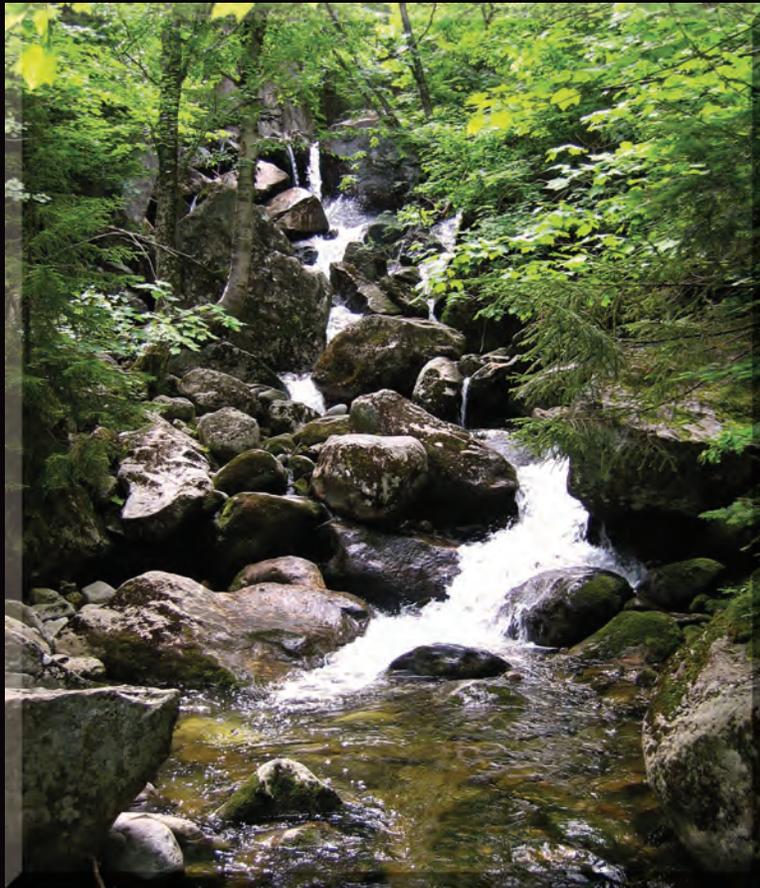


Prepared in cooperation with the National Park Service

Characterization of Major-Ion Chemistry and Nutrients in Headwater Streams Along the Appalachian National Scenic Trail and Within Adjacent Watersheds, Maine to Georgia



Scientific Investigations Report 2011–5151

U.S. Department of the Interior
U.S. Geological Survey



Front cover. Bumpus Brook above Stairs Falls on the Howker Ridge Trail of Mount Madison in Coos County, New Hampshire.
(Photograph published with permission from Nancy Gaudreau)

Back cover. Appalachian National Scenic Trail in the Pisgah National Forest, east of Roan Highlands, North Carolina.
(Photograph published with permission from Nancy Gaudreau)

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By Denise M. Argue, Jason P. Pope, and Fred Dieffenbach

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**U.S. Department of the Interior
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U.S. Department of the Interior
KEN SALAZAR, Secretary

U.S. Geological Survey
Marcia K. McNutt, Director

U.S. Geological Survey, Reston, Virginia: 2012

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Contents

Acknowledgments	iii
Abstract	1
Introduction.....	2
Purpose and Scope	4
Description of the Study Area	5
Delineation of Study Area	5
Geology.....	5
Topography	7
Precipitation and Temperature.....	7
Hydrology	8
Physiographic and Ecological Divisions.....	9
Previous Investigations.....	15
Sources of Water-Quality Data.....	16
Acid Rain Monitoring Program.....	17
Coweeta LTER Program	17
Hubbard Brook LTER Program.....	17
Delaware Water Gap National Recreation Area.....	17
Great Smoky Mountains National Park.....	17
Virginia Trout Stream Sensitivity Study (VTSSS).....	19
White Mountain National Forest.....	19
Environmental Monitoring and Assessment Program (EMAP).....	19
Temporally Integrated Monitoring of Ecosystems and Long Term Monitoring Program (TIME/LTM).....	19
National Stream Survey Program	19
Wadeable Stream Assessment Program.....	19
Methods of Analysis.....	20
Quality Assurance and Compilation of Water-Quality Data	20
Quality Assurance.....	20
Data Compilation.....	20
Ancillary Data Sources.....	21
Hydrologic Attributes	21
Environmental Attributes	25
Site Selection.....	25
Criteria for Selection of Nonadjacent Sampling Sites.....	25
Selected Sites and Data Aggregation	26
Statistical Methods.....	36
Characterization of Selected Field Properties, Major-Ion Chemistry, Acid Neutralizing Capacity, and Nutrients.....	37
Field Properties	37
Major Ions.....	39
Acid Neutralizing Capacity.....	46
Nutrients.....	47

Effects of Environmental Attributes on Water Quality.....	48
Elevation.....	49
Geology.....	49
Land Cover.....	51
Atmospheric Deposition.....	51
Implications of Using Available Data and Considerations for Future Monitoring.....	55
Summary.....	56
Selected References.....	58
Appendix 1. Ancillary and Water-Quality Variable Definitions and Catchment Data (on CD-ROM).....	63

Figures

1. Map showing location of the Appalachian National Scenic Trail and study area.....	3
2. Photograph showing the Appalachian National Scenic Trail north of Roanoke, Virginia.....	4
3. Map showing the percentage of forested land cover in the study area.....	6
4. Photograph showing the Appalachian National Scenic Trail passing through an open field on Cross Mountain near Shady Valley, Tennessee.....	7
5. Photograph showing the Appalachian National Scenic Trail on Franconia Ridge, near Franconia, New Hampshire.....	8
6. Photograph showing a first-order stream, typical of the high-elevation streams that are crossed by the Appalachian National Scenic Trail.....	9
7. Map showing U.S. Forest Service ecological sections (ecosections) that intersect the study area.....	13
8. Photograph showing the Appalachian National Scenic Trail passing over Little Hump in North Carolina through the region known as the “balds”.....	14
9. Map showing hydrologic subregions that intersected and were used as geographic subdivisions of the study area.....	23
10. Schematic diagram showing examples of the nested relation of National Hydrography Dataset <i>Plus</i> catchments with larger delineated hydrographic units such as subwatersheds, and drainage areas defined for a set of nested catchments.....	24
11. Index map showing areas covered by figures 12 and 13.....	27
12. Maps showing first- and second-order catchments from the National Hydrography Dataset <i>Plus</i> that are adjacent to the Appalachian National Scenic Trail and were used to characterize physical attributes of the trail environment from <i>A</i> , Maine to Vermont, <i>B</i> , Massachusetts to Maryland, <i>C</i> , Maryland to Virginia, and <i>D</i> , Virginia to Georgia.....	28
13. Maps showing the spatial distribution of and the number of sampling sites in National Hydrography Dataset <i>Plus</i> catchments used in the level 1 inventory of first- and second-order streams along the Appalachian National Scenic Trail, <i>A</i> , Maine to Vermont, <i>B</i> , Massachusetts to Maryland, <i>C</i> , Maryland to Virginia, and <i>D</i> , Virginia to Georgia.....	32
14. Boxplots showing comparisons of concentrations of <i>A</i> , pH, <i>B</i> , specific conductance, <i>C</i> , acid neutralizing capacity, <i>D</i> , calcium, <i>E</i> , magnesium, <i>F</i> , sodium, <i>G</i> , potassium, <i>H</i> , sulfate, <i>I</i> , chloride, <i>J</i> , nitrate, <i>K</i> , ammonia, <i>L</i> , total nitrogen, and <i>M</i> , total phosphorus, by U.S. Forest Service ecological sections (ecosections), from catchments that contain selected first- and second-order streams along the Appalachian National Scenic Trail.....	44

15. Map showing major geologic units within the study area	50
16. Boxplots showing comparison of concentrations, by major geologic groups, of <i>A</i> , pH, <i>B</i> , specific conductance, and <i>C</i> , acid neutralizing capacity from catchments that contained selected first- and second-order streams along the Appalachian National Scenic Trail	52
17. Maps of 1994 annual wet-deposition estimates for <i>A</i> , sulfate and <i>B</i> , nitrate for the eastern United States, including the study area	53
18. Boxplots showing wet-deposition estimates from 1994 of <i>A</i> , sulfate and <i>B</i> , nitrate by U.S. Forest Service ecological sections (ecosections) for all first and second order catchments in the study area	54

Tables

1. Description of landscapes, geology, and primary land cover for physiographic provinces and U.S. Forest Service ecological sections.....	10
2. Appalachian National Scenic Trail level 1 inventory of data sources used, project acronym, number of sampling sites, number of records, and the period of record for the water-quality data initially compiled.....	18
3. Types and sources of ancillary data used in this study	22
4. Threshold values, by subregion, of selected physical attributes used to screen nonadjacent sampling sites for inclusion in the water-quality summary of selected sampling sites along the Appalachian National Scenic Trail.....	36
5. Summary statistics of selected physical attributes, by U.S. Forest Service ecological sections (ecosections), from catchments that contain selected sampling sites along the Appalachian National Scenic Trail	38
6. Summary statistics of concentrations of selected water-quality constituents from catchments that contain selected sampling sites along the Appalachian National Scenic Trail	39
7. Water temperature and dissolved oxygen concentrations by U.S. Forest Service ecological sections (ecosections) and by season from selected sampling sites along the Appalachian National Scenic Trail	40
8. Summary statistics of selected water-quality constituents by U.S. Forest Service ecological sections (ecosections) from catchments that contain selected sampling sites in headwater streams along the Appalachian National Scenic Trail.....	41
9. Comparison among U.S. Forest Service ecological sections (ecosections) of the percentages of catchments with acid neutralizing capacity classified as acidic, sensitive, or insensitive	46
10. Comparison of median catchment concentrations of nutrients and the percentages of median concentrations greater than estimated national background concentrations from selected sampling sites along the Appalachian National Scenic Trail.....	47
11. Comparison, by nutrient ecoregion, of median catchment concentrations of total nitrogen and total phosphorus and the percentages of median catchment concentrations greater than U.S. Environmental Protection Agency's nutrient criteria from selected sampling sites along the Appalachian National Scenic Trail.....	48
12. Rho values from Spearman correlations of the elevations of catchments and the percentages of developed and agricultural land cover with concentrations of selected water-quality constituents in catchments that contained selected sampling sites along the Appalachian National Scenic Trail.....	49
13. Rho values from Spearman correlations of elevation with selected environmental attributes of catchments that contain selected sampling sites along the Appalachian National Scenic Trail	49

Conversion Factors, Abbreviations, and Acronyms

Multiply	By	To obtain
Length		
inch (in.)	2.54	centimeter (cm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
Area		
square mile (mi ²)	259.0	hectare (ha)
square mile (mi ²)	2.590	square kilometer (km ²)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

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

Vertical coordinate information is referenced to the North American Vertical Datum of 1988 (NAVD 88).

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius ($\mu\text{S}/\text{cm}$ at 25°C).

Concentrations of chemical constituents in water are given in milligrams per liter (mg/L), micrograms per liter ($\mu\text{g}/\text{L}$), micromoles per liter ($\mu\text{mol}/\text{L}$), and microequivalents per liter ($\mu\text{eq}/\text{L}$).

Concentrations of chemical constituents in wet-atmospheric deposition are given in kilograms per hectare (kg/ha).

Acronyms

ANC	acid neutralizing capacity
ATC	Appalachian Trail Conservancy
CAAA	Clean Air Act Amendments of 1990
EMAP	Environmental Monitoring and Assessment Program
LTER	Long Term Ecological Research
LTM	Long Term Monitoring
NADP	National Atmospheric Deposition Program
NHD	National Hydrography Dataset
NPS	National Park Service
NSF	National Science Foundation
NWIS	National Water Information System
STORET	STORage and RETrieval database operated by the U.S. Environmental Protection Agency
TIME	Temporally Integrated Monitoring of Ecosystems
USEPA	U.S. Environmental Protection Agency
USFS	U.S. Forest Service
USGS	U.S. Geological Survey
VTSSS	Virginia Trout Stream Sensitivity Study

Characterization of Major-Ion Chemistry and Nutrients in Headwater Streams Along the Appalachian National Scenic Trail and Within Adjacent Watersheds, Maine to Georgia

By Denise M. Argue¹, Jason P. Pope², and Fred Dieffenbach³

Abstract

An inventory of water-quality data on field parameters, major ions, and nutrients provided a summary of water quality in headwater (first- and second-order) streams within watersheds along the Appalachian National Scenic Trail (Appalachian Trail). Data from 1,817 sampling sites in 831 catchments were used for the water-quality summary. Catchment delineations from *NHDPlus* were used as the fundamental geographic units for this project. Criteria used to evaluate sampling sites for inclusion were based on selected physical attributes of the catchments adjacent to the Appalachian Trail, including stream elevation, percentage of developed land cover, and percentage of agricultural land cover.

The headwater streams of the Appalachian Trail are generally dilute waters, with low pH, low acid neutralizing capacity (ANC), and low concentrations of nutrients. The median pH value was slightly acidic at 6.7; the median specific conductance value was 23.6 microsiemens per centimeter, and the median ANC value was 98.7 milliequivalents per liter ($\mu\text{eq/L}$). Median concentrations of cations (calcium, magnesium, sodium, and potassium) were each less than 1.5 milligrams per liter (mg/L), and median concentrations of anions (bicarbonate, chloride, fluoride, sulfate, and nitrate) were less than 10 mg/L.

Differences in water-quality constituent levels along the Appalachian Trail may be related to elevation, atmospheric deposition, geology, and land cover. Spatial variations were summarized by ecological sections (ecosections) developed by the U.S. Forest Service. Specific conductance, pH, ANC, and concentrations of major ions (calcium, chloride, magnesium, sodium, and sulfate) were all negatively correlated with elevation. The highest elevation ecosections

(White Mountains, Blue Ridge Mountains, and Allegheny Mountains) had the lowest pH, ANC, and concentrations of major ions. The lowest elevation ecosections (Lower New England and Hudson Valley) generally had the highest pH, ANC, and concentrations of major ions. The geology in discrete portions of these two ecosections was classified as containing carbonate minerals which has likely influenced the chemical character of the streamwater. Specific conductance, pH, ANC, and concentrations of major ions (calcium, chloride, magnesium, sodium, and sulfate) were all positively correlated with percentages of developed and agricultural land uses at the lower elevations of the central region of the Appalachian Trail (including the Green–Taconic–Berkshire Mountains, Lower New England, Hudson Valley, and Northern Ridge and Valley ecosections). The distinctly different chemical character of the streams in the central sections of the Appalachian Trail is likely related to the lower elevations, the presence of carbonate minerals in the geology, higher percentages of developed and agricultural land uses, and possibly the higher inputs of sulfate and nitrate from atmospheric deposition.

Acid deposition of sulfate and nitrate are important influences on the acid-base chemistry of the surface waters of the Appalachian Trail. Atmospheric deposition estimates are consistently high (more than 18 kilograms per hectare (kg/ha) for sulfate, and more than 16 kg/ha for nitrate) at both the highest and lowest elevations. However, the lowest elevation (Green–Taconic–Berkshire Mountains, Lower New England, Hudson Valley, Northern Glaciated Allegheny Plateau, and Northern Ridge and Valley ecosections) included the largest spatial area of sustained high estimates of atmospheric deposition.

Calcium-bicarbonate was the most frequently calculated water type in the Lower New England and Hudson Valley ecosections. In the northern and southern sections of the Appalachian Trail mix-cation water types were most prevalent and sulfate was the predominate anion. The predominance of the sulfate anion in the surface waters of the northern and southern ecosections likely reflects the influence of sulfate deposition. Although the central portion of the Appalachian Trail has the largest spatial area of high atmospheric acid

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deposition, the lower ionic strength waters in the northern and southern ecoregions of the Appalachian Trail may have been more adversely affected by acid deposition.

The low ionic strength of the streams in the White Mountains, Blue Ridge Mountains, and Allegheny Mountains ecoregions makes parts of these regions susceptible to seasonal or event-driven episodic acidification, which can be detrimental to health of aquatic and terrestrial ecosystems. Median catchment ANC values were classified into three groups—acidic, sensitive, and insensitive. The White Mountains, Blue Ridge Mountains, and Allegheny Mountains ecoregions included the highest frequency of catchments classified as acidic or sensitive. More than 56 percent of the catchments from the White Mountains ecoregion were classified as sensitive to acidic inputs. In the Blue Ridge ecoregion, 1.6 percent of the catchments were classified as acidic, and 38.2 percent of the catchments were classified as sensitive to acidic inputs. In the Allegheny Mountains ecoregion, 17.6 percent of the catchments were classified as acidic, and 29.4 percent of the catchments were classified as sensitive to acidic inputs.

Median concentrations of nitrogen species were less than 0.4 mg/L, and median concentrations of total phosphorus were less than 0.02 mg/L along the Appalachian Trail. A comparison of median catchment concentrations of nutrients to estimated national background concentrations demonstrated that concentrations along the Appalachian Trail are generally lower. A comparison of median concentrations of total nitrogen and total phosphorus to the U.S. Environmental Protection Agency's (USEPA) nutrient criteria for the Eastern U.S. ecoregions showed that the concentrations of total nitrogen in the northern section of the Appalachian Trail were generally higher than the USEPA criterion. Similarly, median concentrations of total phosphorus in the southern regions of the Appalachian Trail were approximately twice as high as USEPA criteria. Sections of the Appalachian Trail are adjacent to modest amounts of agricultural and developed land areas. These nonforested land areas may be contributing to the percentage of catchments in which concentrations of total nitrogen and total phosphorus are higher than USEPA nutrient ecoregion criteria.

Introduction

The level 1 inventory is a process used by the Water Resources Division of the National Park Service (NPS), to provide descriptive water-quality information for key water resources at NPS units throughout the United States. The Appalachian National Scenic Trail (Appalachian Trail) is a unit of the National Park System that extends along almost the entire Appalachian Mountain range in the Eastern United States (fig. 1). The Appalachian Trail passes from Maine to Georgia through 14 states, 6 national parks, 8 national forests, 1 national wildlife refuge, and a variety of lands owned by

federal, state, local, and nonprofit organizations (National Park Service, 2008). The Appalachian Trail is administered through a cooperative management system in which responsibilities are shared among the NPS, the U.S. Forest Service (USFS), the nonprofit Appalachian Trail Conservancy (ATC), and other organizations. More than 99 percent of the Appalachian Trail lies on protected land (National Park Service, 2008), and the trail traverses a wide variety of landscapes characteristic of the Appalachian Mountains.

The Appalachian Trail was originally conceived by Benton MacKaye, an early 20th Century conservationist, as a footpath (fig. 2) that linked a series of small isolated communities (MacKaye, 1921). While some of MacKaye's original visions did not materialize, the trail itself did come together as a footpath that provides hikers the ability to traverse a largely intact wilderness located along the crest of the Appalachian Mountains. In recent years, as natural systems in the United States have been increasingly affected by human activities, including urbanization, pollution, habitat fragmentation, and invasive species, there has been an increased awareness and appreciation of the Appalachian Trail for its value as an intact corridor of protected natural lands and as a study area for research on the effects of human disturbance and variations in climate over time on natural systems (Shriver and others, 2005).

The quality of water resources along the Appalachian Trail were identified by the NPS as a critical measure of the environmental health of the Appalachian Trail (Shriver, 2005). A fundamental understanding of the natural-resource conditions along the Appalachian Trail is essential for the NPS to manage Appalachian Trail water resources in a way that is consistent with its mission. Water resources along the Appalachian Trail include streams, rivers, lakes, ponds, seeps, springs, wetlands, and wells. The form, structure, and occurrence of these water resources vary considerably, and their characteristics and occurrence may depend on the geology, climate, and the terrestrial ecological systems in particular areas. The water resources along the Appalachian Trail serve many uses, providing a source of drinking water for hikers, visitors, and wildlife; providing recreational, scenic and aesthetic value; habitat for plants and animals; and a source of water for downstream uses, such as public water supplies, fisheries, and hydropower generation.

An assessment of the quality of water resources along the Appalachian Trail has not been previously undertaken, although a variety of studies have been performed within specific regions and individual park units through which the Appalachian Trail passes. The current review conducted by the U.S. Geological Survey (USGS), in cooperation with the NPS, comprises a level 1 inventory of available water-quality data (1923–2009) along the Appalachian Trail. The NPS requested the USGS to perform a level 1 water-quality inventory of the Appalachian Trail to enable NPS to develop baseline water-quality information for key water resources that are defined as those waters that are essential to the central cultural, historical, or natural-resource-management themes of the park or



Figure 1. Location of the Appalachian National Scenic Trail and study area.



Figure 2. The Appalachian National Scenic Trail (AT) north of Roanoke, Virginia. Symbol on the sign is an emblem for AT. (Photograph courtesy of Joseph Ayotte, U.S. Geological Survey)

that provide habitats for threatened or endangered plants and animals. The focus of this report is on headwater streams that represent one common, or ‘characteristic’ water resource that is key along the Appalachian Trail. This information will enhance the ability of NPS to manage park resources, could have direct relevance for future resource-monitoring activities, and may serve as a foundation from which changes in water quality could be assessed over time.

Purpose and Scope

This report summarizes the objectives, methods, and results of analyses of water-quality data compiled by the USGS for headwater streams (classified as first- and second-order streams in the Strahler stream-order system) along and near the Appalachian Trail from Maine to Georgia. Specific objectives of this project include (1) compiling water-quality data collected along or near the Appalachian Trail;

(2) determining the spatial coverage of water-quality data; (3) developing a method by which data could be screened to determine suitability for inclusion in water-quality summaries; (4) providing summary statistics of the concentrations of selected constituents typically used to describe basic water chemistry; (5) describing natural and anthropogenic factors that may explain the observed variability in water quality; and (6) evaluating how data can help guide future water-quality-monitoring considerations. The parameters and constituents selected for analysis in this report include pH, specific conductance, dissolved oxygen, water temperature, acid neutralizing capacity (ANC), bicarbonate, calcium, chloride, fluoride, magnesium, potassium, silica, sodium, sulfate, ammonia, nitrate, total nitrogen, and total phosphorus. The focus is on basic chemical quality of headwater streams and the report does not include data on microbiological characteristics, trace elements, and other constituents that are commonly related to drinking water quality.

In an attempt to compile the most extensive inventory of water-quality data that characterize headwater streams along and nearby the Appalachian Trail, a method for incorporating sampling sites not adjacent to the Appalachian Trail (hereafter referred to as nonadjacent) was developed. The developed methodology for selecting nonadjacent sampling sites helped to ensure that the environmental setting of the selected nonadjacent sampling sites was representative of the Appalachian Trail environment and therefore appropriate for inclusion in this water-quality characterization. In this report, the term ‘Appalachian Trail environment’ (not spatially defined) is used to refer to the general characteristics of the landscape features and surrounding area and resources in the immediate vicinity of the Appalachian Trail.

Description of the Study Area

The Appalachian Trail is an approximately 2,175-mi-long footpath that follows the crest of the Appalachian Mountain range in the eastern United States. From its northern end in central Maine to its southern end in northern Georgia, the Appalachian Trail passes through 14 states, including New Hampshire, Vermont, Massachusetts, Connecticut, New York, New Jersey, Pennsylvania, Maryland, West Virginia, Virginia, North Carolina, and Tennessee (Shriver and others, 2005). The Appalachian Trail passes through a wide variety of landscapes representative of the Appalachian Mountains, including topographic classes such as high mountain ridges and peaks, rolling foothills, plateaus, and river valleys.

Land along the Appalachian Trail is most commonly forested (fig. 3), with occasional open grassy (fig. 4) and rocky areas (fig. 5), and intermittent agricultural and developed areas (Dieffenbach, 2011). Farmland used for both row crops and pasture is also adjacent to many parts of the Appalachian Trail, but agricultural land is much more common in the mid-Atlantic than in other areas. The Appalachian Trail traverses land that is typically sparsely populated and relatively undeveloped, but it also passes near some large population centers, particularly in New York and Virginia. The Appalachian Trail actually passes through thirteen cities and towns defined as Urbanized Areas or Urban Clusters by the U.S. Census, including the New York–Newark Urbanized Area in New York and New Jersey, the Allentown–Bethlehem Urbanized Area in Pennsylvania, and the Roanoke Urbanized Area in Virginia (U.S. Census, 2003). Overall, the Appalachian Trail constitutes a protected corridor of relatively undeveloped land where important natural ecosystems of the Appalachian highlands are preserved.

Land along the Appalachian Trail is subject to many of the same environmental problems that threaten natural areas in other places. Threats to the health of the Appalachian Trail environment include atmospheric ozone; atmospheric deposition of sulfur, nitrogen, and mercury; impaired visibility; pressure on rare and endangered wildlife and vegetation; invasive species; climate change and variability; and changes in land

use; particularly from encroaching development (Shriver and others, 2005).

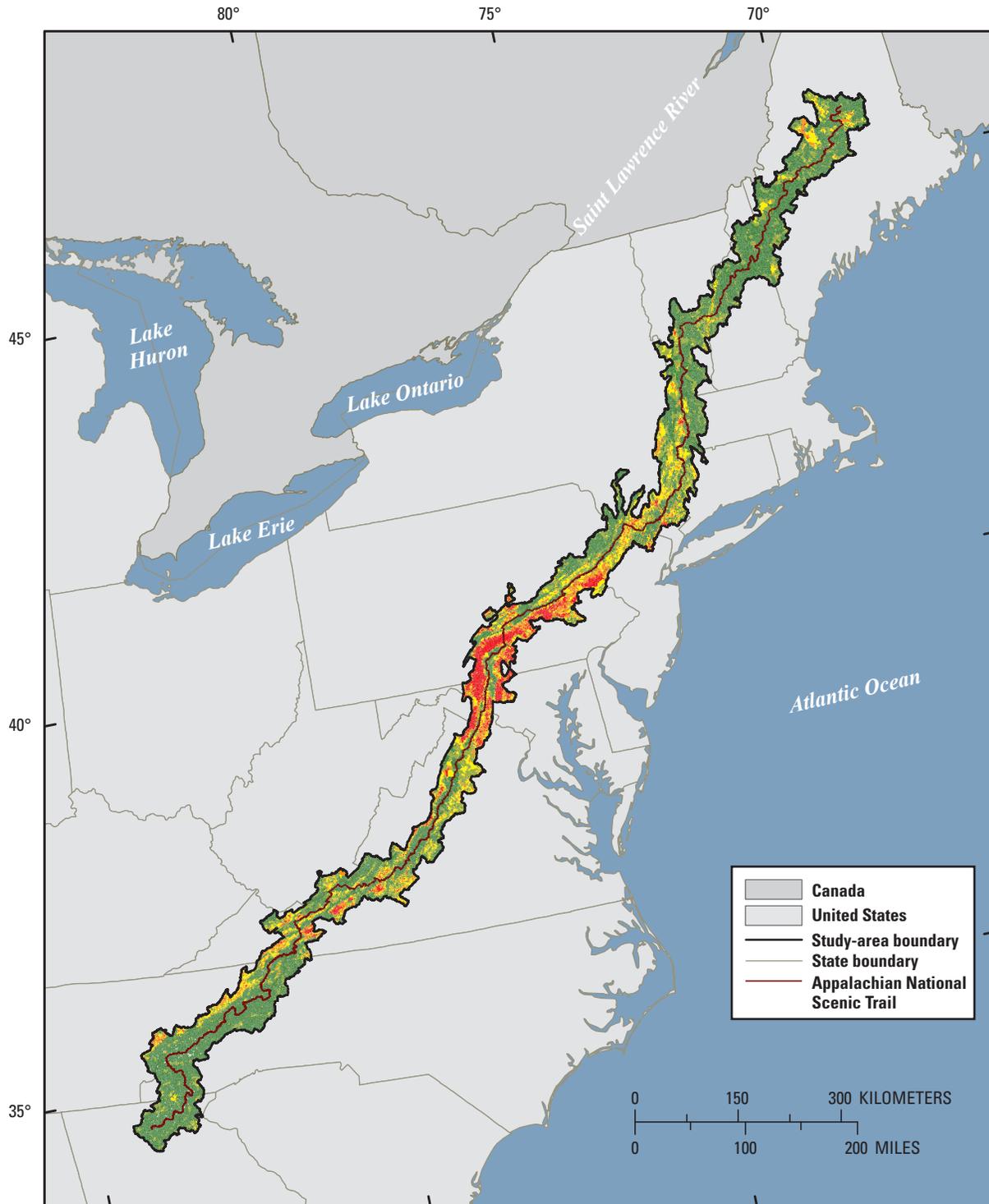
Delineation of Study Area

The Appalachian Trail is delineated and protected by a right-of-way corridor typically extending about 500 ft on either side of the footpath. While the Appalachian Trail can be most narrowly defined as the area within this 1000-ft-wide corridor, a broader area of interest was needed to capture as much relevant water-quality data as possible for a level 1 assessment of the quality of water resources in the Appalachian Trail environment. In consultation with the NPS, a discrete study area for this investigation was defined on the basis of hydrologic boundaries to provide a geographic scope with hydrologic relevance to the Appalachian Trail. This study area was specifically defined as the intersections of the boundaries of watersheds (10-digit hydrologic units) (U.S. Department of Agriculture, 2005) not more than 5 mi from the Appalachian Trail corridor. This area of interest is known as the HUC10 shell (Dieffenbach, 2011). The HUC10 shell, referred to as study area in this report, incorporates an area that is approximately 41,779 mi² and extends approximately 15 mi on either side of the Appalachian Trail; it is much wider in some places and narrower in others owing to the different sizes of the watersheds composing the boundary (fig. 1).

