Effects of Hydrophyte Community Structure on Atrazine and Alachlor Degradation in Wetlands

K.E. Lee, D.G. Huggins, E.M. Thurman [1]

Abstract

This research assessed the effects of the hydrophyte community structure in wetland mesocosms on the degradation of two commonly used herbicides, atrazine and alachlor. The research was conducted for 383 days at the University of Kansas Nelson Environmental Study Area near Lawrence, Kansas. Wetland treatments, consisting of three mesocosms each, included open-water mesocosms with no or limited macrophyte communities, mesocosms with a predominate submergent hydrophyte community (Potamogeton spp. and Najas quadalupensis), and mesocosms dominated by an emergent hydrophyte community (Typha latifolia and T. augustifolia). Atrazine and alachlor were added to wetland mesocosms to obtain approximate concentrations of 25 g/L each. Atrazine mass loss was more rapid in the emergent mesocosms than in the open or submergent mesocosms. The dissipation half-life of atrazine mass in the emergent mesocosms was 58-70 days compared to 85-115 days for the open and submergent mesocosms. Alachlor dissipated more rapidly than atrazine under all treatments. More than 50% of the alachlor concentration and mass were lost within 21 days under all treatments (dissipation half-life of alachlor mass ~ 10 to 20 days). Deethylatrazine (DEA) was a metabolite of atrazine detected in all mesocosms. The mean DEA-to-atrazine ratio (DAR) under all treatments increased during the two growing seasons and stabilized during the winter when biological communities and processes are relatively inactive. The DAR was significantly different among the treatments (emergent > submergent > open) for the first 126 days. These results indicate that (1) hydrophytes were not as important as other factors in alachlor degradation, and (2) wetland hydrophyte community structure (i.e. open, submergent, or emergent) was the primary ecological determinant of atrazine degradation rate.

Keywords: Atrazine, Alachlor, Degradation, Wetlands, Hydrophytes, Community structure.

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Introduction

Atrazine (2-chloro-4-ethylamino-6-isopropylamine-s-triazine) and alachlor [2 - chloro-N-(2,6 - diethylphenyl) -N- (methoxymethyl)-acetamide] are the two most widely applied herbicides in the United States (Gianessi and Puffer, 1991) and are frequently detected in surface water. Atrazine is persistent in streams and even more persistent in reservoirs. For example, Schottler and Eisenreich (1994) found that atrazine in the Great Lakes had a half-life on the order of years. Buser (1990) reported that atrazine loss from lakes was related primarily to export and not degradation. Goolsby et al. (1993) reported more frequent herbicide detections in reservoirs than in streams, as well as longer herbicide residence times.

Herbicide persistence in water may be a result of a lack of herbicide contact with microorganisms and organic matter, which are found primarily in soils (Goolsby et al., 1993). In addition, when reservoirs continually receive incoming herbicides, concentrations remain high and degradation may not be as rapid as the inflow or inputs of contaminants (Stamer and Zelt, 1994). Alachlor appears to be less persistent than atrazine in surface water environments (Schottler et al., 1994; Stamer and Zelt, 1994; Grover and Cessna, 1991).

Previous research has shown that herbicides in aquatic systems result in species-composition shifts and reduction in productivity (deNoyelles et al., 1982; Dewey, 1986; Huggins,1990; Kettle and deNoyelles, 1990). In addition, conventional water-treatment processes only remove from 0-14% of atrazine; therefore, deterioration of drinking-water supplies is also a concern (Miltner et al., 1989).

Wetlands, acting as buffer strips between agricultural fields and aquatic systems, could improve water quality by removing contaminants through plant uptake or adsorption by organic rich soils and subsequent microbial decomposition (Pullin and Hammer, 1989). Transpiration by wetland plants translocates contaminants into the soil where degradation or adsorption may occur. Although the use of wetland systems as filters to remove contaminants has been proposed, little is known about the efficiency of wetlands in herbicide removal. Moreover, less is known about the relative efficiency of different types of wetlands to sequester and(or) degrade herbicides. Few field studies have investigated the degradation of atrazine and alachlor within wetlands composed of differing hydrophyte community structures. The objectives of this research were to design and conduct a field study for investigation of atrazine and alachlor fate in wetlands with different hydrophyte communities, and to Identify relations between vegetation type and degradation rate.

