Hydrologic and Geochemical Controls on Pesticide and Nutrient Transport to Two Streams on the Delmarva Peninsula

Scientific Investigations Report 2004-5051

Cover. The upper Pocomoke River Watershed is extremely flat with poorly drained soils and abundant artificial drainage.

[Photograph by Allen C. Gellis, U.S. Geological Survey]

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by Scott W. Ator, Judith M. Denver, and Michael J. Brayton

125 years of science for America ★ ★ ★ ★ ★ *1879–2004*

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.
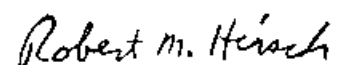
The USGS implemented the National Water-Quality Assessment (NAWQA) Program to support national, regional, and local information needs and decisions related to water-quality management and policy. Shaped by and coordinated with ongoing efforts of other Federal, State, and local agencies, the NAWQA Program 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

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Associate Director for Water

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Conversion Factors and Vertical Datum

Multiply	By	To obtain
Length		
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
Area		
square mile (mi^2)	259.0	hectare
square mile (mi^2)	2.590	square kilometer (km^2)
Flow rate		
cubic foot per second (ft^3/s)	0.02832	cubic meter per second (m^3/s)
cubic foot per second (ft^3/s)	448	gallon per minute (gal/min)
Mass		
Pound, avoirdupois (lb)	0.4536	kilogram (kg)
Load		
microgram per second ($\mu g/s$)	0.0036	gram per hour (g/h)

Temperature in degrees Celsius ($^\circ$C) may be converted to degrees Fahrenheit ($^\circ$F) as follows:

$$^\circ F = (1.8 \times {}^\circ C) + 32$$

Vertical datum: In this report, vertical coordinate information is referenced to the National Geodetic Vertical Datum of 1929 (NGVD 29) and (where noted) to the North American Datum of 1983 (NAD83).

Altitude, as used in this report, refers to distance above or below sea level.

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (μS/cm at 25 $^\circ$C)

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter (μg/L).

Hydrologic and Geochemical Controls on Pesticide and Nutrient Transport to Two Streams on the Delmarva Peninsula

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Abstract

Pesticides and nutrients move from application areas through ground water and surface runoff to streams on the Delmarva Peninsula. The relative importance of different transport media to the movement of these compounds in different watersheds is related to locally variable hydrologic and geochemical conditions among areas of regionally similar land use, geology, and soils. Consideration of such local variability is important to land-management efforts or future environmental investigations on the Peninsula.

Chemical analyses of samples collected over a multiyear period from two streams on the Delmarva Peninsula were analyzed along with similar available analyses of ground water to document the occurrence of pesticides and nutrients, and illustrate important processes controlling their movement through watersheds to streams. The upper Pocomoke River and Chesterville Branch drain predominantly agricultural watersheds typical of the Delmarva Peninsula. Chesterville Branch drains a watershed of moderate relief, good drainage, and a permeable surficial aquifer that ranges in thickness from about 15 to 25 meters. The upper Pocomoke River Watershed, however, is extremely flat with poorly drained soils and abundant artificial drainage. Influences on the chemistry of water in each stream were determined from seasonal patterns in the concentrations of selected constituents from 1996 through 2001, and relations with streamflow.

Nutrients and pesticides are detectable throughout the year in the upper Pocomoke River and Chesterville Branch. Water in both streams is typically dilute, slightly acidic, and well oxygenated, and nitrate and phosphorus concentrations generally exceed estimated natural levels. Pesticide concentrations are generally low, although concentrations of selected metabolites commonly exceed 1 microgram per liter, particularly in Chesterville Branch. Nitrate and metabolites of pesticide compounds are apparently transported to Chesterville Branch preferentially through ground water in the surficial aquifer, although selected pesticide parent compounds and less soluble nutrients move primarily in surface runoff. Conversely, the relative proportion of discharge from surficial and partially confined aquifers is the most important factor controlling the chemistry of water in the upper Pocomoke River. Surface runoff in the larger and predominantly flat upper Pocomoke River Watershed is apparently limited to particularly significant precipitation events. Transport of pesticides in surface runoff becomes important in both watersheds during such events. Instantaneous loads of pesticides in streams typically stabilize or continue to increase with increasing flow even after runoff begins, although in-stream concentrations may decrease due to dilution.

Introduction

Synthetic organic pesticides are present in streams and aquatic ecosystems in many parts of the United States and the world (Larson and others, 1997; Fuhrer and others, 1999; Nowell and others, 1999; Capel and others, 2001). Many streams also contain nutrients (including nitrogen and phosphorus compounds) at concentrations exceeding natural levels (Fuhrer and others, 1999). Although pesticide and nutrient applications are useful for many purposes, excessive levels of these compounds in the environment may cause a variety of adverse ecological or human-health effects. An understanding of the hydrologic, geochemical, and other factors affecting the transport of pesticides and nutrients from areas of application to streams and other surface-water bodies is fundamental to the safe and effective use of these chemicals.

The occurrence and distribution of pesticides and nutrients in streams are related to physical and chemical transport

and transformation processes as well as application rates (Larson and others, 1997; Capel and others, 2001). Pesticides and nutrient compounds are applied for a variety of agricultural, commercial, and domestic purposes (Puckett, 1995; Aspelin, 1997). These compounds can move from areas of application to streams in several ways, including direct discharge from point sources, direct fallout in precipitation or from spraying, overland flow in storm runoff, or through ground water or the unsaturated zone. The time of travel from the original source to a stream is a function of the dominant physical transport mechanisms and potential transformation processes that may alter the original compound. During transport, nutrients and pesticides can be transformed to other related compounds through physical, chemical, or biological processes (Larson and others, 1997; Capel and others, 2001).

The movement of nutrients and pesticides in the environment is related to the mobility and persistence of each individual compound, as well as local hydrologic, geologic, atmospheric, and soil conditions. Although relatively soluble compounds such as nitrate and metolachlor can move in streams and ground water, less soluble chemicals such as phosphorus often attach to soil particles and may only move in overland runoff or streams during periods of relatively high flow (Fuhrer and others, 1999). Airborne transport may be considerable for volatile compounds or those that are dispersed during application (Puckett, 1995; Majewski and others, 1998). Streams are particularly vulnerable to contamination as they may carry surface runoff from urban and agricultural areas as well as ground-water discharge (Larson and others, 1997). The persistence of nutrients in water depends largely on biologic uptake, chemical transformations, and sedimentation. Nitrate, for example, is extremely soluble but may be converted to nitrous oxide or nitrogen gas through denitrification by anaerobic bacteria. Pesticides, by design, are not incorporated as easily into non-target living plants and animals. Although some pesticides can remain in the environment for years, many newer compounds are designed to decompose more rapidly (Fuhrer and others, 1999). Newer pesticides are generally more soluble and therefore more mobile and less likely to adhere to soil and sediment (Larson and others, 1997).

Although nitrogen and phosphorus are essential for healthy plant and animal populations, excessive nutrients can be damaging to aquatic ecosystems. Algal blooms caused by surplus nitrogen or phosphorus may block sunlight from the water column and disrupt photosynthesis in submerged aquatic plants. The biochemical oxygen demand (BOD) from the subsequent death of the algae may consume dissolved oxygen in the stream and cause eutrophication (Fuhrer and others, 1999). In 1999, the Chesapeake Bay was listed as "impaired" under the Clean Water Act due to harmful effects of excess nutrients and sediment (Phillips, 2002).

Pesticides can also cause unintended harmful effects on aquatic ecosystems and human health. Possible human-health effects from overexposure to pesticides include cancer, reproductive and nervous-system disorders, and

acute toxicity (Fuhrer and others, 1999). Recent studies have shown that low concentrations of herbicides may disrupt endocrine and hormonal activity in certain amphibians and other aquatic species (Hayes and others, 2002). It is also possible for some pesticides to bioaccumulate in fish and other organisms, and to move along the food chain and thus disturb the ecosystem at a larger scale (Nowell and others, 1999).

Purpose and Scope

Hydrologic and geochemical factors affecting the transport of pesticides and nutrient compounds to two streams in different environmental settings on the Delmarva Peninsula are described in this report. Major-ion and nutrient concentrations in samples collected from the nontidal upper Pocomoke River and Chesterville Branch in eastern Maryland (fig. 1) were analyzed to identify major factors affecting the variability of water chemistry in each stream. Stream chemistry was also compared to the known chemistry of ground water in upstream aquifers to determine the dominant sources of flow to each stream in different seasons and under different flow conditions. Periods of significant surface runoff were determined from streamflow records and concentrations of suspended sediment and relatively insoluble compounds. Concentrations of selected herbicides, herbicide metabolites, and nutrient compounds in these streams were examined to identify natural factors affecting their transport through watersheds in different environmental settings on the Peninsula. Implications of these natural hydrologic and geochemical factors for agricultural and other land-management practices are also discussed.

Analyses presented in this report are based largely on data collected from the mid–1990s through 2001. Specific conductance, pH, and concentrations of dissolved oxygen, silica, calcium, magnesium, sodium, potassium, chloride, sulfate, bicarbonate, iron, and manganese (hereafter collectively referred to as "major ions") were measured along with suspended sediment and selected total and dissolved nitrogen and phosphorus species in samples collected at one site above the head of tide between 1996 and 2001 in Chesterville Branch and 1999 and 2001 in the upper Pocomoke River in eastern Maryland. Pesticide analyses are based on samples collected between 1999 and 2001 from each stream.

Acknowledgments

The Delmarva Peninsula

The Delmarva Peninsula is located within the Coastal Plain Physiographic Province and includes most of the State of Delaware, and parts of Maryland and Virginia east of the Chesapeake Bay (fig. 1). The Peninsula is characterized by flat and gently rolling topography. The drainage network includes a series of streams that originate in the central upland and become tidal within 16 km (kilometers) downstream (Shedlock and others, 1999). The largest nontidal watershed is less than 300 km^2 (square kilometers), and most watersheds are less than 26 km^2 in area. Land use on the Peninsula is predominantly rural; only about 7 percent of the land is urbanized (Denver and others, 2004). About half (48 percent) of the Peninsula is used for agriculture; much of the agricultural land is used to grow corn and soybeans for poultry feed. More than 600 million broiler chickens were produced on the Peninsula in 2000 (Garbarino and others, 2003).

The Delmarva Peninsula is underlain by a wedge of unconsolidated sediments that includes a series of confined aquifers and associated confining beds overlain by an extensive surficial aquifer that is unconfined over most of the Peninsula. The surficial aquifer is an important source of water supply, recharge to underlying confined aquifers, and base flow to streams. It is composed mostly of quartz and other minerals that are generally resistant to weathering (Cushing and others, 1973). The surficial aquifer is generally sandy at the surface in the central part of the Peninsula where it is composed mostly of fluvial and marginal marine sediments, and finer grained near the coast in areas dominated by tidal marsh and wetland sediments.

Patterns in sedimentation and geomorphology on the Delmarva Peninsula have resulted in several different hydrogeologic settings. These settings have been delineated on the basis of geomorphology and the thickness and texture of surficial sediments and underlying confining beds at several different scales by different methods (Shedlock and others, 1993; Bachman and others, 1998; Ator and others, *in press*). The general hydrogeologic conditions described by each method are similar, and range from well-drained settings with incised stream channels and surficial aquifers as thick as tens of meters, to poorly drained settings with flat topography and ditched stream channels overlying surficial sands. In the northern and central part of the Peninsula, stream channels may incise through the surficial aquifer into underlying confined aquifers and confining beds. On the flanks of the Peninsula, the surficial aquifer is thin or absent, topography is very flat, and stream channels and ditches are commonly tidal.

The typically sandy unconfined surficial aquifer on the Delmarva Peninsula is vulnerable to anthropogenic contamination from a variety of sources, including septic-system discharges and applications of fertilizer, pesticides, lime, and manure. Hamilton and others (1993) found concentrations of nitrate[1] above 3 mg/L (milligrams per liter) in unconfined ground water from most areas of the Peninsula; the highest concentrations were beneath agricultural areas. Nitrate concentrations have increased since the late 1980s at moderate depths in well-oxygenated parts of the surficial aquifer, although concentrations remain very low in poorly oxygenated ground water (Denver and others, 2004). Very low concentrations of herbicides (below Federal drinking-water standards), primarily those associated with corn and soybean crops, have been measured in shallow ground water near agricultural fields, as well as in nontidal streams during base-flow conditions (Koterba and others, 1993; Denver and others, 2004).

The Upper Pocomoke River

The upper Pocomoke River drains a watershed of approximately 155 km^2 above the USGS stream gage near Willards, Maryland (fig. 2). Elevations in the watershed range from about 8 to 24 m (meters) above sea level, and the topography is generally flat with occasional sand dunes. Soils are generally moderately permeable but poorly drained (U.S. Department of Agriculture, 1970) and the water table is shallow (generally less than 2 m below land surface during wet periods). Tributaries are low gradient with sluggish flow and are typically channelized. Ditches to promote drainage of agricultural fields are common; the Pocomoke River Watershed (including areas downstream of Willards, Maryland) contains an estimated 1,930 km of artificial ditching (Bricker and others, 2003).

Land use in the upper Pocomoke River Watershed is 45 percent agricultural with interspersed forest and swamps (Vogelmann and others, 1998). Corn, soybeans, and small grains are the predominant crops, and poultry farms are located throughout the watershed. In 1997, more than 320 million broiler chickens were produced in Sussex County, Delaware and Wicomico and Worcester Counties, Maryland (the three counties in the watershed) (U.S. Department of Agriculture, 1999). Manure generated from the intensive poultry production is typically applied to nearby agricultural fields; nutrient application rates in the area are among the highest in the Chesapeake Bay Watershed (Brakebill and Preston, 1999). Recent estimates of annual nitrogen and phosphorus applications in the form of manure for parts of the Pocomoke River Watershed are greater than 6 million pounds for nitrogen and 1.5 million pounds for phosphorus (Brakebill and Preston, 1999). An additional

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[1] Concentrations of nitrogen species are presented in this report as equivalent concentrations of elemental nitrogen. Nitrate concentrations also include any measurable nitrite.
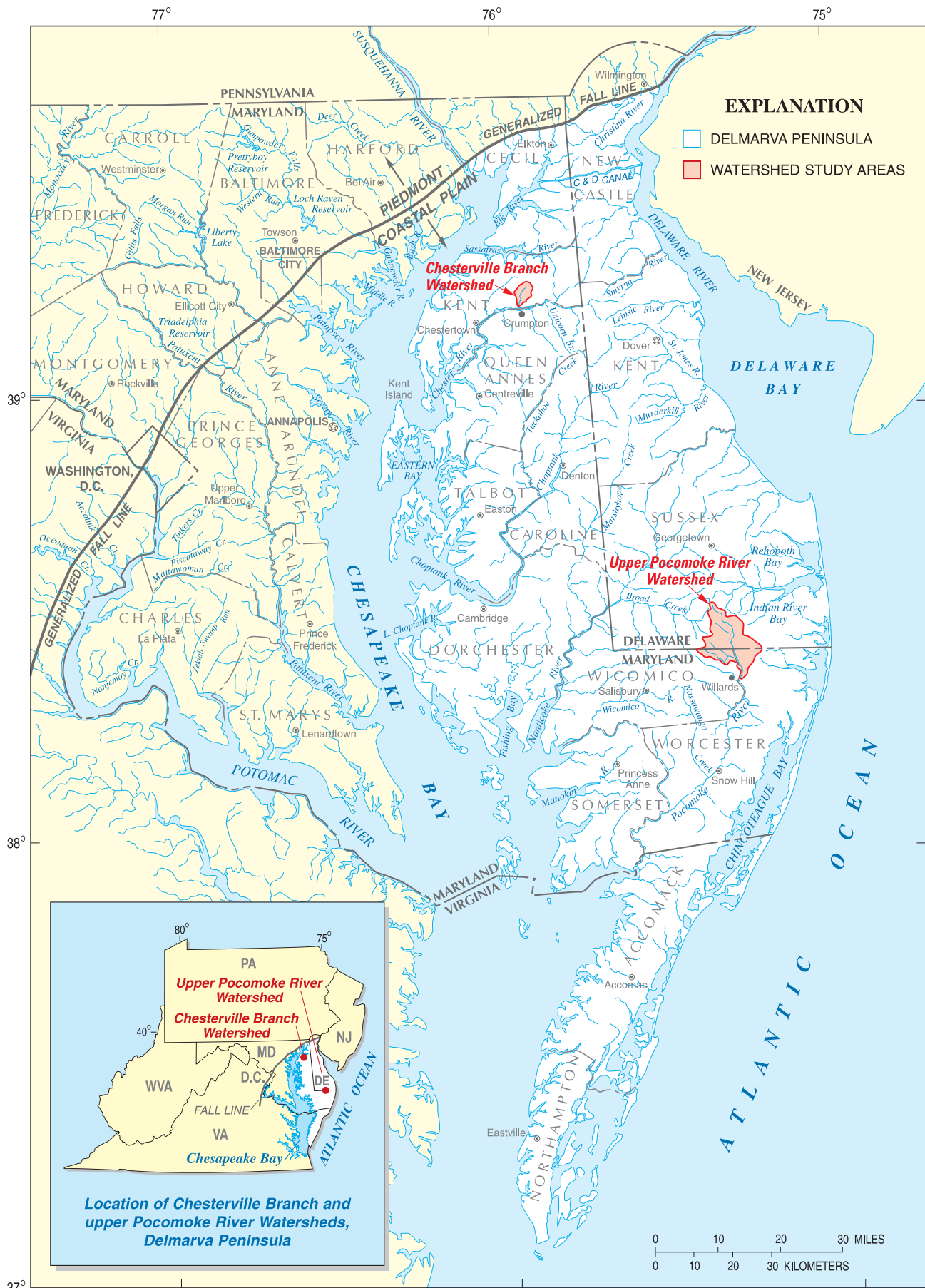
Figure 1. Location of Delmarva Peninsula, and Chesterville Branch and upper Pocomoke River Watersheds.

estimated 2 million pounds of nitrogen and 1.5 million pounds of phosphorus are applied annually in the form of commercial fertilizers. The most commonly used agricultural pesticides in Wicomico and Worcester Counties (which contain the Maryland part of the upper Pocomoke River Watershed) include alachlor, atrazine, glyphosate, metolachlor, oxyfluorfen, and simazine (Maryland Department of Agriculture, 1999).

The surficial aquifer underlying the upper Pocomoke River Watershed is complex and heterogeneous (fig. 3) (Owens and Denny, 1978, 1979; Ramsey and Schenck, 1990; Andres and Howard, 2000, 2002). It includes the Beaverdam Sand (mostly sand with thin beds of gravel at its base), overlain by 3 to 6 m of discontinuous clay, silt, and some peat of the Walston Silt and Omar Formation, which form confining units where present. These deposits are in turn overlain by 3 to 6 m of the Parsonsburg Sand, an eolian sandy unit interspersed with clay and silt. Organic-rich loamy sand and silt are present in shallow parts of the Parsonsburg Sand (Owens and Denny, 1978, 1979). Surficial sediments in the primarily swampy northeastern part of the watershed include fine sand, silt, clayey silt, and organic matter of the Cypress Swamp Formation (Andres and Howard, 2000).

