Wet Deposition of Current Use Pesticides at a Rural Location on the Delmarva Peninsula: Impact of Rainfall Patterns and Agricultural Activity

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Event-based precipitation samples were collected during the main agricultural season (April–September) over 4 years (2000–2003) at one site in the Choptank River Watershed on the Delmarva Peninsula. The samples were analyzed for 19 agricultural pesticides to determine the contribution of wet deposition as a source of these compounds to the Chesapeake Bay and the factors affecting the temporal trends in deposition. Chlorothalonil was detected most frequently (92% samples) followed by metolachlor (66%) and endosulfans (49%). Although chlorothalonil is the single biggest contributor to pesticide flux (33–46%), pesticide wet deposition is dominated by herbicides (46–61%), with the greatest fluxes occurring during the time of herbicide application on corn and soybeans. The analysis suggests that the extent of wet deposition of herbicides depends on the timing of precipitation relative to herbicide application. The insecticide and fungicide flux was greater in years with above-average rainfall (2001 and 2003), suggesting that for these pesticides deposition flux is dependent on the total amount of rainfall in the agricultural season. The data indicate that the use of chlorpyrifos, an organophosphate insecticide which is on the Toxics of Concern list for the Bay, is on the increase. Total pesticide flux ranged from 90 μg/m^2 (2001) to 180 μg/m^2 (2000). Wet deposition can account for up to 10–20% of the annual loadings of pesticides to the Bay.

KEYWORDS: Pesticides; precipitation; Delmarva Peninsula; Choptank; wet deposition; agriculture

INTRODUCTION

The Choptank River watershed is an intensely agricultural region. It is part of the Chesapeake Bay estuarine drainage area where pesticide application rates are among the highest in the United States (*1*). The watershed is located on the Delmarva Peninsula (**Figure 1**), a rural, agricultural region. Corn, soybeans, wheat, fruits and vegetables are the main agricultural commodities. Maryland counties on the Peninsula used ∼2.1 × 10^3 tons of pesticides in 2000 (*2*). Aquatic organisms in the Bay, its tributaries, and associated wetlands may be at risk from exposure to pesticides (*3*). Research shows that exposure to agricultural pesticides can alter both functional and structural aspects of the estuarine microbial food web (*4*). For instance, it has been found that long-term exposure to low levels of atrazine may lead to shifts in species sensitivity and potential alterations in phytoplanktonic population dynamics (*5*). Similarly, exposure to endosulfan and chlorpyrifos adversely affects abundance of

bacteria and heterotrophic ciliates and flagellates, respectively, in an estuarine environment (*4*).

A major portion of the pesticide load to the Bay is expected to occur via runoff contributions to its tributaries. However, aerial deposition, which is recognized as a major pathway for organic contaminant loading to water bodies (*6, 7*), may also be a significant source of pesticides. Pesticides are effectively scavenged from the atmosphere by rainfall (*8, 9*) and have been detected in precipitation throughout the world. Pesticides of concern include chlorpyrifos, atrazine, and endosulfan among others because of their widespread use and/or high toxicity potential (*10, 11*).

The Chesapeake Bay has a large surface area to mean water volume ratio and receives 75–100 cm of precipitation annually, which makes the atmosphere a likely source of contaminants (*12*). For example, it is estimated that a fourth of the total nitrogen load to the Bay comes from atmospheric deposition (*13*). The Chesapeake Bay region is not well characterized with respect to the presence of pesticides in the atmosphere. The existing studies are few, sporadic, and mostly short term (*14*–*18*). Long-term monitoring is required to better understand the different factors affecting the wet deposition of pesticides in this region. Concentrations in precipitation depend not only upon the amount of pesticides present in the atmosphere but also on

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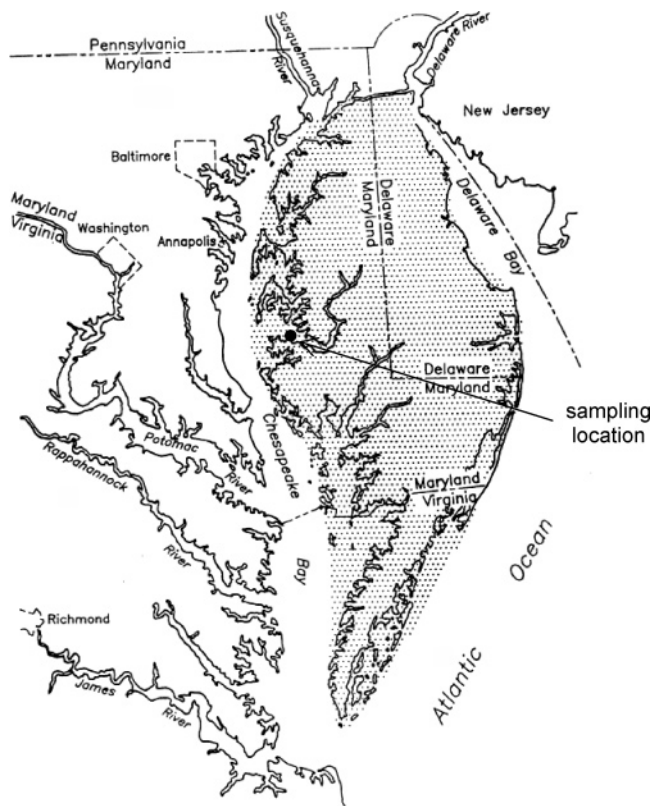
Figure 1. Sampling site along the Choptank River, Delmarva Peninsula.

the amount, intensity, and timing of rainfall (*19*). Moreover, the usage of pesticides varies from year to year in response to weather conditions and farming practices.

This study was undertaken to elucidate the effects of agricultural activity and rainfall patterns on the wet depositional fluxes of current use pesticides in the region. The importance of wet deposition as a source of these compounds to the Bay has also been investigated.

EXPERIMENTAL PROCEDURES

Precipitation Sampling. Precipitation samples were collected from April to September for the years 2000−2003 at one site on the campus of the University of Maryland, Horn Point Environmental Laboratory, near the mouth of the Choptank River in Cambridge, MD (38° 36′ 04″ N, 76° 07′ 47″ W) (**Figure 1**). The site is adjacent to a 10-m meteorological tower in an open field with no large obstructions within at least 100 m and no agricultural production in the immediate proximity (at least 800 m).

