

## EFFECT OF SEDIMENT ON THE FATE OF METOLACHLOR AND ATRAZINE IN SURFACE WATER

PAMELA J. RICE,\*† TODD A. ANDERSON,‡ and JOEL R. COATS§

†U.S. Department of Agriculture, Agricultural Research Service, Soil and Water Management Research, St. Paul, Minnesota 55108

‡The Institute of Environmental and Human Health, Texas Tech University, Lubbock, Texas 79409, USA

§Pesticide Toxicology Laboratory, Department of Entomology, Iowa State University, Ames, Iowa 50011, USA

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**Abstract**—In aquatic environments, pesticides can partition between the dissolved phase and particulate phase depending on the type of suspended sediment present and the physical and chemical properties of the pesticides and water. Particulate matter and sediment can alter the bioavailability of contaminants to organisms and therefore influence their toxicity and availability for microbial degradation. Experiments were conducted to determine the degradation of atrazine (6-chloro-*N*-ethyl-*N'*-(1-methylethyl)-1,3,5-triazine-2,4-diamine) and metolachlor (2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(methoxyprop-2-yl)acetamide) in surface water, and to evaluate the contribution of sediment to their dissipation. Sediment significantly reduced concentrations of atrazine and metolachlor in the surface water as a result of greater degradation, evident by increased quantities of degradates in the surface water, and the partitioning of the herbicide or herbicide degradates in the sediment. First-order 50% dissipation time (DT50) values for atrazine and metolachlor were 42 and 8 d in the surface water–sediment incubation systems, which were almost four times less than the DT50s calculated for the sediment-free systems. The results of this research illustrate the importance of sediment in the fate of pesticides in surface water. Greater comprehension of the role of sediment to sequester or influence degradation of agrichemicals in aquatic systems will provide a better understanding of the bioavailability and potential toxicity of these contaminants to aquatic organisms.

**Keywords**—Herbicides Dissipation Degradation Metabolites

## INTRODUCTION

Pesticide use in agricultural and urban areas has resulted in nonpoint source and point source contamination of surface water and groundwater [1–3]. Runoff/erosion of pesticides and soil from agricultural fields is a large contributor to water-quality degradation. It is estimated that 1 to 6% of soil-applied herbicides may be lost to aquatic environments in runoff and drainage from agricultural fields [4,5]. A number of agrichemicals have been detected in surface waters [3] and several studies have demonstrated significant negative effects of agrichemicals on aquatic organisms and ecosystems [6,7]. In addition to concerns of potential adverse effects on aquatic life, degraded water quality impacts the use of surface waters for drinking water supplies and recreation.

In 2002, atrazine (6-chloro-*N*-ethyl-*N'*-(1-methylethyl)-1,3,5-triazine-2,4-diamine) and metolachlor (2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(methoxyprop-2-yl)acetamide) were applied to 62 and 15% of the acreage planted in corn in the midwestern United States (Illinois, Indiana, Iowa, Minnesota, Nebraska, Ohio, and Wisconsin), which resulted in the application of 35,762,000 (16,235,948 kg) and 10,230,000 pounds (4,644,420 kg) of atrazine and metolachlor, respectively [8]. Physiochemical properties of pesticides, soil properties, and factors such as climatic conditions, farming practices, pesticide usage, spray drift, intensity and timing of rainfall after pesticide application, and soil erosion with runoff are important in governing the quantity of pesticides that occur in streams. Pesticides may be transported in the dissolved phase or particulate phase of runoff depending on their water solubility and sorption to soil [9,10]. Atrazine and metolachlor are

relatively water-soluble herbicides that are moderately adsorbed to soil and primarily transported to surface water and groundwater in the dissolved phase [11]. The widespread use of these moderately soluble and mobile herbicides has led to the frequent detection of atrazine and metolachlor in surface water and groundwater [1–3].

Although dissipation of extractable pesticides from surface water is the net result of volatilization, assimilation by aquatic organisms, sorption, abiotic and biotic degradation, or a combination of these [12–14], the present study only addresses the dissipation of atrazine and metolachlor through degradation, sorption, and volatilization. Laboratory studies were conducted to measure changes in metolachlor and atrazine concentrations in the water of surface water and surface water–sediment incubation systems. Mass balance analyses were performed to determine the role of degradation, sorption to the sediment, and volatilization on the herbicide's elimination from the surface water. Herbicide and degradate concentrations measured in nonsterile and autoclaved incubation systems were compared to better understand the influence of microbial degradation of metolachlor and atrazine in these systems. Results of this research (dissipation rates, partitioning characteristics, and mass balance data) can be utilized in predictive models to more accurately assess environmental behavior and to perform risk assessment analyses.

## MATERIALS AND METHODS

*Sample collection*

Surface water and sediment cores were collected from the Iowa State University Horticulture Station Pond (Ames, IA, USA). Pond water samples were stored in sterile 4-L bottles

\* To whom correspondence may be addressed (pamrice@umn.edu).

Table 1. Summary of pesticides and degradates evaluated

	Metolachlor <sup>a</sup>	Atrazine <sup>b</sup>
Water solubility	530 ppm at 20°C	33 ppm at 27°C
Vapor pressure	$1.3 \times 10^{-5}$ mm Hg at 20°C	$3.0 \times 10^{-7}$ mm Hg at 20°C
Sorption coefficient ( $K_{oc}$ )	200	100
Degradates	Carbinol <sup>c</sup> Morpholinone <sup>e</sup>	DEA <sup>d</sup> DIA <sup>f</sup> DDA <sup>g</sup> HYA <sup>h</sup> DEHYA <sup>i</sup> DIHYA <sup>j</sup>

<sup>a</sup> Metolachlor = [U-<sup>14</sup>C]metolachlor (2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(methoxyprop-2-yl)acetamide; 98.9% radiochemically pure).

<sup>b</sup> Atrazine = [U-<sup>14</sup>C]atrazine (6-chloro-*N*-ethyl-*N'*-(1-methylethyl)-1,3,5-triazine-2,4-diamine; 98.2% radiochemically pure).

<sup>c</sup> Carbinol = *N*-(2-ethyl-6-methylphenyl)-2-hydroxy-*N*-(2-methylethyl)-acetamide; CGA 40172, 98.4% pure).

<sup>d</sup> DEA = [U-<sup>14</sup>C]deethylatrazine (2-chloro-4-amino-6-(isopropylamino)-*s*-triazine; 94.8% radiochemically pure).

<sup>e</sup> Morpholinone = 4-(2-ethyl-6-methylphenyl)-5-methyl-3-morpholinone.

<sup>f</sup> DIA = [U-<sup>14</sup>C]deisopropylatrazine (2-chloro-4-(ethylamino)-6-(amino)-*s*-triazine; 92.9% radiochemically pure).

<sup>g</sup> DDA = [U-<sup>14</sup>C]didealkylatrazine (2-chloro-4,6-diamino-*s*-triazine; 98.8% radiochemically pure).

<sup>h</sup> HYA = [U-<sup>14</sup>C]hydroxyatrazine (2-hydroxy-4(ethylamino)-6(isopropylamino)-*s*-triazine; 97.5% radiochemically pure).

<sup>i</sup> DEHYA = [U-<sup>14</sup>C]deethylhydroxyatrazine (2-hydroxy-4-amino-6(isopropylamino)-*s*-triazine).

