8

CONTAMINANTS FLUX

Convenors: Dr. James Sanders and Mr. Richard Batiuk

Toward a Sustainable Coastal Watershed:
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DEFINING THE NATURE, EXTENT, AND MAGNITUDE OF BAY TOXICS PROBLEMS: FINDINGS FROM THE BASINWIDE STRATEGY REEVALUATION

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Abstract: The Chesapeake Bay Program's Toxics Subcommittee conducted comprehensive reevaluation of the 1989 Basinwide Toxics Reduction Strategy during 1992-93. The objectives of this strategy reevaluation were to define:

- What we now know about the nature, extent, and magnitude of Bay toxics problems
- What steps we should take to reduce and prevent impacts from toxics.
- What information we still need to determine the additional actions need to be taken.

The subcommittee investigated and evaluated the complex nature of the Bay's toxics conditions and problems through a two-year schedule of meetings, research workshops, and information-gathering forums. Key to building a technical consensus on the nature and extent of the Bay's toxics conditions and problems was a series of seven critical issue forums.

The major findings from these critical issue forums and the overall strategy reevaluation including documentation of severe localized toxicity problems, evidence of toxic effects in areas previously thought to be uncontaminated, and widespread low levels of toxics in all Bay habitats sampled are presented in this paper, along with a summary of areas and issues to be emphasized in the revised basinwide strategy currently under development.

Toward a Sustainable Coastal Watershed:
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OCCURRENCE AND YIELDS OF TRIAZINE HERBICIDES IN THE SUSQUEHANNA RIVER AND TRIBUTARIES DURING BASE-FLOW CONDITIONS IN THE LOWER SUSQUEHANNA RIVER BASIN, PENNSYLVANIA AND MARYLAND, JUNE 1993

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Abstract : Concentration of triazine herbicides, stream discharge, and drainage area data were used to estimate yields of triazine herbicides for 43 individual surface-water sites in the lower Susquehanna River basin, including the Susquehanna River at Danville, Harrisburg, and Marietta, and the basin outflow at Conowingo Dam. Yields of triazine herbicides also were determined for 6 major tributaries and for 33 subbasins that represent the Piedmont physiographic province and the Appalachian Mountains and Great Valley sections of the Ridge and Valley physiographic province. Detectable concentrations of triazine herbicides, ranging from 0.1 to 1.0 µg/l (micrograms per liter) were measured in water samples from 39 of the 43 surface-water sites. No detections were made in samples from two sites that represent forested subbasins, the Susquehanna River at Danville, and the West Branch Susquehanna River at Lewisburg. Median concentrations of triazines ranged from 0.45 to 0.55 µg/l for subsets of samples representing the Ridge and Valley and Piedmont physiographic provinces in limestone and noncarbonate bedrock settings.

Loads and yields of triazine herbicides are smaller for the Ridge and Valley physiographic province than for the Piedmont physiographic province. A ranking on the basis of instantaneous load of the major tributaries sampled during this study of stream base flow is Conestoga River > Swatara Creek > Muddy Creek > Pequea Creek > East Mahantango Creek > West Branch Susquehanna River. A ranking on the basis of instantaneous yield is Muddy Creek > Conestoga River > Pequea Creek > Swatara Creek > East Mahantango Creek > West Branch Susquehanna River.

INTRODUCTION

The Susquehanna River is the largest tributary to the Chesapeake Bay, draining approximately 27,100 mi^2. An understanding of the amounts of chemical constituents entering Chesapeake Bay from tributary rivers has been identified as part of the research needed to manage the Bay ecosystem. In past years, nutrients were a focus of research. More recently, a list of organic compounds and trace elements of concern has been identified (Chesapeake Bay Program 1991). Atrazine, a triazine herbicide applied chiefly to corn crops, is on the “toxics of concern” list.

Purpose and Scope

This paper presents the triazine herbicide concentrations from a synoptic survey of the Susquehanna River and its tributaries. Data are given on site locations, stream discharge, and concentration of triazine herbicides in stream water. Concentrations of triazines from two analytical techniques are given for selected sites and are used to relate concentrations of triazine herbicide residue to concentrations of atrazine and other triazine compounds. The results are for individual samples collected from 43 sites representing the Susquehanna River, selected major tributaries, and smaller tributaries in four major regions of corn production in the lower Susquehanna River basin. Yields of triazine herbicides are estimated by use of drainage basin area as a first approximation for this paper.

Setting

The Lower Susquehanna River basin comprises 9,300 mi^2 of agricultural, forest, and urban land primarily in the Piedmont and Ridge and Valley physiographic provinces of southcentral Pennsylvania and northern Maryland (figure 1). Atrazine use and the relation to corn cropping are described together with stream flow conditions and timing of herbicide applications to provide a setting and context for the design of the survey.

Atrazine Use and Corn Cropping

Atrazine is the primary triazine herbicide used for control of broadleaf weeds in corn and other row crops throughout the lower Susquehanna River basin. In the mid-1980s, on the basis of product labeling, rates of atrazine application in corn may have been as high as 2 lb/acre (pounds of active ingredient per acre of cropland). Label changes in 1993 for atrazine lowered the recommended annual application rate to 1.6-2.0 lb/acre (Horstmeier 1993). Estimates of annual application rates vary in both Pennsylvania and Maryland. In Pennsylvania, the 1990-92 annual application rate on cornfields was estimated to be between 1.2 and 1.3 lb/acre (Knopf 1990, Hopple 1992). In Maryland, the 1987-89 annual application rate on cornfields was estimated to be 1.5 lb/acre (Gianessi and Puffer 1990, p. 2). An average annual application rate of

Figure 1. Subunits and sites representing major physiographic and bedrock lithologic settings for June 1993 synoptic survey of triazine herbicide occurrance in streams, in the lower Susquehanna River basin, Pennsylvania and Maryland.