Rain samples were collected on an event basis using a modified MIC-B rain sampler (Meteorological Instrument Center, Ontario, Canada) having a 0.2 m² stainless steel funnel covered with a rain sensor activated lid. Each rain event was any precipitation collected during a 24-h period from 10 a.m. one day to 10 a.m. (± 1 h) the following day. Rainwater passed through a filter-cartridge assembly. Particles were retained on the filter, whereas pesticides in the dissolved phase were retained on the solid-phase extraction (SPE) cartridge. Samples with volume of <50 mL, representing <0.025 cm of rainfall, were not analyzed. After a rain event, the cartridge and filter were removed, stored at 20 °C, and shipped to the U.S. Department of Agriculture, Beltsville, MD, for analysis. More details on the sample collection, extraction procedures, and efficiencies can be found in Kuang et al. (*20*).

A total of 203 rain samples were collected from April to September in the 4 years of sampling from 2000 to 2003. There were 17 rain events where the rainfall was below the sample cutoff size of 50 mL and were discarded. Hence, the dataset includes >90% of the rain events that occurred from April to September for the 4 years. Fewer events

were received in 2001 and 2002 (36 and 39, respectively), whereas 67 and 62 events were received in 2000 and 2003, respectively. Median volumes for each year ranged from 0.8 L in 2002 to 1.7 L in 2003. For the year 2003, sampling was terminated on September 15 due to Hurricane Isabelle. In some years additional samples were collected in March or in October and November to assess concentrations outside the main agricultural season (*n* = 39).

Pesticide Extraction. The SPE cartridges were dried using high-purity (>99.9%) nitrogen gas. Absorbed analytes were eluted with 6 mL of dichloromethane (DCM) followed by 9 mL of 3:1 acetone/acetonitrile (MeCN) solvent mixture. The resulting extracts were concentrated to a volume of 1.0 mL under a gentle stream of high-purity (>99.9%) nitrogen gas, exchanged into MeCN, and quantitatively transferred to a 2-mL amber glass vial. Pesticide recoveries from dissolved-phase rainwater following our collection and extraction method ranged from 68 to 104% (*20*). The collection capacity of the SPE sorbent material was assessed by placing two cartridges in series and extracting several volumes (up to 10 L) fortified with a mixture of target analytes through the sampler. For the majority of the compounds, the extraction efficiency was lowest at 10 L (*21*). The maximum rain sample volumes reported for 2000, 2002, and 2003 were the only rain events in those years that exceeded 10 L (except for another 11 L sample in 2003). It is probable that the measured pesticide concentrations from these high-volume events are lower than the actual values. The data presented in this paper are for dissolved-phase pesticide concentrations only; previous work has shown that particle-phase pesticides are not present above the limit of quantitation at the typical sample volumes collected (*20*).

Instrumental Analysis. Pesticide concentrations in rain extracts were determined using a Hewlett-Packard (HP) (Palo Alto, CA) 5890 gas chromatograph coupled to an HP 5989A mass spectrometer (GC-MS) in selected-ion monitoring mode using electron impact (EI) and negative chemical ionization (NCI) mass spectrometry. Samples from 2000 were analyzed as in Kuang et al. (*20*). For samples from 2001−2003 the chromatographic conditions were as follows: in EI mode, injection volume, 1 μL; column, J&W DB-1MS, 30 m, 0.25 mm i.d., 0.25-μm thickness; flow rate through the column, 1 mL/min; temperature program, 90 °C, raised at 5 °C/min to 150 °C, then at 2 °C/min to 166 °C, and finally at 5 °C/min to 280 °C for 2 min; interface, 300 °C; quadrupole, 100 °C; source, 200 °C; injector, 270 °C. For the analysis of samples from 2003, a DB-17MS column (J&W) was used as it was observed that it gave a better separation for 6-amino-2-chloro-4-ethylamino-*s*-triazine (CEAT) and 6-amino-2-chloro-4-isopropylamino-*s*-triazine (CIAT). In NCI mode, the injection volume was 2 μL. The chromatographic conditions were as follows: column, J&W DB-17MS, 30 m, 0.25 mm i.d., 0.25-μm thickness; flow rate through the column, 1.4 mL/min; temperature program, 130 °C, raised at 6 °C/min to 205 °C for 4.5 min and then at 6 °C/min to 300 °C for 5.5 min; interface, 300 °C; quadrupole, 150 °C; source, 200 °C; injector, 290 °C.

Beginning in 2001, 20 μL of atrazine-*d*₅ (54 ppm) and 20 μL of PCB-204 (4 ppm) were used as internal standards. The method of internal standards using a five-point calibration curve (ranging from 0.005 to 0.25 ppm for NCI and from 0.05 to 2.0 ppm for EI) was used for sample quantification.

Target Pesticides. Our target analytes in this study included those pesticides that are typically used on corn, soybeans, and vegetables, as well as a few transformation products (**Table 1**). Eight compounds were analyzed in the EI mode and the remaining in NCI mode on the GC-MS. Target herbicides were the triazines (simazine, atrazine, and transformation products CIAT and CEAT), chloroacetanilides (ac-etochlor, alachlor, and metolachlor), and dinitroanilines (trifluralin and pendimethalin). Insecticides included organochlorines [endosulfans, α and β isomers, as well as the transformation product sulfate, lindane (γ-HCH) and its transformation product α-HCH], organophosphates (chlorpyrifos and its degradation product, the oxon, diazinon, malathion). Chlorothalonil was the only fungicide in the study. Chlorpyrifos, malathion, endosulfan, and endosulfan sulfate are among the compounds on the Toxics of Concern List for the Chesapeake Bay (*24*).

Quality Assurance/Quality Control. The quality control and assurance procedures have been described in Kuang et al. (*20*), and method detection limits (MDLs) developed for target analytes are

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Table 1. Usage of Some Pesticides in Maryland

pesticide	class	target crops in Maryland	usage in Maryland eastern shore counties (tons) 1997[a]	usage in Maryland eastern shore counties (tons) 2000[b]	Henry's constant[c] (Pa-m³/mol)
acetochlor	H	corn	71	7	2.2E−08
alachlor	H	corn, soybeans	51	2	2.1E−03
atrazine	H	corn	127	138	2.5E−04
chlorothalonil	F	vine crops,[d] greens,[e] potatoes, tomatoes, orchard fruits[f]	6	13	2.2E−02
chlorpyrifos	I	corn, orchard fruits, strawberries	14	8	7.4E−01
diazinon	I	melons, greens, orchard fruits	2	3	7.2E−02
endosulfan	I	vine crops, orchard fruits, tomatos, potatoes	0.3	0.3	2.9E−02
glyphosate[g]	H	soybeans, corn, barley, wheat	106	245	<1.4E−07
malathion	I	strawberries	1	2	1.1E−03
metolachlor	H	corn, soybeans, greens, potatoes, tomatoes	237	145	2.4E−03
pendimethalin	H	soybeans, tomatoes, greens	27	18	1.2E+00
simazine	H	corn, orchard fruits, strawberries	46	78	9.8E−05
trifluralin	H	greens, tomatoes	1	14	1.5E+00

[a] Source: Maryland Pesticide Statistics for 1997 (*23*). [b] Source: Maryland Pesticide Statistics for 2000 (*2*). [c] Source: The ARS Pesticides Properties Database (*22*). [d] Squash, cucumber, watermelon, musk melon, cantaloupe, pumpkin. [e] Green peas, greean beans, collards. [f] Orchard fruits include apples and peaches. [g] Glyphosate is not a target pesticide and is included here solely for comparison.

