SUMMARY OF AND FACTORS AFFECTING PESTICIDE CONCENTRATIONS IN STREAMS AND SHALLOW WELLS OF THE LOWER SUSQUEHANNA RIVER BASIN, PENNSYLVANIA AND MARYLAND, 1993-95

by Robert A. Hainly, Tammy M. Zimmerman, Connie A. Loper, and Bruce D. Lindsey

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http://wwwrvares.er.usgs.gov/nawqa/nawqa_home.html

FOREWORD

The U.S. Geological Survey (USGS) is committed to serve the Nation with accurate and timely scientific information that helps enhance and protect the overall quality of life, and facilitates effective management of water, biological, energy, and mineral resources. Information on the quality of the Nation's water resources is of critical interest to the USGS because it is so integrally linked to the long-term availability of water that is clean and safe for drinking and recreation and that is suitable for industry, irrigation, and habitat for fish and wildlife. Escalating population growth and increasing demands for the multiple water uses make water availability, now measured in terms of quantity *and* quality, even more critical to the long-term sustainability of our communities and ecosystems.

The USGS implemented the National Water-Quality Assessment (NAWQA) Program to support national, regional, and local information needs and decisions related to water-quality management and policy. Shaped by and coordinated with ongoing efforts of other Federal, State, and local agencies, the NAWQA Program is designed to answer: What is the condition of our Nation's streams and ground water? How are the conditions changing over time? How do natural features and human activities affect the quality of streams and ground water, and where are those effects most pronounced? By combining information on water chemistry, physical characteristics, stream habitat, and aquatic life, the NAWQA Program aims to provide science-based insights for current and emerging water issues. NAWQA results can contribute to informed decisions that result in practical and effective water-resource management and strategies that protect and restore water quality.

Since 1991, the NAWQA Program has implemented interdisciplinary assessments in more than 50 of the Nation's most important river basins and aquifers, referred to as Study Units. Collectively, these Study Units account for more than 60 percent of the overall water use and population served by public water supply, and are representative of the Nation's major hydrologic landscapes, priority ecological resources, and agricultural, urban, and natural sources of contamination.

Each assessment is guided by a nationally consistent study design and methods of sampling and analysis. The assessments thereby build local knowledge about water-quality issues and trends in a particular stream or aquifer while providing an understanding of how and why water quality varies regionally and nationally. The consistent, multi-scale approach helps to determine if certain types of water-quality issues are isolated or pervasive, and allows direct comparisons of how human activities and natural processes affect water quality and ecological health in the Nation's diverse geographic and environmental settings. Comprehensive assessments on pesticides, nutrients, volatile organic compounds, trace metals, and aquatic ecology are developed at the national scale through comparative analysis of the Study-Unit findings.

The USGS places high value on the communication and dissemination of credible, timely, and relevant science so that the most recent and available knowledge about water resources can be applied in management and policy decisions. We hope this NAWQA publication will provide you the needed insights and information to meet your needs, and thereby foster increased awareness and involvement in the protection and restoration of our Nation's waters.

The NAWQA Program recognizes that a national assessment by a single program cannot address all water-resource issues of interest. External coordination at all levels is critical for a fully integrated understanding of watersheds and for cost-effective management, regulation, and conservation of our Nation's water resources. The Program, therefore, depends extensively on the advice, cooperation, and information from other Federal, State, interstate, Tribal, and local agencies, non-government organizations, industry, academia, and other stakeholder groups. The assistance and suggestions of all are greatly appreciated.

Robert M. Hirsch
Associate Director for Water

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CONVERSION FACTORS AND ABBREVIATIONS

Multiply	by	To obtain
Length		
inch (in.)	25.4	millimeter
foot (ft)	0.3048	meter
mile (mi)	1.609	kilometer
Area		
acre	0.4047	hectare
square mile (mi^2)	2.590	square kilometer
Mass		
pound, avoirdupois (lb)	0.4536	kilogram
Application Rate		
pounds per acre per year [(lb/acre)/yr]	1.121	kilograms per hectare per year
Temperature		
degree Fahrenheit (°F)	°C = 5/9 × (°F – 32)	degree Celsius

Other Abbreviations:

L, liter
µg/L, micrograms per liter
µL, microliter
µm, micrometer
mm, millimeter
lb/yr, pounds per year

Chemical concentrations used in this report are given in micrograms per liter (µg/L), a metric unit. Micrograms per liter is a unit expressing the concentration of chemical constituents or compounds in solution as weight (micrograms) of solute per unit volume (liter) of water. For concentrations less than 7,000 µg/L, the numerical value is the same as for concentrations in parts per billion.

Summary of and Factors Affecting Pesticide Concentrations in Streams and Shallow Wells of the Lower Susquehanna River Basin, Pennsylvania and Maryland, 1993-95

by Robert A. Hainly, Tammy M. Zimmerman, Connie A. Loper, and Bruce D. Lindsey

ABSTRACT

This report presents the detection frequency of 83 analyzed pesticides, describes the concentrations of those pesticides measured in water from streams and shallow wells, and presents conceptual models of the major factors affecting seasonal and areal patterns of pesticide concentrations in water from streams and shallow wells in the Lower Susquehanna River Basin. Seasonal and areal patterns of pesticide concentrations were observed in 577 samples and nearly 40,000 pesticide analyses collected from 155 stream sites and 169 shallow wells from 1993 to 1995. For this study, shallow wells were defined as those generally less than 200 feet deep.

The most commonly detected pesticides were agricultural herbicides—atrazine, metolachlor, simazine, prometon, alachlor, and cyanazine. Atrazine and metolachlor are the two most-used agricultural pesticides in the Lower Susquehanna River Basin. Atrazine was detected in 92 percent of all the samples and in 98 percent of the stream samples. Metolachlor was detected in 83 percent of all the samples and in 95 percent of the stream samples. Nearly half of all the analyzed pesticides were not detected in any sample. Of the 45 pesticides that were detected at least once, the median concentrations of 39 of the pesticides were less than the detection limit for the individual compounds, indicating that for at least 50 percent of the samples collected, those pesticides were not detected. Only 10 (less than 0.025 percent) of the measured concentrations exceeded any established drinking-water standards; 25 concentrations exceeded 2 µg/L (micrograms per liter) and 55 concentrations exceeded 1 µg/L. None of the elevated concentrations were measured in samples collected from streams that are used for public drinking-water supplies, and 8 of the 10 were measured in storm-affected samples.

The timing and rate of agricultural pesticide applications affect the seasonal and areal concentration patterns of atrazine, simazine, chlorpyrifos, and diazinon observed in water from wells and streams in the Lower Susquehanna River Basin. Average annual pesticide use for agricultural purposes and nonagricultural pesticide use indicators were used to explain seasonal and areal patterns. Elevated concentrations of some pesticides in streams during base-flow and storm-affected conditions were related to the seasonality of agricultural-use applications and local climate conditions. Agricultural-use patterns affected areal concentration patterns for the high-use pesticides, but indicators of nonagricultural use were needed to explain concentration patterns of pesticides with smaller amounts used for agricultural purposes.

Bedrock type influences the movement and discharge of ground water, which in turn affects concentration patterns of pesticides. The ratio of atrazine concentrations in stream base flow to concentrations in shallow wells varied among the different general rock types found in the Lower Susquehanna River Basin. Median concentrations of atrazine in well water and stream base flow tended to be similar in individual areas underlain by carbonate bedrock, indicating the connectivity of water in streams and

shallow wells in these areas. In areas underlain by noncarbonate bedrock, median concentrations of atrazine tended to be significantly higher in stream base flow than in well water. This suggests a deep ground-water system that delivers water to shallow wells and a near-surficial system that supplies base-flow water to streams. In addition to the presence or absence of carbonate bedrock, pesticide leaching potential and persistence, soil infiltration capacity, and agricultural land use affected areal patterns in detection frequency and concentration differences between samples collected from streams during base-flow conditions and shallow wells.

INTRODUCTION

The National Water-Quality Assessment (NAWQA) Program is a nationwide, long-term U.S. Geological Survey (USGS) study to assess the quality of our Nation's waters. The full-scale NAWQA Program was implemented over a 6-year period in 51 separate study units. The study units are river basins or aquifer systems that range from about 1,200 to 50,000 mi^2 and include about 60 to 70 percent of the Nation's water use. The design of the NAWQA Program, as described by Gilliom and others (1995), includes four interrelated components: 1) retrospective analysis, 2) occurrence and distribution assessment, 3) trend and change assessment, and 4) case studies of sources, transport, fate, and effects. The goals of two of these components—the assessment of occurrence and distribution and case studies in relation to pesticides in the water column—are addressed in this report.

Studies began in 1991 in the Lower Susquehanna River Basin NAWQA study unit, hereafter termed "the study unit." The bulk of the water-quality sampling was completed during 1993-95, the intensive phase. Following this phase, interpretive reports were completed and a low intensity water-quality sampling program was conducted from 1997-2000. Topics for national synthesis and retrospective analysis include pesticides, volatile organic pesticides, nutrients, and suspended sediment.

The investigation of pesticides, the focus of this report, began with compilation and analysis of available data. Pesticide use for agricultural purposes in the study unit ranks high nationally (Gianessi and Puffer, 1991). In a few counties in the southern part of the study unit, application rates of pesticides are among the highest in the Nation (Barbash and Resek, 1996), making the effects of pesticide usage on the environment and human health a topic of concern.

Purpose and Scope

This report presents the detection frequencies of all analyzed pesticides, describes the concentrations measured in water from streams and shallow wells, and presents conceptual models of the major factors affecting seasonal and areal patterns of pesticide concentrations in water from wells and streams in the Lower Susquehanna River Basin.

The report is limited to an overview of pesticide concentrations measured in water from shallow wells (generally less than 200 ft deep) and streams in the study unit during the 1993-95 water years (the 12-month period October 1 to September 30 designated by the calendar year in which it ends) and a detailed analysis of five selected pesticides. Concentrations of 46 selected pesticides were analyzed in all samples. Concentrations of an additional 37 pesticides were measured in slightly more than half of the samples. A total of nearly 40,000 pesticide concentrations measured in 577 samples obtained from 169 ground-water wells and 155 stream water-quality sites are summarized.

Acknowledgments

The authors acknowledge significant efforts by the Lower Susquehanna River Basin NAWQA team in the collection of data for this report. In addition, thanks are given to the report review and production team for constructive comments that improved the quality and presentation of the study results and the document.

PREVIOUS INVESTIGATIONS

Numerous studies have been conducted to describe the occurrence of pesticides in water from wells and streams in the study unit. From 1970 to 1990, 10 ground-water studies, 8 surface-water studies, and 2 studies that focused on both ground and surface waters were done. Atrazine was frequently detected in ground-water and/or surface-water samples in many of these studies. Concentrations of atrazine and other detected pesticides rarely exceeded maximum contaminant levels for drinking water supplies. Ground-water studies were done at national, basin-wide, and local scales and will be summarized briefly in the paragraphs to follow. Ranges of concentrations for frequently detected pesticides are given when possible, but detection limits among the studies may have varied.

Two national well-water surveys included wells located in the study unit. Both studies determined the occurrence of a broad suite of pesticides in water from nearly 1,500 wells nationwide (Holden and others, 1992; Klein and others, 1993; U.S. Environmental Protection Agency, 1990a, 1990b). The work of Holden and others (1992) and Klein and others (1993) summarized one national survey in which the detection frequency of the pesticide alachlor was the primary focus. Less than 1 percent of the estimated six million existing private domestic wells had detectable levels of alachlor (Holden and others, 1992). The other national well-water survey included analyses of 126 pesticides and pesticide degradates. Atrazine and DCPA acid metabolites were most commonly found; maximum concentrations were 7.0 and 2.4 μg/L, respectively. Pesticide concentrations were generally low and rarely exceeded any established U.S. Environmental Protection Agency (USEPA) drinking-water guidelines (U.S. Environmental Protection Agency, 1996). Both studies were designed to provide information on frequency of detection and concentration of pesticides in wells on a nationwide basis; therefore, it was not possible to extract specific information on wells found in the Lower Susquehanna River Basin.

Several well-water studies also were completed from 1970 to 1990 in the study unit. These studies were performed in areas where the predominant land use was agriculture. A well-water study by Fishel and Lietman (1986) determined the effectiveness of agricultural best-management practices on herbicide and nitrate-nitrogen concentrations. Water was collected in the heavily farmed, 188-mi^2 Conestoga River Basin from 42 wells and 1 spring in an area of the Piedmont Physiographic Province underlain by carbonate bedrock. High herbicide concentrations (atrazine, 3 μg/L; simazine, 3.4 μg/L; alachlor, 3.0 μg/L) were measured and were associated with agricultural practices. Another study performed by Hippe and others (1994) analyzed concentrations of triazine and chloroacetamide herbicides and nutrients in ground water from wells and springs in an agricultural area in southcentral Pennsylvania near Carlisle. This study area was in the Great Valley Section of the Ridge and Valley Physiographic Province underlain by carbonate bedrock. Herbicides were detected, but none of the samples had concentrations that exceeded the USEPA Maximum Contaminant Level's (MCL's). For example, atrazine concentrations ranged from 0.1 to 0.2 μg/L—much less than the USEPA MCL for atrazine (3 μg/L).

Two studies were completed in intensely agricultural areas of the Mahantango Creek watershed. Both studies analyzed waters from about 20 wells to determine the occurrence of 9 different pesticides (alachlor, atrazine, carbofuran, chlorpyrifos, cyanazine, fonofos, metolachlor, simazine, and terbufos) in the Appalachian Mountain Section of the Ridge and Valley Physiographic Province underlain by sandstone and shale bedrock (Pionke and others, 1988; Pionke and Glotfelty, 1989). The study by Pionke and others (1988) also analyzed waters for 2,4-D and dicamba, but due to analytical problems, these two pesticides were not included in the study by Pionke and Glotfelty (1989). Atrazine was the pesticide most commonly detected in both studies but was measured at concentrations mostly less than 0.1 µg/L.

A ground-water study by Harrison and others (1995) analyzed waters from 189 private wells in rural corn-producing regions of Pennsylvania. Water samples were analyzed to determine the occurrence of 11 pesticides (alachlor, atrazine, carbofuran, chlorpyrifos, cyanazine, 2,4-D, dicamba, metolachlor, pendimethalin, simazine, and terbufos) in several of Pennsylvania's physiographic provinces. Atrazine and 2,4-D were the most prevalent pesticides detected in the samples. None of the detections exceeded the USEPA drinking-water guidelines except for water from one well that was used only for irrigation purposes. Another ground-water study by Becher (1996) analyzed waters from a network of wells and springs for a broad suite of constituents including seven herbicides (alachlor, atrazine, cyanazine, metolachlor, propazine, simazine, and toxaphene). Alachlor, atrazine, and simazine were the only herbicides detected in samples. Atrazine was detected most frequently; concentrations were generally less than 0.31 µg/L. The study was an assessment of wells in 10 valleys and 7 counties in Pennsylvania in the Cambro-Ordovician carbonate rocks of the Appalachian Mountain Section of the Ridge and Valley Physiographic Province.

Studies were conducted on major tributaries to the Chesapeake Bay. An assessment of the three major Chesapeake Bay tributaries—the Susquehanna, Potomac, and James Rivers—was completed by Lang (1982). Waters from the Susquehanna River at Conowingo Dam in Conowingo, Md., were analyzed for a seasonal characterization of organochlorine and organophosphorus insecticides and chlorophenoxy-acid herbicides. Atrazine and 2,4-D were the pesticides most frequently detected. Minimum concentrations reported as zero were below the minimum detection limit for that pesticide. Concentrations ranged from 0 to 1.2 µg/L for atrazine and 0 to 0.3 µg/L for 2,4-D.

Fishel (1984) collected data on various water-quality characteristics of the Susquehanna River at Harrisburg, Pa., to determine the relative contribution of constituent loads in the Susquehanna River to the Chesapeake Bay. Waters were analyzed for a suite of selected herbicides and insecticides. The herbicides atrazine and 2,4-D were detected most frequently; atrazine concentrations ranged from 0 to 3.4 µg/L, and 2,4-D ranged from 0 to 0.41 µg/L.

A study by Breen and others (1995) assessed the presence of triazine herbicide concentrations in the Susquehanna River and selected tributaries. Samples were collected from 43 sites that represented four major regions of corn production in the Lower Susquehanna River Basin. Triazine herbicides were detected in 39 of 43 sites; concentrations ranged from 0.1 to 1.0 µg/L. Triazine herbicides were more likely to be found in streams of the Piedmont Physiographic Province than in the Ridge and Valley Physiographic Province. A study by Hainly and Kahn (1996) evaluated the occurrence and transport of agricultural herbicides in the Susquehanna and Potomac Rivers. A total of 43 samples was collected in June 1994, and of the 47 pesticides included in the analysis, atrazine, metolachlor, simazine, alachlor, and cyanazine were the most commonly detected. Atrazine, metolachlor, and simazine ranged from 0 to 10 µg/L, 0 to 10 µg/L, and 0 to 1.4 µg/L, respectively. Herbicide concentrations were usually considerably less than the USEPA MCL’s. Land use was a key factor affecting herbicide concentrations. The highest concentrations were in areas where large amounts of corn were planted.

An assessment of pesticide occurrence in small streams by Truhlar and Reed (1975) was conducted to determine the magnitude of pesticide contamination in four basins with drainage areas ranging from 1.26 to 46.2 mi^2 with differing land uses (forested, general-farming, residential, and orchard-farming) in Pennsylvania. Another objective of the study was to determine whether or not the pesticides were present in amounts harmful to human or aquatic life. The study area included two basins within the study unit—Bixler Run in western Perry County and a tributary of Spring Creek in Dauphin County. Waters were analyzed to determine concentrations of chlorinated hydrocarbon insecticides and chlorophenoxy-acid herbicides. The insecticides DDT and dieldrin were detected most frequently. No pesticide concentrations exceeded established health standards.

Studies were conducted in basins within the Piedmont Physiographic Province where the predominant land use is agriculture. Two of these studies were completed in the Pequea Creek Basin (Ward, 1987; Ward and Eckhardt, 1979). Stream-water samples were analyzed to determine concentrations of organochlorine and organophosphate insecticides and chlorophenoxy-acid and triazine herbicides. The pesticides detected most frequently in the basin were atrazine, 2,4-D, dieldrin, DDT, heptachlor epoxide, and lindane. Atrazine concentrations ranged from 0 to 24 µg/L, and 2,4-D ranged from 0 to 1.2 µg/L. A similar study by Lietman and others (1983) determined the effects of land use on the water quality of receiving streams. Data were collected to quantify nonpoint-source loadings from four specific subbasins: 1) forest, 2) cornfield, 3) rural residential, and 4) pasture. Waters were analyzed for triazine herbicides and alachlor, a chloroacetamide herbicide. Atrazine, simazine, and prometon were detected frequently in the base-flow samples. Reported atrazine concentrations ranged from 0 to 3.9 µg/L during base flow. Lietman and Hall (1991) report atrazine concentrations ranging from 0 to 200 µg/L during storms. The highest concentration was in a composite storm sample collected from the cornfield site after herbicide application.

Two studies analyzed for pesticides in ground and surface waters and are most like the NAWQA Lower Susquehanna River Basin study. Lietman and Hall (1991) analyzed for triazine herbicides and the chloroacetamide herbicides, alachlor and metolachlor, in the intensely farmed Pequea Creek and Conestoga River watersheds in Lancaster County, Pa. The study was part of the Chesapeake Bay and Rural Clean Water Programs. Atrazine was the herbicide most frequently detected in water samples; atrazine concentrations ranged from 0 to 200 µg/L. Detections were commonly reported for simazine, cyanazine, alachlor, and metolachlor. The U.S. Department of Agriculture (1992) studied the Conestoga Headwaters during a Pennsylvania Rural Clean Water Program project. The project evaluated the severity of nonpoint-source pollutants on water quality. Best-management practices were implemented on the basis of the findings. Waters were analyzed for a broad suite of constituents including seven herbicides (atrazine, simazine, cyanazine, dieldrin, alachlor, metolachlor, and propazine). In the Regional Study area, atrazine, alachlor, and metolachlor were detected most frequently, and more than 35 percent of the 28 wells sampled in agricultural areas underlain by carbonate bedrock had detectable atrazine concentrations (greater than or equal to 0.2 µg/L). Atrazine and simazine concentrations in surface-water samples generally ranged from 0 to 1.0 µg/L and 0 to 1.3 µg/L, respectively.

The review of previous studies showed that geographical and technical gaps in pesticide data existed. The Lower Susquehanna River Basin NAWQA study helps to fill in those gaps and adds to the work of past studies by looking at spatial and temporal distributions of pesticides analyzed. In addition, numbers of detections in surface and ground water are reported for a broader spectrum of pesticides than was previously examined for the entire basin.

Initially, Breen and others (1991) described water-quality objectives for the Lower Susquehanna River Basin NAWQA Program in which the key issues included 1) contamination of surface and ground water by pesticides used in agricultural and urban areas and by other organic chemicals, and 2) the extent of and processes involved in ground-water contamination in limestone karst and in highly fractured-rock aquifers. The NAWQA study by Hainly and Kahn (1996) furthered the understanding of these key issues by measuring pesticide concentrations of surface-water sites in agricultural areas and by determining streamflow yields in carbonate systems. The NAWQA study by Breen and others (1995) identified triazine herbicide concentrations during base-flow conditions on the Susquehanna River and selected tributaries. The Lower Susquehanna River Basin NAWQA study, the study on which this report is based, is the first basin-wide well and streamwater assessment of pesticide concentrations in agricultural, urban, and forested areas. The study revisits some settings studied by others and examines water from wells and streams in the five major hydrogeologic settings, determined by physiology and bedrock type, in the study unit. These settings were further subdivided by incorporating land-use activity. Nationwide consistency in sampling and analytical methods used by the NAWQA Program will allow the use of these pesticide data in a national study of pesticide occurrence and will determine the magnitude of pesticide concentrations detected in streams and shallow wells, nationally.

DESCRIPTION OF STUDY AREA

The Susquehanna River drains about 27,000 mi^2 in New York, Pennsylvania, and Maryland. About 80 percent of the Susquehanna's watershed lies within Pennsylvania. From its headwaters near Cooperstown, N.Y., the Susquehanna River flows 447 mi to the Chesapeake Bay. In terms of total discharge at the mouth and its drainage area, the Susquehanna is the largest river on the eastern seaboard of the United States, the 18th largest in the United States (Kammerer, 1987), and is the largest tributary to the Chesapeake Bay, providing about one-half of the total freshwater to the Bay.

The study unit consists of the lower 9,200 mi^2 of the basin from where the West Branch and main stem of the Susquehanna River join near Sunbury, Pa., downstream to the Chesapeake Bay at Havre de Grace, Md. (fig. 1). The study unit also contains an area of about 150 mi^2 that includes parts of the Northeast Creek and Elk River Basins located upstream from the Fall Line. The Fall Line is an approximate boundary defined by the contact between the Piedmont and Coastal Plain Physiographic Provinces. Northeast Creek and Elk River drain directly into Chesapeake Bay. In this report, the term "Lower Susquehanna River Basin" (the study unit) is meant to include this small area that drains directly to the Bay. A detailed description of the study area and the hydrogeologic settings and environmental subunits can be found in Risser and Siwiec (1996).

Climate and Hydrology

Mean annual air temperature in the Lower Susquehanna River Basin is near 50°F. Mean daily air temperatures vary widely throughout the year, from the low 20's in January to the mid 70's in July. The mean annual precipitation is about 40 in. The areas that generally receive the most precipitation are the western edge and the southeastern part of the basin, primarily because of the mountain ridges and the Atlantic Ocean, respectively.

Runoff in the study unit, as indicated by the flow measured at the streamflow-gaging site on the Susquehanna River at Conowingo, Md., near the mouth, averaged about 20.5 in. annually for the period 1968-95 (James and others, 1995). This amount of runoff is slightly more than half of the average annual precipitation in the study unit. Natural streamflows vary seasonally or monthly. In general, streamflows are highest during March and April. About 60 percent of the annual streamflow is during the period February to May. Evapotranspiration during the growing-season months of July, August, and September reduces streamflow to its smallest amounts of the year. During these months, streamflow is primarily from ground-water sources. According to analyses of 24 streamflow-gaging sites in the study unit, 55 to 88 percent of annual streamflow is from ground water.

Climate and hydrology affect pesticide concentrations in water from wells and streams by determining the length of time that agricultural activities occur each year (the growing season) and the crops that grow best in that climate. This directly affects the amount and type of pesticide applied to cropland. The variability of runoff rates in the study unit and the seasonality of climate and hydrology affect the volume of water and concentrations in the streams. The seasonality of ground-water contributions to streamflow also affects in-stream pesticide concentrations.

