Effects of Acidic Deposition on Aquatic Resources in the Southern Appalachians with a Special Focus on Class I Wilderness Areas

Prepared for the Southern Appalachian Mountains Initiative (SAMI)

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EXECUTIVE SUMMARY

The Southern Appalachian Mountains Initiative (SAMI) was established to address concerns about the adverse effects of air pollution on environmental resources in the Southern Appalachians. Acidic deposition and its effects on surface waters is a major air pollution issue in this area. This report has two main objectives:

1. Summarize the existing state of knowledge about the effects of acidic deposition on surface water resources in the Southern Appalachians.
2. Evaluate and make recommendations on the use of available methodologies for predicting future changes in the aquatic effects of acidic deposition in the Southern Appalachians.

The major findings of this report are as follows.

Factors Controlling the Response of Surface Waters to Acidic Deposition

The two major processes influencing the response of surface waters in the Southern Appalachians to acidic deposition are sulfate/nitrate retention and base cation mobilization. The amount of watershed sulfate/nitrate retention controls how much of the incoming anions from deposition reach the lake/stream. The degree of base cation mobilization controls the cation composition entering surface waters. If the entering anions are all balanced by base cations, there is little effect on the acid-base status of the water and consequently little effect on aquatic biota. However, if the anions are balanced by significant concentrations of acid cations (H^+, Al), surface water acidity increases and there can be significant adverse effects on many aquatic species. Base cation mobilization is controlled primarily by the composition of the watershed bedrock and soils and is reflected in surface water acid neutralizing capacity (ANC).

Current Status of Aquatic Resources

Lakes in the Southern Appalachians are mostly reservoirs and are not very numerous (estimated total of 71 lakes > 4 ha in the southern Blue Ridge). The Eastern Lake Survey found no acidic lakes; 5% of the lakes had ANC ≤ 50 µeq/L and would be considered sensitive to acidic deposition.

Acidic and very low ANC streams are located in small (< 20 km^2), upland, forested catchments in areas of base-poor bedrock. The National Stream Survey estimated (in 1986) that of the 62,200 km of streams on 1:250,000-scale maps in the acid-sensitive part of the SAMI region, 815 km (1%) were acidic and 4,410 km (7%) had ANC ≤ 50 µeq/L. In these acidic Southern Appalachian streams, sulfate and nitrate from atmospheric deposition are the dominant source of acid anions, and the low pH (median = 4.7) and high levels of inorganic monomeric aluminum (median = 364 µg/L) are causing damage to aquatic biota. Watersheds in the SAMI region are currently retaining significant proportions of the incoming sulfur and nitrogen from acidic deposition.

The SAMI Class I wilderness areas are much more sensitive to acidic deposition than the region as a whole. Based on geology, physiography, and stream chemistry, the 10 Class I areas in the SAMI region can be aggregated into four groups for assessing the aquatic effects of acidic deposition:

1. West Virginia Plateau: Dolly Sods and Otter Creek wilderness areas
2. Northern Blue Ridge: James River Face wilderness area and Shenandoah National Park

3. Southern Blue Ridge: Great Smoky Mountains National Park, Joyce Kilmer/ Slickrock, Linville Gorge, Shining Rock, and Cohutta wilderness areas

4. Alabama Plateau: Sipsey wilderness area

In terms of adverse aquatic effects of acidic deposition, the four Class I groups can be ranked: West Virginia Plateau >> Northern Blue Ridge > Southern Blue Ridge > Alabama Plateau.

Streams in the West Virginia Plateau Class I areas had the highest percentage of acidic stream length (53% in Otter Creek, 82% in Dolly Sods), the highest sulfate and inorganic aluminum concentrations, and the lowest pH of any of the Class I areas. Organic acids play a significant role in a portion (13%) of the stream length in Otter Creek, but the rest of the stream length in both areas was dominated by acid anions from deposition. Streams in both Otter Creek and Dolly Sods are heavily impacted by acidic deposition. The Alabama Plateau Class I area (Sipsey) is of least concern for acidic deposition impacts because sulfate appears to be at steady state with deposition and this area has higher streamwater ANC concentrations.

The Plateau areas retain less sulfate than do the Blue Ridge areas, so any delayed effect of acidic deposition will be more pronounced in the Blue Ridge. Watershed soils in all the Blue Ridge wilderness areas retain most of the sulfate entering from deposition. In these areas, low ANC streams are common and some acidic streams are found in areas of resistant bedrock and/or higher elevations. Streams in the northern Blue Ridge areas have higher sulfate concentrations than streams in the southern Blue Ridge areas and appear to be more influenced by acidic deposition.

The southern Blue Ridge areas stand out from the other Class I areas in terms of having the highest streamwater nitrate concentrations (lowest nitrogen retention). It appears that nitrate is breaking through these watersheds and is entering streams in concentrations that approach and sometimes exceed sulfate concentrations.

Few detailed studies of episodic acidification have been conducted in forested watersheds in the Southern Appalachian Mountains. However, results from several field studies suggest that streams in the region with antecedent baseflow ANC values below about 25 µeq/L (2,280 km or 4% of the 1:250,000-scale stream network) may experience substantial depressions in pH (> 0.5 units) and increases in inorganic aluminum concentrations (> 50 µg/L) during major rainstorm and snowmelt periods.

Chemical properties of surface waters that are most important in influencing biological responses to acidic deposition are pH, aluminum, and calcium concentrations.

Many aquatic species cannot survive, reproduce, or compete in acidic waters. Thus, with increasing acidity, the "acid-sensitive" species are lost and species richness (the number of species living in a given lake or stream) declines. These changes in aquatic community structure occur at chronic pH levels <6.0–6.5. Ecosystem level processes, such as decomposition, nutrient cycling, and productivity, are fairly robust and are affected only at relatively high levels of acidity (e.g., chronic pH <5.0–5.5).

Biological damage is occurring in this region due to the high levels of inorganic aluminum and low pH in acidic streams. Direct quantification of the extent of biological effects, however, is not possible from existing data.

Current Trends in Acidification Impacts

There are few long-term monitoring sites in the SAMI region from which to draw conclusions about trends. In the control watersheds at Coweeta (North Carolina Blue Ridge) and White Oak Run in Shenandoah National Park, sulfate concentrations in streamwater have been increasing over the last 10-20 years. The sulfate increases at these sites are consistent with a gradual saturation of soils in the region with sulfate from deposition, and have been predicted by acidification models.

It is likely that many parts of the SAMI region have undergone increases in stream nitrate over the past several decades. At Fernow Experimental Forest in the West Virginia Appalachian Plateau, streamwater nitrate concentrations have increased from near zero to 50–60 µeq/L at baseflow from 1970 to the present. In the Great Smoky Mountains National Park, streamwater nitrate shows strong correlations with elevation and forest age, with the highest concentrations occurring at high elevations (where deposition is highest) and in areas of old-growth forest, where biological demand for nitrogen is lowest.

More recently, chemical trends in Shenandoah National Park have been altered as a result of forest defoliation by gypsy moth larvae. Defoliation has resulted in large increases in streamwater nitrate, decreases in sulfate, and little change in ANC or pH at baseflow.

Data do not exist to determine trends in the episodic acidification of surface waters related to atmospheric deposition in the Southern Appalachian Mountains. However, episodic mobilization of nitrate resulting from recent forest defoliation by the gypsy moth caterpillar has been shown to exacerbate episodic changes in ANC, pH, and aluminum in streams in the region.

There are virtually no data from which to draw quantitative conclusions about recent trends in biological condition due to acidification.

Methodologies for Predicting Impacts of Acidic Deposition on Aquatic Resources

The two dynamic watershed models that would be most useful for a SAMI assessment are ILWAS and MAGIC. Both these models attempt to describe the major processes controlling surface water response to acidic deposition and require information on deposition, watershed attributes, soils, hydrologic flow, and water chemistry. ILWAS models more processes with more compartments than MAGIC and thus requires more data input and has a greater computational complexity. Both models were extensively tested in the National Acid Precipitation Assessment Program (NAPAP) and there was no evidence that either model was more accurate than the other. Most of the NAPAP modeling effort focused on sulfur dynamics. A number of models that examine nitrogen dynamics have been developed in the past few years (MAGIC-WAND, MERLIN, PnET-CN).

Several models are available for predicting future episodic effects on surface waters in the region; these models were all developed by linking a long-term acidification model (e.g., MAGIC) with a hydrological mixing model (e.g., a two-component mixing model). Although major uncertainties are associated with applying any of these models, the models are expected to predict the occurrence of biologically significant episodic effects prior to the onset of chronic acidification effects.

Modeling of biotic effects of acidic deposition has focused mainly on fish. Fish effects models are either empirical, toxicity based, or a combination of the two. The model used in the NAPAP assessment was based on calculating an Acid Stress Index (ASI) derived from surface water pH, ANC, and inorganic aluminum. The ASI values were related to field observations of fish distributions to set critical ASI values for effects on sensitive, intermediate, and tolerant fish species.

Results from NAPAP Assessments

The Direct/Delayed Response Project and the NAPAP Integrated Assessment projected future acidification based on the MAGIC model at a subset of the National Stream Survey sites in the mid-Appalachians (Pennsylvania, Maryland, Virginia, West Virginia) and the southern Blue Ridge.

NAPAP future projections (50 year) in the mid-Appalachians show that at 1985 rates of deposition, the number of acidic streams is projected to triple, while the number with ANC ≤ 50 μeq/L would increase by a factor of 1.6. At sulfur deposition 20% and 30% greater than 1985 levels, the number of acidic streams is projected to increase by factors of 5.4 and 6.2, respectively. A 20% to 30% reduction in sulfur deposition would be necessary to prevent further acidification.

NAPAP future projections (50 year) in the southern Blue Ridge show that 1985 deposition rates are projected to increase the percentage of acidic streams from 0 to 10%; the number of streams with ANC ≤ 50 μeq/L is projected to increase by a factor of 1.6. At sulfur deposition 20% and 30% greater than 1985 levels, the number of acidic streams is projected to increase to 10% of the modeled population; the number of streams with ANC ≤ 50 μeq/L would increase by a factor of 2.2. A 30% to 50% reduction in sulfur deposition would be necessary to prevent further acidification.

Recommendations for SAMI Assessment

We recommend that MAGIC be used to model surface water acid-base chemistry and that the PnET-CN model be used to input time to nitrogen saturation into MAGIC. We also recommend that the regression approach of Eshleman be applied to MAGIC projections to predict episodic changes in stream chemistry. For modeling effects on fish, we recommend the acid stress index (ASI) approach.

We have outlined four possible levels of effort for the SAMI assessment:

1. Level 1: Qualitative summary of existing modeling information
2. Level 2: Re-run MAGIC model at existing regional network sites with new SAMI deposition scenarios.
3. Level 3: Collect new field data and run the MAGIC model for three acidic/low ANC sites in each of the Class I wilderness area groups (e.g., West Virginia Plateau). Also collect the information needed to run the PnET-CN nitrogen model and the episodic acidification model. Do for one, two, three, or all groups as resources allow.
4. Level 4: Do Level 3 analyses for the regional network of sites in the SAMI region.

Fish Effects: Fish effects can be added through the ASI approach in levels 2–4. However, field information on the relationship between fish distributions and ASI values needs to be collected and evaluated to set critical ASI levels.

Uncertainties in the absolute magnitudes and timing of aquatic effects projections are high, but we have confidence in the projected direction of change and in the relative amounts of change. Thus, we are fairly comfortable with running the models and making conclusions about the relative differences in aquatic effects among different deposition scenarios. However, we are uncomfortable with using the absolute results (e.g., acidic stream length or stream length that has lost fish due to acidic deposition) of these models because of their high uncertainty. We are very uncomfortable with taking these absolute results, linking them together with absolute results from other effects models (e.g., visibility, ozone), running them all through a socio-economic valuation model, and using some kind of overall "cost" estimate as the decision making tool for evaluating different emissions scenarios.

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GLOSSARY

ANC	Acid Neutralizing Capacity
ASI	Acid Stress Index
DDRP	Direct/Delayed Response Project
DOC	Dissolved Organic Carbon
ELS	Eastern Lake Survey
EPA	Environmental Protection Agency
ETD	Enhanced Trickle Down
FISH	Fish in Sensitive Habitats (Shenandoah National Park Project)
GSMNP	Great Smoky Mountains National Park
IA	Integrated Assessment (1990 NAPAP report)
ILWAS	Integrated Lake Watershed Acidification Study
LAF	Lake Acidification and Fisheries model
MAGIC	Model of Acidification of Groundwater in Catchments
MAGIC-WAND	MAGIC - With Aggregated Nitrogen Dynamics model
MERLIN	Model of Ecosystem Retention and Loss of Inorganic Nitrogen
MIDAPP	Mid-Appalachians (as region modeled in DDRP)
N	Nitrogen
NADP/NTN	National Atmospheric Deposition Program/National Trends Network
NAPAP	National Acid Precipitation Assessment Program
NBS	Nitrogen Bounding Study
NHEERL	National Health and Environmental Effects Research Laboratory
NSS	National Stream Survey
NSWS	National Surface Water Survey
PnET-CN	Net Photosynthesis and Evapo-Transpiration (PnET) - Carbon and Nitrogen (CN) model
S	Sulfur
SAMI	Southern Appalachian Mountains Initiative
SBRP	Southern Blue Ridge Province (as region modeled in DDRP and IA)
SOS/T	State of Science/Technology (1990 NAPAP reports)
USGS	United States Geological Survey
VTSSS	Virginia Trout Stream Sensitivity Study

1. INTRODUCTION

The Southern Appalachian Mountains Initiative (SAMI) was established to address concerns about the adverse effects of air pollution on environmental resources in the Southern Appalachians. Acidic deposition and its effects on surface waters is a major issue associated with air pollution in this area. For this study, we define the Southern Appalachians as the Blue Ridge, Ridge and Valley, and Appalachian Plateau provinces (as defined by Fenneman, 1938) in the states of Alabama, Georgia, Kentucky, North Carolina, South Carolina, Tennessee, Virginia, and West Virginia (Figure 1). This report has two main objectives:

1. Summarize the existing state of knowledge about the effects of acidic deposition on surface water resources in the Southern Appalachians.
2. Evaluate and make recommendations on the use of available methodologies for predicting future changes in the aquatic effects of acidic deposition in the Southern Appalachians under alternate deposition scenarios.

In this report, we examine the SAMI region as a whole, but the primary focus is on the 10 Class I wilderness areas located in the Southern Appalachians (Figure 1).

A comprehensive study of the effects of acidic deposition in the United States was completed under the National Acid Precipitation Assessment Program (NAPAP) in 1990. This study was documented in the 27 volumes of NAPAP's State of Science/Technology (SOS/T) report. The following six reports pertain to our objectives:

SOS/T #9	Current Status of Surface Water Acid-Base Chemistry	L. Baker et al., 1990
SOS/T #10	Watershed & Lake Processes Affecting Surface Water...	Turner et al., 1990
SOS/T #11	Historical Changes in Surface Water Acid-Base Chem...	Sullivan, 1990
SOS/T #12	Episodic Acidification of Surface Water ...	Wigington et al., 1990
SOS/T #13	Biological Effects of Changes in Surface Water ...	J. Baker et al., 1990
SOS/T #14	Methods for Projecting Future Changes in Surface ...	Thornton et al., 1990

These SOS/T reports contain detailed reference lists that document the work done before 1990. In general, we cite the appropriate SOS/T report for our summaries and conclusions, rather than all the pertinent pre-1990 literature. To bridge the gap between 1990 and 1995, we have compiled an annotated bibliography of pertinent literature published after 1990. The annotated bibliography focuses on surface waters in the SAMI region but it also includes some citations relating to acidic deposition effects in general.

The first part of this report summarizes our current understanding of acidic deposition effects, broken down into sections on important processes (Section 2), current status of aquatic resources (Section 3), and current trends in acidification (Section 4). Each section addresses surface water chemistry, episodic effects, and biological effects. A

Figure 1. Map of the Southern Appalachian study area showing the location of the Class I wilderness areas.

review of assessment methodologies appears in Section 5, followed by results from other predictive assessments in Section 6. Section 7 provides recommendations for the SAMI assessment. The report concludes with an annotated bibliography of post-1990 literature in Section 9.

1.1 Terminology

The terminology used to describe acid-base status can get rather confusing. In order to avoid problems, we follow the conventions developed during NAPAP. In brief, it is important to understand the following distinctions:

Acidity is the amount of acid in a sample, usually measured on the pH scale ($-\log[H^+]$).

Acid Neutralizing Capacity (ANC) is a measure of the ability of a water sample to neutralize acid inputs (determined by acid titration). ANC is used as the main indicator of the sensitivity of a surface water to acid inputs.

Acidic refers to a water sample that has lost all ANC. By definition, we consider waters with ANC ≤ 0 to be acidic (not pH < 7). Most waters with ANC ≤ 0 have pH < 5.3.

Acidification refers to declines in ANC or pH over time. Acidified waters had higher ANC or pH in the past. A lake or stream may have acidified but not be acidic (e.g., ANC decline from 80 to 40 µeq/L).

1.2 The SAMI Region

The SAMI region consists of three, somewhat linear, southwest-to-northeast trending physiographic provinces. From east to west, they are the Blue Ridge Mountains, Valley and Ridge, and Appalachian Plateau (Figure 1). Streams are the dominant aquatic resource in this region.

In Virginia, the Blue Ridge Mountains make up a narrow complex ridge lying between the Piedmont and the Great Valley of the Valley and Ridge Province (Figure 1). In the southern Blue Ridge, the range broadens into a range of uniformly dissected mountains with elevations ranging from 500 m to 2000 m above sea level. The highest mountains in the eastern United States are found in the southern Blue Ridge. Bedrock typically is composed of Cambrian and Precambrian metamorphosed sedimentary and complex gneissic and plutonic rocks.

The Valley and Ridge Province (Figure 1) is composed of a series of folded Paleozoic sedimentary rock layers, resulting in a sequence of valleys separated by narrow, parallel, linear ridges. The ridges typically are composed of more resistant sandstones, whereas limestone and shale formations are common in the valley bottoms. The proportion of ridge area to valley area is quite variable throughout the province. The streams often show a trellis drainage pattern due to the valley and ridge structure.

In West Virginia, the Appalachian Plateau Province (Figure 1) is separated from the Valley and Ridge Province to the east by a steep outfacing escarpment (e.g., Allegheny Front). The southern part of the Appalachian Plateau is often referred to as the Cumberland Plateau. The rocks in the Appalachian Plateau Province are younger than those in the other provinces, and clastic conglomerates, sandstones, and shales predominate. The mountains of the Appalachian Plateau are the result of severe plateau dissection.

2. FACTORS CONTROLLING AQUATIC RESPONSE TO ACIDIC DEPOSITION

2.1 Overview

Watershed soils/geology and hydrology are the major factors controlling streamwater ANC response to acidic deposition. In fact, on a regional scale, there is no relationship between deposition and surface water ANC (L. Baker et al., 1990). Two watersheds a mile apart can have vastly different responses to acidic deposition; one can be acidic, while the other is so well buffered that deposition poses no problem. Quantifying the effects on any one stream will tell very little about the effects across the region. Thus, a study of the effects of acidic deposition should be related to the *population* of streams in the study region.

The NAPAP SOS/T Processes Report summarizes the major processes influencing the response of surface water acid-base chemistry to acidic deposition. Figure 2 presents a summary figure from that report (Turner et al., 1990). For the SAMI region, the two most important processes are base cation neutralization reactions (cation exchange, geologic weathering) and anion retention/mobility (Elwood, 1991). The synthesis statement of Turner et al. (1990) provides a summary of the effects of acidic deposition on surface waters:

> "The magnitude of change in water chemistry parameters in response to acidic deposition and changes in watershed drainage chemistry may range from an equivalent increase in base cation concentrations to a reduction of 50 or more µeq/L ANC, to a shift from a low ANC or acidic, organic-dominated system, or to a sulfate-dominated system with little change in ANC or pH. The first response is probably most common. In the latter two cases, the net effect of atmospheric deposition of S on lake and stream chemistry is a shift toward systems that are dominated by mineral acidity and that have higher concentrations of inorganic aluminum which is toxic to aquatic organisms."

In the SAMI region, the major control that determines the ability of a watershed to buffer its surface waters against the influence of acidic deposition is its base cation mobilization ability. Watersheds that have soils with high base saturation/cation exchange capacity and/or highly weatherable geologic material have streams and lakes virtually unaffected by acidic deposition. The abundance of available base cations in these systems balances the added sulfate/nitrate from deposition, preventing any depression of ANC or pH. Systems that can't balance the added sulfate/ nitrate from deposition with base cations have decreased ANC/pH and/or increased inorganic aluminum. In the SAMI region, the most important factors controlling the supply of base cations are the watershed soil and the bedrock type.

2.2 Acidic Deposition

2.2.1 Current Pattern

Relative to "pristine" deposition, acidic deposition contains elevated concentrations of sulfate, nitrate, acidity, base cations, and ammonia. There are two types of deposition: wet (e.g., rain, snow, sleet, hail) and dry (e.g., aerosols, gases, particulates). The amount and content of wet deposition are much better known than the amount and content of dry deposition. Deposition throughout the SAMI area would be considered acidic (Figure 3). In the Southern Appalachians, the amount of

Figure 2. Conceptual diagram of (a) major processes and (b) hydrologic flowpaths that control surface water acid-base chemistry. Taken from Figure 10-41 in Turner et al., 1990.

acidic deposition decreases from north to south. For example, if we use the volume weighted 1995 wet deposition pH as an indicator of acidic deposition, the deposition in northern West Virginia (pH=4.3) has twice the acidity (pH is log scale) of that in northern Alabama (pH=4.6). Similar patterns occur in the deposition of sulfate and nitrate, as well (NADP/NTN, 1996).

On a national scale, there is a close relationship between sulfate deposition and sulfate concentration in lakes and streams (L. Baker et al., 1990). The same general pattern is evident, although less clear, for the relationship between nitrate/ammonia deposition and nitrate concentration in streams of the eastern United States (Kaufmann et al., 1991). Lakes and streams in the SAMI region are an exception to the national deposition/surface water sulfate relationship. Sulfate concentrations in these southeastern lakes and streams are much lower than would be expected, given their sulfate deposition levels, due to substantial retention of sulfate by adsorption in the soils of their watershed.

2.2.2 Historical Evidence for Acidification

It would be very valuable if the current status of acid sensitive streams in the region covered by SAMI could be placed in a historical context—that is, if we could know the acid-base status of streams in the region in pre-industrial times. No historical data are available for streams in this region, however, and the kinds of retrospective techniques (e.g., paleolimnology) that yield historical records in other regions (Sullivan et al., 1992) are not applicable to streams. Historical data from the Catskill Mountains, a northern extension of the same physiographic province that makes up much of the SAMI region, suggest that large changes in streamwater chemistry have occurred (Stoddard, 1991). While small streams in the Catskills show signs of acidification over the past 50 years, many large streams have actually increased in ANC and base cation concentrations, presumably due to watershed disturbances.

In the absence of historical information on stream chemistry and biology for the SAMI region, we are forced to use a historical context based on deposition and estimated deposition. Husar et al. (1991) report that the northern and southern parts of the SAMI region probably have experienced differences in historical sulfur deposition. In West Virginia and Virginia, S deposition rates rose from a background near 4 kg/ha/yr in the late 1800s to a peak near 30 kg/ha/yr around 1970. Since that time, S deposition rates have declined, although they still remain high, relative to background rates (ca. 25 kg/ha/yr).

In the southern Blue Ridge, S deposition rates were not significantly different from background rates prior to the 1950s. Husar et al. (1991) also report similar information for Florida, and it seems likely that the region from the southern Blue Ridge southward has undergone the same history. Beginning in the 1960s, S deposition increased significantly in this region, to near 20 kg/ha/yr, and there was no evidence of a decline in deposition through 1984, the last year of data reported by Husar et al. (1991).

Similar historical estimates for nitrogen deposition are not available, because of the difficulty of translating nitrogen emissions rates into reliable estimates of deposition (Husar, 1986). Husar et al. (1991) do document the changes in N emissions that have occurred in the area upwind of the southeastern United States. Nitrogen emissions began rising ca. 1900, with a significant part of the increase occurring after 1940. Current rates of emission (ca. 7 million tons of NO_2 per year) in the Southeast are almost twice those in the northeastern United States.

2.3 Hydrologic Flow Path

Watersheds in which the greatest proportion of the flow is through shallow, more acidic soils have surface waters with lower ANC than watersheds in which a large proportion of the flow is through deeper, more weatherable materials. The longer the flowpath, the more intimate the contact with weathering soil and rock and the longer the time available to acquire solutes through biogeochemical reactions (Turner et al., 1990).

2.4 Anion Mobility/Retention

Watershed soils typically contain acid cations (H^+, Al^{n+}) in abundance. The mobile anion hypothesis explains how acid anions (bicarbonate, sulfate, nitrate, organics) are needed to transport acid cations from soils into lakes and streams. Thus, cation leaching in soils is controlled by the availability of mobile anions. In systems affected by acidic deposition, elevated levels of SO_4^{2-} and NO_3^- leach either equivalent amounts of base cations (medium to high base saturation soils) or acid cations (low base saturation soils). Thus, the mobility of the SO_4^{2-} and NO_3^- through the watersheds is an important factor controlling the response of surface waters to acidic deposition (Turner et al., 1990). If all the SO_4^{2-} and NO_3^- derived from deposition were retained within the watershed, there would be little surface water response to acidic deposition.

