Effects of Acidic Deposition on Aquatic Resources in the Central Appalachian Mountains

A Shenandoah Watershed Study Report **2004**

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This report and other Shenandoah Watershed Study documents are available at:

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Abstract

Acidic emissions in the United States, primarily sulfur dioxide and nitrogen oxide generated by electric utilities, increased dramatically from the late 1800s through the 1970s. Since the 1970s, emissions of sulfur dioxide have decreased, largely in response to regulatory controls. However, even after emission reductions required by the Clean Air Act Amendments of 1990 are attained (in 2010), emissions of acidic forming compounds, and therefore acidic deposition, will still greatly exceed natural background levels.

The central Appalachian Mountain region, defined here as the mountainous areas of Virginia and West Virginia, is exposed to among the highest acidic deposition levels in the United States, and it is one of the two regions of the country most affected by acidic deposition. Within this region, the most-acidic and most-sensitive streams are associated with forested mountain watersheds. Variation in the response of these streams to acidic deposition is mainly due to differences in the properties of watershed soil and bedrock.

Sulfur is the primary determinant of precipitation acidity and sulfate is the dominant acid anion associated with acidic streams in the central Appalachian Mountain region. Although a substantial proportion of atmospherically deposited sulfur is retained in watershed soils, sulfate concentrations in regional streams have increased dramatically as a consequence of acidic deposition. Sulfate has become the dominant solute in many of these streams –a major change in the chemical environment.

The combination of elevated sulfate concentrations and low acid neutralizing capacities in stream water, in addition to the base-poor status of watershed soils, provide strong evidence of historic acidification in a number of mountain streams in the central Appalachian Mountain region. The correlation between stream water acid neutralizing capacity and fish diversity in Shenandoah National Park indicates that acidification-related species losses have occurred and that more losses are likely if acidification continues. The Saint Marys River has a record of biological effects associated with acidification, including the loss of eight out of twelve fish species. As a consequence of elevated sulfur deposition, most of the streams in Otter Creek and Dolly Sods Wildernesses are too acidic to support fish. A number of stream water sampling surveys confirm that similar conditions are present throughout the region.

Recent trend analysis provides evidence for decreasing acidity levels among some of the region’s brook trout streams in response to decreasing sulfur dioxide emissions. However, many streams are continuing to acidify, and the degree of observed recovery is small in relation both to the magnitude of historic acidification and to surface water recovery observed in northeastern regions of the United States. Model-based projections indicate that substantial additional reductions in acidic deposition are needed to prevent continued acidification of streams in the region, and that the rate and degree of recovery will be limited by depletion of calcium and other base cations in watershed soils.

Contents

Cover photograph: Laurel Fork in Virginia's George Washington National Forest

1.0 Introduction

Acidic deposition, or "acid rain" in popular terminology, is an insidious form of pollution. Its origins can be hundreds of miles upwind from its ultimate consequences. Its effects are commonly manifest in highly valued landscapes that are otherwise protected from human impact. Its effects are commonly subtle, a gradual cumulative loss of environmental quality that occurs on time scales of decades and presents few noticeable effects in the short-term. But in the long-term, the effects of acidic deposition can be dramatic, substantial, and essentially irreversible. Such is the case in the central Appalachian Mountain region, where acidic deposition derived from multiple distant sources affects the remnant wild lands that have been set aside as National Forests, National Parks, and statutory Wilderness.

Figure 1-1: *The Saint Marys River is an acidified native brook trout stream in the Saint Marys Wilderness of Virginia's George Washington National Forest (see Section 3.2).*

Although implementation of the 1990 Clean Air Act Amendments (CAAA) is likely to reduce the impact of acidic deposition on surface water resources in many regions of the United States, certain areas, including the central Appalachian region, remain at risk (USEPA, 1995). It has been shown, based on the acid-base chemistry of surface waters, that the central Appalachian region is one of the two areas of the United States most affected by acidic deposition (Baker et al., 1991). As summarized by Herlihy et al. (1993), streams in the central Appalachian region are especially susceptible to acidification due to elevated rates of acidic deposition, the delayed-response properties of regional soils, and the presence of watersheds with base-poor bedrock. Church et al. (1992) concluded that further acidification of central Appalachian region streams can be expected as a consequence of continuing acidic deposition. More recently, Bulger et al. (2000) predicted that future losses of native brook trout (*Salvelinus fontinalis*) populations in the streams of western Virginia will be substantial unless acidic deposition reductions are much greater than the 1990 CAAA will provide.

Figure 1-2:

Otter Creek is an acidified native brook trout stream in the Otter Creek Wilderness of West Virginia's Monongahela National Forest (see Section 3.3).

