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Nutrients and Organic Compounds in Deer Creek and South Branch Plum Creek in Southwestern Pennsylvania, April 1996 through September 1998

by *Donald R. Williams and Mary E. Clark*

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NATIONAL WATER-QUALITY ASSESSMENT PROGRAM

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FOREWORD

The mission of the U.S. Geological Survey (USGS) is to assess the quantity and quality of the earth resources of the nation and to provide information that will assist resource managers and policy makers at Federal, State, and local levels in making sound decisions. Assessment of water-quality conditions and trends is an important part of this overall mission.

One of the greatest challenges faced by water-resources scientists is acquiring reliable information that will guide the use and protection of the Nation's water resources. That challenge is being addressed by Federal, State, interstate, and local water-resource agencies and by many academic institutions. These organizations are collecting water-quality data for a host of purposes that include: compliance with permits and water-supply standards; development of remediation plans for a specific contamination problem; operational decision on industrial, wastewater, or water-supply facilities; and research on factors that affect water quality. An additional need for water-quality information is to provide a basis on which regional- and national-level policy decisions can be based. Wise decisions must be based on sound information. As a society we need to know whether certain types of water-quality problems are isolated or ubiquitous, whether there are significant differences in conditions among regions, whether the conditions are changing over time, and why these conditions change from place to place and over time. The information can be used to help determine the efficacy of existing water-quality policies and to help analysts determine the need for and likely consequences of new policies.

To address these needs, the Congress appropriated funds in 1986 for the USGS to begin a pilot program in seven project areas to develop and refine the National Water-Quality Assessment (NAWQA) Program. In 1991, the USGS began full implementation of the program. The NAWQA Program builds upon an existing base of water-quality studies of the USGS, as well as those of other Federal, State, and local agencies. The objectives of the NAWQA Program are to:

- Describe current water-quality conditions for a large part of the Nation's freshwater streams, rivers, and aquifers.
- Describe how water quality is changing over time.
- Improve understanding of the primary natural and human factors that affect water-quality conditions.

This information will help support the development and evaluation of management, regulatory, and monitoring decisions by other Federal, State, and local agencies to protect, use, and enhance water resources.

The goals of the NAWQA Program are being achieved through ongoing and proposed investigations of 59 of the Nation's most important river basins and aquifer systems, which are referred to as study units. These study units are distributed throughout the Nation and cover a diversity of hydrogeologic settings. More than two-thirds of the Nation's freshwater use occurs within the 59 study units and more than two-thirds of the people served by public water-supply system live within their boundaries.

National synthesis of data analysis, based on aggregation of comparable information obtained from the study units, is a major component of the program. This effort focuses on selected water-quality topics using nationally consistent information. Comparative studies will explain differences and similarities in observed water-quality conditions among study areas and will identify changes and trends and their causes. The first topics addressed by the national synthesis are pesticides, nutrients, volatile organic compounds, and aquatic biology. Discussions on these and other water-quality topics will be published in periodic summaries of the quality of the Nation's ground and surface water as the information becomes available.

This report is an element of the comprehensive body of information developed as part of the NAWQA Program. The program depends heavily on the advice, cooperation, and information from any Federal, State, interstate, Tribal, and local agencies and the public. The assistance and suggestions of all are greatly appreciated.

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CONVERSION FACTORS AND ABBREVIATIONS

<u>Multiply</u>	<u>By</u>	<u>To obtain</u>
Length		
foot (ft)	0.3048	meter
mile (mi)	1.609	kilometer
Area		
square mile (mi ²)	2.590	square kilometer
acre	0.004047	square kilometer
Volume		
cubic foot (ft ³)	0.02832	cubic meter
Flow (volume per unit time)		
cubic foot per second (ft ³ /s)	0.02832	cubic meter per second
Concentration in water		
milligram per liter (mg/L)	1.0	part per million
microgram per liter (µg/L)	1.0	part per billion
Mass		
pound, avoirdupois (lb)	0.4536	kilogram
ton, short (2,000 lb)	0.9072	megagram
Temperature		
degree Celsius (°C)	°F = 1.8 (°C) + 32	degree Fahrenheit (°F)

Abbreviations

Abbreviation	Definition
<	less than
2,4-D	(2,4-dichlorophenoxy) acetic acid
2,4-DB	4-(2,4-dichlorophenoxy) butyric acid
2,4,5-T	(2,4,5-trichlorophenoxy) acetic acid
2,4,5-TP	(4,5-trichlorophenoxy) propionic acid
ALMN	Allegheny & Monongahela River Basins Study Unit
BDMC	4-Bromo-3,5-dimethylphenyl-n-methylcarbamate
DCPA	dimethyltetrachloroterephthalate
DDE	dichlorodiphenyldichloroethylene
DDT	dichlorodiphenyltrichloroethane
DNOC	4,6-dinitro-o-cresol
E	estimated
EPTC	S-ethyl dipropylthiocarbamate
GC/MS	Gas chromatography/Mass spectrometry
H	herbicide
H ⁺	hydrogen ion
HA	health advisory
HCH	hexachloro-cyclohexane
HPLC	high-performance liquid chromatography
I	insecticide

LRL	laboratory reporting level
MCL	maximum contaminant level
MCPA	(4-chloro-2-methylphenoxy) acetic acid
MCPB	4-(4-chloro-o-tolyloxy) butyric acid
MDL	method detection limit
MTBE	methyl tert-butyl ether
NAE	National Academy of Engineers
NAS	National Academy of Sciences
NAWQA	National Water-Quality Assessment Program
NWQL	National Water Quality Laboratory
SPE	solid-phase extraction
URL	Universal Resource Locator
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
VOC	volatile organic compound

All forms of nutrients discussed in this report represent concentrations as either nitrogen or phosphorus. For example, a nitrate concentration expressed as 10 mg/L refers to a nitrate concentration of 10 mg/L as nitrogen; dissolved orthophosphate concentration expressed as 10 mg/L refers to a dissolved orthophosphate concentration of 10 mg/L as phosphorus.

NUTRIENTS AND ORGANIC COMPOUNDS IN DEER CREEK AND SOUTH BRANCH PLUM CREEK IN SOUTHWESTERN PENNSYLVANIA, APRIL 1996 THROUGH SEPTEMBER 1998

By Donald R. Williams and Mary E. Clark

ABSTRACT

This report presents results of an analysis of nutrient and pesticide data from two surface-water sites and volatile organic compound (VOC) data from one of the sites that are within the Allegheny and Monongahela River Basins study unit of the National Water-Quality Assessment Program of the U.S. Geological Survey. The Deer Creek site was located in a 27.0 square-mile basin within the Allegheny River Basin in Allegheny County. The primary land uses consist of small urban areas, large areas of residential housing, and some agricultural land in the upper part of the basin. The South Branch Plum Creek site was located in a 33.3 square-mile basin within the Allegheny River Basin in Indiana County. The primary land uses throughout this basin are mostly agriculture and forestland.

Water samples for analysis of nutrients were collected monthly and during high-flow events from April 1996 through September 1998. Concentrations of dissolved nitrite, dissolved ammonia plus organic nitrogen, and dissolved phosphorus were less than the method detection limits in more than one-half of the samples collected. The median concentration of dissolved nitrite plus nitrate in South Branch Plum Creek was 0.937 mg/L and 0.597 mg/L in Deer Creek. The median concentration of dissolved orthophosphate was 0.01 mg/L in both streams. High loads of nitrate were measured in both streams from March to June. Concentrations of dissolved ammonia nitrogen, dissolved nitrate, and total phosphorus were lower during the summer months. Measured concentrations of nitrate nitrogen in both streams were well below the U.S. Environmental Protection Agency

(USEPA) maximum contaminant level (MCL) of 10 mg/L.

Water samples for analysis of pesticides were collected throughout 1997 in both streams and during a storm event on August 25–26, 1998 in Deer Creek. Samples were collected monthly at both sites and more frequently during the spring and early summer months to coincide with application of pesticides. Seventy-eight pesticides and 7 pesticide metabolites were analyzed in 31 samples collected in Deer Creek and in 18 samples collected in South Branch Plum Creek. Of the 85 pesticides and pesticide metabolites analyzed, 25 of the pesticides were detected at least once in Deer Creek, and 20 of the pesticides were detected at least once in South Branch Plum Creek. Atrazine was the most commonly detected pesticide in both streams. There was a distinct seasonal pattern of atrazine, simazine, and metolachlor concentrations measured at both sites.

Prometon was detected in 3 of the 18 samples collected in South Branch Plum Creek in 1997 and in 28 of the 31 samples collected in Deer Creek in both 1997 and 1998. Prometon generally is applied in conjunction with asphalt paving projects and is commonly used in residential areas. The highest measured concentrations of prometon detected in Deer Creek were in the five storm samples collected on August 25–26, 1998.

At the Deer Creek site, 9 of the 25 pesticides detected throughout the study were detected only in the sample collected on June 13, 1997. Those nine pesticides included acifluorfen, bentazon, bromoxynil, dicamba, dichlorprop, fenuron, linuron, MCPA, and neburon. Nine other pesticides also were detected in that sample.

All concentrations of pesticides were well below established drinking-water guidelines. The maximum measured concentration of diazinon in Deer Creek (0.097 µg/L) and South Branch Plum Creek (0.974 µg/L) exceeded the aquatic life guideline of 0.009 µg/L established by the National Academy of Sciences/National Academy of Engineers. The maximum measured concentration of azinphos-methyl in South Branch Plum Creek (an estimated value of 0.033 µg/L) exceeded the chronic aquatic-life guideline of 0.01 µg/L established by the USEPA.

Twenty-five samples were collected from Deer Creek and analyzed for volatile organic compounds (VOCs). Of 87 VOCs analyzed for, 22 were detected at least once, and 12 were gasoline-related compounds. Acetone, benzene, carbon disulfide, meta/paraxylene, methyl chloride, MTBE, p-isopropyl toluene, toluene, and 1,2,4-trimethylbenzene were each detected in five or more samples. VOCs generally were detected during the colder winter months and not frequently during the summer months.

The maximum measured concentrations of benzene, ethylbenzene, o-dichlorobenzene, styrene, and toluene were two or more orders of magnitude lower than the MCLs established by the USEPA.

INTRODUCTION

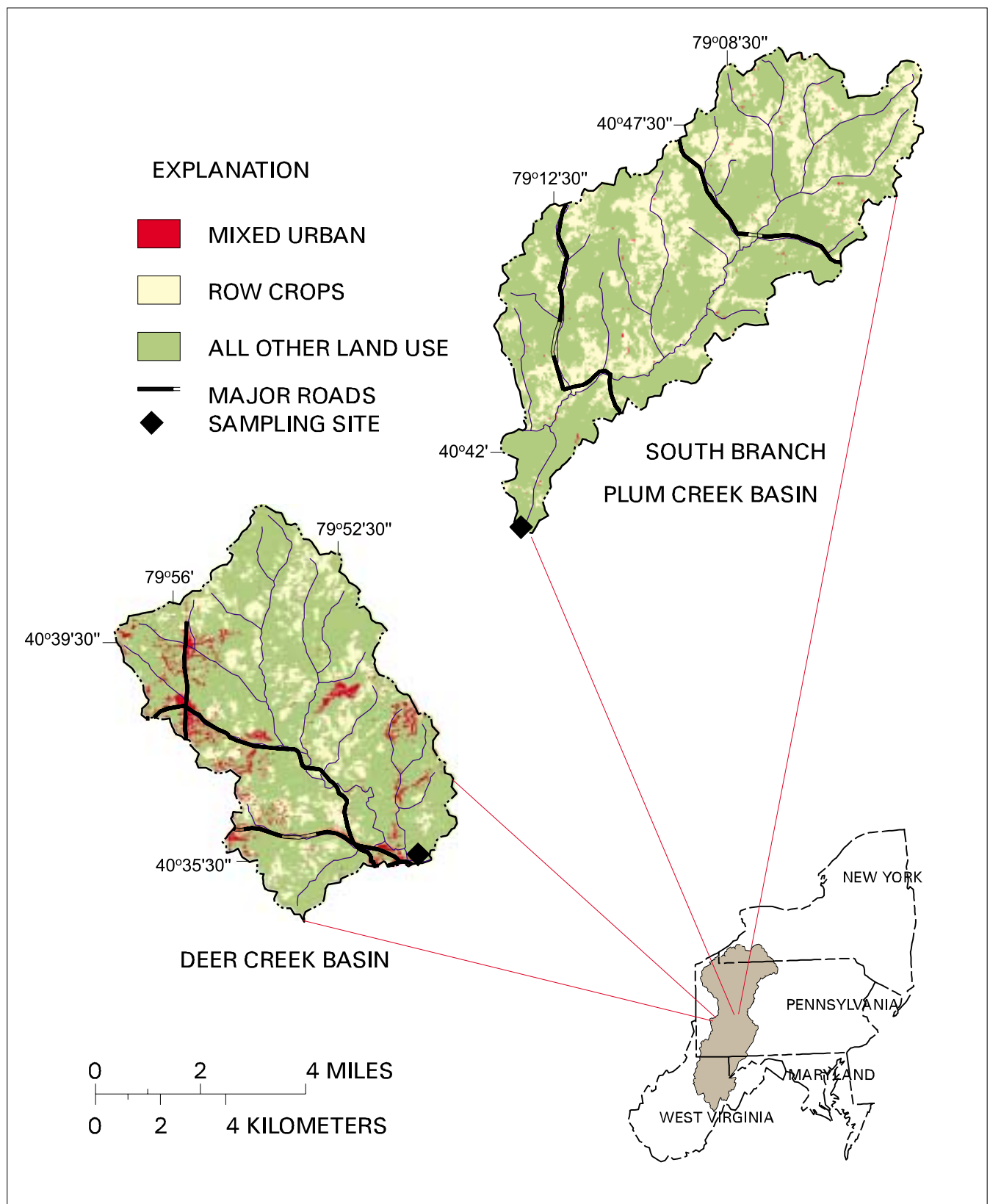
The Allegheny and Monongahela River Basins (ALMN) study unit was one of the second group of 18 study units in which investigations were begun in 1994 as part of the U.S. Geological Survey's (USGS) National Water-Quality Assessment (NAWQA) Program. Historical water-quality data were compiled and analyzed in 1994 and 1995. Intensive water-quality sampling was conducted in 1996–98 at 10 fixed sites established throughout the study unit. Five of the fixed sites are integrator sites that represent water-quality conditions of streams and rivers in heterogeneous large basins commonly affected by complex combinations of land-use settings, point sources, and natural influences. The remaining five sites are indicator sites that

represent water-quality conditions of streams in generally smaller basins with relatively homogeneous land-use settings. The South Branch Plum Creek and Deer Creek sites are indicator sites within the ALMN study unit. Land use in the South Branch Plum Creek Basin is primarily agriculture and forestland, and land use in the Deer Creek Basin is a combination of residential housing, recreational land (golf courses), light industrial, many paved areas, and some agricultural. The drainage areas of these two sites are similar—the South Branch Plum Creek Basin covers an area of 33.3 mi² and the Deer Creek Basin covers an area of 27.0 mi². The location of the two basins and land use within each basin are shown in figure 1.

Although the primary water-quality issue in the ALMN study unit is the effects of coal mining and acidic mine drainage from abandoned coal mines on the surface- and ground-water resources, nutrients and pesticides from agricultural, residential, and commercial areas and volatile organic compounds (VOCs) from residential and commercial areas also are significant concerns. The occurrence and concentration of nutrients, pesticides, and VOCs in ground and surface water and their relation to human and aquatic health criteria are water-quality issues of national and regional interest being addressed by the NAWQA Program.

PURPOSE AND SCOPE

This report presents and compares concentrations and yields of nutrients and concentrations of pesticides in Deer Creek, a stream that drains a predominantly residential basin, and in South Branch Plum Creek, a stream that drains a predominantly agricultural basin. VOC concentrations measured in Deer Creek also are presented. Water samples were collected at Deer Creek near Dorseyville, Pa., and South Branch Plum Creek near Five Points, Pa., for analysis of a broad range of compounds using a sampling strategy designed to characterize seasonal variations and a wide range of streamflow conditions. Effects of residential and agricultural land use on water



Base from U.S. Geological Survey
1:2,000,000 and 1:100,000 Digital Data

Figure 1. Location of Deer Creek and South Branch Plum Creek Basins and land use within the basins.

quality were examined by comparing concentrations and yields between the two sites.

Water samples for analysis of nutrients were collected monthly and during selected high-flow periods from April 1996 through September 1998. The nutrients analyzed included dissolved nitrite plus nitrate, dissolved ammonia, dissolved ammonia plus organic nitrogen, total ammonia plus organic nitrogen, dissolved orthophosphate as phosphorus, dissolved phosphorus, and total phosphorus. For brevity, all forms of nutrients discussed in this report represent concentrations as either nitrogen or phosphorus. For example, a nitrate concentration expressed as 10 mg/L refers to a nitrate concentration of 10 mg/L as nitrogen, and a dissolved phosphorus concentration of 10 mg/L refers to a dissolved phosphorus concentration of 10 mg/L as phosphorus. Pesticide analyses included those for 77 compounds and 7 selected pesticide metabolites. In 1997, samples for analysis of pesticides were collected at least monthly and more frequently during the months of March through June. Samples for analysis of VOCs (87 compounds) were collected at least monthly and bi-weekly during the colder months of 1997 at the Deer Creek site. Intermittent VOC samples were collected in 1998 in Deer Creek. Samples collected throughout a significant storm event at the Deer Creek site on August 25–26, 1998, were analyzed for nutrients, pesticides, VOCs, and major ions.

FIELD AND LABORATORY METHODS

Streamflow measurements were made in accordance with standard USGS procedures (Rantz and others, 1982) and were used to develop stage-discharge relations. Water samples for nutrients and pesticide analyses were collected, processed, and transported according to methods described by Shelton (1994). Water samples for VOC analyses were collected, processed, and transported according to methods also described by Shelton (1997). All field water-quality determinations were performed on the samples by use of protocols

outlined in the National Field Manual for the Collection of Water-Quality Data (Wilde and Radtke, 1998). Samples to be shipped for full laboratory analysis of nutrients and pesticides were processed in the field in a van outfitted as a laboratory. Field processing of nutrient and pesticide samples included sample filtration and preservation and extraction of filtered samples for analysis of pesticides through solid-phase extraction (SPE) cartridges (Zaugg and others, 1995; Werner and others, 1996). Samples for VOC analyses were processed at streamside immediately after sample collection, well away from vehicles, other processing activities, or other potential contamination sources. The processed nutrient, pesticide, and VOC samples were shipped on ice to the USGS National Water Quality Laboratory (NWQL) in Arvada, Colo., where the samples were analyzed. Samples were shipped by priority mail (next day delivery).

Nutrient samples were analyzed according to methods described by Fishman (1993). In October 1997, the NWQL changed the method detection limit (MDL) for dissolved ammonia nitrogen from 0.015 mg/L to 0.02 mg/L. In the data used in this report, no concentrations of dissolved ammonia nitrogen were between the two MDL values; therefore, the current MDL of 0.02 is depicted in all figures except figure 4, as noted. Concentrations of 47 pesticides were determined by C-18 SPE and capillary-column gas chromatography/mass spectrometry (GC/MS). Concentrations of 39 pesticides were determined by Carboapak-B SPE and high-performance liquid chromatography (HPLC). Pesticide samples were analyzed according to methods described by Zaugg and others (1995) and Lindley and others (1996) for GC/MS determinations and Werner and others (1996) for HPLC determinations. VOC samples were analyzed by use of a recently approved method for determination of low concentrations of VOCs in water (Connor and others, 1998). VOC concentrations were determined by purge-and-trap isolation and concentration and capillary-column GC/MS.

