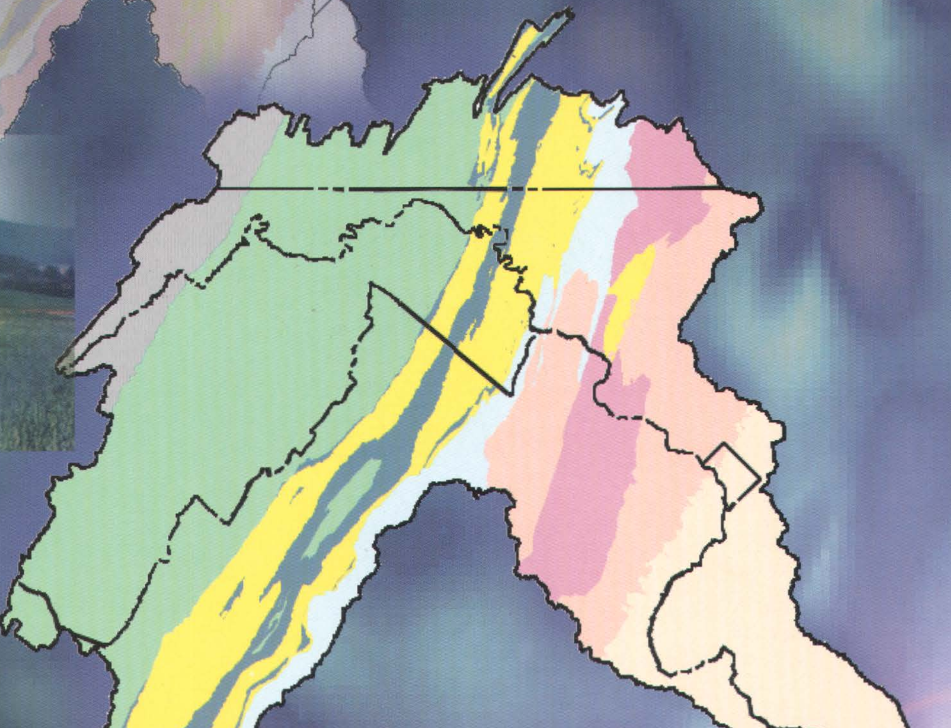
DESIGN AND IMPLEMENTATION OF A SAMPLING STRATEGY FOR A WATER-QUALITY ASSESSMENT OF THE POTOMAC RIVER BASIN



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SURVEY

WATER-RESOURCES INVESTIGATIONS REPORT 96-4034

Agencies and organizations represented on the Potomac River Basin study unit Liaison Committee.

District of Columbia Department of Consumer and Regulatory Affairs, Washington, D.C.

District of Columbia Water Resources Research Institute, University of the District of Columbia, Washington, D.C.

Interstate Commission on the Potomac River Basin, Rockville, Maryland

Johns Hopkins University, Baltimore, Maryland

Maryland Department of the Environment, Baltimore, Maryland

Maryland Department of Natural Resources, Maryland Geological Survey, Baltimore, Maryland

Maryland Water Resources Research Institute, University of Maryland, College Park, Maryland

Metropolitan Washington Council of Governments, Washington, D.C.

Pennsylvania Department of Conservation and Natural Resources, Bureau of Topographic and Geologic Survey, Harrisburg, Pennsylvania

Pennsylvania Department of Environmental Protection, Division of Assessments and Standards, Harrisburg, Pennsylvania

Pennsylvania Environmental Resources Research Institute, Pennsylvania State University, University Park, Pennsylvania

Resources For the Future, Washington, D.C.

U.S Army Corps of Engineers, Baltimore District, Baltimore, Maryland

U.S. Department of Agriculture, Agricultural Research Service, Beltsville, Maryland

U.S. Department of Agriculture, Natural Resources Conservation Service, Annapolis, Maryland

U.S. Environmental Protection Agency, Chesapeake Bay Program, Annapolis, Maryland

U.S. Environmental Protection Agency, Region III, Philadelphia, Pennsylvania

U.S. Fish and Wildlife Service, Annapolis, Maryland

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Virginia Department of Environmental Quality, Bridgewater, Virginia

Virginia Division of Mineral Resources, Charlottesville, Virginia

Virginia Water Resources Research Center, Virginia Polytechnic Institute and State University, Blacksburg, Virginia

West Virginia Department of Environmental Protection, Charleston, West Virginia

West Virginia Geological and Economic Survey, Morgantown, West Virginia

West Virginia Water Resources Institute, West Virginia University, Morgantown, West Virginia

DESIGN AND IMPLEMENTATION OF A SAMPLING STRATEGY FOR A WATER-QUALITY ASSESSMENT OF THE POTOMAC RIVER BASIN

By James M. Gerhart and John W. Brakebill

U.S. GEOLOGICAL SURVEY

Water-Resources Investigations Report 96-4034
Baltimore, Maryland
1996

U.S. DEPARTMENT OF THE INTERIOR
BRUCE BABBITT, Secretary
U.S. GEOLOGICAL SURVEY
Gordon P. Eaton, Director

For additional information write to:

District Chief
U.S. Geological Survey, WRD
8987 Yellow Brick Road
Baltimore, Md. 21237

Copies of this report can be purchased from:

U.S. Geological Survey
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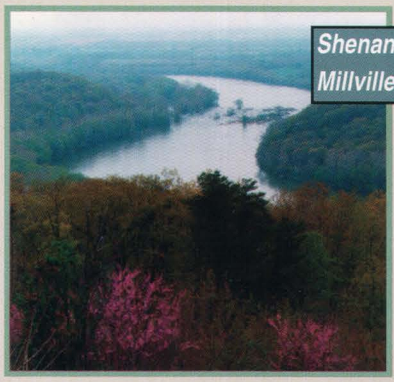
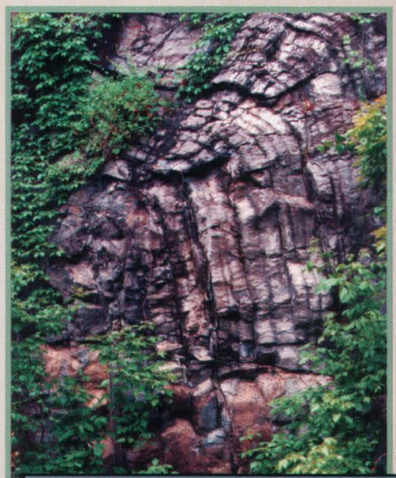
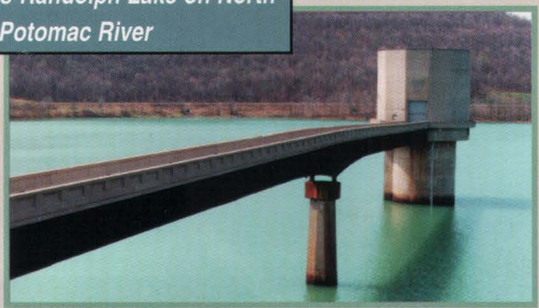


Shenandoah River overlook near Millville, West Virginia



Folded limestone near Front Royal, Virginia



Jennings-Randolph Lake on North Branch Potomac River

INTRODUCTION

In 1991, the U.S. Geological Survey (USGS) began a comprehensive assessment of water-quality conditions in the Potomac River Basin as part of the National Water-Quality Assessment (NAWQA) Program. Water quality in the Potomac River Basin has been extensively monitored, studied, and assessed for most of the last century. The majority of these studies have focused on specific aspects of water quality in selected areas of the basin. The assessment of water quality in the Potomac River Basin by the NAWQA program is designed to be more comprehensive than the scope of these previous studies. The NAWQA design includes physical and chemical aspects of surface-water and ground-water quality as well as the biological aspects of surface-water quality in the entire basin. A sampling strategy that meets the goals of the NAWQA program while answering specific water-quality related questions is the first step in a long-term comprehensive water-quality assessment of the Potomac River Basin.

In order to enhance the exchange of information about water-quality issues of regional and local interest in the Potomac River Basin, a liaison committee consisting of representatives who have water-resources responsibilities from Federal, State, and local agencies, universities, and the private sector was established. This committee assisted in the scope and design of study products and the review of planning documents and reports. A complete list of agencies and organizations represented on the Potomac River Basin liaison committee is provided on the inside cover of this report.

NATIONAL WATER-QUALITY ASSESSMENT PROGRAM

The NAWQA program was developed to address important questions about the Nation's water quality, including:

(1) What is the quality of the Nation's water?
(2) Is water quality getting better or worse?
(3) Have water-quality programs in the past resulted in significant water-quality improvements?

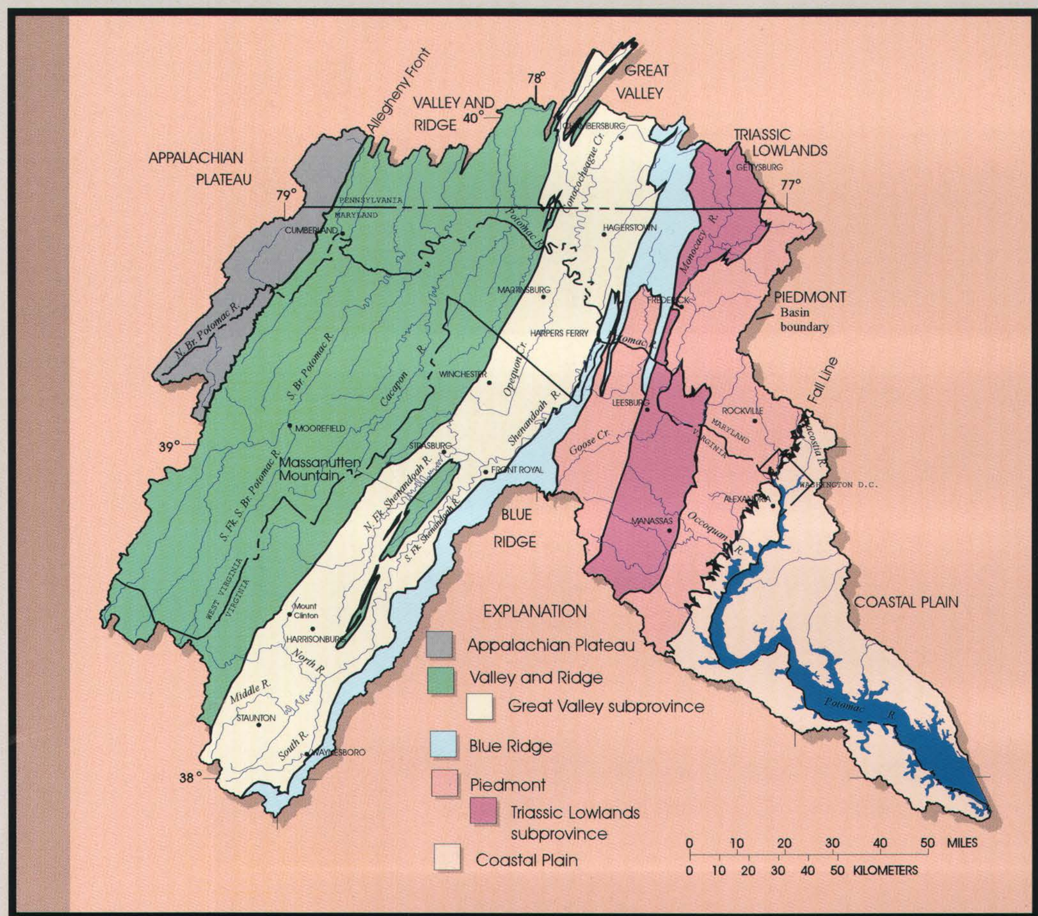
The NAWQA program began in 1986 with the establishment of seven pilot study units. In 1991, 20 study units were selected to begin. When fully implemented in 1997, the NAWQA program will consist of 60 study units conducted on a rotational basis investigating major river basins and aquifer systems that will account for about one-half of the Nation's land area and two-thirds of the Nation's water use and population. Each study unit will have a design that addresses the major water-quality issues and yields a comprehensive assessment of water quality within the study unit. In addition, because of the use of similar study-unit designs and standard data-collection proto-


Great Falls

cols, results from all 60 study units can be aggregated into a national assessment of water-quality conditions.

The goals of the NAWQA program and each study unit are to:
(1) Describe current water-quality conditions in surface and ground water;
(2) Define long-term trends in surface-water and ground-water quality; and
(3) Identify, describe, and explain the major natural and human factors affecting the observed water-quality conditions and trends.

1 Physiographic provinces and subprovinces in the Potomac River Basin.



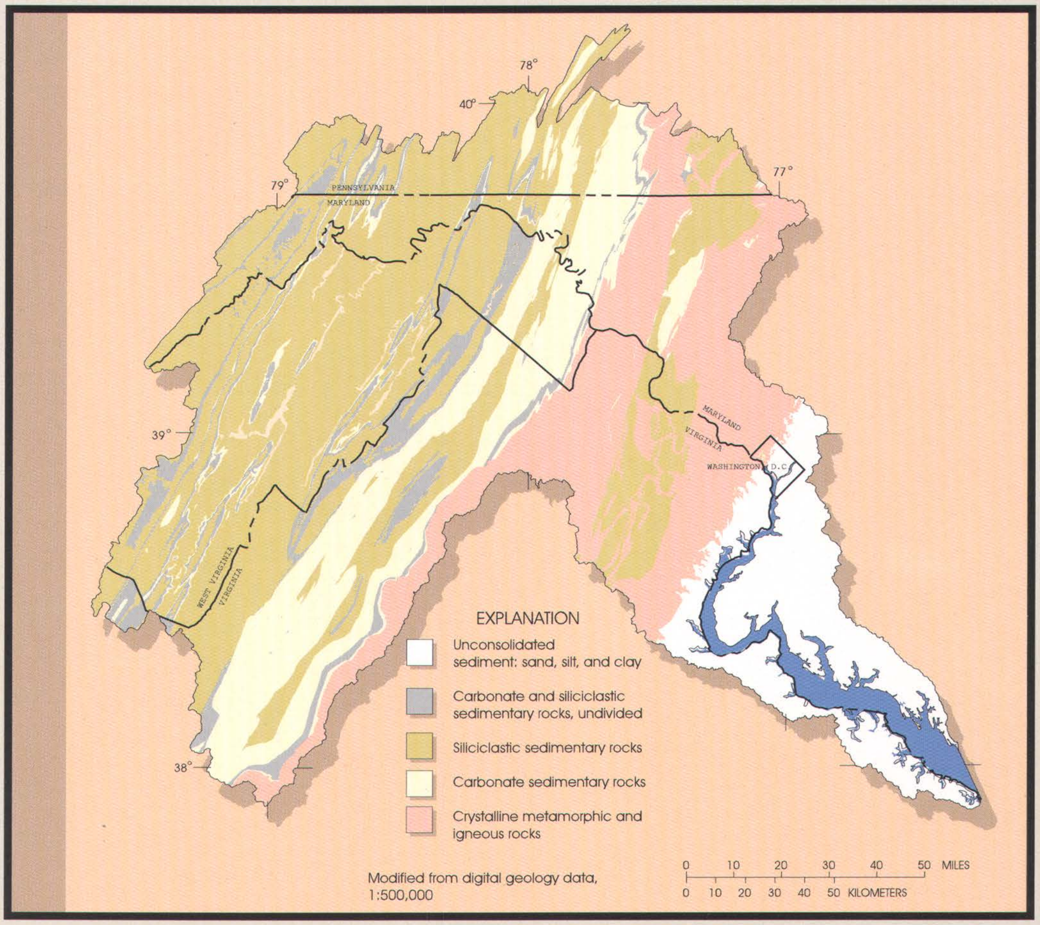
Activities in each NAWQA study unit are organized around four major components:
(1) Retrospective analysis of existing water-quality data to discover the strengths and weaknesses of available data, and to set priorities for study-unit data collection;
(2) Occurrence and distribution assessment of water-quality conditions by sampling surface and ground water, and evaluation of sampling results in relation to natural and human factors affecting those conditions;
(3) Long-term trend and change assessment based on a strategy derived from the results of the retrospective analysis and the occurrence and distribution assessment, and using ancillary information about changes in the factors affecting water-quality conditions; and
(4) Case studies of sources, transport, fate, and effects of selected contaminants to address important questions about the processes controlling water-quality conditions.