The growing season covers periods of normally high and low streamflow and extends from April through September. It ranges from 160 days in the northern areas to 200 days in the south. On the average, slightly more than one-half of the annual

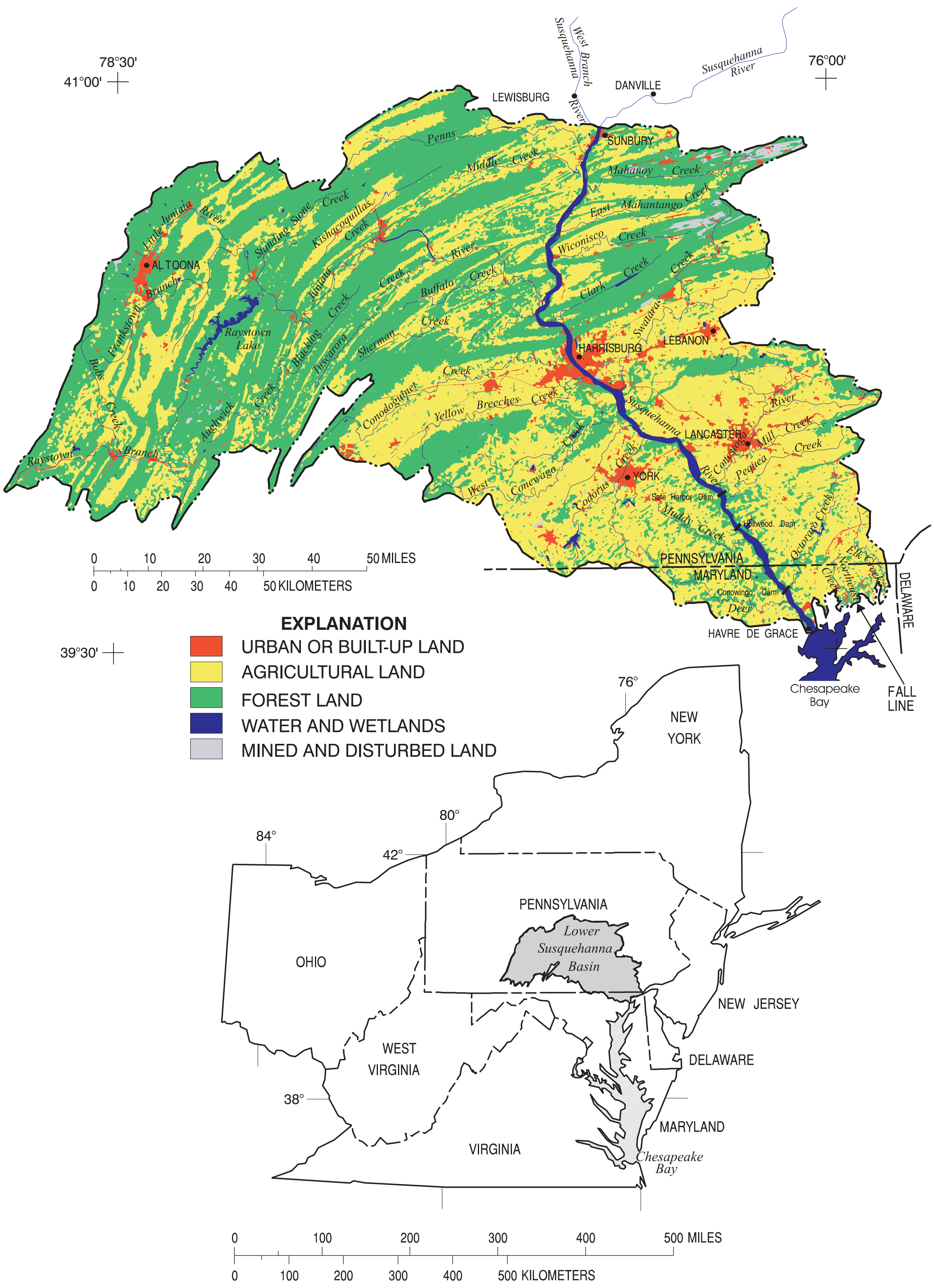


Figure 1. Major physical features and generalized land use in the Lower Susquehanna River Basin study unit, Pennsylvania and Maryland.

precipitation is received during the nongrowing season (October through March), allowing much of this quantity to be available for recharge to ground water. A major part of the precipitation that falls during the growing season is during the early months of the growing season (April through June)—a time when pesticide applications for agricultural purposes are most common. This provides a mechanism for localized atmospheric transport of spray clouds and removal of recently applied pesticides from the soil surface and subsequent transport to streams by runoff.

The climate of the study unit is controlled by a prevailing westerly circulation of air and the proximity of the basin to the Atlantic Ocean—the source for most precipitation in all but the western part of the study unit. The western part of the study unit has a humid continental climate characterized by large seasonal temperature variations and the eastern part has a more coastal-type climate characterized by moderated temperatures and precipitation amounts somewhat greater than the other parts of the basin (U.S. Geological Survey, 1991). Majewski and Capel (1995) report that high agricultural use of pesticides in the Midwestern and Mid-Atlantic parts of the United States may be one source for pesticides detected in rain and air. Common air circulation patterns may facilitate atmospheric transport of pesticides to the study unit.

Hydrogeologic Settings and Environmental Subunits

Hydrogeologic setting includes the environmental factors of physiography, bedrock type, and soils. Differences within the study unit for these factors are generally defined by major physiographic provinces or province sections and bedrock type. The study unit contains parts of five physiographic provinces: the Appalachian Plateau, Ridge and Valley, Blue Ridge, New England, and Piedmont (Berg and others, 1989). Together, the Ridge and Valley and Piedmont Physiographic Provinces account for 97 percent of the study unit. The Ridge and Valley Physiographic Province accounts for the northwestern two-thirds of the study unit and is characterized by valleys and long, narrow, and relatively steep ridges that trend southwest to northeast. The Great Valley Section of the Ridge and Valley Physiographic Province is located along the eastern edge of the province and in the central part of the study unit. It features a fairly wide and relatively flat valley floor. The Piedmont Physiographic Province covers the southeastern third of the study unit and is characterized by gently rolling hills.

Physiography affects water quality and pesticide concentrations in the study unit by controlling the route that precipitation must follow through the flow system on its way to a discharge point on the Susquehanna River. Physiography also determines the amount of time the precipitation is in contact with materials such as soil, rock, and vegetative cover that affect the chemical content of surface and ground waters.

Bedrock in the study unit has a complex structure and is diverse in type (Berg and others, 1980). Metamorphic and igneous crystalline rocks (for example, schist, gneiss, gabbro, and quartzite) crop out in the southeastern part of the basin. Carbonate rocks (limestone and dolomite) crop out predominantly in two east-west trending bands near the southcentral part of the basin, in a southwest to northeast band in the northwestern part of the study unit, and in thin ribbons in the center of the basin. The remaining area of the study unit is underlain by rocks consisting of sandstone, shale, and siltstone, hereafter termed sandstone and shale.

Bedrock type plays a major role in controlling the chemical composition of ground water and stream base flow. Ground water with elevated dissolved solids, hardness, and pH are the result of weathering of carbonate rocks. The median hardness of ground-water samples from carbonate rocks is about three times the median for sandstone and shale rocks and about six times the median for crystalline rocks (Taylor and Werkheiser, 1984). In addition, because of fractures common in carbonate rocks, aquifers in carbonate bedrock areas tend to have a rapid hydrologic response and are well-connected to the surface hydrologic system. The fractured rock also allows for the fairly rapid movement of dissolved constituents, such as some pesticides, to the aquifer.

Soils cover the bedrock throughout most of the study unit and were formed by physical and chemical weathering of bedrock. Soils formed by chemical weathering generally exhibit the chemical characteristics of the parent rock type and can be categorized into major groups by the type of parent material. The location of the soil groups is generally inferred by the location of each bedrock type within the study unit. Soil groups based on their capacity for infiltration in the study unit include the influences of the parent material but also include the characteristics of slope and thickness. Soils weathered from carbonate bedrock are generally considered to have an excellent infiltration capacity; those from crystalline rocks are considered to have good capacities, and those from sandstone and shale rocks are labeled as having good to poor capacities.

Soil-infiltration capacity affects the movement of precipitation, irrigation water, and soluble pesticides to ground water. Soil type also affects the availability of organic material and clay in the soil, which, in turn, influences transport processes in the soil. Chemical processes such as dissolution and adsorption are major factors in the transport and fate of pesticides. The location of rich agricultural soils, formed by the weathering of carbonate rocks, is also an important factor to consider. The location of this soil type encourages the use of the land for intense agricultural purposes and determines areas where pesticides might be applied and, potentially, areas of high agricultural pesticide use.

In the Lower Susquehanna River Basin, five major hydrogeologic settings, determined by physiography and bedrock type, are present: 1) crystalline rocks in the Piedmont and Blue Ridge Physiographic Provinces, 2) carbonate rocks in the Piedmont Physiographic Province, 3) sandstone and shale rocks in the Piedmont Physiographic Province, 4) carbonate rocks in the Ridge and Valley Physiographic Province, and 5) sandstone and shale rocks in the Ridge and Valley Physiographic Province.

Land use is an important environmental factor in describing pesticide use for both agricultural and nonagricultural purposes. In the study unit, land use is evenly divided between 47 percent agriculture and 47 percent forest, based on 1970’s data (Risser and Siwiec, 1996). However, local variations in this ratio exist. In the southern half of the basin (the Piedmont Physiographic Province and the Great Valley Section of the Ridge and Valley Physiographic Province) agriculture dominates (fig. 1). Nearly three-quarters of the land in the southern half of the basin is used for agricultural purposes. In the northern half of the basin (the Appalachian Mountain Section of the Ridge and Valley Physiographic Province) about two-thirds of the land is forested and one-third is used for agricultural purposes. Because the majority of pesticide use in the study unit is for agricultural purposes, the location and density of agricultural land use is an important factor to consider when describing factors affecting pesticide concentrations in the environment.

In comparison, about one-third of the Chesapeake Bay Basin has herbaceous agricultural land cover and slightly more than half of the basin is covered by forests (Langland and others, 1995). Most of the remainder of the Bay Basin is covered by urban land uses and water. In the Chesapeake Bay Basin, most agricultural land use is in the Piedmont Physiographic Province, the Great Valley Section of the Ridge and Valley Physiographic Province, and the eastern shore area of Maryland in the Coastal

Plain Province. In the Potomac River Basin, the next largest basin in the Bay watershed, the intensity of agriculture is similar to the study unit only in the Piedmont Physiographic Province (Fisher, 1995).

More recent studies in selected areas of the Lower Susquehanna River Basin indicate land use is changing. Since the 1970’s, 5-10 percent of the cropland in the Piedmont Physiographic Province and the Great Valley Section of the Ridge and Valley Physiographic Province has been converted to urban land uses (Petersen and others, 1992), which indicates a possible trend in pesticide use and type in these areas from agricultural to homeowner and commercial purposes.

In order to study the land-use diversity and hydrogeologic settings within the study unit, environmental subunits, hereafter termed subunits, were established. The subunits combine the physical and hydrogeologic factors of physiography and topography, bedrock type, and predominant land-use activity. This classification method produced more subunits than could be studied in this phase of the NAWQA Program. Along with input from a local group of interested environmental and water-resource managers, the NAWQA staff selected seven subunits that would address high-priority water-quality issues. The selected subunits allowed an assessment of water-quality conditions in agricultural areas underlain by carbonate bedrock and comparisons between agricultural, urban, and forested land uses in different hydrogeologic settings.

Water samples were collected in the following subunits: (1) agricultural areas underlain by crystalline bedrock in the Piedmont Physiographic Province, (2) agricultural areas underlain by carbonate bedrock in the Piedmont Physiographic Province, (3) agricultural areas underlain by carbonate bedrock in the Great Valley Section of the Ridge and Valley Physiographic Province, (4) urban areas underlain by carbonate bedrock in the Great Valley Section of the Ridge and Valley Physiographic Province, (5) agricultural areas underlain by carbonate bedrock in the Appalachian Mountain Section of the Ridge and Valley Physiographic Province, (6) agricultural areas underlain by sandstone and shale in the Appalachian Mountain Section of the Ridge and Valley Physiographic Province nearest to the Susquehanna River, and (7) forested areas underlain by sandstone and shale in the Appalachian Mountain Section of the Ridge and Valley Physiographic Province (fig. 2 and table 1).

Table 1. *Description of environmental subunits where pesticide samples were collected in 1993-95 in the Lower Susquehanna River Basin study unit, Pennsylvania and Maryland*

Environmental subunit	Physiographic province (section)	Topographic setting	Dominant bedrock type	Dominant land use	Percentage of study unit
Piedmont crystalline agricultural	Piedmont	Hilltop and hillside	Igneous and metamorphic	Agriculture	9.8
Piedmont carbonate agricultural	Piedmont	Valley	Limestone and dolomite	Agriculture	4.7
Great Valley carbonate agricultural	Ridge & Valley (Great Valley)	Valley	Limestone and dolomite	Agriculture	3.0
Great Valley carbonate urban	Ridge & Valley (Great Valley)	Valley	Limestone and dolomite	Urban	.6
Appalachian Mountain carbonate agricultural	Ridge & Valley (Appalachian Mountain)	Valley	Limestone and dolomite	Agriculture	4.6
Appalachian Mountain sandstone and shale agricultural	Ridge & Valley (Appalachian Mountain)	Valley and hillside	Sandstone, siltstone, and shale	Agriculture	6.3
Appalachian Mountain sandstone and shale forested	Ridge & Valley (Appalachian Mountain)	Valley and hillside	Sandstone, siltstone, and shale	Forest	34.2

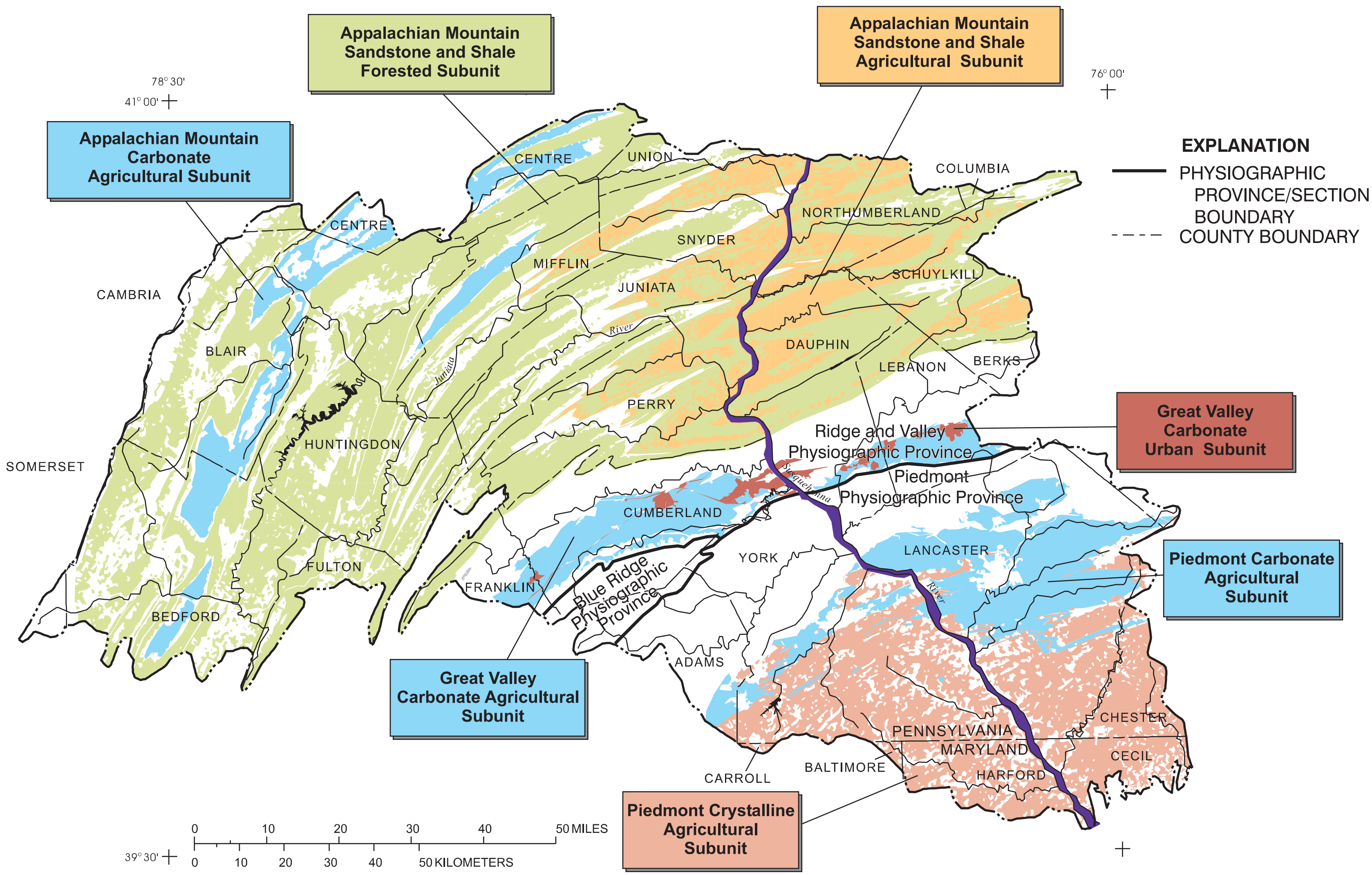


Figure 2. Subunits within the Lower Susquehanna River Basin study unit, Pennsylvania and Maryland.

PESTICIDE USE

Herbicides are used extensively in the study unit for the control of numerous weeds that affect the growth of corn, alfalfa, soybeans, and small grain crops. Weed-control programs are designed to control the growth and spread of weeds so that they will not adversely affect the use and the value of cropland, reduce the yield or the quality of crops, or increase the costs of production and harvest (Hippe and others, 1994). Most herbicide applications in the study unit are to row crops, especially corn and soybeans. Pasture and unplanted cropland receive very little herbicide treatment (Anderson and Gianessi, 1995). Row crops, and some cover crops, commonly receive one or more herbicide applications. Cover crops, such as forage, and small-grain crops, like alfalfa, barley, wheat, and oats, receive fewer herbicide applications because they leave little room for weed growth and do not require applications for weed control. Herbicide combinations are sometimes used for more effective weed control. Multiple applications are common and generally include some combination of pre-plant applications of selective or nonselective herbicides and pre-emergent and post-emergent applications of selective herbicides (Hippe and others, 1994). Additionally, nonselective burndown herbicides are sprayed on fields after small grain crop cuttings or along with no-till operations.

Little information is available concerning herbicide use for nonagricultural purposes. For this reason, determining the direct effect of nonagricultural applications on water quality is difficult to define and is generally only implied. Herbicides applied for these purposes will be discussed in a qualitative manner only. Nonagricultural uses of herbicides include weed control on golf courses, public lands, and homeowner lawns and vegetation-clearing along railways, highways, and transmission lines throughout the growing season. Weed-control application frequency for nonagricultural purposes ranges from routine application by commercial operations to sporadic application on an as-needed basis by private homeowners.

Estimates of herbicide use for agricultural and nonagricultural purposes indicate greater than 99 percent of all herbicide use is for agricultural purposes (Barbash and Resek, 1996, p. 175). In addition, agricultural pesticide use is considerably more extensive, areally, than nonagricultural use. Even though data are not available to estimate the herbicide amounts used for nonagricultural purposes in the study unit, it should not be considered insignificant. A compilation of national pesticide-use data by Barbash and Resek (1996) indicate commercial sod operations, lawn-care services, and golf courses are three of the top five pesticide uses. Nationally, about 35 percent of the available turf has almost 6 lb of active ingredient applied per acre on an average annual basis (Barbash and Resek, 1996, p. 109). In comparison, average application rates for atrazine on corn crops in the study unit range from 0.5 to 1.5 lb of active ingredient per acre per year (Anderson and Gianessi, 1995).

Insecticides and fungicides are applied on a routine basis only where recurring problems are known. Generally, such pesticides are applied to remedy sporadic problems and may be applied anytime throughout the growing season before the crop matures. This type of application program also is used to control insects and fungi associated with turf damage on homeowner lawns and golf courses and to control insects in structures. Insecticides like chlorpyrifos and diazinon are applied more commonly for home and garden use than for agricultural use. Nonagricultural uses are estimated to account for 50 to 70 percent of the chlorpyrifos and 90 to 98 percent of the diazinon used in the United States (Barbash and Resek, 1996, pp. 172-175). Most agricultural use of insecticides and fungicides is applied to orchard crops. Almost all fruit and vegetable crops in the study unit receive some kind of insecticide treatment (Anderson and Gianessi, 1995).

STUDY METHODS

The selection of streams and shallow wells for the collection of water-quality samples for pesticide analysis was directed by the design of the various water-quality studies being conducted as part of the NAWQA Program. The issues addressed by the water-quality studies ranged from local scale (the effects of agricultural practices on pesticides in ground-water wells and streams) to national scale (the occurrence, distribution, and concentrations of pesticides in ground-water wells and streams). The objectives of the stream water-quality studies were addressed by designing and conducting both long-term monitoring (up to 3 years) and synoptic studies. The ground-water synoptic studies focused on specific land-use types or areas underlain by similar bedrock types. Sampled wells were generally less than 200 ft deep and less than 20 years old. For a more detailed description of the design of water-quality studies, site-selection procedures, the implementation of the studies, and site and basin characteristics, see Siwiec and others (1997).

Water-quality studies conducted by the NAWQA Program in the Lower Susquehanna River Basin study unit may be broadly categorized into four major types: long-term monitoring of streams, basinwide synoptic studies of streams, subunit synoptic studies of ground water and streams, and focused synoptic studies of streams. Synoptic studies were completed over periods of 1 day to 2 weeks. Basinwide synoptic studies designed to cover a broad geographical area, subunit synoptic studies conducted in areas of homogeneous physiography and bedrock type and, in most cases, land use or land cover, and synoptic studies focused on a small geographic area or a particular water-quality issue were used to collect pesticide samples from streams.

Long-term monitoring consisted of the collection of samples at fixed intervals at seven streams, each representing one of seven major environmental subunits in the Lower Susquehanna River Basin (fig. 3). Sample-collection frequency ranged from weekly to monthly depending on the season and the stream. From four of these seven streams, water samples were collected routinely for pesticide analysis. At these streams, the number of water samples collected over a 2-3-year period ranged from nearly 50 to slightly more than 100. Less than five water samples for pesticide analysis were collected from each of the three remaining streams during the same period. Most fixed-interval water samples were collected during base-flow conditions, but some samples were collected during storm-affected flow conditions (see Appendix for explanation). For two of the streams, water samples for pesticide analysis were collected over the hydrograph of several storms during the early growing season of 1995. A total of 250 pesticide samples was collected at the long-term monitoring sites from 1993 to 1995 (Siwiec and others, 1997, table 2, p. 12).

A total of 22 synoptic studies were conducted in the study unit for the analysis of pesticides in ground water and streams from 1993 to 1995 (Siwiec and others, 1997). One basinwide synoptic study of streams was conducted in 1993. That study was an analysis of triazine herbicides at 47 stream sites located throughout the study unit. Subunit and focused synoptic studies also were conducted for the analysis of pesticides in streams (fig. 3). Six subunit synoptic studies in streams were conducted in the study unit; the number of sites sampled in each subunit ranged from 10 to 17 sites. Focused synoptic studies were conducted for the analysis of pesticides in streams; eight focused synoptic studies were conducted in the study unit, and the number of sites sampled in each study ranged from 5 to 19 sites. Subunit synoptic studies were conducted for pesticide analysis in ground water. Seven subunit synoptic studies were conducted; the number of wells sampled in each subunit generally

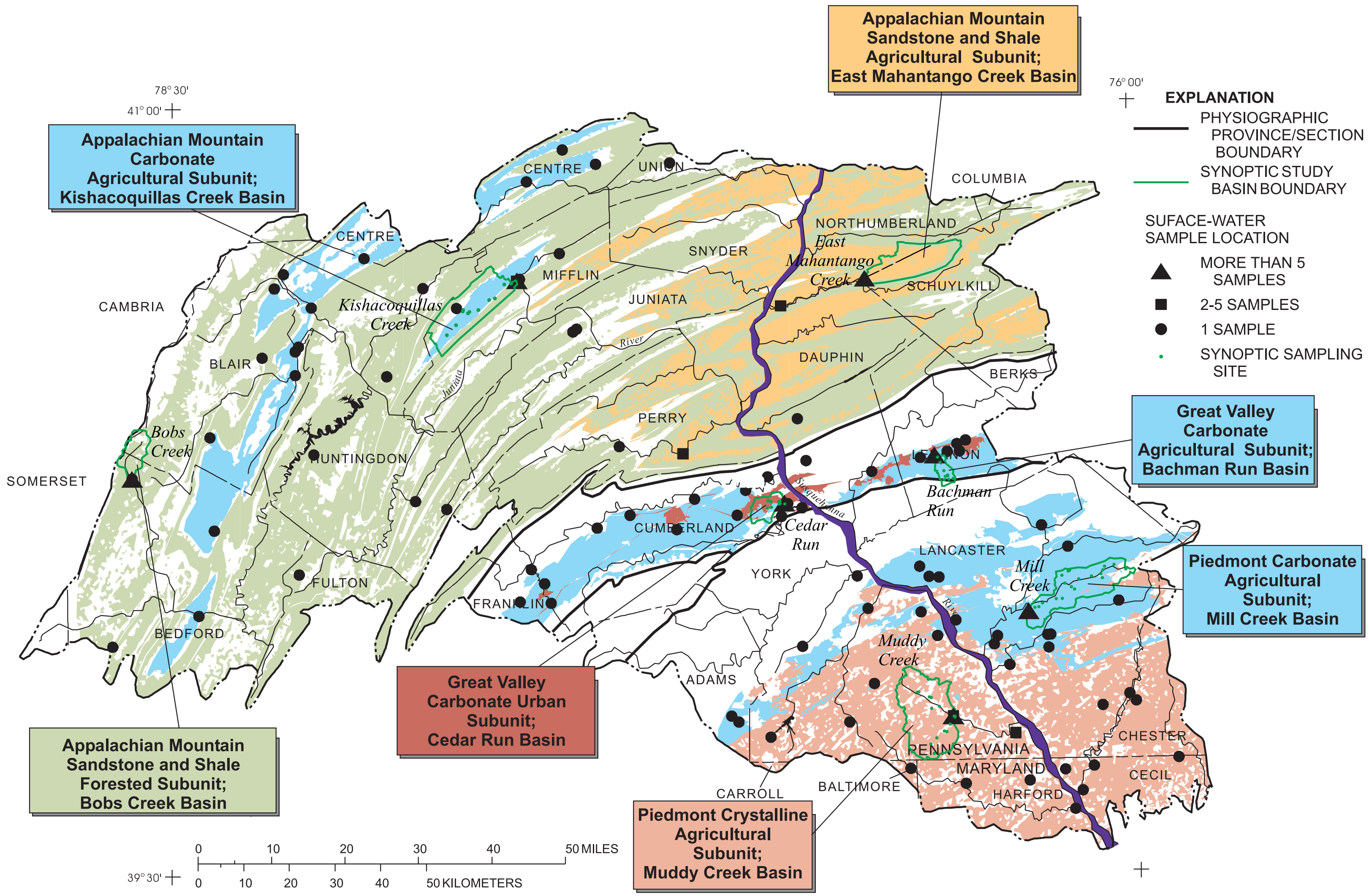


Figure 3. The Lower Susquehanna River Basin study unit, counties, major environmental subunits, and location of long-term monitoring basins and stream sites where pesticide samples were collected from 1993 to 1995.

ranged from 20 to 30. Water samples were collected for pesticide analysis from 169 wells (fig. 4). In all synoptic studies, wells and streams were sampled one time only.

Data Collection and Analysis

The process for selecting target analytes for pesticide analyses in the NAWQA Program involved consideration of several factors (Robert J. Gilliom, U.S. Geological Survey, written commun., 1994). The primary factors were (1) pesticides with annual applications greater than 8,000 lb of active ingredient, (2) pesticides previously and currently analyzed in various monitoring and survey programs by other agencies such as USEPA and National Oceanic and Atmospheric Administration (NOAA), (3) pesticides with USEPA Drinking Water Regulations and Health Advisories, (4) pesticides on the USEPA Priority Pollutant List, (5) results of published reports in which pesticides were reported in ground and surface water, (6) pesticides and metabolites that have a high potential for leaching into ground water, (7) pesticides that are highly toxic to mammals or aquatic life but have a low national use, (8) input from NAWQA study units on pesticides of major concern in the study units, and (9) new pesticides that are replacing discontinued pesticides. The pesticides analyzed for in this study, other selected information, and estimated annual-use data for the study unit and for the Commonwealth of Pennsylvania are listed in table 2. In addition, seven pesticides applied in the study unit but not analyzed in the water-quality samples were included in the table because of their relatively high use in the study unit (>20,000 lb/yr). Agricultural pesticide-use estimates for the Lower Susquehanna River Basin (table 2) were obtained from Anderson and Gianessi (1995). Estimates for statewide agricultural pesticide use were obtained from Gianessi and Puffer (1991, 1992a, 1992b).