QUALITY-CONTROL METHODS AND RESULTS

QUALITY-CONTROL METHODS

In an effort to quantify accuracy, precision, presence of laboratory contamination, and analytical bias, several quality-control (QC) samples were collected during the sampling period. Collection and processing of the sample may introduce potential sources of variability and bias that limit the interpretation of the water-quality data. For nutrient, pesticide, and VOC data, the NAWQA Program recommends the use of a series of field-equipment blanks, replicates, surrogates, and field-matrix spikes to determine data validity. Descriptions of the different quality-control samples and collection procedures are detailed by Mueller and others (1997) for the nutrient and pesticide data and by Shelton (1997) for the VOC data. Solutions of inorganic- or organic-free water that did not contain the analytes of interest at detectable levels were used in preparation of a field blank. A volume of the blank water was poured through all equipment used in sample collection and then processed in the same manner as an environmental sample. Field-equipment blanks are important in establishing the potential bias from contamination of sampling and processing equipment. Replicate samples were prepared by dividing the environmental samples into two equal volumes. Each subsample was then processed as a separate sample. Replicates are designed to determine post-collection precision of values. A surrogate solution was added to every environmental pesticide sample. The surrogate solution contained known concentrations of compounds not expected to be present in the environment but to behave similarly to selected target analytes found in the environment. Data from the surrogates were used to assess recoveries and precision of the analytical method for the targeted analytes. A field-matrix spike containing the series of organic compounds used in the analytical schedule was added to an environmental pesticide replicate. The pesticide sample and the spiked sample were analyzed. Data from the spiked sample were used to determine extraction and elution recov-

eries from the filtered water and to evaluate the accuracy and precision of the results.

In addition to the processing and submission of quality-control samples, the data were reviewed routinely for results that seemed unreasonable on the basis of previous data, anion/cation balance, and statistics.

QUALITY-CONTROL RESULTS

Nutrient Split Replicates

The results of six split replicate samples analyzed for nutrients are presented in table 11 of the appendix. Fifty-eight percent of the analyses showed no difference between the split samples. Relative differences between environmental split samples ranged from 0 to 91 percent. The median relative difference was 0 percent. On the basis of the nutrient QC results, the conclusion was that nutrient concentrations in the environmental samples were of sufficiently high quality to meet the study's objectives of detection of nutrient presence or absence, determination of concentration distribution in time and space, and comparisons to water-quality guidelines.

Pesticide Split Replicates

The results of a split replicate for pesticide compounds analyzed by GC/MS and HPLC methods are presented in table 12. Ninety-one percent of pesticide compounds analyzed by GC/MS analyses showed no difference between the split samples. For the remaining 9 percent, or five compounds, the relative difference ranged from 3 to 33 percent. There was no relative difference between environmental split samples for HPLC analyses. The surrogate recoveries varied in each instance. Relative differences for the surrogate recoveries ranged from 6 to 9 percent. The difference in recoveries suggests that most analytes associated with schedule yield quantitative information.

Pesticide Surrogate Recoveries

The recovery ranges for surrogates added to pesticide samples are shown in figure 15 at the back of this report. Recoveries for all surro-

gates added to the sample for GC/MS analysis were between 70 and 130 percent. Recoveries for the surrogate added to the sample for HPLC analysis were between 60 and 120 percent. Since recoveries for all surrogates used in each method were above 60 percent, the results yield quantitative information.

Pesticide Spikes

At each site, a set of split replicates was spiked for analytes in GC/MS and HPLC methods. The results of these analyses are shown in table 13. Eighty-seven percent of the GC/MS method spike recoveries fell within the expected recovery range of 60 to 140 percent. The median for all GC/MS recoveries was 104 percent. Eighty-two percent of the spike recoveries from the HPLC method fell within the expected recovery range of 60 to 140 percent. The median for all HPLC method recoveries was 78.5 percent.

VOC Blanks

Four blank VOC samples were prepared on four different occasions (table 14 of the appendix). The first blank sample was collected indoors in the equipment storage area. The three other samples were field blanks prepared on site at Deer Creek. The first sample showed low level detections of nine analytes, indicating a potential source of VOCs in the storage area. The sampling equipment was relocated. The second sample showed detections of three analytes with estimated values below the MDL. This indicated the main source of VOCs had been removed. The third sample showed detections of two analytes with estimated values below the MDL. The fourth sample showed no detections of the VOC analytes. Samples collected for VOC analysis prior to March of 1997 may be biased high due to the source of VOCs in the area where equipment was stored during that time.

SOURCES OF NUTRIENTS AND ORGANIC COMPOUNDS

SOURCES OF NUTRIENTS

Nutrients are chemical elements essential to plant and animal nutrition. Nonpoint nutrient sources are a major contributor to nutrients in the hydrologic environment. For example, in the first 20 study units of the NAWQA Program, it was estimated that about 90 percent of nitrogen and 75 percent of phosphorus originated from nonpoint sources; the remaining percentages were from point sources (U.S. Geological Survey, 1999). Combustion of fuels at high temperatures releases nitrogen oxide to the atmosphere. This nitrogen oxide undergoes chemical alterations that produce hydrogen ions and finally nitrate. In addition to nitrate, ammonia nitrogen also is present in precipitation. More than 3 million tons of nitrogen are deposited in the United States each year from the atmosphere (U. S. Geological Survey, 1999). The highest deposition rates of atmospheric nitrogen (greater than 2 tons per square mile) are in a broad band from the upper Midwest through the Northeast. This atmospheric nitrogen is derived either naturally from chemical reactions or from the combustion of fossil fuels, such as coal and gasoline. Nitrogen and phosphorus are affected by chemical and biological processes that change their form and transfer them to or from water, soil, biological organisms, and the atmosphere.

Several compounds of nitrogen and phosphorus can be dissolved in water or they can travel with or attach to sediment particles in water. Nitrogen and phosphorus are only two of the many elements, termed nutrients, required to sustain healthy plant growth. In sufficiently high concentrations, however, these nutrients cause excess biological growth that can adversely affect water quality. Nitrogen is introduced to the aquatic system in the forms of nitrate, ammonia, organic nitrogen, or molecular nitrogen. Rapid transformation between forms of nitrogen occurs through the generation of short-lived intermediate forms.

Nitrite is a primary intermediate form in this process. Although essential for algal and macrophyte growth, nitrite and nitrate in high concentrations can be harmful if consumed by warm-blooded animals. Nitrite reacts with hemoglobin resulting in oxygen-transport impairment. Nitrate can be harmful if converted to nitrite in the gastrointestinal tract.

Some major nonpoint nutrient sources to streams include fertilizers applied to cropland and landscapes, animal wastes, decomposition of organic matter, sewage effluent, atmospheric deposition, and dissolution of phosphorus-bearing minerals. Nitrogen and phosphorus are important macronutrients for crop productivity, commonly added to soil as fertilizer. Although fertilizers have long been considered one of the major sources of nutrient enriched waters, animal feedlots are gaining more attention. Increasing livestock populations in concentrated areas result in a high level of nitrate contribution to the aquatic system. Because the nitrate ion is not strongly bound to soil, it is readily transported through the soil by water.

Phosphorus is a component of sewage and some industrial effluents and is always present in animal metabolic waste (Hem, 1985). Little phosphorus applied as fertilizer leaches from the soil because of its transformation to relatively insoluble hydroxyapatite in alkaline soils.

The primary nutrient source in the surface water of South Branch Plum Creek Basin and Deer Creek Basin is fertilizer. Fertilizers are applied to crops in the South Branch Plum Creek Basin from April through June; applications vary on the basis of crop type and weather. Most agricultural fertilizer is applied prior to or at planting in May and June, and more is applied to corn than to any other crop. In the fall, some fertilizers are applied to pastures and to fields planted to winter wheat. In the Deer Creek Basin, fertilizers are applied to landscaped areas—private lawns, recreational areas, and golf courses—during periods of vigorous plant growth, which generally is from April through June. Frequently, an early fall application also is made on lawns.

SOURCES OF ORGANIC COMPOUNDS

Pesticides are typically synthetic organic compounds introduced into the environment for many purposes. Pesticides commonly are used in agriculture, forestry, transportation (weed control along roadsides and railways), urban and suburban areas (control of pests in homes, buildings, gardens and lawns), lakes and streams (control of aquatic flora and fauna), and various commercial and industrial settings. From a National perspective, agricultural pesticide use provides the greatest potential for contamination of surface waters; nonagricultural uses of pesticides also are substantial, however, and may be the dominant source to surface waters in some areas. Pesticide use in residential and urban areas has undergone major changes over the last several decades. The growth of suburban areas, the rise of the lawn-care industry, the development of new herbicides and insecticides, and the virtual replacement of organochlorine insecticides with alternative compounds have influenced the amounts and types of pesticides applied in residential and urban areas. The atmosphere also can be a significant pesticide source. Nearly every pesticide investigated has been detected in air, rain, snow, and fog across the Nation at different times of the year. Pesticides are widely used in the rural areas in the South Branch Plum Creek Basin and in the urban and suburban areas in the Deer Creek Basin. Pesticide contamination of surface waters is a critical National issue because of the potential toxicity of pesticides to aquatic ecosystems and to humans. However, their potential toxicity is difficult to evaluate because of inadequate information on effects of low-level mixtures, transformation products, and seasonal exposure. The pesticide data collected in South Branch Plum Creek and Deer Creek in the ALMN study unit and in other NAWQA study units throughout the United States may provide information to address some of these unknowns.

VOCs are a class of organic compounds found in virtually all natural and synthetic materials. The production of synthetic organic chemicals (many of which are VOCs) has

increased by more than an order of magnitude between 1945 and 1985 (Ashford and Miller, 1991). VOCs are present in many household items such as deodorants and perfumes, cleaning and polishing products, paints, adhesives, refrigerants, and ink. VOCs also are used as general anesthetics, to decaffeinate coffee, and in the production of pharmaceuticals, pesticides, and fuels. VOCs are present in combustion exhaust and chlorinated drinking water. VOCs are released into the environment during their production, distribution, storage, handling, and use and can enter the surface-water system from many point and nonpoint sources. Some VOC sources in surface waters include industrial and municipal waste-water discharges, urban and residential runoff, precipitation, and accidental spills of crude petroleum and fuel products. VOCs have chemical and physical properties that allow the compounds to move freely between water and air phases of the environment. They generally have low molecular weights, high vapor pressures, and low-to-medium water solubilities (Rathbun, 1998). VOCs can be significant environmental contaminants because many are mobile, persistent, and toxic. The presence of VOCs in surface water is a matter of increasing concern, and many VOCs are the focus of Federal regulations related to water quality (Leahy and Thompson, 1994). The land uses

throughout the Deer Creek Basin, with its residential and urban areas, shopping malls, commercial and light industrial areas, and many miles of roadways and many acres of paved parking areas, provide a potential optimum source of VOCs that can accumulate and eventually be transported into Deer Creek.

NUTRIENTS IN DEER CREEK AND SOUTH BRANCH PLUM CREEK

Water samples for analysis of nutrients were collected at the Deer Creek and South Branch Plum Creek monitoring sites from April 1996 through September 1998. Samples were collected monthly and during high-flow events throughout the sampling period. Samples were analyzed for eight nutrient compounds (table 1).

Results of analyses of the water samples were used to compare nutrient concentrations in streamflow in a basin in which land use is predominantly agriculture and forestland (South Branch Plum Creek) to a mostly suburban basin (Deer Creek) comprising mainly residential housing areas, shopping centers, light industrial companies, golf courses, and some agricultural land in the headwaters. The drainage areas above the monitoring sites were similar in size. Many

Table 1. Nutrients analyzed in water samples collected from Deer Creek and South Branch Plum Creek from April 1996 through September 1998

PARAMETER CODE	COMPOUND NAME	MINIMUM REPORTING LEVEL (MG/L)
00608	Nitrogen, Ammonia, As N, Dissolved	0.01, 0.02
00613	Nitrogen, Nitrite, As N, Dissolved	.01
00623	Nitrogen, Ammonia+organic, As N, Dissolved	.20
00625	Nitrogen, Ammonia+organic, As N, Total	.20
00631	Nitrogen, Nitrate+nitrite, As N, Dissolved	.05
00665	Phosphorus, As P, Total	.01
00666	Phosphorus, As P, Dissolved	.01
00671	Phosphorus, Orthophosphate, As P, Dissolved	.01

factors, both environmental and human, influence the nutrient concentrations. These factors include precipitation, runoff, instream processes, soil types, proximity to the source or sources, and land use.

In this report, nitrate refers to the sum of nitrate plus nitrite, as reported by the USGS laboratory. Nitrite concentrations commonly were less than the laboratory detection level of 0.01 mg/L, making its contribution to nitrate plus nitrite negligible. Laboratory and field data for all samples are published in the annual data reports for the Ohio River and St. Lawrence River Basins (Coll and Siwicki, 1996–98).

CONCENTRATIONS OF NUTRIENTS

Most nutrients fall within comparable ranges for each stream (fig. 2). The range and median concentrations of total phosphorus were similar in both streams. Concentrations of dissolved nitrite, dissolved ammonia plus organic nitrogen, and dissolved phosphorus were less than the MDL in more than one-half the samples collected at each site. Concentrations of the other nutrients sampled were detected more frequently at levels above the detection limit. For example, dissolved nitrate plus nitrite concentrations in South Branch Plum Creek ranged from <0.05 to 2.58 mg/L; the median concentration was 0.937 mg/L. Concentrations in Deer Creek ranged from <0.05 to 1.44 mg/L; the median concentrations was 0.597 mg/L. Concentrations of dissolved ammonia nitrogen in South Branch Plum Creek ranged from <0.015 to 0.079 mg/L and the median was 0.03 mg/L; whereas the range in Deer Creek was <0.015 to 0.138 mg/L and the median was 0.02 mg/L. Dissolved orthophosphate concentrations ranged from <0.01 to 0.031 mg/L and the median was 0.01 mg/L in South Branch Plum Creek; the range was <0.01 to 0.062 mg/L and the median was 0.01 mg/L at Deer Creek. In South Branch Plum Creek, the maximum concentration of dissolved nitrate plus nitrite is twice the maximum concentration measured in Deer Creek, and the median concentration at South

Branch Plum Creek is over one and one-half times the median measured in Deer Creek. Although the maximum concentrations of dissolved ammonia and dissolved orthophosphate in South Branch Plum Creek are approximately twice the level of those measured at Deer Creek, the median concentrations of the two sites are similar.

Concentrations of dissolved ammonia, dissolved nitrate, dissolved orthophosphate, and total phosphorus were examined with relation to streamflow (fig. 3). The concentrations of dissolved nitrate and total phosphorus tend to increase with increasing streamflow. In contrast, concentrations of dissolved orthophosphate and dissolved ammonia show no trend with respect to streamflow, but the concentrations appear to be higher after storm events. The correlation coefficients for these four nutrients are listed in table 2.

SEASONALITY OF NUTRIENTS

Dissolved nitrate concentrations for April 1996 to September 1998 are related to season (fig. 4). The nitrate concentrations are high from March to June in South Branch Plum Creek and Deer Creek. This is most likely because of higher fertilizer applications to crops and lawns and lower algal uptake rates during the growing season, April through September. After a brief low during the late summer months, the nitrate concentration increases. The correlation between nutrient concentrations and growing season is much stronger in Deer Creek than in South Branch Plum Creek (table 3).

The concentrations of dissolved ammonia, dissolved nitrate, and total phosphorus are strongly influenced by season (fig. 4). These constituents tend to have lower concentrations during the summer months. This is likely because of lower fertilizer application rates and runoff rates and increased uptake by algae and aquatic vegetation during this period. In contrast, concentrations of dissolved orthophosphate remained nearly constant throughout the period sampled in South Branch Plum Creek. In midsummer, 1997,

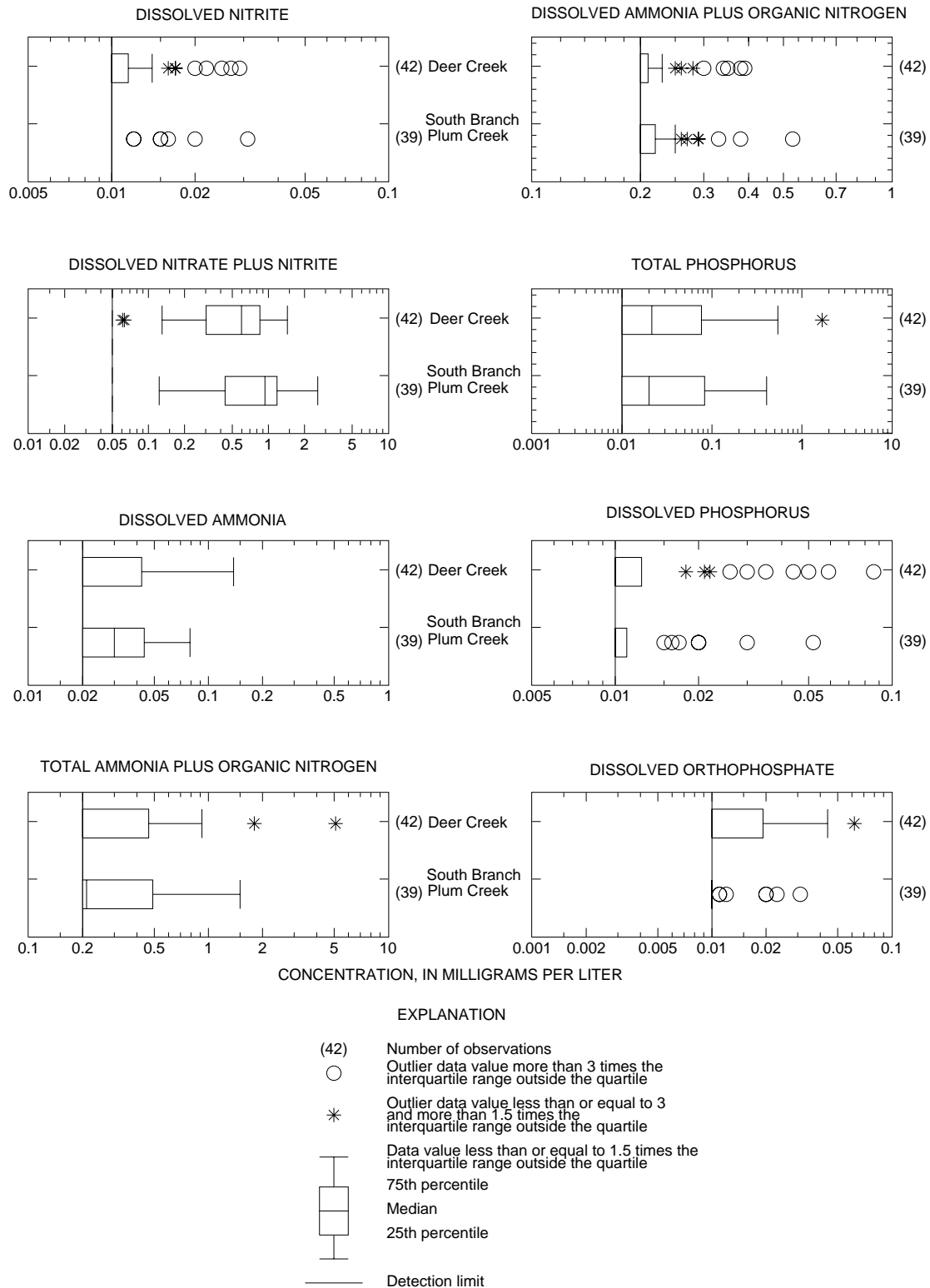


Figure 2. Concentrations of nutrients in Deer Creek and South Branch Plum Creek from April 1996 through September 1998.