Methods

To accomplish the research objectives, a field study (March 1993 through June 1994) was conducted using wetland mesocosms. The field study was conducted at the University of Kansas Nelson Experimental Area near Lawrence, Kansas. Nine mesocosms (0.01 hectare in size) were manipulated to create three distinct treatments. Treatments, consisting of three mesocosms each, included open-water mesocosms with no or limited macrophyte communities, mesocosms with a predominate submergent hydrophyte community (Potamogeton spp. and Najas quadalupensis), and mesocosms dominated by an emergent hydrophyte community (Typha latifolia and T. augustifolia). Atrazine and alachlor were introduced into each wetland mesocosm to produce a target concentration of 25 micrograms per liter (g/L) for each herbicide.

Hydrophyte cover (percent) and(or) density (stems/m^2) were measured monthly. Water samples (1 L) were collected from three randomly selected locations within each mesocosm on each of 10 sampling dates during the first 126 days of the 383-day study. There was a gap in sample collection between day 126 and 251 during the non-growing season. Thereafter (day 251 through day 383), water samples were collected at three random locations within each mesocosm and then composited into one sample on each of 8 sampling dates. Water samples were stored on ice and transported to the laboratory for processing. One hundred and twenty-three ml of each sample were filtered through a 0.75-micrometer glass fiber filter and transferred to a cleaned, baked, amber glass bottle for herbicide analyses. Atrazine, alachlor, deethylatrazine, and deisopropylatrazine analyses were performed using methods of Thurman et al. (1990) and Meyer et al. (1993).

Results and Discussion

Herbicide data are first discussed in terms of concentration. Because initial herbicide concentrations were not equal in all mesocosms, the data were standardized to percent loss to compare concentration loss among treatments. Percent loss of herbicide concentration was calculated starting with day 6 as zero loss. Day 6 was chosen as the initial point because there was less variance in the three sample concentrations and because mixing was assumed to be complete. In addition, herbicide-concentration measures were converted to mass values to eliminate variation in concentrations caused by precipitation and evapotranspiration (volume change), and mass values were standardized to percent loss for treatment comparisons.

Atrazine

The concentration of atrazine declined in all mesocosms during the 383-day study. The most rapid loss occurred between day 6 (July 16, 1993) and day 75 (September 23, 1993) when the concentration decreased from an average of 25 μg/L to approximately 5 μg/L in all mesocosms. During the remaining 308 days, atrazine concentration slowly declined from approximately 5 μg/L to less than 2 μg/L. The percent of atrazine concentration lost in the emergent treatment was generally greater than the loss in either the open or submergent treatment throughout the

