Concentrations and Transport of Atrazine in Surface Water of the Delaware River-Perry Lake System, Northeast Kansas, July 1992 Through September 1995

United States Geological Survey Water-Supply Paper 2489

Prepared in cooperation with the Kansas State Conservation Commission, Kansas State University, and the Kansas Department of Agriculture

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By LARRY M. POPE, LESLEY D. BREWER, GREG A. FOLEY, and SCOTT C. MORGAN

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CONVERSION FACTORS, ABBREVIATIONS, AND VERTICAL DATUM

Multiply	By	To obtain
acre	4,047	square meter
acre-foot (acre-ft)	1,233	cubic meter
cubic foot per second (ft^3/s)	0.02832	cubic meter per second
foot (ft)	0.3048	meter
inch (in.)	25.4	millimeter
mile (mi)	1.609	kilometer
pound (lb)	453.6	gram
pound per acre (lb/acre)	1.121	kilogram per hectare
pound per square mile (lb/mi^2)	175.1	gram per square kilometer
square mile (mi^2)	2.590	square kilometer

Temperature can be converted to degrees Celsius (°C) or degrees Fahrenheit (°F) by the equations:

$$°C = 5/9\ (°F - 32)$$
$$°F = 9/5\ (°C) + 32.$$

Sea level: In this report, "sea level" refers to the National Geodetic Vertical Datum of 1929—a geodetic datum derived from a general adjustment of the first-order level nets of the United States and Canada, formerly called Sea Level Datum of 1929.

Water year: A water year is a 12-month period, from October 1 through September 30, designated by the calendar year in which it ends. Years are water years in this report unless otherwise stated.

Crop year: A crop year, as used in this report, is a 12-month period from April 1 through March 31, designated by the calendar year in which it begins.

Concentrations and Transport of Atrazine in Surface Water of the Delaware River-Perry Lake System, Northeast Kansas, July 1992 Through September 1995

By Larry M. Pope, Lesley D. Brewer, Greg A. Foley, *and* Scott C. Morgan

Abstract

A study of the distribution and transport of atrazine in surface water in the 1,117 square-mile Delaware River Basin in northeast Kansas was conducted from July 1992 through September 1995. The purpose of this report is to present information to assess the present (1992–95) conditions and possible future changes in the distribution and magnitude of atrazine concentrations, loads, and yields spatially, temporally, and in relation to hydrologic conditions and land-use characteristics.

A network of 11 stream-monitoring and sample-collection sites was established within the basin. Stream-water samples were collected during a wide range of hydrologic conditions throughout the study. Nearly 5,000 samples were analyzed by enzyme-linked immunosorbent assay (ELISA) for triazine herbicide concentrations. Daily mean triazine herbicide concentrations were calculated for all sampling sites and subsequently used to estimate daily mean atrazine concentrations with a linear-regression relation between ELISA-derived triazine concentrations and atrazine concentrations determined by gas chromatography/mass spectrometry for 141 dual-analyzed surface-water samples.

During May, June, and July, time-weighted, daily mean atrazine concentrations in streams in the Delaware River Basin commonly exceeded the value of the 3.0-μg/L (micrograms per liter) annual mean Maximum Contaminant Level (MCL) established by the U.S. Environmental Protection Agency for drinking-water supplies. Time-weighted, daily mean concentrations equal to or greater than 20 μg/L were not uncommon. However, most time-weighted, daily mean concentrations were less than 1.0 μg/L from August through April.

The largest time-weighted, monthly mean atrazine concentrations occurred during May, June, and July. Most monthly mean concentrations between August and April were less than 0.50 μg/L. Large differences were documented in monthly mean concentrations within the basin. Sites receiving runoff from the northern and northeastern parts of the Delaware River Basin had the largest monthly and annual mean atrazine concentrations.

Time-weighted, annual mean atrazine concentrations did not exceed the MCL in water from any sampling site for either the 1993 or 1994 crop years (April–March); however, concentrations were larger during 1994 than during 1993. Time-weighted, annual mean concentrations in water from among the 11 sampling sites during the 1993 crop year ranged from 0.27 to 1.5 μg/L and from 0.36 to 2.8 μg/L during the 1994 crop year. Furthermore, concentrations in samples from the outflow of Perry Lake were larger during the first 6 months of the 1995 crop year than during the previous year.

Flow-weighted, annual mean atrazine concentrations were larger than time-weighted, annual mean concentrations in water from all sampling

sites upstream of Perry Lake, and samples from several sites had concentrations that were substantially larger than the MCL. This difference explained why time-weighted, annual mean concentrations in the outflow of Perry Lake were larger than corresponding time-weighted concentrations in water from sampling sites upstream of Perry Lake. Flow-weighted, annual mean concentrations in water from among the 11 sampling sites during the 1993 crop year ranged from 1.0 to 4.4 μg/L and from 1.0 to 8.9 μg/L during the 1994 crop year.

Statistically significant linear-regression equations were identified relating the percentage of subbasin in cropland to time- and flow-weighted, average annual mean atrazine concentrations. The relations indicate that time-weighted, average annual mean atrazine concentrations may not exceed the MCL in water from subbasins with at least about 70-percent cropland. However, flow-weighted, average annual mean atrazine concentrations may exceed the MCL when the percentage of cropland is greater than about 40 percent.

Approximately 90 percent of the annual atrazine load is transported from May through July. Atrazine loads and yields were larger during the 1993 crop year than during the 1994 crop year because of much greater runoff in 1993. Yields at sampling sites upstream of Perry Lake ranged from 2.4 to 17 lb/mi^2 (pounds per square mile) during the 1993 crop year and from 0.29 to 4.4 lb/mi^2 during the 1994 crop year. Loads and yields were largest at sampling sites receiving runoff from the northern and northeastern parts of the Delaware River Basin. A statistically significant linear-regression equation was identified relating percentage of subbasin in cropland to atrazine yields.

About 283,000 lb (pounds) of atrazine are applied each year in the Delaware River Basin. Annual atrazine loads (5,200 and 2,000 lb), yields (4.7 and 1.8 lb/mi^2), and transport ratios (1.8 and 0.7 percent) were estimated for the entire Delaware River Basin for the 1993 and 1994 crop years, respectively. Differences between the 1993 and 1994 crop years are the result of differences in rainfall amounds and subsequent runoff volumes.

INTRODUCTION

Crop yields have increased during the last 40 years due in part to the use of herbicides in reducing weed growth and competition for moisture and nutrients. However, concern on the part of water suppliers, health officials, and the public also has increased regarding the safe and effective use of herbicides.

Since about 1960, atrazine has been used as a pre- and post-emergent herbicide in the production of corn, grain sorghum, sugar cane, pineapple, and certain other plants and has become the most extensively applied herbicide in the United States (U.S. Environmental Protection Agency, 1989). Nonagricultural uses include nonselective weed control around commercial and industrial areas and along railroad rights-of-way. About 95 percent of the atrazine applied in the United States is used in corn and grain sorghum production (CIBA-GEIGY Corporation, 1992). Atrazine is the most consistently detected herbicide in Kansas surface-water samples. Eastern Kansas streams and lakes show the most consistent patterns of pesticide detection, which are probably related to land use and runoff conditions (Butler and Arruda, 1985).

The widespread use of atrazine may pose a potential threat to public-water supplies in areas where it is used intensively because of possible adverse effects on human health and potential toxicity to aquatic life (Hersh and Crumpton, 1987; Kettle and others, 1987; Stay and others, 1989). In 1992, the U.S. Environmental Protection Agency (1992) established an annual mean Maximum Contaminant Level (MCL) for atrazine of 3.0 μg/L (micrograms per liter) in finished drinking-water supplies.

Because of concerns that some surface-water supplies in northeast Kansas may exceed the MCL for atrazine, the Kansas State Board of Agriculture (currently the Kansas Department of Agriculture) conducted a series of hearings concerning the extent of atrazine contamination. As a result of these hearings, which indicated that long-term average concentrations of atrazine in Perry Lake (a Federal reservoir located at the downstream end of the Delaware River Basin, fig. 1) may exceed the 3.0-μg/L MCL, the Nation's first inland surface-water Pesticide Management Area (PMA) was established in the Delaware River Basin in

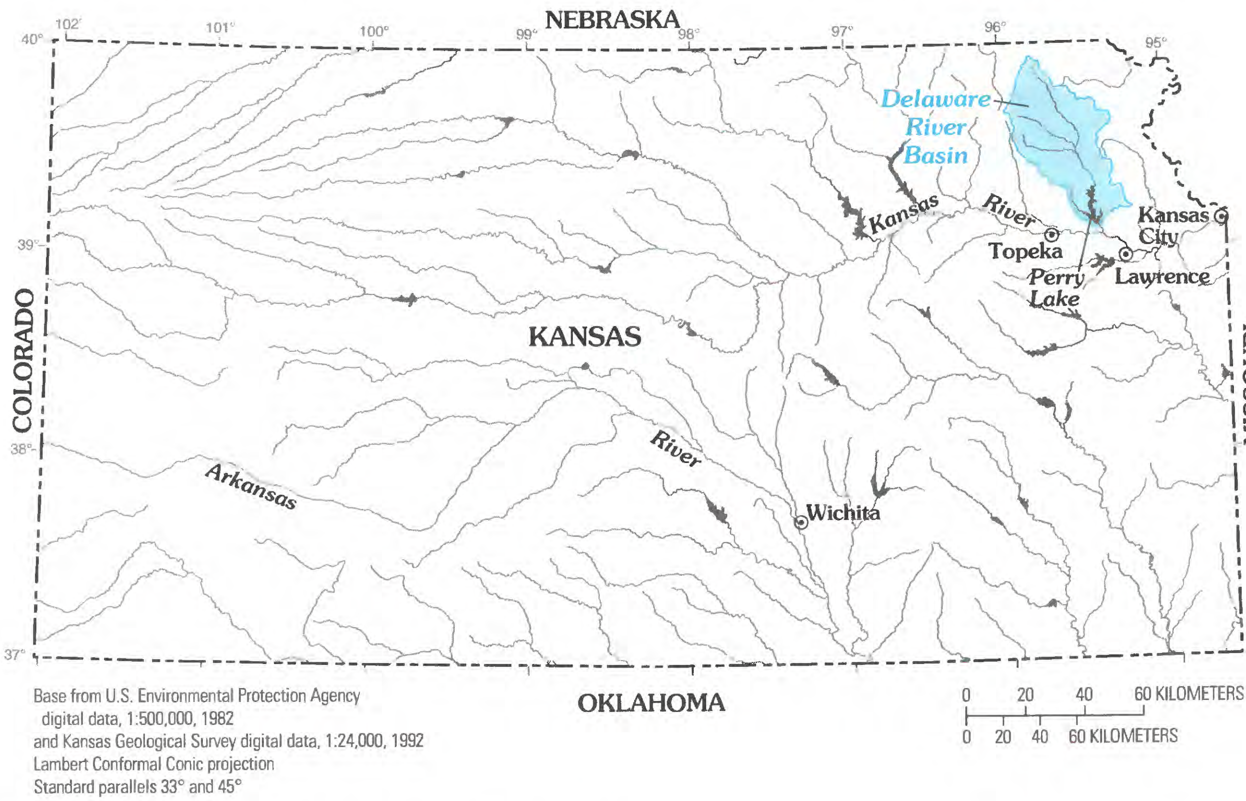


Figure 1. Location of Delaware River Basin in northeast Kansas.

April 1992 by the Kansas State Board of Agriculture. The goal of the PMA is to limit the input of atrazine into surface water in the Delaware River Basin. Components of the PMA included voluntary management and conservation practices, education, monitoring, research, enforcement, and evaluation.

Public-water supplies are withdrawn from Perry Lake and the Delaware River upstream of Perry Lake. Withdrawals from Perry Lake supply two rural-water districts and several Federal- and State-owned recreational areas. Water from Perry Lake receives no special treatment to remove atrazine from the finished water, and there is the potential for annual mean concentrations of atrazine in these public supplies to exceed the MCL (Stamer and Zelt, 1994). Additionally, discharge from Perry Lake enters the Kansas River, which serves as a supply source for the city of Lawrence and the Kansas City, Kansas, metropolitan area.

A study of the distribution and transport of atrazine in the 1,117-mi^2 Delaware River Basin in northeast Kansas was conducted by the U.S. Geological Survey (USGS) in cooperation with the Kansas State Conservation Commission, Kansas State University, and the Kansas Department of Agriculture from July 1992 through September 1995 as supported in part by the Kansas State Water Plan Fund. Data and results from this study will be used by State and Federal conservation, regulatory, research, and informational agencies to: (1) evaluate the perception of a long-term atrazine problem in the basin, (2) identify areas of the basin where additional educational activities may be required, (3) evaluate the effectiveness of selected land-management and agricultural practices, and (4) improve the understanding of herbicide transport in areas of similar agriculture and hydrology.

Purpose and Objectives

The purpose of this report is to present the information necessary to assess the present and possible future changes in the distribution and magnitude of atrazine concentrations, loads, and yields spatially, temporally, and in relation to hydrologic conditions and land-use characteristics. Specific objectives of this report are to: (1) present estimates of annual mean concentrations and loads of atrazine, (2) compare annual mean atrazine concentrations determined by this study with historical data and explain observed differences, (3) reduce the uncertainty of atrazine information by presenting the results of intensified spatial and temporal sampling, and (4) define relations between the occurrence of atrazine in surface water to natural and human factors.

Description of Study Area

Physiography and Topography

The Delaware Basin, shown in figure 1, is an 1,117-mi^2 area located entirely within northeast Kansas. The Delaware River Basin is in the Dissected Till Plains Section of the Central Lowlands physiographic province (Fenneman, 1946). The Dissected Till Plains Section is characterized by dissected deposits of glacial till that consist of silt, clay, sand, gravel, and boulders that overlie bedrock of primarily shale and limestone with some sandstone. Drainage channels are well entrenched by tributaries flowing south to the Kansas River. Maximum local relief is about 200 ft.

Generally, the Delaware River Basin can be divided into two main topographic areas, the lowlands and uplands. The lowlands occur along the streams. They vary in width from 0.25 to 0.75 mi and generally are level and fairly well drained. The uplands are subdivided into smooth to gently sloping areas, steeply sloping areas, and rough hilly areas. The smooth to gently sloping areas are on broad divides, generally at some distance from the larger streams. The steeply sloping areas are in the vicinity of the streams. The rough hilly areas are along the creeks (Eikleberry and Templin, 1960).

Surface-Water Hydrology

The Delaware River is a tributary of the Kansas River and on average contributes about 9 percent of the annual flow in the Kansas River downstream at DeSoto, Kansas (Geiger and others, 1994). A prominent hydrologic feature of the basin is Perry Lake, which is a Federal reservoir formed by the construction of a 7,750-ft-long rolled-earth-filled dam completed in 1969. The multipurpose pool has a surface area of 11,150 acres, with a storage of 209,500 acre-ft, at an elevation of 891.5 ft above sea level. The flood-control pool has a surface area of 25,300 acres, with a storage of 725,300 acre-ft, at an elevation of 920.6 ft above sea level.

Perry Lake provides flood protection on the Delaware River and is used in conjunction with other U.S. Army Corps of Engineer projects to provide flood control on the Kansas, Missouri, and Mississippi Rivers. The lake serves as a public water-supply source and provides recreational opportunities for fishing, skiing, swimming, and boating, while the surrounding public lands provide for camping, picnicking, hunting, hiking, and many other outdoor activities. Perry Lake also provides 150,000 acre-ft of storage for future water-supply needs.

Streamflow in the basin during the growing seasons (April through September) of 1993 and 1994 was a contrast of extremes as evidenced by percentage differences from long-term monthly mean streamflow rates at Delaware River near Muscotah, Kansas (fig. 2). In 1993, streamflow exceeded long-term means in April, May, and especially in July when streamflow was nearly 1,100 percent greater than the mean. In 1994, however, streamflow did not exceed the long-term mean in any month of the growing season and was considerably less than the mean in April, June, August, and September.

Land Use

Land use in the Delaware River Basin (fig. 3) is typical of the agricultural region of the Midwestern United States. Agriculture accounts for about 85 percent of the land use within the basin, with about 40 percent in crops such as corn, grain sorghum, soybeans, and wheat (Pope, 1995). The remaining agricultural land is devoted to pasture and rangeland. Nearly all cropland is nonirrigated. Only about 1.5 percent of the agricultural land in the basin is irrigated (U.S. Soil Conservation Service, 1987). The most intensely cultivated parts of the study area are the extreme northern and northeastern sections.

Climate

The climate of the study area is controlled by the movement of frontal air masses over the open inland-plains topography, and seasonal temperature and precipitation extremes are common. During the summer months, the weather is dominated by warm, moist air from the Gulf of Mexico or hot, dry air from the desert southwest, and temperatures near or above 100 ^{o}F can occur. Winter months are characterized by influxes of cold, dry polar air with temperatures as low as -20 ^{o}F. Mean annual precipitation is about 36 to 38 in., with more than 70 percent of this occurring during the growing season, April through September (Dickey and

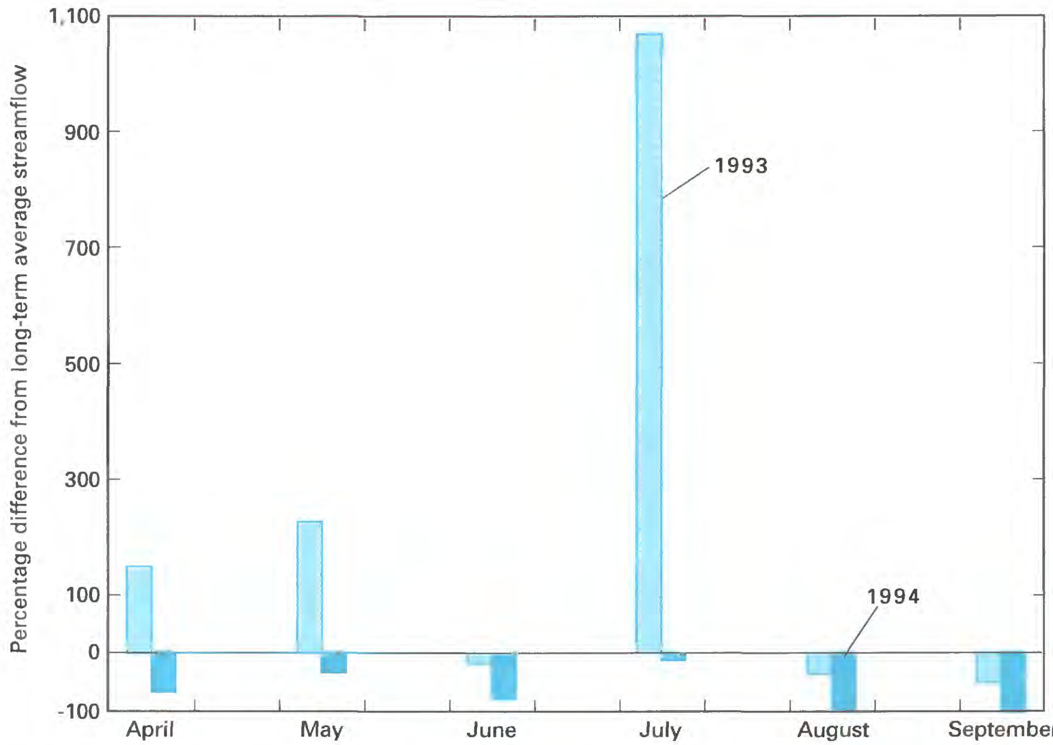


Figure 2. Percentage difference from long-term (1969–92) monthly mean streamflow of Delaware River near Muscotah, Kansas (sampling site 4, fig. 4), for April through September 1993 and 1994.

others, 1977). Mean annual runoff is about 8 in. (Stamer and others, 1994). The average annual snowfall for northeastern Kansas is about 20 in.

Precipitation during the early part of the spring and the latter part of the fall occurs in association with frontal air masses that produce low-intensity rainfall of regional coverage and relatively lengthy duration. Summer precipitation generally occurs as evening or early morning thundershowers of short duration that can produce large amounts of rain. In May and June, 3 to 5 in. of rain may fall in 24 hours (Eikleberry and Templin, 1960). This is the time when much of the cropland has been recently tilled and planted, which results in limited cover on the soil surface. The intense rains may produce a large volume of runoff and commonly cause floods and severe sheet and gully erosion.

The average date of the last frost in spring is about April 19. The latest frost recorded was on May 15. The average date of the first frost in autumn is about October 15. The earliest frost recorded was on September 17. The average growing season is about 179 days (Eikleberry and Templin, 1960).

Uses and Properties of Atrazine

The occurrence of atrazine in water in the Delaware River Basin originates as a result of its use in the production of corn and grain sorghum. Atrazine is the most extensively used herbicide in the basin for pre- and postemergent control of selected broadleaf weeds and annual grasses. Its effectiveness lies in its ability to inhibit the photosynthetic reaction and, thus, the cellular production of glucose and adenosine triphosphate, an energy source for other cellular chemical reactions (Kleiner and Orten, 1966).

Atrazine may be used alone, in tank mixes with other herbicides such as alachlor and metolachlor, or as part of a premix with acetochlor, alachlor, bentazon, bromoxynil, butylate, cyanazine, dicamba, dimethenamid, imazethapyr, or propachlor. Atrazine and its many combinations may be surface applied or incorporated into the soil profile as a preplant and(or) preemergent up to 45 days before planting or as postemergent weed control when mixed with crop-oil concentrate in water (Regehr and others, 1994).

