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## Wet Deposition and Air–Water Gas Exchange of Currently Used Pesticides to a Subestuary of the Chesapeake Bay

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The shallow nature of the Chesapeake Bay makes it vulnerable to both runoff and atmospheric inputs of anthropogenic chemicals. The project goal was to determine agricultural pesticide concentrations in air and rain and to calculate gas exchange fluxes to a Chesapeake Bay subestuary. Rain, air, and surface water samples were collected from April 17 to July 2, 1995 from the Chesapeake Biological Laboratory research pier in Solomons, MD. Of the 16 pesticides studied, chlorothalonil had the highest maximum air concentration ( $6.8 \text{ ng/m}^3$ ). Maximum wet deposition flux measurements were highest for methyl parathion ( $3.4 \text{ } \mu\text{g/m}^2\text{-d}$ ), malathion ( $1.8 \text{ } \mu\text{g/m}^2\text{-d}$ ), metolachlor ( $1.3 \text{ } \mu\text{g/m}^2\text{-d}$ ), and atrazine ( $1.3 \text{ } \mu\text{g/m}^2\text{-d}$ ). Air–water gas exchange fluxes calculated for chlorpyrifos and metolachlor ranged from  $-20$  to  $68 \text{ ng/m}^2\text{-d}$  and  $-41$  to  $-0.05 \text{ ng/m}^2\text{-d}$ , respectively, with negative values indicating net gas absorption. The major equilibration transfer direction for chlorpyrifos was from water to air, while for metolachlor the direction was from air into the surface waters. The total wet deposition load was  $-210$  and  $-7100 \text{ ng/m}^2$ , respectively, for chlorpyrifos and metolachlor during the study period with a net gas exchange loss of chlorpyrifos of  $290 \text{ ng/m}^2$  and a net gain of metolachlor of  $-260 \text{ ng/m}^2$ .

### Introduction

The Chesapeake Bay estuarine drainage system contains  $57\,000 \text{ km}^2$  of harvested crop lands. In 1987 the Chesapeake Bay estuarine drainage area received the highest pesticide application of any coastal area in the nation, with over 2.1 million kg per year (1). More recent estimates of pesticide usage in Maryland alone are 3.7 million kg per year in 1994 (excluding wood treatment) (2). Information is limited on the loadings of these chemicals to the Chesapeake Bay watershed through atmospheric deposition routes.

Previous work by Glotfelty et al. (3), carried out in the early 1980s, is the most detailed report on herbicide

concentrations in air, rain, and water in a Chesapeake Bay subestuary. Wu (4) also measured the herbicide atrazine in rain in the late 1970s from a site within Maryland on the Delmarva peninsula. However, atrazine use rates in the region have decreased significantly since these studies were completed and the number of pesticides used in the region has increased, establishing the need for more accurate information on pesticide loading rates.

In the 1990s Goolsby et al. (5) published a study of herbicides in rainfall from sites across the Midwest and Northeastern United States (1990–1991) including some stations located in the Chesapeake Bay watershed estimating a herbicide wet deposition rate of  $10\text{--}25 \text{ } \mu\text{g/m}^2 \text{ y}$  for most of the region. McConnell et al. (6) also estimated air–water gas exchange fluxes of chlorpyrifos in the Chesapeake Bay main stem from over-water samples collected in 1993. The goal of this study was to provide high-resolution data from the most important pesticide application period in the region with concentrations of selected herbicides, insecticides and fungicides in air, event-based wet deposition fluxes of these compounds, and gas exchange flux estimates for chlorpyrifos and metolachlor. While these data are limited to one location within the Chesapeake Bay system, and concentration differences are expected across the region, trends observed in this study should represent a useful reference for future researchers.

### Experimental Methods

**Sample Collection Methods.** Details of sampling and analytical methods are presented elsewhere (6–8) and are summarized here. Paired air and surface water samples were collected every other day from April 17 to June 2 and every Monday and Friday from June 8 to June 26, 1995 at the Chesapeake Biological Laboratory research pier located near the mouth of the Patuxent River in Solomons, MD [ $38^\circ 43' \text{N}$ ,  $76^\circ 42' \text{W}$ ] (Figure 1). Dissolved-phase concentration data from water samples collected in this study have already been published (7). Rain samples were collected on an event basis from April 17 to July 2, 1995. The air samples were collected over 12 h periods using a high-volume air sampler (Model GPNY1123, Grasby General Metal Works, Village of Cleves, OH) mounted to the research pier approximately 1.5 m above the water's surface. Air was pulled at an average rate of  $0.5 \text{ m}^3/\text{min}$  through a  $20.3 \times 25.4 \text{ cm}$  rectangular glass fiber filter (Gelman A/E) followed by two  $7.6 \times 7.6 \text{ cm}$  cylindrical polyurethane foam (PUF) plugs held in a glass sleeve. The sample volumes ranged from 342 to  $461 \text{ m}^3$  for all samples except one collected on 4/25/95 at  $822 \text{ m}^3$ .

Two-liter surface water samples were collected and processed using a solid-phase adsorbent methodology (7). Rain samples were collected using a round  $1\text{-m}^2$  surface area stainless steel funnel mounted on a steel frame. The rain sampler was also placed at the end of the pier and was equipped with a stainless steel lid that was removed manually just prior to rain events. Rainwater was captured using a stainless steel can placed underneath the funnel. Between rain events, the funnel was cleaned by wiping with precleaned glass wool and rinsing with 5–10 L of organic carbon-free water followed by 0.5–1 L reagent grade methanol.