Geology

The distinctive rolling-to-mountainous topography of the Appalachian Mountains is the product of the geologic development of this region. Repeated mountain-building episodes resulting from continental collisions, followed by hundreds of millions of years of weathering and erosion, have shaped the Appalachian Mountains to its current conformations. This complex geologic history has resulted in rocks ranging in age from billions of years to about 140 million years (National Park Service, 2008). The geology includes a range of rock types, from folded and faulted sedimentary rocks such as limestone, sandstone, and shale, to metamorphic rocks such as schist and gneiss, to extensive intrusive rocks such as granites, as well as localized volcanic rocks. North of central Pennsylvania, continental glaciation during the Pleistocene Era further sculpted the landscape, leaving behind features characteristic of glacial environments, including many ponds (National Park Service, 2008). The underlying geology is important because it is a fundamental aspect of the region: variations in the weathering rates of differing types of rocks, combined with geologic features such as faults and folds, have a substantial effect on drainage patterns, slopes, elevations, and many other topographic features. Additionally, variations in mineralogy may substantially affect surface-water chemistry, especially in smaller watersheds where base flow may be dominant.

6 Major-Ion Chemistry and Nutrients in Headwater Streams Along the Appalachian National Scenic Trail, Maine to Georgia



State-line boundaries from North American Political Boundaries layer
 U.S. Geological Survey 1:10,000,000-scale digital data
 Albers Conic projection, NAD 1983

Percentages of forested land cover
 from the National Hydrography Dataset *Plus*
 (U.S. Environmental Protection Agency, 2006b)

EXPLANATION

Forest cover, in percent

	0 to 20
	greater than 20 to 40
	greater than 40 to 60
	greater than 60 to 80
	greater than 80 to 100

Figure 3. The percentage of forested land cover in the study area.



Figure 4. The Appalachian National Scenic Trail passing through an open field on Cross Mountain near Shady Valley, Tennessee. (Photograph published by permission of Nancy Gaudreau)

Topography

High elevations and steep slopes generally characterize the relief of the land in the immediate vicinity of the Appalachian Trail. Considerable variation in elevation exists along the Appalachian Trail, ranging from 124 ft above sea level where it crosses the Hudson River at Bear Mountain, New York to 6,643 ft at Clingmans Dome in Tennessee (National Park Service, 2008). The highest elevations and steepest slopes are generally in northern New England and in the southern Appalachians, whereas the lowest elevations are in the states of New York, New Jersey, Pennsylvania, and Maryland. Along the Appalachian Trail, the high ridges of the Appalachian Mountains are occasionally dissected by major river valleys such as the valleys of the Hudson, Susquehanna, and Potomac, which are characterized by flat to rolling terrain.

Precipitation and Temperature

The climate in the vicinity of the Appalachian Trail is highly variable owing to the substantial range in latitude,

elevation, and prevailing weather patterns. Cool summers and very cold winters are common in the northern areas around the Appalachian Trail, whereas hot summers and temperate winters are common in the southern areas, even at high elevations. At the northern end of the Appalachian Trail in Maine, the mean annual temperature during the period 1971 through 2000 was 3.9°C, and the mean annual precipitation was 39.0 in. (U.S. Department of Commerce, 2003). The mean daily temperature in Maine over this period ranged from -12.2°C in January to 18.3°C in July (PRISM Climate Group, 2006a). By comparison, the mean annual temperature at the southern end of the Appalachian Trail in north-central Georgia over the same period was approximately 15°C, and the mean annual precipitation was 55.9 in. (U.S. Department of Commerce, 2003). In Georgia, the mean daily temperature over this period ranged from 5°C in January to 25°C in July (PRISM Climate Group, 2006a). The mean annual precipitation along the Appalachian Trail was approximately 52.0 in. during the period 1971 through 2000 (PRISM Climate Group, 2006b).



Figure 5. The Appalachian National Scenic Trail on Franconia Ridge, near Franconia, New Hampshire. (Photograph courtesy of Ann Chalmers, U.S. Geological Survey)

Snowfall was measured between 1971 and 2000 at 12 long-term weather stations in the study area (National Climate Data Center, 2005). The greatest annual snowfall during this period was observed at Mount Washington, New Hampshire, where there was a mean annual value of 26.3 ft of measurable snowfall (National Climatic Data Center, 2005). Excluding the exceptional snowfall at Mount Washington, mean annual snowfall measured at stations in the study area ranged from 7.6 ft in Millinocket, Maine, to 0.82 ft in Knoxville, Tennessee (National Climatic Data Center, 2005). Variation in snowfall appears to be related primarily to latitude, although elevation and other climate factors also affect total annual snowfall.

In general, temperature and precipitation both increase from north to south along the Appalachian Trail. However, extreme climatic variations over small distances in the Appalachian Mountains result from local topographic and orographic effects. One example is Mount Washington in

New Hampshire, which has a mean annual precipitation of 102 in. at the summit (elevation 6,259 ft), while Berlin, N.H. (elevation 928 ft), a town only 18 mi away, has an average annual precipitation of 40.0 in. (U.S. Department of Commerce, 2003).

Hydrology

The Appalachian Trail crosses about 1,700 streams and 100 rivers from Maine to Georgia (fig. 6). Most of these streams are ‘low-order’ intermittent, first-, and second-order streams (Matt Robinson, National Park Service, written commun., 2006). These low-order streams are of particular interest because they are considered to be representative of the forested, mountainous, and high-elevation terrain that characterizes most of the Appalachian Trail environment. Larger streams and rivers—such as the Connecticut, the Hudson, and



Figure 6. A first-order stream, typical of the high-elevation streams that are crossed by the Appalachian National Scenic Trail. Brokenback Run is a tributary to the Hughes River near Nethers, Virginia. (Photograph courtesy of Jason Pope, U.S. Geological Survey)

the Potomac—are typically at lower elevations, and because the water quality is reflective of larger drainage basins and multiple contributing land uses that originate outside of the Appalachian Trail environment, they are not necessarily characteristic of the Appalachian Trail water resources. Consequently, these large stream and rivers, while important are beyond the scope of this report.

Physiographic and Ecological Divisions

Physiographic provinces are large-scale divisions that represent the topographic expression of the land surface and the geology and geologic history of a region (Fenneman and Johnson, 1946). Each province exhibits specific characteristics resulting from distinct combinations of geology, hydrology, precipitation, and temperature. Consequently, these provinces provide general geographic areas that help to describe

variations in the environment within the study area. The Appalachian Highlands Physiographic Division encompasses the entire study area, and within this division are six physiographic provinces (from north to south along the Appalachian Trail): New England, St. Lawrence Valley, Valley and Ridge, Appalachian Plateaus, Blue Ridge, and Piedmont. The St. Lawrence Valley Physiographic Province only intersects a very small area of the study area in west-central Vermont. This province does not represent any significant spatial region of the Appalachian Trail study area and was therefore not included in the following discussion. The five physiographic provinces that do represent the Appalachian Trail study area are listed in table 1.

A similar but more detailed classification scheme provided by the USFS uses the concept of ecological subregions to incorporate the distinctive biological and ecological aspects of the landscape with the physical features at several levels

Table 1. Description of landscapes, geology, and primary land cover for physiographic provinces and U.S. Forest Service ecological sections.

Physiographic province ¹	U.S. Forest Service ecological section ²	Landscape	Geology	Primary land cover
New England	Aroostook Hills and Lowlands	Gently rolling outwash plain with scattered low mountains. Highly modified by glaciation.	Sometimes weakly metamorphosed sedimentary formations, including sandstones, limestones, and shales.	Ranges from boreal conifers to broadleaf deciduous trees.
	Maine–New Brunswick Foothills and Lowlands	Broad central plain with areas of gently sloping hills and low, rounded mountains.	Sedimentary rocks with intruded granites.	Spruce-fir and maple, beech, birch.
	Central Maine Coastal and Embayment	Glacially scoured, dissected plain. Flat to gently rolling.	Metasedimentary and metavolcanic, with scattered granitic plutons.	Spruce-fir, mix of oak, hickory, maple, beech, and birch.
	White Mountains	Dissected highlands with rounded mountains and many glacial features.	Metasedimentary rocks, including quartzite, slate, and schist, intruded by extensive igneous areas including granite, diorite, gabbro, and basalt.	Spruce-fir, maple, beech, birch, and aspen.
	Vermont–New Hampshire Upland	Maturely dissected plain with open, low mountains and isolated hills.	Metamorphosed sedimentary rocks such as quartzite, slate, and schist, as well as areas of gneiss and a band of volcanic rocks.	Maple, beech, birch, and aspen.
	Green–Taconic–Berkshire Mountains	Ranges from nearly flat-topped plateaus with scattered isolated hills to sharp ridges with deep valleys. Previously glaciated.	Quartzite, schist, metavolcanics, gneiss, and amphibolite.	Maple, beech, birch, and aspen.
	Lower New England	Broad, hilly plateaus of lower elevations.	Complex mix of sedimentary, igneous, and metamorphic rocks.	Mix of oak, hickory, maple, beech, birch, aspen, and pine.
	Valley and Ridge	Hudson Valley	Lowland formed from glacial lake plain, bordered by high escarpments.	Mix of carbonates, shales, siltstones, and sandstones, with areas affected by metamorphism.
Northern Ridge and Valley		Broad parallel ridges and valleys trending from northeast to southwest.	Carbonates underlying valleys separated by low sandstone ridges.	Mix of oak and hickory.
Allegheny Mountains		Dissected plateau resulting in landscape of sharp ridges, low mountains, and narrow valleys.	Sedimentary and metamorphic units, including sandstones, carbonates, siltstones, and shales.	Mix of oak, hickory, maple, beech, and birch.
Central Ridge and Valley		Maturely dissected landscape of open hills with folded, faulted, and uplifted belt of parallel valleys and ridges.	Sedimentary rock formations, dominated by carbonates.	Small areas of remaining natural forest include oak, hickory, pine, and white, red, and jack pine. Agricultural and urban land cover is common.

Table 1. Description of landscapes, geology, and primary land cover for physiographic provinces and U.S. Forest Service ecological sections.—Continued

Physiographic province ¹	U.S. Forest Service ecological section ²	Landscape	Geology	Primary land cover
Appalachian Plateaus	Catskill Mountains	Previously glaciated, deeply dissected plateau of mountainous terrain, with many peaks above 3,000 feet.	Fine sandstones, conglomerates, siltstones, and shales.	Mix of maple, beech, birch, oak, and hickory.
	Northern Glaciated Allegheny Plateau	Previously glaciated, dissected plateau of rounded ridges and moderate relief.	Sedimentary, including sandstones, siltstones, and shales.	Mix of maple, beech, birch, oak, hickory, and aspen.
	Northern Cumberland Mountains	Long mountains and dissected uplands.	Flat-lying sandstone units, incised by erosion.	Mix of oak and hickory.
Blue Ridge	Blue Ridge Mountains	System of high ridges and peaks separated by narrow valleys. Southern section is much wider and has higher mountains.	Mostly metamorphic rocks such as schist and gneiss, with some intrusive rocks such as granites and pegmatites, and occasional volcanics.	Deciduous to mixed forest at lower elevations, with distinctive spruce-fir forest at high elevations.
Piedmont	Northern Appalachian Piedmont	Dissected plain extending from mountains to coast. Hilly to rolling, with a few high ridges.	Combination of sedimentary and mixed metamorphic rocks including marble, quartzite, slate, schist, and gneiss.	Oak, hickory and pine.
	Southern Appalachian Piedmont	Dissected, irregular plain. Slightly rolling, with isolated hills and low mountains.	Mostly highly metamorphosed crystalline rocks weathered into deep, infertile, clayey soils.	Forests of oak-pine and loblolly-shortleaf pine. Cultivated agricultural areas are common.

¹ Physiographic provinces are from Fenneman and Johnson, 1946.

² U.S. Forest Service ecological sections and descriptions are from Keys and others, 1995.

of geographic resolution (Keys and others, 1995). Of most interest to the current project were the ecological sections, which are described by Keys and others (1995) as “large land areas of relatively homogeneous physical and biological components that interact to form environments of similar productive capabilities, response to disturbances, and potential for resource management”; ecological sections defined by the USFS (Keys and others, 1995) are referred to in this report as ecosections. These ecosections are useful for describing the Appalachian Trail environment in more detail than that provided by the more general physiographic provinces. The study area intersects 17 ecosections mapped by Keys and others (1995). These ecosections are described in table 1, where they are presented in groups corresponding to physiographic province. The ecosections are shown in figure 7.

The New England Physiographic Province encompasses the Appalachian Trail study area from Maine to southern New York. Much of this province is characterized by a relatively cool climate because of both northern latitudes and high elevations. Winters are long with continual snow cover. This province includes several broad river valleys as well as peaks that are moderate in elevation (over 4,920 ft) with many peaks above treeline (Keys and others, 1995). The White Mountains of New Hampshire include the highest elevations on the Appalachian Trail north of Virginia, with Mt. Washington reaching over 6,200 ft (Keys and others, 1995). The underlying geology in the New England Physiographic Province is quite complex, resulting from multiple episodes of sedimentation, metamorphism, and intrusion, followed by extensive shaping of the landscape by glaciation. Ecosections within the New England Physiographic Province describe local ecological landscapes, with primary distinctions resulting from differences in geology, elevation, and the influence of coastal climatic conditions. Within the study area, the New England Physiographic Province includes seven ecosections: Aroostook Hills and Lowlands, Maine–New Brunswick Foothills and Lowlands, Central Maine Coastal and Embayment, White Mountains, Vermont–New Hampshire Upland, Green–Taconic–Berkshire Mountains, and Lower New England.

The Valley and Ridge Physiographic Province encompasses much of the western highlands of the Appalachian Mountains from New York to Georgia. Geologically, this province is characterized by folded and faulted sedimentary rocks. In general, the landscape is one of moderately high and narrow ridges approximately 1,500 to 3,500 ft in elevation and separated by long, wide valleys, with both trending northeast to southwest, approximately parallel to the Appalachian Trail (Keys and others, 1995). The ridges are formed by relatively resistant sandstone, and the valleys are underlain by shale and carbonate rocks (Keys and others, 1995). The pattern of ridges and valleys results in a trellis-style drainage pattern for streams and rivers of this province. Within the study area, the Valley and Ridge Physiographic Province includes four ecosections: Hudson Valley, Northern Ridge and Valley, Allegheny Mountains, and Central Ridge and Valley.

The Appalachian Plateaus Physiographic Province is in southern New York and Pennsylvania and also along the southern part of the Virginia–West Virginia border. The Appalachian Trail never passes through the Appalachian Plateaus, but the province intersects the study area on the western edge. The Appalachian Plateaus are structural plateaus formed from relatively flat-lying sedimentary rocks that have been dissected by streams into an area of high relief. The northern section has been glaciated. Within the study area, the Appalachian Plateaus Physiographic Province encompasses three ecosections: Catskill Mountains, Northern Glaciated Allegheny Plateau, and Northern Cumberland Mountains.

The Blue Ridge Physiographic Province extends from central Pennsylvania to Georgia and is traversed by the Appalachian Trail over most of that distance, except for a large section in southwestern Virginia where the Appalachian Trail passes into the Valley and Ridge. On its eastern boundary, the Blue Ridge is distinguished by a steep escarpment separating it from the Piedmont province to the east, with relief of 1,000 to 1,600 ft in many places along this boundary (Keys and others, 1995). The Blue Ridge province is a narrow band (less than 12 mi wide) in its northern section and is characterized by a chain of relatively high mountain peaks ranging in elevation from approximately 3,000 to 4,000 ft and underlain primarily by metamorphic rocks, along with some plutonic and volcanic rocks, all highly resistant to weathering (Keys and others, 1995). The Blue Ridge province is much wider (approximately 75 mi) in the southern section, including areas in North Carolina, Tennessee, and Georgia, and is characterized by a system of high ridges forming several distinct mountain ranges separated by relatively narrow valleys. Most of this portion of the Blue Ridge province is underlain by metamorphic rocks such as gneiss and schist, with some intrusive rocks such as granites and pegmatites, and occasional volcanics (Keys and others, 1995). In this southern section, the Blue Ridge province includes numerous peaks and ridges with elevations exceeding 4,900 ft. The highest mountains of the Appalachian Trail are in this part of the province, including Clingmans Dome in Tennessee (Keys and others, 1995). This province includes some distinctive ecological environments, known as mountain balds (fig. 8). Within the study area, the Blue Ridge Physiographic Province includes only the Blue Ridge Mountains ecosection, which consists of deciduous to mixed forests at lower elevations and distinctive spruce-fir forests at elevations above 4,900 ft (Keys and others, 1995). Many lower slopes of the Blue Ridge Mountains were cleared for agriculture in the 1800s, and most areas were selectively logged by the early 1900s (Keys and others, 1995), though some isolated areas of old-growth forest remain. The high elevations and steep slopes of this ecosection result in considerable orographic variations in temperature and precipitation.

The Piedmont Physiographic Province comprises the eastern foothills and lowlands adjacent to the high mountains of the Blue Ridge province immediately to the west. The Piedmont province is not crossed by the Appalachian Trail

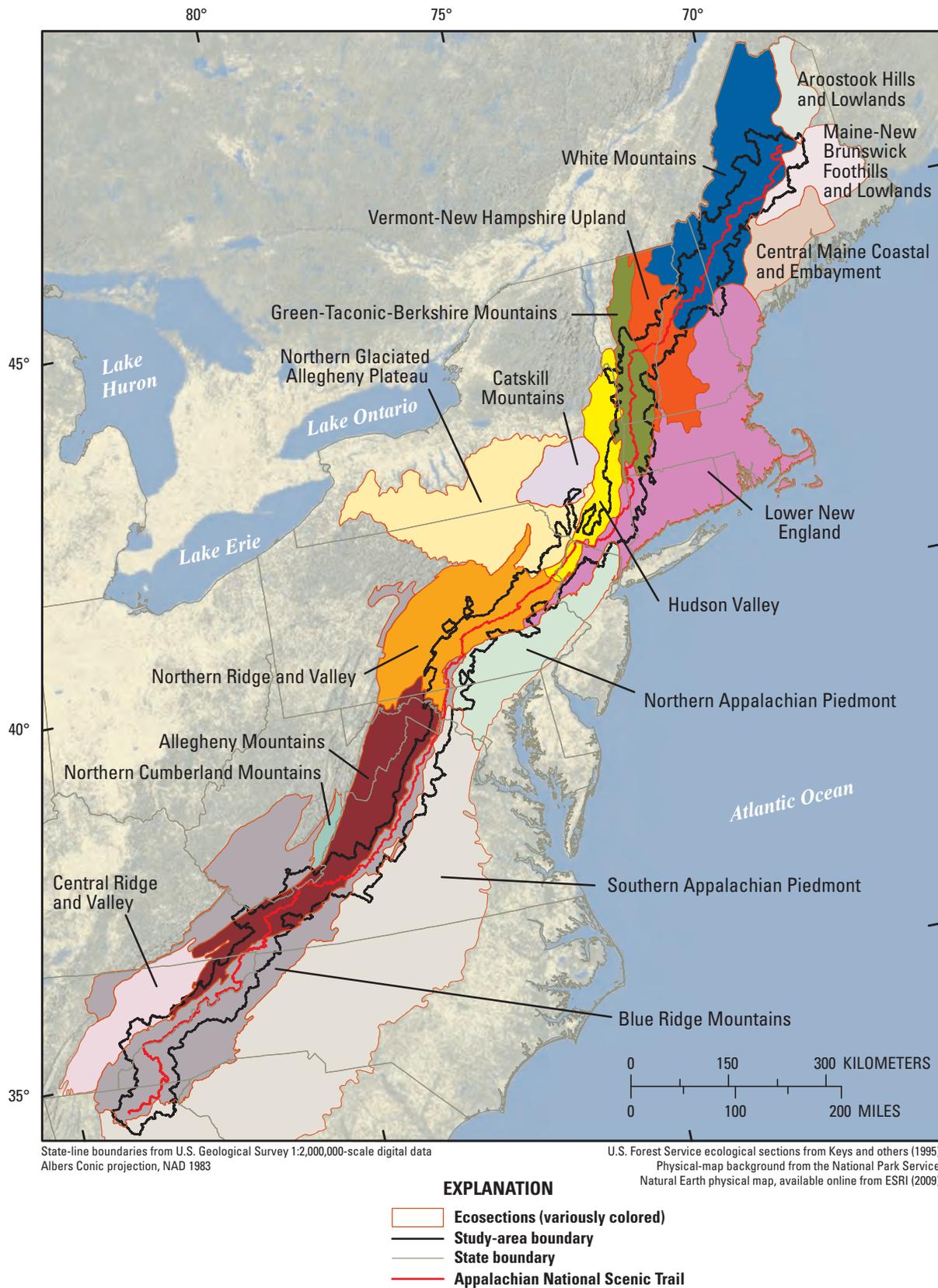


Figure 7. U.S. Forest Service ecological sections (ecosections) that intersect the study area.



Figure 8. The Appalachian National Scenic Trail passing over Little Hump in North Carolina through the region known as the "balds." (Photograph courtesy of Ann Chalmers, U.S. Geological Survey)

but is on the eastern edge of the study area from southern New York to Georgia. The terrain of the Piedmont province ranges in elevation from approximately 330 to 1,640 ft and is underlain by metamorphic and igneous rocks that are the remnants of the tectonic events that formed the Appalachian Mountains (Keys and others, 1995). Hydrologically, this region is traversed by a number of wide river valleys that drain the eastern side of the Appalachians. Within the study area, the Piedmont province includes the Northern Appalachian Piedmont and Southern Appalachian Piedmont ecosections.

Previous Investigations

Although no assessment of the water quality along the entire Appalachian Trail has been completed, water quality has been the focus of numerous investigations within or near portions of the Appalachian Trail. While too many studies have been done to allow a review of each in this report, results from some of the more comprehensive and (or) ongoing investigations can be summarized. Many of these studies have focused on the affects of acid deposition as it relates to the acidification of surface-water bodies and the subsequent degradation of aquatic ecosystems. Generally, studies have found that the combination of regionally high inputs of acidic deposition, coupled with the generally low ionic strength of the surface waters and base-poor soils, makes the water resources of the Appalachian Mountains and nearby areas vulnerable to the detrimental effects of acidic deposition. Assessment of water quality conducted near regions of the Appalachian Trail have also correlated variations in land use, such as higher percentages of agricultural land or developed land, with variations in water quality.

The acidification of surface waters by acid deposition in many areas near the Appalachian Trail has been well documented. Driscoll and others (2001) reported that 41 percent of the lakes in the Adirondack Mountains and 15 percent of the lakes in New England have exhibited chronic or episodic acidification. Furthermore, they reported that 83 percent of affected lakes are acidic because of acidic deposition. Kahl and Scott (1988) documented the significant role of atmospheric deposition in the acid-base chemistry of high-elevation lakes in Maine. In addition, it was concluded that lakes in Maine at elevations higher than approximately 2,000 ft were more dilute, less buffered, and probably more vulnerable to acidic deposition than low-elevation lakes in Maine.

Acid-base chemistry in small streams in the Appalachian Mountains of Virginia (including Shenandoah National Park (Sullivan and others, 2004; Webb and others, 2004; Cosby and others, 2006; Rice and others, 2007) and the Blue Ridge Mountains of North Carolina and Tennessee including Great Smoky Mountains National Park and Coweeta Long-Term Ecological Research area (Cook and others, 1994; Robinson and others, 2008; John Schwartz, University of Tennessee, Department of Civil and Environmental Engineering, written commun., 2008; Cai and others, 2009) has been studied for years, and the effects of acidic deposition have been well

documented. Approximately 93 percent of streams in the western mountains of Virginia were classified as sensitive to the effects of acidic deposition, 49 percent were classified as extremely sensitive, and 10 percent were classified as acidic (Charles and Christie, 1991). Of 54 low-order streams and 67 lakes sampled in the southern Blue Ridge Mountains, no surface-water bodies were classified as acidic, although the waters of this region also have low ionic strength and are sensitive to acidic inputs (Charles and Christie, 1991).

Surface waters that are classified as acidic or sensitive to acidic deposition are of interest because of the negative effects that acidic water can have on terrestrial and aquatic ecosystems. Seasonal and (or) event-driven increases in discharge that temporarily depress ANC in a water body are collectively referred to as episodic acidification. The occurrence and effects of episodic acidification have been well documented in surface waters in the Northeast (Driscoll, 1985; Wigington and others, 1996; Baker and others, 1996; Baldigo and Murdoch, 1997; Driscoll and others, 2001; Lawrence and others, 2004), in the Blue Ridge Mountains (Hyer and others, 1995; Rice and Bricker, 1995; Rice and others, 2005; Cosby and others, 2006), and in the Great Smoky Mountains National Park (Deyton and others, 2009; Neff and others, 2008). One way that repeated exposure to episodic acidification affects terrestrial ecosystems in the Appalachian Mountains is that the increased concentration of anions in acidic deposition leaches and depletes base cations from soils (Lawrence, 2002; Bailey and others, 2005; Cosby and others, 2006; Elias and others, 2009) and researchers have shown that depletion of base cations from soil has negatively affected forest health (Driscoll and others, 2001; Bailey and others, 2005; Elias and others, 2009). One effect of episodic acidification on aquatic life is the decrease in the ANC or pH can facilitate the release of aluminum from the soil, specifically monomeric aluminum, which can be toxic to fish (Driscoll, 1985; Baldigo and Murdoch, 1997). Studies conducted in the Northeastern United States to investigate the harmful effects of inorganic monomeric aluminum on brook trout (*Salvelinus fontinalis*) reported both temporary and long-term harmful effects on fish populations (Baker and others, 1996; Baldigo and Murdoch, 1997). Neff and others (2008) demonstrated the detrimental effects of episodic acidification on the health of brook trout (*Salvelinus fontinalis*) in the Great Smoky Mountains National Park.

Rice and others (2005) developed a model to predict the vulnerability of streams in Shenandoah National Park to episodic acidification. The model indicated that large areas of the park are vulnerable to sustained intervals of episodic acidification that could be harmful to fish populations, and that the geology, elevation, and size of the drainage area are effective predictors of susceptibility to episodic acidification. Sullivan and others (2007) used ANC to evaluate variations in the spatial distribution of acid-sensitive and acid-affected streams in relation to watershed features in the southern Appalachian Mountains. Findings from this study suggest that elevation, lithology, size of the drainage area, and forest type can be useful predictors of acid-sensitive and acid-affected watersheds.

Since the passage of the Clean Air Act Amendments of 1990 (CAAA), the responses of surface-water-chemistry in acid-sensitive regions along the Appalachian Trail to reductions in sulfur dioxide and nitrogen oxides imposed by the CAAA have been studied. The USEPA's Acid Rain Program has reported substantial reductions of sulfur dioxide and nitrogen oxides in atmospheric deposition (U.S. Environmental Protection Agency, 2010a). Researchers' have examined the reactions of surface waters to these reductions in acidic deposition, and reported that concentrations of sulfate and, to a lesser extent, nitrate in surface water decreased after sulfate and nitrate in deposition had decreased (Driscoll and others, 1998; Driscoll and others, 2003; Stoddard and others, 2003; Kahl and others, 2004; Webb and others, 2004; Monteith and others, 2007; U.S. Environmental Protection Agency, 2010a). Many of these studies assessed the recovery of surface waters to changes in atmospheric deposition as reflected by increases in ANC and (or) pH coupled with decreases in concentrations of sulfate. Stoddard and others (2003) and Kahl and others (2004) reported that the response rates of surface waters varied and lagged behind decreases in deposition, but that surface waters with the lowest ANC and pH gave the largest and most rapid response.

These studies, which measured the responses of surface-water-chemistry to reductions in acidic deposition from the CAAA, also demonstrated that these measures of change (increases in ANC and (or) pH and decreases in concentrations of sulfate) could be attributed to or be impeded by other environmental alterations. Stoddard and others (2003) and Rosfjord and others (2007) both reported that in the glaciated regions of the Northeast, concentrations of calcium and magnesium in soil have continued to decline despite the reduced input of anions from acidic deposition. Rosfjord and others (2007) noted that increasing surface-water concentrations of chloride caused by road-salting practices have altered the acid-base chemistry in affected watersheds, and that this interaction is complicating the assessment of the response of surface waters to changes in acidic deposition. Stoddard and others (2003) noted that increases in the natural organic acidity of surface waters also is complicating the assessment of recovery since passage of the CAAA. Monteith and others (2007) determined that increases in concentrations of dissolved organic carbon were proportional to decreases in the deposition of sulfate and sea salt. Webb and others (2004) reported that in the mountains of western Virginia, sulfate deposition in precipitation decreased by approximately 40 percent from 1995 to 2000, although concentrations of sulfate in streamwater did not decline to a similar extent. Their findings corroborate and refine the conclusion from Kahl and others (2004) that the retention of sulfur in watershed soils in some regions of western Virginia affected the apparent disconnect between changes in sulfate deposition and concentrations of sulfate in streamwater. Furthermore, defoliation caused by the gypsy-moth infestation in the mid-1980s to mid-1990s may confound the interpretation of trends in ANC over time (Webb and other, 2004). The

defoliation and subsequent recovery from the infestation produced a temporary increase and then a decrease in nitrate concentrations that likely caused a corresponding decrease and increase in the ANC. They concluded that it would be difficult to discern what respective proportions of the recent increases in ANC in this region could be attributed to the recovery from the gypsy-moth infestation and the reductions in sulfate deposition.

Hickman and Fischer (2007) and Siemion and Murdoch (2010) summarized streamwater quality in the Delaware Water Gap National Recreation area in Pennsylvania and New Jersey. Both studies reported positive correlations between water-quality constituents and the percentage of agricultural land cover in the drainage area. Specifically, Siemion and Murdoch (2010) showed that ANC and the concentrations of calcium, potassium, nitrate, total dissolved nitrogen, and dissolved phosphorus were correlated with the percentage of agricultural land cover. Hickman and Fischer (2007) also noted that wetlands in the Delaware River drainage area appeared to influence water quality in the Delaware Water Gap National Recreation area. Hickman and Fischer (2007) used linear regression to predict the differences in water quality between current (2002–2004) and future conditions.

