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Herbicide and Insecticide Loadings from the Susquehanna River to the Northern Chesapeake Bay

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The Susquehanna River watershed has a large drainage area (71200 km^2) containing heavy agricultural land usage. The river provides approximately half the total freshwater input to the Chesapeake Bay. Water samples were collected at Conowingo Dam near the mouth of the river every 9 days from February 1997 through March 1998. Atrazine, its transformation product 6-amino-2-chloro-4-(isopropylamino)-*s*-triazine (CIAT), and metolachlor were found in the highest concentrations with maximums of 500, 150, and 330 ng/L, respectively. The annual mass loads for atrazine, CIAT, metolachlor, simazine, and 6-amino-2-chloro-4-(ethylamino)-*s*-triazine (CEAT) from the Susquehanna River to the Chesapeake Bay were 1600, 1600, 1100, 820, and 720 kg/year, respectively. Annual loadings of insecticides and organochlorine compounds ranged from 2.8 kg/year for α-HCH to 34 kg/year for diazinon. Strong correlations between loading data from this and previous studies and total annual water discharge through the dam were used to estimate total metolachlor and atrazine loads (12400 and 9950 kg, respectively) to the northern Chesapeake Bay from 1992 to 1997.

KEYWORDS: Chesapeake Bay; rivers; pesticides; herbicides; agriculture

INTRODUCTION

The Chesapeake Bay is the largest estuary in the United States, and it provides important transport, fishery, and recreational resources to the Mid-Atlantic region. Since the 1960s there has been a marked decline in the water quality of the bay (*1*−*3*). As a means of reversing this trend, surrounding states committed to significantly reduce point and nonpoint source pollution loads as part of the 1987 Chesapeake Bay Agreement signed by the U.S. Environmental Protection Agency, the State of Maryland, the Commonwealths of Pennsylvania and Virginia, and the District of Columbia (*4*). This commitment was strengthened in 1994 and again in the Chesapeake 2000 agreement when the parties agreed to reduce or eliminate the input of chemical contaminants to levels that result in no toxic or bioaccumulative impact on human health or the living resources of the bay (*5*, *6*).

Portions of the Chesapeake Bay and its tributaries are surrounded by land known for intensive agricultural activity. About 30% of the land in the bay watershed is used in agriculture, and current estimates indicate that tens of metric tons of pesticides are used in the estuarine drainage area of the Chesapeake Bay annually (*7*, *8*). Some pesticides and their transformation products are toxic to aquatic organisms and wildlife (*9*−*11*). These loads may have potentially toxic impacts on human populations and wildlife within this ecosystem. However, studies of the annual inputs and fate of agricultural pesticides to the bay are limited (*12*−*14*).

The Susquehanna River provides 90% of the freshwater flow to the upper half of the bay and 50% overall (*15*). The Susquehanna River watershed (area = 71200 km^2) contains large areas of intensive agricultural activity. The lower Susquehanna watershed, located in Pennsylvania, comprises 47% agricultural lands (*15*). Because this watershed has such a large drainage area and contains heavy agricultural land usage, riverine inputs of currently used pesticides from the Susquehanna River are likely one of the most important sources of these chemicals to the bay. Previous studies by Foster and Lippa (*13*) and Foster et al. (*14*) provide loadings of some agricultural chemicals for the period between 1992 and 1994.

This paper is the result of sample collections from the mouth of the Susquehanna River over a 14-month period from February 1997 to March 1998. Concentrations of 17 pesticides and transformation products are reported and compared with published data from other tributaries of the Chesapeake Bay. Daily mass loadings of these pesticides along with average daily flow rates through the Conowingo Dam are presented to observe temporal trends and determine possible sources and persistence in the watershed. Results of this study are the most detailed description of agricultural pesticide loadings from the Susquehanna River to the Chesapeake Bay to date and will assist in determining the relative contribution of this tributary to the overall pesticide budget of the Chesapeake Bay.