0.9 lb/acre for atrazine in cornfields was determined by a survey of pesticide use during 1989-91 on 256 farms in Lancaster County, Pennsylvania. (Bingaman et al. 1993). The range of 0.16 to 2.0 lb/acre reported by Bingaman and others suggests the application rate is, in general, likely to be quite variable on corn acreage throughout the basin. Moreover, the intensity of corn production varies with changes in physiography, topography, and soil type, all largely controlled by the bedrock geology.

The Piedmont physiographic province has the largest total area of agricultural land (1.22 million acres or 1,900 mi^2). Agricultural land accounts for 70 percent of the total Piedmont area (Mitchell et al. 1977). In contrast, agricultural land is 30% of the 5,400 mi^2 in the Appalachian Mountains section of the lower Susquehanna River basin.The intensity of row cropping for corn in the Piedmont make this part of the basin rank the highest in the amount of atrazine used.

Accurate estimates of corn acreage for individual subbasins are the ideal for estimating atrazine use. These data are not available at the time of this writing; therefore, generalized intensities of corn row cropping were assigned for the purposes of this paper.

The intensities were estimated in the four subunits chosen for study by the following:

"corn factor" = (fraction of cropland in subunit in corn) x (fraction of subunit in agricultural use).

The fraction of total cropland in corn for the subunit was estimated from county-based values from the 1987 Census of Agriculture (U.S. Department of Commerce 1989). The fraction of the subunit in agricultural use was estimated from land use data for the mid-1970s (Mitchell et al. 1977). The factor was then multiplied by 100 to give a whole number for relative comparison between subunits.

Streamflow Conditions and Timing of Herbicide Application

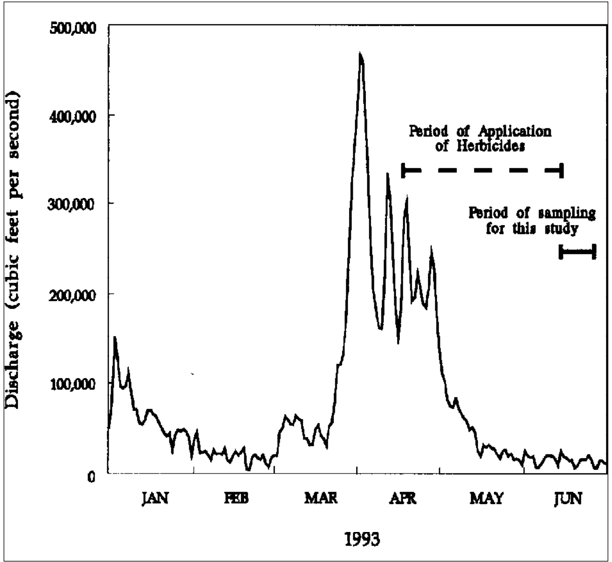

Figure 2. Discharge of Susquehanna River at Conowingo Dam, in period preceding and during the June 1993 synoptic survey of triazine herbicide occurrence in streams.

Streamflow conditions preceding the survey were affected by a heavy snowpack from several winter storms. Melting of the snowpack and above normal rainfall contributed to record flows in the Susquehanna River at Conowingo Dam, Maryland., during April 1993 (figure 2). May 1993 was a dry month; rainfall for the Susquehanna River basin was 50% or more below normal (National Oceanic and Atmospheric Administration 1993) and contributed to lower-than-normal streamflows. During the period June 1-10, daily rainfall totals of 0.1 in (inches) or more were recorded on 1, 8, 9, and 10 June at selected weather stations in the lower Susquehanna River basin. There was no more than a trace of rain during 11-17 June . Most of the sampling was during 14-17 June. Streamflows at nine sample sites during mid-June were exceeded 65% to 75% of the time (table 1). Thus, streams were at base flow when samples were collected. This flow comes from groundwater inflow or flow from springs to the stream channel.

Flow regulation at Conowingo Dam accounts for the high sampled flow shown in table 1 for the Conowingo site. This explains the relatively small percentage of time the sampled flow was exceeded.

Timing of herbicide applications may vary in the southern and northern parts of the basin because of variations in the southern to northern onset of spring planting. Timing of spring planting is related to temperature and precipitation patterns. The period extending from the middle of April to the middle of June is when seeds are sown and is generally the period of high use for preemergent and some postemergent herbicides

Table 1. Assesment of flow conditions in the lower Susquehanna River basin during June 1993 synoptic sampling program. Abbreviation: N / A = not available because of lack of sufficient data for analysis.

Site Number and Name	Sampled Flow (ft^3/s)	Percentage of Time Exceeded (ft^3/s)	Long-Term Mean June Flow	Percentage of Time Exceeded	Month Sampled Fow Similar to: (Monthly Mean ft^3/s)
37 Lewisburg	3,160	70	9,200	40	August (3,340)
36 Danville	5,640	65	10,680	40	July (6,280)
26 Dalmatia	42.3	>77	181	35	August (78)
38 Harrisburg	9,960	75	26,490	40	August (11,600)
39 Hershey	223	73	597	39	August (322)
40 Marietta	13,300	70	2 8,920	40	August (11,800)
41 Conestoga	323	65	500	40	August (376)
42 Pequea C	157	N / A	N / A	N / A	N / A
03 Muddy C	166	N / A	N / A	N / A	N / A
43 Conowingo	46,400	30	38,360	40	May (49,500)

(figure 2). Near the end of the high-use period is when herbicide concentrations in stream water are expected to be at a maximum for the year.

