Release of Atrazine (^{14}C) from Two Undisturbed Submerged Sediments over a Two-Year Period

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Through water erosion and runoff, sediment-adsorbed atrazine can undergo sedimentation and accumulation at the bottom of water bodies and become potential sources of atrazine to the water column. The purpose of this study is to determine the fate and release of atrazine (^{14}C) to the water column from two simulated undisturbed submerged sediments at two temperature treatments (5 and 24 °C) over a 2-year period. Atrazine residue (^{14}C) was released from the two sediments and was, primarily, diffusing from the sediment pore water to the water columns. The amount released was affected by sediment type and is related to the sediment's adsorption/desorption capacity. Larger amounts of residue (^{14}C) were released to the water columns at 5 °C than at 24 °C. Atrazine degraded in the shallow submerged anaerobic sediment's water columns over the 2-year period. Less than 2% (percent of applied in atrazine equivalent) of extractable atrazine and metabolites remained in the sediment after 2 years. The amount of nonextractable atrazine residue (^{14}C) was significantly higher in sediments at 24 °C than at 5 °C. In conclusion, atrazine accumulating in shallow undisturbed submerged sediments from nonpoint sources would most likely degrade and/or become nonextractable over time and would have a low probability of becoming a significant source to the water body. The conditions where accumulation and future release of atrazine have a greater potential to occur are under very cold temperatures with low adsorption capacity sediments.

Keywords: *Atrazine; submerged sediments; temperature; release*

INTRODUCTION

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine) is a major agricultural herbicide that has been extensively used since about 1956 to control weeds primarily in corn (Zea mays L.) and grain sorghum [Sorghum bicolor (L.) Moench]. It is also classified as a moderately persistent herbicide in the environment (Weed Science Society of America, 1994). Therefore, atrazine has become the most widely detected herbicide in surface water systems of the United States (Poinke et al., 1988; Spalding et al., 1989; Maas et al., 1995; Ma and Spalding, 1997). It has been estimated that about 2−5% of applied atrazine is lost to surface water systems through runoff (Wauchope, 1978). In a review, Larson et al. (1997) estimated that about 0.3−2% of applied atrazine is lost annually to surface waters. For example, from 1983 to 1993, total loads of atrazine entering Lake Erie (monitored from five stations in the Western and Central parts) ranged from 500 to 20000 kg year^{-1} (Richards et al., 1996). Also, the timing of rainfall with respect to application affects atrazine concentrations in surface water systems. Seasonal peak concentrations of atrazine usually occur shortly after application through runoff and erosion during storm events (Thurman et al., 1992).

The presence of atrazine in surface waters is a concern because of its potential adverse impact on human and animal health and aquatic ecosystems. The major factors that influence the toxicity of atrazine are its bioavailability and persistence in the water system. In general, atrazine is resistant to microbial attack in aqueous systems (Muir, 1991) and, therefore, can persist for long periods of time (years) in stationary waters (Solomon et al., 1996). However, available data suggests that abiotic degradation of atrazine to hydroxyatrazine does occur in surface waters (Solomon et al., 1996; Ma and Spalding, 1997).

Sediment-adsorbed atrazine from eroding soils can undergo sedimentation and accumulation at the bottom of water bodies on a regular seasonal basis. These buried sediments could then become long-term, low-level sources of the herbicide to the water column. Also, the physicochemical properties, as well as the biological populations of submerged sediments, are very different from that of arable soils. Such environments are usually characterized by large volumes of water over the sediment, are less aerated, and experience less dramatic temperature fluctuations. Sediments also tend to have a greater clay content, greater humic material content, and have strong anaerobic conditions prevailing in the bulk of the material (Gambrell et al., 1984).