**Sample Extraction and Analysis Methods.** PUF plugs were extracted using a Soxhlet apparatus for 16 h with chromatographic grade petroleum ether (J. T. Baker). Selected glass fiber filters were extracted with dichloromethane (DCM) (J. T. Baker) for those samples with highest gas-phase pesticide

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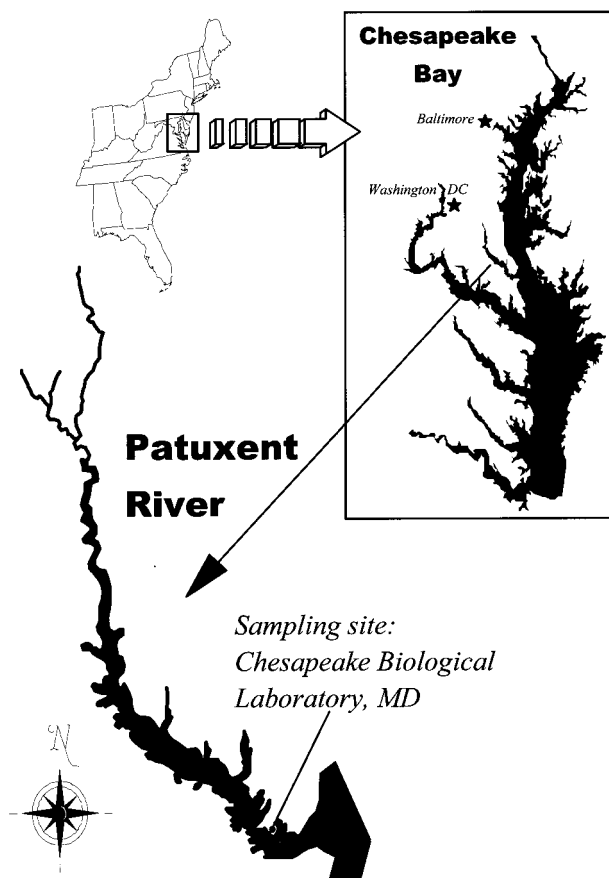


FIGURE 1. Map of the Chesapeake Bay with study site on the Patuxent River in Solomons, MD, indicated.

concentrations. Extracts were concentrated by rotary evaporation to 5–10 mL and further reduced to 0.5 mL using a gentle stream of high purity (99.9%) nitrogen gas.

Two-liter river water samples and 2-L aliquots of each rain sample (lower volumes if less rain collected) were filtered

through a 0.7  $\mu$ m glass fiber filter (Whatman GF/F). The filtered water was spiked with an extraction efficiency surrogate of 500 ng of atrazine- $d_5$ -ethylamine and extracted using a 0.25 g ENVI-Carb graphitized carbon solid-phase extraction cartridge (Supelco, Inc., Bellefonte, PA). Pesticide residues were eluted from the cartridges using 8 mL of 1:1 DCM:methanol followed by 2 mL of methanol, and extracts were reduced to a final volume of 1.0 mL for analysis. Filter samples were not extracted in this study, and only dissolved-phase concentrations are presented in this report.

Sample extracts were analyzed for 16 compounds (Table 1) (9–14). Concentrations of pesticides in the air, surface water, and rain extracts were determined using a Hewlett-Packard 5890 gas chromatograph coupled to a Hewlett-Packard 5989A mass spectrometer in selected-ion monitoring mode using electron-impact and negative chemical ionization mass spectrometry (7, 8).

**Quality Control.** High purity pesticide standards (>99% purity) were obtained from AccuStandard (New Haven, CT). Isotopically labeled internal standards (Cambridge Isotopes, Andover, MA), phenanthrene- $d_{10}$  and diazinon- $d_{10}$  as well as triphenyl phosphate, pentachloronitrobenzene (PCNB), and 2,2',3,4,4',5,6,6'-octachlorobiphenyl (PCB 204), were added to sample extracts before analysis. Quantification was based on the integrated area of the largest mass ion in the compound spectra. Positive identification was also ensured by retention time ( $\pm 0.30$  min of the standard retention time) and the presence of the qualifying ion(s) within 20% of the qualifying/quantifying ion ratio as was found in the standard. All analytes were chromatographically resolved.

The instrumental limit of detection (LOD) for each compound in each matrix was calculated using standard procedures established by USEPA for the analysis of pollutants (15). Using blank extracts, noise peaks in a window around the compound retention times were integrated to determine the concentration value that corresponded to an instrument signal/noise ratio of 3 (Table 1). Results from replicate blanks were averaged. None of the field blanks or control samples contained pesticides at levels above the baseline noise level with the exception of  $\alpha$ - and  $\beta$ -endosulfan in water and rain. Missing values for the recovery and LOD

TABLE 1. Usage, Physical Properties, Percent Recovery, and Limits of Detection (LOD) Values for Air, Water, and Rain Samples