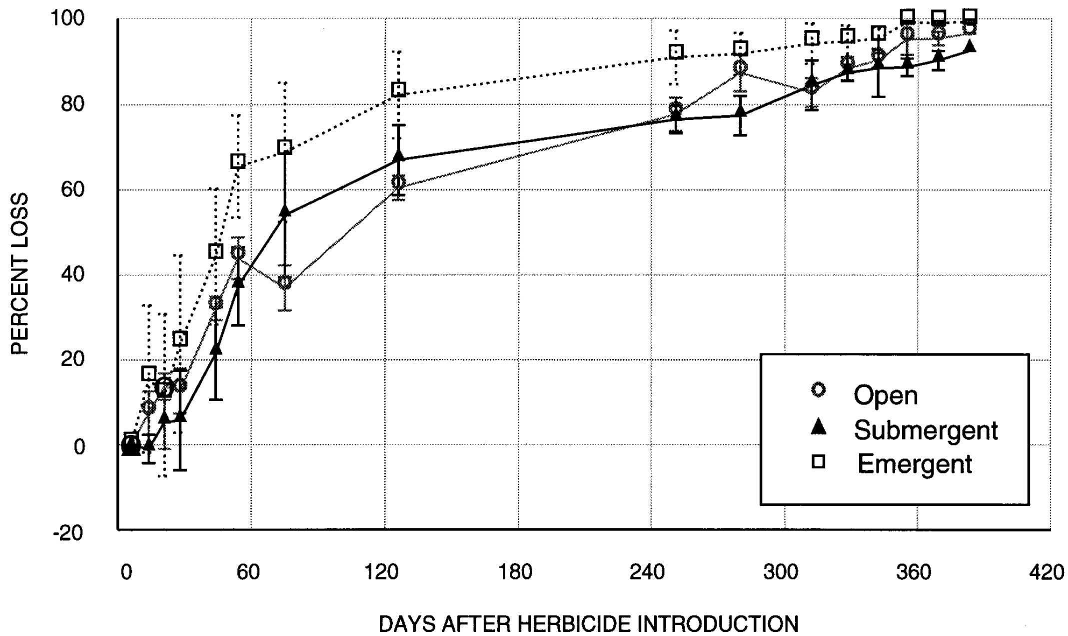

Figure 1. Mean atrazine mass (percent loss) for open, submergent, and emergent treatments. Bars show standard deviation.

study (Table 1). This greater loss in concentration in the emergent treatment suggests that the emergent hydrophyte community either directly or indirectly enhanced atrazine loss. The dissipation half-life for atrazine concentration during the 383-day study (Table 2) was shorter for the emergent treatment (62-73 days) than the open (94-99 days) or the submergent (96-112 days) treatment. These results suggest that the change in atrazine concentration was related to plant community type (i.e., highest in emergent hydrophyte systems).

Analyses of atrazine mass loss also identified significant temporal and spatial differences. A pattern of more rapid atrazine mass loss was observed in the emergent mesocosms when compared to open and submergent mesocosms. At day 54, atrazine mass percent loss in the open and submergent mesocosms ranged from 27-47%, whereas in the emergent mesocosms the losses were greater (52-72%). This trend continued throughout the first 251 days of the study (Table 1; Fig. 1). A two-way analysis of variance (ANOVA) (Zar, 1984) of atrazine mass percent loss showed a significant difference between treatments ($p < 0.05$). The post hoc Duncan's test (Zar, 1984) indicated that the open and submergent treatments formed a low-percent-loss group while the emergent treatment formed the high-percent-loss group. Whereas dilution accounts for some of the variability in concentration change especially during precipitation, it is clear from the mass data that losses were occurring through other mechanisms. These results indicate the important role of the emergent plants in atrazine mass loss.

The mean atrazine mass half-life estimates for open water and submergent treatments (89 and 107 days, respectively) were greater than the estimate for the emergent treatment (65 days). Half-lives in this study for atrazine mass loss in the

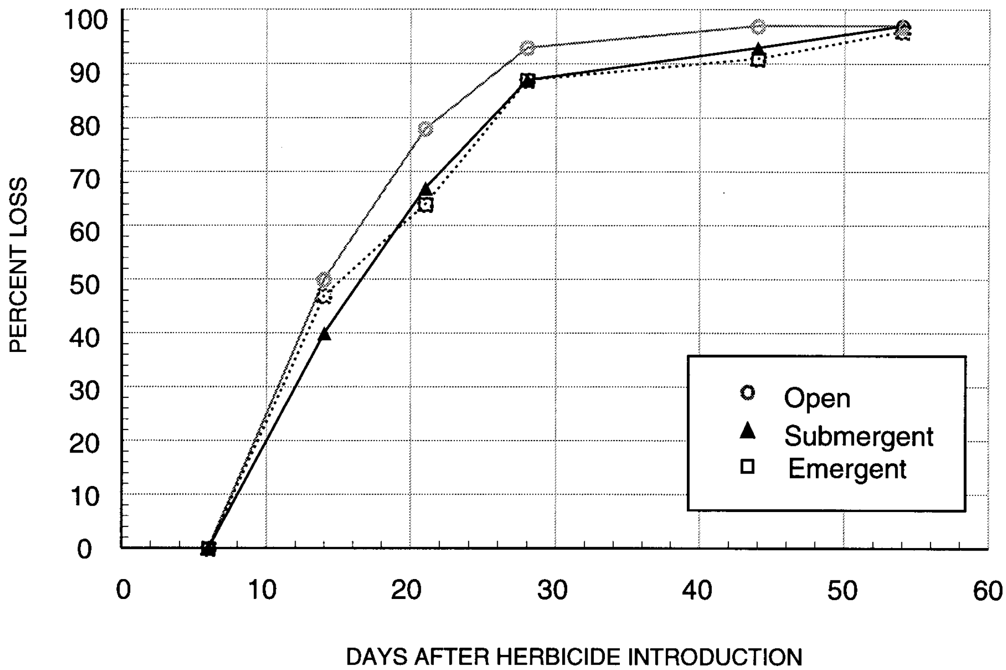

Figure 2. Mean alachlor mass (percent loss) for open, submergent, and emergent treatments.

