Ecotoxicology and Environmental Safety **43,** 35–37 (1999)
Environmental Research. Section B
Article ID eesa.1998.1751, available online at http://www.idealibrary.com on IDEAL®

Effect of Simulated Sunlight on Atrazine and Metolachlor Toxicity of Surface Waters

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Received February 2, 1998

Atrazine and metolachlor are the two most widely used herbicides in the United States; through non-point-source runoff both herbicides may cause toxicity to aquatic organisms. Toxicity changes were measured for atrazine and metolachlor in surface waters after exposure to simulated sunlight (0, 20, and 40 kJ/m^2) using a Xenon Weather-Ometer. A Microtox toxicity test, using the marine luminescent bacterium *Vibrio fischeri*, was conducted on deionized, river, and bay water samples mixed with atrazine or metolachlor herbicide (12 mg/liter) after exposure to simulated sunlight. Microtox test (EC_{50}%) results demonstrated that the toxicity decreased with increasing light intensity for both herbicides in river and bay water. These results also indicate that the toxicity of the bay water, with high concentrations of organic and suspended matter, was reduced, for both herbicides, compared with the toxicity of the river water, possibly through photodegradation of pesticides.

Key Words: **atrazine; metolachlor; river water; bay water; simulated sunlight; photodegradation; toxicity; microtox.**

INTRODUCTION

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-*s*-triazine) and metolachlor [2-chloro-*N* -(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl) acetamide] are the two most widely used herbicides in the United States (USGS, 1992; Masse *et al*., 1994). Non-point-source runoff of these herbicides can cause toxicity to aquatic organisms and affect surface water quality (Arjoon *et al*., 1991). The degree of herbicide transport depends on several factors such as application rate, herbicide persistence and mobility, rainfall, topography, and the climate; the temperature and intensity of the sun often determine the persistence of pesticide compounds (Wauchope *et al*., 1994). Solar radiation is responsible for transformations of pesticides in the aquatic environment and photochemical reactions are induced by the solubilized or adsorbed molecules in water bodies (Pelizetti *et al*., 1992). Changes in environmental chemicals in water can be affected through photocatalytic reactions triggered by ultraviolet radiation. The surface waters, such as bay and river waters, have different abiotic conditions that can affect the persistence, mobility, bioavailability, photodegradation, and toxicity of pesticides (Durand *et al*., 1991). Little is known about the toxicity of atrazine and metolachlor in surface waters after natural photodegradation by sunlight.

The microtox toxicity test has been used in herbicide degradation, interaction with various aquatic systems, bioavailability, and toxicity studies (Dieter *et al*., 1994; Gupta and Baummer, 1996; Karuppiah *et al*., 1997). The objective of this study was to measure the effect on toxicity (Microtox EC_{50}%) of atrazine and metolachlor in surface waters after exposure to simulated sunlight.

MATERIAL AND METHODS

Sample Preparation

The river water (top 3 in.) was sampled from Manokin River, Princess Anne, Maryland, and the bay water (top 3 in.) was sampled from Chesapeake Bay at Deal Island, Maryland. The physicochemical characteristics were measured at the sampling sites; the samples were shipped on ice to the Environmental Science Research Laboratory at the University of Maryland Eastern Shore. All the water samples were filtered using 0.45-μm filters (Corning, New York, NY) with vacuum suction prior to light exposure. Emulsifiable concentrates of atrazine (41% a.i) and metolachlor (91% a.i) (Ciba–Geigy, Greensboro, NC) were used to prepare 12 mg/liter concentrations [toxicity of atrazine and metolachlor to various aquatic organisms ranges from 0.005 to 30 mg/liter (Ward and Ballantine, 1985; Uhler, 1991; Karuppiah *et al*., 1997)] in distilled deionized, river, and bay waters, respectively. Samples were stored at 4°C.

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0147-6513/99 $30.00

Simulated Sunlight Exposure

All sample solutions (20 ml) were placed in 25-ml glass vials (I-Chem, VWR Scientific, Philadelphia, PA) prior to exposure to simulated sunlight. The samples were placed on a merry-go-round rack in the Ci35A Xenon Weather-Ometer (Atlas Electric Device Co., Chicago, IL). The exposure intensities were 0, 20, and 40 kJ/m^2 (Lin *et al*., 1996).

Toxicity Analyses

Toxicity of the samples was measured using marine luminescent bacteria, *Vibrio fischeri* (Microtox). Microtox is a bacterial assay using luminescent bacteria that was developed by Beckman Instruments, Inc. (Bulich, 1984). Based on the reduction in bioluminescence of the marine bacterium *V. fischeri* by the toxicants, the toxicity (EC_{50}%) of atrazine or metolachlor in distilled deionized, river, and bay waters exposed to simulated sunlight intensities (0, 20, and 40 kJ/m^2) was measured using the Microtox Toxicity Analyzer Model 2055. A low EC_{50}% value indicates high toxicity. Microtox has been used in toxicity testing of various chemicals including pesticides (Somasundaram *et al*., 1990; Dieter *et al*., 1994; Karuppiah *et al*., 1997), methyl tertiary butyl ether (MTBE) (Gupta and Lin, 1995), and biodegradation of herbicide (Gupta and Baummer, 1996). The EC_{50}% was calculated using the software (Version 7.08) supplied by Beckman Instruments Inc.

Statistical Analyses

Least significant differences (LSDs) were calculated ($P \leq 0.05$) for mean comparisons of three replicates using Statistix (1994) (Version 4.0).