compound	usage in MD <sup>a</sup> (kg a.i./yr)	usage in Patuxent Watershed <sup>b</sup> (kg a.i./yr)	vapor pressure (mPa) <sup>c</sup>	aqueous solubility (mg/L) <sup>c</sup>	melting point (°C)	air recovery (% $\pm$ SD) <i>n</i> = 6	air LOD (pg/m <sup>3</sup> $\pm$ SD) <i>n</i> = 3 <sup>d</sup>	water/rain recovery (% $\pm$ SD) <i>n</i> = 3 <sup>d</sup>	water/rain LOD (ng/L $\pm$ SD) <i>n</i> = 6 <sup>d</sup>
acetochlor	32 000	430	5.9 <sup>e</sup>	233 <sup>e</sup>	liquid	85 $\pm$ 9	12.0 $\pm$ 1.5	84 $\pm$ 4	0.035 $\pm$ 0.006
alachlor	119 000	5400	4.1 <sup>f</sup>	342 <sup>g</sup>	40 <sup>g</sup>	85 $\pm$ 9	18.0 $\pm$ 1.0	83 $\pm$ 5	0.040 $\pm$ 0.008
atrazine	529 000	6800	1.3 <sup>f</sup>	970 <sup>g</sup>	174 <sup>g</sup>	80 $\pm$ 4	8.0 $\pm$ 1.5	98 $\pm$ 3	0.030 $\pm$ 0.006
atrazine- $d_5$						97 $\pm$ 1	8.0 $\pm$ 1.5	85 $\pm$ 7 ( <i>n</i> = 58)	0.030 $\pm$ 0.005
CIAT						83 $\pm$ 3	8.0 $\pm$ 1.5	99 $\pm$ 3	0.040 $\pm$ 0.005
chlorothalonil	35 000	1300	1.3 <sup>h</sup>	107 <sup>f</sup>	250–251 <sup>g</sup>	85 $\pm$ 3	2.0 $\pm$ 0.5		
chlorpyrifos	109 000	16 000	3.6 <sup>g</sup>	2.90 <sup>g</sup>	41–42 <sup>g</sup>	77 $\pm$ 4	2.0 $\pm$ 0.5	92 $\pm$ 6	0.005 $\pm$ 0.002
cyanazine	39 000	750	0.005 <sup>f</sup>	4400 <sup>f</sup>	167 <sup>g</sup>	86 $\pm$ 6	15.0 $\pm$ 3.0	76 $\pm$ 9	0.050 $\pm$ 0.025
diazinon	4600	480	8.0 <sup>f</sup>	40 <sup>g</sup>	liquid	81 $\pm$ 8	9.0 $\pm$ 1.5	94 $\pm$ 5	0.035 $\pm$ 0.005
technical endosulfan	2500	320							
$\alpha$ -endosulfan			6.2 <sup>i</sup>	3.7 <sup>i</sup>	106 <sup>h</sup>	77 $\pm$ 3	4.6 $\pm$ 0.8		
$\beta$ -endosulfan			3.2 <sup>i</sup>	21 <sup>i</sup>	207–209 <sup>h</sup>	69 $\pm$ 9	3.5 $\pm$ 0.3		
malathion	55 000	3500	5.3 <sup>g</sup>	130 <sup>g</sup>	liquid	89 $\pm$ 8	12.0 $\pm$ 1.0	92 $\pm$ 8	0.025 $\pm$ 0.002
methyl parathion	3000	0	1.6 <sup>g</sup>	76 <sup>g</sup>	35 <sup>g</sup>	60 $\pm$ 10	11.0 $\pm$ 3.0	70 $\pm$ 6	0.042 $\pm$ 0.008
metolachlor	983 000	6600	1.7 <sup>f</sup>	530 <sup>f</sup>	liquid	91 $\pm$ 9	8.0 $\pm$ 0.8	85 $\pm$ 7	0.030 $\pm$ 0.006
pendimethalin	86 000	6100	7.8 <sup>g</sup>	0.7 <sup>g</sup>	54–58 <sup>g</sup>	71 $\pm$ 10	24.0 $\pm$ 2.2	92 $\pm$ 5	0.048 $\pm$ 0.009
simazine	70 000	1600	0.08 <sup>g</sup>	500 <sup>g</sup>	225–227 <sup>g</sup>	81 $\pm$ 4	10.5 $\pm$ 1.8	96 $\pm$ 8	0.050 $\pm$ 0.007

<sup>a</sup> Represents estimated usage in Maryland for 1995 (2). <sup>b</sup> Values based on Maryland county pesticide usage (2) multiplied by the fraction of the county in the watershed (7). <sup>c</sup> Vapor pressure and aqueous solubility for chemicals in the solid phase at room temperature are adjusted to subcooled liquid values using the melting point  $T_m$  (deg. K) to calculate a fugacity ratio  $F$  from the equation  $F = \exp[-0.023(T_m - 298)]$  which assumes a  $\Delta S$  of 56 J/mol K (9). <sup>d</sup> Instrumental detection limits,  $n$  = number of blanks averaged. <sup>e</sup> No temperature information provided (10). <sup>f</sup> Reference 11, 20–25 °C. <sup>g</sup> Reference 12, 20–25 °C. <sup>h</sup> Reference 13, 40 °C. <sup>i</sup> Reference 14, 25 °C.

TABLE 2. Summary of Air Concentrations and Wet Deposition Flux Data for Solomons, MD, April 17–July 26, 1995

compound	air <sup>a</sup>					wet deposition <sup>b</sup>				
	freq (%)	min.	max.	date of max.	mean $\pm$ SD <sup>c</sup>	freq (%)	min.	max.	date of max.	total flux <sup>d</sup>
acetochlor	0					17	11	70	April 23	140
alachlor	30	26	3800	June 2	180 $\pm$ 690	79	13	1100	June 22	4900
atrazine	0					96	5	1300	June 2	6400
CIAT	0					96	9	460	April 23	3600
chlorothalonil <sup>e</sup>	87	8	6800	June 8	990 $\pm$ 1700	0				
chlorpyrifos	100	15	2000	May 25	200 $\pm$ 390	100	1	81	June 6	210
diazinon	20	15	180	May 27	18 $\pm$ 36	0				
$\alpha$ -endosulfan <sup>f</sup>	100	7	680	June 19	170 $\pm$ 170	0				
$\beta$ -endosulfan <sup>f</sup>	73	3	210	June 2	45 $\pm$ 58	0				
malathion	30	13	2300	June 12	120 $\pm$ 420	50	8	1800	June 2	5200
methyl parathion	0					29	120	3400	May 4	5500
metolachlor	53	17	2700	June 2	250 $\pm$ 580	96	4	1300	June 12	7100
pendimethalin	0					46	14	320	June 2	1100

