Fluvial Loadings of Selected Organonitrogen and Organophosphorus Pesticides to Chesapeake Bay

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The annual loads of nine organonitrogen and organophosphorus pesticides were determined from March 1992 to February 1993 above the fall lines of the Susquehanna, Potomac, and James Rivers, the three largest tributaries of Chesapeake Bay. Sampling at the fall lines of the three tributaries was conducted during base- and storm-flow hydrologic conditions, and surface water concentrations of the organo-N/P pesticides were measured using large-volume liquid–solid extraction and gas chromatography/mass spectrometry. Annual loads of the organo-N/P pesticides were directly correlated with field application rates and stream discharge with the exception of alachlor, which had relatively low fall line loads in all three tributaries. The influxes of pesticides and other organic contaminants contributed by the tributaries are being compared with identified nonpoint sources in Chesapeake Bay.

INTRODUCTION

The impacts of trace contaminants on the water quality of and living resources inhabiting Chesapeake Bay are ultimately governed by the magnitude of contaminant influxes from the major tributaries and other sources. To better understand contaminant dynamics in Chesapeake Bay, the Chesapeake Bay Fall Line Toxics Monitoring Program (CBFLP) was established in 1990 to quantify trace contaminant fluxes to the bay's tidal waters contributed through fluvial transport (CBP, 1994). From March 1992 through February 1993 a study was initiated through the CBFLP with the aim of developing and implementing an ultratrace analytical method for the determination of the annual loads of selected organonitrogen and organophosphorus (organo-N/P) pesticides (Godfrey et al., 1995) above the fall lines of the Susquehanna, James, and Potomac Rivers. Together these three rivers account for ca. 75% of the annual freshwater discharge in Chesapeake Bay.

Detection frequencies of the organo-N/P pesticides in surface water samples analyzed in conjunction with the CBFLP prior to 1992, employing 1-L sample extractions with dichloromethane followed by analysis using gas chromatography (Wershaw et al., 1987), were undesirably low for seven of nine constituents, leading to a high level of censoring of the analytical data for fall line load estimations (CBP, 1993). Because the tributary fall line loads reported by the CBFLP will be used to compare input mass balances of organic contaminants in Chesapeake Bay with other sources, such as atmospheric deposition, it was desirable to limit censoring of the analytical data to a level ≤70%. Therefore, an analytical method was developed, consisting of the liquid–solid extraction (LSE) of 10-L surface water samples followed by gas chromatographic/mass spectrometric (GC/MS) analysis, which provided detection limits of ca. 1 ng/L for the analysis of selected organo-N/P pesticides in surface water samples.

Organic contaminant LSE from surface water has traditionally been accomplished using Amberlite-XAD nonionic resins (Junk et al., 1974; Van Rossum and Webb, 1978; Diagnault et al., 1988), C_{18} bonded-phase silicas (C_{18}BPS) (Steinheimer and Ondrus, 1986; Junk, 1988; Brooks et al., 1989; Bogus et al., 1990; Johnson and Fendinger, 1991; Brouwer et al., 1992; Kwakman et al., 1992; Loconto, 1992; Cai et al., 1993; Meyer and Mills, 1993; Barcello et al., 1993; Foreman et al., 1993), graphitized carbon black (GCB) (Bacaloni et al., 1980; Mangani et al., 1981; Borra et al., 1986; Di Corcia and Samperi, 1990; Di Corcia and Marchetti, 1991, 1992), polyurethane foam (Basu and Saxenak, 1978), and Tenax resin (Pankow et al., 1988). Numerous reports exist which describe the isolation of pesticides from water samples of 1 L or less using C_{18}BPS particles packed in sorbent cartridges or embedded in fibrous Teflon membrane disks. Given the demonstrated broad applicability of both C_{18}BPS and GCB in the isolation and enrichment of both polar and nonpolar pesticides from many diverse compound classes in water samples in the 1-L volume range, these sorbents were selected for extraction of the organo-N/P pesticides from 10-L surface water samples.

The central hypothesis of the present study was that the loads of selected organo-N/P pesticides to the bay's tidal waters via the major tributaries could be estimated by (i) sampling the major tributaries during base- and storm-flow hydrologic conditions at the river fall lines, (ii) applying low detection limit techniques in the analysis of the pesticides in surface water samples, and (iii) integrating monthly organo-N/P pesticide concentration measurements with continuous stream discharge data. The importance of obtaining accurate load estimates for heavily applied organo-N/P pesticides in stream runoff across the Chesapeake watershed is directly linked to developing prudent water quality management strategies to protect this invaluable resource from further deterioration.