The first 6 years of each study unit, known as the first intensive phase, focuses on the retrospective analysis and the occurrence-and-distribution components. It is designed to address some of the high-priority water-quality issues affecting the basin. Following some initial study-unit planning, analysis of existing water-quality data is conducted to help guide the design of the first intensive phase, followed by a 3-year period of increased emphasis on sampling and analysis. Water-quality data resulting from these sampling activities are interpreted between field sampling seasons and related to possible natural and human factors affecting water-quality conditions. Summary reports conclude the first intensive phase of the study unit, followed by activities with a lesser emphasis on sampling. The second intensive phase of the study unit is scheduled to begin in 2001.

Nitrogen, phosphorus, and pesticides are the focus of special attention for the first 20 study units, including the Potomac River Basin study unit which began its first intensive phase in 1991. The NAWQA program has identified these compounds as high-priority water-quality issues for which national assessment is needed and they are the emphasis of the sampling approaches for the first 20 study units. In order to answer important questions about nitrogen, phosphorus, and pesticides in the Nation's water resources, information generated in the retrospective-analysis and occurrence-and-distribution components of the first 20 study units will be synthesized into a national assessment.

PURPOSE AND SCOPE

The purpose of this report is to describe the water-quality sampling strategy designed to meet the objectives of the first intensive phase of the Potomac River Basin study unit of the NAWQA program. This report also describes the design considerations that guided the development of the sampling strategy. The water-quality sampling strategy, developed during late 1991 and early 1992, was implemented from August 1992 through September 1995. The strategy consist of surface-water, ground-water, and biological sampling approaches applied on basin-wide, intermediate, and small scales, and addresses spatial and temporal aspects of water-quality conditions. Information for each sampling approach includes objectives, site-selection criteria, number of sites, types of samples collected, general sample-collection methods, sampling frequency, characteristics measured, laboratory analytes, and the contribution of the sampling approach to an integrated water-quality assessment. More specific information about sample-collection methods is available in other publications, some of which are listed at the end of this report.



2 General geology in the Potomac River Basin.

DESCRIPTION OF THE POTOMAC RIVER BASIN STUDY UNIT

The Potomac River Basin encompasses 14,670 square miles in four states and the District of Columbia (Virginia 5,723 square miles, Maryland 3,818 square miles, West Virginia 3,490 square miles, Pennsylvania 1,570 square miles, District of Columbia 69 square miles). Major population centers include Alexandria, Front Royal, Harrisonburg, and Winchester, Va.; Cumberland, Frederick, and Hagerstown, Md.; Harpers Ferry and Martinsburg, W.Va.; Gettysburg and Chambersburg, Pa.; and Washington, D.C. About 75 percent of the basin's 1990 population lived in the Washington, D.C., metropolitan area.

3 **Streamflow characteristics for selected major streams**

Stream name	Location of stream gage	Drainage area, in square miles	Mean-annual streamflow, in million gallons per day	Mean-annual runoff, in inches per year
North Branch Potomac River[1]	Cumberland, Md.	875	830	19.94
South Branch Potomac River	Springfield, W. Va.	1,471	855	12.22
Conococheague Creek	Fairview, Md.	494	382	16.29
Shenandoah River	Millville, W. Va.	3,040	1,757	12.15
Monocacy River	Frederick, Md.	817	607	15.62
Potomac River	Washington, D.C.	11,560	7,737	14.06

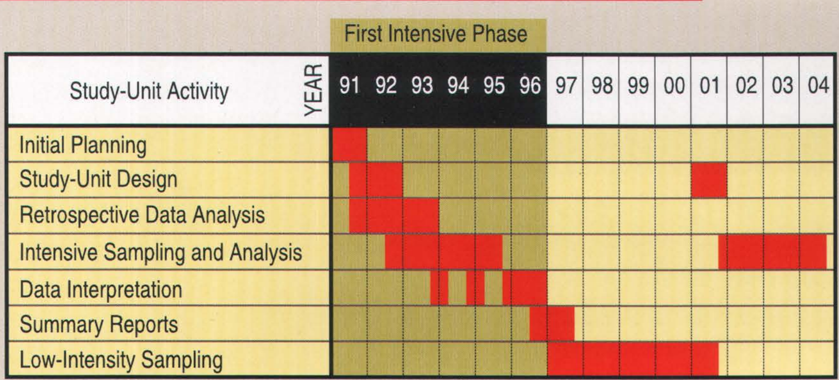
1 Streamflow regulated since 1982.

Water withdrawals from basin streams and aquifers for human purposes averaged about 5.7 billion gallons per day in 1985, about 74 percent of the average daily flow of the Potomac River at Washington, D.C. More than 95 percent of all withdrawals were from streams, with most of the water being used for power generation. Withdrawals for public water supply were about 570 million gallons per day. Ground water supplied about 58 million gallons for domestic use.

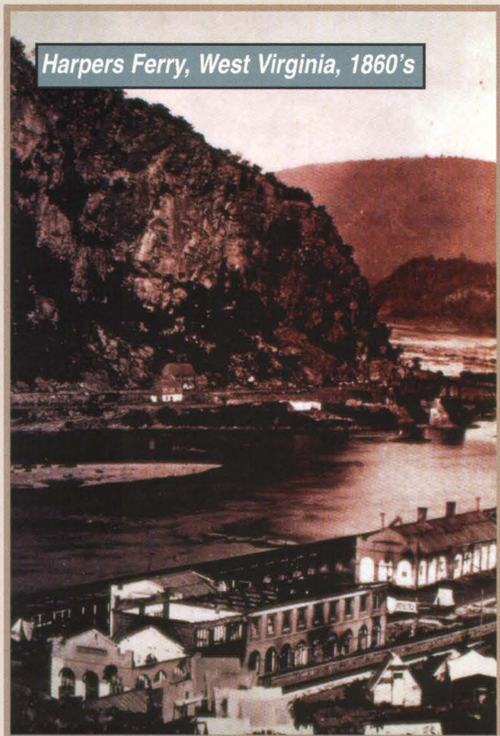
Forest and agriculture are the dominant land uses in the basin. In 1985, 52 percent of the basin was forested, 32 percent was used for agriculture, 12 percent was urban, and 4 percent was for miscellaneous uses.

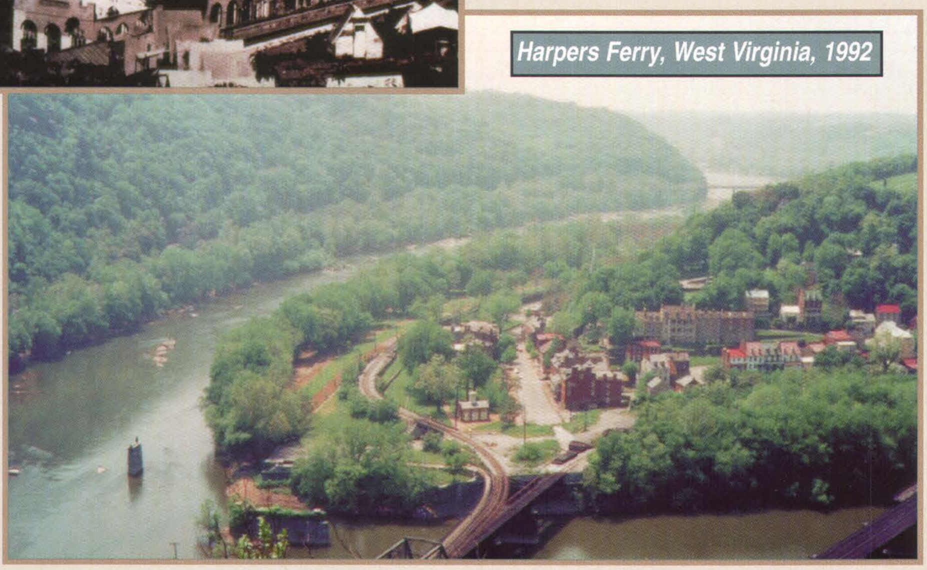
Seven physiographic provinces and subprovinces--the Appalachian Plateau, Valley and Ridge, Great Valley, Blue Ridge, Piedmont, Triassic Lowlands, and Coastal Plain--are included in the Potomac River Basin. Many of the differences among physiographic settings are related to geology. Four major types of rock are present in the basin: siliciclastic sedimentary (shale and sandstone), carbonate sedimentary (limestone and dolomite), crystalline metamorphic and igneous (gneiss, schist, and diabase dikes), and unconsolidated sediments (sand, silt, and clay). Where settings are underlain by bedrock, the bedrock is covered by a mantle of weathered rock material, called regolith.

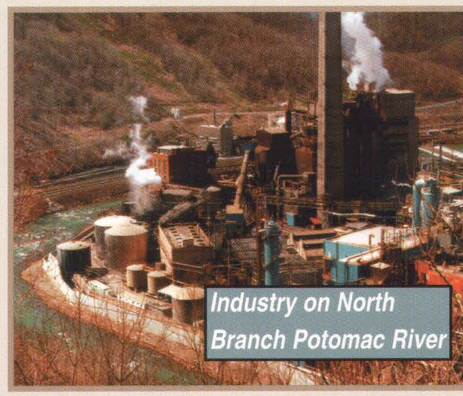
The long-term average flow of the Potomac River at Washington, D.C., is about 7.7 billion gallons per day, which accounts for about 15 percent of the freshwater inflow to the Chesapeake Bay. The Potomac River is fresh and free-flowing from its headwaters to just upstream from Washington, D.C., where it becomes tidally influenced. Downstream from Washington, D.C., near Indian Head, Md., the river becomes brackish and from there its salinity gradually increases until it flows into the Chesapeake Bay. Average-annual runoff differs among the major tributaries in the Potomac River Basin--the



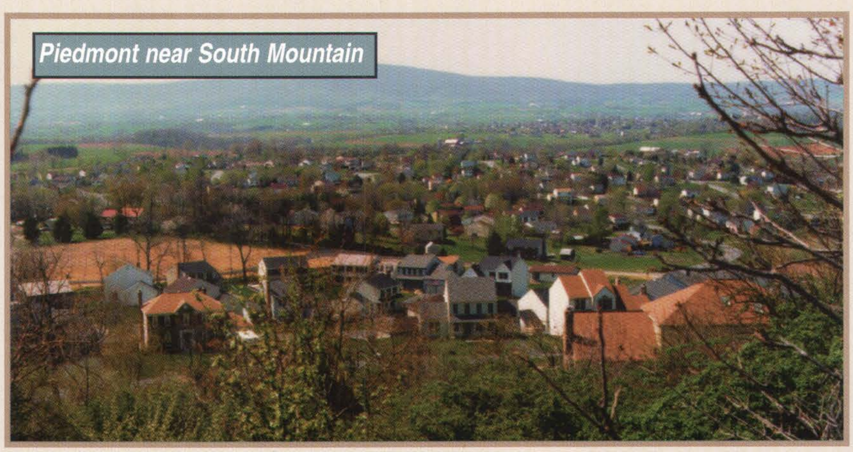
4 **General Study-Unit Schedule**


Harpers Ferry, West Virginia, 1860's


Harpers Ferry, West Virginia, 1992


Industry on North Branch Potomac River

North Branch Potomac, South Branch Potomac, Shenandoah, and Monocacy Rivers, and Conococheague Creek--and ranges from about 12 to 20 inches per year. About one-half of the runoff in the basin is contributed by ground-water inflow to streams. Ground water is present in fractures in bedrock and in pore spaces in unconsolidated sediments and regolith; the most productive aquifers are in the carbonate bedrock and the unconsolidated sediments.

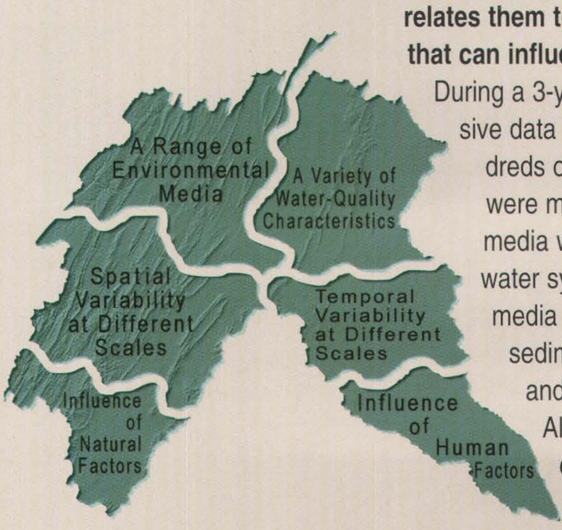

Piedmont near South Mountain

Water quality in the Potomac River Basin can be affected by a wide variety of human activities. Coal mining, sewage-treatment-plant effluent, urban runoff, agricultural runoff, industrial discharges, atmospheric deposition, and septic systems are just some of the possible causes of water-quality problems in the basin. These activities have led to elevated levels of acidity, sediment, bacteria, pesticides, nitrogen, phosphorus, metals, and other potentially harmful contaminants in streams and ground water in parts of the Potomac River Basin. As a result, some uses of the basin's water resources, such as water supply, fishing, and recreation, have been impaired in parts of the basin.

DESIGN CONSIDERATIONS

AN INTEGRATED ASSESSMENT

An integrated water-quality assessment addresses a broad array of water-quality properties in several environmental media at various spatial and temporal scales and relates them to natural and human factors that can influence the quality of water. During a 3-year period (1992-95) of intensive data collection and analysis, hundreds of water-quality characteristics were measured in five environmental media within surface-water and ground-water systems. Sampled surface-water media include streamwater, streambed sediments, aquatic biological tissues, and aquatic biological communities. Also, ground-water samples were collected from wells.



These data can be analyzed in various combinations and interpreted in relation to natural and human factors to develop a preliminary integrated water-quality assessment for the Potomac River Basin. This first intensive phase represented the initial step toward an integrated water-quality assessment. Subsequent phases of the study unit will expand and complete the integrated assessment. In addition, data from 60 NAWQA study units with similar integrated designs can be combined to form regional and national assessments.

A variety of water-quality properties, including physical, chemical, and biological characteristics, were measured during the first intensive phase of the study unit. Physical characteristics included streamflow, water temperature, sediment grain size, ground-water levels, and other characteristics that aid in the interpretation of water-quality data. Chemical characteristics included pH, dissolved oxygen, and concentrations of a broad range of chemical compounds including the nationally important compounds of nitrogen, phosphorus, and pesticides. Biological characteristics included the quantitative description of fish, benthic-invertebrate, and algae communities in streams and descriptions of stream habitat.

Water-quality characteristics were measured at different spatial and temporal scales. Surface-water-quality characteristics were measured in large major tributaries and the Potomac River (draining thousands of square miles), and in intermediate and small streams (draining hundreds to tens of square miles). Water-quality characteristics in surface water were measured at a variety of sampling frequencies ranging from single synoptic samplings to repetitive weekly samplings. Ground-water-quality characteristics were measured in widely dispersed wells distributed over large areas (hundreds of square miles) and in closely spaced wells distributed over small study sites (hundreds of acres). Ground-water sampling frequency ranged from single samples to several samples per season.

The interpretation of water-quality data and the natural and human factors that can influence the quality of water completes the integrated assessment. Natural factors used to interpret water-quality data in the first intensive phase of the study unit included physiography, geology, climate, and hydrology. Human factors included municipal, industrial, and commercial point-source discharges to streams and nonpoint sources related to urban, agricultural, and forested land use and land cover.