In anaerobic sediments, biotransformations of atrazine are generally expected to be slower than under aerobic conditions (Goswami and Green, 1971). They suggested that the degradation pathway for atrazine in submerged sediments is most likely through dealkylation by facultative aerobic microorganisms. At lower depths in the soil profile, atrazine has been shown to have a lower half-life in saturated soil conditions than

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Table 1. Selected Chemical and Physical Properties of Two Sediments Generated from the Cullen and Emporia Soils and Initial Atrazine Concentrations at the Start of the Study

							atrazine concentrations	
sediment	silt (%)	clay (%)	pH[a]	OC[b] (%)	CEC ($cmol_c\ kg^{-1}$)	K_d ($L\ kg^{-1}$)	sediment ($\mu g\ g^{-1}$)	water column ($\mu g\ mL^{-1}$)
Emporia	88	12	5.1	1.6	2.4	1.21	1.99 ± 0.005	0.047 ± 0.001
Cullen	62	38	6.4	2.2	6.8	1.95	2.50 ± 0.009	0.032 ± 0.001

[a] pH in 1:1 soil to water (0.1 M $CaCl_2$) ratio. [b] OC = organic carbon.

in unsaturated conditions (Kruger et al., 1993). Adsorption to soil plays a major role in the bioavailability of atrazine. In soil systems, chemicals that are sorbed are generally less available for uptake and biodegradation (Weber et al., 1993). Also, the longer the residence time in the soil, the less bioavailable it becomes (Alexander, 1995). In wetland soils with high organic matter contents (12−15%), atrazine was shown to be more strongly adsorbed than what has been reported for arable agricultural soils (Mersie and Seybold, 1996). Specific information on atrazine's persistence and potential accumulation in submerged sediments with subsequent release to the water column is needed to predict atrazine's potential impact on aquatic ecosystems.

The objective of this study is to determine the fate and release of ^{14}C-labeled atrazine residue from two simulated submerged sediments left undisturbed over a period of 2 years under water columns. Both the sediments and water columns are incubated at two temperatures, 5 and 24 °C. The finer fraction of two important agricultural soils in Virginia are used to simulate sediments from eroding soils.

MATERIALS AND METHODS

Sediment. The Cullen (Clayey, mixed, thermic Typic Hapludults) and Emporia (Fine-loamy, siliceous, thermic Typic Hapludults) soil series are important agricultural soils in Virginia that have had no previous history of atrazine application and were used to generate sediment for this study. Soil samples were collected from the A horizon, 0−25 cm for the Cullen soil and 0−20 cm for the Emporia soil. Samples were then air dried and passed through a 2-mm sieve. Only the less than 53-μm soil fraction (silt and clay) was used because this fraction adsorbs and transports most of the herbicide residues (Ghadiri and Rose, 1991). Sediments were generated by wet sieving (53-μm sieve) the soils in 0.01 M $CaCl_2$ solution. The $CaCl_2$ solution was used to flocculate the sediment and allow settling; excess solution was siphoned off. The sediment generated from this process will be referred to as Emporia sediment and Cullen sediment. Sediment characteristics determined were pH in 0.01 M $CaCl_2$ (McLean, 1982), organic carbon (OC) content by the Walkley−Black procedure (Nelson and Sommers, 1982), particle size by the pipet method (Sheldrick and Wang, 1993), cation-exchange capacity (CEC), and acidity. Acidity and CEC were determined by A&L Laboratories (Richmond, VA). Sediment characteristics are described in Table 1.

