Herbicide Concentrations in and Loads Transported by the Conestoga River and Pequea Creek, Lancaster County, Pennsylvania, 1992-95

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CONVERSION FACTORS AND ABBREVIATIONS

Multiply	By	To obtain
	Length	
foot (ft)	0.3048	meter
mile (mi)	1.609	kilometer
	Area	
square mile (mi^2)	2.590	square kilometer
acre	0.004047	square kilometer
	Discharge	
cubic foot per second (ft^3/s)	0.02832	cubic meter per second
	Mass	
pound (lb)	0.4536	kilogram
pound per acre (lb/acre)	112.1	kilogram per square kilometer
pound per square mile per year ($(lb/mi^2)/yr$)	0.1751	kilogram per square kilometer per year

Abbreviated water-quality units used in report:

micrograms per liter (μg/L)

micrometer (μm)

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ABSTRACT

Water samples were collected from four streams in Lancaster County from 1992 through 1995 and analyzed for selected herbicides. Samples were collected from the Little Conestoga Creek near Churchtown, Mill Creek (a tributary to the Conestoga River) at Elshelman Mill Road near Lyndon, the Conestoga River at Conestoga, and Pequea Creek at Martic Forge. Most samples were collected from stormflow that occurred during the growing season. Samples were analyzed for alachlor, aldrin, atrazine, chlordane, cyanazine, dieldrin, malathion, metolachlor, propazine, simazine, and toxaphene. Most samples had detectable concentrations of alachlor, atrazine, metolachlor, and simazine, and the loads of these constituents that were transported during each of the 4 years were computed.

Of the samples collected from each of the streams—Little Conestoga Creek, Mill Creek, Conestoga River, and Pequea Creek—10, 12, 15, and 18 percent, respectively, had atrazine concentrations greater than 3.0 micrograms per liter, the U.S. Environmental Protection Agency maximum contaminant level. Loads of atrazine, metolochlor, and simazine were greater than loads of any other herbicides. The largest loads were transported during 1994. Loads of atrazine transported by the four streams during periods of stormflow from May to September 1994 totaled 3.46, 28.3, 263, and 46.8 pounds, respectively. The total loads of atrazine transported by the four streams—Little Conestoga Creek, Mill Creek, Conestoga River, and Pequea Creek—during calendar year 1994 were 6.48, 54.1, 498, and 102 pounds, respectively. A little less than half the atrazine load transported by each stream—45, 39, 42, and 42 percent, respectively—was transported during storms that occurred from May through September.

Average annual yields of atrazine for the period 1992-95 were 0.59, 0.64, 0.68, and 0.51 pounds per square mile from the Little Conestoga Creek, Mill Creek, Conestoga River, and Pequea Creek, respectively. Average annual yields of simazine were 0.36, 1.2, 0.54, and 0.48 pounds per square mile, respectively, and average annual yields of metolachlor were 0.46, 0.49, 0.54, and 0.31 pounds per square mile, respectively. Less than 1 percent of both the atrazine and metolachlor that was applied to all basins was transported by streamflow.

INTRODUCTION

Concern about the influence of toxic chemicals in Chesapeake Bay ecosystems has focused interest on agrichemicals and the contribution of these compounds from predominantly agricultural areas. Lancaster County in southeastern Pennsylvania is a highly productive agricultural area whose waters drain into the Chesapeake Bay by way of the Susquehanna River. About two-thirds (631 mi^2) of the County is drained by two streams, the Conestoga River and Pequea Creek. Agricultural chemical-management initiatives have been proposed by the Pennsylvania Department of Agriculture (Bingaman and others, 1994) for selected drainage areas in the Conestoga River Basin and for most of Pequea Creek Basin, but only limited information is available on the occurrence and transport of agrichemicals from these areas. In response to the need for additional information, the U.S. Geological Survey (USGS), in cooperation with the Susquehanna River Basin Commission, investigated the occurrence of 11 agricultural herbicides in the Conestoga River Basin and the Pequea Creek Basin.

About 60 percent of both the Conestoga River Basin (Ott and others, 1991) and Pequea Creek Basin (Lietman and others, 1983) are used for agriculture. Corn is the major crop, and other important crops include alfalfa, soybeans, and tobacco. A survey of agricultural herbicide usage at 256 farms in the Pequea Creek Basin, Mill Creek Basin, and parts of the Conestoga River Basin reported the use of 69 different herbicide chemicals during the period 1989-91 (Bingaman and others, 1994). The herbicides metolachlor and atrazine accounted for 50 percent of the total amount (41,371 lb) of herbicide applied to 12,592 tillable acres over the 3-year period. Average application rates were 0.304 lb per tillable acre per year for metolachlor and 0.248 lb per tillable acre per year for atrazine.

Herbicide applications in agricultural areas in southeastern Pennsylvania generally are made only once a year, in early May at the start of the growing season. As a result, herbicide concentrations in streams are highest during periods of stormflow in May and June (Lietman and others, 1983). Herbicide concentrations in stormflows that occur during July, August, and September tend to decrease with time, either because of degradation of the herbicides from sunlight or their attachment to soil particles, from moderate levels in July to lowest levels in September. In general, concentrations measured in streamflow (base flow and stormflow) are lowest from October through April.

Purpose and Scope

This report presents summaries of observed concentrations of herbicides in streamflow and provides estimates of loads of selected herbicides transported by the Conestoga River and Pequea Creek in Lancaster County, Pa. The concentrations and loads data were evaluated to determine:

1. partitioning of herbicide transport between base flow and stormflow,

2. temporal variation in herbicide loads, and

3. percentage of applied herbicides that are transported in streamflow.

Annual and seasonal loads for five herbicides are estimated from 1992 to 1995 for four streams that drain predominantly agricultural areas.

Description of Study Area

The Conestoga River and Pequea Creek drain 631 mi^2 of Lancaster County in southeastern Pennsylvania (fig. 1). The two streams enter the Susquehanna River about 30 mi above the point where the Susquehanna River enters the Chesapeake Bay. Herbicide and streamflow data were collected from the Conestoga River just upstream of the Susquehanna River, from two tributaries to the Conestoga River (Little Conestoga Creek and Mill Creek), and from Pequea Creek just upstream of the Susquehanna River.

Water samples from Little Conestoga Creek were collected at a streamflow-gaging station near Churchtown (USGS number 01576085). The drainage area of the basin upstream from the station is 5.82 mi^2; about 50 percent of the basin is underlain by carbonate rock. Koerkle and others (1996) reported that 68 percent of the Little Conestoga Creek Basin was used for agriculture and that 50 percent of the agricultural land was in row crops. About 90 percent of the area in row crops was in corn. Other row crops in the basin were tobacco, soybeans, and vegetables. About 24 percent of the basin is forested and about 1 percent is urban. Farmsteads compose about 5 percent of the agricultural area in the basin.