Despite these bleak assessments, concern about acidic deposition impacts on aquatic systems in the central Appalachian region came relatively late. Earlier concerns about the problem in the United States tended to focus on the Adirondacks region in New York, where the linkage between acidic deposition and loss of fish populations in lakes was recognized by the 1970s (Driscoll et al., 1991). Although acidic and acidifying streams were previously known to exist at various locations in the central Appalachians, the extent of the problem, as well as the degree of association with acidic deposition, was not well established until surveys of regional stream water quality were conducted in the 1980s (Lynch and Dise, 1985; Kaufmann et al., 1988; Webb et al., 1989). Concern about acidic deposition effects on aquatic systems reached particular prominence with the

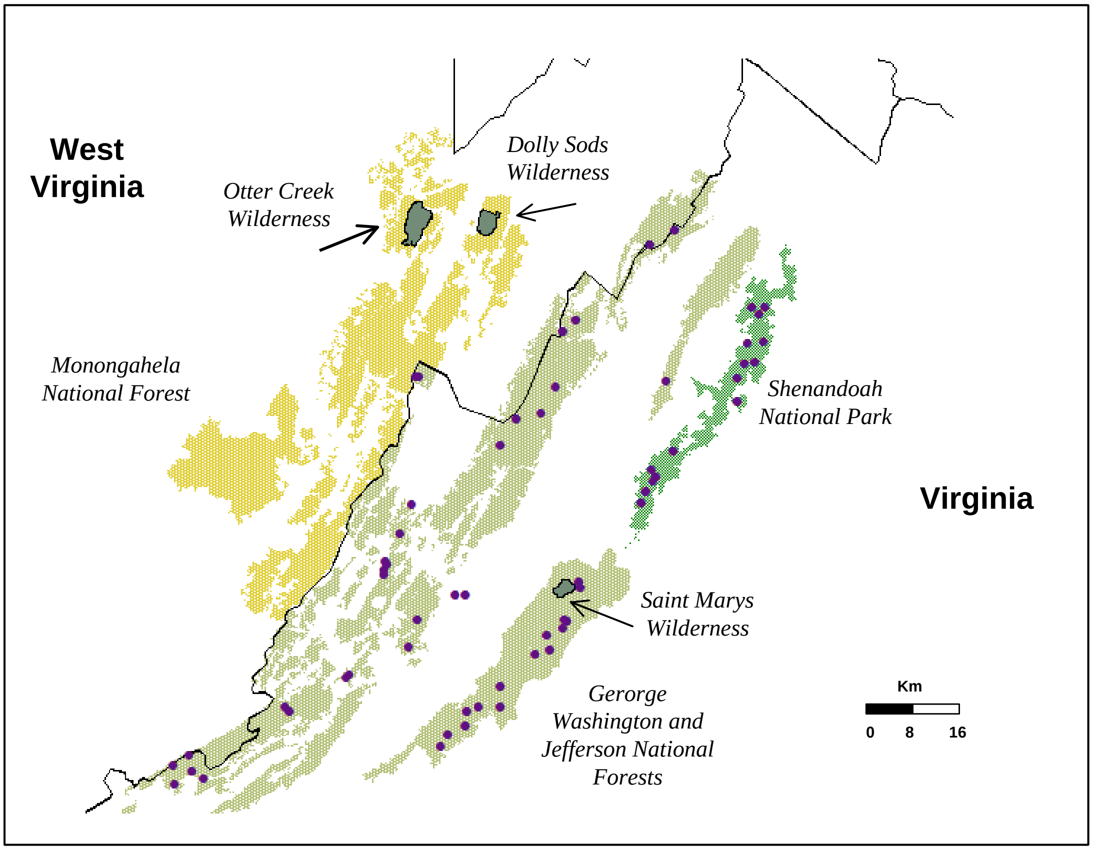


Figure 1-3: *Central Appalachian mountain region case study areas considered in this report. Shaded areas indicate public lands. The points represent data collection sites on native brook trout streams. These sites are sampled through the Virginia Trout Stream Sensitivity Study, a part of the Shenandoah Watershed Study. Additional sampling sites on native brook trout streams are located south of the area depicted (see Figure 3-33).*

completion of the Southern Appalachian Assessment, an effort undertaken by resource agencies that served both to establish the vulnerability of the region's brook trout habitat and document its recreational and aesthetic value (SAMAB, 1996).

Much of the attention currently given to the acidic deposition problem is focused on prospects for recovery of acidified aquatic systems following the reductions in acid-forming emissions mandated by the 1990 CAAA. Despite recent declines in acidic deposition and some encouraging evidence for initial recovery, the degree of recovery has been limited and impairment of surface waters due to acidic deposition continues (Stoddard et al., 2003; Webb et al., 2004). As described in this report, acidification of native brook trout streams is continuing in western Virginia, and the conditions that prevent recovery among these streams are present throughout the central Appalachian region.