2.4.1 Sulfur

Of the two major anions in deposition, SO_4^{2-} received a major share of the attention during the NAPAP process. In many parts of the United States, there is little retention of SO_4^{2-} within the watershed. Observed lake/ stream SO_4^{2-} concentrations are roughly the same as calculated surface water SO_4^{2-} concentrations, assuming evapoconcentration of SO_4^{2-} in deposition. These surface waters are considered to be in "steady-state" with SO_4^{2-} in deposition. A notable exception to this pattern is represented by the lakes and streams in the southeastern United States, where most of the incoming SO_4^{2-} is retained in the watershed and does not reach the lake or stream (L. Baker et al., 1990). The H^+ and Al^{n+} in soils thus does not reach the lake or stream either.

Soils adsorb SO_4^{2-} according to a concentration-dependent function. They continue to adsorb SO_4^{2-} until the concentration of adsorbed SO_4^{2-} reaches equilibrium with SO_4^{2-} in the soil solution. Different soils have different equilibrium points and SO_4^{2-} adsorption capacities. The adsorption capacity is thought to be directly related to the amount of Fe/Al oxide in soil and inversely related to soil pH and organic matter content. The higher the SO_4^{2-} adsorption capacity, the longer it will take for atmospherically derived SO_4^{2-} to break through the watershed and enter surface water. In the Southern Appalachians, much of the SO_4^{2-} is still being adsorbed in the watershed and the response to atmospheric deposition is considered to be "delayed." Watersheds currently in SO_4^{2-} steady state either never had much SO_4^{2-} adsorption capacity or the SO_4^{2-} adsorption sites have been filled by a longer history of deposition, such that their response to SO_4^{2-} deposition is considered "direct." A big remaining question is the reversibility of SO_4^{2-} adsorption. It is not well known what happens when SO_4^{2-} deposition declines. It is likely that SO_4^{2-} adsorption will show some degree of irreversibility; SO_4^{2-} desorption will not follow the same path as adsorption (Turner et al., 1990).

2.4.2 Nitrogen

In the past several years, our scientific understanding of the impacts of long-term N deposition to forested watersheds has undergone significant improvement. Although S deposition has been the focus of most research on acid deposition effects in the past decades, we now recognize that N deposition is also a threat to the integrity of aquatic and terrestrial systems, especially in areas that historically have received elevated levels of N deposition (Aber et al., 1989; Driscoll and Schaefer, 1989; Murdoch and Stoddard, 1992). The danger is that relatively undisturbed watersheds, aside from elevated deposition, may through time become N saturated. Nitrogen saturation has been variously defined, but central to all definitions is the concept that the supply of nitrogenous compounds from the atmosphere exceeds the demand for these compounds on the part of watershed plants and microbes (Skeffington and Wilson, 1988; Aber et al., 1989). Under conditions of N saturation, forested watersheds that previously retained nearly all N inputs, due to a high demand for N by plants and microbes, begin to undergo higher loss rates of N. These losses may be in the form of leaching to surface waters or to the atmosphere through denitrification.

The key processes of the N cycle that affect acidification of soils and surface waters are assimilation, mineralization, nitrification, and denitrification. Nitrogen assimilation is the uptake and metabolic use of N by plants and soil microbes. Because N is the most commonly limiting nutrient in forest ecosystems in North America (Cole and Rapp, 1981; Vitousek and Howarth, 1991), assimilation plays a key role in the development of N saturation. The form of N used by terrestrial ecosystems strongly affects the acidifying potential of N deposition. Ammonium uptake is an acidifying process (i.e., uptake of NH_4^+ releases one mole of H^+ per mole of N assimilated), whereas biological uptake of NO_3^- is an alkalinizing process (i.e., uptake of NO_3^- consumes one mole of H^+ per mole of N assimilated).

Mineralization is the bacterial decomposition of organic matter, releasing NH_4^+ that can subsequently be nitrified to NO_3^-. Mineralization is an important process in watersheds, as it recycles N that would otherwise be tied up in soil organic matter following the death of plants, or as leaf litter. Nitrification is the oxidation of NH_4^+ to NO_3^-; it is mediated by bacteria and fungi in both the terrestrial and aquatic parts of watersheds. It is an important process in controlling the form of N released to surface waters by watersheds, as well as in controlling the acid-base status of surface waters. Nitrification is a strongly acidifying process, producing two moles of H^+ for each mole of nitrogen (NH_4^+) nitrified. Because nitrification in forest soils transforms NH_4^+ into NO_3^-, the acidifying potential of deposition (attributable to N) is often defined as the sum of NH_4^+ and NO_3^-, assuming that all N will leave the watershed as NO_3^- (Hauhs et al., 1989).

Denitrification is the biological reduction of NO_3^- to produce gaseous forms of reduced nitrogen (N_2 , NO, or N_2O). Denitrification is an anaerobic process (i.e., it occurs only in environments where oxygen is absent), whose end product is lost to the atmosphere. It is always an alkalinizing process, consuming one mole of H^+ for every mole of N denitrified. In terrestrial ecosystems, denitrification occurs in boggy, poorly drained soils, or in anaerobic microsites. It has traditionally been considered a relatively unimportant process outside of wetlands (Post et al., 1985), although it may be locally important after such events as spring snowmelt and heavy rain storms, when soil oxygen tension is reduced (Melillo et al., 1983; Groffman et al., 1993). On a watershed scale, denitrification is not likely to be an important sink for N (Bowden, 1986; Bowden and Bormann, 1986), because it is limited by the availability of anaerobic sites (Klemedtsson and Svensson, 1988).

A number of factors may predispose watersheds to become N saturated, including elevated N deposition, stand age, and high soil N pools (Stoddard, 1994). High rates of N deposition play a clear role, as the ability of forest biomass to accumulate N must be finite. At very high, long-term rates of N deposition, the ability of forests and soils to accumulate N is exceeded, and the only remaining pathway for loss of N (other than runoff) is denitrification. High rates of N deposition may favor increased rates of denitrification, but many watersheds lack the conditions necessary for substantial denitrification (e.g., low oxygen tension, high soil moisture, and temperature).

Another important factor in N loss from watersheds is the age of the forest stands. A loss in the ability to retain N is a natural outcome of forest maturation, as both older trees and those that occur later in a successional sequence grow more slowly and therefore exhibit lower N demand (Vitousek and Reiners, 1975). Uptake rates of N into vegetation are generally maximal around the time of canopy closure for conifers, and somewhat later (and at higher rates) in deciduous forests, due to the annual replacement of canopy foliage in these ecosystems (Turner et al., 1990). Finally, soil N status may also affect N loss rates; where large soil N pools exist, they imply that soil microbial processes that are ordinarily limited by the availability of N are instead limited by some other factor (e.g., availability of labile organic carbon, or another inorganic nutrient), and contribute to the likelihood that watersheds will leach NO_3^- (Johnson, 1992; Joslin et al., 1992). To be N saturated, both the vegetational and soil microbial N demands of a watershed must be fulfilled; the existence of large soil N pools suggests that the second of these requirements may be easily met.

2.5 In-lake and In-stream Processes

A number of processes operating within lakes and streams can modify their acid-base chemistry, including SO_4^{2-}/NO_3^- retention mechanisms and base cation production. These processes are most important, however, in waters with long residence times (Turner et al., 1990). Thus, they would be expected to be of minor importance in streams and reservoirs in the SAMI region.

2.6 Other Acidity Sources

In addition to acidic deposition, the two other major sources of acid anions for lakes and streams are natural organic acids and oxidation of watershed sulfur compounds. Lakes and streams naturally acidic due to organic acids are found in areas where bedrock and soils are resistant to weathering and where there is a large buildup of organic matter. These naturally acidic waters are typically colored from high dissolved organic carbon (DOC) concentrations and are often found in places of low-relief terrain and poor drainage (Turner et al., 1990). Lakes and streams may also be acidic due to oxidation of naturally occurring sulfur compounds within their watersheds. This process is similar to acidic deposition in that a sulfuric acid solution is carried into the receiving water, but the sulfur source is internal to the watershed rather than deposited on it. The source of the sulfur is usually bedrock that contains sulfide (e.g., Anakeesta Formation in the Great Smoky Mountains or pyrite (FeS_2) associated with coal seams in the Appalachian Plateau). Significant SO_4^{2-} mobilization from internal sources, however, usually requires some kind of watershed disturbance (mining or road cut) to expose bedrock materials to water/air.

3. CURRENT STATUS OF AQUATIC RESOURCES

3.1 Surface Water Acid-Base Chemistry

3.1.1. Regional Status

As part of NAPAP, EPA conducted a National Surface Water Survey (NSWS) of lakes and streams in acid-sensitive areas of the United States. In the SAMI area, lakes were sampled in the Southern Blue Ridge subregion during the Eastern Lake Survey (ELS). The National Stream Survey (NSS) sampled streams throughout the SAMI region, except for the western parts of the Appalachian Plateau (Figure 4). The western part of the plateau was not sampled in the NSS because existing data at the time indicated that it had high ANC (> 400 µeq/L).

The results of the NSWS reflect chronic, not worst-case episodic, acid-base conditions (see Section 3.2). Due to the probability basis of the sample, and its regional extent, the NSWS is the best picture we have about the regional status and extent of chronic acid-base chemistry (L. Baker et al., 1990). For this report, we have used two ANC criteria to define acid-base status: acidic (ANC ≤ 0) and low ANC (≤ 50 µeq/L). In the SAMI region, acidic streams are those most affected by acidic deposition; they typically have pH in the 4's and low 5's and they have elevated levels of inorganic monomeric aluminum that is toxic to fish. Surface waters with ANC between 0 and 50 µeq/L are not chronically acidic, but many of them become acidic during storm events or snowmelt (episodes). During these episodes, they experience the low pH and elevated aluminum levels of chronically acidic systems (see section 3.2). Acidic deposition does not usually cause substantial environmental impacts in surface waters with ANC > 50 µeq/L.

3.1.1.1 Lakes. In the Southern Blue Ridge subregion, the ELS sampled lakes in both the Piedmont and Blue Ridge physiographic provinces between southern Virginia and northern Georgia (L. Baker et al., 1990). The following analysis (Table 1) reflects only those lakes in the Blue Ridge part of the SAMI region. The ELS lake population was determined by listing all lakes (with surface area > 4 ha) in the study region present on 1:250,000-scale USGS topographic maps. The ELS sampled 45 lakes in the Blue Ridge during fall 1984, after overturn; 90% of the estimated total population of 71 lakes were reservoirs. It was estimated that 5% of the lakes (3 lakes) had ANC ≤ 50 µeq/L. No sample lakes were acidic and 1% had pH < 6. The lakes had very low SO_4^{2-}, NO_3^-, and DOC concentrations (Table 2). Given that most of these lakes are reservoirs, it appears that they have large enough drainage areas to buffer inputs from acidic deposition. For SAMI, lakes can thus be considered of minor interest with respect to acidic deposition impacts due to:

- The low percentage of sensitive systems
- The low lake density in the study area (for comparison there are > 2000 lakes in the Adirondack Mountains of New York)
- Lack of a significant lake resource in the Class I areas

Lakes are not discussed further in any of the remaining sections of this report.

3.1.1.2 Streams. The NSS sampled the stream network in the SAMI area present on 1:250,000-scale USGS topographic maps (those with watershed areas < 155 km^2). The NSS used a randomized, systematic approach to selecting stream segment sample sites. Chemistry was sampled at both the upstream and the downstream ends of each segment (Kaufmann et al., 1991). In the SAMI study

Figure 4. Map of the acid-sensitive part of the Southern Appalachians sampled in the National Stream Survey. Areas outside the NSS study boundary were expected to have ANC > 400μeq/L.

Table 1. Estimates of Regional Acid-base Status for Streams and Lakes in the Southern Appalachians from National Surface Water Survey Data. For streams, the sampling unit was stream segments. Streams were sampled at both the upstream and downstream ends of each segment. The sampling unit for lakes was individual lakes.

Region	Percent ANC ≤ 0 µeq/L Upper — Lower End	Percent ANC ≤ 50 µeq/L Upper — Lower End	Estimated Population Total Upper — Lower End
Blue Ridge Streams	0% — 0%	12% — 2%	4,850 — 4,350
Valley and Ridge Streams			
Ridges	10% — 0%	25% — 2%	3,160 — 2,720
Valleys	0% — 0%	0% — 0%	2,990 — 4,350
Appalachian Plateau Streams	5% — 2%	31% — 24%	8,940 — 8,780
All Streams	4% — 1%	20% — 11%	19,900 — 20,200
Southern Blue Ridge Lakes	0%	5%	71

region, 306 segment ends were sampled, statistically representing 19,900 upstream segment ends and 20,200 downstream ends (or 62,000 km of stream). Streams were sampled in the spring during 1985 and 1986. There was a strong upstream/downstream gradient in the NSS data; ANC increased in the downstream direction due to increasing mobilization of base cations. For example, 12% of the stream segments in the Blue Ridge had low ANC (≤ 50 µeq/L) at the upstream ends versus only 2% at the downstream ends (Table 1). Overall, 4% of the stream segments were acidic at the upstream ends in the SAMI part of the NSS study area (1% at the downstream end).

Of the three physiographic provinces, the Appalachian Plateau had the highest proportion of acidic (5%) and low ANC (31%) streams. Streams acidic because of acid mine drainage were screened out of the NSS population and are not included in any of the estimates presented here (Herlihy et al., 1990). In the Valley and Ridge province, the effects of acidic deposition are restricted to the ridges. Low ANC streams are very rare or absent (none were observed in the NSS sample) in the valleys, due to the easily weatherable bedrock (e.g., limestone). Streams on the ridges are more sensitive to acidification due to the resistance to weathering of the bedrock geology. Thus ridges have less ability to neutralize acidic deposition. At the upstream ends, 10% of the ridge streams were acidic and 25% had low ANC (Table 1). The ANC increases rapidly as streams flow down off the ridges. At the downstream ends, none of the sample segments were acidic and only 2% had low ANC.

There is also a gradient in the percentage of acidic and low ANC streams from the northern to the southern parts of the SAMI region. Acidic and low ANC stream segments are more common in Virginia/West Virginia (26%) than in the six southern SAMI states (8%). This is probably due to a combination of higher S and N deposition and lower SO_4^{2-} retention in the more northern watersheds.

The NSS data from the SAMI region indicated that acidic streams and streams with very low ANC were almost all located in small (< 20 km^2), upland, forested catchments in areas of base-poor, weathering-resistant, bedrock (Herlihy et al., 1993). By interpolating between segment ends, NSS estimates for the whole SAMI region show that of the 62,200 km of stream length on 1:250,000-scale maps, 815 km (1%) were acidic and 4,410 km (7%) had ANC ≤ 50 µeq/L. Sulfate and NO_3^- from atmospheric deposition are the dominant sources of acid anions in these acidic NSS Southern Appalachian streams. As a group, they had low pH (median = 4.7) and high levels of inorganic monomeric aluminum (median = 364 µg/L) that can cause damage to aquatic biota (Table 2).

The NSS data also reflect distinct patterns of SO_4^{2-} retention among the three physiographic provinces. Streamwater SO_4^{2-} concentrations in the Appalachian Plateau were near steady state with respect to SO_4^{2-} deposition, whereas Blue Ridge streams were retaining large amounts (> 50%) of incoming SO_4^{2-} deposition. Valley and Ridge streams showed intermediate levels of SO_4^{2-} retention (Herlihy et al., 1993).

3.1.2 Relationship of Stream ANC to Geology

Several investigators have described the association between bedrock geology and the ANC of streams in the northern Blue Ridge (Lynch and Dise, 1985; Bricker and Rice, 1989). Lynch and Dise (1985) described a strong correlation ($r^2 = 0.95$) between bedrock distribution and streamwater ANC in Shenandoah National Park; percentile distributions of streamwater ANC are distinctly different for the park's five major bedrock types. In theory, the distribution of bedrock types within the region should provide a basis for predicting the ANC of unsampled streams in the region, as well as for explaining the ANC of sampled streams. In practice, however, the success of this approach on regional scales is limited by the generality of much of the geologic information available for the Southern Appalachians. Herlihy et al. (1993) had little success in relating geological information at the 1:250,000 map scale to stream ANC in data from the 1987 synoptic component of the Virginia Trout Stream Sensitivity Study (VTSSS). This map scale was too coarse to adequately characterize small streams. Thus, a geological approach to predicting ANC works well in areas for which geologic maps are available at high levels of detail. Just recently, a detailed geologic lithofacies map for the Southern Appalachians has been developed to provide regional-scale information on stream ANC (Peper et al., 1995). It may prove to be a useful tool for regionalizing acidic deposition impacts, but the predictive power of this new map against observed stream ANC needs to be tested.

3.1.3 Detailed Analysis of Class I Areas

A major focus of the SAMI effort is to evaluate air pollution effects on the Class I wilderness areas in the Southern Appalachians. Stream networks from both 1:100,000-scale and 1:24,000-scale USGS topographic maps were digitized for each of the eight smaller Class I areas (see Appendix A). Stream networks for the two largest Class I areas (two national parks) and the region were taken from the digitized version of the 1:100,000-scale blue-line network (from EPA River Reach File – Version 3).

In the entire SAMI study region (Figure 1), there are just under 200,000 km of streams at the 1:100,000 scale (Table 3). Roughly 60% of this length is in the acid-sensitive part

Table 2. Median Values (with First and Third Quartiles in Parentheses) for Major Ion Chemistry in Streams in Class I Wilderness Areas and in the Entire Southern Appalachians. Year(s) of data collection and number of observations (n) are given below the wilderness area name; data sources are discussed in text.

Wilderness Area	ANC (µeq/L)	pH	Sulfate (µeq/L)	Nitrate (µeq/L)	Chloride (µeq/L)	DOC (mg/L)
Dolly Sods 1994 (n=34)	-18 (-53 - -3)	4.7 (4.3-5.1)	105 (91-115)	4 (2-6)	11 (9-12)	2.2 (1.7-3.1)
Otter Creek 1994 (n=63)	-28 (-82 - 11)	4.6 (4.1-6.0)	129 (111-153)	6 (1-14)	9 (8-10)	2.0 (0.9-3.1)
Shenandoah NP 1981-1982 (n=47)	82 (21-120)	6.7 (6.0-6.9)	85 (66-103)	7 (3-23)	28 (25-32)	-----
James River Face 1991-1994 (n=8)	25 (22-44)	6.3 (6.1-6.5)	68 (54-74)	0 (0-0)	19 (18-20)	-----
Great Smoky Mt. NP 1994-1995 (n=337)	44 (24-64)	6.4 (6.2-6.6)	31 (18-46)	15 (6-29)	14 (12-16)	-----
Joyce Kilmer/Slickrock 1992-1994 (n=9)	70 (53-80)	-----	-----	7 (6-11)	-----	-----
Shining Rock 1992-1995 (n=9)	70 (65-80)	6.8 (6.7-7.0)	-----	7 (6-7)	-----	-----
Cohutta 1992-1994 (n=16)	41 (26-56)	6.5 (6.2-6.6)	35 (25-53)	14 (9-21)	24 (21-28)	1.8 (1.4-2.5)
Sipsey 1991-1993 (n=30)	245 (120-699)	7.3 (6.8-7.6)	94 (83-106)	2 (1-3)	33 (32-34)	2.2 (1.6-2.7)
SAMI Region Streams [a] 1986 NSS (N=19,940)	172 (65-491)	7.1 (6.5-7.5)	135 (62-229)	16 (4-34)	36 (18-68)	1.0 (0.7-1.7)
Acidic SAMI Streams [a] 1986 NSS (N=730)	-24 (-35 - -24)	4.7 (4.5-4.7)	142 (117-229)	0.3 (0.2-3.5)	16 (12-25)	1.4 (1.0-1.7)
S. Blue Ridge Lakes [a]	152	6.8	29	1	25	1.0

1984 ELS (N=71)	(87-246)	(6.7-7.0)	(23-36)	(0-6)	(18-42)	(1.2-1.5)

[a] Regional estimate for SAMI region streams is calculated using National Stream Survey (NSS) data (Figure 4) for the upstream segment end population (extrapolated from 154 sample streams). The Southern Blue Ridge lake estimate is extrapolated from 45 lakes sampled in the Eastern Lake Survey (L. Baker et al., 1990).

--- Not measured, no data found.

Table 3. Surface Area and Stream Length at 1:100,000 and 1:24,000 Map Scales for Streams in the Southern Appalachians and in Class I Wilderness Areas.

Region	Land Area (km^2)	1:100,000 Scale Stream Length (km)	1:24,000 Scale Stream Length (km)
SAMI REGION			
Blue Ridge	44,950	40,200	-----
Valley and Ridge	78,980	60,600	-----
Appalachian Plateaus	117,100	97,800	-----
Total SAMI region	240,700	198,600	-----
Acid-sensitive part (NSS boundary)	142,700	117,800	-----
CLASS I AREAS			
Dolly Sods	43	25	29
Otter Creek	81	57	85
Shenandoah National Park	788	259	-----
James River Face	35	30	44
Great Smoky Mountain National Park	2,300	2,035	-----
Joyce Kilmer/Slickrock	69	73	159
Linville Gorge	44	21	38
Shining Rock	75	44	102
Cohutta	121	140	208
Sipsey	52	70	108
CLASS I TOTAL	3,608	2,754	-----

----- = not determined.

of the Southern Appalachians as defined by the NSS study boundary (Table 3; Figure 4). At the same map scale, there are 2,754 km of streams in the 10 Class I areas (1.4% of the total in the SAMI region); 74% of the total Class I stream length is in the Great Smoky Mountains National Park and 9% is in Shenandoah National Park. The eight smaller Class I areas have a total length of 466 km at the 1:100,000 map scale and 773 km at the 1:24,000 map scale (Table 3). Based on geology, physiography, and stream chemistry, the 10 Class I areas in the SAMI region can be aggregated into four groups for assessing the aquatic effects of acidic deposition:

1. West Virginia Plateau: Dolly Sods and Otter Creek wilderness areas
2. Northern Blue Ridge: James River Face wilderness area and Shenandoah National Park
3. Southern Blue Ridge: Great Smoky Mountains National Park and Joyce Kilmer/Slickrock, Linville Gorge, Shining Rock, and Cohutta wilderness areas
4. Alabama Plateau: Sipsey wilderness area

For each of these wilderness areas, we gathered as much information on stream chemistry as possible. Summary statistics of available chemical data can be found in Table 2. We also estimated SO_4^{2-} and NO_3^- steady-state concentrations for each Class I area by identifying the 3–5 NSS sample streams closest to each area. As part of the Direct/ Delayed Response Project (DDRP; Church et al., 1989; 1992), the steady-state concentrations of SO_4^{2-} and NO_3^- in streamwater for each NSS site were estimated by interpolating available precipitation, runoff, and S and N deposition isopleths. Sulfate steady-state estimates incorporated estimates of dry deposition. The N steady-state estimates were based on wet deposition only and are almost certainly underestimated (Table 4). We calculated percent S and N retention for each Class I area using the observed median streamwater concentration for each area and the median of the 3–5 steady-state estimates from the closest NSS sites. Although these are rather rough estimates, they give a reasonably good picture of the differences in retention capabilities of the Class I areas and the potential for delayed response to acidic deposition.

Available stream chemistry data were also overlain on the digitized 1:100,000-scale stream network maps. The entire 100,000-scale map stream length was then ordered into the following classes, similar to the ones developed by Herlihy et al. (1991) for NSS data:

1. ANC ≤ 0
2. $0 <$ ANC ≤ 50 μeq/L
3. ANC > 50 μeq/L
4. Organic dominated (DOC > 5 mg/L)
5. No data

Stream length between two sample points with the same class was assumed to reflect that class. If the class changed between sample points, the stream length was split in half to reflect each of the sample points. Stream length between a sample point and a confluence or upstream termination was assumed to have the class of the sample point. The stream length in each of the five classes was then calculated from the digitized stream map (Table 5). A DOC level of 5 mg/L was used to distinguish streams whose acid anion source is primarily organic, rather than inorganic anions from deposition. None of the available data from the Class I areas had streamwater SO_4^{2-} concentrations indicative of a predominantly watershed source (e.g., acid mine drainage). Thus, we did not include a

Table 4. Observed and Estimated Steady-state Sulfur and Nitrogen Concentrations for Streams in Class I Wilderness Areas of the Southern Appalachians. Observed data are the median concentrations from Table 2. Steady-state values are based on precipitation, runoff, and deposition isopleth maps that were interpolated for each NSS site by the DDRP. Value in the table is the median of the 3–5 NSS sample streams closest to each wilderness area. Percent retention is calculated as (steady-state - observed)/steady-state * 100.

Wilderness Area	Observed Sulfate (μeq/L)	Steady-state Sulfate (μeq/L)	Percent Sulfur Retention	Observed NO_3+NH_4 (μeq/L)	Steady-state NO_3+NH_4 (μeq/L)	Percent Nitrogen Retention
Dolly Sods	105	177	41%	4	61	93%
Otter Creek	129	177	27%	6	61	90%
Shenandoah NP	85	196	57%	7	93	93%
James River Face	68	213	68%	0	99	100%
Great Smoky Mt. NP	31	104	70%	15	43	65%
Joyce Kilmer/Slickrock	---	112	---	7	46	85%
Shining Rock	---	86	---	7	41	83%
Cohutta	35	103	66%	14	40	65%
Sipsey	94	95	1%	2	60	97%

--- Not measured, no data found.