Headwater stream chemistry is also important because of its subsequent effects on the water quality of downstream resources and aquatic communities. The effect of headwater streams on downstream water quality has been well documented (Alexander and others, 2007; Freeman and others, 2007; Nadeau and Rains, 2007). Alexander and others (2007) used a mass-balance watershed model based on stream networks in the northeastern United States to demonstrate the substantial contribution that first-order, headwater streams have on higher order streams with respect to mean annual flows and solute transport. Findings from this work showed that hydrologic and biogeochemical processes in headwater streams were physically and biochemically connected to the water quality downstream. Furthermore, the high proportional total length of headwater streams in the total stream length of a typical river drainage system (commonly over two-thirds) underscores the profound influence of the water quality of headwaters streams on the ecological integrity of streams and rivers at local and regional scales (Freeman and others, 2007).

Sources of Water-Quality Data

Many different projects with unique objectives have collected water-quality data from sampling sites along the Appalachian Trail. One of the primary objectives in compiling this level 1 water-quality inventory was to assess water-quality data from sites along or near the Appalachian Trail for use in determining water-quality conditions representative of the Appalachian Trail environment. Focus was given to data that had been collected at first- and second-order streams near the Appalachian Trail. Data were retained for consideration if the record included spatial information (latitude and longitude)

and at least one water-quality constituent of interest, and if the data could be reasonably aggregated and compared with other datasets.

The data compiled for this project were collected by Federal, State, and university water-quality research programs. Data sources include the USGS; the U.S. Environmental Protection Agency (USEPA); the NPS; the USFS; the National Science Foundation (NSF), including the Long-Term Ecological Research (LTER) Program; the Water Resources Research Center at the University of Massachusetts, Amherst; and the Department of Environmental Sciences at the University of Virginia. Water-quality data from all of these sources were obtained in a variety of electronic formats.

Initially, data were obtained from the USGS's National Water Information System (NWIS) and USEPA's STORage and RETrieval (STORET) databases (including Legacy STORET) (Dean Tucker, National Park Service, written commun., 2008). NWIS and STORET are national data warehouses for chemical, physical, and biological data from water, sediment, and tissue samples. More than 10 million records of water-quality data from about 16,800 sampling sites within 20 mi of the Appalachian Trail were obtained for this project (table 2). The data obtained from NWIS and STORET constituted about 95 percent of all data initially compiled and included chemical, physical, and biological data. Data were from numerous projects with different objectives, methods of collection and analysis, and scales of focus. The remaining (approximately 5 percent) data were obtained from ten specific water-quality programs focused on areas near the Appalachian Trail. Many of these programs were designed to evaluate the effects of acidic deposition on surface-water resources.

Acid Rain Monitoring Program

The Acid Rain Monitoring (ARM) project is a program of the Water Resources Institute of the Massachusetts Water Resources Research Center at the University of Massachusetts, Amherst. The ARM project began in 1983 for the purpose of determining the sensitivity of Massachusetts lakes and streams to acidic deposition and evaluating trends in acidification (Acid Rain Monitoring, 2008). The data obtained from this program consist of more than 3,100 water-quality records from approximately 70 sampling sites (table 2). Samples typically were analyzed for pH, major ions, ANC, and some trace elements. Findings from this program are summarized in Godfrey (1998).

Coweeta LTER Program

The Coweeta experimental forest is part of the NSF's LTER Program, which supports long-term ecological research across a wide range of geographic scales. The LTER network includes 26 study areas primarily in the United States. Two of these study areas, Coweeta in North Carolina and Hubbard Brook in New Hampshire, are near the Appalachian Trail.

The Coweeta LTER study area focuses on the effects of disturbance and environmental gradients on biogeochemical cycling, and on the underlying watershed ecosystem processes that regulate and respond to the ecological cycles. The USFS also conducts research at the Coweeta LTER site independently and in collaboration with the NSF's LTER program. The USFS investigations primarily focus on the interaction between forest health and the water quality of streams. Coweeta furnished more than 13,000 water-quality records from 74 sampling sites (table 2). Samples typically were analyzed for pH, specific conductance, ANC, major ions, nutrients, and organic carbon. However, specific studies at Coweeta address many different facets of ecosystem interaction (Coweeta Long Term Ecological Research, 2010).

Hubbard Brook LTER Program

The Hubbard Brook experimental forest is in the White Mountain National Forest, New Hampshire. It is part of the NSF's LTER program and is managed by the USFS Northern Research Station. Onsite research is broad based and includes studies relating to hydrology, biology, geology, and chemistry of the forest and its associated aquatic ecosystems (Likens, 1985; Likens and Bormann, 1995). The data obtained from this program consist of 16,900 water-quality records from 5 sampling sites (table 2). Samples typically were analyzed for pH, major ions, and nutrients. However, specific studies at Hubbard Brook also address many different facets of ecosystem interaction (Hubbard Brook Long Term Ecological Research, 2010).

Delaware Water Gap National Recreation Area

Water-quality data were collected from 13 small streams in the Delaware Water Gap National Recreation Area (New York, New Jersey, and Pennsylvania) from July 2002 to September 2003 (table 2). These streamwater samples were analyzed for ANC, major ions, nutrients, carbon, and aluminum at the USGS New York Water Science Center laboratory (Jason Siemion, U.S. Geological Survey, written commun., 2009).

Great Smoky Mountains National Park

There are two components to the Great Smoky Mountains National Park water-quality program: Noland Divide water-quality monitoring and a park-wide water-quality survey. The Noland Divide is in the middle of Great Smoky Mountains National Park near the border of North Carolina and Tennessee. It is a small (17.4 ha), forested, high elevation (5,500 to 6,300 ft) watershed. This watershed was selected for long-term monitoring because its geographic location, high elevation, and underlying geology tend to make the watershed vulnerable to the effects of acidic deposition

18 Major-Ion Chemistry and Nutrients in Headwater Streams Along the Appalachian National Scenic Trail, Maine to Georgia

Table 2. Appalachian National Scenic Trail level 1 inventory of data sources used, project acronym, number of sampling sites, number of records, and the period of record for the water-quality data initially compiled.

[NPS, National Park Service; USEPA, U.S. Environmental Protection Agency; USFS, U.S. Forest Service; STORET, STOrage and RETrieval; USGS, U.S. Geological Survey]

Data source	Appalachian Trail project data source acronym	Number of sampling sites	Number of records	Period of record
Acid Rain Monitoring Program; Water Resources Institute of Massachusetts, Amherst	ARM	73	3,148	1983–2008
National Science Foundation’s Long-Term Ecological Research Program, North Carolina	Coweeta LTER	74	13,640	1998–2009
National Science Foundation’s Long-Term Ecological Research Program, New Hampshire	Hubbard Brook LTER	5	16,900	1963–2005
Delaware Water Gap National Recreation Area ¹	DEWA	13	10,815	2002–2003
Great Smoky Mountains National Park; the Noland Divide and the park-wide water-quality-monitoring programs; NPS	GRSM	92	55,636	1991–2007
Virginia Trout Stream Sensitivity Study; University of Virginia, NPS, USEPA, USFS, Virginia Department of Game and Inland Fisheries, and Trout Unlimited	VTSSS	353	5,148	2002–2003
White Mountain National Forest, New Hampshire (Hornbeck and others, 2001)	WMNF	210	78,781	1967–1999
Environmental Monitoring and Assessment Program; USEPA	EMAP	225	20,273	1993–1998
Temporally Integrated Monitoring of Ecosystems Project and Long Term Monitoring Project; USEPA	TIME/LTM	618	280,911	1979–2005
National Stream Survey; USEPA	NSS	274	46,586	1985–1986
Wadeable Stream Assessment; USEPA	WSA	293	6,264	2004
STORET Legacy Data Center; USEPA	Legacy STORET	7,385	6,296,007	1939–1998
STORET Data Warehouse; USEPA	STORET	3,491	1,083,586	1968–2007
National Water Information System; USGS	NWIS	3,698	2,643,058	1923–2008

¹ Water-quality data from the USGS New York Water Science Center (Jason Siemion, U.S. Geological Survey, written commun., 2009)

(Cook and others, 1994; Robinson and others, 2008; John Schwartz, University of Tennessee, Department of Civil and Environmental Engineering, written commun., 2008; Cai and others, 2009). The Great Smokey Mountain park-wide water quality-monitoring project began in October 1993 and initially collected water samples from 367 sampling sites throughout the park that represented a range of elevations, geology types, and disturbance histories. Throughout the project, water-quality samples were collected at various intervals and subsets of sampling sites during base-flow conditions. The data obtained from these two programs consist of more than 55,000 water-quality records from 92 sampling sites (table 2). Samples typically were analyzed for pH, specific conductance, ANC, major ions, nutrients, and some trace elements. Findings from both projects are summarized in annual NPS reports and various research publications including: Cook and others 1994; Neff and others, 2008; Robinson and others, 2008; Cai and others, 2009; Deyton and others, 2009.

Virginia Trout Stream Sensitivity Study (VTSSS)

The Virginia Trout Stream Sensitivity Study (VTSSS) collects data related to water chemistry in the Shenandoah National Park and the mountains of western Virginia for the general purpose of monitoring the quality of native brook trout streams. VTSSS data collected within Shenandoah National Park is coordinated with ongoing broad-based monitoring of water quality by the Shenandoah Watershed Study (University of Virginia, 2010). The data obtained from the VTSSS consist of more than 5,100 water-quality records from 353 sampling sites (table 2). Samples typically were analyzed for pH, specific conductance, ANC, and major ions.

White Mountain National Forest

In 2001, the USFS compiled a database of water-quality data for the White Mountain National Forest, located in central New Hampshire (Hornbeck and others, 2001). The data obtained from this study consist of more than 78,700 water-quality records from 210 sampling sites (table 2). Samples typically were analyzed for pH, specific conductance, ANC, major ions, nutrients, and trace elements.

Environmental Monitoring and Assessment Program (EMAP)

The USEPA initiated the Environmental Monitoring and Assessment Program (EMAP) in the late 1990s to monitor and assess the status and trends in ecological resources of the United States. The program evolved into a research program aimed at the development of tools for translating environmental-monitoring data from multiple spatial and temporal scales into assessments of current ecological conditions and forecasts of risks to natural resources. EMAP data used in this project were from small streams (first- through third-order streams)

located within the study area. The data obtained from this program consist of more than 20, 200 water-quality records from 225 sampling sites (table 2). Samples typically were analyzed for pH, specific conductance, ANC, major ions, nutrients, and organic carbon.

Temporally Integrated Monitoring of Ecosystems and Long Term Monitoring Program (TIME/LTM)

The USEPA's Temporally Integrated Monitoring of Ecosystems (TIME) project was developed as a special study within EMAP. The focus of the TIME program is to track the trends in the acid/base chemistry of acid-sensitive lakes in the northeast and streams in the central Appalachians (Stoddard and others, 1996). The primary objective of the Long Term Monitoring (LTM) program is to detect long-term trends in the acid/base status of lakes and streams across a gradient of acidic deposition nationally. The LTM network consists of a subset of lakes and streams that are particularly sensitive to acidity with most sampling-site records extending back to the early 1980s. The TIME and LTM are currently (2011) ongoing studies, and their data are commonly used together (U.S. Environmental Protection Agency, 2010b). The data obtained from these two programs consist of more than 280,000 water-quality records from 618 sampling sites (table 2). Samples were typically analyzed for pH, specific conductance, ANC, major ions, nutrients, organic carbon and inorganic carbon.

National Stream Survey Program

The USEPA's National Stream Survey program was designed to classify and characterize streams that are presently acidic or that have low ANC. In addition, the National Stream Survey program sought to identify streams appropriate for intensive long-term monitoring. The data obtained from this program consist of more than 46,500 water-quality records from 274 sampling sites (table 2) (U.S. Environmental Protection Agency, 2010c). Samples typically were analyzed for pH, specific conductance, ANC, major ions, nutrients, organic carbon, and inorganic carbon.

Wadeable Stream Assessment Program

The USEPA's Wadeable Stream Assessment program collected data for water-quality, biological, and physical-attribute assessments from wadeable streams and rivers across the United States (U.S. Environmental Protection Agency, 2006c). For this program, wadeable streams were defined as first-through fifth-order streams. The goal of the Wadeable Stream Assessment was to report on the condition of small streams in the United States and to establish a baseline with which to compare results from future studies. The data obtained from this program consist of more than 6,200 water-quality records from 293 sampling sites (table 2).

Methods of Analysis

Water-quality data and ancillary spatial data were compiled from numerous sources to develop a comprehensive inventory appropriate for describing the water quality of headwater streams along the Appalachian Trail. An inventory and assessment of the water quality of headwater streams of the Appalachian Trail requires an explicit definition of what is meant by the phrase “water quality of the Appalachian Trail.” A careful consideration of project objectives and an initial evaluation of data suggested that the specific area of interest should be larger than the immediate environment of the approximately 1000-ft-wide Appalachian Trail corridor to include relevant water-quality data. However, it also was apparent that inclusion of all water-quality data from first- and second-order streams within the study area would be too broad to be useful. Spatial data that delineates hydrologic boundaries and spatial data that characterizes environmental landscape attributes were used together to develop a method of site selection that resulted in an inventory of water-quality data representative of headwater streams along the Appalachian Trail. Environmental attributes also were used to describe possible anthropogenic and natural factors that may be influencing water quality. Water-quality data selected for inclusion in the resource characterization were aggregated to minimize the influence of intensively monitored sites and areas. The water quality of headwater streams along the Appalachian Trail was described through the use of computed summary statistics, comparisons of variations in summary statistics along the Appalachian Trail, and associations between water quality and environmental attributes.

Quality Assurance and Compilation of Water-Quality Data

Prior to analyzing the water-quality datasets described above, several quality-assurance measures were applied to identify potential errors in the reported water-quality values and to minimize issues that originated from combining data from multiple sources. Quality assurance steps taken to review the water-quality data included: removal of water-quality records determined to be inappropriate for use in analyses; assignment of an Appalachian Trail project site name to unify all records from the same sampling site; censorship of some nutrient values; and conversion of reported concentrations to standardized units.

Quality Assurance

Water-quality data were evaluated to determine if reported values were reasonable and appropriate for use in analyses. Three measures were used to determine if data were appropriate for use: comparison to USEPA criteria; comments or remark codes; and cation-anion balance. The USEPA has

established typical ranges for many constituents and properties. These typical ranges, at one time, were used to screen data entered in STORET (National Park Service, 1998); all data were checked to ensure that they were within typical ranges. Water-quality values identified as suspect were then evaluated individually by comparing the values to other data from that site or similar nearby sites. Comments and remarks codes were evaluated to determine the quality of the reported value. Approximately, 16 percent of the samples selected had enough major ion data reported to calculate an ion balance. Ion balances were calculated on equivalent concentrations using procedures described by Hem (1992). Cation and anion concentrations were within 10 percent of each other for 93 percent of the sampling sites with sufficient data. The quality-assurance actions included:

- 255 records removed for exceeding the USEPA typical ranges,
- 43 records removed because the remarks code indicated that the value was compromised,
- 172 records of major ion data removed because the value was reported as zero, and
- 23 records removed because the cation/anion balance exceeded 10 percent.

These 493 water-quality records composed less than 0.003 percent of the data initially obtained.

Data Compilation

The uniqueness of each sampling site was evaluated relative to other nearby sampling sites through comparison of site-identification data, site names, and proximity. This step determined that approximately 10 percent of the sampling sites appeared in more than one of the datasets. A project-site name was created to unify all water-quality records from a sampling site. For the purposes of this quality-assurance step, sampling sites were considered identical if they had the same site name and were less than 330 ft apart. Sampling sites that had the same identifier and were more than 330 ft apart were retained as separate sampling sites. This method might have eliminated many duplications of sampling sites but also may have merged a small number of sampling sites that were actually unique. Considering the large number of sampling sites with data and the size of the study area, combining sampling sites in this manner probably affected the overall data-compilation effort to a minimal extent.

Data compiled for this study were from both unfiltered and filtered samples. Major ions, nitrate, and ammonia are generally in the dissolved form in these natural waters that are mainly in undisturbed landscapes. For this reason, data values from unfiltered (commonly referred to as total) and filtered (commonly referred to as dissolved) samples were combined for most constituents. More than 75 percent of major-ion samples used in this study were from filtered

samples. Approximately 68 percent of ammonia samples were from unfiltered samples, and more than 87 percent of nitrate samples were from filtered samples. All total nitrogen and total phosphorus values used in analysis were from unfiltered water samples.

The issue of multiple detection limits for each constituent is inherent in a compiled dataset from a variety of sources that includes analyses from 1923 through 2009 (median year = 1995). The minimum detectable concentration for a constituent is dependent on at least the following factors: the water matrix, sample-collection protocols, method of analysis, quality-control measures implemented by the analyzing laboratory, and objectives of the water-quality investigation. Concentrations below the minimum detectable concentration for a water-quality constituent are often censored and identified with a remark character indicating that the concentration is less than the minimum detectable concentration. Fewer than 0.3 percent of major-ion concentrations and approximately 28 percent of nutrient concentrations were reported as less than the respective minimum detectable concentrations. To the extent possible, reported values were retained and used as received. However, some nitrate and ammonia concentrations were reported as exceptionally low (less than 0.008 mg/L for nitrate and less than 0.01 mg/L for ammonia). These exceptionally low values were censored to improve the comparability of datasets by use of the following criteria:

- Concentrations of nitrate reported below 0.008 mg/L as N were set to less than 0.008 mg/L, the USGS National Water Quality Laboratory's Long-Term Method Detection Level for nitrate (Childress, 1999). As a result, 3,835 concentrations of nitrate reported below 0.008 mg/L were censored to less than 0.008 mg/L as N.
- Concentrations of ammonia reported below 0.01 mg/L as N were set to less than 0.01 mg/L as N, the USGS National Water Quality Laboratory's Long-Term Method Detection Level for ammonia (Childress, 1999). As a result, 3,700 concentrations of ammonia reported below 0.01 mg/L as N were censored to less than 0.01 mg/L as N.

The titration procedure used to measure ANC depends on whether the water is expected to be buffered primarily by carbonate solutes, most commonly carbonate and bicarbonate. In this case, the titration proceeds to theoretical pH endpoints for carbonate species (pH values near 8.3 for carbonate and 4.5 for bicarbonate). The ANC of low-ionic-strength waters, like those in some regions along the Appalachian Trail, is generally presumed not to be controlled by the carbonate system; in this case, the Gran titration is used. The Gran titration measures the presence of species other than carbonate that contribute to ANC; the method requires detailed acidimetric data over the entire titration, is carried out to pH values of 3.5 or lower, and can result in a negative ANC value (Gran, 1952).

Reported values of ANC were determined by a variety of titration procedures. For the purposes of this inventory, if the

sample was unfiltered and a titration was performed, it was considered to represent ANC. Approximately 50 percent of the values of ANC were determined by using Gran titration, of which 85 percent were from the section of the Appalachian Trail south of Maryland. To use as much available data as possible and to provide information regarding ANC in the northern section of the Appalachian Trail, all ANC data were combined regardless of the titration procedure. More frequent occurrence of low or negative ANC values in the southern section compared to the central and northern sections of the Appalachian Trail may be an artifact of the higher percentage of ANC determined through the use of the Gran titration method in the southern section of the Appalachian Trail.

Reported water-quality values were converted to ensure that units of concentrations were standardized and to ensure that the same species was analyzed for each constituent. Water analyses were initially reported primarily with four different units for concentration: micrograms per liter ($\mu\text{g/L}$), mg/L, $\mu\text{eq/L}$, and $\mu\text{mol/L}$. Water-quality constituents were converted as needed and are primarily summarized in mg/L. All ANC values are reported in $\mu\text{eq/L}$. Bicarbonate is reported as mg/L as bicarbonate. Ammonia, nitrate, and total nitrogen are reported as mg/L as nitrogen. Total phosphorus is reported as mg/L as phosphorus. Nitrogen and phosphorus species conversions were based on procedures from Mueller and others (2005).

Ancillary Data Sources

Two primary types of ancillary spatial information were used: spatial data delineating hydrologic boundaries, and descriptive spatial data that characterized attributes of the environment, such as land cover. Descriptive spatial data were particularly useful in determining that the environmental setting of nonadjacent sampling sites were very similar to the Appalachian Trail environment. Therefore, it is likely that the water quality also would be representative of the Appalachian Trail environment. Ancillary spatial datasets also were used to help determine differences in the environmental settings of sampling sites where water quality varied along the Appalachian Trail. The spatial datasets used include information pertaining to physiography, land cover, and atmospheric deposition. A list of spatial data sources used for hydrologic and environmental attributes is shown in table 3.

Hydrologic Attributes

The extent of the study area and divisions within the study area were delineated by using the boundaries of hydrologic units (U.S. Department of Agriculture, 2005). Hydrologic-unit boundaries delineate successively smaller surface-water drainage areas of major rivers or the combined drainage areas of a series of rivers (Seaber and others, 1987). Hydrologic units used for this project include watersheds (also known as 10-digit hydrologic units) that were used to define

Table 3. Types and sources of ancillary data used in this study.

Data type	Source
Hydrologic attribute data	
NHDPlus	U.S. Environmental Protection Agency, 2006
Boundaries of hydrologic units	U.S. Department of Agriculture, 2005
Environmental attribute data	
Ecological subdivision	Keys and others, 1995
Stream elevation	U.S. Environmental Protection Agency, 2006
Land-cover data	U.S. Environmental Protection Agency, 2006
Slope	U.S. Environmental Protection Agency, 2006
Elevation	Gesch, 2007
Air temperature	PRISM Climate Group, 2006a
Precipitation	PRISM Climate Group, 2006b
Soils data (STATSGO2)	U.S. Department of Agriculture, Natural Resource Conservation Service, 2006
Geologic data	King and Beikman, 1974; Reed and Bush, 2005
Annual precipitation-weighted mean sulfate concentration	National Atmospheric Deposition Program, 1994a
Annual precipitation-weighted mean nitrate concentration	National Atmospheric Deposition Program, 1994b
Nutrient ecoregions	U.S. Environmental Protection Agency, 2000

the extent of the study area, and subregions (also known as 4-digit hydrologic units) that were used to create subdivisions within the study area (fig. 9).

Delineation and characterization of the Appalachian Trail environment within the study area and characterization of the environmental setting of sampling sites was completed through the use of data from National Hydrography Dataset Plus (NHDPlus). NHDPlus is a suite of geospatial data products that have been developed to work in concert (U.S. Environmental Protection Agency, 2006a). The building blocks of NHDPlus were the medium-resolution National Hydrography Dataset (NHD), the National Elevation Dataset (30-meter), and the National Watershed Boundary Dataset. The fundamental feature of the NHDPlus dataset is the delineation of a catchment. A catchment is defined as the incremental drainage area for a single NHD hydrologic feature such as a stream segment (fig. 10). Stream segments and associated catchments are linked and nested so that the drainage area for a specific hydrologic feature includes its incremental drainage (catchment) area as well as the full cumulative drainage area upstream from that feature, including the headwaters (Johnston and others, 2009) (fig. 10). The NHDPlus geospatial database also contains derived physical attributes for each catchment, including slope, elevation of stream segments (hereafter referred to as stream elevation), and size of drainage area, as well as data integrated from other

geospatial datasets, such as the National Land Cover Dataset (1992) (U.S. Geological Survey, 2000). Comparisons in differences in the size of drainage areas along the Appalachian Trail could not be assessed because of the varying resolution of the underlying hydrography data used in NHDPlus and the influence that this resolution disparity may have had in the delineation of catchment boundaries.

Catchments were used as the fundamental geographic units for this project because of the wealth of landscape data provided by NHDPlus for these small hydrologic units. Catchment boundaries were used to delineate and describe the Appalachian Trail environment, and water-quality data were aggregated and summarized by catchments. Two physical attributes of catchments (stream elevation and land-cover information) were used to screen sites for inclusion in the water-quality summary and were tested as possible explanatory variables for observed variations in water-quality data. In addition, data for slope of the catchment, mean annual precipitation, and mean annual temperature were evaluated for correlations with environmental and water-quality variables. Strahler stream-order values available for every catchment through an NHDPlus extension were important in the site-selection process for defining first- and second-order streams. (Datasets that have been developed to provide additional information integrated with NHDPlus are referred to as data extensions.)

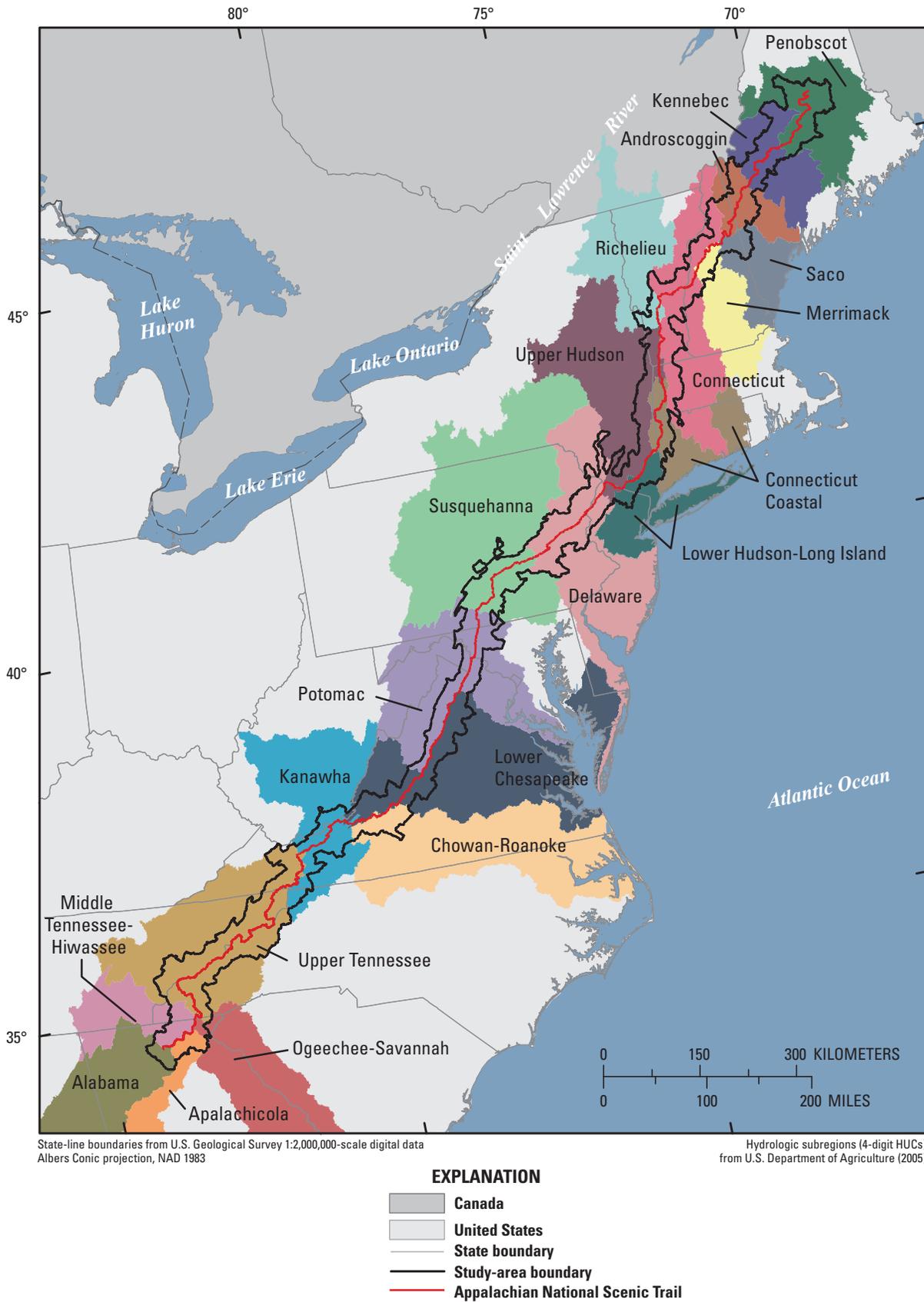
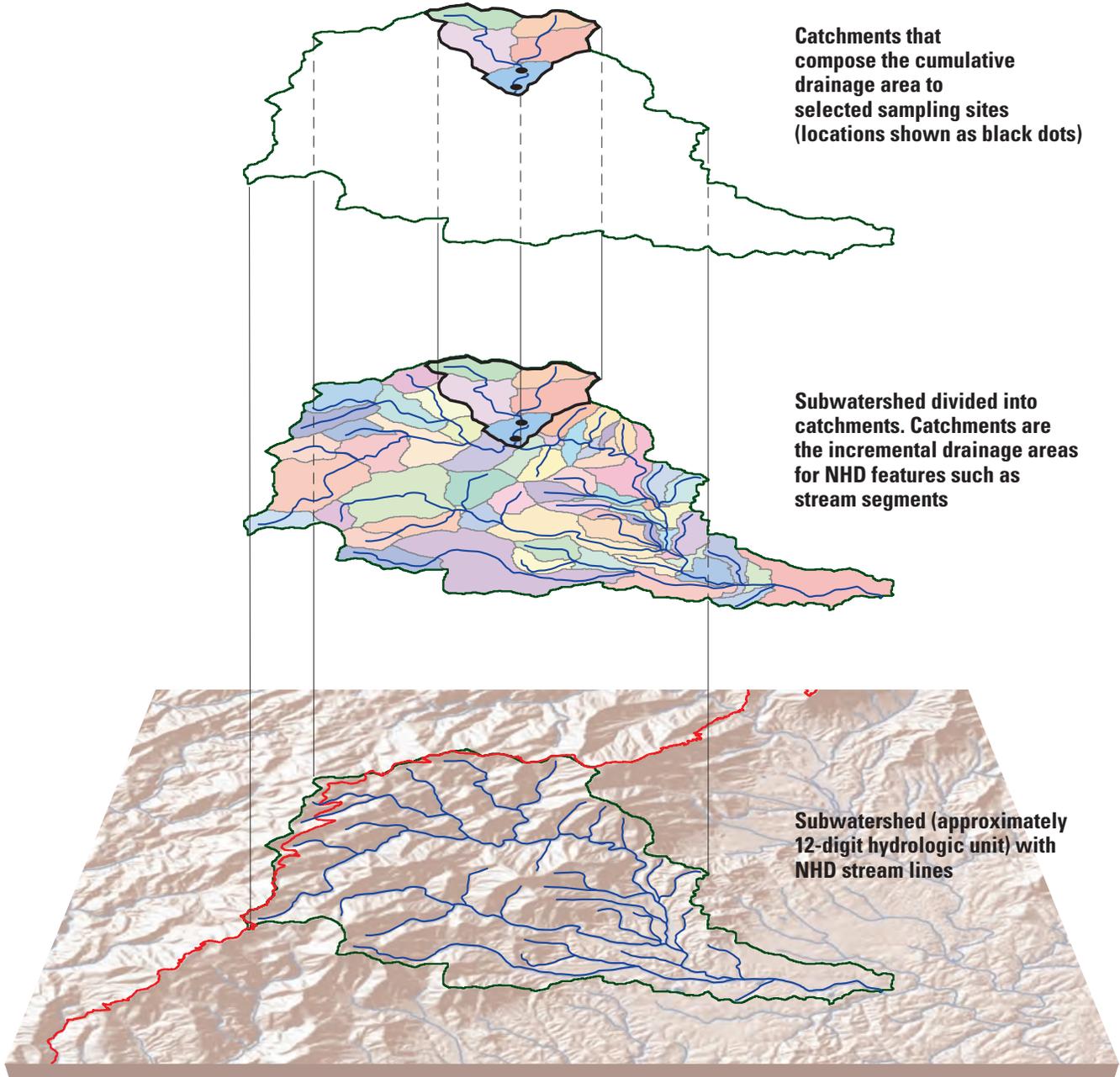


Figure 9. Hydrologic subregions (variously colored) that intersected and were used as geographic subdivisions of the study area.