Figure 3. Land use in the Delaware River Basin, 1992.

Atrazine (2-chloro-4-ethylamino-6-isopropylamine-s-triazine), one of the triazine herbicides, is a white, odorless, crystalline solid with a water solubility (at 22 °C) of 70 mg/L (milligrams per liter). Atrazine is relatively stable in the aquatic medium under environmental pH conditions, and degradation in soil is mainly by photolysis and microbial processes. The products of degradation are dealkylated metabolites, hydroxyatrazine, and nonextractable (bound) residues. Atrazine and the dealkylated metabolites are relatively mobile, whereas hydroxyatrazine is immobile (U.S. Environmental Protection Agency, 1989).

Previous Studies in the Delaware River Basin

In 1986, as part of its National Water-Quality Assessment (NAWQA) Program, the USGS began a study of surface-water quality in a 15,300-mi^2 area of the lower Kansas River Basin in southeastern Nebraska and northeastern Kansas. The Delaware River Basin is a subbasin of the lower Kansas River Basin.

From January 1989 through February 1990, water samples were collected at least monthly from the Delaware River near Muscotah, Kansas (sampling site 4, fig. 4), and the Delaware River below Perry Dam, Kansas (sampling site 11, fig. 4), as part of the lower Kansas River Basin NAWQA study. Atrazine concentrations from the Delaware River near Muscotah, Kansas, were smallest in January, March, and April before the spring 1989 herbicide application and largest in May, June, and July after application. The largest determined atrazine concentration was 22 µg/L in June 1989. The mean atrazine concentration for the 1989 calendar year, based on 16 samples, was 2.8 µg/L (Stamer and others, 1994).

In contrast to the unregulated upstream reach of the Delaware River, atrazine concentrations in water samples collected from the Delaware River at the outflow of Perry Lake showed little or no seasonal variability. Concentrations of atrazine gradually decreased from 5.0 µg/L in January 1989 to 1.7 µg/L in February 1990. The mean atrazine concentration for the 1989 calendar year was 3.5 µg/L, based on 13 samples (Stamer and others, 1994).

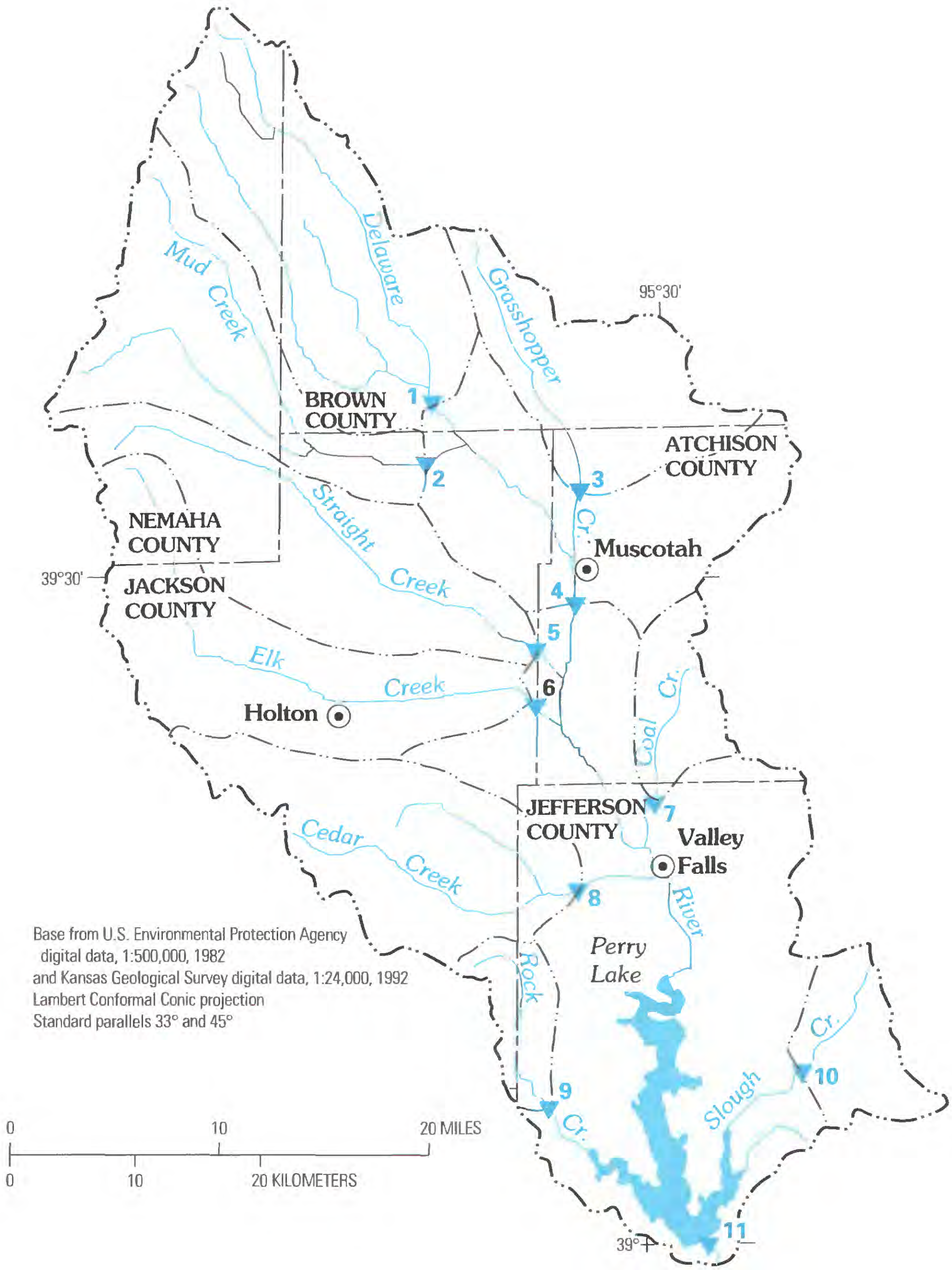
The USGS through its Toxic Substances Hydrology Program began a series of regional studies in a 10-state Midwest area in 1989 to address the issue of contamination of surface water by agricultural chemicals. The Delaware River Basin was included in these studies. Only three samples were collected from the Delaware River near Muscotah, Kansas (sampling site 4, fig. 4), during 1989. These were too few samples to draw specific conclusions about any one site or basin, but when all 149 stream sites in the Midwest area were evaluated, some generalized conclusions were reached. First, the herbicides detected most frequently and in the largest concentrations were atrazine, alachlor, cyanazine, and metolachlor. Second, herbicide concentrations during the postapplication period generally were one or two orders of magnitude larger than those measured before application and in the fall during low streamflow. Third, atrazine is the most persistent of the major herbicides in surface water of the Midwest (Goolsby and others, 1990).

Between April and June 1990, 32 samples were collected from Delaware River near Muscotah, Kansas (sampling site 4, fig. 4), as a continuation of the regional study begun by Goolsby and others (1990). Two of these 32 samples were collected in April, 18 in May, and 12 in June (Scribner and others, 1994). The mean concentrations of atrazine for these monthly sample groups were 0.32, 6.7, and 13 µg/L, respectively. The mean atrazine concentration of all 32 samples was 8.9 µg/L. Most of these samples were collected during storm runoff and at a time of the year when the largest concentrations would be expected.

DATA-COLLECTION AND ANALYSIS METHODS

Data-collection methods for this study were designed to provide a base of information adequate to calculate daily mean streamflow rates and daily mean triazine herbicide concentrations. These data in turn would be used to estimate monthly and annual mean concentrations and loads of atrazine, to determine loading rates for each of the subbasins within the Delaware River Basin, and to determine the relations between these characteristics and possible causal factors such as percentage of basin in cropland.

A network of 11 streamflow-monitoring and sampling sites was established in the Delaware River Basin in July 1992. The sites were geographically distributed to acquire information on most of the major subbasins within the Delaware River Basin. Sampling-site names and locations are given in table 1, and the corresponding map locations are shown in figure 4.



EXPLANATION

Boundary of Delaware River Basin

Subbasin boundary

9 **Sampling site**—Number corresponds to map-index number used in tables

Figure 4. Location of sampling sites in the Delaware River Basin.

Streamflow

Stream-stage records at the 10 stream sites upstream of Perry Lake (fig. 4) were collected with either a manometer, bubble-gage sensor system (sampling sites 1, 3, 4, and 10) or a stilling-well and float (sampling sites 2, 5, 6, 7, 8, and 9) combination (Buchanan and Somers, 1978). Stream stage was recorded in 15-minute increments and was related to periodic current-meter streamflow measurements (Buchanan and Somers, 1976) to develop and adjust stage-streamflow ratings (Kennedy, 1983) for each sampling site. Streamflow at sampling site 11 (Delaware River below Perry Dam, Kansas) was calculated on the basis of a relation between service-gate openings at Perry Dam and Perry Lake water-surface elevation.

A continuous record of stream stage was obtained at the manometer-equipped sampling sites. During winter and periods of extreme low flow, the stage-sensing float at the stilling-well sites may have been frozen in ice or out of water. Daily mean streamflow for these periods was estimated on the basis of hydrologic comparisons with nearby continuous-record sites, periodic streamflow measurements, and weather records. Daily mean streamflow for all sampling sites is presented in Pope and others (1996, tables 14–24).

Sample Collection

Samples for determination of triazine herbicide concentrations were collected either automatically using ISCO Model 3700 samplers capable of collecting 1 to 24 discrete 350-milliliter samples or manually

Table 1. Description of sampling-site locations and drainage areas in the Delaware River Basin

Map-index number (fig. 4)	U.S. Geological Survey site identification number	Site name	County	Drainage area (square miles)
1	06889990	Delaware River near Horton, Kansas	Brown	143
2	06889992	Mud Creek near Horton, Kansas	Jackson	99.0
3	06890092	Grasshopper Creek near Muscotah, Kansas	Atchison	93.3
4	06890100	Delaware River near Muscotah, Kansas	Atchison	431
5	06890350	Straight Creek near Muscotah, Kansas	Atchison	124
6	06890380	Elk Creek near Larkinburg, Kansas	Atchison	139
7	06890450	Coal Creek west of Coal Creek Church, Kansas	Jefferson	27.0
8	06890490	Cedar Creek west of Valley Falls, Kansas	Jefferson	68.1
9	06890595	Rock Creek northeast of Meriden, Kansas	Jefferson	21.7
10	06890810	Slough Creek west of Oskaloosa, Kansas	Jefferson	37.0
11	06890900	Delaware River below Perry Dam, Kansas	Jefferson	1,117

by dipping a sample bottle near the centroid of flow. Automatic samplers were installed at sampling sites 1–10. Sampling site 11 was sampled manually. Automatically collected samples generally were removed from the samplers within 24 hours of collection. The samples were subsequently transported to the USGS laboratory in Lawrence, Kansas, and refrigerated until analyzed.

Triazine concentrations may vary considerably during periods of runoff when fluctuations in concentrations of two orders of magnitudes are common. To define this variability, several samples per day generally were collected during periods of runoff. Samples were collected automatically during these periods at 3- to 8-hour intervals depending on the size of the sampling-site drainage basin, season, and anticipated storm characteristics. Samples were collected manually during periods of low or stable flow, during winter, prior to anticipated rainfall, and at other times when the automatic samplers were not operational. Samples were collected July 1992 through March 1995 at sampling sites 2, 8, 9, and 10 and July 1992 through September 1995 at sampling sites 1, 3, 4, 5, 6, 7, and 11 (fig. 4).

Sample Analysis

Procedures

All samples selected for determination of atrazine concentrations were analyzed by enzyme-linked immunosorbent assay (ELISA). ELISA systems have been used previously in detecting herbicides in surface water (Goolsby and others,1990; Thurman and others, 1990, 1991, 1992; Scribner and others, 1994). The ELISA system chosen for this study was the Atrazine RaPID Assay test developed and manufactured by Ohmicron (Newtown, Pennsylvania). This ELISA is based on combining selective antibodies attached to solid supports, with sensitive enzyme reaction, to produce analytical systems capable of detecting very low levels of chemicals (Baum, 1991). The immunochemical reaction contributes high selectivity due to extraordinary discriminatory capability of the antibodies and high sensitivity because of the powerful catalytic ability of enzymes. The selected analytical system is based on the use of magnetic particles as the solid support and means of separation. Because the particles are dispersed evenly throughout the reaction mixture, they allow rapid reaction kinetics, provide for precise addition of antibody, and facilitate ease of use.

Although ELISA methods are sensitive to the presence of atrazine (0.04-μg/L detection level), the methods are not totally specific to atrazine; other triazine compounds such as ametryn, prometon, prometryn, propazine, and possibly the degradation products of atrazine can be detected (Thurman and others, 1990). Therefore, results of these methods are reported as concentrations of triazine herbicides even though only small concentrations, if any, of these other triazine compounds are detected by gas chromatography/mass spectrometry (GC/MS) procedures. GC/MS also was used to analyze selected samples, as discussed later in this report.

During the immunoassay test (fig. 5), 200 μL (microliters) of each settled water sample was transferred to disposable polystyrene test tubes. Atrazine enzyme conjugate (horseradish peroxidase), 250 μL, was added along with 500 μL of atrazine antibody-coupled paramagnetic particles (rabbit anti-atrazine covalently bound to paramagnetic particles). The test tubes were vortexed for 2 seconds. After 15 minutes, a magnetic-separation rack was used to separate the magnetic particles. After 2 minutes, the tubes were rinsed with distilled water and blotted twice and the magnetic-separation rack removed. Color solution (hydrogen peroxide and 3,3',5,5'-tetramethylbenzidine) was added and vortexed for 2 seconds. After 20 minutes, the color was fixed by adding a solution of 0.5-percent sulfuric acid. The percentage absorbance was read at 450 nanometers on a photometer.

Quality Assurance

Analytical quality assurance consisted of duplicate analyses of selected stream samples, analysis of atrazine standard-reference samples, and analysis of blank-water samples. Precision and reproducibility of the ELISA were evaluated by duplicate analyses on randomly selected stream samples. An analytical method with a high degree of precision generally produces similar results on duplicate samples. Table 2 summarizes the results of 294 duplicate analyses. The mean concentrations of duplicate groups A and B are essentially the same, the variances are similar, and the correlation coefficient between the two groups is 0.997. The correlation coefficient, an expression of the degree of the linear relation, ranges from -1.0 to 1.0. If all data points plot on a straight line and the relation is inverse or direct, the correlation coefficient will be

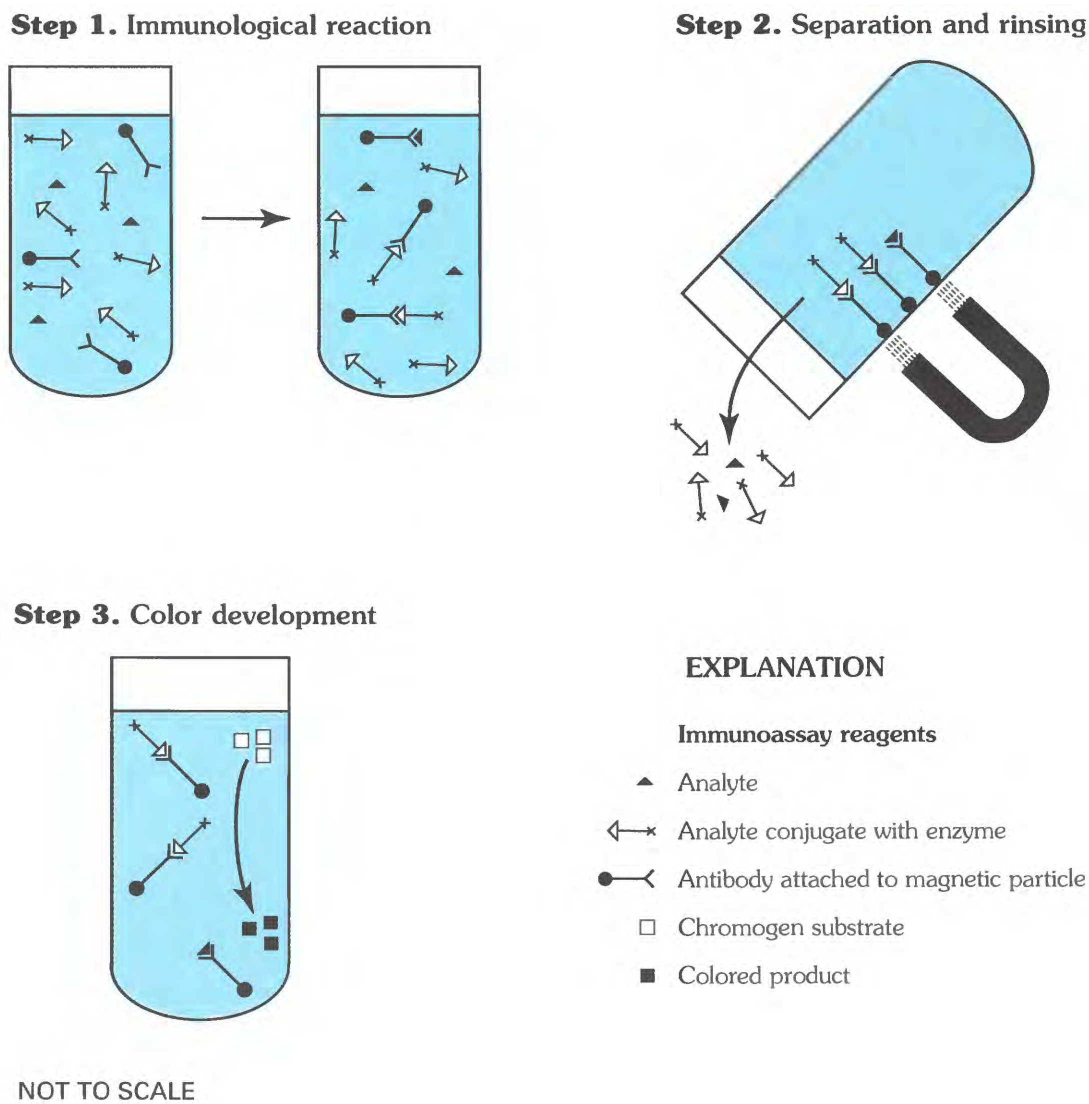


Figure 5. Three major steps in the immunoassay procedure.

-1.0 or 1.0, respectively. However, if the data points are randomly scattered, the correlation coefficient will be zero, and no linear relation exists. The larger the magnitude of the correlation coefficient, the stronger the relation (Blalock, 1972, p. 376–377). These results indicate that the ELISA used in this study has a high degree of precision.

The accuracy of the ELISA was evaluated on the basis of 461 analyses of 13 standard-reference samples (table 3). With the exception of the three smallest atrazine reference concentrations (0.10, 1.00, and 1.15 µg/L), the mean concentrations of the analytical results were all within plus or minus 9 percent of the atrazine reference values. Generally, the ELISA tended to overestimate the actual concentration with the exception of reference samples greater than 4.0 µg/L, which on average, were underestimated by about 4 percent.

The probability of the ELISA producing a false-positive result was examined through the analysis of 158 blank-water samples, which were analyzed throughout the duration of this study. Of these 158 analyses, five reported detectable concentrations of atrazine, a false-positive rate of 3.2 percent. None of these false positives were greater than 0.08 µg/L. Because of the small percentage of false positives, associated small concentrations, and the fact that in most stream samples the atrazine concentration was many times larger than the false-positive values, potential analytical error introduced by false positives was not a concern in this study.

Table 2. Statistical summary of duplicate analyses of selected water samples from the Delaware River Basin by enzyme-linked immunosorbent assay

	Duplicate samples	
	A	B
Number of analyses	294	294
Mean concentration (micrograms per liter)	2.39	2.41
Variance (micrograms per liter)	18.3	19.4
Correlation coefficient	0.997	

Table 3. Statistical summary of standard-reference sample concentrations determined by enzyme-linked immunosorbent assay

	Standard-reference sample concentration (micrograms per liter)												
	0.1	1.00	1.15	1.19	1.21	2.20	2.22	2.30	3.00	3.78	4.00	4.17	5.00
Number of determinations	12	17	7	50	49	7	35	44	164	30	7	32	7
Minimum	.06	.96	1.21	1.05	.98	2.22	1.98	1.86	2.57	3.41	3.82	3.20	4.58
Maximum	.24	1.74	1.49	1.48	1.60	2.60	2.70	2.97	3.54	4.71	4.33	5.00	5.70
Mean	.14	1.22	1.35	1.26	1.28	2.39	2.32	2.37	3.07	4.05	4.06	3.99	4.80
Percentage difference	40	22	17	5.9	5.8	8.6	4.5	3.0	2.3	7.1	1.5	-4.3	-4.0

CONCENTRATIONS OF ATRAZINE

Most previous studies of concentration and transport of atrazine have restricted the number of samples collected and analyzed because of the expense of traditional GC/MS analysis. Consequently, the conclusions pertaining to mean concentrations and loads of atrazine presented in these previous studies may be based on a few samples randomly distributed throughout a year. Because atrazine is applied to farmland each year and subsequently transported in spring and summer runoff, there exist large seasonal and hydrological variability in concentrations in surface water (Goolsby and others, 1990; Thurman and others, 1991; Scribner and others, 1994; Pope, 1995). Unless these variabilities are taken into consideration when planning surface-water studies of atrazine occurrence and movement, conclusions about mean concentrations and loads may represent only crude estimates and(or) be biased either low or high depending on the temporal and hydrological distribution of the samples.