2.0 Background

The susceptibility of surface waters to acidification can be attributed to the coincidence of elevated rates of acidic deposition and sensitive watersheds. The following sections of this report describe these two factors in relation to surface water acidification in the central Appalachian region. A subsequent section provides background information concerning the effects of acidification on aquatic life. This sets the stage for descriptions of surface water acidification in specific areas within the general region.

2.1 Elevated Rates of Acidic Deposition

The main source of acidic deposition in the United States is anthropogenic emissions of acid-forming compounds, primarily sulfur dioxide and nitrogen oxide from the burning of fossil fuels. The largest contributor to these emissions nationwide is the electric power industry, which, according to recent estimates, now accounts for 60 percent of all sulfur dioxide and 26 percent of all nitrogen oxide emissions (USEPA, 2000). As indicated by isopleth maps depicting annual average pH and deposition of sulfur and nitrogen species in precipitation, acidic deposition rates in the central Appalachian region are consistently among the highest in the United States (for example, see Figure 2-1).

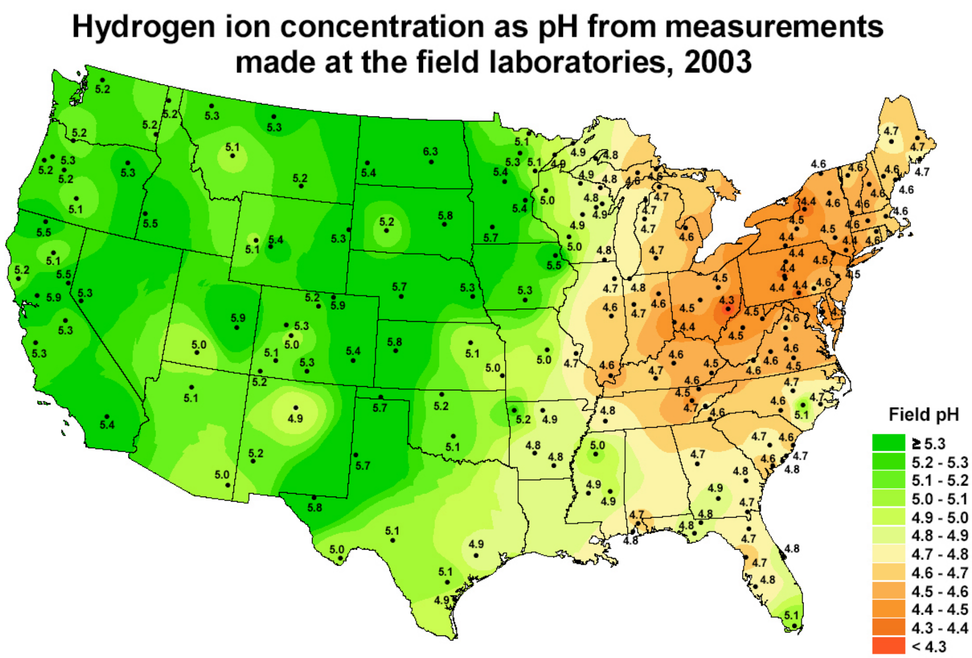


Figure 2-1: *Acidity of precipitation (measured as pH) at monitoring sites of the National Atmospheric Deposition Network (after NADP, 2004). The central Appalachian region consistently receives among the most-acidic precipitation in the United States.*