Table 5. Length of Stream (km) in Various ANC Classes in Class I Wilderness Areas in the Southern Appalachians. This analysis is based on the 1:100,000-scale mapped stream length. Year(s) of data collection and number of unique stream sample points (n) are given below the wilderness area name; data sources are discussed in the text. The percentages below the lengths are based on percent of the total stream length with measured stream chemistry data.

Wilderness Area	ANC ≤ 0 (μeq/L)	ANC 0-50 (μeq/L)	ANC > 50 (μeq/L)	Organic Dominated	No Data
Dolly Sods 1994 (n=28)	20.6 (82%)	4.6 (18%)	0	0	0
Otter Creek 1994 (n=45)	28.5 (53%)	8.9 (17%)	9.4 (18%)	6.7 (13%)	3.9
Shenandoah NP 1981-1982 (n=47)	--- (6%)	--- (19%)	--- (75%)	---	---
James River Face 1991-1994 (n=8)	0	20.5 (92%)	1.7 (8%)	0	7.6
Great Smoky Mt. NP 1994-1995 (n=337)	32 (4%)	336 (46%)	368 (50%)	0	1,300
Joyce Kilmer/Slickrock 1992-1994 (n=9)	0	8 (36%)	14 (64%)	0	51
Shining Rock 1992-1995 (n=9)	0	0	10 (100%)	0	34
Cohutta 1992-1994 (n=15)	0	102 (96%)	4.8 (4%)	0	33.2
Sipsey 1991-1993 (n=10)	0	13.6 (37%)	23.3 (63%)	0	33.1

--- = Length estimates not made; percentage estimates based on sample percentages.

watershed SO_4^{2-} source class in this classification system. There were a few sites in the Great Smoky Mountains National Park, however, that had SO_4^{2-} concentrations somewhat higher than typical, indicative of a watershed SO_4^{2-} contribution from the weathering of bedrock containing sulfide (Anakeesta formation, see section 3.1.3.3).

3.1.3.1. West Virginia Appalachian Plateau. The Dolly Sods and Otter Creek Class I wilderness areas are located about 25 km apart in the Appalachian Plateau of northeastern West Virginia (Figure 1). Both areas are drained by a third-order (1:100,000-scale) stream. The Dolly Sods wilderness (43 km^2) is drained by Red Creek but the headwaters of the stream lie outside the wilderness area. The area is mainly a plateau top dissected by Red Creek and its tributaries. Elevations in the Dolly Sods range from 2600 to 3900 ft. The Otter Creek wilderness (81 km^2) contains almost the entire Otter Creek watershed. Elevations range from 1800 to 3900 ft. Both areas have similar bedrock geology (West Virginia, 1968), underlain by numerous formations, including the Pottsville, Allegheny, Conemaugh, and Mauch Chunk. These formations are dominated by sandstone and shale and are all associated with coal deposits. The geology maps also indicate the presence of Greenbrier limestone in the downstream ends of each of the major creeks. In addition to the streams in the area, there are 7.5 ha of small ponds in the Dolly Sods wilderness. Both wilderness areas also contain vernal pools and a number of bogs and wetlands that serve as habitat for amphibians in the area.

An extensive synoptic survey of chemistry data for the Dolly Sods and Otter Creek wilderness areas was undertaken by the U.S. Forest Service in May, 1994. The survey sampled a total of 78 sites in Otter Creek and 43 sites in Dolly Sods (Webb, 1995). Figures 5 and 6 show the ANC of the sample sites on the 100,000-scale stream network. The Dolly Sods area is strongly affected by acidic deposition. All the streams in the Dolly Sods had ANC $\leq$ 50 µeq/L and 82% of the stream length was acidic (Table 5). The interquartile range in pH was 4.3 to 5.1. None of the streams had high DOC (max = 4.7, median = 2.2 mg/L), so organic acids are unlikely to be an important source of acidity. Some of the vernal pools sampled in Dolly Sods, however, did have high DOC (max = 10 mg/L). Sulfate concentrations (median = 105 µeq/L, Table 2) were lower than steady-state estimates (177 µeq/L), indicating about 40% retention within the watershed (Table 4). There was no evidence of any watershed sources of SO_4^{2-} (maximum stream SO_4^{2-} = 143 µeq/L). Concentrations of the other acid anions were very low (Table 2).

In the Otter Creek wilderness, the majority of the stream length was acidic (53%), 17% had ANC between 0 and 50 µeq/L, and 18% had ANC > 50 µeq/L (Table 5; Figure 6). Another 13% of the stream length was heavily influenced by organic anions (DOC between 5 and 8.5 mg/L). This stream length is probably influenced more by organic acids than acidic deposition. For the wilderness area as a whole, the interquartile range in pH was 4.1–6.0. Interpretation of this information is complicated by the fact that a limestone doser is operated on the main stem of Otter Creek to ameliorate the acidic conditions (see Figure 6 for location). The resulting chemical change from the doser is quite apparent in Figure 6. The main stem of Otter Creek had high ANC for ~ 4 km and low ANC for ~ 3 km downstream of the doser before becoming acidic again. This section of the creek would probably be acidic in the absence of the limestone additions. The only naturally high ANC stream section is a tributary in the northwest corner of the wilderness area (Figure 6). Although SO_4^{2-} concentrations were higher in

Figure 5. Stream ANC classification for the 1:100,000-scale USGS map stream network in the Dolly Sods wilderness area. The dots indicate sample sites.

Figure 6. Stream ANC classification for the 1:100,000-scale USGS map stream network in the Otter Creek wilderness area. The dots indicate sample sites.

Otter Creek than in Dolly Sods (median of 129 vs. 105 µeq/L), there still do not appear to be any significant watershed sources of SO_4^{2-}. The maximum SO_4^{2-} concentration in any stream in Otter Creek was 224 µeq/L, only 26% higher than the expected steady state value of 177 µeq/L for this wilderness area (Table 5).

In summary, both the Otter Creek and the Dolly Sods wilderness areas in the West Virginia Plateau lie on base-poor, resistant bedrock and have very high percentages (70%, 100%, respectively) of acidic and low ANC streams. In the vast majority of the systems, the acid anions in the streamwater are dominated by anions from deposition. Among acidic streams in these two areas, inorganic monomeric aluminum concentrations (interquartile range = 52–112 µg/L for Dolly Sods, 140–348 µg/L for Otter Creek) were above threshold levels for adverse biological impacts (see Section 3.3).

It is virtually impossible to quantify the degree of acidification in these systems. Anecdotal reports indicate that these systems were "always acidic" or are "naturally acidic." It is hard to assess what that means quantitatively (pH < 7?, turns litmus paper red?). It is very difficult to compare ANC and pH measurements of 50 years ago to current measurements. Also, these systems were probably receiving acidic deposition 50 years ago. A likely scenario is that in pre-industrial times, these streams had very low ionic strength, almost distilled water supersaturated with CO_2 (ANC levels of 0–20 µeq/L, pH in the low 5s, and little aluminum). If so, then the degree of acidification over the last 150 years would be about 0.5–1 pH unit, 20–40 µeq/L of ANC, and 50–250 µg/L of inorganic aluminum. This would be consistent with the historic pH and ANC changes reported from paleolimnological analysis of sediment cores in many deposition-dominated acidic lakes in the Adirondack Mountains of New York (Sullivan, 1990, Sullivan et al., 1992).

3.1.3.2 Northern Blue Ridge. Shenandoah National Park and the James River Face wilderness area are both located in the Blue Ridge Mountains in the northern and middle parts of Virginia, respectively (Figure 1). Shenandoah National Park is a thin linear band straddling a 110-km segment of the Blue Ridge (788 km^2) over an elevation range of 600–4050 ft above sea level. Logging, farming, and mining occurred in various parts of the park before its establishment in 1935. There are five major bedrock formations in the park: the Old Rag (a coarsely crystalline granite), Pedlar (feldspathic granodiorite), Catoctin (a metamorphosed basalt), Hampton (phyllite, shale, sandstone, and quartzite), and the Antietam (sandstone and quatzite) (Lynch and Dise, 1985). As discussed in Section 3.1.2, there is a strong relationship between geology and ANC in the park. The Hampton and Antietam formations in the southwestern part of the park are most resistant to weathering and have the streams with the lowest ANC. The streams in the park are virtually all first and second order (1:100,000 scale), draining east and west off the crest of the Blue Ridge. The James River Face wilderness area (35 km^2) is located on the southern bank of the James River, where it cuts through the Blue Ridge Mountains. Elevation ranges from 650 to 2950 ft above sea level. The streams are almost all first order and drain outwards from the high-elevation area in the middle of the wilderness area (Figure 7). The geologic formations in the James River Face are from the Chilhowee Group (sandstone and quartzite) and are similar to the Hampton and Antietam formations found in the southwestern part of Shenandoah National Park. There is also a minor amount of the Pedlar Formation in the James River Face (Virginia, 1963).

Figure 7. Stream ANC classification for the 1:100,000-scale USGS map stream network in the James River Face wilderness area. The dots indicate sample sites.

The most comprehensive survey of streams in Shenandoah National Park was conducted by Lynch and Dise (1985) in 1981 and 1982. Sample sites were not selected with a statistical design and we did not attempt to make estimates of the lengths in various chemical classes. Based on flow-weighted annual average data from 47 of these sites, covering 70% of the park area, Cosby et al. (1991) reported that 6% of the sample sites were acidic and 25% had ANC ≤ 50 µeq/L (Table 5). Over 300 streams were sampled in the mountains of western Virginia as part of the VTSSS (Cosby et al., 1991). Eight of these sites were within or on streams draining from the James River Face wilderness area (Figure 7). According to chemistry data from the VTSSS collected at these sites between 1991 and 1994, virtually all (92%) the stream length had ANC between 0 and 50 µeq/L (Table 5). Anion chemistry in the Shenandoah is similar to that of the James River Face; median SO_4^{2-} values were 85 and 68 µeq/L, and median NO_3^- values were 7 and 0 µeq/L, respectively (Table 2). ANC and pH are lower in the James River Face due to the concentration of more resistant bedrock in that wilderness area compared to Shenandoah Park. Both areas retain most of the incoming SO_4^{2-} (57–68%) and almost all the incoming N (Table 4).

3.1.3.3. Southern Blue Ridge. Most of the land area and stream length in the SAMI-region Class I wilderness areas are in the Great Smoky Mountains National Park (GSMNP; Table 3). The GSMNP (2,300 km^2) is located on the Tennessee/North Carolina border in an area of uplifted sedimentary rock. Elevations in the park range from 900 to 6640 ft. Bedrock is primarily sandstone with some limestone (Elwood et al., 1991). Many investigators have noted that one of the formations (Anakeesta) contains pyrite that can be oxidized to sulfuric acid when exposed to air and water during watershed disturbances (landslides, road cuts). The state geologic map also notes the presence of sulfidic bedrock in other formations within the park (e.g., Copperhill, Boyd Gap; North Carolina, 1985).

Based on a number of biogeochemical studies, the following conclusions can be made about streams in GSMNP (Silsbee and Larson, 1982; Elwood et al., 1991; Cook et al., 1994; Flum and Nodvin, 1995).

- As in Shenandoah National Park, bedrock geology is a good predictor of general streamwater ANC status.
- Low ANC (≤ 50 µeq/L) streams are common in the park.
- Acidic streams exist in the park, primarily at higher elevations.
- ANC tends to be lower and NO_3^- tends to be higher at higher elevations.
- Nitrate and SO_4^{2-} concentrations are comparable in many streams; in higher elevation catchments, NO_3^- concentrations are often greater than SO_4^{2-} concentrations. Streams in watersheds with a history of logging have lower NO_3^- than streams in unlogged watersheds. Thus, N/forest dynamics play a major role in controlling stream anion chemistry in GSMNP.
- Most of the incoming SO_4^{2-} and N is retained within the watershed in the majority of the studied streams.
- Streams that were acidic and had SO_4^{2-} concentrations > ~65 µeq/L probably are influenced by sulfide mineral weathering and are in watersheds containing the Anakeesta Formation.
- Higher ANC systems (> 100 µeq/L) probably are influenced by limestone weathering and are concentrated in the far western end of the park.

On the 1:100,000-scale maps, there are 2,035 km of streams. Elwood et al. (1991) report a length of 1,173 km of streams in the GSMNP capable of supporting trout and/or small-mouth bass. Flum and Nodvin (1995) have conducted a large survey of streamwater chemistry in GSMNP. Using their data, we calculated average spring chemistry for their sample sites by averaging all March, April, and May chemistry data they collected in 1994 and 1995. These streams (337 sites) had very low ionic strength, and had median SO_4^{2-} and NO_3^- concentrations of 31 µeq/L and 15 µeq/L, respectively (Table 2). These medians signify a 70% retention of deposition SO_4^{2-} and 65% retention of deposition NO_3^- (Table 4). These 337 sites represent 736 km of the 2,035 km of streams on the 100,000-scale maps in GSMNP. Of this assessed length, 4% (32 km) was acidic and 46% (336 km) had ANC between 0 and 50 µeq/L (Table 5).

The expected steady-state SO_4^{2-} concentration in GSMNP is 104 µeq/L. Typically, SO_4^{2-} concentrations are much lower than steady state but streams with higher SO_4^{2-} do exist in GSMNP, probably due to bedrock sulfide weathering. In the Flum and Nodvin (1995) data, 9 of the 337 sites had $SO_4^{2-} > 100$ µeq/L (maximum=248 µeq/L), corresponding to about 8 km of stream length (1% of total assessed length). Of the 23 stream sites that were acidic, 11 had $SO_4^{2-} > 65$ µeq/L and 1 had $SO_4^{2-} > 100$ µeq/L.

The Joyce Kilmer/Slickrock wilderness area (69 km^2) contains the headwaters of Slickrock and Little Santeetlah Creeks and is adjacent to the southwest boundary of the GSMNP. As such, it has geology and topography similar to those of the GSMNP and the conclusions listed above for GSMNP are probably applicable to the Slickrock wilderness area. Elevations in the Slickrock wilderness area range from 2000 to 5300 ft and the bedrock geology is composed primarily of the Copperhill (metagraywacke, slate, schist) and Boyd Gap Formations (slate, metasiltstone, and metagraywacke). Both formations have notations on the geologic maps indicating that they contain sulfidic bedrock (North Carolina, 1985). We were able to obtain chemistry data for 9 stream sites in the Slickrock wilderness area from Bill Jackson and Richard Burns with the U.S. Forest Service in Asheville, North Carolina (Figure 8; unpublished data). These 9 sites represent about 22 km of the 73 km of streams on the 100,000-scale map of the area; about one-third of the assessed stream length had ANC between 0 and 50 µeq/L and the rest had ANC > 50 µeq/L (Table 5).

The Linville Gorge wilderness area covers a stretch of the Linville River roughly 20 km long as it flows through Linville Gorge. Other than the Linville River, there are virtually no aquatic resources in this wilderness area (see Appendix A). It is highly unlikely that the Linville River is acid-sensitive. In any event, water quality is not an air-quality related value for the Linville Gorge wilderness area (Bill Jackson, pers. comm.). Thus, we will not assess its acid-base status any further.

The Shining Rock wilderness area (75 km^2) drains parts of the headwaters of the East Fork of the Pigeon River in North Carolina, just north of the South Carolina border. Elevations in this area range from 3300 to 6000 feet. The bedrock geology is primarily from the Tallulah Falls Formation, a locally sulfidic muscovite-biotite gneiss (North Carolina, 1985). We were able to obtain chemistry data for 9 stream sites in the Shining Rock wilderness area from Bill Jackson and Richard Burns with the U.S. Forest Service in Asheville, North Carolina (Figure 9; unpublished data). All 9 sites had ANC between 50 and 100 µeq/L. These 9 sites represented about 10 km of the 44 km of streams on the 100,000-scale map of the area

(Table 5).

Figure 8. Stream ANC classification for the 1:100,000-scale USGS map stream network in the Joyce Kilmer/Slickrock wilderness area. The dots indicate sample sites.

Figure 9. Stream ANC classification for the 1:100,000-scale USGS map stream network in the Shining Rock wilderness area. The dots indicate sample sites.

The Cohutta wilderness area (121 km^2) drains the headwaters of the Conasauga and Jacks rivers in northern Georgia. Elevation ranges from 1000 to 3900 feet and the bedrock is composed primarily of mica and graphite schists, gneiss, and amphibolite (Georgia, 1976). David Wergowske (pers. comm.), from the U.S. Forest Service Chattahoochee-Oconee National Forest provided streamwater chemical data from 15 sites in the Cohutta. Data were collected during 1992-1994 and represent about three-fourths of the 145 km of streams represented on the 1:100,000-scale maps of the wilderness area (Figure 10). Virtually all (96%) of the sampled stream length had ANC ≤ 50 µeq/L but was not acidic (Table 5). Streamwater chemistry in Cohutta was very similar to that observed in the GSMNP. Streams have very low DOC (median=1.8 mg/L) and high NO_3^- concentrations (median=14 µeq/L) relative to the rest of the SAMI region. Roughly two-thirds of the incoming SO_4^{2-} and NO_3^- is retained within the watershed (Table 4). Thus, watersheds in Cohutta are "leaking" nitrogen.

3.1.3.4 Alabama Appalachian Plateau. The Sipsey wilderness area (52 km^2) in northern Alabama is located in the Cumberland Plateau (southern part of the Appalachian Plateau). The area is drained by Sipsey Fork, formed by the confluence of Thompson and Hubbard creeks. The headwaters of this basin lie outside the wilderness area boundary. Elevation ranges from 500 to 1000 ft. A study of the stream chemistry in the Sipsey wilderness area was undertaken by Dr. G. Milton Ward of the University of Alabama during 1991–1993. He described the results in a series of reports to the U.S. Forest Service (Ward, 1991, 1992, 1993). Parts of this wilderness area (around mainstem Sipsey Fork) are underlain by the Bangor limestone formation and the streams draining this formation have such high ANC levels that they are not likely ever to be affected by acidic deposition (Table 2, Figure 11). Other parts of this wilderness area are drained by bedrock of the Pottsville (pebbly quartzose sandstone) and Parkwood (shale, sandstone) formations (Osborne et al., 1989). These streams have lower ANC and may be sensitive to acidic deposition. Just over half (52%) of the 100,000-scale map stream length in the area was sampled for stream chemistry (Table 2). Sampling was concentrated on the mainstem Sipsey Fork and major tributaries. Within the half of the network that was sampled, 63% (including Sipsey Fork) had very high ANC (200–800 µeq/L) and the other 37% (14 km) had ANC levels of 40–50 µeq/L (Figure 11). In terms of anion chemistry, Sipsey is the only Class I area that appears to be at steady state with respect to SO_4^{2-} deposition (i.e., little to no watershed SO_4^{2-} retention). Thus, a delayed response to S deposition is unlikely in this area. Nitrate, on the other hand, is largely retained in the watershed (Table 4).

3.1.4 Class I Area Summary

Upon comparing results, it is clear that the smaller Class I areas are much more sensitive to acidic deposition (higher percentages of low ANC streams) than their specific regions as a whole (Table 6). In terms of adverse aquatic effects of acidic deposition, the four Class I groups can be ranked: West Virginia Plateau >> Northern Blue Ridge > Southern Blue Ridge > Alabama Plateau.

Streams in the West Virginia Plateau Class I areas had the highest percentage of acidic stream length (53% in Otter Creek, 82% in Dolly Sods), the highest SO_4^{2-} and inorganic aluminum concentrations, and the lowest pH of any of the Class I areas. They are currently heavily impacted by acidic deposition. The Sipsey wilderness area is of least concern for acidic deposition impacts because

Figure 10.Stream ANC classification for the 1:100,000-scale USGS map stream network in the Cohutta wilderness area. The dots indicate sample sites.

Figure 11.Stream ANC classification for the 1:100,000-scale USGS map stream network in the Sipsey wilderness area. The dots indicate sample sites.

Table 6. Summary of Acidic and Acid-sensitive Stream Percentages in Class I Wilderness Areas and Other Aggregate Physiographic Regions of the Southern Appalachians. Data for the Class I wilderness area is from Table 5 and is based on the 1:100,000-scale stream network. % total length assessed refers to the percentage of the length of streams in the region with which there were available data to infer ANC status.

REGION	% Assessed Length with ANC ≤ 0 (µeq/L)	% Assessed Length with ANC ≤ 50 (µeq/L)	Total Length (km)	% Total Length Assessed (had Data)
WEST VIRGINIA PLATEAU				
Dolly Sods Wilderness Area	92	100	25	100%
Otter Creek Wilderness Area	53	70	57	93%
Entire Province - NSS (n=37)	5	17	14,100	100%
NORTHERN BLUE RIDGE				
Shenandoah National Park	6**	25**	n=47**	**
James River Face Wilderness Area	0	92	30	75%
Entire Province - NSS (n=13)	0	4	8,700	100%
Virginia Blue Ridge - VTSSS	6**	42**	n=147**	**
SOUTHERN BLUE RIDGE				
Great Smoky Mt. National Park	4	50	2,035	36%
Slickrock Wilderness Area	0	36	73	30%
Shining Rock Wilderness Area	0	0	44	23%
Cohutta Wilderness Area	0	96	140	77%
Entire Province - NSS (n=55)	0	7	10,800	100%
Entire Province - WINGER	2**	4**	n=62**	**
ALABAMA PLATEAU				
Sipsey Wilderness Area	0	37	70	53%

** Estimate reflects percentage of sample size, not length. Representativeness of the sample to the population is unknown and may not accurately reflect the entire population. The sample size used in the estimate is shown in the Total Length column.

VTSSS - Estimates are based on the Virginia Trout Stream Sensitivity Study data (Webb et al., 1989a).

NSS - Estimates based on weighted extrapolation from probability sample data from the National Stream Survey (Kaufmann et al., 1988); stream network from 1:250,000 scale maps.

WINGER - Estimates are based on study by Winger et al., 1987.

SO_4^{2-} appears to be at steady state and it has higher streamwater ANC concentrations. The Plateau areas retain less SO_4^{2-} than do the Blue Ridge areas so any delayed effect of acidic deposition will be more pronounced in the Blue Ridge. Watersheds in both of the Blue Ridge areas retain the majority of the entering SO_4^{2-} from deposition. Low ANC streams are common and some acidic streams are found in areas of resistant bedrock and/or higher elevations. The northern Blue Ridge areas have higher sulfate concentrations than the southern Blue Ridge areas and seem to be more influenced by acidic deposition. The southern Blue Ridge areas stand out from the other Class I areas in terms of having the highest NO_3^- concentrations (lowest N retention). It appears that NO_3^- is breaking through these watersheds and is entering streams in concentrations that approach and sometimes exceed SO_4^{2-} concentrations.

3.2 Episodic Chemical Conditions

Most of the research on (and modeling of) acidification of surface waters has dealt with the problem of chronic acidification over relatively long time scales (years to centuries) and most regional assessments of surface water acid-base status have focused on average annual conditions or on so-called "index" periods. However, transient changes in acid-base status associated with hydrological events (i.e., those occurring during snowmelt and rainfall periods) represent a potentially important acidification process— known as episodic acidification—in regions that receive acidic deposition, including the entire SAMI region. In this section of the report, we briefly summarize the synthesis documents pertaining to the problem of episodic acidification of surface waters, namely NAPAP State of Science and Technology Report 12, entitled *Episodic Acidification of Surface Waters Due to Acid Deposition* (Wigington et al., 1990), and the NAPAP *1990 Integrated Assessment Report* (NAPAP, 1991). This summary focuses on the factors most likely to control episodic acidification of surface waters and on the techniques that can be used to quantify current regional and local-scale episodic acidification impacts. In the second part of the section, we focus our discussion specifically on surface waters of the Southern Appalachians, including those in the Class I wilderness areas.

3.2.1 Synopsis of Synthesis Documents

Episodic acidification is defined as the process by which lakes and streams experience short-term decreases in ANC, generally during hydrological events and over time scales varying from several hours to several weeks. ANC depressions are usually accompanied by changes in concentration of one or more of the following: hydrogen ion, base cations, dissolved organic carbon, sulfate, nitrate, and various forms of dissolved aluminum. In highly acid-sensitive lakes and streams (chronically low levels of ANC), episodic ANC depressions are usually accompanied by increases in hydrogen ion concentrations (i.e., decreases in pH) and increases in dissolved aluminum concentrations. These transient increases in hydrogen ion and aluminum concentrations can cause significant nonlethal stress or increased mortality of some species and life stages of fish and other aquatic organisms (Wigington et al., 1990).

In a thorough review and synthesis of results published from studies of episodic acidification conducted in the United States, Canada, and Europe, Wigington et al. (1990) were able to draw four important conclusions:

1. Episodic acidification is a ubiquitous process in streams and drainage lakes and is not necessarily symptomatic of anthropogenically produced chronic acidification (i.e., episodic acidification occurs both in waters that are chronically acidic and in those that are not). However, episodic and chronic acidification are clearly related, as

the magnitude of ANC depressions is usually larger in intermediate to high ANC systems than in low ANC or acidic systems, and the lowest minimum ANC and pH levels occur during episodes in surface waters with low pre-episode ANC levels. These observations at least qualitatively support the explanation that ANC *dilution* is an important component of episodic acidification.

