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Degradation of Atrazine in Subsoils, and Groundwater Mixed with Aquifer Sediments

C. J. Rodriguez,* J. M. Harkin

Water Resources Center and Environmental Toxicology Center, University of Wisconsin, Madison, Wisconsin 53706, USA

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Atrazine (2-chloro-4-ethylamino-6-isopropylamino-*s*-triazine) is widely used for control of broadleaf weeds in the cultivation of corn, and other crops (Uhler, 1991). Traces of atrazine and its chlorinated degradation products deethylatrazine (DEAT), deisopropylatrazine (DIAT) and deethyl-deisopropylatrazine (DEDIAT) in groundwater is a public concern that has prompted the U.S. Environmental Protection Agency (EPA) to review current usage of this possible human carcinogen (USEPA, 1994). Chlorinated atrazine degradation products are considered to be as toxic as parent material (Belluck et al., 1991). Chemical hydrolysis of chlorinated residues is thought to detoxify these compounds. Despite frequent detection of atrazine and its chlorinated degradation products in groundwaters of several states (Kolpin et al., 1996), little is known about their fate in subsoils and aquifers. Most degradation studies of atrazine have focused on breakdown materials at or near the soil surface, placing particular emphasis on the disappearance of the parent compound with no regard to the mechanism or pathway of atrazine degradation. Biodegradation of atrazine residues is expected to be slower in subsurface environments because microbial numbers and soil organic matter content decrease with depth. Therefore, chlorinated degradation products of atrazine in groundwater are generally ascribed to leaching from overlying topsoil where most microbial activity takes place, and not to in-situ degradation of atrazine.

The object of this study was to determine whether chlorinated degradation products of atrazine can be formed in subsurface soils and aquifer materials, and be detoxified by dechlorination or totally degraded. The rates and extent of atrazine degradation were determined under aerobic conditions in subsurface soils and aquifer materials from strata underlying two widely different Wisconsin soil types. Reaction kinetics were examined in sterilized (γ-irradiation) and nonsterilized samples to differentiate rates of microbial and chemical modification.

MATERIALS AND METHODS

The Waunakee and Arena sites are two representative atrazine-contaminated Wisconsin agricultural areas overlain respectively by a silt loam and a sandy soil. The hydrologic and geologic characteristics of both sites, and the extent of groundwater contamination by atrazine and chlorinated dealkylated products have

Present address: Department of Environmental Health, School of Public Health, Medical Sciences Campus, P.O. Box 365067, University of Puerto Rico, San Juan, Puerto Rico 00936-5067
Correspondence to: C. J. Rodríguez

been extensively studied (Levy, 1993; Lowery et al., 1994). Waunakee aquifer sediments were collected aseptically from a borehole drilled with a solid-stem auger to water-table depth using a 122 cm x 7.6 cm stainless steel tube (lined with a sterilized polycarbonate liner) with a core retainer. The inner core was used for degradation studies. Groundwater was obtained from a polyvinyl chloride piezometer voided several times with a peristaltic pump to ensure sampling of recharge rather than standing water into a sterilized 4-L amber bottle. Core Waunakee subsoil samples were obtained below the topsoil A horizon with Oakfield sampling tubes and bucket augers. In a laminar-flow hood, the exposed subsoil from core samples was removed and the inner unexposed core sampled for degradation studies. Arena aquifer sediments and subsoils were collected with a 5.6-cm diameter bucket auger. Arena aquifer sediments were obtained by first drilling to the capillary fringe with an 8.1-cm diameter bucket auger and then using a 6.8-cm diameter bucket auger to drill to the water table (about 3 m). Continuous collection of aquifer sediment was conducted with a 5.6-cm diameter bucket auger. Subsamples from Arena sediments were taken from the core center and placed in sterilized Teflon-lined screw-cap glass jars for degradation studies. Groundwater collection and processing followed the procedures for the Waunakee site. Subsoil, aquifer sediments, and groundwater samples from Waunakee and Arena were transported to the laboratory in a cooler, and stored at 4°C or 11°C. Physico-chemical and biological characteristics of the subsoils and sediments are presented in Table 1. The physico-chemical composition of the groundwater sample from Waunakee was as follows: pH 8.2; specific conductance 660 µS; alkalinity 335 mg $CaCO_3$/L; microbial plate counts (1.4 x 10^4 CFU/mL); water table 1.9 m. The composition of the Arena groundwater was: pH 6.1; specific conductance 170 µS; alkalinity 5 mg $CaCO_3$/L; microbial plate counts (2.6 x 10^4 CFU/mL); water table 2.9 m. Analytical reference standards of atrazine and its degradation products were provided by Ciba-Geigy, Greensboro, NC and are listed elsewhere with their percent purity, chemical names and structures (Rodríguez and Harkin, 1995). [2,4,6-^{14}C]Atrazine (sp. act. 20.9 µCi/mg, radiochemical purity 97.8%) was purified by TLC to 99% because of decomposition during storage.