<sup>a</sup> Air concentrations in units of pg/m<sup>3</sup>,  $n = 30$ . Frequency is the percentage of detections out of total samples collected. <sup>b</sup> Wet deposition flux in units of ng/m<sup>2</sup> – per rain event,  $n = 24$ . Frequency is the percentage of detections out of total samples collected. <sup>c</sup> Arithmetic mean of concentrations  $\pm$  SD, with 0.5 (limit of detection value) substituted for samples with concentrations below the limit of detection. <sup>d</sup> Total flux (ng/m<sup>2</sup>) from April 17–June 26, 1995. A total of 200 mm rain was received over the study period. <sup>e</sup> Chlorothalonil was not recovered from SPE cartridge. <sup>f</sup> Endosulfan was not quantified in rain due to matrix interferences.

of  $\alpha$ -endosulfan and  $\beta$ -endosulfan in water and rain is attributable to interferences from the ENVI-Carb cartridge-sorbent material that coeluted with the two endosulfan isomers preventing quantification in samples.

Recovery values for target compounds extracted from air samples were >81% (Table 1) for all compounds except chlorpyrifos (77%), endosulfan I (77%), endosulfan II (69%), methyl parathion (60%), and pendimethalin (71%). Recovery values for target pesticides extracted from water and rain samples were >83% with the exception of cyanazine (76%) and methyl parathion (70%). Extraction efficiency of the method was also measured by the recovery of atrazine-*d*<sub>5</sub> surrogate from air and rain/water samples. Recovery results were high and consistent with an average of 85%  $\pm$  7% and 97%  $\pm$  1% for rain/water and air, respectively. The water extraction procedure proved unsatisfactory for the recovery of chlorothalonil from water samples due to the inability to elute chlorothalonil from the ENV-Carb sorbent.

## Results and Discussion

The closest and most likely source of pesticides in the vicinity of our sample collection station is from agricultural activity and volatile losses from pesticide applications in the Patuxent River watershed. Eighteen percent of the Patuxent river watershed is used for agriculture (16). Corn and soybeans comprise 75% of the crops planted, but significant acres of wheat, tobacco, and barley are also grown in this area (17).

In the Patuxent River watershed and in the surrounding region, corn crops are usually planted in early May, and the herbicides atrazine and metolachlor are generally applied together at the time of planting. Soybeans and tobacco are planted in June, and the herbicides metolachlor and/or alachlor are usually applied during planting. Insecticides such as chlorpyrifos, diazinon, malathion, and endosulfan or fungicides such as chlorothalonil may be applied to vegetable crops during the summer, depending on weather and pest population conditions. Wheat and barley crops that are usually grown over the winter require little pesticide treatment. A more detailed description of the Patuxent River watershed, pesticide usage in the watershed, and trends in water concentrations in the river from this study has recently been published (7).

**Pesticide Concentrations in Air.** Several factors have been shown to influence pesticide volatilization rates, including application method, meteorological and soil conditions, plant canopy extent and types, and the physical and chemical characteristics of the compounds are all important factors

(11). Overall, pesticides with a combination of high use rates, relatively high liquid-phase vapor pressures, and persistence in soil and the atmosphere would be expected to be present in the atmosphere at the highest concentrations.

Chlorpyrifos, atrazine, metolachlor, and alachlor have the highest estimated annual use rates in the Patuxent river watershed (Table 1) and in the state of Maryland (2) for those compounds included in the study. Comparatively, diazinon, pendimethalin,  $\alpha$ -endosulfan, and acetochlor have the highest liquid-phase vapor pressures (5.9–8 mPa) (Table 1). Malathion, alachlor, chlorpyrifos, and  $\beta$ -endosulfan have moderate vapor pressures ranging from 3.2 to 5.3 mPa. The remaining compounds have vapor pressures lower than 1.7 mPa.

The persistence of any pesticide in soil will be highly variable depending on specific soil conditions, moisture, and temperature conditions. Overall, atrazine is likely the most persistent of our target analytes. Under dry or cold conditions, atrazine can persist for more than 1 year (18). Acetochlor, chlorothalonil, chlorpyrifos, endosulfan, metolachlor, pendimethalin, and simazine are all moderately persistent in soils with half-lives of 2–3 months (18–22). Atmospheric persistence is more difficult to gauge as very few studies of gas phase reactions of these compounds have been conducted. Using all these factors as a rough guide, the seven chemicals most likely to be observed in the atmosphere are as follows: chlorpyrifos, pendimethalin, chlorothalonil, atrazine, metolachlor, endosulfan, and acetochlor.

Results from analysis of 10 of the 30 total air filter samples revealed that none of the target analytes were present in the particulate phase at levels above the LOD. Therefore, all results presented are gas-phase concentrations. Larger sample volumes might have resulted in detections of pesticides on the particle-phase material. With the exception of pendimethalin, acetochlor, and atrazine, which were not detected in any air samples (Table 2), results from our project agreed with predictions based on usage, vapor pressures, and soil persistence. Compounds that were observed in the highest atmospheric concentrations, beginning with the highest maximum concentration, were chlorothalonil, alachlor, metolachlor, malathion, and chlorpyrifos. Only chlorpyrifos and  $\alpha$ -endosulfan were observed in all 30 air samples, and chlorothalonil and  $\beta$ -endosulfan were found in 86% and 73% of samples, respectively. Despite their predicted low persistence in soil, alachlor and malathion were present in air at high concentrations over short periods of time possibly due to their moderate vapor pressures and/