Sediment/Water Column Setup. Sediment-adsorbed atrazine was prepared by mixing a sediment suspension (1475 g dry weight bases) with 0.01 M $CaCl_2$ aqueous solution in 2-L flasks to produce a 1:1 sediment to solution ratio. Technical-grade and ^{14}C-labeled atrazine in 0.01 M $CaCl_2$ solution (specific activity of 135 Mbq $mmol^{-1}$ and radiochemical purity of 98%) were added to the sediments to provide a final concentration of 2.8 μg of atrazine per g of sediment on a dry weight basis. The ^{14}C-labeled atrazine concentration was 0.27 kBq g^{-1}. The flasks were shaken on an orbital shaker at 200 oscillations min^{-1} for 24 h at 23 ∓ 2 °C. Subsamples of 25 g (dry weight basis) of sediment treated with atrazine were transferred to the bottom of 250-mL graduated cylinders without touching the side walls; sediments were allowed to settle in the cylinders for 4 h. The supernatant (about 4 mL) from each cylinder was siphoned and replaced with river water (James River) up to the 250 mL level with minimum disturbance to the sediment (1:10 sediment:water ratio). The radioactivity was measured in 1 mL of the siphoned solution by liquid scintillation spectrometry (LSS) with quenching correction by the external standardization method. The amount of atrazine adsorbed to the sediment was determined as the difference between the initial concentration and the solution concentration. From this, atrazine adsorption coefficients (K_d) were determined: K_d = atrazine adsorbed to sediment ($\mu g\ kg^{-1}$) ÷ atrazine in solution at equilibrium ($\mu g\ L^{-1}$). The sediment in the cylinders was allowed to settle for 24 h, and then it was placed in temperature-controlled chambers set at 5 or 24 °C. After the 24-h period, 1-mL water column samples were analyzed for ^{14}C activity to establish time-zero atrazine concentrations. Glass stopper lids were placed on the columns allowing for about 25−30 mL of headspace. A factorial treatment design was used consisting of two sediment types, two water temperatures (5 and 24 °C), and three replications for a total of 12 cylinders.

Atrazine and Metabolite Extraction and Analysis. At each sampling time (14, 28, 112, 168, 252, 336, 504, and 672 days), 1-mL water column samples were taken for ^{14}C analysis using LSS. During sampling there was minimal disturbance to the water columns; cylinder lids were removed while sampling. At the 672-day sampling time, water columns were siphoned and the sediments and solution stored at −18 °C until analyzed for atrazine and its metabolites. Metabolites analyzed were deethylatrazine (2-amino-4-chloro-6-isopropylamino-s-triazine; DEA), deisopropylatrazine (2-amino-4-chloro-6-ethylamino-s-triazine; DIA), hydroxyatrazine (2-hydroxy-4-ethylamino-6-isopropylamino-s-triazine; HA), and deethylhydroxyatrazine (2-amino-4-hydroxy-6-isopropylamino-s-triazine; DEHA). The redox potential (E_h) of the sediments and solution were measured at 112 and 252 days of sampling using redox combination (pH) electrodes. Redox potentials of the sediments ranged from 265 to −267 mV, indicating that anaerobic conditions prevailed. In general, the sediments at 24 °C had lower redox potentials and were generally lower in the Cullen sediments. Redox potentials of the solution ranged from 50 to 290 mV, indicating milder reducing conditions.

Atrazine and its metabolites were sequentially extracted from 15 to 20 g sediment samples 2 (dry weight basis): once with 80 mL of 0.01 M $CaCl_2$ aqueous solution, 3 times with 25 mL of a methanol/water mixture (4:1, v/v), and 3 times with 25 mL of methanol/water/formic acid (20:5:1, vlv/v) for a total of seven extractions. The pH of the methanol/water/formic acid extracting solution was 3.2. At each sequence in the extraction, the mixture was shaken for 45 min at 23 ± 2 °C and then centrifuged at 2012 g for 20 min. One milliliter of the supernatant was sampled and analyzed for ^{14}C using LSS. Nonextractable ^{14}C was determined on each sediment sample by combusting 300−500 mg of sediment (dry weight basis) mixed with an equivalent amount of cellulose in a biological oxidizer and by trapping the released $^{14}CO_2$. The trapped $^{14}CO_2$ was then counted using LSS.

A reverse-phase high-pressure liquid chromatography (HPLC) system was used for the analysis of atrazine and its metabolites. Terbuthylazine (2-*tert*-butylamino-4-chloro-6-ethylamino-1,3,5-triazine; TBA) (99%) was used as an internal standard for atrazine, DEA, and DIA, whereas hydroxypropazine (2-hydroxy-4,6-di[isopropylamino]-1,3,5-triazine; HP) (98%) was used as the internal standard for DEHA and HA. The HPLC