EXPLANATION

- Appalachian National Scenic Trail
- Subwatershed boundary
- Catchment boundaries
- Cumulative drainage area
- National Hydrography Dataset streamline
- Sampling site

Figure 10. Schematic diagram showing examples of the nested relation of National Hydrography Dataset *Plus* (NHD*Plus*) catchments with larger delineated hydrographic units such as subwatersheds, and drainage areas defined for a set of nested catchments.

Environmental Attributes

Ecoregions defined by the USFS were used to group water-quality data and to relate spatial attributes to variations in water-quality data. Geologic data from Reed and Bush (2005) and King and Beikman (1974) were used to group catchments by major lithology type and evaluate variations in water quality. Concentrations of total nitrogen and total phosphorus were compared to USEPA nutrient criteria by nutrient ecoregions (U.S. Environmental Protection Agency, 2000; 2002b). Concentrations of ammonia, nitrate, total nitrogen, and total phosphorus were compared to estimated background concentrations developed by the USGS (Dubrovsky and others, 2010).

Environmental attributes from most of the following spatial datasets were assigned based on the attribute values at the geographic center of each catchment. Topographic elevation data used to evaluate water-quality variations associated with elevation were assigned from digital elevation maps (Gesch, 2007). Land-cover data were obtained from *NHDPlus*, which contains information integrated from the National Land Cover Dataset from 1992. Mean annual precipitation and temperature data were obtained from the PRISM Climate Group (PRISM Climate Group, 2006a; b). Soils data were obtained from the Natural Resources Conservation Service's State Soil Geographic database (U.S. Department of Agriculture, 2006). Soils data used in the analysis included average range in permeability, average range in bulk density, average range in organic matter content, average percentage of clay content, average percentage of silt content, and average percentage of sand content. Precipitation-weighted annual concentrations of sulfate and nitrate in precipitation were obtained from the National Atmospheric Deposition Program (NADP) as continuous rasters interpolated from measurements at NADP sites (National Atmospheric Deposition Program, 1994a, b). Continuous rasters of yearly estimated sulfate and nitrate deposition (in mass per unit area) were computed from NADP concentration rasters and PRISM estimated annual mean precipitation rasters (PRISM Climate Group, 2006b) by using a method developed by Latysh and Wetherbee (in press).

Site Selection

The evaluation and selection of available sampling sites for this study were based on the stream-order, the proximities of the sites to the Appalachian Trail, and the environmental settings of the sampling sites. Sampling sites were assigned to an *NHDPlus* catchment through GIS analysis, and the environmental setting of each sampling site was characterized by the physical attributes compiled from available spatial data for the catchment. All selected sampling sites were on first- and second-order streams as determined by available data from *NHDPlus*.

All catchments that contained first- and second-order streams and directly adjacent to the Appalachian Trail were identified. Catchments defined as adjacent to the Appalachian

Trail included those for which the catchment polygon geographically intersected the Appalachian Trail corridor in a GIS analysis. These catchments, hereafter called adjacent catchments, encompass the headwaters that drain the Appalachian Mountains along the Appalachian Trail and were considered to represent the hydrologic environment of the Appalachian Trail. There are 2,565 first- and second-order adjacent catchments in the Appalachian Trail study area. *NHDPlus* data were used to evaluate and describe physical landscape characteristics associated with the adjacent catchments and thereby characterize the hydrologic environment of the Appalachian Trail headwater streams (figs. 11 and 12A–D).

The collective environment for all adjacent catchments was over 88 percent forested land, approximately 8 percent agricultural land, 2 percent open water or wetlands, and 1 percent developed land. However the Appalachian Trail environment differed widely along the trail. Adjacent catchments in the state of Maine were approximately 90 percent forested land, 7 percent water, and 3 percent bare rock. In contrast, the adjacent catchments in Pennsylvania and Maryland were approximately 65 percent forested land, more than 30 percent agriculture land, and more than 2 percent developed land. Approximately 25 percent of the length of the Appalachian Trail is in Virginia. The adjacent catchments in Virginia were 89 percent forested land, 10 percent agricultural land, and less than 1 percent developed land. The adjacent catchments in the state of Georgia were more than 99 percent forested land. For this investigation, data collected from all sampling sites within adjacent catchments were retained for analysis because these sampling sites were considered to be representative of the hydrologic environment of the Appalachian Trail. A total of 309 adjacent catchments contained at least one sampling site selected for water-quality analysis in this study.

Criteria for Selection of Nonadjacent Sampling Sites

Sampling sites within the study area but not adjacent to the Appalachian Trail were evaluated for inclusion in this inventory to increase the amount of water-quality data used to describe the water resources of the Appalachian Trail. Physical attributes of adjacent catchments were compared with all other first- and second-order catchments in the study area. Through this analysis, it was determined that stream elevation, the percentage of the drainage area classified as developed land, and the percentage of the drainage area classified as agricultural land were the most important criteria to determine if nonadjacent sampling sites were similar to the Appalachian Trail environment.

The maximum stream elevation was used as the elevation variable for site selection rather than the maximum topographic elevation of the catchment because it more closely relates to the elevation at which a headwater streams forms. Developed land was defined to include low- and high-intensity residential, as well as commercial, industrial, and

transportation land cover. Land cover characterized as agricultural included pasture and row crops.

Stream-elevation and land-cover data from the adjacent catchments were aggregated by hydrologic subregion. The number of adjacent catchments varies by subregion and is related to topography and to the proportion of the Appalachian Trail within the subregion. Summary statistics of elevation and land-cover information from adjacent catchments within each subregion were used to develop criteria for the selection of nonadjacent sampling sites by subregion. Hydrologic subregions were selected for the aggregation of adjacent catchment attributes because they provided reasonable and informative geographic divisions of major landscapes within the study area. The 21 subregions that intersect the Appalachian Trail are shown in figure 9.

Nonadjacent sampling sites within the study area were selected for inclusion in the water-quality analysis if the following subregion criteria were met: (1) the stream elevation was equal to or greater than the lowest stream elevation of an adjacent catchment within the same subregion; (2) the percentage of agricultural land in the drainage area of the catchment did not exceed the 75th percentile for adjacent catchments within the same subregion; and (3) the percentage of developed land in the drainage area of the catchment did not exceed the 75th percentile for adjacent catchments within the same subregion (table 4).

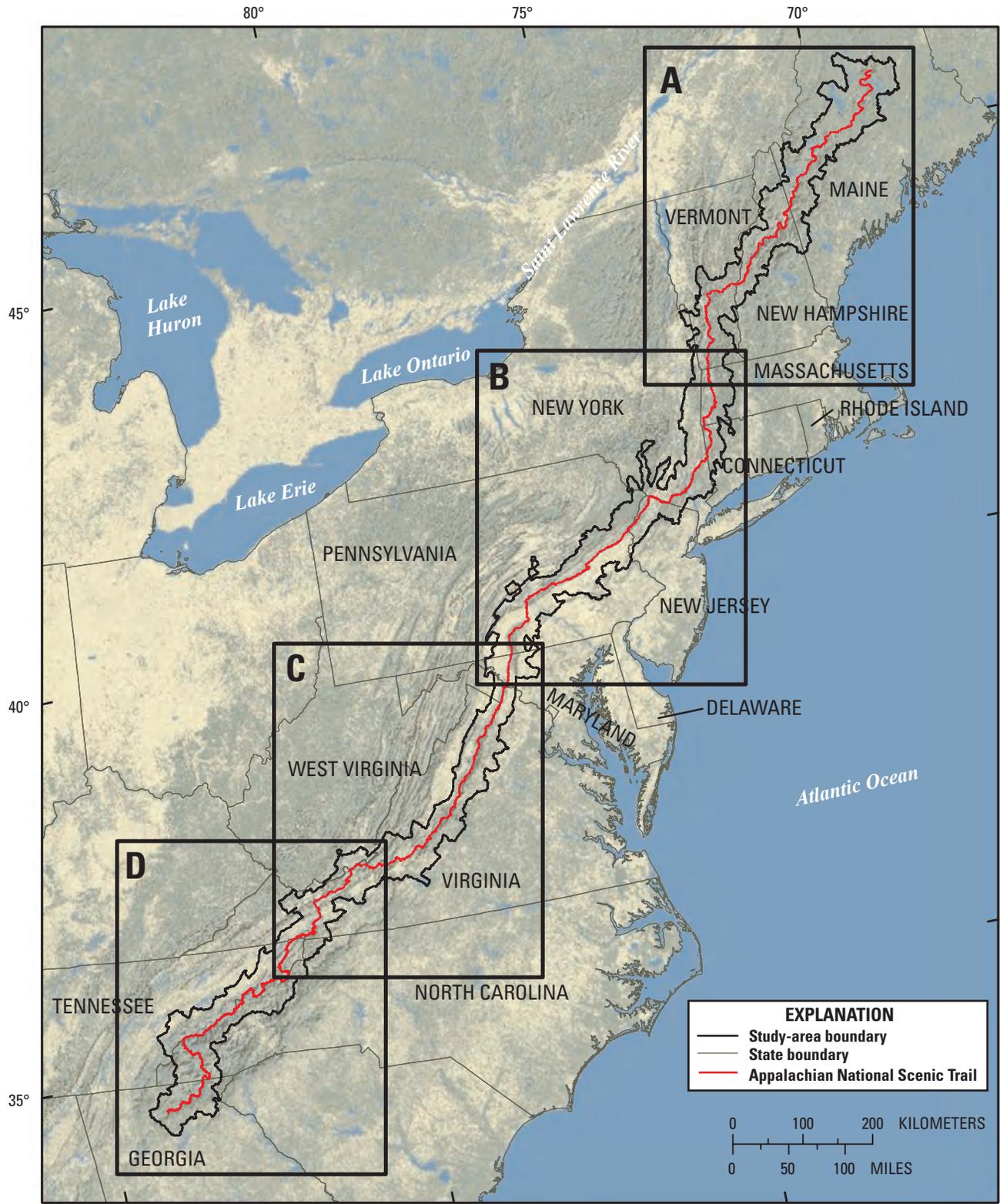
The thresholds for each of the criteria differ among the subregions and reflect the geographic variations in topography and land cover along the Appalachian Trail. The highest stream elevations were in the northern and southern subregions of the Appalachian Trail (table 4), while the lowest stream elevations were in subregions that coincide with the Hudson River Basin: the Upper Hudson, and the Lower Hudson–Long Island subregions (table 4). The thresholds for the percentage of developed land in the drainage area for all subregions were all less than 3 percent (table 4). In other words, nonadjacent sampling sites were never selected with developed land cover of 3 percent or greater in the drainage area. The threshold for the percentage of developed land in the drainage area was 0 for the 6 most southern subregions. Therefore, nonadjacent catchments could be selected in these subregions only if they contained no developed land cover. The subregions with the highest thresholds for the percentage of agricultural land cover were the Delaware (17.2 percent), the Susquehanna (26.8 percent), and the Potomac (27.7 percent) (table 4). Consequently in these subregions, nonadjacent sampling sites which had modest amounts of agricultural land cover in the drainage area were included in this inventory. The minimum stream-elevation thresholds in these subregions were useful in limiting the number of sampling sites retained with modest amounts of agricultural land cover.

Selected Sites and Data Aggregation

The final dataset for use in this project consisted of 1,817 stream-sampling sites in 831 different catchments that represent approximately 450 different first- and second-order streams. Some catchments contained multiple sampling sites and some streams were represented by multiple catchments. There were 946 adjacent sampling sites and 871 nonadjacent sampling sites in the final dataset. Specific areas that contain numerous selected sites include the White Mountain National Forest in New Hampshire (fig. 13A), the Delaware Water Gap National Recreation Area in Pennsylvania and New Jersey (fig. 13B), the Shenandoah National Park in Virginia (fig. 13C), and the Great Smoky Mountains National Park in Tennessee and North Carolina (fig. 13D). Some areas had relatively few selected sampling sites with available water-quality data, with the most notable data gaps in Maine (fig. 12A). Only seven sampling sites in the State of Maine met the project criteria and were retained for analysis. Central Vermont, western Massachusetts, and Georgia also had few sampling sites retained for water-quality analysis (figs. 13A–B, D).

In addition to spatial disparities in the number of sites, the number of times each site was sampled and the constituents analyzed for each sample also were highly variable. The number of times a selected site was sampled ranged from one to more than a thousand. The most frequently sampled sites were primarily in the Shenandoah National Park. Approximately 58 percent of the sites used in this study were sampled at least five times. Thirty-eight percent of the sampling sites used in this study were sampled only once.

To mitigate a potential bias resulting from disparities in the spatial locations of sampling sites and in the frequencies of sampling, the data were aggregated in four steps: (1) data were aggregated by sampling site and date to determine a daily median value for each constituent; (2) daily median values were aggregated by sampling site and year to determine an annual median value for each constituent (for example, if 300 daily median values of pH were recorded at a sampling site in one year, the median of these 300 pH values was determined as the annual median value for that year); (3) annual median data were aggregated by site, thus reducing the data to one median annual value for each constituent at that site for the entire sampling period in years; and (4) data were aggregated by National Hydrography Dataset Plus (NHDPlus) catchments to a single median value for each constituent in each catchment. Sampling sites in the same catchment are on the same stream segment (fig. 10). The number of sampling sites within a catchment ranged from 1 to 55; however, 542 of the 831 catchments contained only one sampling site. The resulting values (hereafter referred to as catchment values or concentrations) for each constituent were used to assess water quality along the Appalachian Trail and are available in addition to ancillary data in the catchment-data worksheet of appendix 1.



State-line boundaries from U.S. Geological Survey 1:2,000,000-scale digital data
Albers Equal-Area Conic projection, NAD 1983

Base physical-map background is from U.S. National Park Service
Natural Earth physical map, available online from ESRI (2009)

Figure 11. Index map showing areas covered by figures 12 and 13.

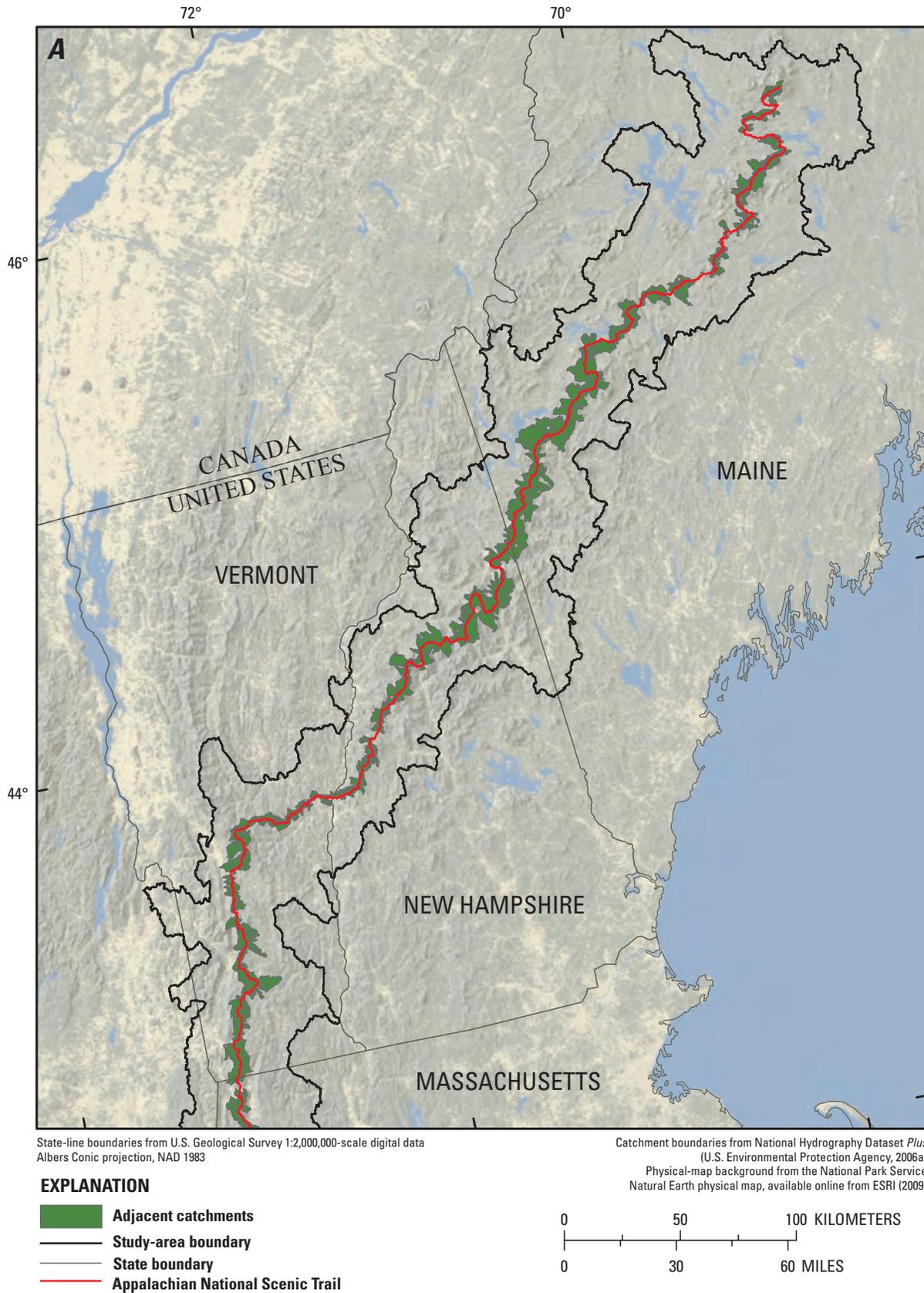


Figure 12. First- and second-order catchments from the National Hydrography Dataset *Plus* (NHD*Plus*) that are adjacent to the Appalachian National Scenic Trail and were used to characterize physical attributes of the trail environment from *A*, Maine to Vermont, *B*, Massachusetts to Maryland, *C*, Maryland to Virginia, and *D*, Virginia to Georgia.

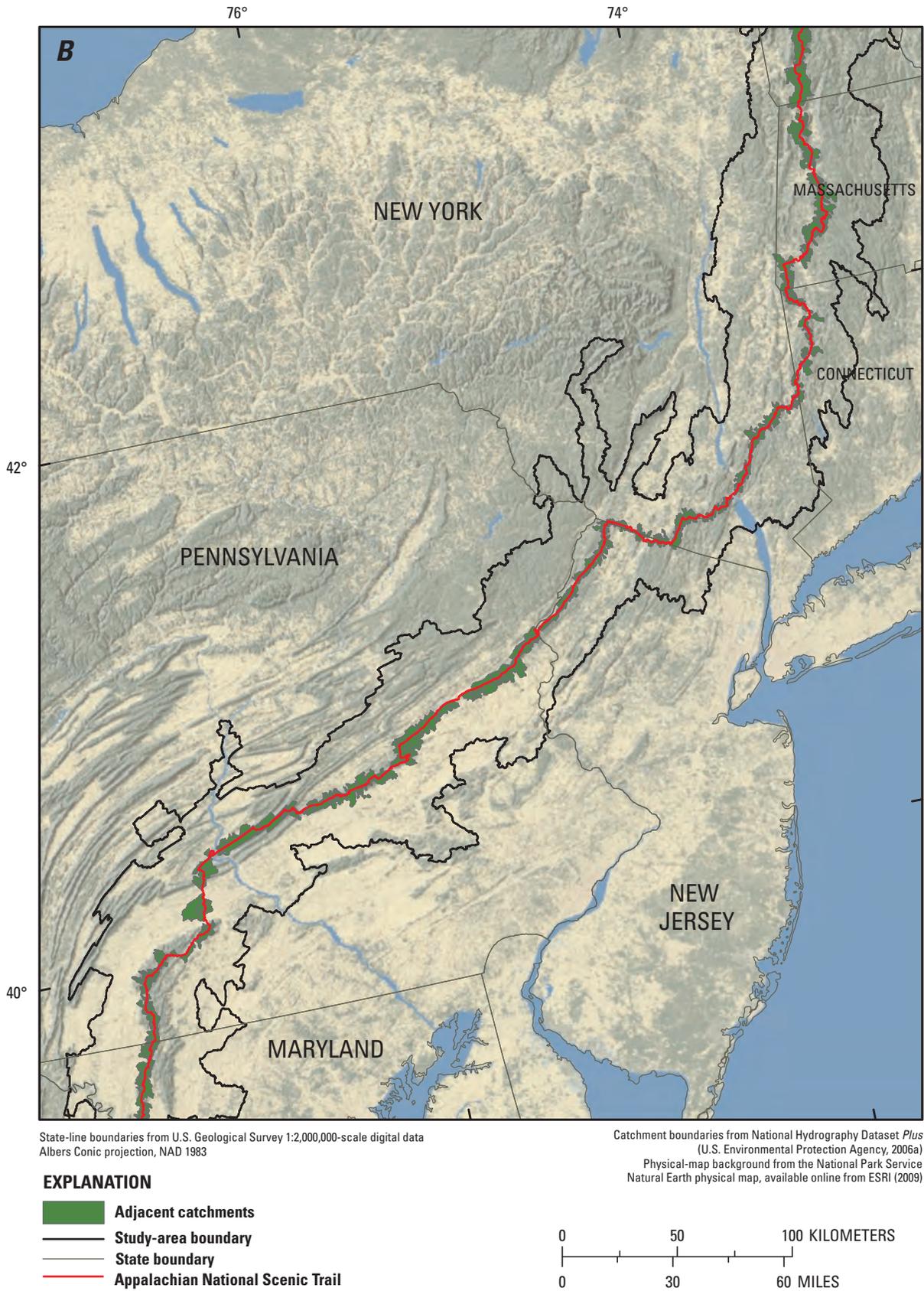


Figure 12. —Continued

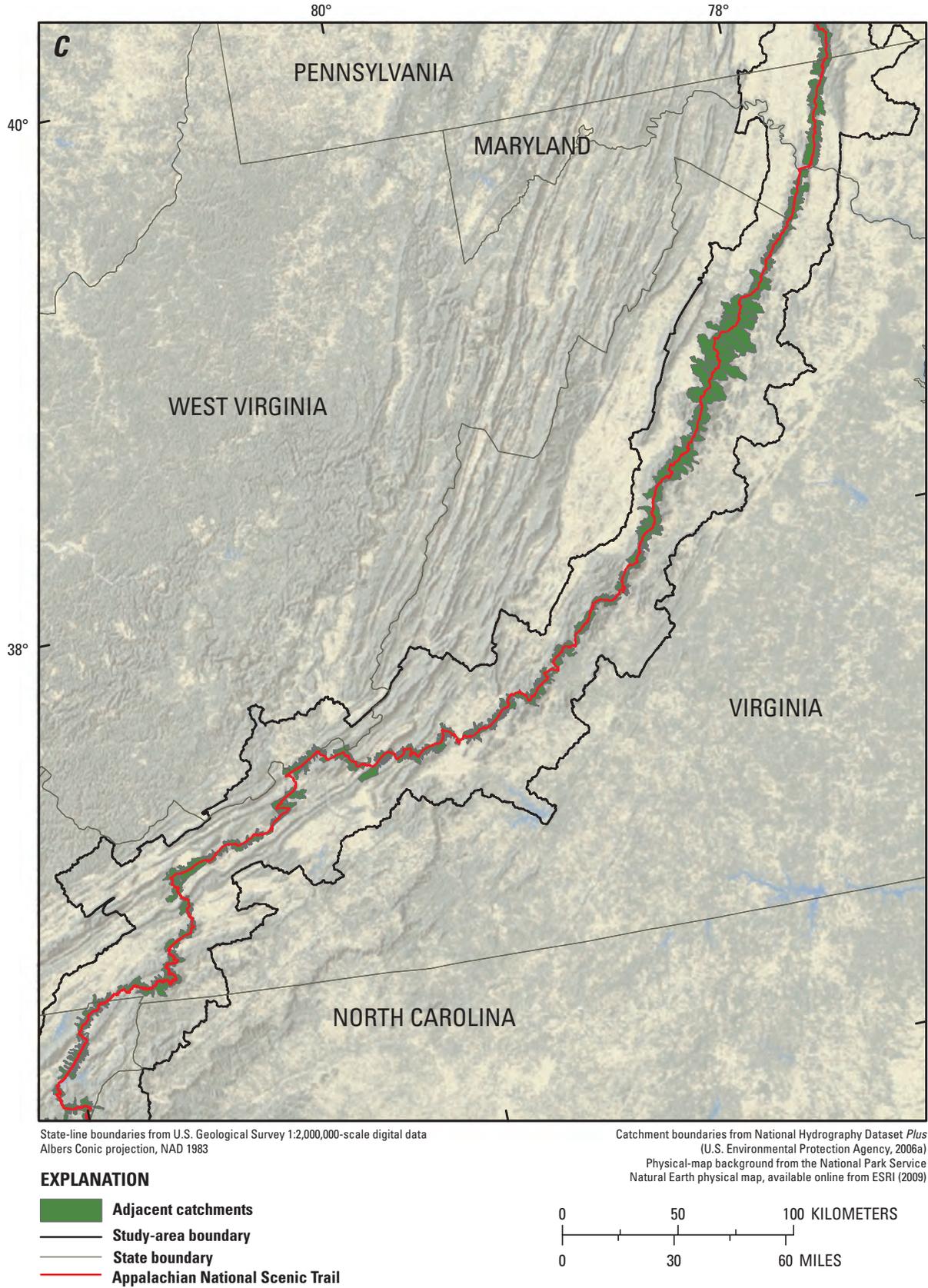
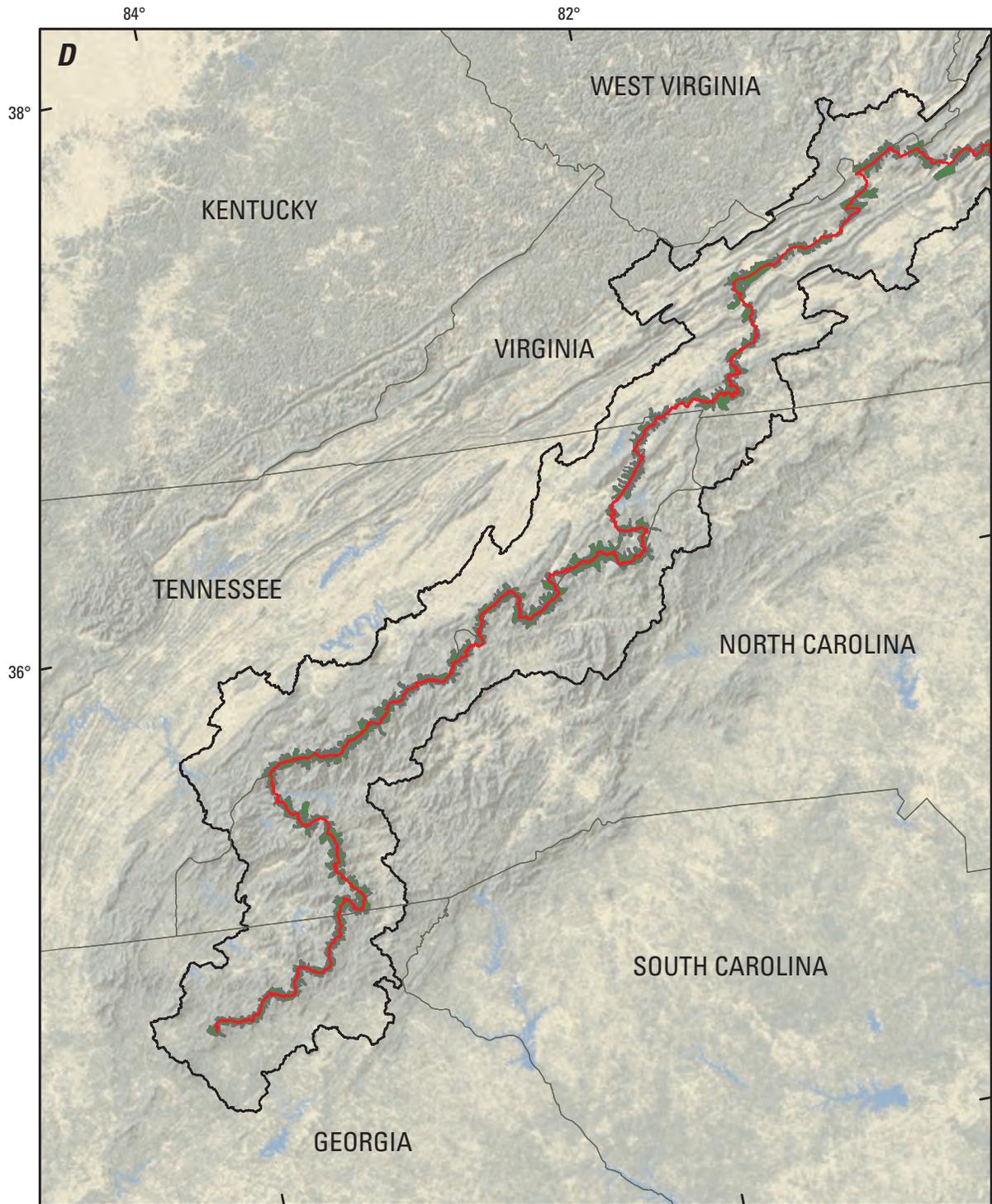