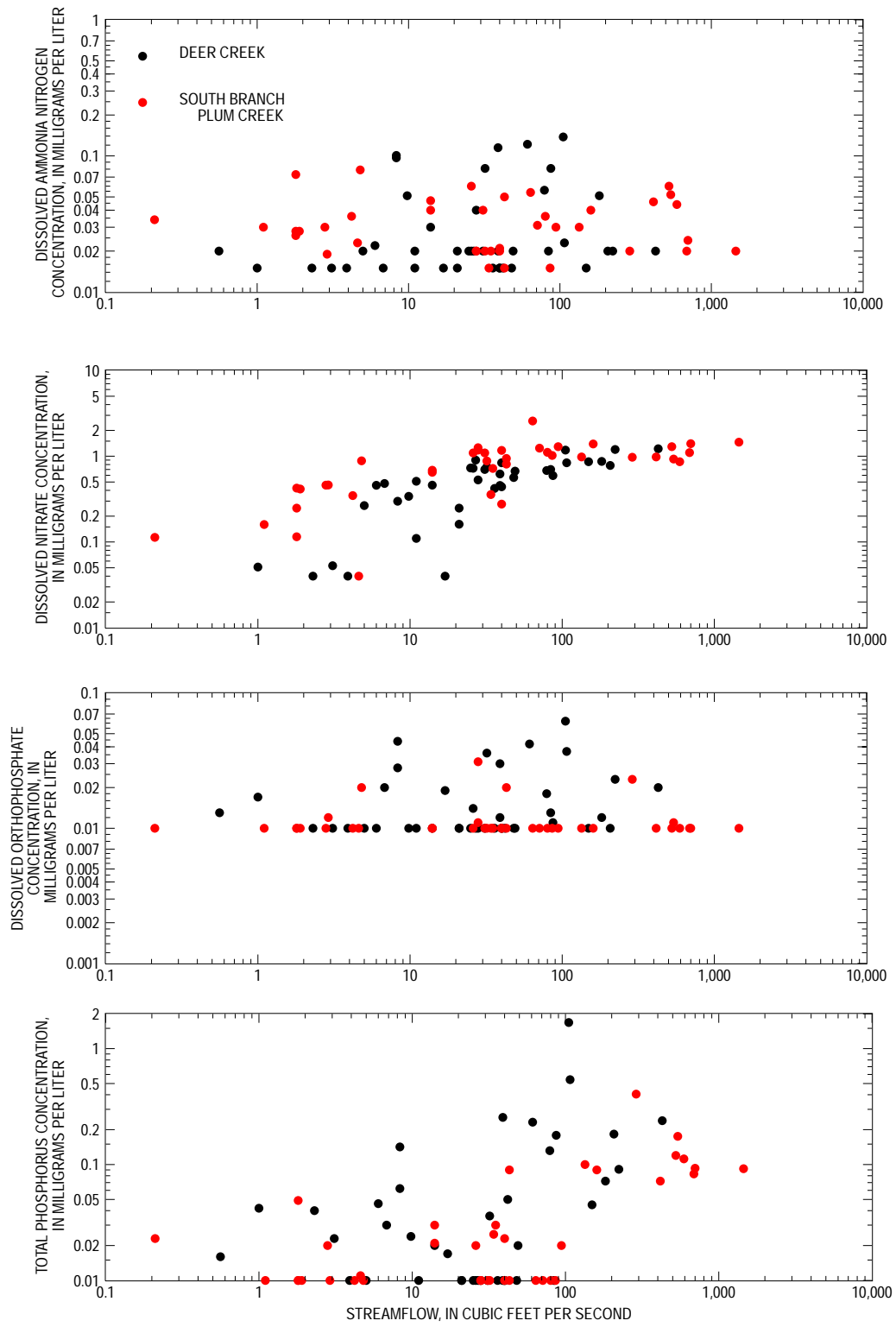


Figure 3. The relation between nutrient concentrations and streamflow at Deer Creek and South Branch Plum Creek, April 1996 through September 1998.

Table 2. Correlation between streamflow and nutrient concentrations in Deer Creek and South Branch Plum Creek

CONSTITUENT	DEER CREEK		SOUTH BRANCH PLUM CREEK	
	CORRELATION	P-VALUE	CORRELATION	P-VALUE
Dissolved ammonia	0.014	0.930	-0.043	0.795
Dissolved nitrate	.579	.000	.375	.019
Dissolved orthophosphate	.140	.378	-.082	.621
Total phosphorus	.259	.098	.454	.004

orthophosphate concentrations at Deer Creek begin to show some seasonality. This may be the result of new residential development in the Deer Creek Basin. Higher concentrations of dissolved ammonia, dissolved nitrate, and total phosphorus seem to be related to fertilizer application periods to agricultural areas, lawns, and landscaped areas upstream of the sampling site in each basin. Storm events during the growing season may be responsible for the variability from the seasonal signature for dissolved nitrate, dissolved ammonia, and total phosphorus.

Water samples for analysis of nutrients were collected in Deer Creek throughout a storm from August 25 to August 26, 1998 (fig. 5). Constituent concentrations generally follow the stream hydrograph. Dissolved ammonia concentrations rise only slightly, peak, and recede in conjunction with the streamflow. The concentrations of total phosphorus and dissolved orthophosphate rise quickly but only decrease slightly as the streamflow recedes. The dissolved nitrate concentrations remain higher than pre-storm levels, even as the streamflow returns to normal conditions. This is possibly due to the dissolution of the nitrate component of the fertilizer. The resulting high nitrate solution in

the topsoil drains to a low spot in the field and then discharges to the stream, rather than draining through the less permeable topsoil and discharging to the ground water.

In order to determine how the two basins respond under similar conditions of streamflow and season, flow was classified into three regimes—normal, low, and high flows—and seasons into growing season and dormant season (fig. 6). Low flow was defined as those streamflows below the 10th percentile, and high flow was defined as those streamflows above the 90th percentile. The growing season was defined as the period from April through September. Statistical significance of the difference in medians was determined by a Wilcoxon Signed-Rank Test on season and a Kruskal-Wallis test on streamflow event with 95-percent confidence level. A p-value equal to or less than 0.05 was considered statistically significant. This breakdown shows median concentrations of dissolved ammonia are slightly higher during the dormant seasons and low flows in the South Branch Plum Creek Basin. In the Deer Creek Basin, median concentrations of dissolved ammonia do not vary on the basis of flow event or season. At both sites, median concentrations of dissolved nitrate are statistically highest during the

Table 3. Correlation between season and nutrient concentrations in Deer Creek and South Branch Plum Creek

CONSTITUENT	DEER CREEK		SOUTH BRANCH PLUM CREEK	
	CORRELATION	P-VALUE	CORRELATION	P-VALUE
Dissolved ammonia	0.545	0.000	0.214	0.191
Dissolved nitrate	.211	.180	.000	1.000
Dissolved orthophosphate	.510	.001	.125	.449
Total phosphorus	.355	.021	.174	.290

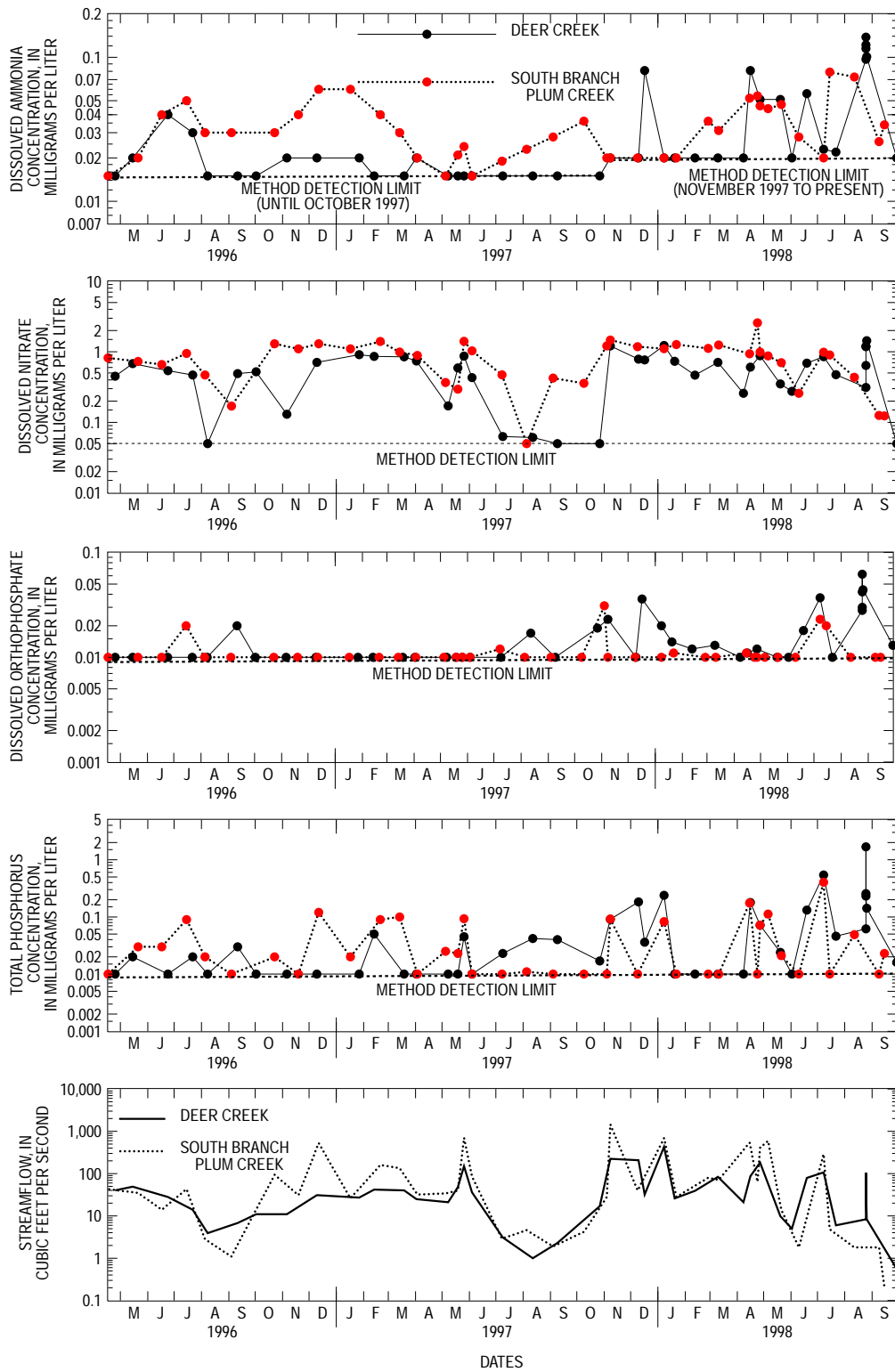


Figure 4. Seasonal variation of nutrient concentrations in Deer Creek and South Branch Plum Creek from April 1996 through September 1998.

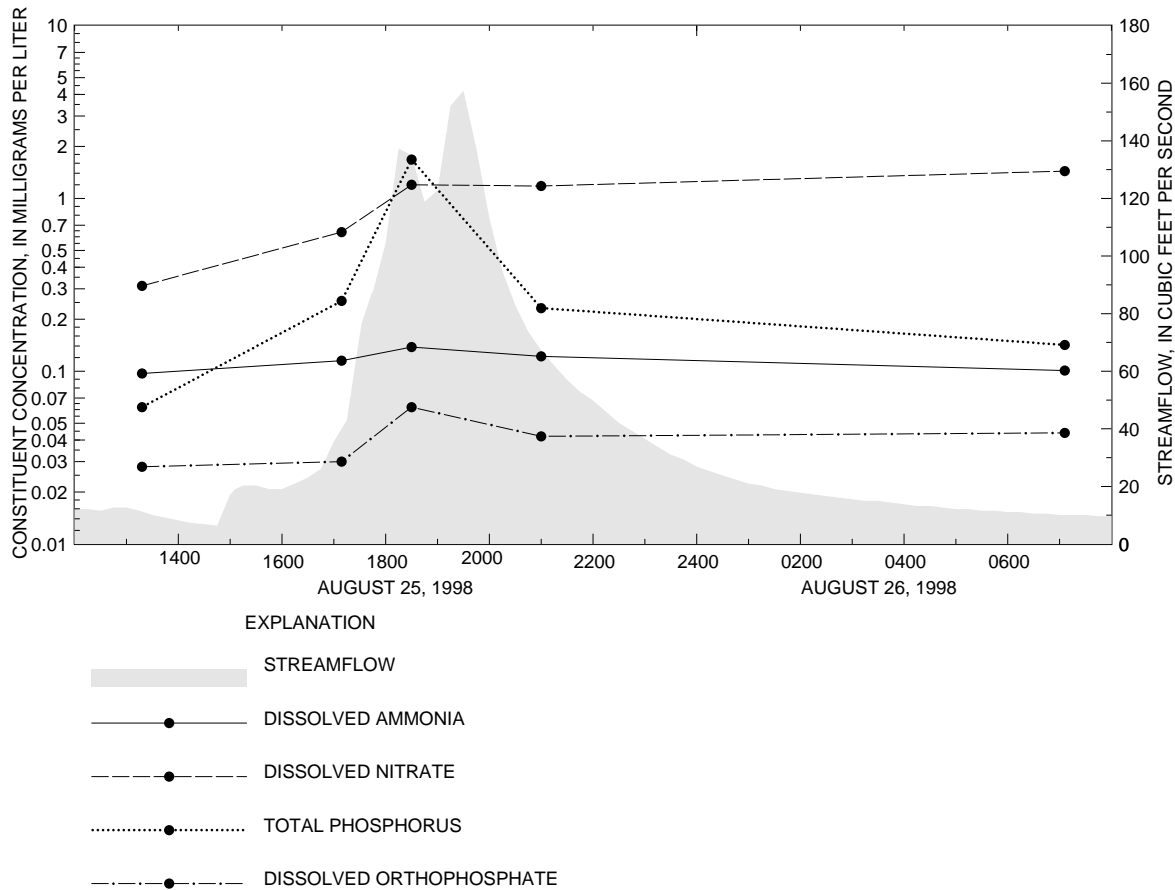


Figure 5. Nutrient concentrations sampled during a storm in Deer Creek on August 25–26, 1998.

dormant season and during high flows. During the growing and dormant seasons and throughout the flow regime, most concentrations of dissolved orthophosphate in South Branch Plum Creek were below the MDL of 0.01 mg/L. Only four samples collected during the growing season and two samples collected during the dormant season had concentrations of dissolved orthophosphate higher than the MDL. In Deer Creek, dissolved orthophosphate concentrations were higher than the MDL of 0.01 mg/L in more than 50 percent of the samples collected, and neither season nor flow event caused statistically significant differences in median concentrations of dissolved orthophosphate. Total phosphorus concentrations in South Branch Plum Creek were consistently lower than those in Deer Creek Basin. At both sites, median concentrations of total phosphorus were slightly but not statistically

higher during the growing season but were significantly higher during high-flow events than during normal or low-flow events.

The application of fertilizers and primary productivity of algae may be the major factors affecting nutrient concentrations. Neither stream receives appreciable inflows of industrial or sewage effluent. Although a few small feedlot operations are present in the South Branch Plum Creek Basin, animal waste is not a major contributor to nutrient concentrations. Total phosphorus concentrations are actually higher in the Deer Creek Basin, where there are no feedlot operations. In both streams, the concentrations of total phosphorus were highest during storm events in the growing season, indicating the possible effect of seasonal application rather than the effects of sewage discharges or feedlot operations.

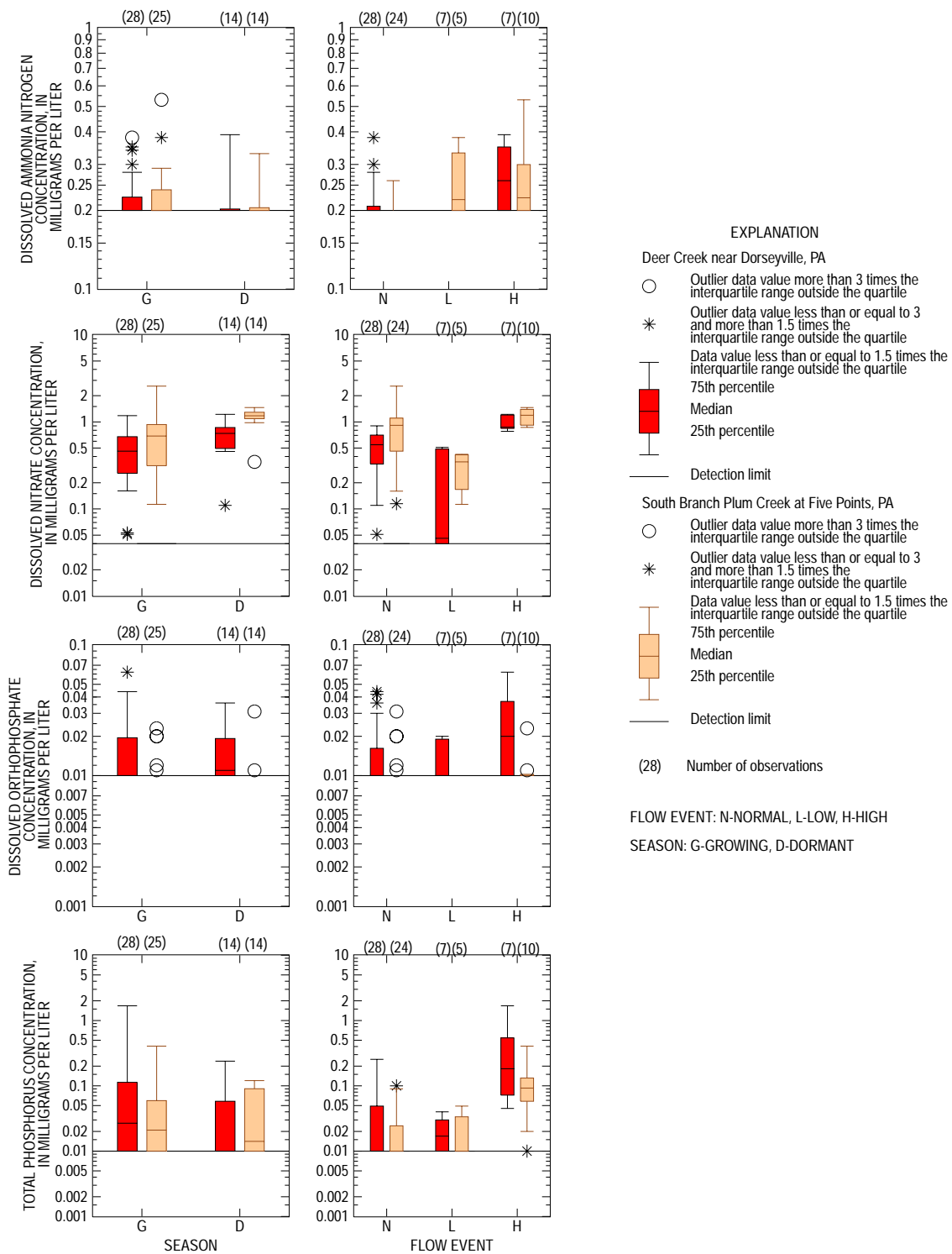


Figure 6. Nutrient concentrations by season (growing and dormant) and flow event (normal, low, or high) in Deer Creek and South Branch Plum Creek.

The U.S. Environmental Protection Agency (USEPA) maximum contaminant level (MCL) for nitrate-nitrogen is 10 mg/L. The recommended level for total phosphorus is 0.1 mg/L (U.S. Environmental Protection Agency, 1986). Concentrations of nitrate and total phosphorus measured in South Branch Plum Creek and Deer Creek were well below these levels.

PESTICIDES IN DEER CREEK AND SOUTH BRANCH PLUM CREEK

Water samples for analysis of pesticides were collected at the Deer Creek and South Branch Plum Creek monitoring sites from January through December 1997 and during a storm at the Deer Creek site on August 25–26, 1998. Samples were collected monthly and more frequently during the spring and early summer months to coincide with pesticide application to crops. At the Deer Creek site, samples were routinely collected once each month in January, February, and September through December, twice each month in July and August, and weekly in March through June. At the South Branch Plum Creek site, samples were routinely collected once each month in January, February, and July through December and twice each month in March through June. The samples were collected to compare pesticide concentrations in streamflow from a basin in which land use is predominantly agriculture and forestland (South Branch Plum Creek) to a basin with land use that is mostly suburban (Deer Creek), mainly residential housing areas, shopping centers, light industrial, golf courses, and some agricultural land. Samples were analyzed for 77 pesticides and 7 pesticide metabolites (table 4). Laboratory analyses and field data for all samples are published in the annual data reports for Pennsylvania for the Ohio River and St. Lawrence River Basins (Coll and Siwicki, 1997–98).

The pesticides targeted for analyses in the Deer Creek and South Branch Plum Creek Basins included herbicides, insecticides, and one fungicide (table 4). Herbicides are used to

control weeds that compete with crops in agricultural areas and home gardens, to control broad-leaf weeds on lawns and turf, and to defoliate utility, railroad, and highway rights-of-way. Herbicides prevent or inhibit the growth of weeds that compete for nutrients and moisture needed by crops and are generally applied before, during, or after planting. Insecticides are used in agricultural, urban, and suburban areas to control insects and to protect the crop seeds in storage prior to planting. Fungicides are used to control the spread of fungal diseases of plants.