Water Quality Criteria forTriazine Herbicides

In the United States, criteria are established for atrazine, cyanazine, and simazine in drinking water; however, no criteria are established for the protection of aquatic life. For drinking water, the maximum contaminant level and health advisory level concentrations are 3 µg/l (micrograms per liter) for atrazine, 1 µg/l for cyanazine, and 4 µg/l for simazine (U.S. Environmental Protection Agency, 1990). Canadian water quality guidelines for protection of freshwater aquatic life are 2 µg/l for atrazine, 2 µg/l for cyanazine, and 10 µg/l for simazine. These guidelines are intended to protect fish, vascular plants, and algae (Canadian Council of Resource and Environment Ministers 1993).

METHODS

Design of the Survey

The survey of triazine herbicide occurrence and yield was designed as a reconnaissance of waters in the Susquehanna River and waters in tributaries draining subbasins of differing physiography and bedrock lithology. Land use and relative intensity of row cropping for corn also were considered in the design and in the selection of subbasins for sampling. Of the 22 permutations of physiography, bedrock lithology, and major land uses that define subunits for a stratified study design, the survey was to assess four major subunits with different intensities of

Table 2. Site and subbasins for the June 1993 synoptic Survey of triazine herbicides in streams lower Susquehanna River basin. Abbreviation: N / A = not available.

row cropping for corn (figure 1).

Designation of subbasins

For the tributaries, sites 01-10 and 41-42 represent the Piedmont physiographic province and sites 11-35 represent the Ridge and Valley physiographic province (figure 1, table 2). Carbonate bedrock (limestone) and noncarbonate bedrock subbasins were selected in each of the two provinces.

In the Piedmont, the noncarbonate bedrock is crystalline and underlies the Conowingo Creek, Deer Creek, Muddy Creek, and Octoraro Creek subbasins represented by sites 01-09. The corn factor for the Piedmont crystalline subunit is estimated to range from 35 to 42.

Limestone bedrock underlies the Mill Creek subbasin (site 10) and underlies most of the Conestoga River basin (site 41). Mill Creek is a tributary of the Conestoga River. The corn factor for the Piedmont limestone subunit is the highest for the subunits surveyed and is estimated at a value of 48.

In the Ridge and Valley, the noncarbonate bedrock that predominates in the Appalachian Mountains section is sandstone and shale and underlies the Schwaben Creek, East Mahantango Creek, and Wiconisco Creek subbasins represented by sites 11-28. The shaded area designated as “Ridge and Valley Sandstone and Shale Subbasins” in figure 1 includes only the sandstone and shale of the central Susquehanna River valley. The same lithologies also are present in the Juniata River basin, but this basin was not part of the survey design.The corn factor for the Ridge and Valley sandstone and shale subunit is estimated to be less than 35.

Limestone bedrock underlies many valleys in the Ridge and Valley physiographic province. The survey was limited to limestone underlying the central parts of the Great Valley section and represented by sites 29-35. This subunit, in and around Harrisburg, Pennsylvania, is being developed for residential and commercial use; housing tracts in suburbs are displacing cornfields. In this subunit, stream-water chemistry is impacted by development and streams are more distant from the cornfields than in the three other subunits where agricultural and forest land dominate.The corn factor for the subunit in the Great Valley section of the Ridge and Valley physiographic province underlain by limestone is estimated to range from 39 to 43.

Selection of Sites

Sites were selected for three of the four subunits with the primary objective of establishing representative geographic coverage of the subunits. The three subunits in the Piedmont and Great Valley were represented in this manner. The Ridge and Valley sandstone and shale subunit was approached with the primary objective of describing the occurrence of triazine herbicides in the East Mahantango Creek watershed from its headwaters, where the work of Gburek (1977), Pionke et al. (1988), and Pionke and Glotfelty (1989) is based to its mouth. Geographic coverage for this subunit is more restricted than for the other three subunits; however, the East Mahantango Creek drainage is believed to be representative of agricultural valleys underlain by noncarbonate bedrock in the Ridge and Valley physiographic province.

Sample Collection and Analysis

A reconnaissance of sites on tributaries was conducted prior to the synoptic survey to ensure access and to choose the discharge measurement and water quality sampling sections. Water samples were collected at the rate of about 10 per day during 14-17 June 1993. The final sample for the survey was collected on 21 June at Conowingo Dam, Maryland. Measurements of water and air temperature, barometric pressure, pH, specific conductance, alkalinity, and dissolved oxygen were made at the time each sample was collected.

Stream discharge was determined for all 43 sample collection sites. At nine sites on the Susquehanna River and the large tributaries, (sites 26 and 36-43) (table 2), a stage measurement from a U.S. Geological Survey (USGS) streamflow-gaging station and the existing stage-discharge relation were used to determine stream discharge. At four additional sites (sites 2, 10, 20, and 32), stage measurements from (USGS) streamflow-gaging stations established in 1993 for the National Water-Quality Assessment Program study and the existing stage-discharge relation were used. At the other 30 sites, a discharge measurement was made in the same stream section where the water quality sample was collected. Sample collection and discharge measurement were done concurrently by a two-person team at most sites.