<sup>j</sup> DIHYA = [U-<sup>14</sup>C]deisopropylhydroxyatrazine (2-hydroxy-4(ethylamino)-6(amino)-*s*-triazine).

at 4°C. Sediments cores (10.5 × 18 cm) were collected with a Par Aide golf cup cutter (Lino Lakes, MN, USA). Ten randomly selected sediment cores were composited for each of the three replicates, sieved (2.4-mm diameter), and stored at 4°C. Replicate composite samples were analyzed according to standard protocol to characterize physical and chemical properties, pH 7.8, 88% sand, 8% silt, 4% clay, 1.3% organic matter, and 9.9 meq/100 g cation exchange capacity (A&L Mid West Laboratories, Omaha, NE, USA).

### Chemicals

[U-<sup>14</sup>C]Metolachlor ([<sup>14</sup>C]MET), [U-<sup>14</sup>C]atrazine ([<sup>14</sup>C]ATR), and their degradates were gifts from Ciba-Geigy (Greensboro, NC, USA; Table 1) [11].

### Incubation systems

**Treatments.** Four treatments, which included nonsterile surface water (NS-SW), nonsterile surface water and nonsterile sediment (NS-SW + NS-SED), sterile surface water (ST-SW), and sterile surface water and sterile sediment (ST-SW + ST-SED), were evaluated for each herbicide. Three randomly selected systems from each treatment were sacrificed and extracted within hours of the herbicide application and 16 and 60 d after application.

**Assembly of nonsterile surface water and nonsterile surface water-sediment systems.** Surface water solutions containing pond water-Hoagland's nutrient solution-ultrapure water (1:1:4, v/v/v) were treated with either [<sup>14</sup>C]MET or [<sup>14</sup>C]ATR at a concentration of 200 μg/L to ensure sufficient radioactivity for the detection of degradates. One hundred fifty milliliters of herbicide-treated surface water was added to each empty French square bottle (NS-SW) or French square bottle containing 50 g (dry wt) of sediment (NS-SW + NS-SED). Test systems were capped with a polytetrafluoroethylene-covered neoprene stopper, sealed with paraffin film, and incubated in a temperature-controlled greenhouse (25 ± 2°C) with a 14:

10 h light:dark photoperiod for the duration of the experiment (0, 16, or 60 d).

**Assembly of sterile surface water and sterile surface water-sediment systems.** For the sterile incubations systems, surface water and sediments were autoclaved for 1 h at 121 ± 2°C on two consecutive days before application of metolachlor or atrazine. Sterilization of the autoclaved surface water and sediment was evaluated with microbial plate counts of autoclaved surface water or sediment slurries applied to trypticase soy agar plates and plates containing nutrient agar with rose bengal and streptomycin. One hundred fifty milliliters of sterile herbicide-treated surface water was added to each empty French square bottle (ST-SW) or French square bottle containing 50 g (dry wt) of autoclaved sediment (ST-SW + ST-SED). Each test systems was capped with a polytetrafluoroethylene-covered neoprene stopper, sealed with paraffin film, and incubated in a temperature-controlled greenhouse (25 ± 2°C) with a 14:10 h light:dark photoperiod for the duration of the experiment (0, 16, or 60 d). Autoclaved incubation systems were handled in a laminar flow hood, by using sterile techniques, to minimize microbial contamination, survival, and growth during the study.

### Measurement of volatilization and mineralization

Polyurethane foam and a vial containing 10 ml of 0.1 N NaOH were suspended above the treated surface water in each incubation chamber to trap volatile [<sup>14</sup>C]-organic chemicals and <sup>14</sup>CO<sub>2</sub>, respectively, produced from the degradation and mineralization of the herbicides. The NaOH and polyurethane foam traps were changed periodically (weekly for NaOH and biweekly for polyurethane foam), which also allowed for frequent aeration of the incubation chambers to maintain aerobic conditions. Once removed from the incubation chambers, polyurethane foam traps were placed in vials containing 20 ml of hexane for a minimum of 4 h to extract organic volatiles. Scintillation cocktail (Ultima Gold<sup>TM</sup>, Packard Instrument,

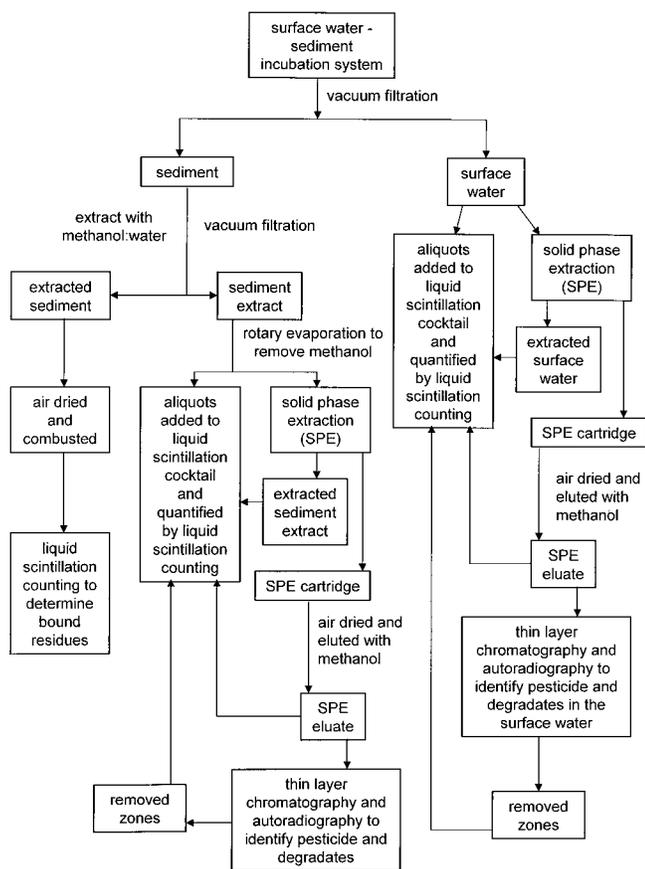


Fig. 1. Diagram of the sediment and surface water extraction scheme.

Downers Grove, IL, USA) was added to each of two aliquots of the NaOH trapping solution and hexane extract and the percentages of applied  $^{14}\text{C}$  associated with  $^{14}\text{CO}_2$  and volatile  $^{14}\text{C}$ -organic chemicals were quantified by liquid scintillation counting with a Rack-Beta<sup>®</sup> model 1217 liquid scintillation counter (Pharmacia LKB Biotechnology, Gaithersburg, MD, USA).

#### Extraction of herbicides and degradates from the surface water

At the completion of each incubation period (0, 16, or 60 d), sediment was separated from the surface water of the surface water-sediment systems by using vacuum filtration (Fig. 1). Atrazine, metolachlor, and their degradates were removed from the surface water solutions of both the surface water and surface water-sediment systems by using preconditioned Supelclean Envi-18<sup>™</sup> 6cc solid-phase extraction (SPE) cartridges (Supelco, Bellefonte, PA, USA) with an applied vacuum (50 kPa). Aliquots of the surface water that passed through the cartridge were added to scintillation cocktail and radioassayed to determine the percentage of applied  $^{14}\text{C}$  that is characterized as unknown polar degradates. The SPE cartridges were air-dried, and the herbicides and herbicide degradates were eluted with 10 ml of methanol. The quantity of  $^{14}\text{C}$  in the methanol eluates was determined by adding aliquots of the eluate to scintillation cocktail and measuring radioactivity by liquid scintillation counting. Herbicides and degradates in the methanol eluates were identified and quantified as described in the section on analyses of herbicides and degradates.