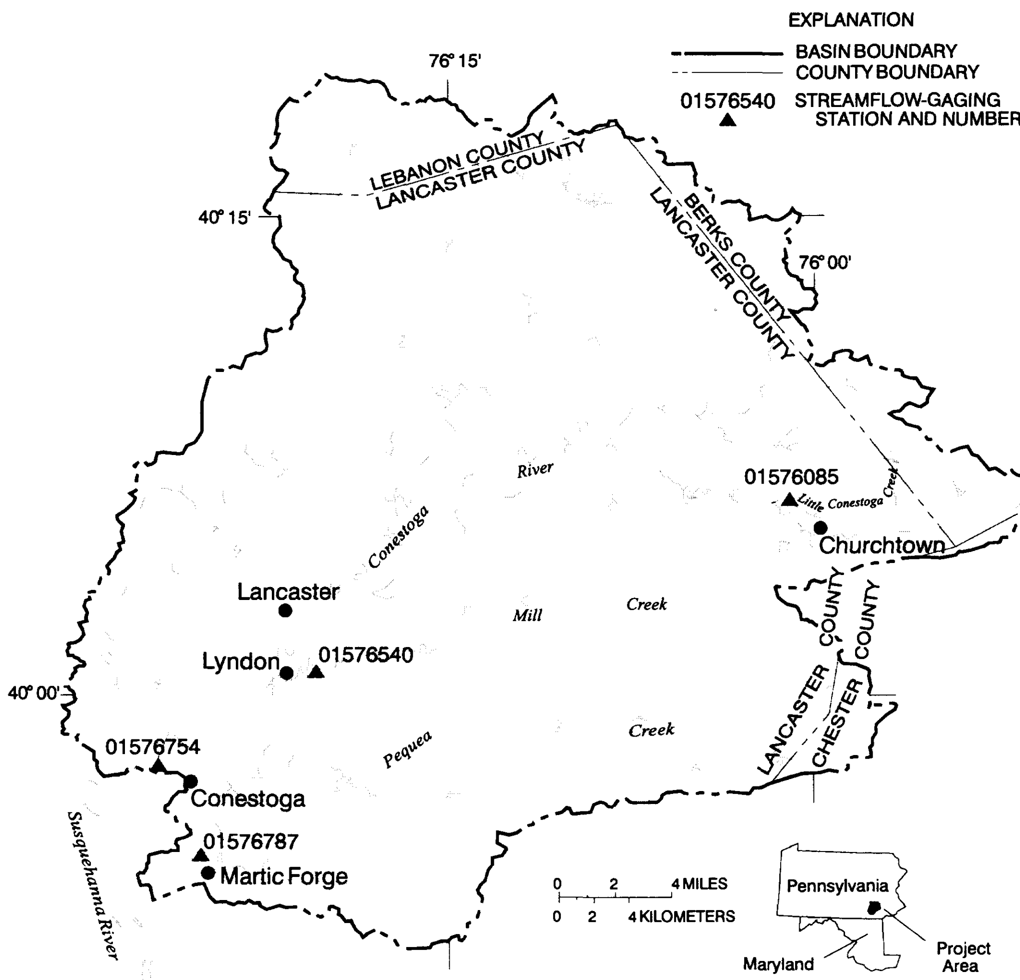

Figure 1. Location of data-collection sites in Lancaster County, Pennsylvania.

Mill Creek was sampled at a streamflow-gaging station at Eshelman Mill Road near Lyndon (USGS number 01576540), about 2 mi upstream of the Conestoga River. The drainage area of the basin upstream from the station is 54.2 mi^2. Ninety percent of the Mill Creek Basin is underlain by carbonate rock, and about 85 percent was in agricultural land use. Land area planted in row crops was not determined, but agricultural practices in the basin are similar to those in the Little Conestoga Creek Basin, where half of the agricultural land was in row crops. An estimated 42 percent of the Mill Creek Basin was planted in row crops in 1992, and about 90 percent of the area in row crops was planted in corn. About 9 percent of the Mill Creek Basin is forested, and about 6 percent is urban.

The Conestoga River was sampled at a streamflow-gaging station at Conestoga (USGS number 01576754), about 2 mi upstream of the confluence with the Susquehanna River. The drainage area of the basin upstream from the station is 470 mi^2, and about 59 percent of the basin is underlain by carbonate rock. Sixty percent of the Conestoga River Basin is in agriculture. An estimated 30 percent of the basin was in row crops in 1992, and about 93 percent of the area planted in row crops was planted in corn. The city of Lancaster is entirely within the basin, and the total urban area is about 15 percent of the basin (Langland and others, 1995). About 23 percent of the basin is forested; most of the forested area is along the northern edge of the basin.

Pequea Creek was sampled at a streamflow-gaging station at Martic Forge (USGS number 01576787), about 3 mi above the confluence with the Susquehanna River. The drainage area of the Pequea Creek Basin upstream from the station is 148 mi^2, and 63 percent of the basin is underlain by carbonate rock. Ward (1987) reported land-use data for the basin that was based on aerial photographs obtained twice in 1978 by the U.S. Environmental Protection Agency (USEPA) Photographic Interpretation Center. At that time, about 68 percent of the basin was in agriculture, 31 percent of the basin was in row crops, and 29 percent of the basin was planted in corn. Ward reported that about 20 percent of the basin was forested and that about 9 percent was urban. Since that time, some agricultural and forested areas have been converted to urban areas, especially in that part of the basin near the city of Lancaster.

Acknowledgments

Planning support for this project was provided by the Pennsylvania Department of Environmental Protection (PaDEP) and the USEPA. Data on herbicide application rates were provided by the Pennsylvania Department of Agriculture.

METHODS OF DATA COLLECTION AND ANALYSIS

The emphasis of this project was to determine loads of herbicides that are transported in streamflow. Most of the annual load of herbicides was thought to be transported during periods of stormflow that occur in the first 3 to 4 months after herbicide application in conjunction with spring planting. A storm was considered to occur if the stream stage increased at least 0.2 ft from the prevailing base-flow conditions. In general, about 10 storms can be expected to cause storm runoff in the study area during the period May through September of any given year. However, funding constraints did not permit sampling during all runoff periods.

A time-stratified sampling schedule was implemented because the total number of samples was limited. During the first 2 years of the project, stormflow samples (three samples per storm) were collected during four storms that occurred during the period May through July, one storm in September, and one storm in February. In addition, base-flow samples were collected once in each of the 5 months (May through September) during which stormflow sampling was scheduled. Data collected in the first 2 years indicated few detectable concentrations of herbicides in samples that were collected during storms in September and February. Therefore, to better define periods of detectable herbicide concentrations given the limited number of samples available, the sampling schedule was modified. Beginning in 1993, sampling of the stormflows that occur in February and September was discontinued, and the four stormflow samplings scheduled for May through July were changed to the first seven stormflow periods after the planting of corn.

Samples that were analyzed for alachlor, atrazine, cyanazine, metolachlor, and simazine were collected from Mill Creek at Eshelman Mill Road as part of the USGS Lower Susquehanna River National Water-Quality Assessment (NAWQA) project (Breen and others, 1991). The objective of the NAWQA project is to determine the quality of the stream over time and to relate the quality of the stream to the aquatic life in the stream.

Data-Collection Methods

All samples that were collected during the first 2 years (1992-93) of the study were collected by using manual depth-integrating techniques. Automatic water samplers that were modified for sampling of organic compounds were installed at the streamflow-gaging stations at Little Conestoga Creek near Churchtown, Mill Creek at Eshelman Mill Road, and Pequea Creek at Martic Forge before the 1994 growing season. Both automatic and depth-integrated samples were collected at these three sites during 1994 and 1995. All samples were collected in baked glass containers that were chilled to 4 °C and delivered within 24 hours to the PaDEP Bureau of Laboratories for analysis of the whole-water sample.

Samples for the NAWQA project were collected at a pre-established interval with a frequency of about two per month from March 1993 through September 1994. Most samples were collected during periods of base flow. Samples were filtered through a 0.7-µm filter, chilled to 4 °C, and shipped to the USGS National Water Quality Laboratory (NWQL) in Denver, Colo., for analysis.

Laboratory Methods

Whole water (unfiltered) samples were analyzed for alachlor, aldrin, atrazine, chlordane, cyanazine, dieldrin, malathion, metolachlor, propazine, simazine, and toxaphene at the PaDEP Bureau of Laboratories. USEPA Analytical Method 608 was used for most of the compounds, but a substitute detector (nitrogen-phosphorus detector (NPD) was used in place of an electron-capture detector (ECD)) when analyzing for the triazines (atrazine, propazine, simazine). Both ECD and NPD detectors were used (as a means of confirmation) for determining concentrations of alachlor, cyanazine, and metolachlor.

Clean sample (those with minimal interferences) reporting limits specified by the PaDEP Bureau of Laboratories at the start of the project are listed in table 1. Actual reporting limits for herbicide concentrations were considerably variable, particularly during the first year of the project. The primary reason for this variation was the presence of substantial amounts of sediment in the water samples. Changes in procedures during the course of the project reduced the sediment problem greatly. A secondary reason for variations in the reporting limits was a change in the analytical equipment used by the PaDEP Bureau of Laboratories.