2. The characteristics of episodes are determined largely by changes in hydrological flowpaths during rainfall and snowmelt events. During baseflow periods, streamflow is derived largely from drainage of relatively alkaline groundwater, whereas during stormflow periods, both pre-event and event water can be routed through either acidic upper soil layers (as subsurface stormflow) or across the soil surface as overland flow (as saturation overland flow). In drainage lakes in cold temperate regions where surface ice forms, inverse thermal stratification accentuates the episodic acidification response by restricting the hydrological mixing of snowmelt and ambient lake water under ice cover.

3. Episodic acidification can be attributed to several different anthropogenic and natural processes, including direct inputs of mineral acids (sulfuric and nitric) from the atmosphere during events, antecedent deposition of mineral acids to watershed soils (chronic or antecedent "conditioning"), hydrological dilution, nitrification, organic acid production, and deposition of neutral sea salts. Any one or several of these mechanisms may be operative in a particular watershed. In many watersheds of the northeastern and mid-Atlantic regions of the United States, atmospheric deposition appears to be operating in conjunction with several natural processes to generate episodes with lower minimum ANC and pH and higher dissolved aluminum levels. Most likely atmospheric deposition is affecting episodic acidification in these (and perhaps other) regions by providing direct inputs to surface waters, by conditioning watersheds during antecedent periods, and by reducing chronic ANC levels. Thus, relatively small ANC depressions are capable of creating acidic, high Al conditions in streams and lakes.

4. Modeling of episodic acidification has been only moderately successful, due primarily to a lack of understanding of hydrological pathways and biogeochemical reactions. Several fairly simple empirical models have been successfully linked to surface water survey databases to provide crude estimates of regional episodic acidification impacts on streams in the eastern United States and on lakes in the Adirondack Mountains of New York.

While these conclusions were based on a relatively large number of field studies, the authors also concluded that a clear scientific consensus regarding the primary causes of episodic acidification had not yet emerged. In addition, the report concluded that there was little knowledge of the regional extent or environmental significance of episodic acidification in any of the regions where field studies had been conducted and that statistically rigorous population estimates of current or future episodic acidification impacts could not be made with data that were available at the time.

Finally, the possible biological significance of episodic acidification had not been properly addressed at the time the synthesis document was written (Wigington et al., 1990). To address these assessment issues, Wigington et al. (1990) identified several critical knowledge gaps:

1. Additional field data collected with high temporal resolution in various geographic regions of the United States (in particular the southeastern, upper midwestern, and western regions) that could be used for calibrating simple models of episodic acidification for estimating current regional impacts.
2. Long-term episodic data for describing the behavior of systems over longer time periods.
3. New techniques for quantifying watershed-scale hydrological flowpaths.
4. Better understanding of biogeochemical processes involving nitrogen, sulfur, and natural organic acids.

The 1990 NAPAP assessment of current and future acidification impacts of acidic deposition recognized that assessments based solely on chemical conditions during index periods (i.e., periods approximating average annual or seasonal conditions) did not account for the worst-case chemical conditions that usually occur during extreme hydrological events. However, due to the rather large uncertainties associated with incorporating episodic acidification into the regional assessment framework, model-based projections of watershed responses to emissions reduction scenarios were not formulated to account for changes in episodic acidification over long time periods.

3.2.2 Current Episodic Acidification Impacts in the Southern Appalachians

As summarized by Wigington et al. (1990), field studies of current episodic acidification impacts have been conducted on at least two continents (North America and Europe), including many physiographic regions of the United States and much of Canada. As previously observed, episodic acidification has been found to be virtually ubiquitous; therefore, episodes must be accounted for in any overall scheme to assess the current acid-base status of surface waters, either at local or regional scales. For several regions of the eastern United States, models have been employed to predict current episodic acidification impacts. Most of these modeling studies have unfortunately been based on extremely limited data sets. The following paragraphs summarize our current understanding of episodic acidification in the Southern Appalachians at the two scales of interest—local and regional.

3.2.2.1 Local Scale. Wigington et al. (1990) specifically identified the southeastern United States as a region for which no complete data sets on episodic acidification were available and for which incomplete data were available for fewer than 10 streams in the entire region. Declines in pH and ANC were noted in all studies, but only one study reported minimum episodic pH values below 5.0 (Raven Fork, North Carolina). Since 1990, however, data from several intensive studies of episodic acidification in the Southern Appalachians have been reported (Miller-Marshall, 1993; Hyer et al., 1995; Eshleman et al., 1995; Nodvin et al., 1995), from which local episodic impacts can be quantified. These studies suggest that streams with antecedent baseflow ANC values less than about 25 µeq/L may experience substantial depressions in pH (as much as one unit) and increases in dissolved Al concentrations (perhaps as much as 100 µg/L). Streams with higher antecedent baseflow ANC values probably experience much smaller changes in pH and Al concentrations.

Another interesting aspect of this problem, addressed by Eshleman et al. (1995), was the effect of insect defoliations on the episodic mobilization of nitric acid and the associated acidification response. At White Oak Run in Shenandoah National Park, a statistical analysis of 13 years of data suggested that mean episodic depressions of ANC have increased by about a factor of 2 since the first outbreak of forest defoliation by the gypsy moth caterpillar during the summer of 1990; the mean episodic change in NO_3^- concentration also has increased by about 12 µeq/L, while the mean episodic dilution of C_B has decreased from -8.5 µeq/L to -1.7 µeq/L during the same period. Episodic changes in SO_4^{2-} have remained the same, however.

3.2.2.2 Regional Scale. Eshleman (1988) estimated regional-scale episodic acidification impacts in the Southern Appalachians using an empirical two-component mixing model with minimal calibration. Eshleman (1988) estimated that 5–7% of the population of Southern Appalachian stream reaches sampled during the National Stream Survey may become acidic (ANC < 0) during extreme hydrological conditions, compared to 0–3% during typical spring baseflow conditions. Recently, Hyer et al. (1995) presented results from an intensive study of episodic acidification of three streams in Shenandoah National Park (Virginia) that support the use of the two-component mixing model of ANC and provide data for model parameterization. No comparison of the model parameters has been conducted, although the data are available to do so. Additional field data are needed, however, to determine the robustness of the model (and of the existing parameters) for quantifying regional impacts in other regions of the Southern Appalachians (including Class I areas).

3.3 Biological Effects of Acidic Deposition

3.3.1 Synopsis of Synthesis Documents

The NAPAP SOS/T report on biological effects (J. Baker et al., 1990) states that there is no doubt that acidification, at pH levels as high as 6.0–6.5, results in changes in biological communities. All major groups of aquatic organisms have been affected, but individual species differ greatly in acid tolerance. Two readily observable consequences are (1) shifts in species composition and (2) reduction in the total number of species in a body of water. Ecological processes are more robust than some acid-sensitive species. A general summary of the biological changes associated with declining pH is shown in Table 7.

It is more difficult to state precisely the magnitude of community effects on a regional scale. The report provides guidelines and methods for estimating the magnitude of effects, given regional differences in data availability. The use of suggested models provides three significant advances: (1) improved definition of chemical ranges critical for specific biological responses, (2) quantification of the interactions among pH, aluminum, and calcium (the most important parameters for understanding biological responses in this context) at realistic, regional levels, and (3) estimates of the current and projected numbers of lakes and streams unsuitable for fish due to acidification. However, given the complexity of natural systems, it would be misleading to consider model outputs as absolute; although sources of uncertainties in models have been identified, their influence on model outputs can be only partly quantified.

The discussions of biological effects cover all components of aquatic communities (algae,

Table 7. General Summary of Biological Changes Anticipated with Surface Water Acidification, Expressed as a Change in pH. Taken from Table 13-37 in the NAPAP SOS/T report (J. Baker et al., 1990).

pH Decrease	General Biological Effects
6.5 to 6.0	Small decrease in species richness of phytoplankton, zooplankton, and benthic invertebrate communities resulting from the loss of a few highly acid-sensitive species, but no measurable change in total community abundance or production Some adverse effects (decreased reproductive success) may occur for highly acid-sensitive species (e.g., fathead minnow, striped bass)
6.0 to 5.5	Loss of sensitive species of minnows and dace, such as blacknose dace and fathead minnow; in some waters decreased reproductive success of lake trout and walleye, which are important sport fish species in some areas Visual accumulations of filamentous green algae in the littoral zone of many lakes, and in some streams Distinct decrease in the species richness and change in species composition of the phytoplankton, zooplankton, and benthic invertebrate communities, although little if any change in total community biomass or production Loss of a number of common invertebrate species from the zooplankton and benthic communities, including zooplankton species such as *Diaptomus silicis, Mysis relicta, Epsichura lacustris*; many species of snails, clams, mayflies, and amphipods, and some crayfish
5.5 to 5.0	Loss of several important sport fish species, including lake trout, walleye, rainbow trout, and smallmouth bass; as well as additional non-game species such as creek chub Further increase in the extent and abundance of filamentous green algae in lake littoral areas and streams Continued shift in the species composition and decline in species richness of the phytoplankton, periphyton, zooplankton, and benthic invertebrate communities; decrease in the total abundance and biomass of benthic invertebrates and zooplankton may occur in some waters Loss of several additional invertebrate species common in oligotrophic waters, including *Daphnia galeata mendotae, Diaphanosoma leuchtenbergianum, Asplanchna priodonta*; all snails, most species of clams, and many species of mayflies, stoneflies, and other benthic invertebrates Inhibition of nitrification
5.0 to 4.5	Loss of most fish species, including most important sport fish species such as brook trout and Atlantic salmon; few fish species able to survive and reproduce below pH 4.5 (e.g., central mudminnow, yellow perch, and in some waters largemouth bass) Measurable decline in the whole-system rates of decomposition of some forms of organic matter, potentially resulting in decreased rates of nutrient cycling Substantial decrease in the number of species of zooplankton and benthic invertebrates and further decline in the species richness of the phytoplankton and periphyton communities; measurable decrease in the total community biomass of zooplankton and benthic invertebrates in most waters. Loss of zooplankton species such as *Tropocyclops prasinus mexicanus, Leptodora kindtii*, and *Conochilis unicornis*; and benthic invertebrate species, including all clams and many insects and crustaceans Reproductive failure of some acid-sensitive species of amphibians such as spotted salamanders,

	Jefferson salamanders, and the leopard frog

zooplankton, benthic invertebrates, fish, amphibians, and waterfowl) and major ecological processes. However, quantitative methods and models, plus regional discussions, cover only fish responses. The reasons for this limitation include data availability (historical and experimental), as well as the ability to make direct linkages between water chemistry and toxic mechanisms in fish.

The major conclusions of this SOS/T report are shown in italics (J. Baker et al., 1990) and discussed in the following subsections.

3.3.1.1 Chemical Factors Influencing Biota. The most important chemical properties of surface waters influencing biological responses to acid-base chemistry are pH, aluminum, and calcium.

Surface water pH is probably the most important of the three; decreases in pH (particularly at levels below 6.0–6.5) have been shown to produce negative effects on many aquatic animals. Species (and life history stages within species) differ greatly in tolerance to acid conditions; in brook trout, for example, adults do not typically disappear from streams until baseflow pH falls below 5.5, but sublethal effects on the growth of young fish are detectable when pH drops below 6.5. Increased H+ concentration (decreased pH) has been shown to be directly toxic itself, but perhaps more importantly in nature, increased acidity mobilizes aluminum, which is toxic under acidic conditions, even though it is harmless under acid neutral conditions. Animals typically tolerate lower pH values in the absence of aluminum. Aluminum is the most abundant metal in the Earth's crust, and is virtually ubiquitous in terrestrial environments. The aqueous chemistry of aluminum is complex, and it can exist in multiple chemical forms differing in toxicity in solution; inorganic monomeric aluminum is thought to be the most toxic form. Organically bound aluminum is relatively nontoxic, so waters with high organic content usually contain little toxic aluminum. Concentrations of inorganic monomeric aluminum above 30–50 µg/L cause adverse effects in the most sensitive organisms; concentrations over 100 µg/L affect many organisms.

Many aquatic animals are more sensitive to acid conditions when calcium concentrations are low. Calcium ameliorates the negative effects of acid conditions by directly supporting the physiological processes and structures damaged by H+ and aluminum in fish. Small changes in calcium concentration can produce substantial changes in response; most of the benefits of increased calcium concentration are evident at concentrations of 150 µeq/L, and further increases produce smaller improvements.

3.3.1.2 Effects on Species Richness. A number of the species that commonly occur in surface waters susceptible to acidic deposition cannot survive, reproduce, or compete in acidic waters. Thus, with increasing acidity, the "acid-sensitive" species are lost and species richness (the number of species living in a given lake or stream) declines. These changes in aquatic community structure occur at chronic pH levels <6.0–6.5.

Acid-sensitive species occur in all groups of aquatic organisms. The drop in species richness is most dramatic between pH 5 and 6. For example, many species of minnows, zooplankton, mollusks, and mayflies are adversely affected at chronic pH levels between 5.5 and 6. Long-term declines in pH from 5.5 to 5.0 result in the loss of several important sport fish species, including lake trout, rainbow trout, walleye, and smallmouth bass. Brook trout generally cannot survive or reproduce successfully at pH levels below 4.8–5.2. Few fish are found at pH levels below 4.5. Both chronic and acute (episodic) acidification contribute to species loss; episodic acidification is more pronounced in streams than in lakes.

3.3.1.3 Effects on Ecosystem Level Processes. Ecosystem level processes, such as decomposition, nutrient cycling, and productivity, are fairly robust and are affected only at relatively high levels of acidity (e.g., chronic pH <5.0–5.5).

Among nonvertebrate organisms, acid-sensitive species lost in the early stages of acidification are "replaced" to some degree by acid-tolerant organisms; as a result, the net change in total community productivity is relatively small; however, less information is available for system-level processes than for community structure, so subtle effects on system processes may not yet have been detected.

3.3.1.4 Recovery of Biological Communities. Relatively few studies have been conducted on the recovery of biological communities following reductions of acid inputs. Nevertheless, it is predicted that, with decreasing acidity, acid-sensitive species would reappear and species richness would increase.

Much of the information on recovery is derived from liming experiments, involving the addition, in most cases, of calcium carbonate. With few exceptions, this treatment results in improved water quality, to levels that would support more acid-sensitive species. Problems in interpreting these results remain. Although liming adds calcium, decreases in acid precipitation may reduce surface water calcium. Preliminary results from Norway suggest that fish community declines have continued in the last 10–15 years in regions where acid deposition has decreased. In these low calcium waters (50–100 µg/L), small decreases in calcium have apparently offset the benefits of lower acid and aluminum concentrations. In contrast, preliminary results from Ontario indicate improved biological status following reductions in atmospheric loading; calcium levels there tend to be higher than in Norway. Rates of recovery are poorly known in general, but algae appear to recover more rapidly than other groups of organisms. Additional research on recovery (and management steps to accelerate it) is much needed.

3.3.1.5 Developing Regional Models. Laboratory toxicity experiments and field surveys provide an adequate basis for quantifying the relationship, on a regional scale, between changes in pH, aluminum, and calcium and acidity-induced stress on fish populations. Thus, toxicity-based models, field-based models, and models that combine laboratory and field data can be used to evaluate the biological significance of projected changes in acid-base chemistry, given alternate deposition and emission scenarios.

Regional assessments of the effects of surface water acidification on fish require two components: the expected distribution of fish in the area in the absence of acidification effects (baseline status) and the ways to predict changes in the fish community as a function of water chemistry changes (prediction). The NAPAP Integrated Assessment developed two procedures for determining baseline status: (1) habitat evaluations based on fish habitat requirements known from the literature and (2) field-based empirical models that rely on statistical associations between fish status and measured habitat characteristics. Three procedures have been developed for prediction. The first, using toxicity models, predicts conditional mortality rates, or an acidic stress index (ASI), based on water chemistry and fish mortality in laboratory bioassays. The second procedure uses field-based empirical models, relating fish status to water chemistry. In the third procedure, models combining toxicity and field survey data were developed. Two types of models are available, Bayesian models and the Lake Acidification and Fisheries framework.

Development of baseline status is often more difficult and less precise than prediction. The approaches for the NAPAP Integrated Assessment vary among regions, due to fish data availability. Methods for conducting regional assessments of potential effects on fish in Mid-Appalachian streams include habitat evaluation for baseline status, and both toxicity models and field-based models for prediction of acidification effects.

3.3.1.6 Documentation of Effects on Fish. The loss of fish populations and/or absence of fish species as a result of acid-base chemistry has been documented for some lakes and streams in several regions of the United States. Applications of fish response models suggest that the percentage of NSWS waters with acid-base chemistry unsuitable for acid-sensitive fish species ranges from <5% in the Upper Midwest to nearly 60% for upper stream reaches in the Mid-Atlantic Coastal Plain. An estimated 23% of the Adirondack lakes and 18% of the Mid-Appalachian streams classified as potential brook trout habitat currently have acid-base chemistry unsuitable for brook trout survival.

Good quality survey data on the regional status of fish communities in the United States are limited; other natural and human factors also affect fish distributions. As a result, effects caused by acidification can be difficult to document. Nevertheless, intensive studies at a small number of sites in Mid-Appalachian streams have documented toxic conditions during episodes, fishkills, and loss of fish populations as a result of increasing stream acidity. An estimated 18% of potential brook trout streams in the Mid-Appalachians are too acid for brook trout survival; in about 30% of the streams, ASIs indicate that conditions are too acid for more acid-sensitive species that might be expected there.

In the southern Blue Ridge, few systems currently have baseflow pH levels detrimental to fish. However, these streams have low buffering capacity, and are vulnerable during increases in acidity, especially episodically.

Acidification of mountain streams in the SAMI region apparently has consequences outside the SAMI region. Declines in anadromous fish stocks may be explained partly by acidification. Nearly 60% of upper reaches of streams entering the Mid-Atlantic Coastal Plain are unsuitable for acid-sensitive species. Anadromous fishes (those that are spawned in freshwater, spend various amounts of time there, migrate to seawater where they attain sexual maturity, and then return to freshwater to spawn) have been shown to be among the most acid-sensitive fish in their freshwater phase. These species include Atlantic salmon, striped bass, and blueback herring; all show acid-induced stress at pH levels of 6.0–6.5. The contribution of acidification to losses of these species is difficult to evaluate because other factors such as overfishing and habitat loss also affect them.

3.3.2 Current Biological Impacts in the Southern Appalachians

The NAPAP synthesis documents (J. Baker et al., 1990) did not use regional boundaries perfectly coincident with the SAMI region. However, two of the regions overlap with the SAMI study area and the conclusions of the NAPAP study are applicable to surface waters in the SAMI region. The NAPAP mid-Appalachians region covers the SAMI study area in Virginia and West Virginia, plus most of Pennsylvania, western Maryland, and the Catskill Mountains of New York. The NAPAP Interior Southeast region consists of parts of the Piedmont and the SAMI study region (Figure 1) south of the Virginia/North Carolina, and Kentucky/Tennessee state lines.

3.3.2.1 Mid-Appalachians. In the mountains of western Virginia, the high-elevation, low ANC headwater streams in the area have fish assemblages dominated by eastern brook trout, the only salmonid native to the region (Cosby et al., 1991). Stocking with brown and rainbow trout is partly responsible for displacing brook trout from low-elevation reaches, but it has not displaced brook trout from habitats at higher elevations. The reaches farthest upstream contain brook trout or no fish at all. Farther downstream, mottled sculpins and blacknose dace co-occur with brook trout.

The extent of aquatic biological responses to acidic deposition has not been studied region-wide in the Mid-Appalachians. A study in western Maryland measured aluminum, calcium, pH, and fish abundance in 79 trout streams (Morgan et al., 1990). The mean pH of streams with fish was 7.1, compared with 5.4 for fishless streams; no brook trout were found in streams with baseflow pH < 5.5. In situ bioassays on brook trout and other fish species in the Mid-Appalachians have demonstrated adverse affects, including altered spawning behavior, reduced egg viability, decreased hatching rate, reduced survival, and reduced growth.

The current status and trends regarding region-wide acidification effects in the mid-Appalachians is difficult to assess because of the absence of large-scale fish surveys. In the SAMI region, losses of fish species associated with increasing stream acidity have been reported in Virginia (Little Stony Creek and St. Mary's River; Webb et al., 1989a,b) and in West Virginia (Cranberry River drainage; Zurbuch et al., 1986). In Pennsylvania, a study of 61 streams in the Laurel Hills region showed that 16% of the sites were fishless. Fishless streams had significantly lower pH values than streams with fish and they did not have acid mine drainage impacts. All the fishless streams were in largely undisturbed forests with base-poor bedrock types (Sharpe et al., 1987). Also in Pennsylvania, fish kills due to pH depressions during rainfall events have been confirmed in some Appalachian Plateau streams Wigington et al., 1993).

A three-year project on the effects of acid-base chemistry on fish communities in mountain streams in Virginia was started in Shenandoah National Park in 1992 (Bulger et al., 1995). Both chronic and episodic acidification are occurring in these streams. Biological differences in low ANC versus high ANC streams include fish species richness, population density, condition factor, age, size, and bioassay survival. In particular, both episodic and chronic mortality occurred in young brook trout exposed in low ANC streams, but not in high ANC streams (MacAvoy and Bulger, 1995), and blacknose dace in low ANC streams were in poor condition relative to dace in high ANC streams (Dennis and Bulger, 1995; Dennis et al., 1995). In the same study, blacknose dace and brook trout from a low ANC stream were able to detect and avoid acid pulses simulating an acid episode in the laboratory; they could also find neutral pH refugia (Newman and Dolloff, 1995). Predictive models relating fish status to future water chemistry are to be produced.

Dennis (1995) lists 26 species of fish found in Shenandoah National Park (based on the park's Fishery Management Plan). Ranges of critical pH for nine of these species were reported by Baker and Christensen (1991), who estimated average pH thresholds for a variety of negative effects observed in several studies for each species. Paine Run, which hosts three fish species, has been studied intensively since 1992 as part of the park's Fish in Sensitive Habitats (FISH) Project (Bulger et al., 1995). Episodic pH values within the critical range of all nine species have been recorded in this stream, and Paine

Run's baseflow pH (5.7–6.0) is within the critical pH range for two of the nine species whose critical pH range is reported by Baker and Christensen (1991). One of these two species, blacknose dace (critical pH range: 5.6–6.2), occurs in Paine Run, but individuals from that stream are significantly smaller than blacknose dace from higher ANC streams (Dennis and Bulger, 1995). Indeed, pH as low as 4.11 has been recorded for a small tributary of Paine Run (Dennis, 1995). It seems clear that elements of the fish community of Shenandoah Park are vulnerable to habitat loss resulting from future decreases in stream pH.

The NAPAP SOS/T report used two approaches to assess acidification effects in the Mid-Appalachian region: (1) ASI values calculated from pH, calcium, and inorganic monomeric aluminum using NSS index chemistry (see Section 5.3.3) and (2) a brook trout presence/absence model based on streams in western Maryland (Morgan et al., 1990) and southeastern Pennsylvania (Sharpe et al., 1987).

There are about 63,000 km of total stream length in the NSS-I target population in the Mid-Appalachian region. About 24% (15,000 km) of the NSS-I target population stream length exhibits sensitive fish ASI values > 10, indicating chemistry conditions unsuitable for acid-sensitive fish species. The highest ASI values occur in the western part of the region.

Potential brook trout habitat in the region was defined by the following criteria: elevation > 400 m, stream gradient 0.4–17%, and Strahler stream order (1:24,000-scale map) < 4. The entire mid-Appalachian region is within the zoogeographic range of brook trout, so all streams meeting the criteria were assumed to be potential brook trout habitat. About 37% (23,000 km) of the NSS-I target population can be considered potential brook trout habitat. Of these, 18% (4,100 km) have ASI-sensitive values > 30, indicating conditions unsuitable for brook trout.

3.3.2.2 Interior Southeast Streams. In Great Smoky Mountains National Park, fish surveys conducted periodically since the 1930s indicate a steady decline in brook trout range; similar declines in brook trout range have occurred elsewhere in the SAMI region. The reasons include habitat loss through logging, overfishing, and competition from introduced brown and rainbow trouts. Acidification is not considered a major factor yet, though brook trout do not occur in streams whose pH values approach 5.0. The only documented fish kills in the area associated with stream acidity have occurred at fish rearing facilities; these incidents involved introduced rainbow and brown trout, which are more acid sensitive than brook trout.

No adverse effects of acidic deposition on biota have been demonstrated conclusively so far in the southern Blue Ridge province (SBRP), except in fish hatcheries supplied by Raven Fork (North Carolina). Several fish kills of brown trout and rainbow trout in holding tanks supplied with water from Raven Fork have occurred during storms (Jones et al., 1983). Stream acidification was implicated as the cause of the fish kills based on observed streamwater pH/aluminum levels and the lack of trout mortality in limed streamwater. Elsewhere in the region, the relationship established elsewhere between low pH and species diversity indicates that any decreases in streamwater pH may produce decreases in species richness. As in the mountains of Virginia, fish assemblages in the low-order, high-elevation streams at risk are dominated by trout species, especially brook trout and rainbow trout, joined (moving downstream) by mottled sculpin and blacknose dace, creek chub and longnose dace, then assemblages of introduced salmonids, minnows, suckers, and darters. Aquatic invertebrate species richness and pH are positively correlated in this province, suggesting that declines in pH would result in declines in benthic macroinvertebrate diversity (Baker and Christensen, 1991).