#### Extraction of herbicides and degradates from the sediment

Atrazine, metolachlor, and their degradates were extracted from the sediment with three 150-ml aliquots of methanol-ultrapure water (9:1, v/v; Fig. 1). The sediment and sediment extract were separated by vacuum filtration, and sediment on the filter paper was allowed to air-dry. Methanol in the sediment extract was removed by rotary evaporation, and the remaining extract was brought to a final volume of 100 ml with ultrapure water to ensure that the aqueous sediment extract contained less than 5% methanol. Aliquots of the extract were added to 5 ml of liquid scintillation cocktail and radioassayed to quantify the radioactivity of the sediment extract. Atrazine, metolachlor, and their degradates were removed from the aqueous sediment extracts by using preconditioned Supelclean Envi-18 6cc SPE cartridges, and the quantity of unknown polar degradates and  $^{14}\text{C}$  in the methanol eluates was determined by liquid scintillation counting. Herbicides and degradates were identified and measured as described in the following section.

#### Analyses of herbicides and degradates from the surface water and sediment extracts

A portion of the methanol eluates, representing  $0.03 \mu\text{Ci}$ , was concentrated under  $\text{N}_2$  in a warm-water bath and spotted on  $20 \text{ cm} \times 20 \text{ cm} \times 250 \mu\text{m}$  normal-phase silica gel 60 F-254 plates (Fisher Scientific, Pittsburg, PA, USA) along with radiolabeled and nonradiolabeled herbicide and degradate standards (Fig. 1). Plates containing  $^{14}\text{C}$ MET, carbinol (*N*-(2-ethyl-6-methylphenyl)-2-hydroxy-*N*-(2-methylethyl)-acetamide), and 4-(2-ethyl-6-methylphenyl)-5-methyl-3-morpholinone and the eluates from surface water and sediment extracts of  $^{14}\text{C}$ MET-treated systems were developed in a hexane-methylene chloride-ethyl acetate (6:1:3, v/v/v) solvent system [15]. The  $^{14}\text{C}$ ATR,  $^{14}\text{C}$ deethylatrazine (2-chloro-4-amino-6-(isopropylamino)-*s*-triazine [ $^{14}\text{C}$ DEA]),  $^{14}\text{C}$ deisopropylatrazine (2-chloro-4-(ethylamino)-6-(amino)-*s*-triazine [ $^{14}\text{C}$ DIA]),  $^{14}\text{C}$ didealkylatrazine (2-chloro-4,6-diamino-*s*-triazine [ $^{14}\text{C}$ DDA]),  $^{14}\text{C}$ hydroxyatrazine (2-hydroxy-4(ethylamino)-6(isopropylamino)-*s*-triazine [ $^{14}\text{C}$ HYA]), deethylhydroxyatrazine (2-hydroxy-4-amino-6(isopropylamino)-*s*-triazine [DEHYA]), and deisopropylhydroxyatrazine (2-hydroxy-4(ethylamino)-6(amino)-*s*-triazine [DIHYA]), and the water and sediment extracts from the  $^{14}\text{C}$ ATR-treated systems were spotted on the normal-phase silica gel plates and developed in a chloroform-methanol-formic acid:water (100:20:4:2, v/v/v/v) solvent system (Ciba-Geigy). The locations of the nonradiolabeled standards were identified with an ultraviolet lamp (254 nm). X-Omat<sup>™</sup> Kodak diagnostic film (Eastman Kodak, Rochester, NY, USA) was placed in contact with each plate and developed after four weeks to produce an autoradiogram, which located the extracted  $^{14}\text{C}$ -labeled compounds. The distance between the initial sample application area and the center of each developed sample spot was measured. The silica gel was divided into zones according to identified sample locations. Each zone was removed from the plate, added to 5 ml of scintillation cocktail, and radioassayed in a liquid scintillation counter. The SPE-bound  $^{14}\text{C}$  was calculated as the difference between the percentage of  $^{14}\text{C}$  measured in the sediment extract or surface water before SPE and the sum of the percentage of radioactivity in the SPE aqueous sample waste and SPE methanol eluate.

Table 2. Distribution of [<sup>14</sup>C]metolachlor and [<sup>14</sup>C]metolachlor degradates in surface water and sediment (reported as percentage of applied <sup>14</sup>C)

	16-d incubation <sup>a</sup>			60-d incubation <sup>a</sup>		
	NS-SW <sup>b</sup>	NS-SW + NS-SED <sup>b</sup>		NS-SW <sup>b</sup>	NS-SW + NS-SED <sup>b</sup>	
	Water	Water	Sediment	Water	Water	Sediment
Metolachlor <sup>c</sup>	61.2 A	23.7 B	6.6 C	27.0 D	0.7 E	0.6 E
Extractable degradates <sup>d</sup>	18.5 F	37.4 G	5.2 C	46.3 H	60.6 A	9.2 I
Carbinol <sup>e</sup>	1.0 E	3.3 J	0.7 E	1.4 E	7.8 C	0.7 E
Morpholinone <sup>f</sup>	1.2 E	9.3 I	0.3 E	5.7 C	10.0 I	1.4 E
Polar degradates <sup>g</sup>	1.2 E	2.9 J	0.2 E	5.7 C	8.6 I	0.7 E
Unknown degradates <sup>h</sup>	15.1 K	21.9 L	4.0 J	33.5 M	34.2 M	6.4 C
Sediment-bound residues			21.4 L			20.0 N
Total <sup>14</sup> C in water	79.7 O	61.1 A		73.3 P	61.3 A	
Total <sup>14</sup> C in sediment		33.2 M			29.8 Q	
CO <sub>2</sub>	0.2 E	0.1 E		0.2 E	0.2 E	
Organic volatiles	0.0 E	0.0 E		0.0 E	0.0 E	
SPE loss <sup>i</sup>	16.0 K	6.4 C		9.6 I	7.8 C	
Total <sup>14</sup> C	95.9 R	100.8 S		83.1 T	99.1 U	

<sup>a</sup> Incubated in a temperature-controlled greenhouse (25 ± 2°C) with a 14:10 h light:dark photoperiod for the duration of the experiment. Means in each row followed by the same letter are not statistically different (*p* = 0.05).

<sup>b</sup> NS-SW = nonsterile surface water system without sediment; NS-SW + NS-SED = nonsterile surface water–sediment system.

<sup>c</sup> Metolachlor = (2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(methoxyprop-2-yl)acetamide.

<sup>d</sup> Extractable degradates = sum of extractable degradates including the carbinol, morpholinone, polar, and unknown degradates.

<sup>e</sup> Carbinol = *N*-(2-ethyl-6-methylphenyl)-2-hydroxy-*N*-(2-methylethyl)-acetamide.

<sup>f</sup> Morpholinone = 4-(2-ethyl-6-methylphenyl)-5-methyl-3-morpholinone.

<sup>g</sup> Polar degradates = unknown metolachlor degradates in the solid-phase extraction (SPE) aqueous extract.

<sup>h</sup> Unknown degradates in the SPE solvent eluate.

<sup>i</sup> Solid-phase extraction loss = % of applied <sup>14</sup>C measured in the soil extract before SPE – sum of % applied <sup>14</sup>C measured in the SPE aqueous extract and solvent eluates.

### Quantifying sediment-bound residues

Air-dried extracted sediment (0.5 g dry wt) was mixed with hydrolyzed starch (0.1 g), and combusted in a Packard sample oxidizer (Packard Instruments) to determine the quantity of unextractable sediment-bound residues (Fig. 1). The resulting <sup>14</sup>CO<sub>2</sub> was trapped in Carbo-Sorb® E mixed with Permafluor V (Packard Instrument) and <sup>14</sup>C was quantified by liquid scintillation counting. The combustion efficiency was 98.7 ± 3.62%. Six pellets were combusted for each sample.

