¹) were still detected (Raju et al. 1993).

VI. Management Practices

Specific management practices influence atrazine movement. Tillage, atrazine formulation and placement, fertilizer type, application, and placement, previous crop history, and crop residues are some of the variables that change the characteristics of atrazine movement (Baker and Mickelson 1994). These practices affect transformation, retention, and transport processes in soil. For instance, tillage systems affect various soil properties such as soil moisture, temperature, pH, organic matter, water flow characteristics, and microbial populations, which in turn can affect all three processes. Atrazine movement is usually studied under one management practice at a time; however, interactions of these practices challenge our ability to predict the net effect on its persistence and movement in soil. In the following section, the effect of single management variables is discussed.

A. Tillage

Effect on Persistence. It is difficult to generalize the effects of tillage on atrazine persistence, dissipation, and movement because tillage influences so many soil characteristics. Differences in tillage practices have been reported to decrease, increase, or have no effect on its persistence in soil. Several studies have reported no effect on atrazine dissipation. For example, in a sandy loam soil, persistence was not significantly different in fields under no-tillage and conventional tillage management (Gish et al. 1994). In another study, similar dissipation in both no-till and conventional tillage systems was attributed to the low pH of the soil resulting from long-term application of NH_4NO_3 , which catalyzed hydrolysis to HA (Ghadiri et al. 1984). Although the moldboard tillage soil profile had consistently higher atrazine concentrations, only in one instance was it significantly different than in the no-till system (Sauer et al. 1990). Also, in soils under no-till and moldboard tillages, it was never detected at quantifiable levels below the 15-cm depth at four sampling times during the growing season. Tillage had little significant effect on the overall distribution and dissipation of atrazine in soil, although moldboard-plow plots usually had the largest amounts at a given sampling time (Weed et al. 1995).

In contrast, other studies have reported differences in dissipation due to tillage. Dissipation was faster in reduced tillage systems than in conventional tillage systems, as evidenced by reduced carryover under reduced tillage (Burnside and Wicks 1980). Residues in the surface 10 cm of soil in conventional tillage plots averaged 2.6 times more atrazine than in no-tillage plots, regardless of the difference in the rainfall patterns (Sadeghi and Isensee 1992, 1994). Total atrazine from the 0- to 50-cm depth was also generally lower under no-till than under conventional till treatments (Isensee and Sadeghi 1994).

Persistence also has been reported to increase when volatilization losses

decrease. A 50% reduction in atrazine volatilization losses was observed under no-tillage relative to tilled fields (Weinhold and Gish 1994). This decrease was attributed to the protection of the soil surface by mulch, which decreased volatilization losses by half (Gish et al. 1995a).

Surface Runoff and Leaching. The effect of tillage on the amount of atrazine detected in surface runoff and leachate also is difficult to generalize. In most cases, environmental conditions during the study play a more important role in the losses than tillage. For example, in a study by Logan et al. (1994), tillage had little effect on water flow or atrazine losses in runoff and tile drainage; however, loss was greatly influenced by crop type and weather. Tillage (conventional, zero, and ridge tillage) had no significant effect on runoff volume, distribution between surface and sub-surface runoff, herbicide concentration, or herbicide loss (Gaynor et al. 1992). Concentration and loss in tile drainage water was minimal (less than 0.13% of applied) but ranged from 0.01 in moldboard-plow to 0.13% in no-tillage systems (Buhler et al. 1993). In contrast, conservation tillage (ridge tillage and zero tillage) increased surface runoff 42% and decreased tile drainage discharge 15% compared with conventional tillage, but total field runoff was the same from all tillages. Conservation tillage altered the mechanism of atrazine loss compared with conventional tillage, but environmental factors after its application were more important than tillage in determining total loss (Gaynor and van Wesenbeeck 1995).

In a Wisconsin study, conservation tillage systems reduced both runoff and soil loss; however, atrazine concentrations in runoff water and sediment in these systems were at times greater than with conventional tillage (Sauer and Daniel 1987). Reduced runoff volumes and erosion with conservation tillage systems usually offset higher pesticide concentrations in runoff, resulting in little difference in tillage with respect to total atrazine loss. Maximum loss was 5.8% of applied.

In areas with high amounts of summer precipitation, losses in no-till systems were generally greater than in plowed systems, perhaps due to more structured soils with less exposed sorption sites and more macropores. In general, maximum atrazine concentrations and mean amounts in pan lysimeter percolates collected at a depth of 122 cm were greater under no-tillage, where more leachate was collected than under conventional tillage (Hall et al. 1989). In another study, Hall et al. (1991) reported that percentage losses in root zone leachates were greater under no-tillage than under conventional tillage corn. However, the opposite was true for runoff losses, and the magnitude of loss was less for runoff than for leaching. Isensee and Sadeghi (1994) also reported greater leaching below 10 cm under no-till than under conventional till.

A moldboard-plow treatment in the fall reduced atrazine residues in the soil in the spring because plowing resulted in some soil dilution of the residues and also moved the residues below the sampling depth. Ridge

tillage systems had higher spring residues than zero tillage, apparently because of reduced atrazine dissipation on the drier ridge tops (Gaynor et al. 1987).

Over a 4-yr period, there was twice as much runoff volume from conventional tillage compared to chisel-plow and no-tillage (Blevins et al. 1990). Atrazine loss in runoff was least in chisel plow, while conventional tillage and no-till losses were about the same. During a 2-yr period, <1% of applied atrazine was lost in runoff, and most of this occurred between application and corn canopy closure. Less runoff and atrazine loss occurred from areas planted in continuous corn in no-tillage areas than in conventional tillage areas (Triplett et al. 1978).