emergent treatment (58-70 days) were between half-lives reported for soils (30-60 days) (Harris, 1967), and those reported for surface water (65-150 days) (Klassen and Kadoum, 1979; Yoo and Solomon, 1981; deNoylles et al., 1982; Bacci et al., 1989). Atrazine loss was greater in the emergent mesocosms than in the open and submergent mesocosms. Atrazine half-lives calculated from experimental-pond mass data from Huggins (1990) revealed a similar trend of extended half-lives in open ponds (~170 days), in contrast to more heavily vegetated ponds (60-90 days).

The greater loss of atrazine in the emergent mesocosms indicates that this plant community directly and(or) indirectly affects the loss of atrazine in wetland mesocosms. Rapid uptake by plants and large biomass surface area for herbicide adsorption may offer an explanation for the increased loss rate in the emergent treatment. Greater adsorption to the soil also could be a factor, as a result of plants translocating the herbicides into the soils through transpiration. In addition, once atrazine comes in contact with the soil, a greater amount of microbial degradation may occur.

Alachlor

Alachlor concentration declined more rapidly than atrazine concentration in all mesocosms. For example, 58-84% of the alachlor concentration was lost by day 21 as compared to 11-38% for atrazine concentration loss on the same date (Tables 1 and 3), Eckhardt et al. (in press) also reported greater persistence of atrazine than alachlor in soils, and Schnoor et al. (1982) found that alachlor degraded more rapidly than atrazine in surface water. There does appear to be a slight difference in

Table 1. Atrazine concentration and mass (percent loss) for wetland mesocosms at days 21, 54, 75, 126, and 251.

Mesocosm Treatment	Mesocosm Identification Number	Day 21		Day 54		Day 75		Day 126		Day 251	
		Concentration (% loss)	Mass (% loss)	Concentration (% loss)	Mass (% loss)	Concentration (% loss)	Mass (% loss)	Concentration (% loss)	Mass (% loss)	Concentration (% loss)	Mass (% loss)
Open	2	30	14	34	47	77	43	82	64	86	82
	8	30	11	38	38	73	41	85	59	85	77
	9	28	10	29	46	67	34	81	59	81	74
Submergent	3	14	0.1	35	40	67	43	81	61	81	75
	4	24	10	40	45	83	71	89	74	89	80
	5	27	7	30	27	81	48	88	63	88	75
Emergent	6	11	0.6	42	52	70	50	87	71	87	84
	7	38	38	62	70	83	74	94	84	94	93
	10	16	5	60	72	88	80	96	90	96	95

Table 2. Atrazine concentration and mass (half-lives) for all wetland mesocosms during the 383-day study period.

Mesocosm Treatment	Mesocosm Identification Number	Concentration Half-Life (days)	Mass Half-Life (days)
Open	2	99	88
	8	98	94
	9	94	85
Submergent	3	112	108
	4	96	102
	5	101	115
Emergent	6	73	70
	7	72	63
	10	62	58

Table 3. Alachlor concentration and mass (percent loss) for wetland mesocosms at days 14, 21 and 44.

Mesocosm Treatment	Mesocosm Identification Number	Day 14		Day 21		Day 44	
		Concentration (% loss)	Mass (% loss)	Concentration (% loss)	Mass (% loss)	Concentration (% loss)	Mass (% loss)
Open	2	73	65	84	81	97	98
	8	55	40	82	78	96	96
	9	58	46	80	75	96	96
Submergent	3	40	27	60	54	88	88
	4	55	45	74	70	95	95
	5	60	47	82	77	97	97
Emergent	6	-	-	58	51	82	83
	7	60	54	78	79	93	95
	10	50	39	68	64	93	93