### Calculations and statistical analyses

First-order reaction kinetics [16] were used, in which the rate of degradation is directly proportional to the concentration

$$dC/dt = -kC \quad (1)$$

where *k* is the first-order rate constant and *C* is the concentration after time *t*. Logarithms of the concentrations were plotted against the incubation times (0, 16, and 60 d) to give a straight line with a slope proportional to the rate constant

$$\ln C = \ln C_0 - kt \quad (2)$$

where *C*<sub>0</sub> is the initial concentration. Timed for 50% dissipation (DT50) were calculated by the formula

$$DT50 = 0.693/k \quad (3)$$

Analysis of variance and least-square means were utilized to determine significant difference between treatments.

## RESULTS AND DISCUSSION

### Recovery of applied <sup>14</sup>C

In order to characterize the fate and distribution of metolachlor and atrazine in the surface water–sediment incubation systems, mass balances of the applied chemicals are necessary. We could account for all <sup>14</sup>C applied as the sum of remaining extractable metolachlor (0.1–64%), or atrazine (5–85%), extractable degradates (0.9–61%), unextractable sediment-bound residues (6 to 28%), CO<sub>2</sub> resulting from mineralization (<1%), volatile organic chemicals (<1%), and residues bound to SPE cartridge packing (5–23%). Overall, the average mass balance was 96.3 ± 6.8% for all metolachlor treatments and 99.8 ± 3.6% for all atrazine treatments.

### Metolachlor

*Change in surface water concentrations.* Metolachlor concentrations were more rapidly reduced in the water of the surface water–sediment incubation systems than in the sediment-free incubation systems. After 16 and 60 d, only 23.7 and 0.7%, respectively, of the applied metolachlor remained in the water of the surface water–sediment systems, whereas 61.2 and 27.0% remained in the water of the sediment-free system (Table 2). The quantity of metolachlor remaining in the water of the sediment-free system was almost 34 times greater than the quantity measured in water column of the surface water–sediment system at 60 d. Time for 50% dissipation was 33 and 8 d for surface water and surface water–sediment systems, respectively (Table 3). Volatilization did not contribute to the reduction in metolachlor concentrations be-

Table 3. First-order time for 50% dissipation (DT50) values of metolachlor and atrazine

Incubation system <sup>a</sup>	Sediment	Autoclaved	Metolachlor		Atrazine	
			DT50 <sup>b</sup> (d)	( <i>r</i> <sup>2</sup> )	DT50 <sup>b</sup> (d)	( <i>r</i> <sup>2</sup> )
NS-SW	No	No	33	(0.94)	150	(0.76)
NS-SW + NS-SED	Yes	No	8	(0.97)	42	(0.99)
ST-SW	No	Yes	97	(0.86)	177	(0.69)
ST-SW + ST-SED	Yes	Yes	8	(0.69)	117	(0.78)

<sup>a</sup> One hundred fifty milliliters of herbicide-treated surface water (SW) or 150 ml of herbicide-treated surface water and 50 g (dry wt) of sediment (SW + SED). NS = nonsterile; ST = autoclaved for 1 h at 121 ± 2°C on two consecutive days; NS-SW = nonsterile surface water; NS-SW + NS-SED = nonsterile surface water and nonsterile sediment; ST-SW = autoclaved surface water, ST-SW + ST-SED = autoclaved surface water and autoclaved sediment.

<sup>b</sup> DT50 = time for 50% dissipation; calculated based on first-order reaction kinetics.

cause no organic volatiles were measured in either system (Table 2). After 60 d, more than one quarter of the applied <sup>14</sup>C had partitioned with the sediment and more than one half was identified as metolachlor degradates in the water, suggesting that both sorption and degradation (biotic, abiotic, or both) are important to the reduction of metolachlor in the surface water of the surface water–sediment systems.

**Sorption to sediment.** The percentages of applied <sup>14</sup>C associated with the sediment at 16 and 60 d represented 33.2% and 29.8% of the applied <sup>14</sup>C, respectively (Table 2). Characterization of the sediment extracts showed that sediments contained both [<sup>14</sup>C]metolachlor and [<sup>14</sup>C]metolachlor degradates. The ratios of metolachlor to metolachlor degradates extracted from the sediment at 16 and 60 d were 1:1 and 1:15, respectively. Although the total quantity of extractable <sup>14</sup>C from the sediment remained relatively constant from 16 d (11.8%) to 60 d (9.8%), the percentage of extractable degradates almost doubled (from 5.2% to 9.2%), whereas the percentage of extractable metolachlor was reduced by an order of magnitude (from 6.6% to 0.6%). Unextractable sediment-bound residues represented approximately 20% of the applied <sup>14</sup>C (21.4% at 16 d and 20.0% at 60 d).

**Degradation.** Extractable degradates represented 37.4 and 18.5% of the applied <sup>14</sup>C in the water of the surface water–sediment systems and the sediment-free systems, respectively, at 16 d (Table 2). After 60 d, more than 45% of the applied <sup>14</sup>C was characterized as metolachlor degradates. Less than 1% of the applied metolachlor remained in the water of the surface water–sediment system, whereas 27.0% remained in sediment-free surface water system. The quantity of extractable degradates detected in the water was 87 times greater than the quantity of metolachlor extracted from the water of the surface water–sediment system at 60 d. A greater percentage of the applied <sup>14</sup>C was identified as carbinol, morpholinone, and polar degradates (degradation products of which we did not have known standards) in the water of the surface water–sediment systems compared to the sediment-free systems. The increase in polar degradates measured in the water of the water–sediment system possibly is the result of the formation of carboxylic acid and sulfonic acid degradates, which were not identified with the methods of extraction and analysis utilized in this study. LeBaron et al. [17] reported that the carboxylic acid degradate of metolachlor, the oxidized version of the carbinol degradate, was the major degradation product of metolachlor in soil. In addition, Aga et al. [18] identified an ethanesulfonic acid metabolite of metolachlor, which is formed via a glutathione conjugation pathway in soil. The presence of sediment in the surface water–sediment systems may have

enhanced the formation of these degradates relative to the sediment-free system. Unknown less-polar degradates, measured in the SPE solvent eluates, accounted for 34% of the applied <sup>14</sup>C for both incubation systems at 60 d. Mineralization of [<sup>14</sup>C]metolachlor to [<sup>14</sup>CO<sub>2</sub>] was minimal (≤0.2%).

**Biotic versus abiotic degradation.** Pesticides can undergo biotic degradation (biodegradation, cometabolism, conjugation, and accumulation) and abiotic degradation (chemical hydrolysis and photochemical degradation), which may occur simultaneously [19,20]. Distinguishing between abiotic and biotic transformations of pesticides often is difficult. In an attempt to assess the influence of microbial degradation on the reduction of metolachlor concentrations from the surface water, additional studies were conducted with autoclaved (sterile) surface water systems (ST-SW). Metolachlor concentrations were significantly (*p* < 0.001) greater in the operationally defined sterile water of the sediment-free surface water system relative to the nonsterile system (ST-SW = 63.8% and NS-SW = 27.0% at 60 d; Fig. 2A). The quantity of total degradates detected in the water of the ST-SW systems was three times less than the quantity of total degradates measured in the water of the NS-SW systems (NS-SW = 46.3% and ST-SW = 13.8%). The first-order half-life of metolachlor was 97 d in the ST-SW system and 33 d in the NS-SW system (Table 3). Photodegradation of metolachlor in lake water has been shown to enhance metolachlor dissipation with near-surface half-lives of 22 and 205 d in the summer and winter, respectively [12]. The detection of degradates in the ST-SW systems suggests that abiotic degradation occurred, which may have included photodegradation. The difference in quantity of degradates measured in the nonsterile and sterile surface water systems demonstrates greater biotic than abiotic degradation of metolachlor in these surface water systems (assumption: ST-SW = 13.8% degradates = 13.8% abiotic degradation; NS-SW = 46.3% degradates, therefore 46.3 – 13.8 = 32.5% biotic degradation).