Water samples at sites that could be waded were collected by use of an equal width increment (EWI) method (Ward and Harr, 1990). A DH-81 sampler equipped with 1l (liter) Teflon or glass sample containers was used to collect water subsamples. Subsamples were composited in 3l Teflon bottles. For sites on the Susquehanna River and major tributaries, samplers were lowered from bridges and samples were

Table 3. Comparison of imunoassay and GC/MS results for concentrations of triazine compounds in stream water collected14-21 June 1993, in the lower Susquehanna River basin. Abbreviations: OGRL = U.S. Geological Survey Organic Geochemistry Research Laboratory, Lawrence, Kansas; NWQL = U.S. Geological Survey National Water-Quality Laboratory, Arvada, Colorado; PaDER = Pennsylvania Department of Environmental Resources Bureau of Laboratories, Harrisburg, Pennsylvania; Imm = enzyme-linked immunosorbent assay (ELISA); GC / MS = gas chromatography / mass spectrometry; a double dash line incentration not measured by analytical technique.

Concentration, in micrograms per Liter

	Site 10 Mill Creek			Site 20 East Mahantango Creek			Site 32 Cedar Run		
Compound	OGRL Imm	OGRL GC/MS	NWQL GC/MS	OGRL Imm	OGRL GC/MS	NWQL GC/MS	OGRL Imm	OGRL GC/MS	NWQL GC/MS
Triazines, total	0.53	– -	–	0.71	–	–	0.44	– -	–-
Atrazine	0.23	0.14	–	0.40	0.56	–	---	0.27	0.17
Deethylatrazine	–-	.35	.08	–-	.13	.08	–-	.36	.10
Simazine	– -	.65	.46	–-	<.05	<.05	–	.05	<.05
Cyanazine	__	<.05	<.05	–-	.17	.17	__	<.05	<.05
Prometon	– -	<.14	.10	–-	<.05	<.05	__	.20	.12

	Site 40 Susquehanna River ar Marietta		Site 41 Conestoga River	
Compound	OGRL Imm	PaDER GC / MS	OGRL Imm	PaDER GC / MS
Triazines, total	0.24	– -	0.72	– -
Atrazine	–-	0.15	–-	0.23
Propazine	–-	<.20	–-	<.20
Simazine	–-	0.6	–-	.46
Cyanazine	–-	<.40	–-	<.40

collected in glass containers. Subsamples were composited in plastic churns.

All water samples for herbicide analyses were filtered through a fiberglass membrane with 0.7 mm openings into amber glass bottles. The bottles were fired prior to use to remove organic residues. Sampling equipment was cleaned after each sample was collected by use of a Liquinox soap wash and several rinses with deionized water. Before a sample was collected, the equipment was rinsed with stream water to remove traces of the deionized water. Bottles containing water samples were kept chilled to 4° C and shipped chilled to the laboratories by overnight express delivery.

Triazine herbicide residue concentrations were measured by use of a triazine immunoassay technique (ELISA, or enzyme-linked immunosorbent assay) at the USGS Organic Geochemistry Research Laboratory (OGRL) in Lawrence, Kansas. Details of the analytical method and data for cross-reactivity of the immunoassay to triazine compounds other than atrazine are given in Pomes et al. (1991) and Thurman et al. (1990). The minimum reporting level, 0.1 µg/l as atrazine, is the smallest measured concentration of triazine herbicide residue that may be reliably reported using the immunoassay analytical method.

Triazine herbicide residue concentrations from the immunoassay were compared to concentrations of individual triazine compounds from gas chromatography/mass spectrometry (GC/MS) for five sites. Splits of water samples from sites 10, 20, and 32 were analyzed by GC/MS at the OGRL and at the USGS National Water-Quality Laboratory (NWQL) in Arvada, Colorado. Splits of water samples from sites 40 and 41 were analyzed by GC/MS at the Pennsylvania Department of Environmental Resources

Figure 3a. Concentration of triazine herbicides in water from streams representing four corn-growing areas of the lower Susquehanna River basin, Pennsylvania and Maryland.

Figure 3b. Load of triazine herbicides in water from streams representing four corn-growing areas of the lower Susquehanna River basin, Pennsylvania and Maryland.

Figure 3c. Yield of triazine herbicides in water from streams representing four corn-growing areas of the Lower Susquehanna River basin, Pennsylvania and Maryland.

(PaDER) Bureau of Laboratories in Harrisburg. The results, compared in table 3, show the concentrations from the immunoassay method to be 0.2 - 0.3 µg/l larger than the mean concentrations of atrazine determined by GC/MS at the two USGS laboratories. The concentrations from the immunoassay method were 0.1 - 0.5 µg/l larger than the concentrations of atrazine determined by GC/MS at the PaDER laboratories. Thus, the triazine herbicide residue concentrations determined by triazine immunoassay and reported in units of µg/l as atrazine in this paper may overestimate the concentration of atrazine in the water samples.

Table 4. Concentration of triazine herbicides and load and yield estimates for triazine herbicides at sites representing subbasins underlain by crystalline bedrock in the Piedmont physiographic province, in the lower Susquehanna River basin.

The concentrations from immunoassay can be interpreted as a sum of the concentrations of selected triazine residues that are reactive in the ELISA method. The GC/MS results for the other triazine compounds (table 3) indicate concentrations that, when summed, would approximate the immunoassay result only at East Mahantango Creek (site 20). The summation of concentrations of triazine compounds measured by GC/MS for the other two sites results in total concentrations larger than the immunoassay concentration results. Although inaccurate, the immunoassay results can be used as a good first approximation of triazine concentrations in these stream water samples.