MATERIALS AND METHODS

Reagents and Standards. The nine organo-N/P pesticides, including simazine, prometon, atrazine, diazinon, alachlor, malathion, metolachlor, cyanazine, and hexazinone, were purchased from Chem Service, Inc. (West Chester, PA) as neat compounds with a purity >97%. All acquired solvents were

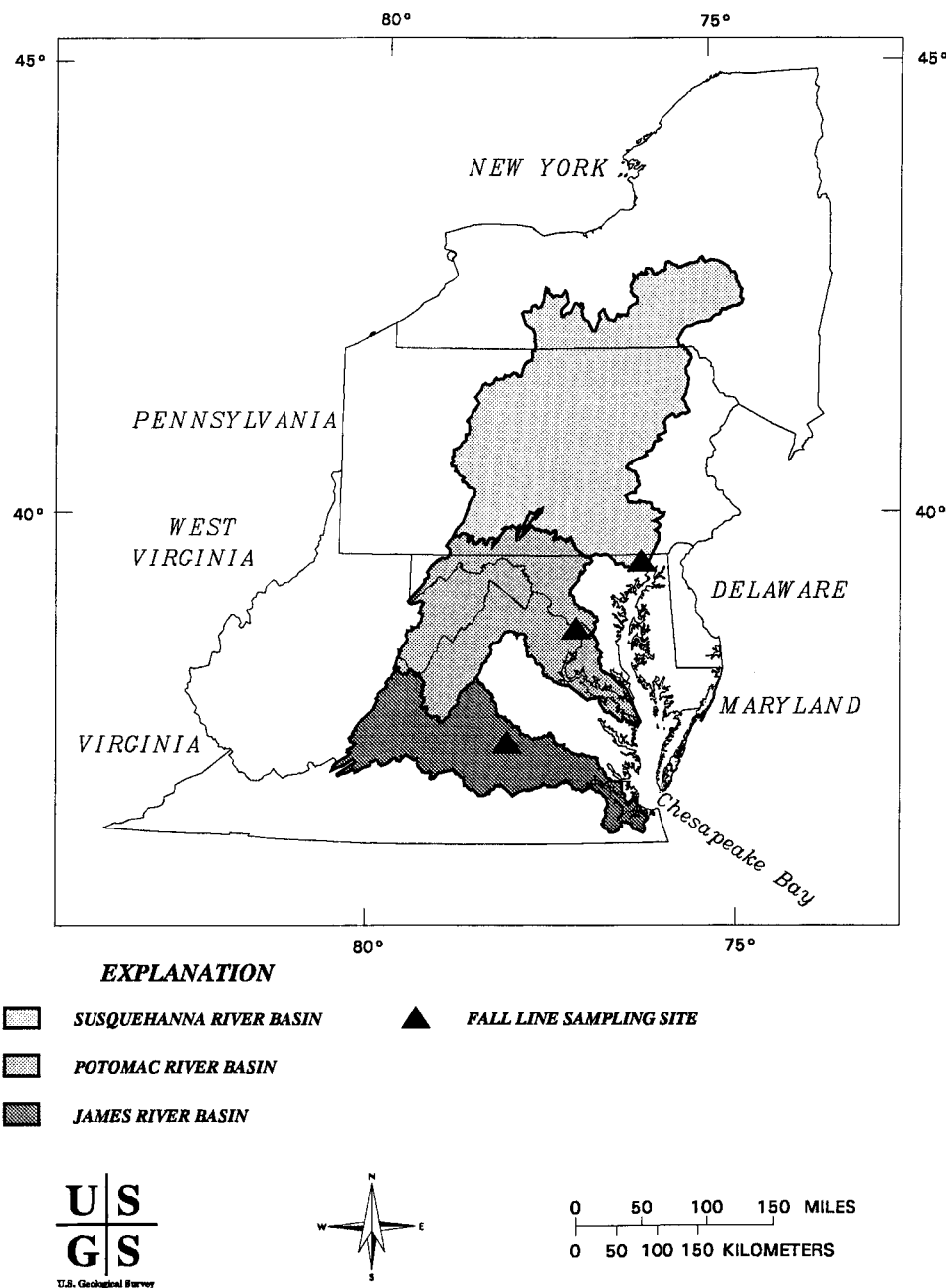* Author to whom correspondence should be addressed [fax (703) 993-1055; e-mail gfoster@gmu.edu].

Figure 1. Map of Mid-Atlantic United States showing the Chesapeake Bay watershed (shaded region) and the location of tributary sampling stations at the Susquehanna, Potomac, and James River fall lines (triangles).

of high purity from Burdick and Jackson (Muskegeon, MI). GCB (40/120 mesh) was obtained in bulk form from Supelco, Inc. (Bellefonte, PA), and 10-g C_{18}BPS cartridges were purchased prepacked from Varian (Harbor City, CA).

Sample Collection and Preparation. Surface water samples were obtained from the Susquehanna River at Conowingo, MD, from the Potomac River at Chain Bridge, Washington, DC, and from the James River at Cartersville, VA, from March 1, 1992, through February 28, 1993 (Figure 1). The numbers of base- and storm-flow samples collected at each river fall line are listed in Table 1. Surface water sampling of the Susquehanna and James River fall lines was performed by the U.S. Geological Survey using an equal-discharge increment method (Ward and Harr, 1990). Surface water samples from the Potomac River fall line were acquired through the operation of an automated sample retrieval system built and maintained by Virginia Tech (Post and Grizzard, 1987). The samples obtained from the Susquehanna and James River fall lines were placed directly in precleaned 37.5-L stainless steel milk cans and immediately processed on-site. Surface water samples obtained from the Potomac River fall line were placed in milk cans and transported to George Mason

University (GMU) for immediate processing. Duplicate samples were acquired and composited for three or four of the base-flow collections at each fall line.