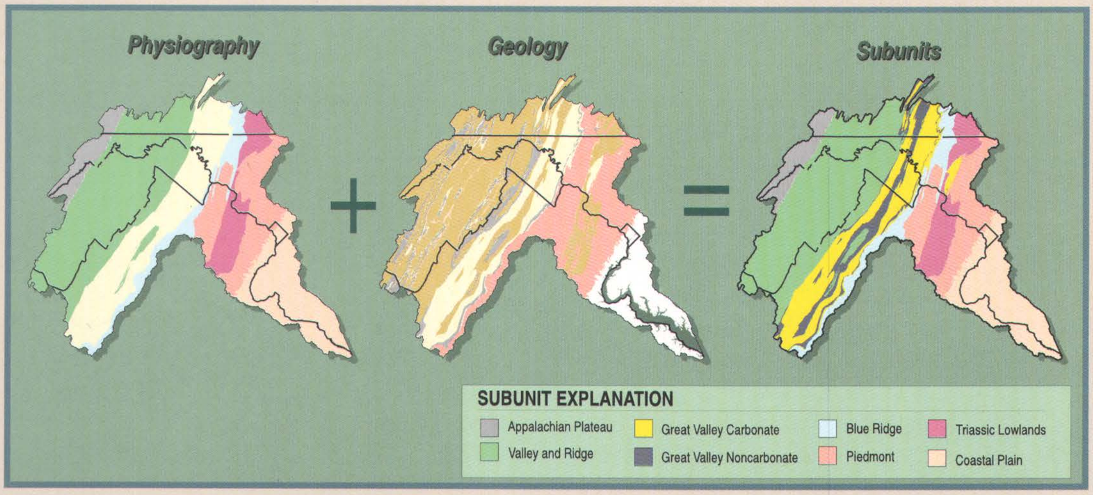
SUBDIVISION AND PRIORITIZATION

The environmental setting of the Potomac River Basin is very complex because of the many diverse natural and human factors present in the basin. These factors, in various combinations in different parts of the basin, are the principal influences on water quality. Their relative influence on water quality must be understood to assess the water quality in the basin. The natural and human factors that are responsible for most of the water-quality variability throughout the Potomac River Basin were identified and used to develop a framework within which to assess the water quality in the basin. In this process, sometimes referred to as "stratification", the geographic distribution of the most influential natural and human factors was used to subdivide the basin into major subareas having relatively distinct environmental settings consisting of relatively homogeneous combinations of natural and human factors, and therefore relatively similar water quality.

Physiography and geology were determined to be the two most influential natural factors affecting water quality in the basin. Differences in physiography across the basin, partly the result of geology, affect water quality primarily through topographic characteristics such as altitude, relief, and slope. The primary geologic factor that influences water quality is the type of rock. Different types of rock have different effects on water quality, primarily resulting from differences in chemical composition of the rocks and their hydrologic characteristics.

The Potomac River Basin was subdivided into eight major subunits based on the geographic distribution of physiographic and geologic characteristics in the basin. Because physiography is partly the result of geology, it is not surprising that the resulting distribution of subunits closely resembles the distribution of physiographic provinces and subprovinces. Six of the subunits—the Appalachian Plateau, Valley and Ridge, Blue Ridge, Piedmont, Triassic Lowlands, and Coastal Plain—were delineated solely on physiography. Differences in type of rock were considered to be important enough in the Great Valley physiographic subprovince to further

5 **Combining physiography and geology resulted in 8 subunits used in the first intensive phase.**



6 Selected information about subunits

Subunit	Area, in square miles	1990 population, in thousands	Dominant type of rock	Major land use, in percentage of subunit area[1] Forest	Agriculture	Urban
Appalachian Plateau	660	35	Siliciclastic sedimentary	82	13	2
Valley and Ridge	5,054	187	Siliciclastic sedimentary	80	18	1
Great Valley Carbonate	2,216	498	Carbonate sedimentary	15	74	11
Great Valley Noncarbonate	929	141	Siliciclastic sedimentary	39	52	8
Blue Ridge	918	67	Crystalline metamorphic	78	17	4
Piedmont	1,770	1,697	Crystalline metamorphic	24	48	27
Triassic Lowlands	1,018	347	Siliciclastic sedimentary	21	64	14
Coastal Plain	2,105	1,699	Unconsolidated sediments	36	16	23

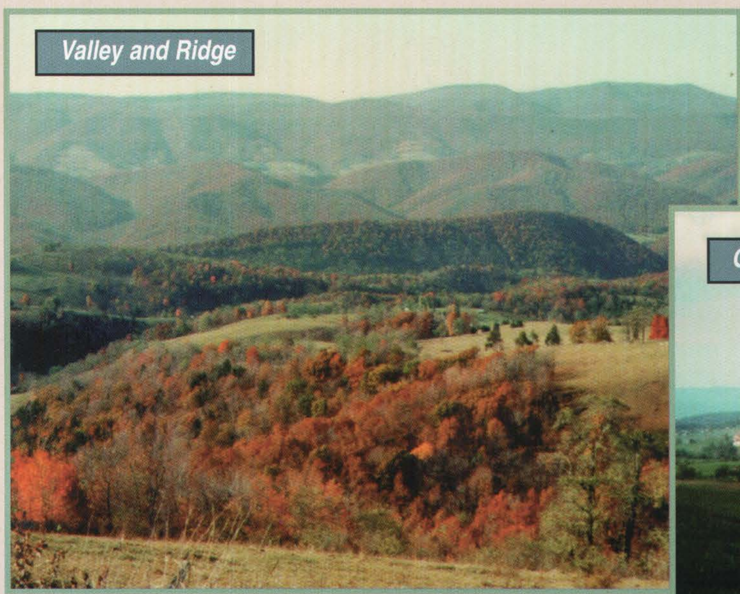
[1]From mid-1970's land-use data. Urban areas updated using 1990 census data.

High-priority subunit for first intensive phase — Targeted land use within high-priority subunit

subdivide that subprovince into carbonate and noncarbonate subunits. The eight resulting subunits are used in the first intensive phase of the study unit as the primary framework for the assessment of water quality in the basin, and they form the basis for much of the water-quality sampling strategy that is described later.

As a result of the subdivision process, each of the eight subunits is characterized by a relatively distinct combination of physiography and type of rock that is expected to result in a relatively distinct natural water-quality signature. The Appalachian Plateau subunit is characterized by narrow valleys, steep ridges, and high local relief, and is underlain primarily by sandstone and shale. The Valley and Ridge subunit, the largest subunit in the basin, is characterized by long narrow valleys underlain by limestone, dolomite, and shale, and steep ridges capped by more resistant sandstone. An outlier of the Valley and Ridge subunit, Massanutten Mountain, is located south of Strasburg, Va., in the adjacent Great Valley subprovince. The Great Valley Carbonate subunit and the Great Valley Noncarbonate subunit are both located in the broad, flat Great Valley subprovince, but are underlain by limestone and dolomite, and shale, respectively. An outlier of the Great Valley Carbonate subunit is located in the Piedmont Province near Frederick, Md. Characterized by a fairly continuous, high, narrow ridge, the Blue Ridge subunit is underlain by metamorphosed volcanic and other crystalline rocks. Gently rolling hills and moderate to low relief characterize both the Piedmont and Triassic Lowlands subunits, with the primary natural difference between the two subunits being the type of rock. The Piedmont subunit is underlain by schist, gneiss, and other crystalline metamorphic rocks, whereas the Triassic Lowlands subunit is underlain mostly by sandstone and shale. The final subunit, the relatively flat Coastal Plain, is underlain by a gently sloping series of unconsolidated sand, silt, and clay units.

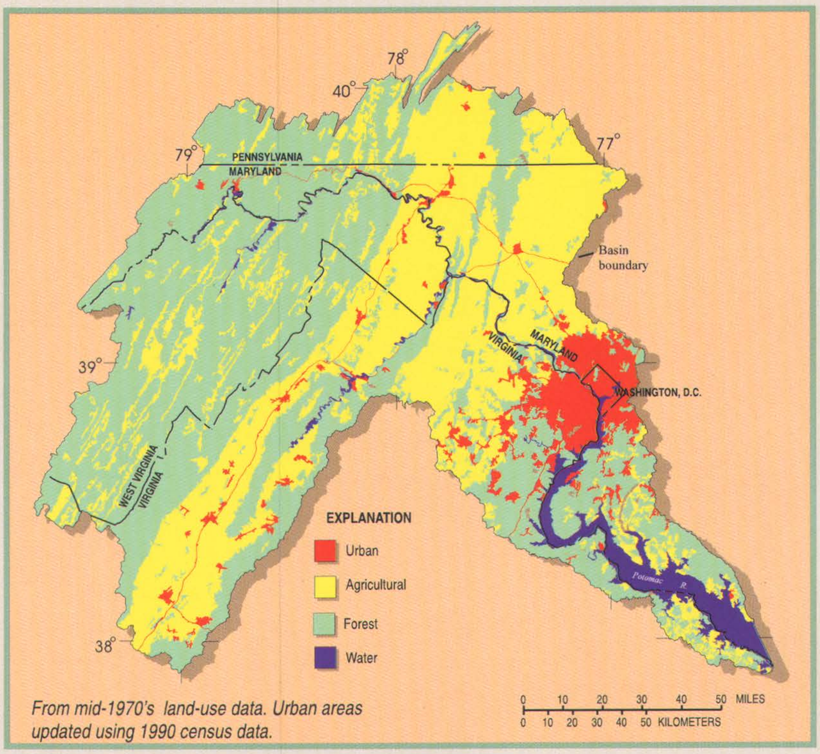
Land use was considered to be the most influential human factor affecting water quality in the basin. The natural water-quality signature in each of the eight subunits, determined primarily by physiography and type of rock, is overwritten by the signature of the major land uses in each subunit. The geo-


Valley and Ridge


Great Valley

graphic distribution of forested, agricultural, and urban land uses within each subunit was used to further subdivide each subunit into three smaller subareas, resulting in 24 combinations of physiography and rock type (eight subunits) and land use (three major land uses). Most of the water-quality differences in the Potomac River Basin are expected to be related to the physiographic, rock-type, and land-use differences inherent in these 24 subareas.

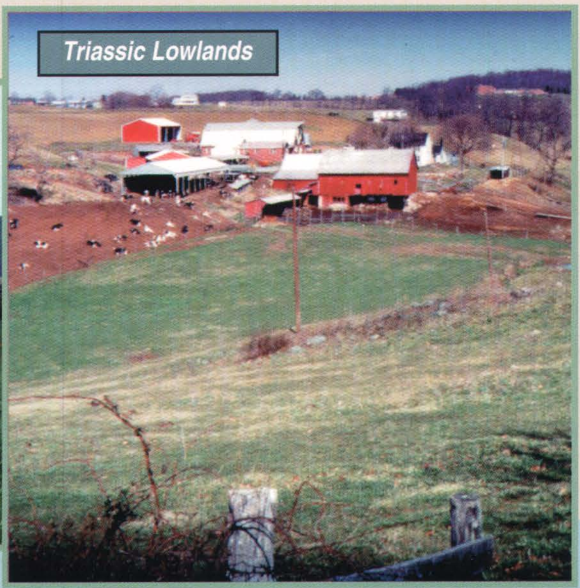
Subunits and land uses within subunits were prioritized for water-quality assessment in the first intensive phase of the study unit. The prioritization was made based upon recommendations of the study-unit liaison committee, which consisted of representatives from 25 Federal, State, and regional agencies and universities. Key factors considered in this prioritization were the distribution of population and land use within subunits, and the results of retrospective analysis of existing data in order to focus study-unit resources in the parts of the basin with the most relevance to overall water quality in the basin. Four of the eight subunits—Valley and Ridge, Great Valley Carbonate, Piedmont, and Triassic Lowlands—were selected for emphasis in the first intensive phase of the study unit. These four high-priority subunits encompass nearly 60 percent of the basin population and 70 percent of the basin area. Agricultural land use was targeted in all four high-priority subunits while urban land use was targeted in the Great Valley Carbonate, Piedmont, and Triassic Lowlands. Forest land use was targeted in the Valley and Ridge subunit as forest covers about 80 percent of this largest subunit.



From mid-1970's land-use data. Urban areas updated using 1990 census data.

7 **Major land uses in the Potomac River Basin**

Subsequent intensive phases of the study unit will address the remaining subunits and land uses in more detail. The heavily populated Coastal Plain subunit was not emphasized in the first intensive phase because of resource constraints. The Coastal Plain subunit contains the Potomac River estuary and those reaches of the basin's streams that are tidally influenced. Because the Coastal Plain was not selected as a high-priority subunit, the sampling strategy for the first intensive phase focused on the fresh, nontidal water resources of the basin, in the areas generally north and west of Washington, D.C.



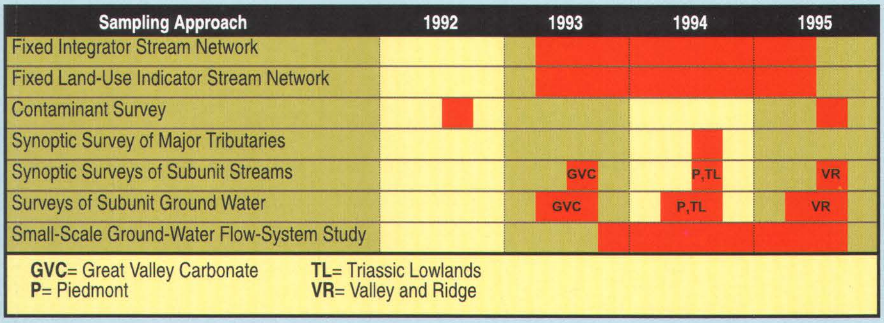
SAMPLING STRATEGY: OVERVIEW OF SAMPLING APPROACHES

Seven sampling approaches comprise the water-quality sampling strategy in the first intensive phase of the Potomac River Basin study unit. Five of the sampling approaches address surface-water resources and two address ground-water resources. Each approach involves the measurement of a set of water-quality characteristics in one or more environmental media at one or more spatial and temporal scales.

The seven sampling approaches were conducted during 1992-95. Three of the approaches—fixed integrator stream network, fixed land-use indicator stream network, and small-scale ground-water flow-system study—were conducted continuously over periods of 2 years or more. The term "fixed" refers to stream sampling sites which are

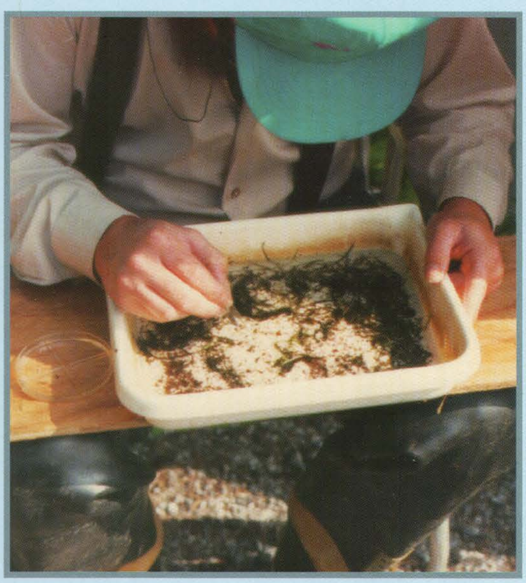
Sampling approach	Number of sampling sites	Water-quality characteristics and environmental media	Spatial scale	Temporal scale
Fixed Integrator Stream Network	6	Field measurements and chemical concentrations in water; fish, benthic- invertebrate, and algae communities; stream habitat.	Large streams	Monthly
Fixed Land-Use Indicator Stream Network	5	Field measurements and chemical concentrations in water; fish, benthic-invertebrate, and algae communities; stream habitat.	Intermediate and small streams	Weekly to monthly
Contaminant Survey	26	Concentrations of contaminants in streambed sediments and aquatic biological tissues.	Large, intermediate, and small streams	One time
Synoptic Survey of Major Tributaries	23	Field measurements and chemical concentrations in water.	Large and intermediate streams	One time
Synoptic Surveys of Subunit Streams	12 - 27 *depending on subunit*	Field measurements and chemical concentrations in water; benthic-invertebrate and algae communities; stream habitat.	Small streams	One time
Surveys of Subunit Ground Water	23 - 29 *depending on subunit*	Field measurements and chemical concentrations in water.	Subunits	One time
Small-Scale Ground-Water Flow-System Study	29	Field measurements and chemical concentrations in water.	Small flow system	1-10 samples over one year

8 General information about sampling approaches geographically "fixed" and are routinely sampled over long periods of time for a broad range of chemical constituents, ecological surveys, and continuous streamflow. These sampling sites form the basis for long-term trend, transport, and integrated physical, chemical, and biological studies within and among the different cycles of the NAWQA program.



9 **General schedule for sampling approaches**

The other four approaches—contaminant survey, synoptic survey of major tributaries, synoptic surveys of subunit streams, and surveys of subunit ground water—were one-time sampling events conducted over periods of several weeks to months. The four approaches that were conducted over shorter time periods were completed primarily between late spring and late summer when nitrogen, phosphorus, and pesticides, the compounds selected for special attention by the NAWQA program, were expected to be at their highest concentrations in basin water resources. The synoptic surveys of subunit streams and the surveys of subunit ground water were scheduled for the same time in each of the four high-priority subunits, so that the sampling results could be compared within subunits with more confidence.