Rosemond et al. (1992) report strong relationships between measures of benthic invertebrate community status and water chemistry in Great Smoky Mountains National Park. Baseflow pH values were 4.5–6.8, and inorganic monomeric aluminum was 3–197 µg/L. Total invertebrate density (excluding the acid-tolerant chironomids) and species richness were higher in the high pH streams; these effects were attributed to direct effects on invertebrate survival rather than on food availability.

Assessment of biological effects is limited to ASI toxicity models (see Section 5.3.3) because no region-wide surveys of chemistry and fish status are available. The highest acidic stress levels occur in the high-elevation areas of the southern Blue Ridge. Extreme acidic stress levels (ASI-sensitive values > 50) occur much less frequently than in other regions. About 24% (63,000 km) of the NSS-I target population stream length has ASI-sensitive values over 10, indicating conditions unsuitable for acid-sensitive species. Much of the acid-related stress in this region results from the very low calcium levels which are typical of regional geology classes.

Potential brook trout habitat in the region was defined by the following criteria: elevation > 1000 m, stream gradient 0.4–17%, and Strahler stream order (1:24,000-scale map) < 4. These criteria include only streams within the Southern Blue Ridge subregion, but all are within the zoogeographic range of brook trout. About 46% (24,000 km) of the NSS-I target population can be considered brook trout habitat; of this percentage, 11.5% (1,400 km) has ASI-sensitive values > 30. Perhaps 10% of streams otherwise suitable for brook trout are unavailable because of acidification; this estimate, however, contains much uncertainty. We do not have sufficient information to construct probability of presence models.

4. RECENT TRENDS IN ACIDIFICATION IN THE SOUTHERN APPALACHIANS

4.1 Trends in Surface Water Chemistry

Within the SAMI Class I areas, temporal trend information is available only for streams in Shenandoah National Park. In the late 1980s, White Oak Run and Deep Run both showed significant increases in SO_4^{2-} and decreases in pH (Ryan et al., 1989). At Coweeta, in the North Carolina Blue Ridge, there were no significant trends in acidity but there was a significant increase in SO_4^{2-} concentration (average of 0.7 µeq/L/yr) in all control watersheds between 1974 and 1982 (Swank and Waide, 1988). The SO_4^{2-} increases at these sites are consistent with a gradual saturation of soils in the region with SO_4^{2-} from deposition, and have been predicted by acidification models (Church et al., 1992). More recently, the SO_4^{2-} trends in Shenandoah National Park have been greatly altered as a result of forest defoliation by gypsy moth larvae (Webb et al., 1995). Defoliation has resulted in large increases in streamwater NO_3^- (up to 60 µeq/L), decreases in SO_4^{2-}, and little change in ANC or pH at baseflow. During storms, however, the increased leaching of NO_3^- in these watersheds has led to an increase in episodic acidification, with ANC decreases during episodes nearly twice the magnitude previously observed (Eshleman et al., 1995). We do not currently know how the streams will respond as the forests recover from defoliation.

It is likely that many parts of the SAMI region have undergone increases in NO_3^- over the past several decades. There are few data to verify this pattern, but it is supported by the few time-series data that do exist, and by the current patterns of streamwater NO_3^- distribution in the region. At Fernow Experimental Forest in West Virginia, NO_3^- concentrations have increased from near zero to 50–60 µeq/L at baseflow from 1970 to the present (Stoddard, 1994). In the Great Smoky Mountains National Park, NO_3^- shows strong correlations with elevation and forest age (Cook et al., 1994; Flum and Nodvin, 1995), with the highest concentrations (up to 100 µeq/L) occurring at high elevations (where deposition is highest; Shubzda et al., 1995) and in areas of old-growth forest where biological demand for nitrogen is lowest (Stoddard, 1994; Nodvin et al., 1995). It is very likely that a combination of high rates of N deposition, coupled with forest maturation in the park, have led to accelerated rates of N loss in the Smokies, and that this trend will continue as maturation of the forests at lower elevation progresses.

We do not know what effect the presumed increase in streamwater NO_3^- has had in the Smokies, but it is likely to have led to substantial cation depletion and ultimately to soil acidification in the region (Johnson and Lindberg, 1992). Many of the same streams that now show elevated NO_3^- concentrations are either chronically or episodically acidic (Flum and Nodvin, 1995; Nodvin et al., 1995).

4.2 Trends in Episodic Effects

It has been proposed that episodic changes in surface water pH during stormflow conditions may represent an "early warning" of sustained, chronic acidification impacts associated with regional-scale acidic deposition. However, only a few experimental or modeling studies of long-term changes in episodic conditions have been conducted, due to a general lack of data with which to statistically evaluate trends or to parameterize an appropriate predictive acidification model (Neal et al., 1992; Hooper and Christophersen, 1992; Eshleman et al., 1995). One of these studies (Eshleman et al., 1995) was conducted within the SAMI region in Shenandoah National Park.

Two modeling studies have been conducted using the predictive acidification model, MAGIC (see section 5.1.2.2). The study by Neal et al. (1992) used MAGIC in two-component mode (i.e., MAGIC was calibrated for two distinct soil horizons and the resulting solutions were mixed according to known proportions based on chemical hydrograph separations). The technique was applied to the Afon Gwy catchment in mid-Wales, with results demonstrated in the forms of (1) 3-month sequences of hydrogen ion and inorganic aluminum concentrations and (2) chemical duration curves for hydrogen ion and aluminum. The most important finding in the study was that aluminum concentrations in the stream did not recover as rapidly as had previously been thought, in response to reductions in sulfur deposition. The second modeling study, by Hooper and Christophersen (1992), of long-term episodic changes in stream chemistry at Panola Mountain (Georgia) largely supported the hypothesis that stormflow conditions provide an “early warning”; while baseflow chemistry gradually became acidic over a 50-year modeling period, acidification of two upper soil layers occurred more rapidly, causing acidic conditions during stormflow periods. Although this work was located geographically outside the SAMI region, the results of Hooper and Christophersen (1992) appear to provide a reasonable hypothesis for long-term changes in episodic conditions in other southern Appalachian mountain waters.

The analytical study of Eshleman et al. (1995) involved the use of a hydrological separation program and long-term daily flow and weekly chemical data from White Oak Run, Virginia. A statistical analysis of 13 years of daily discharge data and weekly streamwater composition data for White Oak Run in Shenandoah National Park was performed in order to quantify episodic changes in composition and to identify long-term trends in episodic acidification attributable to both natural and anthropogenic processes. An objective hydrological separation technique was used to identify more than 100 “stormflow/baseflow pairs” in the database, from which episodic chemical changes could be quantified. Univariate statistical analysis suggested that mean episodic depressions of ANC in White Oak Run have increased by about a factor of 2 since the first outbreak of forest defoliation by the gypsy moth caterpillar during the summer of 1990; in addition, the mean episodic change in NO_3^- concentration has increased by about 12 µeq/L, while the mean episodic dilution of C_B has decreased from -8.5 µeq/L to -1.7µeq/L during the same period. Episodic changes in SO_4^{2-} have remained the same, however. The results indicate that natural processes such as insect defoliations can contribute to episodic acidification through mobilization of NO_3^-. Results from the study did not demonstrate any long-term changes in episodic conditions associated with atmospheric deposition, presumably due to the larger, overwhelming influence of the gypsy moth defoliations. Other experimental and modeling studies of long-term trends in episodic conditions are needed for the SAMI region.

4.3 Trends in Biological Effects

It is difficult to quantify trends in biological condition because few datasets have good biological data over time. It is also difficult to differentiate the effects of acidic deposition from other anthropogenic effects. Thus, it is not possible to make a definitive statement about trends in biological effects related to acidic deposition in the SAMI region. There is at least one stream in the area, however, in which fish declines are probably the result of acidification: the St. Mary's River in George Washington National Forest in the Virginia Blue Ridge. Surveys in 1988, compared to those in the 1930s, showed declines in acid-sensitive fish and invertebrates, coincident with lower pH values (Webb et al, 1989a,b).

5. METHODOLOGIES FOR PREDICTING FUTURE EFFECTS OF ACIDIC DEPOSITION

5.1 Surface Water Chemical Models

A large number of models have been developed over the years to predict and/or explain surface water chemical response to acidic deposition. These models fall into two general categories: steady state, and dynamic. Most of these models were comprehensively reviewed and cited in the NAPAP SOS/T Report #14 (Thornton et al., 1990) and the next two subsections briefly summarize those findings. Most of the NAPAP modeling effort focused on sulfur chemistry. It has become more apparent over the last 5 years, however, that NO_3^- is increasing in some areas and needs to be treated more explicitly. Thus, a number of modeling efforts have recently been developed to incorporate N dynamics in future projections of surface water acid-base chemistry.

5.1.1 Steady-state Models

Steady state refers to the condition in which outputs equal inputs. In other words, after a perturbation such as acidic deposition, lake or stream chemistry (output) will eventually reach an equilibrium with the new chemical input levels. In general, steady-state models use current water chemistry to estimate steady-state conditions for both preindustrial conditions and the eventual future condition for a given level of acidic deposition. Steady-state models have no explicit time component; the lake or stream is assumed to be in equilibrium with atmospherically deposited SO_4^{2-} in both the past and future scenarios. Future changes in ANC are then usually estimated from the change in SO_4^{2-} either empirically or by using a charge-balance approach that calculates ANC decline as some fraction of the change in SO_4^{2-}. This fraction has been named the Henriksen F-factor (after its inventor) and relates the proportion of added SO_4^{2-} that is balanced by increased base cation concentration. Thus, an F=1 means that all the additional SO_4^{2-} is balanced with additional base cations (no ANC or pH decline). An F=0 indicates that no base cations are released and that all the added SO_4^{2-} is balanced against a decline in ANC (additional H^+ or Al^{n+}). As one would expect, steady-state models using the F-factor approach are very sensitive to the value of F used in the model, and various approaches have been used to estimate F. Thornton et al. (1990) concluded that most steady-state models were not appropriate for use in the NAPAP assessment because they had: (1) unrealistic assumptions concerning the level of watershed neutralization (F-factor), (2) a lack of biological relevance (no aluminum predictions), and (3) problems in applying the models outside the regions for which they were first developed.

5.1.2 Dynamic Models

Whereas steady-state models have no explicit time component, dynamic models project water chemistry for specific days, months, or years. Dynamic models integrate our current understanding about the hydrological and biogeochemical processes that occur as acidic deposition falls on watersheds and is transported into lakes and streams. The modeled mechanisms include hydrologic flow routing, soil-water interactions (including soil-water contact time), anion retention, base cation exchange, mineral weathering, and other watershed processes (e.g., vegetative uptake and organic interactions). The mechanisms are modeled with varying degrees of complexity among the different dynamic models but they are all are much more complex and time consuming and they have larger data input requirements than steady-state models. The two dynamic watershed models of most use to an assessment of the aquatic effects of acidic deposition in the SAMI region are the ILWAS (Integrated Lake-Watershed Acidification Study) and MAGIC (Model of Acidification of Groundwater in Catchments) models.

5.1.2.1 ILWAS. The ILWAS model (Chen et al., 1983; Gherini et al., 1985) was developed as a research tool to further understanding about the processes affecting acid-base chemistry in Adirondack lakes. It is a process-oriented model that uses both equilibrium and rate-limited expressions to describe the mass balances for acid-base chemistry. ILWAS has three modules: canopy, hydrologic/soil, and within lake. ILWAS is quite complex; it models more processes with more compartments (e.g., soil layers) than the other dynamic models. Thus it has greater input data requirements and is more time consuming to run and calibrate. ILWAS requires daily meteorological data, weekly or monthly deposition chemistry, watershed vegetation types and coverage, watershed attributes, physical/chemical soil data, lake/stream hydrological data, and initial water chemistry. All in all, it requires specification of more than 200 parameters, coefficients, and initial conditions for model calibration. Model results can be output over a range of time steps from daily to annual.

5.1.2.2 MAGIC. MAGIC (Cosby et al., 1985a,b; 1986a,b) is a lumped parameter model of intermediate complexity developed to project the long-term effects (decades to centuries) of acidic deposition on responses in average annual stream or lake chemistry. It was originally developed for streams in Shenandoah National Park. MAGIC was formulated to be parsimonious in selecting processes for inclusion in the model. It assumes that only a few key processes influence the long-term response of watersheds to acidic deposition. MAGIC has a separate hydrologic flow routing component that runs on a daily time step. Hydrologic data are averaged and the rest of the MAGIC model has a monthly or annual time step. MAGIC has two soil layers and a lake/stream component, and both equilibrium and rate-limited expressions are used to describe the mass balances for acid-base chemistry. MAGIC requires annual meteorological/ deposition data, watershed attributes, physical/chemical soil data, lake/stream hydrological data, and initial water chemistry. Model results can be output seasonally or annually. It does not simulate episodic responses.

A regional MAGIC model has been developed to project the acid-base status of regional stream/lake populations rather than individual sites (Hornberger et al., 1986, 1987). Regional MAGIC is structurally and functionally similar to MAGIC for individual sites. It has the same data input requirements. The major difference is that in Regional MAGIC, inputs and outputs are in the form of regional distributions, not individual values. Regional MAGIC is also calibrated differently; a set of simulated watersheds is generated by random sampling from the input distribution data and then calibrated to fit an observed distribution of water chemistry from a regional survey. It is important to note that the output projects how a regional distribution will change over time and reflects simulated watersheds. It cannot be used to project conditions for any specific watershed or geographic location within the region.

5.1.3 Nitrogen Models

Three models of nitrogen dynamics are being used currently, or are being developed, to assess the acid-base status of surface waters. One of the models (MAGIC-WAND) is incorporated directly into the MAGIC model. The others provide input that can be used to set up the MAGIC model to run with the influences of N deposition included. Each model is described briefly here.

5.1.3.1 Model of Acidification of Groundwater in Catchments – With Aggregated Nitrogen Dynamics (MAGIC-WAND). MAGIC-WAND is a direct modification of the MAGIC model that includes some simple representations of the N cycle (Cosby, pers. comm.). Nitrogen is assumed to be present only in solution in soil water. Nitrogen inputs to the system are in the form of inorganic N added to the soil solution, and are represented as atmospheric deposition and mineralization. The rates for these inputs must be entered *a priori*. Nitrogen losses from the system are represented as hydrologic runoff and denitrification. Transformations included in the model are nitrification and uptake. The primary limitation of MAGIC-WAND is that it includes no internal feedbacks (e.g., mineralization rates must be entered *a priori*, and do not depend on changes in other processes or on N pools). Its major strength is that it is directly incorporated into MAGIC, so that direct outputs of the variables of interest (e.g., time series of ANC) can be made.

5.1.3.2 Model of Ecosystem Retention and Loss of Inorganic Nitrogen (MERLIN). MERLIN is a stand alone nitrogen-cycling model, adapted from the Generalized Ecosystem Model (GEM; Rastetter et al., 1991). It is probably the most realistic of the three models available, and therefore also requires the most detailed inputs (Cosby, pers. comm.). The processes in MAGIC-WAND are included in MERLIN, not as driving variables, but calculated from internal state variables. The carbon and N pools of the terrestrial compartments (photosynthetic biomass, wood, litter, labile organic matter, refractory organic matter, etc.) are modeled explicitly and the carbon:nitrogen ratios in these pools feed back and affect the N transformation processes. Data on the carbon and N pool sizes in each compartment, plus all the fluxes between compartments, are needed for calibration. The realistic nature of this model (particularly the division of soil organic matter into labile and refractory pools) is clearly advantageous. Its major drawback is the detailed input data required to run the model; many of the transformation rates (e.g., into and out of the soil organic matter pools) are not known for many sites. This is still a rapidly developing model, and the results of its application to any existing sites are not yet available.

5.1.3.3 Net Photosynthesis and Evapo-Transpiration (PnET) – Carbon and Nitrogen (CN) Model. PnET-CN (Aber and Federer, 1992) has evolved from a relatively simple model of gross and net photosynthesis to one that now includes cycles of water, carbon, and nitrogen in a monthly time step (Aber et al., in press). Because it evolved from a "tree-growing model," it focuses on the effects of forest development, and the terrestrial processes that accompany it, on N dynamics. The latest version of the model includes litter decomposition and turnover, as well as transfers between terrestrial compartments (roots, foliage, wood, and soil), and incorporates site history (land use disturbance) into the transformation rates between compartments. The model has been applied to a large number of sites with remarkable success, especially considering that it is not truly "calibrated" (e.g., the model parameters are not tuned so that they reproduce current conditions before the model is run to predict future conditions) to each site. For example, it accurately reproduces the record of NO_3^- outputs from the Hubbard Brook control watershed for the last three decades (Aber et al., in press). Although the model requires a large number of parameters to run, it has been very successfully applied using literature values for different forest types (e.g., hardwoods vs. conifers). The key site-specific variables needed to run the model successfully are climatic variables (temperature and precipitation), foliar N content, and land use history.

5.2 Episodic Chemical Models

The 1990 NAPAP assessment of current and future acidification impacts of acidic deposition recognized that assessments based solely on chemical conditions during "index periods" (i.e., periods that approximate average annual or seasonal conditions) did not account for the "worst-case" chemical conditions that usually occur during extreme hydrological events. However, because of the rather large uncertainties associated with incorporating episodic acidification into the regional assessment framework, model-based projections of watershed responses to emissions reduction scenarios were not formulated to account for changes in episodic acidification over long time periods.

Since completion of the 1990 NAPAP assessment, several modeling approaches have been utilized to predict future episodic chemical responses to a variety of emissions/ deposition reduction scenarios (Neal et al., 1992; Hooper and Christophersen, 1992; Eshleman et al., 1995), although none has yet been applied to a watershed in the SAMI region. Two of the published studies were conducted on individual watersheds and utilized the MAGIC model, while one of the studies was conducted at the regional scale and utilized a regional modeling approach. Depending upon the nature of the integrated assessment desired by SAMI (local scale or regional scale), any one of these three approaches could be employed to address the issue of episodic changes in surface water acid-base status resulting from changes in deposition loadings. Two key issues that will need to be addressed before conducting such an assessment are: (1) the assumptions inherent in each of the modeling approaches and (2) the availability of watershed and surface water data for model calibration and testing.

5.3 Modeling the Effects of Acidic Deposition on Fish Communities

The primary goal of the mathematical/ statistical models that evaluate the effects of acidic deposition on fish communities is to predict future effects on biological resources based on projected changes in water chemistry. Few models for regional assessment of acidification have been developed, and most deal only with fish responses; most of these deal with fish species presence or absence, but more sophisticated response variables are increasingly being modeled. This report considers three kinds of models: field-based empirical models, toxicity models, and models that combine toxicity (laboratory) data with field observations.

5.3.1 Empirical Models

Empirical or field-based models are based on associations between fish status and water chemistry as they exist in nature, and are typically constructed from survey data. The future values of variables that turn out to be most strongly correlated with fish status are estimated with the model, and fish status is predicted from its association with those variables. These models make two assumptions: (1) the systems surveyed are in steady state, and (2) the observed associations between fish status and water chemistry accurately reflect what would occur over time.

These empirical models do not assume that the variables most strongly associated with fish status (or with greatest predictive capacity) in a given data set directly control fish status in a mechanistic way, although the mechanistic linkages are often easy to imagine. For example, ANC often shows a strong relationship to fish status, but it is clear that fish do not respond directly to ANC; however, ANC controls pH, which controls aluminum, which is toxic. Likewise, variables that have well-understood mechanistic effects on fish do not always show strong empirical relationships with fish status in survey data. An example is calcium, which ameliorates acid stress; it is not always a good predictor of fish status, because healthy populations exist at high as well as low calcium concentrations, in the absence of acid stress; in the presence of acid stress, most of the benefits of elevated calcium are achieved at 150 µg/L, and further increases produce smaller improvements. Fish presence or absence, measures of fish population status, or the number of fish species (richness) in a body of water or region have been estimated with empirical models. Multiple regression analysis is usually the statistical tool used in empirical models, with either a two-state response variable, such as presence or absence, using logistic regression, or a multiple-state or continuous response variable, using standard regression.

In all cases, the data set must be purged of bodies of water which have known explanations for fish loss other than acidification, if the remaining differences among lakes or streams are to be attributed to acidification effects on fish. In this connection, two other physical attributes of bodies of water must be taken into account in modeling efforts: size and elevation. For example, larger lakes and lakes at lower elevation tend to support more species of fish, all else being equal. For the SAMI region, focusing on mountain streams, size and elevation are probably correlated to some extent, so smaller streams and streams at higher elevation are expected to host fewer species.

5.3.2 Toxicity Models

Toxicity models are covered in some detail in this synopsis because they provide the opportunity for near-term assessments of acidification effects on fish populations in the SAMI region. J. Baker et al. (1990) define toxicity models in the context of acidification as mathematical functions fitted to fish responses in laboratory studies with constant levels of pH, inorganic monomeric aluminum, and calcium. Regression models are then used to estimate the acidification effects on fish associated with aluminum, pH, and calcium levels measured in the field. Because they are based on variables with known toxic (aluminum and pH) or mitigating (calcium) effects, the mechanistic linkages between fish response and acid-base chemistry are established at the outset. This is an advantage, but two important disadvantages to toxicity models remain: (1) the field survey data used as input frequently do not capture the extreme events to which sensitive life stages of fish may be exposed in nature and (2) the model output is best at estimating percent mortality in laboratory studies and cannot easily be interpreted directly as a population level response. The primary advantage of toxicity models is that they can deal with the joint effects of pH, aluminum, and calcium.

5.3.3 Combined Toxicity-Field Models — he Acid-Stress Index

The approach used to model the effects of acidity on fish in the 1990 NAPAP assessment converted the joint effects of pH, inorganic monomeric aluminum, and calcium into a single, biological response variable, called the acid stress index (ASI). Three criteria were used for the data sets used to create the ASI toxicity models. The first was that aluminum, calcium, and pH were measured as part of the experimental design. Secondly, the data sets were based on observations of fish mortality as opposed to sublethal stresses; the reasons being that mortality is most often used as an observational endpoint, and, while sublethal stresses are important, they are difficult to interpret as population level effects. Lastly, the data sets were based on observations of early life stages; the reasons being that there are large number of such studies, early stages are usually the most sensitive stage, and early life stage mortality has a clear effect on population recruitment.

Toxicological experimental elements of the Lake Acidification and Fisheries (LAF) framework (Mount et al., 1988a,b) were specifically designed to produce results that could be incorporated into regression models; thus the LAF data are an important resource for the ASI models. The four freshwater species used in the LAF framework were brook and rainbow trouts, smallmouth bass, and white sucker. Four levels of fish sensitivity to acidity were modeled: tolerant, intermediate, sensitive, and anadromous. Since not all fish species potentially affected by acidification can be practically modeled, three species from the LAF data were used in toxicity models as reasonable representations of the range of responses possible in fish communities.

1. Tolerant Toxicity model: 21-day survival of brook trout fry.

2. Intermediate Toxicity model: 8-day survival of smallmouth bass alevins.

3. Sensitive Toxicity model:

21-day survival of rainbow trout fry.

It became necessary to incorporate an even more sensitive life form after it was discovered that anadromous species (those that are spawned in freshwater, spend various amounts of time there, then migrate to seawater, attain sexual maturity, then return to freshwater to spawn) are among the most acid-sensitive fish in their freshwater phase, even more sensitive than rainbow trout. Example of such species include Atlantic salmon, striped bass, and blueback herring; all show acid-induced stress at pH levels of 6.0–6.5. Thus a fourth toxicity model was developed specifically for use in the Mid-Atlantic Coastal Plain, using 4-day survival of blueback herring alevins as the basis for the anadromous model. This fourth model would be relevant only in estimating effects of acidification outside the SAMI region.

5.3.3.1 Acid Stress Index Model Structure. The proportion of fish surviving a toxic exposure was regressed as a function of the values of pH, Al, and Ca, using maximum likelihood regression; considerable literature exists to support this choice of model; the predicted variable was converted to percent mortality (0–100%), and adjusted for "background" (not due to acid stress) mortality. The mortality percentage due to acid stress is referred to as "conditional mortality rate" and called the acid stress index (ASI). Thus higher values of ASI indicate greater stress caused specifically by acidification. It is a characteristic of the water whose chemistry is modeled.

For each toxicity data set, alternative models structures were evaluated using various combinations of pH, inorganic Al, and Ca, plus squared and interactive terms. The final coefficients included for each of the four models were based on three criteria.

1. Visual (graphical) examination of the model fit to the data set and realism of the model output outside the range of chemistry variables tested.

2. Statistical significance of model parameters (only variables significant at $p < 0.05$ were included).

3. Model r^2, calculated by the goodness-of-fit chi-square for the intercept-only model (X) to the goodness-of-fit chi-square for the full model (Y).

The variables used in the toxicity models are pH in standard units, Al in µg/L, and Ca in µeq/L. The model r^2 values were 0.70, 0.80, 0.79, and 0.78 for tolerant, intermediate, sensitive, and anadromous models, respectively. The intercept and coefficients for each of the four models may be found in Table 13-42 of SOS/T 13 (J. Baker et al., 1990). The generalized model structure is:

$$ASI\ (\%\ mortality) = 100/[1 + \exp(a + b_i x_i)]$$

where x_i are values of the three chemical variables and b_i are their coefficients. Some restrictions were placed on model output. The ASI was assumed to be zero at pH > 8.0, and at Ca concentrations > 2000 µeq/L; inorganic Al concentrations were assumed to be zero at pH > 6.5.