RESULTS

Micortox toxicity (EC_{50}%) analyses of distilled deionized, Chesapeake Bay, and Manokin River waters revealed no toxicity (Table 1). Exposure to simulated sunlight of 20 and 40 kJ/m^2 intensity significantly ($P \leq 0.05$) reduced the toxicity (Microtox EC_{50}%) of distilled deionized, Chesapeake Bay, and Manokin River waters mixed with atrazine or metolachlor (Table 2). Distilled deionized, bay, and river waters mixed with atrazine exposed to simulated sunlight at all intensities exhibited less toxicity (Microtox EC_{50}%) than the waters mixed with metolachlor (Table 2).

Chesapeake Bay water samples exposed to simulated sunlight at all intensities exhibited less toxicity compared with the distilled deionized and river waters mixed with atrazine or metolachlor. Chesapeake Bay water mixed with atrazine after exposure to 40 kJ/m^2 simulated sunlight demonstrated no toxicity. Manokin River water (mixed with atrazine or metolachlor) after exposure to simulated sunlight at all intensities exhibited higher toxicity than the distilled deionized water or bay water mixed with atrazine or metolachlor (Table 2).

TABLE 1

Physicochemical Characteristics (Mean of Three Replicates) of Distilled Deionized Water, Chesapeake Bay Water, and Manokin River Water

Parameter	Distilled deionized water	Bay water	River water	LSD[a]
pH	7.0	8.5	8.1	0.23
Conductivity (mS/cm)	0.016	15.19	0.15	0.03
Temperature (°C)	22.4	9.1	11.0	0.12
Salinity (% NaCl)	0	1	0	NV[b]
Dissolved oxygen (mg/liter)	9.26	9.75	9.09	0.06
Turbidity (NTU)	0	0	0	NV
Total dissolved solids (mg/liter)	ND[c]	9.70	0.09	0.08
Organic matter (mg/liter)	ND	1.65	0.03	0.02
Toxicity (Microtox EC_{50}%)	NT[d]	NT	NT	NV

[a] Least significant difference ($P \leq 0.05$).
[b] No value.
[c] Not detected.
[d] Not toxic.

DISCUSSION

Physicochemical parameters that revealed differences among the three types of water were conductivity, organic matter, and total dissolved solids (Uhler, 1991; Pelizetti *et al*., 1992; Gupta and Baummer, 1996); the Chesapeake Bay water, compared with the Manokin River and distilled deionized waters, had the highest values for all these parameters (Table 1).

The results indicate that the reduction in toxicity of the waters was directly proportional to the intensity of

TABLE 2

Toxicity (Microtox EC_{50}%, Mean Values) of Distilled Deionized Water, Chesapeake Bay Water, and Manokin River Water Mixed with Atrazine or Metolachlor (12 mg/liter)

Herbicide	Light intensity (kJ/m^2)	Deionized distilled water	Chesapeake Bay water	Manokin River water	LSD[a]
Atrazine	0	30.17 ± 0.58[b]	45.82 ± 2.05	29.26 ± 0.58	2.47
	20	35.35 ± 0.31	63.56 ± 1.62	33.85 ± 1.01	2.23
	40	75.95 ± 4.32	NT[c]	72.63 ± 1.54	5.29
Metolachlor	0	24.45 ± 0.92	26.39 ± 0.23	22.39 ± 0.10	1.09
	20	29.86 ± 1.22	32.26 ± 0.74	27.06 ± 0.46	1.73
	40	38.04 ± 1.23	42.38 ± 1.84	29.04 ± 1.17	2.89

[a] Least significant difference ($P \leq 0.05$).
[b] Mean ± SD.
[c] Not toxic.

simulated sunlight exposure, suggesting photodegradation of the pesticide on exposure to simulated sunlight. Katayama and Matsumara (1991) indicated that degradation of pesticides in aquatic systems can be enhanced by light energy. Breakdown of pesticides appears to be faster in summer than in winter due to the presence of higher light intensity (Uhler, 1991). Photodegradation of xenobiotics such as Aroclor 1254 is also enhanced by higher intensity of simulated sunlight (Lin *et al*., 1996).

Photodecomposition of atrazine in the environment occurs immediately, whereas only a small amount of metalochlor is lost due to photodegradation (Buttle, 1990; Kochany and Maguire, 1994). Photodegradation of pesticides is faster in salt water than in fresh water (Durand *et al*., 1991; Laws, 1993). Photodegradation of herbicides is enhanced in substrates that contain high concentrations of organic matter and inorganic chemicals that act as photosensitizers (Pelizetti *et al*., 1992). Various studies have found that the degradation rates are enhanced by the presence of particulate, organic matter, dissolved substances through the attenuation of sunlight, secondary photoreactions, and chemical or physical interactions that change the speciation or availablity of the pesticides (Durand *et al*., 1991).

Kochany and Maguire (1994) reported that the photodegradation of metolachlor was slower in freshwater samples than in distilled water. Due to the slower rate of photodegradation of pesticides in river water, the river water samples were more toxic than the distilled deionized water samples mixed with atrazine or metolachlor.

CONCLUSIONS

The following ecotoxicologically significant conclusions can be made on the basis of this study:

i. The toxicity of atrazine and metolachlor in surface waters is reduced on exposure to simulated sunlight possibly through photodegradation.

ii. The toxicity of atrazine is reduced at a faster rate than the toxicity of metolachlor by simulated sunlight in surface waters.

iii. Toxicity reduction of atrazine and metolachlor by simulated sunlight is higher in bay water than in fresh water.

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