Estimation of Atrazine Concentrations from Triazine Concentrations

The study of the Delaware River Basin described in this report had the advantage of recently developed methods (ELISA) for rapid, efficient, and relatively inexpensive analysis of samples. The reduced analytical cost allowed for the collection and analysis of a large number of samples to, in effect, verify triazine concentrations during all seasons and under all streamflow conditions. The number of samples analyzed from each sampling site during this study is given in table 4. Data from these individual sampling sites were used to calculate daily mean triazine concentrations.

Selected samples were analyzed by both ELISA and GC/MS methods to define the relation between ELISA triazine concentrations and GC/MS-derived atrazine concentrations. This relation was used to estimate daily mean atrazine concentrations.

Time-Weighted, Daily Mean Triazine Concentrations

As previously described in the "Sample Collection" section of this report, multiple samples for the analysis of triazine concentrations by ELISA were collected on days with storm runoff. During low flow, a single sample was collected every few days. Daily mean triazine concentrations for days with multiple samples were calculated using a midinterval-subdivision method similar to that used for the computation of

Table 4. Number of samples from each sampling site analyzed by enzyme-linked immunosorbent assay for triazine concentrations from July 1992 through September 1995

Sampling-site map-index number (fig. 4)	Number of discrete triazine determinations
1	511
2	469
3	571
4	500
5	533
6	487
7	460
8	451
9	349
10	378
11	211
Study total	**4,920**

a daily mean streamflow water-surface elevation as described by Kennedy (1983). This method produces a time-weighted, daily mean concentration. An example of this calculation method is presented in table 5.

Total hours (time interval) associated with each discrete concentration in table 5 are equal to one-half the time since the previous concentration to one-half the time to the next concentration. For the first concentration, the time interval is from the beginning of the day (0 hours) to one-half the time to the second concentration. For the last concentration, the time interval is from one-half the time since the previous concentration to the end of the day (24 hours). The time-weighted, mean concentration is equal to the summation of the products of concentration (C) multiplied by the time interval (H) for each individual concentration divided by total hours (24).

Time-weighted, daily mean triazine concentrations for days of low streamflow were estimated on the basis of previously collected single samples. Generally, linear interpolation between days with low-flow samples was used to estimate time-weighted, daily mean concentrations for the intervening days between samples. This is considered to be an acceptable method because triazine concentrations during low flow vary little and generally show a continued and steady decline. However, in cases where a low-flow sample was not collected prior to storm runoff, the last previously defined concentration was held constant throughout the period preceding the runoff, or an estimate of prerunoff concentration was made on the basis of either initial runoff concentrations or judgement of previously defined concentration and hydrologic responses, followed by linear interpolation. Time-weighted, daily mean triazine concentrations for sampling sites 1–10 from July 1992 through March 1995 are presented in Pope and others (1996, tables 25–34), and time-weighted, daily mean triazine concentrations for sampling site 11 from July 1992 through September 1995 are presented in Pope and others (1996, table 35).

Time-Weighted, Daily Mean Atrazine Concentrations

The ELISA procedure, although very sensitive to atrazine, may not be totally specific to atrazine. Therefore, the daily mean triazine concentrations presented in Pope and others (1996, tables 25–35) may reflect, in part, other cross-reacting compounds with a chemical structure similar to atrazine. Because the MCL for atrazine is an annual mean and is based solely on the concentration of atrazine, it is necessary to estimate time-weighted, daily mean atrazine concentrations from the ELISA-derived triazine concentrations. To do this, 141 samples were analyzed by both ELISA to determine a triazine concentration and GC/MS to determine an atrazine concentration. Correlation and linear-regression analyses were used to relate these two procedurally derived concentrations. A plot of these data is presented in figure 6.

Linear-regression analysis was used to define the relation between ELISA-determined triazine concentrations and GC/MS-determined atrazine concentrations. The procedure develops an equation useful for estimating one variable from another and is in the form:

$$Y = a + bx, \qquad (1)$$

where

Y is the predicted (estimated) concentration of atrazine, in micrograms per liter, as computed by equation 1;

a is the y-intercept value, a constant determined by the regression analysis;

b is the slope of the regression line, a constant determined by the regression analysis; and

Table 5. Example calculation of time-weighted, daily mean triazine concentration for a day with multiple samples

[--, no sample; µg/L, micrograms per liter]

Sampling site 1 (fig. 4) May 31, 1993			
Hour of day	Concen- tration (C) (µg/L)	Total hours (H)	C x H
0	--	--	--
1	19	2.0	38
2	--	--	--
3	14	2.0	28
4	--	--	--
5	17	2.0	34
6	--	--	--
7	22	3.0	66
8	--	--	--
9	--	--	--
10	--	--	--
11	17	4.0	68
12	--	--	--
13	--	--	--
14	--	--	--
15	10	5.0	50
16	--	--	--
17	--	--	--
18	--	--	--
19	--	--	--
20	--	--	--
21	6.5	6.0	39
22	--	--	--
23	--	--	--
24	--	--	--
	Sum	24.0	323
Time-weighted, mean concentration (µg/L) = 323/24=13			

x is the concentration of triazine, in micrograms per liter, as determined by ELISA.

Initially, correlation and regression analyses were conducted using all 141 data pairs (fig. 6). Results of these analyses are given in table 6. Although the correlation between the two analytical procedures is high (0.967) and the probability that the relation exists only by chance is extremely small (p-value = 1.36×10^{-85}), the slope coefficient of the ELISA value (independent variable) is 0.728, which means that prior to the addition of the y-intercept value (0.207) the ELISA triazine concentration is reduced by 27 percent in estimating GC/MS atrazine concentrations. For example, using this relation, an ELISA value of 3.0 µg/L would convert to an estimated atrazine concentration of 2.4 µg/L [(0.728)(3.0)+0.207)]. There is a substantial decrease from an ELISA triazine concentration to a GC/MS atrazine concentration; therefore, further regression analyses were performed to determine if this large a decrease was indicative of the full range of ELISA concentrations. The standard error of estimate (SEE) presented in table 6 is equivalent to the standard deviation of points about the regression line and, for a normal distribution, two-thirds of the points should be within one standard deviation above and below the regression line (Riggs, 1968, p. 22)

An examination of the data plot in figure 6 indicates that data scatter increases at concentrations larger than about 5.0 µg/L. This scatter may have a substantial effect on determining the regression parameters. This observation was tested by splitting the data set into two groups—one with ELISA concentrations less than 5.0 µg/L and the other with ELISA concentrations greater than 5.0 µg/L. Correlation and regression analyses were performed on both these data groups. Results are presented in table 6.

The regression results in table 6 indicate that ELISA triazine concentrations less than 5.0 µg/L almost are a one-to-one estimator for atrazine concentrations based on a slope of 0.966. However, at very small ELISA concentrations, the addition of the y-intercept value (-0.083) may represent a large percentage change in the estimated atrazine concentration compared to the corresponding ELISA concentration. For example, an ELISA triazine concentration of 0.10 µg/L would estimate an atrazine concentration of 0.014 µg/L [(0.10)(0.966)-0.083]; an 86-percent reduction from the ELISA concentration. However, from the perspective of a monthly or annual mean concentration or load, this will be insignificant because at other times of the month or year concentrations or loads could be several orders of magnitude larger and, thus, have a much greater effect on the calculated mean or total load.

The regression analysis for the greater-than-5.0-µg/L data group shows a slightly lower correlation coefficient (0.914) and a much reduced slope (0.732) when compared to the results of the less-than-5.0-µg/L

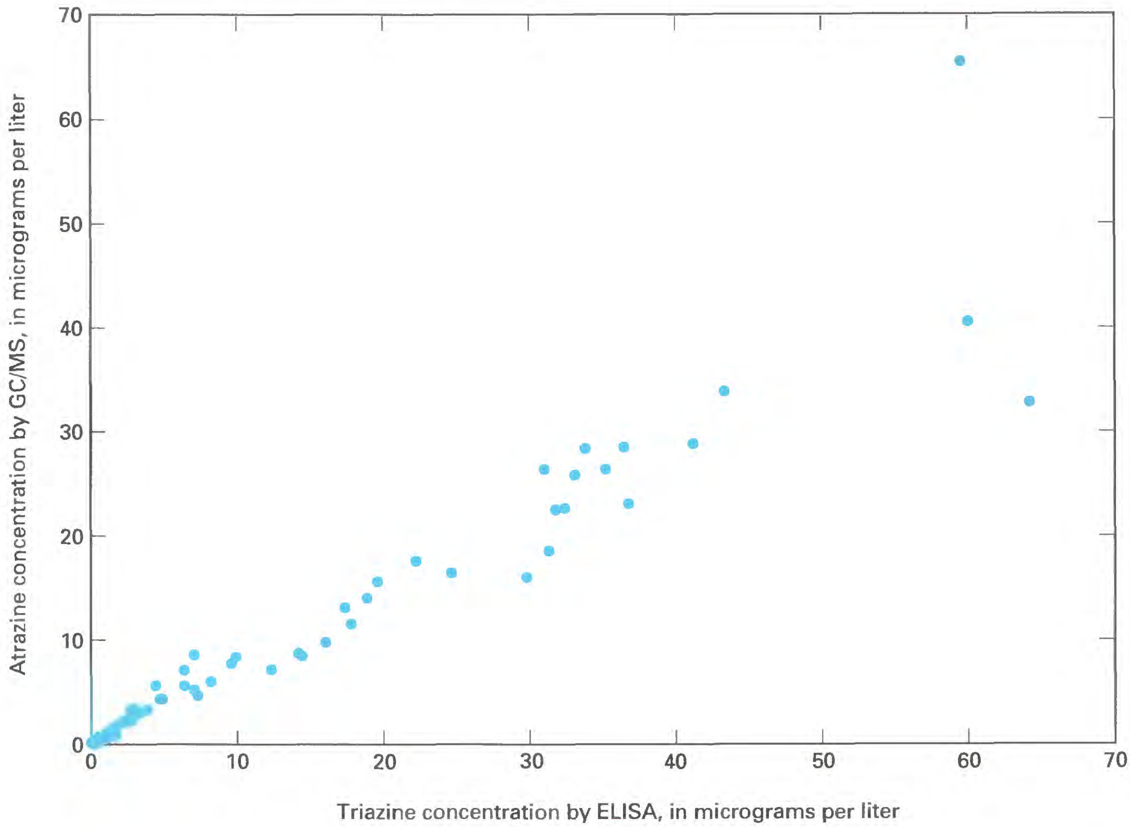


Figure 6. Relation between triazine concentrations determined by enzyme-linked immunosorbent assay (ELISA) and atrazine concentrations determined by gas chromatography/mass spectrometry (GC/MS) for 141 samples from the Delaware River Basin, July 1992 through July 1994.

data group (table 6). The greater-than-5.0-µg/L analysis closely resembles the results of the all-data-set analysis and seems to indicate that the scatter of these 32 data pairs in the greater-than-5.0-µg/L group have the most effect on the result of the all-data-set regression analysis. Two reasons for this may be: (1) samples with large triazine concentrations may contain larger quantities of other herbicides or degradation products of atrazine that cross react in the ELISA analysis producing an erroneously large estimated atrazine concentration (Thurman and others, 1990); and (2) the analytical range of the ELISA method is 0.04–5.0 µg/L, and sample concentrations greater than 5.0 µg/L need to be diluted to within this analytical range. This dilution process may introduce variability into the analytical results of these samples and, consequently, increase data scatter at larger triazine concentrations. This potential dilution error may be associated with either the ELISA and(or) the GC/MS procedures.

Currently (1996), atrazine is a restricted-use herbicide with an enforceable annual mean MCL of 3.0 µg/L in finished water supplies (U.S. Environmental Protection Agency, 1992). Because results from this study may be used by regulatory agencies for comparison to that standard, the need for reliable estimates of daily mean atrazine concentrations is critical, particularly in the immediate magnitude of the enforceable standard. Therefore, in this report, two regression relations are used for estimating time- and flow-weighted, daily mean atrazine concentrations—one for ELISA concentrations less than or equal to 5.0 µg/L and another for ELISA concentrations greater than 5.0 µg/L. The results of regression analyses for these relations are presented in table 6 and shown with their respective data sets and regression equations in figure 7.

Estimated time-weighted, daily mean atrazine concentrations were calculated from the time-weighted, daily mean triazine concentrations presented in Pope and others (1996, tables 25–35). These estimated daily mean values subsequently were used to calculate monthly and annual mean concentrations at all sampling sites and used in calculations of

Table 6. Summary of linear-regression analysis relating concentrations of atrazine (dependent variable), in micrograms per liter, determined by gas chromatography/mass spectrometry to concentrations of triazine compounds (independent variable), in micrograms per liter, for selected water samples from the Delaware River Basin

[N, number of analyses; r, correlation coefficient; SEE, standard error of estimate, in micrograms per liter (μg/L); p-value, probability value]

Data set	N	r	Regression parameters		SEE	p-value
			Slope	y-intercept		
All concentration data	141	0.967	0.728	0.207	2.47	1.36×10^{-85}
Concentration less than 5.0 μg/L	109	.979	.966	-.083	.22	1.75×10^{-75}
Concentration greater than 5.0 μg/L	32	.914	.732	.054	5.29	2.68×10^{-13}

atrazine transport (loads and yields). The equation used for estimating atrazine concentrations from triazine concentrations less than or equal to 5.0 μg/L contains a negative component (-0.083). As a result, atrazine concentrations estimated from triazine concentrations less than 0.09 μg/L are negative. Because negative concentrations are illogical and it is unlikely that a true zero concentration now occurs in this system, all calculated negative daily mean atrazine concentrations arbitrarily were set at a concentration of 0.01 μg/L.

Temporal and Spatial Distribution

Time-weighted, daily mean atrazine concentrations in samples from streams in the Delaware River Basin commonly exceeded the value of the MCL during May, June, and July (fig. 8). Time-weighted, daily mean concentrations equal to or greater than 20 μg/L were not uncommon during this period. However, time-weighted, daily mean concentrations greater than the value of the MCL were rare at other times of the year. Most time-weighted, daily mean concentrations were less than 1.0 μg/L from August through April.

Time-weighted, daily mean atrazine concentrations during the period immediately following application (April through early June) generally responded directly to streamflow; when streamflow increased, so did atrazine concentrations, However, after about August, time-weighted, daily mean atrazine concentrations increased little, regardless of streamflow conditions.

The atrazine-streamflow relation shown in figure 8 was characteristic of all 10 sampling sites upstream of Perry Lake; however, the magnitude of time-weighted, daily mean concentrations and duration of those concentrations varied considerably between sampling sites. Sampling site 3 (Grasshopper Creek, fig. 8*A*) had the largest time-weighted, daily mean atrazine concentrations and greatest number of days exceeding the value of the MCL of any sampling site. Sampling site 8 (Cedar Creek, fig. 8*C*) had the smallest time-weighted, daily mean concentrations and fewest days greater than the value of the MCL. In general, the largest time-weighted, daily mean concentrations occurred at sampling sites receiving runoff from the northern and northeastern parts of the Delaware River Basin. This difference may be the result of differences in the extent of cropland (fig. 3) in the subbasins (fig. 4).

Time-weighted, daily mean atrazine concentrations in water from Perry Lake, as determined from samples of the lake outflow (sampling site 11, fig. 4), are affected largely by the timing and magnitude of inflow (fig. 9). Late-season runoff in November and December 1992, combined with preapplication runoff in March and April 1993 (fig. 8), decreased time-weighted, daily mean concentrations in the lake from about 3.0 μg/L in October 1992 to about 0.4 μg/L in May 1993. Runoff from the basin upstream of the lake during these periods contained small atrazine concentrations ranging from about 0.01 to about 0.90 μg/L. Most atrazine application in 1993 was delayed until May or June because of wet field conditions.

Postapplication runoff in 1993 produced substantial increases in time-weighted, daily mean atrazine concentrations in the outflow of Perry Lake. Measured concentrations peaked at about 3.6 μg/L in mid-July during a period of severe flooding, as shown by the increase in lake water-surface elevation (fig. 9);

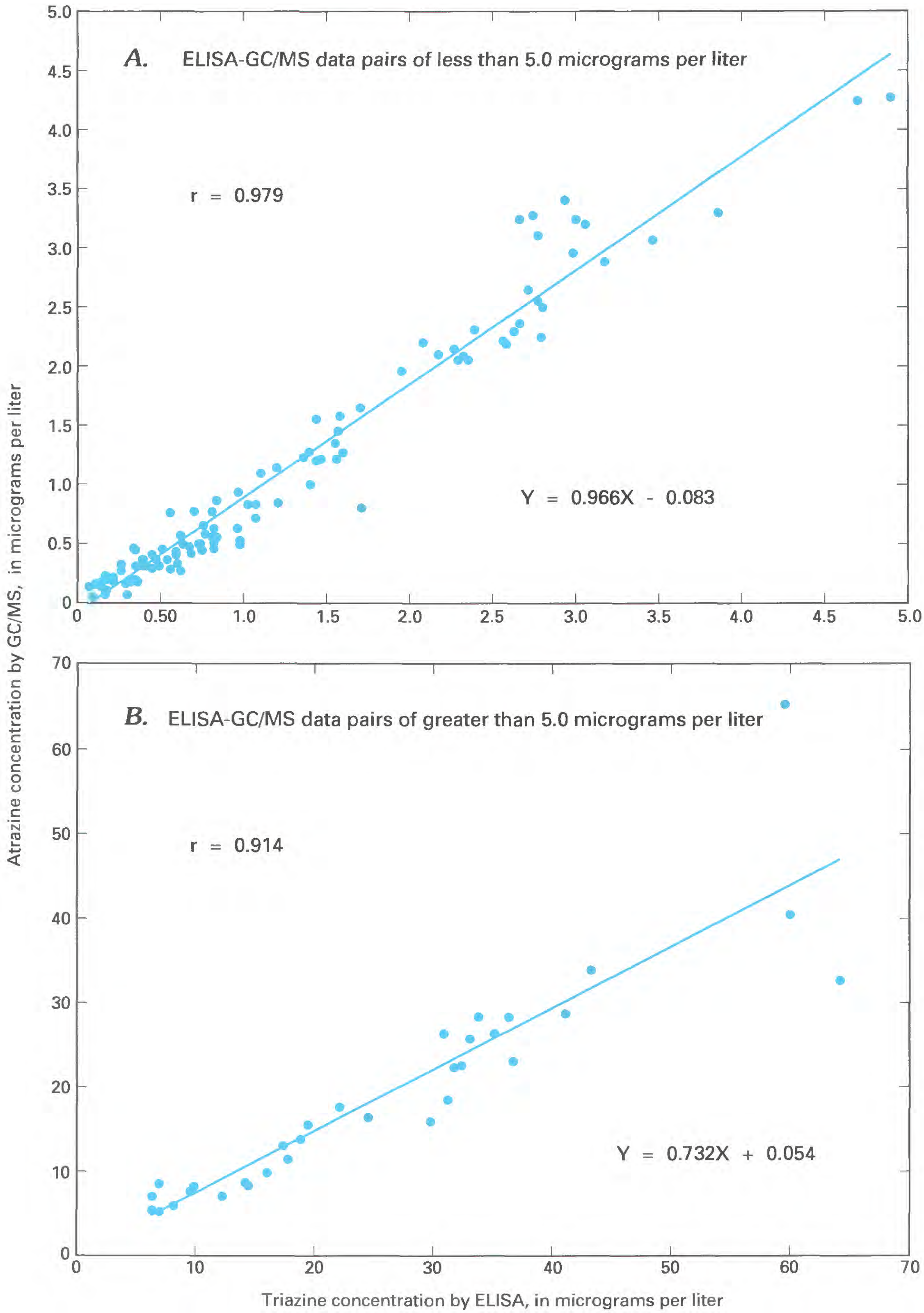


Figure 7. Relation between triazine concentrations determined by enzyme-linked immunosorbent assay (ELISA) and atrazine concentrations determined by gas chromatography/mass spectrometry (GC/MS) for data pairs of (*A*) less than 5.0 and (*B*) greater than 5.0 micrograms per liter, July 1992 through July 1994.