Table 2. Method Detection Limits (MDLs), Observed Concentrations, and Wet Depositional Fluxes for the Target Pesticides for the Sampling Period April–September 2000–2004

pesticide	MDL (ng/L)	% detection	2000 conc. range (ng/L)	2000 conc. av (ng/L)	2000 flux (μg/m²)	2001 conc. range (ng/L)	2001 conc. av (ng/L)	2001 flux (μg/m²)	2002 conc. range (ng/L)	2002 conc. av (ng/L)	2002 flux (μg/m²)	2003 conc. range (ng/L)	2003 conc. av (ng/L)	2003 flux (μg/m²)	r[a] dep flux vs sample vol
acetochlor	1.30	17	14–170	2.1	1.32	20–85	6.6	3.06	50–360	20	7.82	11–220	14	11.2	*0.08*
α-endosulfan	0.23	31	1.3–31	0.8	0.53	0.4–5.2	1.2	0.55	0.1–2.4	0.3	0.12	0.2–1.4	0.4	0.41	0.42
α-HCH	0.40	2	0.4	0.1	0.03	ND	NA	NA	0.03–0.5	0.1	0.04	22	0.7	0.02	0.46
alachlor	1.30	25	9.5–450	16	9.88	7.7–490	14	6.31	6.2–150	15	5.83	5.3–73	3.4	2.69	*0.03*
atrazine	1.30	44	22–900	44	27.4	4.7–520	26	12.1	21–470	35	13.6	10–800	18.5	15.1	*0.01*
β-endosulfan	0.22	47	0.3–81	2.4	1.48	0.4–7.7	1.6	0.75	0.1–2.4	0.6	0.23	0.3–11	2.0	1.53	0.35
CEAT	2.10	0	ND	NA	NA	ND	NA	NA	ND	NA	NA	ND	NA	NA	NA
chlorothalonil	1.60	92	12–2000	130	80.8	5.6–510	86	41.2	6.1–1100	78	30.1	2.0–380	91	61.7	0.47
chlorpyrifos	0.45	39	1.0–29	1.0	0.61	0.5–8.9	1.2	0.67	0.4–180	4.5	1.75	0.7–17	2.3	1.33	0.25
chlorpyrifos oxon	2.03	3	1.3–650	4.6	2.91	2.7–75	8.1	3.71	ND	NA	NA	4.4–48	1.5	1.34	0.15
CIAT	1.80	18	21–130	4.6	2.86	11–150	7.77	3.57	13–260	12	4.46	3.4–18	0.8	0.69	0.00
diazinon	1.96	20	13	0.3	0.21	10–39	0.5	0.23	3.1–150	6.2	2.39	10–160	18	14.6	0.26
endosulfan sulfate	0.50	34	1.0–14	0.4	0.28	0.9–3.4	0.6	0.27	0.2–7.5	0.9	0.34	0.7–4.2	0.7	0.88	0.51
γ-HCH	0.54	15	1.5–22	0.8	0.53	0.3–7.1	1.2	0.53	0.3–6.3	0.8	0.32	0.7–3.6	0.3	0.32	0.32
malathion	0.88	7	1.9–360	1.5	0.94	31.5	0.2	0.17	7.3	0.1	0.04	4.2–83	5.9	1.80	*0.05*
metolachlor	1.20	66	4.3–1000	53	33.1	11–370	38	17	1.4–590	51	19.8	0.8–800	40	32.1	*0.11*
pendimethalin	1.20	12	20–83	4.8	3.04	12–96	3.7	2.19	14–150	4.5	1.72	2.8–76	4.3	3.45	0.17
simazine	2.00	10	18–500	16	10.2	–[b]	–	–	19–160	4.0	1.55	55–130	6.0	4.77	*0.04*
trifluralin	0.37	17	ND	NA	NA	0.2–7.4	0.1	0.08	0.1–12	0.3	0.11	0.2–24	1.2	0.75	0.15
total					176			90.2			90.2			155	

[a] Pearson's corelation coefficient. Numbers in italics are not significant at α = 0.05. [b] Data not available due to problem with interfering ions.

provided in **Table 2**. To ensure that there was no bias in results due to possible contamination of the sampler, once every month a field blank was collected by pouring 4 L of distilled water into the rain sampler funnel and processing it in the same way as a sample. A total of 17 field blanks were collected for the sampling period April−September 2001−2003. Some analytes occurred above the MDL in nine of these field blanks; chlorothalonil in eight, trifluralin in four, and metolachlor and α-HCH in one blank each. The field blanks having chlorothalonil above the MDL all fell during the summer. On the basis of the standard deviation for the amount of chlorothalonil seen in the blanks, a new summertime MDL of 4.2 ng/L was calculated for a 4-L volume. Therefore, an MDL for chlorothalonil of 1.6 ng/L was used for samples collected from April to June and an MDL of 4.2 ng/L was used for July−September samples for all 4 years. Trifluralin amounts in field blanks were very close to the MDL. Metolachlor occurred in one field blank from April 2002, and the amount present in samples from this month was much higher than in the blank. α-HCH occurred in the blank from September 2003 and surprisingly was not present in any sample from this month. Considering the timing of occurrence of these compounds in the blanks and their levels with respect to MDLs and amount present in samples, it was decided not to apply any corrections to the samples for trifluralin, metolachlor, and α-HCH.

For the regression analyses performed in this study, the level of significance has been set at 5% (i.e., α = 0.05), and *p* values (i.e., actual observed level of significance) are reported throughout the text.