The aquifer configuration and the extensive network of drainage ditches result in complex patterns of ground-water flow that change seasonally as the water table rises and falls. Flow paths are generally highly localized and short in the Parsonsburg Sand, and longer in the Beaverdam Sand (Patrick Phillips, U.S. Geological Survey, written commun., 1991; Hamilton and others, 1993). When the water table is high, short flow paths to drainage ditches comprise an important part of streamflow. During drier periods, when the ditches are dry or flow is stagnant, longer flow paths in the Parsonsburg Sand and the Beaverdam Sand maintain base flow in the Pocomoke River and its major tributaries. Ground water is generally 35 to 50 years old in the Beaverdam Sand, but less than 15 years old in the Parsonsburg Sand (Dunkle and others, 1993).

Chesterville Branch

Chesterville Branch drains an approximately 15-km^2 watershed and flows directly into the tidal part of the Chester River (fig. 4). Elevations range from less than 6 to greater than 27 m above sea level, with broad, gently sloped uplands and deeply incised stream channels. Soils are typically moderately well-drained to well-drained on the uplands, with moderately poorly drained soils in narrow flood plains. The water table ranges from near the land surface in the stream channels to about 6 m below land surface on upland watershed divides.

Land use in the Chesterville Branch Watershed is about 93 percent agricultural, of which about 21 percent is cultivation of plant nursery stock. The remaining agricultural land is used for corn, soybean, and small grain production. Forested areas comprise the remaining 7 percent and occur primarily in narrow bands in riparian zones (Vogelmann and others, 1998). Although nutrient applications to agricultural

areas of the Chesterville Branch Watershed are unknown, application rates for the larger Chester River Watershed are generally much lower than for parts of the Pocomoke River Watershed. Estimated annual applications of nitrogen and phosphorus from manure are less than 0.5 and 0.2 million pounds (respectively), and estimated applications of commercial fertilizer total 0.5 to 2 million pounds of nitrogen, and 0.2 to 0.5 million pounds of phosphorus (Brakebill and Preston, 1999). The pesticides most commonly used for agriculture in Kent County, Maryland (which includes the Chesterville Branch Watershed) include acetochlor, atrazine, glyphosate, metolachlor, and simazine (Maryland Department of Agriculture, 1999).

The surficial aquifer underlying the Chesterville Branch Watershed includes deeply weathered sands and gravels of the Pensauken Formation (the Columbia aquifer) and the underlying weathered glauconitic sands of the upper Aquia Formation (the Aquia aquifer) (fig. 5) (Hamilton and others, 1993; Bachman and others, 2002). The surficial aquifer may also contain fine to medium marine sand of the Old Church Formation (fig. 5) (Hansen, 1992), although these sediments are typically very thin within the Chesterville Branch Watershed (Bachman and others, 2002). The lower part of the Aquia Formation contains a low permeability silt-clay that forms a 6- to 10-m confining layer (Bachman and others, 2002). The uppermost confined aquifer beneath the confining layer is the Hornerstown aquifer, which includes glauconitic sand in the upper part of the Hornerstown Formation (Hansen, 1992) (also known as the Hornerstown Sand, Owens and Minard, 1962). The surficial aquifer ranges in thickness from about 15 m at the northern edge of the watershed to about 25 m near Crumpton, Maryland (Bachman and others, 2002).

The surficial aquifer is unconfined throughout the watershed. Ground water in the aquifer ranges in age from several years near the water-table surface to greater than 30 years near the base of the aquifer in ground-water discharge areas (Dunkle and others, 1993). Chesterville Branch is incised into the surficial aquifer and perennial throughout the watershed. Water in the confined Hornerstown aquifer is consistently greater than 40 years old (Bachman and others, 2002).

Data Collection and Analysis

Water samples were collected to characterize the chemical composition of selected streams on the Delmarva Peninsula and to describe the variability of stream chemistry during different seasons and flow conditions. Data analyses were selected to identify major factors affecting the variability of water chemistry in each stream, including major transport processes in each watershed, and dominant sources of flow to each stream in different seasons and under different flow conditions.
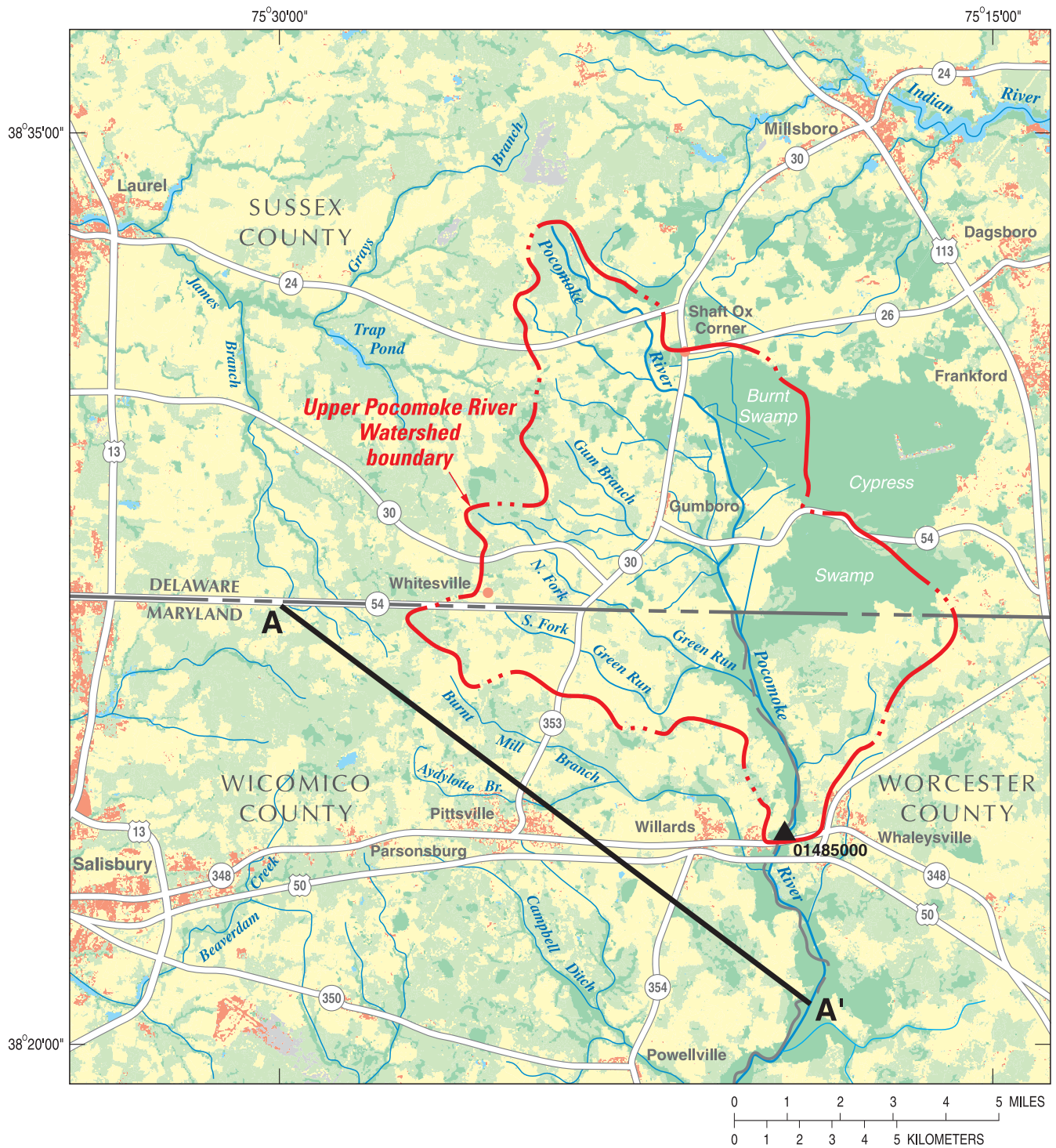
Figure 2. Land use and land cover in the upper Pocomoke River Watershed and vicinity and line of section A-A'.
(Refer to figure 3 for hydrogeologic cross section.) (Land cover from U.S. Geological Survey National Land Cover Database [NLCD].) (Vogelmann and others, 1998)

A   **A'**
(Northwest)   *(Southeast)*

FEET   METERS

100   30
75   20
50
25   10

Route 54   Route 353   Aydlotte Branch   Route 348   Route 50   Route 354   Pocomoke River

Land surface

WALSTON   SILT

PARSONSBURG SAND

Sea Level

OMAR FORMATION   Sea Level

ALLUVIUM

-25   -10
BEAVERDAM SAND
-50   -20

VERTICAL SCALE GREATLY EXAGGERATED

0   1   2   3 MILES
0   1   2   3 KILOMETERS

EXPLANATION

AQUIFER   —— GEOLOGIC CONTACT

CONFINING LAYER

Figure 3. Hydrogeologic cross section A-A' in the vicinity of the upper Pocomoke River Watershed. *(Line of section shown in figure 2; modified from Owens and Denny, 1979.)*

Data Collection

Water-quality data were collected periodically by the USGS from the late 1990s through September 2001 from the upper Pocomoke River near Willards, Maryland, and Chesterville Branch near Crumpton, Maryland. One sampling location was selected on each stream near an existing stream gage above the head of tide. The frequency of sampling at each stream varied slightly over time depending on the objectives and design of participating projects and programs. Routine sampling of the upper Pocomoke River began in June 1999 as part of the NAWQA Program. Sampling was conducted approximately monthly until March 2001; subsequent samples were collected twice a month. Relatively intensive sampling of Chesterville Branch for nutrients and (less frequently) suspended sediment and major ions began in July 1996 as part of the River Input Monitoring project, a cooperative effort between the USGS and the State of Maryland to quantify nutrient loads to Chesapeake Bay (Sprague and others, 2000). Samples were typically collected at least monthly; additional samples were collected during selected high-flow events to support calibration of empirical load models (Smith and others, 1997; Yochum, 2000). Additional samples were collected at Chesterville Branch between February 1999 and

September 2001 as part of the NAWQA Program and the Landscape Indicators for Pesticides Study (LIPS), a cooperative effort between the USGS and the U.S. Environmental Protection Agency to develop empirical models predictive of pesticide occurrence in streams (Pitchford and others, 2000). Approximately two samples per month were collected from Chesterville Branch through October 1999 as part of these programs; subsequent sampling was conducted monthly. NAWQA and LIPS samples from both streams were analyzed for selected pesticides and pesticide metabolites, as well as nutrients and major ions.

Stream samples were collected, processed, and analyzed using procedures designed to minimize contamination while ensuring results representative of sampled conditions (Shelton, 1994). Specific conductance, dissolved oxygen, and pH were measured directly in the stream (Wilde and Radtke, 1998). Instantaneous streamflow (discharge) during sample collection was also measured in the stream (Rantz and others, 1982) or noted on existing stream gages at each site (U.S. Geological Survey, 1950–2001). Depth-integrated water samples were collected at equal-width intervals along a cross section of the stream perpendicular to flow and combined into a single composite. Subsamples for analysis of dissolved constituents were passed through a 0.45-µm

Figure 4. Land use and land cover in the Chesterville Branch Watershed and vicinity and line of section B-B'. *(Refer to figure 5 for hydrogeologic cross section.) (Land cover from Kent County Digital Orthophoto Quarter Quadrangle, Maryland Department of Natural Resources, 1996.)*
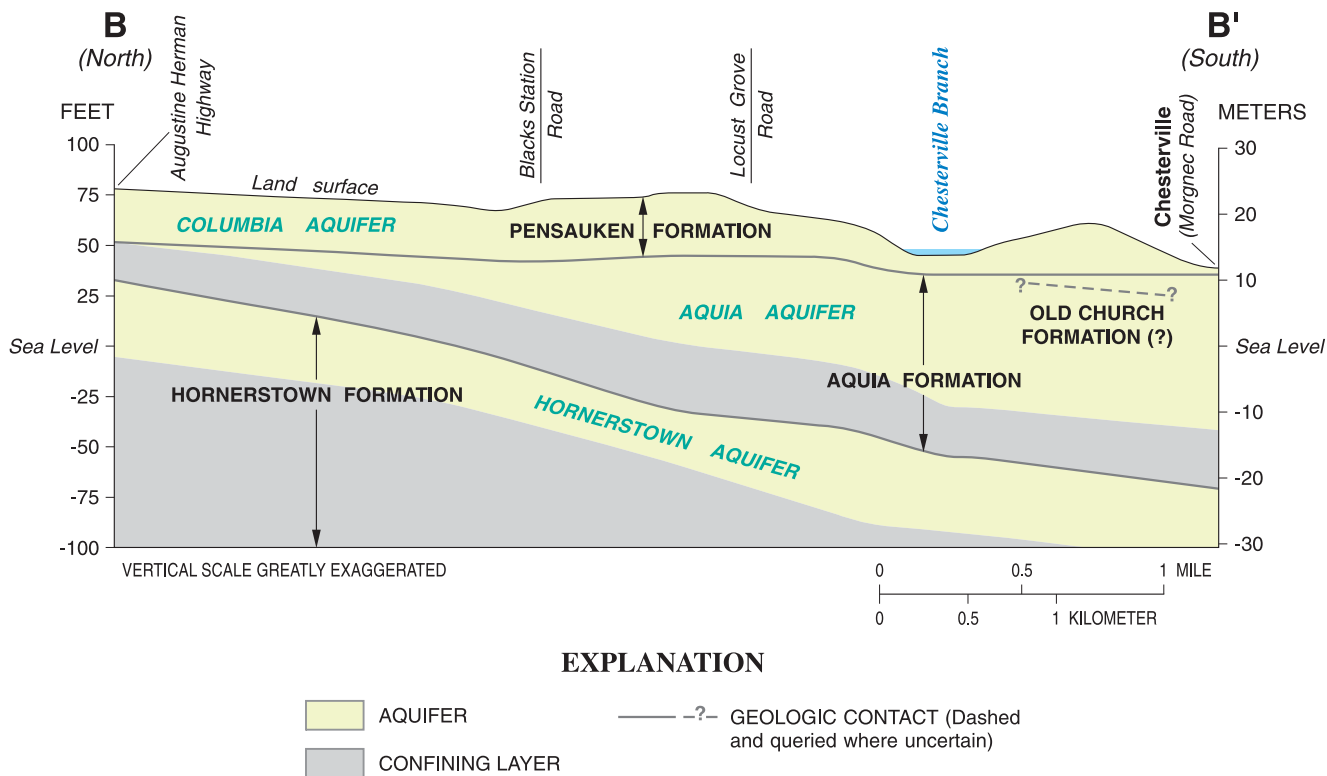
Figure 5. Hydrogeologic cross section B-B' through the Chesterville Branch Watershed and vicinity. *(Line of section shown in figure 4; modified from Bachman and others, 2002.)*

(micrometer) cellulose-nitrate capsule filter (for inorganic analytes) or a 0.7-µm baked glass-fiber filter (for pesticides and metabolites). Subsamples intended for analysis of selected nutrients and cations were preserved with sulfuric acid and nitric acid, respectively. Bicarbonate concentrations were computed on the basis of alkalinity titrations conducted in the field (Wilde and Radtke, 1998). Suspended sediment concentrations were measured as described in Sholar and Shreve (1998). All other subsamples were chilled to 4 degrees Celsius and shipped overnight to the USGS Organic Geochemistry Research Laboratory in Lawrence, Kansas (for analyses of selected pesticide metabolites; Zimmerman and others, 2000; Lee and others, 2001) or the USGS National Water-Quality Laboratory in Denver, Colorado (for all other analyses; Zaugg and others, 1995). A mild detergent solution and deionized water were used to clean all reusable sampling equipment between sites (Wilde and others, 1998).

Field blanks, split-replicates, and (for pesticides) field spikes (Mueller and others, 1997) were collected and analyzed to estimate bias and variability in reported analyte concentrations (table 1). Analyses of field blanks suggest that reported concentrations contain minimal bias due to contamination during sample collection, processing, or shipment.