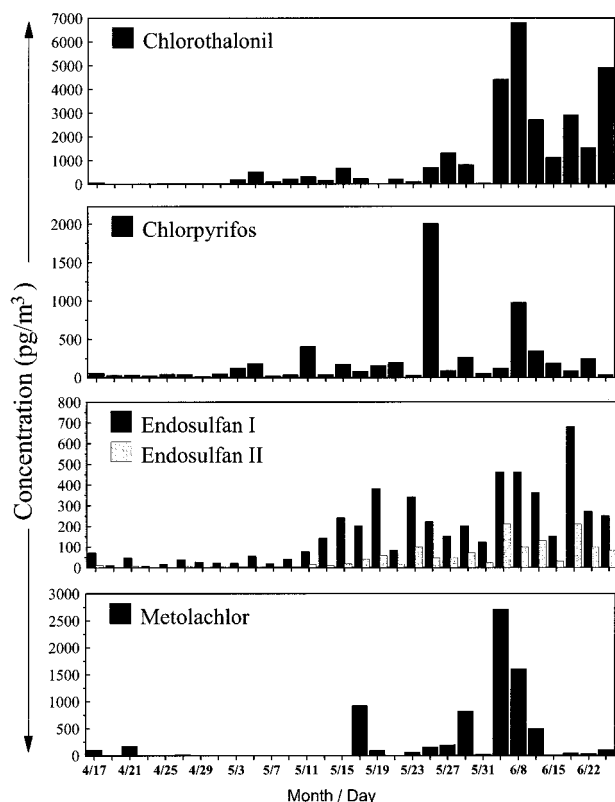


FIGURE 2. Concentrations in air ( $\text{pg}/\text{m}^3$ ) over the Patuxent River in Solomons, MD, of five commonly detected pesticides, April 17–June 26, 1995. Dates listed on X-axis represent only those days when samples were collected.

or highly localized use near the sampling site.

Chlorothalonil is a widely used fungicide that may be applied on multiple occasions on many fruits and vegetables, depending on weather conditions, to control botrytis infections (17). This chemical is also included in some home gardening products. Maximum concentrations of chlorothalonil in air were observed in June (Figure 2), and the arithmetic mean concentration over the study period was  $990 \pm 1700 \text{ pg}/\text{m}^3$ . The higher concentrations observed in the early summer appear to coincide with the expected peak use period when mature crops require increased protection from botrytis spoilage.

Metolachlor concentrations in air ranged from  $17 \text{ pg}/\text{m}^3$  to a maximum value of  $2700 \text{ pg}/\text{m}^3$  on June 2, 1995, with an arithmetic mean value of  $250 \text{ pg}/\text{m}^3$ . Concentrations of metolachlor in air were below our detection limit for 14 sampling days in April and early May, and then concentrations peaked to maximum values in early June before decreasing later in the month (Figure 2). These results were surprising in that metolachlor was detected during soybean planting season in June but not during the corn planting season in early May; however, higher soil temperatures in June may have lead to higher air concentrations. Alachlor was observed in only nine air samples, but, as with metolachlor, peak concentrations coincided with soybean planting.

None of the other herbicides, acetochlor, atrazine, simazine, or cyanazine, were detected in air. This finding is consistent with vapor pressure values of the triazine herbicides which are lower than metolachlor. Pendimethalin has a relatively high vapor pressure value and use rate; however, it was not found in any air sample above the LOD, perhaps because this compound has been shown to adsorb strongly to most soil types (21).

Chlorpyrifos concentrations in the air from April 17 through June 26, 1995 ranged from 15 to  $2000 \text{ pg}/\text{m}^3$  with a mean value of  $200 \text{ pg}/\text{m}^3$ . Levels were very low during the early spring and then increased in late May to early June before declining again in late June (Figure 2). The sharp increase in gaseous chlorpyrifos concentration in late spring may be a result of regional usage of the insecticide and from increased volatilization rates as air and soil temperatures increase.

The only other reported concentrations of chlorpyrifos in the atmosphere in the Chesapeake Bay region were measured over the main stem of the Chesapeake Bay in 1993. Over-water concentrations averaged  $29 \text{ pg}/\text{m}^3$  and ranged from  $2 \text{ pg}/\text{m}^3$  in March to a maximum of  $97 \text{ pg}/\text{m}^3$  in June over the southern portion of the Bay (6). While the temporal trend of maximum concentrations observed in June in 1993 mimics the trends found at the Patuxent site, higher concentrations observed in the 1995 study may reflect a closer proximity to sources.

In contrast to chlorpyrifos, diazinon and malathion were only detected sporadically throughout the study despite relatively high vapor pressure values for both compounds and moderate use rates for malathion. Methyl parathion was not detected in any air samples, but reported use rates of this compound are also very low (Table 1). Lack of persistence in soil for all three of these organophosphate insecticides (21) is also a likely reason for the absence of these chemicals in the atmosphere.

Despite low reported use rates in the Patuxent watershed and in the state of Maryland (2), low levels of  $\alpha$ -endosulfan were detected in every air sample. Concentrations increased throughout the study period to a maximum of  $680 \text{ pg}/\text{m}^3$  in mid-June. The  $\beta$ -endosulfan isomer was also detected in the majority of samples, but the maximum observed concentration was only  $210 \text{ pg}/\text{m}^3$ .

The two endosulfan isomers are always applied together in a technical mixture containing an  $\alpha/\beta$  ratio of 2.3 (23). However, the  $\alpha$ -endosulfan isomer has a higher vapor pressure than  $\beta$ -endosulfan (Table 1). The ratio of the  $\alpha/\beta$  isomer concentrations measured at the Patuxent site was higher than in the technical mixture with an average ratio value of  $5.6 \pm 3.8$ , consistent with differences in vapor pressure. The ratio value averaged  $9.3 \pm 4.9$  during the first month of the study (4/17–5/17) and decreased to  $3.9 \pm 1.2$  during the second month of the study (5/19–6/26). Results suggest that endosulfan contained in soils and plant material are being released in response to increases in temperatures through the study period. It appears that temperatures at the beginning of the period were high enough to volatilize the  $\alpha$ -isomer more than the  $\beta$ -isomer. A more detailed study of endosulfan isomer concentrations in response to temperatures is currently underway.