system consisted of an LC-8, 4.6 i.d. × 150 mm deactivated C8 (3 μm spherical silica) column, which was deactivated for analysis of organic bases, dual Waters 510 pumps with a control module, a 717+ Autosampler, and a 996 Photodiode Array Detector. The software from Waters, Millennium 2010 Chromatography Manager, was used for system control, data acquisition, and data analysis. The organic portion (solvent A) of the mobile phase was methanol. The aqueous portion (solvent B) of the mobile phase was 20:1 (v/v) buffer/methanol, and the buffer was a 10 mM ammonium acetate (pH = 5.68) aqueous solution. The atrazine metabolites were base-line separated with a gradient elution. The first gradient was with solvent B for 1 min, then it was linearly increased to 100% solvent A in 20 min, then decreased to 100% with solvent B in 5 min and held at this point for another 5 min. The retention times of the analytes were 10.22 min for DEHA, 13.32 min for DIA, 15.32 min for DEA, 16.25 min for HA, 17.92 min for HP, 18.92 min for atrazine, and 20.28 min for TBA. Method detection limits (MDL) for atrazine, HA, DEA, DIA, and DEHA were 0.12, 3.1, 0.05, 4.9, and 3.6 μg mL^{-1}, respectively.

Chemicals. Reference standards used in this study were atrazine (98%), DEA (94%), DIA (98%), DEHA (97%), and HA (97%). Atrazine and HP were purchased from Riedel-deHaën (Seelze, Germany), and the other standards were obtained from Novartus Corp. (Greensboro, NC). All reagents used were either HPLC or analytical grade. Stock solutions of atrazine, DEA, DIA, and terbuthylazine were prepared in methanol at 500 μg mL^{-1} and stored at −118 °C. Stock solutions of HA, HP, and DEHA were made in a mixture of methanol:water: formic acid (25:74:1, v/v/v) and stored at −18 °C. Herbicide standards were freshly prepared by serial dilution of the stock solution in methanol:water (25:75, v/v) mixtures.

RESULTS AND DISCUSSION

The Cullen sediment has a higher organic C content and contains more clay than the Emporia sediment (Table 1). Organic matter and, to a lesser extent, clay content controls the adsorption of atrazine in soils (Hamaker and Thompson, 1972; Laird et al., 1992; Seybold et al., 1994). As expected, the atrazine adsorption coefficient (K_d) obtained for the Cullen sediment was higher than what was obtained for the Emporia sediment (Table 1). Therefore, initial sediment concentrations of atrazine, at the start of the study, were larger for the Cullen sediment; concentrations were about 2.5 μg g^{-1} for Cullen and 2.0 μg g^{-1} for Emporia sediments. These concentrations represent the amount of atrazine sorbed to the sediment plus the amount in solution in the interstitial particle spaces (pore water). Sediment concentrations of atrazine resulting from nonpoint sources have been found to range from 5.7 to 44 ng g^{-1} in sediments of Essex coast, U.K. (Fletcher et al., 1994), and up to about 500 ng g^{-1} in sediments of northeastern Britany, France (Gueune and Winnett, 1994). In the present study, atrazine concentrations in the sediments are much greater than what would normally occur in the natural environment from nonpoint sources but could be similar to concentrations that could occur from a point source, such as a chemical spill. We wanted to simulate a worst-case scenario.

Initial water column concentrations of atrazine above the Cullen sediment were about 0.033 μg mL^{-1}, and concentrations above the Emporia sediment were about 0.047 μg mL^{-1} (Table 1). In the natural environment, concentrations of atrazine in receiving waters have been found to range up to about 20 μg L^{-1} (Solomon et al., 1996). Other chemical characteristics of the water column water are presented in Table 2.

Release of Atrazine Residue (^{14}C) from Undisturbed Sediment. Water column concentrations of ^{14}C were monitored over a 2-year period (Figure 1). ^{14}C was released from the two sediments with larger amounts being released from the Emporia sediment. The chemical form of the ^{14}C released was not determined. However, initially, atrazine probably was the major compound released and over time atrazine metabolites (Mersie et al., 1998b). In general, for the water columns at 24 °C, ^{14}C concentrations reached a maximum within 28 days and then declined sharply, while for the water columns at 5 °C, ^{14}C concentrations reached a maximum within about 120 days, which did not decline significantly from that level for the duration of the study (Figure 1). The pore water of the sediments at the start contained a larger concentrations of atrazine than did the water columns above them, creating a diffusion gradient from the sediment pore water to the water column. The initial increases in ^{14}C concentrations of the water columns are primarily coming from the sediment pore water. Also, desorption of weakly sorbed atrazine could also be contributing to initial increases in water column ^{14}C concentrations.