Among pesticides, only metolachlor was detected in field blanks, and concentrations were invariably less than the laboratory reporting level of 0.013 µg/L (micrograms per liter). Concentrations of major ions and nutrients in field blanks were similarly insignificant when compared to routine laboratory reporting levels. Median spike recoveries for pesticides were generally near 100 percent; reported recoveries for only 8 of 47 compounds were less than 70 percent or greater than 130 percent. Reported concentrations for these compounds may substantially differ from true environmental concentrations. Sample matrix effects or other reasons for poor analytical recovery are well documented for some of these compounds (Zaugg and others, 1995). Variability in sampling and analytical results estimated on the basis of replicate analyses is also generally minimal, particularly for major ions and nutrients. Estimated variability in reported pesticide concentrations is typically greater (often more than 10 percent), although these estimates were generated from only two to four analyses (table 1). A review of a much larger set of replicate samples collected from around the United States as part of the NAWQA Program (Martin, 2002) may be more indicative of the reliability of reported pesticide concentrations. Further information on variability in reported concentrations of pesticides and selected metabo-

Table 1. *Estimated uncertainty in reported concentrations of major ions, suspended sediment, nutrients, and pesticides in Chesterville Branch near Crumpton, Maryland (1996–2001) and the upper Pocomoke River near Willards, Maryland (1999–2001)*

[B_N, number of field blanks; B_{ND}, number of blanks in which compound was detected; B_{MAX}, maximum reported concentration in field blanks in which compound was detected; S_N, number of field spikes; S_{MED}, median recovery from field spikes; %, percent; S_{IQR}, interquartile range of recovery from field spikes; R_N, number of replicate sets; R_{NAGREE}, number of replicate sets within which compound was consistently detected or not detected; R_{UNC}, estimated uncertainty in reported concentrations; NC, not computed because no replicate sets had consistent detected concentrations; N, nitrogen; ESA, ethanesulfonic acid; OA, oxanilic acid; MET, metabolite]

Compound or Ion	Contamination Bias			Sampling and Analytical Uncertainty					
	B_N	B_{ND}	B_{MAX}[1]	S_N	S_{MED} (%)	S_{IQR} (%)	R_N	R_{NAGREE}	R_{UNC}[2] (%)
Calcium	7	4	0.03	0	-	-	9	9	0.3
Magnesium	7	0	-	0	-	-	9	9	0.1
Sodium	7	2	0.05	0	-	-	9	9	0.5
Potassium	7	0	-	0	-	-	9	9	0.8
Silica	11	3	0.14	0	-	-	13	13	0.6
Sulfate	7	0	-	0	-	-	9	9	0.4
Chloride	7	0	-	0	-	-	9	9	1.2
Suspended Sediment	2	0	-	0	-	-	13	13	5.7
Iron	7	1	6.6	0	-	-	9	9	5.4
Manganese	11	0	-	0	-	-	10	10	0.3
Ammonia plus Organic N	13	2	0.06	0	-	-	17	17	2.6
Ammonia plus Organic N, total	13	3	0.16	0	-	-	17	17	8.1
Nitrate	13	3	0.03	0	-	-	17	17	1.2
Phosphorus	13	3	0.002	0	-	-	17	17	8.6
Phosphorus, total	13	3	0.001	0	-	-	17	15	1.6
Acetochlor	5	0	-	7	113	10	4	4	6.3
Acetochlor ESA (MET)	2	0	-	0	-	-	2	2	34.6
Acetochlor OA (MET)	2	0	-	0	-	-	2	2	17.7
Alachlor	5	0	-	7	119	13	4	4	2.4
Alachlor ESA (MET)	2	0	-	0	-	-	2	2	4.8
Alachlor OA (MET)	2	0	-	0	-	-	2	2	5.5
2, 6-diethylaniline (MET)	5	0	-	7	90	13	4	4	NC
Alpha BHC	5	0	-	7	92	29	4	4	NC
Atrazine	5	0	-	7	103	8	4	4	1.3
Desethylatrazine (MET)	5	0	-	7	73	22	4	4	1.7
Benfluralin	5	0	-	7	78	29	4	4	NC
Butylate	5	0	-	7	103	8	4	4	NC
Carbaryl	5	0	-	7	169	193	4	4	NC
Carbofuran	5	0	-	7	178	203	4	4	21.1
Chlorpyrifos	5	0	-	7	100	21	4	4	6.3
Cyanazine	5	0	-	7	126	23	4	4	NC
DCPA	5	0	-	7	101	15	4	4	NC
Diazinon	5	0	-	7	104	21	4	4	NC
Dieldrin	5	0	-	7	108	32	4	4	NC
Disulfoton	5	0	-	7	62	35	4	4	NC
EPTC	5	0	-	7	105	6	4	4	NC
Ethalfluralin	5	0	-	7	90	36	4	4	NC
Ethoprop	5	0	-	7	107	18	4	4	NC
Fonofos	5	0	-	7	104	26	4	4	NC

Table 1. *Estimated uncertainty in reported concentrations of major ions, suspended sediment, nutrients, and pesticides in Chesterville Branch near Crumpton, Maryland (1996–2001) and the upper Pocomoke River near Willards, Maryland (1999–2001)—Continued*

Compound or Ion	Contamination Bias			Sampling and Analytical Uncertainty					
	B_N	B_{ND}	B_{MAX}[1]	S_N	S_{MED} (%)	S_{IQR} (%)	R_N	R_{NAGREE}	R_{UNC}[2] (%)
Lindane	5	0	-	7	97	26	4	4	NC
Linuron	5	0	-	7	135	45	4	4	NC
Malathion	5	0	-	7	127	17	4	4	NC
Methyl-azinphos (MET)	5	0	-	7	201	40	4	4	NC
Metolachlor	5	3	0.011	7	114	22	4	4	1.1
Metolachlor ESA (MET)	2	0	-	0	-	-	2	2	6.4
Metolachlor OA (MET)	2	0	-	0	-	-	2	2	7.3
Metribuzin	5	0	-	7	108	22	4	4	NC
Molinate	5	0	-	7	108	11	4	4	NC
Napropamide	5	0	-	7	121	23	4	4	NC
p, p'-DDE (MET)	5	0	-	7	59	13	4	4	NC
Parathion	5	0	-	7	108	46	4	4	NC
Methyl-parathion (MET)	5	0	-	7	102	37	4	4	NC
Pebulate	5	0	-	7	105	6	4	4	NC
Pendimethalin	5	0	-	7	107	25	4	4	NC
Permethrin	5	0	-	7	53	12	4	4	NC
Phorate	5	0	-	7	79	28	4	4	NC
Prometon	5	0	-	7	97	10	4	4	1.5
Pronamide	5	0	-	7	105	16	4	4	9.6
Propachlor	5	0	-	7	128	13	4	4	NC
Propanil	5	0	-	7	112	18	4	4	NC
Propargite	5	0	-	7	127	20	4	4	NC
Simazine	5	0	-	7	109	28	4	4	0.9
Tebuthiuron	5	0	-	7	139	23	4	4	NC
Terbacil	5	0	-	7	125	52	4	4	NC
Terbufos	5	0	-	7	84	21	4	4	NC
Thiobencarb	5	0	-	7	106	12	4	4	NC
Triallate	5	0	-	7	104	7	4	4	NC
Trifluralin	5	0	-	7	84	31	4	4	NC

[1] In milligrams per liter or (for iron and metolachlor) micrograms per liter.

[2] Estimated uncertainty is the median of the relative standard deviation of reported concentrations for replicate sets in which the compound was detected in all replicates. The relative standard deviation is the standard deviation divided by the mean.

lites is available in Zaugg and others (1995), Zimmerman and others (2000), and Lee and others (2001).

Ancillary data were compiled to support the analysis and interpretation of observed water chemistry in Chesterville Branch and the upper Pocomoke River. Ground-water chemistry in surficial and near-surface aquifers within or near each watershed has been measured at various times since the late 1980s (see below). Base-flow chemistry in selected tributaries of each stream was measured during late winter and spring 2000 as part of the LIPS project (Pitchford and others, 2000).

Data Analysis

Exploratory and nonparametric data-analysis techniques were selected to identify significant sources of water to Chesterville Branch and the upper Pocomoke River during different seasons and under different flow conditions, and to relate those sources to observed pesticide and nutrient concentrations. All statistical tests were evaluated at the 95-percent confidence level (α=0.05). Correlation among continuous variables was evaluated through the use of scatter plots and correlation (Spearman's rho) matrices (Helsel and Hirsch, 1992; Conover, 1999). Rank-sum tests (large-sample approximation with correction for ties; Conover, 1999) were used to compare water quality in each stream during different seasons; samples were assigned to relatively "wet" (December through May) or "dry" (June through November) seasons on the basis of long-term streamflow records (U.S. Geological Survey, 1950–2001). Rank-transform analysis of variance (ANOVA) tests and rank-sum tests were also used to compare pesticide and metabolite concentrations within each stream. Data were censored to a common level for each compound and censored data were set to zero before ranks were computed for correlation, rank-sum, or ANOVA tests (Helsel and Hirsch, 1992). Trilinear diagrams (Piper, 1944) were used to compare stream chemistry during different seasons to the chemistry of tributaries during late winter and spring base flow, and to that of ground water in different aquifers in the contributing watersheds.

Principal-components analysis (PCA) (Hamilton, 1992; Helsel and Hirsch, 1992) was used to identify underlying patterns in the concentrations of major ions and nutrients in each stream. Concentrations of different major ions and nutrient species are typically well correlated with each other and thus good candidates for PCA. Data were censored to a common level, and rare censored values were set to zero to separate them from values detected at the reporting level. Concentrations were ranked prior to analysis. PCA has been previously used to interpret stream chemistry in the Potomac River Watershed (Miller and others, 1997) and the Chesapeake Bay Watershed (Liu and others, 2000).

Available historical streamflow data (U.S. Geological Survey, 1950–2001) were used to estimate long-term average relative contributions of ground-water discharge and surface runoff to the upper Pocomoke River and Chesterville Branch. The proportion of base flow contributing to mean daily streamflow for each day in each stream was estimated on the basis of the rise and recession of streamflow in

response to precipitation. The estimates were computed using the HYSEP computer program with the local-minimum method (Sloto and Crouse, 1996). Estimates computed using such techniques may be questionable for short time periods, but may be useful for comparing hydrologic conditions among similar watersheds.

Water Chemistry in the Upper Pocomoke River and Chesterville Branch Watersheds

The chemistry of water in the upper Pocomoke River and Chesterville Branch reflects the predominance of ground-water discharge from well-weathered siliciclastic surficial sediments and agriculture in their contributing watersheds. Concentrations and trends in stream chemistry are related to natural aquifer conditions and agricultural practices that affect ground-water chemistry in the contributing watersheds. Discussion of the water chemistry in the upper Pocomoke River and Chesterville Branch during the period of this study (1996–2001) begins with a review of previous work on ground-water chemistry in each watershed, including possible chemical changes that may occur as ground water discharges to each stream and its tributaries.

Hydrologic studies began in both watersheds as part of the NAWQA program in 1987 (Hamilton and others, 1993). In the upper Pocomoke River Watershed, a local-scale study area was established near an existing USGS stream gage on the Pocomoke River near Willards, Maryland. A similar study was established including the Chesterville Branch and adjacent Morgan Creek Watersheds near Locust Grove, Maryland. Boreholes were drilled within each watershed to provide information on aquifer characteristics, and wells were installed to allow for collection of ground-water samples for chemical analyses. Flow measurements were made and stream samples were also collected periodically. These data were analyzed in conjunction with soil, geologic, and land-use data to describe the effects of agriculture on ground- and surface-water quality in these watersheds.

Research has continued within and near both watersheds as part of NAWQA and other programs of the USGS (Dunkle and others, 1993; Reilly and others, 1994; Böhlke and Denver, 1995; Phillips and Donnelly, 2003), the U.S. Environmental Protection Agency (Hantush and Marino, 2001; Bachman and others, 2002), and State and local agencies (Sprague and others, 2000). These studies have contributed to the understanding of the processes controlling the movement of water and chemicals in these watersheds through the interpretation of geologic data, isotopic tracer studies, and dating and modeling of ground-water flow and chemistry.

Ground Water in the Upper Pocomoke River Watershed

Shallow ground-water chemistry in the upper Pocomoke River Watershed is affected by geologic conditions and agricultural applications of fertilizer, lime, and manure. The natural chemistry of ground water in the Parsonsburg Sand is

a calcium-sodium-sulfate type (Hamilton and others, 1993). Concentrations of silica and other ions from dissolution of silicate minerals are relatively low because of the short residence time of water in the Parsonsburg Sand. Natural sources of organic matter in sediments are probably a major source of sulfate in ground water (Puckett, 1987). Organic matter and fine-grained sediments in the Parsonsburg Sand result in variable oxidation conditions in shallow ground water, which affect the transport and transformation of nutrients.

Agricultural applications of inorganic fertilizer, lime, and poultry manure affect water chemistry in the Parsonsburg Sand. Nitrate concentrations range from less than 1 mg/L to greater than 60 mg/L in ground water (Hamilton and others, 1993; Phillips and Donnelly, 2003). The highest concentrations are associated with samples from shallow wells in areas of manure application. Many of the samples with the lowest concentrations contain excess (nonatmospheric) dissolved nitrogen gas, which indicates possible nitrate removal through denitrification. Concentrations of phosphorus and dissolved ammonium and organic nitrogen are highest in ground water in anoxic parts of the Parsonsburg Sand. Chloride, calcium, and magnesium from agricultural sources also contribute to the major-ion chemistry of shallow ground water (Patrick Phillips, U.S. Geological Survey, written commun., 1991).

Pesticides commonly used on corn and soybean crops and their metabolites are present at low levels in ground water in the Parsonsburg Sand. Atrazine, acetochlor, alachlor, metolachlor, simazine, prometon, and carbofuran have occasionally been detected, usually at concentrations below 0.1 µg/L (U.S. Geological Survey, 1950–2001). Selected pesticide metabolites have also been detected, often at concentrations higher than those of corresponding parent compounds.

Ground water in confined parts of the Beaverdam Sand is generally anoxic, with high concentrations of silica, bicarbonate, and iron (Patrick Phillips, U.S. Geological Survey, written commun., 1991; Hamilton and others, 1993). The typically low concentrations of chloride, nitrate, and nitrogen gas indicate that ground water has been largely unaffected by agricultural chemicals. Concentrations of orthophosphate and ammonium are generally higher in the Beaverdam Sand than in some parts of the Parsonsburg Sand (U.S. Geological Survey, 1950–2001), and are likely derived from natural sources in the organic sediments of the overlying confining layer. Some parts of the Beaverdam Sand are hydraulically connected with the overlying Parsonsburg Sand where the confining bed is thin or absent (fig. 3). In these areas, ground-water chemistry is a mixture of the two water types (Patrick Phillips, U.S. Geological Survey, written commun., 1991). Pesticides and other agricultural chemicals have not typically been detected in water from the Beaverdam Sand, except in areas in hydraulic connection with the Parsonsburg Sand (Hamilton and others, 1993; U.S. Geological Survey, 1950–2001).

Surface-water chemistry in the upper Pocomoke River Watershed is affected to varying degrees by discharge of ground water from the Parsonsburg and Beaverdam Sands. In general, as stream order increases from the ditched headwaters to the main river channel, increasing concentrations of sodium and silica suggest an increase in the proportion of flow coming from the deeper, older flow paths in the Beaverdam Sand (Patrick Phillips, U.S. Geological Survey, written commun., 1991). Conversely, nitrate concentrations and concentrations of other chemicals from agricultural sources are generally highest in the headwater ditches, and decrease downstream.

Ground Water in the Chesterville Branch Watershed

Water chemistry in the surficial aquifer reflects the influence of agriculture in the Chesterville Branch Watershed. Predominant dissolved ions include calcium, magnesium, and nitrate, which are typical of agricultural areas in sandy Coastal Plain sediments on the Delmarva Peninsula (Hamilton and others, 1993). Effects of agricultural activities are apparent in all ground-water samples collected from the surficial aquifer in the watershed, reflecting the fact that fertilizer and lime applications predate the early 1970s, the oldest recharge dates of most surficial ground water (Hamilton and others, 1993). Ground water in the surficial aquifer is aerobic and nitrate is stable to the base of the aquifer (Hamilton and others, 1993). Concentrations of nitrate are as high as 15 mg/L, with a median near 10 mg/L. There is evidence of denitrification in water from the deepest wells screened near the interface between the surficial aquifer and the confining bed at the base of the Aquia Formation (Böhlke and Denver, 1995). This may be caused by upward discharge of water from the confined Hornerstown aquifer to Chesterville Branch (Bachman and others, 2002).

Pesticides that are commonly used on corn, soybean, and nursery crops and their metabolites have been detected in ground water from the Chesterville Branch Watershed. The most commonly detected compounds are atrazine, simazine, metolachlor and their metabolites. Concentrations of parent compounds are generally below 1 µg/L; metabolites are generally detected at levels that are an order of magnitude or more greater than parent compounds. Several other herbicides and insecticides are less frequently detected. Pesticides are also detected in surface water under base-flow conditions (Shedlock and others, 1999).

In the Chesterville Branch Watershed, concentrations of nitrate and other ions from agricultural sources in ground water generally decrease with depth, along flow paths, and with increasing age. This trend is related to changes in fertilizer application rates since around the 1940s, rather than denitrification (Böhlke and Denver, 1995). Much of the nitrate in ground water is discharged directly to surface water through sandy streambed sediments. Although most of Chesterville Branch has a forested riparian zone (fig. 4), most of the ground water discharging to streams moves along deeper flow paths and bypasses the shallow sediments of the riparian zone where nitrate may be removed from the system. Aerobic ground-water samples have been collected
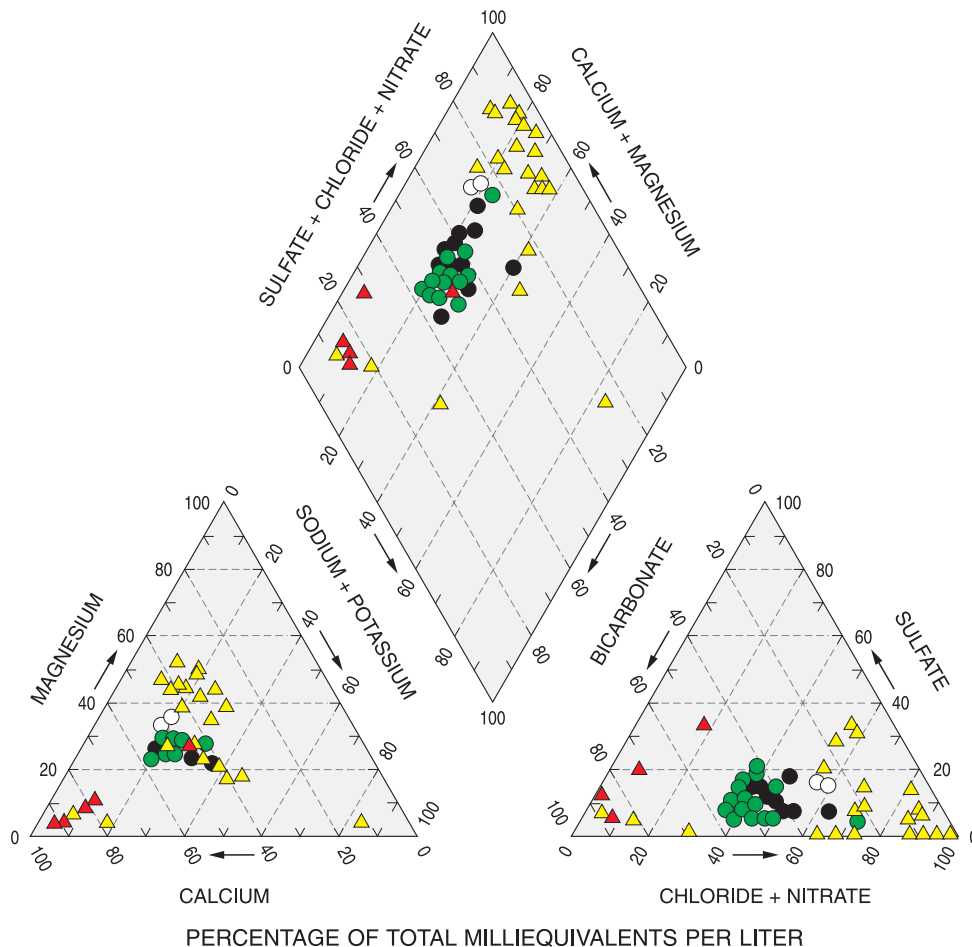
Figure 6. Summary of stream and ground-water chemistry in the Chesterville Branch Watershed.

beneath streambeds in aquifer discharge areas (Böhlke and Denver, 1995).

Concentrations of nitrate and other ions in surface water during base flow are similar to those in ground water. Nitrate concentrations in Chesterville Branch near Crumpton, Maryland, in the early 1990s ranged from about 9 to 10 mg/L during base flow, and decreased during periods of surface runoff (Böhlke and Denver, 1995). Base-flow concentrations of nitrate are highest upstream where younger flow paths with higher concentrations of nitrate discharge, and generally decrease downstream as the proportion of older water from deeper flow paths increases (Böhlke and Denver, 1995). Similar nitrogen isotope ratios in ground water and surface water indicate that the nitrate discharging to Chesterville Branch is relatively unaltered by denitrification (Böhlke and Denver, 1995). Some loss of nitrate is

likely in surface water from biotic uptake and reaction with organic matter.