Majewski et al. (24) have published results from a study of pesticide concentrations in air along the Mississippi River. The Midwest region, while much larger and more heavily farmed than our study area, has similar cropping patterns. For those compounds that were target analytes in both studies, in general, maximum air concentrations in the Majewski study were a factor of  $2 \times$  higher than in this study. For example, maximum metolachlor and alachlor concentrations observed in the our study were  $2.7$  and  $3.8 \text{ ng}/\text{m}^3$ , respectively, while Majewski et al. found  $5.6$  and  $8.8 \text{ ng}/\text{m}^3$  as maximum levels for the same compounds. A major difference between the studies is that Majewski detected atrazine in air, while this chemical was not detected in our work. This may be due to higher use rates in the midwestern region compared with the Chesapeake Bay.

**Wet Deposition Fluxes.** Rainfall occurred frequently throughout the study period (Figure 3) for a total of 24 discrete rain events and a total of 20 cm of rain. Atrazine, CIAT,

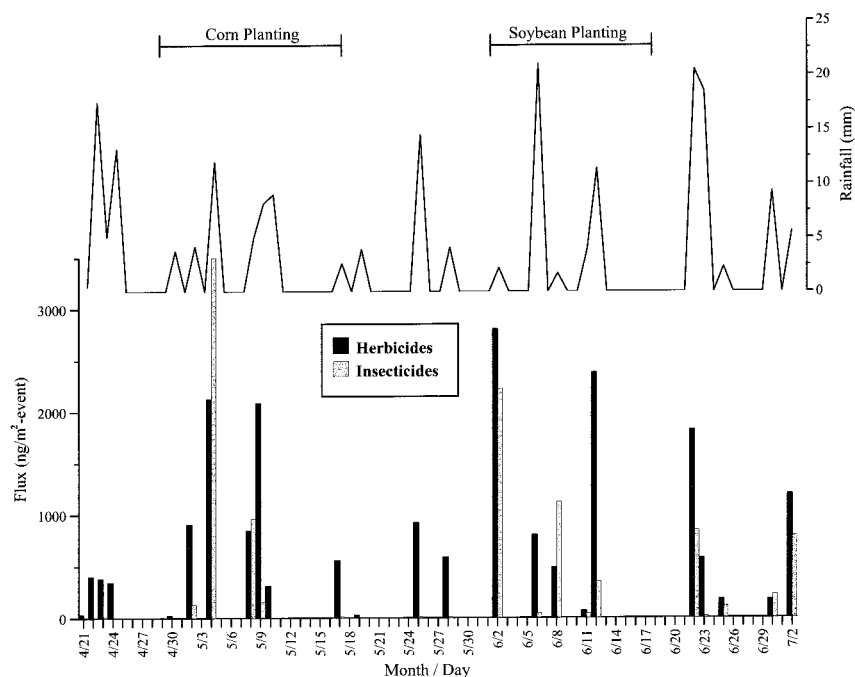


FIGURE 3. Precipitation received (mm) from April 21 to July 2, 1995 and flux (ng/m<sup>2</sup>-event) of herbicides (acetochlor, alachlor, atrazine, metolachlor, pendimethalin) and OP insecticides (chlorpyrifos, malathion, methyl parathion) per each rain event.

chlorpyrifos, and metolachlor were detected consistently throughout the study in >95% of samples (Table 2). Alachlor was detected less frequently (79% of samples), while malathion and methyl parathion were detected only in short, large pulses. Pendimethalin and acetochlor were detected sparingly at low levels throughout the study. Chlorothalonil and endosulfan could not be quantitated due to matrix interference problems.

Comparisons of pesticide concentrations in rainwater can be misleading as concentrations may decrease during a rain event due to dilution. High pesticide concentrations in rainwater can be observed during a very brief rain event, while a more significant storm may deliver more pesticide mass to a region despite lower overall rainwater concentrations. Consequently, results are presented here in ng/m<sup>2</sup>-event to indicate the magnitude of mass deposited.

While atrazine and CIAT were not detected in our air samples, these compounds were major components of the wet deposition flux. Atrazine and CIAT flux ranged from 5 to 1300 and 9–460 ng/m<sup>2</sup> per event, respectively, suggesting that these compounds were actually present in the air but at levels below our limits of detection. These relatively soluble compounds are likely efficiently scavenged from the air column during rain events. The maximum flux rates for metolachlor and alachlor were similar to atrazine at 1300 and 1100 ng/m<sup>2</sup>-event, respectively. The herbicides pendimethalin and acetochlor contributed less to the total herbicide flux. Herbicides such as atrazine and alachlor have previously been detected in rainwater from Maryland watersheds (3–5).

While the insecticide chlorpyrifos has the highest use rate of any pesticide in the Patuxent River watershed on our target list (Table 1, usage rates in agricultural and nonagricultural applications), the wet deposition flux of this compound was consistent but low throughout the project. Chlorpyrifos is used for termite and roach control in residential and urban areas. Therefore, that fraction used in agriculture, and thus easily available to the atmosphere, may be less than predicted. However, malathion and methyl parathion, having much lower estimated use rates and a lower frequency of occurrence, contributed more to the overall insecticide wet

deposition load through large pulses. A comparison of the total herbicide and total organophosphate insecticide flux throughout the study (Figure 3) indicates that while herbicides are more heavily used in the region, insecticides contribute more in atmospheric loadings in relation to their use rates. More work is needed to examine wet deposition loads and determine variability in flux rates of pesticides in the Chesapeake Bay watershed and the actual contribution to overall pesticide loadings to the Bay.