Figure 12. —Continued



State-line boundaries from U.S. Geological Survey 1:2,000,000-scale digital data
Albers Conic projection, NAD 1983

Catchment boundaries from National Hydrography Dataset *Plus*
(U.S. Environmental Protection Agency, 2006a)

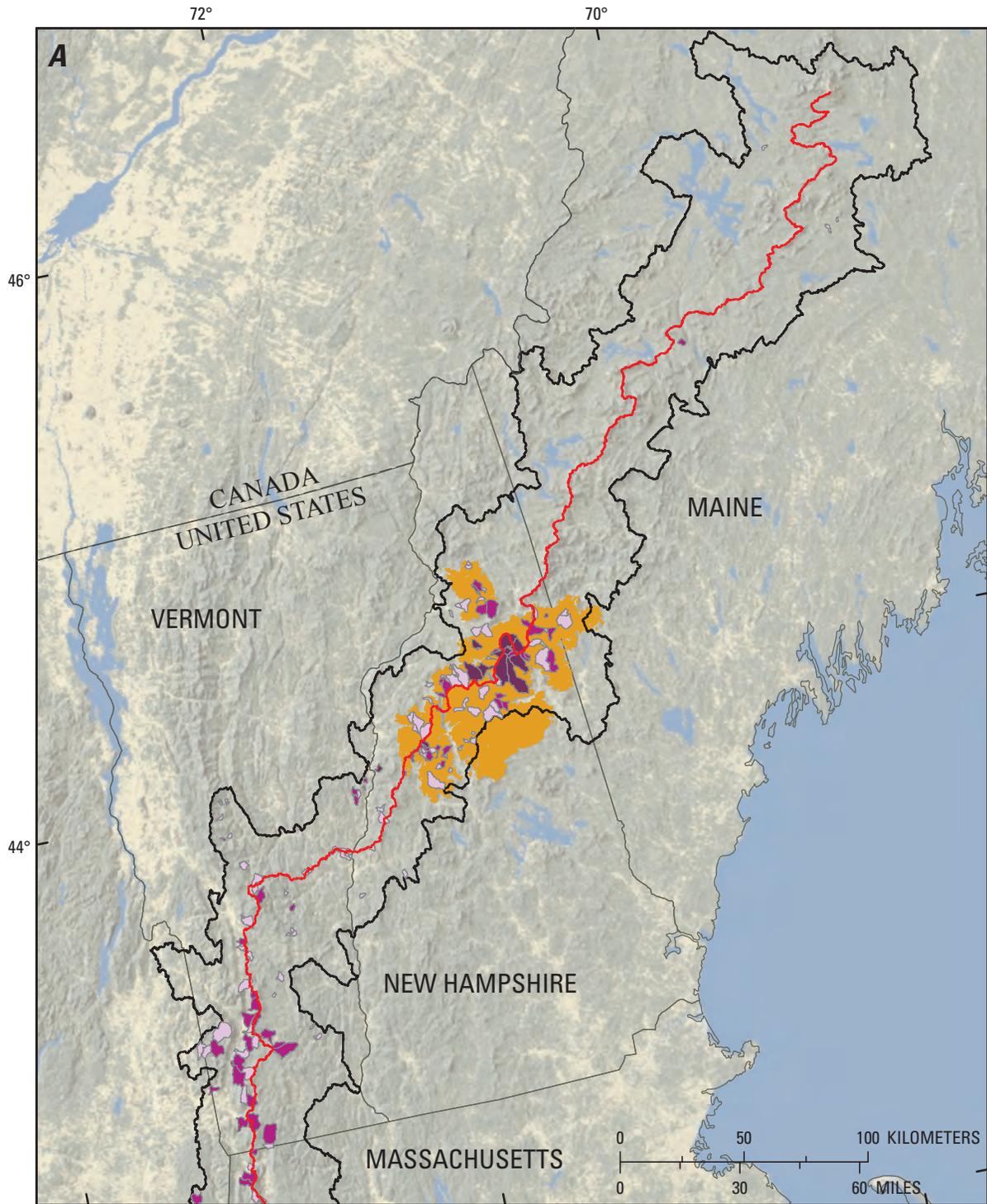
Physical-map background from the National Park Service
Natural Earth physical map, available online from ESRI (2009)

EXPLANATION

- Adjacent catchments**
- Study-area boundary**
- State boundary**
- Appalachian National Scenic Trail**



Figure 12. —Continued



State-line boundaries from U.S. Geological Survey 1:2,000,000-scale digital data
Albers Conic projection, NAD 1983

Catchment boundaries from National Hydrography Dataset *Plus*
(U.S. Environmental Protection Agency, 2006a)
Physical-map background from the National Park Service
Natural Earth physical map, available online from ESRI (2009)

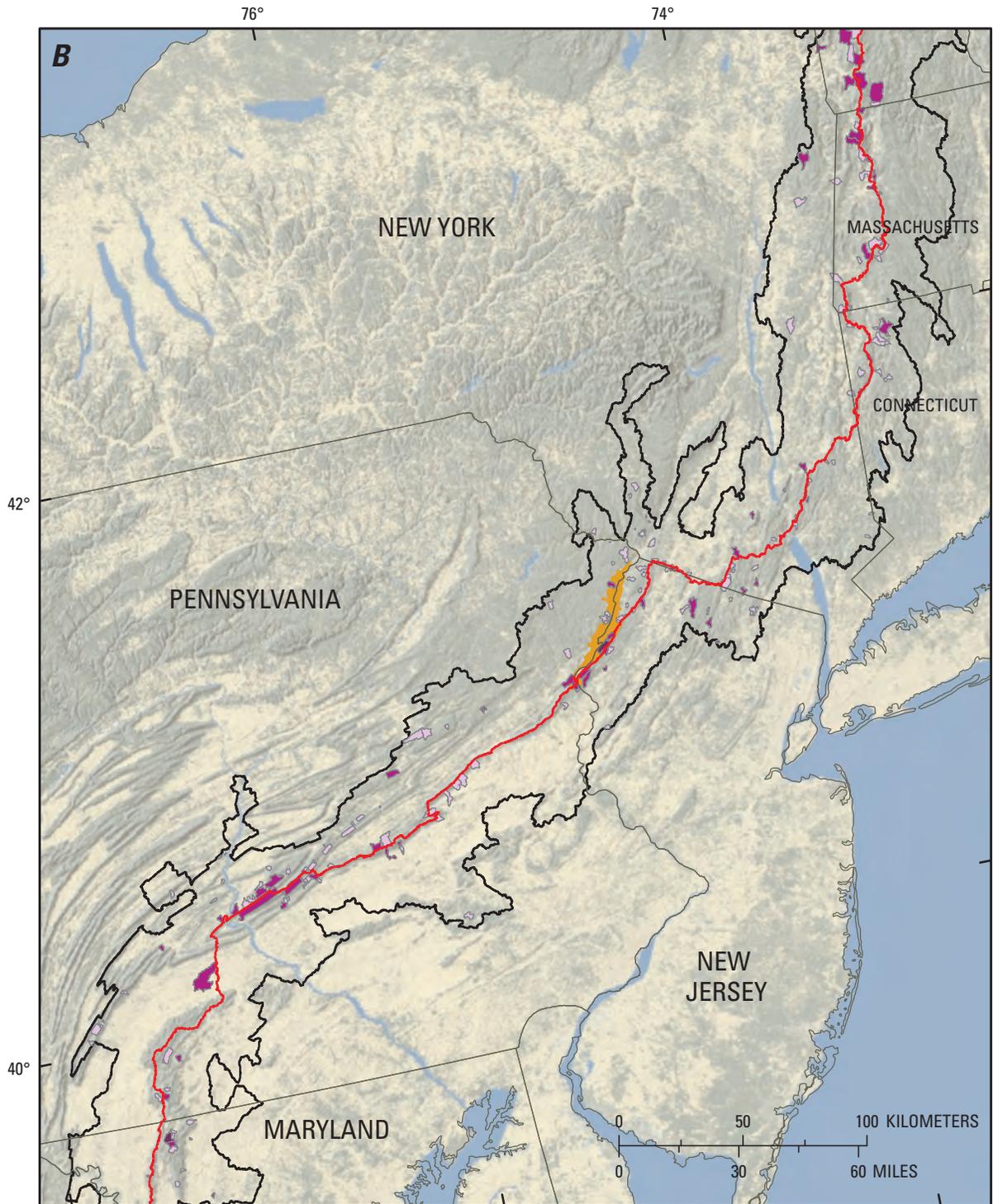
EXPLANATION

Selected catchments
Number of sampling sites

	1 to 2
	3 to 5
	6 to 55

	White Mountain National Forest
	Study-area boundary
	State boundary
	Appalachian National Scenic Trail

Figure 13. The spatial distribution of and the number of sampling sites in National Hydrography Dataset *Plus* (NHD*Plus*) catchments used in the level 1 inventory of first- and second-order streams along the Appalachian National Scenic Trail, A, Maine to Vermont, B, Massachusetts to Maryland, C, Maryland to Virginia, and D, Virginia to Georgia.



State-line boundaries from U.S. Geological Survey 1:2,000,000-scale digital data
Albers Conic projection, NAD 1983

Catchment boundaries from National Hydrography Dataset *Plus*
(U.S. Environmental Protection Agency, 2006a)
Physical-map background from the National Park Service
Natural Earth physical map, available online from ESRI (2009)

EXPLANATION

- Selected catchments**
Number of sampling sites
- 1 to 2
 - 3 to 5
 - 6 to 55

- Delaware Water Gap National Recreation Area
- Study-area boundary
- State boundary
- Appalachian National Scenic Trail

Figure 13. —Continued

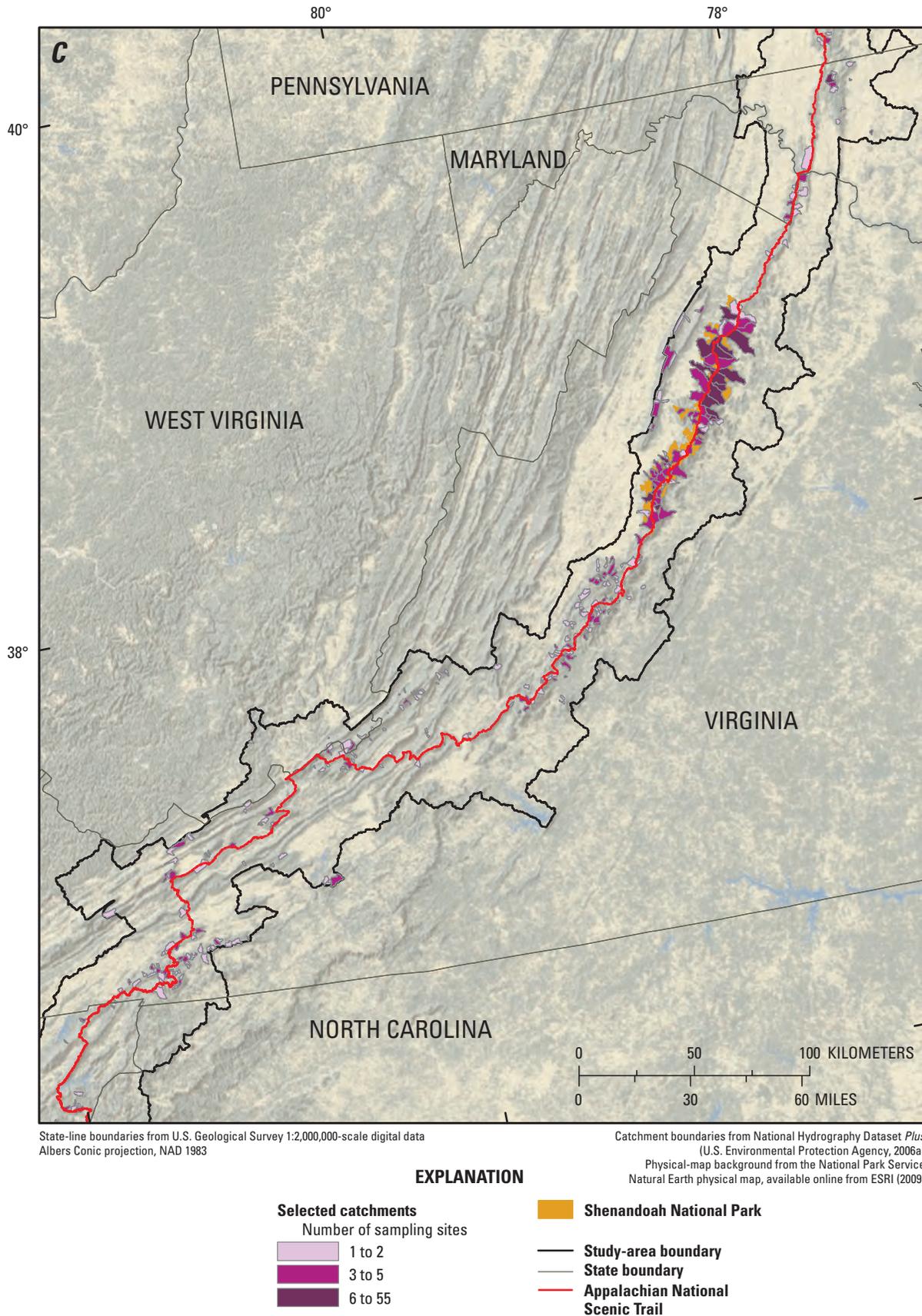
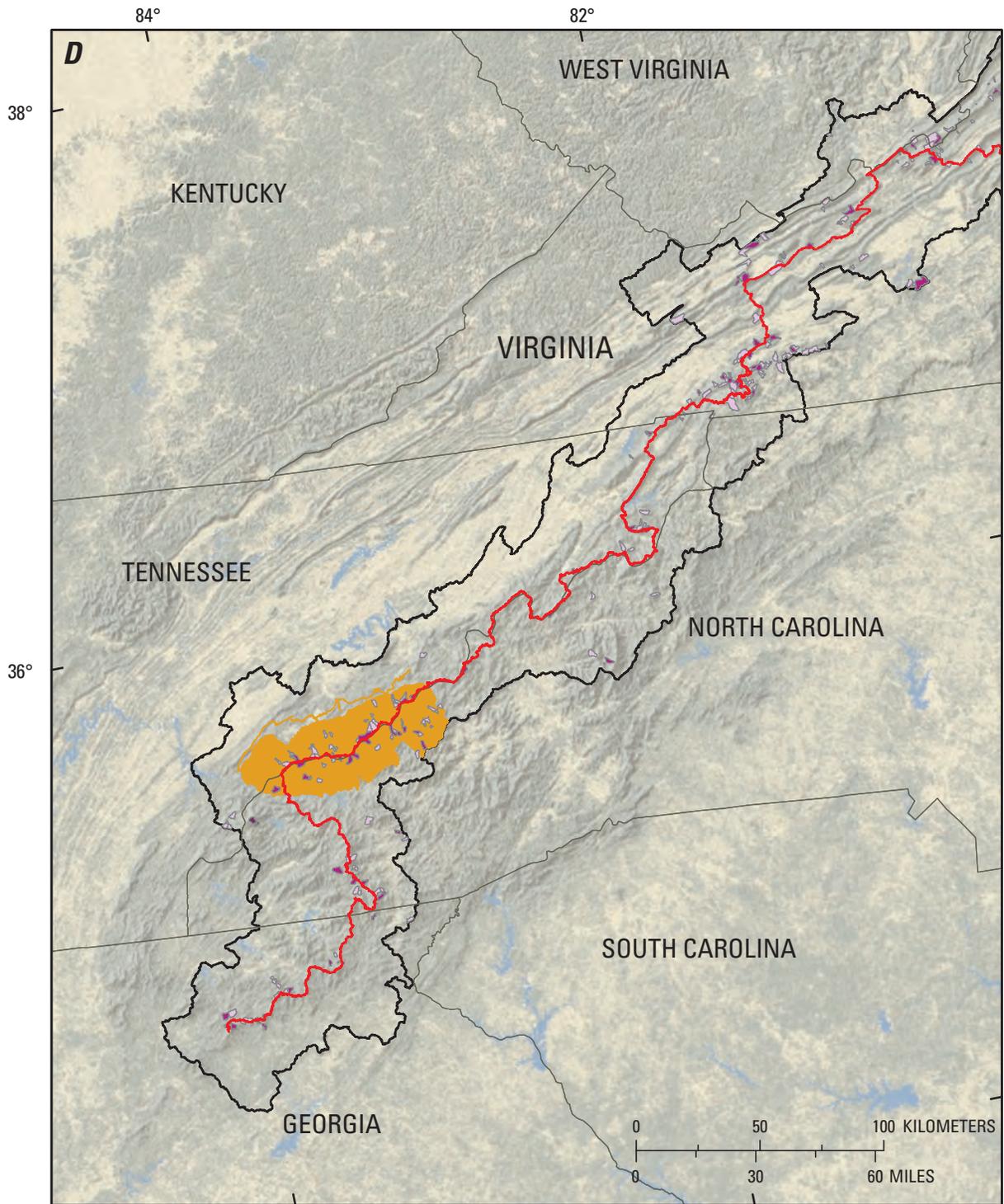


Figure 13. —Continued



State-line boundaries from U.S. Geological Survey 1:2,000,000-scale digital data
Albers Conic projection, NAD 1983

Catchment boundaries from National Hydrography Dataset *Plus*
(U.S. Environmental Protection Agency, 2006a)
Physical-map background from the National Park Service
Natural Earth physical map, available online from ESRI (2009)

EXPLANATION

- | | |
|---|---|
| <p>Selected catchments
Number of sampling sites</p> <ul style="list-style-type: none"> 1 to 2 3 to 5 6 to 55 | <ul style="list-style-type: none"> Great Smoky Mountains National Park Study-area boundary State boundary Appalachian National Scenic Trail |
|---|---|

Figure 13. —Continued

Table 4. Threshold values, by subregion, of selected physical attributes used to screen nonadjacent sampling sites for inclusion in the water-quality summary of selected sampling sites along the Appalachian National Scenic Trail.

[Subregions are listed in approximate order from north to south; ft, feet]

Subregion (hydrologic unit name)	Hydrologic unit code	Number of adjacent catchments	Minimum stream elevation (ft)	75th percentile of developed land cover (percent)	75th percentile of agricultural land cover (percent)
Penobscot	0102	182	492	0	0.04
Kennebec	0103	73	487	0.03	0.10
Androscoggin	0104	74	1,015	0.01	0.05
Saco	0106	10	1,243	0.18	0.06
Merrimack	0107	36	1,012	0.04	0.37
Connecticut	0108	152	374	0.39	5.68
Richelieu	0201	41	658	0.71	5.92
Upper Hudson	0202	142	227	2.98	13.3
Connecticut Coastal	0110	136	347	1.25	10.8
Lower Hudson–Long Island	0203	52	0	1.47	0.83
Delaware	0204	141	291	0.71	17.2
Susquehanna	0205	129	332	0.12	26.8
Potomac	0207	199	220	0.65	27.7
Lower Chesapeake	0208	247	652	0.01	3.63
Chowan–Roanoke	0301	69	1,199	0.23	5.25
Kanawha	0505	147	1,895	0	15.8
Upper Tennessee	0601	597	1,318	0	1.06
Middle Tennessee–Hiwassee	0602	66	2,279	0	0.10
Ogeechee–Savannah	0306	26	2,728	0	0
Apalachicola	0313	37	2,323	0	0.12
Alabama	0315	9	1,904	0	0

Statistical Methods

Selected data compiled for this study were statistically analyzed to characterize the water quality along the length of the Appalachian Trail using Version 9.3 of SAS (SAS Institute, 2008). Summary statistics were computed by robust Regression on Order Statistics which uses a probability plot of the logarithms of the data to account for datasets that include multiple detection limits (Helsel and Cohn, 1988; Helsel, 2005). In the robust Regression on Order Statistics method of analysis, detected values were used when available, while estimations were used for the censored portions of the distribution. In the combined dataset, each constituent had two to eight different detection limits, likely due to differences in laboratory analysis methods. Results less than the maximum detection limit for each constituent were considered estimated (Helsel, 2005). Dashed lines represent estimated values in box plots while estimated values in tables were reported by using italicized text.

Water-quality data were grouped by ecosections and by major geologic units, and the Kruskal-Wallis statistical test

was used to determine if there were statistical differences in water-quality data within these groupings. If a significant difference was found, Tukey's multiple-comparison test was used to determine which group differed significantly (Helsel and Hirsch, 1992). Results from the Tukey's multiple-comparison tests are shown by use of letters on the figures in this report; groups having the same letter underneath them are not significantly different. Groups that contained fewer than five values are shown as boxplots but were not compared statistically. A Spearman rank correlation (ρ) test was used to determine the strength of association between two variables and to identify environmental attributes that might have influenced water quality along and near the Appalachian Trail. Physical attributes (elevation, slope, and size of the drainage area) and land-cover, soils, temperature, and precipitation data were tested to determine the extent to which each variable is correlated with water-quality data. The level of significance for all tests was set at 0.05. Significant ρ values less than 0.4 are generally not discussed in this report because the correlations were considered weak.

Characterization of Selected Field Properties, Major-Ion Chemistry, Acid Neutralizing Capacity, and Nutrients

Water-quality data from the selected sampling sites were aggregated, summarized, and used to describe the basic character of and variations in the water quality along the Appalachian Trail. Concentrations and relative proportions of solutes in surface waters are primarily determined by the types of sediments and bedrock underlying the surface waters, residence time, atmospheric deposition, and climate. These environmental attributes vary over the length of the Appalachian Trail, and water chemistry also varies as a reflection of these changes. Nine of the 17 USFS ecoregions had sufficient sampling sites with relevant water-quality data and were used for describing variations in water quality along the Appalachian Trail. The nine ecoregions were the White Mountains, Vermont–New Hampshire Upland, Green–Taconic–Berkshire Mountains, Lower New England, Hudson Valley, Northern Glaciated Allegheny Plateau, Northern Ridge and Valley, Blue Ridge Mountains, and Allegheny Mountains ecoregions (fig. 7). Water-quality data from the White Mountains, Blue Ridge Mountains, and Allegheny Mountains ecoregions typically demonstrated similar chemical concentrations that were markedly lower than concentrations measured in samples collected from the other ecoregions.

Differences in selected physical attributes among ecoregions may help to indicate factors that influence variations in water quality along the Appalachian Trail. Physical attributes of the catchments that contained selected sampling sites are summarized by ecoregion in table 5. The highest median elevations were in the southern (Allegheny Mountains and Blue Ridge Mountains, 2,495 and 2,474 ft respectively) and the northern (White Mountains and Green–Taconic–Berkshire Mountains, 2,064 and 1,394 ft respectively) ecoregions (table 5). Median slope values were greatest (steepest slopes) in the ecoregions with the highest elevations, including the Allegheny Mountains, White Mountains, and Blue Ridge Mountains ecoregions (table 5). The median percentage of developed land in drainage areas of catchments in the Lower New England ecoregion was the highest (0.53 percent) (table 5). The Northern Ridge and Valley, Hudson Valley, Vermont–New Hampshire Upland, and Green–Taconic–Berkshire Mountains ecoregions contained the highest median percentages of agricultural land in the drainage areas of catchments (7.47, 4.09, 3.92, and 2.98, respectively) (table 5).

Field Properties

Temperature affects the life cycles and activity of aquatic organisms and the rates and equilibria of biogeochemical reactions (Allen, 1995). Aggregated surface-water catchment temperature data for the 69 year period between March 1939 and November 2008 ranged from 2.6 to 25.2°C (table 6). Most

temperature values (56.7 percent) were less than 12°C, which may be indicative of cool headwater streams. Water temperatures greater than 20°C, which is generally considered an in stream upper limit for the protection of aquatic health, were recorded in 170 catchments (U.S. Environmental Protection Agency, 2006b). These warm temperatures were primarily observed between the months of July and September and were measured in all regions along the Appalachian Trail (including catchments with elevations greater than 2,500 ft). Water temperatures were related to season, elevation, and latitude. Catchments in the northern section of the Appalachian Trail generally had the coolest water temperatures in all seasons, whereas catchments in the central and southern sections of the Appalachian Trail generally had the warmest water temperatures in all seasons (table 7).

Dissolved oxygen is important in maintaining healthy stream biota because oxygen is necessary for the survival of many aquatic organisms, and is affected by many factors including ambient temperatures, atmospheric pressures, and ionic or biological activity. Catchment concentrations of dissolved oxygen ranged from 3.8 to 12.9 mg/L, with a median value of 9.5 mg/L (table 6). Five catchments had concentrations of dissolved oxygen less than 6 mg/L, which is generally considered the lower limit for the protection of aquatic health (U.S. Environmental Protection Agency, 2006b). Concentrations of dissolved oxygen appeared to be related to temporal variations, such as seasonal differences (table 7).

The pH of a water body is a measure of the Hydrogen ion (H^+) concentration. pH helps to characterize the acid-base status of the water and has relevance to many water chemistry measures. Natural waters generally have pH values in the range of 6.5 to 8.5 (Hem, 1992). Catchment pH values ranged from 4.0 to 8.9 with a median value of 6.7 (table 6), with approximately 38 percent of the catchments (302) having pH values less than 6, pH values of 6, are generally considered an instream lower limit for the protection of aquatic health (U.S. Environmental Protection Agency, 2006b).

Statistical similarities and differences in median catchment pH values among the nine ecoregions are shown in figure 14A. Median pH values from the White Mountain ecoregion are the lowest and statistically unique among the other eight ecoregions (median pH = 6.1) (fig. 14A, table 8). The Vermont–New Hampshire Upland, Green–Taconic–Berkshire Mountains, Lower New England, and Hudson Valley ecoregions have the highest median catchment pH values of 7.1 to 7.4 (fig. 14A, table 8).

Specific conductance is a measure of the ability of water to conduct an electric current and is related to the concentration of dissolved solids (Hem, 1992) and is reported as microsiemens per centimeter ($\mu S/cm$). Median catchment specific conductance values ranged from 4.0 to 761 $\mu S/cm$ with a median value of 23.8 $\mu S/cm$ (table 6). Approximately 75 percent of the catchments had specific conductance values less than 50.0 $\mu S/cm$ (table 6).

The White Mountains, Green–Taconic–Berkshire Mountains, Blue Ridge Mountains, and Allegheny Mountains

Table 5. Summary statistics of selected physical attributes, by U.S. Forest Service ecological sections (ecosections), from catchments that contain selected sampling sites along the Appalachian National Scenic Trail.

[ft, feet]

Ecological section	Number of catchments	Minimum	Median	Maximum
White Mountains	82	712	2,064	3,950
Vermont–New Hampshire Upland	25	430	971	1,985
Green–Taconic–Berkshire Mountains	71	689	1,394	2,818
Lower New England	36	381	833	1,490
Hudson Valley	30	302	722	1,332
Northern Glaciated Allegheny Plateau	13	548	873	1,158
Northern Ridge and Valley	57	417	804	1,703
Blue Ridge Mountains	369	522	2,474	5,351
Allegheny Mountains	88	955	2,495	4,091
Slope				
White Mountains	82	0.00	0.06	0.20
Vermont–New Hampshire Upland	22	0.00	0.03	0.13
Green–Taconic–Berkshire Mountains	81	0.00	0.03	0.11
Lower New England	37	0.00	0.02	0.08
Hudson Valley	20	0.00	0.02	0.09
Northern Glaciated Allegheny Plateau	14	0.01	0.03	0.12
Northern Ridge and Valley	45	0.00	0.01	0.08
Blue Ridge Mountains	330	0.01	0.07	0.35
Allegheny Mountains	88	0.01	0.05	0.19
Percentage of developed land cover				
White Mountains	82	0.00	0.00	1.08
Vermont–New Hampshire Upland	22	0.00	0.13	6.45
Green–Taconic–Berkshire Mountains	81	0.00	0.38	20.0
Lower New England	37	0.00	0.53	15.1
Hudson Valley	20	0.00	0.41	27.2
Northern Glaciated Allegheny Plateau	14	0.00	0.03	0.41
Northern Ridge and Valley	45	0.00	0.05	23.6
Blue Ridge Mountains	330	0.00	0.00	10.0
Allegheny Mountains	88	0.00	0.00	3.08
Percentage of agricultural land cover				
White Mountains	82	0.00	0.01	5.40
Vermont–New Hampshire Upland	22	0.08	3.92	35.5
Green–Taconic–Berkshire Mountains	81	0.00	2.98	24.0
Lower New England	37	0.00	0.64	17.0
Hudson Valley	20	0.16	4.09	25.3
Northern Glaciated Allegheny Plateau	14	0.05	0.17	3.98
Northern Ridge and Valley	45	0.00	7.47	67.0
Blue Ridge Mountains	330	0.00	0.19	41.1
Allegheny Mountains	88	0.00	0.24	17.1

Table 6. Summary statistics of concentrations of selected water-quality constituents from catchments that contain selected sampling sites along the Appalachian National Scenic Trail.