The discussion of concentrations measured in environmental and quality-assurance samples collected from streams and wells will be focused on five pesticides—atrazine, simazine, pendimethalin, chlorpyrifos, and diazinon. These pesticides were selected to represent a range of amounts used for agricultural purposes and a range of detection frequencies in wells and streams. Other factors considered were toxicity, as indicated by the existence of health-advisory guidelines, and susceptibility to leaching (table 3). Atrazine and simazine are representative of the triazine herbicide group and pendimethalin is a dinitroaniline herbicide. Chlorpyrifos and diazinon are organophosphate insecticides.

Measured pesticide concentrations were compared to the drinking-water MCL's or maximum contaminant level goals (MCLG) but were not evaluated from a regulatory standpoint. For drinking water, an MCL is exceeded when the average concentration over a pre-defined period of time is higher than the MCL. Because typically only one sample was collected per site and the samples were not from public drinking-water supplies, it is not possible to determine if the MCL was exceeded from a regulatory standpoint. Drinking-water standards were used for comparison because there are no ambient water-quality criteria or suggested guidelines for the protection of aquatic organisms available for these pesticides.

Each pesticide analyzed by the USGS National Water Quality Laboratory (NWQL) in Arvada, Colo., for this study has a corresponding method detection limit (MDL), which is the minimum concentration of a substance that can be identified, measured, and reported with 99-percent confidence that the analyte concentration is greater than zero (Timme, 1995, p. 92). Nondetected concentrations are assigned a value of less than (<) the MDL and can be any concentration less than the MDL, including zero

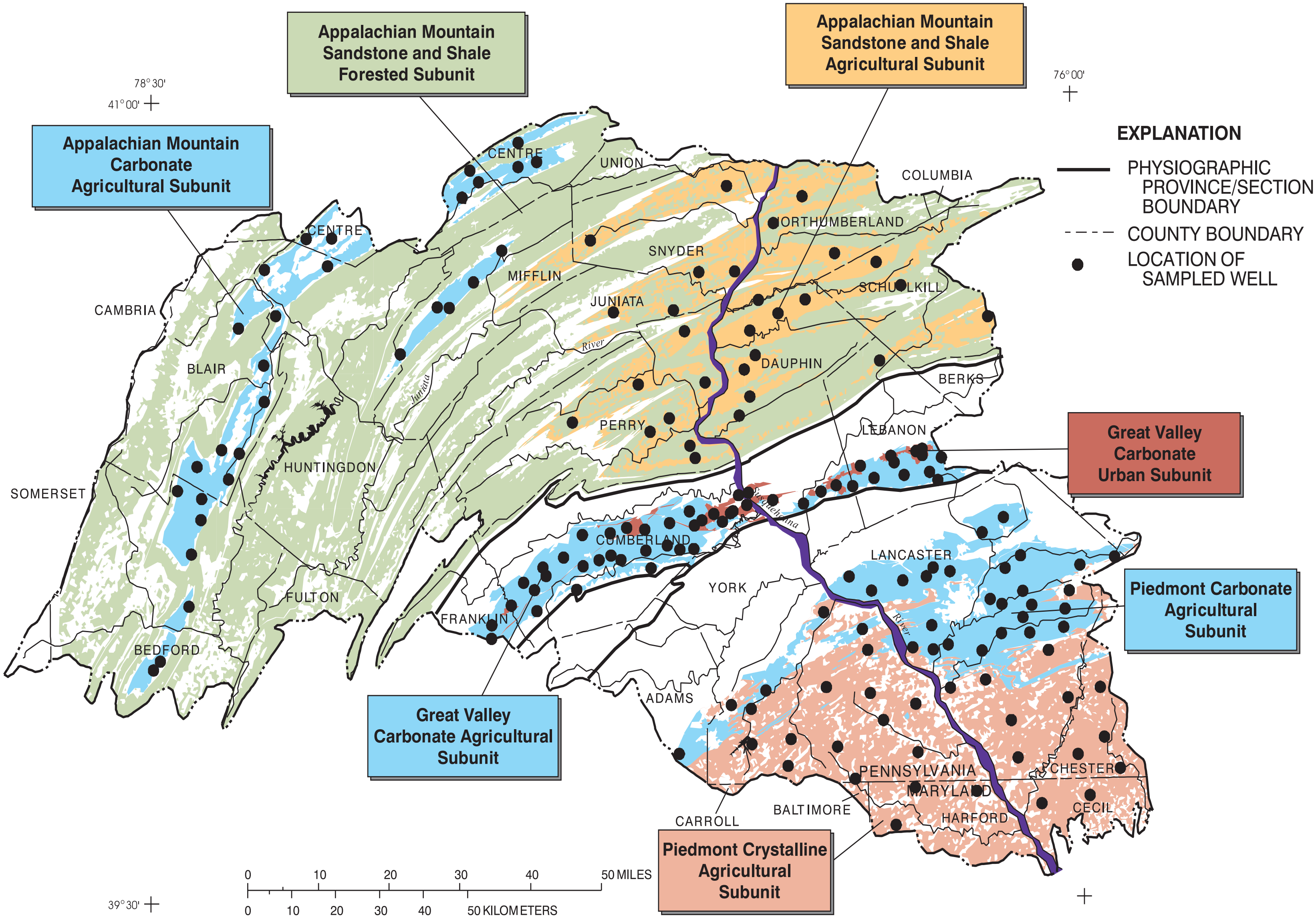


Figure 4. The Lower Susquehanna River Basin study unit, counties, major environmental subunits, and location of shallow ground-water wells where pesticide samples were collected from 1993 to 1995.

Table 2. *Pesticides for which ground- and surface-water samples were analyzed in the Lower Susquehanna River Basin study unit from 1993 to 1995 and information on water-quality standards and pesticide use*

[Shaded pesticides were analyzed by the gas chromatography/mass spectrometry method (Sandstrom and others, 1992; Zaugg and others, 1995); unshaded pesticides were analyzed by the high performance liquid chromatography method (Werner and others, 1996); Parameter code, 5-digit number used in the U.S. Geological Survey computerized data system, NWIS, to uniquely identify a specific constituent*; Italicized* pesticides indicate those pesticides that were not analyzed in this study but commonly are used in Pennsylvania; *, Restricted-use pesticide; NWIS, National Water Information System; LSR, Lower Susquehanna River Basin; MCL, Maximum Contaminant Level; MCLG, Maximum Contaminant Level Goal; --, not established; µg/L, micrograms per liter; lb/yr, pounds per year]

Pesticide	NWIS parameter code	Selected trade name(s)	MCL or MCLG[1] (µg/L)	Amount applied for agricultural use (lb/yr)	
				LSR Basin[2] (1990-1994)	Statewide-Pa. (1988)
		Herbicides[3]			
Acetochlor	49260	Harness, Surpass	--	--	--
Acifluorfen	49315	Blazer, Scepter	--/zero	--	13,300
Alachlor*	46342	Lasso, Alanox	2	127,000	514,000
Atrazine*	39632	AAtrex, Trac	3	417,000	1,610,000
Atrazine, desethyl	04040		--	--	--
Benfluralin	82673	Balan, Benefin, Bonalin	--	--	--
Bentazon	38711	Basagran, Forte	--/20	324	13,000
Bromacil	04029	Hyvar, Uragan	--	--	--
Bromoxynil	49311	Buctril, Brominex	--	19,100	[4]630
Butylate	04028	Sutan+, Genate Plus	--	--	121,000
Chloramben	49307	Amiben, Vegiben	--	1,730	9,560
Clopyralid	49305	Lontrel, Stinger	--	--	--
Cyanazine*	04041	Bladex, Fortrol	--/1	98,500	450,000
DCPA*	82682	Dacthal	--	2,160	11,200
Dicamba, mono-acid-	38442	Banvel, Metambane	--	21,300	112,000
Dichlobenil	49303	Barrier, Casoron	--	--	2,380
Dichlorprop, mono-acid-	49302	Weedone, Corasil	--	--	--
Diethylanaline	82660		--	--	--
Dinoseb[6]	49301	Premerge, DNBP	7	--	--
Diuron	49300	Karmex, Direx	--	2,740	28,900
EPTC	82668	Eptam, Alirox	--	895	202,000
Ethalfluralin	82663	Sonalan, Curbit	--	441	--
Fenuron	49297		--	--	--
Fluometuron	38811	Cotoran, Meturon	--	--	--
Glyphosate	39941	Roundup, Rodeo	700	21,300	526,000
Linuron*	82666	Lorox, Linex	--	45,300	60,100
MCPA, mono-acid-	38482	Chiptox, Weedar	--	10,200	36,900
MCPB, mono-acid-	38487	Thistrol, Tropotox	--	<10	514
Metolachlor	39415	Dual, Pennant	--	470,000	1,410,000
Metribuzin	82630	Lexone, Sencor	--	9,660	12,600
Molinate	82671	Ordram, Molinam	--	--	--
1-Naphthol	49295		--	--	--
Napropamide	82684	Devrinol, Naproguard	--	2,110	15,100
Neburon	49294	Neburex, Propuron	--	--	--
Norflurazon	49293	Predict, Zorial	--	505	6,520

Table 2. *Pesticides for which ground- and surface-water samples were analyzed in the Lower Susquehanna River Basin study unit from 1993 to 1995 and information on water-quality standards and pesticide use*—*Continued*

[Shaded pesticides were analyzed by the gas chromatography/mass spectrometry method (Sandstrom and others, 1992; Zaugg and others, 1995); unshaded pesticides were analyzed by the high performance liquid chromatography method (Werner and others, 1996); Parameter code, 5-digit number used in the U.S. Geological Survey computerized data system, NWIS, to uniquely identify a specific constituent; *Italicized* pesticides indicate those pesticides that were not analyzed in this study but commonly are used in Pennsylvania; *, Restricted-use pesticide; NWIS, National Water Information System; LSR, Lower Susquehanna River Basin; MCL, Maximum Contaminant Level; MCLG, Maximum Contaminant Level Goal; --, not established; µg/L, micrograms per liter; lb/yr, pounds per year]

Pesticide	NWIS parameter code	Selected trade name(s)	MCL or MCLG[1] (µg/L)	Amount applied for agricultural use (lb/yr)	
				LSR Basin[2] (1990-1994)	Statewide-Pa. (1988)
Herbicides—Continued					
Oryzalin	49292	Surflan, Snapshot	--	483	2,000
Paraquat	--	Cyclone, Gramoxone	--	28,900	91,400
Pebulate	82669	Tillam	--	4,570	17,800
Pendimethalin	82683	Prowl, Squadron	--	137,000	257,000
Picloram, mono-acid-*	49291	Grazon, Tordon	500	--	--
Prometon	04037	Pramitol	--	--	--
Pronamide*	82676	Kerb, Propyzamid	--	2,350	--
Propachlor	04024	Prolex, Ramrod	--	<10	2,200
Propham	49236	Chem-Hoe, Birgin	--	--	--
Silvex, mono-acid-[6]	39762	2,4,5-TP, Fenoprop	50	--	--
Simazine	04035	Princep, Aquazine	4	10,700	106,000
Tebuthiuron	82670	Spike, Tebusan	--	--	--
Terbacil	82665	Sinbar	--	5,750	[4]3,390
Thiobencarb*	82681	Bolero, Saturn	--	--	--
Triallate[6]	82678	Far-Go, Avadex BW	--	--	--
Triclopyr, mono-acid-	49235	Grandstand, Turflon	--	--	--
Trifluralin	82661	Herbiflan, Treflan	--	9,780	[4]2,580
2,4-D, mono-acid-	39732	Miracle, Dacamine	70	30,500	144,000
2,4-DB, mono-acid-	38746	Butyrac	--	24,500	84,000
2,4,5-T, mono-acid-[6]	39742	Weedar	--	--	--
Insecticides[5]					
Aldicarb*	49312	Temik, Sanacarb	7	--	--
Aldicarb Sulfone	49313	Standak, Aldoxycarb	7	--	--
Aldicarb Sulfoxide	49314		7	--	--
Azinphos, Methyl*	82686	Acifon, Guthion	--	23,600	87,700
Carbaryl	82680	Sevin, Slam	--	10,500	56,300
Carbofuran*	82674	Furadan, Carbodan	40	23,600	189,000
Carbofuran, 3-Hydroxy-	49308		--	--	--
Chlorpyrifos	38933	Dursban, Scout	--	94,600	614,000
Cryolite	--	Kryocide, Prokil	--	21,600	92,000
DDE, p,p	34653		--	--	--
Diazinon	39572	Basudin, Knox-Out	--	2,460	19,200
Dieldrin[6]	39381	Panoram D-31	--	--	--
Disulfoton*	82677	Disyston, Disultex	--	--	2,600
DNOC[6]	49299	Elgetol, Trifocide	--	--	--
Esfenvalerate	49298	Asana XL, Sumi-alpha	--	1,170	6,030

Table 2. *Pesticides for which ground- and surface-water samples were analyzed in the Lower Susquehanna River Basin study unit from 1993 to 1995 and information on water-quality standards and pesticide use—Continued*

[Shaded pesticides were analyzed by the gas chromatography/mass spectrometry method (Sandstrom and others, 1992; Zaugg and others, 1995); unshaded pesticides were analyzed by the high performance liquid chromatography method (Werner and others, 1996); Parameter code, 5-digit number used in the U.S. Geological Survey computerized data system, NWIS, to uniquely identify a specific constituent; *Italicized* pesticides indicate those pesticides that were not analyzed in this study but commonly are used in Pennsylvania; *, Restricted-use pesticide; NWIS, National Water Information System; LSR, Lower Susquehanna River Basin; MCL, Maximum Contaminant Level; MCLG, Maximum Contaminant Level Goal; --, not established; µg/L, micrograms per liter; lb/yr, pounds per year]

Pesticide	NWIS parameter code	Selected trade name(s)	MCL or MCLG[1] (µg/L)	Amount applied for agricultural use (lb/yr)	
				LSR Basin[2] (1990-1994)	Statewide-Pa. (1988)
		Insecticides—Continued			
Ethoprop*	82672	Mocap, Ethoprophos	--	--	--
Fonofos*	04095	Capfos, Dyfonate	--	17,600	151,000
HCH, alpha[6]	34253	(none)	--	--	--
HCH, gamma*	39341	Lindane, Lintox	0.2	--	--
Malathion	39532	Cythion, Maltox	--	24,800	104,000
Methiocarb	38501	Draza, Mesurol	--	--	--
Methomyl	49296	Lannate, Lanox	--	13,700	54,600
Methyl Bromide	34413	Meth-O-Gas, Celfume	--	64,200	--
Oxamyl*	38866	Vydate L	200	4,620	16,200
Parathion, Ethyl[6]	39542	Parathion, Panthion	--	22	--
Parathion, Methyl*	82667	Penncap-M, Paraton	--	10,600	22,700
Permethrin, cis	82687	Ambush, Pounce	--	7,200	52,200
Phorate*	82664	Thimet, Granutox	--	2,680	48,100
Propargite[6]	82685	Comite, Ornamite	--	3,220	26,700
Propoxur	38538	Baygon, Suncide	--	--	--
Terbufos*	82675	Counter, Pilarfox	--	20,100	99,600
		Fungicide[7]			
Captan	39640	Orthocide, Merpan	--	160,000	288,000
Chlorothalonil	49306	Bravo, Daconil 2787	--	--	92,000
Mancozeb	--	Manzate, Aimcozeb	--	52,700	326,000
Ziram	81827	Pomarsol Z, Mezene	--	25,800	107,000

[1] U.S. Environmental Protection Agency, 1996.
[2] Anderson and Gianessi, 1995.
[3] Gianessi and Puffer, 1991.
[4] Possible discrepancy in the way the two studies determined the percentage of crop treated.
[5] Gianessi and Puffer, 1992a.
[6] Not registered for use in Pennsylvania.
[7] Gianessi and Puffer, 1992b.

Table 3. *Summary of characteristics of pesticides selected for detailed analysis*

[MCL, Maximum Contaminant Level; HAL, Health Advisory Limit; NR, not rated]

Pesticide	Characteristics considered				
	Generalized agricultural-use category[1]	Frequency of detection in streams[2]	Frequency of detection in wells[2]	Health advisory exists?, type	Leaching potential[3]
			Herbicides		
Atrazine	High	High	High	Yes, MCL	High
Pendimethalin	High	Low	Low	No	NR
Simazine	Low	High	Medium	Yes, MCL	Medium
			Insecticides		
Chlorpyrifos	High	Low	Low	Yes, HAL	Low
Diazinon	Low	Low	Low	Yes, HAL	Low

[1] Arbitrarily selected, High = >90,000 pounds per year (1990-1994 average); Low = <12,000 pounds per year (1990-1994 average) (Anderson and Gianessi, 1995).
[2] Arbitrarily selected, High = >90 percent; Low = <20 percent.
[3] Hippe and Hall, 1996, pages 44-45.

(censored data). Methods used to account for censored data are described in each section that dealt with censored data.

Streamwater and ground-water samples for pesticide analysis were collected and processed in accordance with methods described by Shelton (1994) and by Koterba and others (1995), respectively. Samples were collected from wadeable streams with a US-DH-81 sampler and glass or Teflon bottles using the Equal-Width-Increment (EWI) and depth-integrated methods. Samples from unwadeable streams were collected in 3-L Teflon bottles with a US-D-77 TM sampler suspended from a bridge. In addition to the equipment-cleaning protocols described in Shelton (1994) and Koterba and others (1995), all sampling and processing equipment was rinsed with native water before sample collection. Sample splitting was conducted with a Teflon cone (decaport) splitter (Capel and others, 1995). Water samples for pesticide analysis were filtered using 142-mm diameter, baked, glass-fiber filters with 0.7-μm pore size on an aluminum-plate filter stand and collected in 1-L, baked and amber-colored glass bottles. A Teflon diaphragm pump and Teflon tubing were used to force the water sample through the filter membrane. Water samples were collected at each site for analysis of 46 pesticides by gas chromatography/mass spectrometry (GCMS) (Sandstrom and others, 1992; Zaugg and others, 1995). All ground-water and some streamwater samples were analyzed for an additional 37 pesticides by high-performance liquid chromatography (HPLC) (Werner and others, 1996) (table 2).

For surface-water synoptic surveys, the methods used for sample collection and processing were similar to those used for samples collected at the long-term monitoring sites and were in accordance to methods provided by Shelton (1994). During synoptic surveys, samples were generally collected using hand samplers and the EWI and depth-integrated methods unless the streams were too narrow or depths were too shallow. In this case, a sample was collected without the use of a sampler and from the center of flow. Laboratory methods and analyses were identical to those used for long-term monitoring site streamwater samples, with the exception that no water samples collected for pesticide analyses were analyzed by HPLC for the 37 additional pesticides. A more detailed description of the methods used for the collection and processing of surface-water samples in the Lower Susquehanna River Basin can be found in Siwiec and others (1997). Shelton (1994) provides specific guidance on surface-water sample collection for the NAWQA Program.

Ground-water samples were collected in a sampling chamber from a Teflon sampling hose connected to an outside spigot, pressure tank, or directly to a sampling pump. All sampling lines and connections between the faucet and the sampling chamber were Teflon or stainless steel. All bottles were filled inside the sampling chamber to minimize the potential for contamination by dust or other atmospheric contaminants. Powderless latex gloves were worn during sampling. As with the surface-water samples, ground-water samples for pesticide analysis were filtered using 0.7-µm pore size, 142-mm diameter, baked, glass-fiber filters. Water samples were collected at each site for analysis by GCMS and HPLC. Refer to Siwiec and others (1997) for a more detailed description of the methods used for the collection and processing of ground-water samples.

All water samples for pesticide analysis were kept chilled and stored away from sunlight until they were processed. The samples for analysis by GCMS were filtered through a solid-phase extraction (SPE) cartridge in the Pennsylvania District Laboratory following the guidelines in Shelton (1994) and Manning and others (1994). The SPE cartridge was sent chilled to the NWQL for elution and analysis of pesticides. Samples for analysis by HPLC were shipped chilled in 1-L, baked and amber-colored glass bottles to the NWQL, which did the SPE. All laboratory analyses were performed at the NWQL.

Water samples collected during ground water and stream-synoptic surveys were characterized as base-flow condition samples. Synoptic surveys were designed to represent non-recharge or base-flow conditions and were conducted only when ground-water discharge dominated the supply of flow to the region’s streams. Base-flow or storm-affected stream conditions were designated for water samples collected from streams. Analysis of regional streamflow was based on evaluations of hydrographs from streams near the sampled basins. Hydrographs of water levels in wells were used to verify that ground-water samples were being collected during non-recharge periods.

To characterize water samples collected from streams at the long-term monitoring sites, base-flow samples were those collected a sufficient amount of time after a significant storm event so that the flow in the stream was reasonably stable and predominantly supplied by ground-water discharge. A more detailed description of the algorithm used is given in the Appendix.

Statistical Analysis Methods

All statistical analysis methods used in this report are described in Helsel and Hirsch (1992). Statistical Analysis Systems (SAS Institute Inc., 1990) software was used to complete the statistical tests. Other than summary statistics (mean, median, standard deviation, and percentiles), the only other statistical tests and methods employed in this analysis were contingency tables using the Chi-square statistic and the Kruskal-Wallis test. The Chi-square statistic was used to determine if the difference between the number of detections and nondetections of two data sets was statistically significant. The Kruskal-Wallis test was used to determine if differences between the medians of two data sets were statistically significant.

Quality-Assurance Procedures

Three types of quality-assurance data are available for analysis—surrogate pesticide concentrations and recoveries, spiked and unspiked replicates, and equipment and field blanks. Surrogates are organic pesticides injected into all filtered water samples prior to extraction by the SPE cartridge to provide quality control by monitoring for matrix effects and gross sample-processing errors. Surrogates are expected to behave similarly chemically and physically to target analytes in terms of SPE recovery and are not expected to occur in the environment (Timme, 1995; Werner and others, 1996).

A field blank is analyte-free water carried through the entire sample collection, field processing, preservation, transportation, and laboratory handling process as an environmental sample and is used to identify possible contamination introduced during data collection. An equipment blank is similar to a field blank, but equipment blanks are not exposed to field conditions and are normally done in the laboratory. Blanks are acceptable if the amount of analyte in the blank water is less than the MDL (Sandstrom, 1994).

Sequential-replicate samples were collected immediately following the collection of the environmental samples using the same type of equipment and collection methods. Sample replicates are submitted as quality-control samples to determine the precision and random error of the NWQL analyses, assuming negligible change in water chemistry between samples. A spike is the addition of a known quantity of one or more pesticides of interest to the sample prior to analysis, which yields data on the results (accuracy) that can be expected from a suite of similar samples when used with a synthetic matrix. The spike is used to verify analytical method performance by recovery of analytes in that synthetic matrix (Timme, 1995).

Quality-assurance samples were collected at a ratio of about one for every five environmental samples. For surface-water samples, the ratio of environmental sample replicates (spiked or unspiked) to field blanks was about 2:1. All ground-water replicate samples were spiked. Blank or replicate samples were collected at 10 percent of all sites.

Replicates or spiked replicates were collected immediately following collection of the environmental samples. Spiked replicates for pesticides had 100 µL of a solution added that was prepared specifically for the GCMS and HPLC analytes by the NWQL. Concentrations of unspiked replicate samples were used to analyze the precision of NWQL methods and consistency of sampling techniques (assuming the water chemistry remained unchanged between subsequent replicate samples), and concentrations of spiked replicate samples were used to analyze the accuracy of NWQL methods.

A ground-water equipment blank was conducted at the beginning of the first year of sampling; all subsequent ground-water blanks were field blanks conducted to assess the equipment decontamination procedures and contamination introduced at the sampling site. Surface-water blanks, on the other hand, were collected in the field during the first year of sampling, after which equipment blanks were conducted in the laboratory. Following the collection and processing of surface- and ground-water environmental samples, the equipment was cleaned and set up for the processing of samples using pesticide-grade organic-free water. The processing of blank-water samples followed the same method as that used for the environmental samples.

Organic-free and pre-analyzed inorganic-free water were used for blank samples for surface-water samples. Pesticide-grade organic-free water was used for all ground-water blank samples.

QUALITY-ASSURANCE RESULTS

Quality-control procedures for the Lower Susquehanna River Basin NAWQA study included the use of surrogates and the collection of sample blanks (field and equipment) and sample replicates. According to Horowitz and others (1994), quality-control samples must be collected for any sampling and analysis program because without quality-control information, the quality of the data can not be evaluated or qualified.

Surrogates

Surrogate pesticide recoveries were compared to NWQL reagent water recoveries for the HPLC surrogate, BDMC, and the three GCMS surrogates, isotopically-marked diazinon-d_{10} and *alpha*-HCH-d_6, and tebuthylazine (table 4). Surrogate recoveries outside the range of the NWQL mean recoveries indicate the recovery performances were affected by the environmental matrix of the sample. All the mean values for the GCMS surrogates for surface-water storm samples, surface-water base-flow samples, and ground-water samples were higher than the NWQL mean reagent water recoveries (table 4). Surrogate recoveries for environmental study-unit samples performed equivalently to the NWQL mean reagant water recoveries. This indicates that the results for GCMS analyses were reliable. The HPLC surrogate, BDMC, had a mean recovery for all samples that was consistently lower than the NWQL mean reagent water recovery of 81 percent (table 4). According to Werner and others (1996), BDMC has not performed as expected, consequently the ability to infer performance for an individual sample has been limited.

Table 4. *Statistical summary of surrogate recoveries (in percent) from National Water Quality Laboratory reagent water and from environmental samples collected from the Lower Susquehanna River Basin study unit*

[Max, maximum; Min, minimum]

Surrogate	National Water Quality Laboratory mean reagent water recovery (percent)	Surrogate recoveries from environmental samples (percent)								
		Surface water storm-affected (n = 109)			Surface water base flow (n = 299)			Ground water (n = 169)		
		Max	Mean	Min	Max	Mean	Min	Max	Mean	Min
BDMC	[1] 81	118	59	2	189	49	0	276	71	0
Diazinon-d_{10}	[2] 88	166	114	56	182	108	47	163	91	0
alpha-HCH-d_6	[2] 90	152	98	72	150	96	60	172	92	66
Tebuthylazine	[2] 100	285	114	88	173	111	72	141	105	80

[1] Pirkey and Horodyski, 1994.
[2] Zaugg and others, 1995.