Stream Chemistry in the Upper Pocomoke River and Chesterville Branch

Water in the upper Pocomoke River and Chesterville Branch is typically dilute and slightly acidic. The median pH and specific conductance measured during sampling from the late 1990s through 2001 in the upper Pocomoke River were 5.9 and 120 μS/cm (microsiemens per centimeter), respectively; median pH and specific conductance in Chesterville Branch were 6.5 and 159 μS/cm, respectively. Both streams are also generally well-oxygenated; measured dissolved oxygen levels exceeded 4 mg/L during every sampling trip to each stream. Aqueous chemistry in Chesterville Branch is generally dominated by dissolved chloride, nitrate,
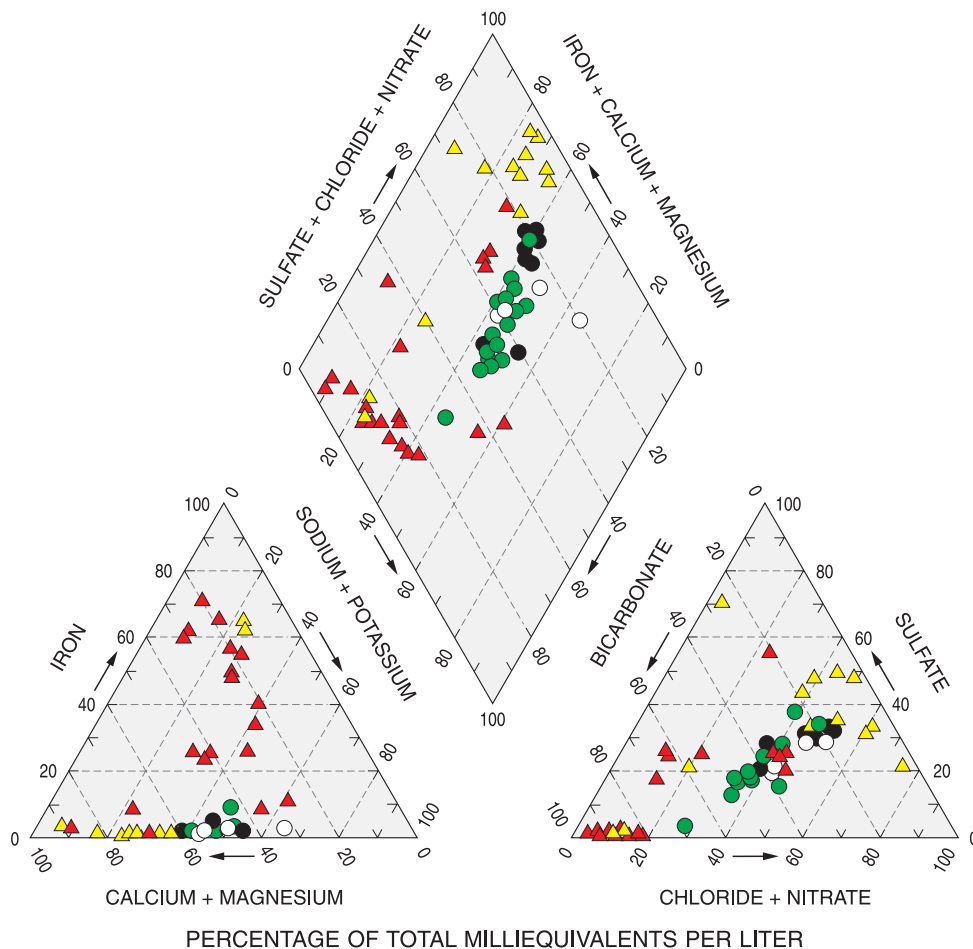
Figure 7. Summary of stream and ground-water chemistry in the upper Pocomoke River Watershed.

bicarbonate, and calcium, with lesser amounts of sodium, potassium, and magnesium (fig. 6). Aqueous chemistry in the upper Pocomoke River is similar, but more variable (fig. 7). Sulfate is a more significant anion in the upper Pocomoke River than in Chesterville Branch, and measured iron concentrations were as high as 2.3 mg/L. The maximum concentration of dissolved iron among samples from Chesterville Branch was 0.3 mg/L.

Nutrients were detectable in nearly every sample collected from both streams (table 2). Nitrate, ammonia plus organic nitrogen, and phosphorus were detectable in all 32 samples collected from the upper Pocomoke River and in over 90 percent of samples collected from Chesterville Branch. Among nitrogen compounds, nitrate typically occurred at higher concentrations than more reduced species

in both streams, although concentrations of ammonia and/or organic nitrogen may be higher during certain seasons or under certain flow conditions. Median nitrate and total phosphorus concentrations in both streams exceeded 0.09 and 0.02 mg/L, respectively (table 2)—the estimated median concentrations in natural streams of the United States (Clark and others, 2000). Most of the phosphorus transport probably occurs in the particulate phase; median total phosphorus concentrations were three to four times higher than those of dissolved phosphorus in both streams. A similar review of median concentrations of total and dissolved ammonia plus organic nitrogen suggests that slightly less than half of the in-stream transport of those species occurs in the particulate phase in both streams (table 2).

Table 2. *Summary of analytical results for samples collected from the upper Pocomoke River (1999–2001) and Chesterville Branch (1996–2001) and analyzed for nutrients or pesticide compounds*

[Compounds or ions detected in at least 50 percent of samples from either stream are shown in **bold**. N, nitrogen; ESA, ethanesulfonic acid; OA, oxanilic acid; MRL, most common minimum reporting level; n, number of samples; Freq, detection frequency in percent; Med, median concentration; Max, maximum concentration; mg/L, milligrams per liter; µg/L, micrograms per liter; <, less than]

Compound or Ion	Units	MRL	Pocomoke River near Willards, Maryland				Chesterville Branch near Crumpton, Maryland			
			n	Freq	Med	Max	n	Freq	Med	Max
Ammonia plus Organic N	mg/L as N	0.2	32	100	0.65	1.84	130	96	0.35	1.63
Ammonia plus Organic N, total	mg/L as N	0.1	32	100	0.81	2.78	129	98	0.54	2.50
Nitrate	mg/L as N	0.05	32	100	1.96	4.95	128	100	5.31	8.57
Phosphorus	mg/L	0.01	32	100	0.03	0.72	130	89	0.02	0.76
Phosphorus, total	mg/L	0.05	32	100	0.09	1.22	129	95	0.08	1.28
Acetochlor	µg/L	0.002	32	34	<0.004	0.073	40	3	<0.005	0.023
Acetochlor ESA	µg/L	0.05	21	95	0.55	1.33	36	3	<0.05	0.34
Acetochlor OA	µg/L	0.05	21	100	0.22	1.18	36	0	<0.05	<0.20
Alachlor	µg/L	0.002	32	75	<0.010	0.014	40	100	0.047	0.482
Alachlor ESA	µg/L	0.05	21	100	0.91	1.38	36	100	2.19	4.65
Alachlor OA	µg/L	0.05	21	95	0.19	0.50	36	100	0.66	4.14
2,6 diethylaniline	µg/L	0.003	32	0	<0.003	<0.003	40	3	<0.003	<0.003
Alpha-BHC	µg/L	0.002	32	0	<0.005	<0.005	40	0	<0.002	<0.005
Atrazine	µg/L	0.007	32	94	0.020	0.541	40	100	0.039	4.10
Desethylatrazine	µg/L	0.006	32	78	0.006	0.219	40	100	0.115	0.215
Benfluralin	µg/L	0.002	32	0	<0.010	<0.010	40	0	<0.002	<0.010
Butylate	µg/L	0.002	32	0	<0.002	<0.002	40	0	<0.002	<0.002
Carbaryl	µg/L	0.003	32	9	<0.041	0.186	40	30	<0.003	0.064
Carbofuran	µg/L	0.02	32	3	<0.020	<0.030	40	40	<0.060	0.103
Chlorpyrifos	µg/L	0.005	32	0	<0.005	<0.005	40	30	<0.004	0.014
Cyanazine	µg/L	0.004	32	3	<0.018	<0.018	40	8	<0.004	<0.018
DCPA	µg/L	0.002	32	9	<0.003	<0.003	40	0	<0.002	<0.003
Diazinon	µg/L	0.002	32	6	<0.005	0.031	40	13	<0.002	0.005
Dieldrin	µg/L	0.001	32	0	<0.005	<0.005	40	0	<0.001	<0.005
Disulfoton	µg/L	0.017	32	0	<0.021	<0.021	40	0	<0.017	<0.021
EPTC	µg/L	0.002	32	3	<0.002	0.010	40	3	<0.002	0.002
Ethalfluralin	µg/L	0.004	32	0	<0.009	<0.009	40	0	<0.004	<0.009
Ethoprop	µg/L	0.003	32	0	<0.005	<0.005	40	0	<0.003	<0.005
Fonofos	µg/L	0.003	32	0	<0.003	<0.003	40	0	<0.003	<0.003

Table 2. *Summary of analytical results for samples collected from the upper Pocomoke River (1999–2001) and Chesterville Branch (1996–2001) and analyzed for nutrients or pesticide compounds—Continued*

| Compound or Ion	Units	MRL	Pocomoke River near Willards, Maryland				Chesterville Branch near Crumpton, Maryland			
			n	Freq	Med	Max	n	Freq	Med	Max
Lindane	µg/L	0.004	32	0	<0.004	<0.007	40	0	<0.004	<0.004
Linuron	µg/L	0.002	32	0	<0.035	<0.035	40	8	<0.002	0.036
Malathion	µg/L	0.005	32	0	<0.027	<0.027	40	5	<0.005	0.034
Methyl-azinphos	µg/L	0.001	32	0	<0.050	<0.050	40	0	<0.001	<0.050
Metolachlor	**µg/L**	**0.013**	**32**	**97**	**0.061**	**0.617**	**40**	**100**	**0.395**	**5.39**
Metolachlor ESA	**µg/L**	**0.05**	**21**	**100**	**5.09**	**8.42**	**36**	**100**	**2.41**	**4.72**
Metolachlor OA	**µg/L**	**0.05**	**21**	**100**	**1.88**	**3.05**	**36**	**100**	**0.79**	**2.36**
Metribuzin	µg/L	0.004	32	6	<0.006	<0.010	40	3	<0.004	0.062
Molinate	µg/L	0.004	32	0	<0.002	<0.005	40	0	<0.004	<0.004
Napropamide	µg/L	0.003	32	0	<0.007	<0.007	40	3	<0.003	0.053
p, p' DDE	µg/L	0.006	32	0	<0.003	<0.006	40	0	<0.006	<0.006
Parathion	µg/L	0.004	32	0	<0.007	<0.007	40	0	<0.004	<0.007
Methyl-parathion	µg/L	0.006	32	0	<0.006	<0.006	40	0	<0.006	<0.006
Pebulate	µg/L	0.004	32	0	<0.002	<0.004	40	0	<0.004	<0.004
Pendimethalin	µg/L	0.004	32	0	<0.010	<0.010	40	10	<0.004	0.018
Permethrin	µg/L	0.005	32	0	<0.006	<0.006	40	0	<0.005	<0.006
Phorate	µg/L	0.002	32	0	<0.011	<0.011	40	0	<0.002	<0.011
Prometon	**µg/L**	**0.018**	**32**	**75**	**<0.015**	**0.065**	**40**	**3**	**<0.018**	**<0.018**
Pronamide	**µg/L**	**0.004**	**32**	**0**	**<0.004**	**<0.004**	**40**	**78**	**0.016**	**0.286**
Propachlor	µg/L	0.007	32	0	<0.010	<0.010	40	0	<0.007	<0.010
Propanil	µg/L	0.004	32	0	<0.011	<0.011	40	0	<0.004	<0.011
Propargite	µg/L	0.013	32	0	<0.023	<0.023	40	0	<0.013	<0.023
Simazine	**µg/L**	**0.011**	**32**	**66**	**<0.011**	**0.213**	**40**	**100**	**0.375**	**5.67**
Tebuthiuron	µg/L	0.01	32	0	<0.016	<0.016	40	0	<0.010	<0.016
Terbacil	µg/L	0.007	32	0	<0.034	<0.034	40	0	<0.007	<0.034
Terbufos	µg/L	0.013	32	0	<0.017	<0.017	40	0	<0.013	<0.017
Thiobencarb	µg/L	0.002	32	0	<0.005	<0.005	40	0	<0.002	<0.005
Triallate	µg/L	0.001	32	0	<0.002	<0.002	40	0	<0.001	<0.002
Trifluralin	µg/L	0.002	32	0	<0.009	<0.009	40	13	<0.002	<0.009
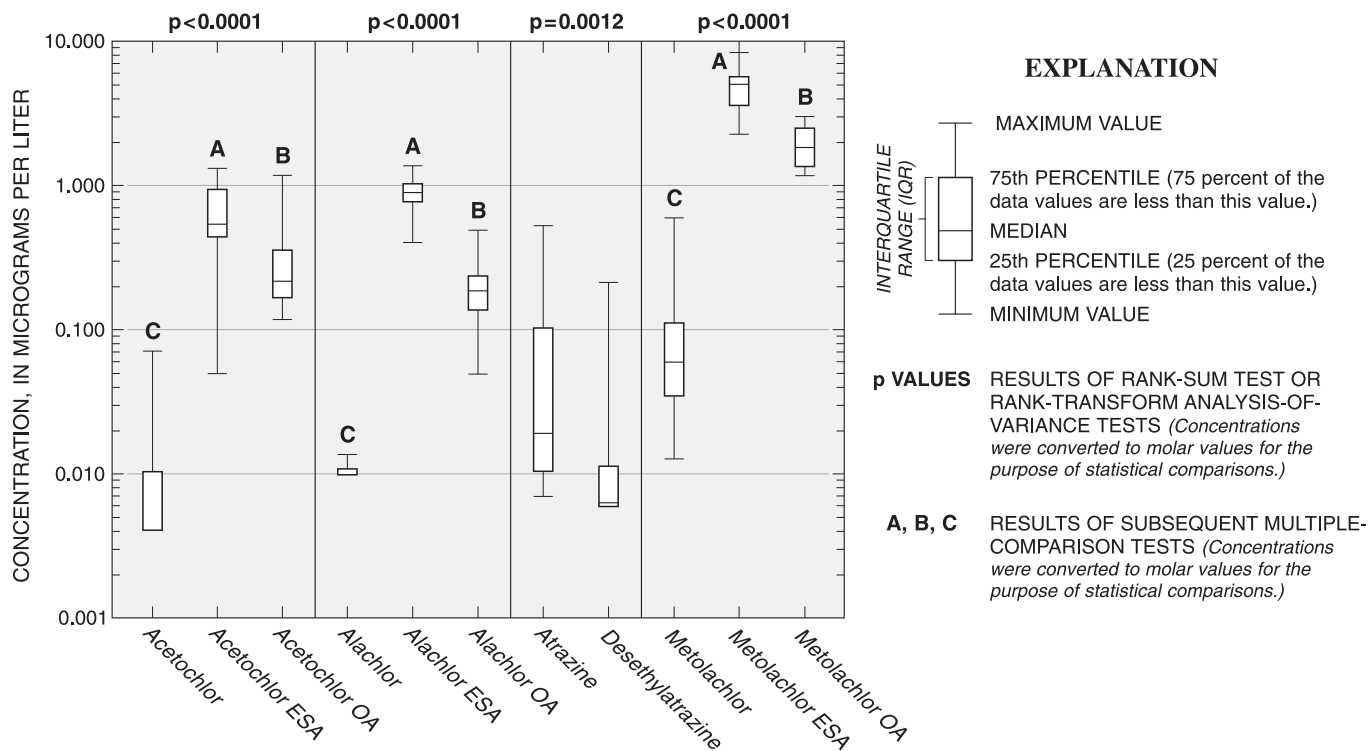
Figure 8. Concentrations of selected pesticides and metabolites in the upper Pocomoke River, 1999-2001. *Concentrations of metabolites of alachlor, acetochlor, and metolachlor typically exceeded concentrations of their parent compounds, although concentrations of atrazine were typically greater than those of desethylatrazine.*

Selected pesticides are present year-round in both the upper Pocomoke River and Chesterville Branch. Although concentrations of parent compounds rarely exceeded 1 µg/L, metabolite concentrations were commonly higher (table 2). Of the 53 pesticides and metabolite compounds for which stream samples were analyzed, 28 were detected in at least one sample from either stream. The most frequently detected pesticide compounds were all herbicides or herbicide metabolites (table 2), as might be expected considering that applications of herbicides generally far exceed those of insecticides or fungicides in agricultural areas (Aspelin, 1997). Every sample collected from Chesterville Branch contained detectable concentrations of two triazine herbicides (atrazine and simazine) and two acetanilide herbicides (alachlor and metolachlor), as well as selected metabolites of each (table 2). Ethanesulfonic (ESA) and oxanilic acid (OA) metabolites of acetanilide herbicides were also detected in every sample from the upper Pocomoke River, although parent compounds were detected slightly less frequently and at lower concentrations than were the metabolites.

