Bull. Environm. Contam. Toxicol. 24,411-414 (1980)

Enrichment of the Agricultural Herbicide Atrazine in the Microsurface Water of an Estuary

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Some of the surface films that are frequently observed in estuarine waters result from the accumulation of water-insoluble metabolic and decay products, particularly from the planktonic organisms which reside in the upper strata of waters (DIETZ & LAFOND 1950). These natural slicks are not the result of petroleum, detergent, or other pollution. The major constituents of these natural surface films are surface-active substances such as fatty acids, fatty esters, fatty alcohols, and triglycerides (GARRETT 1976, LARRSON et al. 1974). Three major mechanisms are known to promote the enrichment of these products in the microsurface film: diffusion, convection currents, and rising air bubbles (DUCE et al. 1972).

Microsurface films often concentrate various pollutants, including heavy metals such as lead, iron, copper, and nickel (DUCE et al. 1972); chlorinated hydrocarbons such as PCBs (BIDLEMAN & OLNEY 1974) and DDT compounds (SEBA & CORCORAN 1969); and petroleum hydrocarbons (MORRIS & CULKIN 1974). The majority of enrichment studies have been conducted in the open ocean over comparatively short sampling periods. Relatively few studies of natural surface films in estuarine systems have been reported. This paper summarizes the results of a study of the herbicide atrazine in such a system.

Atrazine, one of the most commonly used herbicides for corn on the Atlantic coastal plain, is primarily utilized for preemergence control of broadleaf weeds and grasses in cornfields. The increased use of atrazine and our awareness of transport of pesticides from agricultural lands led us to study the distribution and concentration of atrazine in the Rhode River estuary.

MATERIALS AND METHODS

Between June, 1977 and November, 1978, microsurface and bulk subsurface (depth = approx. 0.3 m) water samples were collected twice a week from a station near the head of the Rhode River, a subestuary of the Chesapeake Bay near Annapolis, Maryland (38° 53', 70° 32'). The Rhode River has a surface area of 485 ha, a mean water depth of 2 meters, and a watershed of 3332 ha. Forest, pasture, and row crops are the major land uses. Corn, tobacco, and hay are the principal crops. Atrazine is one of the herbicides most commonly applied to cornfields on the watershed. The sampling station is a mudflat where Muddy Creek, the principal freshwater drainage to the Rhode River, enters the main tidal basin.

Using a technique described by GARRETT (1965), microsurface water was collected with a 16 mesh stainless steel screen that samples the top 100-150 um of the water surface. Bulk surface water samples were collected in a

0007-4861/80/0024-0411 $01.00

glass bottle at a depth of approximately 0.3 m. Approximately 4 liters of microsurface or 15 liters of bulk surface water was taken for herbicide analysis. Five grams of calcium chloride were added to the water sample for each liter of water. The water sample was left overnight at about 5° C and then filtered through a 142 mm Gelman type AE glass fiber filter to separate solid particles from the dissolved phase. The glass fiber filters, which had been previously cleaned with a water extraction procedure, were then extracted with a 1:3 mixture of toluene and dichloromethane. After filtration, solid particles were extracted with 200 mL of a 1:9:10 toluene/hexane/dichloromethane mixture in Soxhlet extractors. Herbicides in the dissolved phase were extracted in a separatory funnel first with 100 mL of dichloromethane. Grade V alumina (15 g H_2O and 85 g Al_2O_3) was used in the subsequent clean up procedure. A gas chromatograph equipped with a Hall electrolytic detector in the nitrogen mode was used for quantitation. The chromatographic conditions are 1.8 m x 4 mm glass columns packed with 3% OV-17 on 80/100 mesh Gas Chrom Q 190° column temperature, 65 mL/min He flow rate. Recovery studies from six replicate samples each of which consisted of four liters of distilled and deionized water spiked with 2 ug atrazine, were 90 ± 8%. Another 1.8 m x 4 mm glass column packed with 1% Carbowax 20 M on 100/120 Gas Chrom Q was used for confirmation of atrazine for selected samples.

RESULTS AND DISCUSSION

Atrazine was detected in the water of the Rhode River throughout the entire June-December sampling period in both 1977 and 1978 (Fig. 1). The maximum atrazine concentration (3.3 ug/L) was detected on August 4, 1977, in a microsurface sample collected within a heavy slick. Atrazine concentration in the Rhode River decreased at the end of October, both in microsurface and bulk surface water. Atrazine concentration in the bulk surface water varied from 0.003 to 0.19 ug/L, with a mean value of 0.04 ug/L. Atrazine concentration in the microsurface water samples was generally in the range of 0.01 to 0.59 ug/L, with a mean value of 0.13 ug/L.