Table 1. Properties of soils and sediments.

Site	Texture	Depth[1] (m)	pH	Organic matter (%)	Sand (%)	Silt (%)	Clay (%)	Plate Counts CFU[2] (x10^6/gdw)
Arena								
subsoil	sand	0.9 - 1.5	5.8	0.1	98	0	2	15.5 ± 1.1
sediment	sand	3.3 - 4.0	6.6	0.1	98	0	2	1.4 ± 0.1
Waunakee								
subsoil	silty clay loam	0.7 - 1.1	6.9	1.5	13	57	30	49.2 ± 4.6
sediment	sandy loam	2.0 - 2.7	8.1	0.3	71	19	10	2.7 ± 1.3

[1]Sediments were collected starting from water table

[2]CFU is a colony-forming unit in 5% PTYG (Balkwill and Ghiorse, 1985)

In a laminar flow hood, under aseptic conditions, the equivalent of 25 g oven-dry subsoils and aquifer sediments were placed in pre-weighed, sterilized 225-mL glass

bottles closed with Teflon-lined screw-caps. To prepare aquifer slurries, 25mL aliquots of groundwater were added to glass bottles containing sediments. Incubation bottles were similar to those described by Marinucci and Bartha (1979). Half of the replicate samples were sterilized commercially by γ-irradiation generated by a ^{137}Cs source of 4 Mrd (Isomedix Co., Libertyville, IL). Triplicate subsoil and aquifer slurry samples were spiked with filtered-sterilized (0.2 µm filter Supor-200, Gelman Sciences Inc., Ann Arbor, MI) aqueous [^{14}C]atrazine at a rate of 0.4 µg/g. Distilled deionized water (DDW) was added to subsoil samples to provide an approximate moisture content of 90% water holding capacity. Sample bottles were incubated aerobically in the dark at 11 ± 1 °C and sampled after 1, 30, 60, 90, 150, 210, and 270 d. DDW was added as necessary to restore initial weight.

For the extraction of atrazine residues, a mixture of 100 mL acetonitrile and 5 mM phosphate buffer (pH 7) in a ratio of 4:1 was added to each bottle. Samples were shaken mechanically for 45 min, kept 16 h in a water bath at 42 ± 2 °C, and reshaken for 45 min after the sediment settled. For subsoil samples, the supernatant was filtered through a 9-cm diameter Whatman glass microfibre filter 934-AH in a Buchner funnel into a 500-mL Erlenmeyer flask. The sample was reshaken with 50 mL acetonitrile/buffer for 30 min, and the slurry filtered on the Buchner funnel. The bottle was rinsed with 50 mL acetonitrile and the rinsate used to wash the soil on the filter. The combined extract was evaporated to 15-20 mL in a 500-mL round-bottom flask on a rotary evaporator at 40 °C. The extract was filtered with a Nalgene 25-mm, 0.45-µm nylon filter (Rochester, NY), and transferred into a Teflon-lined screw-cap 50-mL test tube. Atrazine residues were extracted from the aqueous soil extract 5 times with 4 mL ethyl acetate (EtOAc) by vortex mixing for 1 min, N_2-evaporating to dryness and dissolved in methanol. Groundwater and aquifer sediments were separated by centrifugation in Nalgene 250-mL screw-cap Teflon centrifuge bottles centrifuge (Beckman GPR centrifuge, GH 3.7 rotor). The sediment was extracted as previously described for subsoil samples with separation of the extract from the sediment by centrifugation, not by filtration. The groundwater was extracted with EtOAc. Radioactivity in subsoil and aquifer slurry samples was determined with a Rackbeta Model 1209 liquid scintillation counter (LKB-Wallac, San Francisco, CA). Thin-layer chromatography (TLC) separation and quantitation of atrazine and its degradation products was accomplished as previously described (Rodríguez and Harkin, 1995) except that the developing solvent consisted of 100:20:4:2 (v:v:v:v) chloroform:methanol:formic acid:water (method of Ciba-Geigy Corp., Greensboro, NC). $^{14}CO_2$ from subsoil and aquifer slurry samples was collected in a trapping system similar to that of Marinucci and Bartha (1979). Residual ^{14}C in subsoils and aquifer sediments after extraction with acetonitrile/buffer was determined in an R.J. Harvey Model OX-600 biological material oxidizer. Analysis of variance (ANOVA) for linear regression analysis, and Tukey's Studentized Range test ($p = 0.05$) for comparison among means were obtained using the general linear mode procedure (GLMP) from an SAS system (SAS Institute Inc., Gary, NC). Zero-order and first-order reaction models were used to examine the kinetics of atrazine degradation (Alexander, 1994).