Blanks

Approximately 95 percent of the equipment and field blanks collected as part of this study contained no measurable concentrations. Three blanks contained trace amounts of several pesticides at or near the respective minimum detection limits. Atrazine was detected in all of these blanks in the 0.003 - 0.004-µg/L range. Desethyl atrazine (estimated 0.005 µg/L), metolachlor (0.006 µg/L), trifluralin and benefluralin (both 0.002 µg/L), triallate (0.001 µg/L), and pronamide (0.013 µg/L) also were detected in one blank. Therefore, pesticide concentrations below these detected concentrations will be qualified as potentially due to contamination from an unknown source and cannot, with assurance, be attributed to sampled concentrations.

Overall, it is considered highly unlikely that cross contamination occurred between samples because of the high percentage of blank samples collected following the processing of a sample with measurable concentrations and equipment cleaning in which no pesticides were detected. An evaluation of 1992-95 NAWQA pesticide blank data shows the number of pesticide detections in blanks from the Lower Susquehanna River study unit was similar to detections from other NAWQA study units across the United States (Martin and others, 1999).

Replicates

Ninety-eight percent of replicate concentration measurements for atrazine, simazine, pendimethalin, chlorpyrifos, and diazinon were within two standard deviations of the environmental concentration measurements. About 85 to 95 percent of the replicated pairs for pendimethalin, chlorpyrifos, and diazinon had concentrations less than the detection limit; therefore, these data do not give a great deal of quantitative information about the precision of the analyses. Concentrations measured in 80 percent of the replicate samples for atrazine and 67 percent of the replicate samples for simazine were within 10 percent of the concentrations measured in the environmental samples. No temporal trends in precision of replicate concentration measurements were observed.

The mean recoveries for atrazine, simazine, chlorpyrifos, and diazinon in spiked replicate samples were between 94 and 100 percent; the mean recovery for pendimethalin in the same group of spiked-replicates was 74 percent. Recoveries were generally within two standard deviations of the mean. Diazinon, for example, had a mean recovery of 95 percent and a standard deviation of 12 percent. About 95 percent of the recoveries for diazinon were within the range of two standard deviations (71 and 119 percent).

SUMMARY OF DETECTED PESTICIDES AND MEASURED CONCENTRATIONS

The results of an analysis of detection frequency for all pesticide data and a detailed analysis of the concentrations of five selected pesticides will be discussed in the following sections. Tables are provided that compare the agricultural-use ranking for the pesticide to the detection frequency and the median and maximum concentrations.

Detection Frequency of Measured Pesticides

The detection frequency was determined for each pesticide analyzed in all water samples from wells and streams. Pesticides were grouped (table 5) alphabetically by pesticide type: herbicide, insecticide, or fungicide. Included were 53 herbicides, 29 insecticides, and 1 fungicide. Several pesticides have median concentrations less than the MDL (nondetects), indicating low numbers of detections.

Forty-six percent of the herbicides, insecticides, and fungicides analyzed were not detected in any of the 577 samples. Herbicides were detected most frequently, and about 60 percent of all herbicides analyzed were detected at least once. Approximately 45 percent of all insecticides analyzed were detected at least once. The only fungicide analyzed in the study was chlorothalonil, and it was not detected in any of the samples. Of the 83 pesticides analyzed, 55 are registered for use in Pennsylvania. The remainder are either classified as restricted-use pesticides or are not registered for use in Pennsylvania. Of the 55 pesticides registered for use in Pennsylvania, 23 were not detected in any samples collected within the study unit. Only 7 of the 19 pesticides analyzed that were classified as restricted-use pesticides were not detected in any samples collected within the study unit.

Agricultural-use rankings were compared to detection frequency. The five pesticides with the highest agricultural-use rankings in the study unit from 1990 to 1994 were atrazine, metolachlor, captan, pendimethalin, and alachlor (Anderson and Gianessi, 1995) (table 5). The detection frequencies of the herbicides atrazine and metolachlor were 91 and 83 percent, respectively. Captan, a fungicide, was not included in the standard suite of pesticides analyzed for this study. The detection frequencies of the herbicides pendimethalin and alachlor were 13 and 37 percent, respectively.

The most commonly detected pesticides were agricultural herbicides—atrazine, metolachlor, simazine, prometon, alachlor, and cyanazine. Atrazine and desethyl atrazine, a metabolite of atrazine, were detected more frequently (91 and 92 percent, respectively) than any other pesticides analyzed. Desethyl atrazine recovery performances were poor and because of this, all concentrations of desethyl atrazine were marked as ‘estimated’ values to qualify the results. Because of the national importance of desethyl atrazine, the pesticide remains on the suite of pesticides analyzed (Zaugg and others, 1995) in spite of its poor recovery. Metolachlor was the second most frequently detected compound. It was detected in 478 of the 577 samples (83 percent) (table 5). All of the herbicides detected most frequently are used for weed control, and with the exception of prometon, they are used primarily for weed control on corn and grain crops.

Table 5. *Pesticides (listed alphabetically by pesticide type), the Method Detection Limit for the pesticide, the rank of its use for agricultural purposes in the study unit, frequency of detection in ground and surface water, and median and maximum measured concentrations, Lower Susquehanna River Basin study unit, 1993-95*

[*Italicized* pesticides indicate those pesticides that were not analyzed in this study; *, Restricted-use pesticide; MDL, statistically determined method detection limit in micrograms per liter; µg/L, micrograms per liter; --, not available; <, less than]

Pesticide	MDL (µg/L)	Agri-cultural use rank[1]	Number of samples	Detection frequency (percent) 0 20 40 60 80 100	Concentration (µg/L) Median	Maxi-mum
Herbicides						
Acetochlor	0.002		314		<0.002	1.5
Acifluorfen	.035		304		<.035	.64
Alachlor*	.002	5	577		<.002	3.4
Atrazine*	.001	2	577		.120	12
Atrazine, Desethyl	.002		577		.094	1.0
Benfluralin	.002		577		<.002	.039
Bentazon	.014	47	304		<.014	.88
Bromacil	.035		304		<.035	.12
Bromoxynil	.035	22	304		--	--
Butylate	.002		577		<.002	.016
Chloramben	.011		304		--	--
Clopyralid	.050		304		--	--
Cyanazine*	.004	6	577		<.004	3.9
DCPA*	.002	40	577		<.002	.72
Dicamba, mono-acid-	.035	19	304		<.035	.21
Dichlobenil	.020		304		<.020	.21
Dichlorprop, mono-acid-	.032		304		--	--
Diethlyanaline	.003		577		<.003	.01
Dinoseb[2]	.035		304		--	--
Diuron	.020	36	304		<.020	.64
EPTC	.002	43	577		<.002	.21
Ethalfluralin	.004	46	577		--	--
Fenuron	.013		304		--	--
Fluometuron	.035		304		--	--
Glyphosate	--	20	0		--	--
Linuron*	.002	11	577		<.002	.54
MCPA, mono-acid-	.050	28	304		<.050	.1
MCPB, mono-acid-	.035		304		--	--
Metolachlor	.002	1	577		.032	11
Metribuzin	.004	30	577		<.004	.15
Molinate	.004		577		--	--
1-Naphthol	.007		304		--	--
Napropamide	.003	41	577		<.003	.07
Neburon	.015		304		--	--
Norflurazon	.024	44	304		--	--
Oryzalin	.019	45	304		<.019	.05
Paraquat	--	13	0		--	--
Pebulate	.004	34	577		<.004	.053
Pendimethalin	.004	4	577		<.004	.24
Picloram, mono-acid-*	.050		293		--	--

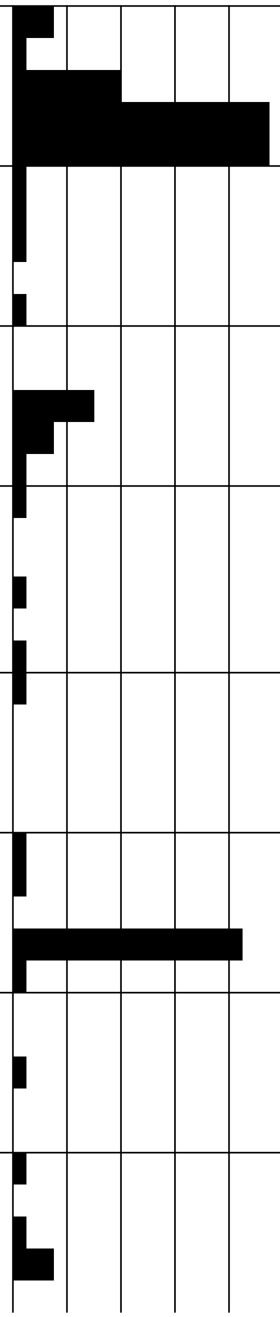


Table 5. *Pesticides (listed alphabetically by pesticide type), the Method Detection Limit for the pesticide, the rank of its use for agricultural purposes in the study unit, frequency of detection in ground and surface water, and median and maximum measured concentrations, Lower Susquehanna River Basin study unit, 1993-95—Continued*

[*Italicized* pesticides indicate those pesticides that were not analyzed in this study; *, Restricted-use pesticide; MDL, statistically determined method detection limit in micrograms per liter; µg/L, micrograms per liter; --, not available; <, less than]

Pesticide	MDL (µg/L)	Agri-cultural use rank[1]	Number of samples	Detection frequency (percent) 0 20 40 60 80 100	Concentration (µg/L) Median	Maxi-mum
Herbicides—Continued						
Prometon	0.018		577		0.022	1.5
Pronamide*	.003	39	577		.013 (one detection)	
Propachlor	.007		577		<.007	.036
Propham	.035		304		--	--
Silvex, mono-acid-[2]	.021		304		--	--
Simazine	.005	25	577		.031	7.6
Tebuthiuron	.010		577		<.010	.12
Terbacil	.007	32	561		<.007	.34
Thiobencarb*	.002		577		--	--
Triallate[2]	.001		577		--	--
Triclopyr, mono-acid-	.050		304		--	--
Trifluralin	.002	29	577		<.002	.028
2,4-D, mono-acid-	.035	9	304		<.035	1.4
2,4-DB, mono-acid-	.035		304		--	--
2,4,5-T, mono-acid-[2]	.035		304		--	--
Insecticides						
Aldicarb*	.016		304		--	--
Aldicarb Sulfone	.016		301		--	--
Aldicarb Sulfoxide	.021		301		--	--
Azinphos, Methyl*	.001	16	561		<.001	.41
Carbaryl	.003	27	577		<.003	.65
Carbofuran*	.003	18	577		<.003	.48
Carbofuran, 3-Hydroxy-	.014		304		--	--
Chlorpyrifos	.004	7	577		<.004	.09
Cryolite	--	17	0		--	--
DDE, p,p	.006		577		<.006	.005
Diazinon	.002	38	577		<.002	.06
Dieldrin[2]	.001		577		<.001	.019
Disulfoton*	.017		577		--	--
DNOC[2]	.035		304		--	--
Esfenvalerate	.019	42	304		--	--
Ethoprop*	.003		577		<.003	.052
Fonofos*	.003	23	577		<.003	.015
HCH, alpha[2]	.002		577		--	--
HCH, gamma*	.004		577		--	--
Malathion	.005	15	577		<.005	.13

Table 5. *Pesticides (listed alphabetically by pesticide type), the Method Detection Limit for the pesticide, the rank of its use for agricultural purposes in the study unit, frequency of detection in ground and surface water, and median and maximum measured concentrations, Lower Susquehanna River Basin study unit, 1993-95—Continued*

[*Italicized* pesticides indicate those pesticides that were not analyzed in this study; *, Restricted-use pesticide; MDL, statistically determined method detection limit in micrograms per liter; µg/L, micrograms per liter; --, not available; <, less than]

Pesticide	MDL (µg/L)	Agri-cultural use rank[1]	Number of samples	Detection frequency (percent) 0 20 40 60 80 100	Concentration (µg/L)	
					Median	Maxi-mum
Insecticides—Continued						
Methiocarb	0.026		304		--	--
Methomyl	.017	24	301		<0.017	0.19
Methyl Bromide[3]	.2	8	0		--	--
Oxamyl*	.018	33	301		--	--
Parathion, Ethyl[2]	.004	48	577		--	--
Parathion, Methyl*	.006	26	577		<.006	.051
Permethrin, cis	.005	31	577		--	--
Phorate*	.002	37	577		--	--
Propargite[2]	.013	35	577		--	--
Propoxur	.035		297		--	--
Terbufos*	.013	21	577		.030 (one detection)	
Fungicides						
Captan	--	3	0		--	--
Chlorothalonil	.035		302		--	--
Mancozeb	--	10	0		--	--
Ziram	--	14	0		--	--

[1] This ranking was determined using the information in table 2 (p. 19)—amount applied in the study unit basin (1990-94).

[2] Not registered for use in Pennsylvania.

[3] This pesticide was analyzed as a volatile organic compound and was not analyzed as a pesticide for this study.

Pesticide detections in well and stream samples were compared for 83 pesticides (table 6). Approximately 53 percent of all herbicides and 17 percent of all insecticides analyzed were detected in well-water samples and approximately 51 percent of all herbicides and 48 percent of all insecticides analyzed were detected in stream samples. Base-flow samples accounted for nearly 75 percent of the stream samples, and approximately 45 percent of all herbicides and 41 percent of all insecticides analyzed were detected in base-flow samples. Storm-affected samples account for the remainder of the stream samples, and approximately 51 percent of all herbicides and 41 percent of insecticides analyzed were detected in storm-affected samples. The percentage of pesticide detections was higher in stream samples for 25 of the 28 total pesticides detected in both ground and surface waters. For example, the herbicide atrazine was detected in 98 percent of the stream samples but in only 75 percent of the well-water samples.

Table 6. *Pesticides commonly used in Pennsylvania, pesticides analyzed, and number of detections in water from streams during storm-affected and base-flow conditions and water from ground-water wells, Lower Susquehanna River Basin study unit, 1993-95*

[*Italicized* pesticides indicate those pesticides that were not analyzed in this study but are commonly used in Pennsylvania; *, Restricted-use pesticide; --, not available]

Pesticide	Storm-affected stream samples		Base-flow stream samples		Ground-water samples	
	Number of samples	Number of detections	Number of samples	Number of detections	Number of samples	Number of detections
Herbicides						
Acetochlor	72	34	142	10	100	0
Acifluorfen	40	0	96	1	168	1
Alachlor*	109	81	299	116	169	18
Atrazine*	109	109	299	292	169	126
Atrazine, Desethyl	109	109	299	289	169	131
Benfluralin	109	13	299	0	169	1
Bentazon	40	0	96	0	168	4
Bromacil	40	0	96	0	168	1
Bromoxynil	40	0	96	0	168	0
Butylate	109	2	299	2	169	1
Chloramben	40	0	96	0	168	0
Clopyralid	40	0	96	0	168	0
Cyanazine*	109	52	299	102	169	11
DCPA*	109	52	299	35	169	0
Dicamba, mono-acid-	40	1	96	0	168	1
Dichlobenil	40	0	96	0	168	1
Dichlorprop, mono-acid-	40	0	96	0	168	0
Diethlyanaline	109	1	299	1	169	1
Dinoseb[1]	40	0	96	0	168	0
Diuron	40	4	96	5	168	6
EPTC	109	10	299	3	169	2
Ethalfluralin	109	0	299	0	169	0
Fenuron	40	0	96	0	168	0
Fluometuron	40	0	96	0	168	0
Glyphosate	--	--	--	--	--	--
Linuron*	109	14	299	9	169	1
MCPA, mono-acid-	40	1	96	1	168	0
MCPB, mono-acid-	40	0	96	0	168	0
Metolachlor	109	109	299	279	169	90
Metribuzin	109	17	299	11	169	1
Molinate	109	0	299	0	169	0
1-Naphthol	40	0	96	0	168	0
Napropamide	109	7	299	5	169	1
Neburon	40	0	96	0	168	0
Norflurazon	40	0	96	0	168	0
Oryzalin	40	0	96	0	168	1
Paraquat	--	--	--	--	--	--
Pebulate	109	0	299	1	169	2
Pendimethalin	109	49	299	25	169	1
Picloram, mono-acid-*	40	0	96	0	157	0

Table 6. *Pesticides commonly used in Pennsylvania, pesticides analyzed, and number of detections in water from streams during storm-affected and base-flow conditions and water from ground-water wells, Lower Susquehanna River Basin study unit, 1993-95*—*Continued*

[*Italicized* pesticides indicate those pesticides that were not analyzed in this study but are commonly used in Pennsylvania; *, Restricted-use pesticide; --, not available]

Pesticide	Storm-affected stream samples		Base-flow stream samples		Ground-water samples	
	Number of samples	Number of detections	Number of samples	Number of detections	Number of samples	Number of detections
Herbicides—Continued						
Prometon	109	94	299	236	169	71
Pronamide*	109	0	299	0	169	1
Propachlor	109	4	299	2	169	0
Propham	40	0	96	0	168	0
Silvex, mono-acid-[1]	40	0	96	0	168	0
Simazine	109	107	299	272	169	83
Tebuthiuron	109	50	299	84	169	12
Terbacil	104	2	288	8	169	1
Thiobencarb*	109	0	299	0	169	0
Triallate[1]	109	0	299	0	169	0
Triclopyr, mono-acid-	40	0	96	0	168	0
Trifluralin	109	18	299	0	169	1
2,4-D, mono-acid-	40	9	96	5	168	1
2,4-DB, mono-acid-	40	0	96	0	168	0
2,4,5-T, mono-acid-[1]	40	0	96	0	168	0
Insecticides						
Aldicarb*	40	0	96	0	168	0
Aldicarb Sulfone	40	0	96	0	165	0
Aldicarb Sulfoxide	40	0	96	0	165	0
Azinphos, Methyl*	104	7	288	18	169	0
Carbaryl	109	52	299	21	169	7
Carbofuran*	109	11	299	19	169	4
Carbofuran, 3-Hydroxy-	40	0	96	0	168	0
Chlorpyrifos	109	41	299	24	169	0
Cryolite	--	--	--	--	--	--
DDE, p,p	109	2	299	2	169	4
Diazinon	109	28	299	13	169	2
Dieldrin[1]	109	7	299	14	169	8
Disulfoton*	109	1	299	0	169	0
DNOC[1]	40	0	96	0	168	0
Esfenvalerate	40	0	96	0	168	0
Ethoprop*	109	2	299	1	169	0
Fonofos*	109	5	299	4	169	0
HCH, alpha[1]	109	0	299	0	169	0
HCH, gamma*	109	0	299	0	169	0
Malathion	109	15	299	5	169	0
Methiocarb	40	0	96	0	168	0
Methomyl	40	1	96	0	165	0
Methyl Bromide	--	--	--	--	--	--
Oxamyl*	40	0	96	0	165	0
Parathion, Ethyl[1]	109	0	299	0	169	0

Table 6. *Pesticides commonly used in Pennsylvania, pesticides analyzed, and number of detections in water from streams during storm-affected and base-flow conditions and water from ground-water wells, Lower Susquehanna River Basin study unit, 1993-95—Continued*

[*Italicized* pesticides indicate those pesticides that were not analyzed in this study but are commonly used in Pennsylvania; *, Restricted-use pesticide; --, not available]

Pesticide	Storm-affected stream samples		Base-flow stream samples		Ground-water samples	
	Number of samples	Number of detections	Number of samples	Number of detections	Number of samples	Number of detections
Insecticides—Continued						
Parathion, Methyl*	109	1	299	1	169	0
Permethrin, cis	109	0	299	0	169	0
Phorate*	109	0	299	0	169	0
Propargite[1]	109	0	299	0	169	0
Propoxur	38	0	93	0	166	0
Terbufos*	109	0	299	1	169	0
Fungicides						
Captan	--	--	--	--	--	--
Chlorothalonil	38	0	96	0	168	0
Mancozeb	--	--	--	--	--	--
Ziram	--	--	--	--	--	--

[1] Not registered for use in Pennsylvania.

In October 1994, the herbicide acetochlor was added to the list of pesticides analyzed by the GCMS method. It is a selective preemergent herbicide used on corn to control weeds and grasses and has restricted registration for use in the United States to replace some of the more widely used corn herbicides such as atrazine, metolachlor, and alachlor. Acetochlor's restricted registration is contingent on concentration limits that have been set for stream and ground-water samples. These limits can not be exceeded or registration will be revoked (Lindley and others, 1996). In the Lower Susquehanna River Basin study unit, 314 samples were analyzed for acetochlor, and of those, 44 (14 percent) had measurable concentrations (table 5). Storm-affected stream samples had the highest number of detections; acetochlor was detected in 34 of 72 samples (47 percent).

Concentrations of Selected Pesticides

The discussion of concentrations of pesticides measured in streams and wells will be focused on five compounds—atrazine, simazine, pendimethalin, chlorpyrifos, and diazinon. For data-analysis purposes, concentrations designated as less than the MDL were assigned a concentration of one-half the MDL (table 7). Measured concentrations were compared to MCL's established by the USEPA. Of the five selected pesticides, MCL's have been established only for atrazine and simazine (table 7). The data for this study are listed in the USGS annual water-data reports (Durlin and Schaffstall, 1994; 1996; 1997).

Of the nearly 40,000 pesticide concentrations measured in water samples from streams and shallow wells, only 7 measurements (less than 0.018 percent) exceeded any established MCL or MCLG for drinking water. All of the concentrations that exceeded the drinking-water standards were in samples from streams not used as drinking-water supplies, and five of the seven exceedances were in samples collected during three storm events during June, when agricultural applications on row crops

Table 7. *Statistical summary of atrazine, simazine, pendimethalin, chlorpyrifos, and diazinon concentrations in water samples collected within the Lower Susquehanna River Basin study unit,1993-95*

[µg/L, micrograms per liter; MCL, Maximum Contaminant Level; MDL, Method Detection Limit; --, not available; n, number of samples; Percentiles, percentage of samples in which pesticide concentrations were less than or equal to those shown (in µg/L); P10, tenth percentile; P25, twenty-fifth percentile; P75, seventy-fifth percentile; P90, ninetieth percentile]

Pesticide	MCL (µg/L)	MDL (µg/L)	Pesticide concentration, in µg/L														
			Storm-affected stream water samples (n=109)					Base-flow stream water samples (n=299)					Ground-water samples (n=169)				
			P10	P25	Median	P75	P90	P10	P25	Median	P75	P90	P10	P25	Median	P75	P90
Atrazine	3.0	0.001	0.064	0.085	0.16	0.34	1.01	0.04	0.093	0.13	0.21	0.31	<0.001	<0.001	0.05	0.19	0.36
Simazine	4.0	.005	.016	.028	.044	.10	.81	<.005	.018	.041	.076	.28	<.005	<.005	<.005	.015	.051
Pendimethalin	--	.004	<.004	<.004	<.004	.019	.045	<.004	<.004	<.004	<.004	<.004	<.004	<.004	<.004	<.004	<.004
Chlorpyrifos	--	.004	<.004	<.004	<.004	.008	.016	<.004	<.004	<.004	<.004	<.004	<.004	<.004	<.004	<.004	<.004
Diazinon	--	.002	<.002	<.002	<.002	.005	.018	<.002	<.002	<.002	<.002	<.002	<.002	<.002	<.002	<.002	<.002

are common. Concentrations of four agricultural herbicides—alachlor, atrazine, cyanazine, and simazine—exceeded the standards. Concentrations during storm events are elevated due primarily to surface-runoff contributions and are expected to be short-lived. Simazine concentrations in samples from two streams exceeded the MCL during base-flow conditions.

A comparison of the median concentrations of the five selected pesticides shows concentrations in storm-affected stream samples are higher than concentrations in ground-water and stream base-flow samples (table 7). Simazine, for example, has a median concentration of 0.044 µg/L in storm-affected stream samples—this means that 50 percent of the storm-affected concentrations were above 0.044 µg/L and 50 percent of the concentrations were below 0.044 µg/L. The median concentrations of simazine for base-flow stream samples (0.041 µg/L) and ground-water samples (<0.005 µg/L) were lower than those of the storm-affected stream samples (table 7). Again using simazine as an example and looking at the ninetieth (P90) percentiles, storm-affected stream samples had a concentration of 0.81 µg/L—this means that 10 percent of the concentrations were higher than 0.81 µg/L. Concentrations at the ninetieth percentile for base-flow stream samples (0.28 µg/L) and ground-water samples (0.051 µg/L) were again lower than that of the storm-affected stream samples (table 7).

Differences between median concentrations may not be statistically significant due to the variability of concentrations within each data subset and the variability of the number of samples between data subsets. The Kruskal-Wallis test (Helsel and Hirsch, 1992, p. 159-163) was used to compare storm-affected and base-flow and base-flow and ground-water median concentrations and determine statistical significance for atrazine and simazine. The test indicated statistically significant differences in median concentrations for the storm-affected to base-flow and base-flow to ground-water comparisons for both pesticides. A confidence level of 95 percent ($\rho \leq 0.05$) was used to determine statistical significance.

The comparison of pesticide detection frequency and concentration data (tables 5, 6, and 7) indicated that not only does atrazine have the highest detection frequency of the pesticides analyzed, but it consistently has the highest concentrations in both ground and surface waters. This result was found despite the fact that, on an annual basis, more metolachlor than atrazine is applied to agricultural land (table 2) in the Lower Susquehanna River Basin. Atrazine is second only to metolachlor as the most-used herbicide for agricultural purposes in the study unit (table 5). Approximately 417,000 lb and 470,000 lb of active ingredient of atrazine and metolachlor are applied annually. Determining the reason for this discrepancy was not within the scope of this study.

Atrazine was detected in 98 percent of stream samples and 75 percent of the well-water samples. Of the samples in which there were detections of atrazine, 50 percent had concentrations between 0.093 and 0.21 µg/L for the base-flow stream samples and between <0.001 and 0.19 µg/L for the ground-water samples. These concentration ranges correspond to the twenty-fifth (P25) and seventy-fifth (P75) percentiles (table 7).

Another of the selected pesticides, the insecticide diazinon, had a median concentration of <0.002 µg/L for all samples (table 7), a comparatively low median concentration in relation to atrazine. Diazinon was detected in only 13 of 299 (4 percent) samples of stream base flow and in 2 of 169 (1 percent) ground-water samples. For agricultural purposes in the study unit, diazinon is a low-use pesticide with approximately 2,460 lb of active ingredient applied annually (table 2) and was ranked 38 out of 48 pesticides in terms of annual usage (table 5).