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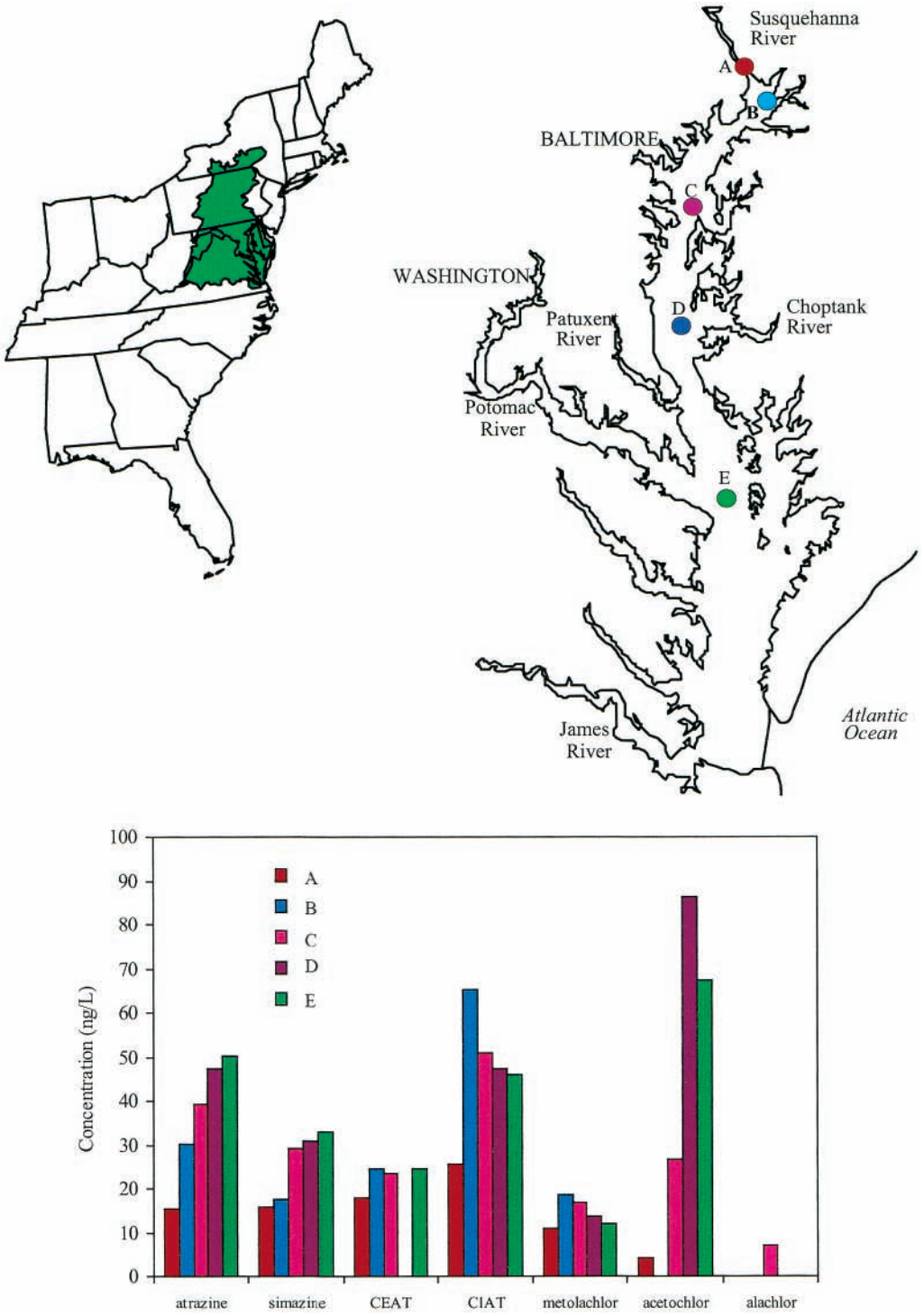

Figure 1. Map of the Chesapeake Bay watershed and the Chesapeake Bay with sampling locations. Site A is the Conowingo Dam, and sites B–E indicate collection sites used in February 1997. The graph is water concentrations of herbicides and their breakdown products measured at sites A–E on February 24–27, 1997.

MATERIALS AND METHODS

Sample Collection. The Conowingo Dam is located in Harford County, MD, 16 km upstream from the Susquehanna River mouth (39° 39′ 26″ N and 76° 10′ 31″ W). The length of the dam is 1417 m, and the depth of the dam is 32 m. The surface area of the Conowingo Reservoir is 36 km^2, the length 22.5 km, and the volume of water impounded by the dam 397 million m^3 (*16*). Water residence time in the reservoir varies according to river flow conditions. One hundred percent of Susquehanna River water flows through or over the Conowingo Dam (*15*).

Susquehanna River water samples were collected every 9 days from the center of the outflow of the Conowingo Dam for a 14-month period from February 1997 to March 1998 (**Figure 1**, site A) for a total of 41 sample collection days. In February 1997, samples were also collected during an EPA-funded cruise of the Chesapeake Bay at Turkey Point, near the mouth of the Susquehanna River (39 26.00 N and 76 0.01 W) and at the 104 site, near the Chesapeake Bay Bridge (39 01.02 N and 76 21.00 W), on February 24, at the mouth of the Potomac River (VA056D, 37 57.00 N and 76 10.00W) on February 25, and off the Choptank River (38 38.93 N and 76 25.04 W) on February 26, 1997 (**Figure 1**, sites B−E, respectively).

At the Conowingo Dam, water from the outflow of the dam was sampled from a catwalk 5−6 m above the water surface using a portable, submersible, stainless steel, groundwater pump (Fultz, model

SP-201-A) from a 1−2-m depth through a 5.4-m-long Teflon tube. Water samples were collected in 18-L stainless steel pressurizable tanks. Two tanks of water were collected on each sample date. Samples were transported to the laboratory for processing and analysis.

The tanks were cleaned before sample collection using a dilute soap solution, followed by tap water, followed by reagent grade deionized water, and finally chromatographic grade acetone. Tanks were kept closed during transport. The pump was cleaned before sampling by pumping tap water followed reagent grade deionized water through the system for 10−20 min.

Sample Processing. Water samples were filtered within 4−6 h of collection. The stainless steel tanks were pressurized with high-purity N_2 gas (20 psi, 140 kPa), and water was forced through two stainless steel filter holders (Millipore) in series. The first filter head contained a 90-mm-diameter Whatman graded density glass microfiber prefilter (1-μm pore size), and the second filter head contained a 14.2-cm-diameter Whatman GF/F filter (0.7-μm pore size). The filtered water was split into three, 10-L aliquots in three precleaned stainless steel pressurizable tanks. The filter papers were folded to protect particles, wrapped in solvent-rinsed aluminum foil, and stored in the freezer (−15 °C) until extraction.

Filtered water samples were generally extracted on the day of collection with the exception of February 27, April 23, July 13, and July 31, when cans were kept in cold storage (4 °C) for 2−3 days until extraction. Ten-liter water samples were extracted using solid phase extraction cartridges (IST Isolute, ENV+ sorbent, 500-mg sorbent mass, 6-mL reservoir volume) using positive pressure (20 psi, ~140 kPa of N_2) on each tank and negative pressure on the cartridges (15 mmHg vacuum) using a vacuum manifold (Supelco) with an approximate flow rate of 50−100 mL/min through the cartridge. Cartridges were preconditioned with 6 mL of dichloromethane (DCM), 6 mL of acetone, and 6 mL of organic-carbon-free deionized water. After extraction, cartridges were wrapped in aluminum foil and stored at −15 °C until elution.