RESULTS AND DISCUSSION

Agricultural Activity and Pesticide Usage. Agriculture is the state of Maryland's largest commercial industry and contributes more than $17 billion in revenue annually. The major crops in Maryland include corn, soybeans, small grains (barley, wheat, oats), vegetables (potatoes, tomatoes), nursery products, and fruits (apples, melons, etc.). Agricultural activity is mainly concentrated in the counties on the Delmarva Peninsula. The soil type in this region is mainly clay-loam. Besides being the major producers of potatoes, tomatoes and green peas, these counties accounted for 62% of corn, 72% of soybeans, 70% of wheat, and 48% of barley produced in the state in 2002 (*25*).

Vegetables such as potatoes and peas are among the first to be planted (early in March) and harvest begins at the end of June. Potatoes are rotated with other crops such as corn and vegetables, whereas peas are followed by soybeans, lima beans,

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and other vegetables. Row crops such as cantaloupes, water-melons, cucumbers, and tomatoes are planted from early April to the middle of June. Corn planting begins in April, whereas soybeans are planted at the beginning of May. Wheat and barley are winter grains and are often used as cover crops. They are sown in late fall and harvested in spring.

Herbicides comprised 46% of all pesticides used in the United States in 2001 (*26*) followed by insecticides (9%) and fungicides (6%). Typically, herbicides are applied at the time of planting; atrazine and metolachlor are often applied together at corn planting, metolachlor and/or alachlor/acetochlor are applied during soybean planting. Metolachlor, pendimethalin, and trifluralin are among the herbicides that are applied pre-emergence on potatoes, late-planted peas, and tomatoes. Some crops also require post-emergent herbicide application. In Maryland (as per the statistics available from 1997, *27*) acetochlor and atrazine are used exclusively on corn (**Table 1**). Metolachlor and alachlor are used on both corn and soybeans, whereas pendimethalin and trifluralin are used on vegetables. In 1997, in excess of 36 tons of glyphosate was used on corn and 62 tons on soybeans in Maryland (*27*). The increased acreage of glyphosate-tolerant corn and soybeans (RoundUp-Ready) and consequently greater use of use of glyphosate is the likely reason for the sharp decrease in the use of traditional corn herbicides, such as acetochlor and alachlor, from 1997 to 2000 (**Table 1**).

Insecticides are used to combat insects and mites and are used mostly on vegetables and fruits. Depending on plant physiology and soil and weather conditions, plants may be susceptible to one or more insects during the different stages of their lifecycle. The timing and total number of insecticide applications can vary considerably from year to year, as influenced by the timing and level of infestation. Endosulfan is used for the control of aphids (tomatoes, potatoes, melons, peaches, and apples) during May–June, for beetles (potatoes, tomatoes, and pumpkins) during April–May, and also for whiteflies on pumpkins later in the season. Most of the agricultural uses of lindane (γ-HCH), another organochlorine, have been banned by the U.S. EPA. However, it can be used as a seed treatment on corn, soybeans, wheat, barley, peas, cantaloupes, and squash (*28*) and hence has been included in this study. The organophosphates malathion, chlorpyrifos, and diazinon were the top three organophosphate insecticides used in the United States in 2001 (*26*). In Maryland, chlorpyrifos is used mainly on corn for the control of ear-damaging pests such as the European corn borer, which strikes in May–June. In response to the Food Quality Protection Act of 1996, the U.S. EPA has canceled its use on tomatoes and has greatly reduced its use on apples and peaches (*29*). Diazinon is used for the control of maggots (peas, watermelons, and pumpkins) in spring. It can also be used on worms (potatoes and tomatoes) in May–June. One of the uses of malathion is also to control mites in strawberries.

Chlorothalonil is the primary fungicide used on fruits and vegetables for the treatment of diseases, such as blight, leaf spots, mildew, and fruit rots. It was the most used fungicide in Maryland in 2000 (5.5 tons of active ingredient, *2*). The intensity of the disease depends on weather conditions; *early blight* occurs during warm rainy or humid weather, whereas *late blight* is favored under cool, wet conditions. For tomatoes and pumpkins disease control is achieved with preventive pesticide treatments. Fungicides are typically applied every 7–14 days.

Thus, the major herbicide application period is from March to May. Insecticides are likely to be applied during late spring and summer. Fungicide application would depend on rainfall
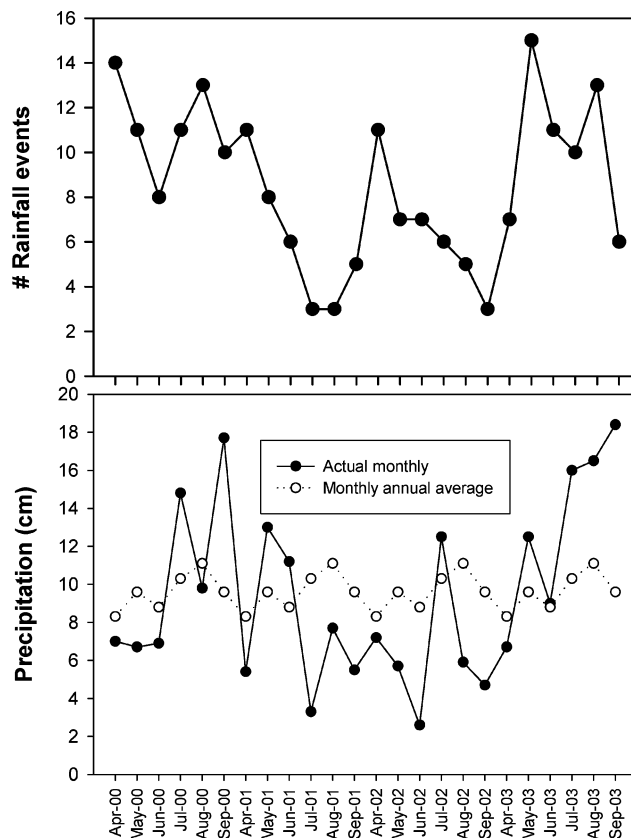

Figure 2. Number of rainfall events and amount of precipitation received (centimeters) on a monthly basis during the sampling period (April–September 2000–2003).

patterns. Greater use of fungicides is expected during years with greater rainfall quantities.

Trends in Precipitation. During the course of this project a wide range of rainfall patterns were observed (**Figure 2**), ranging from drought conditions in 2002 (39 cm rainfall) to above-average rainfall in 2003 (79 cm). The largest number of rain events was observed in 2000 (67), and the fewest events were observed in 2001 (36). The drought year of 2002 was dominated by the largest event of the entire 4-year sampling period, a 6.5 cm rainfall on July 24, 2002, representing 17.3% of the total rainfall for the entire season (*31*). For any given year and month, the highest number of rain events occurred in May 2003 ($n =$ 15). The years 2000 and 2003 (as well as 2001 and 2002) were very similar in terms of the amount of rainfall received and the frequency of rain events. For the years 2000–2002, it rained frequently during April, whereas the frequency was quite low in 2003. Seasonable weather in spring 2002 resulted in corn being planted at a faster rate than in the other years. However, crop plantings were delayed in 2003 due to excess moisture from the snow and rain received in the region during the winter of 2002–2003 (*32*).