Table 2. Chemical Characteristics of the Water Columns

chemical	concentration (mg L^{-1})	chemical	concentration (mg L^{-1})
Ca	250	Cu	0.057
Mg	4.27	K	8.85
Fe	0.053	NH_4-N	0.036
Mn	ND[a]	NO_3-N	0.21
S	0.75	PO_3	0.076
Zn	ND	Cl	8450

[a] ND = not detected.

The significant decline in water column ^{14}C concentrations at the 24 °C temperature was much greater in the Emporia water columns than in the Cullen water columns (Figure 1). The decrease in ^{14}C concentrations in the Emporia water columns at the 24 °C temperature was about 40% of the amount applied, which is greater than the 11% that was lost from the columns at the end of the 2 years from all sources (water and sediment) (Table 3). This indicates that about 29% of the ^{14}C was readsorbed to the surface of the sediment. The decrease in water column ^{14}C concentrations could be due to readsorption of atrazine to the sediment surface (Mersie et al., 1998b) and/or atrazine degradation into metabolites that are readsorbed to the sediment surface. Hydroxyatrazine is strongly adsorbed to soils and sediments (Seybold and Mersie, 1996; Mersie and Seybold, 1996) and has been indicated as the primary degradation product of atrazine in water (Solomon et al., 1996; Ma and Spalding, 1997). Atrazine degradation to hydroxyatrazine is considered to be primarily a chemical process, which depends on pH. Chemical hydrolysis to HA is generally faster at lower pHs (Armstrong et al., 1967) and faster in the presence of soil than without (Jordan et al., 1970). Degradation to HA and its adsorption to the surface of the sediment is probably occurring. Also, atrazine mineralization and loss through $^{14}CO_2$ evolution from the water columns could be occurring. If mineralization occurred, $^{14}CO_2$ would become dissolved in water as $CO_{2(aq)}$ and rapidly establish equilibrium with water to form the weak acid H_2CO_3. The rate of gas diffusion in water is about 1/10000 the rate in air (Bohn et al., 1979), so very little $^{14}CO_2$ will escape to the headspace above the water columns, except in water near the surface. Therefore, loss of $^{14}CO_2$ from the water columns would be minimal. However, $^{14}CH_4$ and $^{14}CO_2$ could have been lost from the columns