SAMPLING STRATEGY: FIXED INTEGRATOR STREAM NETWORK

Objectives of the Fixed Integrator Stream Network

Determine occurrence and spatial and temporal distribution of basic chemical compounds and biological communities in large streams.

Relate stream chemistry and biological communities to land use and other factors.

Estimate amounts of nitrogen and phosphorus that are transported by large tributary streams and the Potomac River.

Brief Description of the Fixed Integrator Stream Network

Sites: *Five large tributary stream sites and one site on the Potomac River.*

Schedule: *Each site sampled monthly for streamwater and annually for biological communities. Streamwater also sampled during selected high-streamflow events. Sampled spring 1993 through spring 1995.*

Streamwater: *Field measurements, suspended sediment, major ions, nitrogen, phosphorus, and organic carbon in width- and depth-integrated samples collected during different flow conditions; pesticide samples at one site.*

Biological Communities: *Fish, benthic-invertebrate, and algae communities and stream habitat description in stream reaches averaging 700 feet in length.*

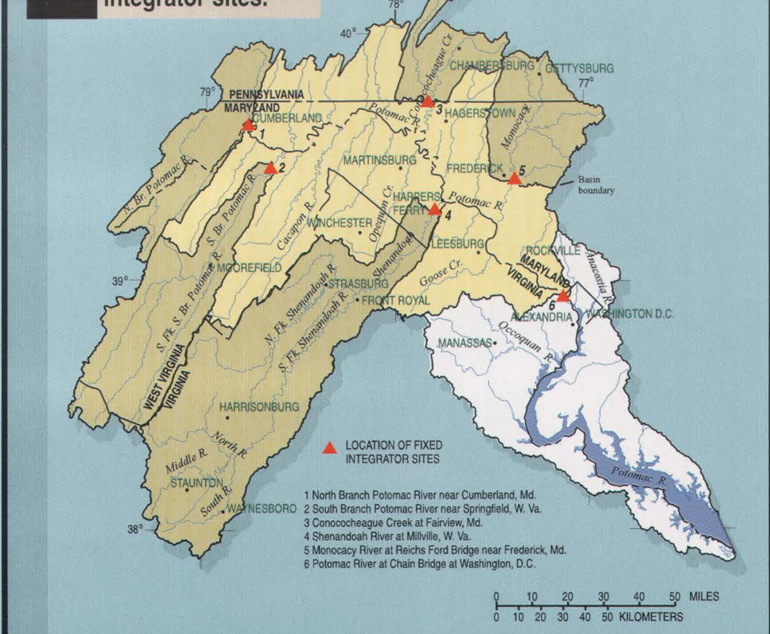
Integrator stream sites drain large areas and represent the combined effects of all natural and human water-quality factors in the watersheds they drain. Streamwater samples from an integrator stream site contain an aggregate of all dissolved chemical compounds transported from throughout the site's drainage area. Biological communities at an integrator stream site also are influenced by the composite effect of all the factors present in the drainage area. For these reasons, sampling of streamwater and biological communities at key integrator stream sites in a river basin provides a measure of overall surface-water quality for the basin.

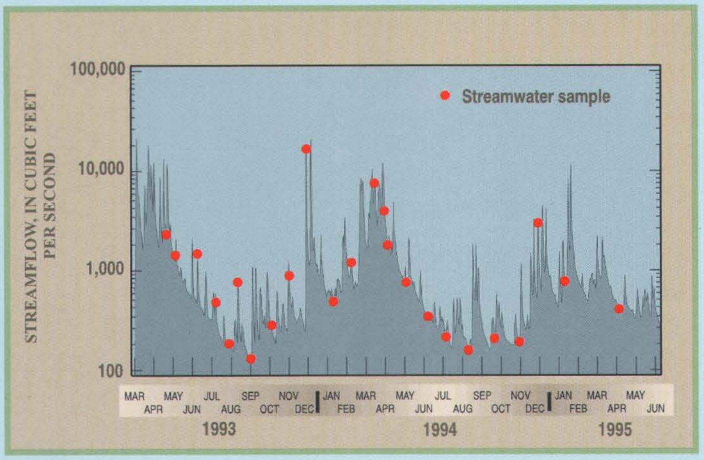
The principal objectives of the fixed integrator stream network are to determine the occurrence of basic chemical compounds and biological communities in important large streams in the Potomac River Basin, including the Potomac River, and determine how the compounds and communities are spatially and temporally distributed. A secondary objective is to relate basic stream chemistry and biological communities to land use and other natural and human factors. Finally, an objective that is important because of its relevance to the Chesapeake Bay as well as the NAWQA program is the estimation of the amounts of nitrogen and phosphorus that are transported by large tributary streams and the Potomac River.

Six fixed integrator stream sites were selected for water-quality sampling in this approach. Five of the sites are near the mouths of major tributaries and one is on the Potomac River; all six coincide with long-term USGS stream-gaging stations. The five major basin tributaries that are included in this sampling approach are the North Branch Potomac River, South Branch Potomac River, Conococheague Creek, Shenandoah River, and Monocacy River. The site on the Potomac River is located near the western boundary of Washington, D.C., and drains 11,560 square miles, including the drainage areas of the other five integrator stream sites. These sites were selected on the basis of their large drainage areas, their integration of multiple land uses, their inclusion of all basin subunits west of Washington, D.C., and their relative importance to water quality in the basin.

Water-quality sampling at the six fixed integrator stream sites for the first intensive phase of the study unit began in the spring of 1993 and ended in the spring of 1995, a period of about 25 months. Streamwater samples were routinely collected at each site on an approximately monthly schedule. In addition, several samples were collected each year during various high-

10 **Location of fixed integrator sites.**





11 **Sampling frequency at the Monocacy River fixed integrator site.**

streamflow conditions because concentrations and the transport of contaminants are often greatest during these events. Streamwater-sampling frequency at the Shenandoah River integrator site was increased to once every 2 weeks during the 1993 growing season as part of a more detailed assessment of stream quality in the Great Valley Carbonate subunit. Other studies have shown that agricultural chemicals are transported mostly during the growing season. Sampling of biological communities was conducted annually at each site, except at the Potomac River site where river conditions did

not allow community sampling.

Streamwater samples were collected by use of cross-sectionally-integrated methods. These methods composite samples from many points across the stream and from the water surface to the streambed, assuring that the sample is truly representative of the average flowing streamwater. Most samples were collected from bridges at the sites because of the depth of these large streams, especially during high streamflow conditions. All streamwater samples were collected using sampling equipment constructed from inert materials and by use of clean-sampling protocols that ensured no contaminants were introduced during sampling and handling. Measurements of water temperature, pH, specific conductance, dissolved oxygen, and alkalinity were done in the field. Samples were then processed in the field and shipped to the USGS National Water-Quality Laboratory (NWQL) in Arvada, Colo., for analysis. Laboratory analytes included suspended sediment, major ions, nitrogen, phosphorus, and organic carbon. Samples from the Shenandoah River integrator site also were analyzed for selected pesticides during the 1993 growing season.

Biological communities--benthic-invertebrate, algae, and fish--serve as indicators of the quality of water in which they live, complementing physical and chemical data collected at each site. Stream habitat was described in detail at each site to provide baseline data on environmental setting and to help identify limiting physical factors for biological communities. Community samples were collected and composited over stream reach of about 500 to 1,000 feet in length. Quantitative benthic-invertebrate and algae samples were collected from riffles and pools, and qualitative benthic-invertebrate and algae samples were collected from all possible habitats to generate a complete list of taxa present within the sampling reach. Benthic-invertebrate and algae samples were collected according to USGS protocols and sent to the USGS NWQL for quantification and identification to the species level. Fish were collected primarily by electrofishing techniques and were identified, counted, measured, and weighed, and external anomalies were noted before being returned to the stream.

Beyond meeting the stated objectives of the fixed integrator stream network, the stream-chemistry and biological-community data collected in this sampling approach contribute significantly to an integrated assessment of water quality in the Potomac River Basin. The data are the source of the basic-chemistry and biological-community components of the comprehensive description of stream quality at large stream sites, enabling stream chemistry and biological communities to be related. The data provide the large-scale end-member descriptions of stream quality at different spatial and temporal scales, laying the groundwork for future trend analysis for basic chemistry and biological communities at these important large stream sites.

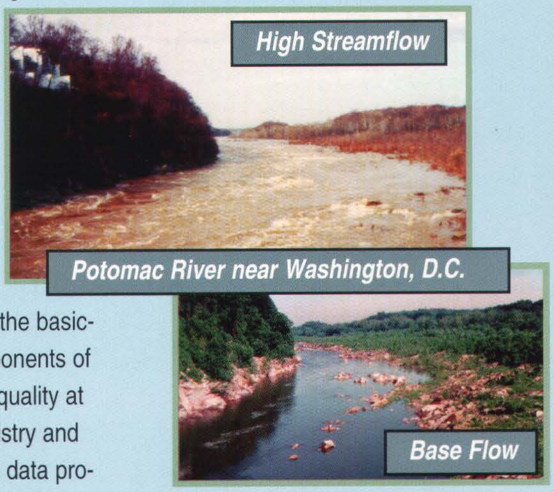
How Does the Fixed Integrator Stream Network Contribute to an Integrated Water-Quality Assessment?

Provides basic-chemistry and biological-community components to a comprehensive description of stream quality at fixed integrator stream sites.

Provides large-scale component of an evaluation of stream quality at different spatial and temporal scales.

Provides data that can be used to relate stream chemistry to biological communities for large-scale sites.

Provides data that initialize a long-term data set for trend analysis for stream chemistry and biological communities.



Potomac River near Washington, D.C.

SAMPLING STRATEGY: FIXED LAND-USE INDICATOR STREAM NETWORK

Objectives of the Fixed Land-Use Indicator Stream Network

Determine occurrence and spatial and temporal distribution of basic chemical compounds and biological communities in small and intermediate streams in high-priority subunits and targeted land uses.

Determine occurrence and distribution of pesticides in streams in selected high-priority subunits and targeted land uses.

Relate stream chemistry and biological communities to land use and other factors.

Estimate amounts of nitrogen, phosphorus, and pesticides that are transported by streams in these important settings.

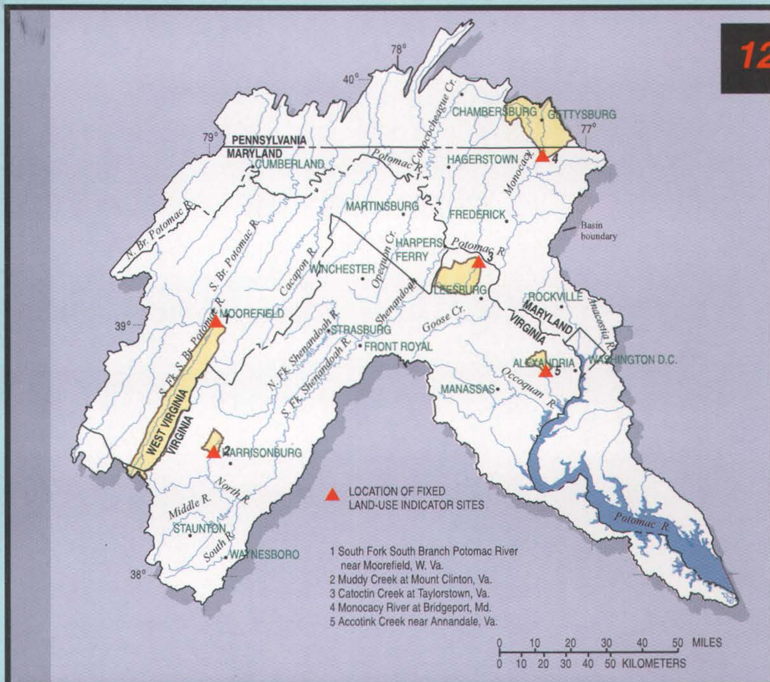
Brief Description of the Fixed Land-Use Indicator Stream Network

Sites: *Five small and intermediate stream sites representing high-priority subunits and targeted land uses.*

Schedule: *Each site sampled monthly for streamwater and annually for biological communities. Three sites sampled weekly for streamwater during a growing season. Sampled spring 1993 into summer 1995.*

Streamwater: *Field measurements, suspended sediment, major ions, nitrogen, phosphorus, and organic carbon in width- and depth-integrated samples collected during different flow conditions; pesticide samples collected at three sites.*

Biological Communities: *Fish, benthic-invertebrate, and algae communities and stream-habitat description in stream reaches averaging 700 feet in length; multiple reaches at two sites.*



12 Location of fixed land-use indicator sites

Indicator stream sites drain small to intermediate watersheds having relatively homogeneous environmental settings. Whereas larger integrator sites drain parts of several basin subunits containing multiple land uses, smaller indicator sites drain parts of an individual subunit that are characterized by a single land use or a representative combination of land uses. Consequently, streamwater and biological-community samples from indicator stream sites have water-quality signatures that are indicative of targeted land uses within specific subunits. The sampling of key indicator stream sites in a river basin provides a measure of the relative contributions of important individual environmental settings to overall surface-water quality in the basin.

The objectives of the fixed land-use indicator stream network for the Potomac River Basin study unit generally are similar to those of the fixed integrator stream network. The objectives include the determination of the occurrence and distribution of basic chemical compounds and biological communities, the determination of the relation of water quality to land use and other factors, and the estimation of nitrogen and phosphorus transport in the sampled streams. These objectives differ from those of the fixed integrator stream network only in terms of the size and complexity of the watershed. The objectives for the fixed land-use indicator stream network apply to small and intermediate streams in individual high-priority subunits and targeted land uses rather than large streams draining multiple subunits and land uses. One important expansion of the scope of the objectives for the fixed land-use indicator stream network is the addition of selected pesticides to the list of laboratory analytes for selected indicator sites.

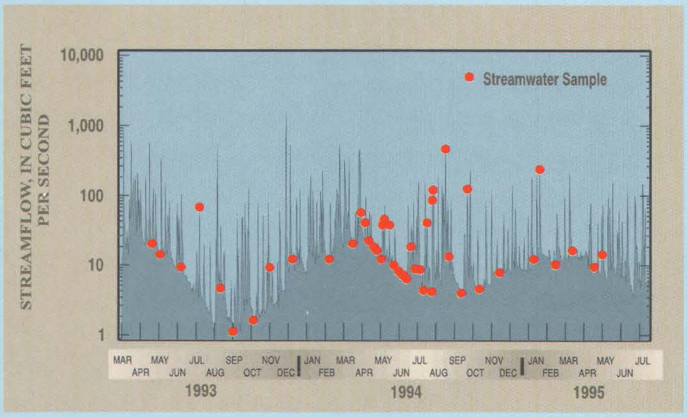
Electrofishing at Monocacy River

Five fixed land-use indicator stream sites were selected for water-quality sampling in the first intensive phase of the Potomac River Basin study unit. The five fixed land-use indicator sites and the high-priority subunits and targeted land uses they represent are: (1) South Fork South Branch Potomac River, W. Va.—Valley and Ridge, mixed forest and agriculture; (2) Muddy Creek, Va.—Great Valley Carbonate, agriculture; (3) Catoctin Creek, Va.—Piedmont, mixed agriculture and forest; (4) Monocacy River, Pa. and Md.—Triassic Lowlands,

agriculture; and (5) Accotink Creek, Va.—Piedmont, urban. All five sites are located at streamflow-gaging stations. Drainage areas range from approximately 14 square miles (Muddy Creek) to 283 square miles (South Fork South Branch Potomac River). The sites were selected for their ability to capture the effects of a single high-priority subunit and its characteristic targeted land uses.

The five fixed land-use indicator stream sites were sampled for a period of about 27 months, from the spring of 1993 into the summer of 1995. Streamwater samples were collected approximately monthly and during selected high-streamflow conditions at each site, the same sampling frequency as the fixed integrator stream network. At three of the indicator sites, streamwater-sampling frequency was increased to about weekly during one growing season. These sites and the year of intensive sampling are: (1) Muddy Creek, Va.—1993; (2) Monocacy River, Pa. and Md.—1994; and (3) Accotink Creek, Va.—1994. Biological-community sampling was conducted annually at each of the five land-use indicator sites.

