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Persistence and Movement of Atrazine in a Salt Marsh Sediment Microecosystem

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Pesticides enter salt marshes in runoff from agricultural lands or through direct or near-by application. Concern has been raised that the tidal action in the salt marsh that functions to trap sediment and nutrients (Odum 1971) may also function to concentrate pesticides to harmful levels. Studies have been conducted to evaluate the effect of pesticides on representative species of salt marsh ecosystems (Edwards and Davis, 1975, Maly and Ruber 1983). These studies have shown that (1) toxic responses are associated with concentrations indicitive of point sources (e.g. spills and direct application) rather than from non-point sources (e.g. agricultural runoff) and (2) the natural systems rapidly recover, even from high concentrations. Another research approach has been to examine a basic salt marsh process; pesticide impact on the hetrotropic microbial population which degrades vegetation to detritus (Caplan et al. 1984; Bourquin et al. 1976). Such disruption would adversely affect the energy flow, productivity, and nutrient cycling of the salt marsh. However, the hetrotrophic microbial population was not disrupted by two insecticides that they evaluated. Thus, one is left to speculate that some other process, such as pesticide adsorption to salt marsh sediment, which is often high in organic carbon content, may function as a trap reducing pesticide input to the estuarian environment. The organic carbon content of natural sediment has been shown to be the primary factor controlling adsorption of xenobiotic compounds (Karickhoff et al. 1979). Adsorption usually results in a significant reduction in pesticide availability.

This paper describes the use of a modified salt marsh microecosystem to evaluate persistence and movement of atrazine in salt marsh sediment under simulated tidal flux and continuous flooding conditions. Atrazine persistence was also compared under normal field conditions.

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MATERIALS AND METHODS

The overall procedures and design of a salt marsh microecosystem, as described by Caplan et al. (1984), were modified for this study (Figure 1a & 1b). In brief, a timer controlled air pump drives "percolator" water pumps that flood the tidal chamber (start of high tide sequence) and keep a float at the water surface (Figure 1a). The float holds the intake of a drain line above the water. When the air supply is turned off (start of low tide sequence), the pumps stop and the float sinks, thus submerging the drain line (Figure 1b). Twice every 24 h (11:00 a.m. and 11:00 p.m.) the timer turns on the air pumps for four h time periods of high tide. Sediment containers were designed and built to simulate both surface and subsurface water movement during tidal fluctuations (Figure 2).

Treated and untreated sediment (obtained from a tidal marsh area in the Wye River [a subestuary of the Chesapeake Bay]; air dried, sieved to <2 mm; organic carbon content of 11.2%) were layered into the sediment containers as follows: 165 g untreated sediment was added to a depth of 5 and 10 cm at opposite ends of the container, thus forming a 40% slope. The sediment was covered with 0.5 mm polypropylene mesh (2.5 x 15 cm). Next, a mesh divider (2.5 x 5 cm) was positioned vertically 7.5 cm from either end and 25 g quantities of untreated sediment were placed on both sides. Additional mesh (2.5 x 7.5 cm) was placed over the soil and 25 g untreated sediment was placed on the lower side of the divider. Twenty-five g of sediment treated with [^{14}C]atrazine (44.0 uci/mg; 96% purity) at the rate of 4 ppm was added to the upper side of the divider. The screen defines four sampling units, designated as treated (T) and untreated 1, 2, and 3 (UT-1, UT-2, and UT-3, respectively) (Figure 2). Seven sediment chambers were prepared for each microecosystem tank. Atrazine mobility and persistence in continuously submerged sediment was determined by placing 25 g quantities of sediment treated with [^{14}C] atrazine (same rate as above) in seven 50-ml beakers. These beakers were placed in the reservoir side of the microecosystem tank. Seventeen L of estuarian water (collected from the Wye River; 9.5 PPT salinity) were poured into each tank after the sediment chambers and beakers were in place. The sediment was allowed to equilibrate with the water for 24 h before the pumps were turned on. Two hundred gram quantities of field soil (sand, silt, clay and organic carbon contents of 37.3, 46.3, 16.4, and 0.99%, respectively) were treated with [^{14}C] atrazine at the rate of 4 PPM and moistened to 20% (w/w). All treatments were replicated twice.