RESULTS AND DISCUSSION

In subsoils, the disappearance rate of 0.4 µg/g [2,4,6 ^{14}C]atrazine was faster in nonsterile than in sterile samples from the Waunakee site, while atrazine degradation was faster in sterile subsoils from the Arena site (Figure 1 and Table 2). The apparent higher atrazine degradation rate in sterile versus nonsterile Arena

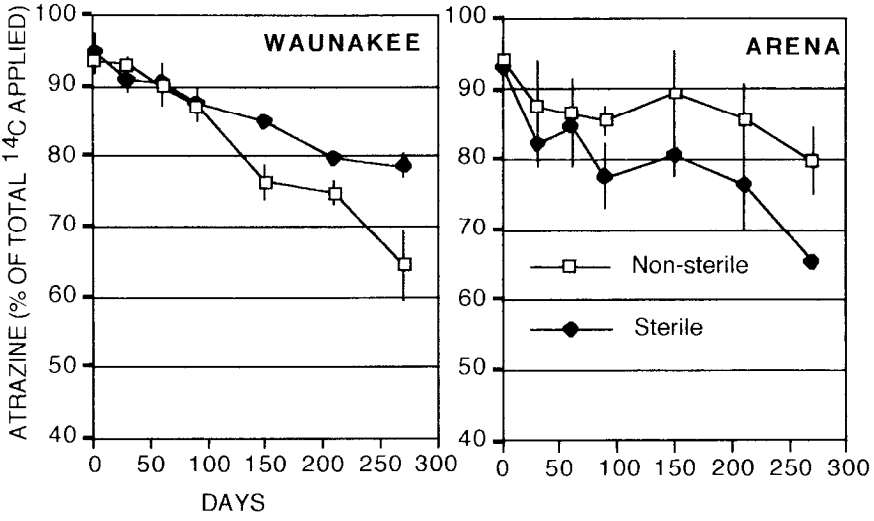

Figure 1. [^{14}C]Atrazine persistence in subsoils under sterile and nonsterile conditions based on TLC analysis. Data points represent triplicates (n=3), except for 270 d in which n=2, ± standard deviation.

Table 2. Zero-order formation rate constants (k) of ethyl acetate-extractable atrazine degradation products in subsoils after 270 d incubation at 11 ± 1 °C.

	Waunakee		Arena	
	(k ± SE[1]) x 10^{-3} (%/day)	r^2	(k ± SE[1]) x 10^{-3} (%/day)	r^2
DEAT				
nonsterile	60.9 ± 2.4	0.972**	1.86 ± 0.28	0.714**
sterile	8.02 ± 1.5	0.619**	-0.05 ± 0.29	0.002
difference	+52.9		+1.9	
DIAT				
nonsterile	9.90 ± 0.64	0.931**	2.27 ± 0.22	0.850**
sterile	4.02 ± 0.70	0.646**	0.47 ± 0.17	0.304*
difference	+5.9		+1.8	
HOAT				
nonsterile	5.84 ± 0.43	0.910**	1.96 ± 0.28	0.736**
sterile	6.37 ± 0.50	0.900**	8.35 ± 0.99	0.800**
difference	-0.5		-6.4	
DEDIAT				
nonsterile	7.71 ± 0.48	0.935**	nd[3]	
sterile	nd[3]		nd[3]	
difference	+7.71			

[1]SE is standard error

2*, ** significant at the 0.05 and 0.001 probability levels, respectively

[3]nd is not detected

Table 3. Distribution of ^{14}C residues in nonsterile subsoils from the Waunakee site[1].