13 Sampling frequency at fixed land-use indicator site at Accotink Creek.



Streamwater samples were collected by use of the same equipment and protocols, and were analyzed for the same chemical compounds, as the samples collected from the fixed integrator stream network. One difference from the fixed integrator stream network was that during storm events at the urbanized Accotink Creek, an automatic sampler was used to help collect samples during high-streamflow conditions. Another difference was the weekly collection of streamwater samples for selected pesticide analyses during one growing season at three of the five indicator sites—Muddy Creek, Monocacy River, and Accotink Creek. Biological-community sampling was conducted at each site in the same manner as at the fixed integrator stream sites. A difference is that at two of the five land-use indicator sites—Muddy Creek and Accotink Creek—three adjacent stream reaches rather than one were sampled for benthic invertebrates, algae, and fish to determine the variability of biological communities on a small scale.

Streamwater-chemistry and biological-community data from the fixed land-use indicator stream network contribute to an integrated water-quality assessment of the basin in many ways. The data yield important components of the comprehensive descriptions of stream quality at the five sites and supply the small-scale and intermediate-scale components to a basinwide evaluation of stream quality. The routine sampling frequency at the fixed land-use indicator sites as basin streamflow conditions were changing provides a frame of reference in which the results of synoptic samplings can be properly interpreted. Data from the indicator sites can be used to relate stream chemistry to biological communities at small and intermediate stream sites, initializing a long-term data set useful in analyzing trends in stream chemistry and biological communities at these sites. The data also provide stream-quality information that can be compared to ground-water-quality information provided by data collected in other sampling approaches. Finally, the degree of confidence with which biological-community data from single stream reaches can be said to represent a stream, can be determined from the biological-community data collected at triplicate reaches at two of the indicator sites.

How Does the Fixed Land-Use Indicator Stream Network Contribute to an Integrated Water-Quality Assessment?

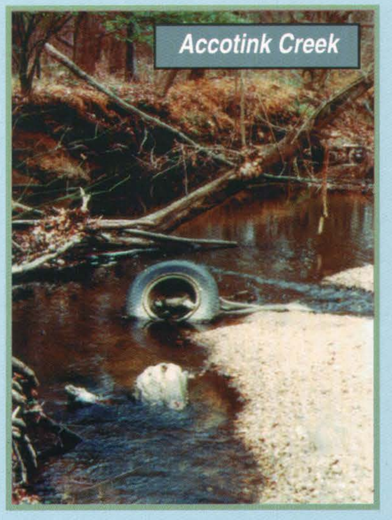
Provides basic-chemistry and biological-community components to a comprehensive description of stream quality at fixed indicator stream sites.

Provides small- and intermediate-scale components of an evaluation of stream quality at different spatial and temporal scales.

Provides data that can be used to relate stream chemistry to biological communities for small- and intermediate-scale sites in important settings.

Provides data that initialize a long-term data set for trend analysis for stream chemistry and biological communities.

Provides data that can be used to relate stream quality to regional ground-water quality.



SAMPLING STRATEGY: CONTAMINANT SURVEY OF STREAMBED SEDIMENTS AND AQUATIC BIOLOGICAL TISSUES

Objectives of the Contaminant Survey of Streambed Sediments and Aquatic Biological Tissues

Determine occurrence and spatial distribution of trace-element and organic contaminants in streambed sediments and aquatic biological tissues.

Relate presence of contaminants to potential contamination sources.

Brief Description of the Contaminant Survey of Streambed Sediments and Aquatic Biological Tissues

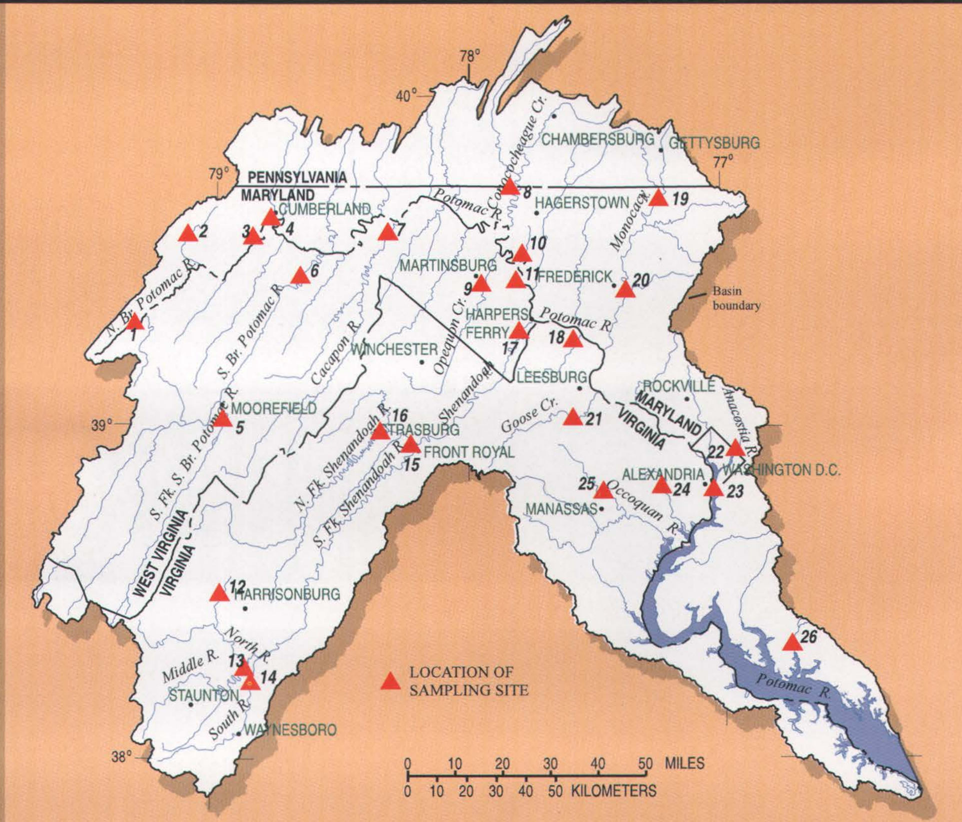
Sites: *26 stream sites.*

Schedule: *Each site sampled once. Twenty-two sites sampled in August 1992, and four sites sampled summer, 1995.*

Streambed Sediments: *Trace elements, organochlorine pesticides, semivolatile organic compounds, and PCB's in samples composited from various locations at each site.*

Clam and Fish Tissues: *Trace elements, organochlorine pesticides, and PCB's in samples composited from numerous clams and fish at each site.*

Many trace elements and synthetic organic compounds do not easily dissolve in streamwater, but instead tend to accumulate in streambed sediments and aquatic biological tissues. At sufficiently high concentrations, trace elements and synthetic organic compounds can act as contaminants that can adversely affect the health of aquatic life. Moreover, once in the food chain, these trace elements and synthetic compounds can adversely affect the health of terrestrial animals and humans as well. For this reason, trace elements and synthetic organic compounds in streambed sediments and aquatic biological tissues are particularly relevant for inclusion in assessments of water quality.



1 North Branch Potomac River at Steyer, Md.
2 Savage River near Barton, Md.
3 North Branch Potomac River at Pinto, Md.
4 North Branch Potomac River near Cumberland, Md.
5 South Fork South Branch Potomac River near Moorefield, W. Va.
6 South Branch Potomac River near Springfield, W. Va.
7 Cacapon River near Great Cacapon, W. Va.
8 Conococheague Creek at Fairview, Md.
9 Opequon Creek near Martinsburg, W. Va.
10 Marsh Run at Grimes, Md.
11 Potomac River at Shepherdstown, W. Va.
12 Muddy Creek at Mount Clinton, Va.
13 Middle River near Grottoes, Va.
14 South River at Harriston, Va.
15 South Fork Shenandoah River below Cabin Run at Front Royal, Va.
16 North Fork Shenandoah River near Strasburg, Va.
17 Shenandoah River at Millville, W. Va.
18 Catoctin Creek at Taylorstown, Va.
19 Monocacy River at Bridgeport, Md.
20 Monocacy River at Reichs Ford near Frederick, Md.
21 Goose Creek near Leesburg, Va.
22 Anacostia River near Bladensburg, Md.
23 Potomac River near Alexandria, Va.
(Sediment collected below Oxon Creek at Washington, D.C.)
24 Accotink Creek near Annandale, Va.
25 Bull Run near Manassas, Va.
26 St. Clement Creek near Clements, Md.

14 **Location of streambed-sediment and aquatic-biological-tissue sampling sites.**

The primary objective of the contaminant survey is to determine the occurrence and spatial distribution of trace-element and organic contaminants in streambed sediments and aquatic biological tissues in the Potomac River Basin. A secondary objective is to determine how the occurrence and distribution of these contaminants may be related to natural and human sources of contamination in the basin.

Twenty-six stream sites were selected for sampling in the contaminant survey with drainage areas ranging from less than 20 to nearly 12,000 square miles. Sampling sites were selected to maximize the probability of detection of trace-element and organic contaminants. Therefore, most sites were selected downstream of known or suspected point sources of contamination or in areas where nonpoint sources of contamination are prevalent. A few sites also were selected in areas with suspected low probability of detection of contaminants.

Samples of streambed sediments were collected at all 26 sites during low streamflow conditions; 22 sites were sampled in August 1992 and 4 were sampled in the summer of 1995. Sediment samples were collected at each site by using a scoop or dredge constructed from inert materials to skim off the top 1 inch of streambed sediments. Samples were collected from multiple depositional zones within stream reaches averaging about 300 feet in length and were composited in glass jars. Samples were sieved to obtain only the finer-grained sediments to which these types of contaminants are most likely to attach. Sediment samples were analyzed at the USGS NWQL for trace elements, including arsenic, cadmium, lead, and mercury; organochlorine insecticides, including chlordane, DDT, dieldrin, and heptachlor; semivolatile organic compounds, including anthracene, chrysene, naphthalene, and pyrene; and PCB's.

Samples of aquatic biological tissues were collected at a subset of the 26 sites where sediments were collected. Samples of Asiatic clams (Corbicula fluminea) were collected at 16 sites and usually consisted of hundreds of individuals from the stream reach at the site. Samples of fish (catfish, bass, suckers, or sunfish) were collected by electrofishing techniques at 12 sites. Fish samples were composites of 4 to 8 individuals from each site. Whole-fish samples for analysis of organic contaminants, and extracted livers for analysis of trace elements were analyzed for a subset of the contaminants analyzed in sediment samples. Contaminants that do not accumulate in tissues were eliminated from the tissue analyses.

In addition to meeting the two explicit objectives of the contaminant survey, the contaminant data can be used to contribute to an integrated water-quality assessment of key streams in the Potomac River Basin. The contaminant data in combination with other physical, chemical, and biological data collected through other sampling approaches at some of the same sites can be used to develop a comprehensive, multidisciplinary description of stream quality for those sites. Also, in conjunction with other data from some of the same sites and ancillary information on potential contaminant sources, these data can contribute to a comprehensive evaluation of contamination sources at each site.

How Does the Contaminant Survey Contribute to an Integrated Water-Quality Assessment?

Provides contaminant component to a comprehensive description of stream quality at fixed sites.

Provides contaminant component to a comprehensive evaluation of all potential contamination sources for fixed sites.

Provides data that initialize a long-term data set for possible trend analysis for contaminants.

SAMPLING STRATEGY: SYNOPTIC SURVEY OF MAJOR TRIBUTARIES

Objectives of the Synoptic Survey of Major Tributaries

Determine occurrence and spatial distribution of nitrogen, phosphorus, and pesticides in major tributaries.

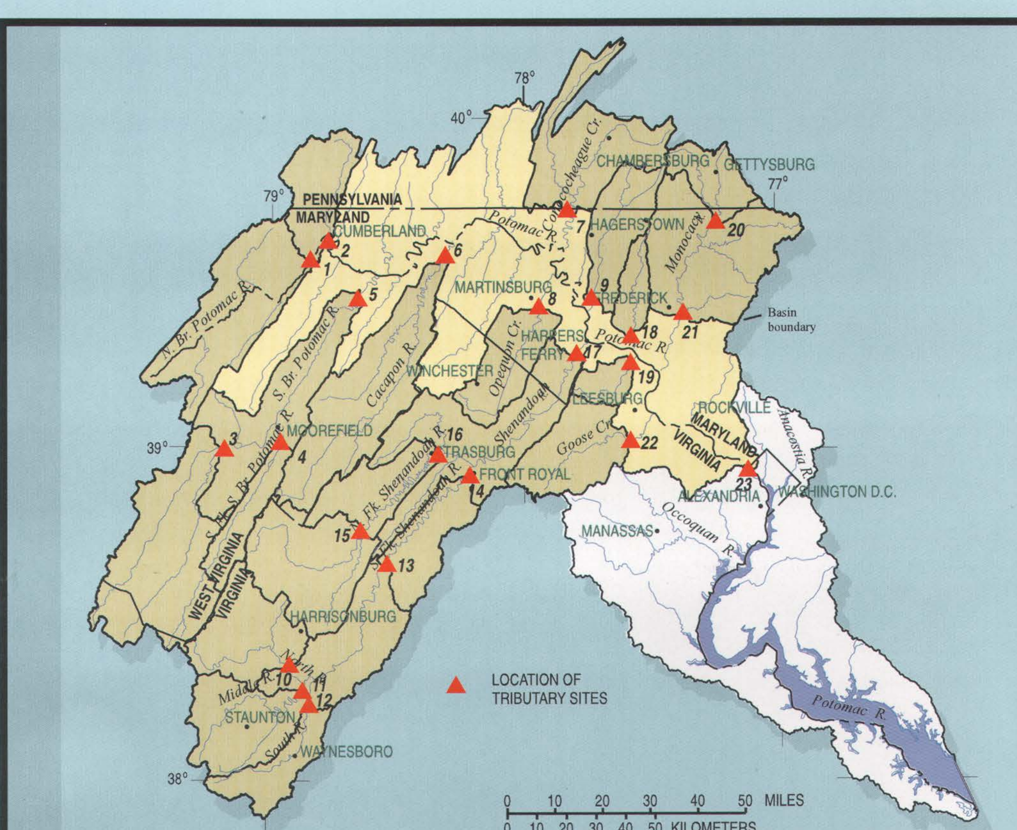
Relate concentrations and amounts of nitrogen, phosphorus, and pesticides in major tributaries to potential sources in tributary watersheds.

Brief Description of the Synoptic Survey of Major Tributaries

Sites: *23 major tributaries, including Potomac River and all fixed sites.*

Schedule: *Each site sampled once in early June 1994.*

Streamwater: *Field measurements, suspended sediment, nitrogen, phosphorus, and pesticides in width- and depth-integrated samples collected during stable intermediate-flow conditions.*



1 North Branch Potomac River at Pinto, Md.
2 North Branch Potomac River near Cumberland, Md.
3 South Branch Potomac River near Petersburg, W. Va.
4 South Fork South Branch Potomac River near Moorefield, W. Va.
5 South Branch Potomac River near Springfield, W. Va.
6 Cacapon River near Great Cacapon, W. Va.
7 Conococheague Creek at Fairview, Md.
8 Opequon Creek near Martinsburg, W. Va.
9 Antietam Creek near Sharpsburg, Md.
10 North River near Burketown, Va.
11 Middle River near Grottoes, Va.
12 South River at Harriston, Va.
13 South Fork Shenandoah River near Luray, Va.
14 South Fork Shenandoah River at Front Royal, Va.
15 North Fork Shenandoah River at Mt. Jackson, Va.
16 North Fork Shenandoah River near Strasburg, Va.
17 Shenandoah River at Millville, W. Va.
18 Catoctin Creek at Olive, Md.
19 Catoctin Creek at Taylorstown, Va.
20 Monocacy River at Bridgeport, Md.
21 Monocacy River at Jug Bridge near Frederick, Md.
22 Goose Creek near Leesburg, Va.
23 Potomac River at Chain Bridge at Washington, D.C.