Contaminant-free double-distilled water was prepared by redistilling laboratory supply distilled water using a Corning (Corning, NY) Mega-Pure water purifier and further extracting organic substances from double-distilled water via 10-g C_{18}-BPS cartridges. Contaminant-free distilled water was collected in precleaned 4-L amber glass bottles and stored at 3 °C until use.

Each surface water sample was pumped via a positive displacement pump (Model QB, Fluid Metering Inc., Oyster Bay, NY) at 1 L/min through a stacked configuration of a 15-cm (diameter) Whatman GF/D (Whatman International Ltd., Maidstone, England) glass fiber filter (25-μm nominal pore diameter) overlaying a 15-cm (diameter) Whatman GF/F glass fiber filter (0.7-μm nominal pore size) housed in a 142-mm Millipore (Millipore Corp., Bedford, MA) stainless steel filtration apparatus. The filter holder had been customized by the addition of a PTFE Teflon O-ring in place of the original Viton O-ring to minimize sample contamination and analyte reaction. The filtered water was collected in separate precleaned

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Table 1. Sampling Summary

Susquehanna River Fall Line (39° 39′ 31″ Latitude, 76° 10′ 28″ Longitude) Sampling Dates

base flow (when $q < 2266$ m^3/s)[a]   1992 (March 6,* April 3, May 12, June 19,* July 15, Sept 2,* Nov 18*)
     1993 (Jan 8)

storm flow (when $q > 2266$ m^3/s)[b]   1992 (March 29, March 30, March 31, April 22, April 23, Nov 25, Nov 30)

Potomac River Fall Line (38° 55′ 46″ Latitude, 77° 07′ 02″ Longitude) Sampling Dates

base flow (when $h/t <\pm 1.2$ cm/min)[a]   1992 (March 20,* April 22,* May 29, June 30,* Aug 4,* Oct 6,* Dec 9)
     1993 (Jan 26)

storm flow (when $h/t >\pm 1.2$ cm/min)[b]   1992 (June 11)

James River Fall Line (37° 40′ 15″ Latitude, 78° 05′ 10″ Longitude) Sampling Dates

base flow (when $q < 340$ m^3/s)[a]   1992 (March 13,* April 10,* May 20,* June 24,* July 22, Sept 3, Oct 28)
     1993 (Jan 28)

storm flow (when $q > 340$ m^3/s)[b]   1992 (April 23, April 24, April 26, April 27, April 28, Nov 23, Nov 25, Dec 11, Dec 12)
     1993 (Feb 23, Feb 24, Feb 25)

[a] Base flow hydrologic criteria for individual tributary: q = stream discharge at fall line; h/t = stream gauge height at the fall line divided by time, representing the rising and falling limbs of the storm hydrographs. *Indicates dates when duplicate samples were collected. [b] Storm flow criteria for individual tributary (nomenclature identical to base flow).

milk cans for subsequent spiking and extraction. Total suspended particulate matter concentrations were determined by collecting samples during filtration and applying standard methods (Strickland and Parsons, 1972).

The organo-N/P pesticides were extracted from the surface water samples and distilled water by using LSE procedures similar to that described previously by Foreman et al. (1993). Briefly, 10 L of water was passed through LSE sorbent cartridges configured in a stacked, front and back, arrangement. For the extraction of Susquehanna and James River surface water and distilled water, the front and back sorbent cartridges contained 4 and 2 g of GCB, respectively. For the extraction of Potomac River surface water and distilled water, two 10-g C$_{18}$BPS cartridges were used in a similar arrangement. Water was pumped through the sorbent cartridges using Model RHB or Model QB (Fluid Metering) pumps at flow rates of 50−75 mL/min. Upon extraction of the samples, the sorbent cartridges were rinsed with 10 mL of contaminant-free distilled water, wrapped in aluminum foil, put into zip-lock plastic bags, and placed in an ice chest. The sorbent cartridges were eluted within 24 h of returning to the laboratory. The sorbent cartridges were dewatered and eluted with 60 mL of cyclohexane/2-propanol (Foreman et al., 1993). The eluents were reduced in volume to either 0.2 or 0.5 mL via rotary flash evaporation and nitrogen gas blowdown, and the organo-N/P pesticides were subsequently analyzed by using GC/MS.

Field blanks were performed on-site during each Susquehanna and James River base-flow sampling. Field blanks consisted of a contaminant-free distilled water rinse of all of the sample collection equipment. Field blanks were placed in precleaned milk cans and filtered and extracted in the normal fashion. Approximately 4−8 L of contaminant-free distilled water was used for the field blank. The field blanks were processed prior to the filtration and extraction of the surface water samples. Laboratory blanks were performed intermittently using identical procedures.

