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Contribution of Hydroxylated Atrazine Degradation Products to the Total Atrazine Load in Midwestern Streams

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The contribution of hydroxylated atrazine degradation products (HADPs) to the total atrazine load (i.e., atrazine plus stable metabolites) in streams needs to be determined in order to fully assess the impact of atrazine contamination on stream ecosystems and human health. The objectives of this study were (1) to determine the contribution of HADPs to the total atrazine load in streams of nine midwestern states and (2) to discuss the mechanisms controlling the concentrations of HADPs in streams. Stream samples were collected from 95 streams in northern Missouri at preplant and postplant of 1994 and 1995, and an additional 46 streams were sampled in eight midwestern states at postplant of 1995. Samples were analyzed for atrazine, deethylatrazine (DEA), deisopropylatrazine (DIA), and three HADPs. Overall, HADP prevalence (i.e., frequency of detection) ranged from 87 to 100% for hydroxyatrazine (HA), 0 to 58% for deethylhydroxyatrazine (DEHA), and 0% for deisopropylhydroxyatrazine (DIHA) with method detection limits of 0.04−0.10 μg L^{-1}. Atrazine metabolites accounted for nearly 60% of the atrazine load in northern Missouri streams at preplant, with HA the predominant metabolite present. Data presented in this study and a continuous monitoring study are used to support the hypothesis that a combination of desorption from stream sediments and dissolved-phase transport control HADP concentrations in streams.

Introduction

Atrazine usage on cropland of the midwestern United States has resulted in contamination of surface and groundwaters throughout the region by the parent compound and its stable degradation products (*1*−*6*). With respect to atrazine degradation products, most of these studies focused on contamination of surface and groundwaters by the chlorinated degradation products because of their greater water solubility and lower soil adsorption compared to the parent. However, hydroxylated atrazine degradation products (HADPs), particularly hydroxyatrazine (HA), are the major degradation products of atrazine in most soils (*7*−*11*).

HADPs form in the environment via chemical, biological, and photochemical hydrolysis of atrazine or dealkylated atrazine metabolites, resulting in replacement of Cl with a hydroxyl group at the 2-position of the triazine ring (*7*−*17*). In soil or water, the rate of hydrolysis is enhanced by extremes in pH, dissolved organic matter, sorption to soil colloids, and the presence of photosensitizing compounds, such as nitrate and humic acids (*7, 12, 13, 16, 18*).

HADPs have been shown to be more persistent in soils than atrazine and chlorinated atrazine metabolites (*8, 11, 19*). On the basis of laboratory incubation studies, half-life estimates in surface soils were 32−165 days for HA, 14−50 days for atrazine, and 17−33 days for chlorodealkylated atrazine metabolites (*11, 19, 20*). Baluch et al. (*19*) reported HA half-life estimates of greater than 100 days for three of the five soils studied. Winkelmann and Klaine (*11*) concluded that HA would persist longer in soils than atrazine or chlorinated atrazine metabolites, and it would build up in surface soils if atrazine was applied annually. Capriel et al. (*8*) reported that the HADPs accounted for the majority of the ^{14}C remaining in the bulk soil and humic fraction nine years after application of ^{14}C-atrazine. Supercritical fluid extraction of this soil resulted in recovery of greater amounts of hydroxyatrazine than atrazine (*21*). Using an extracting agent designed to recover compounds sorbed to soils by both cation exchange and hydrophobic interactions, Lerch et al. (*22*) reported that ^{14}C-HADPs accounted for 88% of extractable bound residues from a soil spiked with ^{14}C-atrazine and incubated for 120 days. Thus, the persistence of HADPs in surface soils indicates that the potential exists for HADPs to contaminate surface or groundwaters, particularly in the midwestern United States where atrazine use has been greatest over the last 30 years.

Recent work by Cai et al. (*23*) reported 10−30 ng L^{-1} HA in groundwater of eastern Nebraska. Atrazine concentrations in these same well samples were approximately 100-fold higher, indicating the much greater leaching potential of the parent compared to HA. Lerch et al. (*5*) reported that HADPs were not detected in shallow groundwater samples from the Claypan Soil region of northeastern Missouri using methods with a detection limit of 0.04−0.1 μg L^{-1} (*24*). Studies under field and laboratory conditions have reported greater leaching potential of atrazine and its chlorinated degradation products compared to HA (*25*−*27*). Schiavon (*25*) showed that only 0.4% of the applied [^{14}C]HA leached beyond the top 24 cm of soil compared to 13% for [^{14}C]atrazine, 16.6% for [^{14}C]-deethylatrazine (DEA), and 11.1% for [^{14}C]deisopropylatrazine (DIA) after 1 year under field conditions. Using soil thin-layer chromatography, Kruger et al. (*27*) reported that HA was nearly immobile in surface and subsurface soils.

The low leaching potential of the HADPs compared to atrazine and its chlorinated degradation products reflects their greater sorption to surface soils. Several studies have reported that adsorption of *s*-triazines to clays and soil organic matter is related to the dissociation constant (pK_a) of the compound (*12, 28*−*30*). For example, *s*-triazines having a pK_a in the range 4−5, which includes the HADPs, exhibit stronger sorption to soil colloids than s-triazines with a pK_a near 2. The greater sorption of the higher pK_a triazines occurs because of mixed-mode binding to soils (*22*) while triazines with a pK_a near 2 are limited to hydrophobic interactions as their primary binding mechanism to soils (*12, 29*). Since the pH at colloid surfaces is approximately 0.5−2 pH units lower