15 **Location of major-tributary-synoptic-sampling sites.**

Nitrogen, phosphorus, and pesticides in streamwater contribute to some of the water-quality problems affecting the Potomac River. Furthermore, because the Potomac River provides 15 percent of the freshwater inflow to the Chesapeake Bay, the amounts of these potential contaminants that are transported by the Potomac River also are important to the health of the Chesapeake Bay. The effective implementation of programs designed to reduce the amounts of nitrogen, phosphorus, and pesticides in the Potomac River must start with an understanding of which major Potomac River tributaries contribute the largest amounts of these compounds. A synoptic sampling of streamwater in major tributaries, at a time of year when the transport of nitrogen, phosphorus, and pesticides is expected to be near its peak, provides a first-cut measure of each major tributary's relative contribution of these compounds.

The determination of the occurrence and spatial distribution of nitrogen, phosphorus, and selected pesticides in the major streams that feed the Potomac River is the primary objective of the synoptic survey of major tributaries. A secondary objective is to establish the relations between the concentrations and amounts of nitrogen, phosphorus, and pesticides in major tributaries and the probable sources of these potential contaminants in the watersheds that drain to the major tributaries.

Twenty-two major tributaries of the Potomac River west of Washington, D.C., were selected for streamwater sampling. These streams were selected on the basis of their large drainage areas and their ability to represent the various sources of nitrogen, phosphorus, and pesticides in the Potomac River Basin. They included five of the six fixed integrator stream network sites and the three largest sites in the fixed land-use indicator stream network. Other major tributaries include the South Branch Potomac River, Cacapon River, Opequon Creek, Antietam Creek, Catoctin Creek (Md.), and Goose Creek, as well as seven sites in the Shenandoah River Basin to gain additional insight into the distribution of nitrogen, phosphorus, and pesticides within this important large tributary. Drainage areas for the 22 major tributaries range from about 90 square miles (Catoctin Creek, Va.) to 3,040 square miles (Shenandoah River), with a median drainage area of 500 square miles. In order to provide a measure of the composite effect of all tributaries, a 23rd site, the Potomac River integrator site at Washington, D.C., was also sampled.

A single streamwater sample was collected at each of the 23 sampling sites during June 5-16, 1994. This time period was selected because it was a time of stable intermediate-streamflow conditions throughout the Potomac River Basin and because it followed the spring high-streamflow conditions and spring applications of agricultural chemicals, a combination of conditions expected to result in high transport rates of nitrogen, phosphorus, and pesticides in streamwater. No major storms occurred in the Potomac River Basin for at least 10 days prior to the sampling period, which optimizes the potential for meaningful comparisons among sampling sites.

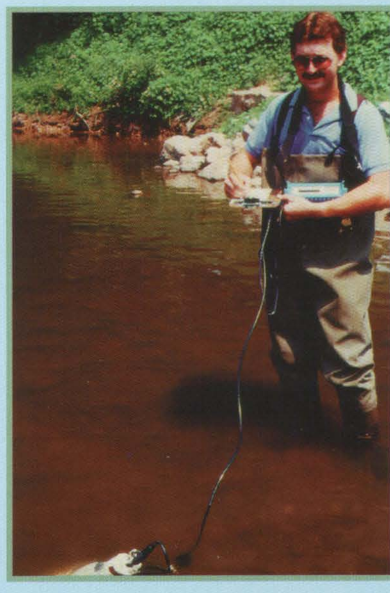
Streamwater samples were collected using the same flow-weighted and cross-sectionally-integrated methods used for the fixed integrator and land-use indicator stream networks. Sampling equipment was constructed from inert materials and clean-sampling protocols were employed. Field measurements included streamflow, water temperature, pH, specific conductance, dissolved oxygen, and alkalinity. Samples were processed and shipped to the USGS NWQL for analysis of nitrogen, phosphorus, and selected pesticides. Samples also were analyzed for suspended sediment.

The nitrogen, phosphorus, and pesticide data obtained in this sampling approach provide two important components to an integrated water-quality assessment of the Potomac River Basin. First, this approach is the only one that provides pesticide data for most of the fixed integrator and land-use indicator sites. Second, this sampling approach provides higher spatial resolution on the distribution of nitrogen, phosphorus, and pesticides in streamwater for some of the fixed integrator stream sites, most notably the Shenandoah River site.

How Does the Synoptic Survey of Major Tributaries Contribute to an Integrated Water-Quality Assessment?

Provides pesticide component to a comprehensive description of stream quality at fixed sites.

Provides higher spatial resolution on nitrogen, phosphorus, and pesticides for watersheds nested within fixed-site drainages.



SAMPLING STRATEGY: SYNOPTIC SURVEYS OF SUBUNIT STREAMS

Objectives of the Synoptic Surveys of Subunit Streams

Determine occurrence and spatial distribution of chemical compounds and biological communities in small streams in high-priority subunits.

Relate stream chemistry and biological communities to land use and other factors.

Brief Description of the Synoptic Surveys of Subunit Streams

Sites: *Selected small streams in high-priority subunits:*

27 in Great Valley Carbonate
25 in Piedmont
12 in Triassic Lowlands
25 in Valley and Ridge.

Schedule: *Each site sampled once:*

Great Valley Carbonate in summer of 1993
Piedmont and Triassic Lowlands in summer of 1994
Valley and Ridge in summer of 1995.

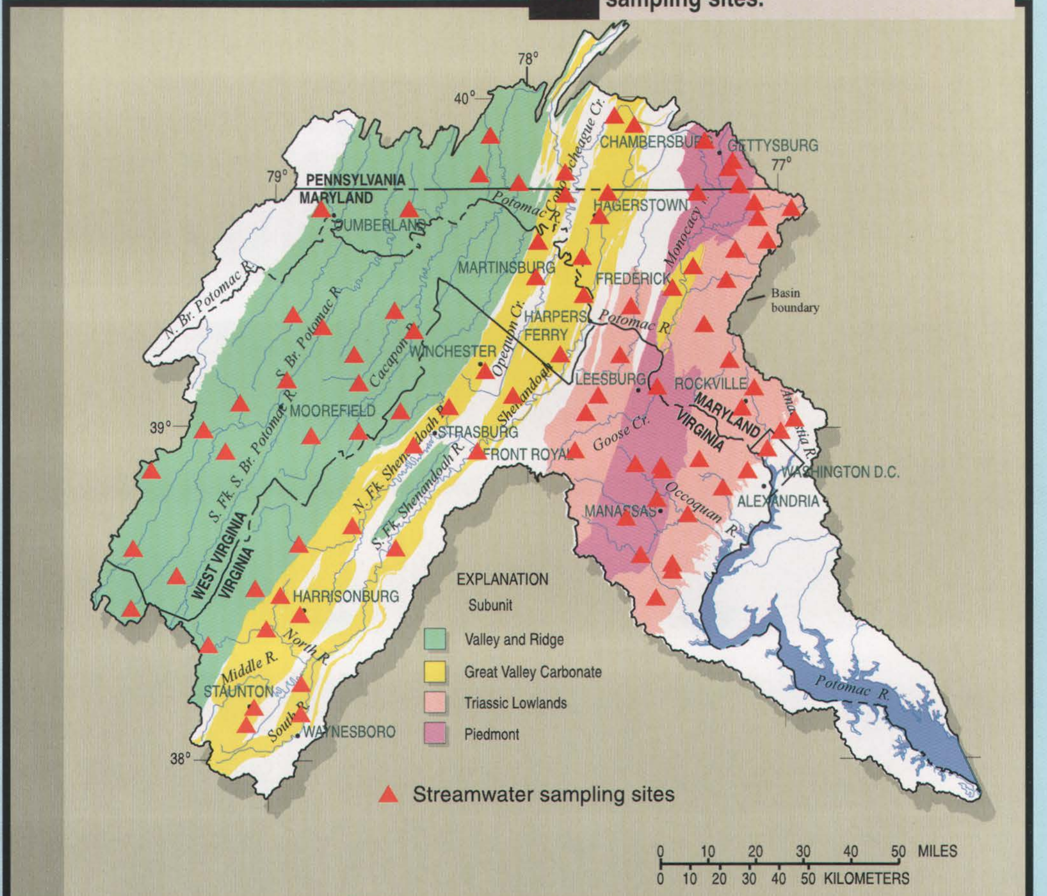
Streamwater: *Field measurements, suspended sediment, major ions, nitrogen, phosphorus, and pesticides in width- and depth-integrated samples collected during low-flow conditions.*

Biological Communities: *Benthic-invertebrate and algae communities and stream-habitat description in stream reaches averaging 200 feet in length.*

The chemical and biological quality of the major tributaries to the Potomac River are largely determined by the quality of the numerous smaller streams that combine to form them. Major differences among subunits in the quality of these smaller headwater streams are due to diversities in physiography and type of rock. Small-scale variability in land use and other factors also can contribute to significant differences in stream quality within subunits. Because the great majority of streams in the Potomac River Basin are of this headwater type, a critical component of a basin water-quality assessment is the evaluation of the quality of these smaller streams. A sampling of streamwater and biological communities in a representative number of small streams throughout a subunit provides a measure of overall stream quality for that subunit.

The principal objective of the synoptic surveys of subunit streams is to determine the occurrence and spatial distribution of chemical compounds and biological communities in small streams

16 **Location of subunit stream-survey sampling sites.**



throughout high-priority subunits. A secondary objective is to relate the observed stream chemistry and biological communities to land use and other influencing factors.

Sampling sites for this approach were selected in the four high-priority subunits--the Great Valley Carbonate, Piedmont, Triassic Lowlands, and Valley and Ridge subunits. Eighty-nine sites were selected for subunit surveys: 27 in the Great Valley Carbonate subunit; 25 each in the Piedmont and Valley and Ridge subunits; and 12 in the Triassic Lowlands subunit. Sampling sites were selected on small streams draining watersheds representing the major land uses in each subunit, such that the number of sampling sites for each land use is roughly proportional to the amount of that land use present in the subunit. For example, in the Great Valley Carbonate subunit, where agricultural land use accounts for about 75 percent of the area of the subunit, 19 of 27 sites were selected on streams draining agricultural watersheds. Drainage areas for sampling sites in this approach generally range from about 5 to 20 square miles. Site selection was based on office analysis using a geographic information system, followed by field reconnaissance.

For each high-priority subunit, all sites were sampled once during a period of 2 to 3 weeks in late summer. Sites in the Great Valley Carbonate subunit were sampled in 1993; sites in the Piedmont and Triassic Lowlands subunits were sampled in 1994; and sites in the Valley and Ridge subunit were sampled in 1995. Two sites within the outlier of the Great Valley Carbonate subunit near Frederick, Md. were sampled in 1994. All samples were collected during similar low-streamflow conditions to facilitate comparisons of results within and among subunits.

A single sample of streamwater was collected at each site using flow-weighted and cross-sectionally-integrated sampling methods. All samples were collected using equipment constructed from inert materials and processed according to clean-sampling protocols. Streamflow, water temperature, pH, specific conductance, dissolved oxygen, and alkalinity were measured in the field at each site. The samples were analyzed at the USGS NWQL for major ions, nitrogen, phosphorus, and selected pesticides. Samples also were analyzed for suspended-sediment concentrations.

The benthic-invertebrate community was sampled at each site in the four high-priority subunits. The algae community was sampled at all sites except those in the Valley and Ridge subunit. Quantitative community samples were collected from riffles in stream reaches of about 100 to 300 feet in length. In addition, qualitative community samples were collected and composited from all possible habitats in the reaches at most sites. All benthic-invertebrate and algae samples were sent to the USGS NWQL for analysis. Basic stream habitat measurements and descriptions also were recorded at each site.

Synoptic surveys of subunit streams are one of the most valuable approaches in an integrated water-quality assessment of the Potomac River Basin. They provide the small-scale stream-chemistry and biological-community data needed to characterize surface-water quality in high-priority subunits. Synoptic surveys provide data that can be used to establish relations between stream chemistry and biological communities, and between stream quality and ground-water quality measured in other approaches. They provide data that can be used to compare stream quality among high-priority subunits and among targeted land uses within and across subunits. They also provide finer spatial resolution on stream chemistry and biological communities within larger watersheds sampled in other approaches. They allow the results of sampling at fixed land-use indicator stream sites in a high-priority subunit to be placed in perspective with regard to the range of conditions in a subunit. Finally, the synoptic surveys of streams conducted in the four high-priority subunits can serve as the first step in a possible long-term series of synoptic surveys at the same sites to evaluate trends in stream chemistry and biological communities in the subunits.

How Do the Synoptic Surveys of Subunit Streams Contribute to an Integrated Water-Quality Assessment?

Provide small-scale information on stream chemistry and biological communities in high-priority subunits.

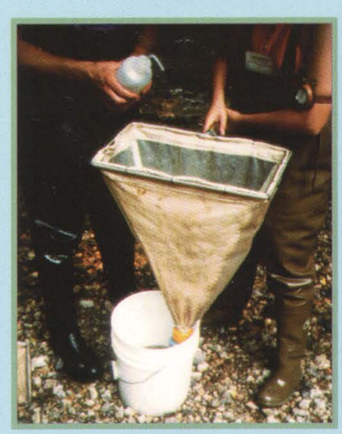
Provide data that can be used to relate stream chemistry to biological communities for small-scale sites.

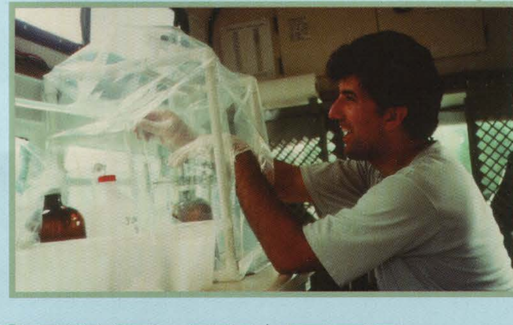
Provide data that can be used to relate stream quality to ground-water quality.

Provide data that can be used to compare stream quality among subunits.

Provide data that can be used to compare stream quality in major land uses among subunits.

Provide data that initialize a long-term data set for possible trend analysis for stream chemistry and biological communities.





SAMPLING STRATEGY: SURVEYS OF SUBUNIT GROUND WATER

Objectives of the Surveys of Subunit Ground Water

Determine occurrence and spatial distribution of chemistry of relatively shallow ground water in high-priority subunits and targeted land uses.

Relate ground-water chemistry to land use, type of rock, and other factors.

Brief Description of the Surveys of Subunit Ground Water

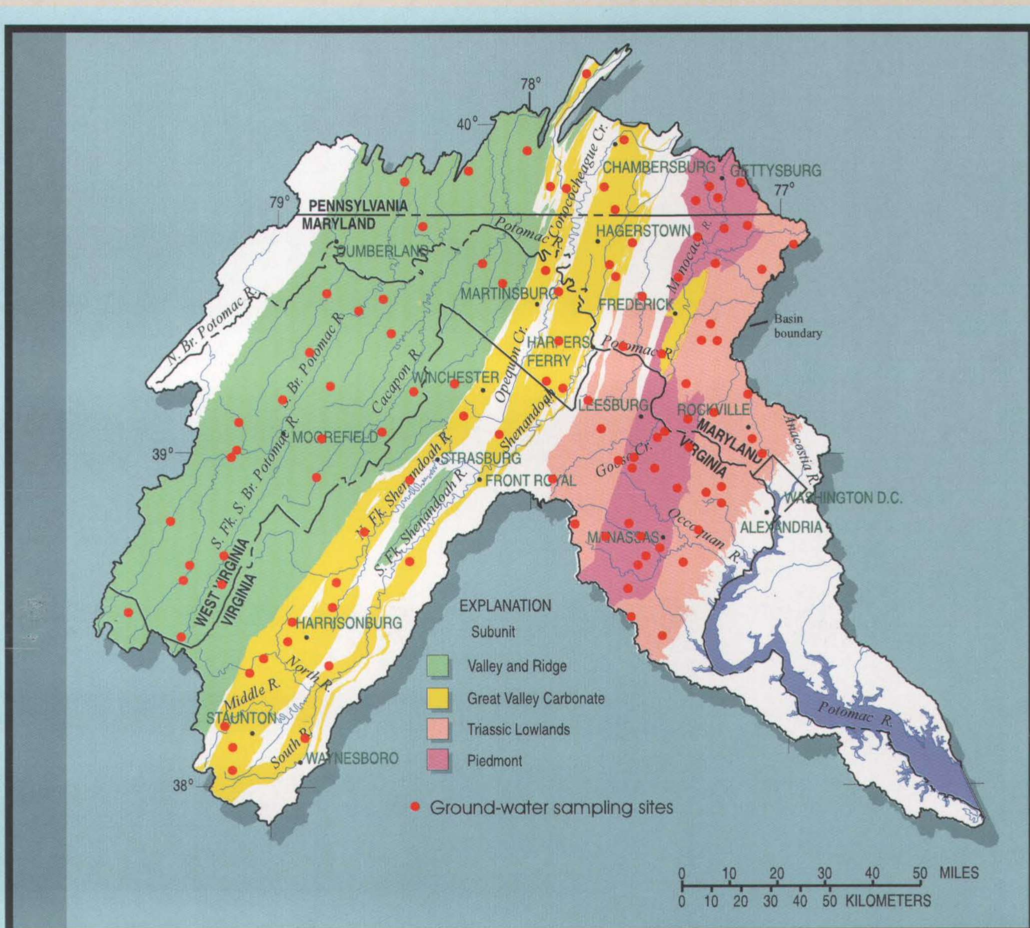
Sites: *Randomly selected, relatively shallow, domestic wells in high-priority subunits—*

29 in Great Valley Carbonate
25 in Piedmont
23 in Triassic Lowlands
28 in Valley and Ridge.