5.3.3.2 Acid Stress Index Model Evaluation. In regional applications of the toxicity models, outputs are intended to represent index responses of tolerant, intermediate, and sensitive fish species, rather than just the species for which the models were developed. Index or baseflow levels of pH, Al, and Ca were used to calculate ASI values for individual water bodies. To determine the suitability of this approach, two types of evaluations were executed: interspecies comparisons and comparison to field population responses. For interspecies comparisons, the focus was on the applicability of the sensitive model to estimates of effects on other sensitive species. Agreement between the experimental mortalities of common shiner and blacknose dace, typical of a group of sensitive cyprinid fish, and the output of the sensitive model predictions of mortality was considered adequate.

ASI values were also compared to field observations of fish population responses. Predictions (ASI values) derived from lab studies do not include natural variation in chemistry or other variables which affect survival in nature. Nor do these predictions consider biological compensation (positive effects on the survivors due to reduced density resulting from deaths of some of the population). Nevertheless, it is clear that the ASI has value as an index, based on comparisons with three data sets from (1) Adirondack lakes, (2) Ontario lakes, and (3) western Maryland streams. For lakes, the likelihood of presence of brown bullhead was about 50% when the ASI-tolerant values were about 30; thus, waters with an ASI value > 30 would appear, on average, to have acid-base chemistry unsuitable for the survival of brown bullheads. Brook trout were lost from waters (likelihood of occurrence = 50%) at ASI-tolerant values above 10. The likelihood of occurrence was 50% when ASI-intermediate values were near 80 for lake trout and ASI-sensitive values were near 80–90 for common shiner.

The relationship between ASI and fish presence/absence clearly differs between streams and lakes. Stream fish populations appear to be affected at much lower values of ASI. Since ASI values are calculated from the index (baseflow) chemistry values, this difference in response probably reflects the more significant role of episodic acidification in streams versus lakes. As a result, both brook trout and blacknose dace presence/absence appeared to be best represented by the sensitive model in streams, with reference ASI values of >30 and >10 for brook trout and blacknose dace, respectively.

Although there is not a one-to-one relationship between ASI and population-level effects, the NAPAP study concluded that toxicity-based model outputs can be useful as an index of probable acidification stress at the population level. As a result, reference levels of ASI were associated with the following fish responses for *streams* (Table 13-43 in SOS/T 13, J. Baker et al., 1990):

- ASI-intermediate values > 30: Loss of all species
- ASI-sensitive values > 30: Loss of brook trout
- ASI-sensitive values > 10: Loss of acid-sensitive species, e.g. minnows

It is very important to note that ASI models constructed from lab experiments taken by themselves appear to underestimate the acidification stress experienced by populations in nature. For example, streams that have lost brook trout populations have index values of pH, Al, and Ca that would result in as little as 30% mortality of the more sensitive rainbow trout fry in lab bioassays (see above, ASI-sensitive > 30, associated with loss of rainbow trout populations). This is no doubt caused in part by temporal and spatial variation in chemistry, e.g., episodes of poor water quality which occur during sensitive life stages of fish. It would be preferable to include episodes into predictions of fish status, but regional-scale data sets are lacking, and exposures during episodes are themselves difficult to characterize. Thus, given the uncertainties and limitations regarding chemical variation in nature, the NAPAP Assessment used ASI values based on index chemistry, but interpreted them in light of reference ASI values based on field observations as indices of probable population effects.

6. PREDICTIVE STUDIES OF ACIDIC DEPOSITION EFFECTS IN THE SOUTHERN APPALACHIANS

6.1 NAPAP Modeling Efforts

The NAPAP efforts to model future changes consisted of the Direct/Delayed Response Project (DDRP) and the 1990 Integrated Assessment (IA). In the SAMI region, both efforts focused on the potential effects of acidic deposition on surface water ANC during the spring baseflow index period defined and sampled by the NSS. The time horizon for these analyses was 50 years, starting in 1985. The primary processes modeled were (1) the retention of deposited sulfur within watersheds and (2) the supply of base cations from watersheds to surface waters. These two processes had been identified by a National Academy of Sciences panel as the most important watershed processes affecting or mediating long-term surface water acidification (NAS, 1984).

The DDRP (Church et al., 1989, 1992) and IA (NAPAP, 1991) modeled streamwater chemistry responses to various deposition scenarios in two regions of the eastern United States: the Mid-Appalachians (MIDAPP) and the Southern Blue Ridge Province (SBRP). The SBRP modeling region is entirely within the SAMI region, but it does not include parts of the Blue Ridge located in Virginia and northern North Carolina. The MIDAPP modeling region contains all the acid-sensitive SAMI study region in Virginia and West Virginia, plus large parts of Pennsylvania and the Catskill region of New York.

Three watershed models were applied to streams in the SBRP:

1. The Model of Acidification of Groundwater in Catchments, MAGIC (Cosby et al., 1985a,b; 1986a,b).
2. The Enhanced Trickle Down (EDT) model (Lee, 1987; Nikolaidis et al., 1988; Schnoor et al., 1986).
3. The Integrated Lake-Watershed Acidification Study (ILWAS) model (Chen et al., 1983; Gherini et al., 1985).

These models integrated the current understanding of how various watershed processes interact and respond to acidic deposition. The three models used common datasets for forcing functions (e.g., rainfall, runoff, atmospheric deposition) and used data aggregated from the DDRP soils database for state variables such as soil physical and chemical characteristics (Church et al., 1992).

Although absolute values of modeled concentrations of constituents varied in comparisons for individual watersheds, Church et al. (1989) reported that projections of changes in ANC among the models were remarkably consistent *on a regional basis*. Rather than repeating costly and time consuming duplicative modeling analyses, Church et al. (1992) used only the MAGIC model for projections in the MIDAPP. They reported that MAGIC was by far the easiest, quickest, and least expensive to apply. For the same reasons, NAPAP (1991) used MAGIC as the primary method for projecting and comparing the chemical responses of SBRP and MIDAPP streams to various deposition scenarios in the 1990 Integrated Assessment Report.

The DDRP and IA modeling efforts were intended to estimate the general direction and the relative magnitude of possible future changes in surface water acid-base chemistry under alternative scenarios of atmospheric sulfur deposition (Church et al., 1992). The projections of these models were not intended to be forecasts of future conditions, but tools to evaluate the relative effectiveness of alternative emission controls. The modeled stream population for all three assessments is the downstream ends of NSS stream segments with drainage areas < 30 km^2. In addition, only streams with ANC < 200 µeq/L and no substantial watershed sources of sulfate or chloride were included in the MIDAPP population. These criteria eliminated about 30% of the NSS target population in the SBRP and 42% in the MIDAPP, and restricted the model inferences to the subset of streams likely to respond to acidic deposition inputs over the next several decades. However, the projections were calibrated on the downstream ends of the NSS stream reaches and estimate the chemistry for these ends. ANC at the lower ends of these streams was generally higher than at the upstream ends (Table 1), so these projections overestimate ANC and underestimate changes in ANC for the upper ends. For these reasons, the model baseline conditions will not agree with the NSS current status estimates that include streams over a broader size and disturbance spectrum.

6.1.1 Model Results

The basic results and conclusions of the IA agree with the DDRP results of Church et al. (1989, 1992), and primarily the IA results appear in the following outline of future modeling projections. Furthermore, we have borrowed freely from Church et al. (1989, 1992) and NAPAP (1991) in the wording of most of these conclusions. Both the DDRP and the IA modeled a projection of current deposition and defined it as the 1985 level. All deposition scenarios extend to 50 years beyond 1985. The basic results and conclusions of the future modeling efforts are as follows.

6.1.1.1 Sensitivity to Acidification. Three percent of the modeled MIDAPP stream population currently is acidic and 15% has ANC ≤ 50 µeq/L. The streams in the MIDAPP highlands with lowest ANC are generally restricted to small, forested watersheds at relatively high elevations (> 300 m). These streams are expected to be the most sensitive to acidic deposition. None of the streams sampled by the NSWS in the SBRP was chronically acidic, but 12% of the modeled subpopulation had ANC ≤ 50 µeq/L. Streams in the SBRP may be responsive to changes in acidic deposition, but the response is delayed more than that of MIDAPP streams because watershed soils are retaining more sulfate from acidic deposition. Church et al. (1989) estimated that their watersheds are currently retaining three-quarters of the atmospherically deposited sulfur on the average, but projected that their soils will become more saturated with sulfur over time. As a result, they project that watershed sulfur retention will decline, increasing sulfate concentrations in the surface waters of this region. The response is projected to be marked over the next 50 years at either current or increased levels of sulfur deposition, as are decreases in streamwater ANC. Superimposed upon this effect is a relatively minor acidification effect of base cation depletion (Church et al., 1989).

6.1.1.2 Projections for Current and Increased Deposition. Streams in the MIDAPP and SBRP are projected to acidify (decrease in ANC over time) under current levels of deposition (Figure 12). Streamwater concentrations of sulfate are projected to increase substantially over the next 50 years, accelerating both cation leaching from soils and the projected acidification of surface waters. Median ANC of streams in the MIDAPP and SBRP would decrease about 20 µeq/L over 50 years at current levels of atmospheric sulfur deposition, because less sulfate is being retained by soils over time. ANC would change by about 3 to 4 µeq/L in addition to the 20 µeq/L decrease for each

Figure 12. Future projections of stream ANC and pH after 50 years for 6 sulfate deposition scenarios for (a) Mid-Atlantic Highlands (includes Pennsylvania, Maryland, and New York) and (b) Southern Blue Ridge. Taken from Figures 4.4-7 and 4.4-9 in 1990 NAPAP Integrated Assessment. CSC are the current (1985) simulated conditions at year 0. The six future deposition scenarios are:

-50%:	Current levels for 5 years, ramp down 50% over 10 years, then constant.
-30%:	Current levels for 5 years, ramp down 30% over 10 years, then constant.
-20%:	Current levels for 5 years, ramp down 20% over 10 years, then constant.
0:	Current deposition level for 50 years.
+20%:	Ramp up 20% above current levels over 25 years, then constant.
+30%:	Ramp up 30% above current levels over 25 years, then constant.

kg/ha/yr change from current sulfur deposition over 50 years. Under current levels of deposition over 50 years, 46% of streams would experience ANC declines of ≥ 10 µeq/L;15% of streams would experience pH declines of ≥ 0.3 units.

In the MIDAPP, a decline in the regional median ANC of about 25 µeq/L is projected over 50 years. After 50 years at current levels of deposition, 10% of MIDAPP streams are projected to be acidic and 24% would have ANC ≤ 50 µeq/L (Figure 12). At sulfur deposition 20% and 30% greater than current levels, the number of acidic MIDAPP streams is projected to increase by factors of 5.4 and 6.2, respectively, over the next 50 years. In the SBRP, projections suggest that after 50 years at current levels of deposition, about 10% of the streams will be acidic and 15% will have ANC ≤ 50 µeq/L (Figure 12). A 20% increase in deposition would result in an increase to 10–12% acidic streams and 23–26% with ANC ≤ 50 µeq/L.

6.1.1.3 Reduced Deposition Scenarios. With reduced deposition, projected changes in streamwater sulfate will ultimately respond to the level of deposition. Model projections suggest that a 20–30% reduction in sulfur deposition would be necessary to prevent further acidification in MIDAPP streams over the next 50 years; reductions of 30–50% would be required in the SBRP. Because of the substantial amount of sulfate adsorption in SBRP soils, a delay in the reduction of sulfur deposition would be expected to result in acidification greater than that which would occur with no delay. These effects would occur beyond the 50-year time frame modeled.

6.1.1.4 Chemical Conditions for Fish. The projected acidic stress indices for sensitive fish species suggest that biological conditions in low ANC MIDAPP streams will deteriorate under current deposition levels. The simulated current percentage of MIDAPP stream segments with downstream end water chemistry unsuitable for sensitive fish species (e.g., rainbow trout, blacknose dace) is 21%. With a 30% increase in sulfur deposition, this percentage is projected to increase to 34%. With a 50% decrease in sulfur deposition, it would remain at 21%. A 25-year delay in the reduction of sulfur deposition is projected to increase the number of MIDAPP streams unsuitable for sensitive fish species by 6% during the 50-year modeling period. If unsuitable chemical conditions eliminate reproducing populations of fish and other aquatic biota from some streams, they will have to recolonize these streams from other locations and may not return until well after chemical conditions permit. Estimates of fish response were not made for streams in the SBRP because the IA researchers did not find field information relating fish status to stream acid-base chemistry and felt that the uncertainties of extrapolating models developed elsewhere were too great (NAPAP, 1991).

6.1.1.5 Uncertainties in Model Projections. Uncertainties in the projections for timing of aquatic effects are high because of uncertainties in sulfate adsorption-desorption dynamics and in the relative importance of weathering versus cation exchange processes (NAPAP 1991). Additional uncertainty results from the fact that acidification from nitrogen deposition was not considered in the modeling. However, limited field observations of ANC trends in MIDAPP streams are in the low end of the predicted range of modeled ANC changes. Conclusions regarding future effects from acidic deposition are considerably more uncertain in the SBRP than in the MIDAPP, primarily because of the difficulty of predicting future changes in sulfur retention by soils. Effects are likely to occur beyond the 50-year time frame used in the modeling.

6.2 Nitrogen Bounding Study

Most of the efforts at dynamic modeling of watershed acidification that were carried out as part of NAPAP (see section 6.1) did not consider the potential influence of changes in watershed nitrogen retention on model forecasts. The Nitrogen Bounding Study (NBS; Van Sickle and Church, 1995), whose results were also reported as part of the Acid Deposition Standard Feasibility Study (U.S. Environmental Protection Agency, 1995) was an attempt to bracket the potential effects that nitrogen saturation might have on future acidification. The NBS used the modeling techniques of the DDRP, several different scenarios for future nitrogen and sulfur deposition, and hypothetical time sequences for nitrogen saturation to predict the percentages of streams that would be either chronically acidic (ANC < 0) or susceptible to episodic acidification (ANC < 50 µeq/L) in the future.

In the case of the Mid-Appalachian region, the study predicted that 8% of streams would become acidic at current rates of nitrogen deposition and forecasted rates of sulfur deposition (roughly half of 1985 rates), if nitrogen saturation occurs in 50 years. Approximately 40% of streams would be episodically acidic under the same scenario. If the time to nitrogen saturation is expanded to 250 years, current rates of N deposition would lead to chronic acidification in 4% of streams and episodic acidification in 28% of streams.

The NBS predicted much lower rates of acidification in the southern Blue Ridge, where 4% (chronic) and 16% (episodic) of streams would be acidified with a time to saturation of 50 years. With a 250-year time to saturation, the models predicted no streams would be chronically acidic, and 14% would be susceptible to episodic acidification. These modeling results are somewhat at odds with information about the current status of streams in the SBRP. Some streams in Great Smoky Mountains National Park are acidic and have high nitrate concentrations. These streams tend to occur at high elevations, whereas the DDRP sampling design was based on the lower elevation downstream segment end population. Thus, the NBS results based on the DDRP are biased toward lower elevation streams (Cook et al., 1994), leading to more conservative forecasts for future acidity.

7. RECOMMENDATIONS FOR SAMI ASSESSMENT

7.1 Model Recommendations

We recommend that the SAMI assessment use the MAGIC model for any quantitative future projections of surface water acid-base status. The steady-state models are not appropriate for the Southern Appalachians. In addition to the arguments against steady-state models listed in section 5.1.1, streams in the SAMI region are not at steady state. The time required to reach steady state is one of the major unknowns that needs to be modeled in the SAMI assessment. Of the two dynamic watershed models (ILWAS and MAGIC) suitable for SAMI, MAGIC is by far the easiest, quickest, and least expensive to apply. The two models do have some real differences in terms of some projections (especially among alternate deposition scenarios in the southern Blue Ridge). Both models were extensively tested during the NAPAP assessment and there was no evidence that either model was more accurate than the other. Although ILWAS is more complex and models more processes and compartments, complexity does not necessarily make the model results more accurate. Therefore, it seems more cost-effective to select the more economical MAGIC model.

We recommend the use of the PnET-CN model as the nitrogen model for use in further assessments, because of its track record of applicability to a variety of sites with relatively little site-specific information. It would require some regional compilation of climate data and land use histories, as well as the collection of foliar nutrient samples from all sites of interest (a fairly straightforward task). One of the primary outputs of PnET-CN is the time to nitrogen saturation. This information could easily be incorporated into runs of the MAGIC model, to produce desired forecasts of acid-base status, given various scenarios of sulfur and nitrogen deposition (as well as climate change, if desired).

To make projections about the effects of episodic acidification on streams in the SAMI region, we recommend linking the regression model approach of Eshleman (1988) to MAGIC model projections. This step would provide a first approximation of the likely magnitude of episodic impacts. The regression model is fairly robust, can be applied on a regional basis, and has already been shown to be linkable to MAGIC. The regression equations, however, should be recalibrated using new data from studies in the Shenandoah and Great Smoky Mountains National Parks.

For doing future projections of the effects of acidic deposition on fish, we recommend using the acid stress index (ASI) approach used in the NAPAP assessment. Calcium, pH, and aluminum values can be obtained from MAGIC output to calculate ASIs under alternate deposition scenarios. Critical ASI values can then be obtained by comparing current fish distributions to current ASI levels.

7.2 Levels of Assessment

For SAMI, we've devised four levels of effort for doing an aquatic effects assessment. Each additional level will require more resources but will give a more complete assessment. The final choice of an assessment approach will require decisions about the nature and objective of the assessment. For example, will the assessment focus on streams in the entire SAMI region, the acid-sensitive part of the region, or just the Class I areas? Should the assessment just look at sulfur deposition or sulfur and nitrogen? How quantitative does the answer need to be? How different are the various emission management options or deposition scenarios? As the SAMI assessment is still in its formative stages, our recommended levels span a wide range of options. The final decision will depend heavily on the final choice of the SAMI assessment objective.

7.2.1 Level 1

A very simple qualitative assessment could be made by examining the existing results of the DDRP and NAPAP Integrated Assessment. For example, Figure 12 in this report gives a reasonably good idea of the relative effects of various sulfur deposition scenarios on the regional population of streams in the mid-Appalachians and southern Blue Ridge. This analysis focuses on the region as a whole, not the Class I areas. As the Class I areas comprise some of the most sensitive systems in the SAMI region, inferences to them could be made by examining what happens to the most sensitive streams in the regional distribution.

7.2.2 Level 2

An analysis that would require no new collection of data would involve redoing the DDRP/NAPAP Assessment at the existing DDRP sites using new deposition scenarios provided by SAMI. The data currently exist to run MAGIC at all these sites and to calculate fish ASI values using MAGIC output. This activity would provide a quantitative regional estimate of stream acid-base status for each of the SAMI deposition scenarios. This level has two major shortcomings. One drawback is that it really does not handle changes in nitrogen deposition/dynamics; the assessment would remain driven by sulfur deposition. Secondly, as in level 1, level 2 focuses on the region as a whole, not the Class I areas that may be of primary interest to SAMI. As in level 1, some inference to the Class I areas could be made by examining what happens to the most sensitive streams in the region, but it would not be very quantitative or applicable to any specific Class I area.

7.2.3 Level 3

Level 3 efforts would be geared toward using the most current methodologies for making the projections of the aquatic effects of acidic deposition. The analysis should be done by Class I wilderness area groups (e.g., West Virginia Plateau, southern Blue Ridge). It could be done for just one group or as many of the groups as resources allow. We would, however, make the Sipsey wilderness area group a low priority and focus efforts in the other three areas. We would recommend field efforts to collect new data on soils, watershed attributes, and hydrology for three low ANC watersheds (along the available ANC gradient) in each group. Where water chemistry information is sparse or lacking (see 7.4), a probability sample of 30–50 streams in the wilderness area group should be conducted to aid in regionalizing to the entire area group. This task would be relatively simple in the smaller areas but might require some extra effort in the GSMNP. Data necessary to run the PnET-CN nitrogen model and episodic acidification model (foliar chemistry, land use, and hydrologic information) should be collected at the same time. MAGIC and PnET-CN models would be used to make future projections about average annual streamwater chemistry. The episodic model would be linked to the MAGIC output to predict episodic acidity. ASI values could then be calculated for both episodic and chronic conditions to estimate the effects on fish. All the models would need to be calibrated and run under the SAMI deposition scenarios. This approach would allow for the best available projections for the modeled Class I wilderness area groups.

7.2.4 Level 4

A level 4 analysis would consist of conducting the level 3 analysis for each of the DDRP stream sites (level 2) to allow regional projections that take both nitrogen and sulfur dynamics into account. This work would involve collecting additional information at these sites to run PnET-CN.

7.2.5 Fish Assessment

A fish assessment could be added to Level 2, 3, or 4 quite easily using the ASI approach. However, field information on the relationship between fish distributions and ASI values needs to be collected and evaluated in order to set critical ASI levels for sensitive, intermediate, and tolerant fish species.

7.3 Limitations and Relationship to a SAMI Integrated Assessment

One of the conclusions of the NAPAP assessment was that "Uncertainties in the absolute magnitudes and timing of aquatic effects projections are high, but we have confidence in the projected direction of change and in the relative amounts of change." We believe that this conclusion has two important implications for the SAMI assessment:

1. Emission management options or deposition scenarios that result in very small changes in sulfur and nitrogen deposition will not cause distinguishable differences in aquatic effects. The resolution of the models is not that high.

2. Transferring absolute aquatic model projections (e.g., miles of acidic streams) into a broader integrated effects model has a large potential for significant errors. The models are reasonably good for evaluating the relative differences of different deposition scenarios. Thus, we are fairly comfortable with running the models and making conclusions about the relative differences in aquatic effects among various deposition scenarios. However, we are uncomfortable with using the absolute results (e.g., length of acidic streams) of these models. We are very uncomfortable with taking these absolute results, linking them together with absolute results from other effects models (e.g., visibility, ozone), running them all through a socio-economic valuation model, and using some kind of overall "cost" estimate as the decision making tool for evaluating different emissions scenarios. From the aquatic perspective, future projections about miles of acidic streams or miles of streams that will have impaired or absent fish populations have very large uncertainties due to model structure, sensitivity, calibration, and definition of the target population.

7.4 Data Availability

The surface water chemistry and watershed data required to run the MAGIC model exist at 35 streams in the southern Blue Ridge and 36 streams in the mid-Appalachians that were sampled in the NSS and DDRP. Note that only 17 of the 36 streams in the mid-Appalachians were in the SAMI states of West Virginia or Virginia. Data also exist to run the MAGIC model in the streams of Shenandoah National Park where the MAGIC model was developed. We are not aware of any other locations in the SAMI region where sufficient watershed, soils, water chemistry, and hydrologic data are available or are in a form ready to run MAGIC.

Available water chemistry data sets exist in many of the Class I areas in varying degrees of resolution. The magnitude of the "No Data" column in Table 5 relates the degree of completeness. High-resolution data sets exist for Otter Creek, Dolly Sods, and the Shenandoah National Park. Data sets with good resolution exist for James River Face and

Cohutta. More complete data need to be collected in Sipsey, Slickrock, and Shining Rock wilderness areas. Data exist for 359 stream sites in the Great Smoky Mountains National Park. These sites, however, represent only about one-third of the stream length in the park. A population-level assessment is likely to require a probability survey of the park's 2,035 km of streams (Table 3).

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West Virginia. 1968. *Geologic Map of West Virginia*. 1:250,000 scale. West Virginia Geological and Economic Survey, Charleston.

Wigington, P.J., Jr., T.D. Davies, M. Tranter, and K.N. Eshleman. 1990. *Episodic Acidification of Surface Waters Due to Acidic Deposition*. NAPAP Report 12. In: *National Acid Precipitation Assessment Program, Acidic Deposition: State of Science and Technology*. Volume II. National Acid Precipitation Assessment Program, Washington, D.C.

Wigington, P.J., Jr., et al. 1993. *Episodic Acidification of Streams in the Northeastern United States: Chemical and Biological Results of the Episodic Response Project*. EPA/600/R-93/190. U.S. Environmental Protection Agency, Washington, D.C.

Winger, P.V., and others. 1987. Sensitivity of high-elevation streams in the Southern Blue Ridge Province to acidic deposition.

Zurbuch, P.E., R. Menendez, and J.E. Woodrum. 1986. *West Virginia Dogway Fork Project Cooperative Acid Precipitation Mitigation Program*, Annual Report 1986. Cooperative Agreement No. 14-16-009-85-945. Report from the West Virginia Department of Natural Resources to the Eastern Energy and Land Use Team, US Fish and Wildlife Service, Kearneysville, WV.

9. ANNOTATED BIBLIOGRAPHY

This annotated bibliography provides up-to-date information on papers published since the 1990 NAPAP SOS/T reports, focusing particularly on articles of regional significance to SAMI and on those that present significant new general findings.

Baker, J.P., J. Van Sickle, C.J. Gagen, D.R. DeWalle, W.E. Sharpe, R.F. Carline, B.P. Baldigo, P.S. Murdoch, D.W. Bath, W.A. Kretser, H.A. Simonin, and P.J. Wigington, Jr. 1996. Episodic acidification of small streams in the northeast United States: Effects on fish populations. *Ecol. Appl*. 6:422-437.

This paper largely summarizes the results from the experimental field studies of fish populations in the 13 ERP streams first reported on by Wigington et al. (1993).