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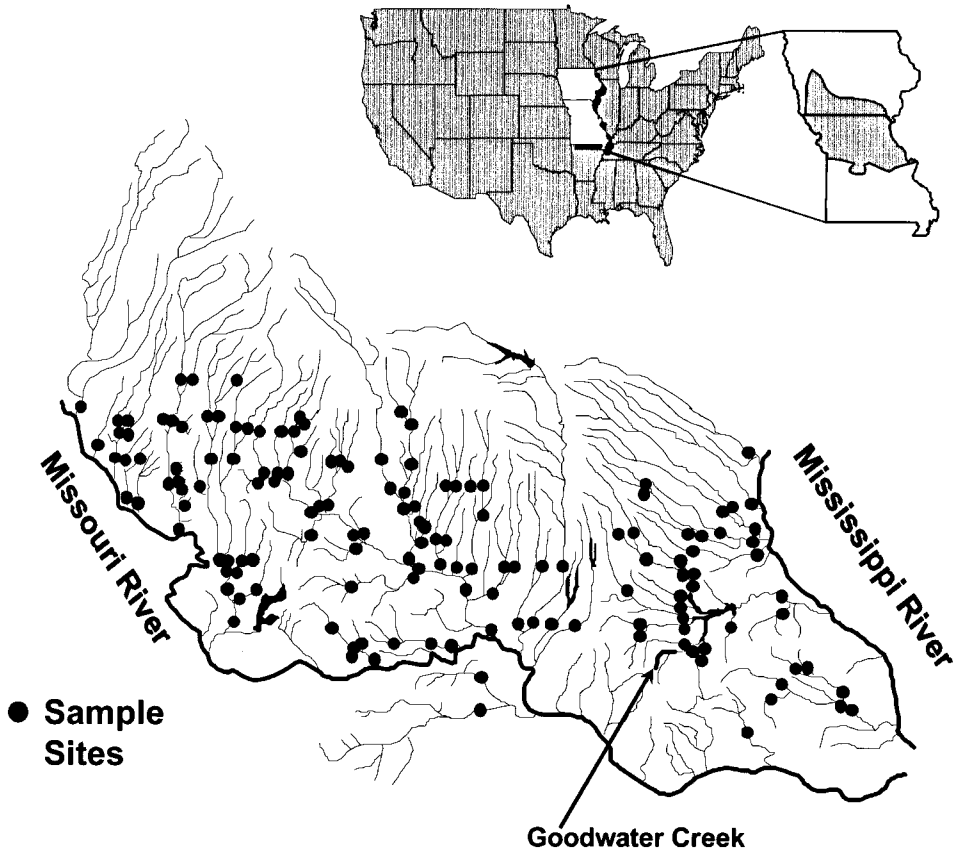

FIGURE 1. Sample locations for northern Missouri streams.

than the bulk soil solution (*12*), cation exchange is a significant binding mechanism for HADPs in many agricultural soils. On the basis of the low mobility and relatively high sorption of HADPs to soil, their potential to significantly contaminate groundwater is apparently very low.

In contrast, HADPs have been shown to contaminate surface waters at concentrations of 2−3 orders of magnitude greater than reported for groundwater (*5, 31, 32*). Adams and Randtke (*31*) detected HA at 1−2 μg L^{-1} in samples from two eastern Kansas reservoirs. Cai et al. (*32*) reported HA concentrations of 0.25−2.7 μg L^{-1} in runoff water from the Beaver Creek watershed in southcentral Nebraska. Lerch et al. (*5*) reported concentrations of 0.18−5.7 μg L^{-1} for HA, <0.12−1.9 μg L^{-1} for deethylhydroxyatrazine (DEHA), and <0.12−0.72 μg L^{-1} for deisopropylhydroxyatrazine (DIHA) in Goodwater Creek, a predominantly agricultural watershed in northeast Missouri (Figure 1). During the 2.5 year monitoring period of the study, frequency of HADP detections were 100% for HA, 25% for DEHA, and 6% for DIHA. In addition, HA levels in Goodwater Creek were generally equal to or greater than atrazine or DEA concentrations from late summer through early spring. The chemical characteristics of HADPs combined with the long-term use of atrazine have likely resulted in persistence of HADPs in surface soils throughout the Midwestern United States (*11, 22*). Thus, widespread contamination of HADPs in midwestern streams is probable. The primary objective of this study was to determine the contribution of HADPs to the total atrazine load in streams of nine midwestern states. As part of this objective, the prevalence (i.e., frequency of detections) and concentrations of HADPs in midwestern streams are compared to atrazine and its chlorinated metabolites. A secondary objective was to discuss the mechanisms controlling the concentrations of HADPs in streams.

Experimental Section

Chemicals and Standard Materials. Hydroxyatrazine (HA) (2-hydroxy-4-ethylamino-6-isopropylamino-*s*-triazine), deethylhydroxyatrazine (DEHA) (2-hydroxy-4-amino-6-isopropylamino-*s*-triazine), and deisopropylhydroxyatrazine (DIHA) (2-hydroxy-4-ethylamino-6-amino-*s*-triazine) were 94−99% pure (Ciba-Geigy Corp. Greensboro, NC). Atrazine (2-chloro-4-ethylamino-6-isopropylamino-*s*-triazine) was 98% pure (Ultra Scientific, N. Kingstown, RI), and deethylatrazine (DEA) (2-chloro-4-amino-6-isopropylamino-*s*-triazine) and deisopropylatrazine (DIA) (2-chloro-4-ethylamino-6-amino-*s*-triazine) were 97% pure (Crescent Chemical Co., Inc., Hauppauge, NY). All solvents used were HPLC grade. All chemicals used for routine and confirmation analyses of HADPs, atrazine, DEA, and DIA have been previously described (*5, 24, 33*).

Stream Sampling. The primary study region was northern Missouri. Sampling of northern Missouri streams encompassed about 140 locations representing 95 streams and 14 separate river systems which were sampled at preplant (March and April) and postplant (May to July) of 1994 and 1995 (Figure 1). Baseflow conditions (i.e., groundwater as the source of streamflow) existed for both sample dates in 1994 and preplant 1995. Runoff conditions predominated for the postplant 1995 samples. In order to sample the approximately 140 northern Missouri streams in 2 weeks or less, grab samples were taken at all sites. A single point was sampled in the main flow path for smaller streams. To obtain a more representative sample for the larger rivers, two to three grab samples were taken in a transect at the main flow paths. The samples were transported in iced coolers (approximately 2−4 °C) and filtered through 0.45 μm nylon filters within 1−3 days of collection. For larger streams, all samples were mixed just before filtration to provide a single composite sample. Filtered samples were then stored