Schedule: *Each site sampled once:*

Great Valley Carbonate in summer of 1993
Piedmont and Triassic Lowlands in summer of 1994
Valley and Ridge in summer of 1995.

Ground Water: *Field measurements, major ions, nitrogen, phosphorus, pesticides, organic carbon, radon, uranium, and tritium in samples collected after complete well purge.*

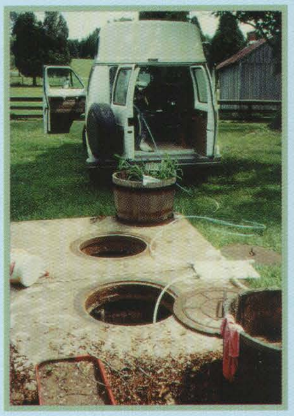


17 **Location of subunit ground-water survey sampling sites.**

Ground water is the primary source of drinking water in rural areas of the Potomac River Basin. Most rural basin residents obtain their water supply from drilled wells that are less than about 500 feet deep. Thus, for public-health reasons, it is important that ground water be included in an integrated water-quality assessment. In addition, because more than one-half of basin streamflow is derived from ground-water inflow to streams, the inclusion of ground water in an assessment also contributes to the understanding of stream quality.

The surveys of subunit ground water in selected high-priority subunits and targeted land uses have two major objectives. The first is to determine the occurrence and spatial distribution of ground-water chemistry in important, relatively shallow aquifers. The second objective is to relate differences in ground-water chemistry to natural and human factors including type of rock and land use.

Ground-water sampling sites (wells) were selected in the four high-priority subunits determined to be of the highest priority for the first intensive phase of the study unit. Ground-water samples were collected from 29 wells in the Great Valley Carbonate, 25 in the Piedmont, 23 in the Triassic Lowlands, and 28 in the Valley and Ridge subunits. A randomized selection procedure was used to generate latitude and longitude coordinates within all four major subunits for potential sampling sites, followed by field reconnaissance to locate the nearest suitable wells to those random coordinates. In most cases, relatively shallow, privately owned,



domestic wells were selected as sampling sites. Specific well-selection criteria included well depth (generally less than 300 feet), recent well-construction date, absence of water-treatment systems, and existing submersible pumps. In the Piedmont and Triassic Lowlands subunits, where multiple land uses may equally influence ground-water quality, wells to be sampled were randomly selected regardless of the land use in which they were located. In the Great Valley Carbonate and Valley and Ridge subunits, where agricultural land use is a dominant factor in determining ground-water quality, wells were randomly selected only within the agricultural areas of the subunit. Three forested sites in the Valley and Ridge subunit were selected without using the random method, while the outlier of the Great Valley Carbonate subunit located in the Piedmont Province near Frederick, Md., was not considered in the selection process.

Wells were sampled for each high-priority subunit during the summer months. The survey in the Great Valley Carbonate subunit was conducted during the summer of 1993; the surveys in the Piedmont and Triassic Lowlands subunits were conducted in the summer of 1994, and the Valley and Ridge survey was conducted in the summer of 1995. These sampling periods were selected to correspond with the sampling periods for the synoptic surveys of subunit streams to facilitate valid comparisons between the ground-water and stream data sets within each subunit. In the Potomac River Basin, the summer months are a time of relatively stable ground-water levels following the relatively higher levels of the winter and spring months.

A single sample was collected from each selected well in each of the four sampled subunits. Before the sample was collected, the well was pumped until field measurements of water temperature, pH, specific conductance, and dissolved oxygen became stable at the wellhead, indicating that the source of the pumped water was the aquifer and not water that had been stored in the well casing. Using this method, at least one and usually two to three well volumes were removed from the wells before the sample was collected. All equipment that came in contact with the water sample after it left the well was constructed from inert materials, and all processing of the samples was done by use of clean-sampling protocols. At the time of sample collection, measurements of water temperature, pH, specific conductance, dissolved oxygen, and alkalinity were recorded. The samples were then shipped to the USGS NWQL for analysis for major ions, nitrogen, phosphorus, organic carbon, and selected pesticides. Samples also were analyzed for radon, uranium, and tritium. For each sampled site, well characteristics were documented and land uses surrounding the well were mapped.

The surveys of subunit ground water play an important role in an integrated water-quality assessment of the Potomac River Basin. The surveys provide data that can be used to compare and contrast ground-water quality among subunits and among land uses. The results of the ground-water surveys can be used to determine the relation between the chemistry of ground water and the chemistry and biological communities of streams. The surveys conducted in the four high-priority subunits can be used as the initial step in a possible trend analysis of ground-water chemistry in the subunits. Finally, the survey of ground-water chemistry in the Great Valley Carbonate subunit provides a frame of reference within which to evaluate the results of the small-scale ground-water flow-system study that is described in the next section.

How Do the Surveys of Subunit Ground Water Contribute to an Integrated Water-Quality Assessment?

Provide data that can be used to compare ground-water quality among subunits.

Provide data that can be used to compare ground-water quality in agricultural land uses among subunits.

Provide data that can be used to relate regional ground-water chemistry to stream chemistry and biological communities at various scales.

Provide data that initialize a long-term data set for possible trend analysis for ground-water quality.

18 **Land uses were mapped within one-half mile of each ground-water sampling site in the four major subunits.**

EXPLANATION

- Cr Cropland
- P Pasture
- R Residential
- Wo Woodland
- FB Farm Building
- Un Unused Cropland

SAMPLING STRATEGY:
SMALL-SCALE GROUND-WATER FLOW-SYSTEM STUDY

Objectives of the Small-Scale Ground-Water Flow-System Study

Determine occurrence and spatial and temporal distribution of nitrogen, phosphorus, and pesticides in shallow ground water on a small scale for a targeted land use in a high-priority subunit.

Relate nitrogen, phosphorus, and pesticide occurrence and distribution to land use and other factors on a small scale.

Evaluate the transport of nitrogen, phosphorus, and pesticides from the land surface to ground water and from ground water to streams, and the associated time of travel, on a small scale.

Brief Description of the Small-Scale Ground-Water Flow-System Study

Sites: *Numerous sampling sites in a small agricultural study area in the Great Valley Carbonate subunit:*

16 shallow observation wells
5 sites on a small stream
8 drive points in the streambed.

Schedule: *Each well, stream site, and drive point sampled at least once; some sampled up to 10 times; spring 1994 through summer 1995.*

Ground Water: *Field measurements, major ions, nitrogen, phosphorus, pesticides, organic carbon, radon, tritium, and chlorofluorocarbons in samples collected after complete well purge.*

Streamwater: *Field measurements, major ions, nitrogen, phosphorus, pesticides, and organic carbon.*

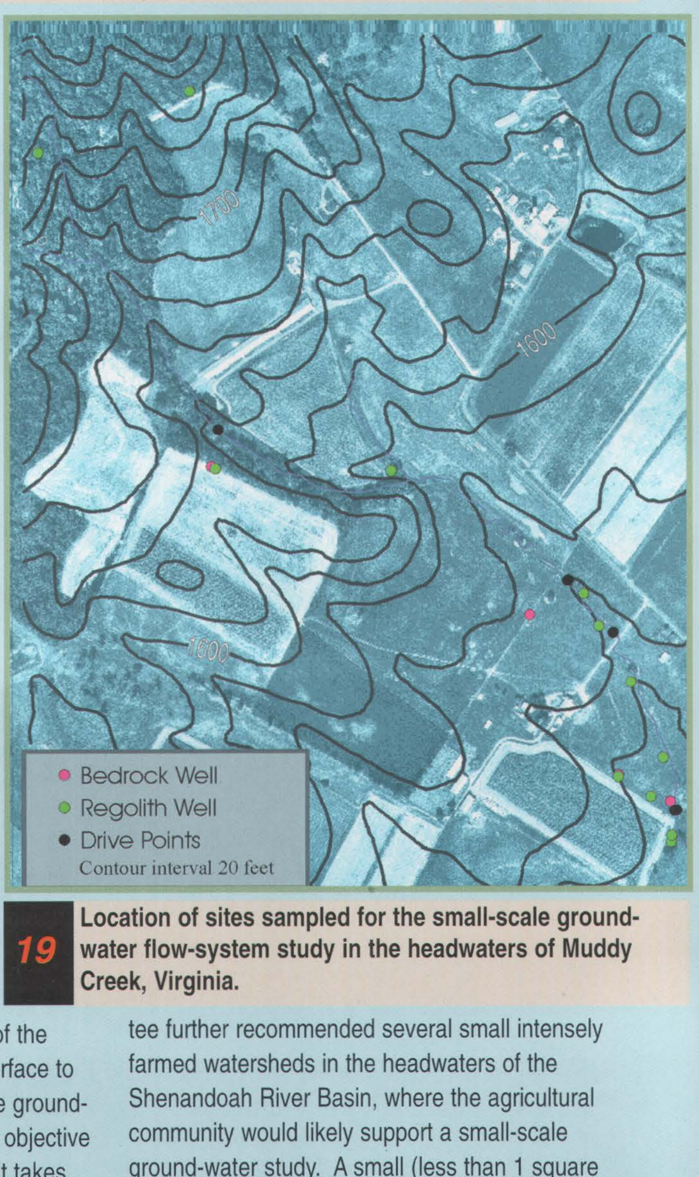
Other Data: *Continuous ground-water levels continuous cores, gamma and caliper logs, samples from nearby domestic wells, precipitation amounts, stream stage, and aquifer properties.*

Small-scale studies of ground-water quality are essential to the understanding of the processes by which ground-water quality is influenced by land use and other factors. When these processes are identified and quantified through a small-scale study, the resultant understanding can be extrapolated upward in scale to assist in the interpretation of the results of larger-scale approaches such as the surveys of subunit ground water. Small-scale studies of ground-water quality are expensive and logistically demanding; therefore, only one such study was conducted during the first intensive phase of the Potomac River Basin study unit.

The small-scale ground-water flow-system study has three major objectives. The first is to determine the occurrence, spatial distribution, and temporal variability of selected contaminants in ground water at a small scale in an important basin setting. Another objective is to relate the occurrence and distribution of the ground-water contaminants to land use and other factors. Perhaps the most important objective of the small-scale ground-water flow-system study approach is to develop an understanding of the transport of the contaminants from land surface to the ground-water-flow system and from the ground-water-flow system to streams. Part of this objective involves the estimation of how much time it takes for the contaminants to move through the ground-water-flow system to nearby streams.

A small study area was selected in an agricultural setting in the Great Valley Carbonate subunit. On the basis of input from the study-unit liaison committee, it was decided that the most important influence on basin ground-water quality is the surface application of agricultural chemicals (nitrogen, phosphorus, and pesticides) in areas underlain by carbonate rocks. The liaison committee further recommended several small intensely farmed watersheds in the headwaters of the Shenandoah River Basin, where the agricultural community would likely support a small-scale ground-water study. A small (less than 1 square mile) area was selected in the headwaters of Muddy Creek north of Harrisonburg, Va. This small-scale study area is nested within the fixed land-use indicator stream site located on Muddy Creek at Mount Clinton, Va.

Several types of water-quality sampling sites were established in the small-scale study area. Sixteen shallow (less than 100 feet) observation wells were installed, as were eight drive points in the beds of small streams traversing the study



19 **Location of sites sampled for the small-scale ground-water flow-system study in the headwaters of Muddy Creek, Virginia.**

area. In addition, five sites were selected on the small streams for sampling of streamwater. The observation wells were located to provide ground-water information for the several specific topographic, geologic, and land-use settings present in the small study area, with a concentration of observation wells at the downgradient end of the local flow system. Twelve of the wells were installed in the weathered material (regolith) overlying bedrock and four were installed in bedrock.

Water-quality samples were collected at least once from all well, drive-point, and stream sampling sites. Repetitive sampling was conducted at nearly all sites, with most sites being sampled 5 to 10 times from the spring of 1994 through the summer of 1995. Sampling extended over two growing seasons to maximize information during the times when agricultural chemicals were applied and when ground-water recharge was at its highest.

Ground-water and drive-point samples were collected after complete purging of the water standing in the wells and drive points, and the stabilization of field measurements at the wellhead. Stream samples were collected from well-mixed reaches at the five sampling sites on small streams. Clean-sampling protocols and equipment made from inert materials were used to collect and process all samples. Water temperature, pH, specific conductance, dissolved oxygen, and alkalinity were measured in all samples in the field. Subsamples were sent to the USGS Northeastern Region Research Laboratory in Reston, Va., for analysis for major ions, nitrogen, and phosphorus. Other subsamples were sent to the USGS NWQL for analysis of organic carbon and selected pesticides. Selected samples also were analyzed for radon, tritium, and chlorofluorocarbons at the NWQL. In addition, most samples also were analyzed for selected herbicides (such as atrazine and metolachlor) using immunoassay kits.

A wide variety of other hydrologic, geologic, and climatological data were collected to support and explain the water-quality data. This ancillary information includes precipitation data, continuous ground-water levels, lithologic descriptions of well cuttings, borehole geophysical logs, continuous lithologic cores, stream stage, aquifer properties derived from slug tests in wells, detailed geologic mapping, and data from suction lysimeters. Additionally, a synoptic sampling of 10 domestic wells and 1 spring in the vicinity of the small study area was conducted in the spring of 1995 to place the results of the small-scale study in a slightly more regional context.

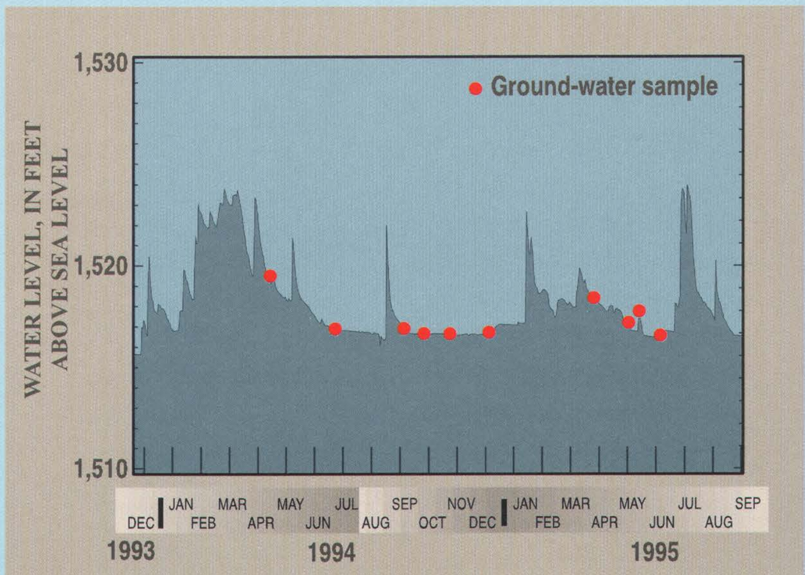
The primary role of the small-scale ground-water flow-system study in an integrated water-quality assessment of the Potomac River Basin is to collect the small-scale information needed to properly evaluate regional ground-water quality results. The data provide spatial and temporal frames of reference for the more regional data from the ground-water survey conducted in the Great Valley Carbonate subunit. The data also provide information that can be used to determine the relation between ground-water quality and stream quality on a small scale. Finally, the work conducted in the small-scale ground-water flow-system study during the first intensive phase of the study unit serves as the initialization of a long-term data set that can be used for possible trend analysis of ground-water quality in the study area and for investigating how ground-water quality is influenced by changes in agricultural practices over time.