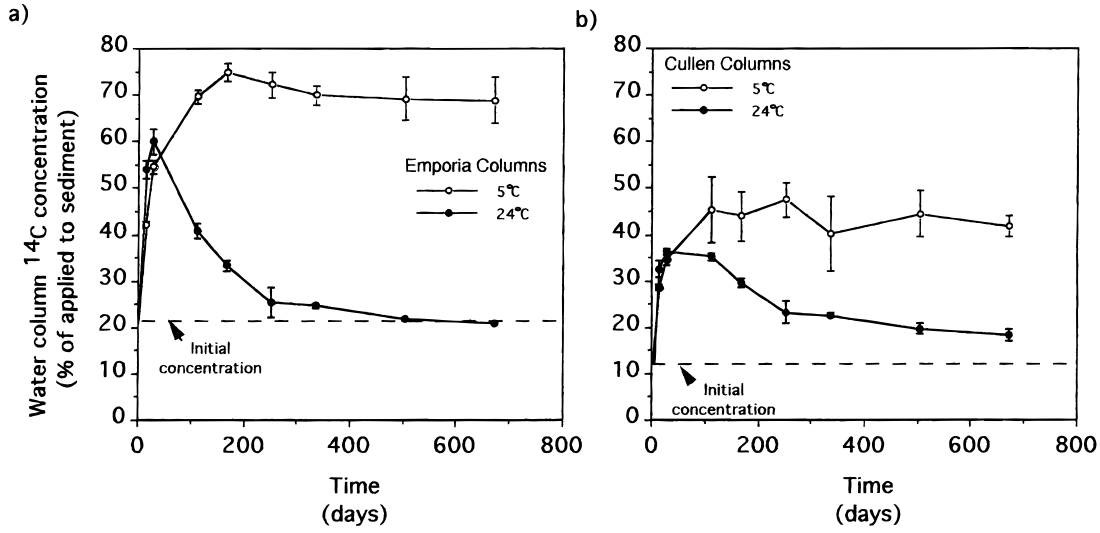

Figure 1. Release of ^{14}C (expressed as percent of ^{14}C applied to sediment in atrazine equivalent) released from spiked sediments incubated at 24 and 5 °C for 2 years: (a) Emporia sediment and (b) Cullen sediment.

Table 3. Atrazine and ^{14}C Residue Concentrations Remaining in the Water Column and Sediment after Two Years

			% applied to sediment (atrazine equivalent)					
			extraction from sediment					
sediment	temp (°C)	chemical	water	MeOH/water	MeOH/water/FA	unextractable	water column	total
Cullen	5	^{14}C	5.97(0.96)[a]	12.30(2.86)	5.46(0.70)	13.06(2.42)	41.86(2.24)	78.60
		atrazine	0.009(0.005)	0.005(0.005)	0.004(0.002)		1.505(0.395)	
Cullen	24	^{14}C	1.91(0.14)	7.02(0.33)	6.28(0.22)	25.71(7.92)	18.32(1.35)	59.24
		atrazine	0.013(0.013)	0.005(0.005)	0.003(0.001)		0.591(0.078)	
Emporia	5	^{14}C	4.66(0.16)	11.36(0.14)	3.65(0.60)	14.43(3.34)	68.80(4.97)	102.9
		atrazine	0.109(0.099)	0.104(0.089)	0.081(0.024)		6.444(1.027)	
Emporia	24	^{14}C	1.49(0.18)	6.96(0.71)	6.48(0.66)	43.06(13.56)	21.03(0.75)	79.02
		atrazine	0.048(0.022)	0.029(0.006)	0.121(0.039)		0.62(0.104)	

[a] Numbers in parentheses are standard errors.

through air bubbles that formed and were observed escaping from the sediment, especially from the 24 °C columns. Loss of atrazine through volatilization from the water's surface is considered negligible because of its low vapor pressure (Solomon et al., 1996).

Maximum levels of ^{14}C released from the sediments (after subtracting out the initial ^{14}C concentration) to the water columns at 24 °C were about 38% and 24% of the amount applied to the Emporia and Cullen sediments, respectively. In water columns at 5 °C, maximum levels of ^{14}C released (after subtracting out the initial ^{14}C concentrations) were about 52% and 33% of the amount applied to Emporia and Cullen sediments, respectively (Figure 1). This shows that the temperature affected the amount and rate of ^{14}C released from the sediments. Larger amounts of ^{14}C were released from the sediments incubated at 5 °C than at 24 °C. This indicates that atrazine could be degrading at a faster rate at 24 °C, lowering its concentration in the sediment pore water leaving less to diffuse into the water column (Mersie et al., 1998b). Greater amounts of ^{14}C released during the first two sampling times in columns at 24 °C in combination with the longer time period it took to reach maximum ^{14}C concentrations in columns at 5 °C indicates a faster rate of diffusion at the warmer temperature treatment.

The Emporia sediment released larger amounts than did the Cullen sediment (Figure 1). Differences between the sediments in the amount released could be due, in part, to differences in their adsorption/desorption capacities and initial pore water concentrations. The Emporia sediment has a smaller capacity to adsorb atrazine (and its metabolites) and, thus, had a larger initial pore water concentration of atrazine available to diffuse into the water columns. All columns started out with the same amount of atrazine that was distributed between the sediment and solution. Also, the desorption capacity of the sediments differ. Seybold and Mersie (1996) showed that atrazine is more readily desorbed from the Emporia soil ($K_f = 1.51$) than from the Cullen soil ($K_f = 1.85$), indicating that the Emporia sediment more readily desorbs atrazine than the Cullen sediment, which may have contributed to the release of atrazine residue.