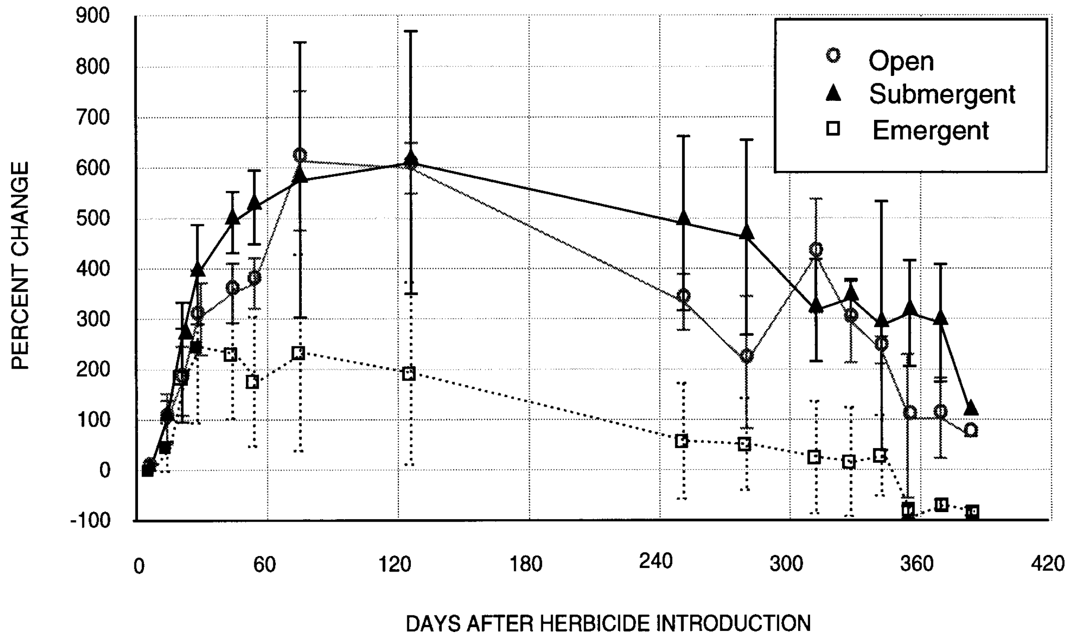

Figure 3. Mean deethylatrazine (DEA) mass (percent change) for open, submergent, and emergent treatments. Bars show standard deviation.

the percent loss of alachlor concentration between treatments. However, the alachlor loss rates in all mesocosms were very rapid, with an average of 90-percent loss by day 44.

Alachlor mass rapidly declined in all mesocosms throughout the study. More than 50% of the alachlor mass was lost by day 21 in all treatments as compared to <1 to 38% lost at day 21 for atrazine mass (Tables 1 and 3). Visual inspection of Fig. 2 reveals a somewhat higher percent loss of alachlor in the open mesocosms on day 21 than in the submergent or emergent mesocosms. However, more than 80% of the alachlor mass was lost by day 44 in all mesocosms. These results indicate that hydrophytes may not be as important as other factors in alachlor degradation.

Deethylatrazine

Atrazine degraded to two metabolites, deethylatrazine (DEA) and deisopropylatrazine (DIA) in all treatments. DEA was detected at greater concentrations than DIA throughout this study. These results are in agreement with other studies of atrazine degradation in soil and surface-water environments (Sirons et al., 1973; Thurman et al., 1991; Eckhardt et al., 1993). In general, the DEA concentration increased rapidly in all mesocosms for the first 54 days during the period of rapid atrazine concentration loss. Precipitation between day 54 and day 75 may have resulted in dilution of DEA concentration. DEA concentration increased between day 75 and day 126 in all mesocosms.