B. Formulation and Amendments

Controlled-release formulations of atrazine have been proposed as a method to reduce its mobility in soil. Ideally, such formulations would only release the amount of chemical into soil solution necessary to control weeds, with the remaining atrazine unavailable for leaching. Starch encapsulation has been shown to reduce atrazine leaching in sand using intact soil cores (Mervosh et al. 1995). In a column study, atrazine leached less as a starch encapsulation than when applied as an acrylic polymer formulation. Effectiveness of acrylic polymers to reduce leaching decreased with water volume and time compared to conventional formulations (Fleming et al. 1992). In a field study, Gish et al. (1994) found starch-encapsulated atrazine less mobile than the conventional formulation.

In contrast, in a 3-d laboratory column study, acrylic polymers slightly reduced atrazine leaching but had no effect in a 92-d field study (Lee and Weber 1993). Addition of 2% polymer by volume to a conventional formulation resulted in no difference in atrazine mobility compared to the conventional formulation but did decrease the movement of metolachlor through sandy soils (Wietersen et al. 1993b).

Controlled release can make atrazine more persistent, thereby increasing the time it is available for leaching. Starch encapsulation greatly increased persistence in the surface 15 cm of soil compared to the dry flowable formulation (Buhler et al. 1994). Increased persistence of atrazine resulted in increased leaching in the soil at 120 d after application compared to conventional formulations. In a field study, Gish et al. (1994) found starch-encapsulated atrazine more persistent than the conventional formulation.

Volatilization of atrazine contributes significantly to environmental contamination. Starch encapsulation decreased atrazine volatilization compared with conventional formulations (Wienhold and Gish 1994; Wienhold et al. 1993). Surface mulch and a starch-encapsulated formulation decreased volatilization losses by a factor of 4 compared to conventional formulation on bare soil, whereas surface mulch decreased volatilization losses by half (Gish et al. 1995a).

Numerous other amendments have been used to control atrazine persistence and movement. For instance, while pig manure slurry and cow manure did not affect leaching through soil, they both increased the soil half-life by 50% (Rouchaud et al. 1994). Addition of dairy manure increased the rate of atrazine mineralization, whereas corn meal decreased and $(\text{NH}_4)_2\text{HPO}_4$ inhibited mineralization (Gan et al. 1996). Amendments applied at 2.1 t total carbon per ha to a sandy, coarse-textured soil reduced atrazine leaching in this order: waste-activated carbon \gg digested municipal sewage sludge $>$ animal manure; under saturated flow conditions 0.3%, 57%, and 67% of applied atrazine was in the leachate, respectively, compared to 77% in the untreated soil (Guo et al. 1991b). These amendments also reduced atrazine phytotoxicity (Guo et al. 1991a).

C. Other Management Practices

Application methods can affect atrazine persistence and movement. Runoff of atrazine, when applied in 50-cm-wide bands, was reduced 69% compared with a broadcast application. The greater reduction in loss by runoff associated with reduced application was attributed to movement into the soil profile (Gaynor and van Wesenbeeck 1995). Banding over 50% of a corn row reduced atrazine concentrations in lysimeter leachate by 43% (from 1.6 to 0.9 $\mu\text{g L}^{-1}$) compared with broadcast applications (S.A. Clay, unpublished data). Greater amounts were lost in runoff 1, 7, and 30 d after preemergence compared to that applied postemergence applications (Pantone et al. 1992). The greatest amount in runoff was $<2\%$ of the applied. The injection slot created by fertilizer application increased atrazine movement when atrazine application and the fertilizer injection slot overlapped (Clay et al. 1994). The increased movement resulted from the physical disturbance of the soil and from reduction of atrazine sorption to soil by the fertilizer.

Vegetative buffer strips appear to hold promise for protecting water supplies. A 6-m-wide strip of oat (*Avena sativa* L.) at the slope base reduced runoff loss by greater than 64% when atrazine was applied either preemergence or preplant incorporated at 2.2 or 4.5 kg ha^{-1} in corn plots (Hall et al. 1983). Deep rooted poplar trees also appear to hold promise for protecting water supplies (Paterson and Schnoor 1992).

Summary

Atrazine persistence and fate are influenced by many factors, the interactions of which are difficult to predict. Several models, such as LEACHP (Wagenet and Hutson 1989), have been used as tools to estimate losses and identify variables that will impact the magnitude of loss. The LEACHP model was evaluated for predicting atrazine movement in sandy loam, silt loam, and clay loam soils during three consecutive years (two dry and one

wet) in Minnesota (Khakural et al. 1995). Considering the broad range in soil properties and climatic conditions used in testing, the model performed well. However, these are only estimates, and additional field studies need to be conducted to verify model results.

In a report by Fausey et al. (1995), the amount of atrazine found in groundwater throughout the Midwestern region was reported to be much below the MCL. However, specific sites in the Midwest may struggle with atrazine problems from both point and nonpoint sources of contamination. Some states, such as South Dakota, have created groundwater protection areas that alert growers and the public to sensitive areas where contamination may occur because of soil type, depth to groundwater, and distance to public wellheads. Wisconsin has developed a tiered managerial strategy, or zoning approach, in which restrictions are matched to pollution detections (Wolf and Nowak 1996). The USEPA has mandates for states to implement generic management plans to prevent pesticide contamination of groundwater. Chemical-specific plans by states will be required for at least five pesticides, one of which will be atrazine.

Best management practices have been and are continuing to be developed to aid the grower in lessening the adverse impacts of atrazine. With continuing research into understanding the problem and developing solutions, and with adaptation of these recommendations by growers, the use of effective, inexpensive herbicides may continue with minimal off-site environmental effects.

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Manuscript received November 8, 1996; accepted February 4, 1997.