Abiotic transformation of pesticides can occur in sediment by hydrolysis and redox reactions. In many cases of pesticide transformation, a solid phase alters the kinetics of hydrolysis but the degradation products are the same as those resulting from hydrolysis in clear water [20]. The concentrations of metolachlor and metolachlor degradates were measured and compared from sterile surface water (ST-SW) and sterile surface water–sediment incubation systems (ST-SW + ST-SED) treated with [<sup>14</sup>C]metolachlor (Table 4). After 60 d, less than 1% of the applied metolachlor remained in the water of the sterile systems containing sediment, whereas 63.8% remained in the sterile surface water of the sediment-free system. Al-

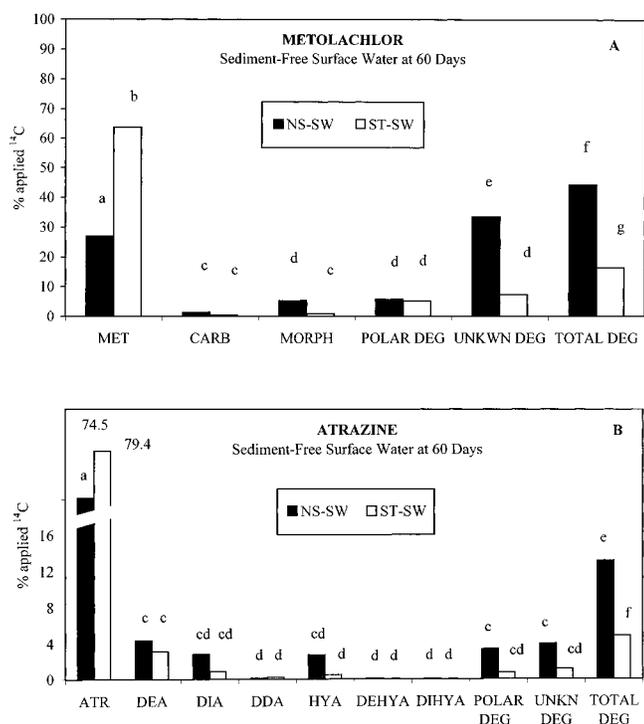


Fig. 2. Influence of microbial degradation on the dissipation of (A) metolachlor and (B) atrazine in sediment-free surface water incubation systems. Bars with the same letter are not statistically different ( $p = 0.05$ ). NS-SW = nonsterile surface water incubation systems; ST-SW = sterile (autoclaved) surface water incubation systems; MET = metolachlor; CARB = carbinol degradate; MORPH = morpholinone degradate; ATR = atrazine; DEA = deethylatrazine; DIA = deisopropylatrazine; DDA = didealkylatrazine; HYA = hydroxyatrazine; DEHYA = deethylhydroxyatrazine; DIHYA = deisopropylhydroxyatrazine; POLAR DEG = polar degradates = unknown degradates in the solid-phase extraction (SPE) aqueous extract; UNKWN DEG = unknown degradates in the SPE solvent eluate; TOTAL DEG = sum of extractable degradates.

though one half of the applied  $^{14}\text{C}$  partitioned with the sediment (52.6%), the twofold greater quantity of degradates measured in the water of the sterile surface water-sediment systems (31.8%) relative to the sterile sediment-free systems (13.8%) suggests greater metolachlor degradation in the presence of the sediment. Sediments were autoclaved and sediment slurries were evaluated for microbial growth before the addition of sterile surface water containing  $^{14}\text{C}$ metolachlor. Assuming that the incubation systems remained sterile, we can estimate that 18% of the degradates measured in the surface water resulted from abiotic degradation associated with the sediment (assumption: ST-SW = 13.8% degradates = 13.8% abiotic degradation; ST-SW + ST-SED = 31.8% degradates, therefore  $31.8 - 13.8 = 18.0\%$  abiotic degradation associated with the presence of the sediment).

Overall, both biotic and abiotic degradation of metolachlor resulted in the reduction of metolachlor concentrations in the surface water of the incubation systems evaluated. The percentages of applied  $^{14}\text{C}$ metolachlor measured as  $^{14}\text{C}$ degradates in the surface water of the incubation systems at 60 d were, from least to greatest, 13.8% (ST-SW) < 31.8% (ST-SW + ST-SED) < 46.3% (NS-SW) < 60.6% (NS-SW + NS-SED). It is no surprise that the greatest quantity of degradates in the surface water occurred in the NS-SW + NS-SED systems, in which microorganisms

Table 4. Distribution of  $^{14}\text{C}$ metolachlor and  $^{14}\text{C}$ metolachlor-degradates in the surface water and sediment of the autoclaved incubation systems (reported as percentage of applied  $^{14}\text{C}$ )

	60-d incubation <sup>a</sup>		
	ST-SW <sup>b</sup>	ST-SW + ST-SED <sup>b</sup>	
	Water	Water	Sediment
Metolachlor <sup>c</sup>	63.8 A	0.8 B	0.1 B
Extractable degradates <sup>d</sup>	13.8 C	31.8 D	24.4 E
Carbinol <sup>e</sup>	0.4 B	0.2 B	0.0 B
Morpholinone <sup>f</sup>	0.9 B	1.7 B	0.8 B
Polar degradates <sup>g</sup>	5.1 F	1.4 B	1.0 B
Unknown degradates <sup>h</sup>	7.4 F	28.5 D	22.6 E
Sediment-bound residues			28.1 G
Total $^{14}\text{C}$ in water	77.6 H		32.6 D
Total $^{14}\text{C}$ in sediment			52.6 I
CO <sub>2</sub>	0.8 B		0.1 B
Organic volatiles	0.0 B		1.2 B
SPE loss <sup>i</sup>	23.2 E		10.9 C
Total $^{14}\text{C}$	101.6 J		97.4 K

<sup>a</sup> Incubated in a temperature-controlled greenhouse ( $25 \pm 2^\circ\text{C}$ ) with a 14:10 h light:dark photoperiod for the duration of the experiment. Means in each row followed by the same letter are not statistically different ( $p = 0.05$ ).

<sup>b</sup> ST-SW = sterile surface water system without sediment; ST-SW + ST-SED = sterile surface water + sterile sediment system. For the sterile incubation systems, surface water and sediments were autoclaved for 1 h at  $121 \pm 2^\circ\text{C}$  on two consecutive days before the application of  $^{14}\text{C}$ metolachlor.

<sup>c</sup> Metolachlor = (2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(methoxyprop-2-yl)acetamide).

<sup>d</sup> Extractable degradates = sum of extractable degradates including the carbinol, morpholinone, polar, and unknown degradates.

<sup>e</sup> Carbinol = *N*-(2-ethyl-6-methylphenyl)-2-hydroxy-*N*-(2-methyl-ethyl)-acetamide.

<sup>f</sup> Morpholinone = 4-(2-ethyl-6-methylphenyl)-5-methyl-3-morpholinone.