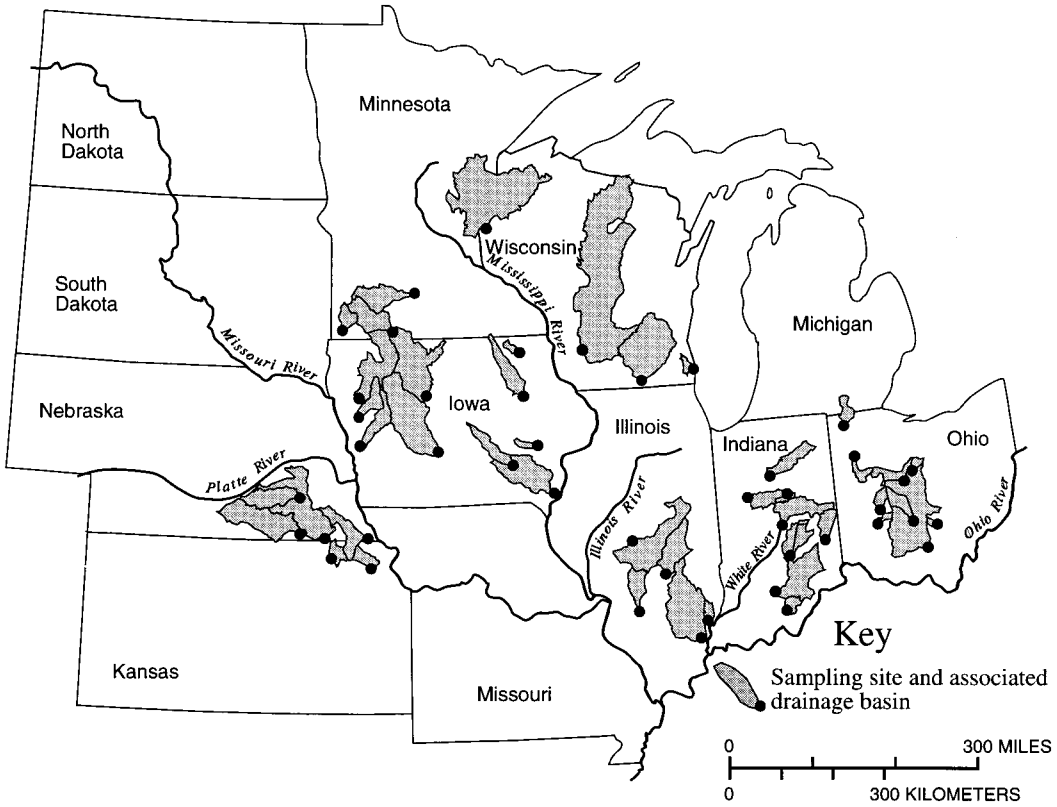

FIGURE 2. Sample locations for midwestern streams.

refrigerated until solid phase extraction cleanup could be performed within 5−15 additional days. Each sample set was scrutinized to ensure that the samples were representative of the corresponding sample date. For instance, a considerable number of samples collected in April 1994 were not representative of preplant conditions based on the presence of alachlor, and significant levels of metolachlor. Previous studies of northern Missouri and midwestern streams indicated that alachlor and metolachlor either were not present or were detected at very low levels under preplant conditions (*1, 33, 34*). In addition, the proximity of sample locations to upstream pesticide dealerships was considered in developing the sampling scheme so that point-sources of herbicides were not a factor.

Another sample set was acquired from 46 locations under runoff conditions at postplant 1995 (May and June) representing eight midwestern states encompassing the Corn Belt region (Figure 2). Details of the sampling procedure and sample handling prior to analysis for atrazine, DIA, and DEA were described previously (*1, 33*). A subsample was transported to the USDA-ARS Water Quality Laboratory in Columbia, MO, and sample cleanup and analyses for the HADPs were conducted within 2−3 months of sampling. In order to distinguish the different regional sample sets, those samples from Missouri will be referred to as northern Missouri streams and those from the eight state midwest region will be referred to as midwestern streams.

Routine Analyses. All sample cleanup and analyses for the HADPs were conducted on filtered samples as previously described (*5, 24*). Briefly, sample cleanup was performed by cation exchange (SCX) solid phase extraction (SPE) followed by quantitation using reverse phase octyl (C_8) high-performance liquid chromatography (HPLC). For the northern Missouri streams, quality assurance samples consisted of field and laboratory blanks and spikes. Spike sample concentrations were either 0.5 μg L^{-1} for preplant samples or 2.0 μg L^{-1} for postplant samples. Duplicate samples were also analyzed to ensure the reproducibility and precision of the method. For the midwestern streams, quality assurance samples consisted of laboratory blanks and spikes as well as field spikes at 2.0 μg L^{-1} and duplicate samples. Final reported concentrations for HA and DEHA were corrected for field spike recoveries. Limits of detection were 0.04 μg L^{-1} for HA and 0.1 μg L^{-1} for DEHA and DIHA. DIHA was not detected in any 1994 samples, and routine analyses for DIHA were not performed on any samples collected in 1995.

Analysis of atrazine, DIA, DEA, and cyanazine were described previously (*5, 35, 36*). For the northern Missouri streams, sample clean-up was performed by C_{18} SPE followed by quantitation using gas chromatography (GC) and N-P detection or reverse phase HPLC and ultraviolet (UV) detection for cyanazine. Cyanazine concentrations and identity were confirmed by GC or GC−mass spectrometry (MS). Quality assurance samples were similar to that described for HADP analysis. Field spike concentrations were 0.2 μg L^{-1} (preplant) or 1 μg L^{-1} (postplant) for DEA and DIA and 1 μg L^{-1} (preplant) or 5 μg L^{-1} (postplant) for atrazine. Limits of detection were 0.04 μg L^{-1} for atrazine and 0.05 μg L^{-1} for DEA and DIA. For the midwestern streams, sample cleanup was also by C_{18} SPE followed by quantitation of atrazine, DEA, DIA, and cyanazine using GC−MS. The quality assurance program was previously described by Scribner et al. (*33*). Limits of detection for the midwestern stream samples were 0.05 μg L^{-1} for all analytes.

Confirmation Analyses. Qualitative confirmation of HA and DEHA was performed using HPLC/MS/MS on the original sample prepared by SCX SPE or on fractions of HA or DEHA (*5*). DIHA confirmation was not performed since it was not detected by routine HPLC analysis. HPLC conditions were Spherisorb S5 propylbenzenesulfonic acid (SCX) stationary phase, 150 mm X 4.6 mm (i.d.) column (Phase Separations, Inc., Norwalk, CT); 50 μL sample injection; and mobile phase flow rate of 1.5 mL min^{-1}. Mobile phases were A, 25% CH_3OH:75% H_2O containing 1 g L^{-1} ammonium

TABLE 1. Prevalence of Atrazine and Atrazine Degradation Products in Northern Missouri and Midwestern Streams

		maximum concentration[a]		prevalance[b]				
				northern Missouri streams				
				preplant		postplant		
compd	detection limit[a]	northern Missouri streams	midwest streams	1994	1995	1994	1995	midwest streams, postplant, 1995
DEHA	0.10	0.86	0.50	0	0	58	55	24
HA	0.04	3.72	2.37	98	99	100	100	87
atrazine	0.04 or 0.05[c]	136	50.4	99	90	100	100	100
DEA	0.05	7.50	6.00	83	42	99	99	96
DIA	0.05	7.37	3.87	60	52	99	98	96