The majority of selected pesticides occur in the upper Pocomoke River and Chesterville Branch in the form of metabolites. Acetochlor, alachlor, and metolachlor occurred in the upper Pocomoke River from 1999 through 2001

almost exclusively in the form of metabolites, particularly ESA (fig. 8). Concentrations of metabolites of atrazine, metolachlor, and alachlor far exceeded those of their parent compounds in Chesterville Branch as well (fig. 9). Pesticide transformations through metabolism or other processes typically occur in the soil zone in areas of application. A review of data from across the United States revealed that less than 2 percent of applied alachlor, atrazine, or metolachlor typically reaches stream networks, but little further in-stream losses of these compounds occur (Capel and Larson, 2001; Capel and others, 2001). Atrazine concentrations in the upper Pocomoke River were greater than those of desethylatrazine (fig. 8), which may indicate that soil conditions in the upper Pocomoke River Watershed do not favor the metabolism of atrazine, or favor the formation of hydroxyatrazine or some other metabolite. Although the formation or movement of OA metabolites may be favored over that of ESA metabolites in coarse-grained soils (at least for metolachlor; Phillips and others, 1999), concentrations of metolachlor ESA and alachlor ESA were generally much higher than those of OA metabolites or parent compounds in both the upper Pocomoke River (fig. 8) and Chesterville Branch (fig. 9).
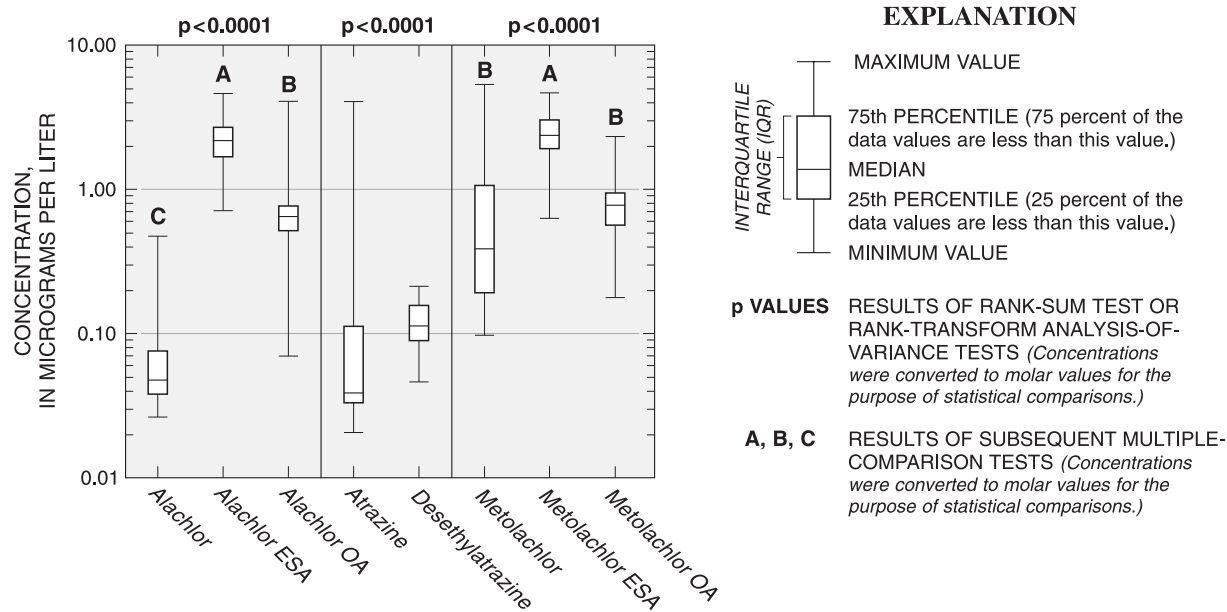
EXPLANATION

	MAXIMUM VALUE
INTERQUARTILE RANGE (IQR)	75th PERCENTILE (75 percent of the data values are less than this value.)
	MEDIAN
	25th PERCENTILE (25 percent of the data values are less than this value.)
	MINIMUM VALUE

p VALUES RESULTS OF RANK-SUM TEST OR RANK-TRANSFORM ANALYSIS-OF-VARIANCE TESTS *(Concentrations were converted to molar values for the purpose of statistical comparisons.)*

A, B, C RESULTS OF SUBSEQUENT MULTIPLE-COMPARISON TESTS *(Concentrations were converted to molar values for the purpose of statistical comparisons.)*

Figure 9. Concentrations of selected pesticides and metabolites in Chesterville Branch, 1999-2001. *Metabolite concentrations typically exceeded concentrations of parent compounds.*

Hydrologic and Geochemical Controls on the Transport of Pesticides and Nutrients

Dominant pathways for the transport of agricultural chemicals to the upper Pocomoke River and Chesterville Branch are related to geologic, topographic, and soil conditions in each watershed and vary mainly with the weather. The distinctive chemistry of ground water derived from within different geologic formations in each watershed provides an opportunity to distinguish the relative contribution of these sources to streamflow as they change seasonally and over individual storm events.

Two principal components explain nearly two-thirds of the variability in water chemistry over the sampling period in each stream. In the upper Pocomoke River, the relative volume of discharge from two ground-water sources is apparently the dominant factor affecting stream chemistry. Surface runoff is evidently less important in the upper Pocomoke River Watershed, but explains nearly half of the variability in the chemistry of Chesterville Branch.

The Upper Pocomoke River

Ground water is a significant hydrologic chemical transport pathway to streams in the upper Pocomoke River Watershed. The first principal component of stream chemistry in the upper Pocomoke River (POCOPC1), which explains nearly half (44 percent) of the overall variability in major-ion and nutrient concentrations in the river, apparently repre-

sents a distinction between two ground-water sources (table 3). POCOPC1 correlates directly with calcium, magnesium, chloride, sulfate, and nitrate (as well as specific conductance), which are typical of agricultural influences observed in ground water from the unconfined Parsonsburg Sand. Inverse correlations with POCOPC1 are strongest for iron and bicarbonate, which are typical of ground water in the Beaverdam Sand.

Contributions of particulates and other relatively insoluble materials from surface runoff are evidently of secondary importance to the chemistry of water in the upper Pocomoke River. The second principal component of stream chemistry (POCOPC2, table 3) is strongly correlated with streamflow (fig. 10), and apparently represents an indicator of flow regime. The relatively strong negative loadings of POCOPC2 with phosphorus and ammonia plus organic nitrogen, as well as (to a lesser extent) potassium and manganese, suggests negative values of POCOPC2 are indicative of a high-flow regime. Phosphorus is relatively insoluble and often bound to sediment; potassium and ammonium (which constitutes most of the ammonia at pH typical of the upper Pocomoke River) may also be adsorbed onto mineral surfaces (Hem, 1985). Organic nitrogen in surface runoff may be indicative of surface applications of poultry manure. The relatively strong direct correlation of POCOPC2 with silica and sodium suggests base flow, especially from the Beaverdam Sand.

As is the case in many areas, the mobility of particulate

Table 3. *Loadings on the first two components from unrotated principal components analysis on major-ion and nutrient data collected from the upper Pocomoke River, 1999–2001*

[Loadings with absolute value greater than 0.70 are shown in **bold**; those with absolute value less than 0.40 are omitted]

| Compound, ion, or physical characteristic	Component 1 (POCOPC1)	Component 2 (POCOPC2)	Communality estimates
Percent of overall variance	44	25	
Specific conductance	**0.8553**		0.7353
Sulfate	**0.9148**		0.8660
Calcium	**0.9278**		0.9193
Magnesium	**0.9389**		0.8908
Nitrate	**0.8893**		0.8675
Chloride	**0.7127**	0.4807	0.7390
Silica		**0.8841**	0.8627
Sodium		**0.8236**	0.7801
Ammonia plus organic nitrogen	0.4009	**-0.8183**	0.8302
Phosphorus, total	-0.4629	**-0.7652**	0.7998
Bicarbonate	-0.6662		0.5887
Iron	-0.6304		0.4212
Manganese	0.6351	-0.5045	0.6579
Potassium	0.6282	-0.5690	0.7183
pH			0.0606
Dissolved oxygen		0.4196	0.3265
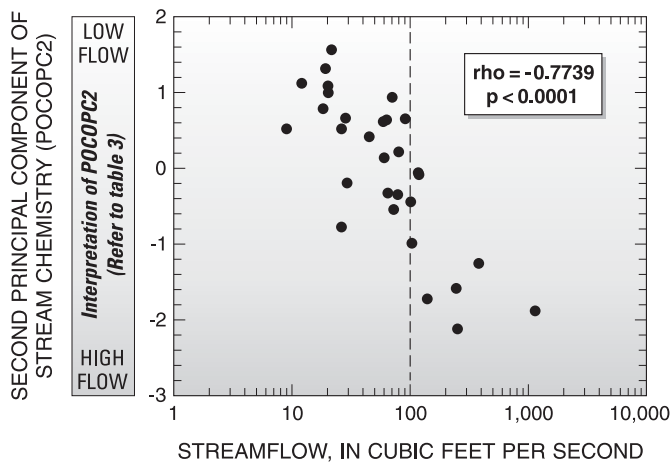
Figure 10. Relation of the second principal component of stream chemistry (POCOPC2) to streamflow in the upper Pocomoke River, 1999-2001. *POCOPC2 decreased significantly with increasing streamflow.*

matter and relatively insoluble chemical species through the upper Pocomoke River Watershed is dependent on relatively high streamflow. In the predominantly flat upper Pocomoke River Watershed, however, direct runoff of precipitation along the land surface contributes significantly to streamflow in the river only during particularly large or intense storm events. Concentrations of total phosphorus and suspended sediment were consistently low when streamflow was less than 100 ft^3/s (cubic feet per second), but increased dramatically above that level (fig. 11). Total flow of 100 ft^3/s in the Pocomoke River near Willards, Maryland, may be an indicator of when overland runoff becomes significant in the watershed. Bank erosion or resuspension of bed load may also contribute to elevated phosphorus or sediment concentrations in the river during periods of high flow.

Periods of significant overland flow in the upper Pocomoke River Watershed are relatively infrequent. POCOPC2 represents only 25 percent of the variability in stream chemistry from 1999 through 2001 (table 3). Hourly streamflow measurements exceeding 100 ft^3/s occurred only about 20 percent of the time between July 1996 and September 2001, and HYSEP estimates indicate that over 70 percent of flow in the upper Pocomoke River is generated from ground-water discharge (table 4).
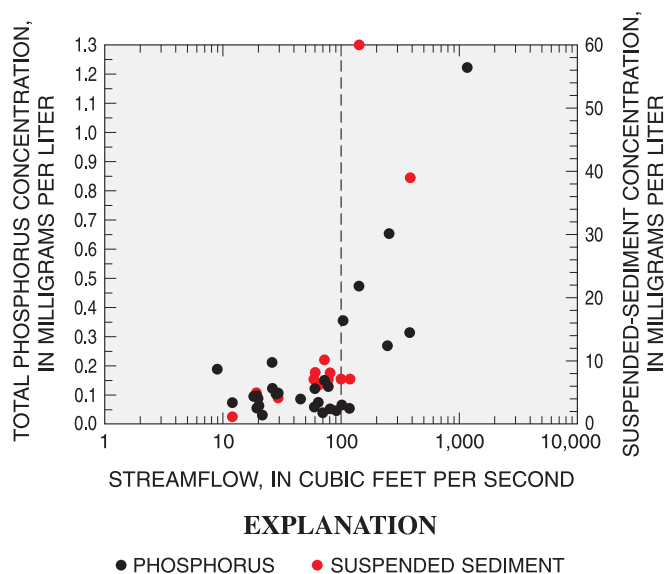
Figure 11. Relation of phosphorus and suspended-sediment concentrations to streamflow in the upper Pocomoke River, 1999-2001. *Concentrations of phosphorus and suspended sediment were typically low until streamflow reached approximately 100 cubic feet per second.*

Unconfined ground water in the Parsonsburg Sand represents an important conduit through which soluble agricultural or other chemicals are transported through the upper Pocomoke River Watershed. Concentrations of these chemicals may be diluted in the river by discharge from the confined Beaverdam Sand, however, particularly during dry periods. The relative contribution of water from the Parsonsburg Sand to that from the Beaverdam Sand increases with increasing streamflow (fig. 12). This relation is apparently related to base flow, however, and is not apparent above 100 ft^3/s where surface runoff may be significant. POCOPC1 is more strongly correlated with streamflow below 100 ft^3/s (rho $= 0.749$, $p < 0.0001$, $n = 22$) than over the entire range of flow conditions (rho $= 0.479$, $p = 0.0075$, $n = 30$) (fig. 12). The relative discharge from the two ground-water sources is probably controlled by the level of the water table in the Parsonsburg Sand. The higher water table during wet periods would induce greater discharge from this aquifer to the upper Pocomoke River and its tributaries. These tributaries are primarily artificial ditches, however, and may contain little or no water during dry periods. Ground-water discharge from the Beaverdam Sand, which is probably fairly consistent over different seasons, would have its greatest influence on stream chemistry during drier periods.

The occurrence of pesticides in the upper Pocomoke River similarly reflects the importance of transport through shallow ground water in the Parsonsburg Sand. Where significant, correlations between pesticide concentrations and streamflow are generally negative (table 5). Ground-water

Table 4. *Summary of streamflow characteristics for the upper Pocomoke River near Willards, Maryland and Chesterville Branch near Crumpton, Maryland, July 1996 through September 2001*

[km^2, square kilometers; ft^3/s, cubic feet per second]

Stream	Drainage area (km^2)	Median estimated percent monthly base flow [1]	Estimated threshold for runoff events [2] (ft^3/s)	Percentage of time exceeding threshold [3]	Number of runoff events [3]	Mean duration of runoff events [4] (hours)
Pocomoke River near Willards, MD	155	72.2	100	20.8	72	133
Chesterville Branch near Crumpton, MD	15	78.8	10	21.6	140	71

[1] Estimated from HYSEP, Sloto and Crouse, 1996. Estimates for Chesterville Branch include August 1996 through September 2001.

[2] Estimated on the basis of stream chemistry.

[3] Estimated on the basis of hourly streamflow measurements, neglecting missing data.

[4] Computed from TE * TT/NE, where TE = percentage of time exceeding threshold (as a proportion), TT = 46,032, the total number of hours between July 1, 1996 and September 30, 2001, and NE = total number of runoff events.
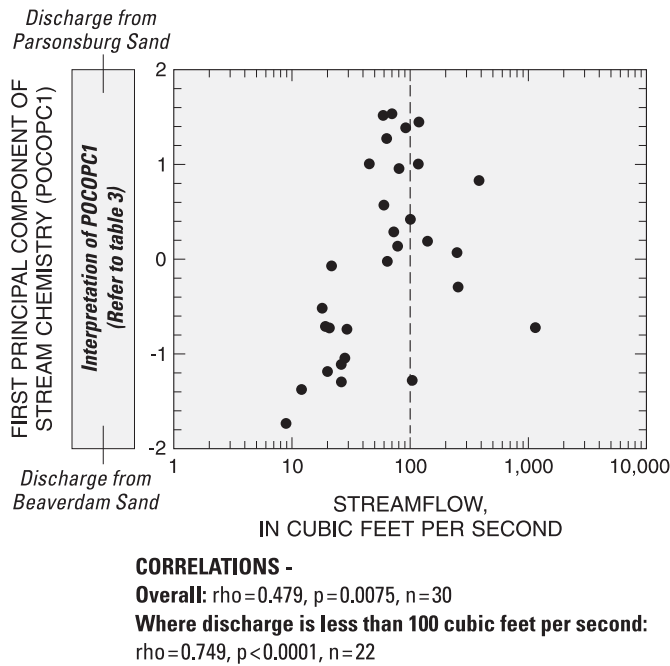
Figure 12. Relation of the first principal component of stream chemistry (POCOPC1) to streamflow in the upper Pocomoke River, 1999-2001. *POCOPC1 was particularly strongly correlated with streamflow below 100 cubic feet per second.*
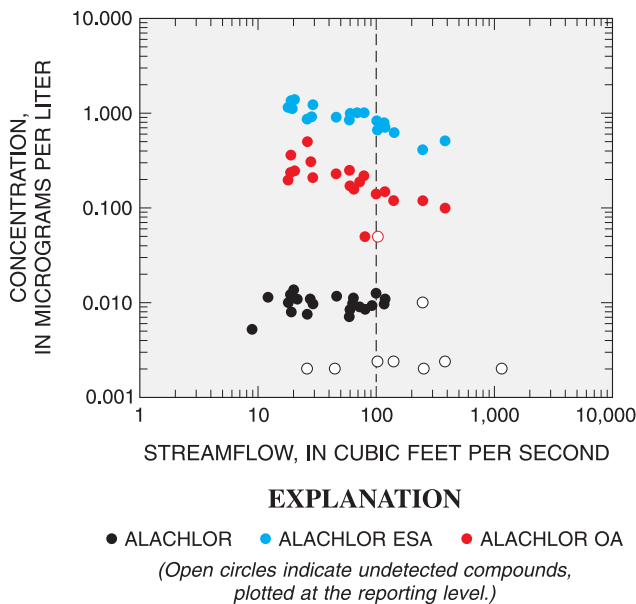

Figure 13. Relation of alachlor and selected metabolites to streamflow in the upper Pocomoke River, 1999-2001. *Concentrations of all three compounds decreased with increasing streamflow (refer to table 6); alachlor was rarely detectable in the river when streamflow exceeded 100 cubic feet per second.*

discharge probably accounts for the entire mass of alachlor in the river; alachlor was rarely detected when streamflow exceeded 100 ft^3/s (fig. 13). Although concentrations of ace-tochlor ESA, metolachlor ESA, and metolachlor OA increase with increasing streamflow (table 5), this is proba-bly indicative of ground-water discharge from the Parsons-burg Sand rather than rainfall or surface runoff. Correlations of both metolachlor metabolites with streamflow are stron-ger below 100 ft^3/s than over the entire range of sampled conditions (fig. 14).

Seasonal variability in major-ion and nutrient chemistry in the upper Pocomoke River reflects the seasonal hydro-logic variability and resulting changes in the relative contri-butions from the Parsonsburg and Beaverdam Sands. POCOPC1 was significantly higher ($p = 0.0252$) between December and May than during the drier period, suggesting a greater relative contribution of flow from the Parsonsburg Sand than from the Beaverdam Sand (table 3, fig. 15). Indi-vidually, concentrations of nitrate, ammonia plus organic nitrogen, sulfate, and manganese were also significantly higher during the wetter period, but concentrations of iron,
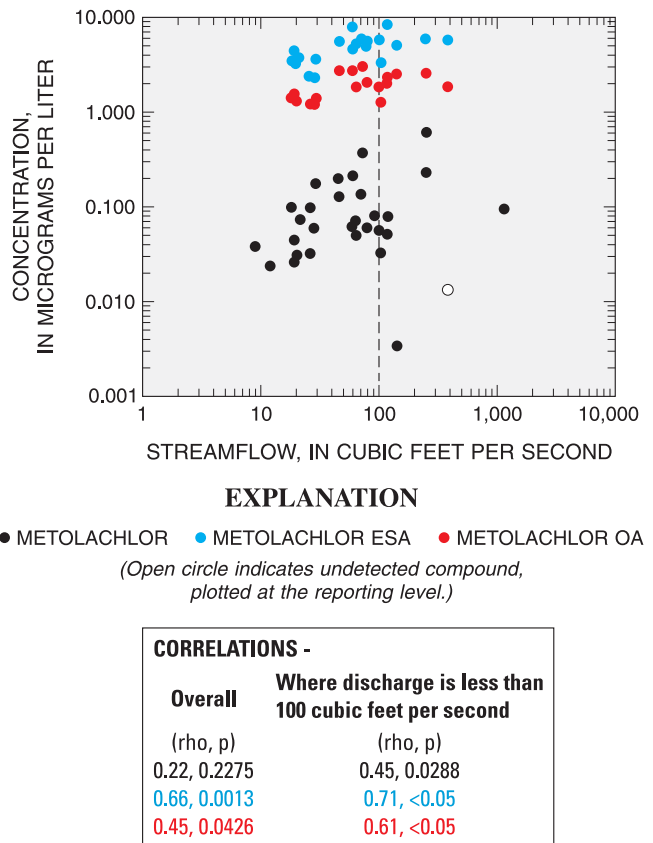

Figure 14. Relation of metolachlor and selected metabolites to streamflow in the upper Pocomoke River, 1999-2001. *Concentrations of all three compounds were particularly strongly related to streamflow at flows less than 100 cubic feet per second.*

Table 5. *Results of comparisons of concentrations of selected pesticides and relative proportions of parent and daughter compounds in the upper Pocomoke River and Chesterville Branch to streamflow and among different seasons, 1999–2001*