<sup>g</sup> Polar degradates = unknown metolachlor degradates in the solid-phase extraction (SPE) aqueous extract.

<sup>h</sup> Unknown degradates in the SPE solvent eluate.

<sup>i</sup> Solid-phase extraction loss = % of applied  $^{14}\text{C}$  measured in the soil extract before SPE - sum of percentage applied  $^{14}\text{C}$  measured in the SPE aqueous extract and solvent eluates.

in the surface water and sediment may contribute to the biodegradation of metolachlor in addition to degradation resulting from abiotic processes.

### Atrazine

**Change in surface water concentrations.** The quantity of atrazine measured in the surface water of the surface water-sediment incubation systems was significantly less than the quantity measured in the surface water of the sediment-free incubation systems. After 60 d, 74.2% of the applied atrazine remained in the surface water of the sediment-free incubation systems, whereas only 36.7% of the applied atrazine was measured in the water of the surface water-sediment systems, representing a 38% reduction (Table 5). Time for 50% dissipation was 150 d and 42 d for surface water and surface water-sediment systems, respectively (Table 3). No  $^{14}\text{C}$ -organic volatiles were measured in either system; therefore, surface water concentrations of atrazine were not reduced as a result of volatilization (Table 5). After 60 d, almost one quarter of the applied  $^{14}\text{C}$  was identified as atrazine degradates in the water, whereas more than 30% had partitioned with the sediment, suggesting that both degradation and sorption are important

Table 5. Distribution of [<sup>14</sup>C]atrazine and [<sup>14</sup>C]atrazine degradates in surface water and sediment (reported as percentage of applied <sup>14</sup>C)

	16-d incubation <sup>a</sup>			60-d incubation <sup>a</sup>		
	NS-SW <sup>b</sup>	NS-SW + NS-SED <sup>b</sup>		NS-SW <sup>b</sup>	NS-SW + NS-SED <sup>b</sup>	
	Water	Water	Sediment	Water	Water	Sediment
Atrazine <sup>c</sup>	85.0 A	74.6 B	7.6 C	74.2 B	36.7 D	5.5 E
Extractable degradates <sup>d</sup>	7.5 C	8.3 F	1.1 G	17.5 H	23.5 I	3.0 J
DEA <sup>e</sup>	2.7 J	2.7 J	0.2 K	4.3 L	7.6 C	0.3 K
DIA <sup>f</sup>	1.4 GM	1.3 GM	0.1 K	2.8 J	4.5 L	0.2 K
DDA <sup>g</sup>	0.1 K	1.7 M	0.0 K	0.1 K	2.6 J	0.0 K
HYA <sup>h</sup>	0.7 G	0.2 K	0.4 K	2.7 J	2.7 J	0.8 G
DEHYA <sup>i</sup>	0.0 K	0.0 K	0.0 K	0.1 K	0.0 K	0.0 K
DIHYA <sup>j</sup>	0.0 K	0.0 K	0.0 K	0.1 K	0.0 K	0.0 K
Polar degradates <sup>k</sup>	1.1 G	1.3 GM	0.3 K	3.4 J	4.7 L	1.5 GM
Unknown degradates <sup>l</sup>	1.5 GM	1.1 G	0.1 K	4.0 L	1.4 GM	0.2 K
Sediment-bound residues			5.1 E			25.6 N
Total <sup>14</sup> C in water	92.5 O	82.9 P		91.7 Q	60.2 R	
Total <sup>14</sup> C in sediment		13.8 S			34.1 T	
CO <sub>2</sub>	0.0 K	0.0 K		0.0 K	0.1 K	
Organic volatiles	0.0 K	0.0 K		0.0 K	0.0 K	
SPE loss <sup>m</sup>	6.8 U	6.0 V		4.3 L	3.0 J	
Total <sup>14</sup> C	99.3 W	102.7 X		96.0 Y	97.4 Z	

<sup>a</sup> Incubated in a temperature-controlled greenhouse (25 ± 2°C) with a 14:10 h light:dark photoperiod for the duration of the experiment. Means in each row followed by the same letter are not statistically different (*p* = 0.05).

<sup>b</sup> NS-SW = nonsterile surface water system without sediment; NS-SW + NS-SED = nonsterile surface water–sediment system.

<sup>c</sup> Atrazine (6-chloro-*N*-ethyl-*N'*-(1-methylethyl)-1,3,5-triazine-2,4-diamine).

<sup>d</sup> Extractable degradates = sum of extractable degradates including the DEA, DIA, DDA, HYA, DEHYA, DIHYA, polar degradates, and unknown degradates.

<sup>e</sup> DEA = deethylatrazine (2-chloro-4-amino-6-(isopropylamino)-*s*-triazine).

<sup>f</sup> DIA = deisopropylatrazine (2-chloro-4-(ethylamino)-6-(amino)-*s*-triazine).

<sup>g</sup> DDA = didealkylatrazine (2-chloro-4,6-diamino-*s*-triazine).

<sup>h</sup> HYA = hydroxyatrazine (2-hydroxy-4(ethylamino)-6(isopropylamino)-*s*-triazine).

<sup>i</sup> DEHYA = deethylhydroxyatrazine (2-hydroxy-4-amino-6(isopropylamino)-*s*-triazine).

<sup>j</sup> DIHYA = deisopropylhydroxyatrazine (2-hydroxy-4(ethylamino)-6(amino)-*s*-triazine).

<sup>k</sup> Polar degradates = unknown metolachlor degradates in the solid-phase extraction (SPE) aqueous extract.

<sup>l</sup> Unknown degradates in the SPE solvent eluate.

<sup>m</sup> Solid-phase extraction loss = % of applied <sup>14</sup>C measured in the soil extract before SPE – sum of % applied <sup>14</sup>C measured in the SPE aqueous extract and solvent eluates.

to the reduction of atrazine in the surface water of the surface water–sediment systems.

**Sorption to sediment.** Fourteen and 34% of the applied <sup>14</sup>C was associated with the sediment at 16 and 60 d, respectively (Table 5). Sediment extracts contained both [<sup>14</sup>C]atrazine and [<sup>14</sup>C]atrazine degradates. Although the quantity of extractable <sup>14</sup>C from the sediment (atrazine + extractable degradates) was similar at 16 and 60 d (8.7 and 8.5%), the quantity of extractable atrazine decreased from 7.6 to 5.5% as the percentage of extractable degradates increased from 1.1 to 3.0%. Sediment-bound residues increased from 5.1 to 25.6%. The fivefold increase of sediment-bound residues from 16 to 60 d may be the result of the degradation of atrazine to hydroxyatrazine, which has been shown to occur as a result of biological, chemical, and photolytic hydrolysis [21–23]. Hydroxylated atrazine degradation products have been detected in surface waters [24]. Hydroxyatrazine has been shown to form electron-transfer complexes with humic substances in soil [25] and is more readily adsorbed than ATR, DEA, and DIA to terrestrial soil [26], wetland soil [27], and aquifer solids [28]. In water–sediment systems treated with [<sup>14</sup>C]atrazine, Mersie et al. [29] observed that increased retention of <sup>14</sup>C by sediment coincided with greater detection of HYA. Runes et al. [30] reported that

HYA was the predominant degradate in the sediment of laboratory wetland microcosm. In this study, sediments were extracted three times with aqueous methanol. Further extraction of the sediment with a mixture of KH<sub>2</sub>PO<sub>4</sub> and CH<sub>3</sub>CN may have resulted in the recovery of additional atrazine degradates, particularly HYA, as reported by Lerch et al. [31,32].