Baker, L.A., A.T. Herlihy, P.R. Kaufmann, and J.M. Eilers. 1991. Acidic lakes and streams in the United States: The role of acidic deposition. *Science* 252:1151-1154.

A short article taken from the NAPAP SOS/T report 9 examining the likely causes of acidity in lakes and streams. It also summarizes the number and proportions of lakes and streams in the U.S. likely to be acidic as a result of acidic deposition.

Bazemore, D.E., K.N. Eshleman, and K.J. Hollenbeck. 1994. The role of soil water in stormflow generation determined from natural tracer and hydrometric techniques. *J. Hydrol.* 162:47-75.

A field study that combined natural tracer methods and hydrometric observations was conducted to estimate the contributions of pre-event soil water to stormflow in a small forested catchment in Shenandoah National Park, Virginia. A three-component model using two naturally occurring tracers (oxygen-18 and chloride) was used to show that pre-event soil water dominated total storm runoff and peak runoff during two major rainfall events. The authors also illustrated that quantitative error analyses are advisable in chemical and isotopic hydrograph separation studies. Field observations suggested that the pre-event water response could be attributed to a threshold-type expansion of hillslope source areas. Results of the study are significant for understanding episodic acidification, because the chemical composition of the three end-members (soil water, groundwater, and throughfall) may vary dramatically in small headwater systems.

Bishop, K.H. 1991. Episodic Increases in Stream Acidity, Catchment Flow Pathways and Hydrograph Separation. PhD dissertation. Department of Geography, University of Cambridge, U.K.

Detailed field investigations (including hydro-isotopic separations using oxygen-18) were conducted at Loch Fleet (Scotland) and Svartberget (Sweden) to test the hypothesis that acid episodes are due primarily to the rapid displacement of pre-event water from the catchment during stormflow events. This hypothesis was confirmed by the field investigation, although the study was unable to identify the specific mechanisms of runoff generation (e.g., saturation overland flow, subsurface stormflow) in the two watersheds. The author also concluded that non-Darcian flow (i.e., macropore flow) could explain the field observations of rapid displacement of pre-event water and increases in stream acidity during storm events.

Bradford, D., C. Swanson, and M. Gordon. 1992. Effects of low pH and aluminum on two declining species of amphibians in the Sierra Nevada, California. *Jour. of Herpetology* 26:369-377.

Bradford, D.F., and M.S. Gordon. 1992. Aquatic amphibians in the Sierra Nevada: Current status and potential effects of acidic deposition on populations. Final report, Contract No. A932-139, California Air Resources Board, Sacramento, CA.

Bradford, D.F., C. Swanson, and M. Gordon. 1994. Effects of low pH and aluminum on amphibians at high elevation in the Sierra Nevada, California. *Can. J. Zool.* 72:1272-1279.

Bradford, D.F., M. Gordon, D. Johnson, R. Andrews, and W.B. Jennings. 1994. Acidic deposition as an unlikely cause of amphibian population declines in the Sierra Nevada, California. *Biological Conservation* 69:155-161.

Toxicity testing indicated that amphibians are at

little risk from low pH in water acidified to a pH level of 5.0, with Al concentrations of 39–80 µg/L. However, the authors observed sublethal effects (reduced growth rate and earlier hatching) for pH as high as 5.25 at the Al concentrations tested. Field survey findings implied that acidic deposition is unlikely to have been a cause of recent amphibian population declines in the Sierra Nevada.

Bulger, A.J., L. Lien, J. Cosby, and A. Henriksen. 1993. Brown trout (*Salmo trutta*) status and chemistry from the Norwegian Thousand Lake Survey: Statistical Analysis. *Can. J. Fish. Aquat. Sci*. 50:575-585.

The relationship between atmospheric sulfate and terrestrial calcium is the main control of acidification processes, but neither one is a good predictor of fish response; this paper provides a useful explanation of this as a general phenomenon, not limited to Norway. It also provides an explanation linking toxic mechanisms and empirical responses of fish populations in nature.

Bulger, A.J., C.A. Dolloff, B.J. Cosby, K.N. Eshleman, J.R. Webb, and J.N. Galloway. 1995. The "Shenandoah National Park: Fish in Sensitive Habitats (SNP: FISH)" Project: An integrated assessment of fish community responses to stream acidification. *Water Air Soil Pollut*. 85:309-314

This paper presents a summary to date of the overall findings of a three-year project on fish community effects and acid-base chemistry in mountains streams in Virginia. Both chronic and episodic acidification are occurring in these streams. Biological differences in low ANC versus high ANC streams include fish species richness, population density, condition factor, age, size, and bioassay survival. Predictive models relating fish status to future water chemistry will be produced by this project.

Carline, R.F., D.R. Dewalle, W.E. Sharpe, B.A. Dempsey, C.J Gagen, and B. Swistock. 1992. Water chemistry and fish community responses to episodic stream acidification in Pennsylvania, USA. *Environ. Pollut*. 78:45-48.

Five undisturbed, wooded streams were studied on the Northern Appalachian Plateau of Pennsylvania for 9 months to determine chemical changes and fish responses that occur during episodic storm runoff. Wild brook trout were found in all streams, although only a remnant population existed in the most acidic stream. Sculpins (*Cottus bairdi* or *C. cognatus*) were collected only in the two streams with the least severe episodes. Mortality of brook trout and sculpins in in-situ bioassays ranged from 0 to about 80% among streams during acidic episodes and was positively related to concentrations of total dissolved Al. Some displaced trout were found near groundwater seeps, where pH was higher and dissolved Al lower than in the main channel.

Church, M.R., and J. Van Sickle. 1995. *Potential Relative Effects of Nitrogen and Sulfur Deposition on Regional Scale Acidification of Surface Waters in the Eastern United States*. U.S. Environmental Protection Agency, Washington, DC.

The Nitrogen Bounding Study used the MAGIC model to predict the future acid-base status of regional populations of surface water sites under several different scenarios for future nitrogen and sulfur deposition, and several different time series for nitrogen saturation.

Church, M.R., P.W. Shaffer, K.N. Eshleman, and B.P. Rochelle. 1990. Potential future effects of current levels of sulfur deposition on stream chemistry in the Southern Blue Ridge Mountains, United States. *Water Air Soil Pollut*. 1990:39-48.

This article concludes that, although little change in surface water chemistry is likely to have occurred due to acidic deposition in the region to date, soils are currently retaining a majority of atmospherically deposited S, and it is likely that marked increases in surface water SO_4^{2-} will occur. Such increases could be accompanied by significant surface water acidification (loss of ANC).

Church, M.R., P.W. Shaffer, K.W. Thornton, D.L. Cassell, C.I. Liff, M.G. Johnson, D.A. Lammers, J.J. Lee, G.R. Holdren, J.S. Kern, L.H. Liegel, S.M. Pierson, D.L. Stevens, B.P. Rochelle, and R.S. Turner. 1992. *Direct/Delayed Response Project: Future Effects of Long-Term Sulfur Deposition on Stream Chemistry in the Mid-Atlantic Region of the Eastern United States*. EPA/600/R-92/186. U.S. Environmental Protection Agency, Washington, D.C.

This is the last in the series of DDRP reports detailing the results of empirical and dynamic modeling of acidification of the regional population of surface waters in several regions. For this report, the results of the Appalachian Plateau, Valley and Ridge, and Piedmont provinces are presented together.

Cook, R.B., J.W. Elwood, R.R. Turner, M.A. Bogle, P.J. Mulholland, and A.V. Palumbo. 1994. Acid-base chemistry of high-elevation streams in the Great Smoky Mountains. *Water Air Soil Pollut*. 72:331-356.

Cook et al. report on seasonal data from eight streams in Great Smoky Mountains National Park on differing types of bedrock. They point out both the effects of the Anakeesta formation on stream chemistry (high SO_4^{2-} and acidic waters) and the effects of high-elevation, old growth forests on NO_3^- concentrations.

Davies, T.D., P.J. Wigington, Jr., M. Tranter, and K.N. Eshleman. 1992. 'Acidic episodes' in surface waters in Europe. *J. Hydrol.* 132:25-69.

This paper largely presents a summary of Section 3.2 of Wigington et al. (1990), NAPAP SOS/T Report 12.

Dennis, T. E., and A. J. Bulger. 1995. Condition factor and whole-body sodium concentration in a freshwater fish: evidence of acidification stress and possible ionoregulatory over-compensation. *Water Air Soil Pollut.* 85: 377-382.

Acidification negatively affects ion regulation in fish. This paper shows that fish in a low ANC stream appear to be able to ion-regulate adequately at current acid-base conditions, but it also suggests that the added metabolic cost of ion regulation in low ANC streams versus high ANC streams my be responsible for slower growth and smaller sized individuals in the low ANC stream.

Dennis, T.E. , S. E. MacAvoy, M. B. Steg and A. J. Bulger. 1995. The association of water chemistry variables and fish condition in streams of Shenandoah National Park (USA). *Water Air Soil Pollut.* 85: 365-370.

This paper demonstrates a strong relationship between water chemistry and fish condition factor, across nine montane streams in Virginia. The variables most strongly related to fish condition were those associated with ANC and SO_4^{2-}, with condition factor poorest in low ANC streams.

DiStefano, R.J., R.J. Neves, L.A. Helfrich, and M.C. Lewis. 1991. Response of the crayfish *Cambarus bartonii bartonii* to acid exposure in southern Appalachian streams. *Can. J. Zool*. 69(6):1585-1591.

Tolerance of crayfish to acidity was rather high (96 hr LC50, range 2.43–2.85 for early juveniles to adults). Lowering the water temperature increased acid tolerance. Nevertheless, the authors state that gradually increasing acidity and loss of watershed buffering capacity could produce sublethal effects, such as altered reproductive activity or changes in early life history stages and more sensitive molt cycle stages, that could damage crayfish populations.

Dow, C.L., D.R. DeWalle, J.A. Lynch, and W.E. Sharpe. 1994. Blizzard's effects on Appalachian stream chemistry assessed. *EOS Trans. Amer. Geophys. Union* 75:389-390.

This short paper provides a description of the hydrochemical changes observed in three small streams in Pennsylvania during an extreme rain-on-snow event that followed the "blizzard of 1993." This storm deposited approximately 90 cm of snow on the study catchments and was followed by about 7 cm of rainfall, which caused the highest sustained (monthly) discharge in the Susquehanna River basin. ANC and pH depressions (and elevated Al concentrations) during the event were quite large, although their absolute magnitude was not found to vary significantly from previously monitored conditions of lesser (hydrological) magnitude. Nitrate and organic anion concentrations were significantly higher than those recorded previously, however, which supported the explanation that flows were attributable to movement of water through shallow soil horizons.

Downey, D.M., C.R. French, and M. Odom. 1994. Low cost limestone treatment of acid sensitive trout streams in the Appalachian Mountains of Virginia. *Water Air Soil Pollut*. 77:49-77.

Based on their results in three streams, the authors suggest that approximately 88% of native trout streams in Virginia, which average 29 µeq/L ANC reduction from acid deposition, could be temporarily restored using single application liming.

Driscoll, C.T., and R. Van Dreason. 1993. Seasonal and long-term temporal patterns in the chemistry of Adirondack lakes. *Water Air Soil Pollut.* 67:319-344.

A long-term (1982-present) monitoring program of 17 Adirondack lakes was conducted to examine temporal patterns in acid-base chemistry. The monitoring results indicated relatively uniform SO_4^{2-} concentrations among the lakes, while ANC variations were largely determined by differences in base cations. Lakes in the southern and western Adirondacks showed the highest levels of NO_3^-, during both peak and baseflow conditions. From an episodic acidification perspective, this paper is significant since it concluded that Adirondack lakes with ANC values < 100 µeq/L during baseflow conditions may experience decreases in ANC to values near or below 0.

Eckhardt, B.W. and T.R. Moore. 1990. Controls on dissolved organic carbon concentrations in streams, southern Quebec. *Can. J. Fish. Aquat. Sci*. 47(8):1537-1544.

DOC concentrations in 42 streams draining small catchments in the Appalachian Uplands and St. Lawrence Lowlands were consistently related to the percentage of wetland in the catchment. The results indicate that stream DOC concentrations may be predicted from easily obtained catchment variables, such as percent wetland.

Englin, J.E., T.A. Cameron, R.E. Mendelsohn, G.A. Parsons, and S.A. Shankle. 1991. Valuation of damages to recreational trout fishing in the upper Northeast due to acidic deposition. Technical Report. NTIS Order No. DE91012029/GAR. Battelle Pacific Northwest Laboratories.

This report documents methods used by NAPAP to model the economic value of changes in recreational fishing due to acidic deposition.

Eshleman, K.N. 1992. Comment on “The episodic acidification of Adirondack lakes during snow-melt” by Douglas A. Schaefer et al. *Water Resour. Res.* 28:2869-2873.

This paper is a technical comment on an earlier paper published in *Water Resources Research* that dealt with the significance of the linear relationship observed by Eshleman (1988) between ANC_{index} and $ANC_{minimum}$ for a group of lakes in the Adirondacks of New York. The author argued that the observed linear relationship is statistically and physically significant and can be applied to an entire population of lakes in the Adirondacks.

Eshleman, K.N. 1995. Predicting Regional Episodic Acidification of Streams in Western Maryland. Report CBRM-AD-95-7. Maryland Department of Natural Resources, Annapolis.

This report used the empirical linear regression model first proposed by Eshleman (1988) and data from two studies of episodic acidification in the Appalachian Plateau to provide an estimate of the number and length of streams in western Maryland that are episodically acidic (ANC < 0) during stormflow periods. The report concluded that about 50% more streams (11% of the population) are acidic during episodes than are acidic during spring baseflow conditions (7% of the population) in the region; the population used corresponds to those streams sampled during the Maryland Synoptic Stream Chemistry Survey (MSSCS) in 1987. An important uncertainty is whether the linear regression model can be applied across all bedrock types found in western Maryland.

Eshleman, K.N., P.J. Wigington, Jr., M. Tranter, and T.D. Davies. 1992. Modelling episodic acidification of surface waters: The state of the science. *Environ. Pollut.* 77:287-295.

This paper largely summarizes Chapter 5 of Wigington et al. (1990), NAPAP SOS/T Report 12.

Eshleman, K.N., P.J. Wigington, Jr., T.D. Davies, and M. Tranter. 1995. A two-component mixing model for predicting regional episodic acidification of surface waters during spring snowmelt. *Water Resour. Res.* 31:1011-1021.

A two-component mixing model of ANC was used to explain two observed features related to the episodic acidification of Adirondack and Catskill mountain surface waters during spring snowmelt: (1) maximum episodic declines in ANC are largest in high ANC systems and increase linearly with antecedent ANC and (2) relative depressions in ANC attributable to dilution of base cations are larger in high ANC systems. The model was calibrated using snowmelt data for 10 Adirondack lakes and was then applied to the regional population of lakes described by the National Lake Survey. The model was also linked to an empirical acidification model for predicting the future extent of episodically acidic (ANC < 0) lakes in the Adirondacks, given various emissions control strategies. Model predictions indicated that 40% reductions in sulfuric acid concentrations will not restore to positive values the ANC of all lakes that are currently acidic during spring snowmelt.

Eshleman, K.N., L.M. Miller-Marshall, and J.R. Webb. 1995. Long-term changes in episodic acidification of streams in Shenandoah National Park, Virginia (U.S.A.). *Water Air Soil Pollut.*85:517-522.

A statistical analysis of 13 years of daily discharge data and weekly streamwater composition data for White Oak Run (WOR) in Shenandoah National Park was performed in order to quantify episodic changes in composition and to identify long-term trends in episodic acidification attributable to both natural and anthropogenic processes. An objective hydrological separation technique was used to identify more than 100 "stormflow/baseflow pairs" in the database, from which episodic chemical changes could be quantified. Univariate statistical analysis suggested that mean episodic depressions of ANC in WOR have increased by about a factor of 2 since the first outbreak of forest defoliation by the gypsy moth caterpillar during the summer of 1990; in addition, the mean episodic change in nitrate concentration has increased by about 12 µeq/L, while the mean episodic dilution of C_B has decreased from -8.5 µeq/L to -1.7 µeq/L during the same period. Episodic changes in SO_4^{2-} have remained the same, however. The results indicate that natural processes such as insect defoliations can contribute to episodic acidification through mobilization of NO_3^-.

Flum, T., and S.C. Nodvin. 1995. Factors affecting streamwater chemistry in the Great Smoky Mountains, USA. *Water Air Soil Pollut*. 85:1707-1712.

Flum et al. summarize the results of synoptic stream chemistry surveys carried out in Great Smoky Mountains National Park during the 1990s. They focus on differences among different types of bedrock and former land use types (e.g., old growth vs. second growth forests) and across elevations. ANC is lowest and NO_3^- is highest in the least disturbed (i.e., old growth) and highest elevation watersheds.

Gagen, C.J., W.E. Sharpe, and R.F. Carline. 1994. Downstream movement and mortality of brook trout (*Salvelinus fontinalis*) exposed to acidic episodes in streams. *Can. J. Fish. Aquat. Sci*. 51(7):1620-1628.

This article describes a study of two streams with severe acidic episodes and two with less severe acidic episodes. Episodes of low pH and high Al concentration were associated with net downstream movement and increased mortality of radio-tagged brook trout. Study populations moved downstream hundreds of meters in the streams with more severe acidic episodes (pH <5.0 and Al >200 µg/L. Median downstream movement in spring was 250 and 900 m after 20 days for fish in the more acidic streams; one-third of the fish were found dead during this time. They found no net movement and no dead fish in the reference streams. Lower stream discharge in fall studies was associated with less severe acidic episodes, less net movement, and no mortality. Water samples collected at individual fish locations indicated that few fish avoided adverse effects of acidic episodes by remaining in microhabitats with higher H and lower Al concentration.

Griffith, M.B., and S.A. Perry. 1993. Colonization and processing of leaf litter by macroinvertebrate shredders in streams of contrasting pH. *Freshwat. Biol*. 30(1):93-103.

This article describes a leaf pack study of four central Appalachian streams. Leaf litter processing rates were fastest in the neutral streams, slowest in the acidic stream, and intermediate in the most alkaline stream. Slower processing rates in the acidic stream were associated with lower total shredder biomass, made up predominantly by small leuctrid and nemourid stoneflies. The differences in processing rates between the more alkaline stream and the neutral streams appeared to be related to taxonomic differences in the shredder assemblages. Insects were dominant in the neutral streams, and amphipods were dominant in the more alkaline stream.

Heath, R.H., J.S. Kahl, S.A. Norton, and I.J. Fernandez. 1992. Episodic acidification caused by the seasalt effect in coastal Maine streams, USA. *Water Resour. Res.* 28:1081-1088.

This field study examined the causes and characteristics of episodic acidification of low-order streams in Acadia National Park (Maine), based on samples collected during stormflow conditions using automated water samplers and analyzed for ANC, pH, DOC, Si, and major ions. The primary conclusion of the study was that the sea-salt effect is the dominant cause of episodic acidification of streams in coastal Maine, owing to a depression in the Na:Cl ratio in surface waters by precipitation. No other contributors to episodic acidification (SO_4^{2-}, NO_3^-, organic acids) were able to explain the magnitude of ANC changes observed.

Herlihy, A.T., P.R. Kaufmann, and M.E. Mitch. 1991. Chemical characteristics of streams in the Eastern United States: II. Sources of acidity in acidic and low ANC streams. *Water Resour. Res.* 27:629-642.

This is part 2 of a two-part paper that summarizes the results of EPA's National Stream Survey, a probability survey of stream chemistry in the mid-Atlantic and southeastern United States. This part of the paper describes the chemical classification scheme used to attribute sources of acidity to organics, mining, and deposition. It then uses the probability design of the Survey to make population estimates of stream numbers in the different acid source classes.

Herlihy, A.T., P.R. Kaufmann, M.R. Church, P.J. Wigington, Jr., J.R. Webb, and M.J. Sale. 1993. The effects of acidic deposition on streams in the Appalachian Mountain and Piedmont region of the mid-Atlantic United States. *Water Resour. Res.* 29:2687-2703.

This article is an assessment of the effects of acidic deposition on streams of the mid-Appalachian and Piedmont region of the U.S. It summarizes all available survey information on the effects of acidic deposition on chronic and episodic stream chemistry, and includes biological effects.

Hooper, R.P., and N. Christophersen. 1992. Predicting episodic stream acidification in the southeastern United States: Combining a long-term acidification model and the end-member mixing concept. *Water Resour. Res.* 28:1983-1990.

This paper addresses the problem of predicting episodic stream acidification through the use of a long-term acidification model (MAGIC) linked to a end-member mixing model. The results of the modeling effort—applied to the Panola Mountain Research Watershed (Georgia)—predicted that the two upper soil levels will dramatically acidify within the next 50 years, causing the streamwater to become unsuitable for sensitive aquatic biota for much of the year.

Hyer, K.E., J.R. Webb, and K.N. Eshleman. 1995. Episodic acidification of three streams in Shenandoah National Park, Virginia (U.S.A.). *Water Air Soil Pollut*. 85:523-528.

The short-term acidification of three streams in Shenandoah National Park was studied to quantify the magnitude of chemical changes accompanying

stormflow conditions and to evaluate the contributions of individual ions to changes in streamwater ANC. An important element of the study was the unique bedrock geology of each of the catchments. Data from 25 storm events were analyzed using the method of Molot et al. (1989). Depressions in pH and ANC were observed in all three streams, although ANC only became negative in the most acid-sensitive stream, Paine Run, which drains a catchment underlain by silici-clastic bedrock. Similar to other studies, SO_4^{2-} and NO_3^- concentrations usually increased during storm events in all streams, although base cation concentrations typically increased. Minimum values of ANC during storm events were best predicted by a linear model using antecedent baseflow ANC as the independent variable.

Johnson, D.W., and S.E. Lindberg, eds. 1992. *Atmospheric Deposition and Forest Nutrient Cycling*. Ecological Studies. Springer-Verlag, New York.

This book summarizes the results of the Integrated Forest Study (IFS), and includes detailed information on the IFS sites in Great Smoky Mountains National Park (3 sites) and at Coweeta. The focus was on detailed measurements of deposition (wet, dry, and cloud), soil solution chemistry, and other aspects of nutrient cycles in forests. This work clearly identifies the high-elevation parts of Great Smoky Mountains National Park as the highest deposition areas in the United States.

Johnson, D.W., W.T. Swank, and J.M Vose. 1993. Simulated effects of atmospheric deposition on nutrient cycling in a mixed deciduous forest. *Biogeochem.* 23:169-196.

Using the NuCM (Nutrient Cycling Model) model, the authors investigated the effects of three S deposition scenarios on biogeochemical cycling of N, P, S, K, Ca, and Mg in a mixed deciduous forest at Coweeta, North Carolina. Ecosystem S and SO_4^{2-} leaching were almost entirely controlled by SO_4^{2-} adsorption via the nature of the Langmuir adsorption isotherm used in NuCM. Both the simulations and field data show that the ecosystem is becoming more S saturated. Varying S deposition had very little effect upon simulated vegetation growth, nutrient uptake, or N cycling but had a strong effect on base cation and P leaching. S deposition effects on soil exchangeable pools of these elements, however, were minimal due to the size of these pools relative to the fluxes.

Kahl, J.S., S.A. Norton, T.A. Haines, E.A. Rochette, R.H. Heath, and S.C. Nodvin. 1992. Mechanisms of episodic acidification of low-order streams in Maine, U.S.A. *Environ. Pollut.* 78:37-44.

Observed chemical changes during hydrological events in low-order streams in Maine were examined in order to understand the mechanisms of episodic acidification in this region. It was generally observed that five processes contribute to episodic depressions in pH and ANC: (1) increases in nitric acid concentrations, (2) increases in organic acidity, (3) increases in the anion fraction of SO_4^{2-}, (4) increases in acidity due to the salt effect in soils, and (5) hydrological dilution of ANC by increased stream discharge. The chemical composition of individual precipitation events was found to be irrelevant in the generation of acidic episodes, with the exception of those primarily attributable to high loadings of neutral salts within the coastal region of Maine.

Kaufmann, P.R., A.T. Herlihy, M.E. Mitch, and W.S. Overton. 1991. Chemical characteristics of streams in the Eastern United States: I. Synoptic survey design, acid-base status and regional chemical patterns. *Water Resour. Res*. 27:611-627.

This is part 1 of a two-part paper that summarizes the results of EPA's National Stream Survey, a probability survey of stream chemistry in the mid-Atlantic and southeastern United States. This part of the paper describes the probability design of the Survey and discusses the regional findings in terms of population estimates of condition.

Kaufmann, P.R., A.T. Herlihy, and L.A. Baker. 1992. Sources of acidity in lakes and streams of the United States. *Environ. Pollut*. 77:115-122.

This paper presents and defends a classification scheme designed to attribute sources of acidity to the lakes and streams of EPA's National Surface Water Survey.

Kobuszewski, D.M., and S.A. Perry. 1993. Aquatic insect community structure in an acidic and a circumneutral stream in the Appalachian Mountains of West Virginia. *J. Freshwat. Ecol*. 8(1):37-45.

The authors report, in comparing benthic macroinvertebrates in two West Virginia streams, that density did not differ between the acidic and circumneutral stream, but species richness and evenness were higher in the neutral stream. Plecoptera and shredders dominated the acidic stream.