Considering the amount of rainfall received during the sampling period, one would expect higher fluxes in 2000 and 2003 as compared to 2001 and 2002. In general, wet deposition of pesticides would be expected to be lowest in 2002. Considering the timing of overall planting progress for corn and soybeans combined with rainfall patterns, conditions for the greatest herbicide wet flux would be found in 2000 and 2001 with less expected in 2002.

Pesticide Detections in Rainfall. As expected, herbicides were most frequently detected in samples collected around the corn and soybean planting season, and concentrations generally

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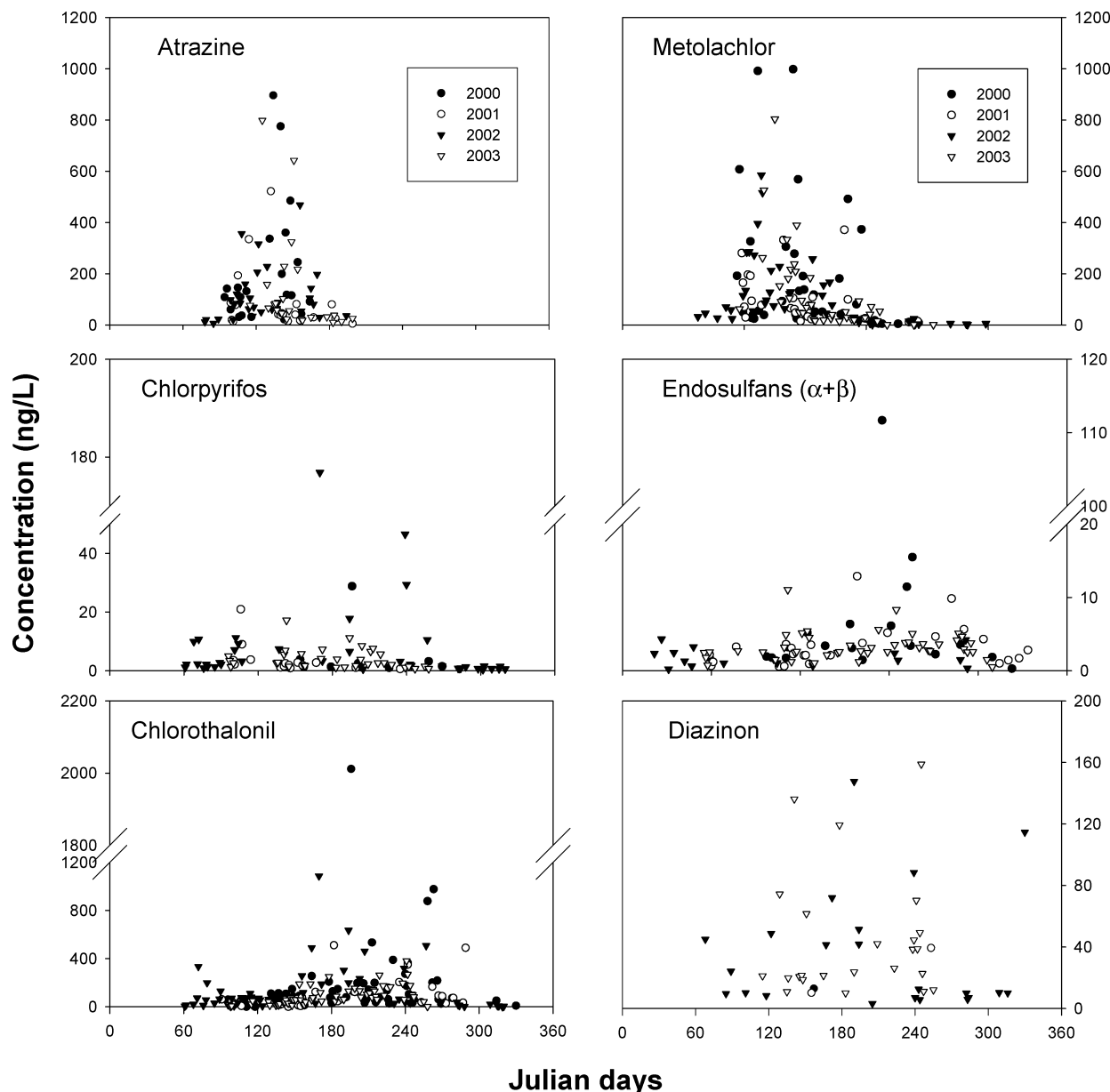
**Figure 3.** Concentrations in precipitation of select pesticides for the years 2000–2003.

declined sharply after the end of June (**Figure 3**). The insecticides, in general, showed a greater variation in their detection and observed concentrations. Most insecticides as well as the fungicide chlorothalonil were detected in low concentrations throughout the year, and concentrations typically peaked in July–August. During the main agricultural season (April–September), chlorothalonil was the most frequently detected pesticide (in 92% samples) (**Table 2**) followed by metolachlor (66%) the endosulfans (α + β) (49%), atrazine (44%), and chlorpyrifos (39%). Pesticides were also detected in samples collected from March (2002), October (2001 and 2002), and November (2000 and 2002). Insecticides and chlorothalonil dominated the pesticide detections for these off-season months; chlorothalonil was detected in 74% samples followed by chlorpyrifos (69%), endosulfans and trifluralin (38% each), and diazinon (33%). Chlorothalonil and pendimethalin were the only compounds detected in samples from November 2000 and October 2001. Although the primary use of pendimethalin (also trifluralin) is on beans (*27*), it can also be used on wheat, barley, and turfgrass. Application of pendimethalin as a pre-emergence herbicide on wheat and barley, which are both winter crops in

the Peninsula, or on golf courses later in the year could explain its occurrence in samples from the cold months. Trifluralin was detected in low concentrations in all samples from March 2002 (*n* = 12), which is in keeping with its use on vegetables. Metolachlor and atrazine were also present in March 2002 samples, which can be explained by the early onset of corn planting in that year due to dry conditions.