Atrazine Residue in Water Columns. At the end of 2 years, the water columns were analyzed for actual concentrations of atrazine and major metabolites remaining (Table 3). As expected, there were greater amounts of atrazine in water columns placed at 5 °C than at 24 °C regardless of sediment type. The largest concentration was 6.4% (of the amount applied to sediment), which occurred in the Emporia water columns. The persistence of atrazine in stationary waters is influenced by the chemical composition of the water body. In a review by Solomon et al. (1996), half-lives of atrazine in aqueous systems varied from 0.2 to 742 days depending on the temperature, light source, sediment type, water constituents, and concentration. In pristine ground waters, atrazine was shown not to degrade after 539 days (Klint et al., 1993) and after 11 months in anaerobic aquifer slurries (Adrian and Suflita, 1994). In the presence of increasing dissolved organic matter and salt concentrations, atrazine half-lives were shown to decrease in aqueous systems (Khan, 1978; Li and

Feldback, 1972). The salt concentration in the water columns of the present study is low (about 80 TDS; Table 2). Most of that is due to the addition of $CaCl_2$ used to flocculate and settle the sediment. The low concentration of atrazine remaining after 2 years indicates that it can degrade in shallow stationary waters containing some nutrients or catalysts.

Total water column concentrations of major atrazine metabolites were less than 2% of the amount applied to sediment (in atrazine equivalent) in all water columns (data not shown). Of the atrazine metabolites, HA concentrations were the highest in water columns incubated at 24 °C (1.6% for Cullen and 1.3% for Emporia sediments). Less than 1% (of the atrazine equivalent amount applied to sediment) of DEA was detected in the water columns; the largest concentrations were found in the Cullen columns at 5 °C. Less than 0.5% (of the atrazine equivalent amount applied to sediment) of DIA was detected in the water columns; the highest concentrations were in the Cullen columns at 5 °C. The very low concentrations of atrazine and metabolites indicate that degradation is occurring and possibly complete mineralization in columns at 24 °C.

There were several peaks in the chromatograms of water samples that did not correspond to atrazine or the major metabolites. Most of the peaks were too broad to correctly integrate and quantify. They could be metabolites further in the atrazine degradation pathway, such as cyanuric acid and ammeline (Erickson and Lee, 1989). Other metabolites were not identified because we did not have the standards.

Atrazine Residue in Sediment. At the end of 2 years, three solvents were used to sequentially remove different sorbed strengths of sediment-bound residues (Table 3). Water was used first to remove the most labile portion, followed by MeOH/water, which removed the next available fraction, and the most resistant portion was extracted by MeOH/water/formic acid. The total amount of atrazine and metabolites that were extracted (all solvents) from the sediments, after 2 years, were less than 1% of the total equivalent amount of atrazine applied to the sediment (Table 3). Slightly greater amounts were extracted from the Emporia sediment than from the Cullen sediment, regardless of temperature. The extractable ^{14}C residue amounts (as percent of applied) are much larger than what was identifiable as atrazine or its major metabolites (Table 3). This discrepancy could be due to loss of atrazine and analogs during extraction and/or transformation to other unidentified metabolites. Also, greater amounts of ^{14}C were extracted from the sediments at 5 °C than at 24 °C, which indicates greater degradation/mineralization and removal of atrazine and its degradation products over time at the warmer temperature. Major metabolites detected were DEA, DIA, HA, and DEHA. As with atrazine, extractable metabolites were slightly greater from the Emporia than from the Cullen sediment. The greater extractable amounts from the Emporia sediment relate to the sediment's greater desorption potential. Of the metabolites, HA had the highest extractable amounts (0.45% from the 5 °C and 0.65% from the 24 °C treatments from the Emporia sediment). Mersie et al. (1998a) reported that acidification of the extraction step with formic acid improved the extractability of HA from Emporia sediment. They indicated that HA was the major metabolite formed in an anaerobic sediment during a 336-day period. Of the three extraction solvents, the amounts extracted with water are the most important under natural conditions. It is this fraction of the residue which will be expected to impact organisms in the sediment pore water and overlaying water column. The amount of atrazine in this fraction was less than 0.15% of the amount applied. The very low extractable concentrations of atrazine and metabolites from simulated sediments after two years indicates that atrazine has a low potential to accumulate and will most likely degrade in shallow anaerobic submerged sediments or become nonbioavailable over time. Jones et al. (1982) found similar results in estuarine sediments. They showed rapid atrazine degradation rates, half-life of 15−20 days, for two estuarine sediments and concluded that there is a low probability that atrazine will accumulate in these sediments.