Computation of Loads and Yields

The triazine herbicide concentrations and the instantaneous discharge measurements were used to compute triazine loads. The load was then divided by the drainage area of the subbasin to obtain the yield. These values are termed "instantaneous load" and "yield" because they are based on instantaneous discharge. Monthly mean discharge was used in separate computations of monthly mean load and yield for sites where the discharge records were available.

Occurrence and Yields of Triazine Herbicides in Susquehanna River and Tributaries

This section presents the results for the tributaries in subbasins representing the four subunits, followed by the results for the Susquehanna River and

Table 5. Concentration of triazine herbicides and load and yield estimates for triazine herbicides at a site representing a subbasin underlain by limestone bedrock in the Piedmont physiographic province, in the lower Susquehanna River basin.

Site Number	Site Name	Date	Time	Triazine Herbicide Concentration (µg / l)	Triazine Herbicide Load (lb / d)	Triazine Herbicide Yield [(lb / d)vlmi^2]
10	Mill Creek near Lyndon, Pa.	06-16-93	0840	0.53	0.1372	0.0025

Table 6. Concentration of triazine herbicides and load and yield estimates for triazine herbicides at sites representing subbasins underlain by sandstone and shale bedrock in the Appalachian Mountains section of the Ridge and Valley physiographic province, lower Susquehanna River basin.

major tributaries. Asubsequent discussion and summary of results integrates the two sets of results and presents an overall view of loads from tributaries and basin yields. The downstream change in triazine concentrations, loads, and yields in the Susquehanna River is documented and discussed. Needs for refinement of results and further study are presented.

Subbasins Representing Four Subunits of Physiography and Bedrock Lithology

Data from four subunits with accompanying tables are presented in this section. The corn factor defined earlier was used as a variable to facilitate comparisons of results among subunits. The relation of the corn factor to observed concentrations, loads, and yields from subbasins in four major subunits in the lower Susquehanna River basin is shown in figure 3. An expanded presentation, that includes an illustration of triazine mass transport, is given for the subunit representing sandstone and shale areas of the Ridge and Valley physiographic province.

Piedmont Physiographic Province Underlain by Crystalline Bedrock

Triazine concentrations in stream water for the nine agricultural subbasins underlain by crystalline bedrock ranged from 0.30 to 0.75 µg/l (figure 3, table 4). The mean and

Figure 4. Schematic of stream network, sampling site locations, and results of June 1993 synoptic survey of triazine herbicide occurrence and yield in the Mahantango and Lykens valleys of the ridge and Valley physiographic provine underlain by sandstone and shale bedrock, in the lower Susquehanna River basin.

median were 0.55 µg/l. The two highest triazine concentrations, 0.75 and 0.71 µg/l, were measured in water samples from South Branch Muddy Creek and Deer Creek, respectively. These adjacent basins are west of the Susquehanna River; Muddy Creek basin is in York County, Pennsylvania, and Deer Creek basin is in York County, Pa., and Baltimore County, Maryland. The lowest concentration of triazine herbicide, 0.30 µg/l, was measured in the West Branch Octoraro Creek. This site is in Lancaster County, east of the Susquehanna River. The concentrations of triazines at the remaining six sites were within 0.09 µg/l of each other.

The triazine loads for the nine crystalline subbasins ranged from 0.0120 to 0.5015 lb/d, representing the Little Conowingo Creek Basin and the Muddy Creek basin at Castle Fin, Pennsylvania., respectively. The highest triazine yields in the subunit, 0.0049 (lb/d)/mi^2), were in the adjacent South Branch Muddy Creek and Deer Creek basins. The triazine yields for these two sites were the second highest of all the sampling sites, draining areas of 28 mi^2 and 24 mi^2, respectively. The West Branch Octoraro Creek basin had the lowest yield, 0.0011 (lb/d)/mi^2. The mean triazine yield was 0.0030 (lb/d)/mi^2; the median yield was 0.0033 (lb/d)/mi^2.

Piedmont Physiographic Province Underlain by Limestone Bedrock

The site on Mill Creek drains an area of approximately 54 mi^2 in central Lancaster County. The concentration of triazines in stream water from this subbasin was 0.53 µg/l (table 5). The triazine herbicide load calculated for the Mill Creek site was 0.1372 lb/d, and the yield was determined to be 0.0025 (lb/d)/mi^2. Mill Creek is a tributary of the Conestoga River, one of the few major tributaries in the study area underlain almost entirely by limestone bedrock. The triazine herbicide concentration in water from the Conestoga River near its mouth was 0.72 µg/l, resulting in a load of 1.25 lb/d. The yield from Conestoga River is 0.0027 (lb/d)/mi^2, similar to the yield for the Mill Creek subbasin (figure 3). This tributary system is an example of a system where a concentration in water at a site in the upper reaches of the basin was smaller than concentrations at the mouth of the tributary. The converse will be described in the following section on sandstone and shale bedrock.

Table 7. Concentration of triazine herbicides and load and yield estimates for triazine herbicides at sites representing subbasins underlain by limestone bedrock, in the Great Valley section of the Ridge and Valley physiographic province, in the lower Susquehanna River Basin.