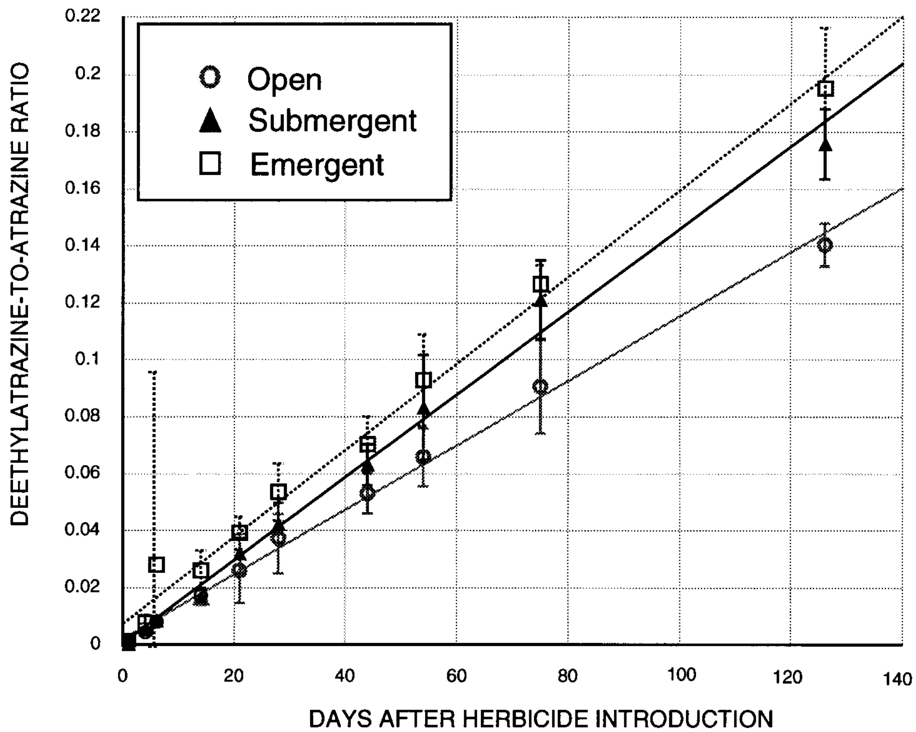

Figure 4. Deethylatrazine-to-atrazine ratios (DAR) for 126 days after herbicide introduction. Bars show standard deviation.

DEA mass increased rapidly during the first 50 to 75 days in all treatments during the period of the most rapid loss of atrazine. The rapid gain in DEA during the early part of the study (during the active growing season) was probably the result of degradation of large amounts of atrazine. Following the peak in DEA mass gain, there was a steady decline for all treatments throughout the remainder of the study. DEA mass in the emergent mesocosms declined at an earlier date (day 75) than in the other treatments (day 126) and remained low throughout the study (Fig. 3). All mesocosms showed a decline in percent gain after day 126 (Fig. 3). A two-way ANOVA, by treatment and date, was computed for DEA mass percent change, and both factors were found to be significant; therefore, a series of date-wise one-way ANOVA's were calculated to assess treatment effects. All date-wise test results indicate the existence of treatment effects, except for day 75. Duncan's post hoc tests revealed that the low DEA mass percent gain group was comprised of only the emergent treatment on all dates through day 328.

The decline in DEA concentration after day 126 did not indicate that degradation of atrazine to DEA had ceased, or had decreased, but that there was less parent herbicide for conversion to DEA and DEA was also degrading. One possible explanation of the relatively smaller gain in DEA mass in the emergent treatment is that DEA degraded more rapidly than it was formed in the emergent mesocosms. Additionally, there may have been greater atrazine loss to adsorption, and(or) plant uptake in the emergent systems, thus reducing the amount of atrazine available for conversion to DEA.