Table 1. Analytical reporting limits for selected herbicides

[All reporting limits are in micrograms per liter; NA, not applicable]

Herbicide	Pennsylvania Department of Environmental Protection reporting limit	National Water Quality Laboratory reporting limit
Alachlor	0.08	0.009
Aldrin	.005	NA
Atrazine	.20	.10
Chlordane	.04	NA
Cyanazine	.40	.013
Dieldrin	.01	.02
Malathion	.1	.014
Metolachlor	.1	.009
Propazine	.2	.10
Simazine	.20	.10
Toxaphene	.4	NA

Filtered-water samples collected for the USGS NAWQA program were analyzed by using USGS Analytical Method O-1126-95 (Zaugg and others, 1995). Reporting limits for this method are listed in table 1. Filtering of the samples, which would remove herbicides that are bound with sediment or other particulate matter, could introduce bias, because the measured concentrations would be expected to be lower than those in the whole-water samples analyzed by PaDEP Bureau of Laboratories. Therefore, the NAWQA data presented in this report represent only base-flow conditions (minimal sediment) and the five herbicides—alachlor, atrazine, cyanazine, metolachlor, and simazine—that are predominantly found in the dissolved (filtered) fraction in water samples. These data probably have minimal bias relative to the whole-water sample determinations.

All herbicide concentrations for samples that were collected during periods of base flow were reviewed for quality assurance. On three occasions, separate samples were collected and analyzed by the NWQL and the PaDEP Laboratory. For the four samples that were analyzed by the NWQL, mean concentrations of alachlor, atrazine, cyanazine, metolachlor, and simazine were <0.009, 0.12, <0.013, 0.051, and 0.33 µg/L, respectively, and for the samples that were analyzed by the PaDEP Laboratory, mean concentrations were <0.08, <0.20, <0.40, 0.13, and 0.54 µg/L, respectively.

Quality-Assurance Procedures

Ascertaining the accuracy of the concentration of herbicides detected in water is regarded to be difficult even for samples in a "clean" matrix, such as drinking water. For example, USEPA Water Supply Study WS030 (D.J., Markovchick, U.S. Geological Survey, written commun., 1992) lists an order of magnitude range in the acceptable analytical results for known concentrations of atrazine and simazine in a clean water matrix. In a matrix of streamwater under stormflow conditions, judging the accuracy of these determinations becomes much more problematic. In an effort to better evaluate the quality of the analytical results, quality-assurance samples were submitted to the PaDEP Bureau of Laboratories and the USGS NWQL. For quality-assurance analyses that were completed at the NWQL, a customized analytical method was used. This method was developed to ensure compatibility with the modified USEPA Method 608 used by PaDEP Bureau of Laboratories.

Quality-assurance procedures for sample collection and analysis consisted of submitting blank, spike, and replicate samples. Blank samples were used to determine if contamination was occurring in any stage of the sample collection and pre-analysis procedures. Spike samples were used to ascertain analytical accuracy. Duplicate samples, field-split from the same aliquot, were used to compare analytical precision.

Blank samples were submitted frequently during the early stages of the project to ensure as quickly as possible that contamination of samples was not a problem. Blank samples were prepared from quality-assured organic-free water that was subject to all the same sampling, compositing, bottling, preservation, and handling procedures as the environmental (stream water) samples. Results of blank-sample analyses indicated no detectable contamination.

In an effort to evaluate interlaboratory precision, spike samples were submitted one time only to both the PaDEP Bureau of Laboratories and to the USGS NWQL. One streamwater sample that was collected in February to minimize the possibility of the sample containing environmental herbicides was split and spiked with atrazine, simazine, and propazine. All spiked samples were submitted in duplicate to both laboratories. Spike concentrations were 0 µg/L, 1 µg/L, and 9 µg/L. Results from PaDEP Bureau of Laboratories (table 2) showed the greatest deviation from the expected values and in duplicate analyses; results ranged from 10 percent below to 140 percent above the expected value and from 6 to 100 percent difference between duplicates. Results from the USGS NWQL showed substantially less deviation but a consistent low bias; results ranged from 30 to 53 percent below the expected value and from 0 to 10 percent difference between duplicates. Both laboratories reported all non-spiked sample analyses as below the reporting limit.

Table 2. Results of quality-assurance spike sample analysis

[µg/L, micrograms per liter; <, less than; PaDEP, Pennsylvania Department of Environmental Protection, Bureau of Laboratories; NWQL, U.S. Geological Survey, National Water-Quality Laboratory]

Compound	Laboratory	Concentration		
		No spike	1-µg/L spike	9-µg/L spike
Atrazine	PaDEP	<0.2	0.9	8.9
		<.2	1.9	8.4
	NWQL	.1	.6	6.0
		.1	.7	5.7
Simazine	PaDEP	<.2	1.4	17.7
		<.2	2.4	15.3
	NWQL	<.1	.6	4.2
		<.1	.6	4.7
Propazine	PaDEP	<.2	.9	8.9
		<.2	2.0	8.4
	NWQL	<.1	.7	5.9
		<.1	.8	5.6

Duplicate samples were submitted on a routine basis. Because of the large number of "less than reporting limit" results, the total number of valid duplicate analyses was 40 analyses divided unequally among 7 constituents. The Relative Percent Difference (RPD), a statistic that represents the difference between two measurements (X_1, X_2) relative to their average, was calculated for the duplicate samples. The RPD is calculated as follows:

$$\mathrm{RPD} = \frac{(2|X_2 - X_1|)}{(X_2 + X_1)} \times 100.$$

RPD's ranged from 0 to about 180 percent (fig. 2); the median RPD was 25 percent. Typically RPD's are greatest at the reporting limit and decrease as constituent concentrations increase. As a group, the RPD's for duplicate samples showed a maximum at concentrations about 10 times the reporting limit. This deviation in maximum RPD's from the reporting limit can be explained in part by the correlation of high concentrations with stormflow conditions. Stormflow samples commonly contain higher concentrations of both sediment and non-target constituents, which increase the likelihood of analytical interference. Analytical precision, and thus RPD, is more difficult to maintain for stormflow samples.

Uncertainty in the data increases with greater RPD's. When loads are calculated by using these data, the resulting uncertainty in the computed loads will consist of the uncertainty in the measured concentrations in combination with the proportion of flow during which a specific concentration occurred. As a result, loads for periods when concentrations are greatest, as in stormflow, will likely have greater uncertainty than those calculated for base-flow periods.

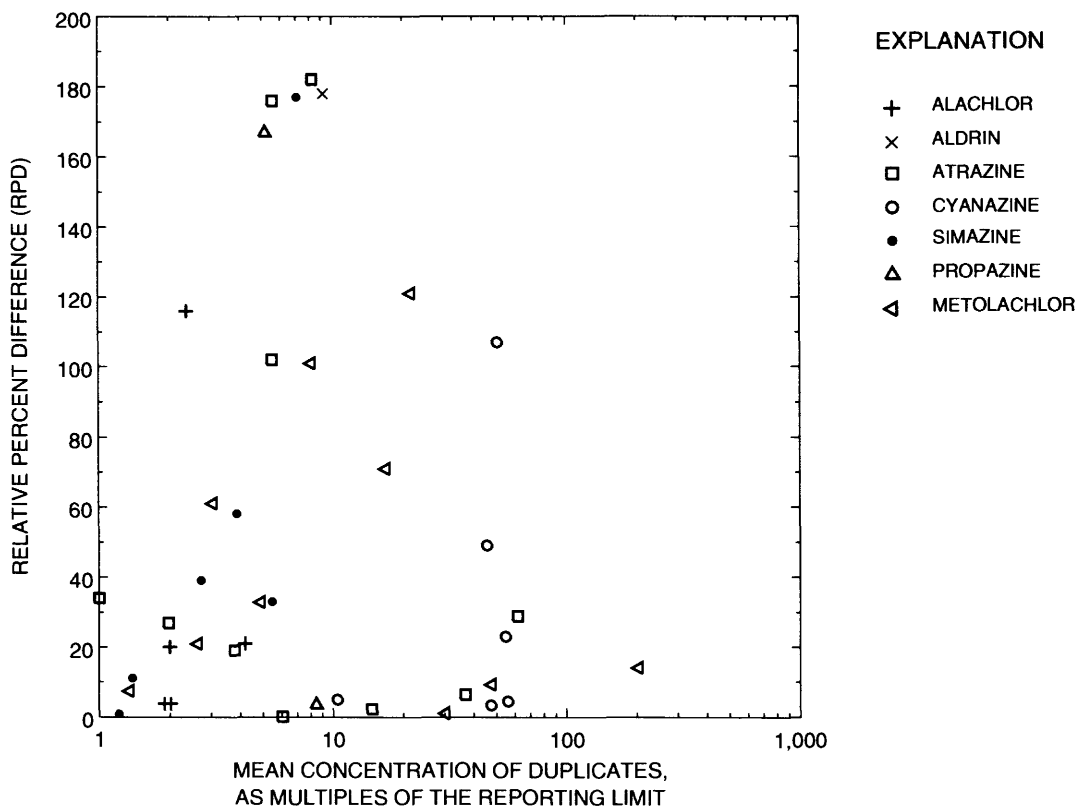

Figure 2. Relative Percent Difference of reported herbicide concentrations in field-split duplicate samples.