The Kruskal-Wallis test could not be used to evaluate differences in median concentrations for pendimethalin, chlorpyrifos, and diazinon because of the large number of samples that had concentrations below the detection limit. For each of these pesticides, contingency tables were used to evaluate if the differences were statistically significant between the number of samples above the detection limit and the number of samples below the detection limit for the following comparisons: storm-affected to base-flow, base-flow to ground-water, and storm-affected to ground-water (table 6). Comparison of data subsets indicate statistically significant differences ($\rho \leq 0.05$) between numbers of samples above and below the detection limit for all comparisons except the diazinon base-flow to ground-water comparison.

Maximum pesticide concentrations in the study unit were measured in storm-affected stream samples. Samples collected during one storm in particular, during the second week of June 1994, provided most of the higher concentrations. Storm-affected stream samples were generally collected during the growing season. Base-flow stream samples were collected throughout the year, whereas ground-water samples were collected only during the summer months of June through August.

FACTORS AFFECTING PESTICIDE CONCENTRATIONS

Pesticide data-collection studies implemented by the Lower Susquehanna River Basin NAWQA study unit were designed, among other things, to provide data to describe areal and temporal variations in pesticide concentrations in ground water and streams. Concentration data from three herbicides—atrazine, simazine, and pendimethalin—and two insecticides—chlorpyrifos and diazinon—will be used to display observed patterns in concentrations. This group of compounds was selected to represent various types of uses, ranges of amounts used for agricultural purposes, and ranges of detection frequencies in water from streams and wells in the study unit. Conceptual models that guide the discussion of the major factors affecting seasonal and areal patterns of pesticide concentrations are described.

Conceptual Models for Major Factors Affecting Pesticide Concentrations

Two factors observed to have a major influence on seasonal patterns of pesticide concentrations in the four streams where data are available are 1) seasonality of applications and climate, and 2) ground-water retention and discharge to streams. The conceptual model for seasonal patterns relates annual and short-term patterns of storm-runoff concentrations observed in streams to the delivery of applied pesticides and the subsequent discharge to streams by surface runoff and ground water. The timing of periods of elevated concentrations in streams will be related to the timing of applications to bare soils and foliage, to the method of transport to the stream, and to the traveltime of water as it passes through the hydrogeologic system.

The conceptual model for areal patterns of pesticide concentrations in streams and shallow wells in the Lower Susquehanna River Basin includes the following factors: 1) areal-application patterns (agricultural and nonagricultural) and initial availability of the pesticide for transport; 2) the pesticides' environmental persistence, affinity for dissolution in water or adsorption to sediment particles, and the infiltration capacity of the soils to which the pesticides are applied; and 3) ground-water retention and discharge to the streams. Many of these factors originate from differences in bedrock type (which affects the percentage of agricultural/nonagricultural land use, infiltration capacity of the soils, and to a limited extent, the ground-water retention and discharge to streams) and differences in the pesticides' chemical properties (which affects the affinity for dissolution and the rate of transformation resulting in degradation).

Factors Affecting Seasonal Concentration Patterns in Streams

Multi-year pesticide-concentration data are available for the description of seasonal patterns. Samples were collected multiple times at three long-term monitoring sites on streams in Pennsylvania: East Mahantango Creek in Schuylkill County (47 samples), Cedar Run in Cumberland County (104 samples), and Mill Creek in Lancaster County (47 samples). At an additional site (Bachman Run in Lebanon County), pesticide-concentration data are available from 53 samples collected over 1 year; these data will be used to describe short-term effects during the application season. Data collected from the streams represent the water quality of four environmental subunits in the study unit. Three of the sites drain basins in which agriculture is the predominant land use. Cedar Run drains a predominantly urban area. The basin upstream of the East Mahantango Creek site is in the Appalachian Mountain Section of the Ridge and Valley Physiographic Province and is underlain by sandstone and shale. The three remaining streams drain basins underlain by carbonate rock. Two basins, Cedar Run and Bachman Run, are located in the Great Valley Section of the Ridge and Valley Physiographic Province, and the third, Mill Creek, is located in the Lowlands Section of the Piedmont Physiographic Province (fig. 3). More detailed information about the environmental setting of these subunits can be found in Risser and Siwiec (1996). More detailed information about basin characteristics, sample-collection frequency, and the types of field and laboratory measurements made at each of the sites can be found in Siwiec and others (1997).

Seasonality of Applications and Climate

Because herbicides are applied shortly before planting or shortly before the emergence of crops, crop-planting information can be used to approximate when herbicides are applied in any given year. This assumption is supported by Barbash and Resek (1996, p. 107) and, for corn, by Crawford (1995). Barbash and Resek suggest crop acreage is a reliable predictor of pesticide use, on a local scale. Crawford showed a relation between percentage of corn planted and the timing of annual peak atrazine concentrations in the White River, Ind. In this report, the progressive amount of acres planted in corn is used to estimate pre-planting, pre-emergent, and post-emergent herbicide-application periods.

The recorded stages of corn crop planting and growth provide estimates of time periods when burndown, pre-emergent, and post-emergent applications may occur. Statewide average 5-day-interval corn planting and growth schedules for 1993 and 1994 are available from the Pennsylvania Department of Agriculture (1996). During these 2 years, the planting of corn generally began by April 25, 10-20 percent of the corn was planted by May 5, and about 85 percent of the total crop was planted by June 5 (figs. 5-7). By mid-July, corn has generally reached a height at which applications cannot be made without crop damage. These stages of planting and growth imply burndown herbicide applications during the month of April, pre-emergent applications during the month of May, and post-emergent applications during the month of June. The three herbicides displayed in figures 5-7 (atrazine, simazine, and pendimethalin) are generally used for pre- and post-emergent applications. Atrazine is applied on soil and foliar surfaces. Simazine and pendimethalin are generally applied to soil surfaces only, and simazine is sometimes applied with other herbicides for burndown purposes. Generally, the herbicides applied during a particular growing season would not be expected to be seen in the environment before April of that season. Concentrations measured in wells and streams prior to April are probably the result of applications during prior years.

Concentrations of atrazine and simazine measured in samples collected during base-flow conditions from three streams at long-term monitoring sites exhibit seasonal patterns (figs. 5-7). Little variation in concentration was measured from September through April. This period coincides with the nongrowing season and the nonapplication period for the three herbicides. A general increase in concentrations of atrazine and simazine in the two streams draining agricultural basins, East Mahantango Creek (fig. 5) and Mill Creek (fig. 6), is observed from May through August, the planting, growing, and herbicide-application seasons. In contrast, Cedar Run (fig. 7) is a predominantly urban basin with some agricultural area in the headwaters of the basin. Variations in stream-water herbicide concentrations that may result from agricultural activity in headwater areas of the basin may be masked by the quantity and quality of flow contributed to Cedar Run by the downstream urban and commercial areas.

While the seasonality of applications appears to play a major role in the seasonal elevation of selected pesticide concentrations in streams, the effects are enhanced by the concurrent seasonality of the climate in the northeastern United States. The long-term averages for precipitation in Pennsylvania show a 60-percent increase from March (low) to July (high) (National Oceanic and Atmospheric Administration, 1995).

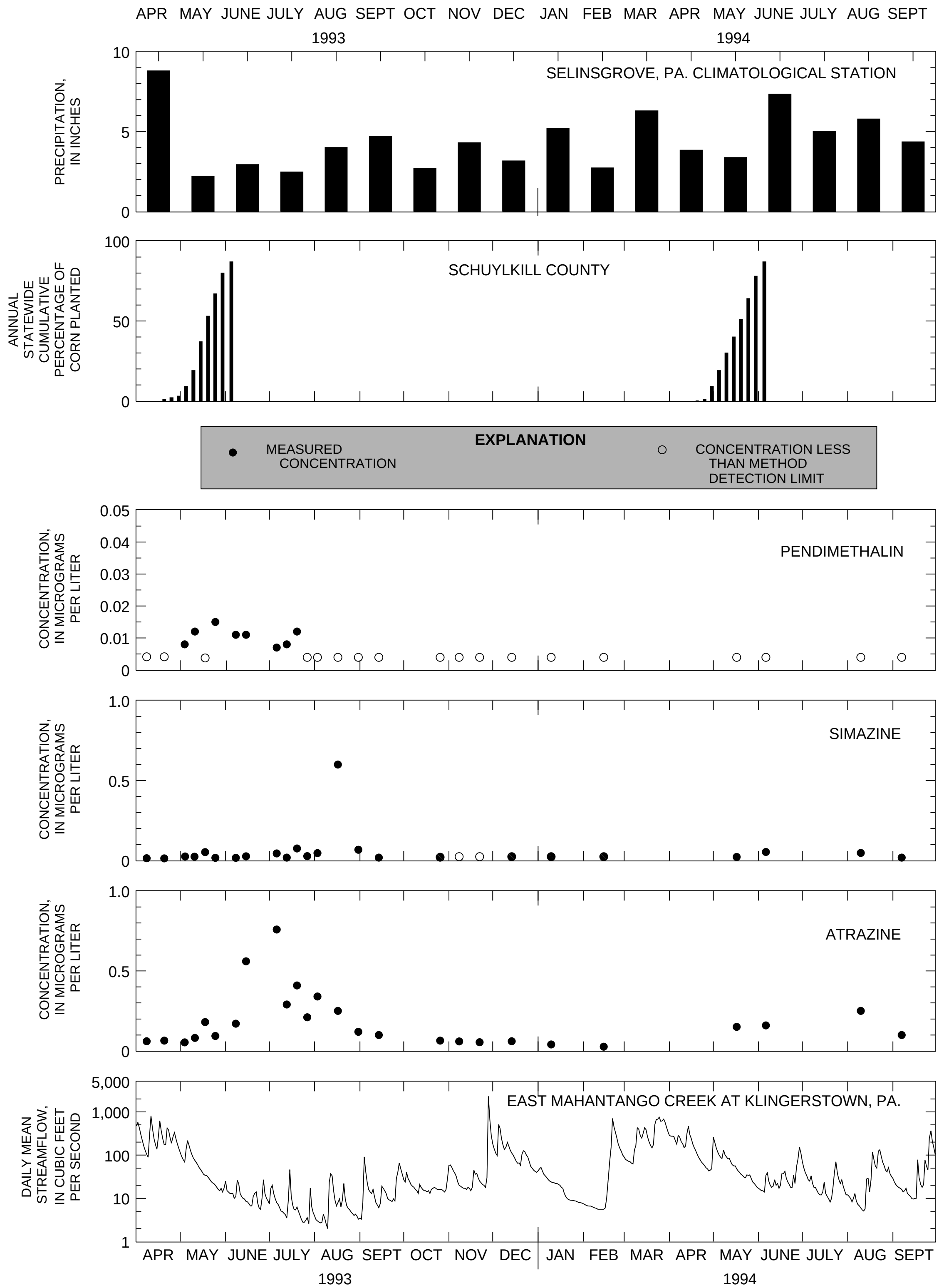


Figure 5. Monthly precipitation and cumulative percentage of corn planted in the East Mahantango Creek Basin and base-flow herbicide concentrations and daily mean streamflow for East Mahantango Creek, 1993-94.

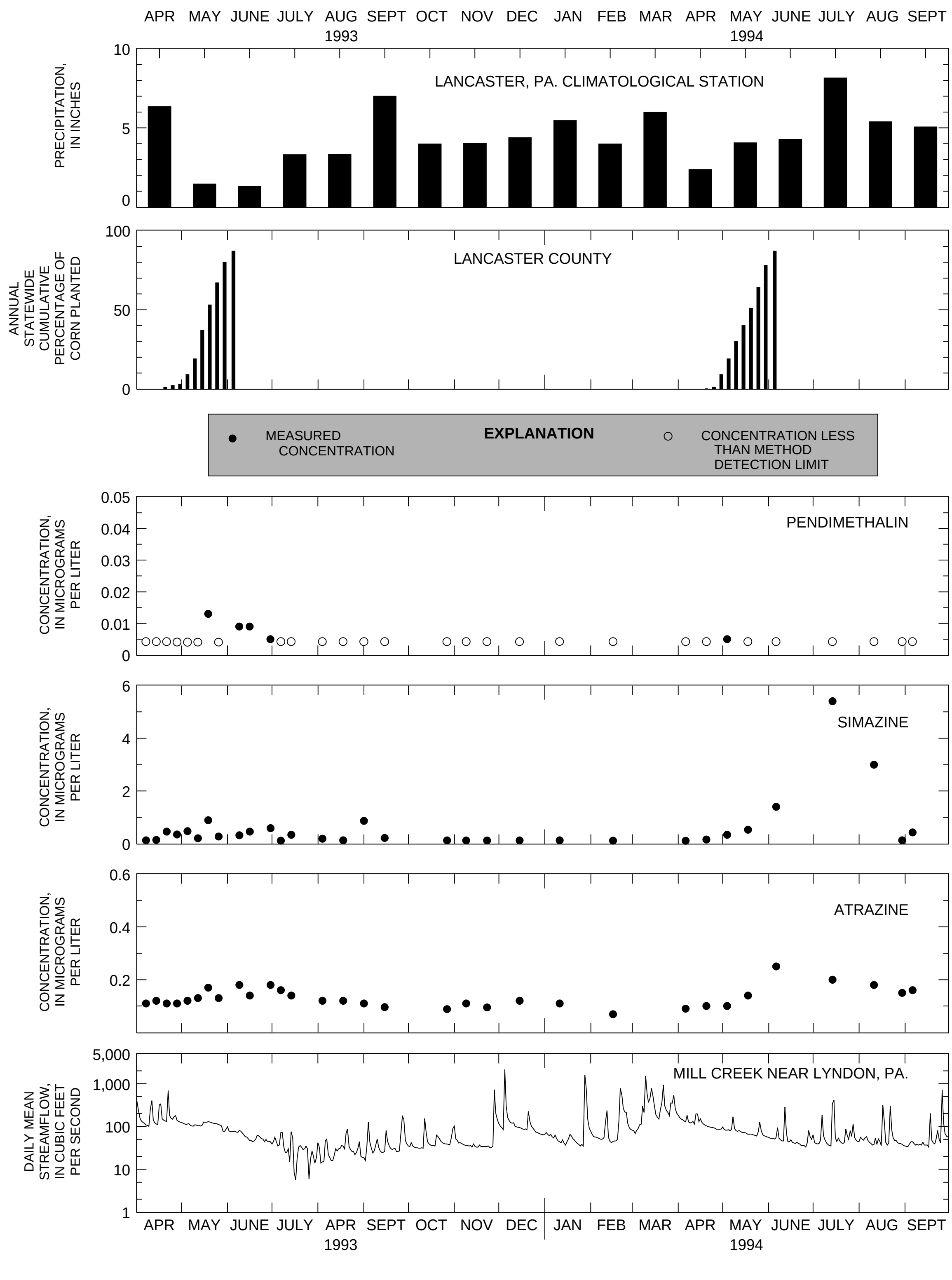


Figure 6. Monthly precipitation and cumulative percentage of corn planted in the Mill Creek Basin and base-flow herbicide concentrations and daily mean streamflow for Mill Creek, 1993-94.

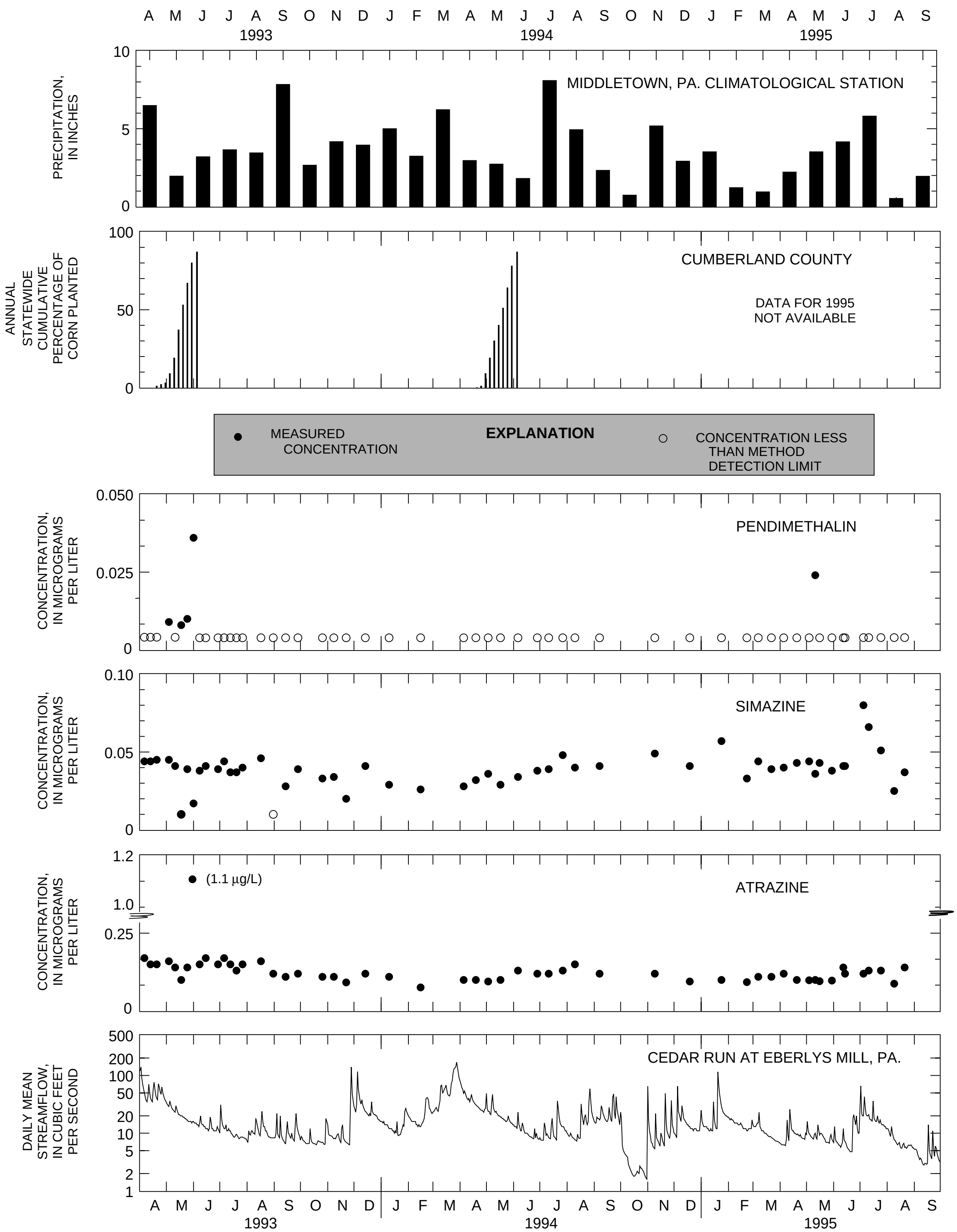


Figure 7. Monthly precipitation and cumulative percentage of corn planted in the Cedar Run Basin and base-flow herbicide concentrations and daily mean streamflow for Cedar Run, 1993-95.

Evapotranspiration is also seasonally low in the spring, which increases the potential for precipitation to recharge ground water. Therefore, soluble pesticides applied during the spring have a higher potential to enter the ground water and eventually discharge to the stream through base flow (figs. 5-7). Compared to long-term average monthly precipitation, precipitation in the spring of 1993 was abnormally low. Studies examining fluxes in concentrations of selected pesticides (including atrazine) in the Susquehanna River above the Fall Line to the northern Chesapeake Bay, also found that the greatest pesticide concentrations coincided with the months of field application (Foster and Lippa, 1996; G.D. Foster, K.A. Lippa, and C.V. Miller, written commun, 1998).

Applied pesticides also can be volatilized or become attached to dust particles and be redeposited during precipitation. Although data of this type were not collected during this investigation, a study that examined samples collected in 23 states from 1990 to 1991 as part of the National Atmospheric Depositional Program/National Trends Network found that about one-third of the samples contained detectable concentrations of triazine and/or acetanilide herbidices (Stamer and others, 1998). Atrazine and alachlor were detected most frequently. Pesticide concentrations in precipitation varied seasonally and corresponded to pesticide-application periods; however, the overall contributions by this delivery method were relatively small (Stamer and others, 1998).

The effect of seasonal stormflow on herbicide transport is shown in figures 8 and 9. During the stormflows sampled in May and June from Cedar Run and Bachman Run, general increases in atrazine concentrations were observed along the rising limb of the hydrograph; the concentration occasionally peaked after the peak in streamflow had passed. This implies that atrazine applied from April through June (application months) is available and is being flushed into the streams during storms. The storm in July shows a decrease in atrazine concentrations along the rising limb of the stream hydrographs—a time when increases were noted during events earlier in the season. Except for the one concentration measured in Bachman Run near the peak of the July 1995 storm, this pattern of decreasing storm concentrations in July is consistent. It implies a reduction from the supply of atrazine available during the months of application.

Studies in other basins in the United States indicate similar patterns in stream concentrations during storms. Crawford (1995) reported atrazine concentrations in the White River at Hazelton, Ind., from 1991 through 1995 were highest during the planting period and the occurrence of peak concentrations was not necessarily related to peak streamflow. In the White River, the concentrations typically were highest during the first one or two runoff periods after application.

A short-term reduction in the atrazine supply also can occur during the application season. The hydrograph of the June 11-14, 1995, storm (fig. 8) shows two successive storms within about 12 hours. The first, with a considerably lower streamflow peak, produced the higher peak concentrations of atrazine of the two storms. This type of transport is common for limited-supply constituents like atrazine.

Concentrations of the insecticides diazinon and chlorpyrifos (figs. 8 and 9) behaved in a manner similar to herbicides during the rising limb of storms but differed significantly during base-flow conditions between storms. Organophosphate insecticides such as these have a relatively high capacity for adsorption to sediment particles. Triazine herbicides like atrazine have a relatively low adsorption potential and have a higher potential to dissolve and be transported in the water, as opposed to by the water through attachment to sediment. Concentrations of diazinon and chlorpyrifos

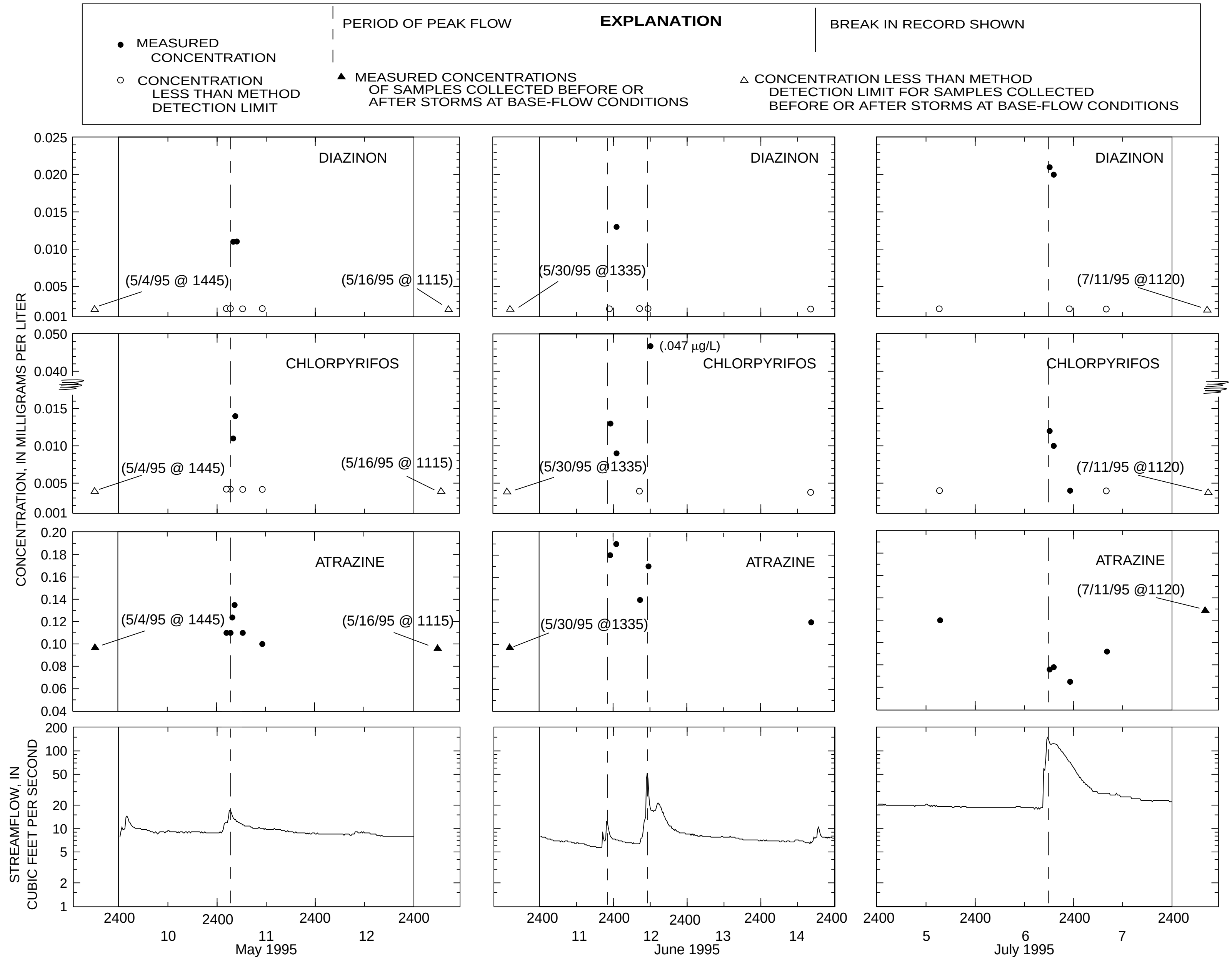


Figure 8. Streamflow and concentrations of diazinon, chlorpyrifos, and atrazine measured in Cedar Run at Eberlys Mill, Pa., before, during, and after selected storms in May through July 1995. [Samples identified as triangles are nearest samples collected before or after storms at base-flow conditions.]