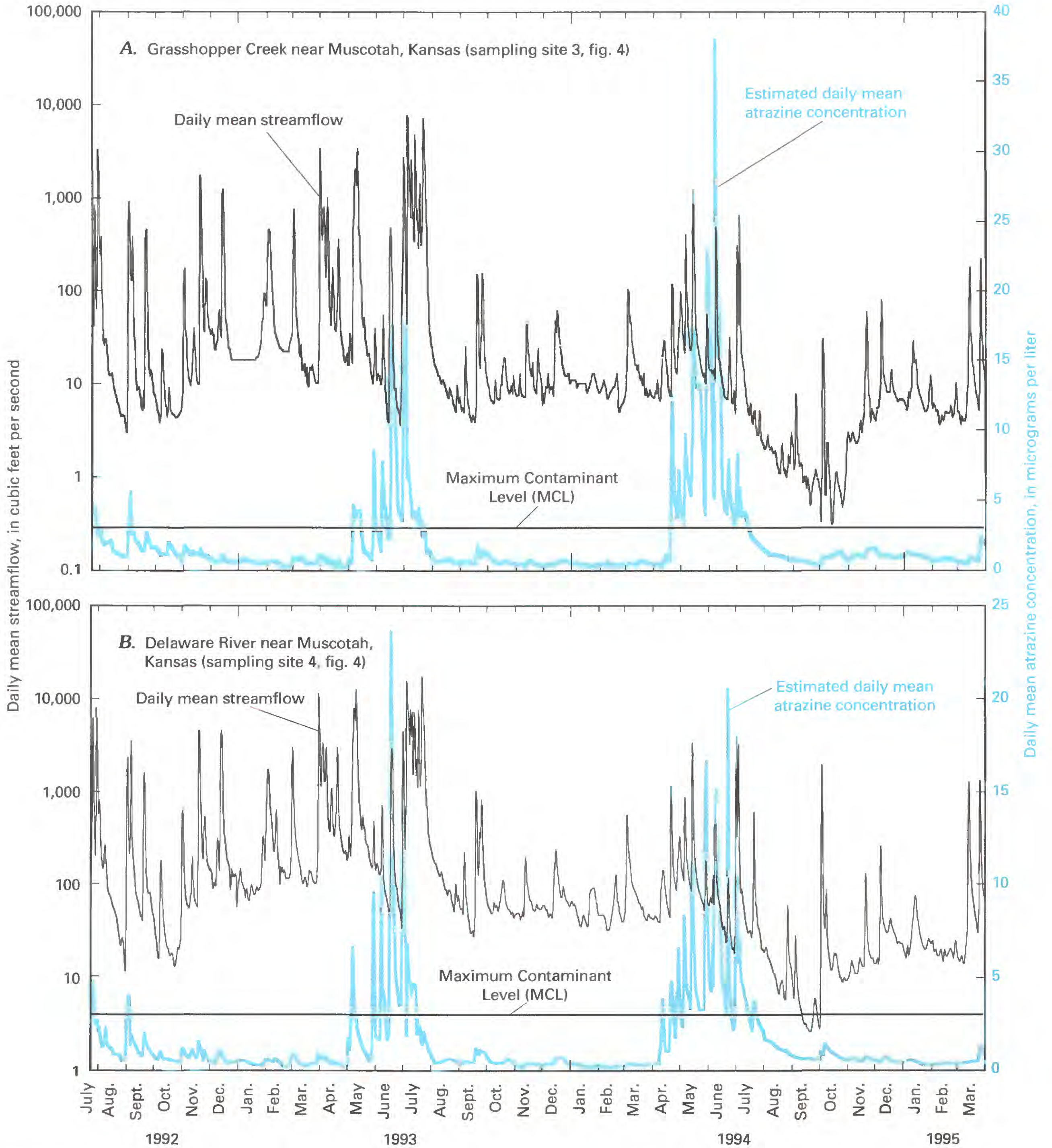


Figure 8. Estimated time-weighted, daily mean atrazine concentrations and daily mean streamflow at selected sampling sites, July 1992 through March 1995.

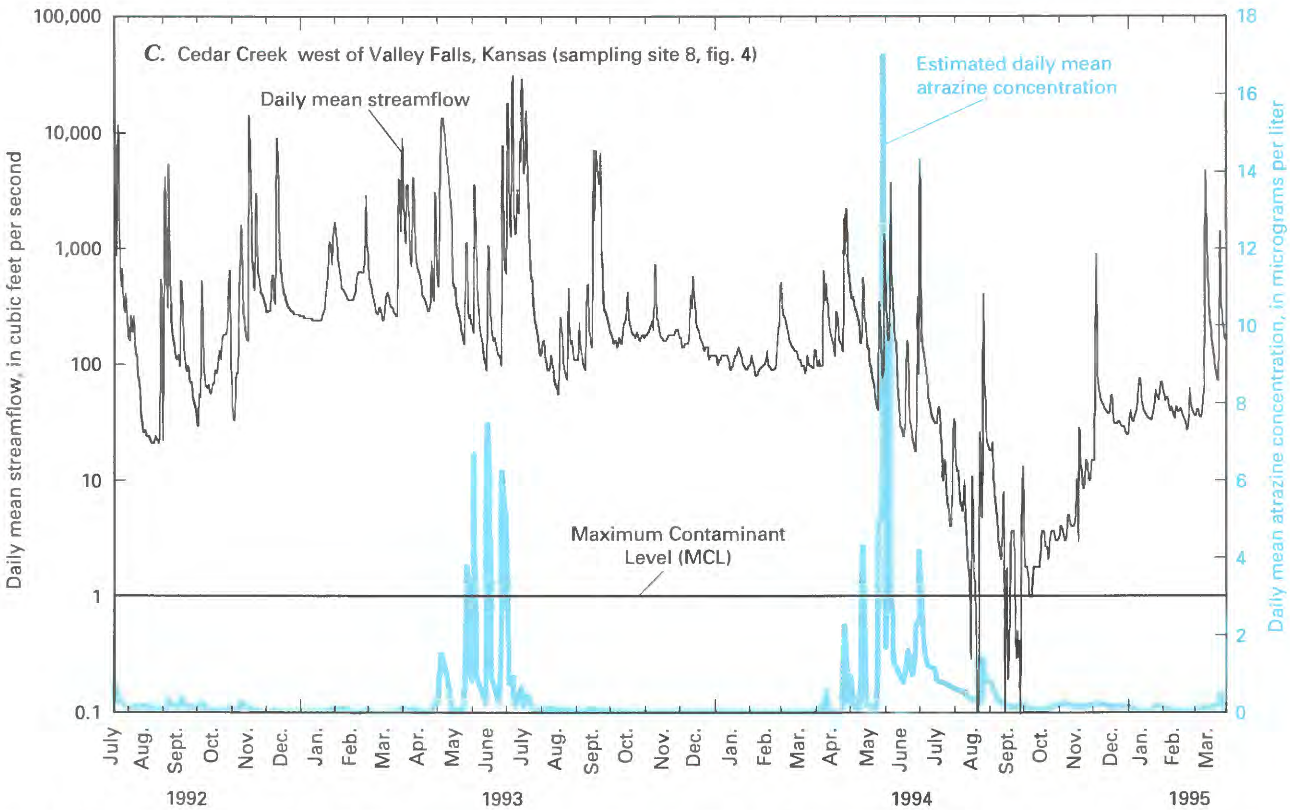


Figure 8. Estimated time-weighted, daily mean atrazine concentrations and daily mean streamflow at selected sampling sites, July 1992 through March 1995—Continued.

however, much of the floodwater (inflow to the lake) from mid- to late July generally contained atrazine concentrations less than 2.0 µg/L (fig. 8*B*). This, combined with daily mean concentrations less than 1.0 µg/L in inflow from August 1993 through March 1994, generally produced decreasing daily mean atrazine concentrations in the outflow of the lake until postapplication runoff in 1994.

Early-season, postapplication runoff in 1994 caused time-weighted, daily mean atrazine concentrations in water from Perry Lake to exceed the value of the MCL even though inflow volumes were small relative to lake volume. Most of the upstream basin runoff occurred in May and early July as evidenced by the small increase in lake water-surface elevations during this period (fig. 9). By late July 1994, atrazine concentrations in samples from the outflow of the lake were greater than 3.0 µg/L. Less-than-average late-season runoff, which normally tends to dilute existing concentrations, did not temper the effects of early-season runoff in 1994. Atrazine concentrations in samples from the lake outflow were greater than 3.0 µg/L through the end of 1994 and gradually declined until postapplication runoff during May and June 1995 produced substantial increases in atrazine concentrations. The largest atrazine concentrations in water from lake outflow recorded during this study occurred during August 1995. Concentrations greater than 5.0 µg/L were common during August 1995.

The large increase in time-weighted, daily mean atrazine concentrations in water from the outflow of Perry Lake during the summer of 1995 probably was the result of a wet spring that delayed most planting and atrazine application until early June, a time when atrazine movement is more likely because of the potential for larger rainfall volume and intensities. This delayed planting effectively reduced the length of the growing season and may have shifted production away from corn, which required a longer than available growing season, to grain sorghum, which is more suited to a short growing season. This possible production shift may have compounded the delayed-application problem because surface application of atrazine is used routinely in grain-sorghum production in the Delaware River Basin. Surface application, as contrasted to soil incorporation, increases the runoff potential of atrazine particularly at a time of year of large rainfall.

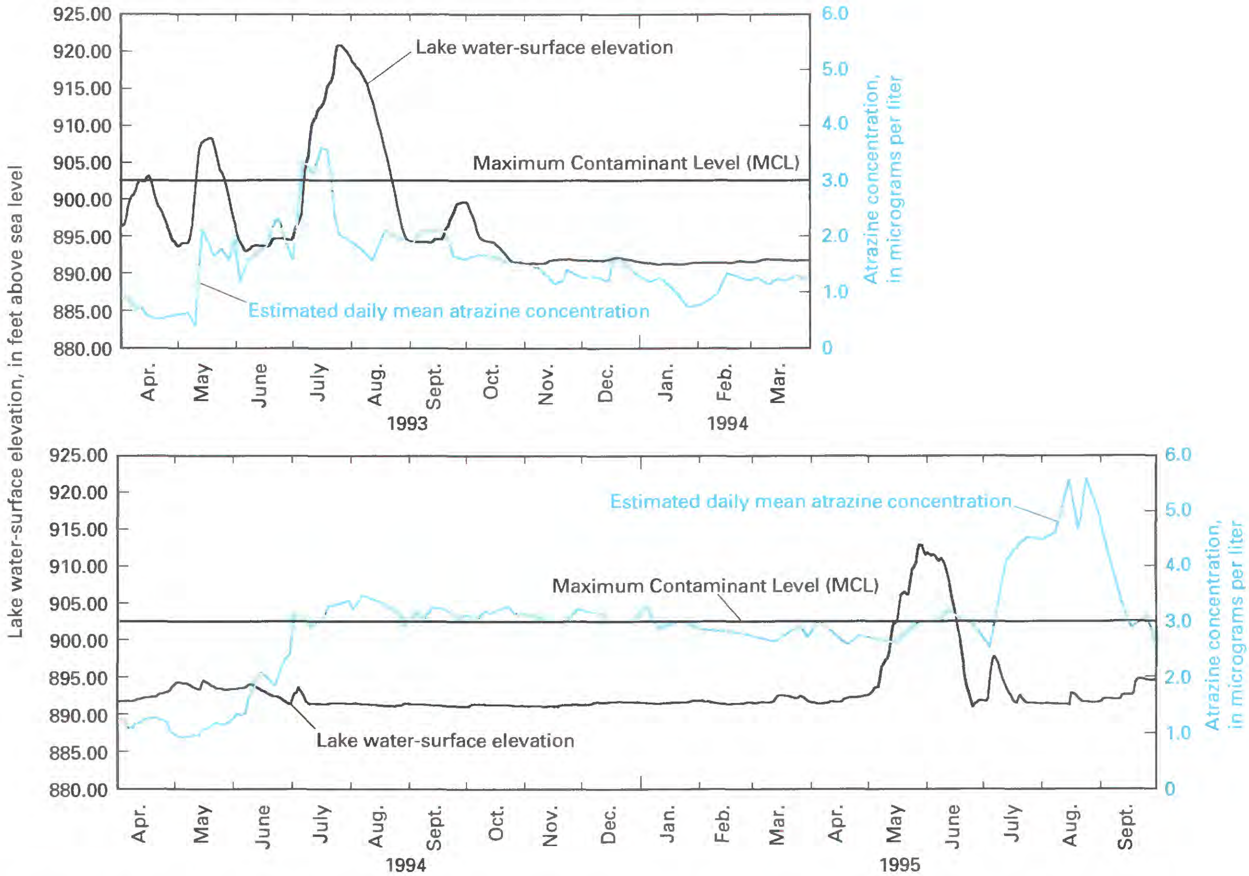


Figure 9. Estimated time-weighted, daily mean atrazine concentrations and Perry Lake water-surface elevations, April 1993 through September 1995.

Time-weighted, monthly mean atrazine concentrations for the sampling sites upstream of Perry Lake (sites 1–10, table 7) reflected patterns similar to those observed in the analysis of daily mean concentrations (fig. 10). The largest monthly mean concentrations were for the months of May, June, and July. At most sampling sites, the largest monthly concentration occurred during June of both the 1993 and 1994 crop years. Monthly mean concentrations from August through April at the 10 upstream sites (sites 1–10) were minimal compared to May through July. August through April rarely had monthly mean concentrations greater than 1.0 µg/L, with most months substantially less than 0.50 µg/L.

Time-weighted, monthly mean concentrations during the 1994 crop year were mostly larger than corresponding monthly mean concentrations during the 1993 crop year (fig. 10). Several factors may be responsible for this difference: (1) preapplication, low-flow concentrations were larger in 1994 than in 1993, thereby establishing a larger baseline concentration preceding planting, application, and runoff; (2) 1994 was a much drier year than 1993 and, consequently, produced below-average streamflow (fig. 2) and potentially reduced the dilution effect from major storm runoff such as occurred during July 1993 (fig. 8); (3) most runoff in 1994 occurred during a short period after May application, which produced larger runoff concentrations for the few storms that did occur (fig. 8); (4) reduced runoff in June and July 1994 may have kept more atrazine available for subsequent runoff later in the year; and (5) the generally larger monthly mean concentrations from August 1994 through March 1995 may have been the result of less-intense rainfall patterns, which allowed more atrazine to move downward into the shallow alluvial ground-water system, with subsequent discharge into streams during the last 8 months of the 1994 crop year. These factors are suggested under the assumption that total basin atrazine application was about the same for both the 1993 and 1994 crop years. If, however, greater application was made in 1994, that in itself would be potential reason for the larger monthly mean atrazine concentrations in 1994. Data currently (1996) are not

Table 7. Time-weighted, monthly and annual mean atrazine concentrations, in micrograms per liter, at 11 sampling sites in the Delaware River Basin, August 1992 through March 1995

	Sampling site (fig. 4)										
	1	2	3	4	5	6	7	8	9	10	11
1992											
Aug.	1.1	0.42	1.6	1.1	0.15	0.19	1.4	0.12	0.44	0.58	2.9
Sept.	1.0	.44	2.1	1.4	.43	.33	.86	.15	.36	.49	2.6
Oct.	.28	.10	1.2	.48	.16	.08	.45	.06	.10	.27	2.6
Nov.	.55	.25	1.1	.76	.32	.16	.56	.07	.19	.99	2.5
Dec.	.35	.09	.57	.41	.06	.04	.24	.02	.09	.67	2.1
1993											
Jan.	.22	.05	.50	.25	.03	.03	.22	.01	.05	.47	1.3
Feb.	.25	.08	.39	.28	.14	.04	.15	.05	.06	.24	.85
Mar.	.34	.14	.57	.32	.07	.04	.18	.02	.06	.21	1.1
Apr.	.44	.15	.47	.32	.10	.05	.36	.02	.13	.29	.64
May	1.2	.46	2.4	2.1	1.4	.95	3.2	.56	.09	.83	1.3
June	6.2	4.4	5.8	5.6	3.8	2.6	5.8	1.5	1.4	2.2	1.8
July	4.1	3.3	5.0	4.1	2.8	1.4	4.8	1.0	3.3	2.6	2.8
Aug.	.53	.14	.59	.43	.02	.05	.89	.06	.33	.48	1.8
Sept.	.60	.23	.77	.53	.16	.28	1.1	.04	.27	.40	1.9
Oct.	.39	.08	.58	.37	.03	.03	.45	.01	.18	.14	1.6
Nov.	.23	.03	.40	.18	.03	.02	.24	.01	.06	.04	1.3
Dec.	.24	.06	.44	.33	.07	.02	.25	.01	.01	.05	1.4
1994											
Jan.	.08	.02	.33	.14	.01	.01	.15	.01	.01	.03	1.0
Feb.	.05	.02	.34	.09	.01	.01	.06	.01	.01	.02	1.1
Mar.	.18	.07	.42	.15	.03	.02	.10	.01	.01	.05	1.2
Apr.	1.7	.55	2.4	1.8	1.1	.38	1.6	.22	.14	1.3	1.2
May	2.4	1.6	10	5.6	2.7	2.1	5.0	.76	.23	2.4	1.0
June	2.9	.74	11	6.7	3.2	1.9	9.1	2.7	1.7	1.5	1.8
July	3.9	3.6	3.2	3.9	3.4	.70	3.0	1.5	1.2	1.8	3.1
Aug.	.98	.92	.97	1.2	.10	.23	1.4	.51	.38	.51	3.3
Sept.	.43	.51	.50	.52	.09	.17	.87	.36	.26	.24	3.1
Oct.	.69	.58	.87	.74	.08	.08	.51	.12	.18	.25	3.2
Nov.	.29	.25	1.1	.46	.06	.08	.32	.19	.16	.33	3.1
Dec.	.30	.19	.94	.38	.03	.02	.29	.19	.05	.26	3.1
1995											
Jan.	.21	.09	.95	.28	.01	.03	.20	.08	.01	.11	3.0
Feb.	.11	.02	.65	.21	.01	.01	.10	.05	.01	.15	2.8
Mar.	.34	.28	.85	.42	.15	.09	.50	.14	.01	.20	2.7
1993 crop year[1] annual mean	1.2	.75	1.5	1.2	.70	.45	1.4	.27	.48	.60	1.5
1994 crop year[1] annual mean	1.2	.78	2.8	1.8	.91	.48	1.9	.57	.36	.75	2.6

[1]Crop year is the 12-month period from April 1 through March 31 and is designated by the calendar year in which it begins.

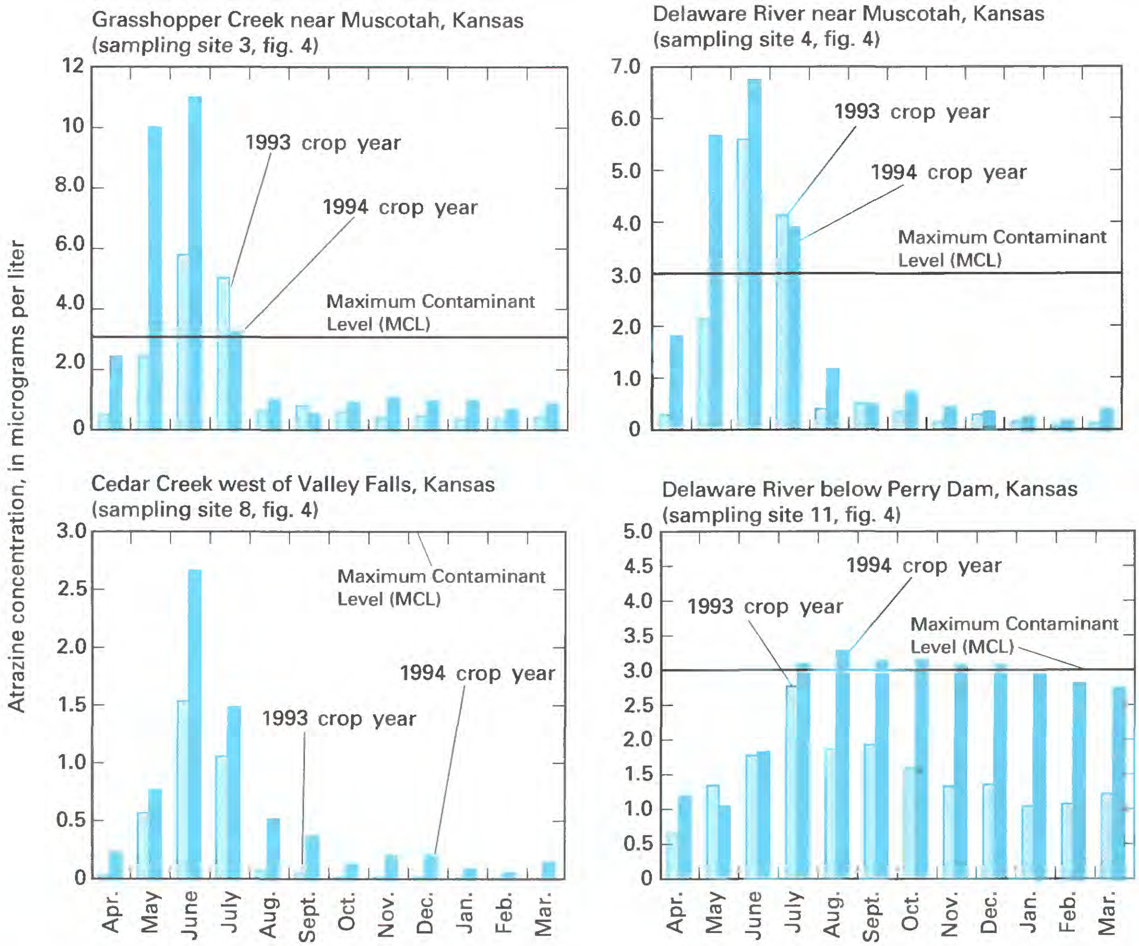


Figure 10. Time-weighted, monthly mean atrazine concentrations for 1993 and 1994 crop years in water from selected sampling sites in the Delaware River Basin.

available to verify differences in annual atrazine application.