[a] Values expressed in units of micrograms per liter. [b] Values expressed in units of percent detection. [c] Detection limit was 0.04 μg L^{-1} for northern Missouri streams and 0.05 μg L^{-1} for midwestern streams.

acetate (NH_4OAc) and 5 mL L^{-1} HOAc, pH 3.5−4; and B, 25% CH_3OH:75% H_2O containing 16 g L^{-1} NH_4OAc, pH 7.0−7.4. Gradient mobile phase conditions were

time (min)	mobile phase A (%)	mobile phase B (%)
0.0	90	10
2.0	90	10
3.0	0	100
7.0	0	100
7.2	90	10
12.5	90	10

The MS/MS system was a Perkin-Elmer Sciex API III Plus (Norwalk, CT), which utilizes an atmospheric pressure chemical ionization (APcI) interface with the HPLC. APcI conditions were interface temperature, 70 °C; heated nebulizer temperature, 425 °C; nebulizer gas, ultrapure N_2 at 0.55 MPa; discharge current, 3 μA. MS/MS conditions were positive ion mode; collision gas, ultrapure Ar/N_2 (90/10) mixture; declustering potential, 50 V; collision energy, 16 V; dwell time, 200 ms with 30 ms pause. Multireaction monitoring (MRM) was used for identification of HA and DEHA. In this technique, the first MS chamber (Q1) screens the mass corresponding to the *m/z* of the protonated molecular ion $[M + H]^+$, then the third MS chamber (Q3) detects a specific mass corresponding to the *m/z* for a known characteristic daughter ion of the analyte after fragmentation in the second chamber (Q2). For HA, Q1 screened *m/z* 198 $[M + H]^+$, and Q3 detected *m/z* 156 $[M - C_3H_7 + 2H]^+$. For DEHA, Q1 screened *m/z* 170 $[M + H]^+$, and Q3 detected *m/z* 128 $[M - C_3H_7 + 2H]^+$. For both compounds, conditions were analogous in that the protonated molecular ion was screened first and the daughter ion detected resulted from the removal of the isopropyl group. The MRM technique, in combination with HPLC, provided three means of compound identification: (1) HPLC retention time; (2) mass screening based on the protonated molecular ion; and (3) detection of a specific daughter ion. HA and DEHA confirmation were performed on 5% of the northern Missouri samples. Confirmation samples encompassed 13 of the 14 major river systems in northern Missouri. Four of the 46 midwestern stream samples were selected for HA or DEHA confirmation so that their presence has been confirmed from Nebraska to Ohio and from Wisconsin to southern Illinois.

Results and Discussion

Prevalence and Concentrations of HADPs in Streams. In northern Missouri streams at preplant, HA was detected in 98−99% of the samples, and DEHA was not detected (Table 1). HA prevalence at preplant was comparable to atrazine, and it was much greater than DEA and DIA in both years (Table 1). At postplant, HA prevalence was 100% in northern Missouri streams and 87% in midwestern streams. HA prevalence in northern Missouri streams was equal to atrazine and slightly greater than DEA and DIA. In the midwestern streams, HA prevalence was somewhat lower than atrazine, DEA and DIA. DEHA prevalence in northern Missouri streams at postplant was similar in each year, with 58% in 1994 and 55% in 1995. DEHA prevalence in midwestern streams was 24%, less than half that of northern Missouri streams. Prevalence of DEHA at postplant was consistently much lower than atrazine, HA, DEA, or DIA in northern Missouri and midwestern streams. DIHA was not detected in either pre- or postplant sample sets in 1994 for the northern Missouri streams. Therefore, no further analyses for DIHA were conducted in 1995.

HA contamination of streams was common at pre- and postplant, but DEHA contamination of streams occurred only at postplant and with much lower frequency than HA or the chlorinated atrazine metabolites. HA was the predominant atrazine degradation product detected in northern Missouri streams under preplant conditions, with much greater prevalence than DEA or DIA. HA prevalence was not dependent upon sample date for northern Missouri streams with 98% or greater prevalence for all four sample sets. The consistently high prevalence of HA showed that a year-round source of this metabolite exists in northern Missouri streams. This further indicated that the mass of HA formed and the persistence of HA in the environment are sufficient to cause year-round stream contamination. DEHA lacks either sufficient mass formed or stability to be present at preplant.

The lower prevalence of HA and DEHA in midwestern streams compared to northern Missouri streams likely resulted from a combination of three factors: differences in the timing of sampling, less HADPs formed in midwestern basins, and dilution in runoff. Most midwestern stream samples were collected at the end of May 1995 while the northern Missouri samples were collected from mid-June to early July. Thus, the midwestern stream samples represented a shorter time between atrazine application and sample collection, and in some basins, atrazine application was probably not completed. Less time since atrazine application and cooler soil temperatures could result in reduced formation and transport of HADPs in midwestern basins compared to northern Missouri basins. This is consistent with the fact that four of the five streams in which HA was not detected were in the northern Corn Belt states of Wisconsin and Minnesota. In addition, the midwestern stream samples were collected during runoff events, possibly diluting HADP concentrations below the detection limit. Lerch et al. (*5*) reported that HA and DEHA concentrations in Goodwater Creek were inversely related to streamflow.

At preplant, median HA concentrations in northern Missouri streams were 0.21 μg L^{-1} in 1994 and 0.23 μg L^{-1} in 1995 (Figure 3). HA concentrations ranged from <0.04 to 0.54 μg L^{-1} in 1994 and <0.04 to 0.75 μg L^{-1} in 1995. Median HA concentration in northern Missouri streams was lower than the median atrazine concentration in 1994, but it was greater in 1995 (Figure 3). Maximum atrazine concentrations

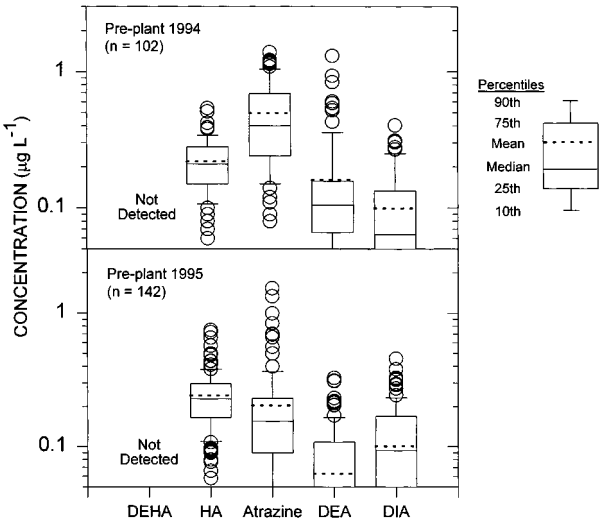

FIGURE 3. Concentrations of atrazine and atrazine degradation products in northern Missouri streams at preplant.