Samples were taken 1, 3, 7, 15, 21, 28, and 35 days after the start of the experiment. Each sediment chamber that was removed was replaced with one filled with silica sand to maintain the same volumetric displacement in the microecosystem tank. Excess water was drained from the sediment chambers and 50 ML beakers for 4 h after removal from the microecosystem tank. The sediment samples (T, UT-1, UT-2, UT-3, and flood) were placed in flasks, mixed, and

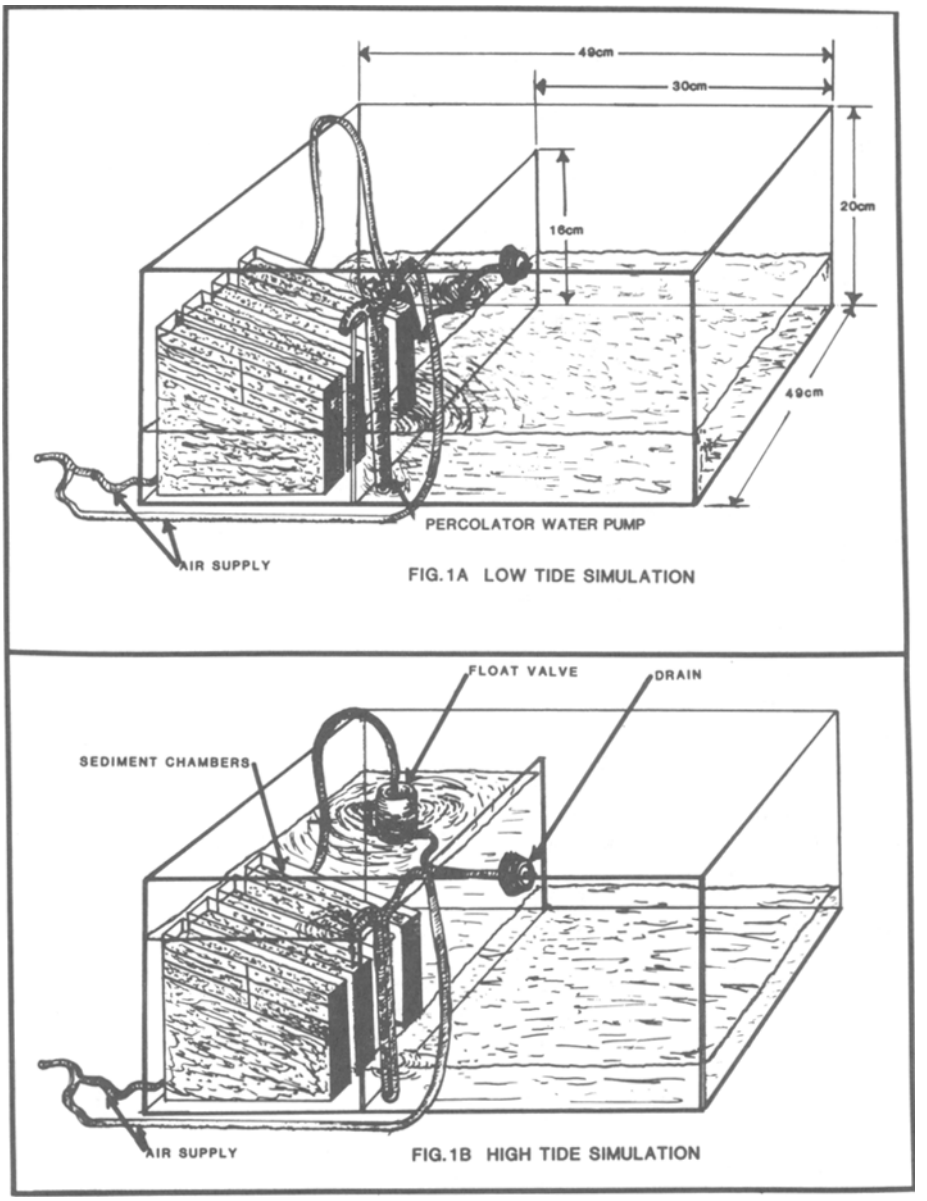

FIGURE 1 SALT MARSH MICROECOSYSTEM

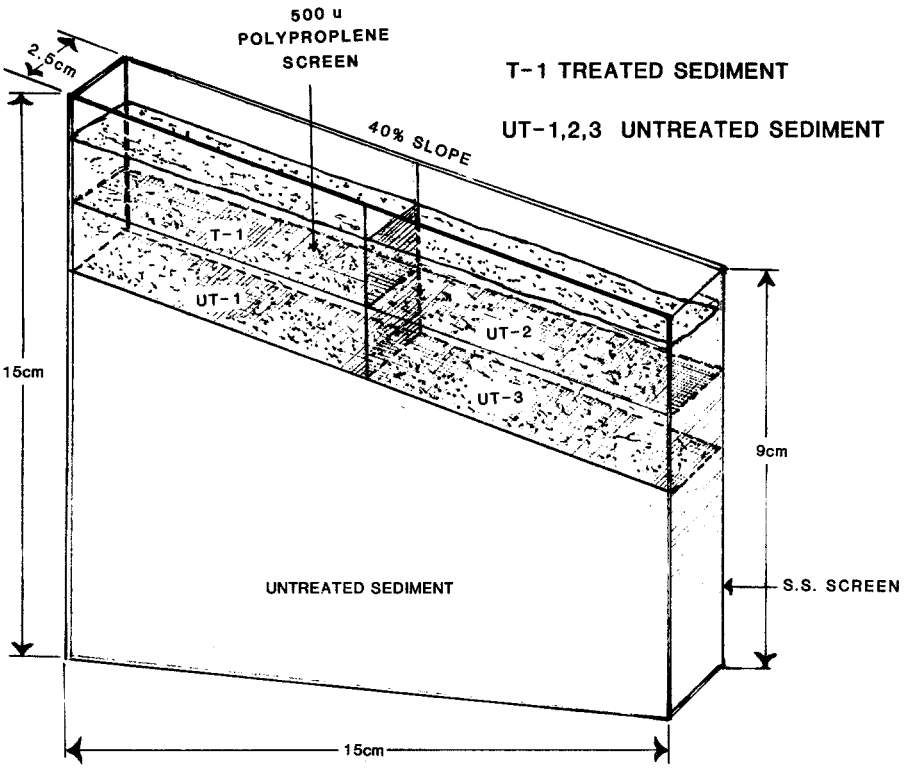

FIGURE 2 SEDIMENT CHAMBER

subsampled for moisture determinations. Subsamples of the field soil were also taken for moisture determinations. Sediment and field soil were extracted and analyzed as follows: moist sediment and field soil (equal to about 10 g dry weight) were shake extracted for 12 h with 25 ml of acetonitrile:H_2O (70:30 V/V) and filtered. Samples of the extract were analyzed by liquid scintillation (LS) for total ^{14}C, and the remaining extract was reduced in volume on a rotary evaporator. The remaining aqueous extract was extracted with ether. The ether was spotted on thin-layer chromatography (TLC) plates (20 x 20 cm silica gel GF-254) with unlabeled atrazine and developed 10 cm using chloroform:ethanol: ethyl acetate (8:1:1, V/V/V). Ether extracts from untreated soil and sediment spiked with [^{14}C] atrazine, were also analyzed by TLC. Plates were autoradiographed using Kodak No-Screen NS-54T X-ray film to locate radioactive compounds, then scraped and total ^{14}C was determined by LS. Extracted sediment and soil was air-dried, mixed, and samples were oxidized to determine bound ^{14}C.

RESULTS AND DISCUSSION