Substantial between-site differences are evident in time-weighted, monthly mean atrazine concentrations in water from the 10 upstream sampling sites. The largest monthly mean concentrations were in water from sites receiving runoff from the northern and northeastern part of the Delaware River Basin (sites 1, 3, 4, and 7), whereas the smallest concentrations were in water from the most downstream locations (sites 8, 9, and 10). For example, monthly mean concentrations at sampling site 3 for June 1993 and 1994 were 5.8 and 11 µg/L, respectively. Corresponding monthly mean concentrations in water from sampling site 8 were 1.5 and 2.7 µg/L, respectively. These differences may be due to differences in land use within the subbasins.

Time-weighted, monthly mean atrazine concentrations in the outflow of Perry Lake (sampling site 11) showed a somewhat similar seasonal-fluctuation pattern to that of the 10 upstream sampling sites, although delayed, attenuated, and persistent (fig. 10). The largest monthly mean concentrations in the outflow of Perry Lake occurred in July 1993 and August 1994 for the two complete crop years monitored in this study. This contrasts with the upstream sites where the largest monthly mean concentrations occurred in June or July in 1993 and 1994.

The magnitude of change in time-weighted, monthly mean concentrations in water from sampling site 11 was not as great as at upstream sites. The maximum change in monthly mean atrazine concentrations between successive months in the outflow of Perry Lake was slightly greater than 1.0 µg/L, whereas an equivalent time-period change in concentration in water from an upstream site may have been several micrograms per liter.

The decline from peak time-weighted, monthly mean concentrations in water from sampling site 11 took several months to produce a substantial decrease.

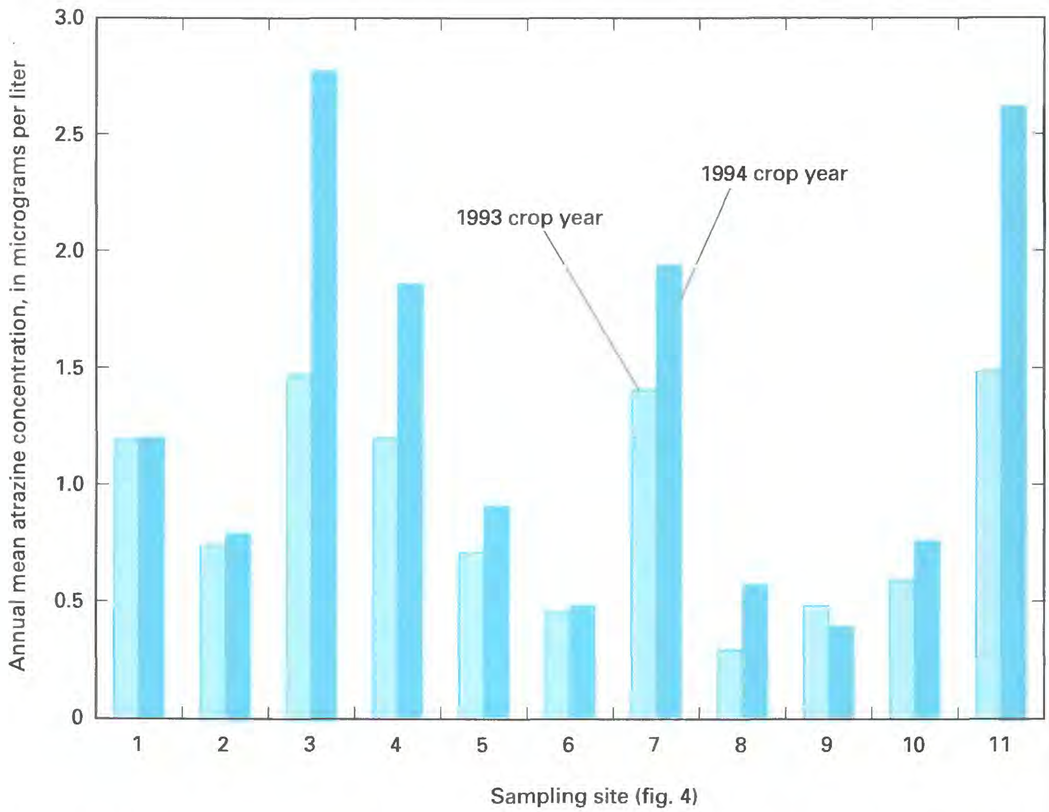


Figure 11. Time-weighted, annual mean atrazine concentrations for 1993 and 1994 crop years in water from 11 sampling sites in the Delaware River Basin.

For example, during the 1994 crop year, monthly mean concentrations peaked at 3.3 µg/L in August and did not decrease to less than 3.0 µg/L until February 1995. The fairly substantial change in monthly mean concentration between June and July 1993 and July and August 1993 represents the inflow and release of large volumes of runoff (approximately three conservation-pool volumes) from near-record floods in early to mid-July 1993. A new maximum water-surface elevation was established for Perry Lake in July 1993. Fluctuations in concentrations this large in Perry Lake are considered to be unusual and do not represent normal, expected conditions.

The aforementioned characteristics of atrazine concentrations in the outflow of Perry Lake are indicative of a large reservoir with substantial storage capacity. Therefore, because of the large solubility of atrazine and its slow degradation rate in water, it is expected that after seasonal peak concentrations are reached in Perry Lake it could take many months before a substantial decrease in monthly mean concentrations is achieved.

Annual mean concentrations in water from 11 sampling sites in the Delaware River Basin are presented in table 7 and a between-site comparison is shown in figure 11. Annual mean concentrations were calculated by summing daily mean concentrations for the crop year and dividing by 365. The derivation of the daily mean concentrations has been discussed previously in the "Time-Weighted, Daily Mean Atrazine Concentrations" section of this report. The resultant annual mean atrazine concentration represents, in effect, a time-weighted, annual mean concentration.

Time-weighted, annual mean concentrations did not exceed the 3.0-µg/L MCL in water from any sampling site for either the 1993 or 1994 crop years; however, concentrations generally were larger in 1994 than in 1993. Annual mean atrazine concentrations during the 1993 crop year ranged from 0.27 µg/L in water from sampling site 8 to 1.5 µg/L in water from sampling sites 3 and 11, and during the 1994 crop year from 0.36 µg/L in water from sampling site 9 to 2.8 µg/L in water from sampling site 3. Concentrations during the first 6 months of the 1995 crop year were larger than in 1994, at least for the outflow of Perry Lake (fig. 9). The 1995-crop-year annual mean concentration in water from the outflow of Perry Lake may exceed the MCL unless substantial inflow to the lake dilutes existing concentrations.

Time-weighted, annual mean atrazine concentrations varied substantially between sampling sites. The previous discussion of monthly mean atrazine concentrations indicated an apparent difference in mean concentrations between sampling sites receiving runoff from the northern and northeastern parts of the basin with those receiving runoff from other parts of the basin. Annual mean concentrations displayed the same pattern. Water from sampling sites 1, 3, 4, and 7 has substantially larger time-weighted, annual mean concentrations than water from sampling sites 8, 9, and 10. For example, the annual mean concentrations in water from site 3 were about five times larger than concentrations in water from site 8 for both crop years (5.6 times larger in 1993 and 4.9 times larger in 1994).

Time-weighted, annual mean atrazine concentrations in the outflow of Perry Lake (sampling site 11) are some of the largest in the Delaware River Basin. This fact seems contrary to the observation that concentrations in the outflow of Perry Lake were smaller at the beginning of each crop year than the calculated annual means. For example, in April 1993, the monthly mean atrazine concentration was about 0.64 μg/L, whereas the 1993 crop year annual mean was 1.5 μg/L. It would follow then that concentrations in at least some inflow streams should have been substantially larger than 1.5 μg/L to raise the annual mean concentration in a body of water as large as Perry Lake to that level. An analysis of flow-weighted, annual mean concentrations was performed to explain this apparent contradiction.

Flow-Weighted Concentrations

All mean atrazine concentrations previously presented in this report are, by the method of calculation, time-weighted concentrations and, as such, can be used to evaluate compliance with Federal drinking-water-quality regulations that, by the nature of the regulation's sampling requirements, approximate time-weighted averages. However, to evaluate the potential effect that a stream may have on a downstream reservoir and to hydrologically evaluate subbasins relative to each other, flow-weighted concentrations are more appropriate.

Flow-weighted, mean concentrations represent, in effect, the average concentration of a specific volume of water. A flow-weighted, annual mean atrazine concentration, therefore, is an estimate of the mean concentration of all the water that flowed past a site during a crop year. Flow-weighted, annual mean atrazine concentrations were calculated by summing the products of daily mean atrazine concentrations multiplied by daily mean streamflow (Pope and others, 1996, tables 14–24) divided by a summation of daily mean streamflow. The estimation of daily mean atrazine concentrations has been discussed previously in this report. Flow-weighted, annual mean atrazine concentrations are given in table 8. Flow-weighted, annual mean concentrations during the 1993 crop year ranged from 1.0 μg/L at sampling site 8 to 4.4 μg/L at sampling site 7 and during the 1994 crop year from 1.0 μg/L at sampling site 9 to 8.9 μg/L at sampling site 3. Flow-weighted, annual mean atrazine concentrations during the 1993 crop year generally were smaller than those during the 1994 crop year because of floods in July 1993, which contained large volumes of runoff with relatively small concentrations of atrazine (fig. 8).

A comparison of the time- and flow-weighted, average annual mean atrazine concentrations for the 1993 to 1994 crop years in water from 11 sampling sites in the Delaware River Basin is presented in figure 12. Time-weighted, average annual mean concentrations are substantially less than the MCL in water from all sampling sites, and none are appreciably larger than concentrations in the outflow of Perry Lake (sampling site 11). However, in water from several sampling sites (1, 3, 4, and 7), the flow-weighted, average annual mean concentrations are considerably larger than both the MCL and the time-weighted, average annual mean atrazine concentrations in the outflow of Perry Lake (sampling site 11).

As was the case regarding time-weighted atrazine concentrations, sites receiving runoff from the northern and northeastern parts of the Delaware River Basin (sites 1, 3, 4, and 7) also have the largest flow-weighted atrazine concentrations. Flow-weighted, average annual mean concentrations (table 8 and fig. 12) ranged from 1.2 μg/L in water from sampling site 9 to 6.6 μg/L at sampling site 3. Time- and flow-weighted, average annual mean atrazine concentrations in the outflow of Perry Lake (sampling site 11) are similar because seasonal and hydrologically related fluctuations common at upstream sites are tempered by the storage and mixing effects of the lake.

Table 8. Flow-weighted, annual mean atrazine concentrations for the 1993 and 1994 crop years, in micrograms per liter, at 11 sampling sites in the Delaware River Basin

Sampling site (fig. 4)	Crop year[1] 1993	1994	Average
1	4.2	4.0	4.1
2	2.9	2.6	2.8
3	4.2	8.9	6.6
4	3.5	5.4	4.4
5	2.2	4.3	3.2
6	1.1	2.2	1.6
7	4.4	6.5	5.4
8	1.0	2.2	1.6
9	1.3	1.0	1.2
10	1.4	5.0	3.2
11	1.6	2.1	1.8

[1]Crop year is the 12-month period from April 1 through March 31 and is designated by the calendar year in which it begins.

Relation to Land Use

Data previously presented indicate large differences in annual mean atrazine concentrations between sampling sites. Water from sampling sites receiving runoff from the northern and northeastern part of the Delaware River Basin (sites 1, 3, 4, and 7) had the largest annual mean concentrations of any of the 11 sampling sites. An implication is that these differences may be due to differences in land use, particularly differences in percentage of subbasins in cropland. This implication was tested with regression analysis relating percentage of subbasin in cropland (independent variable) to average annual mean concentrations for the 1993 to 1994 crop years (dependent variable).

Land-use percentages for selected categories were developed for the subbasin represented by each sampling site from digital land-use data provided by the Data Access and Support Center of the Kansas Geological Survey, Lawrence, Kansas (table 9). The cropland category was the most relevant to a potential relation to atrazine concentrations. Cropland percentages in table 9 include all major crops produced in the Delaware River Basin. These crops include corn, grain sorghum, soybeans, and wheat. Atrazine is not used in the production of soybeans or wheat; therefore, the actual causal relation would be between the percentage of area in corn and sorghum production and atrazine concentrations. However, the percentages of area devoted to individual crop production currently (1996) are not available on a subbasin or basin scale. Therefore, percentage of subbasin in cropland was used as a surrogate variable for percentage of basin in corn and sorghum production.

Results of regression analysis relating time- and flow-weighted, average annual mean atrazine concentrations in water from the 10 sampling sites upstream of Perry Lake to percentage of subbasin in cropland are presented in figure 13. The time- and flow-weighted, average annual mean concentrations are averages of the annual means for the 1993 and 1994 crop years. Sampling site 11 (outflow of Perry Lake) was not included in the regression analysis because it was believed that data from a site with a major reservoir within its basin could not be comparable with data from the upstream sites. This lack of comparability would result from potential water-quality effects of the reservoir due to storage of runoff, time of residence, mixing, atrazine degradation, and completely regulated outflow rates.

Both relations presented in figure 13 are direct and statistically significant. A direct relation is one in which the dependent variable varies in the same direction as the independent variable. In this case, as percentage of subbasin in cropland increases, annual mean atrazine concentration also increases. The significance of a relation is evaluated by the probability value (p-value) calculated from the relation of the two variables. For the purpose of this report, a relation with a p-value less than 0.05 is considered to be statistically significant.

The relations in figure 13 indicate that time-weighted, average annual mean atrazine concentrations may not exceed the 3.0-μg/L MCL in subbasins with at least about 70-percent cropland. However, flow-weighted, average annual mean atrazine concentrations may exceed the MCL when percentage of cropland is greater than about 40 percent of the subbasin.

The relations presented in figure 13 should be valid for any subbasin in the Delaware River Basin as long as the area ratios of individual crops remain at about the same levels as during this study. Although ratios of individual crops to cropland were not available for the Delaware River Basin, these ratios were calculated for each county from data provided by the

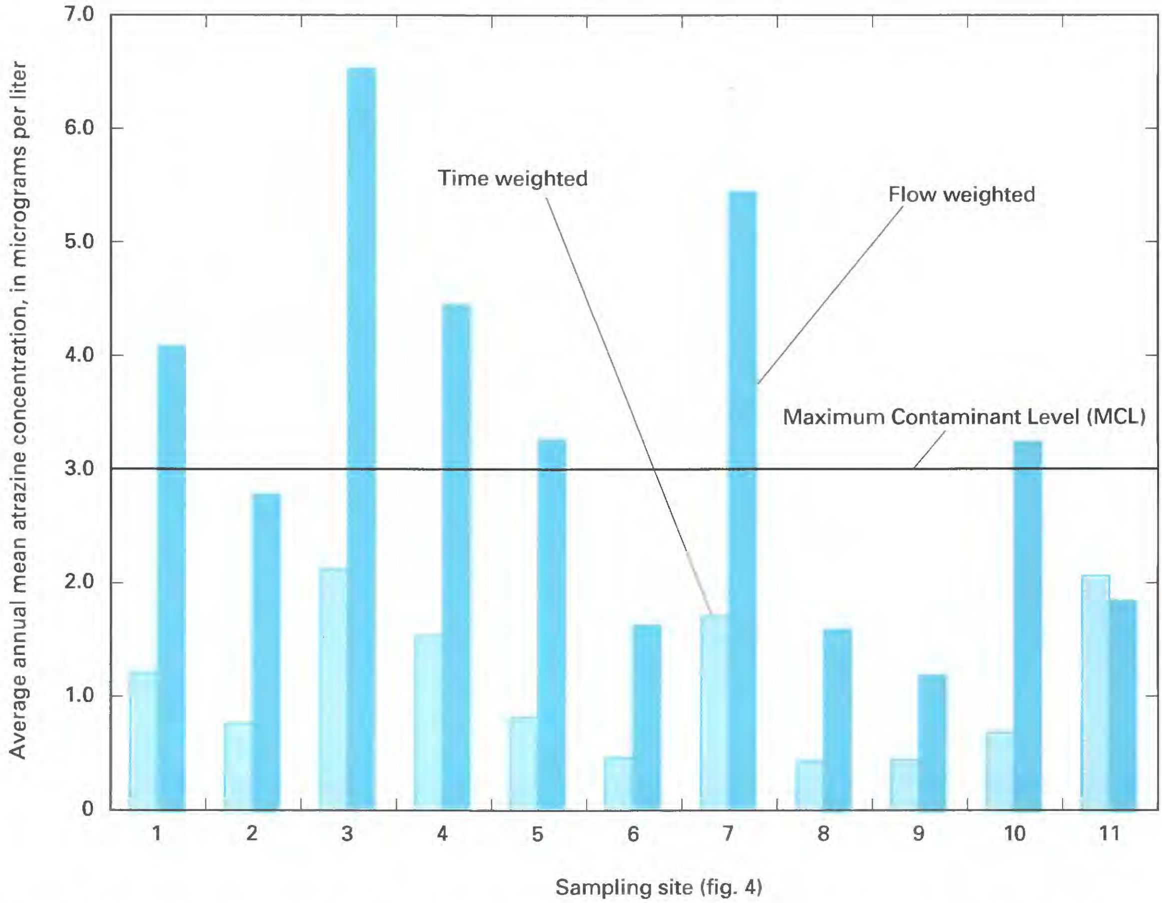


Figure 12. Time- and flow-weighted, average annual mean atrazine concentrations for 1993 and 1994 crop years in water from 11 sampling sites in the Delaware Rvier Basin.

Kansas State Board of Agriculture and U.S. Department of Agriculture (1988–93). Ratios of corn, grain sorghum, soybeans, and wheat areas to total cropland area for the five counties of the Delaware River Basin are given in table 10 for selected years from 1988–93. Generally, corn and grain-sorghum production in the five-county area account for about 44 percent, soybeans 34 percent, and wheat about 22 percent of the total cropland area on a fairly consistent basis.

TRANSPORT OF ATRAZINE

The amount of atrazine transported in a stream is a function of atrazine concentration and volume of water in the stream. A study of herbicide transport in surface water in the Tuttle Creek Lake-stream system of northeast Kansas (Bevans and others, 1995) showed that herbicides with solubilities similar to or greater than that of atrazine are transported in the dissolved phase and do not accumulate in sediment or biota. Therefore, a measure of dissolved atrazine concentration (as provided by ELISA) would provide a reliable estimate for calculation of atrazine load (mass of atrazine). An examination of atrazine loads and yields (load divided by drainage area) is important in determining distributions of atrazine contributions to Perry Lake. Mean atrazine concentrations in Perry Lake are a function of mass of atrazine transported into the lake; therefore, a knowledge of those distributions may help basin planners in directing available resources or educational information to achieve the most positive benefits.

Table 9. Percentages of selected land-use categories for subbasins represented by 11 sampling sites in the Delaware River Basin, 1992

[Percentages from the Data Access and Support Center of the Kansas Geological Survey (Lawrence, Kansas), digital land-use data, 1992]

Land-use category	Sampling site (fig. 4)										
	1	2	3	4	5	6	7	8	9	10	11
Cropland	61	41	65	56	33	23	48	26	32	28	40
Grassland	34	50	31	39	61	69	49	64	63	59	50
Woodland	4	8	2	4	6	7	3	9	4	11	7
Water	0	0	1	0	0	0	0	0	0	1	2
Urban	0	0	1	0	0	1	0	0	0	1	0
Total[1]	99	99	100	99	100	100	100	99	99	100	99

[1]Because of rounding, total may not equal 100.