Before elution, cartridges were dried using a vacuum manifold (15 mmHg). The vacuum pressure was disconnected before cartridge elution. Analytes were removed from the solid phase by sequential elutions with 6 mL of DCM and 9 mL of 3:1 acetone/acetonitrile. The resulting extract was collected and concentrated to 0.5 mL using a gentle stream of high-purity (99.9%) nitrogen and then readjusted to 1.0 mL by adding acetonitrile.

Filter samples were extracted in batches of 20 using a Soxhlet extraction apparatus with chromatographic grade DCM (Burdick and Jackson, high-purity solvent) for at least 8 h. Extracts were reduced to 10 mL using a rotary evaporator. The extract was then passed through approximately 1 g of $NaSO_4$ and 2 g of alumina (Supelco, Supelclean LC-Alumina-N) for cleanup and removal of any residual water, and the column was rinsed with 15 mL of DCM for a total elution volume of 25 mL. The eluant was reduced to 1 mL using a gentle stream of chromatographic grade (99.9%) N_2 gas and exchanged into hexane.

Analytical Methods. Sample extracts were screened for 62 currently used and organochlorine pesticides by gas chromatography ion-trap mass spectrometric detection (Finnigan ITS40). For details, see the paper by Lehotay et al. (*17*). As a result of the screening process, the analyte list was reduced to 26 compounds for detailed analysis. Compounds that were not detected in any sample were eliminated from the analyte list.

Each sample was analyzed using a Hewlett-Packard 5890 capillary gas chromatogram coupled to a 5989 mass spectrometer (GC-MS) using selected-ion monitoring in both electron impact (EI) and negative chemical ionization (NCI) modes (**Table 1**). The injection volume was 2 μL. In EI mode, gas chromatographic conditions were as follows: column, J&W DB-5, 30 m, 0.25-mm-i.d., 0.25-μm thickness; electronic pressure control used to keep flow constant at 1.0 mL/min; temperature program, 130 °C, raised at 5 °C/min to 240 °C and then at 20 °C/min to 280 °C for 5 min; interface, 300 °C; quadrupole, 100 °C; source, 200 °C; injector, 250 °C. In NCI mode, conditions were as follows: column, J&W DB-5, 30 m, 0.25-mm-i.d., 0.25-μm thickness; electronic pressure control used to keep flow constant at 1.0 mL/min; temperature program, 130 °C, raised at 6 °C/min to 280 °C for 5 min; interface, 300 °C; quadrupole, 100 °C; source, 150 °C; injector, 250 °C. The ionization gas was methane at 1.6 Torr.

Table 1. Quality Assurance Results Summary for Dissolved and Particulate Phase Water Samples

		dissolved phase		particle phase	
compound	mass ions monitored (*m*/*z*)	spike recovery (%)	MDL (ng/L)	spike recovery (%)	MDL (ng/L)
		EI Results			
atrazine	200, 205, 173	100 ± 4	1.2	96 ± 5	1.0
simazine	201, 186, 173	110 ± 5	1.6	78 ± 1	1.4
CEAT	173, 158, 145	120 ± 6	1.8	91 ± 4	0.5
CIAT	172, 187, 145	120 ± 5	1.0	38 ± 2	0.3
metolachlor	162, 238	110 ± 3	1.2	100 ± 6	1.2
acetochlor	146, 162, 174	120 ± 9	1.5	96 ± 7	1.4
alachlor	160, 188, 146	110 ± 5	1.4	100 ± 6	1.0
cyanazine	212, 213, 225	130 ± 7	1.8	54 ± 1	1.6
pendimethalin	252, 281, 191	110 ± 9	1.6	100 ± 8	1.4
diazinon	179, 137, 304	110 ± 6	1.2	92 ± 7	1.7
malathion	173, 127, 125, 158	140 ± 12	1.6	99 ± 1	1.7
Diazinon-d_{10}	183, 138, 314	100 ± 8	–[a]	88 ± 7	–
		NCI Results			
trifluralin	335, 336, 305	87 ± 6	0.2	110 ± 4	0.1
chlorpyrifos	313, 315, 214	120 ± 8	0.2	110 ± 5	0.1
α-HCH	71, 255, 257	120 ± 5	0.1	100 ± 5	0.1
γ-HCH	71, 255, 257	120 ± 5	0.2	110 ± 5	0.1
chlorothalonil	266, 268, 264	180 ± 26	0.2	220 ± 3	0.2
α-endosulfan	372, 237	130 ± 6	0.1	110 ± 8	0.1
β-endosulfan	406, 408, 404	132 ± 7	0.2	110 ± 1	1.0
endosulfan sulfate	386, 388, 384	163 ± 7	0.3	150 ± 6	0.2
α-chlordane	266, 410, 237	58 ± 15	0.7	110 ± 8	0.4
γ-chlordane	266, 410, 237	85 ± 11	0.2	120 ± 5	0.1
trans-nonachlor	444, 300, 237	59 ± 7	0.4	110 ± 9	0.2
o,*p*′-DDT	71, 246, 318, 282	120 ± 13	0.3	150 ± 7	0.2
p,*p*′-DDT	71, 318, 283, 250	81 ± 9	0.7	130 ± 4	0.3
p,*p*′-DDE	318, 316, 320	78 ± 6	0.3	110 ± 4	0.2

[a] Diazinon-d_{10} is used as a surrogate and is not an analyte.