Computation of Loads

Herbicide loads transported by Mill Creek at Eshelman Mill Road (the site at which samples were collected for both this and the NAWQA project) were computed by use of four methods. Results of the calculations were reviewed, and the method thought to produce the most nearly correct results was used to compute loads from the other three sites. The four methods that were evaluated included (1) hydrograph subdivision (Porterfield, 1972), (2) use of the relation between instantaneous water discharge and constituent concentration to compute storm loads, (3) a computer method that uses the Minimum Variance Unbiased Estimator (MVUE) model (Cohn and others, 1989), and (4) a method involving a modification of the data input to the MVUE model.

The first method, hydrograph subdivision, can be used to compute loads if a streamflow hydrograph is available and if a concentration graph can be developed from constituent concentration data. Most constituent concentrations change rapidly during periods of stormflow, and several samples are needed to develop concentration hydrographs. The second method, the relation between instantaneous discharge and constituent concentration, can be used if the mean time-weighted concentration during a storm is similar to the mean water-weighted concentration. This is true only for streams that drain very large areas and in which rapid changes in water discharge do not occur. This method was not expected to produce satisfactory results because of the small drainage areas, the rapid changes in water discharge that occur during storms, and the limited availability of constituents (because of the application of herbicides only once a year, the degradation of herbicides in sunlight, and their attachment to soil particles). The third method, the MVUE model (Cohn and others, 1989), is based on the assumption that the supply of a constituent is relatively unlimited and that seasonal changes in constituent concentration can be approximated by use of sine and cosine mathematical functions. This method also was not expected to produce satisfactory results because most of the herbicides are applied only once, in May near the beginning of the growing season. This factor, along with herbicide loss due to leaching, degradation, and transport with earlier runoff, limited the availability of herbicides on the soil from October through April. The bulk of herbicide applications generally are made at the start of the growing season, and earlier studies (Lietman and others, 1983) have shown that herbicide concentrations in streams are highest during storms in May and June. The fourth method, a modification to the MVUE model, was evaluated because the herbicides for which data were collected are supply limited. This method was used to compute loads for the periods May through September, but satisfactory results were not expected because most samples had been collected during periods of stormflow and few samples had been collected during base-flow periods.

Computation of Loads By Using the Traditional Method of Hydrograph Subdivision

The traditional method of calculating loads using subdivision is described in *Computation of Fluvial-Sediment Discharge* by Porterfield (1972). Concentrations of atrazine measured in all but the samples collected during periods of stormflow during the growing season are plotted on figure 3 by months. All samples are plotted regardless of the year in which they were collected. Monthly mean concentrations are shown for the months of May through September, and the mean concentration is shown for the other 7 months. The maximum monthly mean concentration, 0.62 µg/L, was measured in samples collected during June, and the mean concentration for the months of October through April was 0.11 µg/L.

Concentration graphs were developed for each sampled storm by using the constituent-concentration data collected during the storm. An example of a concentration graph is shown on figure 4. The corresponding streamflow hydrograph also is shown. From figure 4, it can be seen that stormflow in Mill Creek began at 1800 on June 26 and ended at 2400 on June 27. During the period of stormflow, three samples were collected for analysis of herbicides—one at 2059 hours and another at 2245 hours on the 26th, and one at 0419 hours on the 27th. The concentrations of herbicides in streamflow on the 26th, prior to the start of stormflow, were assumed to equal June base-flow concentrations. Because of the extensive periods when constituent concentrations were estimated, the concentration curves should be considered only as "gross estimates" of the actual concentrations.

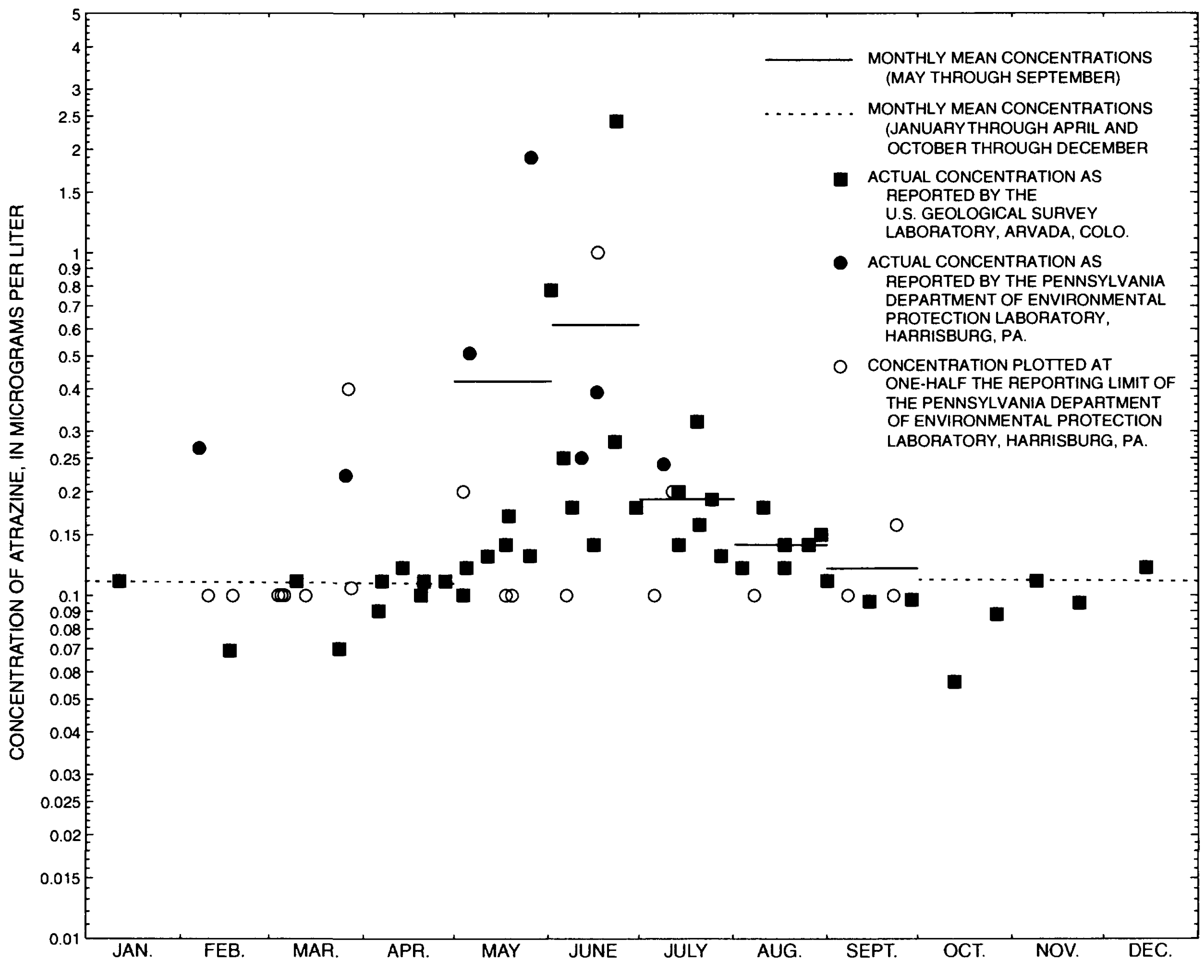

Figure 3. Atrazine concentrations in water samples collected from Mill Creek at Elshelman Mill Road near Lyndon, Pennsylvania, February 1992 through August 1995. Excluded are stormflow samples collected during the months of May through September, 1992 through 1995.