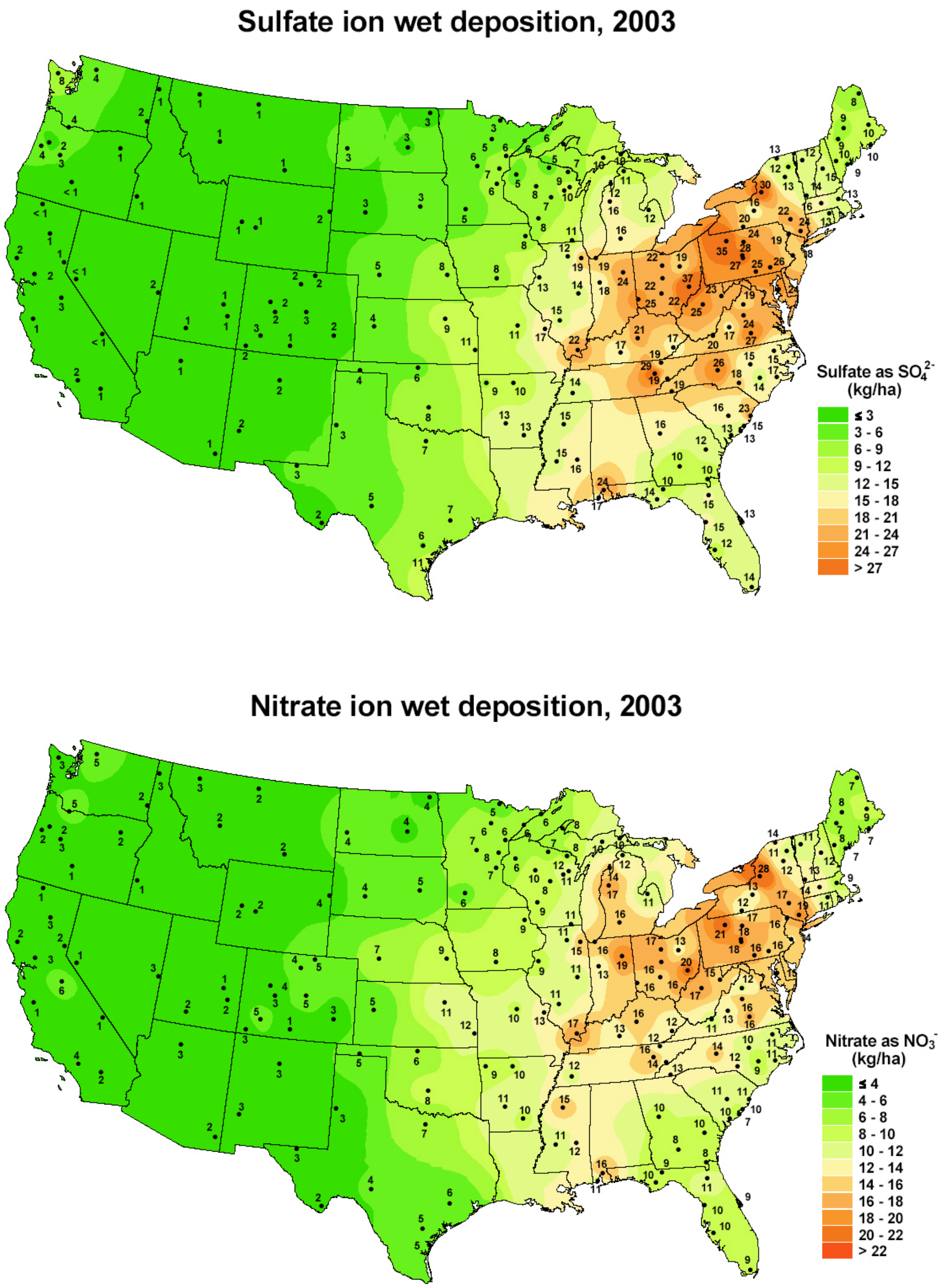


Figure 2-1 (continued): *Regional deposition of sulfate and nitrate ions at precipitation monitoring sites of the National Atmospheric Deposition Network (after NADP, 2004). The central Appalachian region consistently receives among the highest levels of these acidic deposition components.*

A substantial change occurred in both the level and trend of acid-forming emissions during the past few decades, largely in response to regulatory controls. United States emissions of sulfur dioxide and nitrogen oxides peaked around 1970 after increasing amid fluctuations since the late 1800s (Husar et al., 1991). Annual emissions of sulfur dioxide increased between 1900 and 1973 from 9.9 to 31.7 million tons, while emissions of nitrogen oxides increased from 2.6 to 24 million tons (USEPA, 2000). Annual emissions of sulfur dioxide then declined about 38 percent between 1973 and 1998, while emissions of nitrogen oxides leveled off at about the 1973 value (USEPA, 2000). Sulfur dioxide emissions can be expected to decline another 14 percent from 1973 levels by 2010, the target year for compliance with the sulfur emissions cap set by the 1990 CAAA. However, the 1990 CAAA did not set a cap on nitrogen emissions, which are expected to increase in the future with increasing fossil fuel consumption (NAPAP, 1993, 1998).

Reductions in the sulfur component of acidic deposition have generally followed the reductions in sulfur dioxide emissions. Preliminary analysis for the eastern United States indicates that total deposition of sulfur, which includes dissolved, aerosol, particulate, and gaseous forms, declined by an average of 26 percent between 1989 and 1998 (USEPA, 2000). Of more-specific relevance to the central Appalachian region, deposition of sulfate in precipitation in the mid-Appalachian area (West Virginia and Virginia, as well as areas to the north), declined by 23 percent between the periods of 1983-94 and 1995-98 (USGAO, 2000). Legislated reductions in sulfur dioxide emissions have thus achieved reductions in sulfur deposition, and additional reductions can be anticipated through 2010.