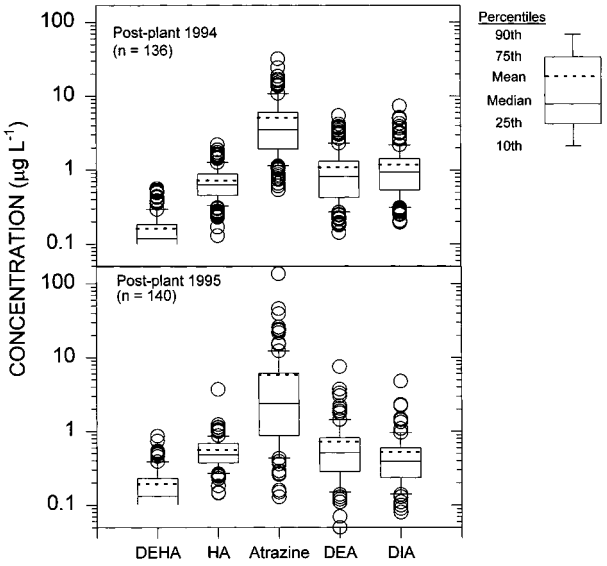

FIGURE 4. Concentrations of atrazine and atrazine degradation products in northern Missouri streams at postplant.

at preplant of both years were greater than maximum HA concentrations by 2−3 times. Median HA concentrations were greater than median DEA and DIA concentrations at preplant for both years, but the concentration ranges were similar for the three metabolites.

At postplant, median HA concentrations increased to 0.63 μg L^{-1} in 1994 and 0.48 μg L^{-1} in 1995 (Figure 4). Post-plant HA concentrations ranged from 0.13−2.22 μg L^{-1} in 1994 and 0.15−3.72 μg L^{-1} in 1995. In midwestern streams, median HA concentration was 0.19 μg L^{-1}, similar to the preplant median concentrations in the northern Missouri streams (Figure 5). However, the HA concentration range in midwestern streams was similar to the northern Missouri streams. Median DEHA concentrations in northern Missouri streams at postplant were 0.12 μg L^{-1} in 1994 and 0.13 μg L^{-1} in 1995 (Figure 4). DEHA exhibited a very narrow concentration range with maximum concentrations of 0.56 μg L^{-1} in 1994 and 0.86 μg L^{-1} in 1995. In midwestern streams, DEHA concentrations were lower than northern Missouri streams with a median concentration of <0.10 μg L^{-1} and a maximum concentration of 0.50 μg L^{-1} (Figure 5). The increased concentrations of HA and DEHA in northern Missouri streams at postplant compared to preplant resulted from new sources

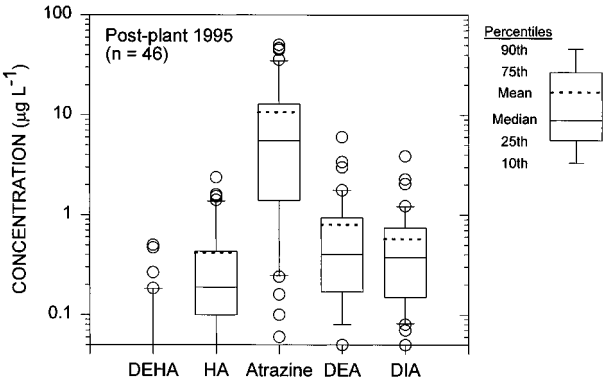

FIGURE 5. Concentrations of atrazine and atrazine degradation products in midwestern streams at postplant, 1995.

of each compound due to the application of atrazine in these basins.

At postplant, median atrazine concentrations in northern Missouri streams were about 5 times higher than median HA concentrations in both years (Figure 4). In 1994, median concentrations of DEA and DIA were 1.3 and 1.5 times greater than HA, respectively. However, median levels of these three metabolites were nearly the same at postplant 1995. In midwestern streams, median HA levels were 29 times lower than median atrazine concentrations and about 2 times lower than median DEA and DIA concentrations (Figure 5). Thus, absolute HA concentrations, as well as concentrations relative to atrazine and chlorinated atrazine metabolites, were significantly lower in midwestern streams than in northern Missouri streams. DEHA levels in comparison to atrazine, DEA, and DIA were consistently much lower in both (postplant) stream sample sets (Figures 4 and 5). In northern Missouri and midwestern streams, median DEHA concentrations were 18−55 times lower than median atrazine concentrations. The prevalence and concentrations of HA in streams throughout northern Missouri and the Midwest showed that it is a major stream water contaminant resulting from the use of atrazine in these basins. Conversely, the consistently low levels and lack of detections under preplant conditions indicated that DEHA was not a significant contaminant in northern Missouri or midwestern streams.

The prevalence and concentrations of DEHA and HA for these two regional data sets are in close agreement with findings reported for a 2.5 year continuous monitoring study of HADPs in Goodwater Creek (*5*). HA was detected in 100% of these samples at similar levels to those reported in this study. HA concentrations were similar to atrazine and typically greater than DEA and DIA, from late summer (September) until atrazine application in April or May. During the first 6 weeks following application, levels of atrazine were as much as 50 times greater than HA, and DEA levels were typically 1.5−5 times greater than HA. DEHA was detected in 25% of the samples from the year-round monitoring study with concentrations generally less than 1 μg L^{-1}, and detections of DEHA usually occurred from June−October. No detections of DEHA were reported from December−April of each year. Thus, these results agreed with the findings presented in this study in which DEHA detections only occurred at postplant.