Pesticides detected in 25 percent or more of the samples collected in Deer Creek in 1997 included atrazine, deethyl atrazine (metabolite), simazine, prometon, metolachlor, and diazinon. The pesticides detected in 25 percent or more of the samples collected in South Branch Plum Creek in 1997 included atrazine, deethyl atrazine (metabolite), cyanazine, simazine, metolachlor, and tebuthiuron. All frequently detected herbicides are used for weed control and, with the exception of prometon, are used primarily for weed control on corn and other grain crops. Non-agricultural herbicide uses include weed control on golf courses, public lands, homeowner lawns, and vegetation-clearing along railways, highways, and transmission lines. Weed control application frequency for non-agricultural purposes ranges from routine application by commercial operations to sporadic application on an as-needed basis by private homeowners.

COMPARISON OF CONCENTRATIONS AND SEASONALITY

The following comparison of pesticide data collected at the two sites is limited to the six most frequently detected pesticides—atrazine, simazine, cyanazine, prometon, metolachlor, and diazinon. Atrazine, cyanazine, simazine, and prometon are triazine herbicides, and metolachlor is an acetanilide herbicide. Triazine and acetanilide herbicides have been used in the United States since the 1940's, and the amounts used in agriculture have risen dramatically in the last 30 years (Larson and others, 1997, p. 194). Atrazine,

Table 4. Pesticides and pesticide metabolites analyzed in water samples collected from Deer Creek and South Branch Plum Creek, January 1997 through August 1998

[Concentrations are in micrograms per liter; MCL, maximum contaminant level; HA, health advisory; HPLC, high performance liquid chromatography; GC/MS, gas chromatography/mass spectrometry; - -, no standard or guideline]

PESTICIDE	TRADE NAME(S)	ANALYSIS METHOD	METHOD DETECTION LIMIT	STANDARD OR GUIDELINE FOR DRINKING WATER (MCL OR HA)	GUIDELINE FOR AQUATIC LIFE
Herbicides					
Acetochlor	Acetochlor and many other names	GC/MS	0.002	--	--
Acifluorfen	Blazer, Tackle	HPLC	.035	--	--
Alachlor	Lasso	GC/MS	.002	¹ 2	--
Atrazine	AAtrex	GC/MC	.001	13	² 2
Benfluralin	Balan, Benefin	GC/MC	.002	--	--
Bentazon	Basagran	HPLC	.014	20	--
Bromacil	Bromax 90, Urox B	HPLC	.035	90	--
Bromoxynil	Buctril, Brominal	HPLC	.035	--	² 5
Butylate	Sutan +	GC/MS	.002	350	--
Chloramben	Amiben	HPLC	.011	100	--
Clopyralid	Lontrel	HPLC	.050	--	--
Cyanazine	Bladex	GC/MS	.004	1	² 2
2,4-D	2,4-D and many other names	HPLC	.035	¹ 70	³ 3
2,4-DB	Butoxone	HPLC	.035	--	--
Dacthal, mono acid	Dacthal, mono acid	HPLC	.017	--	--
DCPA	Dacthal	GC/MS	.002	4,000	--
Deethyl atrazine	metabolite of atrazine	GC/MS	.002	--	--
Dicamba	Banvel	HPLC	.035	200	³ 200
Dichlobenil	Casoron	HPLC	.020	--	³ 37
Dichlorprop	2,4-DP	HPLC	.032	--	--
2,6-Diethylalanine	metabolite of alachlor	GC/MS	.003	--	--
Dinoseb	Basanite and many other names	HPLC	.035	¹ 7	--
Diuron	Diurex and many other names	HPLC	.020	10	³ 1.6
EPTC	Eptam	GC/MS	.002	--	--
Ethalfuralin	Sonalan	GC/MS	.004	--	--
Fenuron	Beet-Kleen	HPLC	.013	--	--
Fluometuron	Cotoran	HPLC	.035	90	--
Liuron	Lorox	GC/MS	.002	--	--
MCPA	MCPA and many other names	HPLC	.050	10	--
MCPB	Thistrol	HPLC	.035	--	--
Metolachlor	Dual	GC/MS	.002	100	² 8
Metribuzin	Lexone, Sencor	GC/MS	.004	200	² 1
Molinate	Ordram	GC/MS	.004	--	--
Napropamide	Devrinol	GC/MS	.003	--	--
Neburon	Neburex, Neburon	HPLC	.015	--	--
Norflurazon	Evital, Zorial	HPLC	.024	--	--

Table 4. Pesticides and pesticide metabolites analyzed in water samples collected from Deer Creek and South Branch Plum Creek, January 1997 through August 1998—Continued

[Concentrations are in micrograms per liter; MCL, maximum contaminant level; HA, health advisory; HPLC, high performance liquid chromatography; GC/MS, gas chromatography/mass spectrometry; - -, no standard or guideline]

PESTICIDE	TRADE NAME(S)	ANALYSIS METHOD	METHOD DETECTION LIMIT	STANDARD OR GUIDELINE FOR DRINKING WATER (MCL OR HA)	GUIDELINE FOR AQUATIC LIFE
Herbicides-Continued					
Oryzalin	Surflan	HPLC	0.019	--	--
Pebulate	Tillam	GC/MS	.004	--	--
Pendimethalin	Prowl	GC/MS	.004	--	--
Picloram	Tordon	HPLC	.050	¹ 500	--
Prometon	Pramitol	GC/MS	.018	100	--
Pronamide	Kerb	GC/MS	.003	50	--
Propachlor	Ramrod	GC/MS	.007	90	--
Propanil	Stampede	GC/MS	.004	--	--
Propham	IPC	HPLC	.035	100	--
Simazine	Princep, Aquazine	GC/MS	.005	¹ 4	³ 10
2,4,5-T	Line Rider and many other names	HPLC	.035	70	--
2,4,5-TP	Silvex	HPLC	.021	¹ 50	³ 1.4
Tebuthiuron	Spike, Graslan	GC/MS	.010	500	--
Terbacil	Sinbar	GC/MS	.007	90	--
Thiobencarb	Bolero	GC/MS	.002	--	--
Triallate	Far-Go	GC/MS	.001	--	² .24
Triclopyr	Garlon	HPLC	.050	--	--
Trifluralin	Treflan and several other names	GC/MS	.002	5	² .10
Insecticides					
Aldicarb	Temik	HPLC	.016	¹ 3	--
Aldicarb sulfone	metabolite of aldicarb	HPLC	.016	¹ 2	--
Aldicarb sulfoxide	metabolite of aldicarb	HPLC	.021	¹ 4	--
Azinphos-methyl	Guthion	GC/MS	.001	--	⁴ .01
Carbaryl	Sevin	GC/MS	.003	700	³ .02
Carbofuran	Furadan	GC/MS	.003	¹ 40	² 1.75
Chlorpyrifos	Dursban, Lorsban	GC/MS	.004	20	⁵ .08
<i>p,p'</i> -DDE	metabolite of DDT	GC/MS	.006	--	--
Diazinon	Diazinon and many other names	GC/MS	.002	.6	³ .009
Dieldrin	Panoram D-31	GC/MS	.001	--	⁵ .36
Disulfoton	Disyston and several other names	GC/MS	.017	.3	³ .05
DNOC	Sinox and several other names	HPLC	.035	--	--
Esfenvalerate	Asana	HPLC	.019	--	--
Ethoprop	Mocap	GC/MS	.003	--	--
Fonofos	Dyfonate	GC/MS	.003	10	--
<i>alpha</i> -BHC	Lindane (impurity)	GC/MS	.002	--	--
Lindane	<i>gamma</i> -HCH	GC/MS	.004	¹ .2	⁵ 2.0

Table 4. Pesticides and pesticide metabolites analyzed in water samples collected from Deer Creek and South Branch Plum Creek, January 1997 through August 1998—Continued

[Concentrations are in micrograms per liter; MCL, maximum contaminant level; HA, health advisory; HPLC, high performance liquid chromatography; GC/MS, gas chromatography/mass spectrometry; - -, no standard or guideline]

PESTICIDE	TRADE NAME(S)	ANALYSIS METHOD	METHOD DETECTION LIMIT	STANDARD OR GUIDELINE FOR DRINKING WATER (MCL OR HA)	GUIDELINE FOR AQUATIC LIFE
Insecticides-Continued					
Malathion	Malathion and many other names	GC/MS	0.005	200	⁴ 0.1
Methiocarb	Mesurol	HPLC	.026	--	--
Methomyl	Lannate and several other names	HPLC	.017	200	--
Methyl parathion	Penncap-M	GC/MS	.006	2	⁴ --
1-Naphthol	metabolite of carbaryl	HPLC	.007	--	--
3-OH-carbofuran	metabolite of carbofuran	HPLC	.014	--	--
Oxamyl	Vydate	HPLC	.018	¹ 200	--
Parathion	Alkron and many other names	GC/MS	.004	--	⁵ .065
<i>cis</i> -Permethrin	Ambush, Pounce	GC/MS	.005	--	--
Phorate	Thimet and several other names	GC/MS	.002	--	--
Propargite	Comite, Omite	GC/MS	.013	--	--
Propoxur	Baygon	HPLC	.035	3	--
Terbufos	Counter	GC/MS	.013	0.9	--
Fungicide					
Chlorothalonil	Bravo	HPLC	.035	--	--

¹Value is the U.S. Environmental Protection Agency (USEPA) maximum contaminant level for drinking water; other values are USEPA lifetime health advisories for a 70-kilogram adult (Nowell and Resek, 1994).

²Canadian Government aquatic-life guidelines (Canadian Council of Resource and Environment Ministers, 1987; updates 1989–91, 1993).

³National Academy of Sciences and National Academy of Engineering aquatic-life guidelines, 1973 (Nowell and Resek, 1994).

⁴U.S. Environmental Protection Agency chronic aquatic-life guidelines (Nowell and Resek, 1994).

⁵U.S. Environmental Protection Agency acute aquatic-life guidelines (Nowell and Resek, 1994).

cyanazine, and simazine are commonly used triazines and are used primarily on corn and other row crops. Atrazine is one of the most studied and most commonly detected herbicides in the hydrologic environment (Larson and others, 1999). Prometon is a triazine herbicide used for total vegetative control on industrial sites, on noncrop areas, and in and under asphalt. The principal mode of action for triazine herbicides is to disrupt the light reaction of photosynthesis. Metolachlor is one of the most commonly used acetanilides. It is a selective herbicide used primarily for pre-emergent and preplant weed control in corn, soybeans, alfalfa, and sorghum. Diazinon is an organophosphorus insecticide and is one of the more commonly used insecticides in urban and resi-

dential areas throughout the United States. Common household uses include insect control on fruits, vegetables, and ornamentals, grub and nematode control in turf soils, and control of cockroaches, silverfish, and ants. The variation in concentrations of the six selected pesticides at the two sites during 1997 is shown in figure 7. The simazine and prometon concentrations that plotted below the MDL are estimated (Zaugg and others, 1995; Werner and others, 1996). All estimated data are believed to be reliable detections but with greater than average uncertainty in quantification.

Land use is an important environmental factor that affects the magnitude of pesticide concentrations in streams. Land use is primarily agriculture and forestland in the South

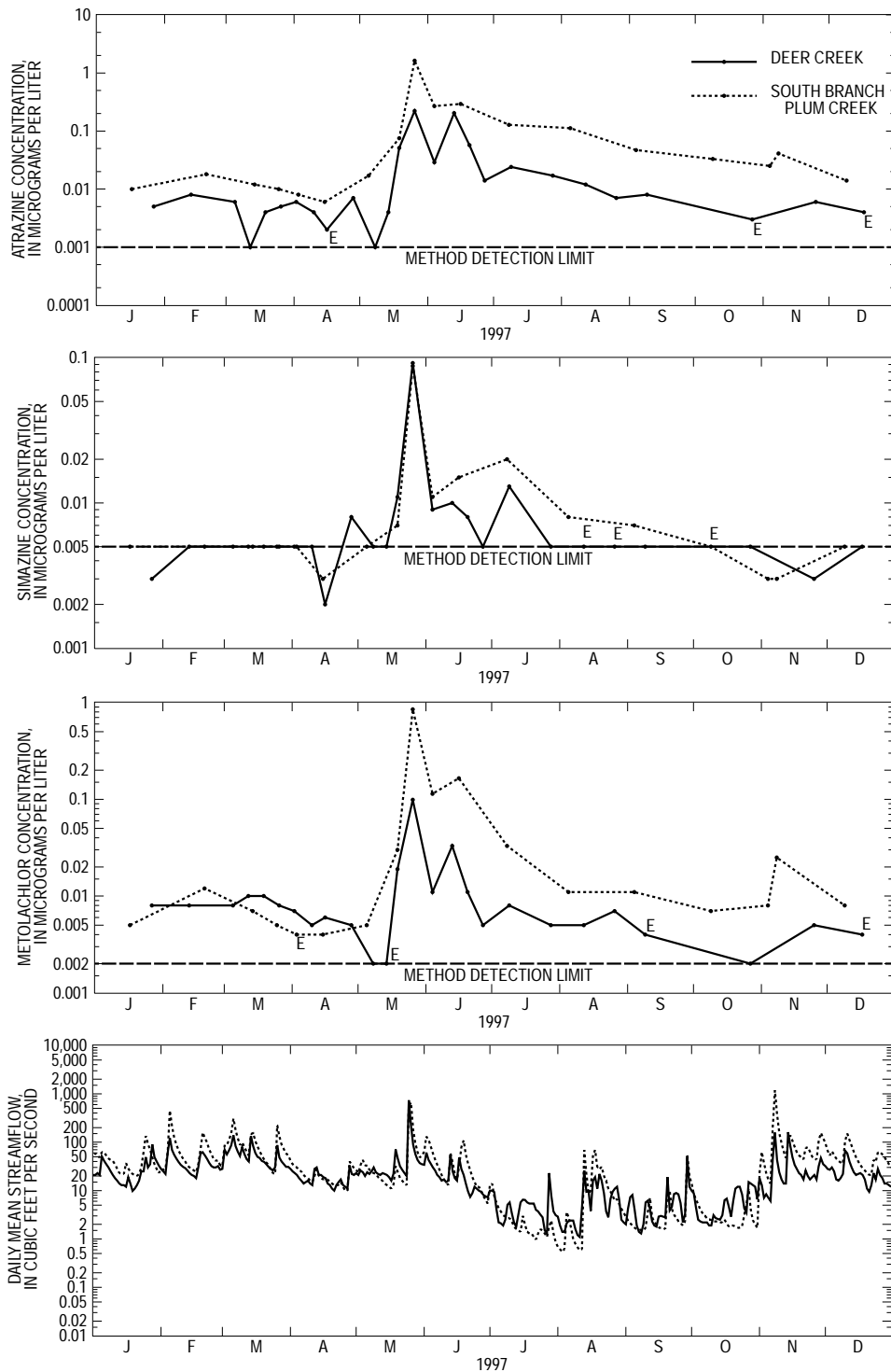


Figure 7. Measured pesticide concentrations and daily-mean streamflow for Deer Creek and South Branch Plum Creek, 1997. [E, estimated value; all values plotted below the method detection limit are estimated values.]

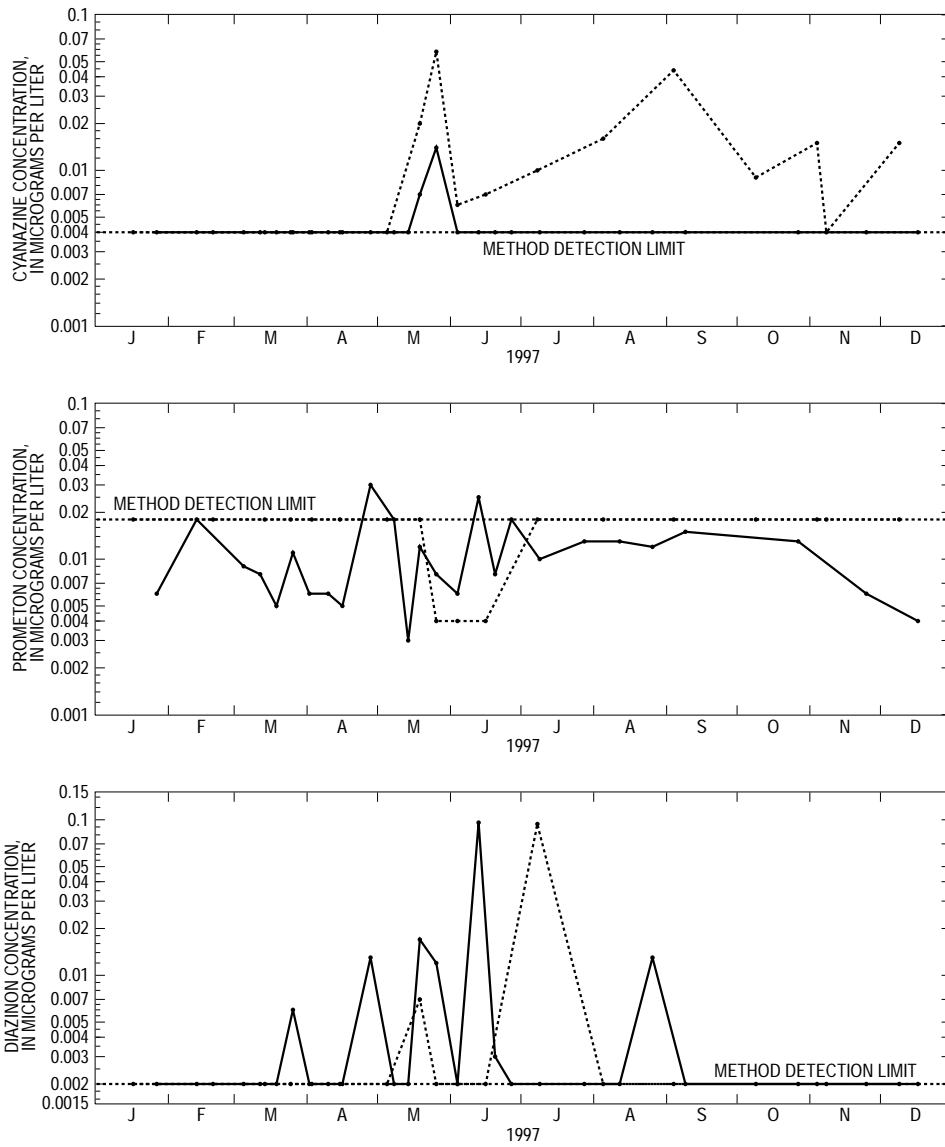


Figure 7. Measured pesticide concentrations and daily-mean streamflow for Deer Creek and South Branch Plum Creek, 1997—Continued.

Branch Plum Creek Basin and residential, urban, forestland, and some agriculture in the Deer Creek Basin. Two other factors, in addition to land use, that can have a significant effect on pesticide concentrations in streams include climate and the period of pesticide application. The growing season in these two basins generally extends from April through September and covers periods of normally high and low streamflow conditions. Most of the annual precipitation falls during the early months of the growing season (April through June), which coincides with the time of year when pesticide application for agricultural purposes and for residential lawn care are generally at a peak. Long-term average monthly precipitation amounts from National Weather Service rain gage data (National Oceanic and Atmospheric Administration, 1997) for Indiana, Pa., which is near the South Branch Plum Creek Basin, and for Natrona Lock and Dam 4 on the Allegheny River, which is near the Deer Creek Basin, are shown in figure 8. These data show a significant amount

of precipitation in both basins during the early months of the growing season.