Current Use Pesticide Wet Flux. Pesticide concentrations in a precipitation sample are influenced by the total amount of rainfall received in that particular event. Rain concentrations are likely to be highest at the beginning of a rain event, with decreasing concentrations as the air is scavenged of airborne residues (*33*). Hence, it is more informative to use mass fluxes of pesticides in precipitation to compare trends. Across the years, the median pesticide flux was highest in the month of May (**Figure 4**), decreased during June, increasing again in July, and dropping steadily during August and September. Herbicides contributed most to the flux in April and May, whereas the flux in September was almost exclusively contributed by insecticides and chlorothalonil. The total pesticide flux for the target compounds were in the range of 90–180 μg/m^2 per season
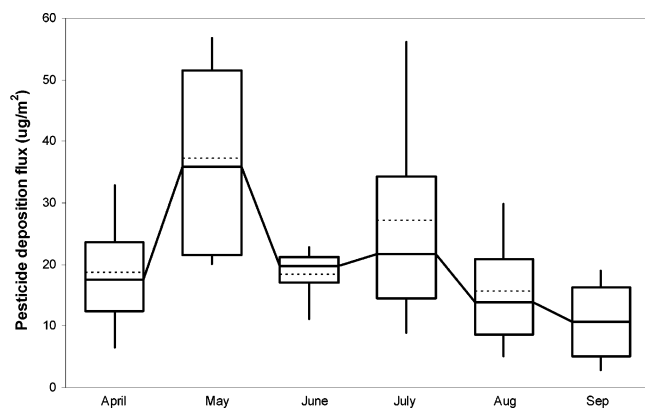
Figure 4. Box plot showing the distribution of pesticide wet flux across months (April–September 2000–2003).
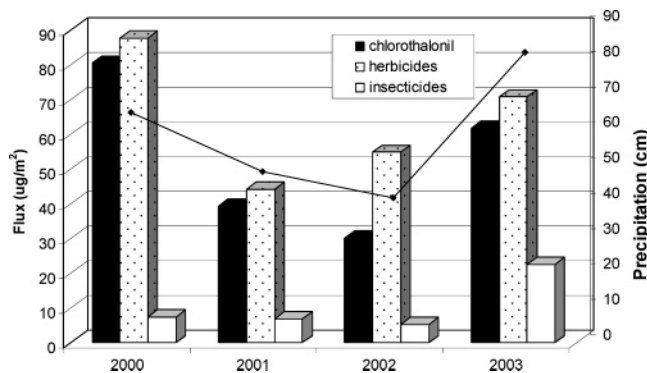
Figure 5. Pesticide flux versus rainfall received during the sampling period (April–September) across the four years.

(**Table 2**). Chlorothalonil was the single biggest contributor to the overall flux (33−46%) followed by metolachlor (19−22%) and atrazine (10−16%).

Herbicides. As a class, herbicides were the biggest contributors comprising 46−61% of the total flux for the months April−September. Because corn and soybeans are the main crops on which herbicides are applied in large quantities, April−May was the time for greatest herbicide flux (except for 2003 when the maximum flux was in June). Herbicide fluxes were not linearly correlated with the rainfall volume in an event (**Table 2**) except for trifluralin and pendimethalin, which were weakly correlated ($r_{trifluralin} = 0.15$, $r_{pendimethalin} = 0.17$; $\alpha = 0.05$). Total herbicide flux also did not vary as the total amount of rainfall (**Figure 5**). Rather, fluxes for herbicides appear to be related to the frequency and timing of precipitation during the planting season (**Figure 2**). Dependence of herbicide flux on the timing of rainfall relative to application has also been reported by Hatfield et al. (*34*). In our study, herbicide flux was least in the year with the wettest spring (2001) and greatest in the year with a dry spring (2000) (**Figure 5**), which is contrary to what was expected. Surprisingly, the numbers of rainfall events from April to June were the same for 2000 and 2003 (33 each) and for 2001 and 2002 (25 each). Hence, the years with the wettest and driest springs (2001 and 2002, respectively) had the same numbers of precipitation events from April to June ($n = 25$). However, in the wettest spring there was no precipitation from April 25 to May 11, missing a major pesticide application period (59% of the corn was planted between April 23 and May 13, 2001, *32*). In contrast, it rained frequently during the corn-planting season of the driest spring (2002) although the volume of rainfall was small. Our data indicate that during the time of

planting smaller but frequent rain events result in greater herbicide flux than infrequent but large rain events.

Atrazine and metolachlor together contributed approximately two-thirds of the total herbicide flux, and their fluxes correlated well with the progress of corn planting. The weekly fluxes for atrazine and metolachlor for the duration of corn planting displayed a weak positive correlation (atrazine, r = 0.41, *p* value = 0.08; metolachlor, *r* = 0.36, *p* value = 0.10) with the frequency of rain events and percentage of corn planted in that week, although (as is evident from the *p* values) the correlations were not statistically significant (at $\alpha = 0.05$). Like atrazine, metolachlor fluxes typically peaked in May. However, in 2002 (driest spring), the highest metolachlor flux was in April. This is consistent with faster progress of corn planting; 40% of corn was planted by the end of April 2002 as compared to 20% in an average year (*31*). However, metolachlor presence in precipitation as late as September and second peaks in July of wet summers (years 2000 and 2003) suggest its use as a broad spectrum herbicide, although the major use is on corn.

Depending on where the samples were collected and the weather conditions, the reported annual wet fluxes of herbicides vary considerably across the United States. In the Midwest (*15, 34, 35*), the atmospheric inputs of atrazine (25−120 μg/m^2) and metolachlor (25−100 μg/m^2) are considerably higher than in our study (atrazine, 12−27 μg/m^2; metolachlor, 17−33 μg/m^2). Higher flux values would be expected in the Midwest region, an area with 43 million acres of corn and 38 million acres of soybeans (combined acreage for the states of Illinois, Indiana, Iowa, Minnesota, and Nebraska for 2002, *36*) versus the Delmarva Peninsula (0.43 million acres of corn and 0.53 million acres of soybeans in 2002, *25*). These studies in the Midwest were conducted in the early to mid 1990s. The introduction of glyphosate and *s*-metolachlor in the late 1990s has changed the herbicide usage in recent years. The acres of soybeans in the United States that were treated with metolachlor dropped from 7% in 1995 to <1% in 2001. For the same period soybeans treated with glyphosate rose from 20 to 76% (*37*). Glyphosate is also increasingly being used on corn. It is likely that the wet deposition flux of atrazine and metolachlor has also decreased in the Midwest since the mid 1990s.