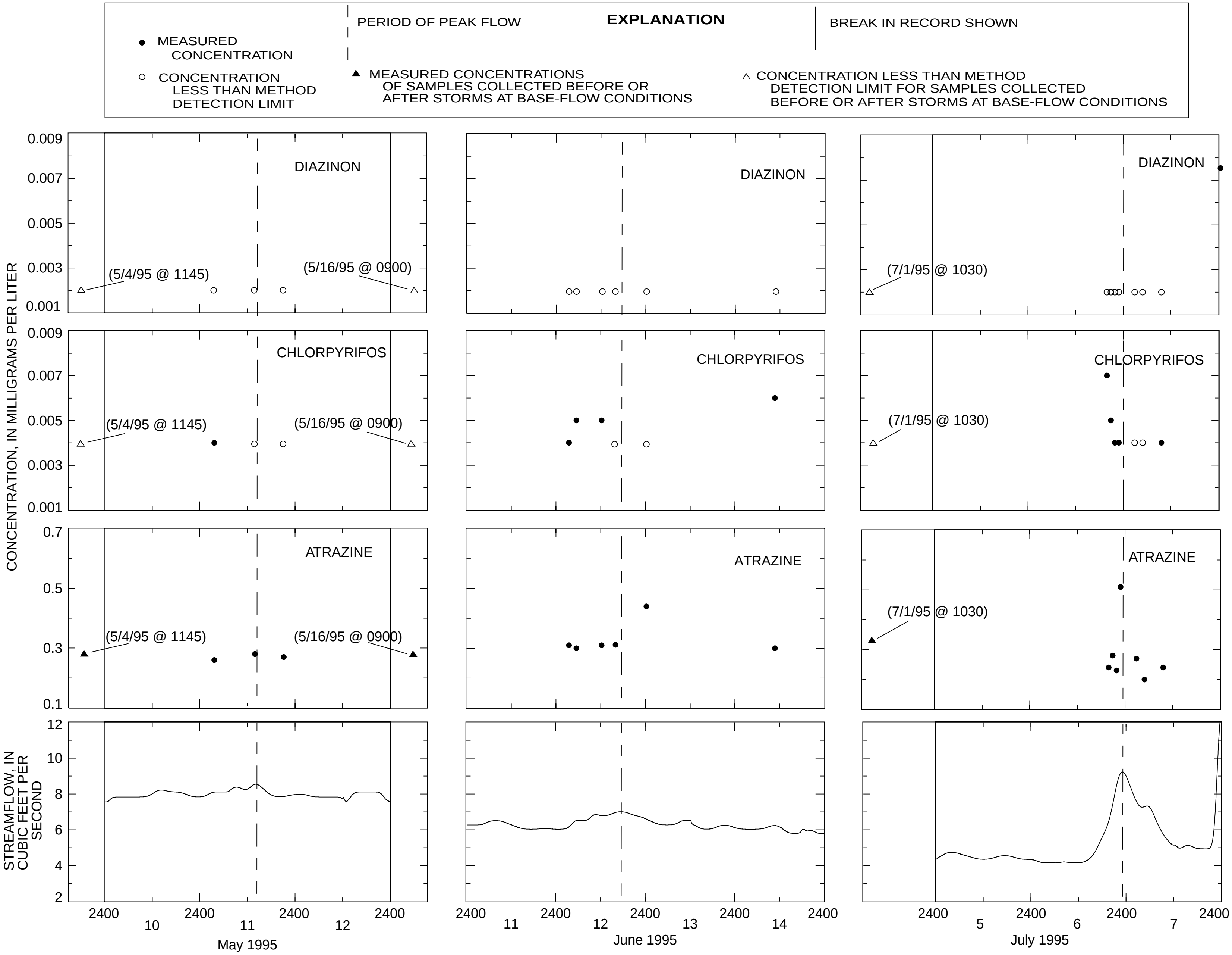


Figure 9. Streamflow and concentrations of diazinon, chlorpyrifos, and atrazine measured in Bachman Run at Annville, Pa., before, during, and after selected storms in May through July 1995. [Samples identified as triangles are nearest samples collected before or after storms at base-flow conditions.]

exceeded the reporting limit only when overland runoff was a significant component of the streamflow. The introduction of these adsorptive pesticides to streams appears to be dependent on the energy supplied by overland runoff to dislodge and transport sediment particles. During all three storm periods shown on figures 8 and 9, not just those early in the season, measurable insecticides concentrations were observed. This is probably because insecticides are applied to control pests throughout the growing season—a pattern unlike the seasonal method used for herbicides applied to corn. Most insecticide applications in the study unit are probably for nonagricultural purposes.

Ground-Water Retention and Discharge

The important role of ground water in the retention of pesticides and their eventual discharge to streams is shown in figures 5-7. Although concentrations varied between the three streams, a relatively constant year-round baseline atrazine concentration was measured in base-flow samples in each stream. In two of the three streams, a similar pattern was observed for simazine. Pendimethalin, a herbicide with a higher potential for adsorption and a lower potential for dissolution than either atrazine or simazine, was rarely measured in base-flow samples.

Measurable in-stream concentrations of herbicides throughout the year in study-unit streams indicate aquifers are constantly transporting a small amount of contaminant to the stream with a reservoir-like effect. In reservoirs, the effect is the result of the mixing of inflow within the impounded pool of water and the discharge of the mixed water through an outlet at a fixed location. The extent of mixing in the reservoir is dependent on several factors, but primarily on residence time. The physical properties of the soils, bedrock, and deep aquifers appear to have a tendency to attenuate the effects of seasonal applications of herbicides and provide a relatively constant baseline release of measurable concentrations to streams from a deep ground-water source replenished during each application season. More shallow ground water is believed to provide the seasonal pulses observed in base flow of streams in the study unit.

The concept of a ground-water reservoir that discharges to stream base flow is supported by other studies. Barbash and Resek (1996) indicate seasonal patterns also have been observed in shallow ground water in the mid-continent of the United States. Generally, low median pesticide concentrations and detection frequencies are maintained throughout the winter months and reach peak concentrations during late spring and early summer. Studies by Goodman (1991) in South Dakota, Libra and others (1993) in Iowa, and Risch (1994) in Indiana also found frequencies of pesticide detection in shallow ground water are significantly lower during the winter than those observed in the spring and summer application periods.

A study by Hippe and others (1994) measured herbicide concentrations in samples collected from springs near Carlisle, Pa., that flow into Conodoguinet Creek, a tributary to the Susquehanna River. The study was conducted from May 1990 through May 1991. The area is underlain by carbonate bedrock and is in the Great Valley Section of the Ridge and Valley Physiographic Province. They found atrazine concentrations in the spring discharges varied little throughout the year. This setting is not unlike the basin characteristics for the Cedar Run Basin (fig. 6) where similar results were observed. The concentrations measured by Hippe appeared to be independent of streamflow and indicated the discharge of a well-mixed reservoir of ground water. Simazine was detected in only 4 of 101 samples collected from the springs sampled in the Conodoguinet Creek Basin, at a minimum reporting level of 0.1 µg/L.

Stamer and Zelt (1994) report a similar release mechanism of pesticides in samples collected from a surface-water reservoir in the Lower Kansas River Basin, and Squillace and Thurman (1992) suggest this type of herbicide transport in the Cedar River in Iowa. Pesticide movement through the hydrologic system is assumed to be slow (on the order of months to years). The approximate age of the water discharged to these streams is 1-10 years, but the application year of the discharged pesticides is unknown. Because of mixing, the discharged herbicides are probably from multiple years of application.

Herbicide and insecticide concentration patterns observed in the Lower Susquehanna River Basin were similar to those observed in streams in the Chesapeake Bay watershed (U.S. Environmental Protection Agency, 1994). Organonitrogen herbicide and organochlorine and organophosphorus insecticide concentrations in stream water that discharged from three major tributaries directly into Chesapeake Bay were measured at the Fall Line, the contact between the Piedmont and Atlantic Coastal Plain Physiographic Provinces. Organonitrogen herbicide concentrations, primarily atrazine, peaked in May or June and dropped to lower levels during the winter months. Organophosphorus insecticides were rarely detected, and organochlorine insecticides did not exhibit the seasonal pattern of herbicides.

Factors Affecting Areal Concentration Patterns in Wells and Streams

The relatively constant and year-round release of soluble herbicides to streams draining areas affected by agricultural land use and the intermittent delivery of relatively non-soluble insecticides to streams described in the previous section are probably the combined result of several factors. Areal patterns of pesticide concentrations and the factors that appear to affect them will be discussed with respect to the following topics: 1) areal application patterns—in agricultural and nonagricultural areas, 2) pesticide persistence and solubility and the infiltration capacity of soils, and 3) ground-water retention and discharge.

Areal Application Patterns

Areal application patterns and detection frequencies of pesticides may vary significantly depending on the percentage of land in agricultural or nonagricultural use in the basin. As would be expected, patterns of pesticide use and detection of pesticides for agricultural purposes reflect patterns of agricultural land use in the study unit (fig. 1). Use of nonagricultural pesticides is usually limited to turf management, roadside vegetation clearing, and residential and garden insect control.

Areal application patterns in agricultural areas

Areal application patterns of selected pesticides for agricultural purposes in the study unit are based on county-level data supplied by Anderson and Gianessi (1995). Applications of the five selected pesticides in Lancaster, York, Cumberland, Adams, and Lebanon Counties, all located in the southern part of the study unit, account for a majority of the annual amount of the pesticides used for agricultural purposes in the study unit (table 8). Lancaster County, an area of intense agriculture, has the highest amounts applied for three of the five pesticides. Applications in Adams County accounted for the highest amounts of the two remaining pesticides. York County receives the second highest amounts for all five pesticides.

Table 8. *Average annual amounts of selected pesticides used for agricultural purposes and rank, by county, in the Lower Susquehanna River Basin study unit, 1990-94*

[Source: Anderson and Gianessi (1995); No data are reported for Cambria, Columbia, and Somerset Counties in Pennsylvania and Baltimore and Carroll Counties in Maryland because less than 5 percent of their respective areas occupy the Lower Susquehanna River Basin; No data are reported for Chester County because pesticide use is reported as negligible in the part of the county within the Lower Susquehanna River Basin; Amount shown for each county has been adjusted by the percentage of the county in the Lower Susquehanna River Basin; LSR, Lower Susquehanna River Basin; lb/yr, average annual amount used in pounds; ---, no known use]

County, state	Percentage of county in LSR	Atrazine		Simazine		Pendimethalin		Chlorpyrifos		Diazinon	
		Amount used (lb/yr)	Rank	Amount used (lb/yr)	Rank	Amount used (lb/yr)	Rank	Amount used (lb/yr)	Rank	Amount used (lb/yr)	Rank
Adams, Pa.	52	9,680	14	3,170	1	3,870	12	5,140	4	1,230	1
Bedford, Pa.	72	10,100	13	324	9	3,310	14	4,030	7	99	6
Berks, Pa.	11	6,400	20	110	18	1,970	18	1,200	20	20	15
Blair, Pa.	100	10,300	12	292	10	10,000	3	4,520	5	93	8
Cecil, Md.	34	8,710	17	637	5	136	22	3,150	13	3	18
Centre, Pa.	27	6,490	19	55	20	2,740	15	1,390	19	1	19
Cumberland, Pa.	100	27,900	3	546	6	8,230	4	6,070	3	142	5
Dauphin, Pa.	100	17,700	6	210	14	6,000	7	3,180	12	23	13
Franklin, Pa.	22	9,660	15	495	7	2,670	16	2,450	17	165	3
Fulton, Pa.	34	1,920	22	16	22	788	20	551	22	---	---
Harford, Md.	37	9,220	16	882	4	155	21	3,330	10	1	20
Huntingdon, Pa.	100	12,600	10	108	19	5,370	8	3,560	9	---	---
Juniata, Pa.	100	10,800	11	245	11	4,950	9	2,850	16	50	10
Lancaster, Pa.	100	107,000	1	1,120	3	33,600	1	22,900	1	154	4
Lebanon, Pa.	85	23,000	4	227	12	7,210	5	4,090	6	20	14
Mifflin, Pa.	100	13,100	9	162	16	3,500	13	3,060	14	25	12
Northumberland, Pa.	62	19,100	5	217	13	6,430	6	2,950	15	39	11
Perry, Pa.	100	16,400	8	166	15	4,860	11	3,320	11	15	16
Schuylkill, Pa.	41	7,470	18	129	17	2,170	17	1,400	18	64	9
Snyder, Pa.	100	16,700	7	406	8	4,910	10	3,640	8	97	7
Union, Pa.	28	4,200	21	44	21	1,330	19	880	21	5	17
York, Pa.	100	68,400	2	1,120	2	22,300	2	11,000	2	220	2
LSR TOTALS[1]		416,850		10,681		136,499		94,661		2,466	

[1] Column totals may not be equal to sum of pesticide use for all counties in LSR Basin shown in table 2 due to rounding.

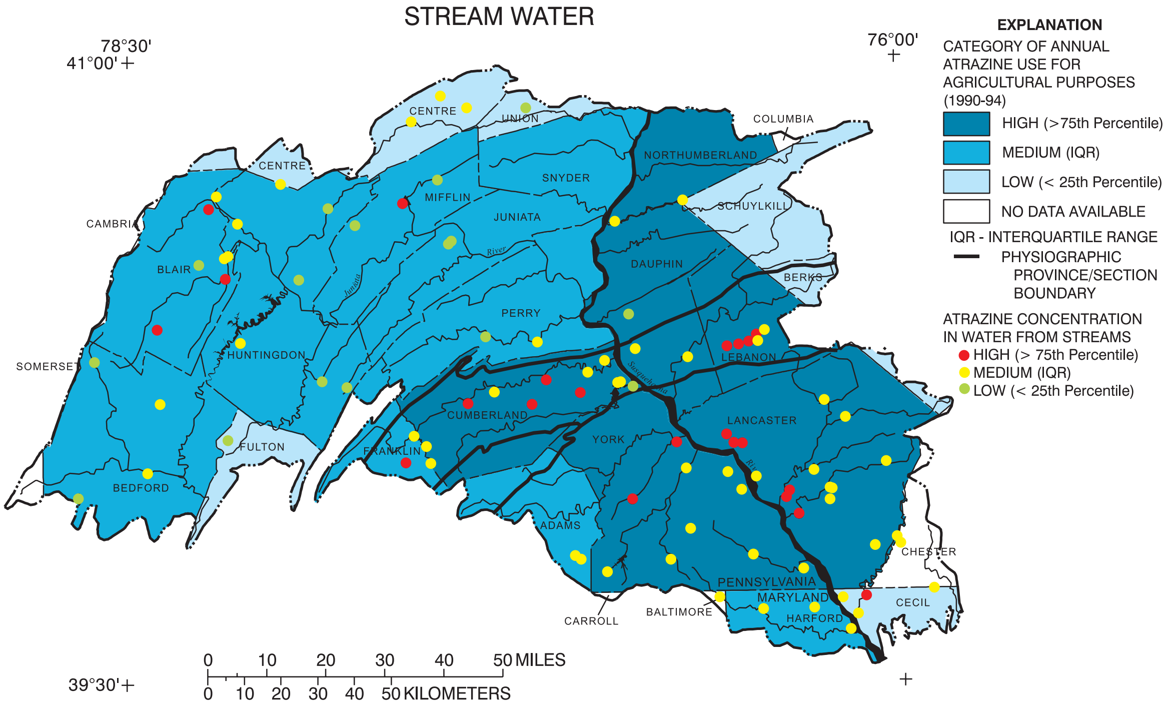
Atrazine use is closely tied to agriculture. Risser and Siwiec (1996) reported that agriculture is the dominant land use in Lancaster, York, Cumberland, Dauphin, and Lebanon Counties—the five southern counties of the Lower Susquehanna River Basin study unit. Sixty percent of the study unit's entire agricultural land use is located in this five-county area that occupies only 35 percent of the study-unit drainage area. Estimated average annual applications of atrazine for agricultural purposes in these five counties comprise about 58 percent of the total applied in the study unit. A similar pattern of use was observed for another pesticide applied mostly for agricultural purposes—pendimethalin.

Agricultural-use application patterns in the study unit were determined by first ranking the average annual amount applied in each county for each of the five selected pesticides. The top 25 percent of the counties, by ranked use, were designated as high-use areas. The bottom 25 percent of the counties, by ranked use, were designated as low-use areas. The remainder of the counties were designated as medium-use areas. Each pesticide was treated separately in determining the county ranks.

Shallow-well synoptic surveys (169 samples) and stream-subunit synoptic surveys (94 samples) were conducted, in part, to determine areal patterns of concentrations. Pesticide concentration patterns were determined in a manner similar to that used for application patterns. Sample measurements collected during subunit surveys including nondetected concentrations were ranked separately. For the multiple-sample long-term monitoring sites, only the single samples collected during the stream synoptic surveys were used in this analysis.

Using this overall ranking for each pesticide, the concentrations were divided into three groups. The top 25 percent of the measured concentrations were designated as high concentrations; the lower 25 percent as low concentrations. The remainder of the concentrations were designated as medium. If the number of detected concentrations for a particular pesticide was small compared to the total number of samples, the measured concentrations were grouped into only two categories—detected and nondetected concentrations. The designations of concentrations in the low, medium, and high categories are simply an arbitrary categorization of the measured concentrations and were determined on the basis of quartile limits. A high designation should not be considered in relation to any existing or proposed health standard and does not imply a risk to human or aquatic ecosytem health.

The pattern of atrazine concentrations detected in these surveys conducted from 1993 to 1995 resembles the pattern of atrazine applications for agricultural purposes (fig. 10). If no relation existed between atrazine application patterns and atrazine concentrations measured in streams and ground water, the areal pattern of samples with high concentrations would be expected to match the distribution of all samples among the atrazine-use areas. The pattern found appears to support a high-use, high-concentration relation. Ten percent of the samples were collected in the low-use areas, and less than 5 percent of the high concentrations were measured in the low-use areas. In contrast, about 60 percent of the samples were collected in high-use areas, and about 75 percent of the concentrations in the high category were measured in the high-use areas. When compared to pendimethalin, atrazine's high solubility in water and low adsorption potential also may explain the frequency and range of detection for atrazine in surface- and ground-water samples.



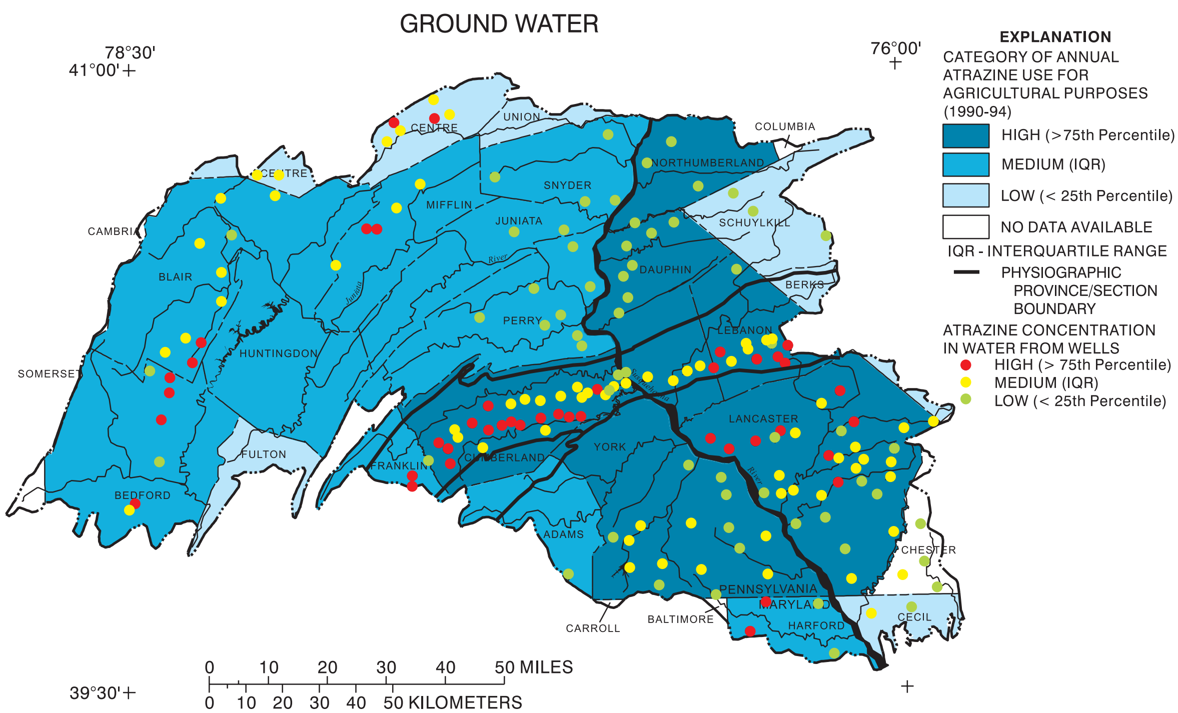


Figure 10. Categorized average annual atrazine agricultural applications, 1990-94, and categorized atrazine concentrations measured in water from streams (subunit synoptic surveys) and ground water (shallow-well synoptic surveys), 1993-95, in the Lower Susquehanna River Basin study unit, Pennsylvania and Maryland.

The high number of nondetected pendimethalin concentrations did not allow a descriptive display of areal concentration patterns or a relation to be established with application patterns (fig. 11). Only three samples (one in a shallow well and two in streams) had detectable concentrations. As indicated during the discussion of factors affecting seasonal patterns of pendimethalin, the low number of detections may be affected by its relatively low solubility in water and relatively high affinity for adsorption to soil.

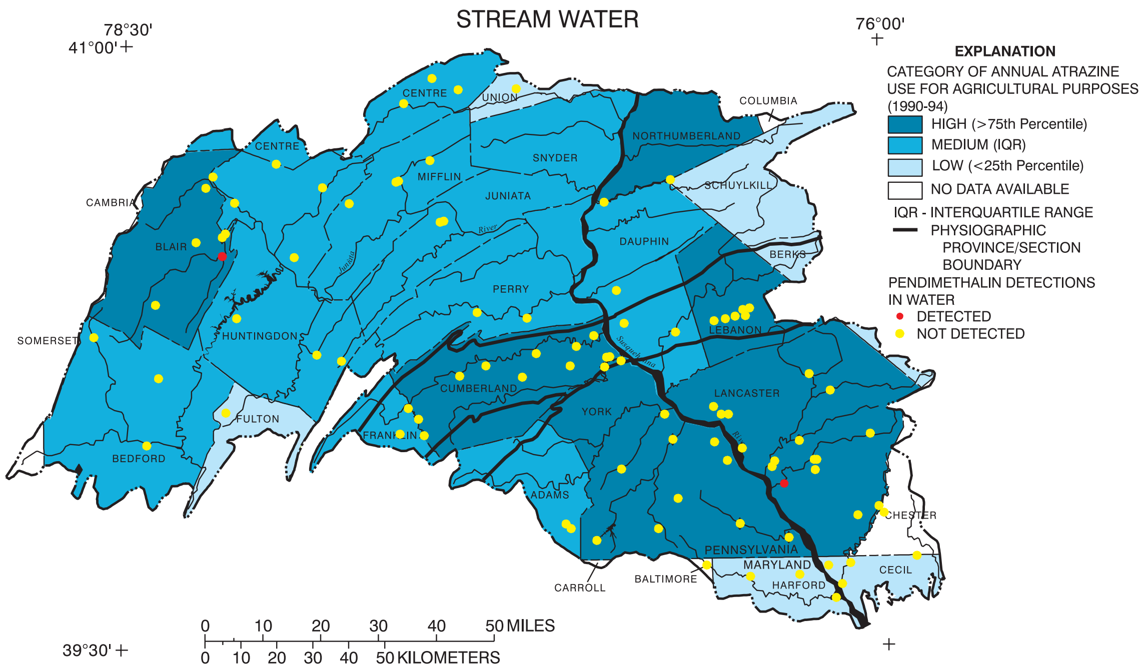
Statistical analysis of the categorized use and concentration data for atrazine and simazine using contingency tables and the Chi-square statistic indicates the level of combined well and stream concentrations of atrazine and simazine and the level of use of each herbicide for agricultural purposes are significantly related at a 95-percent confidence level ($\rho \leq 0.05$). Analyzed separately, well and stream concentrations also are significantly related to use.

Pesticide-use estimates and stream median base-flow pesticide concentrations are shown for five selected pesticides in three environmental subunits of the study unit in figure 12. Pesticide concentrations measured at the long-term stream-monitoring sites and basins were selected to represent those concentrations typically found in the individual subunits. Estimates of agricultural pesticide use in three subunits representing selected environmental settings of the study unit generally were based on pesticide use in the county in which each of the long-term stream monitoring basins are located. The exception to this latter rule was Lancaster County, where a more regionalized approach was used.

Averaged Lancaster and York County pesticide-use data are used to represent the agricultural areas underlain by carbonate bedrock in the Piedmont Physiographic Province (PD-CAR) and the Mill Creek Basin. For most agricultural pesticides, Lancaster County has the greatest use, by far, of an individual pesticide in the study unit. A better estimate of use for the subunit that includes parts of Lancaster County is the average pesticide use in the Lancaster and York County region. York County also has high amounts of agricultural land use, but the intensity of agriculture is less and is more typical of the two subunits that include parts of Lancaster and York Counties.

Lebanon County pesticide-use data represent agricultural areas underlain by carbonate bedrock in the Great Valley Section of the Ridge and Valley Physiographic Province (GV-CAR) and the Bachman Run Basin. Schuylkill County data represent agricultural areas underlain by sandstone and shale bedrock in the Appalachian Mountain Section of the Ridge and Valley Physiographic Province (AM-SIL) and the East Mahantango Creek Basin. Data collected by Pionke and others (1988) indicate pesticide-use estimates for the East Mahantango Creek Basin and Schuylkill County may have been underestimated by Anderson and Gianessi (1995). Because all available pesticide-use data are based on use for agricultural purposes, no estimates are made for pesticide use in the urban area.