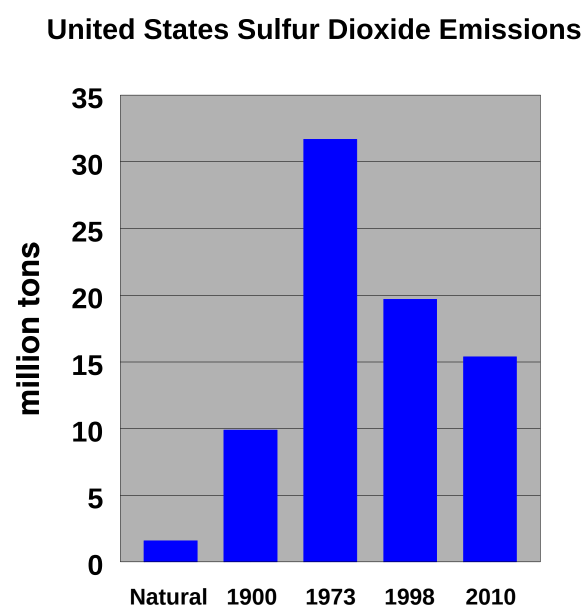


Figure 2-2: *Estimated United States sulfur dioxide emissions. Levels for 1900, 1973, and 1998 are from USEPA (2000). The level for 2010 represents the emission cap required by the 1990 Clean Air Act Amendments. The natural or background level is estimated as 5 percent of the 1973 level.*

The more-critical issue relative to ecosystem effects is the magnitude of anthropogenic emissions in relation to natural emissions (Figure 2-2). Total emissions of both nitrogen and sulfur compounds greatly exceed natural emission levels. Estimates of natural nitrogen emissions in the United States are in the range of 10-11 percent of total nitrogen emissions (NAPAP, 1990; Placet, 1990). Anthropogenic emissions of nitrogen oxides are thus presently about 9 times the natural background level and are expected to increase. Estimates of natural sulfur emissions in the United States are in the range of 1-5 percent of total sulfur emissions (NAPAP, 1990; Placet, 1990). The maximum total annual sulfur dioxide emission level occurred in 1973 at approximately 31.7 million tons (USEPA, 2000). Assuming that as much as 5 percent of the sulfur dioxide emitted in 1973 was derived from non-anthropogenic sources, the natural emission level for sulfur, expressed as sulfur dioxide, is about 1.6 million tons per year. When fully implemented in 2010, the 1990 CAAA will cap anthropogenic sulfur dioxide emissions at 15.4 million tons per year, a value that is at least 9 times the natural background level. Thus, even with anticipated emission reductions, emissions of acid-forming compounds, and hence acidic deposition, will continue to far exceed natural levels.

2.2 Watershed Sensitivity

Watershed response to acidic deposition may involve chronic or episodic change in the acid-base status of surface waters. The term acid-base status refers to the effective balance between acids and bases in solution. Surface water acidification is defined as a loss of acid neutralizing capacity (ANC). Loss of ANC related to acidic deposition occurs when concentrations of strong-acid anions (sulfate and nitrate) increase relative to concentrations of base cations (calcium, magnesium, potassium, and sodium ions). If

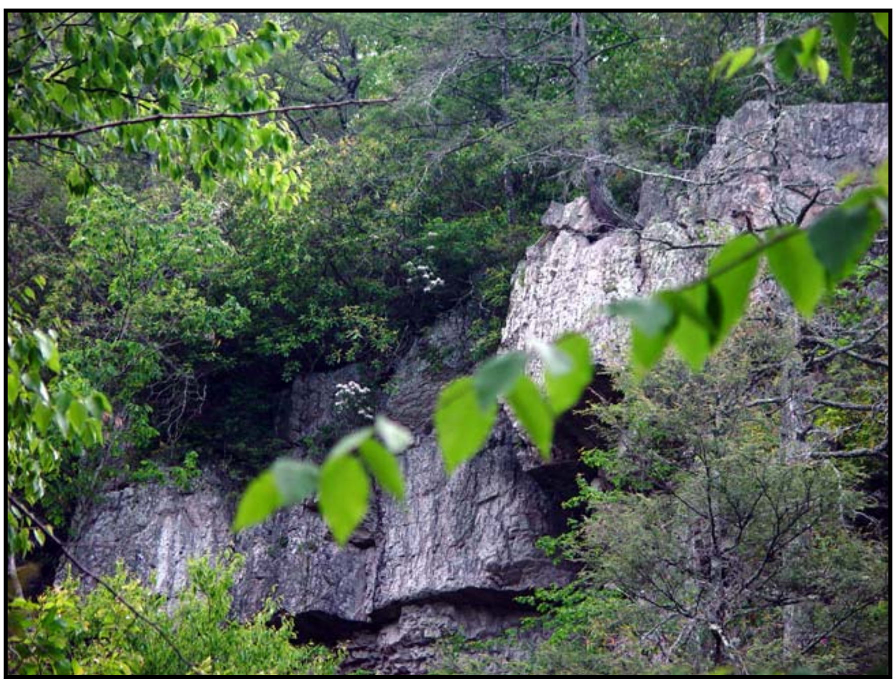


Figure 2-3: *Many of the mountain watersheds in the central Appalachian region are underlain by quartzite and sandstone. Soils that develop from these base-poor and weathering-resistant rocks provide minimal acid neutralizing capacity.*

surface water ANC is reduced to sufficiently low values, acidity may increase, as indicated by a depression in pH, to a range associated with adverse effects on fish and other aquatic life (Baker and Christensen, 1991).