	% of applied ^{14}C						
Incubation days	1	30	60	90	150	210	270
Organic-phase	96.27ab (1.08)	96.89ab (1.19)	98.80a (2.44)	97.36ab (1.01)	92.70bc (2.46)	94.50abc (0.68)	89.95c (3.05)
Atrazine	93.57a (0.34)	92.96a (1.22)	90.04a (2.94)	87.13a (2.31)	76.30b (2.58)	74.65b (1.53)	64.28c (4.86)
DEAT	0.74a (0.14)	2.76a (0.18)	6.12b (0.50)	6.87b (1.28)	11.34c (0.50)	13.56d (0.73)	17.57e (1.18)
DIAT	nd[2]	0.64a (0.02)	1.15b (0.08)	1.44b (0.02)	1.98c (0.25)	2.47d (0.13)	2.69d (0.05)
DEDIAT	nd[2]	nd[2]	0.36ab (0.14)	0.50bc (0.06)	0.98cd (0.13)	1.34d (0.30)	2.16e (0.35)
HOAT	0.43a (0.02)	0.45a (0.05)	0.67ab (0.05)	0.81ab (0.07)	1.18bc (0.14)	1.54cd (0.25)	1.97d (0.51)
Others	1.53a (0.65)	0.08b (0.14)	0.46ab (0.47)	0.62ab (0.13)	0.92ab (0.18)	0.94ab (0.40)	1.28a (0.18)
Aqueous-phase	0.56a (0.29)	0.80ab (0.20)	1.21bc (0.05)	1.56c (0.17)	2.52d (0.15)	3.25e (0.14)	4.22f (0.04)
Non-extractable	0.53a (0.11)	2.09ab (1.40)	2.26ab (0.09)	3.54bc (0.40)	4.06bc (0.04)	6.02cd (1.83)	7.06d (0.40)
$^{14}CO_2$	<0.01	0.01	0.02	0.02	0.05	0.02	0.08
Total recovery	97.36a (0.97)	99.79ab (0.76)	102.29ab (2.42)	102.49ab (0.93)	99.33ab (2.44)	103.79b (2.36)	101.31ab (2.59)

[1]Means (n=3, except for 270-d in which n=2) in each row followed by the same letter are not statistically different (p=0.05) using Tukey's Studentized Range test for comparisons among means; values in parentheses are standard deviations

[2]nd is not detected

subsoils possibly resulted from the poor ^{14}C mass balance obtained with sterile Arena samples which failed to account for 23% of the ^{14}C applied in sterile samples after 270 d (data not shown). Atrazine degradation in aquifer slurries was not significant (data not shown). After 270 d, 85% of the total ^{14}C applied in sterile and nonsterile aquifer slurries was recovered as unchanged atrazine. The minuscule (<0.1%) recovery of $^{14}CO_2$ from subsoils (Tables 3 and 4) and aquifer samples (data not shown), was similar to values from previous studies involving surface soils (Skipper and Volk, 1972; Kruger et al., 1993), subsoils and aquifer materials (Konopka and Turco, 1991; McMahon and Chapelle, 1992; Sinclair and Lee, 1992), where ring cleavage of atrazine by microorganisms is a minor degradation pathway. Atrazine $t_{1/2}$ using first-order kinetics in Arena and Waunakee nonsterile subsoils were 5.2 yr and 1.4 yr, respectively. Atrazine $t_{1/2}$ values were longer than those for surface soils incubated at 25 °C and below. For

Table 4. Distribution of ^{14}C residues in nonsterile subsoils from the Arena site.

	% of applied ^{14}C						
Incubation days	1	30	60	90	150	210	270
Organic-phase	95.72a (0.73)	88.69a (6.43)	88.02a (4.92)	86.79a (1.78)	91.56a (5.70)	88.32a (5.05)	83.15a (4.11)
Atrazine	94.21a (0.68)	87.44ab (6.35)	86.58ab (4.91)	85.48ab (2.00)	89.45ab (5.84)	85.83ab (4.98)	79.67b (4.80)
DEAT	0.59a (0.11)	0.86bc (0.005)	0.86bc (0.01)	0.72ab (0.09)	1.01cd (0.07)	1.08d (0.06)	1.16d (0.07)
DIAT	nd[2]	nd[2]	0.10a (0.02)	0.11a (0.11)	0.34b (0.08)	0.34b (0.06)	0.66c (0.17)
DEDIAT	nd[2]	nd[2]	nd[2]	nd[2]	nd[2]	nd[2]	nd[2]
HOAT	0.44ab (0.13)	0.26a (0.02)	0.45ab (0.02)	0.48abc (0.11)	0.57bc (0.01)	0.74cd (0.14)	0.90d (0.13)
Others	0.48ab (0.24)	0.13a (0.14)	0.03a (0.05)	nd	0.19a (0.19)	0.33ab (0.10)	0.76b (0.47)
Aqueous-phase	2.56a (2.59)	0.69a (0.34)	0.67a (0.08)	0.76a (0.10)	1.59a (0.25)	1.56a (0.29)	2.30a (0.20)
Non-extractable	0.16a (0.08)	0.69b (0.16)	0.70b (0.12)	0.97b (0.08)	1.42c (0.14)	1.41c (0.07)	1.71c (0.35)
$^{14}CO_2$	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	0.01
Total recovery	98.43a (2.94)	90.08a (6.36)	89.39a (4.83)	88.53a (1.80)	94.58a (5.50)	91.29a (4.83)	87.17a (4.26)