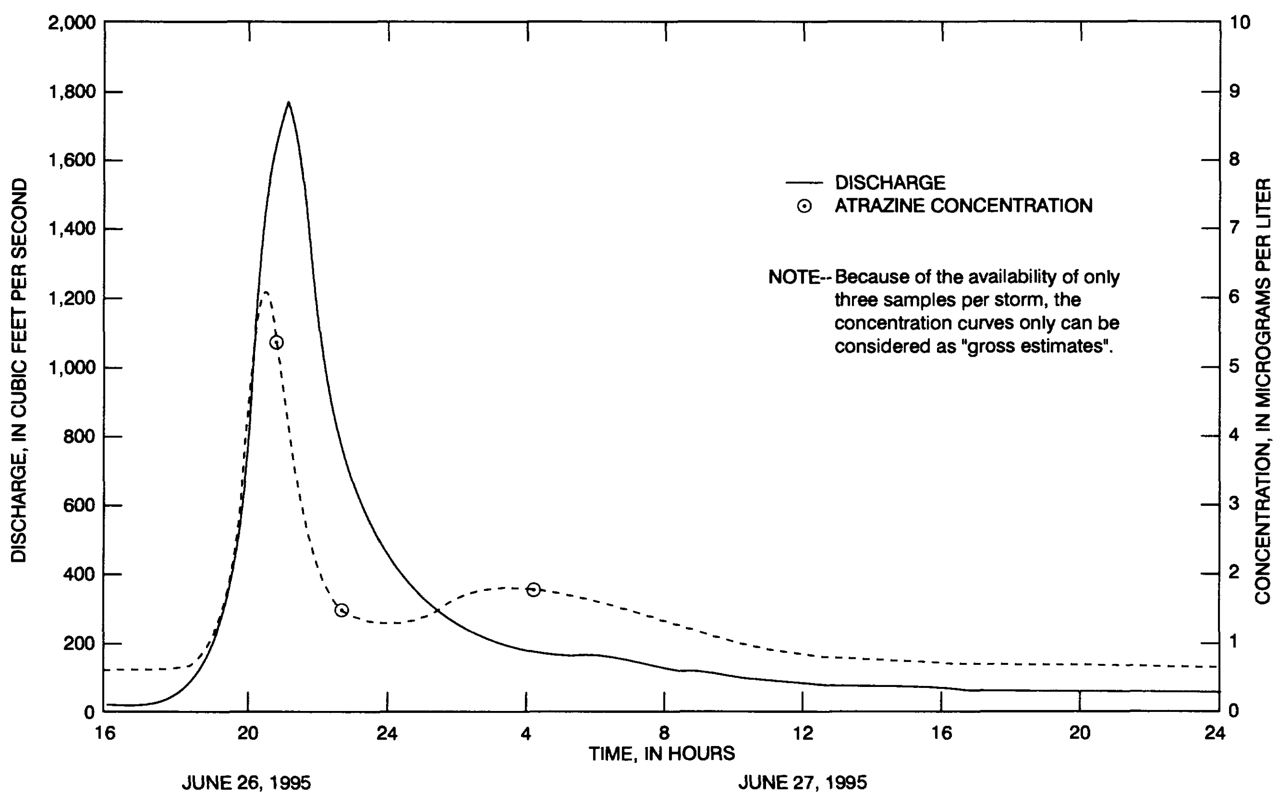

Figure 4. Discharge hydrograph and atrazine concentration graph, Mill Creek at Elshelman Mill Road near Lyndon, Pennsylvania, from June 26 at 1600 hours through June 27 at 2400 hours, 1995.

The concentration of atrazine during base flow (up to the start of storm runoff) was estimated to be 0.62 µg/L. Concentrations at the time of sample collection were 5.36 µg/L at 2059 hours on the 26th, 1.47 µg/L at 2245 hours on the 26th, and 1.74 µg/L at 0419 hours on the 27th. Six time periods were used to subdivide the streamflow and concentration hydrographs for the 2 days beginning with an 18-hour base-flow period, three 2-hour stormflow periods on the 26th, and an 8-hour period and a 16-hour period on the 27th. Results of the computations are listed on table 3.

Table 3. Results of the subdivision of the streamflow hydrograph and the atrazine concentration graph for the storm of June 26 and 27, 1995, Mill Creek at Elshelman Mill Road near Lyndon, Pennsylvania

Date	Time interval	Number of hours	Mean discharge, in cubic feet per second	Mean atrazine concentration, in micrograms per liter	Computed load[1], in pounds
6-26	0000-1800	18	36	0.62	0.09
6-26	1800-2000	2	250	1.3	.15
6-26	2000-2200	2	1,625	4.2	3.08
6-26	2200-2400	2	550	2.0	.49
Subtotal, June 26			229		3.81
6-27	0000-0800	8	200	1.6	.58
6-27	0800-2400	16	78	.75	.21
Subtotal, June 27			119		.79
June 26-27, 1995			174		4.60

[1] Computed load equals number of hours times mean discharge times mean concentration times 0.000225.

Errors associated with this technique involve those inherent in estimating the concentration graph (Porterfield, 1972) during periods when no sample data are available. Errors in the estimation of the concentration graph (fig. 4) can result in large overestimates or underestimates of loads. Similar subdivisions were used to compute loads of alachlor, metolachlor, and simazine. Load data for Mill Creek that were computed by the subdivision method for the years 1992 through 1995 are listed on table 4. Loads that were computed for nonstorm periods from May to September and for October through April also are listed on table 4. For Mill Creek, the percentage of storms with adequate samples for developing concentrations graphs and that occurred during the growing season ranged from 35 percent in 1992, when samples were collected manually, to 89 percent in 1995 when an automatic sampler was used. At Little Conestoga Creek, the range was from 31 to 48 percent of the storms; for the Conestoga River, the range was from 11 to 48 percent; and for Pequea Creek, the range was from 28 to 68 percent.

Computation of Loads By Using the Relation Between Water Discharge and Constituent Concentration

The relation between water discharge and constituent concentration, similar to the relation between water discharge and sediment load shown in Porterfield (1972, p. 56), can be used to estimate constituent loads if sufficient samples were not collected to construct concentration graphs. This technique is based on the assumption that the daily mean water-weighted concentration during a storm is similar to the daily mean time-weighted concentration, which is generally true only for large basins, and that a relation

Table 4. Loads of alachlor, atrazine, cyanazine, metolachlor, and simazine for Mill Creek at Elshelman Mill Road near Lyndon, Pennsylvania, 1992-95

[ft^3/s, cubic feet per second; $(lb/mi^2)/yr$, pounds per mile squared per year; --, no data]

Calendar year	Flow period	Streamflow, in ft^3/s-days	Loads, in pounds				
			Alachlor	Atrazine	Cyanazine	Metolachlor	Simazine
1992	Jan.-Apr. and Oct.-Dec.	10,007	0.36	5.90	--	2.65	6.81
	May-Sept. storms	1,476	.63	10.0	--	3.28	20.5
	May-Sept. nonstorms	4,211	.52	7.58	--	4.57	26.2
	Year	15,694	1.51	23.5	--	10.5	53.5
1993	Jan.-Apr. and Oct.-Dec.	21,838	.81	13.0	--	5.70	14.61
	May-Sept. storms	1,160	.22	3.28	--	2.94	3.28
	May-Sept. nonstorms	7,487	1.02	15.6	--	8.86	44.9
	Year	30,482	2.05	31.9	--	17.5	62.8
1994	Jan.-Apr. and Oct.-Dec.	26,334	1.02	15.6	--	6.90	19.5
	May-Sept. storms	4,614	3.99	28.3	18.0	43.5	33.4
	May-Sept. nonstorms	6,194	.83	10.2	--	7.30	37.1
	Year	37,142	5.84	54.1	--	57.7	90.0
1995	Jan.-Apr. and Oct.-Dec.	15,137	.48	8.86	--	4.01	9.18
	May-Sept. storms	1,836	1.67	12.3	--	12.3	17.0
	May-Sept. nonstorms	4,410	.60	7.34	--	5.24	26.2
	Year	21,383	2.75	28.5	--	21.6	52.4
1992-95	Total	104,701	12.2	138	--	107	259
1992-95	Yield, in $(lb/mi^2)/yr$		.056	.64	--	.49	1.2

between streamflow and the concentration of constituents can be developed. Because herbicide availability is limited, however, concentrations in stormflow change seasonally, and the relations between streamflow and herbicide concentration are difficult to define (fig. 5).