Distilled Water and Matrix Spikes. Ten liters of distilled water or surface water was spiked with 5 mL of a methanol solution containing the entire suite of organo-N/P pesticides immediately after filtration to achieve "spike" concentrations of 10 (C$_{18}$BPS only) or 100 ng/L (C$_{18}$BPS and GCB). (The actual concentration in the surface water samples was the sum of both native and spiked pesticides.)

Because organic compounds dissolved in water are known to undergo sorption to the walls of sample containers, the milk cans were solvent rinsed with 100 mL of cyclohexane/2-propanol (7:3) after extraction, and the solvent rinses were concentrated and analyzed separately by using GC/MS.

Percent recoveries (% rec) were calculated according to the net amount of pesticide recovered from front (only) cartridge isolations. In addition, mass balances were calculated from the amount of pesticide recovered from front and back cartridge isolations, as well as through other sample processing steps relative to the total amount of pesticide spiked in the sample. Standard deviations (SD) were used to quantify the agreement between replicate recovery experiments. In addi-

tion, indeterminate errors were propagated through individual steps in the present method using conventional computational techniques (Harris, 1995). Collection efficiencies (% C_E) were determined from the mass of pesticide eluted from the back cartridge (m_{bc}) relative to the mass eluted from the front cartridge (m_{fc}) according to the following formula:

$$\% \text{ CE} = [1 - (m_{bc}/m_{fc})] \times 100 \qquad (1)$$

Collection efficiencies were used to asses the degree of analyte breakthrough occurring during isolation from water on the solid sorbents.

GC/MS Analysis. Electron impact ionization GC/MS in the multiple ion detection mode was used in the analysis of the organo-N/P pesticides. Three ions were monitored for each of the individual pesticides. The GC/MS system consisted of a Hewlett-Packard (HP) Model 5890A GC, equipped with an HP Model 7673A autosampler (2-μL injections), coupled to a Finnigan MAT (San Jose, CA) Incos 50 mass spectrometer. The GC/MS was controlled using Incos 50 software. The mass spectrometer was operated with a source ionization potential of 70 eV, a source temperature of 200 °C, and an electron multiplier voltage range of 1200−1500 V. GC/MS separations were preformed on a 30 m × 0.25 mm (i.d.) DB-5 (J&W Scientific, Inc., Folsom, CA) bonded-phase (0.25-μm film) fused silica capillary column. Separations were temperature programmed from an initial temperature of 45 °C (1-min hold) and ramped to 285 °C at a rate of 10 °C/min, and the temperature was held at 285 °C for 7 min. The GC/MS was tuned and calibrated daily with perfluorotributylamine. Raw data files produced by the Incos 50 mass spectrometer were archived and converted to PCDS (version 3.0, Finnigan MAT) format for autoquantitation via uploading to an HP Vectra QA/20 microcomputer. The PCDS reports were imported into Quattro Pro spreadsheets (version 2, Borland Associates, Scotts Valley, CA) for numerical processing using customized macro programs.

Primary and internal standards were prepared from the neat compounds. Phenanthrene-d_{10} and chrysene-d_{12} were used as the internal standards for quantitation. The internal standard was added to each sample extract immediately prior to GC/MS analysis. Single calibrations were used to calculate relative retention times (retention time of analyte/retention time of the appropriate internal standard) and relative response factors for each pesticide. Peak identifications were assigned according to relative retention times with a tolerance of ±0.0004 relative unit. Detection limits were calculated from an extrapolated analyte signal-to-noise ratio of three in laboratory blank samples spiked with each of the organo-N/P pesticides.