Land use, seasonality, and streamflow affect the concentrations of the six selected pesticides sampled in the two streams (fig. 7). Four of the pesticides shown in figure 7 (atrazine, simazine, cyanazine, and metolachlor) are herbicides that are generally applied to corn and other agricultural row crops. Other than the extremely high-flow samples collected on May 26, 1997, it appears that concentrations of atrazine, simazine, and metolachlor were more seasonal dependent than flow dependent. Concentrations of these three constituents were not statistically related to streamflow but were statistically related to season. Atrazine was the most commonly detected pesticide in both streams; it was detected in all 18 samples collected from South Branch Plum Creek and in 24 of the 26 samples collected from Deer Creek in 1997. Measured concentrations of atrazine and cyanazine always were higher in South Branch Plum Creek than in Deer Creek. Paired concentrations of atrazine and cyana-

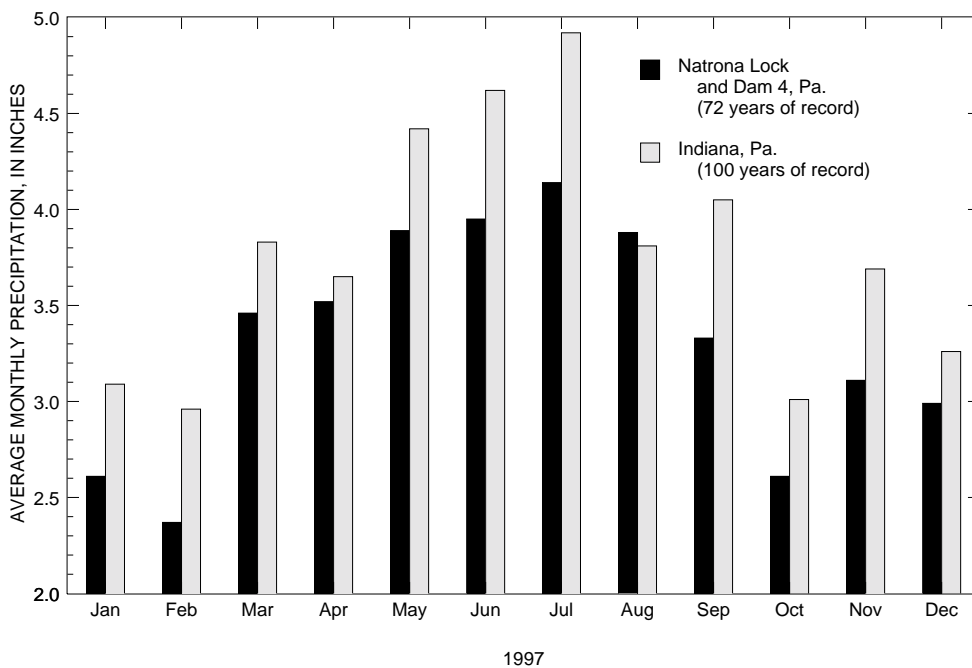


Figure 8. Long-term average monthly precipitation at Natrona Lock and Dam 4, Pa., and Indiana, Pa.

zine produced statistically significant differences in concentrations between the two streams when used in the Wilcoxon Signed-Rank Test. The p-value was 0.005 for atrazine and 0.0035 for cyanazine. The higher concentrations measured in South Branch Plum Creek were attributed to the greater amount of agriculture in that basin. The highest measured concentrations for atrazine, simazine, cyanazine, and metolachlor at both sites were in the high-flow sample collected on May 26, 1997. That high-flow event coincided with the end of the planting season for corn and came at a time shortly after most row-crop pesticides had been applied in both basins. Studies in other basins in the United States indicate similar annual patterns in stream pesticide concentrations. Crawford (1995) reported that atrazine concentrations in the White River at Hazelton, Ind., from 1991 through 1995, were highest during the planting period, and the highest concentrations typically were during the first one or two periods of runoff after application.

On a few isolated occasions, concentrations of simazine and metolachlor were either equal to or slightly greater in Deer Creek than concentrations measured in South Branch Plum Creek. Simazine is used generally for agricultural purposes, but it also is used extensively on fruits and vegetables and for weed control in residential areas, along railways, highways, and transmission lines. This may explain why simazine concentrations were sometimes higher in Deer Creek. Voss and others (1999) reported that atrazine and simazine were found at more than 60 percent of the study sites in 10 urban watersheds in King County, Wash., indicating that these two pesticides were being applied in areas such as rights-of-way, parks, and recreational areas. During a 2-month period from early March until late April, concentrations of metolachlor in Deer Creek were slightly higher than concentrations in South Branch Plum Creek. Differences in concentrations of metolachlor and simazine between the two sites were not statistically significant on the basis of results of the Wilcoxon Signed-Rank Test.

The pattern of decreasing concentrations of atrazine, simazine, and metolachlor at both sites after the peak concentration measured on May 26 implies a reduction in the supply available in the following months. Most corn is planted in May, and most pesticides are applied at planting time. Some of the pesticides are flushed from the land surface to the streams during subsequent surface-runoff periods, but the degradation of the compounds with time is the more significant cause of the depletion of pesticides on the soils. An example of the depletion of pesticide availability can be seen from the two samples collected in the South Branch Plum Creek in November 1997. The routine monthly sample was collected on November 4 at 0930; the streamflow was 28 ft³/s. Four days later on November 8 at 1330, a high-flow sample was collected at a streamflow of 1,440 ft³/s, but the concentration of atrazine only increased from 0.025 to 0.041 µg/L. Simazine concentration remained the same, metolachlor concentration increased from 0.008 to 0.025 µg/L, cyanazine concentration decreased, and prometon and diazinon concentrations were not detected in either sample. The peak streamflow of record for the South Branch Plum Creek site for the 2.5-year study period was 1,620 ft³/s at 1000 on November 8, just 3.5 hours prior to when the high-flow sample was collected.

In recent large-scale studies by the USGS, prometon has been the most commonly detected herbicide in surface water and ground water in urban areas and the third and fourth most commonly detected herbicide in ground water and surface water, respectively, in agricultural areas. It also has been detected in rain (Capel and others, 1999). Prometon has a variety of uses and applications. It is used as a pre-emergent herbicide to control vegetation on bare ground around buildings, fences, and along rights-of-way and is commonly applied to the land surface below layers of asphalt on roads, parking lots, and trails. Prometon was detected in only 3 of the 18 samples collected in South Branch Plum Creek but was detected in 23 of the 26 samples collected in Deer Creek. All three detections in South Branch Plum Creek and 21 of the 23 detections in Deer

Creek were estimated values at low concentrations (fig. 7). Prometon generally is applied at any time of the year depending on its intended uses, and its use in conjunction with asphalt paving generally provides a direct transport route to surface-water resources in residential areas. As the asphalt wears and cracks, prometon in and under it becomes exposed to rain water and can find its way to surface-water drainage. The Deer Creek Basin has a high density of paved areas that could be the major source of prometon measured at the monitoring site. Concentrations of prometon measured in Deer Creek showed no apparent trends (fig. 7). The highest concentrations were measured in the five samples collected during a storm on August 25–26, 1998 (fig. 9). The first sample collected during the storm had a concentration of 0.355 $\mu\text{g/L}$ and the four subsequent samples had progressively decreasing concentrations. Prior to the storm on August 25, the last appreciable amount of precipitation in the Deer Creek Basin was on July 23, 1998. Paving during the period between July 23 and August 25 and the accompanying application of prometon may have been a major source of this pesticide in the five high-flow samples collected during August 25–26, 1998.

The insecticide diazinon is more commonly applied for home and garden use than for agricultural use. Majewski and Capel (1995) report that outdoor applications of diazinon by homeowners in 1990 were about 30 times greater than the amount used for agricultural purposes. Crawford (1996) found significantly higher concentrations of diazinon in streams in urban areas of the White River Basin, Ind., than in agricultural areas. Diazinon concentrations were detected in only 2 of the 18 samples collected from the South Branch Plum Creek in 1997, in 7 of the 26 samples collected from Deer Creek in 1997, and in all 5 samples collected from Deer Creek during August 25–26, 1998. Insecticides are generally applied at times when pest control is necessary, unlike the seasonal application method used for herbicides applied to agricultural crops and to lawns and gardens. Detections of diazinon from samples collected from Deer Creek in 1997 showed no seasonal

pattern (fig. 7); however, five of the seven detections were in samples collected shortly after a peak in streamflow due to overland runoff throughout the basin. Diazinon also was detected in all five of the storm runoff samples collected on August 25–26, 1998. The peak concentration, 0.051 $\mu\text{g/L}$, was measured in the last two samples collected on the streamflow recession (fig. 10).

Cyanazine is applied almost exclusively to corn for weed control. It is more biodegradable and has less residual carryover than atrazine or metolachlor. Cyanazine was present in 10 of 11 samples collected in the South Branch Plum Creek from mid-May through December but was not detected in any of the 7 samples collected from January through early May (fig. 7). It was detected in only 2 of the 28 samples collected in Deer Creek, and those samples were collected in late May on the recession of two significant rises in the stream. The sample collected in Deer Creek on May 26 was collected on the recession of the maximum streamflow recorded for the period of record at the site. Cyanazine was not detected in any of the five streamflow samples collected from Deer Creek on August 25–26, 1998.

MAXIMUM PESTICIDE DETECTIONS

Of the 85 pesticides and pesticide metabolites sampled in Deer Creek and South Branch Plum Creek, 25 of the pesticides were detected at least once in Deer Creek, and 20 of the pesticides were detected at least once in South Branch Plum Creek. At the Deer Creek site, 9 of the 25 pesticides detected during the study were detected only in the June 13, 1997, sample. Nine other pesticides also were detected in that sample. Prior to June 13, 1997, streamflow in Deer Creek had been on a gradual recession (fig. 11) from a moderate peak flow of 111 ft^3/s at 1100 on June 2, 1997. Streamflow gradually receded to a flow of 15 ft^3/s late in the day of June 12. Precipitation and surface runoff on June 12 and 13 resulted in a peak flow of 97 ft^3/s at 0830 on June 13. The sample for pesticide analysis collected from Deer Creek was at 1045 on June 13 at a flow rate of 76 ft^3/s . From late in the day on

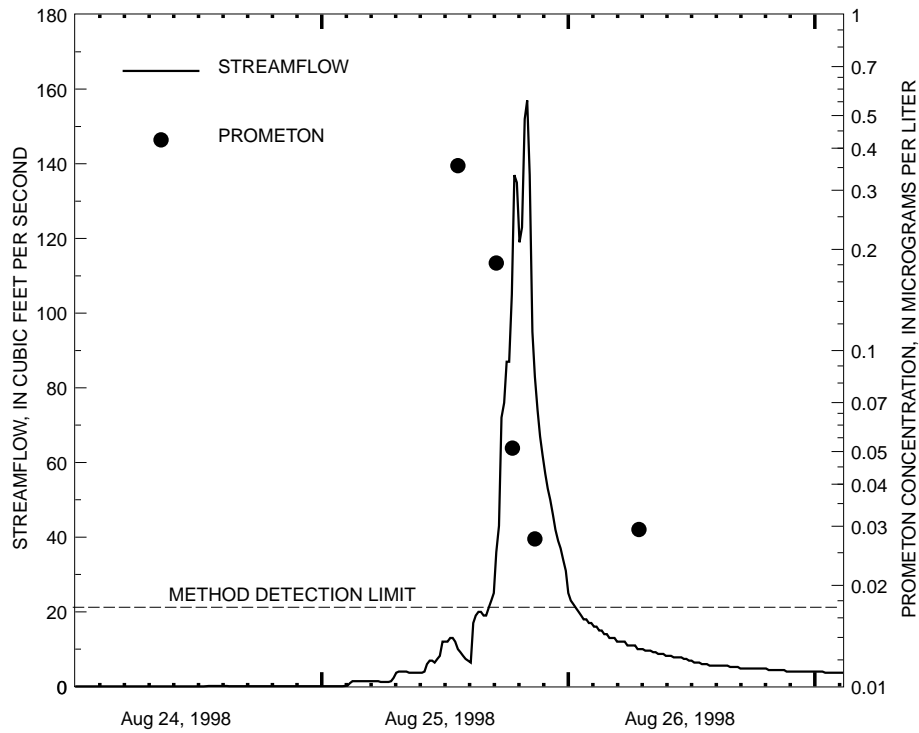


Figure 9. Measured prometon concentrations and streamflow for Deer Creek on August 25–26, 1998.

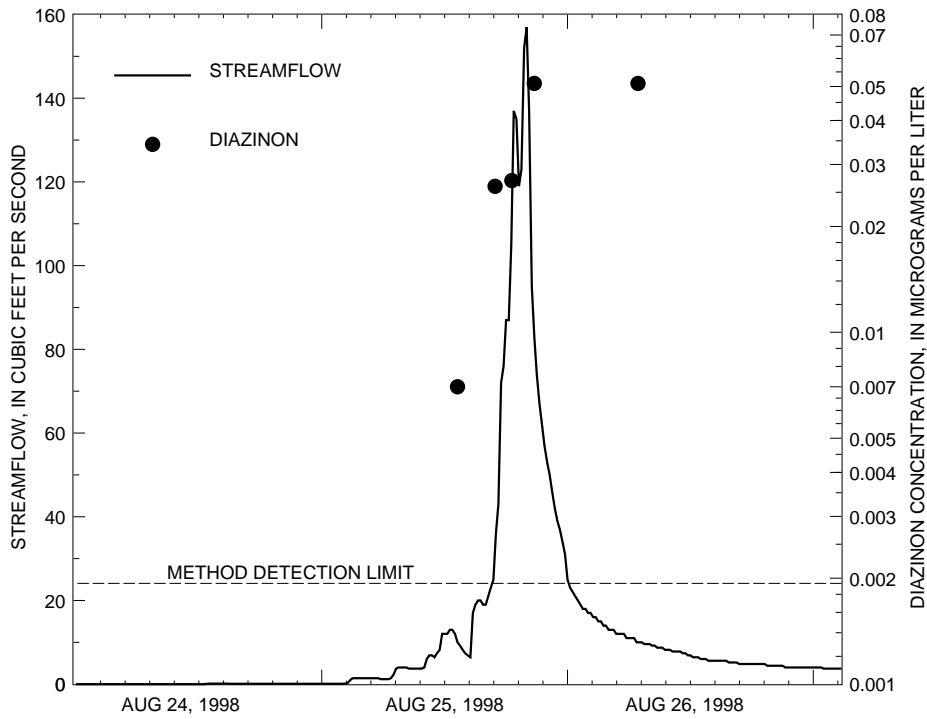


Figure 10. Measured diazinon concentrations and streamflow for Deer Creek on August 25–26, 1998.

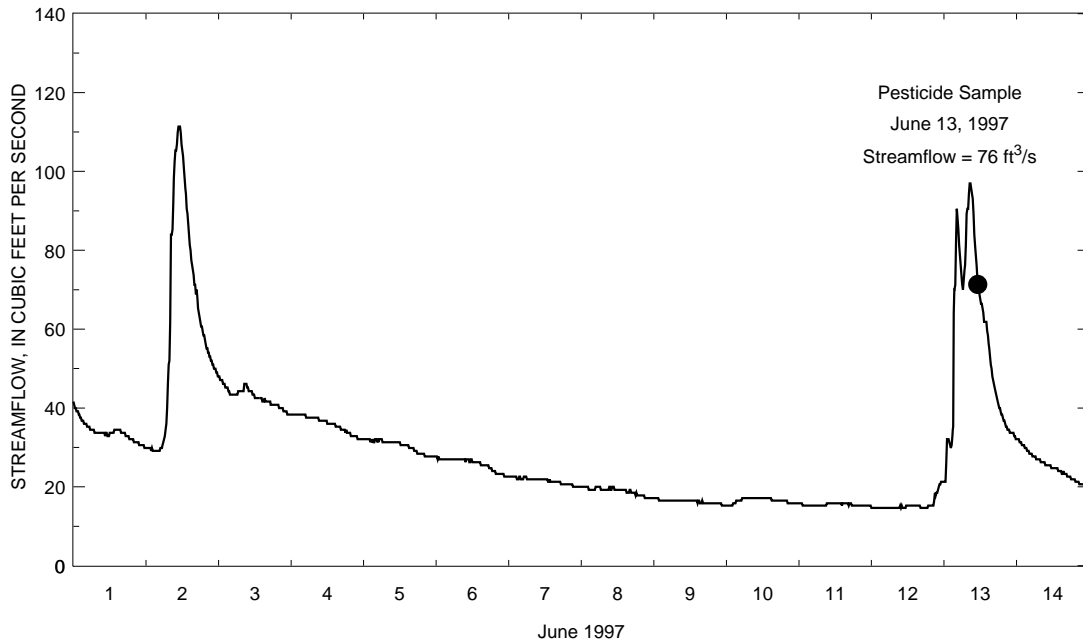


Figure 11. Streamflow hydrograph for Deer Creek near Dorseyville, Pa., from June 1 to 14, 1997.

June 2 to late in the day on June 12, there was no appreciable surface runoff throughout the Deer Creek Basin. Early June is an optimum period for the widespread application of pesticides from individual homeowners, from professional applicators, from utility companies, and from the farmers in the headwater areas of the basin. Most likely, a number of pesticide compounds were applied in the basin prior to the storm on June 12 and 13. When surface runoff occurred on June 12 and 13, many of those pesticides were flushed from the land surface into the stream and were detected in the stream sample. The 18 pesticides detected in the stream sample collected on June 13 and the 9 pesticides that were detected only in that sample are shown in table 5. Four of those nine pesticides (acifluorfen, bentazon, bromoxynil, and MCPA) are classified as selective-post-emergent type pesticides, pesticides expected to be present in mid-June during postemergent weed growth. Three of the 18 pesticides detected in the June 13 sample (dicamba, MCPA, and 2,4-D) are herbicides commonly used by commercial lawn companies

During the period of pesticide application, the greatest number of pesticide compounds usually are detected during the first flush of runoff to streams regardless of the magnitude

of streamflow. The samples collected in Deer Creek on May 26, 1997, represented the highest streamflow sampled for pesticides in Deer Creek in 1997. The streamflow in Deer Creek for the May 26 sample was 149 ft³/s, almost twice the amount of streamflow of the sample collected on June 13 (76 ft³/s). However, 10 pesticides were detected in the May 26 sample compared to 17 pesticides detected in the June 13 sample. The May 26 sample was collected about 40 hours after the initial rise in streamflow and the June 13 sample was collected about 12 hours after the initial rise in streamflow.

HUMAN-HEALTH AND AQUATIC-LIFE CRITERIA

Of the 85 pesticides and pesticide metabolites analyzed in samples collected from Deer Creek and South Branch Plum Creek, human-health criteria were established by the USEPA (1999) for 39 of the pesticides and 2 of the pesticide metabolites. The criteria include maximum contaminant levels (MCLs) and health advisories (HAs). Pesticide MCLs and HAs are based on chronic long-term exposure; therefore, pesticide concentrations in individual samples that exceed these criteria may not necessarily indicate a violation of a

Table 5. Pesticides detected in the water sample collected on June 13, 1997, in Deer Creek

[Concentrations are in micrograms per liter; E, estimated value]

PESTICIDE	CONCENTRATION	USE
<u>Herbicides</u>		
Acifluorfen ¹	0.040	selective, postemergence
Atrazine	.203	selective, season-long weed control
Deethyl atrazine	E .005	degradation product of atrazine
Bentazon ¹	E .050	selective, postemergence
Bromoxynil ¹	E .070	selective contact, postemergence
Dicamba ¹	E .120	broadleaf weed control
Dichlorprop ¹	.040	brush control on rights-of-way
Diuron	.180	young broadleaf and grass weeds
Fenuron ¹	.050	woody plants, deep rooted perennial weeds
Linuron ¹	E .020	selective weed control
MCPA ¹	.100	selective, postemergence
Metolachlor	.033	selective, preemergence
Neburon ¹	.040	selective weed control
Prometon	.025	nonselective
Simazine	.010	selective, annual grasses and broadleaf weeds
2,4-D	1.16	broadleaf weeds
<u>Insecticides</u>		
Carbaryl	E .022	broad spectrum insecticide
Diazinon	.096	commonly used insecticide

¹Pesticide detected only in the June 13, 1997 sample.

standard. The MCL is the maximum permissible annual average concentration of a contaminant in water that is delivered to any use of a public water system. The HA is an advisory guideline for drinking-water exposure over a 70-year lifetime, considering noncarcinogenic adverse health effects. More detail on these types of criteria, their derivation, and their underlying assumptions is provided in Nowell and Resek (1994). Although Deer Creek and South Branch Plum Creek are not used as a drinking-water supply, the MCLs and HAs are offered as a point of reference for comparison to actual concentrations measured in the two streams.