A five-point calibration curve (ranging from 0.25 to 0.005 ng/μL of 17 targeted compounds for NCI and from 2.0 to 0.05 ng/μL of 11 targeted compounds for EI) was injected at the beginning of each sequence of injections with at least one repetition of the calibration curve for every 20 sample injections. Sample results were quantified using the internal standard method. The two internal standards, 685 ng of anthracene-d_{10} and 587 ng of chrysene-d_{12}, were added into 1 mL of sample extract before GC-MS analysis. These two compounds were used for quantifying earlier and later compounds on the chromatograph, respectively.

Ancillary Measurements. Temperature and salinity were measured using a salinity−conductivity−temperature meter (YSI model 33). Salinity was measured at 0 parts per thousand on every occasion except for the dates May 20 (1.0‰) and June 16 (1.2‰). Salinty data for sample collected from the Chesapeake Bay are not available. Temperature ranged from 6 to 30 °C. Water samples were also characterized for total suspended solids (TSS) (0.57−26 mg/L), dissolved organic carbon (DOC) (2.2−12.5 mg/L), and total particulate carbon (PC) (0.23−1.54 mg/L). Data for the average daily flow rates through the Conowingo Dam (107−4600 m^3/s) used in mass loading calculations were provided by Robert McIntyre at the Conowingo Hydro Station (personal communication). Details of analytical techniques used in these ancillary measurements are given elsewhere (*18*).

Quality Assurance. On each sampling date, duplicate 10-L samples, one 10-L river water sample spiked with chlorpyrifos (102 ng), one 10-L deionized water blank, and one 10-L deionized water sample spiked with chlorpyrifos were extracted together to monitor contamination of the extraction equipment and recovery of the analytes. Recoveries of chlorpyrifos were high and averaged 110 ± 16% in distilled water (n = 27) and 94 ± 16% in river water (n = 23).

This extraction method has been shown to be effective at isolating our analytes (*17*). Results of our spike experiments (n = 11 for EI and n = 12 for NCI compounds) with organic-carbon-free water showed that most chemicals were recovered at >80%, with the exceptions of α-chlordane and *trans*-nonachlor at 58%, malathion at 140%, chlo-

rothalonil at 180%, and endosulfan sulfate at 160%. After careful scrutiny, the high recovery values for these chemicals appear to be due to a matrix enhancement effect from material eluted from the cartridge and not due to contamination of the system. However, with the exception of endosulfan sulfate, none of these chemicals were detected consistently in samples. In the future, use of blank samples to create standard curves will be used to eliminate this enhancement. Concentrations of endosulfan sulfate were not adjusted for this enhancement.

In the case of glass fiber filters, one blank filter was extracted along with each batch of samples to observe any contamination from laboratory procedures, and one blank filter was spiked with a mixture of 26 target analytes to monitor the extraction efficiency of the method. An extraction surrogate standard solution in methanol containing 206 ng of diazinon-diethyl-d_{10} (diazinon-d_{10}) was added to samples and controls. Recoveries of diazinon-d_{10} were high and averaged 91 ± 9% (n = 33) for blank filters and 84 ± 21% (n = 37) for river water filters.

The extraction efficiency of the Soxhlet extraction and cleanup procedures was tested using experiments with blank filters. Fourteen replicates were spiked with a standard solution containing ~50 ng of each compound of the 11 target compounds analyzed by EI. For compounds analyzed by NCI, 13 replicates were spiked with a standard solution containing ~5 ng of each of our 17 target compounds. Results of our recovery experiments showed compounds were recovered at >78%, except 6-amino-2-chloro-4-(isopropylamino)-*s*-triazine (CIAT) at 38%, cyanazine at 54%, chlorpyrifos oxon at 14%, chlorothalonil at 220%, endosulfan sulfate at 150%, and *o*,*p*′-DDT at 150% (**Table 1**).

No interfering peaks were found in blank extracts; therefore, high recovery values appear to be due to a matrix enhancement effect. That is, the response factor for some compounds appears to be higher in sample extracts compared with that in clean solvent. This may be due to material in the sample extract occupying active sites in the GC injector port or on the capillary column. This may increase the amount of analyte reaching the detector.

Because no interfering peaks were found in blank samples, detection limits are governed only by instrumental sensitivity and the extraction efficiency of the method. The method detection limit (MDL) for each target compound was determined using techniques defined in the U.S. EPA standard methods. As U.S. EPA protocols require, seven experimental replicates were carried out; the sample matrix was spiked at a low level and processed as a sample (*18*). The MDL value was defined as the *t* value multiplied by the standard deviation of measured replicate concentration (*19*). Detection limits for targeted compound ranged from 0.1 to 1.0 ng/L for NCI analysis and from 1.0 to 1.8 ng/L for EI analysis (**Table 1**).

Mass Loading Calculations. For each compound, a daily mass load was calculated by multiplying the measured average concentration (from duplicate samples) by the average daily flow rate through the Conowingo Dam. A concentration value is available for only 1 day in 9, so the measured values were assigned to the 4 days prior to and after sampling. This assumption is valid as the Susquehanna River is extremely large, the flow is buffered by the presence of the reservoir, and large changes in concentration are not likely to happen quickly. An annual loading value for each chemical was calculated for the period March 1, 1997, through February 28, 1998. For those dates when concentration values were below our quantification limits, a zero load rate was used. The reader should keep in mind when viewing the figures depicting mass loadings that although flow data are available for each day, concentration data are available only for 1 day in 9; thus, the loading values are only estimates for most points on the graphs.