Load Estimation Methods. Annual loads above the fall lines for each of the three rivers were estimated separately by using an interpolation−integration (I−I) model developed in our laboratory. Tributary fall line base-flow loads (L_{BF}) and storm-flow loads (L_{SF}) in kilograms per day were estimated using the following methods, respectively:
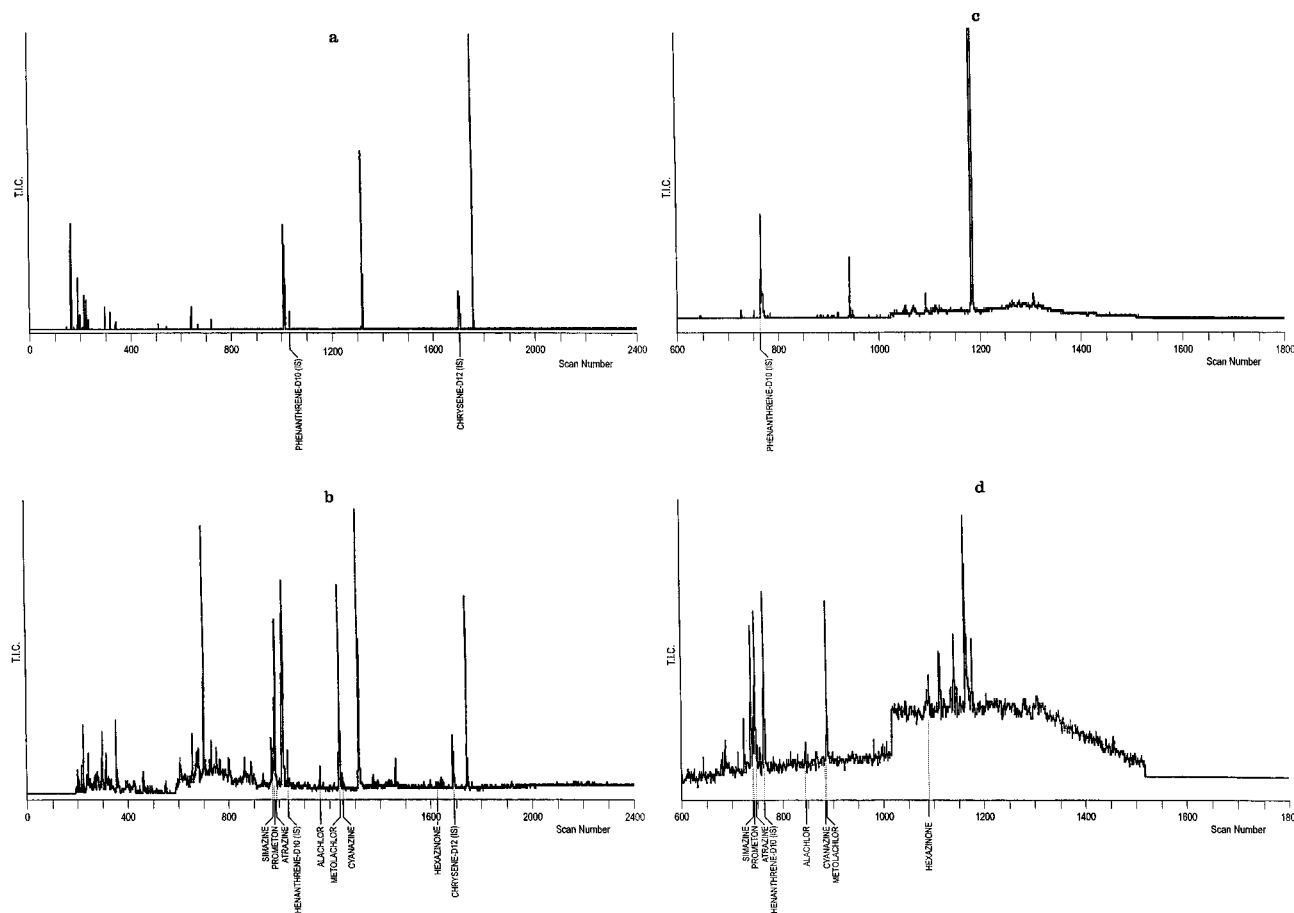
Figure 2. GC/MS ion chromatograms for (a) $C_{18}BPS$ extraction of 10 L of distilled water (blank), (b) $C_{18}BPS$ extraction of 10 L of Susquehanna River surface water (April sample), (c) GCB extraction of 10 L of distilled water (blank), and (d) GCB extraction of 10 L of Potomac River surface water (April sample). Individual peaks are labeled on chromatograms (IS refers to internal standard), which are expressed as relative abundance (0−100%) of the TIC versus scan number. Refer to text for separation conditions.

$$L_{BF} = 10^{3.556} \sum_{j=1}^{N} c_j \sum_{i=-n_j}^{n_j} \bar{q}_{ij} t_{ij} \qquad (2)$$

$$L_{SF} = 10^{3.556} \sum_{l=1}^{M} \sum_{k=1}^{n_l} \bar{q}_{kl} c_{kl} t_{kl} \qquad (3)$$

$\bar{q}_{ij}$ is the mean daily discharge (m^3/s) on ith day of jth period, $\bar{q}_{kl}$ is the mean daily discharge (m^3/s) on kth day of lth storm, c_j is the concentration (dissolved + particulate) of constituent (kg/m^3) in jth period, c_{kl} is the concentration (dissolved + particulate) of constituent on kth day of lth storm, t_{ij} is the hours of base flow on ith day of jth period, t_{kl} is the hours of storm flow on kth day of lth storm, n_j is $0.5 \times$ number of days in jth period, n_l is the number of days per storm, N is the number of periods ($\approx$ number of samples), and M is the number of storms.

Estimated daily L_{BF} and L_{SF} values were summed throughout the sampling period to obtain annual loads. Data censoring was employed in the I−I model whenever an analyte was below the detection limit in the surface water samples. In these cases, both maximum (max) and minimum (min) daily loads were estimated by adjusting the sample concentration to the detection limit (max) in one scenario and to zero (min) in the other and are reported below as load intervals. Mean daily stream discharges were obtained via USGS gaging stations.

RESULTS AND DISCUSSION

Analytical Method Performance. Quantitation of organo-N/P pesticide concentrations in the surface water

samples was never limited by the presence of interferences in the field blanks. Occasional GC/MS peaks had the same retention time and mass-to-charge ratio as the primary quantitation ion of the analyte in some of the field blanks but were detected at concentrations slightly above detection limit values only during times of the year when surface water concentrations of the organo-N/P pesticides were the greatest (i.e., April through July). Identified pesticides in surface water required the presence of at least one confirmatory ion in addition to the primary quantitation ion with the correct relative abundance in GC/MS ion chromatograms. The organo-N/P pesticides were not detected in any of the laboratory blanks.