**Degradation.** Greater quantities of atrazine degradates were detected in the surface water of the surface water–sediment systems than in the sediment-free systems (Table 5). After 60 d, one quarter of the applied <sup>14</sup>C was characterized as atrazine degradates (23.5% extracted from the water and 3.0% extracted from the sediment) in the surface water–sediment systems, whereas only 17.5% was identified as atrazine degradates in the sediment-free systems. This may be the result of greater hydrolysis in the presence of sediment as a result of sorption-catalyzed decomposition [33]. No individual degradate represented more than 8% of the applied <sup>14</sup>C. Deethylatrazine was the most abundant degradate extracted from the water of the sediment-free and surface water–sediment systems at 16 and 60 d. After 60 d, greater quantities of DEA, DIA, and DDA were detected in the water of the surface water–sediment incubation systems compared to the sediment-free systems, whereas levels of HYA, DEHYA, and DIHYA were not sta-

tistically different. Deethylatrazine, DIA, and HYA also were detected in the sediment extract but each represented less than 1% of the applied  $^{14}\text{C}$ . Total unidentified degradates extracted from the water and the sediment accounted for less than 8% of the applied  $^{14}\text{C}$ . The mineralization of  $^{14}\text{C}$ -atrazine to  $^{14}\text{CO}_2$  was insignificant ( $\leq 0.1\%$ ).

**Biotic versus abiotic degradation.** In order to determine the influence of microbial degradation on the reduction of atrazine concentrations from the surface water, additional studies were conducted with autoclaved surface water (ST-SW). At 60 d, greater than 74% of the applied [ $^{14}\text{C}$ ] atrazine remained in both the nonsterile and sterile sediment-free surface water (Fig. 2B). No significant difference was found in the quantities of DEA, DIA, DDA, HYA, DEHYA, and DIHYA extracted from the water of the NS-SW or ST-SW systems after 60 d. However, the sum of degradates (total degradates) was significantly greater ( $p < 0.05$ ) for the nonsterile incubation systems. Extrapolated DT50s of atrazine in the ST-SW and NS-SW systems were 177 and 150 d, respectively (Table 3). The detection of degradates in the ST-SW systems demonstrates that abiotic degradation occurred. However, the difference in quantity of total degradates measured in the nonsterile and sterile surface water systems suggests greater biodegradation than abiotic degradation of atrazine (assumption: ST-SW = 6.8% total degradates = 6.8% abiotic degradation; NS-SW = 17.5% total degradates, therefore  $17.5 - 6.8 = 10.7\%$  biotic degradation).

Mass balance analyses from the sterile sediment-free surface water systems (ST-SW) and the sterile surface water-sediment system (ST-SW + ST-SED) were compared to determine if the presence of sediment influenced the degradation of atrazine (Table 6). Sediments were autoclaved and sediment slurries evaluated for microbial growth before the addition of sterile surface water containing [ $^{14}\text{C}$ ]atrazine. After 60 d, 11% more atrazine was detected in the water of the sterile sediment-free surface water systems (79.4%) compared to the water of the sterile systems containing sediment (68.4%). Seventeen percent of the  $^{14}\text{C}$  applied to the surface water of the ST-SW + ST-SED system was associated with the sediment as unextractable bound residues (6.1%), extractable atrazine (10%), and extractable atrazine degradates (0.9%). The difference in atrazine concentrations in the surface water of the sterile systems apparently was primarily the result of sorption rather than abiotic degradation because concentrations of extractable degradates measured in the surface water of the sediment-free and surface water-sediment systems were identical (6.8%). We were unable to characterize the sediment-bound residues. Some of the unextractable residues possibly are atrazine degradates, primarily hydroxyatrazine. Researchers have reported more rapid hydrolysis of atrazine to hydroxyatrazine in sterilized soil compared to soil-free systems, which suggests that soil catalyzed hydrolysis reactions [34]. Hydroxyatrazine can be formed as a result of photolytic hydrolysis or chemical or biological degradation [21–23]; has been found to be a predominant degradate in sediment [30]; is more readily adsorbed to wetland soils and aquifer solids than atrazine [27,28]; and has a greater sorption coefficient than ATR, DIA, or DEA [26–28], which suggests the sediment-bound residues would primarily consist of HYA. This is further implied by the results of Lerch et al. [31], who reported exhaustive mixed-mode extraction of soil-bound residues from aqueous methanol-extracted atrazine-treated soil, recovered substantial quantities of HYA. Other studies have observed that a greater detection of HYA coincides with the increased retention of  $^{14}\text{C}$  by sediment

Table 6. Distribution of [ $^{14}\text{C}$ ]atrazine and [ $^{14}\text{C}$ ]atrazine degradates in the surface water and sediment of the autoclaved incubation systems (reported as percentage of applied  $^{14}\text{C}$ )

	60-d incubation <sup>a</sup>		
	ST-SW <sup>b</sup>	ST-SW + ST-SED <sup>b</sup>	
	Water	Water	Sediment
Atrazine <sup>c</sup>	79.4 A	68.4 B	10.0 C
Extractable degradates <sup>d</sup>	6.8 D	6.8 D	0.9 E
DEA <sup>e</sup>	3.1 F	1.9 E	0.1 E
DIA <sup>f</sup>	0.9 E	1.3 E	0.1 E
DDA <sup>g</sup>	0.2 E	1.2 E	0.0 E
HYA <sup>h</sup>	0.5 E	0.8 E	0.2 E
DEHYA <sup>i</sup>	0.1 E	0.0 E	0.0 E
DIHYA <sup>j</sup>	0.0 E	0.0 E	0.0 E
Polar degradates <sup>k</sup>	0.8 E	0.6 E	0.3 E
Unknown degradates <sup>l</sup>	1.2 E	1.0 E	0.2 E
Sediment-bound residues			6.1 D
Total $^{14}\text{C}$ in water	86.2 G	75.2 H	
Total $^{14}\text{C}$ in sediment		17.0 I	
$\text{CO}_2$	0.0 E	0.0 E	
Organic volatiles	0.0 E	0.2 E	
SPE loss <sup>m</sup>	19.4 J	5.5 D	
Total $^{14}\text{C}$	105.6 K	97.9 L	

<sup>a</sup> Incubated in a temperature-controlled greenhouse ( $25 \pm 2^\circ\text{C}$ ) with a 14:10 h light:dark photoperiod for the duration of the experiment. Means in each row followed by the same letter are not statistically different ( $p = 0.05$ ).

<sup>b</sup> ST-SW = sterile surface water system without sediment; ST-SW + ST-SED = sterile surface water + sterile sediment system. For the sterile incubations systems, surface water and sediments were autoclaved for 1 h at  $121 \pm 2^\circ\text{C}$  on two consecutive days before the application of [ $^{14}\text{C}$ ]atrazine.

<sup>c</sup> Atrazine (6-chloro-*N*-ethyl-*N'*-(1-methylethyl)-1,3,5-triazine-2,4-diamine).

<sup>d</sup> Extractable degradates = sum of extractable degradates including the DEA, DIA, DDA, HYA, DEHYA, DIHYA, polar, and unknown degradates.

<sup>e</sup> DEA = deethylatrazine (2-chloro-4-amino-6-(isopropylamino)-*s*-triazine).

<sup>f</sup> DIA = deisopropylatrazine (2-chloro-4-(ethylamino)-6-(amino)-*s*-triazine).

<sup>g</sup> DDA = didealkylatrazine (2-chloro-4,6-diamino-*s*-triazine).