The enrichment of atrazine in the microsurface varied from none to about 110x (Table 1). Forty-six percent of the 65 sampling dates had an atrazine enrichment factor of 5x or less. No direct relationship was found between the atrazine enrichment factor and the thickness of slick observed (i.e., heavier slicks did not necessarily contain higher atrazine concentrations in the microsurface layer), but a correlation did exist between season and atrazine enrichment. High enrichment of atrazine in the microsurface occurred between mid-September and late October, both in 1977 and 1978.

Atrazine in the surface film samples exists partly in the dissolved phase and partly in the solid phase in association with suspended particles. Dissolved atrazine generally accounted for more than 80% of total atrazine in the microsurface samples, and amounted to 84% in the bulk surface water. Microsurface concentrations were more variable, and a few samples contained from 50-98% of the total atrazine in particulates in the microsurface layer.

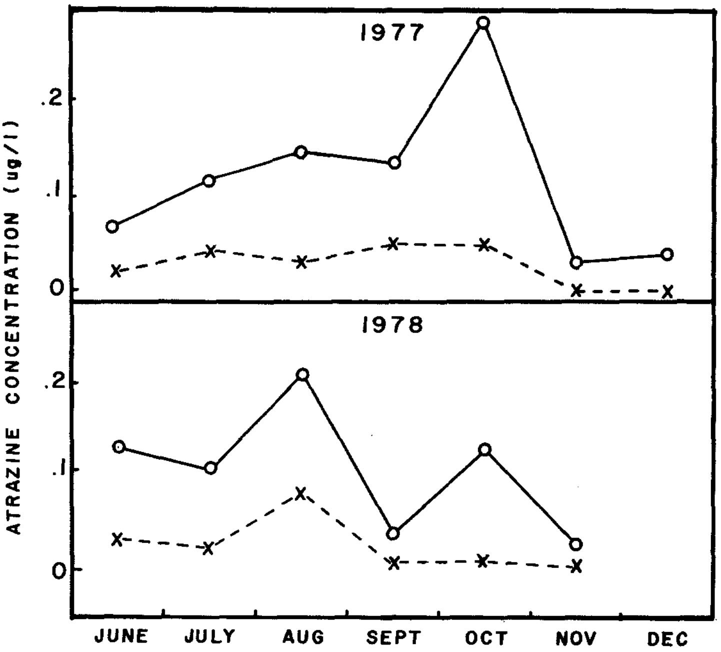

Figure 1. Monthly average atrazine concentration in the microsurface and bulk surface water of a mudflat station in the Rhode River, Maryland. Solid lines are concentrations in microsurface water, broken lines are for atrazine in bulk surface water.

TABLE 1

Enrichment Factor of Atrazine in the Rhode River Microsurface Water. Samples from all seasons combined.

Enrichment Factor*	1	1-5	6-10	11-20	20-30	31-100	110
No. of Samples	2	30	13	9	5	5	1

*The enrichment factor is equal to the microsurface atrazine concentration divided by the bulk surface atrazine concentration.

The screen sampling technique collects surface water film samples 100-150 um thick. It has been estimated that the actual film thickness cannot be more than five times the thickness of the monolayer of organic molecules, which is approximately 2 x 10^{-3} um (DUCE et al. 1972). Assuming all atrazine to be concentrated within this thickness, the actual enrichment of the microsurface (10^{-2} um thick) is approximately 1.5 x 10^{4}. Therefore, atrazine concentration in the actual microsurface probably varied from 150 to 8850 ug/L. It is known that a few parts per billion of

DDT inhibits photosynthesis in marine phytoplankton (WURSTER 1968). The effects of the high concentration of herbicides in the microsurface layer on the diversity and species composition of bacteria, phytoplankton, submerged macrophytes, and zooplankton exposed to the surface microlayer are not known, nor do we understand the extent to which pollutants in the microsurface are transferred to higher trophic levels of the food web. The biological implications of extreme atrazine enrichment at the microsurface from mid-September to the end of October remain to be determined, but the chemical composition of surface films during that period is known to be very different from other seasons, due to the decomposition of large amounts of organic materials. Biological activities are minimal in winter, but more assimilation of organic materials needed as energy sources occurred in spring, summer, and early fall.

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