**Air–Water Gas Exchange.** The theoretical basis for calculating the air–water gas exchange flux of a chemical using simultaneous air and water concentration measurements, along with the air–water partition coefficient or Henry's law constant ( $H$ ) of that compound, has been exhaustively discussed in the literature (6, 25, 26), where  $\text{Flux } (F) = K_{OL}(C_w - C^*)$  and  $C^* = C_a/H$ . Here,  $K_{OL}$  is the overall mass transfer coefficient (m/day) which describes the rate of transfer from water to air,  $C_w$  is the measured concentration of pesticide in the water phase (ng/m<sup>3</sup>), and  $C^*$  is the water concentration in equilibrium with the air concentration,  $C_a$  (ng/m<sup>3</sup>).  $C^*$  is calculated by dividing the measured pesticide concentration in air by the dimensionless Henry's law constant. The dimensionless Henry's Law value ( $H'$ ) is related to the Henry's law constant ( $H$ ) (Pa m<sup>3</sup>/mol) by  $H' = H/RT$ , where  $R$  is the ideal gas law constant (8.3145 Pa m<sup>3</sup>/K mol) and  $T$  is the temperature at the air–water interface (K) (25). The  $H'$  values for chlorpyrifos were corrected for measured water temperature and salinity by empirical formulas derived from laboratory experiments (23). However, no data regarding the salinity effect on  $H'$  values of metolachlor are available, and only preliminary data are available for temperature dependence (27). The following equations describe the temperature and salinity corrections used in our calculations:

$$\log H'_{\text{chlorpyrifos}} = -1186.9/T + 0.173 \text{ distilled water}$$

$$\log H'_{\text{chlorpyrifos}} = -916.3/T - 0.574 \text{ saltwater (33.3‰)}$$

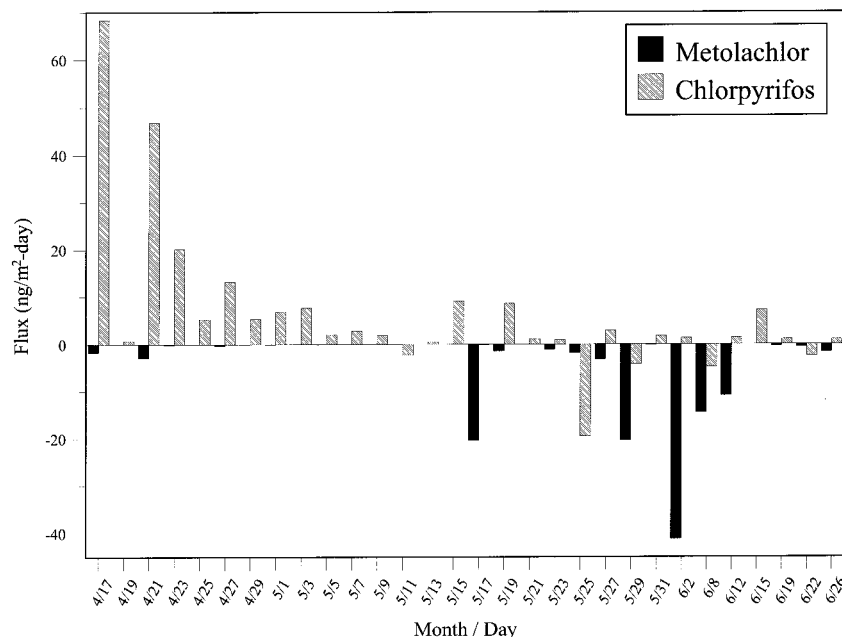


FIGURE 4. Daily gas exchange flux (ng/m<sup>2</sup>-day) for metolachlor and chlorpyrifos across the air–water interface in the Patuxent River, Solomons, MD from April 17 to June 26, 1995. Dates listed on X-axis represent only those days when samples were collected.

$$\log H_{\text{metolachlor}} = -1197.4/T - 1.36 \text{ distilled water}$$

The  $H$  value of chlorpyrifos was adjusted for salinity by interpolating between the  $H$  values observed at 0 and 33‰ salinity to measured salinity values in Patuxent River water. Final  $H$  values calculated for chlorpyrifos and metolachlor ranged from  $1.3 \times 10^{-4}$ – $1.9 \times 10^{-4}$  and  $2.8 \times 10^{-6}$ – $4.3 \times 10^{-6}$  for water temperature and salinity conditions that ranged from 12.9 to 25.9 °C and 12.8–14.8 l, respectively.

Twenty-four h average wind speed values measured at the Chesapeake Biological Laboratory (10-m height) were used to calculate a daily overall mass transfer coefficient ( $K_{OL}$ ) (21) value for chlorpyrifos and metolachlor. In general the average wind speed was < 5 m/s, and  $K_{OL}$  values ranged from  $1.2 \times 10^{-3}$ – $4.0 \times 10^{-3}$  m/day and  $3.3 \times 10^{-5}$ – $9.1 \times 10^{-5}$  m/day for chlorpyrifos and metolachlor, respectively. Over the course of the study, chlorpyrifos and metolachlor were sometimes absent from either the water or air or both. On days where either the air or water concentration was below the LOD, the LOD value was used in the calculation, on days where both values were below the LOD, no calculation was made.

Figure 4 displays the net direction and magnitude of the gas exchange flux for chlorpyrifos and metolachlor. The net flux of chlorpyrifos is from water to air in the early spring when water concentrations are at their maximum (maximum value = 30 ng/L) (7) and air concentrations are near the limit of detection (Figure 2). The net volatilization flux of 68 ng/m<sup>2</sup>-day occurred on the first sampling day (April 17, 1995). The flux decreased to near zero and became negative (net absorption) in late May, when air concentrations are at their maximum (2000 ng/m<sup>3</sup>) and water concentrations were low (<0.005–1.7 ng/L).