Blank and unspiked (native) surface water sample GC/MS total ion chromatograms (TIC) are illustrated in Figure 2 for both the 10-L $C_{18}BPS$ and GCB extractions. The chromatograms demonstrate (a) the favorable signal-to-noise ratio found for the organo-N/P pesticide peaks in the native surface water samples relative to the lab blanks. Many of the organo-N/P pesticides could be quantified at ambient concentrations in the surface water samples for most collections throughout the calendar year. Detection limits for the nine organo-N/P pesticides ranged from 0.5 to 3 ng/L in the GC/MS analysis of the 10-L water samples for this method.

Front cartridge extraction recoveries of the target analytes from $C_{18}BPS$ and GCB for both spiked distilled and surface water are listed in Table 2. All GCB

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Table 2. Front Cartridge C$_{18}$BPS and GCB Extraction Recoveries and Collection Efficiencies of the Pesticides from Spiked 10-L Distilled and Surface Water Samples

	distilled water		surface water	
	front cartridge % rec[a] (dev)[b]	front cartridge % rec ± SD[c]	front cartridge % rec ± SD	% C_E[d]
spike concn. ng/L	100	10	100	
C$_{18}$BPS				
no. of replicates (*n*)[e]	2	3	5	
simazine	75 (14%)	89 ± 10	80 ± 13	96
prometon	81 (1%)	100 ± 10	68 ± 4	94
atrazine	92 (4%)	103 ± 4	90 ± 20	94
diazinon	99 (9%)	94 ± 2	110 ± 20	99
alachlor	91 (8%)	88 ± 13	100 ± 10	96
malathion	100 (1%)	113 ± 1	99 (*n*=1)	97
metolachlor	94 (8%)	94 ± 3	100 ± 20	95
cyanazine	99 (18%)	103 ± 5	90 ± 30	97
hexazinone	80 (*n*=1)	nd[f]	84 (*n*=2)	85
GCB				
no. of replicates (*n*)	3		5	
simazine	53 ± 3	nd	60 ± 20	96
prometon	80 ± 10	nd	60 ± 10	94
atrazine	100 ± 10	nd	70 ± 40	95
diazinon	110 ± 20	nd	90 ± 30	98
alachlor	100 ± 20	nd	80 ± 40	97
malathion	91 ± 7	nd	79 (*n*=2)	98
metolachlor	110 ± 30	nd	90 ± 30	95
cyanazine	100 ± 20	nd	60 ± 20	96
hexazinone	102 ± 7	nd	130 ± 60	86

[a] Mean percent recovery. [b] Precent deviation for duplicates: dev = |% rec$_{rep1}$ − %rec$_{rep2}$|/mean × 100. [c] Standard deviation. [d] % C_E = Mean percent collection efficiency. [e] Number of replicate recovery determinations. [f] nd, not determined.

recoveries for pesticides spiked in surface water were combined because there were no apparent differences in extraction behavior between the Susquehanna and James River sources. Mean extraction recoveries in C$_{18}$-BPS cartridges were ≥80% for each of the pesticides except for simazine in distilled water and prometon in surface water at the 100 ng/L spikes. In GCB cartridge extractions, only simazine was recovered at less than 80% from distilled water, but six of the nine pesticides showed ≤80% recoveries from surface water. Recoveries of the organo-N/P pesticides from spiked surface water were somewhat lower overall in GCB versus C$_{18}$PBS cartridges, and this finding was not attributed to the source of surface water.

Assessment of collection efficiencies and container rinses revealed that none of the organo-N/P pesticides were detected in any of the container rinses in C$_{18}$BPS or GCB extractions. Collection efficiencies were always near 100% in distilled water spikes and were typically near 95% in surface water spikes for both sorbents, indicating breakthrough in either distilled or surface water was minimal for all of the pesticides except hexazinone (Table 2).

The variabilities of the spike recoveries (±SD in Table 2) were usually greater for surface water relative to distilled water for both sorbents. Determinant error was introduced in the corrected recoveries when the amount of spiked pesticide represented less than half of the mass balance in the surface water sample. This was especially apparent for simazine, atrazine, metolachlor, and cyanazine during times of the year when the native concentrations of these pesticides in surface water were the highest. The spiked surface water extraction replicates were conducted throughout the calendar year, and all the results were combined to provide the values in Table 2. Additional assessments of method variabilities were obtained via the propagated indeterminant errors and duplicate analyses of the

Table 3. Error Analysis for Surface Water Concentration Measurements

pesticide	propagated rel error,[a] %	mean % dev of duplicates[b,c]
simazine	11	28
prometon	18	40
atrazine	10	19
diazinon	21	na[d]
alachlor	19	43
malathion	27	na
metolachlor	15	28
cyanazine	21	11
hexazinone	38	37

[a] Relative indeterminate error propagated through sample preparation and GC/MS analysis procedures. [b] Mean percent deviation for duplicate measurements performed for all surface water measurements of the organo-N/P pesticides at the fall lines of the three tributaries (% dev = |rep 1 − rep 2|/mean × 100). [c] A total of 13 duplicate samples were collected and analyzed. [d] na, not applicable.