Ridge and Valley Physiographic Province Underlain by Sandstone and Shale Bedrock

A total of 18 sites were sampled. Triazines were detected in water from 16 of the 18 sites. Overall, the concentrations of triazines in stream water ranged from <0.1 to 1.05 µg/l, displaying the greatest variation within the study area (figure 3, table 6). The highest concentration of triazine herbicide for all the sites in this survey, 1.05 µg/l, was measured in the sample from Deep Creek at Pillow. Excluding the two nondetections, the lowest triazine herbicide concentration, 0.13 µg/l was measured in the sample from Pine Creek at Erdman. Triazine herbicides were not detected in water samples from Pine Creek near Spring Glen and the Wiconisco Creek. Each of these subbasins contains significant areas of forest. The determinable triazine loads for the sandstone and shale subbasins ranged from 0.0010 to 0.0639 lb/d. Because of the low loads, the determinable yields of triazine herbicide ranged from <0.0001 to 0.0011 (lb/d)/mi^2. The mean and median yields for the subbasins were 0.0004 (lb/d)/mi^2, representing the lowest mean triazine herbicide yield for the four different sets of subbasins.

The sandstone and shale subbasins of the Appalachian Mountains section can be divided into three major tributary basins and one minor tributary basin that contribute to the Susquehanna River: the Schwaben Creek basin, the Fidlers Run basin (minor tributary), the Wiconisco Creek basin, and the East Mahantango Creek basin. A simplified diagram of the stream network for the Mahantango valley area is given in figure 4.

The northernmost major tributary basin is the Schwaben Creek basin. As seen in the diagram, this basin does not flow directly into the Susquehanna River, but first enters Mahanoy Creek. Four sites within the Schwaben Creek basin were sampled; triazine herbicide concentrations ranged from 0.20 to 0.68 µg/l. The loads of triazines in stream water ranged from 0.0010 to 0.0142 lb/d. The triazine yields for three of the four sites were 0.0004 (lb/d)/mi^2; the yield for Schwaben Creek at Red Cross was 0.0006 (lb/d)/mi^2.

Fidlers Run is the minor tributary basin that drains directly into the Susquehanna River. The triazine herbicide concentration for this site was 0.29 µg/l. The load of triazines in stream water was determined to be

Table 8. Concentration of triazine herbicides and load and yield estimates for triazine herbicides at sites representing the Susquehanna River and selected major tributaries.

0.0042 lb/d. The triazine herbicide yield was 0.0006 (lb/d)/mi^2.

The Wiconisco Creek drains the southern part of the Lykens valley. Wiconisco Creek basin was represented by two sites, Little Wiconisco Creek and the Wiconisco Creek.Triazine herbicide concentrations displayed the greatest variation of any of the sandstone and shale subbasins. The triazine herbicide concentration forLittle Wiconisco Creek was the second highest in the study area, 1.04 µg/l; the triazine herbicide concentration in water from Wiconisco Creek was below the 0.1 µg/l minimum reporting level.

Tributaries of East Mahantango Creek drain the northern part of the Lykens valley, and flow into the Mahantango

Figure 5. Schematic of stream network, sampling site locations, and results of the June 1993 synoptic survey of triazine herbicide occurrence and yield, in the lower Susquehanna River and major tributaries, Pennsylvania and Maryland.

Valley through water gaps at Erdman and Pillow. In the East Mahantango Creek basin, triazines were detected from the headwaters to the mouth. In the Mahantango valley, concentrations increased in the headwaters part of the basin as streams captured more drainage from the watershed, reaching a maximum of 0.71 µg/l at Klingerstown. Concentrations in Mahantango Creek water downstream of Klingerstown were less than 0.3 µg/l, apparently because of dilution from Pine Creek (figure 4). For the tributaries draining from the Lykens valley into the East Mahantango Creek, the concentrations of triazines ranged from < 0.1 to 1.05 µg/l at Pine Creek near Spring Glen and the Deep Creek at Pillow, respectively. Deep Creek at Pillow also was the site with the highest detectable concentration of triazine herbicide in the entire study area. The discharge of Deep Creek at Pillow is too small to significantly affect the conditions in East Mahantango Creek. The load to the Susquehanna River from East Mahantango Creek is about 0.06 lb/d, resulting in a yield of 0.0004 (lb/d)/mi^2.

East Mahantango Creek is an example of a tributary system where a concentration in water at the mouth is smaller than the concentrations in the upper reaches of the drainage. This type of behavior may be characteristic of streams in the Ridge and Valley physiographic province, where stream hydrology and land use in tributary subbasins can vary in adjacent valleys. If land use and stream hydrology differ between valleys and the streams draining adjacent valleys merge through water gaps, irregular patterns of discharge and concentration will result. Moreover, from the data for the Mahantango valley area, mixing and dilution of waters are important factors controlling instream concentrations of triazine herbicides. Degradation of the triazine compounds in the stream environment may also be a factor contributing to changes in concentration.

Ridge and Valley Physiographic

Susquehanna River at Danville and the West Branch Susquehanna River at Lewisburg (table 8). These two sites are just above the northern boundary of the lower Susquehanna River basin and represent the two major inflows to the study area. Both sites represent drainage from areas of predominantly forested land. This indicates, for the period of sampling, the triazine herbicide concentrations of 0.1 µg/l or more in the river are not originating in the upper Susquehanna River basin. For the remaining sites on the Susquehanna River, triazine herbicide concentrations increased from 0.10 µg/l at Harrisburg to 0.24 µg/l at Marietta and to 0.29 µg/l at Conowingo Dam.