The depositional flux for atrazine in this study (12−27 μg/m^2) is close to what was estimated for northeastern states of the United States (10 μg/m^2, *14*). Some authors (*17, 35*) have reported the detection of atrazine in winter samples. Atrazine was not detected in any sample from October or November in this study, although it was present in air samples from the same time at low concentrations (unpublished data). Long-range transport of atrazine has been suggested as the reason for the presence of atrazine in precipitation in winter months (*17*) and at nonagricultural sites (*38*).

The flux for the triazine degradation product CIAT (0.69−4.5 μg/m^2) was comparable to what has been reported for the Patuxent River watershed (3.6 μg/m^2, *18*). For this study, the fluxes for atrazine and CIAT were well correlated ($r = 0.46$; $p < 0.0001$). Highest CIAT fluxes occurred in the months of April and May in all years. However, unlike atrazine, CIAT had higher fluxes in the drier years (4.5 μg/m^2 in 2002 compared to 0.69 μg/m^2 in 2003). CIAT is formed by the dealkylation of triazine herbicides, which chiefly occurs by microbial degradation in soil but some authors have suggested that atmospheric photolysis may also be a pathway (*39*). In studies from the Midwest, the ratio of CIAT to atrazine (DAR) in atmospheric deposition was 0.4 in spring application. This is higher than the 0.1 that typically occurs in surface water during the first spring flush of herbicides

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during and after application (indicating low degradation in soil) (*40*). The broad range of DAR values in spring samples from our study (0.07–1.5) suggests that atmospheric conversion of triazines to CIAT might be a contributing factor. Low DARs from April–May of 2003 (0.07–0.31) suggest low degradation and are not surprising considering 2003 was marked by delayed corn planting and large rainfall events in the months following April. A large amount of precipitation is likely to have resulted in a greater than normal loss of atrazine in runoff and leaching, making less available for degradation into CIAT. Consequently, May 2003, with the maximum number of rain events in all four years (*n* = 15), had the least CIAT flux (0.69 μg/m^2). DARs were higher in April–May of 2002 (0.24–1.16), which shows that conditions were conducive to degradation (earlier start of corn planting, frequent rain events but low rainfall volume) and could account for maximum CIAT flux occurring in April of 2002 (2.1 μg/m^2).

If wet deposition fluxes directly reflect local usage, alachlor use is on the decrease in the Choptank River watershed, and acetochlor use is on the rise. The total flux for alachlor decreased from 9.9 μg/m^2 in 2000 to 2.7 μg/m^2 in 2003, whereas acetochlor flux increased from 1.3 to 11 μg/m^2 over the same period. Acetochlor is being used mainly for corn (maximum flux in April–May and absence in rainfall beyond June), whereas alachlor is used on both corn and soybeans and is detected more frequently in precipitation. The use of simazine, another herbicide used on corn, is also on the decline in the region. Although data from 2001 are not available, the decrease in flux (10–4.8 μg/m^2), concentrations, and percentage detections (18–4.8%) for simazine from 2000 to 2003 supports this view.

Pendimethalin and trifluralin are more persistent than the other herbicides in this study. They were the only two herbicides to show a weak positive correlation with the amount of rainfall in individual events (**Table 2**), which is consistent with their higher Henry's constant as compared to the other herbicides in this study. Pendimethalin fluxes in the wet years (2000 and 2003) were very similar and were twice as large as in the dry years (2001 and 2002). Moreover, along with metolachlor, pendimethalin and trifluralin were the only herbicides present in precipitation as late as October in 2002. As has been mentioned before, use on winter wheat, barley, and turfgrass could account for the occurrence of trifluralin and pendimethalin in the later months. Trifluralin was not detected in precipitation in 2000; however, for the period 2001–2003, there was a steady increase in fluxes (0.08–0.75 μg/m^2), concentrations, and percentage detections (5.6–44%). It was detected in all samples from March 2002, and flux in that month (0.24 μg/m^2) was more than twice the total flux for the main agricultural season (0.11 μg/m^2). The use of trifluralin in Maryland counties on the Peninsula increased 10-fold from 1997 to 2000, whereas that of pendimethalin fell by 30% in the same period (commensurate with the reduction in maximum application rate recommended by EPA, *41*). Although usage data for the period 2000–2003 are currently not available, our data tend to support a continuing upward trend in usage of trifluralin in this region.

Insecticides and Fungicides. The insecticides and the fungicide chlorothalonil were present in precipitation in all months sampled. The monthly fluxes varied across the years, although they were typically high around July–August. As expected, the insecticide and fungicide fluxes are higher in wetter years (2000 and 2003). The fluxes in individual rain events (for chlorothalonil and the insecticides) showed a statistically significant positive correlation (*r* = 0.15–0.51; α = 0.05) with the amount of rainfall (**Table 2**). These pesticides are applied mainly on

vegetable and fruit crops. Unlike herbicides, which have a narrow window for the bulk of application (pre-emergence), the insecticides and fungicides are often applied on the crops at regular intervals (e.g., every 7–14 days for potatoes and tomatoes), which would explain their frequent presence in atmospheric samples. Their high Henry's constant, lower water solubility (as compared to the herbicides), and more frequent application explain their flux dependence on rainfall volume. In contrast, the herbicides, in general, have a lower Henry's constant and partition into water more readily and are washed out effectively even with a small amount of precipitation.

If wet fluxes are considered to be representative of usage, it appears that the use of diazinon and chlorpyrifos is increasing, whereas the use of endosulfan is decreasing in the region. Diazinon was detected in only one sample each in 2000 and 2001 (in the month of June). The detection frequency and the observed concentrations increased in 2002–2003, and it was present in all sampled months for these years. The detection frequency for chlorpyrifos increased steadily from 2000 (39%) to 2003 (55%). The greatest flux occurred in 2002 (dominated by a single event in August that contributed 54% of the total flux) and the least in 2000. The maximum concentration for α-endosulfan decreased steadily over the years; the concentrations for the β-species and the sulfate also dropped in the years following 2000 (**Table 2**). The decreased contribution of endosulfan to pesticide flux could, in part, be due to the fact that the EPA recommended a decrease in usage owing to its known toxicity to aquatic life (*11*). Malathion was detected sporadically and, in keeping with the general pattern, the detections and fluxes were higher in the wetter years (2000 and 2003). The flux for 2003 was dominated by a single event on June 20, which accounted for 53% of the total flux. Chlorpyrifos and malathion are the organophosphate insecticides among the priority chemicals selected by the Toxics Subcommittee of the Chesapeake Bay Program (*42*). In this context, the apparent increase in the use of chlorpyrifos is a matter of concern.