Water-quality guidelines also have been established by the USEPA and the National Academy of Sciences and National Academy of Engineering (NAS/NAE) for the protection of aquatic life (Nowell and Resek, 1994). The USEPA guidelines include acute and chronic criteria. Acute criteria are based on exposure levels of as much as 1.0 hour, and chronic criteria are based on an exposure time of 1 to

4 days. Aquatic guidelines set by the Canadian Government (Canadian Council of Resource and Environmental Ministers, 1987) are commonly used for pesticides that have not yet been assigned criteria by the USEPA or NAS/NAE. Guidelines for drinking water and/or aquatic life for only those pesticides that were detected in Deer Creek or South Branch Plum Creek and the maximum measured concentrations of those pesticides detected are listed in table 6. The guidelines for drinking water and aquatic life for all 85 pesticides and pesticide metabolites analyzed for in this study are presented in table 4. Four pesticides that have MCLs for drinking water were detected in either Deer Creek or South Branch Plum Creek, but the maximum concentrations of those pesticides were well below the MCLs established by the USEPA. The maximum measured concentration of atrazine in South Branch Plum Creek (1.63 µg/L) was the only pesticide concentration that approached the drinking-water guideline of 3.0 µg/L. The concentrations of two insecticides measured in

Table 6. Guidelines for drinking-water and aquatic-life criteria established for selected pesticides and the maximum measured concentrations in Deer Creek and South Branch Plum Creek

[Concentrations are in micrograms per liter; H, herbicide; I, insecticide; MCL, maximum contaminant level; HA, Health Advisory; —, no standard or guideline; --, all measured values were less than the method detection limit; E, estimated value]

PESTICIDE (TYPE)	STANDARD OR GUIDELINE FOR DRINKING WATER (MCL OR HA)	GUIDELINE FOR AQUATIC LIFE	MAXIMUM MEASURED CONCENTRATIONS	
			DEER CREEK	SOUTH BRANCH PLUM CREEK
Alachlor (H)	¹ 2	—	--	0.008
Atrazine (H)	¹ 3	² 2	0.222	1.630
Azinphos-methyl (I)	—	² .01	--	E .033
Bentazon (H)	20	—	E .050	--
Bromoxynil (H)	—	³ 5	E .070	--
Carbaryl (I)	700	—	E .613	.010
Chlorpyrifos (I)	20	⁴ .08	E .003	.010
Cyanazine (H)	1	² 2	.014	.058
DCPA (H)	4,000	—	E .001	E .002
Diazinon (I)	0.6	⁵ .009	.097	.094
Dicamba (H)	200	⁵ 200	E .120	--
2,4-D (H)	¹ 70	⁵ 3	1.160	1.010
Diuron (H)	10	⁵ 1.6	.400	--
MCPA (H)	10	—	.100	.940
Metolachlor (H)	100	² 8	.099	.851
Prometon (H)	100	—	.355	E .004
Propachlor (H)	90	—	--	.064
Simazine (H)	¹ 4	⁵ 10	.092	.088
Tebuthiuron (H)	500	—	E .004	.021
Terbacil (H)	90	—	E .009	--
Trifluralin (H)	5	² .10	E .002	--

¹Value is the U.S. Environmental Protection Agency (USEPA) maximum contaminant level for drinking water; other values are USEPA lifetime health advisories for a 70-kilogram adult (Nowell and Resek, 1994).

²U.S. Environmental Protection Agency chronic aquatic-life guidelines (Nowell and Resek, 1994).

³Canadian Government aquatic-life guidelines (Canadian Council of Resource and Environment Ministers, 1987; updates 1989-91, 1993).

⁴U.S. Environmental Protection Agency acute aquatic-life guidelines (Nowell and Resek, 1994).

⁵National Academy of Sciences and National Academy of Engineering aquatic-life guidelines, 1973 (Nowell and Resek, 1994).

South Branch Plum Creek and one insecticide measured in Deer Creek slightly exceeded the guidelines established for aquatic life. The maximum measured concentration of diazinon in Deer Creek (0.097 µg/L) and South Branch Plum Creek (0.094 µg/L) exceeded the aquatic-life guideline of 0.009 µg/L established by the NAS/NAE. The maximum measured concentration of azinphos-methyl in South Branch Plum Creek (E 0.033 µg/L) exceeded the chronic aquatic-life guideline of 0.01 µg/L established by the USEPA. In summarizing pesticide data

from 65 sites available from the first phase of the NAWQA Program, Gilliom and others (1999) found that aquatic-life criteria established by the USEPA, Canada, or the International Joint Commission for the Great Lakes were exceeded by at least one compound in one or more samples for about two-thirds of the streams sampled—most commonly by the herbicides atrazine or cyanazine or the insecticides azinphos-methyl, chlorpyrifos, diazinon, or malathion.

VOLATILE ORGANIC COMPOUNDS IN DEER CREEK

Water samples for analysis of VOCs were collected in Deer Creek near Dorseyville, Pa., from January 1997 through August 1998; most samples were collected during 1997. In 1997, samples were collected once each month in January, April–June, August, and September. Samples were collected twice each month in the remaining months. Two samples were collected on July 28, 1997—the first sample at noon was at low flow, and the second at 3 p.m., shortly after a thunderstorm. One sample was collected on March 10, 1998, shortly after a winter frontal system had passed through the area, and one sample was collected on April 16, 1998, during high flow, shortly after a thunderstorm. Five VOC samples were collected during a storm on August 25–26, 1998. During the period January 1997 through August 1998, a total of 25 VOC samples were collected from Deer Creek, and samples were analyzed for 87 VOCs (table 7). Of those 87 VOCs, 22 were detected at least once in the 25 samples collected. The nine VOCs that were detected in 20 percent (5 samples) or more of the samples included acetone, benzene, carbon disulfide, meta/paraxylene, methyl chloride, MTBE, p-isopropyl toluene, toluene, and 1,2,4-trimethylbenzene. Each VOC that was detected, the total number of detections as well as the number of detections in the five storm samples collected on August 25–26, 1998, and the primary use of each compound are listed in table 8. Twelve of the 22 VOCs detected were gasoline-related compounds. Ninety-three percent of all detections of VOCs were below the laboratory reporting level (LRL). The LRL is the reporting level for reliable quantification of the VOCs analyzed. The LRL for all compounds ranged from 0.03 to 5.0 µg/L. Although confirmed detections of the presence of VOCs below the LRL values commonly occurred, accurate quantification in these instances could not be guaranteed, and the values were considered estimates.

SEASONALITY OF VOCs

Temperature is a significant factor affecting the occurrence of VOCs. The concentrations of VOCs in water can increase by a factor of about three to seven when water temperatures decrease from 25°C to 5°C (Lopes and Bender, 1998). These higher levels of VOCs could be caused by an increase in partitioning of VOCs from air into precipitation or slower volatilization from water during cold months. Delzer and others (1996) found that MTBE and benzene were detected more frequently during the winter than the summer. MTBE, benzene, toluene, meta/paraxylene, and naphthalene showed evidence of seasonality in samples collected in Deer Creek. Of the 18 VOC samples collected in 1997 in Deer Creek, MTBE was detected six times in samples collected in January, February, March, November, and December, and benzene was detected six times in samples collected in February, October, November, and December. MTBE also was detected in one of the five storm samples collected on August 25–26, 1998. Benzene was detected in the May 29, 1997, sample and all five storm samples collected on August 25–26, 1998. The May 29, 1997, sample and the August 25–26, 1998, samples were all associated with storm runoff. The seasonal variability in concentrations of MTBE, benzene, toluene, meta/paraxylene, and naphthalene for samples collected in 1997 is shown in figure 12. All five compounds were detected in February, November, and December, and none of the compounds were detected in July through September.

VOCs IN STORMFLOW RUNOFF

VOCs can accumulate on impervious surfaces and can be flushed into the receiving stream during storms. The flushing effect can result in high concentrations in the initial runoff from a storm and relatively lower concentrations during the remainder of the runoff period. Fourteen VOCs were detected in at least one of the five samples collected during the storm on August 25–26, 1998, and six of those VOCs were detected in the samples

Table 7. VOCs analyzed in water samples collected from Deer Creek

[All values are in micrograms per liter; LRL, laboratory reporting level; CAS number, Chemical Abstract Services Number]

PARAMETER CODE	CAS NUMBER	PARAMETER NAME	LRL
77562	630-20-6	1,1,1,2-Tetrachloroethane	0.044
34506	71-55-6	1,1,1-Trichloroethane	.032
34516	79-34-5	1,1,2,2-Tetrachloroethane	.13
34511	79-00-5	1,1,2-Trichloroethane	.064
77652	76-13-1	Freon 113	.032
34496	75-34-3	1,1-Dichloroethane	.066
34501	75-35-4	1,1-Dichloroethylene	.044
77168	563-58-6	1,1-Dichloropropene	.026
49999	488-23-3	1,2,3,4-Tetramethylbenzene	.23
50000	527-53-7	Isodurene	.24
77613	87-61-6	1,2,3-Trichlorobenzene	.27
77443	96-18-4	1,2,3-Trichloropropane	.16
77221	526-73-8	1,2,3-Trimethylbenzene	.12
34551	120-82-1	1,2,4-Trichlorobenzene	.19
77222	95-63-6	1,2,4-Trimethylbenzene	.056
82625	96-12-8	1,2-Dibromo-3-chloropropane	.21
77651	106-93-4	1,2-Dibromoethane	.036
34536	95-50-1	O-Dichlorobenzene	.048
32103	107-06-2	1,2-Dichloroethane	.13
34541	78-87-5	1,2-Dichloropropane	.068
77226	108-67-8	1,3,5-Trimethylbenzene	.044
34566	541-73-1	1,3-Dichlorobenzene	.054
77173	142-28-9	1,3-Dichloropropane	.12
34571	106-46-7	1,4-Dichlorobenzene	.05
77170	594-20-7	2,2-Dichloropropane	.078
81595	78-93-3	Methyl ethyl ketone	1.6
77275	95-49-8	2-Chlorotoluene	.042
77103	591-78-6	2-Hexanone	.7
78109	107-05-1	3-Chloropropene	.2
77277	106-43-4	p-chlorotoluene	.056
77356	99-87-6	p-isopropyl toluene	.11
78133	108-10-1	Methyl isobutyl ketone	.37
81552	67-64-1	Acetone	5
34210	107-02-8	Acrolein	2.0
34215	107-13-1	Acrylonitrile	1.2
34030	71-43-2	Benzene	.1
81555	108-86-1	Bromobenzene	.036
77297	74-97-5	Bromochloromethane	.048
32101	75-27-4	Bromodichloromethane	.048
50002	593-60-2	Bromoethene	.1
32104	75-25-2	Bromoform	.1
34413	74-83-9	Methyl bromide	.15
77342	104-51-8	Butylbenzene	.19
77041	75-15-0	Carbon disulfide	.37
34301	108-90-7	Chlorobenzene	.028

Table 7. VOCs analyzed in water samples collected from Deer Creek—Continued

[All values are in micrograms per liter; LRL, laboratory reporting level; CAS number, Chemical Abstract Services Number]

PARAMETER CODE	CAS NUMBER	PARAMETER NAME	LRL
34311	75-00-3	Chloroethane	0.12
32106	67-66-3	Chloroform	.052
34418	74-87-3	Methyl chloride	.25
77093	156-59-2	cis-1,2-Dichloroethylene	.038
34704	10061-01-5	cis-1,3-Dichloropropene	.09
32105	124-48-1	Dibromochloromethane	.18
30217	74-95-3	Dibromomethane	.05
34668	75-71-8	Dichlorodifluoromethane	.14
34423	75-09-2	Methylene chloride	.38
81576	60-29-7	Ethyl ether	.17
81577	108-20-3	Diisopropyl ether	.098
73570	97-63-2	Ethyl methacrylate	.28
50004	637-92-3	Ethyl tert-butyl ether	.054
34371	100-41-4	Ethylbenzene	.03
39702	87-68-3	Hexachlorobutadiene	.14
34396	67-72-1	Hexachloroethane	.36
77223	98-82-8	Isopropylbenzene	.032
85795	108-38-3 (m) 106-42-3 (p)	m- and p-Xylene	.06
49991	96-33-3	Methyl acrylate	1.4
81593	126-98-7	Methyl acrylonitrile	.57
77424	74-88-4	Methyl iodide	.21
81597	80-62-6	Methyl methacrylate	.35
34696	91-20-3	Naphthalene	.25
77224	103-65-1	n-Propylbenzene	.042
77220	611-14-3	o-Ethyl toluene	.1
77135	95-47-6	o-Xylene	.06
77350	135-98-8	sec-Butylbenzene	.048
77128	100-42-5	Styrene	.042
78032	1634-04-4	MTBE	.17
77353	98-06-6	tert-Butylbenzene	.1
50005	994-05-8	tert-Pentyl methyl ether	.11
34475	127-18-4	Tetrachloroethylene	.1
32102	56-23-5	Carbon tetrachloride	.088
81607	109-99-9	Tetrahydrofuran	9
34010	108-88-3	Toluene	.05
34546	156-60-5	trans-1,2-Dichloroethylene	.032
34699	10061-02-6	trans-1,3-Dichloropropene	.13
73547	110-57-6	trans-1,4-Dichloro-2-butene	.7
39180	79-01-6	Trichloroethylene	.038
34488	75-69-4	Trichlorofluoromethane	.09
39175	75-01-4	Vinyl chloride	.11
77057	108-05-4	Vinyl acetate	5.0

Table 8. VOCs detected in Deer Creek samples and a primary use or source of each compound

VOC	TOTAL NUMBER OF DETECTIONS	NUMBER OF DETECTIONS IN STORM SAMPLES ON AUGUST 25-26, 1998	USE OR SOURCE
Benzene	13	5	Gasoline component
Toluene	13	0	Gasoline component
Acetone	11	5	Solvent and reagent
Methyl chloride	8	4	Refrigerant, catalyst carrier in manufacture of butyl rubber
Carbon disulfide	7	3	Solvent for oils, fats, and rubber and in paint remover
MTBE	7	1	Gasoline component, octane enhancer
P- isopropyl toluene	7	5	Gasoline component
Meta/paraxylene	7	2	Used in insecticides and to synthesize vitamins and pharmaceuticals
1,2,4-trimethyl benzene	6	3	Gasoline component
Naphthalene	4	0	Used in organic synthesis
o-Xylene	4	1	Gasoline component
Ethylbenzene	3	0	Gasoline component
Chloroform	3	2	Solvent
Methylethyl ketone	3	1	Solvent
Styrene	2	1	Used to make plastics
o-Ethyl toluene	2	0	Gasoline component
1,4-Dichlorobenzene	2	1	Gasoline component
O-dichlorobenzene	1	1	Gasoline component
1,3,5-Trimethylbenzene	1	0	Gasoline component
n-Propylbenzene	1	0	Gasoline component
Methyl isobutyl ketone	1	0	Solvent
Freon 113	1	0	Refrigerant, solvent

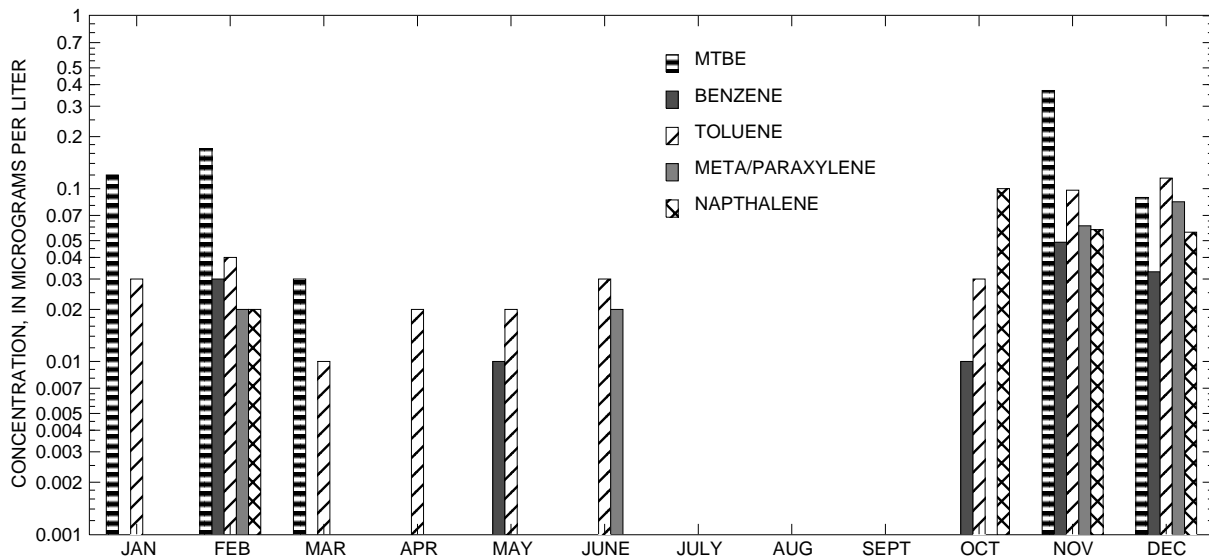


Figure 12. Seasonal patterns in concentrations of MTBE, benzene, toluene, meta/paraxylene, and naphthalene for samples collected in Deer Creek in 1997.

[When two concentrations for a VOC were detected in 1 month, the higher detected concentration was plotted.]

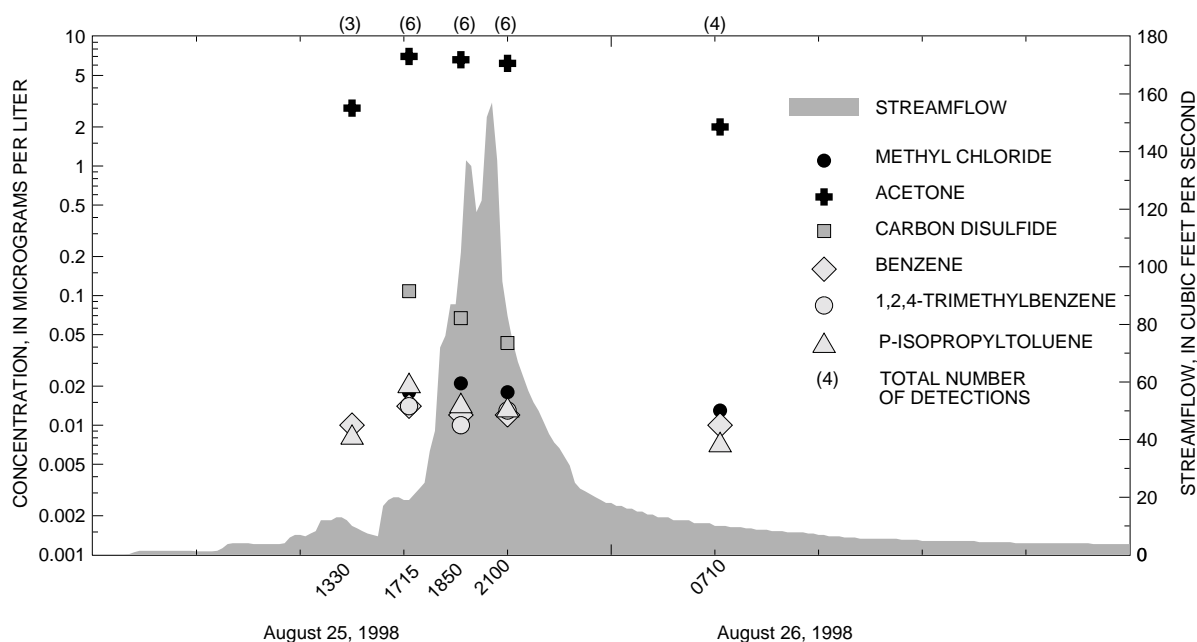


Figure 13. Measured concentrations of methyl chloride, acetone, carbon disulfide, benzene, 1,2,4-trimethyl benzene, and p-isopropyl toluene from samples collected on August 25–26, 1998.

collected on the rise, peak, and recession of the storm hydrograph (fig. 13). The maximum measured concentrations of acetone, carbon disulfide, benzene, 1,2,4-trimethylbenzene, and p-isopropyltoluene were in the sample collected on the rise in the hydrograph at 1715. The maximum concentration for methyl chloride was in the sample collected near the peak in streamflow at 1850. The smallest concentrations of all six compounds were measured in the last or the next to the last sample collected during the runoff period. As mentioned previously, no measurable amount of precipitation had fallen 1 month prior to the storm. During this storm, measured concentrations of VOCs were highest in the initial flush and smallest in the last or next to the last sample showing a flush-off effect (fig. 13).

Fourteen VOCs detected in a sample collected on December 10, 1997 (table 9), may have resulted from a flush of accumulated VOCs from impervious surfaces, in addition to a low water temperature of 5.0°C. Ten of the

14 VOCs were gasoline-related compounds. The sample was collected at 1140 at a streamflow of 127 ft³/s (fig. 14). The peak streamflow was 137 ft³/s and occurred 35 minutes later. No significant runoff occurred during the 10 days prior to when the sample was collected.