Kobuszewski, D.M., and S.A. Perry. 1994. Secondary production of *Rhyacophila minora*, *Ameletus* sp., and *Isonychia bicolor* from streams of low and circumneutral pH in the Appalachian Mountains of West Virginia. *Hydrobiologia* 273(3):163-169.

This article describes a study of three acidic streams and one circumneutral stream in Randolph County, West Virginia. Differences in secondary production of these species were associated with differences in macroinvertebrate community structure.

Kutka, F.J. 1994. Low pH effects on swimming activity of *Ambystoma* salamander larvae. *Environ. Toxicol. Chem*. 13(11):1821-1824.

Results suggest that salamander embryos and larvae may suffer from pH levels below 5.0, even though these levels are not directly lethal. Because of their sensitivity, the authors recommend activity tests with amphibian larvae for use in risk assessments.

Larsen, G.L., S.E. Moore, and B. Carter. 1995. Ebb and flow of encroachment by nonnative rainbow trout in a small stream in the Southern Appalachian Mountains. *Trans. Am. Fish. Soc.* 124:613-622.

The results of this study suggest that encroachment by rainbow trout (nonnative) can exhibit considerable ebb and flow in steep gradient streams of the Great Smoky Mountains National Park. Results also suggest substantial evolutionary adaptation by brook trout to the hydrological conditions in these small streams. We found this paper to be interesting, because similar resistance to rainbow trout invasion in headwater streams has been attributed to the greater tolerance of brook trout to the typically more acidic conditions in steep headwaters.

Lawrence, G.B., M.B. David, and W.C. Shortle. 1995. A new mechanism for calcium loss in forest-floor soils. *Nature* 378:162-164.

Concentrations of root-available calcium have declined in the northeastern United States over the last 60 years. Based on data collected in red spruce forests, the authors propose a mechanism where aluminum (mobilized in the mineral soil by acid deposition) is transported into the forest floor in a reactive form that reduces storage of calcium and thus its availability for root uptake. This would result in potential stress to trees, increased forest demand for calcium, and decreased calcium runoff to surface waters (decreasing surface water ANC).

Loer, S.C., and J.L. West. 1992. Microhabitat selection by brook and rainbow trout in a southern Appalachian stream. *Trans. Am. Fish. Soc*. 121(6):729-736.

We were interested in this paper because it deals with the decreased range of native brook trout in the Great Smoky Mountains National Park, which has been attributed to competition with introduced rainbow trout—a fish not as tolerant of acidity as brook trout. This study reports that young-of-the-year, and to some extent age 1, brook trout shifted to habitat positions farther from overhead cover when rainbow trout numbers were reduced.

MacAvoy, S. E. and A. J. Bulger. 1995. Survival of brook trout (*Salvelinus fontinalis*) embryos and fry in streams of different acid sensitivity in

Shenandoah National Park, USA. *Water Air Soil Pollut.* 85: 439-444.

This paper demonstrates significantly higher mortality of hatchery stock brook trout embryos and fry in field bioassays in low ANC streams compared to high ANC streams in Virginia, both chronically and during acidic episodes.

McQuattie, C.J., S. L. Stephenson, and P.J. Edwards. 1993. Effect of stream acidity on decomposition of sugar maple (*Acer saccharum*) and red oak (*Quercus rubra*) leaves. *Ohio J. Sci*. 93(2):48.

Leaf decomposition of both species was more rapid in a pH 5.6 stream than in a pH 3.2 stream. Authors state that differences were probably due to increased numbers or types of aquatic microorganisms found in the pH 5.6 stream. Acidity level appeared to have a direct effect on cuticular wax structure of the leaves.

Miller-Marshall, L.M. 1993. Mechanisms Controlling Variation in Stream Chemical Composition During Hydrologic Episodes in the Shenandoah National Park, Virginia. MS thesis. Department of Environmental Sciences, University of Virginia, Charlottesville. 165 pp.

This thesis describes both a field investigation of episodic acidification at two sites in Shenandoah National Park and a statistical analysis of long-term weekly stream chemical composition data for four sites in the Park. A major result of the study was that sulfuric acid increases and base cation dilution are the primary mechanisms contributing to the losses of ANC in streams in the Park during hydrological events, although there is evidence that nitric acid has recently become a more important contributor to ANC losses in these streams. These conclusions were based on application of an approach to partitioning ANC losses developed by Molot et al. (1989) and on a newer approach known as the Response Sector Model (RSM).

Morgan, R.P., II, C.K. Murray, and K.N. Eshleman. 1994. Episodic water chemistry changes in a western Maryland watershed. Report CBRM-AD-94-8. Maryland Department of Natural Resources, Annapolis. 125 pp.

This report describes a study of episodic acidification at six sites in the Big Run watershed in western Maryland. A total of 23 hydrological events (including storm fronts, thunderstorms, and snowmelts) were sampled over a 3-year period (1989-92). Antecedent ANC was found to be an excellent predictor ($r^2 = 0.91$) of $ANC_{minimum}$ at the six sites and ANC depressions were largely attributable to increases in sulfuric acid concentrations and dilution of base cations. Nitric and organic acids were secondary contributors to the loss of ANC.

Murdoch, P.S., and J.L. Stoddard. 1992. The role of nitrate in the acidification of streams in the Catskill Mountains of New York. *Water Resour. Res.* 28:2707-2720.

The authors of this paper presented a statistical analysis of long-term (23–70-year records) chemical data from 19 streams and rivers in the Catskill mountains of New York revealing that SO_4^{2-} concentrations are generally declining, while NO_3^- concentrations are increasing. The NO_3^- trend appears to be attributable largely to higher concentrations of NO_3^- during peak flow conditions (particularly spring snowmelt). The magnitude of episodic nitrate increases has increased since about 1970.

Neal, C., A. Robson, B. Reynolds, and A. Jenkins. 1992. Prediction of future short-term stream chemistry—a modeling approach. *J. Hydrol.* 130:87-103.

This paper addresses the problem of predicting future short-term stream chemistry in acidic and acid-sensitive streams under various deposition scenarios. The approach used a hydrograph separation based on ANC, coupled to the two-component version of MAGIC and ALCHEMI. The technique was applied to the Afon Gwyn catchment in mid-Wales, with results demonstrated in the forms of (1) 3-month sequences of hydrogen ion and inorganic aluminum concentrations and (2) chemical duration curves for hydrogen ion and aluminum.

Newman, K., and A. Dolloff. 1995. Responses of blacknose dace (*Rhinichthys atratulus*) and brook char (*Salvelinus fontinalis*) to acidified water in a laboratory stream. *Water Air Soil Pollut*. 85:371-376.

This study was based on Shenandoah National Park fish. Both species actively avoided an acid pulse (ambient pH 7.1 shifted to 5.1) by moving to a pH-neutral refuge, demonstrating at least the potential of two regionally important species to recognize waters with either lethal or sublethal acid-base chemistry and seek better water quality.

Nikolaidis, N.P., P.K. Muller, J.L. Schnoor, and H.L. Hu. 1991. Modeling the hydrogeochemical response of a stream to acid deposition using the enhanced trickle-down model. *Res. J. WPCF*. 63(3):220-227.

The enhanced trickle down model was applied to White Oak Run, a second-order stream in Shenandoah National Park in Virginia. Model results demonstrated the "delayed response" of this system, projecting that SO_4 desorbed from the soils after 40–50 years, assuming no reductions in the current deposition. This finding has significant policy implications, because reduction in deposition levels will not result in a quick recovery of this system.

Nodvin, S.C., H. Van Miegroet, S.E. Lindberg, N.S. Nicholas, and D.W. Johnson. 1995. Acidic deposition, ecosystem processes, and N saturation in a high-elevation southern Appalachian watershed. *Water Air Soil Pollut.* 85:1647-1652.

This paper describes a field study of biogeochemical processes in the Noland Divide watershed in the Great Smoky Mountains National Park (GSMNP). The watershed is dominated by a high-elevation spruce-fir forest that receives the highest loadings of atmospheric S deposition in North America. Watershed NO_3^- export was extremely high, exacerbating the loss of base cations from the system. Stream ANC was extremely low (-10–20 µeq/L) and depressions in pH of a full unit for as long as several weeks were associated with stormflow conditions. Nitrate concentrations actually exceeded SO_4^{2-} concentrations during episodes, which was attributed to substantial SO_4^{2-} retention by sorption and N saturation. The authors conclude that episodic and chronic acidification are moderated by sulfate sorption, but exacerbated by N (nitric acid) release from the watershed soils.

Norton, S.A., R.F. Wright, J.S. Kahl, and J.P. Scofield. 1992. The MAGIC simulation of surface water acidification at, and first year results from, the Bear Brook watershed manipulation, Maine, USA. *Environ. Pollut.* 77:279-286.

A manipulation experiment involving the addition of ammonium sulfate to one of a pair of monitored catchments (East and West Bear Brooks) in eastern Maine was performed; this paper describes results from the first year of the manipulation experiment and the chemical patterns evident in the 3.5 years of antecedent monitoring. The most important aspect of the study from the perspective of assessing episodic acidification was that stormflow conditions in the treated catchment were associated with lower ANC and pH and higher Al concentrations than those observed prior to the manipulation experiment. These results provide additional evidence that the episodic hydrochemical responses of catchments are at least in part a function of the atmospheric deposition loading.

O'Brien, A.K., and K.N. Eshleman. 1996. Episodic acidification of a coastal plain stream in Virginia. *Water Air Soil Pollut.*89:291-316.

This study examined the episodic acidification of an acid-sensitive coastal plain stream in Virginia. All storms sampled showed increases in SO_4^{2-}, with highest concentrations near peak discharge; small increases in base cations and DOC also were found for most storms. Increases in sulfuric acid concentrations were the primary causes of ANC depressions, although organic acids also contributed to ANC loss during winter/spring rainstorms. The chemical results also lend support to the hypothesis that saturation overland flow is the dominant mechanism for transport of solutes to the stream during stormflow conditions.

O'Brien, A.K., K.C. Rice, M.M. Kennedy, and O.P. Bricker. 1993. Comparison of episodic acidification of mid-Atlantic upland and coastal plain streams. *Water Resour. Res.* 29:3029-3039.

Field studies of episodic acidification were conducted in five mid-Atlantic watersheds in three physiographic provinces: Coastal Plain, Valley and Ridge, and Blue Ridge. ANC depressions were largest in watersheds underlain by reactive bedrock, compared to those underlain by quartzites or unconsolidated quartz sands and cobbles. Results from the study clearly demonstrated that sulfuric acid can contribute to episodic ANC depressions in the region, compared to the northeastern United States where nitric acid is the more dominant contributor.

Pinder, M.J., and R.P. Morgan. 1994. Interactions of pH and habitat on cyprinid distributions in Appalachian streams of Maryland. *Trans. Am. Fish. Soc*. 124(1):94-102.

The authors related water chemistry, physical habitat, and watershed characteristics to cyprinid distributions in 56 Appalachian streams in Maryland. Eleven of these streams had pH ≤ 5.3, ANC of ≤ 50 µeq/L, and lacked cyprinids. Gradient was the primary factor affecting cyprinid presence in streams that had pH 6.49 or higher. This indicates that some streams with pH 5.3 or less would have lacked cyprinids in the absence of acidification, but that cyprinid distributions are affected by factors related to stream acidification.

Qualls, R.G., and B.L. Haines. 1992. Biodegradability of dissolved organic matter in forest throughfall, soil solution, and stream water. *Soil Sci. Soc. Am*. J. 56:578-586.

More than 95% of DOC and DON leached by throughfall was removed by soils under oak hickory forest in the southern Appalachians. Soil adsorption rather than decomposition seems responsible for most DON and DOC removal.

Robson, A., K. Beven, and C. Neal. 1992. Towards identifying sources of subsurface flow: A comparison of components identified by a physically based runoff model and those determined by chemical mixing techniques. *Hydrol. Proc.* 6:199-214.

This paper addresses the problem of dynamic modeling of ANC in streams using a modified version of TOPMODEL, in which fixed concentrations are assumed for the two end-members: deep groundwater flow and saturation overland flow components. Results using the modified version of TOPMODEL were then compared with a 2-month synthetic record of ANC (from pH) for a small, spruce-forested catchment in Wales. The comparison is encouraging, except during periods when the saturation overland flow component is a combination of rainwater and subsurface water (and thus the exact chemical composition of this mixture is not well defined). In addition, the results indicated that the assumption of constant composition end-members is not valid over long time periods.

Rosemond, A.D., Reice, S.R., Elwood, J.W., and Mulholland, P.J. 1992. The effects of stream acidity on benthic invertebrate communities in the southeastern United States. *Fresh. Biol*. 27(2):193-209.

This paper reports on strong relationships between measures of the benthic invertebrate community and water chemistry in Great Smoky Mountains National Park. Baseflow pH values were 4.5–6.8, and inorganic monomeric aluminum was 3–197 µg/L. Total invertebrate density (excluding the acid-tolerant chironomids) and species richness were higher in the high pH streams; these effects were attributed to direct effects on the invertebrates rather than on food availability.

Rosseland, B.O., and M. Staurnes. 1994. Physiological mechanisms of toxic effects to acidic water and ecophysiological and ecotoxicological approach. In: C.E.W. Steinberg and R.F. Wright, eds. *Acidification of Freshwater Ecosystems: Implications for the Future*. John Wiley and Sons, Ltd.

This paper is a recent review of toxic mechanisms and fish sensitivities in acidic water. More up-to-date information is provided than was available in 1990-91, but the essential roles of aluminum in ion-regulation failure at the cellular/ organism level, and the loss of early life stages at the population level, have not changed. New relevant areas of emphasis are identified: (1) effects on sensory organs, (2) avoidance responses, (3) sublethal effects on growth, and (4) the greater vulnerability of fish in streams versus lakes.

Rosseland, B.O., I. A. Blakar, A.J. Bulger, F. Kroglund, A. Kvellestad, E. Lydersen, D.H. Oughton, B. Salbu, M. Staurnes, and R. Vogt. 1992. The mixing zone between limed and acidic river waters: Complex aluminum chemistry and extreme toxicity for salmonids. *Environ. Pollut*. 78(1):3-8.

This paper contains an explanation of one of the important consequences of liming, which is being increasingly considered and used in the SAMI region. The mixing zone downstream of the confluence between limed and unlimed acidic waters has unstable aluminum chemistry, and the water can be even more toxic than the unlimed acidic tributary, even though the pH and calcium are higher and the inorganic monomeric aluminum is lower. This phenomenon might occur at any confluence where the mixing waters have very different pH values; it can create a very toxic zone unpassable by fish.

Schaefer, D.A., and C.T. Driscoll. 1993. Identifying sources of snowmelt acidification with a watershed mixing model. *Water Air Soil Pollut.* 67:345-365.

Two-component separations of discharge into old (soil and ground water) and new (snowmelt water) were performed using ionic tracers for 11 Adirondack watersheds; old water contributions ranged from 66% to 90% and no relationship between old water % and soil depth (to till) was found. It was therefore concluded that the magnitude of episodic acidification in Adirondack watersheds is primarily governed by watershed chemical interactions, not by the varying proportions of "old" water during snowmelt.

Schaefer, D.A., C.T. Driscoll, Jr., R. Van Dreason, and C.P. Yatsko. 1992. Reply. *Water Resour. Res.* 28:2874-2876.

This paper was a reply to the technical comment of Eshleman (1992), which again argued that the linear relationship observed by Eshleman (1988) between ANC_{index} and $ANC_{minimum}$ for a group of lakes in the Adirondacks of New York is a statistical artifact.

Shanley, J.B., and N.E. Peters. 1993. Variations in aqueous sulfate concentrations at Panola Mountain, Georgia. *J. Hydrol. Amst.* 146:361-382.

Aqueous SO_4^- concentrations were measured in incident precipitation, canopy throughfall, stem-flow, soil water, groundwater, and streamwater at three locations in a 41-ha forested watershed at Panola Mountain State Park in the Georgia Piedmont. Canopy throughfall, stemflow, and runoff from a bedrock outcrop in the headwaters were enriched in SO_4^- relative to incident precipitation due to washoff of dry deposition that accumulated between storms. Streamwater SO_4^- concentrations during base flow were controlled by low SO_4^- groundwater discharge. As flow increased, an increasing proportion of shallow, high-sulfate groundwater and soil water contributed to streamflow. The dominant control on stream SO_4^- concentration shifted from SO_4^- retention by adsorption in the mineral soil at baseflow to mobilization of SO_4^{2-} from the upper, organic-rich horizons of the soil at high flow.

Shubzda, J., S.E. Lindberg, C.T. Garten, and S.C. Nodvin. 1995. Elevational trends in the fluxes of sulphur and nitrogen in throughfall in the Southern Appalachian mountains: Some surprising results. *Water Air Soil Pollut.* 85:2265-2270.

This study evaluated deposition and throughfall chemistry along an elevational gradient in Great Smoky Mountains National Park. Deposition rates increased with elevation, driven largely by a large input from cloudwater above 1700 m. Nitrogen concentrations in throughfall at the highest elevations were 30% lower than at lower elevation sites. The authors hypothesize that: (1) lower rates of dry deposition among declining forests at high elevations and/or (2) higher rates of canopy uptake of N at high elevations are responsible for the lower N in throughfall at high elevations.

Stoddard, J.L. 1994. Long-term changes in watershed retention of nitrogen: Its causes and aquatic consequences. Pages 223-284 in L.A. Baker, ed. *Environmental Chemistry of Lakes and Reservoirs*. Advances in Chemistry Series, No. 237. American Chemical Society, Washington, DC.

This paper does not deal specifically with the SAMI region, but it does present some results for Great Smoky Mountains National Park, Fernow, Coweeta and other sites. The paper proposes a taxonomic scheme for classifying watersheds according to their stage (Stage 0 through Stage 3) of nitrogen saturation. The control watersheds at Fernow are among the few United States sites at Stage 2, while the Noland Divide watershed in Great Smoky Mountains National Park is the only Stage 3 site identified.

Tranter, M., T.D. Davies, P.J. Wigington, Jr., and K.N. Eshleman. 1994. Episodic acidification of freshwater systems in Canada—physical and geochemical processes. *Water Air Soil Pollut.* 72:19-39.

This paper largely summarizes Section 3.3 of Wigington et al. (1990), NAPAP SOS/T Report 12.

Van Sickle, J., J.P. Baker, H.A. Simonin, B.P. Baldigo, W.A. Kretser, and W.E. Sharpe. 1996. Episodic acidification of small streams in the northeast United States: Effects on fish mortality during field bioassays. *Ecol. Appl.* 6:408-421.

This paper largely summarizes the results from the field bioassays in the 13 ERP streams first reported on by Wigington et al. (1993).

Wang, D., Y. Xia, D. Zhuang, B, Liu, X. Li, Q. Kuang, and S. Wang. 1992. A study of effects of water acidification on aquatic organisms of different trophic levels. *Acta Sci. Circumstant.* 12(1):91-96.

This study assessed the effects of low pH on aquatic organisms at various trophic levels, including zooplankton, mollusks, aquatic insects, algae, and heterotrophic bacteria. The threshold of adverse effects appeared to be pH 5.0–5.5 for most of these organisms.

Webb, J.R., F.A. Deviney, J.N. Galloway, C.A. Rinehart, P.A. Thompson, and S. Wilson. 1994. *The Acid-base Status of Native Brook Trout Streams in the Mountains of Virginia: A Regional Assessment Based on the Virginia Trout Stream Sensitivity Study*. Report submitted to Virginia Department of Game and Inland Fisheries, Charlottesville.

This report provides an assessment of the acid-base status of streams in Virginia that support reproducing populations of native brook trout (*Salvelinus fontinalis)* based on streamwater composition data collected through June 1993. The report describes (1) a stream classification system based on present acid-base status and bedrock geology, (2) trend analysis of changes in streamwater composition during the period of study (1987-1993), and (3) development and application of several models for assessing current impacts and predicting future impacts given a range of sulfur emission reduction levels. An important aspect of the study was the calibration of the linear regression model relating $ANC_{minimum}$ to ANC_{index} for the population of streams; this technique provided a worst-case analysis of acidification impacts under baseflow conditions.

Webb, J.R., B.J. Cosby, K.N. Eshleman, and J.N. Galloway. 1995. Change in the acid-base status of Appalachian Mountain catchments following forest defoliation by the gypsy moth. *Water Air Soil Pollut.* 85:535-540.

Long-term monitoring of the chemical composition of White Oak Run in Shenandoah National Park (Virginia) indicates that changes in acid-base status are associated with forest defoliation by the gypsy moth caterpillar. Increasing concentrations of nitrate, chloride, base cations, and hydrogen ion, as well as decreasing concentrations of sulfate and ANC were observed. In addition, record high levels of hydrogen ion and record low levels of ANC indicate that the magnitude of episodic acidification has increased in this acid-sensitive stream.

Wigington, P.J., Jr., T.D. Davies, M. Tranter, and K.N. Eshleman. 1992. Comparison of episodic acidification in Canada, Europe and the United States. *Environ. Pollut.* 78:29-35.

This paper largely summarizes Section 3.4 of Wigington et al. (1990), NAPAP SOS/T Report 12.

Wigington, P.J., Jr., et al. 1993. *Episodic Acidification of Streams in the Northeastern United States: Chemical and Biological Results of the Episodic Response Project*. EPA/600/R-93/190. U.S. Environmental Protection Agency, Washington, D.C.

This report of a major field project conducted by cooperators for the U.S. EPA addressed

uncertainties about the occurrence, causes, and biological effects associated with episodic acidification of streams in the northeastern United States. The project consisted of intensive studies of chemical and biological effects in 13 streams draining forested watersheds in three study regions: the northern Appalachian plateau in Pennsylvania, the Catskill Mountains in New York, and the Adirondack Mountains in New York. Automated sampling and in-situ monitoring equipment was used to determine the chemical composition of the 13 streams from fall 1988 through spring 1990. Biological studies focused on brook trout and native forage species and utilized in-situ bioassays, radio transmitter studies of fish movement, and fish population monitoring.

Results from the chemical studies clearly indicated the occurrence of acidic episodes with pH < 5 and inorganic monomeric Al concentrations > 150 µg/L in at least two streams in each region. ANC depressions were shown to result from a complex interaction of multiple ions, but base cation dilution was important in all regions. Organic acid pulses were significant in Adirondack streams, while nitric acid pulses dominated the response of the Catskill and Adirondack streams. Only the Pennsylvania streams were regularly affected by episodic pulses of sulfuric acid.

Results from the in-situ field bioassays indicated that mortality was significantly higher during acidic episodes than during nonacidic conditions. In addition, a multiple logistic regression model was used to relate bioassay mortality to summary statistics of time-varying stream chemical composition. In general, the modeling results indicated that mortality could be adequately predicted using a single index of inorganic monomeric Al concentration during stormflow periods; however, a higher percentage of variation in mortality was explained when pH and Ca variables were added to the model.

Results from the fish population studies clearly indicated net downstream movement of fish during events and movement of trout into alkaline refugia—processes that could potentially mitigate the toxic effects associated with individual acid episodes. However, the study results showed that ERP streams with suitable chemical conditions during low flow, but moderate to severe conditions during high flow had higher mortality and lower brook trout density and biomass compared to the nonacidic "control" streams. In general, trout abundance was reduced and acid-sensitive species were absent from ERP streams with median pH < 5.0–5.2 and inorganic Al concentrations > 100–200 µg/L during high flows. Therefore, the authors concluded that episodic acidification can have long-term effects on fish populations and communities in small, acid-sensitive streams.

Wigington, P.J., Jr., J.P. Baker, D.R. DeWalle, W.A. Kretser, P.S. Murdoch, H.A. Simonin, J. Van Sickle, M.K. McDowell, D.V. Peck, and W.R. Barchet. 1996. Episodic acidification of small streams in the northeast United States: Episodic Response Project. *Ecol. Appl.* 6:374-388.

This paper largely summarizes the study areas and objectives of the Episodic Response Project, which were first reported on by Wigington et al. (1993).

Wigington, P.J., Jr., D.R. DeWalle, P.S. Murdoch, W.A. Kretser, and H.A. Simonin. 1996. Episodic acidification of small streams in the northeast United States: Ionic controls of episodes. *Ecol. Appl.* 6:389-407.

This paper largely summarizes the results from the study of chemical changes in the 13 ERP streams first reported on by Wigington et al. (1993).

Appendix A
Stream Networks in the SAMI Class I Wilderness Areas

As part of the analyses done for this report on the SAMI Class I wilderness areas, we digitized the stream networks for the eight smaller Class I areas. We've included these maps in this appendix in case they may be useful for the SAMI assessment or other future SAMI efforts. The stream networks were digitized from the finest map scale available, either a 1:24,000-scale topographic map or a Forest Service Wilderness area map. The presence/absence of a given stream on the 1:100,000-scale topographic map is also given on the maps in this appendix. Thus, a choice in map-scale networks is available.

Figure A-1. Stream network in Dolly Sods wilderness area.

Figure A-2. Stream network in Otter Creek wilderness area.

Figure A-3. Stream network in James River Face wilderness area.

Figure A-4. Stream network in Joyce Kilmer/Slickrock wilderness area.

Figure A-5. Stream network in Linville Gorge wilderness area.

Figure A-6. Stream network in Shining Rock wilderness area.

Figure A-7. Stream network in Cohutta wilderness area.

Figure A-8. Stream network in Sipsey wilderness area.