Computation of Loads By Using the Minimum Variance Unbiased Estimator

The MVUE method (Cohn and others, 1989) is based on the assumption that the supply of a constituent in the streamflow is unlimited, that seasonal changes in constituent concentration can be approximated by use of sine and cosine mathematical functions, that seasonal changes in constituent concentration occur gradually, and that the dataset is not biased. The MVUE model was used to compute loads for 1993 through 1995. Loads were not computed for 1992 because continuous streamflow data were not available for the entire year. Data from this project (mostly storm samples) and the NAWQA project (mostly base-flow samples) were used to compute the loads. Concentrations less than the reporting limit were entered as one-half the reporting limit. The large number of samples collected during storms that occurred during the growing season and the relatively small number collected during all other times tended to bias the data. The model assumes a linear transition in concentrations from one sample in the

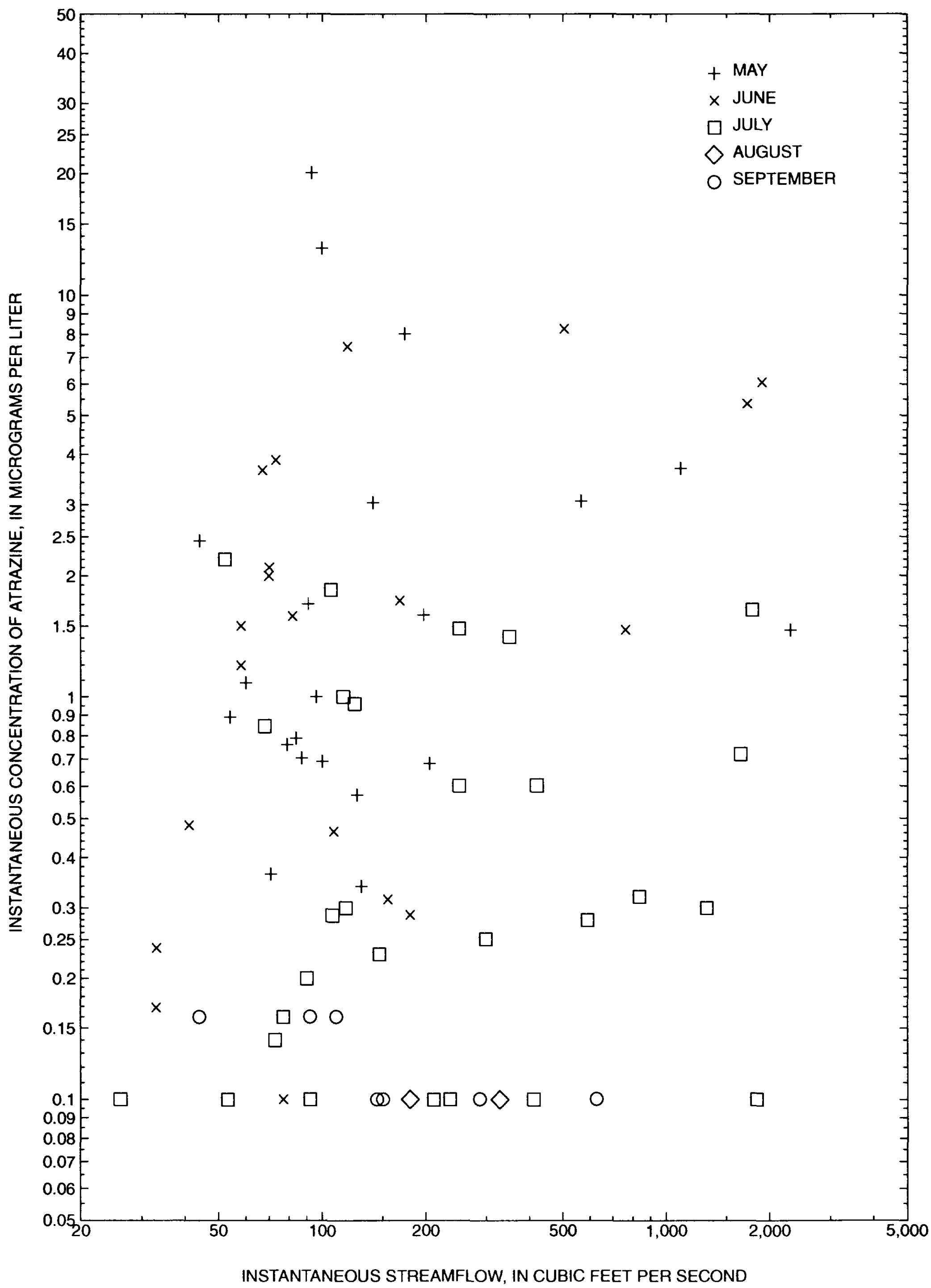

Figure 5. Relation between streamflow and atrazine concentration during periods of stormflow, May to September, 1992 through 1995, Mill Creek at Elshelman Mill Road near Lyndon, Pennsylvania.

dataset to the next. If two storms were sampled but the base-flow period between the storms was not sampled, the model assumes linear changes between the two sets of storm samples and overestimates concentrations for the base-flow period.

Computation of Loads By Using a Modification of the Data and the Unbiased Estimator

A modification of the concentration and streamflow data for use with the MVUE model was made because the herbicides are supply limited and major changes in concentrations occur seasonally. The modification was made to (1) restrict calculations only to the months of May through September, the months when detectable levels of herbicides are commonly observed, and (2) to smooth mathematically the large changes in the concentrations of herbicides observed between those in the stormflow prior to application of herbicides in the spring and the concentration in the first stormflow after application. Calculations were restricted to the May through September period by creating a new set of concentration and streamflow model input data.

Even with the modification, the large number of samples that were collected during storms relative to the small number of samples collected during non-storm periods tended to bias the data. As a result of the bias in the data, herbicide loads computed by the model were significantly greater than the loads computed by the standard method of subdivision.

Selection of Method

Hydrograph subdivision was selected as the best method of those evaluated, and it was used to compute loads at all four sites. The selection was based on a comparison of loads of atrazine transported by Mill Creek during the 1995 growing season when eight of the nine storms were sampled. The loads as calculated by the four methods—subdivision, the relation between concentration and streamflow, original data with the MVUE model, and modified data with the MVUE model—were 12.3, 16.5, 30.5, and 19.5 lb, respectively. Mean water-weighted atrazine concentrations obtained using the four methods of loads computations were 1.2, 1.7, 3.1, and 2.0 µg/L, respectively. Twenty-five samples were collected during eight of the nine storms that occurred during the 1995 growing season. The mean concentration of atrazine in the 25 samples was 1.1 µg/L, about the same as the mean water-weighted concentration obtained with the subdivision method of computing loads.

The overestimation of loads seen with three of the methods—the relation between concentration and streamflow, original data used with the MVUE model, and the modified data used with the MVUE model—is most likely a consequence of using a dataset that does not adequately represent those periods when very small to negligible concentrations of herbicides are normally found. The highest concentrations of herbicides are measured in stormflows during May and June, and many samples were collected during this period. Fewer samples were collected during periods when herbicide concentrations are low, October through April. A second cause of bias in the datasets was the lack of samples during base-flow periods between storms. Computations based on the relation between concentration and streamflow were biased because too few storm and base-flow samples were collected during October through April and too few base-flow samples were collected during May through September. Concentrations computed by the MVUE model were high because very few samples were collected to define the base-flow period when actual concentrations were low.