Contribution of HADPs to Total Atrazine Load. With the inclusion of the HADP concentrations, the total atrazine load (i.e., atrazine plus stable metabolites) in streams of the midwestern U.S. can be calculated. To do this, however, the contribution of DIA from atrazine and cyanazine must be taken into account. DIA formation occurs at about the same rate from either parent source (*37, 38*); therefore, the atrazine-derived DIA was calculated using the proportion of atrazine to cyanazine in the stream water samples. Contributions of

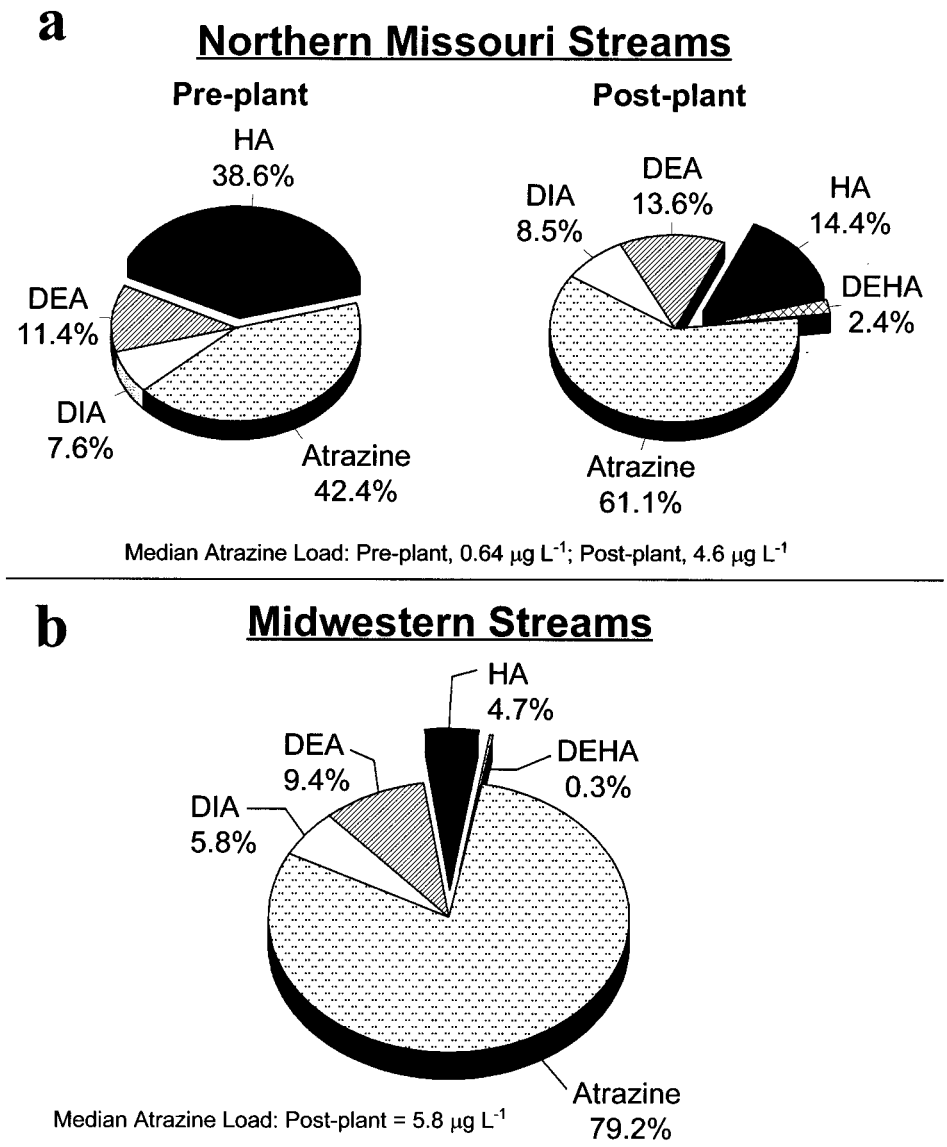

FIGURE 6. Proportion of atrazine and atrazine degradation products to the total atrazine load in streams. (a) northern Missouri streams. (b) midwestern streams. (Charts for the northern Missouri streams represent the average proportions for 1994 and 1995).

DIA from simazine were considered negligible because of its extremely limited use in the midwestern states encompassed by this study (*39*). In northern Missouri streams at preplant, atrazine degradation products accounted for 58% of the total atrazine load, and HA was the predominant degradation product present (Figure 6). At postplant, the parent accounts for the majority of the atrazine load, but the degradation products still represent almost 40% of the atrazine load with 17% of the total as HADPs. The proportion of DEA and DIA did not change appreciably between pre- and postplant, but HA was reduced from 39% to 14% of the atrazine load. Therefore, the major change in the atrazine load between pre- and postplant was an increase in the proportion of the parent and a concomitant decrease in the proportion of HA. Median atrazine loads increased by about 7 times from pre- to postplant, demonstrating the considerable impact that annual atrazine use has on the total load to the streams.

In the midwestern streams, the parent dominates the atrazine load, accounting for 79% of the total. The chlorinated degradation products represented 15% of the atrazine load while the HADPs represented only 5% of the total. Median atrazine load in midwestern streams was 1.2 μg L^{-1} greater than the northern Missouri streams, and the proportion of metabolites to parent was half that of the northern Missouri streams. This result suggested that atrazine degradation rates in northern Missouri basins were greater than the midwestern basins, most likely due to higher soil temperatures during the postplant period. Also, the differences in timing of the midwestern and northern Missouri samples was apparently a factor leading to the increased proportion of metabolites in northern Missouri streams.

Transport Mechanisms Controlling Concentrations of HADPs in Streams. The results of this study and the continuous monitoring study by Lerch et al. (*5*) clearly demonstrate the widespread occurrence of HADPs in streams as well as a year-round source of HA in most northern Missouri streams. Because of the greater significance of HA as a streamwater contaminant and the more extensive research into its environmental behavior, the following discussions of mechanisms responsible for HADP contamination of streams will focus on HA. Potential sources of HA in streams are (1) discharge of HA contaminated groundwater; (2) in-stream biological, chemical, or photolytic hydrolysis of atrazine in the dissolved phase; (3) atmospheric deposition of HA resulting from photolytic hydrolysis of atrazine; (4) transport of dissolved-phase HA in surface runoff; and (5) desorption of HA from suspended and bed sediments. The source or sources of HA must explain the year-round

occurrence of HA, postplant increases in HA concentration, and the relatively high concentration of HA compared to atrazine, DEA, and DIA at preplant.

HA contamination of baseflow is unlikely to be an important source of HA to streams. As previously discussed, HA contamination of groundwater has been reported at levels less than 0.04 μg L^{-1} (*5, 23*), and the relatively strong sorption of HA to soils prevents significant leaching to groundwater. Therefore, HA contamination of baseflow does not account for the observed levels of HA in streams reported in this study or by Lerch et al. (*5*).