RESULTS AND DISCUSSION

To date, the only published studies of pesticide loadings from the Susquehanna River are by Hainly and Kahn (*12*), Foster and Lippa (*13*), and Foster et al. (*14*). Hainly and Kahn's study concentrated on measurements of the five most frequently detected agricultural herbicides (alachlor, metolachlor, atrazine, cyanazine, and simazine), during June 5−16, 1994, and focused on instantaneous measurements of five herbicides over the short term. Foster and Lippa's study was conducted from March 1992 to February 1993 at Conowingo Dam with eight samples collected under base flow conditions and a total of seven samples after three storm events. The second study by Foster et al. (*14*) was carried out over the period from March to December 1994 with a total of 23 samples collected during base flow and storm events. Both Foster studies utilized an interpolation−integration estimator to estimate flux rates and annual loads of target chemicals. These previous measurements will allow us to examine changes in load rates of agricultural pesticides over the past 5−6 years.

Inputs of currently used pesticides to the Susquehanna River and subsequently to the Chesapeake Bay are governed by the agricultural practices used in the watershed, the timing of storm events after major application periods, the properties of the pesticide, and the frequency and intensity of rain events throughout the year. The lower Susquehanna River watershed is located primarily in south central Pennsylvania. Hay/alfalfa is by far the largest crop grown in the state at >1 million acres followed by corn and soybeans. However, hay is not a crop that is pesticide intensive. In the Pennsylvania counties of the lower Susquehanna River watershed, 3000 km^2 of corn and 650 km^2 of soybeans were grown in 1997 (*20*). Corn is generally planted in early May, and soybeans are planted in June. Herbicides are applied at the time of planting. In general, a mixture of atrazine and metolachlor is applied to corn, whereas metolachlor alone is often used for soybeans. Insecticides and fungicides are applied sporadically on a variety of crops throughout the summer and into the early fall months depending on insect populations and weather conditions. The greatest pesticide applications are made from late April through June, although additional applications are made throughout the summer.

The Pennsylvania Department of Agriculture Annual Report states that a total of 202000 kg of metolachlor were used on soybeans during 1997 (*20*). No information on pesticide use on corn in 1997 was available; however, the 1998 report states that 1544 lb of atrazine, 629000 kg of metolachlor, 393000 kg of pendamethalin, 120000 kg of acetochlor, and 78000 kg of chlorpyrifos were used (*21*). The 1999 report (*22*) is limited to information on soybeans and indicates that pesticide usage patterns have changed, with a dramatic increase in glyphosate usage from 10000 kg in 1997 to 131000 kg in 1999, suggesting that farmers are now using "Round-up Ready" soybeans. Metolachlor usage has dropped to 34000 kg. This change in agricultural practices in Pennsylvania indicates that further study of pesticide loadings from the Susquehanna River is needed into the future.

From the pesticide use patterns in 1997, we would expect that the highest concentrations of currently used pesticides would be observed during major application periods and after major storm events (increased flow events). Organochlorine (OC) pesticide concentrations, on the other hand, are not likely to display large changes during the year due to more diffuse sources.

Pesticide Concentrations. As expected from agricultural practices in the watershed, herbicides were present in the highest concentrations, and peak concentrations were observed in the late spring. Atrazine, its transformation product, CIAT, and metolachlor were found in the highest concentrations with maximum values of 500, 150, and 330 ng/L, respectively, after a storm in early June and were found in 100% of samples collected (**Table 2**). This June storm event also produced the maximum concentration for all of the herbicide and herbicide

Table 2. Summary of Pesticide Detection Frequency, Maximum Concentration, Average Concentration, Annual Mass Load, and Maximum Daily Load in Dissolved Phase Water Samples[a]

	herbicides								
	acetochlor	alachlor	atrazine	CEAT	CIAT	cyanazine	metolachlor	simazine	pendimethalin
detection (%)	56	59	100	100	100	59	100	100	17
max concn (ng/L)	99	41	500	64	150	140	330	130	18
av concn (ng/L)	11	9	67	29	64	3	39	37	13
annual load (kg/year)	200	110	1600	720	1600	310	1100	820	53
max daily load (kg/day)	10	4.6	57	13	31	15	38	15	2.1

	insecticides							
	chlorpyrifos	p,p′-DDE	diazinon	α-HCH	γ-HCH	α-endosulfan	β-endosulfan	endosulfan sulfate
detection (%)	96	34	51	72	100	37	57	72
max concn (ng/L)	2	4	28	0.2	9	9	49	6
av concn (ng/L)	0.5	1.9	6.4	0.1	0.3	0.8	2	1
annual load (kg/year)	13	7	34	3	9	4	18	10
max daily load (kg/day)	0.4	0.3	1	0.1	0.3	3	14	2

[a] Compounds from **Table 1** that are not listed were not detected above the quatification limits in any sample.

Table 3. Comparison of Measured Mean Dissolved Phase Concentrations of Pesticide (Nanograms per Liter) in Chesapeake Bay Tributaries[a]

	Susquehanna River			Potomac River	James River	Patuxent River	Choptank River
sampling date:	2/1997–3/1998	3/1994–12/1994	3/1992–2/1993	3/1992–2/1993	3/1992–2/1993	2/1997–11/1997	5/1997–11/1997
reference:	this study	*14*	*13*	*13*	*13*	*17*	*17*
alachlor	9	19	12	12	10		
atrazine	67	81	56	160	61	47	245
cyanazine	25	84	36	114	12		31
p,p′-DDE	2	0.13				1.6	
diazinon	6	5.3	12	10	7	3.3	
α-HCH	0.1	0.15					
γ-HCH	0.3	0.34				0.45	0.3
metolachlor	39	61	31	96	31	9	20
simazine	37	56	24	62	50	18	121

[a] All studies listed involve samples collected at the fall line of the river except for the Patuxent and Choptank studies, in which samples were collected in the tidal portion of the rivers.

transformation products included in the study. Simazine and 6-amino-2-chloro-4-(ethylamino)-*s*-triazine (CEAT) were detected in 100% of samples as well. Other triazine and acetanilide herbicides, cyanazine, alachlor, and acetochlor, were also detected in >50% of samples. The herbicide pendimethalin was detected less frequently.