HERBICIDE CONCENTRATIONS AND LOADS

During the study, 147 samples were collected from Mill Creek; of which 100 were analyzed by the PaDEP Laboratory and 47 were analyzed by the USGS Laboratory. Of the 100 samples analyzed at the PaDEP Laboratory, the herbicides alachlor, atrazine, cyanazine, metolachlor, and simazine were present in concentrations less than the reporting limit in 65, 39, 67, 40, and 22 samples, respectively. Of the 47 samples analyzed at the USGS Laboratory, the herbicides alachlor, atrazine, cyanazine, metolachlor, and simazine were present in concentrations less than the reporting limit in 27, 0, 37, 0, and 0 samples, respectively. Concentrations less than the reporting limit were generally detected in most samples collected from August through April. Concentrations greater than the reporting limit were generally detected in most samples of storm runoff collected in May, June, and July. During the period of data collection, concentrations of atrazine in excess of 3.0 μg/L, the USEPA's maximum contaminant level, were detected in some of the samples collected at all four sites. Concentrations of atrazine greater than 3.0 μg/L were detected in 10 percent of the samples collected from Little Conestoga Creek, in 12 percent of the samples collected from Mill Creek, in 15 percent of the samples collected from the Conestoga River, and in 18 percent of the samples collected from Pequea Creek. Samples sent to the PaDEP Laboratory also were analyzed for aldrin, chlordane, dieldrin, malathion, propazine, and toxaphene, but only a few contained concentrations of those herbicides greater than the reporting limit and, thus, loads could not be computed.

Mean concentrations of alachlor, atrazine, cyanazine, metolachlor, and simazine in samples that were collected during periods of base flow from May through September and mean concentrations in all samples collected from October through April were calculated for all four sites. These mean concentrations were then used to compute loads for base-flow periods from May through September and for all flows from October through April. Because of the NAWQA project, much more data were available to calculate mean concentrations for Mill Creek. Mean concentrations of cyanazine could not be computed for any of the sites because a large number of samples at each site had cyanazine concentrations less than the reporting limit. Loads transported during storms that occurred from May through September were computed by using the subdivision method. Loads transported from Little Conestoga Creek, Conestoga River, and Pequea Creek for the years 1992-95 are listed on tables 5, 6, and 7. Storm loads of cyanazine were computed only for those years in which more than half of the samples that were collected had concentrations greater than the reporting limit.

For the four streams, the percentage of the load of herbicides that was transported during storms that occurred in the May through September period from 1992 to 1995 ranged from 54 to 75 percent for alachlor, from 39 to 45 percent for atrazine, from 49 to 62 percent for metolachlor, and from 14 to 29 percent for simazine (table 8).

Average yields for the 4-year period (1992-95), in pounds per square mile per year of alachlor, atrazine, metolachlor, and simazine, are listed on tables 4, 5, 6, and 7. Differences in average yields among the sites were generally small. Average yields of alachlor ranged from 0.056 (lb/mi^2)/yr for Mill Creek to 0.105 (lb/mi^2)/yr for the Conestoga River. Average yields of atrazine ranged from 0.51 (lb/mi^2)/yr for Pequea Creek to 0.68 (lb/mi^2)/yr for the Conestoga River; average yields of metolachlor ranged from 0.31 (lb/mi^2)/yr for Pequea Creek to 0.54 (lb/mi^2)/yr for the Conestoga River, and yields of simazine ranged from 0.36 (lb/mi^2)/yr for the Little Conestoga Creek to 1.2 (lb/mi^2)/yr for Mill Creek.

Table 5. Loads of alachlor, atrazine, cyanazine, metolachlor, and simazine, Little Conestoga Creek near Churchtown, Pennsylvania, 1992-95

[ft^3/s, cubic feet per second; $(lb/mi^2)/yr$, pounds per mile squared per year; --, no data]

Calendar year	Flow period	Streamflow, in ft^3/s-days	Loads, in pounds				
			Alachlor	Atrazine	Cyanazine	Metolachlor	Simazine
1992	Jan.-Apr. and Oct.-Dec.	1,132	0.04	0.67	--	0.30	0.67
	May-Sept. storms	139.9	.12	2.01	0.606	1.82	.29
	May-Sept. nonstorms	258.4	.03	.351	--	.30	.324
	Year	1,530	.19	3.03	--	2.42	1.28
1993	Jan.-Apr. and Oct.-Dec.	2,913	.12	1.72	--	.77	1.72
	May-Sept. storms	129.2	.04	.41	.189	.28	.14
	May-Sept. nonstorms	312.9	.04	.42	--	.37	.38
	Year	3,356	.20	2.56	--	1.42	2.24
1994	Jan.-Apr. and Oct.-Dec.	4,292	.20	2.50	--	1.12	2.50
	May-Sept. storms	433.8	.59	3.46	3.19	3.98	.60
	May-Sept. nonstorms	383.3	.05	.51	--	.48	.48
	Year	5,109	.84	6.48	--	5.56	3.58
1995	Jan.-Apr. and Oct.-Dec.	1,772	.06	1.05	--	.47	.85
	May-Sept. storms	97.9	.05	.34	.29	.58	.11
	May-Sept. nonstorms	181.8	.02	.25	--	.22	.23
	Year	2,052	.13	1.64	--	1.26	1.18
1992-95	Total load	12,052	1.36	13.7	--	10.7	8.28
1992-95	Yield, in $(lb/mi^2)/yr$		.058	.59	--	.46	.36

Table 6. Loads of alachlor, atrazine, cyanazine, metolachlor, and simazine, Conestoga River at Conestoga, Pennsylvania, 1992-95

[ft^3/s, cubic feet per second; $(lb/mi^2)/yr$, pounds per mile squared per year; --, no data]

Calendar year	Flow period	Streamflow, in ft^3/s-days	Loads, in pounds				
			Alachlor	Atrazine	Cyanazine	Metolachlor	Simazine
1992	Jan.-Apr. and Oct.-Dec.	101,304	3.41	60.2	--	26.8	60.2
	May-Sept. storms	21,097	20.0	98.9	--	136	41.2
	May-Sept. nonstorms	30,077	4.06	58.5	--	35.2	72.8
	Year	152,478	27.4	218	--	198	174
1993	Jan.-Apr. and Oct.-Dec.	254,005	10.1	150	--	67.2	150
	May-Sept. storms	19,510	8.42	38.2	--	30.9	23.1
	May-Sept. nonstorms	48,090	6.42	92.9	--	57.0	134.9
	Year	321,605	25.0	281	--	155	308
1994	Jan.-Apr. and Oct.-Dec.	234,706	9.65	140	--	62.1	140
	May-Sept. storms	42,707	90.1	263	254	262	64.0
	May-Sept. nonstorms	48,931	6.58	95.0	--	58.3	116.6
	Year	326,344	106	498	--	383	320
1995	Jan.-Apr. and Oct.-Dec.	148,906	4.70	88.0	--	39.3	88.0
	May-Sept. storms	23,435	30.1	130	110	198	52.8
	May-Sept. nonstorms	155,334	20.9	301	--	184	389
	Year	200,577	38.6	272	--	271	206
1992-95	Total load	1,001,004	197	1,270	--	1,010	1,010
1992-95	Yield, in $(lb/mi^2)/yr$		.10	.68	--	.54	.54

Table 7. Estimated concentrations and computed loads of alachlor, atrazine, cyanazine, metolachlor, and simazine for Pequea Creek at Martic Forge, Pennsylvania, 1992-95

[ft^3/s, cubic feet per second; $(lb/mi^2)/yr$, pounds per mile squared per year; --, no data]