The annual average wet deposition flux of γ-HCH (lindane) in the Great Lakes (0.25 μg/m^2, adapted from ref *43* using the total surface area of the lakes, 245759 km^2) is similar to that observed in our study (0.32–0.53 μg/m^2), whereas the wet flux for α-HCH (0.32 μg/m^2) is ~10 times higher than observed in this region (0.02–0.04 μg/m^2). Agricultural usage of lindane in the vicinity of the Great Lakes has been suggested (*44*). Although Maryland does not have any reported use of lindane (*2*), it is likely to be used as a seed pretreatment on corn, soybeans, squash etc. (*28*). The fact that γ-HCH was detected most frequently from April to May supports this view. α-HCH occurred sporadically: just one month each in 2000 (September) and 2003 (May), three months in 2002 (April, July, and September), and not at all in 2001. Long-range transport is a possible source of HCHs and along with some local use is likely responsible for the presence of HCHs in precipitation in this region.

Of the insecticide degradation products, endosulfan sulfate flux was highest in the wettest year (2003). Biodegradation of endosulfan in soils is the main pathway for the formation of the sulfate species. Faster degradation of endosulfan in clays under high water content–high temperature regimes (*45*) as well as greater wash out with high rainfall volumes could have contributed to the high flux in 2003. Chlorpyrifos oxon had the greatest flux in 2001. Surprisingly, very high fluxes of chlorpyrifos oxon were received in March and November of 2002, whereas the oxon was not detected at all in the other months of this year. The oxon is formed by photodegradation of the parent

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compound under moist conditions (*46*). The generally dry conditions in 2002 during the main sampling period might account for the nondetection of the oxon in that year.

Chlorothalonil was the only fungicide included in this study. As has been mentioned before, it was the most frequently detected agrochemical and the biggest single contributor to the overall flux. Although it was present in rainfall in all months, the fluxes were typically highest in July−August. Chlorothalonil contributed ∼50−98% of the flux for the months of July−September. The anomaly of the much higher contribution to wet flux as compared to its usage might be explained on the basis of the soil chemistry of this compound. The main degradation pathway for chlorothalonil is by microbial degradation in soil (*47*); it is not broken down by ultraviolet light. The half-life of chlorothalonil in soil after first application is generally short (∼35 days). However, it has been reported that repeated use of chlorothalonil, alone or in combination with other pesticides such as chlorpyrifos, results in suppression of its degradation rate (*48, 49*) and significantly decreases its dissipation rate in soil. The fungicide is typically applied more than once in agricultural operations in this region and is likely to have a longer soil half-life. Thus, it is available for volatilization to the atmosphere over a greater period of time and is detected more frequently in rainfall.

Hence, herbicides and insecticides respond differently to rainfall patterns, reflecting their chemical properties and application patterns. Herbicide fluxes illustrate a higher influence by the timing of application as well as the frequency and distribution of rainfall events relative to application. Insecticide and fungicide fluxes are dependent upon the amount of rainfall in a year. Higher herbicide flux in 2002 (driest year) offset the decrease in insecticide and chlorothalonil flux, resulting in 2001 and 2002 having the same net flux (**Table 2**). Although the April−September sampling period covers the major period when the herbicide flux is received, it is not adequate for the other two classes of pesticides, which may have high fluxes even in the colder months.

Potential Toxicological Risks to Biological Resources in the Chesapeake Bay. Pesticide concentrations in precipitation were at levels likely to raise concern. Chlorothalonil seasonal maximum concentrations (380−2000 ng/L) were close to the 96-h LC_{50} for the Atlantic oyster (3200 ng/L, *50*), a key component of the Chesapeake Bay ecosystem. The U.S. EPA's chronic marine water quality criterion for endosulfan ($\alpha + \beta$) (8.7 ng/L, *51*) was exceeded in ∼3% of the samples, for chlorpyrifos (5.6 ng/L) in 10%, and for malathion (100 ng/L) in one sample. In addition, atrazine seasonal maximum concentrations (470−900 ng/L) approached the level of 1000 ng/L at which sublethal effects have been observed on phytoplanktonic algae, which are an integral part of the estuarine environment (*5*). Even though biota in water bodies are unlikely to be exposed to concentrations present in rainwater due to dilution effects, concentrations in precipitation point to high levels of risk, especially for organisms in shallow water bodies or isolated ponds. It is important to note that our sampling site is distant from any immediate agricultural activity and, as such, is likely to have pesticide concentrations in precipitation closer to background levels for the region. Pesticide fluxes in locations closer to agricultural fields are expected to be higher in response to higher air concentration conditions.

Wet deposition seems to be a significant source of pesticide input to the Chesapeake Bay. Even though concurrent data for the amount of pesticides present in the Bay at the time of this study are not available, several authors (*52−54*) have estimated

Table 3. Estimated Pesticide Loadings to the Chesapeake Bay (Kilograms per Year)

	atmospheric deposition,[a] April–Sept (2000–2004)	annual load rate to the Bay,[b] March 1992–Feb 1993
α-HCH	0.2–0.3	3[c]
alachlor	23–83	126–169
atrazine	102–229	2700
diazinon	2–123	31–153
γ-HCH	3–5	9[c]
malathion	0.3–15	20–180
metolachlor	145–277	1399–1402
simazine	13–85	1050–1090

[a] Based on deposition fluxes from this study for the Chesapeake Bay main stem area (8384 km²). [b] Combined total for the Susquehanna, Potomac, and James Rivers at their fall lines [adapted from Foster (*52*)]. [c] For Susquehanna River from March 1997 to Feb 1998 (*54*).

annual pesticide loadings to the Bay through the main tributaries (Susquehanna, James, and Potomac Rivers, which together provide 80% of the freshwater to the Bay) in the early 1990s. Assuming that the main stem of the Bay (8384 km²) receives the same atmospheric input through wet deposition as recorded at our sampling site, wet deposition accounts for <10% of the triazine herbicide load (**Table 3**). For the acetanilide herbicides (alachlor and metolachlor) the contribution is higher, at ∼10−20% or more. Owing to implementation of pest management practices in the watershed, pollutant loads to the Chesapeake Bay (via sediment transport) from agricultural lands generally declined from 1985 to 2000 (*55*). Hence, pesticide loadings in the waters of the Chesapeake Bay today are likely to be lower than what they were in the early 1990s when the studies estimating these loads in the Bay (*52−54*) were conducted. Keeping in mind the decade-long gap between the aforementioned studies and this study which estimates atmospheric inputs, it is very likely that the contribution of the atmospheric inputs to pesticide loads in the Chesapeake Bay is greater than the 10−20% estimated here.

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