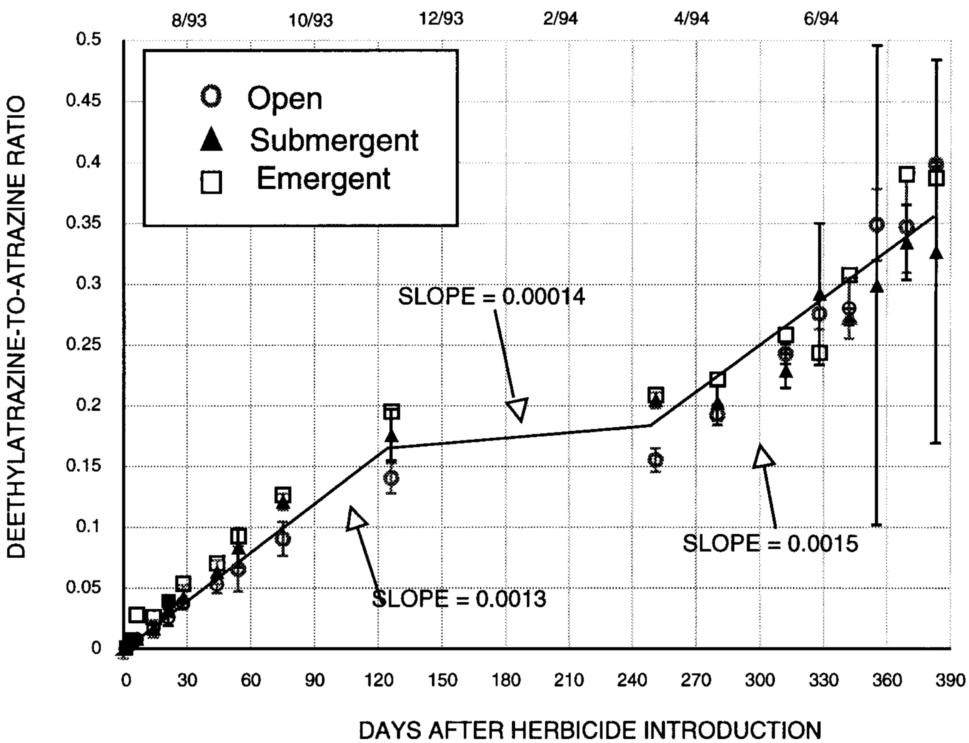

Figure 5. Mean deethylatrazine-to-atrazine ratios (DAR) for 383 days after herbicide introduction. Bars show standard deviation.

Deethylatrazine-to-Atrazine Ratio

The ratio of the concentrations of DEA to atrazine (DAR) has been used as an indicator of atrazine degradation. Adams and Thurman (1991) used the DAR as an indicator of atrazine transport through soil profiles. Fallon (1994) utilized the DAR to determine the relative age of atrazine in a reservoir. In this study, the DAR is a particularly useful degradation indicator because it is not affected by volume changes. The low DAR at the beginning of the study (Fig. 4) was a result of high parent-compound and low metabolite concentrations. The mean DAR increased rapidly in all mesocosms ranging from 0 to 0.19 (depending on treatment) during the first 126 days of the study. At the end of the study (day 383) the DAR values ranged from 0.32 to 0.40. These DAR values are similar to other DARs of < 0.01 to 0.95 reported for surface water (Pereira et al., 1990; Schottler et al., 1994; Thurman et al., 1994). The DARs in the open-treatment mesocosms were generally lower than in other treatments, especially for sample days 75 and 126 (Fig. 4). This graphical interpretation was substantiated by the results of a two-way ANOVA that revealed significant spatial and temporal differences in most DAR values through day 126. A multiple comparison of means (Duncan's test) showed that two treatment groups were formed and that the emergent and submergent treatments comprised the group with the highest DAR values. The DAR increased at similar rates (0.0013 and 0.0015 d^{-1}) in all treatments during two growing seasons and stabilized (0.00014 d^{-1}) during the winter, when the biological community was relatively inactive (Fig. 5).These results indicate that the biological community (i.e.,hydrophytes) affected the degradation of atrazine and the formation of DEA. In addition, the DAR increase coincided with increases in temperature. The potential direct and indirect effects of temperature likely are related to its role in reducing the rate of biological and chemical reactions. DAR values followed a similar pattern for all treatments, but the vegetated treatments clearly enhanced the degradation of atrazine to DEA.

Summary

Data from wetland mesocosms in Kansas indicate that alachlor dissipated more rapidly than atrazine from all mesocosms, and hydrophyte community type did not affect alachlor loss. Atrazine dissipated from emergent mesocosms at a greater rate than from either open or submergent mesocosms. This was evidenced by the loss of concentration, mass, and greater DAR values for the emergent mesocosms. The increase in the deethylatrazine-to-atrazine ratio (DAR) during the two growing seasons is evidence for the important role that the emergent hydrophyte community plays in atrazine loss and degradation. The stabilization of DAR during the winter also substantiates this hypothesis. Temperature could play an active role because it reduces the rate of chemical reactions and biotic activity. Results indicate that plant community type (open, submergent, or emergent) was an ecological determinant of atrazine degradation rate. The plant community may have a direct or an indirect effect on atrazine loss. The plants may provide more substrate for microbes that could actively degrade the atrazine. In addition, the plants could draw atrazine into the soil through evapotranspiration. The atrazine could then be adsorbed to the soil and(or) degraded. In addition, atrazine loss includes plant uptake or adsorption to plant tissue.

The results of this research support the water-quality mitigation function of wetlands and provide information useful to develop appropriate regulations to adequately protect existing wetlands and aid in the design of created or restored wetlands. In addition, this research will provide a baseline upon which to design appropriate field procedures to examine the fate of herbicides at the landscape scale.

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