[°C, degrees Celsius; mg/L, milligrams per liter; $\mu\text{S}/\text{cm}$, microsiemens per centimeter at 25 degrees Celsius; $\mu\text{eq}/\text{L}$, microequivalents per liter; <, less than, *italic text indicates estimated values*]

Property or constituent (reporting units)	Number of catchments	Minimum value	25th percentile	Median value	Mean value	75th percentile	Maximum value
Field properties							
Water temperature (°C)	531	2.6	10.0	12.5	12.9	15.9	25.2
Dissolved oxygen (mg/L)	336	3.8	8.8	9.5	9.5	10.2	12.9
pH (standard units)	790	4.0	6.2	6.7	6.6	7.1	8.9
Specific conductance ($\mu\text{S}/\text{cm}$)	700	4.0	15.4	23.8	43.7	42.7	761
Acid neutralizing capacity ($\mu\text{eq}/\text{L}$)	629	-11.3	38.6	98.7	293	279	4,400
Major ions							
Bicarbonate (mg/L)	163	0.26	3.55	9.64	22.9	24.9	262.0
Calcium (mg/L)	585	0.19	0.83	1.46	3.36	2.92	81.2
Chloride (mg/L)	656	0.20	0.53	0.78	2.76	1.85	150.0
Fluoride (mg/L)	105	< 0.08	< 0.08	< 0.08	0.10	0.10	1.7
Magnesium (mg/L)	625	0.10	0.34	0.64	2.18	1.43	52.0
Potassium (mg/L)	563	0.01	0.34	0.47	0.63	0.77	5.8
Silica (mg/L as SiO_2)	399	0.25	0.60	1.18	9.76	4.99	207.7
Sodium (mg/L)	573	0.21	0.65	1.01	1.94	1.70	84.0
Sulfate (mg/L)	573	0.29	2.07	3.41	5.08	5.50	138.5
Nutrients							
Ammonia (mg/L as N)	283	< 0.01	< 0.01	<i>0.016</i>	<i>0.050</i>	<i>0.038</i>	4.00
Nitrate (mg/L as N)	365	< 0.008	<i>0.045</i>	0.143	0.301	0.356	4.52
Total nitrogen (mg/L as N)	153	< 0.05	0.193	0.350	0.485	0.567	7.10
Total phosphorus (mg/L as P)	215	< 0.004	<i>0.009</i>	<i>0.018</i>	<i>0.052</i>	<i>0.034</i>	4.20

ecosections had the lowest median specific conductance values, which ranged from 17.7 to 25.8 $\mu\text{S}/\text{cm}$. The median specific conductance value from the Blue Ridge Mountains ecosection was the lowest when compared to the other ecosections. In contrast, the Vermont–New Hampshire Upland, Lower New England, Hudson Valley, Northern Glaciated Allegheny Plateau, and the Northern Ridge and Valley ecosections had higher median specific conductance values, which ranged from 41.0 to 108.1 $\mu\text{S}/\text{cm}$ (fig. 14B, table 8).

Major Ions

Major ions summarized in this report are common constituents dissolved in most natural waters and include bicarbonate, calcium, chloride, fluoride, magnesium, nitrate, potassium, silica, sodium, and sulfate (table 6). Median catchment concentrations of cations (calcium, magnesium, sodium, and potassium) were less than 1.5 mg/L and

ranged from 0.47 to 1.46 mg/L (table 6). Median catchment concentrations of anions (bicarbonate, chloride, fluoride, nitrate, and sulfate) ranged more widely than those of cations; all medians were less than 10 mg/L and ranged from less than 0.08 to 9.64 mg/L (table 6).

Major-ion concentrations were compiled to develop water types. Water types can be an efficient way to describe variations in bulk water chemistry and also can be useful in identifying waters that have been contaminated from road salt or deposition. Water types were calculated based on the percentage of milliequivalents of the major ions present within each sample. In most samples compiled for this study, no one cation composed more than 50 percent of the total cations. Sulfate was the most frequently detected predominant anion. Consequently, calcium-magnesium mixed, sulfate was the most frequently determined water type. In the Lower New England and Hudson Valley ecosections however, calcium-bicarbonate was the most frequently calculated water type.

Table 7. Water temperature and dissolved oxygen concentrations by U.S. Forest Service ecological sections (ecosections) and by season from selected sampling sites along the Appalachian National Scenic Trail.

[°C, degrees Celsius; --, insufficient data (fewer than 5 reported values); mg/L, milligrams per liter]

Ecological section	January to March	April to June	July to September	October to December
Water temperature (°C)				
White Mountains	0.5	7.8	13.3	3.9
Vermont–New Hampshire Upland	0.0	10.0	15.6	4.0
Green–Taconic–Berkshire Mountains	1.0	12.0	16.0	5.6
Lower New England	1.0	13.0	18.0	7.0
Hudson Valley	4.1	14.0	17.9	9.5
Northern Glaciated Allegheny Plateau	--	14.3	19.2	--
Northern Ridge and Valley	4.6	12.0	17.0	8.8
Blue Ridge Mountains	5.0	12.1	18.0	9.5
Allegheny Mountains	4.0	10.3	17.0	9.0
Dissolved oxygen (mg/L)				
White Mountains	--	10.4	9.4	12.2
Vermont–New Hampshire Upland	13.6	10.7	8.9	12.3
Green–Taconic–Berkshire Mountains	14.0	10.0	9.2	11.5
Lower New England	11.1	9.2	8.0	9.8
Hudson Valley	13.4	10.0	8.7	11.4
Northern Glaciated Allegheny Plateau	--	--	--	--
Northern Ridge and Valley	12.4	10.4	8.8	11.0
Blue Ridge Mountains	11.9	9.9	8.0	8.4
Allegheny Mountains	11.3	10.0	10.0	10.1

Median concentrations of calcium, magnesium, and sodium (cations) from the Hudson Valley and Lower New England ecosections are among the highest compared to the other ecosections (figs. 14D–G) (table 8). One notable exception is catchment concentrations of magnesium in the Vermont–New Hampshire Upland and Green–Taconic–Berkshire Mountains ecosections of 8.30 and 5.75 mg/L, respectively. Median catchment concentrations of calcium, magnesium, and sodium in the White Mountains, Blue Ridge Mountains, and Allegheny Mountains are among the lowest compared to the other ecosections (figs. 14D–F) (table 8). The White Mountains ecosection also had the lowest median catchment concentration of potassium and was statistically similar only to the Northern Glaciated Allegheny Plateau ecosection (fig. 14G).

Catchment concentrations of common anions were similar to those of cations—generally lowest in the White Mountains, Blue Ridge Mountains, and Allegheny Mountains (figs. 14H–J, table 8). Catchment concentrations of sulfate in these three ecosections were lower than in the other six ecosections and statistically unique in the Blue Ridge Mountain ecosection (fig. 14H). Catchment concentrations of chloride in these three ecosections also were lower than in the other six ecosections and statistically unique in the White Mountains ecosection (fig. 14I). Catchment concentrations

of chloride and sulfate in the Hudson Valley and Lower New England ecosections are generally higher than in the other ecosections (figs. 14H–I, table 8). Catchment concentrations of nitrate were generally lower than concentrations of sulfate and chloride, and the medians for five of the nine ecosections were estimated (fig. 14J, table 8). Catchment concentrations of nitrate were highest in the Northern Ridge and Valley, Green–Taconic–Berkshire Mountains, and Vermont–New Hampshire Upland ecosections: 0.416, 0.330 and 0.261 mg/L, respectively (fig. 14J, table 8).

Overall, major ion concentrations are lower in the White Mountains, Blue Ridge Mountains, and Allegheny Mountains ecosections and higher concentrations in the Lower New England and Hudson Valley ecosections. The Vermont–New Hampshire Upland, Green–Taconic–Berkshire Mountains, Northern Glaciated Allegheny Plateau, and Northern Ridge and Valley ecosections represent the transition zones along the Appalachian Trail between the regions of highest and lowest elevation (table 5). The catchment concentrations of most major ions in these four transitional ecosections are generally lower than or similar to catchment concentrations from the Hudson Valley and Lower New England ecosections and greater than catchment concentrations from the White Mountains, Blue Ridge Mountains, and Allegheny Mountains ecosections.

Table 8. Summary statistics of selected water-quality constituents by U.S. Forest Service ecological sections (ecosections) from catchments that contain selected sampling sites in headwater streams along the Appalachian National Scenic Trail.

[$\mu\text{S}/\text{cm}$, microsiemens per centimeter at 25 degrees Celsius; $\mu\text{eq}/\text{L}$, microequivalents per liter; mg/L , milligrams per liter; <, less than; *italic* text indicates estimated values]

Ecological section	Number of catchments	Minimum	25th percentile	Median	75th percentile	Maximum
pH						
White Mountains	84	4.6	5.6	6.1	6.3	7.3
Vermont–New Hampshire Upland	24	4.0	6.9	7.4	7.6	8.4
Green–Taconic–Berkshire Mountains	82	4.6	6.5	7.2	7.6	8.2
Lower New England	39	5.9	6.8	7.1	7.3	8.3
Hudson Valley	29	5.7	6.9	7.4	7.6	8.9
Northern Glaciated Allegheny Plateau	17	5.6	6.7	6.9	7.1	7.8
Northern Ridge and Valley	66	4.5	6.3	6.6	7.0	7.7
Blue Ridge Mountains	353	4.3	6.3	6.7	6.9	8.4
Allegheny Mountains	96	4.9	5.8	6.6	7.0	8.0
Specific conductance ($\mu\text{S}/\text{cm}$)						
White Mountains	67	13.0	21.8	25.8	30.0	84.8
Vermont–New Hampshire Upland	19	27.0	51.0	84.0	118	351
Green–Taconic–Berkshire Mountains	28	18.0	21.8	27.3	32.0	109
Lower New England	36	39.0	55.5	94.4	144	761
Hudson Valley	28	30.0	47.0	108.1	168	421
Northern Glaciated Allegheny Plateau	16	25.0	46.3	64.8	84.3	124
Northern Ridge and Valley	59	13.7	31.3	41.0	67.0	532
Blue Ridge Mountains	352	4.0	13.1	17.7	27.9	263
Allegheny Mountains	95	7.9	13.2	20.5	37.0	421
Acid neutralizing capacity ($\mu\text{eq}/\text{L}$)						
White Mountains	30	0	23	45	71.0	215
Vermont–New Hampshire Upland	20	0	424	820	1,086	2,680
Green–Taconic–Berkshire Mountains	81	0	140	350	762	3,984
Lower New England	33	84	200	394	960	2,390
Hudson Valley	20	14.2	120	575	901	3,710
Northern Glaciated Allegheny Plateau	12	36.8	135	169	210	352
Northern Ridge and Valley	38	8.35	93.8	164	300	4,400
Blue Ridge Mountains	306	-8.85	31.6	62.4	137	2,280
Allegheny Mountains	85	-11.3	6.8	66.9	204	2,900
Calcium (mg/L)						
White Mountains	76	0.69	1.08	1.71	2.30	3.59
Vermont–New Hampshire Upland	7	2.10	2.30	3.50	22.0	47.0
Green–Taconic–Berkshire Mountains	18	1.35	1.54	2.48	3.45	13.7
Lower New England	28	3.63	4.75	8.08	16.1	39.0
Hudson Valley	18	1.88	4.40	8.47	17.9	49.0
Northern Glaciated Allegheny Plateau	11	2.11	3.07	5.14	5.66	8.04
Northern Ridge and Valley	35	0.19	2.24	3.46	7.50	81.2
Blue Ridge Mountains	313	0.21	0.71	1.06	1.82	27.5
Allegheny Mountains	79	0.19	0.66	1.28	3.42	35.4

Table 8. Summary statistics of selected water-quality constituents by U.S. Forest Service ecological sections (ecosections) from catchments that contain selected sampling sites in headwater streams along the Appalachian National Scenic Trail.—Continued[$\mu\text{S/cm}$, microsiemens per centimeter at 25 degrees Celsius; $\mu\text{eq/L}$, microequivalents per liter; mg/L , milligrams per liter; <, less than; *italic* text indicates estimated values]

Ecological section	Number of catchments	Minimum	25th percentile	Median	75th percentile	Maximum
Magnesium (mg/L)						
White Mountains	63	0.12	0.26	0.35	0.47	0.92
Vermont–New Hampshire Upland	13	0.48	0.94	8.30	13.0	26.0
Green–Taonic–Berkshire Mountains	65	0.28	1.26	5.75	12.0	52.0
Lower New England	28	1.00	1.58	2.68	6.88	15.0
Hudson Valley	18	0.87	1.61	2.50	3.22	17.0
Northern Glaciated Allegheny Plateau	11	0.69	0.95	1.06	1.26	1.71
Northern Ridge and Valley	36	0.10	0.86	1.43	2.43	15.7
Blue Ridge Mountains	313	0.12	0.28	0.49	0.83	8.65
Allegheny Mountains	78	0.16	0.35	0.53	0.80	29.9
Sodium (mg/L)						
White Mountains	64	0.36	0.72	0.97	1.19	3.25
Vermont–New Hampshire Upland	6	1.42	1.65	1.96	4.70	8.00
Green–Taonic–Berkshire Mountains	35	0.21	0.78	1.32	2.56	16.6
Lower New England	24	1.50	2.05	3.00	6.38	84.0
Hudson Valley	19	0.75	1.49	3.90	8.40	22.6
Northern Glaciated Allegheny Plateau	12	0.76	2.05	5.28	7.82	19.0
Northern Ridge and Valley	31	0.51	1.07	2.17	3.20	21.4
Blue Ridge Mountains	307	0.32	0.71	0.99	1.55	20.7
Allegheny Mountains	75	0.22	0.31	0.37	0.60	18.5
Sulfate (mg/L)						
White Mountains	53	2.07	3.32	4.00	4.61	7.63
Vermont–New Hampshire Upland	7	5.00	5.50	8.00	10.50	13.0
Green–Taonic–Berkshire Mountains	32	3.53	5.68	6.97	8.13	15.4
Lower New England	27	5.50	9.10	10.8	14.0	25.0
Hudson Valley	19	7.43	9.75	11.2	16.0	111.0
Northern Glaciated Allegheny Plateau	12	4.06	6.03	6.71	7.72	12.0
Northern Ridge and Valley	40	1.15	4.94	6.59	10.9	79.0
Blue Ridge Mountains	305	0.29	1.44	2.39	3.43	24.0
Allegheny Mountains	78	0.66	2.40	3.10	4.73	138.5
Chloride (mg/L)						
White Mountains	74	0.24	0.37	0.48	0.60	18.8
Vermont–New Hampshire Upland	21	0.20	0.75	2.07	5.15	16.0
Green–Taonic–Berkshire Mountains	71	0.20	0.56	1.75	3.90	20.6
Lower New England	34	0.40	2.43	4.83	12.0	150.0
Hudson Valley	19	0.87	1.60	3.26	12.6	41.1
Northern Glaciated Allegheny Plateau	12	0.57	1.19	8.88	11.3	31.1
Northern Ridge and Valley	35	0.84	1.50	2.50	5.30	52.8
Blue Ridge Mountains	313	0.32	0.54	0.75	0.95	14.2
Allegheny Mountains	77	0.43	0.55	0.65	0.77	48.6

Table 8. Summary statistics of selected water-quality constituents by U.S. Forest Service ecological sections (ecosections) from catchments that contain selected sampling sites in headwater streams along the Appalachian National Scenic Trail.—Continued

[$\mu\text{S/cm}$, microsiemens per centimeter at 25 degrees Celsius; $\mu\text{eq/L}$, microequivalents per liter; mg/L , milligrams per liter; <, less than; *italic* text indicates estimated values]

Ecological section	Number of catchments	Minimum	25th percentile	Median	75th percentile	Maximum
Nitrate (mg/L as N)						
White Mountains	6	<i>0.026</i>	<i>0.030</i>	<i>0.069</i>	0.110	0.560
Vermont–New Hampshire Upland	6	<i>0.023</i>	0.148	0.261	0.430	1.42
Green–Taconic–Berkshire Mountains	15	<i>0.021</i>	0.255	0.330	0.625	0.840
Lower New England	28	<i>0.021</i>	<i>0.058</i>	0.129	0.399	2.00
Hudson Valley	16	<i>0.009</i>	<i>0.022</i>	<i>0.118</i>	0.261	0.928
Northern Glaciated Allegheny Plateau	12	<i>0.019</i>	<i>0.037</i>	<i>0.100</i>	0.310	0.960
Northern Ridge and Valley	37	<i>0.014</i>	0.150	0.416	0.576	4.36
Blue Ridge Mountains	210	< 0.008	<i>0.038</i>	<i>0.127</i>	0.343	4.52
Allegheny Mountains	35	< 0.008	<i>0.015</i>	<i>0.063</i>	0.149	1.85
Ammonia (mg/L as N)						
White Mountains	52	< 0.01	<i>0.010</i>	<i>0.023</i>	<i>0.053</i>	0.175
Vermont–New Hampshire Upland	12	< 0.01	<i>0.013</i>	<i>0.033</i>	<i>0.058</i>	0.120
Green–Taconic–Berkshire Mountains	10	<i>0.015</i>	<i>0.022</i>	<i>0.065</i>	<i>0.088</i>	4.00
Lower New England	21	<i>0.012</i>	<i>0.020</i>	<i>0.035</i>	0.168	0.550
Hudson Valley	11	<i>0.011</i>	<i>0.014</i>	<i>0.024</i>	<i>0.038</i>	0.142
Northern Glaciated Allegheny Plateau	6	<i>0.014</i>	<i>0.028</i>	<i>0.031</i>	<i>0.060</i>	<i>0.061</i>
Northern Ridge and Valley	23	<i>0.014</i>	<i>0.018</i>	<i>0.027</i>	<i>0.060</i>	0.210
Blue Ridge Mountains	136	< 0.01	< 0.01	<i>0.010</i>	<i>0.016</i>	0.750
Allegheny Mountains	12	< 0.01	< 0.01	<i>0.015</i>	<i>0.020</i>	0.030
Total nitrogen (mg/L as N)						
White Mountains	34	<i>0.059</i>	0.315	0.458	0.650	1.38
Vermont–New Hampshire Upland	4	0.420	0.450	0.500	0.570	0.620
Green–Taconic–Berkshire Mountains	12	0.185	0.367	0.413	0.810	0.990
Lower New England	6	0.240	0.290	0.398	0.590	2.30
Hudson Valley	6	0.320	0.380	0.460	0.500	0.604
Northern Glaciated Allegheny Plateau	11	<i>0.064</i>	0.140	0.355	0.485	0.545
Northern Ridge and Valley	22	<i>0.100</i>	0.330	0.530	0.710	7.10
Blue Ridge Mountains	45	<i>0.054</i>	0.124	0.216	0.338	1.91
Allegheny Mountains	11	<i>0.053</i>	<i>0.065</i>	0.119	0.193	0.343
Total phosphorus (mg/L as P)						
White Mountains	13	<i>0.005</i>	<i>0.009</i>	<i>0.010</i>	<i>0.010</i>	<i>0.010</i>
Vermont–New Hampshire Upland	12	< 0.004	<i>0.007</i>	<i>0.008</i>	<i>0.009</i>	<i>0.053</i>
Green–Taconic–Berkshire Mountains	15	< 0.004	< 0.004	<i>0.005</i>	<i>0.009</i>	<i>0.033</i>
Lower New England	13	<i>0.010</i>	<i>0.018</i>	<i>0.020</i>	<i>0.025</i>	<i>0.047</i>
Hudson Valley	11	< 0.004	<i>0.011</i>	<i>0.024</i>	<i>0.030</i>	4.20
Northern Glaciated Allegheny Plateau	13	<i>0.006</i>	<i>0.017</i>	<i>0.035</i>	<i>0.044</i>	0.210
Northern Ridge and Valley	22	<i>0.004</i>	<i>0.011</i>	<i>0.027</i>	<i>0.033</i>	0.113
Blue Ridge Mountains	60	< 0.004	<i>0.009</i>	<i>0.018</i>	<i>0.040</i>	0.200
Allegheny Mountains	11	< 0.004	<i>0.004</i>	<i>0.013</i>	<i>0.020</i>	<i>0.038</i>

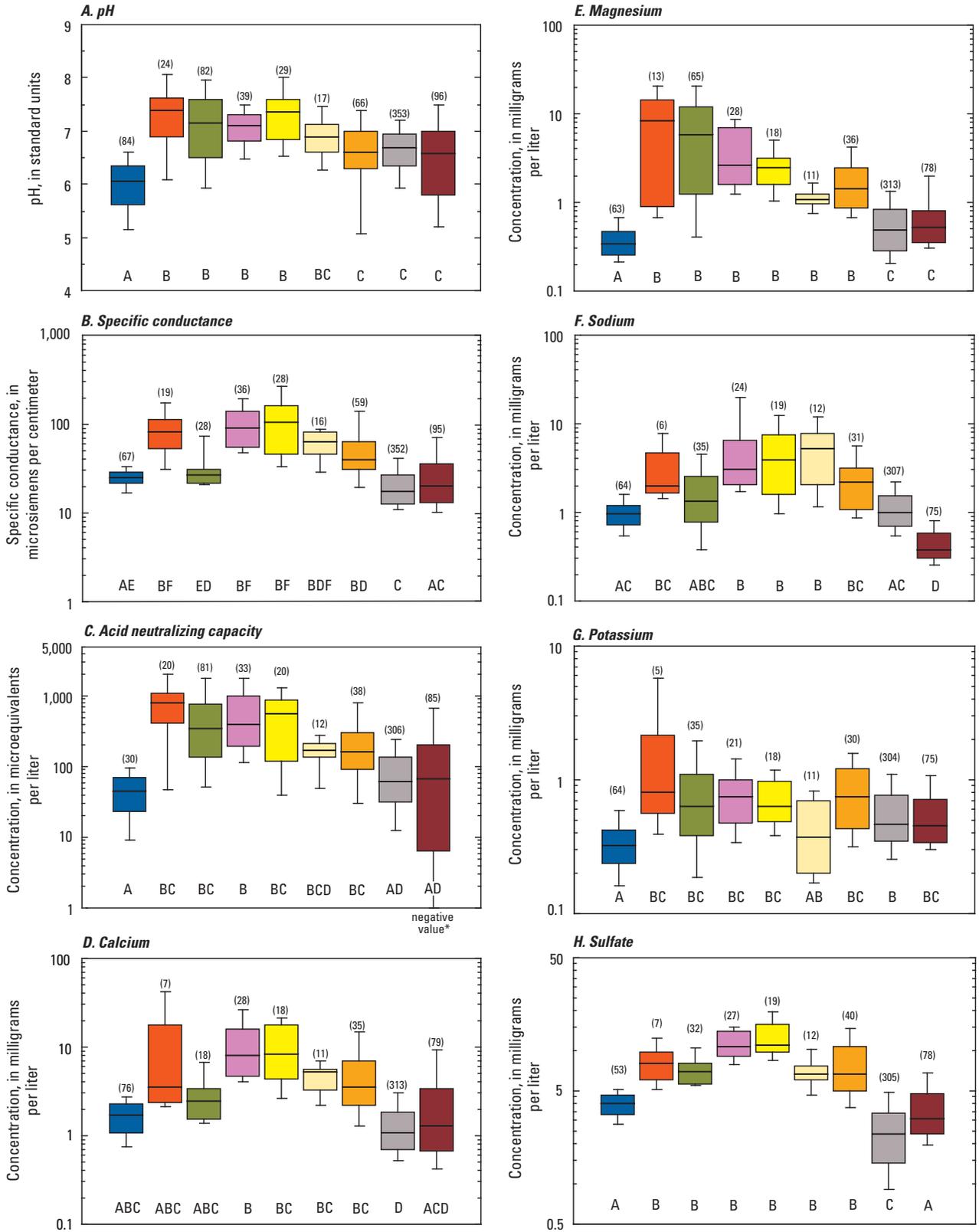


Figure 14. Comparisons of concentrations of *A*, pH, *B*, specific conductance, *C*, acid neutralizing capacity, *D*, calcium, *E*, magnesium, *F*, sodium, *G*, potassium, *H*, sulfate, *I*, chloride, *J*, nitrate, *K*, ammonia, *L*, total nitrogen, and *M*, total phosphorus, by U.S. Forest Service ecological sections (ecosections), from catchments that contain selected first- and second-order streams along the Appalachian National Scenic Trail. Ecosections are displayed left to right in approximate north to south order.

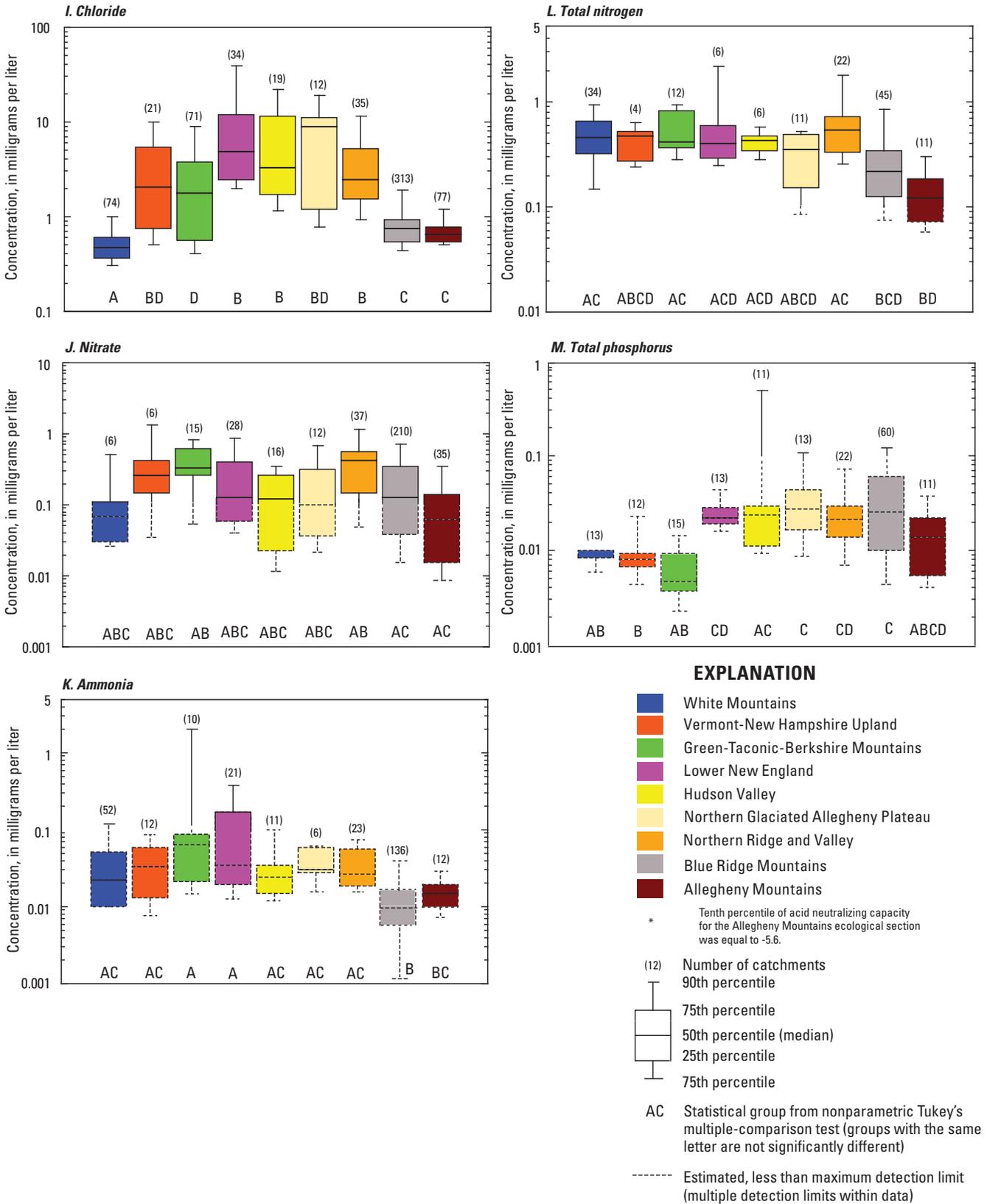


Figure 14. —Continued

Acid Neutralizing Capacity

Acid neutralizing capacity (ANC) is the capacity of a solution, including solutes plus particulates in an unfiltered water sample, to react with and neutralize acid (Rounds, 2006). ANC values, measured in microequivalents per liter ($\mu\text{eq/L}$) help to characterize the acid-base chemistry of water and indicate a net strong base in solution if ANC is positive or a net strong acid if the ANC value is negative. Higher ANC values indicate greater ability to resist acidic inputs from sources such as acid deposition. Catchment values for ANC ranged from -11.3 to $4,400 \mu\text{eq/L}$, with a median ANC value for the entire Appalachian Trail of $98.7 \mu\text{eq/L}$ (table 6).