<sup>h</sup> HYA = hydroxyatrazine (2-hydroxy-4(ethylamino)-6(isopropylamino)-*s*-triazine).

<sup>i</sup> DEHYA = deethylhydroxyatrazine (2-hydroxy-4-amino-6(isopropylamino)-*s*-triazine).

<sup>j</sup> DIHYA = deisopropylhydroxyatrazine (2-hydroxy-4(ethylamino)-6(amino)-*s*-triazine).

<sup>k</sup> Polar degradates = unknown atrazine degradates in the solid-phase extraction (SPE) aqueous extract.

<sup>l</sup> Unknown degradates in the SPE solvent eluate.

<sup>m</sup> Solid-phase extraction loss = % of applied  $^{14}\text{C}$  measured in the soil extract before SPE – sum of % applied  $^{14}\text{C}$  measured in the SPE aqueous extract and solvent eluates.

[29]. This also was noted in our study when the nonsterile and sterile surface water-sediment systems were compared (Tables 5 and 6). The nonsterile system had a greater quantity of HYA extracted from the surface water (0.8% nonsterile and 0.2% sterile) along with a greater percentage of the applied  $^{14}\text{C}$  associated with the sediment (34.1% nonsterile and 17.0% sterile), greater quantities of bound residues (25.6% nonsterile and 6.1% sterile), more extractable degradates (3.0% nonsterile and 0.9% sterile), and less extractable atrazine (5.5% sterile and 10.0% nonsterile).

#### *Metolachlor versus atrazine*

Distribution of  $^{14}\text{C}$  in the surface water and sediment of the [ $^{14}\text{C}$ ]metolachlor- and [ $^{14}\text{C}$ ]atrazine-treated nonsterile surface

water-sediment systems was similar (MET = 61.3% in water and 29.8% in sediment; ATR = 60.2% in water, 34.1% in sediment) despite the greater water solubility and soil sorption coefficient ( $K_{oc}$ ) of metolachlor relative to atrazine (Table 1) [35]. The dissipation of metolachlor from surface water was more rapid than the dissipation of atrazine from surface water. Calculated DT50s of atrazine in the nonsterile surface water and surface water-sediment systems were five times longer than the DT50s of metolachlor in the same incubation systems (Table 3). The 42-d half-life of atrazine in the nonsterile surface water-sediment system was similar to calculated half-lives of atrazine in the Minnesota River (MN, USA) in 1990 and 1991 (21–58 d) [36]. Our observation of longer DT50s for atrazine compared to metolachlor are in agreement with the findings of laboratory experiments and surface water monitoring studies that have shown atrazine to be more prevalent than metolachlor in soil and water, and more frequently detected in surface waters [1,37]. Thurman et al. [38] reported the presence of atrazine in 98% of the 149 surface waters sampled. Goolsby et al. [39] measured pesticide residues in surface waters of the upper midwestern United States and reported that atrazine and metolachlor, some of the most heavily used herbicides in the region, were two of the four most frequently detected herbicides. Atrazine was detected year-round in the majority of streams sampled, whereas metolachlor and DEA, an atrazine degradate, were detected year-round at approximately one half of the sampling sites [39].

#### Environmental relevance

The wide use of pesticides has resulted in human and environmental exposure and prompted questions about the toxicological and ecological effects of pesticides on target and nontarget species. In order to assess potential hazards posed by pesticides, we need to understand their chemistry and behavior in the environment, which will impact their bioavailability, toxicity, and ecological significance.

Whether pesticides in surface water remain in the water column or become associated with sediments will impact their persistence and bioavailability. Dissolved organic matter has been shown to retard photodegradation of metolachlor [12], whereas sterilized soil catalyzed the hydrolysis of atrazine to hydroxyatrazine [34]. Sorption-desorption interactions of pesticides with sediment determine their availability for exposure to sensitive organisms or for microbial degradation. The availability of a pesticide in soil is dependent on how readily the compound is desorbed. Therefore, weakly bound and easily desorbed compounds would be readily available, whereas strongly sorbed or bound residues would be unavailable. Sorption of pesticides to soil can increase with time, demonstrating an aging effect [40].

Abiotic or biotic transformation of pesticides may result in intermediate compounds or environmentally stable degradates that are more or less toxic than the original chemical residue [20]. This was noted with alkyl-aniline metabolites of alachlor and metolachlor that were more toxic to *Vibrio fischeri* than the parent compound [41]. The ecological significance of pesticides and pesticide degradates may be difficult to estimate because of their sorption to particulates and their occurrence as complex mixtures. Typically, atrazine has been found to be nontoxic at environmentally relevant concentrations [42], with atrazine degradates even less toxic than their parent compound [43]. However, atrazine has been shown to have synergistic toxicity in which the presence of atrazine increased the toxicity

of chlorpyrifos, methyl parathion, and diazinon. Researchers speculate this may be the result of atrazine increasing the biotransformation or induction of xenobiotic metabolizing systems, thereby converting other xenobiotics into more- or less-toxic metabolites [44].

These are just a few examples illustrating the importance of understanding the environmental fate and bioavailability of pesticides as they are influenced by sorption and biotic and abiotic transformations. Data collected from this research (dissipation rates, partitioning characteristics, formation of increased sediment-bound residues with time, and the characterization and quantification of extractable degradates in the water and sediment) can contribute to the body of knowledge utilized with predictive models to assess the environmental fate of pesticides and to perform risk assessment analyses.

#### CONCLUSION

The presence of sediment in the surface water-sediment systems enhanced the dissipation of metolachlor and atrazine from the surface water. This was observed when sediment-free and surface water-sediment systems were compared for nonsterile and sterile systems. Volatilization did not contribute to the reduction of metolachlor or atrazine concentrations in the surface water; however, sorption, biodegradation, and abiotic degradation were important.

For metolachlor, approximately one quarter of the applied radioactivity partitioned with the sediment, whereas more than one half was identified as metolachlor degradates in the surface water. Residues in the sediment were primarily unextractable bound residues; however, extractable metolachlor and metolachlor degradates were measured. The presence of sediment did result in the detection of greater quantities of degradates in the surface water of both the autoclaved and nonsterile systems. Sediment-free systems revealed that both abiotic and biotic degradation of metolachlor occurred in the surface water, with the later accounting for a greater percentage of the degradates.

Similar to metolachlor, approximately one quarter of the applied radioactivity associated with atrazine partitioned with the sediment after 60 d. However, unlike metolachlor, the percentage of unextractable-bound residues significantly increased from 16 to 60 d. Atrazine and atrazine degradates were extracted from the sediment but they represented less than one half of the radioactivity measured in the sediment with unidentified bound residues accounting for the rest. In our incubation systems, both abiotic and biotic degradation of atrazine occurred in the sediment-free surface waters. The presence of sediment did reduce the concentration of atrazine remaining in the surface water. The quantity of degradates measured in the water of the nonsterile surface water-sediment systems was greater than the nonsterile sediment-free water but this was not true for the autoclaved systems. Sorption to the sediment apparently was the primary means of atrazine reduction in the sterile surface water-sediment systems; however, we were unable to identify the unextractable sediment-bound residues, which may have resulted from the catalyzed hydrolysis of atrazine to hydroxyatrazine, which is more readily sorbed.

The results of this research illustrate the importance of sediment in the fate of pesticides in surface water. Greater comprehension of the role of sediment to influence degradation and bioavailability of agricultural contaminants in aquatic sys-

tems will provide a better understanding of the potential toxicity of these compounds to aquatic organisms.

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