This pattern of net flux is similar to the results by McConnell et al. (6), who concluded that despite cold water temperatures and lower effective Henry's law constant values favoring absorption, the high surface water concentrations cause net gas exchange fluxes of chlorpyrifos from water to air during March. Additionally, McConnell et al. found that increased temperatures and higher air concentrations in June caused the net flux to be from the air to the water, which is also the finding of this study. The peak air concentration of

2.1 pg/m<sup>3</sup> on May 25, 1995 drives the flux to its greatest negative value (i.e. largest net adsorption) of –20 ng/m<sup>2</sup>-d.

Gas phase metolachlor was adsorbed into the surface water during all days sampled (Figure 4), indicating that deposition dominates gas exchange transport. This is attributable to the relatively high water solubility of metolachlor. The mean gas exchange flux for metolachlor was –0.05 ng/m<sup>2</sup>-day. Flux values are greatest from mid May through mid June when higher air concentrations and low concentrations in the surface water (<0.03–1.2 ng/L) occur. In June, when the water concentrations fall below detection limits and air concentrations increase, the depositional fluxes peak at –41 ng/m<sup>2</sup>-day. Use of the LOD value for the water concentration in the gas exchange calculations gives the most conservative estimates of depositional flux; the true value may be larger in magnitude.

**Comparison of Gas Exchange and Wet Deposition Fluxes.** A comparison of the cumulative inputs or losses due to these two processes for metolachlor and chlorpyrifos is shown in Figure 5 (parts A and B, respectively). Over the course of the study, the cumulative gas exchange loss to the air (290 ng/m<sup>2</sup>-sampling period) and wet deposition input (–210 ng/m<sup>2</sup>-sampling period) of chlorpyrifos essentially offset each other. However, the rate of chlorpyrifos volatile loss through gas exchange flux is high in the beginning of the sampling period and diminishes by the end. The rate of the wet flux remains relatively constant throughout with a few important events at the middle and end of the study. High surface water concentrations in the spring are the controlling factor causing high gas exchange losses of chlorpyrifos. Later, air concentrations are dominant, causing gas and wet deposition.

Wet deposition emerged as the dominant process controlling atmospheric deposition of metolachlor. By the end of the study the net gas exchange load to the surface water was –260 ng/m<sup>2</sup>-sampling period, while wet deposition contributed greater than 25 times more metolachlor (7100 ng/m<sup>2</sup>-sampling period). Wet deposition fluxes, however, will change from year to year with the amount of rain received. Gas exchange is more complicated because it is a bidirectional process and can be both a source and a sink depending on conditions. Both volatilization and deposition occur simultaneously across the air–water interface continuously, and

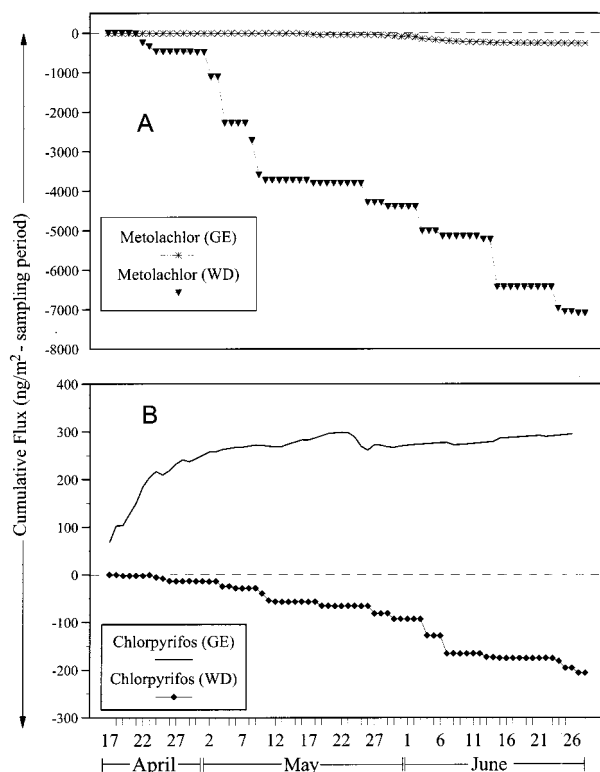


FIGURE 5. Cumulative gas exchange (GE) and wet deposition (WD) fluxes ( $\text{ng}/\text{m}^2 \cdot \text{sampling period}$ ) for metolachlor and chlorpyrifos from April 17 to June, 26, 1995.

the net flux is driven by the concentration gradient across the interface. In this case the concentration gradient of metolachlor was small, therefore limiting the magnitude of the flux.

Results from this one sampling location can be used to calculate a rough estimate of the total atmospheric deposition load of these two chemicals to the entire Patuxent River Watershed (surface area  $2400 \text{ km}^2$ ). While gas exchange can occur across soil and plant surfaces, only air–water gas exchange with the surface water areas of the watershed were considered in this calculation (6% of total watershed area). The wet deposition load is estimated at 0.7 and 18 kg, respectively, for chlorpyrifos and metolachlor during the study period. On the other hand, there was a net loss of 0.04 kg of chlorpyrifos through gas exchange and a net gain of 0.04 kg of metolachlor. Therefore, results indicate that wet deposition is the most important source of both compounds to the watershed. There is, however, likely significant variability in the wet deposition flux rates across the watershed. More work is needed to determine the spatial and temporal trends in these processes in order to further improve our understanding of the behavior of these chemicals in the larger Chesapeake Bay system.

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