Table 10. Ratio of individual crop area to total cropland area by county for selected years from 1988–93

[Data from Kansas State Board of Agriculture and U.S. Department of Agriculture, 1988–93]

Crop	Year	County					Total five-county area
		Atchison	Brown	Jackson	Jefferson	Nemaha	
Corn	1988	0.19	0.23	0.10	0.21	0.07	0.16
	1989	.14	.21	.09	.19	.06	.14
	1992	.20	.24	.16	.25	.08	.18
	1993	.22	.24	.15	.26	.09	.19
Grain sorghum	1988	.23	.17	.30	.21	.49	.29
	1989	.31	.18	.31	.25	.48	.30
	1992	.22	.18	.20	.13	.49	.26
	1993	.19	.16	.20	.12	.47	.24
Soybeans	1988	.41	.39	.33	.44	.19	.34
	1989	.35	.37	.22	.34	.16	.29
	1992	.41	.40	.36	.44	.18	.34
	1993	.45	.44	.42	.47	.22	.39
Wheat	1988	.16	.20	.27	.15	.26	.21
	1989	.20	.25	.37	.22	.30	.26
	1992	.17	.19	.28	.18	.24	.21
	1993	.14	.17	.22	.15	.22	.18

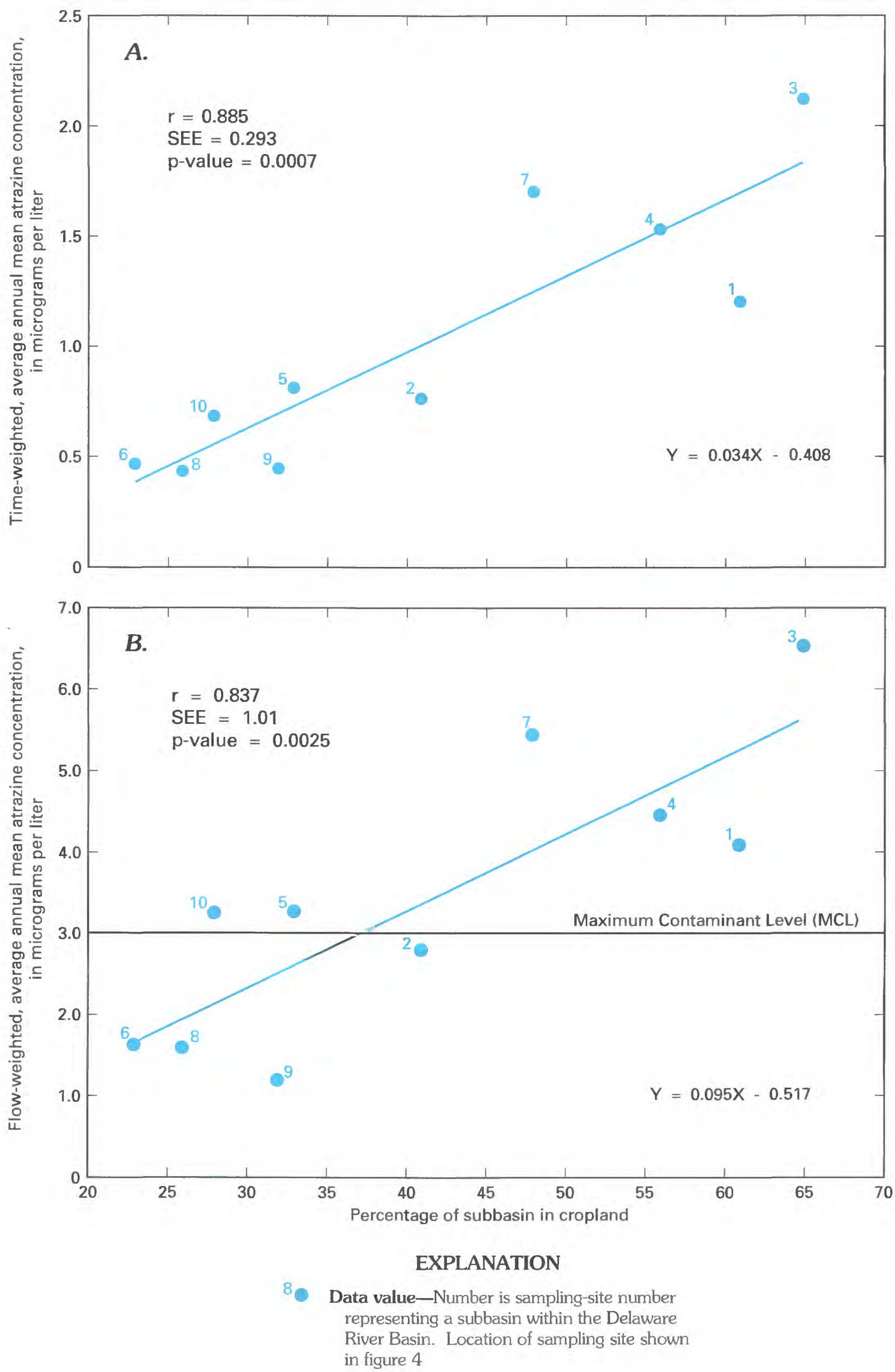


Figure 13. Relations between (*A*) time- and (*B*) flow-weighted, average annual mean atrazine concentrations for 1993 and 1994 crop years and percentages of subbasins in cropland.

Daily loads of atrazine (in pounds) were calculated by multiplying time-weighted, daily mean atrazine concentrations (in micrograms per liter) by daily mean streamflow (in cubic feet per second) and by a unit conversion factor of 0.00538. Estimation of time-weighted, daily mean atrazine concentrations has been discussed previously in this report. Daily mean streamflow at all sampling sites are given in Pope and others (1996, tables 14–24).

Monthly and Annual Atrazine Loads

Monthly and annual atrazine loads were calculated by summing daily loads on a monthly or annual basis. Monthly loads for August 1992 through March 1995 and annual loads for the 1993 and 1994 crop years at 11 sampling sites in the Delaware River Basin are given in table 11.

Atrazine loads are directly related to atrazine concentration and streamflow volume, which means that as concentration and(or) streamflow increase, atrazine loads increase. Monthly or annual variation in either concentration or streamflow will produce variations in atrazine loads. As previously shown (fig. 8), large concentrations and periods of large streamflow generally occur concurrently in northeast Kansas and usually are most pronounced immediately after atrazine application (May–July). As a result, atrazine loads in streams in the Delaware River Basin are typically largest in May, June, and July. For example, figure 14 shows the monthly atrazine load distribution at sampling site 4 for the 1993 and 1994 crop years. Monthly load distribution is highly skewed and temporally restricted to the May through July period on nonregulated streams in northeast Kansas. During this period, which represents 25 percent of the year, 98 percent of the 1993 crop-year annual load was transported, and 91 percent was transported during the same 3 months of the 1994 crop year.

Extreme between-year variations in atrazine loads may occur as a direct result of hydrologic conditions. Figure 14 shows substantial differences in loads between the 1993 and 1994 crop years. These differences reflect the effects of an unusually wet year in 1993 followed by a relatively dry year in 1994 as indicated by deviations from long-term means in monthly streamflow (fig. 2). The most pronounced single monthly loading difference between the 1993 and 1994 crop years occurred in July (fig. 14). The atrazine load in July 1993 was more than seven times larger than the July 1994 load and is the result of major flooding during July 1993 (figs. 2 and 8).

The monthly atrazine load distribution patterns at the outflow of Perry Lake (sampling site 11, fig. 15) are similar to the pattern at sampling site 4 (fig. 14); however, because the outflow of Perry Lake is completely regulated, loads may be more temporally delayed and somewhat more distributed throughout the year relative to nonregulated upstream sites. Atrazine loads for the 1993 crop year were largest in July at sampling site 4 but were largest for August at the outflow of Perry Lake. This difference is due to temporary storage of floodwater in the lake during July 1993 and subsequent release of that water in August (fig. 9). Atrazine load transport for May through July equalled 33 percent of the 1993 crop-year load and 63 percent of the 1994 crop-year load. These outflow loads contrast to 98 and 91 percent of annual loads, respectively, during May through July at sampling site 4.

Skewed, nonrandom distribution of atrazine loads at sampling sites in the Delaware River Basin provide insight into the possible design of sampling programs to monitor loads of agricultural chemicals. The quantification of loads of chemicals in relation to annual application periods requires that monitoring be conducted continually from the time of application through at least July. This should, in most years, ensure an accurate quantification of about 90 percent of the annual load. A monitoring program designed with a limited number of randomly placed samples may not ensure definition during those few flow periods when most of the annual load is transported and may produce results biased extremely high or low depending on when the samples were collected. This becomes more obvious when daily load distribution is examined.

Distribution of daily atrazine loads in Delaware River near Muscotah, Kansas (sampling site 4), is shown in figure 16. Most of the annual transport of atrazine, as previously shown, occurs from May through July, the period immediately following application. Furthermore, a large percentage of the atrazine transported during these months can occur during just a few days. For example, at sampling site 4, the seven largest daily loads in each of the 1993 and 1994 crop years accounted for 45 percent and 67 percent, respectively, of the annual loads. Additionally, short time periods at some of the smaller tributary sites account for even larger percentages of the annual load.

Table 11. Calculated monthly atrazine loads, in pounds and percentage of annual load, for August 1992 through March 1995 and calculated annual loads for the 1993 and 1994 crop years at 11 sampling sites in the Delaware River Basin

Date	Sampling site (fig. 4) 1 Load (pounds)	1 Load (percent of annual load)	2 Load (pounds)	2 Load (percent of annual load)	3 Load (pounds)	3 Load (percent of annual load)	4 Load (pounds)	4 Load (percent of annual load)
1992								
Aug.	14	--	2.9	--	15	--	38	--
Sep.	20	--	13	--	41	--	110	--
Oct.	.61	--	.25	--	1.3	--	3.3	--
Nov.	22	--	8.5	--	26	--	77	--
Dec.	18	--	5.3	--	15	--	54	--
1993								
Jan.	1.4	--	.26	--	2.3	--	4.6	--
Feb.	6.7	--	1.9	--	6.4	--	22	--
Mar.	31	--	10	--	239	--	70	--
Apr.	37	1.5	6.2	0.76	22	1.5	71	1.6
May	280	12	42	5.1	240	16	880	20
June	500	21	240	29	40	2.7	750	17
July	1,600	67	530	65	1,200	80	2,700	61
Aug.	5.3	.22	.40	.049	1.1	.073	8.7	.20
Sep.	9.9	.41	1.6	.20	4.0	.27	22	.50
Oct.	1.7	.071	.27	.033	.90	.060	3.8	.086
Nov.	.84	.035	.11	.013	.83	.055	2.0	.045
Dec.	1.0	.042	.20	.024	1.4	.093	5.1	.12
1994								
Jan.	.22	.009	.055	.007	.57	.038	1.3	.030
Feb.	.11	.005	.035	.004	.42	.028	.75	.017
Mar.	1.2	.050	.32	.039	1.3	.087	2.6	.059
Apr.	33	12	5.8	6.4	18	5.0	69	6.3
May	95	34	54	59	180	50	490	45
June	14	5.0	1.4	1.5	120	33	140	13
July	120	43	24	26	33	9.2	360	33
Aug.	.79	.28	.30	.33	.29	.081	2.9	.26
Sep.	.21	.075	.065	.071	.12	.033	.53	.048
Oct.	12	4.3	1.8	2.0	.33	.092	12	1.1
Nov.	.41	.15	.28	.31	1.3	.36	1.6	.15
Dec.	.94	.34	.52	.57	1.7	.47	2.3	.21
1995								
Jan.	.45	.16	.12	.13	1.5	.42	1.5	.14
Feb.	.18	.064	.023	.025	.50	.14	.62	.056
Mar.	5.8	2.1	2.3	2.5	5.4	1.5	16	1.5
1993 crop year[1]	**2,400**	**102**	**820**	**100**	**1,500**	**101**	**4,400**	**101**
1994 crop year[1]	**280**	**101**	**91**	**99**	**360**	**100**	**1,100**	**101**

Table 11. Calculated monthly atrazine loads, in pounds and percentage of annual load, for August 1992 through March 1995 and calculated annual loads for the 1993 and 1994 crop years at 11 sampling sites in the Delaware River Basin—Continued

Date	Sampling site (fig. 4)							
	5		6		7		8	
	Load (pounds)	Load (percent of annual load)	Load (pounds)	Load (percent of annual load)	Load (pounds)	Load (percent of annual load)	Load (pounds)	Load (percent of annual load)
1992								
Aug.	1.1	--	0.69	--	1.8	--	0.21	--
Sep.	20	--	5.0	--	3.6	--	1.6	--
Oct.	.95	--	.33	--	.13	--	.12	--
Nov.	14	--	7.0	--	4.7	--	1.9	--
Dec.	5.2	--	3.2	--	2.6	--	.96	--
1993								
Jan.	.23	--	.26	--	.41	--	.065	--
Feb.	2.4	--	.64	--	.61	--	.58	--
Mar.	11	--	2.8	--	3.1	--	.34	--
Apr.	8.0	0.90	2.9	0.88	3.6	1.3	1.1	0.50
May	240	27	120	36	70	25	54	25
June	120	13	64	19	12	4.3	23	10
July	520	58	140	42	180	64	140	64
Aug.	.13	.015	.34	.10	.87	.31	.10	.045
Sep.	4.0	.45	6.1	1.8	8.4	3.0	1.3	.59
Oct.	.14	.016	.18	.055	.33	.12	.033	.015
Nov.	.14	.016	.086	.026	.30	.11	.042	.019
Dec.	.42	.047	.16	.048	.60	.21	.034	.015
1994								
Jan.	.048	.005	.035	.011	.10	.036	.019	.009
Feb.	.036	.004	.031	.009	.033	.012	.015	.007
Mar.	.13	.015	.10	.030	.073	.026	.028	.013
Apr.	14	6.1	7.7	5.9	11	9.2	4.7	7.6
May	140	61	73	56	24	20	4.3	6.9
June	18	7.8	34	26	13	11	35	56
July	56	24	15	12	70	58	16	26
Aug.	.10	.043	.47	.36	.36	.30	.23	.37
Sep.	.051	.022	.069	.053	.18	.15	.066	.11
Oct.	.12	.052	.040	.031	.14	.12	.007	.011
Nov.	.14	.061	.098	.075	.20	.17	.020	.032
Dec.	.19	.083	.054	.041	.070	.058	.23	.37
1995								
Jan.	.021	.009	.071	.055	.027	.022	.057	.092
Feb.	.016	.007	.017	.013	.030	.025	.044	.071
Mar.	2.8	1.2	2.50	1.9	.58	.48	1.2	1.9
1993 crop year[1]	**890**	**99**	**330**	**100**	**280**	**98**	**220**	**100**
1994 crop year[1]	**230**	**100**	**130**	**102**	**120**	**100**	**62**	**99**

Table 11. Calculated monthly atrazine loads, in pounds and percentage of annual load, for August 1992 through March 1995 and calculated annual loads for the 1993 and 1994 crop years at 11 sampling sites in the Delaware River Basin—Continued

Date	Sampling site (fig. 4) 9 Load (pounds)	9 Load (percent of annual load)	10 Load (pounds)	10 Load (percent of annual load)	11 Load (pounds)	11 Load (percent of annual load)
1992						
Aug.	0.23	--	0.58	--	730	--
Sep.	1.2	--	.28	--	320	--
Oct.	.012	--	.097	--	11	--
Nov.	1.7	--	7.9	--	530	--
Dec.	1.2	--	8.1	--	910	--
1993						
Jan.	.13	--	2.1	--	85	--
Feb.	.16	--	1.4	--	140	--
Mar.	1.2	--	2.0	--	120	--
Apr.	1.4	1.7	4.9	2.6	280	5.5
May	2.9	3.5	30	16	1,000	20
June	8.4	10	19	10	270	5.3
July	63	77	120	63	420	8.2
Aug.	.23	.28	1.7	.89	2,400	47
Sep.	5.7	7.0	9.4	4.9	51	1.0
Oct.	.34	.41	.64	.34	520	10
Nov.	.094	.11	.18	.095	31	.61
Dec.	.012	.015	.16	.084	73	1.4
1994						
Jan.	.007	.009	.055	.029	33	.65
Feb.	.006	.007	.026	.014	22	.43
Mar.	.009	.011	.097	.051	35	.69
Apr.	1.3	21	37	67	5.3	.56
May	.56	9.0	12	22	130	14
June	3.5	56	1.5	2.7	210	22
July	.70	11	4.1	7.5	260	27
Aug.	.049	.77	.006	.011	17	1.8
Sep.	.000	.000	.005	.009	13	1.4
Oct.	.000	.000	.010	.018	15	1.6
Nov.	.015	.24	.071	.13	13	1.4
Dec.	.040	.64	.057	.10	26	2.7
1995						
Jan.	.002	.032	.19	.35	26	2.7
Feb.	.003	.048	.042	.076	49	5.2
Mar.	.016	.26	.088	.16	190	20
1993 crop year[1]	**82**	**100**	**190**	**98**	**5,100**	**101**
1994 crop year[1]	**6.2**	**99**	**55**	**100**	**950**	**100**

[1]Because of rounding, the annual summation of percentages may not equal 100.

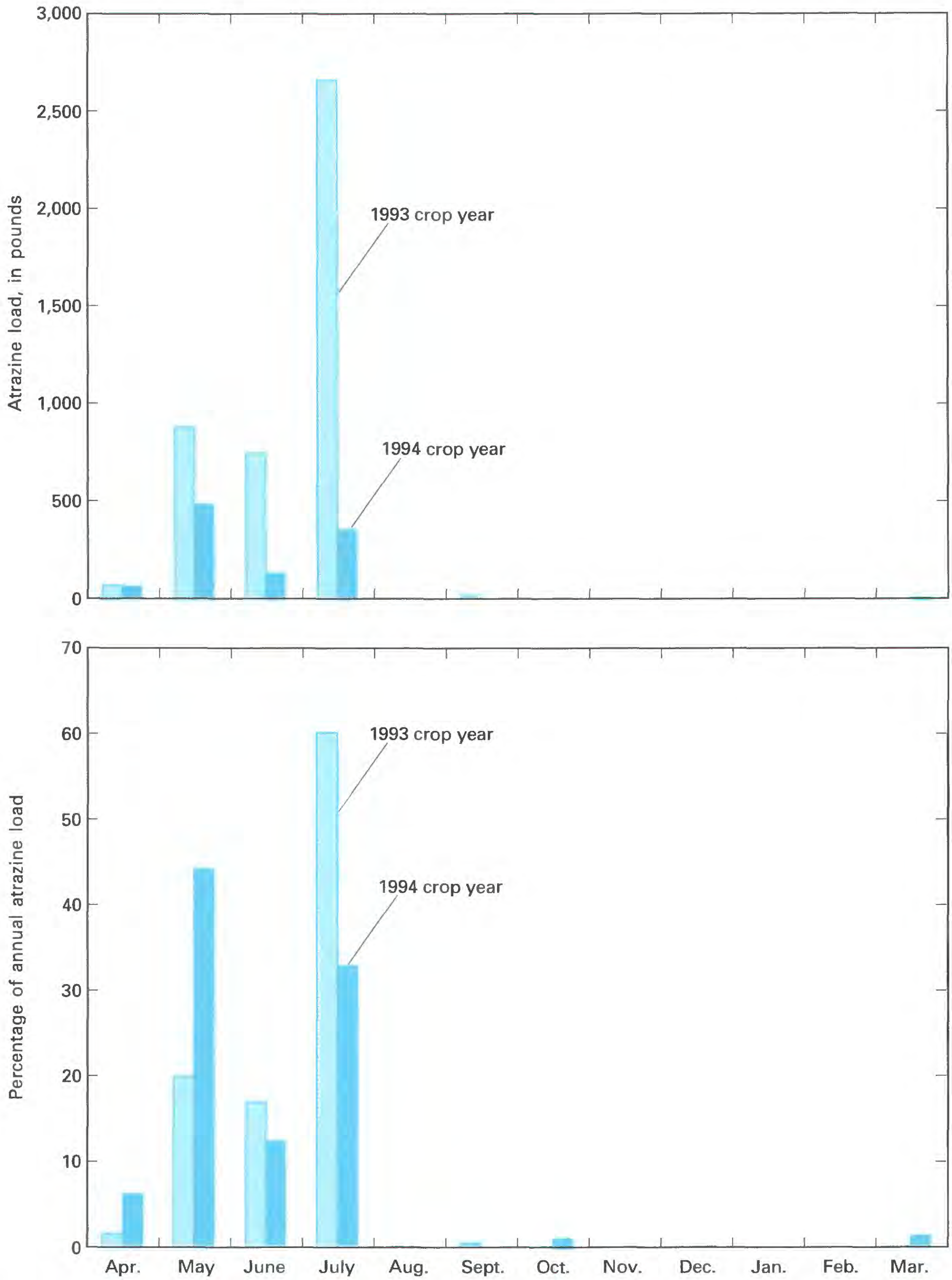


Figure 14. Calculated monthly atrazine load, in pounds and as a percentage of annual load, for Delaware River near Muscotah, Kansas (sampling site 4, fig. 4), for 1993 and 1994 crop years.