[Results are omitted in cases where compound was detected in less than 50 percent of samples, total sample size is less than 20, or (for seasonal comparisons) the number of samples in either season is less than 10. Results in **bold** are significant at *alpha* = 0.05; n, number of samples in correlation of streamflow and concentration; rho, Spearman's rho; *p* value, *p* value from Spearman's test for correlation; n_WET, number of samples collected during the "wet" season (December–May); n_DRY, number of samples collected during the "dry" season (June–November)]

| Chemical variable | Pocomoke River near Willards, Maryland | | | | | | | Chesterville Branch near Crumpton, Maryland | | | | | | |
| | Streamflow[1] | | | Season | | | | Streamflow[1] | | | Season | | | |
	n	rho	*p* value	n_WET	n_DRY	*p* value	Higher season	n	rho	*p* value	n_WET	n_DRY	*p* value	Higher season
Atrazine	32	0.0089	0.9615	13	19	0.1671		**40**	**0.3529**	**0.0255**	20	20	0.2448	
Desethylatrazine	32	0.1573	0.3898	**13**	**19**	**0.0408**	**DRY**	**40**	**-0.4788**	**0.0018**	20	20	0.6948	
Percent Atrazine	**30**	**-0.3932**	**0.0316**	12	18	0.4707		**40**	**0.5937**	**0.0001**	20	20	0.2674	
Acetochlor	32	0.0500	0.7859	13	19	0.4549								
Acetochlor ESA	**21**	**0.5367**	**0.0121**	10	11	1.0000								
Acetochlor OA	21	0.2761	0.2257	10	11	0.6460								
Percent Acetochlor[2]	21	-0.2923	0.1986	10	11	0.6678								
Percent Acetochlor ESA[2]	21	0.3085	0.1736	10	11	0.3242								
Percent Acetochlor OA[2]	21	-0.2319	0.3118	10	11	0.0910								
Alachlor	**32**	**-0.3940**	**0.0257**	13	19	0.4400		40	0.2483	0.1223	**20**	**20**	**0.0119**	**WET**
Alachlor ESA	**21**	**-0.8156**	**0.0001**	10	11	0.0670		36	0.0903	0.6004	19	17	0.5057	
Alachlor OA	**21**	**-0.8238**	**0.0001**	10	11	0.1805		36	0.2977	0.0778	19	17	0.8741	
Ratio of Alachlor ESA/ Alachlor[3]								36	-0.2057	0.2287	19	17	0.0513	
Ratio of Alachlor OA/ Alachlor[3]								36	0.0656	0.7038	19	17	0.0638	
Percent Alachlor[2]	21	-0.1323	0.5676	10	11	0.5720		36	0.1359	0.4295	19	17	0.0900	
Percent Alachlor ESA[2]	21	0.0890	0.7013	10	11	0.8327		**36**	**-0.3973**	**0.0164**	19	17	0.8121	
Percent Alachlor OA[2]	21	-0.1046	0.6519	10	11	0.6221		36	0.2358	0.1663	19	17	0.3665	
Metolachlor	32	0.2195	0.2275	13	19	0.6045		**40**	**0.4638**	**0.0026**	20	20	0.3301	
Metolachlor ESA	**21**	**0.6550**	**0.0013**	10	11	0.0782		36	0.1581	0.3571	19	17	0.2674	
Metolachlor OA	**21**	**0.4463**	**0.0426**	10	11	0.8327		**36**	**0.5120**	**0.0014**	19	17	0.8740	
Ratio of Metolachlor ESA/ Metolachlor[3]	20	0.2272	0.3355					**36**	**-0.3643**	**0.0290**	19	17	0.6920	
Ratio of Metolachlor OA/ Metolachlor[3]	20	0.0707	0.7671					36	-0.1865	0.2761	19	17	0.1885	
Percent Metolachlor[2]	21	-0.3027	0.1823	10	11	0.0910		**36**	**0.3385**	**0.0435**	19	17	0.4957	
Percent Metolachlor ESA[2]	21	0.2884	0.2048	**10**	**11**	**0.0411**	**WET**	**36**	**-0.3938**	**0.0175**	19	17	0.8121	
Percent Metolachlor OA[2]	21	-0.2105	0.3598	**10**	**11**	**0.0411**	**DRY**	36	0.2180	0.2016	**19**	**17**	**0.0379**	**DRY**
Prometon	32	-0.0227	0.9020	**13**	**19**	**0.0087**	**DRY**							
Pronamide								40	0.1461	0.3683	**20**	**20**	**0.0001**	**WET**
Simazine	32	0.1217	0.5071	13	19	0.3282		**40**	**0.3301**	**0.0375**	20	20	0.7150	

[1] Instantaneous streamflow measured at the time of sample collection.

[2] Percentages were computed on a molar basis, only in cases where both parent and daughter compounds were measured and at least one was detected. Censored data were assumed to equal zero.

[3] Ratios were computed on a molar basis, only in cases where both parent and daughter compounds were detected.
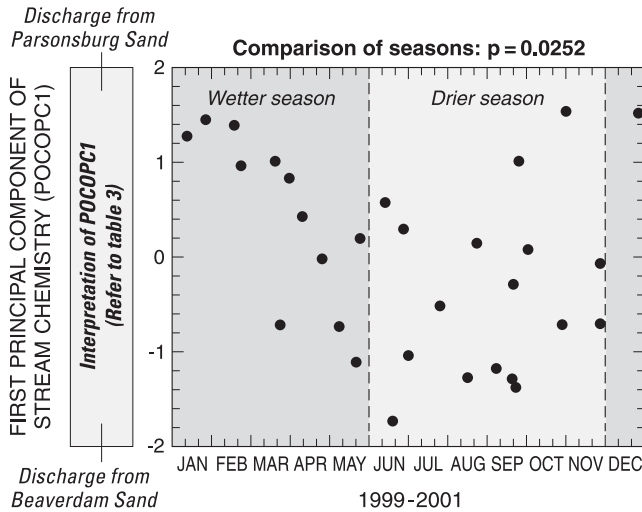
Figure 15. Seasonal variability in the first principal component of stream chemistry (POCOPC1) in the upper Pocomoke River, 1999-2001. *POCOPC1 was significantly greater during the relatively wet season from December through May than during the drier part of the year.*
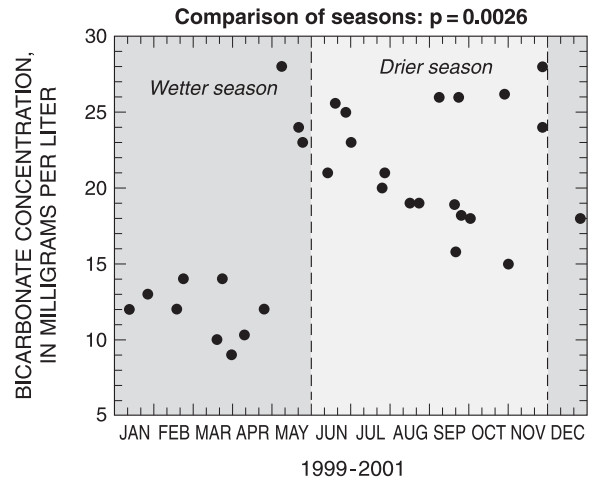

Figure 16. Seasonal variability in bicarbonate concentrations in the upper Pocomoke River, 1999-2001. *Bicarbonate concentrations were typically higher during June through November than during the wetter part of the year.*

bicarbonate, and silica were significantly lower (table 6). Nitrate is indicative of discharge from the Parsonsburg Sand; sulfate and ammonia during the wetter months may also be derived from Parsonsburg discharge, or from organic matter in ditches and other upper Pocomoke tributaries. Iron and bicarbonate represent the influence of discharge of ground water from the Beaverdam Sand during the drier months. The increase in dissolved iron and the sharp increase in bicarbonate concentrations in the upper Pocomoke River in the late spring (fig. 16) may also be the result of the dissolution of amorphous ferric hydroxide in ditch sediments as flow decreases and conditions in the ditches become stagnant and anoxic (Denver, 1986, 1989). A similar seasonal pattern is apparent in figure 7; samples from the upper Pocomoke River during the wetter months were consistently similar to water from the Parsonsburg Sand, but samples from the drier months represented more of a variable mixture from both aquifers, and the effects of stagnant ditch conditions.

Seasonal variability in pesticide concentrations in the upper Pocomoke River is related to application patterns. Concentrations of atrazine and metolachlor were generally highest in the river during the growing season (fig. 17). The relatively rapid response of pesticide concentrations in the upper Pocomoke River to pesticide application in the watershed is likely indicative of drainage from the Parsonsburg Sand through artificial ditching, as well as pesticide transport during relatively unusual periods of surface runoff. Instantaneous pesticide loads increase with increasing streamflow throughout the entire range of sampled condi-
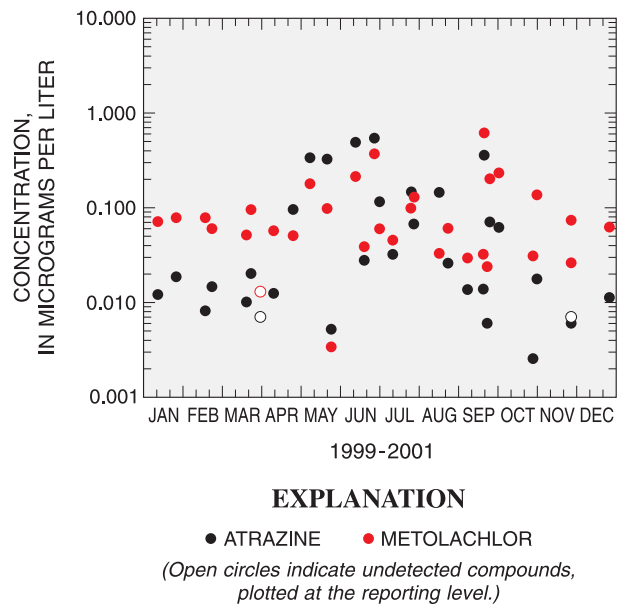

EXPLANATION

● ATRAZINE   ● METOLACHLOR

(Open circles indicate undetected compounds, plotted at the reporting level.)

Figure 17. Seasonal variability in concentrations of atrazine and metolachlor in the upper Pocomoke River, 1999-2001. *Although metolachlor and atrazine were detectable throughout the year, concentrations were generally highest during the growing season following periods of application.*

Table 6. *Results of comparisons of stream chemistry in the upper Pocomoke River (1999–2001) and Chesterville Branch (1996–2001) to streamflow and among different seasons*

[Results in **bold** are significant at alpha = 0.05. Results are omitted in cases where total sample size is less than 20 or (for seasonal comparisons) the number of samples in either season is less than 10. n, number of samples in correlation of streamflow and concentration; rho, Spearman's rho; p value, p value from Spearman's test for correlation; n_{WET}, number of samples collected during the "wet" season (December–May); n_{DRY}, number of samples collected during the "dry" season (June–November)]

Chemical or physical variable	Pocomoke River near Willards, Maryland — Streamflow[1]			Season				Chesterville Branch near Crumpton, Maryland — Streamflow[1]			Season			
	n	rho	p value	n_{WET}	n_{DRY}	p value	Higher Season	n	rho	p value	n_{WET}	n_{DRY}	p value	Higher Season
Specific conductance	31	0.325	0.0743	13	18	0.2885		**124**	**-0.701**	**0.0001**	67	59	0.7599	
Calcium	32	0.268	0.1380	13	19	0.1987		**51**	**-0.750**	**0.0001**	25	27	0.5395	
Magnesium	**32**	**0.385**	**0.0296**	13	19	0.1732		**51**	**-0.442**	**0.0012**	25	27	0.3646	
Sodium	**32**	**-0.542**	**0.0014**	13	19	0.4543		**51**	**-0.596**	**0.0001**	**25**	**27**	**0.0490**	WET
Potassium	**32**	**0.751**	**0.0001**	13	19	0.3374		**51**	**0.421**	**0.0021**	**25**	**27**	**0.0034**	DRY
Silica	**32**	**-0.874**	**0.0001**	**13**	**19**	**0.0148**	DRY	**74**	**-0.693**	**0.0001**	39	37	0.4512	
Sulfate	32	0.334	0.0620	**13**	**19**	**0.0274**	WET	**51**	**0.563**	**0.0001**	25	27	0.1753	
Chloride	32	0.009	0.9619	13	19	0.3001		**51**	**-0.547**	**0.0001**	25	27	0.2375	
Bicarbonate	**31**	**-0.710**	**0.0001**	**13**	**18**	**0.0026**	DRY	**89**	**-0.607**	**0.0001**	**46**	**44**	**0.0001**	DRY
Suspended sediment								**86**	**0.727**	**0.0001**	46	42	0.0930	
Iron	32	-0.343	0.0543	**13**	**19**	**0.0183**	DRY	**51**	**0.512**	**0.0001**	**25**	**27**	**0.0013**	WET
Manganese	**32**	**0.652**	**0.0001**	**13**	**19**	**0.0026**	WET	**52**	**0.294**	**0.0346**	**25**	**28**	**0.0001**	WET
Ammonia plus organic nitrogen	**32**	**0.822**	**0.0001**	**13**	**19**	**0.0316**	WET	**128**	**0.630**	**0.0001**	67	63	0.0556	
Nitrate	**32**	**0.742**	**0.0001**	**13**	**19**	**0.0023**	WET	**126**	**-0.665**	**0.0001**	**66**	**62**	**0.0285**	WET
Phosphorus	32	0.207	0.2551	13	19	0.4314		**128**	**0.747**	**0.0001**	67	63	0.2853	
Phosphorus, total	32	0.269	0.1369	13	19	0.4315		**127**	**0.776**	**0.0001**	67	62	0.1785	

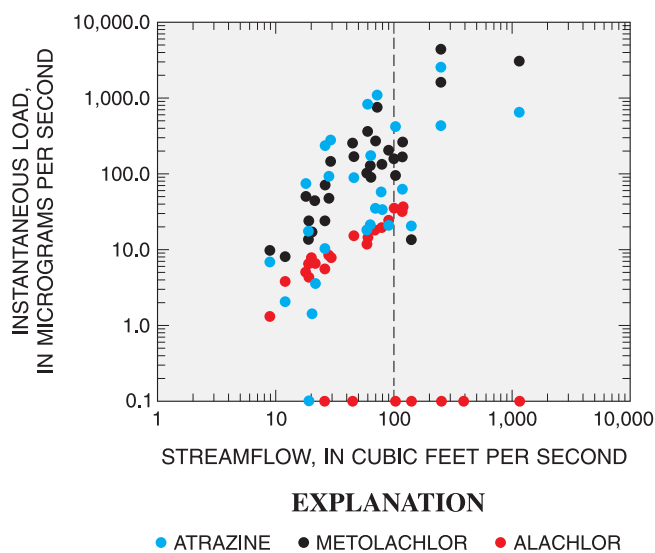[1] Instanteous streamflow measured at the time of sample collection.

Figure 18. Relation of instantaneous loads of selected pesticides to streamflow in the upper Pocomoke River, 1999-2001. *Where compound was not detected, load is plotted at 0.1 micrograms per second. Although loads of atrazine and metolachlor generally increased with increasing streamflow over the entire range of sampled conditions, alachlor was rarely detected in the river when streamflow exceeded 100 cubic feet per second.*

Figure 19. Relation of the first principal component of stream chemistry (CHESPC1) to streamflow in Chesterville Branch, 1997-2001. *Positive values of CHESPC1 are generally indicative of base flow, and strong negative values represent the effects of overland runoff.*

tions in the upper Pocomoke River (fig. 18). Increasing pesticide loads with increasing streamflow below 100 ft^3/s (fig. 18) are likely indicative of the increasing relative importance of discharge from the Parsonsburg Sand. Once surface runoff becomes significant, however, additional amounts of some pesticides are carried in surface runoff to the stream (fig. 18).

Chesterville Branch

Both ground water and overland runoff represent significant pathways for chemical transport to Chesterville Branch and its tributaries. Overland runoff may be a more important transport mechanism in the Chesterville Branch Watershed than in the upper Pocomoke River Watershed due to the greater topographic relief and/or the smaller watershed area. Ground-water transport through the permeable, unconfined Columbia and Aquia aquifers, however, is also important for soluble chemical species. Although stream chemistry in Chesterville Branch is also affected by discharge from the confined Hornerstown aquifer, these effects may be minimal. Even the smallest tributaries draining the relatively thick unconfined aquifer are typically perennial.

The distinction between base flow and surface runoff is apparently of primary importance to the chemistry of water in Chesterville Branch. The first principal component of stream chemistry (CHESPC1) is related to streamflow (fig. 19) and explains nearly half (47 percent) of the variability in major ion and nutrient concentrations (table 7). The
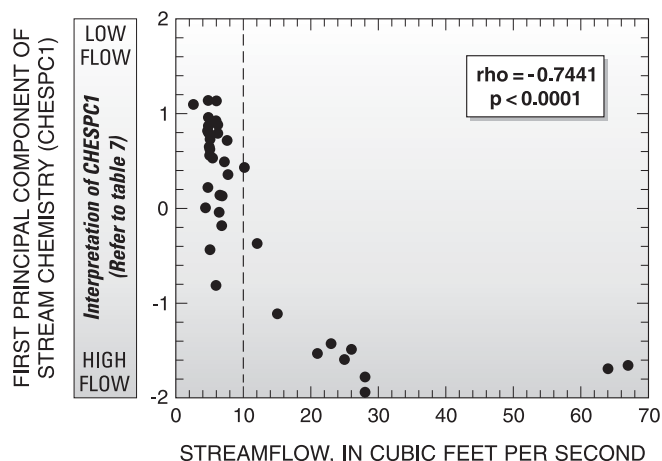
pattern of correlations with CHESPC1 appears to represent a distinction between agricultural chemicals that are relatively soluble and those that are not. Strongly positive values of CHESPC1 associated with low streamflow are correlated with relatively soluble ions typical of ground water in the surficial unconfined aquifer, including calcium, sodium, nitrate, and magnesium. Chemical species with relatively strong negative correlations with CHESPC1 include phosphorus, ammonia plus organic nitrogen, sulfate, and potassium (table 7). These chemicals are commonly transported in overland runoff, often attached to sediment particles.

The second principal component (CHESPC2) represents seasonal variability in the chemistry of water in Chesterville Branch. Positive values of CHESPC2 are correlated with manganese, iron, and dissolved oxygen (table 7) and occur almost exclusively during the relatively wet season from December through May (fig. 20). Negative values of CHESPC2 are correlated with potassium and bicarbonate and occur only during the typically drier period from June through November. Iron is relatively insoluble in oxic conditions (Hem, 1985). Although iron concentrations were generally low in Chesterville Branch, the occurrence of relatively high concentrations of iron and dissolved oxygen in the stream during the wet season suggests some type of chemical disequilibrium. The relatively high concentrations of bicarbonate associated with strongly negative values of CHESPC2 suggests that discharge from the Hornerstown

Table 7. *Loadings on the first two components from unrotated principal components analysis on major-ion and nutrient data collected from Chesterville Branch, 1997–2001*

[Loadings with absolute value greater than 0.70 are shown in **bold**; those with absolute value less than 0.40 are omitted]

Compound, ion, or physical characteristic	Component 1 (CHESPC1)	Component 2 (CHESPC2)	Communality estimates
Percent of overall variance	47	15	
Specific conductance	**0.8483**		0.7321
Sodium	**0.8270**		0.7277
Calcium	**0.8775**		0.7711
Magnesium	**0.7399**		0.5811
Nitrate	**0.7670**		0.7214
Ammonia plus organic nitrogen	**-0.8188**		0.7123
Phosphorus, total	**-0.9271**		0.8748
Potassium	**-0.7094**	-0.4056	0.6677
Sulfate	**-0.7180**		0.6553
Iron	-0.4503	0.6897	0.6783
Manganese		**0.8108**	0.7362
Dissolved oxygen		0.6755	0.5598
Bicarbonate	0.5741	-0.4938	0.5734
Chloride	0.6775		0.4938
Silica	0.6423		0.4141
pH			0.0184

aquifer may be important when the water table is low during the dry season.