The load of triazines from the upper basin was estimated to be less than about 4.7 lb/d (table 8). The load of about 5 lb/d at Harrisburg increased to about 17 lb/d at Marietta. Tributary loading from Swatara Creek, one of four major tributaries between Harrisburg and Marietta, was determined to be about 0.6 lb/d. Three major tributaries between Harrisburg and Marietta—Yellow Breeches Creek, Conewago Creek, and Codorus Creek (figure 5)—

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This survey was only possible with contributions of ideas and hard work from many individuals. The original idea for the survey was proposed by USGS colleagues Robert Gilliom (Sacramento, California) and Michael Thurman (Lawrence, Kansas). Thurman’s laboratory also provided immunoassay analyses. Robert Hainly, USGS (Lemoyne, Pennsylvania), was instrumental in planning and implementing the sampling. Charles Takita, Susquehanna River Basin Commission, collected samples and provided analyses of pesticides for sites at Marietta and Conestoga. Marlin Paul, U.S. Department of Agriculture-ARS (Klingerstown, Pennsylvania), assisted with reconnaissance of sampling sites and obtaining permission to enter private property to access sites in the Mahantango valley.

were not sampled. Thus, the greater-than-threefold increase in triazine herbicide load can not be verified with a summation of tributary loadings. It seems unlikely that any one tributary load would exceed 2 lb/d on the basis of the loads in streams from the Great Valley (table 7). On the basis of a 2 lb/d load, the tributaries would only contribute 50% of the load increase between Harrisburg and Marietta. The triazine herbicide load at Conowingo Dam is anomalous (about 72 lb/d) when instantaneous discharge is used in the computation. At the time of sampling, the outflow discharge at Conowingo Dam was exceptionally high for hydropower production purposes. The monthly mean discharge for June 1993 (table 2), when substituted for instantaneous discharge, resulted in a load of about 21.7 lb/d leaving Conowingo Dam. The loads from Pequea Creek (0.26 lb/d), Muddy Creek (0.50 lb/d), and the Conestoga River (1.25 lb/d) account for the increase in load of triazine herbicides in the Susquehanna River between and Conowingo Dam.

The yields of triazines were calculated by use of both the instantaneous discharge measurements and the monthly mean discharges for June 1993. With the exception of the Conowingo Dam site, the difference between the two yield calculations for each site was within 0.0005 (lb/d)/mi^2 (table 8). Excluding the nondetections at the inflow sites, the yields using the monthly mean discharge ranged from 0.0003 to 0.0033 (lb/d)/mi^2, representing the Susquehanna River at Harrisburg and the Conestoga River, respectively. The Conestoga River and its Mill Creek tributary represent the highest yield for the major tributaries. The estimated load and yield of triazines leaving the Lower Susquehanna River basin at Conowingo Dam was 21.7 lb/d and 0.0008 (lb/d)/mi^2.

SUMMARY OF RESULTS

This study, conducted as part of the USGS's NWQA Program provided (1) information about occurrence and distribution of triazine herbicides in streams of the lower Susquehanna River basin in Pennsylvania and Maryland during base-flow conditions, (2) a preliminary comparison of watershed properties controlling distribution and yield, and (3) a preliminary mass budget for transport of triazine herbicides for base-flow conditions. Analyses by immunoassay of triazine herbicides in samples from 43 sites collected during 14-21 June 1993, indicate widespread occurrence in water at concentrations between 0.1 and 1.05 µg/l as atrazine. Triazine herbicide concentrations did not exceed the U.S. Environmental Protection Agency’s maximum contaminant level for drinking water of 3 and 4 µg/l for atrazine and simazine, respectively. Median concentrations of triazine herbicides ranged from 0.45 to 0.55 µg/l for subsets of samples representing the Ridge and Valley and Piedmont physiographic provinces in limestone and noncarbonate bedrock settings. Loads and yields of triazine herbicides are smaller for streams in the Ridge and Valley underlain by sandstone and shale bedrock than for streams in the Piedmont underlain by limestone or crystalline bedrock. A ranking on the basis of instantaneous load of the major tributaries sampled during this study of stream base flow is Conestoga River > Swatara Creek > Muddy Creek > Pequea Creek > East Mahantango Creek > West Branch Susquehanna River. A ranking on the basis of instantaneous yield is Muddy Creek > Conestoga River > Pequea Creek > Swatara Creek > East Mahantango Creek > West Branch Susquehanna River.

The smaller loads and yields calculated for streams draining the Ridge and Valley watersheds underlain by sandstone and shale are attributable to the low concentrations in water from streams draining of most the Lykens valley subbasins and much lower area-weighted discharge measured in all the streams in the Ridge and Val-

Toward a Sustainable Coastal Watershed:
The Chesapeake Experiment. Proceedings of a Conference
1-3 June 1994. Norfolk, VA
Chesapeake Research Consortium Publication No. 149

ESTIMATION OF TOXIC TRACE ELEMENT LOADS ON THE SUSQUEHANNA AND JAMES RIVERS AT THE FALL LINE, CHESAPEAKE BAY WATERSHED

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Abstract: Estimates were made of loads of toxic trace elements in the Susquehanna and James Rivers where they enter the Chesapeake Bay at the Fall Line. Water samples were collected by depth- and width-integrated sampling methods and analyzed for dissolved and tota-recoverable (acid-extractable) phases of the elements of interest. Ultra-clean collection and processing techniques and inductively coupled plasm-mass spectrometry were used to obtain accurate measures of the normally low trace element concentrations found in river water. Constituent loads were estimated by using of two models: (1) a log-linear regression model, which fits parameters for discharge and temporal variation, and (2) a simple integration model. Total-recoverable concentrations of the elements are positively correlated with the concentrations of suspended sediment, supporting the need for storm-based sampling and a regression-based model for load estimation. Concentrations of dissolved trace elements, however, are randomly distributed through the hydrograph, supporting random sampling and load estimation with the simple integration model.