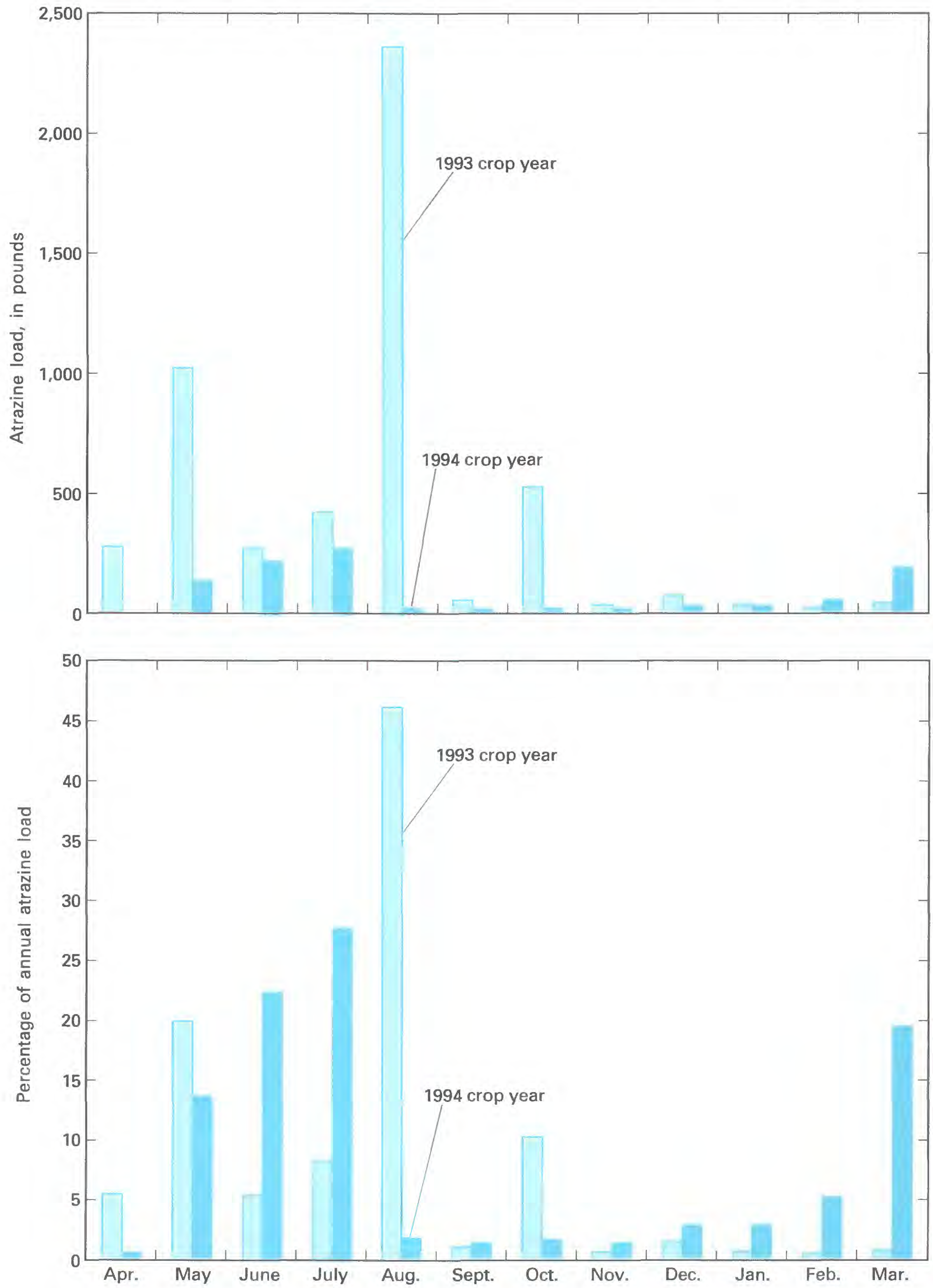


Figure 15. Calculated monthly atrazine load distribution, in pounds and as a percentage of annual load, for Delaware River below Perry Dam, Kansas (sampling site 11, fig. 4), for 1993 and 1994 crop years.

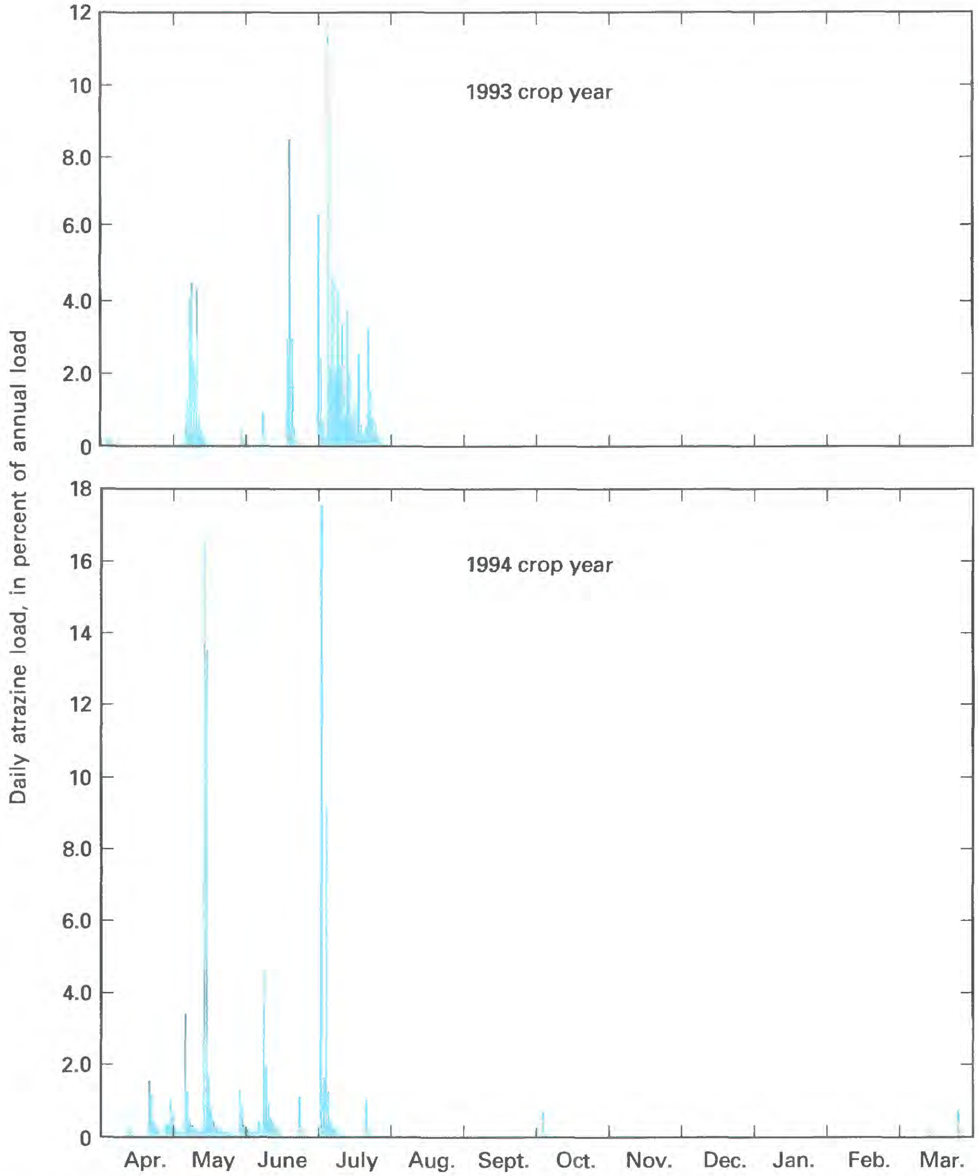


Figure 16. Calculated daily atrazine load as a percentage of annual load for 1993 and 1994 crop years at Delaware River near Muscotah, Kansas (sampling site 4, fig. 4).

The seven largest daily loads in Straight Creek near Muscotah, Kansas (sampling site 5), equalled 53 percent of the 1993 crop-year load and 79 percent of the 1994 crop-year load.

Annual atrazine loads varied considerably between the 1993 and 1994 crop years and among sampling sites (fig. 17). Annual loads during the 1993 crop year were larger than during the 1994 crop year at all sampling sites. The largest relative within-site difference was at sampling site 9 where the annual load of 82 lb during the 1993 crop year was 13 times larger than the 6.2 lb calculated for the 1994 crop year. These differences in annual loads between the 1993 and 1994 crop years are the result of differences in streamflow (runoff) between the 2 years (fig. 2).

Yields and Transport Ratios

Among-site comparisons of atrazine-loading characteristics cannot be made strictly by a comparison of annual atrazine mass (pounds) because of large differences in sampling-site drainage areas and the direct relation between drainage area and streamflow volume. This direct relation gives rise to potentially greater atrazine loads from sampling sites with larger

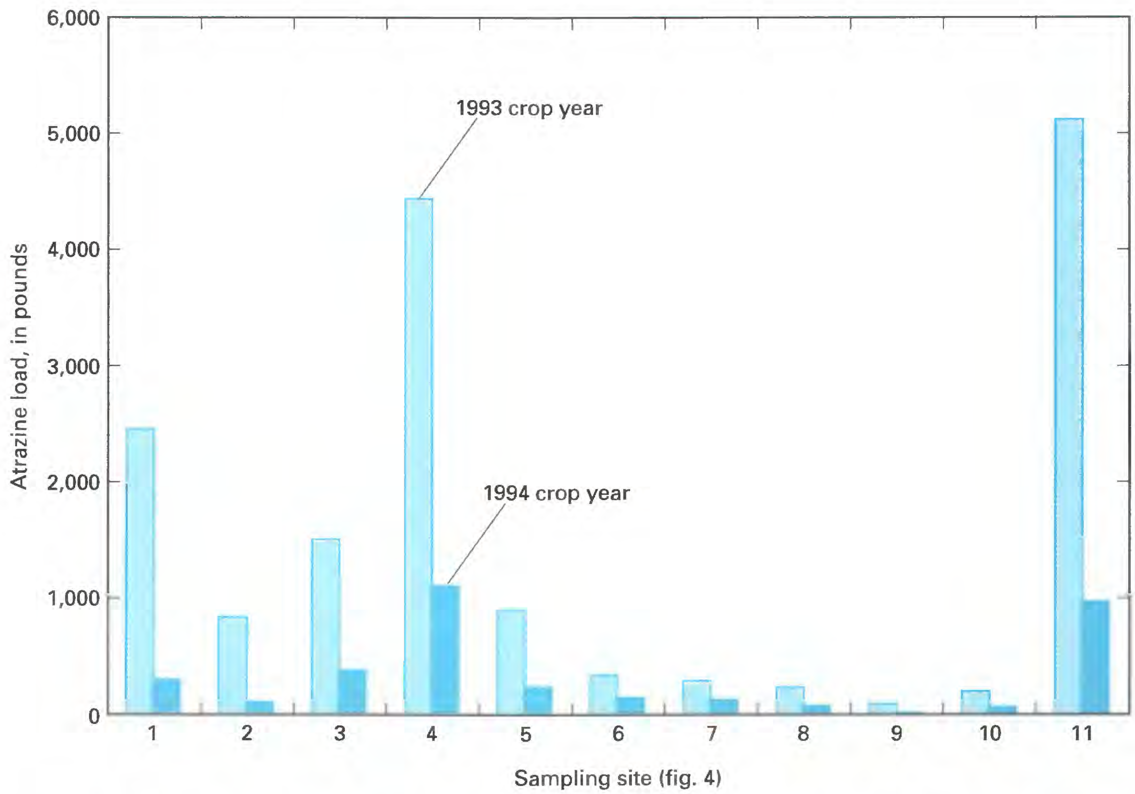


Figure 17. Calculated annual atrazine loads at 11 sampling sites in the Delaware River Basin for 1993 and 1994 crop years.

drainage areas. Therefore, to normalize loads at each site and make direct comparisons possible, annual loads were divided by sampling-site drainage areas. The resulting atrazine yields, in pounds per square mile (lb/mi^2), are presented in table 12 and shown in figure 18.

Atrazine yields were larger during the 1993 crop year than during the 1994 crop year. Yields during the 1993 crop year ranged from 2.4 lb/mi^2 at sampling site 6 to 17 lb/mi^2 at sampling site 1. Yields during the 1994 crop year ranged from 0.29 lb/mi^2 at sampling site 9 to 4.4 lb/mi^2 at sampling site 7. Yields were largest at sampling sites receiving runoff from the northern and northeastern part of the Delaware River Basin (sampling sites 1, 3, 4, and 7) and smallest at those sampling sites in other parts of the basin (sampling sites 6, 8, 9, and 10). These results mirror the results previously discussed in regards to annual atrazine concentrations.

The atrazine yields listed in table 12 for sampling site 11 (outflow of Perry Lake) were calculated from the measured atrazine load at that sampling site but may not represent accurate yields based on total load transported into Perry Lake. Because of the storage capability of Perry Lake, a part of the annual load transported into the lake may be stored there at the end of the crop year (March 31). Therefore, a reasonable estimate of annual atrazine transported from the Delaware River Basin (transported into Perry Lake) must include storage effects.

Annual atrazine transport load from the Delaware River Basin can be estimated by the summation of measured load at sampling site 11 (table 11) plus the difference between estimated atrazine mass in Perry Lake at the end of the crop year (March 31) and the estimated atrazine mass in Perry Lake at the start of the crop year (April 1). Estimates of atrazine mass in Perry Lake were calculated by multiplying the volume (acre-feet) of Perry Lake at either the start or end of the crop year by estimated mean atrazine concentration (micrograms per liter) in the lake and by a unit conversion factor of 0.00272 (table 13). Mean atrazine concentrations in Perry Lake were estimated by averaging concentrations at sampling site 11 (outflow of the lake) from the dates indicated in table 13 to a subsequent date where concentrations started to change substantially as a result of runoff transporting newly applied atrazine.

Table 12. Calculated annual atrazine yields, in pounds per square mile, for the 1993 and 1994 crop years at 11 sampling sites in the Delaware River Basin

Crop year[1]	Sampling site (fig. 4) 1	2	3	4	5	6	7	8	9	10	11
1993	17	8.3	16	10	7.2	2.4	10	3.2	3.8	5.1	4.6
1994	2.0	.92	3.9	2.5	1.9	.94	4.4	.91	.29	1.5	.85
Mean	**9.5**	**4.6**	**10**	**6.2**	**4.6**	**1.7**	**7.2**	**2.1**	**2.0**	**3.3**	**2.7**

[1]Crop year is the 12-month period from April 1 through March 31 and is designated by the calendar year in which it begins.

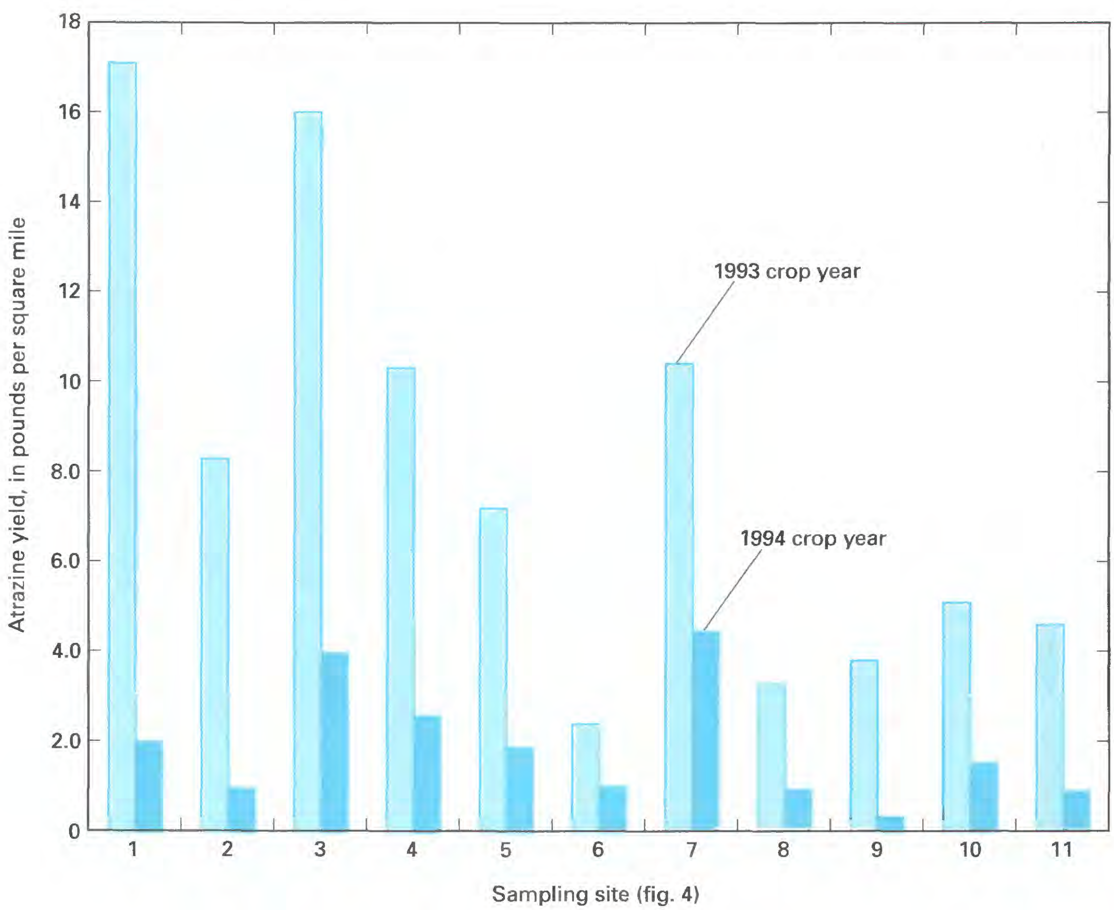


Figure 18. Calculated annual atrazine yields at 11 sampling sites in the Delaware River Basin for 1993 and 1994 crop years.

Table 13. Water-surface elevation, storage, estimated mean atrazine concentration, and mass of atrazine in Perry Lake for selected dates

Date	Water-surface elevation[1] (feet above sea level)	Storage[2] (acre-feet)	Estimated mean atrazine concentration (micrograms per liter)	Estimated atrazine mass (pounds)
April 1, 1993	896.33	269,000	0.60	440
March 31, 1994	891.74	212,000	1.0	580
April 1, 1994	891.75	212,000	1.0	580
March 31, 1995	891.72	212,000	2.7	1,600

[1]From Geiger and others (1994, 1995) or data on file with the U.S. Geological Survey, Lawrence, Kansas.

[2]From U.S. Army Corps of Engineers elevation area-capacity tables for Perry Lake, revised May 1990.

Estimated annual atrazine loads transported from the Delaware River Basin are 5,200 lb [5,100+(580-440)] for the 1993 crop year and 2,000 lb [950+(1,600-580)] for the 1994 crop year. These values, when compared to the measured atrazine loads at sampling site 11 (table 11), indicate that most of the 1993 crop-year annual atrazine load had been transported into and out of Perry Lake by the end of the crop year, whereas during the 1994 crop year, about 50 percent of the annual load was still stored in the lake at the end of the crop year. These differences between crop years reflect differences in hydrologic conditions—a year of near-record floods (1993) compared to a year with less-than-average runoff (1994).

Annual atrazine yields for the Delaware River Basin may be calculated from the estimated annual atrazine loads for the 1993 and 1994 crop years (5,200 and 2,000 lb, respectively) by dividing by drainage area (1,117 mi^2). This produces annual atrazine yields of 4.7 and 1.8 lb/mi^2 for the 1993 and 1994 crop years, respectively. When compared to yields for sampling site 11 (table 12), the 1993 crop-year results are similar, but the 1994 crop-year results are twice as large as presented before lake storage effects were considered. This indicates that in some years much of the annual load of atrazine may be kept in storage in Perry Lake long after the end of the crop year.

The storage effect of atrazine in Perry Lake can have important implications for annual mean atrazine concentrations in the lake when two or more successive years of below-average runoff occur. During years of below-average runoff, atrazine may reside in the lake for many months after being transported there in runoff during May through July. This load-retention effect may increase the mean atrazine concentration in Perry Lake prior to postapplication runoff and the introduction of additional, newly transported atrazine load in subsequent years, thus, compounding the effect.

Atrazine-transport ratio (loss rate) is defined as the amount of atrazine transported relative to the amount applied, expressed as a percentage. The transport ratio for the Delaware River Basin can be estimated subsequent to the following assumptions: (1) the mean percentage (ratio times 100) of cropland devoted to the production of corn and grain sorghum in the Delaware River Basin is the same as the mean for the surrounding five-county area (table 10), and (2) a mean atrazine-application rate can be used for all cropland in corn and grain-sorghum production. The mean percentage of cropland devoted to corn and grain-sorghum production in the surrounding five-county area was about 44 percent in 1992 and 1993 (table 10). Forty percent (285,900 acres) of the Delaware River Basin is cropland (table 9); therefore, 125,800 acres (44 percent) of that is devoted to corn and grain-sorghum production (from assumption 1).

The maximum atrazine-application rate established by PMA voluntary recommendations is 2.25 lb of active ingredient per acre per year. It is believed that 2.25 lb of active ingredient per acre per year is a reasonable estimate of average application rate for the following reasons: (1) the effectiveness of atrazine to inhibit weed development begins to diminish substantially at application rates less than about 2.00 lb/acre, (2) 2.25 lb/acre is 0.25 lb/acre less than the maximum label rate, (3) some producers may inadvertently exceed recommended rates, or (4) producers making both a straight atrazine application and a subsequent premix application may not take into consideration the atrazine that may be included in the premix formulation. However, should the reader of this report believe that 2.25 lb/acre is not a reasonable estimate of average atrazine application, it is a simple calculation to modify the transport ratio.

The atrazine-transport ratio for the Delaware River Basin is the atrazine load transported into Perry Lake divided by the amount applied. The amount applied is equal to the area in corn and grain-sorghum production (125,800 acres) multiplied by the average application rate (2.25 lb/acre). The amount of atrazine applied (283,000 lb) was assumed to be the same for the 1993 and 1994 crop years. The transport ratio was 1.8 percent for the 1993 crop year and 0.7 percent for the 1994 crop year. Differences between these two crop years are hydrologically related, as previously discussed regarding concentrations and loads.

Relation to Land Use

Large variations in annual atrazine yields exist among sampling sites in the Delaware River Basin. Regression analysis was used to determine if percentage of subbasin in cropland could be used to explain this variation. Results of regression analysis relating percentage of subbasins in cropland (table 9) to average annual mean atrazine yields (table 12) at sampling sites 1–10 are presented in figure 19. Sampling site 11 was not used in this analysis for reasons similar to those for not using it in regression analysis relating percentage of cropland to annual mean atrazine concentrations (fig. 13).