How Does the Small-Scale Ground-Water Flow-System Study Contribute to an Integrated Water-Quality Assessment?

Provides spatial and temporal frames of reference for the interpretation of data from the survey of ground-water quality in the Great Valley Carbonate subunit.

Provides data that can be used to relate ground-water quality to stream quality on a small scale.

Provides data that initialize a long-term data set for possible trend analysis for ground-water quality on a small scale, and for monitoring the effects of changing agricultural practices.



20 **Sampling frequency in a regolith well at the small-scale ground-water flow-system site near Mount Clinton, Va.**

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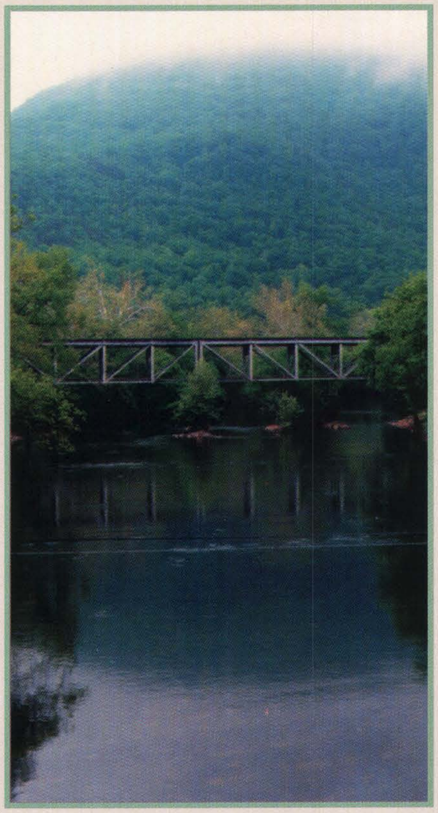


APPENDIX : List of analytes measured in ground water, streamwater, streambed sediments, and aquatic biological tissues.

CONSTITUENTS MEASURED IN GROUND WATER(GW) AND SURFACE WATER (SW)

PHYSICAL PARAMETERS (FIELD)

AIR TEMPERATURE	SW	GW
ALKALINITY	SW	GW
BAROMETRIC PRESSURE	SW	GW
BICARBONATE	SW	GW
CARBONATE, TOTAL	SW	GW
DISCHARGE	SW	
GAGE HEIGHT	SW	
OXYGEN, DISSOLVED	SW	GW
pH	SW	GW
SPECIFIC CONDUCTANCE	SW	GW
WATER TEMPERATURE	SW	GW

MAJOR DISSOLVED CONSTITUENTS AND SELECTED TRACE ELEMENTS

BROMIDE, DISSOLVED		GW
CALCIUM, DISSOLVED	SW	GW
CHLORIDE, DISSOLVED	SW	GW
FLUORIDE, DISSOLVED	SW	GW
IRON, DISSOLVED	SW	GW
MAGNESIUM, DISSOLVED	SW	GW
MANGANESE, DISSOLVED	SW	GW
POTASSIUM, DISSOLVED	SW	GW
SILICA, DISSOLVED	SW	GW
SODIUM, DISSOLVED	SW	GW
SOLIDS, RESIDUE ON EVAPORATION, DISSOLVED	SW	GW
SULFATE, DISSOLVED	SW	GW

NUTRIENTS

NITROGEN, AMMONIA	SW	GW
NITROGEN, NITRITE PLUS NITRATE	SW	GW
NITROGEN, NITRITE	SW	GW
NITROGEN, ORGANIC PLUS AMMONIA,	SW	GW
NITROGEN, ORGANIC PLUS AMMONIA, TOTAL	SW	
PHOSPHORUS, DISSOLVED	SW	GW
PHOSPHORUS, ORTHOPHOSPHATE, DISSOLVED	SW	GW
PHOSPHORUS, TOTAL	SW	

DISSOLVED PESTICIDES

ALACHLOR	SW	GW
ALPHA BHC	SW	GW
ATRAZINE	SW	GW
BENFLURALIN	SW	GW
BUTYLATE	SW	GW
CARBARYL	SW	GW
CARBOFURAN	SW	GW
CHLORPYRIFOS	SW	GW
CYANAZINE	SW	GW
DCPA	SW	GW
DEETHYL ATRAZINE	SW	GW
DIAZINON	SW	GW
DIELDRIN	SW	GW
DISULFOTON	SW	GW
EPTC	SW	GW
ETHALFLURALIN	SW	GW
ETHOPROP	SW	GW
FONOFOS	SW	GW
LINDANE	SW	GW
LINURON	SW	GW
MALATHION	SW	GW
METHYL AZINPHOS	SW	GW
METHYL PARATHION	SW	GW
METOLACHLOR	SW	GW
METRIBUZIN	SW	GW
MOLINATE	SW	GW
NAPROPAMIDE	SW	GW
P, P' DDE	SW	GW
PARATHION	SW	GW
PEBULATE	SW	GW
PENDIMETHALIN	SW	GW
PERMETHRIN	SW	GW
PHORATE	SW	GW
PROMETON	SW	GW
PRONAMIDE	SW	GW
PROPACHLOR	SW	GW
PROPANIL	SW	GW
PROPARGITE	SW	GW
SIMAZINE	SW	GW
TEBUTHIURON	SW	GW
TERBACIL	SW	GW
TERBUFOS	SW	GW
THIOBENCARB	SW	GW
TRIALLATE	SW	GW
TRIFLURALIN	SW	GW

OTHER

CARBON, ORGANIC	SW	GW
CARBON, ORGANIC, SUSPENDED	SW	
CFC		GW
RADON-222		GW
SUSPENDED SEDIMENT	SW	
TRITIUM		GW
URANIUM, NATURAL		GW

CONSTITUENTS IN STREAM BED SEDIMENTS(BS) AND AQUATIC BIOLOGICAL TISSUES(TS)

TRACE METALS, TOTAL

ALUMINUM	BS	TS
ANTIMONY		TS
ARSENIC		TS
BARIUM	BS	TS
BERYLLIUM	BS	TS
BISMUTH	BS	
BORON		TS
CADMIUM		TS
CALCIUM	BS	
CESIUM	BS	
CHROMIUM	BS	TS
COBALT	BS	TS
COPPER	BS	TS
EUROPIUM	BS	
GALLIUM	BS	
GOLD	BS	
HOLMIUM	BS	
IRON	BS	TS
LANTHANUM	BS	
LEAD	BS	TS
LITHIUM	BS	
MAGNESIUM	BS	
MANGANESE	BS	TS
MERCURY		TS
MOLYBDENUM	BS	TS
NEODYMIUM	BS	
NICKEL	BS	TS
NIOBIUM	BS	
PHOSPHORUS	BS	
POTASSIUM	BS	
SCANDIUM	BS	
SELENIUM	BS	TS
SILVER		TS
SODIUM	BS	
STRONTIUM	BS	TS
SULFUR	BS	
TANTALUM	BS	
TIN	BS	
TITANIUM	BS	
URANIUM	BS	TS
VANADIUM	BS	TS
YTTERBIUM	BS	
YTTRIUM	BS	
ZINC	BS	TS

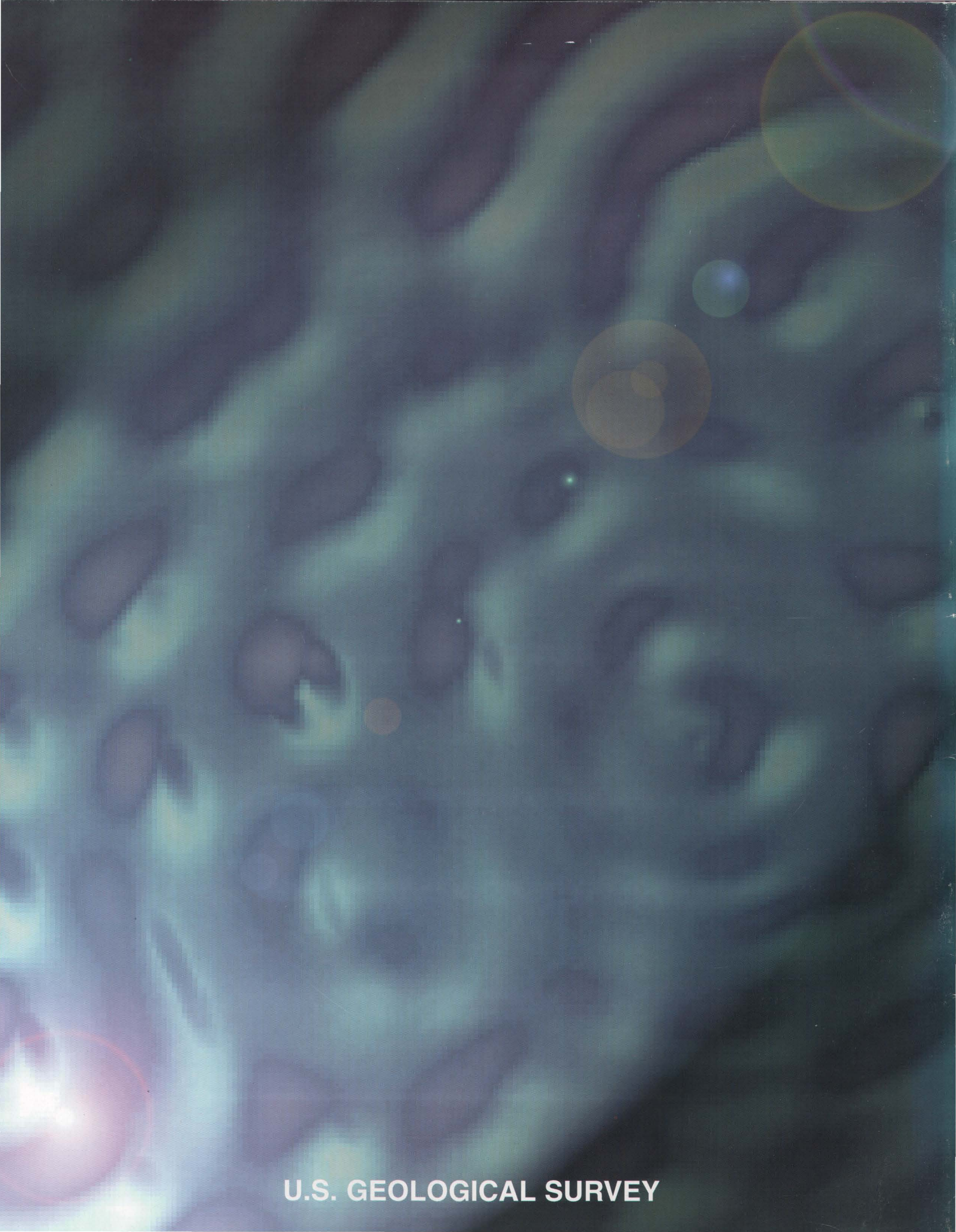
ORGANIC COMPOUNDS

1,2,4-TRICHLOROBENZENE	BS
1,2-DIMETHYLNAPHTHALENE	BS
1,6-DIMETHYLNAPHTHALENE	BS
1-METHYL9H-FLUORENE	BS
1-METHYLBENZO(A)PYRENE	BS
1-METHYLPHENANTHRENE	BS
1-METHYLPYRENE	BS
2,2'-BIQUINOLINE	BS
2,3,5,6-TETRAMETHYLPHENOL	BS
2,3,6-TRIMETHYLNAPHTHALENE	BS
2,4,6-TRICHLOROPHENOL	BS
2,4-DICHLOROPHENOL	BS
2,4-DINITROPHENOL	BS
2,4-DINITROTOLUENE	BS
2,6-DIMETHYLNAPHTHALENE	BS
2,6-DINITROTOLUENE	BS
2-CHLORONAPHTHALENE	BS
2-ETHYLNAPHTHALENE	BS
2-METHYL-4,6-PHENOL	BS
2-METHYLANTHRACENE	BS
3,5-DIMETHYLPHENOL	BS
4-BROMOPHENYL PHENYL ETHER	BS
4-CHLOROPHENYL PHENYL ETHER	BS
4CL-3METHYLPHENOL	BS

4H-CYCLOPENTA(DEF)PHENANTHRENE	BS	
9,10-ANTHRAQUINONE	BS	
9H-FLUORENE	BS	
ACENAPHTHENE	BS	
ACENAPHTHYLENE	BS	
ACRIDINE	BS	
ALDRIN	BS	TS
ALPHA-HCH	BS	TS
ANTHRACENE	BS	
AZOBENZENE	BS	
BENZ(A)ANTHRACENE	BS	
BENZO(B)FLUORANTHENE	BS	
BENZO(G,H,I) PERYLENE	BS	
BENZO(K)FLUORANTHENE	BS	
BENZO{C}CINNOLINE	BS	
BETA-HCH	BS	TS
BIS(2-CHLORO-1-METHYL- ETHYL) ETHER	BS	
BIS(2-CHLOROETHYL) ETHER	BS	
BIS(2-ETHYL HEXYL)PHTHALATE	BS	
BUTYLBENZYLPHTHALATE	BS	
C8-ALKYLPHENOL	BS	
CARBAZOLE	BS	
CARBON, INORGANIC	BS	
CARBON, ORGANIC	BS	
CARBON	BS	
CHLORONEB	BS	
CHRYSENE	BS	
CIS-CHLORDANE	BS	TS
CIS-NONACHLOR	BS	TS
CIS-PERMETHRIN	BS	
DCPA	BS	TS
DELTA-HCH		TS
DIBENZ(A,H)ANTHRACENE	BS	
DIBENZOTHIOPHENE	BS	
DIBUTYLPHTHALATE	BS	
DIELDRIN	BS	TS
DIETHYLPHTHALATE	BS	
DIMETHYLPHTHALATE	BS	
DIOCTYLPHTHALATE	BS	
ENDOSULFAN 1	BS	
ENDRIN	BS	TS
FLUORANTHENE	BS	
HEPTACHLOR EPOXIDE	BS	TS
HEPTACHLOR	BS	TS
HEXACHLOROBENZENE	BS	
HEXACHLOROBUTADIENE	BS	
HEXACHLOROCYCLOPENTADIENE	BS	
HEXACHLOROETHANE	BS	
INDENO(1,2,3-CD)PYRENE 1-METHYL-	BS	
ISODRIN	BS	
ISOPHORONE	BS	
ISOQUINOLINE	BS	
LINDANE	BS	TS
M-DICHLOROBENZENE	BS	
M-NITROPHENOL	BS	
MESITOL	BS	
METHANE BIS(2-CHLORO ETHOXY)	BS	
MIREX	BS	TS
N-NITROSODIPHENYLAMINE	BS	
N-NITROSODIPROPYLAMINE	BS	
NAPHTHALENE	BS	
NITROBENZENE	BS	
o,p' DDD	BS	TS
o,p' DDE	BS	TS
o,p' DDT	BS	TS
o,p' METHOXYCHLOR BN	BS	TS
O-CHLOROPHENOL	BS	
O-DICHLOROBENZENE	BS	
O-NITRO-PHENOL	BS	
OXYCHLORDANE	BS	TS
p,p' DDD	BS	TS
p,p' DDE	BS	TS
p,p' DDT	BS	TS
p,p' METHOXYCHLOR BN	BS	TS
P-CRESOL	BS	
P-DICHLOROBENZENE	BS	
PCB	BS	TS
PENTACHLOROANISOLE	BS	TS
PENTACHLORONITROBENZENE	BS	
PENTACHLOROPHENOL	BS	
PHENANTHRENE	BS	
PHENANTHRIDINE	BS	
PHENOL	BS	
PYRENE	BS	
QUINOLINE	BS	
TOXAPHENE	BS	TS
TRANS-CHLORDANE	BS	TS
TRANS-NONACHLOR	BS	TS
TRANS-PERMETHRIN	BS	
VANADIUM		TS

OTHER

CARBON, INORGANIC	BS	
CARBON, ORGANIC	BS	
CARBON	BS	
LIPIDS		TS
MOISTURE	BS	
WATER PRESENT		TS


U.S. GEOLOGICAL SURVEY