The Susquehanna and James Rivers are major conduits of toxic trace elements to the Bay. Most of the trace element loads are contributed in the particulate phase; estimated loads of total-recoverable trace metals were two to ten times higher than loads in the dissolved phases in both rivers. In 1992, estimated loads of total-recoverable chromium, copper, lead, and zinc in the Susquehanna River, which contributes more than 50% of the fresh water to the Bay, were 56, 66, 47, and 401 metric tons per year, respectively. Estimated loads of trace elements in the James River, were generally 10% to 30% of the loads contributed by the Susquehanna River.

Toward a Sustainable Coastal Watershed:
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SETTLING RATES AND WATER COLUMN RESIDENCE TIMES OF PARTICLE-REACTIVE CONTAMINANTS IN THE CHESAPEAKE BAY

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Abstract: The cycling of hydrophobic organic contaminants (HOCs), including polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbon (PAHs), in the mesohaline Chesapeake Bay was measured by sediment trap deployments from 1990 to 1992. Particulate HOCs were transported in the water column of Chesapeake Bay by suspended organic matter and by resuspended sediments. HOC concentrations in settling solids were remarkably lower than those in suspended organic matter but higher than those in sediments. Using HOCs as tracers, we estimated that 90-100% of particles collected in bottom traps are resuspended sediments while about 50% of HOCs collected in the surface traps are from resuspension. Resuspension fluxes of HOCs measured 2 m above the Bay bottom, up to 5 $\mu g/m^2 \cdot day$ for total PCB and 27 $\mu g/m^2 \cdot day$ for fluoranthene, were 50 and 9 times higher than their settling fluxes from surface waters, respectively, indicating substantial water column recycling. Settling velocities of total PCB measured in surface waters averaged 0.56 ± 0.23 m/day. Transfer time of total PCB from surface to the Bay floor was about 8 hours, which was relatively longer than that of PAHs. However, over short time scales, HOC transport in Chesapeake Bay is controlled by sediment resuspension, which increases HOC residence times in the water column. The high correlation between particulate HOC concentrations and organic carbon contents found in the settling particles results from the partitioning of HOCs into the organic matrix of aquatic particles.

Toward a Sustainable Coastal Watershed:
The Chesapeake Experiment. Proceedings of a Conference
1-3 June 1994. Norfolk, VA
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A MICROCOSM STUDY OF INTERACTIONS BETWEEN SEDIMENT, WATER, AND BIOTA IN CHESAPEAKE BAY

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Abstract: A large-volume microcosm system was used to examine the fluxes of trace elements from Chesapeake Bay sediments, and their influence on the development of the phytoplankton and zooplankton communities. A closed loop, linked microcosm system was developed, where a 500-litter microcosm with sediment in the bottom was linked to a 500-litter water column microcosm by a pump system exchanging 25% of the water between tanks daily. Three sediment treatments were used: a control without sediment, sediment collected from Baltimore Harbor, and sediment collected from the mainstem Chesapeake Bay. Each treatment had replicate linked microcosms. Phytoplankton and zooplankton communities in the water column microcosms were sampled, as was the concentration of trace elements, for approximately one month.

Arsenic concentrations in the Baltimore Harbor and Chesapeake Bay sediment microcosms rose significantly from initial values (approximately 0.4 µg/l) to about 1.0 µg/l , then declined somewhat, while arsenic in the control microcosms declined throughout the later part of the experiment and almost disappeared. Copper concentrations began at approximately 1.0 µg/l and rose consistently in the Baltimore Harbor sediment microcosms, reaching nearly 4.0 µg/l. In the Chesapeake Bay sediment microcosms and control microcosms, copper remained approximately constant.

Phytoplankton and zooplankton communities did not appear to be significantly altered by the different sediment treatments, differences between the replicates of a treatment were approximately the same as differences among treatments, and the communities succession was similar among the treatments.

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ROLE OF BENTHIC COMMUNITIES IN ORGANIC CONTAMINANT TRANSPORT AND FATE: BIOTURBATION, BIOACCUMULATION, AND BIOTRANSFORMATION

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Abstract: We discuss results for a series of laboratory experiments that evaluate macrofaunal effects on the transport and fate of organic contaminant (polycyclic aromatic hydrocarbons, polychlorinated biphenyls) . Our major findings are (1) macrofauna enhance the loss of compounds from the sediment relative to defaunated controls(2) macrofauna effects are similar for all compounds, regardless of hydrophobicity, suggesting that physical transport mechanisms are important; (3) direct resuspension via feeding processes is a potentially important process regulating contaminant flux across the sediment/water interface (4) bioadvective processes are important for contaminant burial, and contaminants become highly concentrated in animal tubes and burrows (5) diffusive processes, as a function of bioirrigation and contaminant physical chemistry have some influence on the final fate of compounds in our systems (6) bioaccumulation is rapid for various organisms regardless of feeding behavior (e.g., surface and head-down deposit feeders, predators), indicating that uptake of contaminants from the dissolved phase may be important. Organic contaminant fate and transport pathways within benthic organisms are important in determining both the direct and indirect effects of organic pollutants on aquatic ecosystems, including trophic transfer of parent compounds and toxic metabolites. Implications for modeling organic contaminant transport and fate in estuarine and coastal systems are discussed.