The effect of tidal fluctuations on atrazine mobility in and recovery from sediment is shown in Table 1. The sediment chambers were designed to evaluate both vertical and lateral movement of atrazine. About 17% of the total ^{14}C moved vertically from the treated to untreated sediment (UT-1) by 3 days. Little additional movement occurred with time. Only 1 to 3% of the total ^{14}C moved laterally to the untreated sediment (UT-2 and UT-3) located down slope from the treated sediment. Adsorption of atrazine to the high organic carbon (11.2%) sediment prevented further movement in either the vertical or lateral directions. In a previous study, K_{OC} values of 300 to 600 were measured in the bottom and suspended sediment (4 to 10% organic carbon) collected from the Wye River (Glotfelty et al. 1984). Rapid adsorption of atrazine to the sediment used in this experiment would thus be expected. Further evidence of atrazine binding is indicated by the decreasing extraction efficiency over time. Total ^{14}C extracted for the treated plus untreated sediment was 76.7% on Day 1, which decreased to about 10% by Day 15, then remained constant for the rest of the experiment. The amount of ^{14}C recovered by oxidation increased concomitantly with the decrease in extracted ^{14}C. Recovery of ^{14}C (expressed as a percent of the initial ^{14}C concentration in the sediment) was about 100% with the exception to two sampling dates. The ratio of extractable to bound (oxidation) ^{14}C was similar for both the flooded sediment and tidal sediment, but actual ^{14}C recovery was lower in the flooded environment. These results are the reverse of what might be expected, i.e., complete recovery in the submerged sediment which has no water flow. The reason for this observation is unknown.

Atrazine extractability from field soil was more complete than from sediment, since the organic carbon content of soil (1.0%) was so much lower than the sediment. Variability in the total recovery of ^{14}C may have been caused by the multiple sampling from one container (each replication) that was periodically remoistened to field capacity. Atrazine is moderately mobile in light textured, low organic matter soils (Helling 1970). Leaching of atrazine by the water additions would likely account for the observed variability.