In the particulate phase filter extracts, traces of our target analytes, chlorpyrifos, γ-chlordane, α-endosulfan, β-endosulfan, endosulfan sulfate, *trans*-nonachlor, and *p,p′*-DDE, were consistently detected. The levels in the particle phase samples, however, were below analytical quantification limits with the exception of atrazine, which was detected above quantification limits only once on September 14, 1997 at a concentration of 2.17 ng/L. These results indicate that the majority of our analytes were present largely in the dissolved phase. Therefore, for our purposes, dissolved phase concentration data were used to calculate mass loading values.

On one occasion during the project, February 1997, water samples were collected at the Conowingo Dam and from four other sites from the main stem of the Chesapeake Bay. Locations of the sample collections are shown in **Figure 1**. Herbicides were detected at all of the sites as were CIAT and CEAT (**Figure 1**). Interestingly, atrazine and simazine concentrations increased from the north of the bay to the south; the sample collected at Conowingo Dam had the lowest concentration for other detected compounds. The presence of acetochlor at concentrations of >60 ng/L at the Choptank River and Potomac River sites is dramatic considering these samples were collected during the winter. These results indicate that studies of loading rates from other tributaries are needed.

Average pesticide concentrations from this study agree well with results from similar studies of the Susquehanna River carried out in 1992 and 1994 by Foster and Lippa (*13*) and Foster et al. (*14*) (**Table 3**). Foster and Lippa also included the James and Potomac Rivers in their study. Other measurements have also been carried out in the Choptank and Patuxent Rivers (*17*). Compared with other tributaries, pesticide average concentrations from the Susquehanna River were generally lower. Atrazine and simazine concentrations in the Choptank River were 3−4 times higher than those of the Susquehanna River; atrazine, cyanazine, metolachlor, and simazine in the Potomac River were 2−4 times higher; and simazine in James River was ∼1.5 times higher than that in the Susquehanna River. This comparison suggests that with regard to concentration alone, the Susquehanna River may not be the largest riverine source of pesticides to the Chesapeake Bay. However, the flow rate of the rivers must be considered to determine the actual loadings to the bay.

Herbicides. As seen in **Figure 2A**, the highest loading rates of atrazine (maximum = 57 kg/day) occurred from mid-May to mid-June as a result of two moderately high river flow events during this period. This trend was mirrored by metolachlor and all of the other herbicides (**Figure 2B**) in the study with the exception of trifluralin, which is not used on corn or soybeans. After the end of June, inputs dropped dramatically to preapplication levels. This is likely due to the very dry conditions

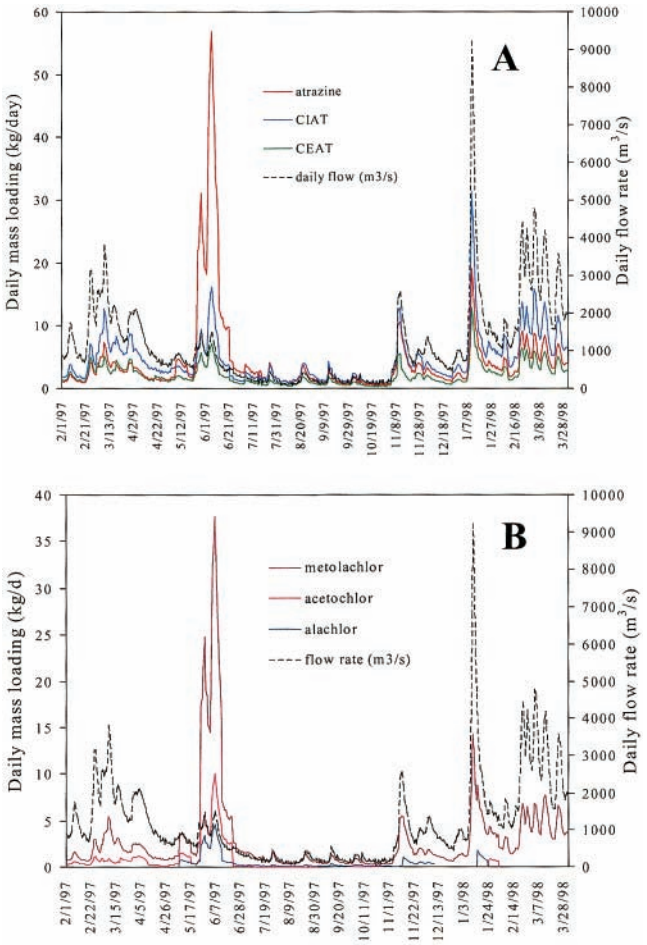

Figure 2. Daily mass loadings (kg/day) for atrazine, CIAT, and CEAT (A) and for metolachlor, alachlor, and acetochlor (B) and daily mean discharge rate (m^3/s) at Conowingo Dam from February 1997 to March 1998.