Table 4. Summary of Organo-N and Organo-P Pesticide Concentrations Observed in Surface Water Samples Collected at the Susquehanna River Fall Line

pesticide	max obsd concn, ng/L	min obsd concn, ng/L	mean concn, ng/L	frequency of detection,[a] %	month of peak concn[b]
simazine	91	2	24	58	May (b)
prometon	19	2	9	42	May (b)
atrazine	290	8	56	90	June (b)
diazinon	18	6	12	10	March (s)
alachlor	23	2	12	37	June (b)
malathion	8	4	6	16	April (s)
metolachlor	140	1	31	90	June (b)
cyanazine	108	4	36	47	June (b)
hexazinone	16	1	5	42	March (s)

[a] Percent of total samples collected during the year for which the pesticide was detected and quantified. [b] Month of the year in which the maximum quantifiable concentration was observed at the river fall line. The letters in parentheses denote the flow regime for the sample which contained the maximum quantifiable concentration: b, base flow; s, storm flow.

surface water samples. The propagated relative errors listed in Table 3 were evaluated for the complete tributary concentration data set and may be applied to the following concentration measurements and esti-mated loads. In addition, the mean percent differences between duplicate analyses combined for all three tributary fall lines are listed in Table 3 for each pesticide.

River Fall Line Concentrations and Loads. Con-centrations of the organo-N/P pesticides detected in the river fall line samples from the Susquehanna, Potomac, and James Rivers varied seasonally (Tables 4−6). The greatest observed concentrations correlated directly with the months of field application, which ranges from April through July in the Mid-Atlantic United States (Pait et al., 1992). Peak concentrations of the organo-N herbicides occurred during May or June at the Susque-hanna and Potomac River fall lines (Tables 4 and 5), but for the James River the greatest concentration occurred during an April storm (Table 6). This storm event in the James River basin in 1992 was exception-ally large, prompting a massive flush and surface runoff throughout the basin. The spring and early summer concentration maxima observed in the Chesapeake Bay tributaries were consistent with temporal trends which have been reported in the Mississippi River (Pereira and Rostad, 1990) and other midwestern U.S. river basins (Thurman et al., 1991, 1992; Schottler et al., 1994). The majority of the surface runoff of the relatively water

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Table 5. Summary of Organo-N and Organo-P Pesticide Concentrations Observed in Surface Water Samples Collected at the Potomac River Fall Line

pesticide	max obsd concn, ng/L	min obsd concn, ng/L	mean concn, ng/L	frequency of detection,[a] %	month of peak concn[b]
simazine	140	6	62	80	June (s)
prometon	17	8	14	60	June (b)
atrazine	580	10	160	93	June (b)
diazinon	10	10	10	6	June (s)
alachlor	21	9	12	33	June (b)
malathion	12	12	12	6	June (s)
metolachlor	360	9	96	87	June (b)
cyanazine	210	10	114	40	June (b)
hexazinone	20	2	9	20	June (s)

[a] Percent of total samples collected during the year for which the pesticide was detected and quantified. [b] Month of the year in which the maximum quantifiable concentration was observed at the river fall line. The letters in parentheses denote the flow regime for the sample which contained the maximum quantifiable concentration: b, base flow; s, storm flow.

Table 6. Summary of Organo-N and Organo-P Pesticide Concentrations Observed in Surface Water Samples Collected at the James River Fall Line

pesticide	max obsd concn, ng/L	min obsd concn, ng/L	mean concn, ng/L	frequency of detection,[a] %	month of peak concn[b]
simazine	370	3	50	50	April (s)
prometon	18	2	6	25	April (s)
atrazine	480	4	61	62	April (s)
diazinon	12	3	7	25	April (s)
alachlor	20	4	10	30	April (b)
malathion	12	3	7	8	April (s)
metolachlor	210	1	31	50	April (s)
cyanazine	25	2	12	38	May (b)
hexazinone	17	1	8	42	April (b)

[a] Percent of total samples collected during the year for which the pesticide was detected and quantified. [b] Month of the year in which the maximum quantifiable concentration was observed at the river fall line. The letters in parentheses denote the flow regime for the sample which contained the maximum quantifiable concentration: b, base flow; s, storm flow.