Using the areas within the subunit boundaries (fig. 2) and the data presented in table 8 and supplied by Anderson and Gianessi (1995), agricultural pesticide-use areal patterns are apparent (fig. 12). When compared to the Great Valley (GV-CAR) and Appalachian Mountain (AM-SIL) agricultural subunits, the counties within the agricultural areas underlain by carbonate bedrock in the Piedmont Physiographic Province (PD-CAR) subunit have the largest masses of atrazine, simazine, chlorpyrifos, and pendimethalin used on a per-acre-of-agricultural-land basis (fig. 12). The agricultural areas underlain by sandstone and shale bedrock in the AM-SIL subunit are where the least amount of pesticides are applied annually for four of the five pesticides. Generally, the subunits underlain by carbonate bedrock are the areas



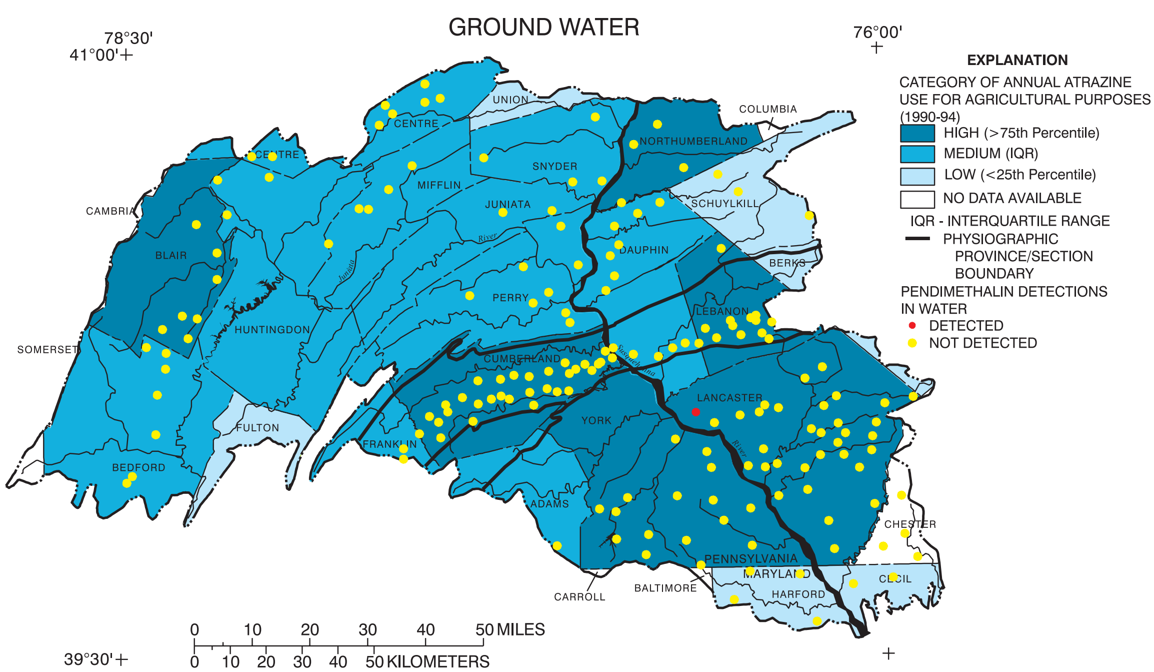


Figure 11. Patterns of average annual pendimethalin agricultural applications, 1990-94, and pendimethalin concentrations measured in water from streams (subunit synoptic surveys) and ground water (shallow-well synoptic surveys), 1993-95, in the Lower Susquehanna River Basin study unit.

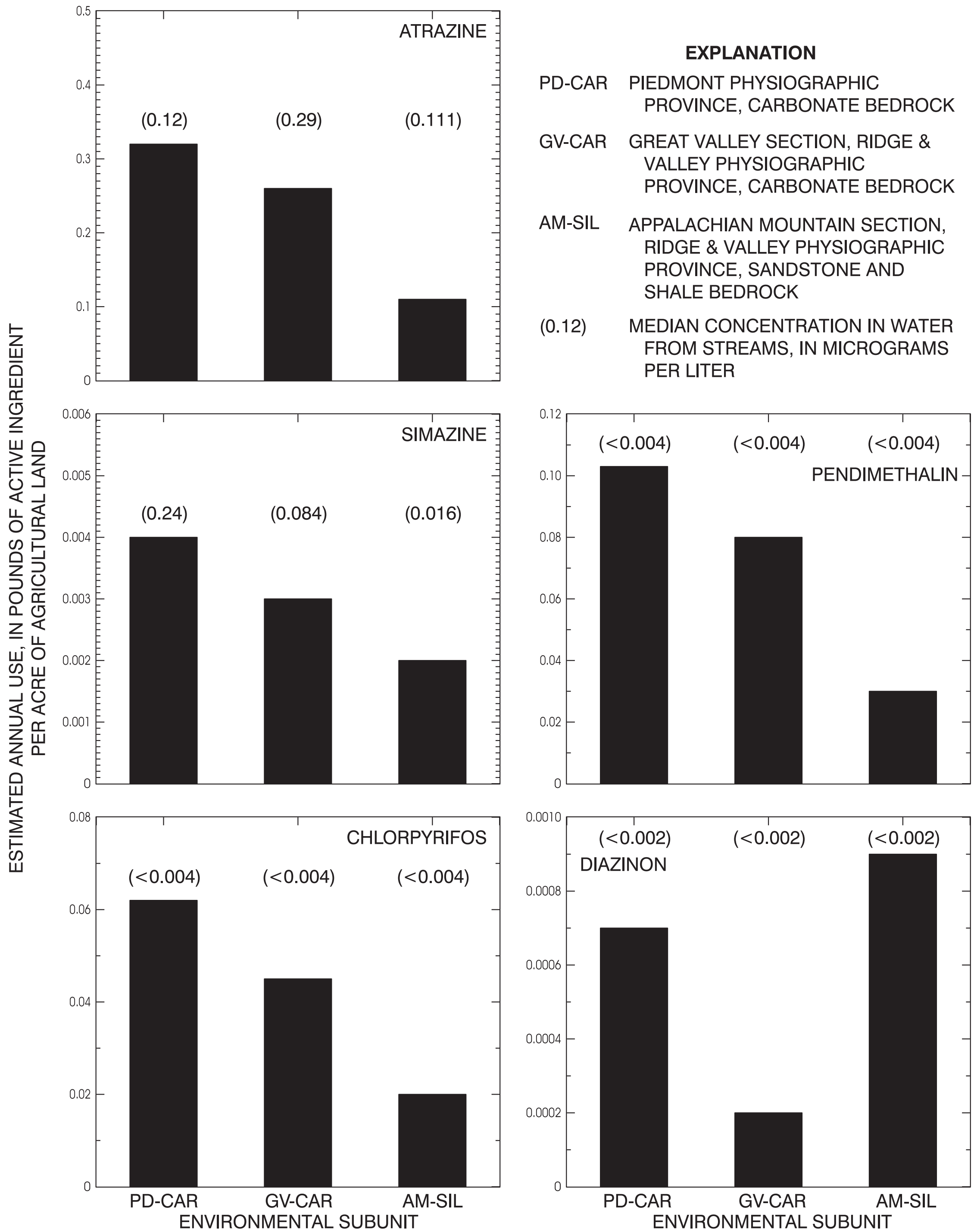


Figure 12. Estimated annual use, 1990-94, for agricultural purposes and the median base-flow concentrations of five selected pesticides observed in water from streams in three environmental subunits of the Lower Susquehanna River Basin study unit where long-term monitoring stream sites were located.

where the most agriculture is located and the most agricultural pesticides are used. This relation of agricultural chemical use, agricultural land use, and carbonate bedrock in the Chesapeake Bay watershed has been reported by others (Hainly and Kahn, 1996; Fisher, 1995).

The relation between pesticide use and concentrations measured in the environment is sometimes used to develop a mass balance for the pesticide. For the selected pesticides, defining the relation between agricultural pesticide use in a subunit and the magnitude of pesticide concentrations measured in the hydrologic environment is a difficult task. Using concentrations of atrazine and simazine measured in streams in three selected subunits (fig. 12), it appears that a general relation may exist between stream concentrations and elevated use in agricultural areas underlain by carbonate bedrock in the Piedmont Physiographic Province and the Great Valley Section of the Ridge and Valley Physiographic Province. Because of a low detection frequency, the determination of a relation between annual use and stream concentration was not possible for pendimethalin, chlorpyrifos, and diazinon. The ability to measure stream-water concentrations of these pesticides may be affected by their relatively low solubility in water and relatively high affinity for adsorption to soil and may not be related to annual application amounts for agricultural purposes.

Areal application patterns in nonagricultural areas

Although pesticides are widely and, in some areas of the study unit, heavily used for agricultural purposes, pesticides also are applied in numerous areas for nonagricultural purposes. Some common nonagricultural herbicide uses include turf management on residential and commercial lawns and golf courses, and vegetation-clearing along railways, highways, and transmission lines. Insecticides commonly are used for pest control in homes and commercial buildings and in private and public gardens. Pesticide amounts used for nonagricultural purposes in areas smaller than nationwide are poorly documented. Barbash and Resek (1996, p. 115) report that, in 1991, pesticide sales to professional applicators and consumers nationwide were slightly more than 20 percent of the sales in the agricultural market. Additionally, Barbash and Resek describe the results of a 1989-90 USEPA study that estimated 73 percent of households, nationwide, used some type of pesticide during 1990.

Little data on nonagricultural pesticide use in the study unit is available. In this report, potential magnitude of pesticide use for nonagricultural purposes in the study unit will be indicated by the percentage of residential land use, excluding urban areas, in the counties within the study unit. The density of residential land use will be used to estimate relative areal patterns in pesticide use for turf management and insect control. A relation between the density of residential areas and the occurrence of insecticides in the environment in a developed area of New York has been demonstrated by Eckhardt and others (1989).

The county-based summary of residential land use (table 9) indicates the highest uses of herbicides for turf management on residential lawns may be in the southern part of the study unit comprising York, Lancaster, Cumberland, Dauphin, and Lebanon Counties. About 70 percent of the residential land use in the study unit is in this five-county area (table 9). In addition, about 80 percent of the public golf courses identified by the Pennsylvania Atlas and Gazetteer (1990) in the study unit are located in this five-county area. Turf management and insect control on golf courses are potentially other uses that may affect pesticide concentrations in water from wells and streams. Insecticides applied to control pests in homes and commercial buildings also may be concentrated in the same five-county area. The areas of residential land use were determined by combining the information available from digital datasets of land use

Table 9. *Cropland and suburban residential land use within the Lower Susquehanna River Basin study unit, by county*

[Source for land-use data: Cropland, U.S. Environmental Protection Agency (1990a); Residential area, Mitchell and others (1977), U.S. Department of Commerce (1991), Hitt (1994); No data are reported for Cambria, Columbia, and Somerset Counties in Pa. and Baltimore and Carroll Counties in Md. because less than 5 percent of their respective areas occupy the Lower Susquehanna River Basin; LSR, Lower Susquehanna River Basin; mi^2, square miles]

County, state	Percentage of county in LSR	Cropland area within county and LSR		Residential area within county and LSR	
		(mi^2)	(percent)	(mi^2)	(percent)
Adams, Pa.	52	140	52	5.2	1.9
Bedford, Pa.	72	164	22	6.2	.9
Berks, Pa.	11	43	45	.8	.9
Blair, Pa.	100	90	17	26.7	5.1
Cecil, Md.	34	32	26	2.5	1.8
Centre, Pa.	27	39	13	1.6	.6
Chester, Pa.	12	29	32	4.2	4.5
Cumberland, Pa.	100	217	40	37.6	6.9
Dauphin, Pa.	100	152	29	47.6	9.0
Franklin, Pa.	22	64	37	1.4	.9
Fulton, Pa.	34	33	22	.3	.2
Harford, Md.	37	40	24	1.4	.7
Huntingdon, Pa.	100	148	17	6.6	.8
Juniata, Pa.	100	102	26	2.1	.5
Lancaster, Pa.	100	552	58	77.2	8.1
Lebanon, Pa.	85	139	45	15.4	4.9
Mifflin, Pa.	100	81	20	9.6	2.3
Northumberland, Pa.	62	129	45	8.8	3.0
Perry, Pa.	100	125	22	5.4	1.0
Schuylkill, Pa.	41	61	19	10.5	3.2
Snyder, Pa.	100	114	35	4.7	1.4
Union, Pa.	28	27	31	1.2	1.4
York, Pa.	100	410	45	59.3	6.5

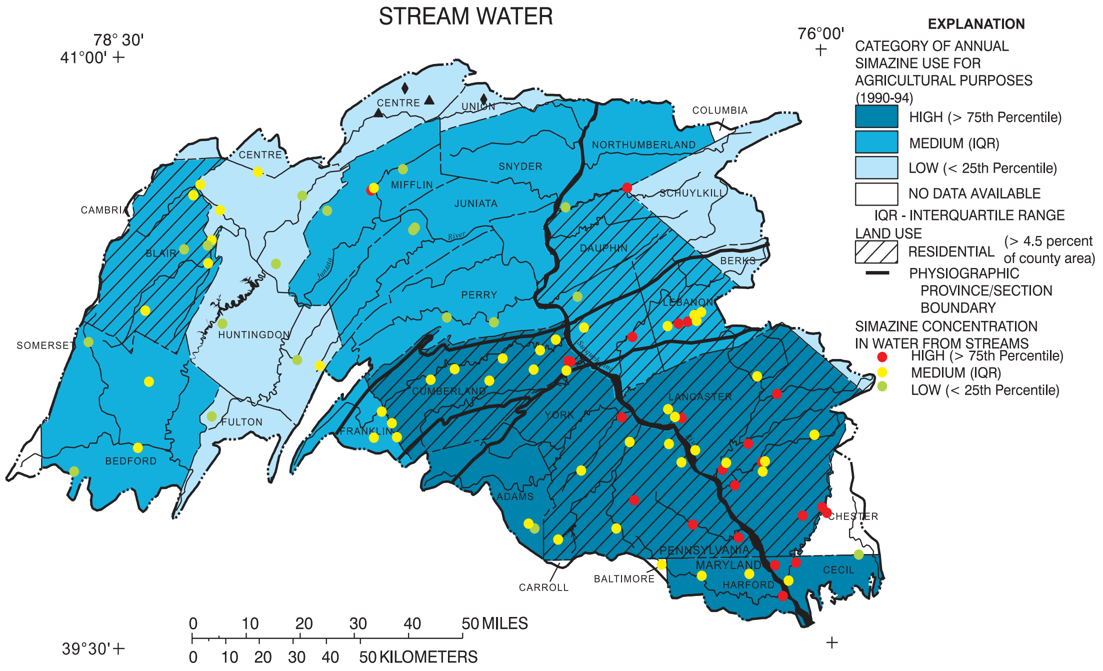
(Mitchell and others, 1977) and 1990 population (U.S. Department of Commerce, 1991). The method for combining the datasets was developed by staff of the NAWQA Program (Hitt, 1994).

Identifying agricultural or nonagricultural uses as the dominant pesticide source in the hydrologic environment is difficult in the study unit because most of the agriculture (fig. 1, table 9), agricultural pesticide use (table 8), residential areas (table 9), and public golf courses are located in a five-county area in the southern part of the study unit. For instance, simazine is used for agricultural purposes (fig. 13, table 8) but is used more extensively on fruits and vegetables than on grain crops. Thirty percent of the total simazine used in the study unit is applied in the five southern counties. Another 30 percent of the simazine used in the study unit on an annual basis is applied in Adams County, where many orchards are located. Simazine also is used for weed control in residential areas along railways, highways, and transmission lines. The multiple uses for simazine, and other pesticides, make it difficult to determine their dominant source in the environment.

Areal patterns of simazine concentration in water from streams and shallow wells (fig. 13) most likely reflect the combined effects of agricultural and nonagricultural uses. Almost all the detected concentrations in the designated high range were in the five-county area in the southern part of the Lower Susquehanna River Basin study unit. Agricultural uses alone do not account for all the higher concentrations detected because samples from streams and wells in Dauphin, Lebanon, and Blair Counties also had concentrations in the higher range, but they are considered to be in the medium-use category for agricultural purposes. Activities associated with the high amount of residential area in these three counties may account for the high concentrations. Most of the high concentrations were measured in water samples collected from streams and shallow wells in locally intensive agricultural areas.

Another pesticide with concentrations that may be affected by nonagricultural use is diazinon. 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. Majewski and Capel (1995) report 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. Very few measurable diazinon detections were found in the Lower Susquehanna River Basin base-flow samples, and statistical analysis using contingency tables shows no statistically significant differences in diazinon detections between the urban basin in the study unit (Cedar Run) and the agricultural basins (Mill Creek, Bachman Run, and East Mahantango Creek). When the data sets were expanded to include storm-affected samples, contingency tables showed statistically significant differences between the number of diazinon detections in samples collected at Cedar Run and those collected at Bachman Run and East Mahantango Creek and also between the expanded data set from Cedar Run and the base-flow samples from Cedar Run. On the basis of this analysis, a significantly higher number of detections were measured in the urban basin due to storm-affected samples when compared to samples from two of the agricultural basins or from the urban basin during base-flow conditions.

The areal simazine and diazinon detection patterns in areas where agricultural pesticide use is not high indicate pesticide applications for agricultural purposes alone may not fully explain the areal patterns in pesticide concentrations observed in water



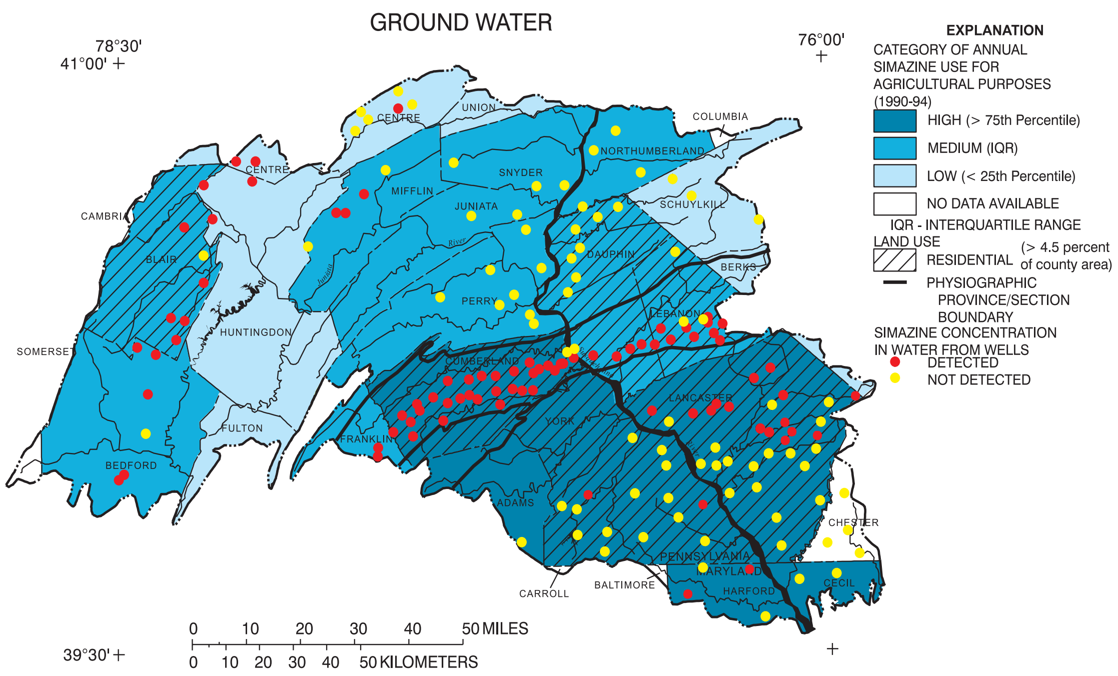


Figure 13. Categorized average annual simazine agricultural applications, 1990-94, counties with high residential land use, and categorized simazine concentrations measured in water from streams (subunit synoptic surveys) and ground water (shallow-well synoptic surveys), 1993-95, in the Lower Susquehanna River Basin study unit.

from streams and shallow wells. The density of residential land use and golf courses are factors that add to the explanation of areal concentration and detection patterns for these two pesticides.

Method of Pesticide Application, Pesticide Persistence and Leaching Potential, and Infiltration Capacity of Soils

The method of pesticide application, pesticide persistence and leaching potential, and infiltration capacity of soils are three factors that affect the fate of a pesticide after application. These factors, along with the previously described seasonal application and climate patterns, play a large part in determining whether an applied pesticide will be transported to ground water and the fraction of the stream pesticide load that will be contributed by a subsurface component.

Three application methods commonly used in the study unit are applications to foliage, applications to the land surface, and incorporation into the soil. Application methods of the five selected pesticides generally differ by the type of control. Herbicides (atrazine, simazine, and pendimethalin) are generally applied to the soil surface but sometimes to weed foliage. Insecticides (chlorpyrifos and diazinon) generally use a foliar application method but are sometimes incorporated into the soil. Those applied to the soil surface would be expected to be more readily available for transport to the subsurface. Another factor that could affect the pesticide transport through the system is the organic-carbon content of the soils. This factor will not be discussed, however, because the organic-carbon content of soils does not vary greatly within the areas studied (Knox and Moody, 1991).

Data collected in this study were not designed to address pesticide persistence. Information from previous investigations of pesticide persistence in the environment are presented to describe the relative degree of availability for leaching and infiltration of atrazine, simazine, pendimethalin, chlorpyrifos, and diazinon. The discussion will be limited to processes initiated by agricultural-use applications of pesticides. Areal patterns of infiltration rates, based on the hydrogeologic framework within the study unit, will be related to detection-frequency differences in streams and shallow wells to further explain areal patterns in pesticide concentrations.

A pesticide’s persistence (normally associated with “half-life”) in the environment is determined by several factors and is generally measured by its rates of volatilization, evaporation, and degradation. Pesticide degradation is a general term used to include the complex transformation and degradation processes of biotransformation, chemical hydrolysis, photolysis, and oxidation-reduction reactions. Most simulations of pesticide fate and transport use the combined losses of evaporation and volatilization and the losses due to degradation to determine the amount available for leaching into ground water or surface transport.

The pesticide leaching potential is affected by several factors, including persistence and solubility. Hippe and Hall (1996) used physical and chemical properties of pesticides described by Wauchope and others (1992) to simulate the fate and transport of four of the five selected pesticides in a carbonate-rock terrain in the Great Valley Section of the Ridge and Valley Physiographic Province in the study unit. The fate and transport of atrazine, simazine, chlorpyrifos, and diazinon were simulated over a 2-year period of near-average annual climatic conditions. Of the factors included in the sensitivity analysis, affinity for adsorption to carbon in the soil and degradation rate had the greatest effects on fate and transport. Two other chemical properties, vapor density and water solubility, were also moderately influential. On the basis of Hippe and Hall’s analysis of the examined pesticides relative to each other, atrazine has a large leaching potential, simazine has a medium leaching potential, and the insecticides, chlorpyrifos and diazinon, have small leaching potentials. The properties of pendimethalin also are described by Wauchope and others (1992). Values given for water solubility and sorption coefficients indicate pendimethalin is more likely to behave in a manner similar to chlorpyrifos and diazinon and will probably have a small leaching potential.

For the purposes of this discussion, a simplistic model is used that assumes the amount of pesticide that reaches ground water is proportional to the amount available for leaching, the physical properties of the pesticide that affect the leaching potential (i.e. pesticide persistence, solubility in water, and affinity for adsorption to soil), and the infiltration rate of the soils to which it is applied. After application and the combined effects of surface processes on the amount of material available for leaching, the movement of pesticides below the land surface is governed primarily by infiltration and the flow of water through the saturated zones. During a normal year and even during slightly less than normal years, precipitation amounts in the study unit are sufficient for crop production. Because of this, irrigation is not a common practice in the study unit and the major source of water applied to the land surface is considered to be precipitation.

Armbruster (1976a) developed an infiltration index for the Susquehanna River Basin using basin characteristics that included physical, climatic, soil, and geologic features. Armbruster (1976b) also published a map providing an infiltration-capacity rating for regions of the Susquehanna River Basin. The infiltration-capacity ratings are based on analyses completed by the U.S. Soil Conservation Service for the Susquehanna River Basin Coordinating Committee (1970).

Topography, soils, and infiltration capacities vary throughout the Lower Susquehanna River Basin study unit. The Appalachian Mountain Section of the Ridge and Valley Physiographic Province accounts for the northwestern two-thirds of the study unit and is characterized by long, narrow forested ridges and agricultural valleys that trend southwest to northeast (fig. 2). The Appalachian Mountain carbonate agricultural subunit and the Appalachian Mountain sandstone and shale agricultural and forested subunits were studied in this Section. The topography of the Appalachian Mountain carbonate subunit is generally flat with wider valleys than those underlain by sandstone and shale, and the carbonate bedrock exhibits typical karst features such as sinkholes and internal drainage. The soils in this subunit have excellent infiltration capacities. The Appalachian Mountain sandstone and shale subunits have valleys that are narrower and steeper than the carbonate valleys due to the more resistant sandstone and shale bedrock and ridges. The soils in Appalachian Mountain sandstone and shale subunits have infiltration capacities that range from good to poor.

The Great Valley Section (fig. 3) borders the eastern edge of the Appalachian Mountain Section of the Ridge and Valley Physiographic Province. The area is a broad 10-15 mi wide valley and is unique in the province. The Great Valley carbonate agricultural and urban subunits were studied in this Section. The topography in the Great Valley subunits is predominantly flat, and the underlying carbonate bedrock also exhibits typical karst features. Soils generally have excellent infiltration capacities except in urban areas where parking lots, buildings, and paved roads reduce infiltration and increase runoff (Lindsey and others, 1997).

The Piedmont Physiographic Province (fig. 2) covers the southeastern third of the study unit. This area is characterized by low, rolling hills and broad valleys. The Piedmont carbonate and crystalline agricultural subunits were studied in this Province. The topography in the Piedmont carbonate subunit is generally flat due to the underlying carbonate bedrock, and flow through the weathered rock can move rapidly through the system. The soil infiltration capacity in this subunit is excellent. The Piedmont crystalline subunit, which is in the southern part of the Piedmont Physiographic Province, is characterized by low rolling hills with underlying bedrock that includes igneous and metamorphic rocks. The soil infiltration capacity in the Piedmont crystalline subunit is good.

Infiltration-capacity ratings are incorporated into figure 14 along with the general hydrogeologic setting of the regions defined by Armbruster (1976b). Detection frequencies of atrazine, simazine, pendimethalin, chlorpyrifos, and diazinon for samples from shallow wells and from streams during all flow conditions from each of the hydrogeologic settings were determined. The pesticides were grouped into the following categories, on the basis of leaching potentials described by Hippe and Hall (1996) and Wauchope and others (1992):

Small leaching potential—pendimethalin, chlorpyrifos, diazinon,

Medium leaching potential—simazine,

Large leaching potential—atrazine.

Pesticide detection frequencies in streams are presented to indicate the relative availability of each pesticide to the hydrologic environment in each hydrogeologic setting. To simplify the graphical presentation and to show the relative differences due to leaching potential, pendimethalin was selected to represent the pesticides with small leaching potentials (fig. 14). Differences or similarities in detection frequencies between water from streams and shallow wells for each of the pesticides are used to indicate the effect of leaching potential and soil infiltration capacity on the delivery of the pesticide to an aquifer.

It appears the probability of an applied pesticide being detected in streams is more related to leaching potential than infiltration capacity of the soils. For water from shallow wells, the probability of a pesticide being detected is related to the pesticide’s leaching potential and the infiltration capacity of the soils in the area where the pesticides are applied. Hydrogeologic settings underlain by carbonate bedrock generally have the highest infiltration capacities. Pesticides, such as atrazine, with a high leaching potential are detected almost as frequently in well water as in streams in these settings. In carbonate settings, pesticides with a smaller leaching potential, such as pendimethalin, tend to have lower detection frequencies in shallow well water and streams than those with larger leaching potentials. Also, in each hydrogeologic setting, the magnitude of the difference between the detection frequencies of wells and streams has a tendency to increase as leaching potential gets smaller.