In-stream biological or chemical hydrolysis of atrazine are also unlikely to be significant sources of HA. At preplant, water temperatures are cold enough (8−12 °C) (*40*) that significant biological hydrolysis of atrazine in the streams would not be expected to occur. Furthermore, biological hydrolysis of atrazine has not been demonstrated in aquatic systems, nor have any aquatic species capable of atrazine hydrolysis been isolated thus far. Significant chemical hydrolysis of atrazine in the dissolved phase would be unlikely since the pH of northern Missouri and midwestern streams is typically near neutral (*33*). Although in-stream hydrolysis of sorbed atrazine may be a significant source of HA (*41*), subsequent desorption would still be required for its release into the dissolved phase.

Of the in-stream hydrolytic processes, photolysis is a potentially significant source of HA. Photolysis of atrazine in water has been shown to occur by direct or indirect reactions with UV light (*15−17, 42−45*). Indirect photolysis occurs via photosensitizers capable of generating ·OH radicals upon absorption of UV light, such as acetone, TiO_2, H_2O_2, dissolved organic matter, and nitrate. However, only the latter two photosensitizers have relevance for stream photolysis of atrazine. Many laboratory studies have shown that photolytic hydrolysis of atrazine in water can occur, but these studies relied on photosensitizers or UV wavelengths which are not environmentally appropriate (*15, 42−44*). Using wavelengths approximating natural sunlight, Minero et al. (*16*) showed that irradiation of atrazine in a humic acid solution resulted in the conversion of about 15% of the atrazine to HA, but several other degradation products were produced through chemical reaction processes such as alkyl chain oxidation, dealkylation, and deamination. Schmitt et al. (*45*) reported that photolysis of atrazine in the presence or absence of humic substances resulted in HA as the main photodegradation product, but the presence of dissolved humic substances decreased HA formation and increased dealkylation reactions. Furthermore, Torrents et al. (*17*) reported that indirect photolysis of atrazine, using nitrate as a photosensitizer, yielded only 3% as HA, with the majority of the degradation products forming via alkyl oxidation and dealkylation reactions. Direct photolysis of atrazine was reported to yield 14% HA and about 9% as chloroalkyloxidized or chlorodealkylated degradation products (*17*). However, direct photolysis is about an order of magnitude slower than indirect photolysis using nitrate as a photosensitizer (*17*). Indirect photolysis using environmentally relevant photosensitizers has resulted in estimated atrazine half-lives of 20−700 h (*16, 17, 45, 46*).

Photolytic hydrolysis of atrazine in streams clearly cannot be discounted as a potentially significant source of HA, but definitive studies of its importance under realistic environmental conditions are lacking. Atrazine photolysis does not result in quantitative formation of HA, but rather, a whole range of products are formed via several mechanisms, and formation of HA is often decreased when photolysis occurs by an indirect mechanism. These photolytic pathways are not consistent with the higher concentrations and prevalence of HA relative to DEA and DIA under preplant conditions reported in this study. Furthermore, photolytic degradation in water is limited to the water surface because of the inability of UV light to penetrate through water (*47*). Under our postplant sampling conditions, high suspended sediment levels existed in most of the streams, and shading by trees will further reduce the amount of UV light reaching the streams. Therefore, the importance of photolysis as a significant source of HA in streams is very questionable.

Atmospheric deposition of HA resulting from photolysis of atrazine is another possible source of HA to streams. Atmospheric transport and subsequent deposition of atrazine in rainwater has been reported at various locations in the Midwest (*48, 49*). Rainwater samples collected from four sites (one in Mississippi, two in Iowa, and one in Minnesota) in spring 1995 were selected for HA analysis because of their relatively high atrazine levels (0.16−0.36 μg L^{-1}). HA was not detected in any of these samples. Therefore, photolytic hydrolysis of atrazine during atmospheric transport is apparently not a significant degradation pathway. Although, dry deposition of HA from the atmosphere is possible, it is unlikely to be a major source of HA in streams because of the low wind erosion rates in the Midwest.

We hypothesize that the processes of dissolved phase transport by surface runoff and desorption of HADPs from stream sediment control the concentrations of HADPs in streams. Under runoff conditions, a combination of dissolved-phase transport by surface runoff and desorption from suspended stream sediments are the sources of HADPs (Figure 7a), while under baseflow conditions, the primary source of HADPs is desorption from bed sediments in the stream (Figure 7b). Dissolved phase transport of HA by surface runoff has been directly measured in edge-of-field samples from a northcentral Missouri field treated with atrazine in 1994. Surface runoff from an event 6−7 days after atrazine application showed HA concentrations of 3.3−5.4 μg L^{-1} in flow-weighted samples taken throughout the course of the event. Thus, surface runoff water has the ability to extract or desorb a fraction of the HA present in the soil. In addition, continuous monitoring of HA in Goodwater Creek showed that HA mass flux was directly related to streamflow, indicating that increased HA mass flux during runoff events resulted from dissolved phase transport (*5*).

Evidence for desorption of HA from sediments as a source of dissolved phase HA in streams is based on several observations of the environmental behavior of HA. First, HA sorption to soils has been shown to be much greater than that of atrazine or its chlorinated degradation products (*27, 29, 50, 51*). Therefore, a greater proportion of HA would be expected to be transported to streams sorbed to the sediment compared to atrazine, DEA, and DIA. Despite the fact that HA has been shown to be the major degradation product of atrazine in most soils (*7−11*), dissolved phase HA concentrations during postplant runoff events reported in this study and by Lerch et al. (*5*) were consistently lower than the concentrations of DEA and DIA. Because of their weaker sorption to soil, DEA and DIA are preferentially transported in the dissolved phase (*27*), resulting in greater stream concentrations than HA during runoff events. In one northern Missouri stream sampled under runoff conditions on June 27, 1995, concentrations of the major degradation products were 5.92 μg L^{-1} for DIA, 6.48 μg L^{-1} for DEA, and 3.72 μg L^{-1} for HA. Furthermore, HA concentrations in Goodwater Creek decreased during postplant runoff events while DEA and DIA concentrations increased (*5*). The lower dissolved phase concentrations of HA during runoff events further supports the hypothesis that the HA concentrations were controlled by desorption from soil or sediment.