Extracts from the tidal sediment, flooded sediment, and field soil were analyzed by TLC. On Day 1, 89% and 93% of the recovered radioactivity was chromatographically identical to atrazine in the sediments and field soil, respectively. By the end of the experiment (Day 35) an average of 18% and 72% of the radioactivity was atrazine, with 54% and 15% of the radioactivity as polar metabolites (^{14}C remaining at the origin) for the sediments and field soil, respectively. Thus, by Day 35, 1.3%, 2.7%, and 5.6% of the extractable radioactivity was atrazine in the tidal sediment, flooded sediment and field soil, respectively.

Table 1. Recovery (Expressed as Percent of Total) of ^{14}C by Extraction plus Combustion from Soil and Sediment Treated with ^{14}C-labeled Atrazine.

Treatment	Days after Start of Experiment							
	1		3		7		15	
	E[a]	O[b]	E	O	E	O	E	O
Tidal								
Treated	66.7±0.8	20.2±0.5	50.5±9.2	26±1.4	17.0±1.6	63.4±8.8	8.9±2.4	66.7±3.2
Untreated 1	0.8±0.8	0.3±0.3	1.3±1.8	3.5±4.5	0.5±0.1	1.2±0.1	0.1±0.1	2.9±2.9
" 2	9.2±2.4	1.6±0.8	9.5±3.3	7.3±5.0	6.4±7.2	10.5±0.2	1.4±0.3	18.6±9.8
" 3	0	0.8±0.8	0.2±0.2	1.9±2.3	0.8±0.3	0.7±0.5	0	1.5±1.4
Sum	76.7	27.9	61.5	38.7	24.7	75.9	10.4	89.7
Total ^{14}C[c]		101.8		110.0		97.2		100.6
Flood	77.8±3.7	22.3±3.7	68.3±7.0	31.8±7.0	41.4±28.5	58.7±28.5	14.5±2.1	85.5±2.1
Total ^{14}C		94.6		91.4		94.7		87.0
Field	89.6±1.6	10.4±1.6	85.3±6.0	14.8±6.0	85.7±1.0	14.3±1.0	81.3±6.1	18.7±6.1
Total ^{14}C		72.0		78.3		77.2		86.9

[a] Shake extracted 10 g wet soil with 25 ml acetonitrile:H_2O (70:30) two times.
[b] Oxidized soil after extraction and air drying.
[c] Total ^{14}C recovered divided by initial ^{14}C content.

Table 1. (Continued).

Treatment	Days after Start of Experiment					
	21		28		35	
	E	O	E	O	E	O
Tidal	7.7±1.2	68.7±6.5	8.0±2.3	66.5±4.0	7.0±0.4	67.2±7.8
Treated	0.4±0.1	2.4±1.3	0.5±0.5	1.5±0.8	0.5±0.2	3.6±2.5
Untreated 1	1.4±0.5	18.8±5.3	2.0±0.3	19.9±8.3	2.1±1.3	18.9±9.5
" 2	0.1±0.1	1.3±0.1	0	1.5±0.1	0	0.8±0.6
" 3	9.6	91.2	10.5	89.4	9.6	90.5
Sum						
Total ^{14}C		88.6		101.7		101.8
Flood	9.4±3.7	90.6±3.7	15.7±5.2	83.3±5.2	14.8±1.9	87.5±1.9
Total ^{14}C		89.3		85.8		80.7
Field	78.6±6.0	21.5±6.0	76.4±0.6	23.6±0.6	78.0±2.1	22.0±2.1
Total ^{14}C		80.1		86.4		92.2

Results of this study indicate that atrazine, a widely used, moderately persistent herbicide, will be rapidly inactivated by adsorption and/or metobolism in estuarian sediment. The magnitude of this inactivation can be estimated from an earlier study on atrazine movement to the Wye River (Glotfelty et al. 1986). In that study we calculated (from adsorption constants) that adsorption to bottom sediment would account for 23% of all atrazine in the headwater areas of the river. That calculation was based on an organic carbon content of 4.4% in the bottom sediment compared to 11.2% in the salt marsh sediment used in this study. Based on these calculations, salt marsh sediment should adsorb 50 to 60% of the atrazine. This is important in estuary-agriculture interface areas (such as the Eastern Shore Areas of the Chesapeake Bay) where much of the runoff from agricultural land enters the estuary through salt marshes. Thus, the water-sediment interactions caused by tidal fluctuations in salt marshes may function to inactivate sediment-borne pesticides.

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