Regression results shown in figure 19 indicate a statistically significant relation ($r = 0.957$, p-value = 0.00001) between percentage of subbasin in cropland and atrazine yields based on data from the 1993 and 1994 crop years. The coefficient of determination (r^2), the square of the correlation coefficient, is a measure of the amount of variation in a dependent variable explained by an independent variable. For this relation, the single variable, cropland, explains almost 92 percent (0.957^2) of the variation in annual yields for sites within the Delaware River Basin. Because the relation in figure 19 is direct, the conclusion is made that those subbasins with relatively large percentages of cropland will produce larger annual yields than subbasins with smaller percentages of cropland. This relation is expected to remain valid as long as individual crop ratios (table 10) do not change substantially within the Delaware River Basin. Annual yields were largest at sampling sites receiving runoff from the northern and northeastern parts of the Delaware River Basin (sampling sites 1, 3, 4, and 7).

ADDITIONAL DATA

Most of the ELISA triazine concentrations determined during this study were used to calculate daily mean concentrations for the 1993 and 1994 crop years. However, additional discrete samples were collected at sampling sites 1, 3, 4, 5, 6, 7, and 11 and analyzed by ELISA from April 1 to September 30, 1995, to provide triazine information through the 1995 growing season. These data are presented in Pope and others (1996, table 36). Data for site 11 in Pope and others (1996, table 36) were used to estimate daily mean atrazine concentrations from April 1 to September 30, 1995, as presented in figure 9.

Concentrations of herbicides other than atrazine were determined by GC/MS analysis of 142 samples (Pope and others, 1996, table 37). These concentrations were determined concurrently with GC/MS determinations of atrazine during the development of an atrazine/ELISA triazine relation (figs. 6 and 7). Of the herbicides other than atrazine presented in Pope and others (1996, table 37) the most frequently detected (detection level of 0.05 µg/L) were the degradation products of atrazine, deethylatrazine (133 detections) and deisopropylatrazine (117 detections), followed by metolachlor (112 detections) and alachlor (63 detections). Maximum concentrations of deethylatrazine and deisopropylatrazine were 3.8 and 1.9 µg/L, respectively; however, most concentrations were substantially less than 1.0 µg/L. No Health Advisory Level (HAL) or MCL has been established by the U.S. Environmental Protection Agency (1995) for the atrazine degradation products.

Alachlor and metolachlor both are used in the production of corn and grain sorghum. Alachlor can be used for preplant, postplant, or postemergent weed control up until the corn is about 5 in. tall (Regehr and others, 1994). Metolachlor is used for preplant control of grasses with some control of broadleaf weeds. Unlike atrazine, alachlor and metolachlor also can be used in soybean production. About 34 percent of the

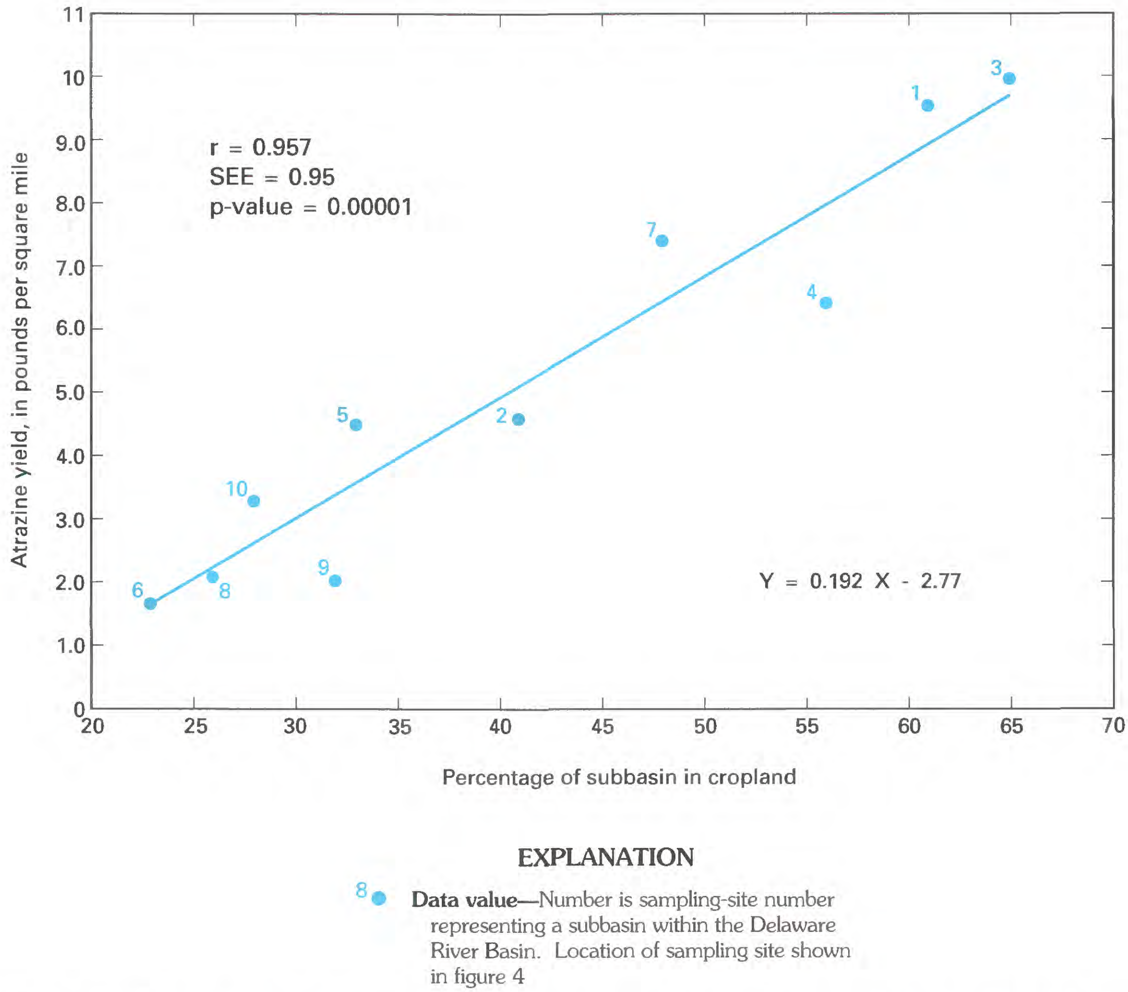


Figure 19. Relation between percentages of subbasins in cropland and average annual mean atrazine yields for 1993 and 1994 crop years at sampling sites 1–10.

crop area in the Delaware River Basin is used for soybean production (table 10).

Concentrations of alachlor and metolachlor generally were less than 1.0 µg/L. Maximum concentrations were 9.4 and 58 µg/L, respectively. The largest concentrations were in samples collected during May and June 1993 at sites receiving runoff from the northern and northeastern parts of the Delaware River Basin. No metolachlor concentration exceeded the 200-µg/L lifetime HAL (U.S. Environmental Protection Agency, 1995); however, 16 alachlor concentrations (11.3 percent) were larger than the 2.0-µg/L MCL.

From January 1993 through December 1994, samples for the determination of biochemical oxygen demand, total suspended solids, selected nutrients, and fecal coliform and fecal streptococcus bacteria were collected manually at all 11 sampling sites in the Delaware River Basin. These samples were collected mostly during low flow and at about 2-week intervals to provide basic water-quality information for the basin. These samples were analyzed at the KDHE laboratory in Topeka, Kansas. Results of these analyses are presented in Pope and others (1996, table 38) in the "Supplemental Information" section of this report.

SUMMARY

Since about 1960, atrazine has been used extensively in the production of corn and grain sorghum in the Midwestern United States. The use of atrazine may pose a potential threat to public-water supplies in areas where it is used intensively because of possible adverse effects on human health and potential toxicity to aquatic life. Because of concerns that some surface-water-supply sources in northeast Kansas may exceed the Maximum Contaminant Level (MCL) established for atrazine in drinking water by the

U.S. Environmental Protection Agency, the Kansas State Board of Agriculture (currently the Kansas Department of Agriculture) conducted a series of hearings concerning the extent of atrazine contamination in northeast Kansas. On the basis of available information which indicated that long-term mean concentrations of atrazine in Perry Lake may exceed the 3.0-µg/L MCL, the Nation's first inland surface-water Pesticide Management Area (PMA) was established in the Delaware River Basin.

A study of the distribution and transport of atrazine in the 1,117 mi^2 Delaware River Basin was conducted by the U.S. Geological Survey in cooperation with the Kansas State Conservation Commission, Kansas State University, and the Kansas Department of Agriculture. Data and results from this study will be used by State and Federal conservation, regulatory, research, and information agencies to: (1) evaluate the perception of a long-term atrazine problem, (2) identify areas where producer-oriented educational activities may be required, (3) evaluate the effectiveness of selected land-management and agricultural practices, and (4) improve the understanding of herbicide transport in areas of similar agriculture and hydrology. The purpose of this report is to present the information necessary to assess the present and possible future changes in the distribution and magnitude of atrazine concentrations, loads, and yields spatially, temporally, and in relation to hydrologic conditions and land-use characteristics.

The Delaware River Basin is an 1,117-mi^2 area located in northeast Kansas. A prominent hydrologic feature of the basin is Perry Lake. Perry Lake is a Federal reservoir with a multipurpose-pool surface area of 11,150 acres and is used for water supply, flood control, and recreational activities. Agriculture accounts for about 85 percent of the land use within the basin, with about 40 percent in crops such as corn, grain sorghum, soybeans, and wheat.

This study, conducted between July 1992 and September 1995, used 11 sampling sites instrumented to record stream stage and to automatically collect stream samples during runoff. These samples were analyzed by enzyme-linked immunosorbent assay (ELISA) for triazine concentrations and subsequently time-weighted to produce daily mean values. Estimates of daily mean atrazine concentrations were calculated from linear-regression relations between ELISA-derived triazine concentrations and atrazine concentrations determined by gas chromatography/mass spectrometry (GC/MS). These relations were based on dual analyses of 141 surface-water samples. Analytical quality assurance included duplicate analyses of selected stream-water samples, analysis of atrazine standard-reference samples, and analysis of blank-water samples.

Daily mean atrazine concentrations in samples from streams in the Delaware River Basin commonly exceeded the 3.0-µg/L MCL during May, June, and July. Daily mean concentrations equal to or greater than 20 µg/L were not uncommon during this period. However, daily mean concentrations greater than the MCL were rare at other times of the year. Most daily mean concentrations were less than 1.0 µg/L from August through April. Daily mean atrazine concentrations in water from Perry Lake were largely affected by the timing and magnitude of inflow.

The largest time-weighted, monthly mean atrazine concentrations in water from the sampling sites upstream of Perry Lake occurred during May, June, and July. In water from most sampling sites, the largest monthly concentrations occurred during June of both the 1993 and 1994 crop years. August through April rarely had monthly mean concentrations greater than 1.0 µg/L, with most months substantially less than 0.50 µg/L. The largest monthly mean concentrations were in water from sites receiving runoff from the northern and northeastern parts of the Delaware River Basin. For example, monthly mean concentrations in water from Grasshopper Creek near Muscotah, Kansas, for June 1993 and 1994 were 5.8 and 11 µg/L, respectively. Corresponding monthly mean concentrations in water from Cedar Creek west of Valley Falls, Kansas, were 1.5 and 2.7 µg/L, respectively. Most monthly mean atrazine concentrations in water from all sites were larger in 1994 than in 1993.

Time-weighted, monthly mean atrazine concentrations in samples from the outflow of Perry Lake showed a somewhat similar seasonal fluctuation pattern to those samples from the 10 upstream sampling sites although larger concentrations were more persistent. For example, during 1994, monthly mean concentrations peaked at 3.3 µg/L in August and did not decrease to less than 3.0 µg/L until February 1995.

Time-weighted, annual mean atrazine concentrations did not exceed the 3.0-µg/L MCL in water from any sampling site for either the 1993 or 1994 crop years; however, concentrations were larger in 1994 than in 1993. Time-weighted, annual mean concentrations in water from the 11 sampling sites during the

1993 crop year ranged from 0.27 to 1.5 µg/L and during the 1994 crop year from 0.36 to 2.8 µg/L. Concentrations in water from the outflow of Perry Lake were larger during the first 6 months of the 1995 crop year than during the same period in 1994. By August 1995, concentrations were greater than 5.0 µg/L. The 1995 crop-year annual mean concentration in water from the outflow of Perry Lake may exceed the MCL unless substantial inflow to the lake dilutes existing concentrations. The largest time-weighted, annual mean atrazine concentrations were in water from sampling sites receiving runoff from the northern and northeastern parts of the Delaware River Basin.

At all sampling sites, except the outflow of Perry Lake, flow-weighted, annual mean atrazine concentrations were considerably larger than time-weighted, annual mean concentrations, and at several upstream sites, the flow-weighted, average annual mean concentration substantially exceeded the MCL. Flow-weighted, annual mean concentrations among the 11 sampling sites during the 1993 crop year ranged from 1.0 to 4.4 µg/L and during the 1994 crop year from 1.0 to 8.9 µg/L.

Statistically significant linear-regression relations (correlation coefficient of 0.837 or better) were identified relating percentage of subbasin in cropland to time- and flow-weighted, average annual mean atrazine concentrations. The relations indicate that time-weighted, average annual mean atrazine concentrations may not exceed the MCL in subbasins with at least about 70-percent cropland. However, flow-weighted, average annual mean atrazine concentrations may exceed the MCL when the percentage of cropland is greater than about 40 percent of the subbasin.

Atrazine loads in streams in the Delaware River Basin typically are largest in May, June, and July. Approximately 90 percent or more of the annual load of atrazine is transported during these 3 months. Annual loads in 1993 were several times larger than loads in 1994 due in large part to a considerably wetter year in 1993, which produced more runoff and associated transport of atrazine.

Atrazine yields were larger during the 1993 crop year than during the 1994 crop year. Yields at the sampling sites upstream of Perry Lake during the 1993 crop year ranged from 2.4 to 17 lb/mi^2 and during the 1994 crop year from 0.29 to 4.4 lb/mi^2. Yields were largest at sampling sites receiving runoff from the northern and northeastern parts of the Delaware River Basin. A statistically significant linear-regression relation (correlation coefficient of 0.957) was identified relating percentage of subbasin in cropland to atrazine yields.

It was estimated that 283,000 lb of atrazine were applied in the Delaware River Basin during each of the 1993 and 1994 crop years. Annual atrazine loads, yields, and transport ratios for the entire Delaware River Basin were estimated for the 1993 and 1994 crop years. Atrazine loads were 5,200 and 2,000 lb, yields were 4.7 and 1.8 lb/mi^2, and transport ratios were 1.8 and 0.7 percent of atrazine applied in the basin, respectively. Differences between the 1993 and 1994 crop years are the result of differences in rainfall amounts and subsequent runoff volumes.

REFERENCES

Baum, E.J., 1991, The advantages of the field-portable enzyme immunoassays: Environmental Lab, On Site News, December/January, 1991/92, unnumbered pages.

Bevans, H.E., Fromm, C.H., and Watkins, S.A., 1995, The occurrence and transport of agricultural pesticides in the Tuttle Creek Lake-stream system, Kansas and Nebraska: U.S. Geological Survey Water-Supply Paper 2419, 34 p.

Blalock, H.M., Jr., 1972, Social statistics: New York, McGraw-Hill Co., 496 p.

Buchanan, T.J., and Somers, W.P., 1976, Discharge measurements at gaging stations: U.S. Geological Survey Techniques of Water-Resources Investigations, book 3, chap. A8, 65 p.

———1978, Stage measurement at gaging stations: U.S. Geological Survey Techniques of Water-Resources Investigations, book 3, chap. A7, 28 p.

Butler, M.K., and Arruda, J.A., 1985, Pesticide monitoring in Kansas surface waters—1973–1984, *in* U.S. Environmental Protection Agency, Perspectives on nonpoint source pollution, Proceedings of a National Conference, May 19–22, 1985: Kansas City, Mo., U.S. Environmental Protection Agency, p. 196–200.

CIBA-GEIGY Corporation, 1992, A review of surface-water monitoring for atrazine in the Chesapeake Bay Watershed (1976–1991): Greensboro, North Carolina, CIBA-GEIGY Corporation, Technical Report 3–92, 3 p.

Dickey, H.P., Zimmerman, J.L., and Rowland, H.T., 1977, Soil survey of Jefferson County, Kansas: U.S. Soil Conservation Service, 67 p.

Eikleberry, R.W., and Templin, E.H., 1960, Soil survey of Brown County, Kansas: U.S. Soil Conservation Service, 32 p.

Fenneman, N.M., 1946, Physical divisions of the United States: Washington, D.C., U.S. Geological Survey special map, 1 sheet, scale 1:7,000,000.

Geiger, C.O., Lacock, D.L., Schneider, D.R., Carlson, M.D., and Dague, B.J., 1994, Water resources data, Kansas, water year 1993: U.S. Geological Survey Water-Data Report KS–93–1, 497 p.

———1995, Water resources data, Kansas, water year 1994: U.S. Geological Survey Water-Data Report KS–94–1, 479 p.

Goolsby, D.A., Thurman, E.M., and Kolpin, D.W., 1990, Geographic and temporal distribution of herbicides in surface waters of the upper Midwestern United States, 1989–90: U.S. Geological Survey Water-Resources Investigations Report 91–4034, p. 86–99.

Hersh, C.M., and Crumpton, W.G., 1987, Determination of growth rate depression of some green algae by atrazine: Bulletin of Environmental Contamination and Toxicology, v. 39, no. 6, p. 1041–1048.

Kansas Geological Survey, 1992, Data Access and Support Center: Lawrence, Kansas, digital data.

Kansas State Board of Agriculture and U.S. Department of Agriculture, 1988–93, Kansas farm facts: Topeka, Kansas (published annually).

Kennedy, E.J., 1983, Computation of continuous records of streamflow: U.S. Geological Survey Techniques of Water-Resources Investigations, book 3, chap. A13, 53 p.

Kettle, W.D., deNoyelles, Frank, Heacock, B.D., and Kadoum, A.M., 1987, Diet and reproductive success of bluegill recovered from experimental ponds treated with atrazine: Bulletin of Environmental Contamination and Toxicology, v. 38, no. 1, p. 47–52.

Kleiner, I.S., and Orton, J.M., 1966, Biochemistry: St. Louis, C.V. Moshy Co., p. 546–547.

Pope, L.M., 1995, Atrazine in surface water and relation to hydrologic conditions within the Delaware River Basin Pesticide Management Area, northeast Kansas, July 1992 through December 1994: U.S. Geological Survey Fact Sheet FS–196–95, 4 p.

Pope, L.M., Brewer, L.D., Foley, G.A., and Morgan, S.C., 1996, Concentrations and transport of atrazine in the Delaware River-Perry Lake system, northeast Kansas, July 1992 through September 1995: U.S. Geological Survey Open-File Report 96–331, 142 p.

Regehr, D.L., Peterson, D.E., Ohlenbusch, P.D., Fick, W.H., Stahlman, P.W., and Kuhlman, D.K., 1994, Chemical weed control for field crops, pastures, rangeland, and noncropland, 1995: Manhattan, Kansas State University, Agricultural Experiment Station, SRP 718, 52 p.

Riggs, H.C., 1968, Some statistical tools in hydrology: U.S. Geological Survey Techniques of Water-Resources Investigations, book 4, chap. A1, 22 p.

Scribner, E.A., Goolsby, D.A., Thurman, E.M., Meyer, M.T., and Pomes, M.L., 1994, Concentrations of selected herbicides, two triazine metabolites, and nutrients in storm runoff from nine stream basins in the Midwestern United States, 1990–92: U.S. Geological Survey Open-File Report 94–396, 144 p.

Stamer, J.K., Gunderson, K.D., and Ryan, B.J., 1994, Atrazine concentrations in the Delaware River, Kansas: U.S. Geological Survey Fact Sheet FS–001–94, 2 p.

Stamer, J.K., and Zelt, R.B., 1994, Organonitrogen herbicides in the lower Kansas River Basin: Journal of American Water Works Association, January 1994, p. 93–104.

Stay, F.S., Katko, A., Rohm, C.M., Fix, M.A., and Larsen, D.P., 1989, Effects of atrazine on microcosms developed from four natural plankton communities: Archives of Environmental Contamination and Toxicology, v. 18, no. 6, p. 866–875.

Thurman, E.M., Goolsby, D.A., Meyer, M.T., and Kolpin, D.W., 1991, Herbicides in surface waters of the midwestern United States—The effects of the spring flush: Environmental Science and Technology, v. 25, p. 1794–1796.

Thurman, E.M., Goolsby, D.A., Meyer, M.T., Mills, M.S., Pomes, M.L., and Kolpin, D.W., 1992, A reconnaissance study of herbicides and their metabolites in surface water of the Midwestern United States using immunoassay and gas chromatography/mass spectrometry: Environmental Science and Technology, v. 26, p. 2440–2447.

Thurman, E.M., Meyer, Michael, Pomes, Michael, Perry, C.A., and Schwab, A.P., 1990, Enzyme-linked immunosorbent assay compared with gas chromatography/mass spectrometry for the determination of triazine herbicides in water: Analytical Chemistry, v. 62, p. 2043–2048.

U. S. Environmental Protection Agency, 1989, Drinking water health advisory—pesticides: Chelsea, Michigan, Lewis Publishers, p. 46.

———1992, Drinking water regulations and health advisories: Washington, D.C., U.S. Environmental Protection Agency, 11 p.

———1995, Drinking water regulations and health advisories: Washington, D.C., U.S. Environmental Protection Agency, 11 p.

U.S. Soil Conservation Service, 1987, National resources inventory: Washington, D.C., U.S. Soil Conservation Service, digital data.