In soil systems, both nonbiological and microbial degradation of atrazine are important (Erickson and Lee, 1989; Blumhorst and Weber, 1994; Mandelbaum et al., 1993; Dao et al., 1979; Kruger et al., 1997). Also, atrazine degradation is suggested to be faster in aerobic than in anaerobic conditions (Erickson and Lee, 1989; Goswami and Green, 1971). In sediments, atrazine was shown to degrade primarily through microbial processes under nitrate-reducing, sulfate-reducing, and methogenic conditions (Wilber and Parker, 1995). The primary substrate under the reducing condition was needed for significant degradation to occur, indicating cometabolic transformations were needed. McCormich and Hiltbold (1966) also reported accelerated degradation of atrazine in soils when a microbial energy source was added. In the present study, it is most likely that both chemical and biological degradation processes are occurring.

The amount of nonextractable ^{14}C in the sediment ranged from 13% to 43% of the amount applied (Table 3) and was higher in columns at 24 °C than at 5 °C. This indicates that at warmer temperatures more ^{14}C residue was able to become bound or nonextractable with time, leaving less available to diffuse into the water column (Mersie et al., 1998a). These results are consistent with Li et al. (1996) in which irreversible uptake was characterized by an effective diffusion coefficient (D) that increased by a factor of 40 from 5 to 35 °C. The compounds are becoming sequestered in inaccessible microsites within the sediment matrix (Alexander, 1995). Bound residue formation could be due to binding to soil organic constituents, incorporation into phenolic polymers, and blockage of voids and, thus, trapping of residues (Khan, 1982; Bollag et al., 1992). Also, degradation can enhance the formation of bound residues by converting atrazine to HA, which has a greater adsorption to soil than the parent compound (Seybold and Mersie, 1996). Others have also reported an increase in the proportion of nonextractable ^{14}C with time (Pignatello and Huang, 1991; Barriuso and Koskinen, 1996; Radosevich et al., 1997).

SUMMARY AND CONCLUSIONS

The release of atrazine, in this study, from simulated undisturbed anaerobic sediments (that could be generated from runoff and erosion) to the water column is primarily a result of initially high concentrations of atrazine in the sediment pore water, which is diffusing into the water columns. However, desorption of weakly sorbed atrazine from the sediment particles could also be occurring. The amount of extractable atrazine in the sediments after 2 years was less than 1% of the amount

applied and less than 7% in the water columns. Accumulation of atrazine in natural sediments from nonpoint sources would probably not result in high pore water concentrations and, thus, would not be a major source to the water column. Atrazine can degrade in simulated shallow anaerobic submerged sediments, and the rate of degradation is affected by sediment type and temperature. The degradation rate is faster at warmer (24 °C) than at colder (5 °C) temperatures. Over time, the amount of nonextractable or bound residue formation is higher at 24 °C than at 5 °C, decreasing the potential for release to the water column at higher temperatures. The potential for release of sediment-adsorbed atrazine to the water column decreases as the sediment temperature increases and with time. The greater the atrazine adsorption capacity of the sediment, the lower the potential for release to the water column. There is a high probability that atrazine from nonpoint sources deposited in shallow undisturbed submerged sediments will degrade or become nonbioavailable (nonextractable) over time and is unlikely to pose a threat by becoming a source for future release to the water column. However, how much atrazine is being deposited and the length of time deposition is occurring will affect future release. The conditions where accumulation and future release of atrazine are most likely to occur are under very cold temperatures with low adsorption capacity sediments.

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