In noncarbonate settings, for a pesticide such as atrazine with a large leaching potential, the detection frequencies in streams and shallow wells are not similar. The detection frequency in water from wells is much lower than the detection frequency in water from streams. This is most likely related to the reduced infiltration capacity of noncarbonate settings in relation to carbonate settings. Pesticides with smaller leaching potentials applied in noncarbonate settings tend to have the lowest detection frequencies in wells and streams and the detection frequency of pesticides in well water is generally lower than the frequency in stream samples.

Detection frequency in shallow wells decreases along the vertical axis from carbonate to crystalline to sandstone and shale bedrock type (from excellent to poor infiltration capacity). Detection frequencies in streams increase along the horizontal axis from small to large leaching potential. Pesticides with a large leaching potential are

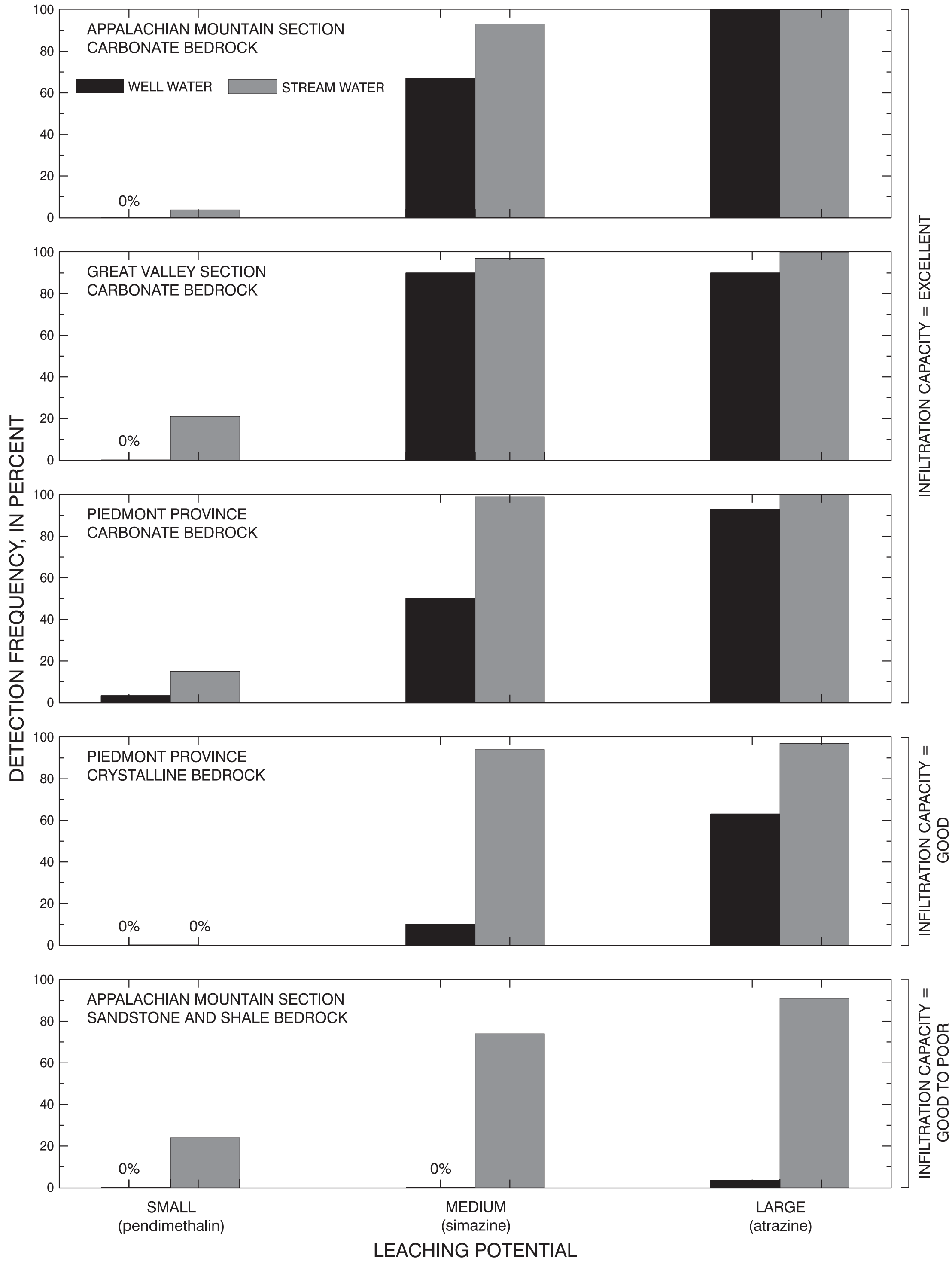


Figure 14. Infiltration-capacity ratings, leaching potential, and frequency of detection for selected pesticides, 1993-95, within various hydrogeologic settings of the Lower Susquehanna River Basin study unit. [Leaching potential groups: small—pendimethalin, chlorpyrifos, diazinon; medium—simazine; large—atrazine.]

expected to be detected most frequently—especially in areas underlain by carbonate bedrock. Conversely, the lowest pesticide detection frequency in streams and shallow wells would be expected in an area with sandstone and shale bedrock type and a low soil infiltration capacity where pesticides with a small leaching potential are applied. Statistical analysis of the categorized infiltration capacity and leaching-potential ratings in relation to the detection-frequency differences for water from streams and shallow wells using contingency tables and the Chi-square statistic indicates differences in well water and stream water detection frequencies are significantly related at a 99-percent confidence level ($\rho \leq 0.01$).

Ground-Water Retention and Discharge

For the purposes of this discussion, ground-water retention is defined as the capacity of an aquifer to attenuate the delivery of a pesticide once it is delivered through some mechanism from the surface. In this sense, the aquifer is treated as a reservoir of dissolved pesticides. The delivery of the pesticides and the magnitude of their concentration is dependent on the hydrologic properties of the aquifer. The dominant transport mechanism to streams is considered to be ground-water and spring discharge. A water sample collected from a stream during base-flow conditions is considered to have one or both of these two sources of discharge as its dominant source.

Based on synoptic sampling data collected for this study, differences in the probability of a particular pesticide being detected in water from a shallow well or from a stream during base-flow conditions in selected subunits are shown in table 10. The summary is similar to the data presented in figure 14 except that land use is not used to subdivide the hydrogeologic settings presented in figure 14 into environmental subunits, and figure 14 includes data from storm samples.

For atrazine, a soluble herbicide used primarily for agricultural purposes, bedrock type appears to explain areal patterns in detection frequency. Atrazine is generally detected at a higher frequency in shallow ground water in carbonate bedrock settings that in noncarbonate settings. For water from streams during base-flow conditions, bedrock type alone does not explain areal patterns in atrazine detection frequency among the subunits. The addition of land use as a factor, and more specifically the dominance of nonforested land use in a subunit, better describes areal patterns of detection frequencies in water collected from streams. The detection frequency of atrazine in streams during base-flow conditions and shallow wells is most similar in carbonate bedrock-agricultural subunits. Subunits with either sandstone and shale bedrock or those dominated by forested land use exhibited the most difference in detection frequencies between water from streams during base-flow conditions and shallow wells. The similarity of detection frequencies in wells and streams in carbonate areas, especially in agricultural areas, indicates a fairly well-connected hydrologic system. Atrazine detection frequency of water discharged to streams from ground water during base-flow conditions is a reasonable representation of detection frequencies in ground water in carbonate settings.

Table 10. *Summary of detection frequency in water from streams (base-flow synoptic surveys) and ground water (shallow-well synoptic surveys) for selected pesticides for various environmental subunits within the Lower Susquehanna River Basin study unit, 1993-95*

[Well water, analyses of water from shallow wells during synoptic surveys; stream water, analyses of water from streams during synoptic base-flow conditions]

Environmental subunit[1]	Pesticide detection frequency (percent)									
	Atrazine		Simazine		Pendimethalin		Chlorpyrifos		Diazinon	
	Well water	Stream water	Well water	Stream water	Well water	Stream water	Well water	Stream water	Well water	Stream water
Piedmont crystalline agriculture (22 well-water samples, 33 stream-water samples)	82	100	9	97	0	0	0	0	0	3
Piedmont carbonate agriculture (30 well-water samples, 31 stream-water samples)	93	100	50	97	3	0	0	3	0	13
Great Valley carbonate agricultural (30 well-water samples, 16 stream-water samples)	100	100	97	94	0	6	0	25	3	0
Great Valley carbonate urban (20 well-water samples, 24 stream-water samples)	90	100	80	96	0	0	0	12	5	8
Appalachian Mountain carbonate agricultural (30 well-water samples, 26 stream-water samples)	100	100	67	92	0	4	0	4	0	0
Appalachian Mountain sandstone and shale agricultural (22 well-water samples, 2 stream-water samples)	4	100	0	50	0	0	0	0	0	0
Appalachian Mountain sandstone and shale forested (7 well-water samples, 16 stream-water samples)	0	62	0	25	0	0	0	0	0	0

[1] See table 1 for a more detailed description of environmental subunits.

Simazine, a herbicide with a lower leaching potential than atrazine, exhibited areal detection frequency patterns similar to atrazine although the magnitude of differences between water from streams and shallow wells is generally greater. Detection frequencies slightly lower than those determined for atrazine were measured in stream waters and markedly lower frequencies were measured in shallow well water in all the subunits except the agricultural areas underlain by carbonate bedrock in the Great Valley Section of the Ridge and Valley Physiographic Province and the agricultural areas underlain by sandstone and shale bedrock in the Appalachian Mountain Section of the Ridge and Valley Physiographic Province. A slightly higher detection frequency was measured in well water than in streams in the agricultural areas underlain by carbonate bedrock in the Great Valley Section of the Ridge and Valley Physiographic Province. On the basis of previous analyses in this report, this result is not expected and may be due to the small sample size for streams. In the agricultural areas underlain by sandstone and shale bedrock in the Appalachian Mountain Section of the Ridge and Valley Physiographic Province, no measurable simazine concentrations were detected in water from wells.

The number of detections of the three remaining pesticides—pendimethalin, chlorpyrifos, and diazinon—were too few in waters from streams during base-flow conditions and shallow wells to support any specific conclusions. The data in table 10 tend to indicate a generalized pattern of higher detection frequencies in samples from base-flow streamwater than in samples from shallow wells in carbonate areas.

The general conclusion of this analysis is that the degree of presence or absence of a pesticide in water from streams during base-flow conditions and wells can be determined fairly well and indirectly by sampling stream water during base-flow conditions or well water in subunits where carbonate bedrock or agricultural land use dominates. This conclusion does not apply to any subunit underlain by sandstone and shale bedrock. The uncertainty of the prediction of presence or absence of a pesticide ranges from high for a soluble pesticide in a carbonate bedrock-agricultural land use subunit to low for a relatively insoluble pesticide in a sandstone and shale bedrock-forested land use subunit.

Combining the data and conclusions provided by figure 14 and table 10 suggests an areal pattern in the study unit determined primarily by bedrock type and secondarily by land use. Land use appears to be a better indicator of initial availability and detection frequency in streams than as an indicator of detection frequency differences between shallow well water and streams. Pesticides applied in carbonate bedrock areas that have a high leaching potential are easily transported through the soils to the aquifer, and the occurrence of pesticides in water discharged to streams is proportional to their occurrence in shallow well water.

Lower proportions of the applied pesticides reach ground water and are discharged to streams in a crystalline bedrock system. A moderate amount of degradation is indicated along transport paths from the surface to the aquifer and from the aquifer to the stream. Of the three major bedrock types in the study unit, sandstone and shale bedrock permit the slowest flow through the system and, therefore, provide the greatest chance for degradation due to time of travel. In this case, very little of the available pesticide reaches the deepest ground-water aquifers and attenuated amounts are seen in stream base flow originating from shallow ground-water zones.

In addition to determining the relative occurrence of pesticides in wells and streams during base-flow conditions in selected subunits, the relatively high frequency of detections for atrazine and simazine provides a concentration data set with sufficient sample size to allow inferences about the relation between concentrations in shallow wells and the water discharged to streams from ground water in selected subunits. The limited number of detections in wells and streams in the Appalachian Mountain-sandstone and shale bedrock-forested subunit does not allow this more detailed analysis. It should be noted, though, that measured concentration levels in streams and shallow wells in the subunit are equivalent (fig. 15).

Relative differences in median atrazine concentrations determined from stream and ground-water samples did not exhibit any areal patterns. In addition, when the relative differences were compared among subunits characterized by bedrock type or land use, no patterns were observed. Two of the four subunits underlain by carbonate bedrock showed higher median concentrations in streams than in wells and two showed lower medians. Two of four subunits where agricultural land use dominates showed higher median concentrations in streams and two showed lower medians than those determined from wells (fig. 15). The magnitude of the differences between median concentrations in wells and streams was generally greatest in nonagricultural or noncarbonate subunits. The similarity of median concentrations in carbonate-bedrock subunits indicates the connectivity of water in streams and shallow wells in these subunits. The range of measured concentrations between the tenth and ninetieth percentiles was also generally greatest in agricultural-carbonate subunits. This implies greater variability in the sources and source concentrations available to aquifers and streams in these subunits.

In the five subunits with sufficient data to analyze, a general areal pattern of higher median concentrations in streams during base-flow conditions than in shallow well water was observed for simazine, regardless of bedrock type or the dominance of agricultural land use in the subunit (fig. 15). This reflects the earlier general observation that less of the available simazine is transported to ground water and also indicates that simazine concentrations in streams are enhanced by some other source. Possible sources could be surficial ones located upstream or others located along the pathway from the aquifer to the stream. The data collected during this study do not allow the identification of these additional simazine sources.

A statistical analysis of the median atrazine concentrations determined for wells and streams in each of the subunits was performed using the Kruskal-Wallis test (Helsel and Hirsch, 1992, p. 159). The test indicated statistically significant differences at a confidence level of 95 percent ($\rho \leq 0.05$) existed between the median atrazine concentrations in shallow well water and base-flow stream water in the urban areas underlain by carbonate bedrock in the Great Valley Section of the Ridge and Valley Physiographic Province, in agricultural areas underlain by crystalline bedrock in the Piedmont Physiographic Province, and in agricultural areas underlain by carbonate bedrock in the Piedmont Physiographic Province. Streams in all three subunits had higher median concentrations during base-flow conditions than shallow wells.

The median atrazine concentrations of streams and shallow wells in two agricultural areas underlain by carbonate bedrock in the Appalachian Mountain and Great Valley Sections located in the Ridge and Valley Physiographic Provinces were not significantly different. No significant difference in the medians infers that the system delivering the pesticides to streams has relatively little effect on the magnitude of the concentration in the stream and that the water in the aquifer is chemically similar, as far as atrazine is concerned, to the water in the stream.

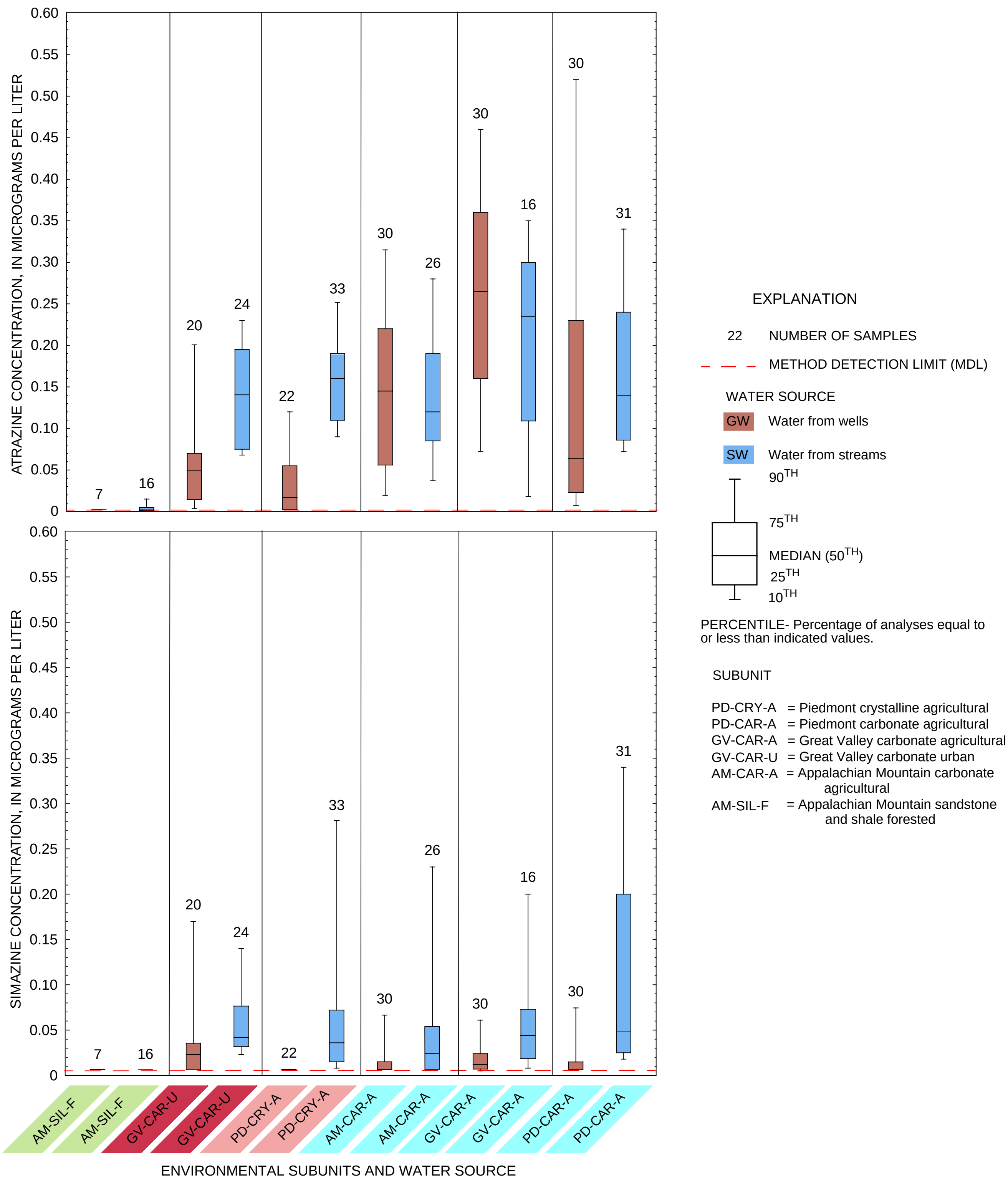


Figure 15. Atrazine and simazine concentrations in wells and streams during base-flow synoptics, 1993-95, in selected environmental subunits, Lower Susquehanna River Basin.

SUMMARY AND CONCLUSIONS

Pesticides in water from wells and streams are an important water-quality issue in the Lower Susquehanna River Basin study unit of the National Water-Quality Assessment Program. Intensive agriculture in parts of the study unit and relatively high amounts of pesticides applied in agricultural areas introduce thousands of pounds of pesticides to the environment each year. Nonagricultural uses of pesticides for turf management and insect control are also a source of these compounds. As a part of the National Water-Quality Assessment Program, concentrations of 53 herbicides, 29 insecticides, and 1 fungicide were measured in water samples from streams and shallow wells located in the Lower Susquehanna River Basin in Pennsylvania and Maryland.

Average annual pesticide application amounts for agricultural purposes in the study unit were determined from crop-specific pesticide application rates and average annual county-based crop acreages. The five pesticides with the highest amounts used for agricultural purposes from 1990 to 1994 were metolachlor, atrazine, captan, pendimethalin, and alachlor.

From 1993 through 1995, a total of 577 samples were collected from 169 shallow wells and 155 stream sites. Samples were collected on a fixed interval over a 1- to 3-year period at four of the stream sites. At two of these four stream sites, samples also were collected over the hydrograph of selected storms.

Conclusions from Analysis of Concentration Data

- Nearly 40,000 concentrations of 83 different pesticide compounds were determined
- Thirty-eight of the 83 compounds were not detected in any of the 577 samples
- About 60 percent of all herbicides analyzed were detected at least once
- Approximately 45 percent of all insecticides analyzed were detected at least once
- The most commonly detected pesticides in the study unit—atrazine, metolachlor, simazine, prometon, alachlor, and cyanazine—are agricultural herbicides primarily used on corn and grain crops
- Atrazine was detected in 98 percent of the stream samples and 75 percent of the well samples
- Approximately 49 percent of all herbicides and 13 percent of all insecticides analyzed in the study unit were detected in well samples
- Approximately 42 percent of all herbicides and 37 percent of all insecticides analyzed were detected in stream samples
- Of the nearly 40,000 pesticide concentrations measured in water from streams and shallow wells, only 7 measurements exceeded any established maximum contaminant level for drinking water (atrazine, simazine, and alachlor); 55 measurements exceeded 1 µg/L, and 24 measurements exceeded 2 µg/L

Conclusions from Analysis of Seasonal Patterns

- Seasonal patterns of atrazine, simazine, pendimethalin, chlorpyrifos, and diazinon concentrations were observed in water from streams during base-flow conditions

- Elevated concentrations in water from streams during base-flow and storm-affected conditions were related to seasonal applications of pesticides for agricultural purposes

- The availability of pesticides for runoff during the application season in a series of storms was related to how recently a previous storm had occurred and not necessarily to the peak discharge of the storm

- Ground-water retention and discharge of pesticides was indicated by a year-round discharge of measurable concentrations of soluble herbicides

- In some cases, relatively constant and year-round concentrations of pesticides and attenuation of the seasonal pulse of elevated concentrations were observed in stream base flow

Conclusions from Analysis of Areal Patterns

- Agricultural-use patterns described many of the areal concentration patterns for the high-use compounds

- Indicators of nonagricultural use such as the location of suburban residential areas were needed to explain concentration or detection frequency patterns for some pesticides such as diazinon and simazine

- The density of residential land use and golf courses may be factors that add to the explanation of areal concentration and detection patterns for simazine and diazinon

- Differences in median concentrations among environmental subunits were related to three coincident factors: agricultural land use, basins underlain by carbonate bedrock, and agricultural pesticide-use patterns

- Ratings of soil infiltration capacity of various hydrologic settings and the persistence of a compound explained some differences in detection-frequency areal patterns in water from streams and wells

- Relatively soluble herbicides, such as atrazine, applied in areas covered by soils formed by the weathering of carbonate bedrock were detected at similar frequencies in water from streams and shallow wells

- Water samples from shallow wells in areas underlain by sandstone and shale provided relatively few detections for compounds with a large leaching potential and no detections for compounds with a smaller leaching potential

- Areal patterns of ground-water retention time and the discharge of an attenuated concentration of a pesticide to streams from ground water were best explained by bedrock type and land use

- Water samples from streams in three of the five environmental subunits comprising the study area had significantly higher atrazine concentrations during base-flow conditions than those concentrations measured in water samples from shallow wells

- Two of the three environmental subunits underlain by carbonate bedrock where agricultural land use dominates had no statistically significant difference in median atrazine concentrations measured in water from shallow wells and streams during base-flow conditions

The data collected in or available to this study did not allow an extensive interpretation of the effect of several factors that influence pesticide concentrations in water from wells and streams. Estimates of agricultural pesticide use are currently based on a summary of application rates and cropping practices developed on a county basis. Agricultural-use estimates based on more-refined stream basin boundaries would enhance the analyses presented in this report. In addition, estimates of pesticide use for nonagricultural purposes would be a valuable complement to the agricultural-use estimates. Additional data collection to further describe concurrent seasonal variations in streams and, especially in shallow wells, would provide invaluable assistance to developing a conceptual model for pesticide transport in streams and aquifers. Flow-path studies and additional samples collected from streams during a storm would aid in the verification of the conceptual model. Finally, the accumulation of data and application of a pesticide fate and transport simulation in other environmental settings within the Lower Susquehanna River Basin would provide a valuable tool for water-resource managers.

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APPENDIX—METHODOLOGY USED TO CHARACTERIZE STREAMFLOW CONDITION

The following methods were used to characterize the streamflow condition represented by samples collected from streams at long-term monitoring sites.

Development of a time-interval estimate for return to base-flow conditions following a storm event

A commonly accepted method used for hydrograph separation,

$N=A^{0.2}$, where N = time interval, in days and A = drainage area, in mi^2, (1)

was used to determine the time interval from the peak of the storm through the falling limb of the hydrograph when ground-water discharge was not the predominant contributor of flow (Viessman and others, 1977). A review of stream hydrographs at the long-term monitoring sites to verify the estimated time intervals indicated this method produced reasonable estimates for six of the seven streams. Examination of hydrographs from East Mahantango Creek generally revealed a slower recession and longer time interval than the estimated value. For this reason, 24 hours was added to the estimated time interval for East Mahantango Creek. Samples collected outside the time interval estimated for each site were considered base-flow samples. Stream hydrographs and precipitation records from nearby sites were used to determine the occurrence and approximate time of a storm peak for samples collected before stage-recording equipment was installed at the long-term monitoring sites or during periods of equipment malfunction.

Application of estimated time interval and determination of storm-affected samples

For days when elevated streamflow was determined to be from a natural event, the fixed interval method of the HYSEP hydrograph separation program (Sloto and Crouse, 1996) was used to separate streamflow into two components, surface runoff (stormflow) and base flow. To negate the elimination of samples collected shortly after relatively minor precipitation events, a day of elevated streamflow was only considered a storm-affected day when the total streamflow for the day was 30 percent greater than the base-flow component for the day. Therefore, only samples collected within the estimated time interval from a storm peak that met or exceeded the 1.3 ratio of total flow to base flow were considered storm-affected samples and excluded from the base-flow sample set.

Consideration of anthropogenic influences on the stream hydrograph

If there was evidence that an observed change in streamflow was due to the anthropogenic release or storage of water and not a runoff event, samples collected within the estimated time interval were considered base-flow samples. This exception only applies to three samples collected from Mill Creek during two periods of elevated stage recorded at the long-term monitoring site. Continuous specific-conductance record at the site was used to confirm the lack of change to water quality during the periods of elevated stage and flow.

Consideration of observed streamflow conditions

A sample collected as a result of either the fixed-interval sampling program or the storm-sampling program that was collected on the rising limb or a rapidly descending falling limb of a hydrograph was considered storm-affected. At the time of collection for these samples, observed streamflow conditions indicated overland runoff was a significant component of streamflow. This rule was applied regardless of whether the storm event produced a total streamflow greater than 30 percent of the computed base-flow component.