Although surface water acidification involves a decrease in both ANC and pH (which is a direct measure of acidity), the relationship between ANC and pH is nonlinear. At lower ANC levels, a given change in ANC results in more change in pH than occurs given the same change in ANC at higher ANC levels. The ANC of surface water is thus an indication of sensitivity to acidification, as well as an indication of present acidity. The degree to which acidic deposition results in chronic, or long-term, loss of ANC in surface water depends mainly upon two watershed processes associated with acid-base status: (1) anion retention in watershed soils; and (2) base-cation release from watershed soils and rocks (Elwood, 1991; Church et al., 1992). The degree to which acidic deposition results in episodic, or short-term, loss of ANC in surface water depends upon the hydrologic flow path associated with high-runoff conditions (Turner et al., 1990; Wigington et al., 1990).

2.2.1 Sulfur Retention in Watershed Soils: A Delayed-Response Mechanism

Sulfate and nitrate, derived from anthropogenic emissions of sulfur dioxide and nitrogen oxides as discussed above, are the primary strong-acid anions associated with acidic deposition in the United States (NAPAP, 1991). Of these two anions, sulfate is the primary determinant of precipitation acidity and the dominant anion associated with acidic streams (NAPAP, 1991; Baker et al., 1991). Although nitrate is also associated with precipitation acidity, nitrate concentrations in upland surface waters are commonly low due to demand for nitrogen as a nutrient in regenerating forests (Aber et al., 1989, 1998; Johnson, 1992). The deposition and fate of sulfur in watersheds has accordingly received most of the attention in assessments of acidic-deposition effects (e.g., NAPAP, 1991; Church et al., 1992).

Although correlations are observed between sulfur deposition measured in precipitation and sulfate concentrations measured in surface waters (Kaufmann, 1988; Baker et al., 1990a), sulfur is not fully mobile in many watersheds systems; some watersheds accumulate or retain sulfur, a process which has the effect of reducing acidity in soil and surface water. Although most watersheds in the northeastern United States do not retain significant amounts of sulfur, watersheds in the southeastern United States commonly retain more than 50 percent of deposited sulfur (Rochelle and Church, 1987; Turner, 1990). This difference in sulfur retention between the two regions is commonly attributed to greater sulfate adsorption capacity in the older and more-weathered southeastern soils (Galloway et al., 1983; Baker et al., 1991). Figure 2-3 illustrates the effect of differences in sulfur retention between the southeastern and northeastern United States in terms of response to reduced sulfur deposition levels.

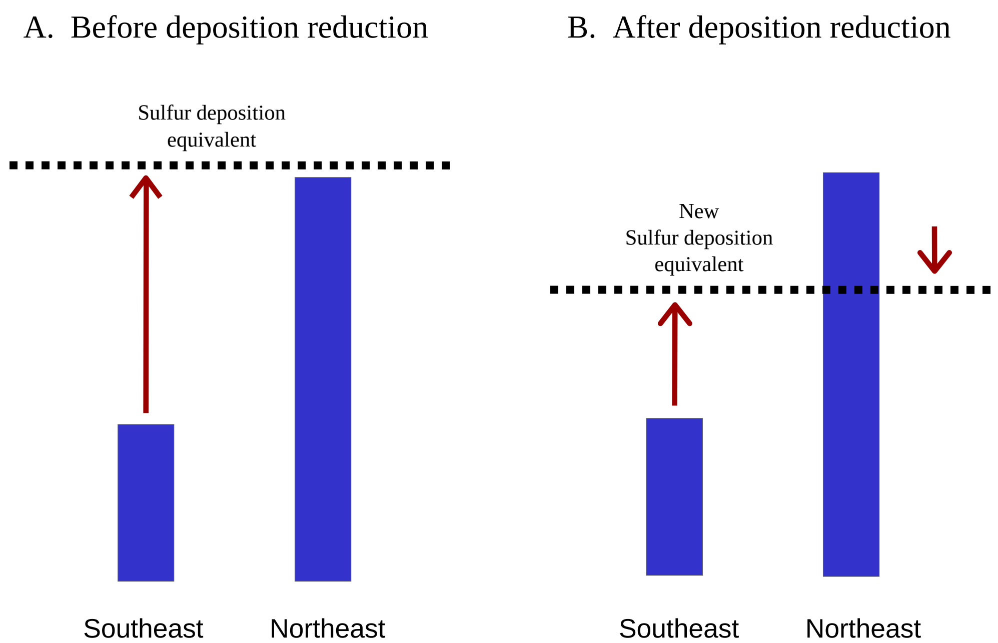


Figure 2-4: *Illustration of the sulfur retention effect on surface water sulfate concentrations.*

The bars represent surface water sulfate concentrations. The arrows indicate trends in surface water sulfate concentrations. The sulfur deposition equivalent is the surface water sulfate concentration given no retention of deposited sulfur in watershed soils.