Surface runoff in the Chesterville Branch Watershed probably becomes significant when total streamflow near Crumpton reaches about 10 ft^3/s. CHESPC1 is strongly correlated with streamflow; strongly negative values indicative of overland runoff occur only at streamflow above 10 ft^3/s (fig. 19). Suspended sediment and total phosphorus occurred at fairly low and consistent concentrations below this level, but were mobilized more significantly at flows greater than 10 ft^3/s (fig. 21). HYSEP estimates suggest that about 79 percent of flow in Chesterville Branch is derived from ground-water discharge (table 4). Flow records at Chesterville Branch, however, date only to 1996, and include several years of severe drought (U.S. Geological Survey, 1950–2001). Although estimated long-term net contributions from base flow are similar to those in the upper Pocomoke River, periods of high flow occurred only about half as often in the upper Pocomoke River Watershed between July 1996 and September 2001, but lasted an average of about twice as long (table 4). Although this pattern is likely due at least in part to the difference in drainage area between the two streams, differences in hydrogeology and topography between the two watersheds are probably also important.

The transport of relatively soluble ions from the land surface to streams in the Chesterville Branch Watershed apparently occurs mainly through the permeable unconfined
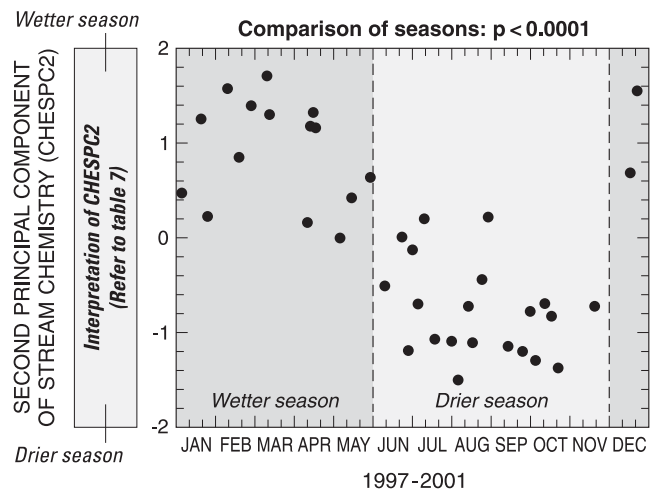

Figure 20. Seasonal variability in the second principal component of stream chemistry (CHESPC2) in Chesterville Branch, 1997-2001. *CHESPC2 was significantly greater from December through May than during the remainder of the year.*
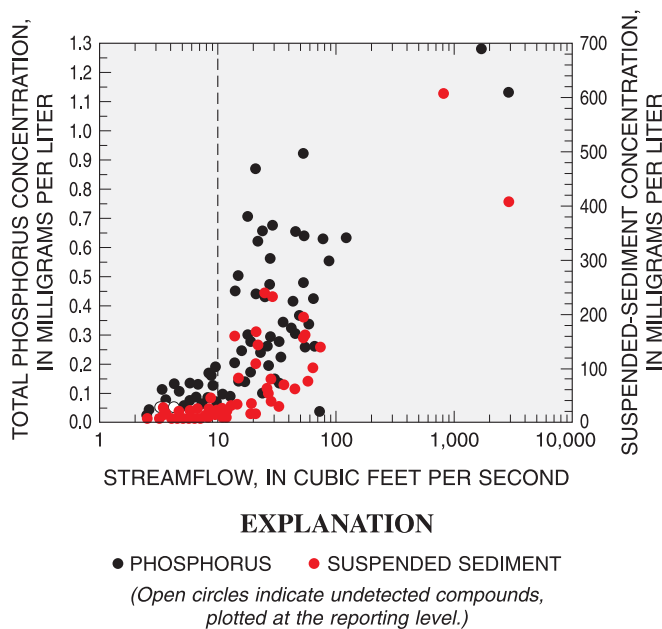
Figure 21. Relation of phosphorus and suspended-sediment concentrations to streamflow in Chesterville Branch, 1996-2001. *Concentrations of phosphorus and sediment were relatively low until streamflow reached approximately 10 cubic feet per second.*

Figure 22. Seasonal variability in the first principal component of stream chemistry (CHESPC1) in Chesterville Branch, 1997-2001. *CHESPC1 was not significantly different between relatively wet (December through May) and dry (June through November) seasons.*

aquifer system. The chemistry of water in Chesterville Branch is evidently minimally affected by discharge from deeper confined aquifers, however, and concentrations of these ions during base flow are not greatly diluted by mixing in the stream. Nitrate, calcium, and magnesium, typical of ground water affected by agriculture, occurred in Chesterville Branch at relatively high concentrations during all seasons (fig. 22); variability is primarily related to flow regime (fig. 19 and table 6). Alachlor, atrazine, metolachlor, simazine, and selected metabolites of each were also detectable throughout the year in Chesterville Branch (fig. 23, table 2).

The transport of pesticides and metabolites to Chesterville Branch occurs through both surface runoff and ground-water discharge. Both parent compounds and metabolites were detectable throughout the year and during all sampled flow regimes (table 2). Although soluble pesticide metabolites may be transported to Chesterville Branch primarily through ground water, parent compounds likely move predominantly in surface runoff. Significant correlations with streamflow over the entire range of sampled conditions are generally positive for parent compounds (including atrazine, metolachlor, and simazine), and negative for most metabolites (table 5). The variability in transport implied by these correlations may be related to solubility or persistence in the soil. ESA and OA metabolites are much more soluble than their parent compounds, and runoff conditions may
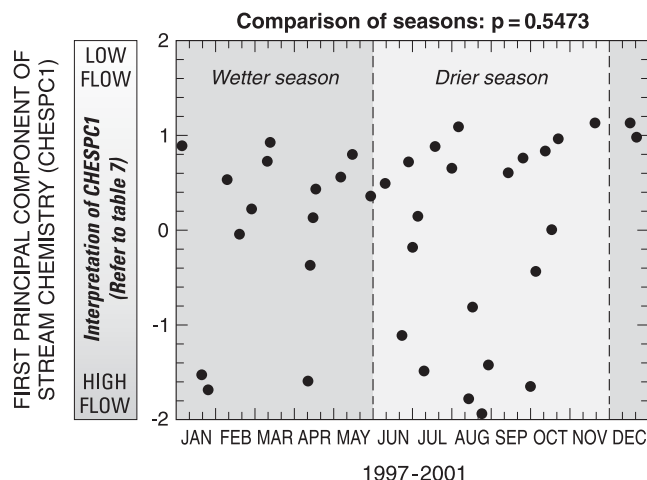
transport parent compounds to streams before they are converted to metabolites (Phillips and others, 1999). Ground-water transport is apparently particularly important for ESA metabolites; relative proportions of these metabolites of metolachlor and alachlor to OA metabolites and parent compounds decreased with increasing streamflow. OA metabolites may be less soluble than ESA metabolites. Although concentrations of most OA metabolites are not related to streamflow, concentrations of metolachlor OA increased with increasing flow (table 5).

The movement of pesticides to Chesterville Branch during wet periods is related to their use and persistence in the watershed as well as to flow conditions. The dependence of pesticide transport on streamflow is probably more complex than is suggested by simple correlations of concentrations with streamflow. Concentrations of selected parent compounds are typically highest near the initiation of surface runoff at around 10 ft³/s, but may decrease or stabilize as flows continue to increase (fig. 24). Instantaneous loads of metolachlor and atrazine, however, apparently stabilize or continue to increase as streamflow in Chesterville Branch increases above 10 ft³/s (fig. 25). The apparent decrease in concentrations of these compounds during high flow is likely the result of simple dilution.

Although pesticide concentrations typically peak during the growing season in Chesterville Branch, seasonal variability in the overall stream chemistry is generally minimal.
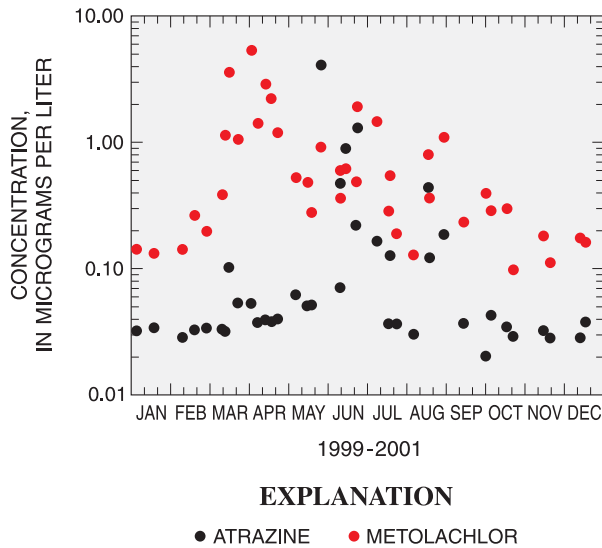
Figure 23. Seasonal variability in atrazine and metolachlor concentrations in Chesterville Branch, 1999-2001. *Although both compounds were detectable throughout the year, concentrations were typically highest following pesticide applications in the spring. Metolachlor concentrations were generally highest in March and April, but atrazine concentrations generally peaked later in the year.*

Figure 24. Relation of concentrations of selected pesticides to streamflow in Chesterville Branch, 1999-2001. *Curves represent spline smoothing. Concentrations were typically highest when streamflow was approximately 10 cubic feet per second.*

Seasonal patterns in pesticide concentrations are probably related to similar patterns in application. From 1999 through 2001, the highest concentrations of metolachlor typically occurred in March or April, but concentrations of atrazine typically peaked later during the growing season (fig. 23). Pronamide concentrations were generally highest early in the year (fig. 26). Although metolachlor and pronamide are often used in pre-emergence applications, atrazine may be used for selective weed control throughout the growing season (Farm Chemical Handbook, 1999). Concentrations of nutrients and most other chemical species are related most significantly to streamflow and are fairly consistent throughout the year (tables 5–6). The unconfined aquifer is relatively thick (as much as 25 m) in the Chesterville Branch Watershed (fig. 5), and the typically perennial headwater streams probably carry discharge from this surficial aquifer throughout the year (Bachman and others, 2002). Conversely, discharge from underlying confined aquifers is probably limited by the relatively small size of the Chesterville Branch Watershed, and is likely significant only during extremely dry periods.
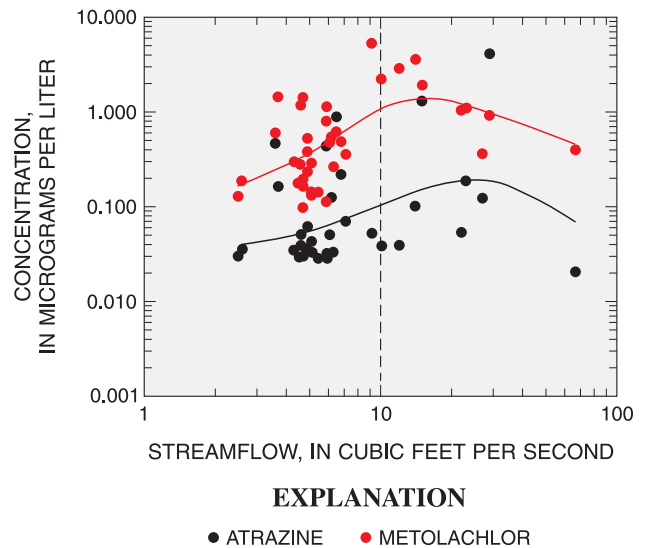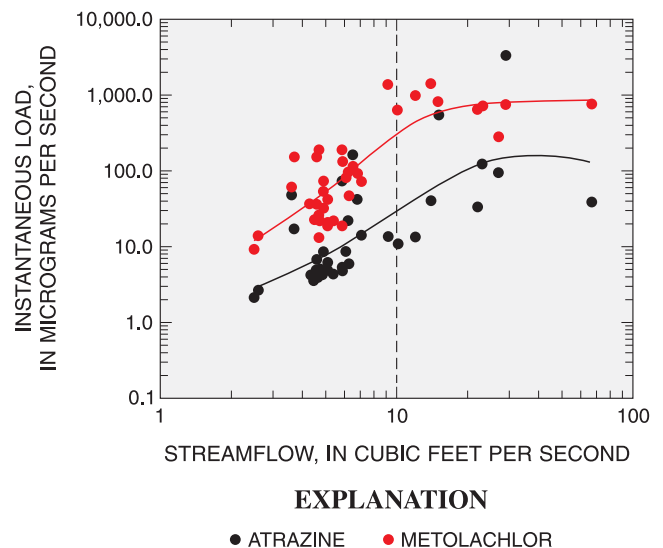

Figure 25. Relation of instantaneous loads of selected pesticides to streamflow in Chesterville Branch, 1999-2001. *Curves represent spline smoothing.*
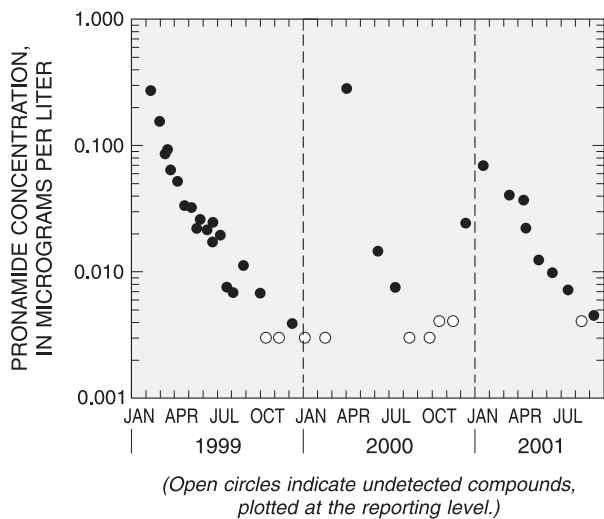
Figure 26. Concentrations of pronamide in Chesterville Branch, 1999-2001. *Concentrations were generally highest early in the year.*

Summary and Conclusions

Water chemistry in the upper Pocomoke River and Chesterville Branch reflects the influence of agriculture and the predominance of permeable siliciclastic surficial sediments in both watersheds. Samples were collected periodically from the late 1990s through 2001 from each stream and analyzed for major ions, nutrients, and selected pesticides and pesticide metabolites as part of the National Water-Quality Assessment and similar programs of the U.S. Geological Survey. Variability in the water chemistry in each stream was analyzed to identify important transport processes in different hydrogeologic settings during different seasons and flow conditions. Excessive nutrients, pesticides, and other agricultural chemicals in streams may be harmful to aquatic biota, and understanding hydrologic and geochemical processes that affect their transport through watersheds can be useful for the safe and effective use of these compounds.

The typically dilute, slightly acidic, and well-oxygenated water in the upper Pocomoke River and Chesterville Branch contains dissolved nitrogen and phosphorus compounds at detectable levels during all seasons and all flow conditions, and concentrations are typically higher than would be expected under natural conditions. Nitrate generally occurs in higher concentrations than ammonia or organic nitrogen,

although concentrations of reduced nitrogen species may be higher during periods of significant surface runoff. Most of the phosphorus transported in the upper Pocomoke River and Chesterville Branch is in the particulate phase.

A review of major ion and nutrient concentrations in the upper Pocomoke River and Chesterville Branch demonstrates the importance of variable topography, geology, and hydrology to stream chemistry in each watershed. In the upper Pocomoke River Watershed, runoff of precipitation over the land surface is limited by the extremely flat topography. Only 25 percent of the variability in measured stream chemistry from 1999 through 2001 is attributable to the distinction between surface runoff and base flow, and a review of long-term records suggests that 72 percent of the flow in the upper Pocomoke River is derived from ground-water discharge. Significant surface runoff in the upper Pocomoke River Watershed probably occurs when flow in the Pocomoke River near Willards, Maryland, reaches about 100 cubic feet per second, although this threshold likely varies seasonally. The primary hydrologic influence on stream chemistry in the upper Pocomoke River is the relative proportion of flow contributed from two ground-water sources. Nearly half (44 percent) of the variability in major ion and nutrient concentrations in the river is related to a distinction between ground-water discharge from the Parsonsburg and Beaverdam Sands. Concentrations of nitrate, calcium, magnesium, and other ions typical of agricultural effects in ground water of the Parsonsburg Sand are generally higher in the upper Pocomoke River when the water table is highest during the winter and spring; concentrations of iron and bicarbonate typical of ground water in the Beaverdam Sand are typically highest in the river during the drier season from June through November.

Surface runoff is more influential on water chemistry in Chesterville Branch than in the upper Pocomoke River. Nearly half (47 percent) of the variability in concentrations of major ions and nutrients in Chesterville Branch is attributable to the distinction between runoff and base flow. Significant surface runoff in the Chesterville Branch Watershed probably begins when total flow in Chesterville Branch near Crumpton, Maryland, reaches about 10 cubic feet per second. Contributions to Chesterville Branch from the Hornerstown aquifer and other confined aquifers are probably limited by the relatively small size of the Chesterville Branch Watershed and the thickness of the surficial aquifer. Most of the first-order tributaries draining the Columbia and Aquia aquifers in the Chesterville Branch Watershed are perennial.

Selected herbicides and herbicide metabolites are detectable throughout the year in both the upper Pocomoke River and Chesterville Branch, although concentrations of most compounds rarely exceed 1 microgram per liter. Analyses for pesticide metabolites may be particularly important in any efforts to compute total pesticide loads or estimate exposures to humans or aquatic ecosystems; metabolite concentrations generally far exceed those of parent compounds in both watersheds. Metabolites of acetochlor, alachlor, and

metolachlor were detected in every sample collected from the upper Pocomoke River, although parent compounds were detected less frequently. Atrazine, alachlor, metolachlor, simazine, and selected metabolites of each were also detected in every sample collected from Chesterville Branch. High detection frequencies for parent compounds as well as metabolites in Chesterville Branch probably reflect the importance of transport through both surface runoff and ground water in that watershed. Relatively low concentrations of desethylatrazine in the upper Pocomoke River suggest that sandy but poorly drained soils typical of the watershed may not favor metabolism of atrazine, or may favor the formation of hydroxyatrazine or some other metabolite.