There were distinct differences in catchment ANC values among the ecosections (fig. 14C). As with pH, the median ANC value for all catchments in the White Mountains ecosection was the lowest of all the ecosections, with a median value of $45.0 \mu\text{eq/L}$ (table 8). Median catchment ANC values from the Blue Ridge Mountains and the Allegheny Mountains were statistically similar and among the lowest: 62.4 and $66.9 \mu\text{eq/L}$, respectively (fig. 14C, table 8). Catchments in the Vermont–New Hampshire Upland ecosection had the highest median ANC value ($820 \mu\text{eq/L}$) (table 8). The catchments from the Green–Taconic–Berkshire Mountains, Lower New England, and Hudson Valley ecosections also had relatively high median ANC values (350 , 394 , and $575 \mu\text{eq/L}$, respectively) (table 8). The three ecosections (White Mountains, Blue Ridge Mountains, and Allegheny Mountains) that had the lowest catchment ANC values also had the lowest catchment concentrations of most major ions (figs. 14D–J) (table 8).

For comparison purposes, catchment ANC values were divided into three categories: ANC values less than zero were defined as acidic, ANC values between 0 and $50 \mu\text{eq/L}$ were classified as sensitive, and ANC values greater than $50 \mu\text{eq/L}$ were classified as insensitive (Kahl and Scott, 1988; Driscoll and others, 2001; Sullivan and others, 2007). Classification as sensitive and insensitive generally refers to the extent that the stream is susceptible to becoming acidic either seasonally or through event-driven episodic acidification. The percentages of catchments that had ANC values classified as acidic, sensitive, or insensitive are shown in table 9.

The ecosections with the most dilute waters—White Mountains, Blue Ridge Mountains, and Allegheny Mountains—had the highest percentages of catchments classified as acidic or sensitive compared to all other ecosections (table 9). The Allegheny Mountains had the highest percentage of catchments classified as acidic (17.6 percent) while 1.6 of the catchments in the Blue Ridge Mountains ecosection were classified as acidic (table 9). The White Mountains ecosection had the highest percentage of catchments classified as sensitive (56.7) (table 9). The White Mountains ecosection contained no catchments that were classified as acidic; however, this may be the result of the titration methods most commonly used to determine ANC values in this ecosection. Most of the ANC data from the Blue Ridge and Allegheny Mountains ecosections were

Table 9. Comparison among U.S. Forest Service ecological sections (ecosections) of the percentages of catchments with acid neutralizing capacity classified as acidic (ANC less than or equal to $0 \mu\text{eq/L}$), sensitive (ANC greater than 0 and less than $50 \mu\text{eq/L}$), or insensitive (ANC equal to or greater than $50 \mu\text{eq/L}$).

[$\mu\text{eq/L}$, microequivalents per liter]

Ecological section	Number of catchments	Percentage of catchments		
		Acidic	Sensitive	Insensitive
White Mountains	30	0	56.7	43.3
Vermont–New Hampshire Upland	20	0	10	90
Green–Taconic–Berkshire Mountains	81	0	9.9	90.1
Lower New England	33	0	0	100
Hudson Valley	20	0	15	85
Northern Glaciated Allegheny Plateau	12	0	8.3	91.6
Northern Ridge and Valley	38	0	13.2	86.8
Blue Ridge Mountains	306	1.6	38.2	60.1
Allegheny Mountains	85	17.6	29.4	52.9

determined by use of Gran's method and therefore are useful in fully characterizing the ANC of these dilute waters. Few of the ANC data from the White Mountains ecosection were determined by use of Gran's method, and therefore low ANC values may be truncated or otherwise not fully determined. Previous investigations in the northeastern United States have shown that a substantial number of lakes are chronically acidic (Kahl and Scott, 1988; Charles and Christy, 2001). This information indicates that surface waters in the White Mountains ecosection are likely to be classified as acidic. The ANC data compiled for this inventory may under represent the extent of regions near or along the Appalachian Trail where noncarbonate alkalinity is a substantial contributor to ANC and where the ANC of streamwaters could be classified as acidic.

Surface waters that have ANC low enough to be classified as acidic or sensitive are prone to seasonal and (or) event driven periods where the water quality is detrimental to the health of aquatic and terrestrial ecosystems. For most forested headwater streams, ANC is generally lower during higher streamflow (Rice and Bricker, 1995; Driscoll and others, 2001; Lawrence and others, 2004). Changes in streamflow can initiate significant changes in the water chemistry through dilution and (or) inputs of ions from deposition. Research on lakes and streams near the Appalachian Trail has helped scientists determine the processes that govern seasonal or event driven episodic acidification. Literature on investigations conducted

in the Northeast, which includes the White Mountains ecoregion, conclude that base-cation dilution is commonly the most important contributor to loss in ANC, coupled with increases of nitrate and dissolved organic carbon (Charles and Christie, 1991; Wigington and others, 1996). In contrast, literature from studies conducted in the southern Appalachian Mountains, which includes the Blue Ridge Mountains and Allegheny Mountains ecoregions, demonstrates that increases in sulfate, dissolved organic carbon, nitrate, and organic acids are more important than base-cation dilution in generating episodic acidification (Cook and others, 1994; Hyer and others, 1995; Deyton and others, 2009). Although streams in the White Mountains, Blue Ridge Mountains, and Allegheny Mountains ecoregions are of similarly low ionic strength and are vulnerable to episodic acidification, the processes in the three ecoregions that cause episodic acidification are distinctly different. Regional variations in watershed characteristics that influence the throughput and fluxes of ions—such as lithology, soil properties, and vegetation—likely play an important role in describing why the processes of episodic acidification are different between the ecoregion in the north and ecoregions in the south.

Nutrients

Nutrients (ammonia, nitrate, total nitrogen, and total phosphorus) in surface water are essential to aquatic life but need to be in appropriate concentrations. Excessively high concentrations of nitrogen can be toxic to fish and harmful to humans. High concentrations of phosphorus can produce an overgrowth of algae, which can degrade aquatic habitats. Source of excess nutrients are commonly associated with developed and agricultural land uses including urban runoff, pesticide use, effluent, and atmospheric deposition. In undeveloped areas, atmospheric deposition and the weathering of rocks and soils are typically the largest contributors (Dubrovsky and others, 2010). In first- and second-order streams along the Appalachian Trail, concentrations of nutrients are typically not high enough to be harmful to aquatic life. Concentrations of nutrients in streams along some regions of the Appalachian Trail may be evaluated through comparisons to estimated background concentrations and to regional nutrient criteria.

Catchment concentrations of ammonia were the lowest among the three nitrogen species with an overall median concentration of 0.016 mg/L (table 6). The highest median concentrations of ammonia were in catchments in the Green–Taconic–Berkshire Mountains ecoregion (0.065 mg/L) (fig. 14K, table 8). Concentrations of total nitrogen were the highest among the three nitrogen species (table 6). Median concentrations of total nitrogen were similar along most of the Appalachian Trail and ranged from 0.355 to 0.530 mg/L for most ecoregions (fig. 14L, table 8). The Blue Ridge Mountains and Allegheny Mountains ecoregions were the exception; these two ecoregions had lower median

concentrations of total nitrogen (0.216 and 0.119 mg/L, respectively; table 8).

Catchment concentrations of total phosphorus ranged from less than 0.004 to 4.20 mg/L, with an estimated median catchment concentration of 0.018 mg/L (table 6). Median catchment concentrations of phosphorus are higher in the middle and southern ecoregions than in the northern ecoregions (fig. 14M, table 8). The region of the Appalachian Trail where concentrations of total phosphorus appeared to change is near the southernmost extent of the most recent glacial advance between the Green–Taconic–Berkshire Mountains and the Lower New England ecoregions. Median catchment concentrations of phosphorus may be higher in the nonglaciated regions of the Appalachian Trail because more abundant deposits of weathered sediments may provide a source of suspended sediment, which typically entrains and transports phosphorus in the streams. Comparative evaluation of the average percentages listed in the State Soil Geographic database of clay and sand in the soil of each ecoregion showed that the middle and southern ecoregions contain more clay-rich soil, while the northern ecoregions contain more sandy soil.

Catchment concentrations of nutrients from selected sampling sites in headwater streams along the Appalachian Trail were compared to estimated national background concentrations (Dubrovsky and others, 2010) (table 10). Estimated national background concentrations were based on data from streams across the Nation in areas with minimal or no development and included sites in semiarid and arid regions (Dubrovsky and others, 2010). Overall catchment concentrations of ammonia, nitrate, total nitrogen, and total phosphorus were lower at sites along the Appalachian Trail

Table 10. Comparison of median catchment concentrations of nutrients and the percentages of median concentrations greater than estimated national background concentrations from selected sampling sites along the Appalachian National Scenic Trail.

[mg/L, milligrams per liter; *italic* text indicates estimated values]

Constituent	Estimated national background concentrations (mg/L) ¹	Median catchment concentrations (mg/L)	Percentage of catchment concentrations greater than estimated national background concentrations
Ammonia	0.025	<i>0.016</i>	35.3
Nitrate	0.24	0.143	36.9
Total nitrogen	0.58	0.35	23.5
Total phosphorus	0.034	<i>0.018</i>	25.1

¹ Estimates for national background concentrations are from Dubrovsky and others, 2010.

as compared to estimated national background concentrations (table 10). However, on a smaller scale, the Vermont–New Hampshire Upland, Green–Taconnic–Berkshire Mountains, Northern Glaciated Allegheny Plateau, and the Northern Ridge and Valley ecoregions had median catchment concentrations of ammonia that were higher than estimated national background concentrations (tables 8 and 10). Additionally, the Vermont–New Hampshire Upland, Green–Taconnic–Berkshire Mountains, and the Northern Ridge and Valley ecoregions had median catchment concentrations of nitrate that were higher than estimated national background concentrations (tables 8 and 10).

The USEPA has developed recommended ecoregional criteria for total nitrogen and total phosphorus that are intended to approximate reference or background concentrations and serve as guidelines to protect against nutrient enrichment (U.S. Environmental Protection Agency, 2000; 2002b). The nutrient ecoregion criteria reflect the regional influences of natural variations in geology, land cover, and climate that affect background concentrations of nutrients. Most of the selected catchments in this study were in one of two nutrient ecoregions, the Nutrient-Poor Largely Glaciated Upper Midwest and Northeast (New York to Maine) and the Central and Eastern Forested Upland (New Jersey to Georgia). Catchment concentrations of total nitrogen and total phosphorus from headwater streams along the Appalachian Trail were compared to USEPA nutrient ecoregion criteria (table 11). Approximately 63.4 percent of catchment concentrations of total nitrogen in the Nutrient-Poor Largely Glaciated Upper Midwest and Northeast nutrient ecoregion were greater than the recommended USEPA nutrient criterion (table 11). Approximately 70.5 percent of the catchment concentrations of total phosphorus in the Central and Eastern Forested Upland nutrient ecoregion were greater than the recommended USEPA nutrient criterion (table 11).

Sections of the Appalachian Trail pass through urban areas and are adjacent to agricultural land (table 5). Intermittent influences from the regions of the Appalachian Trail where the percentages of developed or agricultural land are moderate may be increasing the number of catchments that have concentrations of total nitrogen and total phosphorus greater than the USEPA's nutrient ecoregion criteria. Dubrovsky and others (2010) compared simulated modeled estimations of background concentrations from Smith and others (2003) to the 14 USEPA nutrient ecoregion criteria. This comparison demonstrated that, for the Nutrient-Poor Largely Glaciated Upper Midwest and Northeast and the Central and Eastern Forested Upland nutrient ecoregions, the criteria would be difficult to meet even with only a small percentage of development. Overall concentration of total nitrogen and total phosphorus within the study area are lower than estimated national background concentrations but generally similar or higher than USEPA ecoregion nutrient criteria.

Effects of Environmental Attributes on Water Quality

Variations in water quality along the Appalachian Trail were evaluated with respect to selected environmental attributes to determine how natural or anthropogenic factors may be influencing the water quality of the headwater streams along and near the Appalachian Trail. Physical attributes such as elevation, slope, precipitation, and temperature were explored for correlation with water-quality constituents. Generalized major geologic units were used to group water-quality data along the Appalachian Trail to determine geologic effects

Table 11. Comparison, by nutrient ecoregion, of median catchment concentrations of total nitrogen and total phosphorus and the percentages of median catchment concentrations greater than U.S. Environmental Protection Agency's nutrient criteria from selected sampling sites along the Appalachian National Scenic Trail.

[mg/L, milligrams per liter]

Nutrient	Nutrient ecoregion	Nutrient criterion (mg/L)	Number of catchments	Median catchment concentrations (mg/L)	Percentages of median catchment concentrations greater than nutrient criterion
Total nitrogen	Nutrient-poor largely glaciated Upper Midwest and Northeast	0.38	71	0.42	63.4
	Central and Eastern forested upland	0.31	80	0.28	45.0
Total phosphorus	Nutrient-poor largely glaciated Upper Midwest and Northeast	0.01	82	0.01	51.4
	Central and Eastern forested upland	0.01	95	0.02	70.5

on water quality. Anthropogenic factors such as developed and agricultural land use in the drainage area of headwater streams and atmospheric deposition of sulfate and nitrate in the catchments of headwater streams were evaluated with respect to possible influence on water quality.

Elevation

Catchment pH, ANC, and concentrations of major ions were significantly correlated with elevation along the length of the entire Appalachian Trail (table 12) except in the Lower New England ecosection where pH and most concentrations of major ions were not correlated with elevation. As elevation increases, pH, ANC, and concentrations of major ions decrease. Likewise, most concentrations of nutrients also were negatively correlated with elevation, although rho values were substantially lower than those computed for pH, ANC, and concentrations of major ions (table 12).

Elevation is not directly affecting streamwater chemistry but is more likely a proxy for the synergistic influences of environmental attributes that tend to be correlated with elevational gradients, such as geology, slope, drainage area, precipitation, temperature, and land cover (table 13). Generally, in the Eastern U.S. as elevation increases, drainage areas tend to become smaller and steeper, and geology at elevation tends to be increasingly resistant to weathering. The low residence times of small steep drainages coupled with relatively inert geology yield comparatively more dilute waters compared to surface waters at lower elevations. These types of high elevation landforms typically have little to no agricultural or developed land uses, and receive higher amounts of precipitation in cooler climates which also help to explain the inverse relation between water quality and elevation. The inverse correlation between elevation and streamwater chemistry also has been documented in local and regional investigations of areas along the Appalachian Trail (Cook and others, 1994; Shubzda and others, 1995; Hornbeck and others, 2001; Rice and others, 2005; Likens and Buso, 2006; Sullivan and others, 2007; Robinson and others, 2008). The variation of temperature with latitude along the Appalachian Trail is likely reducing the strength of the relation typically found between elevation and temperature at smaller scales (table 13). Mean annual temperature was negatively correlated with elevation at the ecosection scale.

Geology

Generalized major geologic units from Reed and Bush (2005) were used to group and evaluate differences in water quality. This geologic map was compiled to be used for national or regional assessments of geology and shows the age, distribution, and general character of the rocks (Reed and Bush, 2005). Ten major geologic units underlie the selected catchments and include rocks classified as sedimentary, gneissic, granitic, and volcanic (fig. 15). Most (over

78 percent) of the study area is underlain by sedimentary rocks. Sedimentary rocks classified by Reed and Bush include rocks that have been metamorphosed to varying extents but still retain evidence of their depositional age and origin (Reed and Bush, 2005). The regions of metamorphism are shown by a pattern in figure 15. Approximately 13 percent of the study area is underlain by gneissic rocks, approximately 5 percent is underlain by granitic rocks, and 1.4 percent is underlain by volcanic rocks.

Table 12. Rho values from Spearman correlations of the elevations of catchments and the percentages of developed and agricultural land cover with concentrations of selected water-quality constituents in catchments that contained selected sampling sites along the Appalachian National Scenic Trail.

[All rho values are significant (*p* less than 0.05) from Spearman correlations]

Water-quality parameter or constituent	Elevation	Percentages of land cover	
		Developed	Agricultural
pH	-0.422	0.416	0.517
Acid neutralizing capacity	-0.613	0.557	0.557
Calcium	-0.564	0.522	0.455
Magnesium	-0.675	0.576	0.603
Sodium	-0.563	0.471	0.408
Sulfate	-0.687	0.579	0.451
Chloride	-0.691	0.555	0.565
Nitrate	-0.110	0.307	0.266
Total nitrogen	-0.312	0.423	0.241
Total phosphorus	-0.286	0.173	0.305

Table 13. Rho values from Spearman correlations of elevation with selected environmental attributes of catchments that contain selected sampling sites along the Appalachian National Scenic Trail.

[**Boldface** indicates significant rho values (*p* less than 0.05) from Spearman correlations]

Environmental attributes	Elevation
Slope	0.592
Mean annual precipitation	0.542
Mean annual temperature	0.046
Percentage of developed land cover	-0.599
Percentage of agricultural land cover	-0.568

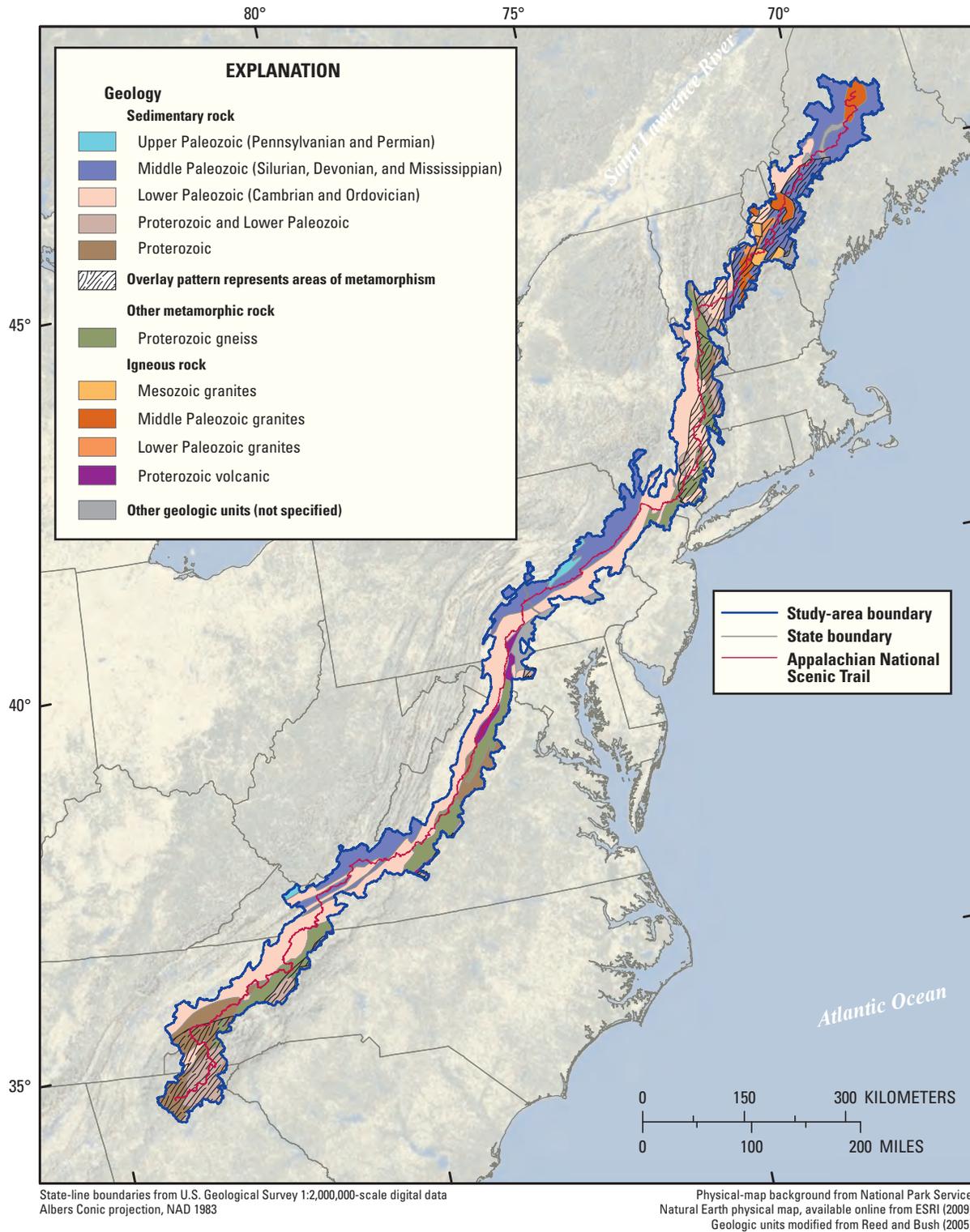


Figure 15. Major geologic units within the study area. Major geologic units that did not underlie catchments from the selected first- and second-order streams within the study are grey.

For evaluation of geology with respect to water quality, the major geologic units were combined into six rock types (sedimentary rocks, metasedimentary rocks, metasedimentary rocks that contain carbonate minerals, gneissic rocks, granitic rocks, and volcanic rocks). The six rock types used in analysis were created by aggregating similar rocks from different geologic ages. For example, the sedimentary rock group included the Late Proterozoic sedimentary rocks, Late Proterozoic and Lower Paleozoic sedimentary rocks, Lower Paleozoic (Cambrian and Ordovician) sedimentary rocks, Middle Paleozoic (Silurian, Devonian, and Mississippian) sedimentary rocks, and the Upper Paleozoic (Pennsylvanian and Permian) sedimentary rocks. The sedimentary group was then subdivided to reflect whether a catchment was in a region of metamorphism and whether the rocks were classified as containing carbonate minerals (King and Beikman, 1974) because these geologic attributes can have a strong influence on the water quality. Granitic major geologic units that were combined into the granitic group included the Lower Paleozoic, Middle Paleozoic, and the Mesozoic granitic rocks. Only one major geologic unit each was adequate for gneissic rocks (Middle Proterozoic gneiss) and volcanic rocks (Late Proterozoic volcanic rocks).

Catchment values of pH, specific conductance, and ANC were compared among the six geologic groups (fig. 16). Generally, sedimentary rocks and metasedimentary rocks had similar median catchment values for pH, specific conductance, and ANC (fig. 16). For the sedimentary rocks, the median pH was equal to 6.6, specific conductance was equal to 23.7, and ANC was equal to 88.7 $\mu\text{eq/L}$. Similarly, catchments in the metasedimentary rocks had a median pH of 6.5, median specific conductance of 20.3, and median ANC of 86.3 $\mu\text{eq/L}$. However, catchment values for pH and ANC were statistically higher in the metasedimentary rocks that were classified as containing carbonate minerals compared to the other two groups of sedimentary rocks (median pH of 7.3; median ANC value of 590 $\mu\text{eq/L}$). The median catchment values of pH in the gneissic and volcanic rocks were statistically similar to that of the metasedimentary rocks that contain carbonate minerals (6.8 and 7.1, respectively) (fig. 16). Additionally, the catchment values of ANC in the volcanic rocks were among the highest with a median value of 220 $\mu\text{eq/L}$ (fig. 16). Catchment pH and ANC values from granitic rocks were the lowest compared to the other rock types (median pH value of 6.0; median ANC value of 57 $\mu\text{eq/L}$) (fig. 16).

The presence of carbonate minerals appears to be the more influential geologic attribute with respect to pH, specific conductance, and ANC in the headwaters along the Appalachian Trail. Catchments were classified as containing carbonate minerals through the use of a national geologic map by King and Beikman (1974), who compiled national geologic data at a finer scale than Reed and Bush (2005) (1:2,500,000 and 1:7,500,000 scales, respectively) and characterized discrete areas of the sedimentary rocks in the region of the Green–Taconic–Berkshire Mountains, Lower New England, and Hudson Valley ecosections as

containing carbonate minerals. This may provide a geologic explanation for generally higher pH, specific conductance, ANC, concentrations of cations, and concentration of anions that are observed in these three ecosections relative to other ecosections (figs. 14A–J).

In general, the coarse scale of the geologic data could not be related to the fine-scale spatial variations in water quality such as variations within ecosections. Sullivan and others (2007), however, produced a lithologic map (at a scale of approximately 1:500,000) based on aggregated geologic map units for the southern Appalachian Mountains and were able to identify lithologies that were more likely to be associated with low-ANC surface water. Sullivan and others (2007) demonstrated that streams in the southern Appalachian Mountains in or downgradient from drainage areas that are predominantly underlain by siliceous lithologies have a greater probability of low ANC. These findings are consistent with other studies that were conducted in and around the Shenandoah National Park in Virginia (Bricker and Rice, 1989; Rice and others, 2005). In addition, these findings demonstrate that, with relatively high-resolution geologic information, significant relations can be determined between water quality and the underlying lithology at relatively fine scales.

Land Cover

The percentages of developed or agricultural land cover in the drainage areas of catchments selected for this inventory were generally low, although sections of the Appalachian Trail do pass through or near major urban areas or agricultural land (table 5). Along the entire Appalachian Trail, the percentages of developed and agricultural land were significantly and positively correlated with pH, ANC, concentrations of major ions, and concentrations of nitrate, total nitrogen, and total phosphorus (table 12). Within ecosections, these correlations were less significant. Insufficient spatial representation of a gradient of developed or agricultural land uses within ecosections may explain why these correlations were significant at the whole study-area scale of Appalachian Trail and not within ecosections. Many studies have demonstrated that land use influences stream quality. Siemion and Murdoch (2010) and Hickman and Fischer (2007) both reported that ANC and concentrations of most major ions and nutrients were positively correlated with agricultural land cover in the Delaware Water Gap National Recreation Area. The percentages of agricultural land cover in these two studies were generally higher than for the selected sampling sites in this project. (figs. 14B–J, table 8).

Atmospheric Deposition

Previous studies of areas near the Appalachian Trail have demonstrated the negative effects of atmospheric deposition on water quality. Atmospheric-deposition data were compared to water-quality data to determine relations between these two datasets. The NADP publishes annual maps of

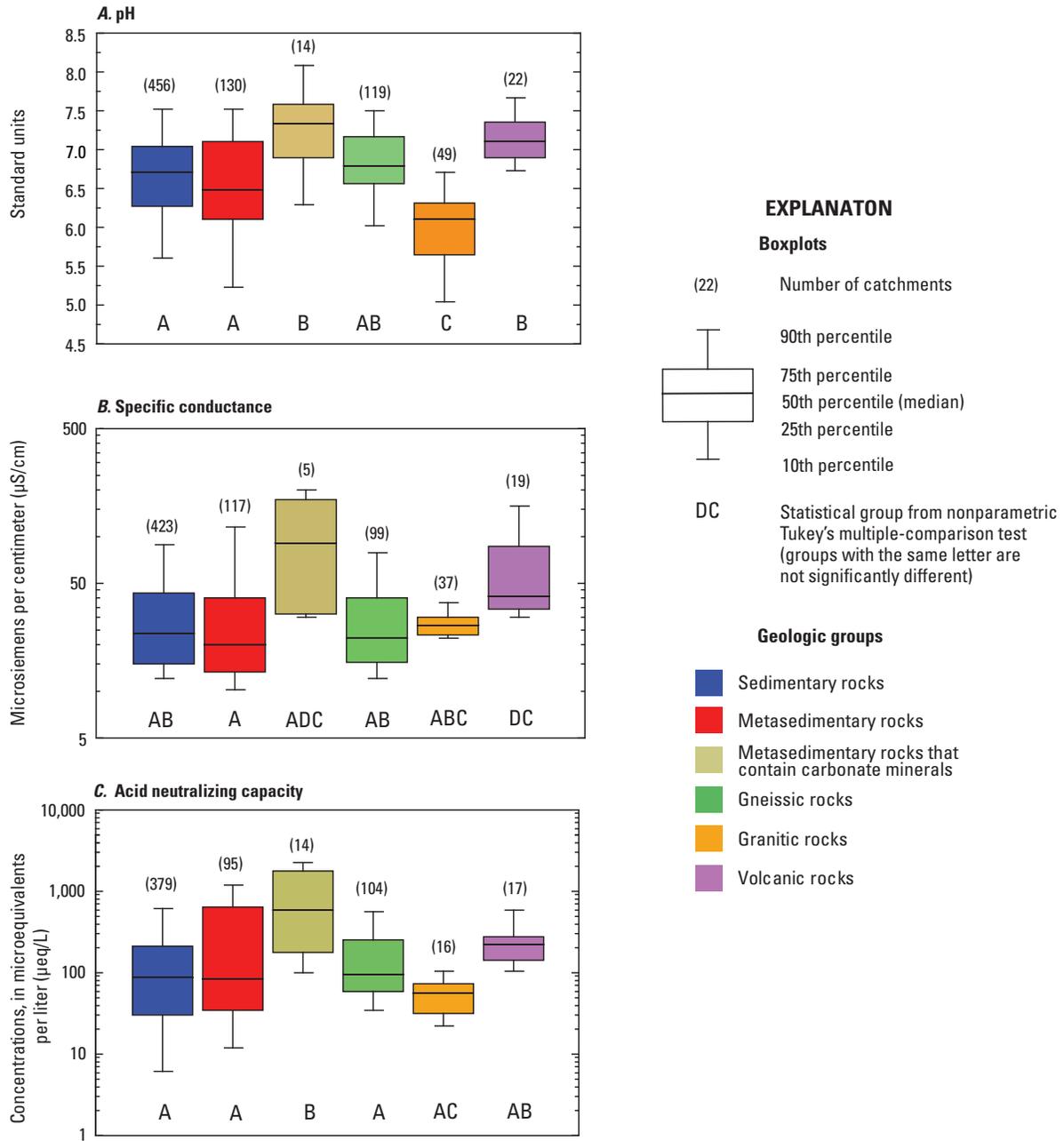
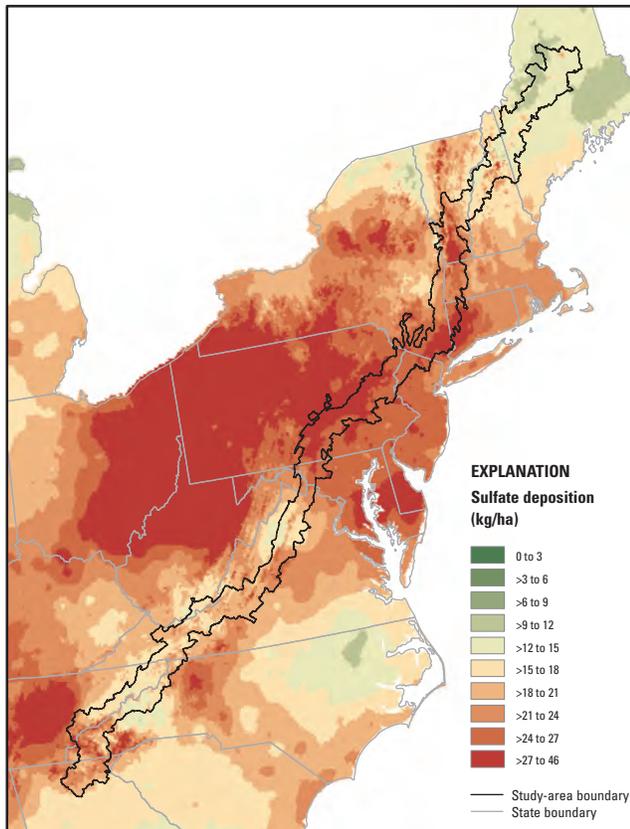


Figure 16. Comparison of concentrations, by major geologic groups, of *A*, pH, *B*, specific conductance, and *C*, acid neutralizing capacity from catchments that contained selected first- and second-order streams along the Appalachian National Scenic Trail.

precipitation-weighted mean concentrations of sulfate and nitrate in precipitation. The values are interpolated from measurements at specific sites (National Atmospheric Deposition Program, 1994a, b). Since most of the sulfate and nitrate data used in this project were collected in the mid-1990s, atmospheric sulfate and nitrate data from the NADP for 1994 were selected for comparison purposes. Atmospheric-deposition rates of sulfate and nitrate were computed by combining the NADP atmospheric-concentration data with high-resolution spatial estimates of precipitation rates for the same year (Laysh and Wetherbee, in press; PRISM Climatic Group, 2006b). The resulting maps of sulfate and nitrate atmospheric deposition (in kilograms per hectare) are shown in figure 17. Mapped values were assigned to catchments in the study area, which enabled the comparison of atmospheric-deposition rates with other catchment attributes and with water-quality data. Atmospheric deposition was estimated by ecosection, including all first- and second-order catchments in the study area and not just the catchments with selected sampling sites.