Second, HA is more persistent in surface soils than atrazine, DEA, DIA, or didealkyl-atrazine (2-chloro-4,6-diamino-*s*-triazine) (*11*), and it is a major component of bound atrazine residues (*8, 21, 22*). Therefore, HA is likely

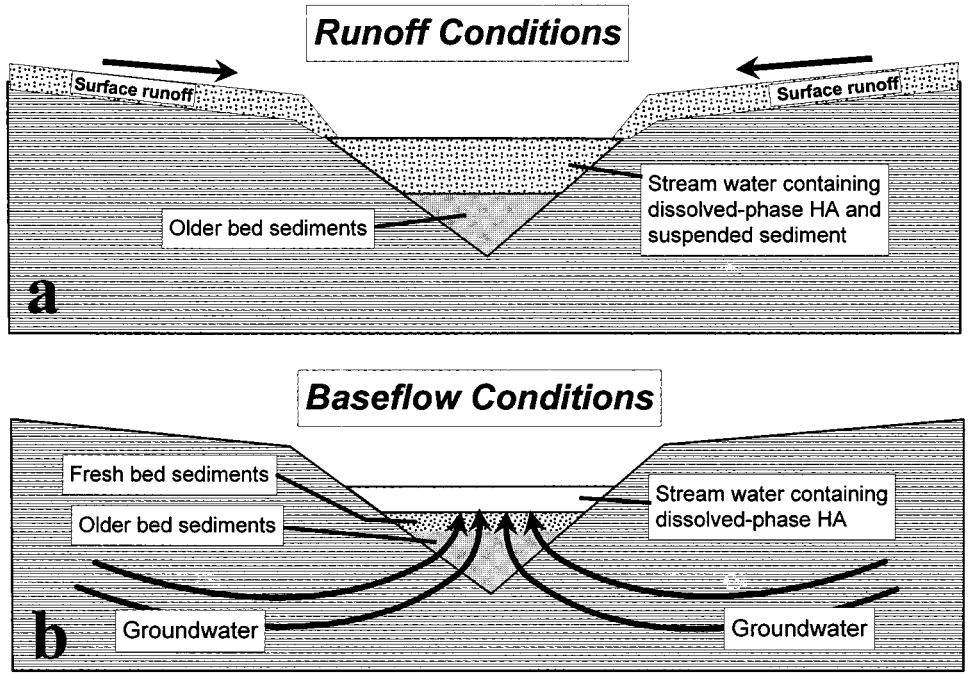

FIGURE 7. Proposed models for the mechanisms controlling HADP concentrations in streams. The figure depicts the cross-sectional view of a stream channel. (a) Under runoff conditions, HA is primarily transported from atrazine-treated fields to the stream in the dissolved phase. An additional source of HA in streams is suspended sediment derived from erosion of HA-contaminated soil. (b) Under baseflow conditions (i.e., groundwater as the source of streamflow), HA is desorbed by groundwater flowing through the HA-contaminated sediments deposited in the stream bed.

to be present in surface soils long after atrazine application. Using a mixed-mode extracting agent [3:1 0.5 *M* KH_2PO_4, pH 7.5:CH_3CN (v/v)] and the extraction procedure of Lerch et al. (*22*), HA has been measured in field soils with a history of atrazine use and in stream bed sediments and freshly deposited bank sediments collected from Goodwater Creek. Field soils (0−15 cm) collected 12−24 months following atrazine application from two sites, one each in Missouri and Iowa, had HA concentrations ranging from 25.1 to 637 $\mu g\ kg^{-1}$, demonstrating that HA does persist in soils. Four stream bed and three fresh bank sediments collected at various locations along Goodwater Creek in October, 1996, varied in HA concentration from <6.5 to 23.0 $\mu g\ kg^{-1}$. HA was detected in two of the four bed sediments and two of the three bank sediments. The persistence of HA in soils and its presence in stream sediments strongly supports our hypothesis that atrazine-treated field soils provide a year-round source of HA-contaminated sediments to streams. Surface runoff events transport soils containing sorbed HA to the stream, as well as transporting HA in the dissolved phase, as previously discussed. Subsequent desorption of HA from contaminated sediments then results in dissolved phase HA under baseflow conditions (Figure 7b).

Third, HA concentrations in Goodwater Creek were inversely related to streamflow (*5*). HA concentrations always increased during low-flow periods, even within a few days following a runoff event. This implied a source of HA to the stream under baseflow conditions. Since the groundwater was not contaminated with HA, and other sources of HA could not explain the observed concentrations, particularly in the winter and early spring months, desorption from stream sediments was the apparent source.

Fourth, box-plots of HA concentrations at postplant (Figures 4 and 5) and HA concentrations reported by Lerch et al. (*5*) for Goodwater Creek invariably showed that HA had a narrower concentration range for the 25th to 75th percentiles than atrazine, DEA, and DIA. This further suggests that the HA concentrations were constrained by some process or processes. As noted earlier, HA concentrations were apparently limited by desorption from field soils under runoff conditions at postplant. Desorption from stream sediments would also be consistent with the low variability in HA concentrations observed under baseflow conditions at postplant.

The evidence for dissolved-phase transport and sediment desorption as the processes controlling HADP concentrations is very strong based on the data reported in this study and by Lerch et al. (*5*). The known behavior of HADPs in the environment further supports our hypotheses about the mechanisms controlling HADP concentrations in streams. Furthermore, the control of dissolved phase concentrations in streams by sediment desorption is likely to be an important mechanism for other highly sorptive pesticides and contaminants. Research is currently underway to optimize the extraction methodology for determination of HADPs in soils and sediments. Additional research is needed to determine HADP desorption isotherms from stream sediments.

Implications for Monitoring Atrazine in Streams. The data presented show the overall importance of HADPs, particularly HA, to the total atrazine load in streams throughout the midwestern U.S. In order to fully assess the effects of management changes or ecological impact, stream monitoring programs should include routine measurement of the major atrazine metabolites (HA, DEA, and DIA) since they can account for 20−60% of the total atrazine load (Figure 6). In addition, the importance of sediment as a source of HADPs in streams should also be considered in designing an atrazine monitoring program. Measurement of HADPs in suspended sediments is warranted since these sediments are a potentially important source of HADP input to the streams (Figure 7a). Therefore, monitoring programs should also include measurement of total suspended sediment and stream flow. Because of the persistence and potential accumulation of HA in surface soils with a history of atrazine use, the impact of reducing atrazine inputs in a watershed may not be immediate with respect to dissolved phase HA

concentrations. Although peak postplant HA levels would be expected to decrease, HA would likely remain at levels similar to the preplant levels reported in this study from late summer through early spring for a period of several years. Assessing the overall impact of atrazine management changes on stream water quality will require long-term measurement of HA in the dissolved phase and in suspended sediments.

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