Calendar year	Flow period	Streamflow, in ft^3/s-days	Loads, in pounds				
			Alachlor	Atrazine	Cyanazine	Metolachlor	Simazine
1992	Jan.-Apr. and Oct.-Dec.	31,908	1.07	19.0	--	8.36	19.0
	May-Sept. storms	6,644	2.42	36.0	--	21.4	24.9
	May-Sept. nonstorms	9,484	1.28	10.2	--	7.10	19.0
	Year	48,036	4.77	65.2	--	36.9	62.9
1993	Jan.-Apr. and Oct.-Dec.	59,718	2.29	35.3	--	15.8	35.3
	May-Sept. storms	5,447	3.91	16.0	--	12.8	7.10
	May-Sept. nonstorms	19,990	2.75	21.4	--	15.1	39.8
	Year	85,155	8.95	72.7	--	43.70	82.2
1994	Jan.-Apr. and Oct.-Dec.	60,884	2.41	36.5	--	16.0	36.5
	May-Sept. storms	7,670	9.55	46.8	28.9	40.56	12.9
	May-Sept. nonstorms	16,883	2.27	18.3	--	12.7	33.9
	Year	85,437	14.2	101.6	--	69.26	83.3
1995	Jan.-Apr. and Oct.-Dec.	39,644	1.22	23.6	--	10.5	23.6
	May-Sept. storms	3,362	3.27	30.2	14.8	15.38	8.98
	May-Sept. nonstorms	10,263	1.40	11.2	--	7.76	20.4
	Year	53,269	5.89	65.0	--	33.64	53.0
1992-95	Total load	271,897	33.8	304	--	183	281
1992-95	Yield, in $(lb/mi^2)/yr$		.057	.51	--	.31	.48

Table 8. Percentage of the annual load of alachlor, atrazine, metolachlor, and simazine transported by storms during the months of May through September, 1992 through 1995 in Little Conestoga Creek near Churchtown, Mill Creek at Elshelman Mill Road near Lyndon, Conestoga River at Conestoga, and Pequea Creek at Martic Forge, Pennsylvania

Site	Time period	Percentage of herbicide transported during May-September storms			
		Alachlor	Atrazine	Metolachlor	Simazine
Little Conestoga Creek	1992	64	66	75	22
	1993	20	16	20	6
	1994	70	53	72	17
	1995	38	21	46	9
Average	1992-95	59	45	62	14
Mill Creek	1992	42	43	31	38
	1993	11	10	17	5
	1994	68	52	75	37
	1995	61	43	57	32
Average	1992-95	54	39	58	29
Conestoga River	1992	73	45	69	24
	1993	34	14	20	7
	1994	85	53	68	20
	1995	78	48	73	26
Average	1992-95	75	42	62	18
Pequea Creek	1992	51	55	58	40
	1993	44	22	29	9
	1994	67	46	58	15
	1995	56	46	46	17
Average	1992-95	56	42	49	19

By use of land-use data and application rates of atrazine and metolachlor presented earlier, the 4-year application and transport (table 9) of alachlor, atrazine, metolachlor, and simazine were calculated. The measured transport of atrazine represents about 0.65 percent of the atrazine applied, and the measured transport of metolachlor represents about 0.40 percent of the metolachlor applied. The percentage of applied atrazine that was transported ranged from 0.47 percent in the Mill Creek Basin to 0.71 percent in the Conestoga River Basin. The percentage of applied metolachlor that was transported by streamflow ranged from 0.23 percent in Pequea Creek Basin to 0.46 percent in the Conestoga River Basin. Simazine use was reported for alfalfa and asparagus (Bingaman and others, 1994). The range in percentage of applied simazine that was transported, from 6.8 to 18.3 percent, suggests additional uses of this herbicide that were not included in the survey.

Table 9. Estimated total application and stream transport of alachlor, atrazine, metolachlor, and simazine during the 4-year period, 1992-95, for the Little Conestoga Creek, Mill Creek, Conestoga River, and Pequea Creek Basins, Lancaster County, Pennsylvania

Basin	Four-year application, in pounds				Four-year stream transport, in pounds				Percentage transported			
	Alachlor	Atrazine	Metolachlor	Simazine	Alachlor	Atrazine	Metolachlor	Simazine	Alachlor	Atrazine	Metolachlor	Simazine
Little Conestoga Creek	779	2,510	3,080	122	1.36	13.7	10.7	8.28	0.17	0.54	0.35	6.8
Mill Creek	9,080	29,300	35,900	1,420	12.2	138	107	259	.13	.47	.30	18
Conestoga River	55,500	179,000	219,000	8,660	197	1,270	1,010	1,010	.36	.71	.46	12
Pequea Creek	19,800	63,900	78,300	3,090	33.8	304	183	281	.17	.48	.23	9.1

SUMMARY AND CONCLUSIONS

Agricultural chemical-management initiatives have been proposed for the Conestoga headwaters and much of the Mill Creek and Pequea Creek Basins in Lancaster County, Pa., by the Pennsylvania Department of Agriculture, the Pennsylvania Department of Environmental Protection, the U.S. Department of Agriculture, and the U.S. Environmental Protection Agency. This report summarizes concentrations of herbicides observed in streamflow and presents estimated loads of selected herbicides transported by four streams in the basins—Little Conestoga Creek, Mill Creek, Conestoga River, and Pequea Creek—in Lancaster County, Pa.

Most agricultural herbicides are applied in agricultural areas only once a year at the start of the growing season, which begins in early May in southeastern Pennsylvania. Samples of storm runoff were collected from May through September of 1992 through 1995 from four stream sites in Lancaster County; those samples were analyzed for the herbicides alachlor, aldrin, atrazine, chlordane, cyanazine, dieldrin, malathion, metolachlor, propazine, simazine, and toxaphene. Most samples had measurable concentrations of alachlor, atrazine, cyanazine, metolachlor, and simazine. Atrazine concentrations greater than 3.0 μg/L were detected in 10, 12, 15, and 18 percent of the samples collected from Little Conestoga Creek, Mill Creek, Conestoga River, and Pequea Creek, respectively.

The hydrograph subdivision method was used to compute loads of alachlor, atrazine, cyanazine, metolachlor, and simazine for sampled storms (May through September). Loads that were transported during periods of base flow from May to September and loads transported during all flows from October through April were estimated from available concentration data. An attempt was made to compute loads by use of three additional methods—the relation between streamflow and constituent concentration, the Minimum Variance Unbiased Estimator (MVUE) model, and a modification of the data input to the MVUE model. All three methods were rejected because the limited availability of concentration data throughout the year appeared to introduce significant error and resulted in an overestimation of loads. Because the highest concentrations of herbicides occur in stormflows during May through September, most samples were collected during this period. Few samples were collected when concentrations of herbicides were low, during base-flow periods from May through September and the months from October through April. Loads computed on the basis of the relation between concentration and streamflow, as well as those computed by the MVUE model, were too high because the relation between concentration and streamflow was biased by the large number of samples with high concentrations.

Loads of atrazine, simazine, and metolachlor were greater than loads of any other herbicides. During the sampling period, the largest loads were transported during 1994. Loads of atrazine that were transported by the four streams—Little Conestoga Creek, Mill Creek, Conestoga River, and Pequea Creek—during 1994 totaled 6.48, 54.1, 498, and 102 lb, respectively; about one-half of the loads at all stream sites were transported during storms that occurred from May through September.

Annual yields of atrazine for the period 1992 through 1995 ranged from 0.51 $(lb/mi^2)/yr$ from the Pequea Creek Basin to 0.68 $(lb/mi^2)/yr$ from the Conestoga Creek Basin. Annual yields of simazine ranged from 0.36 $(lb/mi^2)/yr$ from the Little Conestoga Creek Basin to 1.2 $(lb/mi^2)/yr$ from the Mill Creek Basin, and average yields of metolachlor ranged from 0.31 $(lb/mi^2)/yr$ from the Pequea Creek Basin to 0.54 $(lb/mi^2)/yr$ from the Conestoga River Basin. The percentage of the 4-year (1992-95) atrazine load that was transported during stormflow in the May through September period from the four sites—the Little Conestoga Creek, Mill Creek, the Conestoga River, and Pequea Creek—was 45, 39, 42, and 42 percent, respectively. The percentage of applied atrazine and metolachlor that was transported by streamflow averaged 0.65 and 0.40 percent, respectively.

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