A. *Before deposition reduction: soils in the southeast retain sulfur, and surface water sulfate concentrations increase as retention capacity of soils is exhausted and until the deposition equivalent is attained.*

B. *After deposition reduction: sulfate concentrations in northeastern surface waters decrease to the new deposition equivalent, while sulfate concentrations in southeastern surface waters continue to increase until the new deposition equivalent is attained.*

Although there are other mechanisms of sulfur retention or immobilization in watersheds, including sulfur reduction and biological uptake, these are generally considered less important on regional scales than is adsorption, particularly in upland forests (Turner, 1990). Regardless of mechanism, sulfur retention in watersheds reduces the potential for the acidification of surface waters that is associated with increasing concentrations and mobility of sulfate. However, sulfur retention by adsorption is a capacity-limited mechanism. As the finite adsorption capacity of watershed soils is exhausted, surface waters can increase in sulfate concentration and thus be subject to greater acidification (Johnson and Cole, 1980; Munson and Gherini, 1991; Church et al., 1992).

The boundary between the southeastern region with watersheds that retain sulfur and the northeastern region with watersheds that do not retain sulfur is generally given as the southern limit of the last continental glaciation. Given the importance of sulfur retention among the factors that determine the watershed response to acidic deposition, this boundary in northern Pennsylvania provides a meaningful geographic limit for the central Appalachian Mountain region with respect to acidic deposition effects. It should be noted, however, that this boundary is only approximate.

Herlihy et al. (1993), for example, reviewed information concerning sulfate mobility and retention in watersheds of the central Appalachian region. Although the dissolved mineral composition of most upland streams in this region is dominated by sulfate derived from atmospheric deposition, many streams in the region have not fully realized the effects of this deposition. Some watersheds in the region have high net retention. Others are near the equilibrium condition in which soils are, in effect, sulfur saturated, and sulfur efflux in surface waters equals sulfur influx from atmospheric deposition. Herlihy et al. (1993) concluded that the region is in a state of transition and that net annual sulfur retention in the watersheds of this region will undoubtedly continue to decrease, resulting in increasing stream water sulfate concentrations and further stream acidification.

2.2.2 Base-Cation Release From Watershed Soils and Rock: A Buffering Mechanism

An increase in the concentration of sulfate or other strong-acid anions in surface water will be balanced by an equivalent increase in the concentration of cations. Depending upon the availability of exchangeable base cations in the soil (primarily calcium, magnesium, and potassium ions), the cations associated with increasing concentrations of strong-acid anions can be either acidic or basic. The export of acidic cations (primarily hydrogen and aluminum ions) may contribute directly to loss of ANC, or surface water acidification.

Although the export of base cations serves to reduce direct surface water acidification, it may also contribute to depletion of the base-cation supply in the soil. Figure 2-5 illustrates the process whereby sulfate deposition leeches base cations from watershed soils. As the base-cation supply is reduced, the soil becomes more acidic and an increasing proportion of the exchangeable cation supply consists of hydrogen and aluminum ions (Reuss and Johnson, 1986; Reuss and Walthall, 1990).

The supply of base cations in watersheds can be external or internal. External sources include atmospheric deposition in both precipitation and dry (aerosol, particulate, and gaseous) forms. As indicated by ion-enrichment analysis, internal watershed sources are the main sources of base cations in most upland surface waters of the eastern United States (Baker et al., 1991). The primary internal sources of base cations in most watersheds are mineral weathering and soil exchange. By comparison with exchange reactions, mineral weathering occurs at relatively slow and constant rates (Turner et al., 1990; Munson and Gherini, 1991). Thus, the main source of cations for acid neutralization in most watersheds is the accumulated supply of exchangeable base cations in the soil. However, the size of this supply, and thus the degree to which soil and surface water acidification occurs, is ultimately determined by the availability of base cations in watershed bedrock. As reflected in the low ANC and low base-cation concentrations of stream waters, most of the ridges in the central Appalachian Mountain region are underlain by base-poor bedrock (Webb et al., 1989; Church et al., 1992; Herlihy et al., 1993).