Table 7. Load Intervals for the Organo-N and Organo-P Pesticides above the Fall Lines of the Susquehanna, Potomac, and James Rivers

	load, kg/year			
	Susquehanna River $q = 1030$ m^3/s[a]	Potomac River $q = 293$ m^3/s[a]	James River $q = 210$ m^3/s[a]	rank[b]
simazine	580–610	340	130–140	5
prometon	110–160	56–66	(18–26)[c]	NA
atrazine	1700	780	220	2
diazinon	(8–96)	(3–27)	(20–30)	NA
alachlor	86–97	25–44	15–28	1
malathion	(8–86)	(3–25)	(3–18)	NA
metolachlor	920	390	89–92	3
cyanazine	430–480	220–230	32–43	4
hexazinone	170–180	(6–14)	18–26	NA

[a] Mean annual stream discharge at fall line. [b] Rank of pesticide application rates in the Chesapeake Bay estuarine drainage area for 1987 [from Pait et al. (1992)]; NA indicates pesticide application data were unavailable. [c] Parentheses identify load intervals in which >70% censoring of the fall line concentration data was performed to estimate the annual loads.

soluble organo-N herbicides ensues field application and precipitation events during heavy rainfall in the spring and early summer months. Concentrations of the organo-N/P pesticides decreased exponentially from peak concentrations during spring or summer to near detection limit values during the winter months when most of the labile pesticide residues had been previously flushed from the soils.

Atrazine, cyanazine, metolachlor, and simazine were the most frequently detected pesticides in the tributary fall line samples and had the greatest surface water concentrations (Tables 4–6), generally paralleling pesticide application rates documented for the estuarine drainage area of the bay (i.e., below the tributary fall lines; refer to Table 7). Conversely, alachlor, the most heavily applied organo-N herbicide in the Chesapeake Bay watershed, had surface water concentrations and detection frequencies substantially lower than those observed for atrazine, cyanazine, metolachlor, and simazine in all three tributaries. Glotfelty et al. (1989) have shown that following application of atrazine, simazine, alachlor, and other pesticides to a fallow coastal plain soil in Maryland, first-order air/soil volatilization rate constants were 8- and 49-fold smaller for atrazine and simazine, respectively, than that reported for alachlor. Alachlor has a much larger Henry's law constant than atrazine and the other triazine herbicides

[see Suntio et al. (1988)], typically by an order of magnitude or more. Thus, it appears that the greater air/soil volatilization flux of alachlor relative to the other major organo-N pesticides, along with degradative processes, results in a smaller relative percentage of the application mass balance of alachlor occurring in runoff. It is clearly evident that the concentrations of the organo-N/P pesticides in fluvial transport were not always directly proportional to the documented 1987 field application rates given by Pait et al. (1992); it was assumed the pesticide application rates in 1992 followed the relative order of those reported for 1987.

Detection frequencies of the organo-N herbicides were ≥30% the Susquehanna River fall line for each constituent, for all but hexazinone at the Potomac River fall line and for all but prometon and alachlor at the James River fall line (Tables 4–6). The organo-P pesticides, diazinon and malathion, were detected in only a few of the surface water samples (Tables 4–6). Detection frequencies were <30% for both pesticides for each of the three tributaries. Diazinon and malathion have much lower application rates in the river basins relative to the organo-N herbicides and are labile to oxidation and hydrolysis reactions (Harris, 1981), leading to their low levels observed in fluvial transport.

Estimated annual loads of the organo-N/P pesticides above the fall lines of the three tributaries are presented in Table 7 as load intervals, representing the maximum and minimum estimated loads obtained with eqs 2 and 3. Diazinon and malathion estimated loads were heavily censored for all three tributary fall lines, while for the organo-N pesticide estimated loads only prometon in the James River and hexazinone in the Potomac River fell below the ideal censoring limit. Loads varied among the tributaries in direct correspondence with stream discharge (Table 7). In fact, in all cases where the estimated loads did not exceed 70% censoring, the pesticide loads normalized to drainage area (i.e., kg/km^2/year) differed by less than a factor of 2 among the three river basins.

Because concentrations of the organo-N/P pesticides included in this study have not been reported in the literature for mainstem Chesapeake Bay, the loadings in Table 7 may be used to further estimate steady-state concentrations in mainstem surface water. Treating the bay as a continuously stirred tank with an approximate water volume of 50 km^3 below the tributary fall lines with a flushing time of 1 year (Leister and Baker, 1994),

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and further assuming the maximum loads listed in Table 7 represent 75% of the input mass balance from streams across the entire watershed (in direct proportion to relative discharge of all nine significant tributaries), the estimated annual average concentrations of atrazine, simazine, and metolachlor are 70, 20, and 30 ng/L, respectively, for the mainstem. These calculations indicate that biota in Chesapeake Bay are exposed to long-term low-level concentrations of pesticides the chronic effects of which remain unknown, although these concentrations are well below reported EPA water quality criteria established for freshwater systems (K. Gourdine, U.S. EPA, Region IV, Atlanta, GA, personal communication, 1994). There are presently no clear implications of cause and effect that may be drawn between the estimated annual loads and the health of Chesapeake Bay. Very little is known regarding the toxic effects of submicrogram per liter concentrations of organo-N/P pesticides in freshwater and brackish water ecosystems. Rather, the primary purpose of obtaining fluvial load estimates for trace contaminants is to compare input mass balances among a variety of pathways, providing knowledge that will be useful in developing strategies to significantly reduce transport fluxes in Chesapeake Bay.

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