HUMAN-HEALTH CRITERIA FOR VOCs

The USEPA (1999) has established MCLs for drinking water for 20 of the 87 VOCs analyzed. Only 5 of the 20 compounds were detected in samples collected from Deer Creek. Although the water from Deer Creek is not used as a drinking-water supply, the MCLs for the five compounds are given in table 10 as a point of reference for comparison to the maximum measured concentrations. The maximum measured concentrations of all five compounds were two or more orders of magnitude lower than the established MCLs.

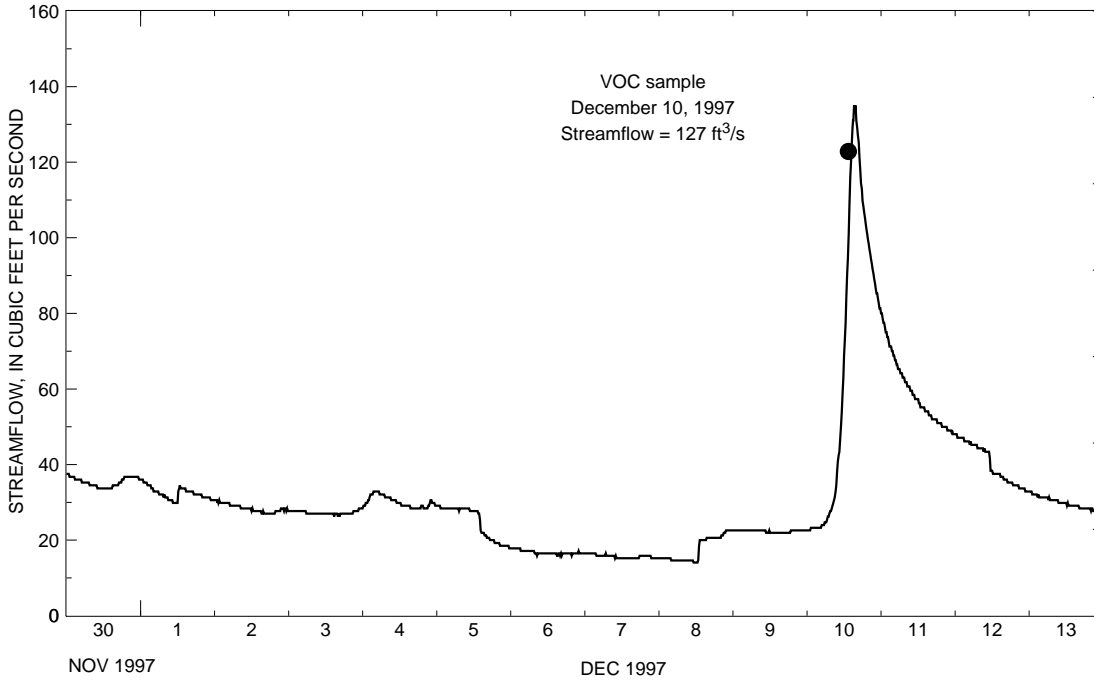


Figure 14. Streamflow hydrograph of Deer Creek prior to and during the storm on December 10, 1997.

Table 9. VOCs detected in Deer Creek on December 10, 1997

[Concentrations are in micrograms per liter; E, estimated value]

VOC	CONCENTRATION
Carbon disulfide	E 0.032
MTBE ¹	E .089
Benzene ¹	E .028
Methyl isobutyl ketone	E .260
Toluene ¹	.115
Ethylbenzene ¹	E .020
Meta/paraxylene	E .084
o-Xylene ¹	E .046
Styrene	E .009
n-Propylbenzene ¹	E .010
1,3,5-Trimethylbenzene ¹	E .020
o-Ethyltoluene ¹	E .016
1,2,4-Trimethylbenzene ¹	E .070
1,4-Dichlorobenzene ¹	E .029

¹Gasoline related compounds.

Table 10. Comparison of the maximum measured concentrations of VOCs in Deer Creek with the current U.S. Environmental Protection Agency maximum contaminant level (MCL)

[Concentrations are in micrograms per liter; E, estimated value]

VOC	MAXIMUM MEASURED CONCENTRATION	USEPA MCL CONCENTRATION
Benzene	E 0.049	5
Ethylbenzene	E .02	700
O-dichlorobenzene	E .01	600
Styrene	E .009	100
Toluene	.115	1,000

SUMMARY AND CONCLUSIONS

The Allegheny and Monongahela River Basins (ALMN) study unit was one of the second group of 18 study units in which investigations were begun in 1994 as part of the U.S. Geological Survey (USGS) National Water-Quality Assessment (NAWQA) Program. Intensive water-quality sampling was conducted in 1996–98 at 10 fixed sites established throughout the study unit. The South Branch Plum Creek and Deer Creek are two of the fixed sites referred to as “indicator sites” that represent water-quality conditions of streams in generally smaller basins with relatively homogeneous land-use settings. The land use in the South Branch Plum Creek Basin is primarily agriculture and forestland. The land use in the Deer Creek Basin is a combination of residential housing, light industrial, numerous shopping malls, many acres of paved parking and highways, and some agriculture.

Water samples for analysis of nutrients were collected monthly and during selected storms from April 1996 through September 1998. The nutrients analyzed included dissolved nitrite plus nitrate, dissolved ammonia, dissolved ammonia plus organic nitrogen, total ammonia plus organic nitrogen, dissolved orthophosphorus, dissolved phosphorus, and total phosphorus. Pesticide samples were collected at least monthly and more frequently during the months of March through June at both sites. The pesticide analyses included 78 pesticides and 7 selected pesticide metabolites. Of the 85 pesticides and pesticide metabolites, 54 were herbicides, 30 were insecticides, and 1 was a fungicide. Samples for analysis of 87 volatile organic compounds (VOCs) were collected at least monthly and twice each month during the colder months of 1997 at the Deer Creek site. In 1998, VOC samples were collected intermittently at Deer Creek. Samples were collected throughout a significant storm event at Deer Creek on August 25–26, 1998, and analyzed for nutrients, pesticides, VOCs, and major ions.

Most nutrient concentrations in samples collected from the two sites were within comparable ranges. Concentrations of dissolved nitrite, dissolved ammonia plus organic nitrogen, and dissolved phosphorus were less than the method detection limit (MDL) in more than half the samples collected at both sites. The median concentrations of dissolved nitrite plus nitrate in South Branch Plum Creek and Deer Creek were 0.937 and 0.597 mg/L, respectively. The median concentrations of dissolved ammonia nitrogen were similar in South Branch Plum Creek and Deer Creek at 0.03 and 0.02 mg/L, respectively, and the median concentration of dissolved orthophosphate was 0.01 mg/L in both streams. Concentrations of dissolved nitrate and total phosphorus tended to increase with increasing flows in both streams, whereas concentrations of dissolved orthophosphate and dissolved ammonia remained fairly constant regardless of the magnitude of streamflow. Nutrient data collected throughout a storm on August 25–26, 1998, show that concentrations of dissolved ammonia, dissolved orthophosphate, and total phosphorus rise, peak, and recede in conjunction with the streamflow. Dissolved nitrate concentrations rise quickly but only decrease slightly as the streamflow recedes. Nitrate concentrations remain much higher than pre-storm levels even as the streamflow returns to normal levels. The U.S. Environmental Protection Agency (USEPA) MCL for nitrate in drinking water is 10 mg/L, and concentrations measured in both streams were well below that level.

Of the 85 pesticides and pesticide metabolites analyzed for in samples collected from both streams, 25 of those pesticides were detected at least once in Deer Creek and 20 of those pesticides were detected at least once in South Branch Plum Creek. Pesticides detected in 25 percent or more of the samples collected in Deer Creek in 1997 included atrazine, deethyl atrazine (metabolite), simazine, prometon, metolachlor, and diazinon. The pesticides detected in 25 percent or more of the samples collected in South Branch Plum Creek

in 1997 included atrazine, deethyl atrazine (metabolite), cyanazine, simazine, metolachlor, and tebuthiuron. Atrazine was the most commonly detected pesticide in both streams. It was detected in all 18 samples collected in South Branch Plum Creek and in 24 of the 26 samples collected in Deer Creek in 1997. Atrazine concentrations were always higher in South Branch Plum Creek than those measured in Deer Creek. This was attributed to the much greater amount of agriculture in the South Branch Plum Creek Basin. Simazine is used generally for agricultural purposes, but it also is used extensively for weed control in residential areas, along railways, highways, and transmission lines. This may explain why simazine concentrations were sometimes higher in Deer Creek than in the agriculture-dominated South Branch Plum Creek.

Atrazine, simazine, and metolachlor concentrations measured at both sites showed a distinct seasonal pattern. Peak concentrations were measured for these three pesticides at both sites on May 26, 1997. After May 26, concentrations decreased throughout the remainder of the year. These pesticides are generally applied from April through June, which coincides with high precipitation periods.

Prometon was detected in only 3 of the 18 samples collected in the South Branch Plum Creek in 1997 but was detected in 28 of the 31 samples collected in Deer Creek in 1997 and 1998. Prometon is generally applied anytime of the year depending on its intended uses, and its use in conjunction with asphalt paving provides a source to surface water in highly residential areas such as in the Deer Creek Basin. Trends in prometon concentrations measured in Deer Creek were not apparent, however, the concentrations measured in the five storm samples collected on August 25–26, 1998, were some of the highest concentrations measured. The highest measured concentration of 0.355 $\mu\text{g/L}$ was in the first storm sample collected, which was about 4 hours after the initial increase in streamflow. The four subsequent samples had progressively decreasing concentrations. The storm followed a dry period of over 30 days during which extensive

asphalt paving probably took place throughout the basin. Asphalt paving is generally accompanied by the application of prometon, which may have been a major source of the prometon detected in the five storm samples collected on August 25–26, 1998.

The insecticide diazinon is more commonly applied for home and garden use than for agricultural purposes and may be the reason for the higher number of detections in Deer Creek than in South Branch Plum Creek. Diazinon detections from samples collected in Deer Creek showed no seasonal pattern, however, five of the seven detections in 1997 were in samples collected on a streamflow recession, shortly after a peak in streamflow when overland runoff was a significant factor throughout the basin. Diazinon also was detected in all five storm samples collected in Deer Creek on August 25–26, 1998.

At the Deer Creek site, 9 of the 25 pesticides detected throughout the study were detected only in the sample collected on June 13, 1997. Those nine pesticides included acifluorfen, bentazon, bromoxynil, dicamba, dichlorprop, fenuron, linuron, MCPA, and neburon. Nine other pesticides also were detected in that sample. The sample was collected on the streamflow recession, about 2 hours after the streamflow had peaked. Prior to that peak flow, no appreciable precipitation was recorded throughout the basin for about a 10-day period from June 2–12. Throughout that 10-day period, which is an optimum time for widespread pesticide application from individual homeowners, professional applicators, utility companies, and farmers, a large diversity of pesticides probably were applied throughout the basin. When surface runoff occurred on June 12th and 13th, many of those pesticides were washed from the land surface into the stream and were detected in the stream sample. The pesticide sample collected in Deer Creek on June 13, 1997, indicates that the period of pesticide application throughout a basin has a significant effect on pesticides detected in streamflow runoff.

Drinking water guidelines were available for seven pesticides detected in Deer Creek and South Branch Plum Creek, but the maximum

measured concentration of those seven pesticides were well below the MCLs established by the USEPA. The maximum measured concentration of atrazine (1.63 µg/L) in South Branch Plum Creek was the only pesticide concentration that approached the drinking-water guideline of 3.0 µg/L.

The maximum measured concentration of diazinon in Deer Creek (0.097 µg/L) and South Branch Plum Creek (0.097 µg/L) exceeded the aquatic-life guideline of 0.009 µg/L established by the NAS/NAE. The maximum measured concentration of azinphos-methyl in South Branch Plum Creek (an estimated value of 0.033 µg/L) exceeded the chronic aquatic-life guideline of 0.01 µg/L established by the USEPA.

Of the 87 VOCs analyzed in Deer Creek in 1997 and 1998, 22 were detected at least once. Twelve of the 22 VOCs detected were gasoline-related compounds. The nine VOCs that were detected in five or more of the samples included acetone, benzene, carbon disulfide, meta/paraxylene, methyl chloride, MTBE, p-isopropyl toluene, toluene, and 1,2,4-trimethylbenzene. Benzene and toluene were detected in more than 50 percent of the samples collected.

The detection of VOCs appears related to temperature; five were detected during the cold winter months but not at all during the summer months. Concentrations of MTBE, benzene, toluene, metaparaxylene, and naphthalene were detected in February, November, and December of 1997 but were not detected in any samples collected in July through September 1997. Of the 18 VOC samples collected in 1997 in Deer Creek, MTBE was detected six times in samples collected in January, February, March, November, and December, and benzene was detected six times in samples collected in February, October, November, and December. Five VOCs were detected in all five samples collected during a storm on August 25–26, 1998. The maximum concentrations of acetone, carbon disulfide, benzene, 1,2,4-trimethylbenzene, and p-isopropyltoluene were measured in the sample collected during the first flush produced by the storm. The smallest concentrations of the five VOCs were measured in the

last or next to the last sample collected, long after the initial flush had depleted the build-up supply of VOCs. The large number of VOCs detected in the sample collected on December 10, 1997, may have resulted from a flush of accumulated VOCs from the impervious surfaces throughout the basin in addition to a low water temperature of 5.0°C. Fourteen VOCs were detected, and 10 of the 14 were gasoline-related compounds. The streamflow in Deer Creek when the sample was collected was 127 ft³/s, and the peak streamflow for that storm occurred just 35 minutes later at 137 ft³/s. No significant runoff had occurred throughout the basin for at least 10 days prior to when the sample was collected.

Five VOCs detected in samples collected in Deer Creek had USEPA drinking-water standards. The maximum measured concentrations of ethylbenzene, o-dichlorobenzene, styrene, and toluene were more than three orders of magnitude lower than the MCL established by the USEPA. The maximum measured concentration of benzene was more than two orders of magnitude lower than the MCL.

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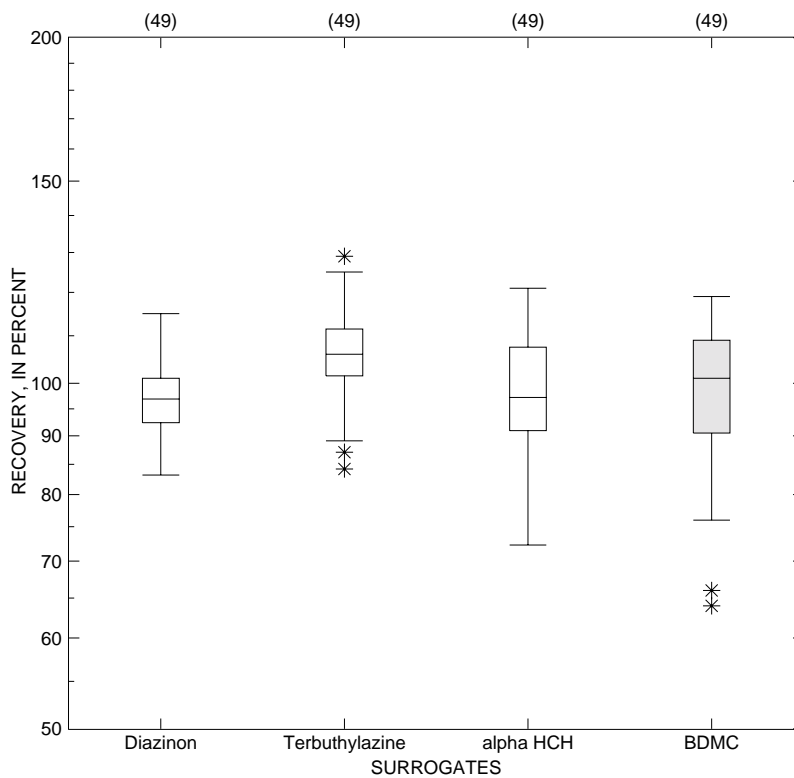
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APPENDIX:
QUALITY-CONTROL DATA



EXPLANATION

GC/MS Surrogate

- (49) Number of observations
- Outlier data value more than 3 times the interquartile range outside the quartile
- * Outlier data value less than or equal to 3 and more than 1.5 times the interquartile range outside the quartile
- Data value less than or equal to 1.5 times the interquartile range outside the quartile
- ▬ 75th percentile
- ▬ Median
- ▬ 25th percentile

HPLC Surrogate

- (49) Number of observations
- Outlier data value more than 3 times the interquartile range outside the quartile
- * Outlier data value less than or equal to 3 and more than 1.5 times the interquartile range outside the quartile
- Data value less than or equal to 1.5 times the interquartile range outside the quartile
- ▬ 75th percentile
- ▬ Median
- ▬ 25th percentile

Figure 15. Distribution of the percent recovery of selected surrogate compounds using gas chromatography/mass spectrometry (GC/MS) or high performance liquid chromatography (HPLC) methods of analysis.

Table 11. Concentrations of nutrients in split replicate native water samples at South Branch Plum Creek and Deer Creek from June 1996 through April 1998

[Concentrations are in milligrams per liter; <, less than]

CONSTITUENT	SOUTH BRANCH PLUM CREEK AT FIVE POINTS, PA.										DEER CREEK NEAR DORSEYVILLE, PA.	
	6/17/96		12/12/96		12/9/97		2/27/98		4/24/98		7/9/97	
	SAMPLE 1	SAMPLE 2	SAMPLE 1	SAMPLE 2	SAMPLE 1	SAMPLE 2	SAMPLE 1	SAMPLE 2	SAMPLE 1	SAMPLE 2	SAMPLE 1	SAMPLE 2
Dissolved orthophosphate	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.013	<0.01	<0.01	<0.01	<0.01
Dissolved nitrate+ nitrite	.66	<.05	1.3	1.3	1.18	1.17	1.12	<.05	2.58	.845	.063	<.05
Dissolved ammonia	.04	.03	.06	.05	<.02	<.02	.036	<.02	.054	.041	<.015	<.015
Dissolved phosphorus	<.01	<.01	.02	<.01	<.01	<.01	<.01	<.01	.016	<.01	<.01	<.01
Dissolved ammonia+ organic nitrogen	<.2	<.2	<.2	<.2	<.1	<.1	<.1	<.1	.26	<.1	<.2	<.2
Total ammonia+ organic nitrogen	<.2	<.2	.6	.3	<.1	<.1	.11	<.1	<.1	<.1	.3	<.2
Total phosphorus	.03	<.01	.12	.07	<.01	<.01	<.01	<.01	<.01	<.01	.023	<.01

Table 12. Concentrations of pesticide compounds analyzed by HPLC and GC/MS methods in filtered split environmental samples, South Branch Plum Creek, December 12, 1997

[Concentrations in micrograms per liter; <, less than]