Pesticide concentrations are typically highest in both watersheds during application periods. The relatively rapid transport from areas of application to streams suggested by this pattern may be related to shallow ground-water flow as well as surface runoff, particularly in the upper Pocomoke River Watershed, where artificial ditches intercept shallow flow paths. In the Chesterville Branch Watershed, conversely, parent compounds are probably transported primarily through surface runoff, but metabolites (particularly ESA metabolites) move primarily through ground water. Both parent compounds and metabolites may be transported to either stream during significant runoff events, however. Although in-stream concentrations of pesticides may decrease due to dilution, instantaneous loads of pesticides in both streams typically stabilize or continue to increase with increasing flow after runoff begins. Most compounds are apparently not completely flushed out of the watershed during the early stages of surface runoff. The continued transport of pesticides after the initiation of surface runoff may be related to the variable length of overland flow paths, and to the amount of pesticides in watershed soils, particularly following application periods.

Consideration of local conditions is important to agricultural and other land or water management in the Delmarva Peninsula and the wider Atlantic Coastal Plain. Although regional patterns and similarities are evident in hydrologic and geochemical conditions across the Peninsula, a review of water chemistry in the upper Pocomoke River and Chesterville Branch illustrates considerable local variability, an understanding of which may be necessary for effective resource management. Nutrient and pesticide transport occurs through both surface runoff and ground water in both watersheds. Airborne transport can also be significant for both types of compounds. A consideration of the relative importance of different transport pathways is necessary for mitigation and other management efforts designed for specific watersheds.

An understanding of local hydrology is also important to environmental studies in any watershed.   Streamflow in the upper Pocomoke River is generated from a variety of sources, including at least two aquifers with very different ground-water quality. Investigating nutrient dynamics or seasonal patterns in geochemistry, aquatic ecology, or other

environmental characteristics in such streams can be complicated by seasonally variable inputs from these sources, as well as biologic uptake and other factors. Analyses of major ions in streams can be extremely useful for interpreting watershed hydrology for environmental studies.

Ground water represents a significant reservoir of dissolved nutrients and pesticides on the Delmarva Peninsula, and likely carries a considerable load of such chemicals to the Chesapeake Bay and other receiving waters. Although confined aquifers may contain little, if any, nutrients, pesticides, or other agricultural chemicals, previous studies have documented the occurrence and persistence of these compounds in surficial aquifers on the Delmarva Peninsula. The occurrence of these compounds at detectable levels in the upper Pocomoke River and Chesterville Branch during baseflow conditions throughout the year further demonstrates that many are successfully transported in ground water through the riparian and hyporheic zone to streams. The slow movement typical of ground water and the resulting lag time between land application and delivery to streams further complicate water-resources management and mitigation strategies.

References Cited

Andres, A.S., and Howard, C.S., 2000, The Cypress Swamp Formation, Delaware: Delaware Geological Survey Report of Investigations 62, 14 p.

_____ **2002,** Results of hydrogeologic studies of the Cypress Swamp Formation, Delaware: Delaware Geological Survey Report of Investigations 64, 16 p.

Aspelin, A.L., 1997, Pesticide industry sales and usage—1994 and 1995 market estimates: U.S. Environmental Protection Agency Report 733-R-97-002, 35 p.

Ator, S.W., Denver, J.M., Krantz, D.E., Newell, W.L., and Martucci, S.K., in press, A surficial hydrogeologic framework for the Mid-Atlantic Coastal Plain: U.S. Geological Survey Professional Paper 1680.

Bachman, L.J., Krantz, D.E., and Böhlke, J.K., 2002, Hydrogeologic framework, ground-water geochemistry, and assessment of nitrogen yield from base flow in two agricultural watersheds, Kent County, Maryland: U.S. Environmental Protection Agency Report EPA/600/R-02/008, 79 p.

Bachman, L.J., Lindsey, B.D., Brakebill, J.W., and Powars, D.S., 1998, Ground-water discharge and baseflow nitrate loads of nontidal streams, and their relation to a hydrogeomorphic classification of the Chesapeake Bay watershed, Middle Atlantic Coast: U.S. Geological Survey Water-Resources Investigations Report 98–4059, 71 p.

Böhlke, J.K., and Denver, J.M., 1995, Combined use of groundwater dating, chemical, and isotopic analyses to resolve the history and fate of nitrate contamination in two agricultural watersheds, Atlantic Coastal Plain,

Maryland: Water Resources Research, v. 31, no. 9, p. 2,319–2,339.

Brakebill, J.W., and Preston, S.D., 1999, Digital data used to relate nutrient inputs to water quality in the Chesapeake Bay Watershed, Version 1.0: U.S. Geological Survey Open-File Report 99–60, available at: *http://md.water.usgs.gov/publications/ofr-99-60/ report.html*.

Bricker, O.P., Newell, W.L., and Simon, N.N., 2003, Bog iron formation in the Nassawango Watershed, Maryland: U.S. Geological Survey Open-File Report 03–346, Online only, available at *http://pubs.usgs.gov/of/2003/ of03-346*.

Capel, P.D., and Larson, S.J., 2001, Effect of scale on the behavior of atrazine in surface waters: Environmental Science and Technology, v. 35, no. 4, p. 648–657.

Capel, P.D., Larson, S.J., and Winterstein, T.A., 2001, The behaviour of 39 pesticides in surface waters as a function of scale: Hydrologic Processes, v. 15, p. 1,251–1,269.

Clark, G.M., Mueller, D.K., and Mast, M.A., 2000, Nutrient concentrations and yields in undeveloped stream basins of the United States: Journal of the American Water Resources Association, v. 36, no. 4, p. 849–860.

Conover, W.J., 1999, Practical nonparametric statistics, 3^d ed.: New York, John Wiley and Sons, Inc., 584 p.

Cushing, E.M., Kantrowitz, I.H., and Taylor, K.R., 1973, Water resources of the Delmarva Peninsula: U.S. Geological Survey Professional Paper 822, 58 p.

Denver, J.M., 1986, Hydrogeology and geochemistry in the unconfined aquifer in west-central and southwestern Delaware: Delaware Geological Survey Report of Investigations 41, 100 p.

_____ 1989, Effects of agricultural practices and septic-system effluent on the quality of water in the unconfined aquifer in parts of eastern Sussex County, Delaware: Delaware Geological Survey Report of Investigations 45, 66 p.

Denver, J.M., Ator, S.W., Debrewer, L.M., Ferrari, M.J., Barbaro, J.R., Hancock, T.C., Brayton, M.J., and Nardi, M.R., 2004, Water quality in the Delmarva Peninsula, Delaware, Maryland, and Virginia, 1999–2001: U.S. Geological Survey Circular 1228, 30 p.

Dunkle, S.A., Plummer, L.N., Busenberg, Eurybiades, Phillips, P.J., Denver, J.M., Hamilton, P.A., Michel, R.L., and Coplen, T.B., 1993, Chlorofluorocarbons (CCl_3F and CCl_2F_2) as dating tools and hydrologic tracers in shallow ground water of the Delmarva Peninsula, Atlantic Coastal Plain, United States: Water Resources Research, v. 29, n. 12, p. 3,837–3,860.

Farm Chemical Handbook, 1999: Willoughby, Ohio, Meister Publishing Company, 1,029 p.

Fuhrer, G.J., Gilliom, R.J., Hamilton, P.A., Morace, J.L., Nowell, L.H., Rinella, J.F., Stoner, J.D., and Wentz, D.A., 1999, The quality of our Nation's waters— Nutrients and pesticides: U.S. Geological Survey

Circular 1225, 82 p.

Garbarino, J.R., Bednar, A.J., Rutherford, D.W., Beyer, R.S., and Wershaw, R.L., 2003, Environmental fate of roxarsone in poultry litter, Part 1, Degradation of roxarsone during composting: Environmental Science and Technology, v. 37, no. 8, p. 1,509–1,514.

Gilliom, R.J., Alley, W.M., and Gurtz, M.E., 1995, Design of the National Water-Quality Assessment Program— Occurrence and distribution of water-quality conditions: U.S. Geological Survey Circular 1112, 33 p.

Hamilton, L.C., 1992, Regression with graphics—A second course in applied statistics: Belmont, California, Duxbury Press, 363 p.

Hamilton, P.A., Denver, J.M., Phillips, P.J., and Shedlock, R.J., 1993, Water-quality assessment of the Delmarva Peninsula, Delaware, Maryland, and Virginia—Effects of agricultural activities on, and distribution of, nitrate and other inorganic constituents in the surficial aquifer: U.S. Geological Survey Open-File Report 93–40, 87 p.

Hansen, H.J., 1992, Stratigraphy of upper Cretaceous and Tertiary sediments in a core hole drilled near Chesterville, Kent County, Maryland: Maryland Geological Survey Open-File Report 93–02–7, 38 p.

Hantush, M.M., and Marino, M.A., 2001, Analytical modeling of the influence of denitrifying sediments on nitrate transport in aquifers with sloping beds: Water Resources Research, v. 37, n. 12, p. 3,177–3,192.

Hayes, T., Haston, K., Tsui, M., Hoang, A., Haeffele, C., and Vonk, A., 2002, Feminization of male frogs in the wild: Nature, v. 419, p. 895–896.

Helsel, D.R. and Hirsch, R.M., 1992, Statistical methods in water resources: Amsterdam, Elsevier Publishers, 522 p.

Hem, J.D., 1985, Study and interpretation of the chemical characteristics of natural water: U.S. Geological Survey Water-Supply Paper 2254, 263 p.

Koterba, M.T., Banks, W.S.L., and Shedlock, R.J., 1993, Pesticides in shallow groundwater in the Delmarva Peninsula: Journal of Environmental Quality, v. 22, p. 500–518.

Larson, S.J., Capel, P.D., and Majewski, M.S., 1997, Pesticides in surface waters—Distribution, trends, and governing factors, v. 3 of Gilliom, R.J., ed., Pesticides in the hydrologic system: Chelsea, Michigan, Ann Arbor Press, 373 p.

Lee, E.A., Kish, J.L., Zimmerman, L.R., and Thurman, E.M., 2001, Methods of analysis by the U.S. Geological Survey Organic Geochemistry Research Group—Update and additions to the determination of chloroacetanilide herbicide degradation compounds in water using high-performance liquid chromatography/mass spectrometry: U.S. Geological Survey Open-File Report 01–10, 17 p.

Liu, Z.J., Weller, D.E., Correll, D.L., and Jordan, T.E., 2000, Effects of land cover and geology on stream chemistry in watersheds of Chesapeake Bay: Journal of the American Water Resources Association, v. 36, no. 6, p. 1,349–1,365.

Majewski, M.S., Foreman, W.T., Goolsby, D.A., and Nakagaki, N., 1998, Airborne pesticide residues along the Mississippi River: Environmental Science and Technology, v. 32, p. 3,689–3,698.

Martin, J.D., 2002, Variability of pesticide detections and concentrations in field replicate water samples collected for the National Water-Quality Assessment Program: U.S. Geological Survey Water-Resources Investigations Report 01-4178, 84 p.

Maryland Department of Agriculture, 1999, Maryland pesticide statistics for 1997: Maryland Department of Agriculture Report MDA-265-99, 56 p.

Maryland Department of Natural Resources, 1996, Digital orthophoto quarter quadrangle: Annapolis, Maryland, scale 1;12,000.

Miller, C.V., Denis, J.M., Ator, S.W., and Brakebill, J.W., 1997, Nutrients in streams during baseflow in selected environmental settings of the Potomac River Basin: Journal of the American Water Resources Association, v. 33, no. 6, p. 1,155–1,171.

Mueller, D.K., Martin, J.D., and Lopes, T.J., 1997, Quality-control design for surface-water sampling in the National Water-Quality Assessment Program: U.S. Geological Survey Open-File Report 97–223, 17 p.

Nowell, L.H., Capel, P.D., and Dileanis, P.D., 1999, Pesticides in stream sediment and aquatic biota— Distribution, trends, and governing factors, v. 4 of Gilliom, R.J., ed., Pesticides in the hydrologic system: Chelsea, Michigan, Ann Arbor Press, 1,001 p.

Owens, J.P., and Denny, C.S., 1978, Geologic map of Worcester County: Maryland Geological Survey, 1 sheet, scale 1:62,500.

_____ 1979, Geologic map of Wicomico County: Maryland Geological Survey, 1 sheet, scale 1:62,500.

Owens, J.P., and Minard, J.P., 1962, Pre-Quaternary geology of the Columbus Quadrangle, New Jersey: U.S. Geological Survey Geologic Quadrangle Map GQ-160, 1 sheet, scale 1:24,000.

Phillips, P.J., Wall, G.R., Thurman, E.M., Eckhardt, D.A., and Van Hoesen, J., 1999, Metolachlor and its metabolites in tile drain and stream runoff in the Canajoharie Creek Watershed: Environmental Science and Technology, v. 33, p. 3,531–3,537.

Phillips, S.W., ed., 2002, The U.S. Geological Survey and the Chesapeake Bay—The role of science in environmental restoration: U.S. Geological Survey Circular 1220, 32 p.

Phillips, S.W., and Donnelly, C.A., 2003, Upper Pocomoke Watershed, p. 50–70, in Lindsey, B.D., Phillips, S.W., Donnelly, C.A., Speiran, G.K., Plummer. L.N., Böhlke, J.K., Focazio, M.J., Burton, W.C., and Busenberg, Eurybiades, 2003, Residence times and nitrate transport in ground water discharging to streams in the Chesapeake Bay Watershed: U.S. Geological Survey Water-Resources Investigations Report 03–4035, 201 p.

Piper, A.M., 1944, A graphical procedure in the geochemical interpretation of water analyses: EOS, Transactions of the American Geophysical Union, v. 25, p. 914–923.

Pitchford, A.M., Denver, J.M., Olson, A.R., Ator, S.W., Cormier, S., Nash, M.S., and Mehaffey, M.H., 2000, Testing landscape indicators for stream condition related to pesticides and nutrients—Landscape indicators for pesticides study for Mid-Atlantic coastal streams (LIPS-MACS): U.S. Environmental Protection Agency EPA-600-R-00-087, 84 p.

Puckett, L.J., 1987, The influence of forest canopies on the chemical quality of water and the hydrologic cycle, in Averett, R.C., and McKnight, D.M., eds. Chemical quality of water and the hydrologic cycle: Chelsea, Michigan, Lewis Publishers, p. 3–22.

_____ 1995, Identifying the major sources of nutrient water pollution: Environmental Science and Technology, v. 29, no. 9, p. 408A–414A.

Ramsey, K.W., and Schenck, W.S., 1990, Geologic map of southern Delaware: Delaware Geological Survey Open-File Report 32, 1 sheet, scale 1:100,000.

Rantz, S.E. and others, 1982, Measurement and computation of streamflow: U.S. Geological Survey Water-Supply Paper 2175, 915 p.

Reilly, T.E., Plummer, L.N., Phillips, P.J., and Busenberg, Eurybiades, 1994, The use of simulation and multiple environmental tracers to quantify ground water flow in a shallow aquifer: Water Resources Research, v. 30, n. 2, p. 421–433.

Shedlock, R.J., Denver, J.M., Hayes, M.A., Hamilton, P.A., Koterba, M.T., Bachman, L.J., Phillips, P.J., and Banks, W.S.L., 1999, Water-quality assessment of the Delmarva Peninsula, Delaware, Maryland, and Virginia– Results of investigations, 1987–1991: U.S. Geological Survey Water-Supply Paper 2355-A, 41 p.

Shedlock, R.J., Hamilton, P.A., Denver, J.M., and Phillips, P.J., 1993, Multiscale approach to regional ground-water-quality assessment of the Delmarva Peninsula, in Alley, W.M., ed., Regional ground-water quality: New York, Van Nostrand Reinhold, p. 563–587.

Shelton, L.R., 1994, Field guide for collecting and processing stream-water samples for the National Water-Quality Assessment Program: U.S. Geological Survey Open-File Report 94–455, 42 p.

Sholar, C.J., and Shreve, E.A., 1988, Quality-assurance plan for the analysis of fluvial sediment by the Northeastern Region, Kentucky District Sediment Laboratory: U.S. Geological Survey Open-File Report 98–384, 20 p.

Sloto, R.A., and Crouse, M.Y., 1996, HYSEP—A computer program for streamflow hydrograph separation and analysis: U.S. Geological Survey Water-Resources Investigations Report 96–4040, 46 p.

Smith, R.A., Schwarz, G.E., and Alexander, R.B., 1997, Regional interpretation of water-quality monitoring data: Water Resources Research v. 33, no. 12, p. 2,781–2,798.

Sprague, L.A., Langland, M.J., Yochum, S.E., Edwards, R.E., Blomquist, J.D., Phillips, S.W., Shenk, G.W., and Preston, S.D., 2000, Factors affecting nutrient trends in major rivers of the Chesapeake Bay Watershed: U.S. Geological Survey Water-Resources Investigations Report 00–4218, 98 p.

U.S. Department of Agriculture, 1970, Soil survey of Wicomico County, Maryland: Soil Conservation Service, 90 p.

_____ 1999, 1997 Census of agriculture, vol. 2, Ranking of states and counties, available at *http://www.nass.usda.gov/census/*.

U.S. Geological Survey, 1950–2001, Water resources data, Maryland and Delaware, water years 1950–2001: U.S. Geological Survey Water-Data Reports MD-DE-50–MD-DE-01, [variously paged].

Vogelmann, J.E., Sohl, T.L., Campbell, P.V., and Shaw, D.M., 1998, Regional land-cover characterization using Landsat and ancillary sources: Environmental Monitoring and Assessment, v. 51, p. 415–428.

Wilde, F.D., and Radtke, D.B., 1998, Field measurements: National field manual for the collection of water-quality data: U.S. Geological Survey Techniques for Water-Resources Investigations, book 9, chap. A6, 177 p.

Wilde, F.D., Radtke, D.B., Gibs, J., and Iwatsubo, R.T., 1998, Cleaning of equipment for water sampling: National field manual for the collection of water-quality data: U.S. Geological Survey Techniques for Water-Resources Investigations, book 9, chap. A3, 70 p.

Yochum, S.E., 2000, A revised load estimation procedure for the Susquehanna, Potomac, Patuxent, and Choptank Rivers: U.S. Geological Survey Water-Resources Investigations Report 00–4156, 49 p.

Zaugg, S.D., Sandstrom, M.W., Smith, S.G., and Fehlberg, K.M., 1995, Methods of analysis by the U.S. Geological Survey National Water-Quality Laboratory—Determination of pesticides in water by C-18 solid-phase extraction and capillary-column gas chromatography/mass spectrometry with selected ion monitoring: U.S. Geological Survey Open-File Report 95–181, 49 p.

Zimmerman, L.R., Hostetler, K.A., and Thurman, E.M., 2000, Methods of analysis of the U.S. Geological Survey Organic Geochemistry Research Group—Determination of chloroacetanilide herbicide metabolites in water using high-performance liquid chromatography-diode array detection and high-performance liquid chromatography/mass spectrometry: U.S. Geological Survey Open-File Report 00–182, 28 p.