[1]Means (n=3, except for 270-d in which n=2) in each row followed by the same letter are not statistically different (p=0.05) using Tukey's Studentized Range test for comparisons among means; values in parentheses are standard deviations

[2]nd is not detected

instance, $t_{1/2}$ in surface soils at 5 °C ranged from 120-271 d (Dao, 1977; Walker and Zimdahl, 1981; Obrador et al., 1993).

More of DEAT was produced in nonsterile (17.6%) than in sterile Waunakee subsoils after 270 d (Tables 2 and 3). Levels of DIAT and DEDIAT increased gradually in nonsterile subsoils from Waunakee, but after 270 d comprised only 2.7% and 2.2% of the ^{14}C applied (Table 3). DEDIAT was not detected in sterile subsoils. DEAT and DIAT levels in Arena subsoils were lower (<1.5%) than those in Waunakee subsoils after 270 d; DEDIAT was not detected (Tables 2 and 4). Formation of N-dealkylated atrazine residues is due to microbial degradation of atrazine, while chemical hydrolysis produced hydroxyatrazine (HOAT) based on the difference in formation rate constants between nonsterile and sterile subsoil samples (Table 2). Adsorption-catalyzed chemical hydrolysis of atrazine to HOAT is considered to be the major pathway of atrazine degradation in surface soils (Armstrong et al., 1967; Winkelmann and Klaine, 1991; Assaf and Turco, 1994). However, this study showed that N-dealkylation reactions of atrazine can occur below the plow layer and predominate over hydrolysis reactions, as was observed with Waunakee subsoils. The faster dealkylation over hydrolysis of atrazine in

nonsterile subsoils from the Waunakee site may be due to low organic matter, low incubation temperature and the almost neutral pH which resulted in less adsorption-catalyzed hydrolysis. The low adsorption over time is reflected in the low levels of nonextractable residues after 270 d (Tables 3 and 4). The greater microbial degradation of atrazine in Waunakee subsoils than in Arena subsoils leading to the formation of chlorinated dealkylated atrazine products probably was due to the presence of a larger and more active microbial population. The accumulation of chlorinated dealkylated products, especially DEAT, indicates that these compounds are resistant to degradation. DEAT was found in higher concentrations than DIAT, confirming that removal of the N- ethyl side chain is favored over dealkylation of the N-isopropyl group (Skipper and Volk, 1972). DEDIAT was probably formed preferentially from N-dealkylation of DIAT (Mills and Thurman, 1994).

No significant chemical or biological degradation of atrazine was observed in aquifer slurries from the Arena and Waunakee sites after 270 d, even though samples from these sites show distinctly different physico-chemical characteristics, e.g. pH and clay content (Table 1). The recalcitrant nature of atrazine to degradation in groundwater and/or aquifer sediments is in agreement with other findings (Konopka and Turco, 1991; McMahon and Chapelle, 1992; Sinclair and Lee, 1992; Klint et al., 1993). Although microbial counts in aquifer materials were lower than in subsoils, their levels were relatively large, corroborating others' findings that aquifer environments contain substantial microbial populations (Balkwill and Ghiorse, 1985). However, the microbial population in the aquifer was inefficient at atrazine degradation despite prior exposure to atrazine residues in groundwater (Levy, 1993; Lowery et al., 1994).

The results of the study do not bode well for the expectation that areas with elevated levels of atrazine or its chlorinated dealkylated metabolites in groundwater or subsoils are likely to recover from processes of natural in situ chemical or microbial detoxification. The chlorinated degradation products of atrazine appear to be resistant to detoxification by dechlorination and/or mineralization, increasing the potential for their transport to groundwater, where no significant atrazine degradation occurs. The resistance of chlorinated dealkylated compounds to degradation in subsoils suggests that they would be as persistent as atrazine in groundwater. This study also supports the deethylatrazine-to-atrazine ratio (DAR) hypothesis for groundwater, which assumes that insignificant atrazine dealkylation to DEAT occurs under aquifer conditions (Adams and Thurman, 1991).

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