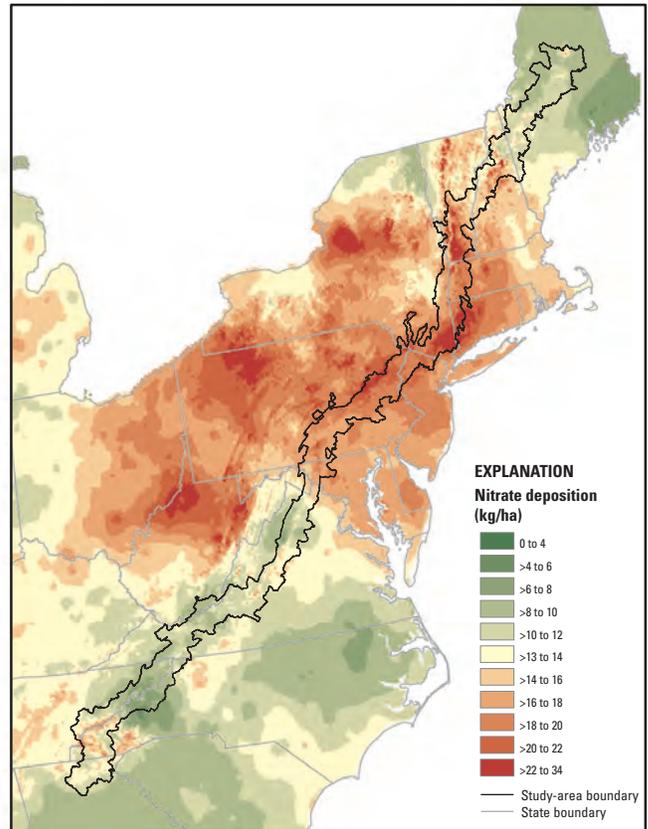
Along the Appalachian Trail, atmospheric deposition is estimated to be high (greater than 20 kg/ha) at both the highest and lowest elevations. The spatially sustained estimates of high deposition (figs. 17 and 18) were broadest in the central portion of the Appalachian Trail, whereas estimates were highest for the highest elevations in the northern and southern sections of the Appalachian Trail. The Green–Taconic–Berkshire Mountains, Lower New England, Hudson Valley, Northern Glaciated Allegheny Plateau, and Northern Ridge and Valley ecosections have median deposition estimates greater than 24 kg/ha for sulfate and greater than 19 kg/ha for nitrate (figs. 18A–B). In the southern region of the Appalachian Trail (Allegheny Mountains and Blue Ridge Mountains ecosections), Great Smoky Mountains National Park has historically received high estimates of deposition. The Integrated Forest Study, which monitored forested sites across the U.S., Canada, and Norway to investigate the effects of acidic deposition on nutrient cycling in forest ecosystems, reported that the Noland Divide Watershed in the Great Smoky Mountains

A. Sulfate



State-line boundaries from U.S. Census Cartographic Boundaries
U.S. Geological Survey 1:5,000,000-scale digital data
Albers Conic projection, NAD 1983
Colorpleth map generated from Laysh and Wetherbee (in press) using NADP and PRISM data

B. Nitrate



State-line boundaries from U.S. Census Cartographic Boundaries
U.S. Geological Survey digital 1:5,000,000-scale digital data
Albers Conic projection, NAD 1983
Colorpleth map generated from Laysh and Wetherbee (in press) using NADP and PRISM data

Figure 17. Maps of 1994 annual wet-deposition estimates for *A*, sulfate and *B*, nitrate for the eastern United States, including the study area. Deposition values were computed using methods from Laysh and Wetherbee (in press) with atmospheric concentration data from the National Atmospheric Deposition Program National Trends Network (National Atmospheric Deposition Program, 1994 a, b) and precipitation from the PRISM climate group (PRISM Climate Group, 2006b).

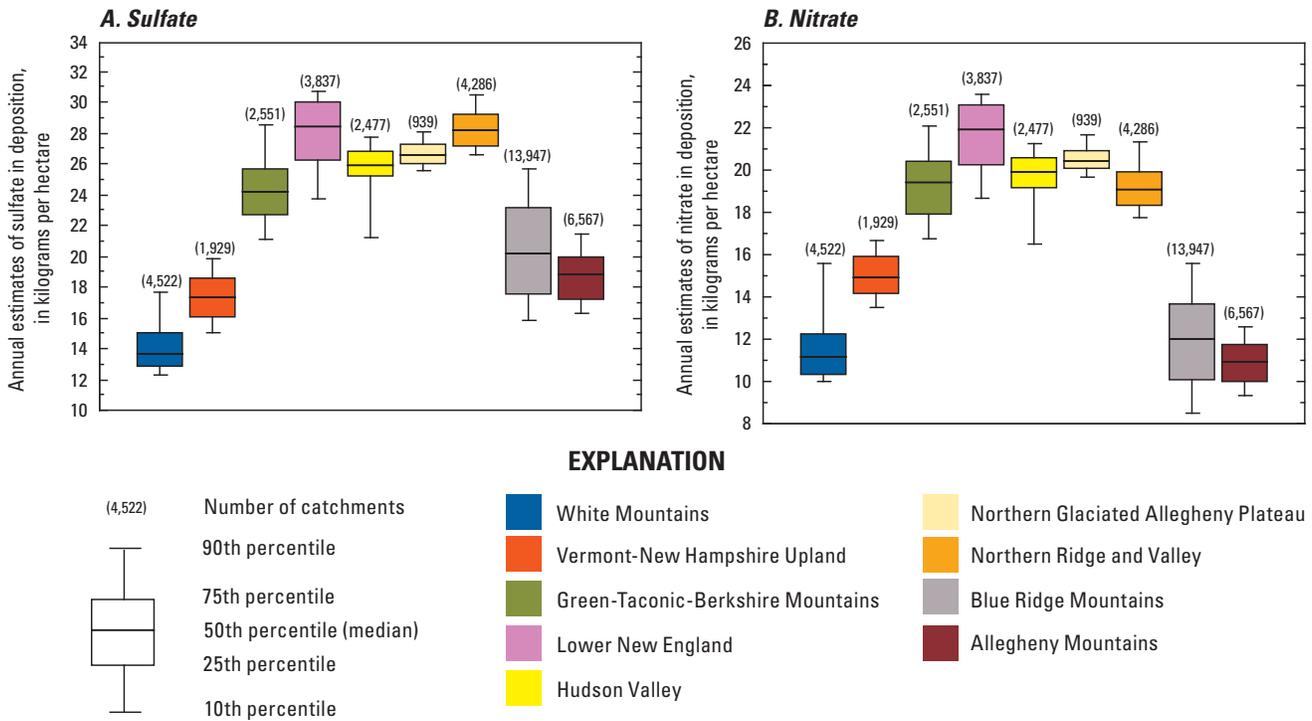


Figure 18. Wet-deposition estimates from 1994 of *A*, sulfate and *B*, nitrate by U.S. Forest Service ecological sections (ecosections) for all first and second order catchments in the study area. Deposition values were computed using methods from Laytsh and Wetherbee (in press) with atmospheric concentration data from the National Atmospheric Deposition Program National Trends Network (National Atmospheric Deposition Program, 1994a, b) and precipitation data are from the PRISM climate group (PRISM Climate Group, 2006b). Ecosections are shown left to right in approximate north-to-south order.

National Park received the highest sulfate and nitrate deposition compared to the other Integrated Forest Study sampling sites (Shubzda and others, 1995). Generally higher elevations are more likely to receive high depositions, however for the five ecosections in the central region of the Appalachian Trail, climatic patterns and possibly sources of sulfate and nitrate, to some extent, outweigh the elevation-induced effects of precipitation on estimates of atmospheric deposition.

Catchment concentrations of sulfate in streamwater were statistically greater in the ecosections that received the highest atmospheric deposition estimates of sulfate (figs. 14H and 18A). However, catchment concentrations of nitrate and total nitrogen in streamwater were not statistically greater in the ecosections that receive the highest atmospheric deposition of nitrate (figs. 14J and L).

Previous studies have demonstrated a link between high concentrations of sulfate in precipitation and sulfate typically being the dominant anion in low-ionic strength waters (Charles and Christie, 1991; Likens and Bormann, 1995; Driscoll and others, 1998; Elliott and others, 2008). Sulfate was most frequently determined to be the predominant anion in waters in the Appalachian Trail study area except in the Lower New England and Hudson Valley ecosections, where

bicarbonate was the most frequently calculated predominant anion. Although the central region of the Appalachian Trail received higher amounts of sulfate deposition, the areas along the Appalachian Trail with waters of lower ionic strength (White Mountains, Allegheny Mountains, Blue Ridge Mountains ecosections) might have been more strongly affected by sulfate deposition.

Reductions in concentrations of sulfate and nitrate in atmospheric deposition related to the CAAA have been observed throughout the Midwest and Eastern United States, specifically in the central Appalachians (U.S. Environmental Protection Agency, 2010) that includes the Green-Taconic-Berkshire Mountains, Lower New England, Hudson Valley, Northern Glaciated Allegheny Plateau, and Northern Ridge and Valley ecosections. Reductions in sulfate have been more significant than reductions in nitrogen—approximately 40 and 20 percent, respectively (U.S. Environmental Protection Agency, 2010). The estimates of atmospheric deposition by ecosection shown in figures 17 and 18 were a reasonable fit for the data compiled for this inventory but may not represent a current estimate (2011) of concentrations in atmospheric deposition.

Trends in concentrations of sulfate and nitrate in streams along the Appalachian Trail were not assessed. Regional investigations that have been completed near the Appalachian Trail reported that concentrations of sulfate and nitrate in surface water are decreasing in response to changes in atmospheric deposition (Driscoll and others, 1998; Driscoll and others, 2003; Stoddard and others, 2003; Kahl and others, 2004; Webb and others, 2004; Monteith and others, 2007). The degree of response is likely to vary along the Appalachian Trail; however, surface waters with the lowest ANC and lowest pH were reported to have shown the largest and most rapid response (Stoddard and others, 2003; Kahl and others, 2004). In the eastern U.S., three processes have been identified that complicate the assessment of surface-water response to decreases in atmospheric deposition: increasing concentrations of chloride from road-salting practices that alter the acid-base chemistry of a watershed, increasing concentrations of dissolved organic carbon, and the retention of sulfate in watershed soils in nonglaciated areas (Rochelle and Church, 1987; Stoddard and others, 2003; Kahl and others, 2004; Webb and others, 2004; Monteith and others, 2007; Rosfjord and others, 2007). These processes will likely play varying roles in assessments of trends in concentrations of sulfate and nitrate in headwater streams along the Appalachian Trail.

The more chemically dilute surface waters in the northern and southern regions of the Appalachian Trail than in the central region of the Appalachian Trail may be attributed to differences in most of the environmental attributes explored (elevation, geology, land use, and deposition). The central region of the Appalachian Trail (including the Lower New England, Hudson Valley, Northern Glaciated Allegheny Plateau, Northern Ridge and Valley, and to a lesser extent the Vermont–New Hampshire Upland and Green–Taconic–Berkshire Mountains ecoregions) generally had the highest catchment values of pH, ANC, and concentrations of major ions. In addition, the catchments in these ecoregions also were the lowest in elevation and contained the highest percentages of developed and agricultural land cover. These three environmental attributes were demonstrated to be positively correlated with catchment pH, ANC, and concentrations of major ions. Portions of ecoregions in the central region of the Appalachian Trail were associated with carbonate geologic units. The presence of carbonate minerals in the geology underlying a catchment could have substantial influence on pH, ANC, and major-ion chemistry. The central region of the Appalachian Trail also was shown to receive the highest estimated concentrations of sulfate and nitrate in atmospheric deposition. It is difficult to discern on the basis of the data compiled for this project whether the type of land cover, the lithology of the underlying geology, inputs of atmospheric deposition, or a combination of these factors is responsible for the distinctly different water quality in the central region of the Appalachian Trail compared to the northern and southern regions of the Appalachian Trail.

Implications of Using Available Data and Considerations for Future Monitoring

The compilation of available water-quality data for this study was useful in identifying regions along the Appalachian Trail where water-quality data are lacking spatially and temporally. As was previously described, there is a notable lack of sampling sites that met this project's criteria in the state of Maine. The spatial density of available sampling sites along the border between Tennessee and North Carolina and north of Great Smoky Mountains National Park also was low, though not as low as in Maine. The spatial gaps were more profound when the data density for specific water-quality constituents was evaluated.

In the 831 catchments where water-quality data was collected, field properties such as pH, specific conductance, temperature, and dissolved oxygen were the most commonly measured parameters. The next most frequently measured type of water-quality data was concentrations of major ions, including, calcium, chloride, magnesium, potassium, sodium, and sulfate. Of the four nutrients of interest, nitrate had the largest number of data values; however, very little nitrate data were available from areas along the Appalachian Trail north of Massachusetts. Ammonia was the most widely collected nutrient, followed by total phosphorus. Spatial coverage of total nitrogen data for the White Mountains of New Hampshire, the southern part of Pennsylvania, and the western mountains of Virginia were moderately good, but lacking for other regions of the Appalachian Trail.

It is important to note a temporal-limitation of the data compiled for this inventory to represent current (2011) water-quality conditions along the Appalachian Trail. Specifically, spatial comparisons of concentrations of sulfate and nitrate may be biased because concentrations of sulfate and nitrate in streamwater have been reported to be declining in response to reductions in deposition related to the CAAA. Much of the data in the northern section region were from the 1980s and would be more representative of water quality influenced by deposition loads of that decade. Whereas, the collection dates of water-quality samples from the southern section (median year = 1997) reflect the inclusion of TIME/LTM stream sites, VTSSS sites, and Great Smoky Mountains National Park sites, at which water-quality data are being actively collected (2011). The comparatively lower concentrations of sulfate and nitrate in streamwater in the Blue Ridge Mountains and Allegheny Mountains ecoregions may reflect the inclusion of more recent (post-2000) data that has responded to decreases in atmospheric deposition.

Water-quality data were not evaluated within the context of hydrologic condition because of the lack of streamflow measurements available for many sites. Future monitoring programs for water quality along the Appalachian Trail should consider locating sampling sites within gaged watersheds, so

that water-quality data can be related to streamflow. Assessments of trends in the water quality of streams over time are frequently done through a comparison of changes in loads or flow-adjusted concentrations. The calculation of load for a given parameter is dependent on both the concentration and streamflow at the time of sample collection. The calculation of relations between streamflow and water quality for streams along the Appalachian Trail would provide a useful tool to evaluate water-quality trends in this environment. Generally, streamgages are placed in larger watersheds; however, the Hubbard Brook and Coweeta LTER areas represent good examples of small watersheds that have generated useful time-series chemical and hydrological data.

The data compiled for this inventory were generally either from the largest national databases of water-quality data (NWIS and STORET), federal agencies (for example, USEPA Wadeable Streams Assessment and National Stream Survey), or from well established programs (i.e. National Science Foundation LTER and the VTSSS). The inclusion of new water quality data in selected catchments and in catchments where data were not compiled for this inventory would improve the spatial and temporal resolution of available data from which to assess water resources. Continued integration of more recent data from the data sources used would be an efficient future effort in making the Appalachian Trail inventory of water-quality data more relevant for continued evaluation of basic water quality and in trend analysis. In addition, an effort to obtain and compile water-quality data from local citizen-based water-quality monitoring programs may be beneficial and facilitate a connection between local and regional scale water-quality issues. These smaller programs are typically initiated and focused on the intention of using scientific information to help locally preserve natural resources; this objective is common with aspects of the NPS mission. Collaborative arrangements to centralize water-quality data among agencies, programs, and researchers interested in the water resources of the Appalachian Trail region may serve to maintain the relevancy of the data compiled for this inventory.

Summary

An inventory of water-quality data was conducted to provide an assessment of water quality in headwater (first- and second-order) streams along the Appalachian National Scenic Trail (Appalachian Trail). The Appalachian Trail is a cooperatively managed National Park along the Appalachian Mountains from Maine to Georgia. Available data on basic chemical quality were compiled from 14 different agencies or projects including the U.S. Geological Survey (USGS); the U.S. Environmental Protection Agency (USEPA); the National Park Service; the United States Forest Service; (USFS); the National Science Foundation, including the Long-Term Ecological Research Program; the Water Resources Research

Center at the University of Massachusetts, Amherst; and the Department of Environmental Sciences at the University of Virginia. To maximize the amount of water-quality data available for use in this inventory and to provide a more robust assessment of the water quality of headwater streams along the Appalachian Trail, a method of sampling-site selection was developed based on proximity, hydrologic boundaries, and environmental settings. Hydrologic boundaries were used to define the watersheds draining the Appalachian Trail, and NHDPlus digital hydrologic data were used to define the catchment as the fundamental areal unit for location information for sampling sites.

The approach used for site selection in this study quantified selected physical attributes of catchments adjacent to the Appalachian Trail to build a criteria matrix by which sampling sites not adjacent to the Appalachian Trail could be compared and evaluated for inclusion. Stream elevation and the percentages of developed and agricultural land cover in the drainage areas of adjacent catchments were used to build the criteria. There were 1,817 sampling sites selected for water-quality characterization. These selected sites were either adjacent to the Appalachian Trail or in landscapes that are locally high in elevation and generally had little to no developed or agricultural land cover in the drainage area.

Water-quality data from sampling sites were aggregated by catchments to reduce the spatial bias of intensively sampled sites and regions and at least one median water-quality value was computed for each of 831 catchments. The number of catchments for which a median value was calculated varies by water-quality parameter. Field properties were the most commonly measured, followed by concentrations of major ions and nutrients. Catchment concentrations of selected water-quality constituents were summarized overall and by USFS ecological sections (termed ecosections in this study). The pH of headwater streams from the Appalachian Trail study ranged from 4.0 to 8.9 with a median value of 6.7. Specific conductance values ranged from 4.0 to 761 microsiemens per centimeter ($\mu\text{S}/\text{cm}$), with a median value of 23.8 $\mu\text{S}/\text{cm}$. Acid neutralizing capacity (ANC) ranged from -11.3 to 4,400 microequivalents per liter ($\mu\text{eq}/\text{L}$) with a median value of 98.7 $\mu\text{eq}/\text{L}$. Catchment concentrations of cations (calcium, magnesium, sodium, and potassium) were low with the median catchment concentration for each of the cations being less than 1.5 milligrams per liter (mg/L). Calcium had the highest median catchment concentration of all the cations (1.46 mg/L). Catchment concentrations of anions (sulfate, chloride, and nitrate) ranged more widely than those of cations. Sulfate had the highest median catchment concentration (3.41 mg/L), followed by chloride (0.78 mg/L). Analysis to characterize water types demonstrated that, for most regions of the Appalachian Trail, no specific cation was predominant. The Lower New England and Hudson Valley ecosections were the exceptions, where the predominant cation in most catchments was calcium. Sulfate was the most frequently detected anion except in the Lower New England and Hudson Valley ecosections where the predominant anion

was bicarbonate. Similar to major ions, nutrient concentrations also were low (median catchment concentrations of total nitrogen and nitrate species were less than 0.4 mg/L, and the median catchment concentration of total phosphorus were less than 0.02 mg/L).

Distinct spatial variations in pH, ANC, and major-ion chemistry were apparent along the length of the Appalachian Trail. The northern and southern regions of the Appalachian Trail (including the White Mountains, Blue Ridge Mountains, and Allegheny Mountains ecoregions) had the lowest catchment pH values. The White Mountains ecoregion was statistically unique and had the lowest median catchment pH value of all the ecoregions (median catchment pH = 6.1). Catchment ANC and concentrations of most major ions also were statistically lower in the White Mountains, Blue Ridge Mountains, and Allegheny Mountains ecoregions compared to the other ecoregions.

The ANC of waters from the White Mountains, Blue Ridge Mountains, and Allegheny Mountains ecoregions were exceptionally low and included negative values. The White Mountains, Allegheny Mountains, and Blue Ridge Mountains ecoregions contained the highest percentage of catchments that were classified as either acidic or sensitive. Low ANC waters are sensitive to seasonal or event-driven episodic acidification. When episodic acidification occurs in a stream, streamwater quality may become harmful to aquatic life.

Catchment concentrations of ammonia, nitrate, total nitrogen, and total phosphorus from selected headwater streams along the Appalachian Trail were generally lower than national estimated background concentrations determined by the USGS for surface waters. The Green–Taconic–Berkshire Mountains and the Northern Ridge and Valley ecoregions were the exceptions. These ecoregions had median catchment concentrations of ammonia more than two times greater than the estimated background concentrations. The Northern Ridge and Valley ecoregion had median catchment concentrations of nitrate greater than the estimated national background concentrations (0.416 and 0.24 mg/L, respectively).

Median catchment concentrations of total nitrogen and total phosphorus were compared to USEPA's ecoregion nutrient criteria. Median concentrations of total nitrogen in approximately 63 percent of catchments in the Nutrient Poor Largely Glaciated Upper Midwest and Northeast were higher than the USEPA regional criterion. Approximately 71 percent of median concentrations of total phosphorus in the Central and Eastern Forested Upland nutrient ecoregion were higher than the USEPA regional criterion. Findings from Dubrovsky and others (2010) suggest that the USEPA criteria in some nutrient ecoregions may be difficult to meet with modest amounts of development or agriculture in the drainage area. Sections of the central region of the Appalachian Trail are adjacent to areas of development and agricultural land. These nonforested land cover types may be contributing to the percentages of catchments that have total nitrogen and total phosphorus concentrations greater than USEPA nutrient criteria.

Spatial variations in water-quality properties of surface waters along the Appalachian Trail were related to elevation, geology, land cover, and atmospheric deposition. Median pH, specific conductance, ANC, and concentrations of major ions (calcium, magnesium, sodium, sulfate, chloride, nitrate, total nitrogen, and total phosphorus) were all negatively correlated with elevation along the Appalachian Trail. For the Lower New England, Hudson Valley, Northern Glaciated Allegheny Plateau, and Northern Ridge and Valley ecoregions, nitrate also was negatively correlated with elevation. Elevation, as such, most likely does not directly affect stream-water chemistry but is more likely a surrogate that represents the combined effects of environmental attributes that are themselves correlated with elevation, including geology, slope, drainage area, precipitation, temperature, and land cover.

Approximately, 78 percent of the study area is underlain by sedimentary or metasedimentary rocks. Most of the remaining study area is underlain by gneissic, granitic, and volcanic rocks (13, 5, and 1.5 percent, respectively). Metasedimentary rocks were further subdivided to distinguish between metasedimentary rock and metasedimentary rocks that contain carbonate minerals. The presence of carbonate minerals appears to be the most influential geologic attribute with respect to pH, specific conductance, and ANC values. Catchments that were classified as being underlain by metasedimentary rocks that contained carbonate minerals had the highest values for pH, specific conductance, and ANC. The Green–Taconic–Berkshire Mountains, Lower New England, and Hudson Valley ecoregions, which contained the highest catchment pH, ANC, and concentrations of most major ions, are underlain, at least in some areas, by metasedimentary rocks that contain carbonate minerals. Catchment values of pH in the gneissic and volcanic rocks were statistically similar to the metasedimentary rocks with carbonate minerals, however, very little of the study area is underlain by these rock types. The granitic rocks occur primarily north of Vermont in the White Mountains ecoregion. Catchments underlain by these granitic rocks contained among the lowest pH, specific conductance and ANC values.

The percentages of developed urban or agricultural land cover in the drainage areas of catchments was significantly and positively correlated with catchment pH, ANC, and concentration of most major ions (calcium, magnesium, sodium, sulfate, chloride, and nitrate). Nutrients were significantly, although weakly, correlated with the two land-cover variables. The regions along the Appalachian Trail that contained high percentages of developed and agricultural land cover in the drainage area were also underlain by major geologic units that may contain carbonate rocks.

Atmospheric deposition of sulfate and nitrate as demonstrated by previous investigations may have led to widespread deleterious effects on the water quality of headwater streams near the Appalachian Trail. Annual atmospheric deposition maps of sulfate and nitrate produced by the National Atmospheric Deposition Program and the USGS demonstrate that portions of the Appalachian Trail receive some of the

highest concentrations of sulfate and nitrate in the eastern United States. The section of the Appalachian Trail that received the overall highest estimates of atmospheric deposition generally contained in the lowest elevations (Green–Taconic–Berkshire Mountains, Lower New England, Hudson Valley, Northern Glaciated Allegheny Plateau, and Northern Ridge and Valley ecosections). Generally, there were higher catchment concentrations of sulfate in the ecosections that received the highest inputs of atmospheric deposition (Green–Taconic–Berkshire Mountains, Lower New England, Hudson Valley, Northern Glaciated Allegheny Plateau, and Northern Ridge and Valley). However, these same ecosections also contained the highest concentrations of most major ions. Sulfate deposition in the ecosections that contain the waters of lowest ionic strength (White Mountains, Blue Ridge Mountains, and Allegheny Mountains ecosections) may have a more profound effect on the chemical character of the surface waters as shown by the predominance of the sulfate anion in surface waters in these ecosections.

In general, the surface waters of the Appalachian Trail environment are dilute in constituents. Although this finding was not unexpected, the low ionic strength of Appalachian Trail surface waters may affect management and preservation strategies. These data also demonstrate that the waters of the central region of the Appalachian Trail, although still dilute, had statistically higher concentrations of most major ions and ANC than the northern and southern sections. Furthermore, the central section of the Appalachian Trail contained some of the highest percentages of developed and agricultural land uses and received the highest estimates of sulfate and nitrate from atmospheric deposition. It is difficult to tell from these data whether the water quality in the central section of the Appalachian Trail has been influenced more by the higher percentages of developed or agricultural land cover, higher inputs of atmospheric deposition, or the lithology of the underlying geology.

Managing the water resources of the Appalachian Trail is a complex and challenging responsibility because the headwater streams are generally dilute and therefore sensitive to atmospheric deposition. As has been demonstrated by previous investigations of discrete sections of the Appalachian Trail and regions near the Appalachian Trail, the water resources of the Appalachian Trail have been altered by atmospheric deposition of sulfate and, to a lesser extent, nitrate. Furthermore, because of the intrinsic connection between headwaters and downstream areas, degradation of the headwaters along the Appalachian Trail most likely has affected the water quality of downstream resources. A specific set of sampling sites that are collocated with continuous flow record sites could be used to assess long-term trends in stream-water chemistry along the Appalachian Trail. The ability to assess and compare changes in streamflow-adjusted water-quality data would provide a clearer characterization of past and current water-quality conditions that would be helpful for resource managers in the management and protection of local catchments and water resources of the Appalachian Trail. The periodic inclusion of

more recent data from data sources used in the Appalachian Trail water-quality inventory would be relatively straightforward and beneficial. Furthermore, an expanded effort to obtain data not compiled (such as water quality from localized citizen based monitoring programs) also would add value and maintain the relevancy of the effort of this inventory. A dynamic and timely database relevant to the Appalachian Trail study area water resources available to the NPS and to the consortium of researchers interested in understanding the impacts of climate change on water quality may facilitate more efficient collaboration to develop strategic ecological sound management practices based on scientific knowledge.

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Appendix 1. Ancillary and Water-Quality Variable Definitions and Catchment Data (on CD-ROM)

Prepared by the Pembroke Publishing Service Center.

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