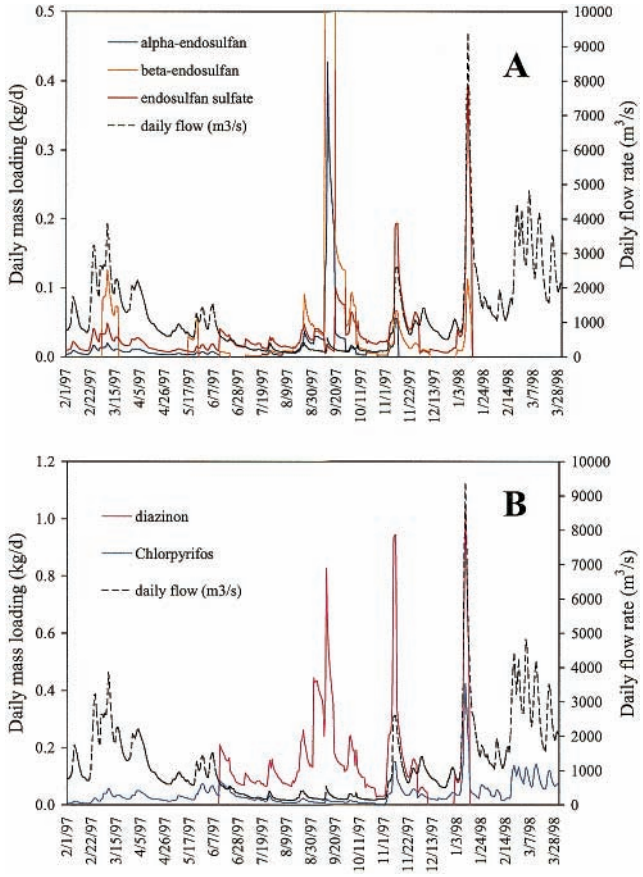

Figure 3. Daily mass loadings (kg/day) for α- and β-endosulfan and endosulfan sulfate (A) and for diazinon and chlorpyrifos (B) and daily mean discharge rate (m^3/s) at Conowingo Dam from February 1997 to March 1998. The maximum load for β-endosulfan is 2 kg/day.

during the summer of 1997 as evidenced by low river flow rates. The herbicides atrazine, metolachlor, and simazine were continually detected, however, throughout the winter months, and two large storms events, the first in mid-November and the second in mid-January, released large amounts of atrazine (maximum loading rates of 11 and 19 kg/day, respectively) and the other herbicides to the bay. Our results support other published information on herbicide persistence. Atrazine has been found to persist in soil for up to 1 year under cold, dry conditions (*23*), and metolachlor and simazine have soil half-lives of 2−3 months (*24*−*26*).

CIAT and CEAT, the major degradation products of atrazine (*27*), have been shown to be more mobile in soil than atrazine (*28*). Evidence of atrazine degradation in soil can also be observed from this data set. During the winter months, loading rates of CIAT are a factor of ∼2 larger than that of the parent compound, and CEAT loading rates are only slightly lower than that of atrazine (**Figure 2A**). Within 2 months of the peak atrazine loading rate, the load of CIAT is equal to that of atrazine. Within 3 months, the loading rate of CIAT surpasses that of atrazine, reaching a factor of 2 greater during the winter months. This trend may be due to a change in sources over the year from runoff of the parent atrazine just after application to a groundwater source containing degraded triazine herbicides during the winter.

Atrazine was detected for a longer period of time than alachlor, which can be attributed, in part, to differences in the physiochemical properties and soil half-lives of these compounds. The soil half-life of alachlor is only ∼15 days (*29*). Thus, the short half-life and higher volatility of alachlor means that a much smaller fraction of the compound applied to cropland is available for leaching into streams.

Insecticides. Results for the insecticides chlorpyrifos, diazinon, and endosulfan also reflected expected use patterns in that maximum loading rates were delayed until the summer and fall months. Despite very low river flow conditions in August and September, loading rates of diazinon were consistently high (maximum summer load = 1 kg/day) (**Figure 3A**). Diazinon is used on fruit crops and is also widely used in residential gardens. Surprisingly, the pulses of diazinon released during the November and January storm events were larger than observed during the summer at 0.9 and 1 kg/day, respectively. However, after January, diazinon was not detected during later storm events, indicating that this chemical is not as persistent in soil as the triazine herbicides.

Inputs of chlorpyrifos, although low, were consistent throughout the study period. This chemical was present in 96% of the samples collected. However, loading rates were linked only to river flow with no obvious application pulse as seen with diazinon. A small increase in input rate relative to flow during late June may indicate runoff from application to corn to control corn root worm. The highest river flow event during the January storm produced the largest input rate, 0.4 kg/day. The presence of this pesticide throughout the year indicates a long environmental half-life and/or a very diffuse and continuous source in the watershed. Chlorpyrifos is used as a termiticide in the foundation of buildings, for roach control, and a for variety of

Table 4. Estimated Annual Load Rates of Pesticides for Major Chesapeake Bay Tributaries (Kilograms per Year)

	Susquehanna River			Potomac River	James River
load estimate dates:	3/1997–2/1998	2/1994–1/1995	3/1992–2/1993	3/1992–2/1993	3/1992–2/1993
reference:	this study	*14*	*13*	*13*	*13*
alachol	110	710	86–97	25–44	15–28
atrazine	1600	2970	1700	780	220
cyanazine	310	3010	430–480	220–230	32–43
metolachlor	1100	2540	920	390	89–92
diazinon	34	220–260	8–96	3–27	20–30
α-HCH	3	11			
γ-HCH	9	18			
simazine	820	1730	580–610	340	130–140