PESTICIDE COMPOUNDS ANALYZED BY HPLC	SAMPLE 1	SAMPLE 2	PESTICIDE COMPOUNDS ANALYZED BY GC/MS	SAMPLE 1	SAMPLE 2	PESTICIDE COMPOUNDS ANALYZED BY GC/MS	SAMPLE 1	SAMPLE 2
2,4,5-T	<0.035	<0.035	Acetochlor	<0.002	<0.002	Terbacil	<0.007	<0.007
2,4,5-D	<.15	<.015	Alachlor	<.002	<.002	Terbufos	<.013	<.013
2,4-DB	<.24	<.24	Atrazine	<.014	<.014	Thiobencarb	<.002	<.002
Silvex (2,4,5-TP)	<.021	<.21	Azinphos-methyl	<.4	<.2	Triallate	<.001	<.001
3-OH-carbofuran	<.14	<.014	Benfluralin	<.002	<.002	Trifluralin	<.002	<.002
DNOC	<.42	<.42	Butylate	<.002	<.002	alpha-BHC	<.002	<.002
Acifluorfen	<.035	<.035	Carbaryl	<.003	<.003	cis-Permethrin	<.005	<.005
Aldicarb	<.55	<.55	Carbofuran	<.003	<.003	p,p'-DDE	<.006	<.006
Aldicarb Sulfone	<.1	<.1	Chlorpyrifos	<.004	<.004			
Aldicarb Sulfoxide	<.021	<.021	Cyanazine	<.15	<.015			
Bentazon	<.014	<.014	DCPA	<.002	<.002			
Bromacil	<.035	<.035	2,6-Diethylalanine	<.003	<.003	"The following are surrogate recoveries, expressed as a percent."		
Bromoxynil	<.035	<.035	Deethyl atrazine	<.0134	<.0127			
Carbaryl	<.008	<.008	Diazinon	<.002	<.002			
Carbofuran	<.12	<.12	Dieldrin	<.001	<.001	Diazinon Surrogate	100	82.2
Chloramben	<.42	<.42	Disulfoton	<.017	<.017	Terbutylazine Surrogate	122	113
Chlorothalonil	<.48	<.48	EPTC	<.002	<.002	alpha HCH Surrogate	109	101
Clopyralid	<.23	<.23	Ethalfuralin	<.004	<.004	BDMC, Surrogate	115	108
Dacthal	<.017	<.017	Ethoprop	<.003	<.003			
Dicamba	<.035	<.035	Fonofos	<.003	<.003			
Dichlobenil	<1.2	<1.2	Lindane	<.004	<.004			
Dichlorprop	<.032	<.032	Linuron	<.002	<.002			
Dinoseb	<.035	<.035	Malathion	<.005	<.005			
Diuron	<.02	<.02	Metolachlor	<.008	<.007			
Fenuron	<.013	<.013	Metribuzin	<.013	<.011			
Fluorometuron	<.035	<.035	Molinate	<.004	<.004			
Linuron	<.018	<.018	Napropamide	<.003	<.003			
MCPA	<.17	<.17	Parathion	<.004	<.004			
MCPB	<.14	<.14	Methyl parathion	<.006	<.006			
Methiocarb	<.026	<.026	Pebulate	<.004	<.004			
Methomyl	<.017	<.017	Pendimethalin	<.004	<.004			
Neburon	<.015	<.015	Phorate	<.002	<.002			
Norflurazon	<.024	<.024	Prometon	<.018	<.018			
Oryzalin	<.31	<.31	Pronamide	<.003	<.003			
Oxamyl	<.018	<.018	Propachlor	<.007	<.007			
Picloram	<.05	<.05	Propanil	<.004	<.004			
Propham	<.035	<.035	Propargite	<.013	<.013			
Propoxur	<.035	<.035	Simazine	<.005	<.003			
Triclopyr	<.25	<.25	Terbutiuron	<.01	<.01			

Table 13. Concentrations of pesticides in native water and percent recovery of spiked concentrations at Deer Creek and South Plum Creek. Percent recovery is calculated as the spiked sample concentration divided by the spike concentration expressed as a percent

[Concentrations are in micrograms per liter; E, estimated value; <less than; --no date available]

PESTICIDE COMPOUNDS ANALYZED BY HPLC	DEER CREEK NEAR DORSEYVILLE, PA.						SOUTH BRANCH PLUM CREEK AT FIVE POINTS, PA.					
	NATIVE WATER	SPIKE CONCEN- TRATION	SPIKED SAMPLE 1	PERCENT RECOVERY	SPIKED SAMPLE 2	PERCENT RECOVERY	NATIVE WATER	SPIKE CONCEN- TRATION	SPIKED SAMPLE 1	PERCENT RECOVERY	SPIKED SAMPLE 2	PERCENT RECOVERY
2,4,5-T	<0.035	0.91	--	--	--	--	<0.035	0.91	0.82	90.2	0.9	99.0
2,4,5-D	<.035	1.12	0.8	71.4	0.8	71.4	<.035	1.12	.87	77.7	.94	83.9
2,4-DB	<.035	.92	.73	79.0	.72	77.9	<.035	.92	.7	75.8	.8	86.6
Silvex (2,4,5-TP)	<.021	.95	.87	92.1	.89	94.2	<.021	.95	.89	94.2	.95	10.5
3-OH-carbofuran	<.014	1.12	.92	82.1	.86	76.8	<.014	1.12	.84	75.0	.88	78.6
DNOC	<.035	.99	E .87	87.7	E.85	85.7	<.035	.99	E.87	87.7	E.91	91.7
Acifluorfen	<.035	1.10	.6	54.5	E.69	62.7	<.035	1.10	.98	89.1	1.04	94.5
Aldicarb	<.016	1.12	.39	34.8	.56	5.0	<.016	1.12	--	--	--	--
Aldicarb Sulfone	<.016	1.18	.3	25.4	.34	28.8	<.016	1.18	.22	18.6	.11	9.3
Aldicarb Sulfoxide	<.021	1.17	.62	53.0	.87	74.4	<.021	1.17	1.1	94.0	.82	7.1
Bentazon	<.014	.95	E .88	92.7	E.93	98.0	<.014	.95	E.87	91.7	.91	95.9
Bromacil	<.035	1.09	.79	72.5	.8	73.4	<.035	1.09	.74	67.9	.79	72.5
Bromoxynil	<.035	.95	.92	97.0	.92	97.0	<.035	.95	.87	91.8	.95	10.2
Carbaryl	<.008	1.07	E 1.12	104.7	E.84	78.5	<.008	1.07	E1.07	10.0	E1.07	10.0
Carbofuran	<.028	1.05	E 1.57	149.5	E1.61	153.3	<.028	1.05	1.04	99.0	.94	89.5
Chloramben	<.011	.00	< .011	--	<.01	--	<.011	.00	<.011	--	E.011	--
Chlorothalonil	<.035	1.10	E .78	7.9	.57	51.8	<.035	1.10	E.29	26.4	E.68	61.8
Clopyralid	<.050	.90	<.05	5.6	<.05	5.6	<.050	.90	.16	17.8	.14	15.6
Dacthal	<.017	.97	E.95	98.3	E.96	99.4	<.017	.97	E.91	94.2	.93	96.3
Dicamba	<.035	.92	.24	26.1	.29	31.6	<.035	.92	.5	54.5	.71	77.3
Dichlobenil	<.020	1.01	E.18	17.8	1.63	161.4	<.020	1.01	E.54	53.5	.58	57.4
Dichlorprop	<.032	.95	.85	89.2	.82	86.0	<.032	.95	.81	85.0	.87	91.3
Dinoseb	<.035	.94	.61	65.0	.69	73.6	<.035	.94	.87	92.8	.92	98.1
Diuron	<.020	1.07	.9	84.1	.91	85.0	<.020	1.07	.88	82.2	.88	82.2
Fenuron	<.013	1.18	.93	78.8	.92	78.0	<.013	1.18	.88	74.6	.94	79.7
Fluometuron	<.035	1.05	1.16	11.5	1.22	116.2	<.035	1.05	.92	87.6	.91	86.7
Linuron	<.018	1.08	.82	75.9	.82	75.9	<.018	1.08	.79	73.1	.78	72.2
MCPA	<.050	.94	.72	77.0	E.86	92.0	<.050	.94	.83	88.8	.89	95.2
MCPB	<.035	.94	.65	69.2	.63	67.1	<.035	.94	.7	74.5	.84	89.5
Methiocarb	<.026	1.06	.89	84.0	.69	65.1	<.026	1.06	.79	74.5	.8	75.5
Methomyl	<.017	1.04	1.16	111.5	.91	87.5	<.017	1.04	.9	86.5	.9	86.5
Neburon	<.015	1.09	.9	82.6	.91	83.5	<.015	1.09	.78	71.6	.79	72.5
Norflurazon	<.024	1.04	1.08	103.8	1.04	10.0	<.024	1.04	.94	9.4	.91	87.5
Oryzalin	<.019	1.14	.8	7.2	.79	69.3	<.019	1.14	.73	64.0	.77	67.5
Oxamyl	<.018	.99	.71	71.7	.56	56.6	<.018	.99	.71	71.7	.64	64.6
Picloram	<.050	1.00	.59	59.0	.39	39.0	<.050	1.00	.72	72.0	.73	73.0
Propham	<.035	1.08	.83	76.9	.8	74.1	<.035	1.08	E.76	7.4	.75	69.4
Propoxur	<.035	1.07	.81	75.7	.81	75.7	<.035	1.07	.83	77.6	.85	79.4
Triclopyr	<.050	.98	.92	94.3	.91	93.2	<.050	.98	.93	95.3	1.03	105.5

Table 13. Concentrations of pesticides in native water and percent recovery of spiked concentrations at Deer Creek and South Plum Creek. Percent recovery is calculated as the spiked sample concentration divided by the spike concentration expressed as a percent—Continued

[Concentrations are in micrograms per liter; E, estimated value; <less than; --no date available]

PESTICIDE COMPOUNDS ANALYZED BY GC/MS	DEER CREEK NEAR DORSEYVILLE, PA.						SOUTH BRANCH PLUM CREEK AT FIVE POINTS, PA.					
	NATIVE WATER	SPIKE CONCEN- TRATION	SPIKED SAMPLE 1	PERCENT RECOVERY	SPIKED SAMPLE 2	PERCENT RECOVERY	NATIVE WATER	SPIKE CONCEN- TRATION	SPIKED SAMPLE 1	PERCENT RECOVERY	SPIKED SAMPLE 2	PERCENT RECOVERY
2,6-Diethylanaline	<0.003	0.1	0.09	90.0	0.09	86.0	<0.003	0.1	0.09	92.5	0.10	97.1
Acetochlor	<.002	.1	.11	106.0	.09	91.0	<.002	.1	.12	119.0	.11	114.0
Alachlor	<.002	.1	.11	108.0	.10	10.0	<.002	.1	.12	116.0	.11	114.0
Atrazine	<.001	.1	.11	108.0	.10	10.0	.112	.1	.13	129.0	.13	127.0
Azinphos-methyl	<.001	.1	.11	11.0	E.11	106.0	<.001	.1	E.34	34.0	E.40	399.0
Benfluralin	<.002	.1	.11	109.0	.10	98.0	<.002	.1	.10	103.0	.10	103.0
Butylate	<.002	.09	.11	119.0	.10	106.7	<.002	.09	.11	117.8	.11	118.9
Carbaryl	<.003	.1	E.17	166.0	E.20	199.0	<.003	.1	E.21	211.0	E.21	207.0
Carbofuran	<.003	.1	E.13	132.0	E.14	142.0	<.003	.1	.21	21.0	E.19	191.0
Chlorpyrifos	<.004	.1	.10	104.0	.10	97.0	<.004	.1	.10	102.0	.10	97.4
Cyanazine	<.004	.1	.09	88.0	.08	84.0	.016	.1	.14	135.0	.12	121.0
DCPA	<.002	.09	.11	118.0	.10	107.8	<.002	.09	.09	104.9	.09	104.9
Deethyl Atrazine	<.002	.1	E.03	25.0	E.02	24.0	E.008	.1	E.05	47.4	E.04	35.6
Diazinon	<.002	.1	.10	99.0	.09	94.0	<.002	.1	.11	111.0	.11	106.0
Dieldrin	<.001	.09	.08	86.0	.08	87.8	<.001	.09	.09	96.7	.09	95.6
Disulfoton	<.017	.09	.05	57.7	.06	67.8	<.017	.09	.09	95.6	.08	89.0
EPTC	<.002	.09	.11	117.8	.10	107.8	<.002	.09	.11	123.3	.11	125.6
Ethalfuralin	<.004	.09	.11	118.9	.10	107.8	<.004	.09	.11	124.4	.11	123.3
Ethoprop	<.003	.09	.10	114.4	.09	104.4	<.003	.09	.11	116.7	.10	114.4
Fonofos	<.003	.1	.10	97.0	.09	92.0	<.003	.1	.11	106.0	.11	105.0
Lindane	<.004	.09	.08	92.2	.09	95.6	<.004	.09	.12	137.8	.11	122.2
Linuron	<.002	.09	.09	95.6	.09	94.4	<.002	.09	.13	146.7	.13	147.7
Malathion	<.005	.1	.10	101.0	.10	95.0	<.005	.1	.12	115.0	.12	115.0
Metolachlor	<.002	.09	.12	127.8	.11	12.0	.011	.09	.13	146.7	.13	143.3
Metribuzin	<.004	.1	.10	104.0	.10	96.0	<.020	.1	.10	96.0	.09	91.0
Molinate	<.004	.1	.10	104.0	.10	10.0	<.004	.1	.10	101.0	.10	104.0
Napropamide	<.003	.1	.09	87.0	.10	95.0	<.003	.1	.11	108.0	.10	98.6
Parathion	<.004	.1	.10	103.0	.11	112.0	<.004	.1	.12	117.0	.12	12.0
Methyl parathion	<.006	.1	.11	108.0	.10	102.0	<.006	.1	.12	123.0	.13	126.0
Pebulate	<.004	.09	.10	113.3	.10	11.0	<.004	.09	.10	115.6	.11	117.8
Pendimethalin	<.004	.1	.09	93.0	.07	74.0	<.004	.1	.11	111.0	.11	112.0
Phorate	<.002	.1	.07	7.0	.07	65.0	<.002	.1	.10	96.0	.09	93.4
Prometon	<.018	.1	.11	106.0	.10	98.0	<.018	.1	.12	122.0	.11	11.0
Propachlor	<.007	.1	.12	116.0	.11	113.0	<.007	.1	.12	119.0	.12	123.0
Propanil	<.004	.1	.11	105.0	.10	98.0	<.004	.1	.11	11.0	.11	11.0
Propargite	<.013	.09	.09	101.1	.09	96.7	<.013	.09	.10	111.1	.09	103.8
Pronamide	<.003	.1	.10	101.0	.10	95.0	<.003	.1	.10	10.0	.10	103.0
Simazine	<.005	.1	.10	97.0	.09	93.0	.008	.1	.11	111.0	.11	106.0
Terbutiuron	<.010	.1	.11	112.0	.11	11.0	<.010	.1	.10	102.0	.11	106.0
Terbacil	<.007	.1	E.07	66.0	E.06	64.0	<.007	.1	E.10	95.7	E.07	67.4
Terbufos	<.013	.1	.09	87.0	.08	82.0	<.013	.1	.11	108.0	.10	101.0
Thiobencarb	<.002	.1	.10	103.0	.10	96.0	<.002	.1	.11	107.0	.11	106.0
Triallate	<.001	.1	.10	95.0	.09	86.0	<.001	.1	.10	97.7	.10	96.6
Trifluralin	<.002	.1	.11	109.0	.10	99.0	<.002	.1	.11	109.0	.11	107.0
alpha-BHC	<.002	.1	.09	94.0	.09	9.0	<.002	.1	.10	10.0	.10	103.0
cis-Permethrin	<.005	.03	.02	5.0	.01	2.0	<.005	.03	.02	53.3	.02	5.0
p,p'- DDE	--	.1	.06	62.0	.03	34.0	<.006	.1	.07	7.8	.07	68.9

Table 14. Concentrations of volatile organic compounds in blank samples collected at Deer Creek, February 2, April 10, and June 5, 1997, and April 16, 1998

[Concentrations are in micrograms per liter; E, estimated value; <, less than; --, no data available]

VOC	02-07-1997	04-10-1997	06-05-1997	04-16-1998	VOC	02-07-1997	04-10-1997	06-05-1997	04-16-1998
Acetone	E1.4	5	4.9	4.9	Freon 113	<0.05	-	<0.032	<0.032
Acrolein	<2	<2	<1.43	--	Tetrahydrofuran	<5	<5	<1.15	<1.15
Acrylonitrile	<2	<2	<1.23	<1.23	Hexachlorobutadiene	<2	<2	<1.142	<1.142
Benzene	<.05	E.005	<.032	<.032	2-Hexanone	<5	<5	<.746	<.746
Bromobenzene	<.05	<.05	<.036	<.036	Isodurene	<.05	--	<.24	<.24
Chlorobenzene	<.05	<.05	<.028	<.028	Methymethacrylate	<1	<1	<.35	<.35
o-Dichlorobenzene	<.05	<.05	<.048	<.048	Ethylmethacrylate	<1	<1	<.278	<.278
1,3-Dichlorobenzene	<.05	<.05	<.054	<.054	Methyl bromide	<.1	--	<.148	<.148
1,4-Dichlorobenzene	E.04	E.007	<.05	<.05	Methyl chloride	<.2	--	<.254	<.254
1,2,3-Trichlorobenzene	<.2	<.2	<.266	<.266	Bromochloromethane	<.1	<.1	<.044	<.044
1,2,4-Trichlorobenzene	<.2	<.2	<.188	<.188	Dibromochloromethane	<.1	<.1	<.182	<.182
1,2,3-Trimethylbenzene	<.05	<.05	<.124	<.124	Dibromomethane	<.1	<.1	<.05	<.05
1,2,4-Trimethylbenzene	E.02	<.05	E.009	<.056	Bromodichloromethane	<.1	<.1	<.048	<.048
1,3,5-Trimethylbenzene	<.05	<.05	<.044	<.044	Dichlorodifluoromethane	<.2	<.2	E.08	<.096
Ethylbenzene	E.009	<.05	<.03	<.03	Methyl iodide	<.05	--	<.076	<.076
n-Propylbenzene	<.05	<.05	<.042	<.042	Carbon tetrachloride	<.05	--	<.088	<.088
Isopropyl-Benzene	<.05	<.05	<.032	<.032	Bromoform	<.2	<.2	<.104	<.104
n-Butylbenzene	<.05	<.05	<.186	<.186	Chloroform	<.1	<.05	<.052	<.052
sec-Butylbenzene	<.05	<.05	<.043	<.048	Trichlorofluoromethane	<.1	--	<.092	<.092
tert-Butylbenzene	<.05	<.05	<.096	<.096	Methyl acrylate	<.2	<.2	<.612	<.612
2-Butene T-1, 4-D	5	--	<.692	<.692	Meth acrylonitrile	<.2	<.2	<.57	<.57
Carbon disulfide	<.05	<.05	<.08	<.08	Methyl ethyl ketone	1.6	--	1.65	1.65
1,2-Dibromoethane	<.1	--	<.036	<.036	Methyl isobutyl ketone	5	--	<.374	<.374
Chloroethane	<.1	<.1	<.12	<.12	Prehnitene	<.05	--	<.23	<.23
1,1-Dichloroethane	<.05	<.05	<.066	<.066	Dichloropropane	<.05	--	<.068	<.068
1,2-Dichloroethane	<.05	<.05	<.134	<.134	2,2-Dichloropropane	<.05	<.05	<.078	<.078
1,1,1-Trichloroethane	<.05	<.005	<.032	<.032	1,3-Dichloropropane	<.05	<.05	<.116	<.116
1,1,2-Trichloroethane	<.1	<.1	<.064	<.064	1,2,3 Trichloropropane	<.2	<.2	<.07	<.07
1,1,1,2-Tetrachloroethane	<.05	<.05	<.044	<.044	Dibromochloropropane	<.5	<.5	<.214	<.214
1,1,2,2-Tetrachloroethane	<.1	<.1	<.132	<.132	3-Chloropropene	<.1	<.1	<.196	<.196
Hexachloroethane	<.05	<.05	<.362	<.362	1,1-Dichloropropene	<.05	<.05	<.026	<.026
Bromoethene	<.1	<.1	<.1	<.1	cis-1, 3-Dichloropropene	<.1	<.1	<.092	<.092
Methylene chloride	<.1	E.01	<.382	<.382	trans-1,3-Dichloropropene	<.1	<.1	<.134	<.134
1,1-Dichloroethylene	<.05	--	<.44	<.44	Styrene	<.05	<.05	<.042	<.042
cis-1, 2-Dichloroethylene	<.05	<.05	<.038	<.038	Toluene	.11	<.05	<.038	<.038
Transdichloroethene	<.05	<.05	<.032	<.032	o-Chlorotoluene	<.05	<.05	<.042	<.042
Trichloroethylene	<.05	--	<.038	<.038	p-Chlorotoluene	<.05	<.05	<.056	<.056
Tetrachloroethylene	<.05	--	<.038	<.038	o-Ethyltoluene	<.05	<.05	<.1	<.1
Diisopropyl ether	<.01	<.01	<.098	<.098	P-Isopropyl toluene	<.05	<.05	<.11	<.11
Ethyl ether	<.01	--	<.17	<.17	Vinyl Acetate	<5	<5	--	--
MTBE	<.1	<.1	<.112	<.112	Vinyl Chloride	<.1	<.1	<.112	<.112
Ethyl tert-butyl ether	<.1	<.1	<.054	<.054	o-Xylene	E.02	<.05	<.064	<.064
tert-Pentyl methyl ether	<.1	--	<.112	<.112	m-and p-Xylene	E.04	<.05	<.064	<.064