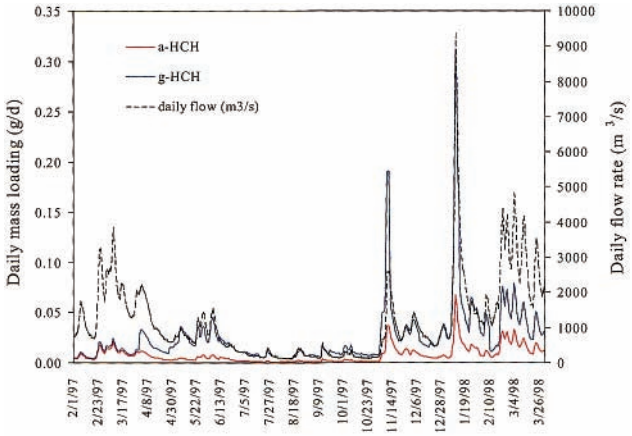

Figure 4. Daily mass loadings (kg/day) for α- and γ-HCH and daily mean discharge rate (m^3/s) at Conowingo Dam from February 1997 to March 1998.

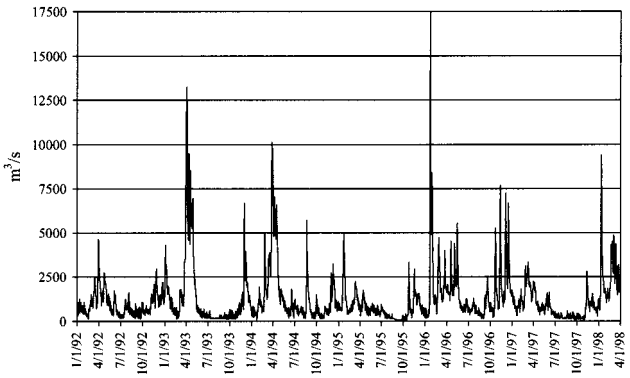

Figure 5. Daily mean discharge rate (m^3/s) at Conowingo Dam from January 1992 to April 1998.

other applications (*30*). Even small inputs of chlorpyrifos to the Bay may be important as chronic toxicity in aquatic species can occur at very low concentrations (*9*).

Endosulfan is used on vegetable row crops such as tomatoes to control the Colorado potato beetle. The technical mixture contains a 70:30 mixture of the α- and β-isomers (*31*, *32*). Two large pulses of endosulfan were observed during August and September (maximum load = 2 and 0.4 kg/day for β- and α-endosulfan, respectively) (**Figure 3B**). Even though the α-isomer is the dominant component of the technical formulation, concentrations of the β-endosulfan isomer were higher in the surface water. This discrepancy can be explained because the liquid phase aqueous solubility of the β-isomer is ~7 times higher than that of the α-isomer (*33*). After application, relatively quick degradation of endosulfan in the watershed is evidenced by the increase in endosulfan sulfate loadings over the parent compounds within 2 months.

The mass loading of organochlorine compounds is dominated by the river flow rate, reflecting a low-level, persistent source in the soil. Hexachlorocyclohexanes (HCHs) were the most prevalent OC detected in the water samples. The load of γ-HCH isomer is higher than that of the α- HCH throughout the year (**Figure 4**). Whereas the technical mixture of HCHs is dominated by the α-isomer, use of this formulation has been banned in most industrialized countries (*34*). Lindane is made up of 90% γ- HCH and is still used in limited applications in the United States. Use of lindane within the Susquehanna River watershed may explain the presence of γ-HCH. A diffuse atmospheric source of γ-HCH to the Susquehanna River watershed is another possible route for this compound.

Comparison with Previous Studies. Previous measurements of pesticide loads from the Susquehanna River in 1992 by Foster and Lippa (*13*) agree extremely well with our results (**Table 4**). For example, Foster and Lippa predicted the annual load of atrazine and metolachlor would be 1700 and 920 kg/year, whereas our results predict 1600 and 1100 kg/year, respectively. However, estimated pesticide loads from 1994 (*14*) are 2−10 times higher than during 1992 or 1997. It is not likely that the number of acres in production or the use rates of these major pesticides would vary so drastically between years; therefore, an examination of water flows in the watershed as a determining factor is warranted.

Daily mean discharge rates measured at the Conowingo Dam were obtained for 1992−1998 (**Figure 5**) from U.S. Geological Survey Station 01578310 (*35*). A comparison of total water discharge for 1992 and 1997, when pesticide loadings were similar, shows results that are also very close, 3.45×10^{10} and 3.31×10^{10} m^3/year, respectively. In contrast, the total water discharge for 1994 was >30% higher, at 4.93×10^{10} m^3/year. If water flow is the dominant factor, this information can be used to give a rough estimate of pesticide loads through the Conowingo Dam from 1992 to 1997. For example, using a correlation between the annual load of atrazine and metolachlor and total annual discharge during the sampling collection periods, a trend line can be developed to estimate loads for the other years between studies.

$$\text{atrazine load (kg/year)} = 8 \times 10^{-8}\,(\text{annual water discharge, m}^3\text{/year}) - 1047,\ R^2 = 0.994$$

$$\text{metolachlor load (kg/year)} = 1 \times 10^{-7}\,(\text{annual water discharge, m}^3\text{/year}) - 2228,\ R^2 = 0.962$$

Using this rough model, the largest loads of atrazine and metolachlor were received in 1996 (3500 and 3460 kg/year, respectively) and the smallest loads in 1995 (950 and 270 kg/year, respectively). The total estimated load over the 6-year

period was 12400 kg of atrazine and 9950 kg of metolachlor. This approach assumes that agricultural practices in the watershed are relatively constant from year to year. Future studies of mass loadings from the Susquehanna River can be used to test this correlation and to evaluate if water discharge normalized annual load rates are dropping or increasing over time.

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