The loss of base cations from soils in base-poor watersheds is a primary consequence of prolonged exposure to acidic deposition, adversely affecting both aquatic and terrestrial components of the ecosystem. As a consequence of base depletion in watershed soils and the comparatively slow replacement of exchangeable base supplies by mineral weathering, the rate of surface water recovery from acidic deposition will be retarded in relation to reductions in acidic deposition, and full recovery may only occur in the context of very long time scales (Galloway et al., 1983; Cosby et al., 1985; Likens et al., 1996).

In addition to neutralizing acidity through soil exchange, base cations are critical nutrients for both aquatic fauna and terrestrial vegetation. Reduced availability of

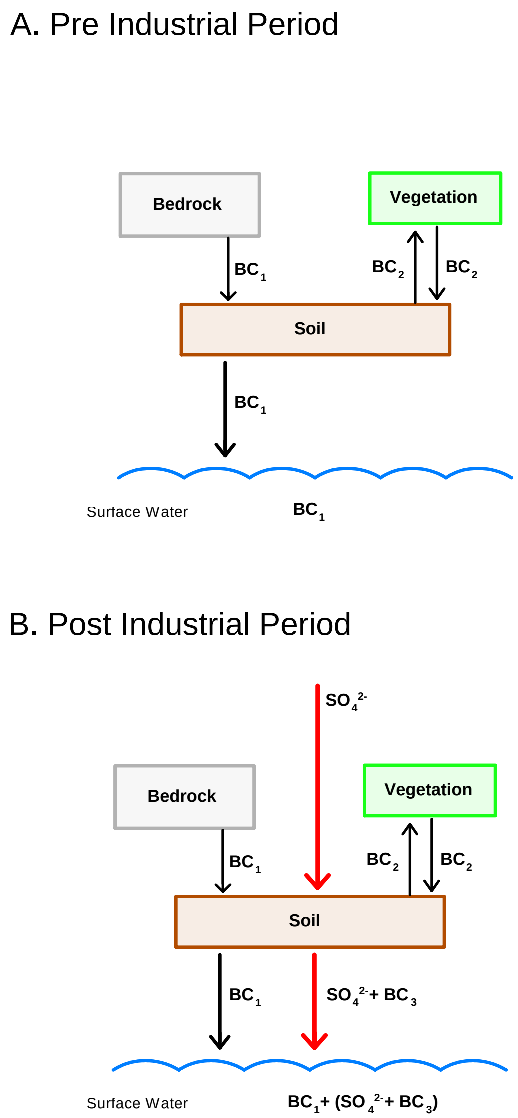


Figure 2-5: *Export of base cations (BC) from watershed soils.*

A. *Pre Industrial Period: The base-cation supply in the soil is stable; losses to surface water are replaced by release from bedrock. Base cations taken-up by vegetation are recycled.*

B. *Post Industrial Period: Sulfate (SO_4^{2-}) moving through the soil leaches base cations. Acidity is buffered at the expense of the base-cation supply. In time, base-poor soils are dominated by the acidic cations, hydrogen and aluminum.*

calcium in surface waters has negative implications for fish. As indicated in Section 2.3, the toxicity of acidity and aluminum are increased when concentrations of calcium are low. Reduced availability of calcium in watershed soils also has negative implications for forest health and productivity. A number of studies have indicated that low calcium supplies in forest soils are associated with reduced potential for forest growth and regeneration (Long et al., 1997; Huntington, 2000; Driscoll et al., 2001).

2.2.3 Hydrologic Flow Path: Determinant of Extreme Conditions

The routing of water as it flows through a watershed determines the degree of contact with acidifying or neutralizing materials. In any given watershed, surface water ANC may vary in time depending upon the proportion of the flow that has contact with deep versus shallow soil horizons; the more subsurface contact, the higher the surface water ANC (Turner et al., 1990). This can be attributed in part to higher base saturation and greater sulfate adsorption capacity in subsurface soils. It may also be related to the accumulation in the upper soil horizons of acidic material derived from atmospheric deposition (Lynch and Corbett, 1989; Turner et al., 1990). Storm flow and snowmelt are often associated with episodes of extreme surface water acidity due to an increase in the proportion of flow derived from water that has moved laterally through the surface soil without infiltration to deeper soil horizons (Wigington et al., 1990).

Hydrologically driven episodic acidification of surface waters has been shown to be a widespread phenomenon (Wigington et al., 1990) and to be associated with acidification effects on aquatic organisms (Baker and Christensen, 1991). It has also been shown to be more severe in waters with chronically low ANC (Wigington et al., 1990),

Figure 2-6:

Paine Run in Shenandoah National Park. Episodic acidification during high-flow conditions has been shown to reduce survival of brook trout eggs and newly hatched fry in Paine Run (see Section 3.1.3).

which indicates that episodic acidification is important in many streams in the central Appalachian region. This has been confirmed by a number of investigators (e.g., Eshleman et al., 1995; Bulger et al., 1995). Episodic acidification may therefore be the limiting condition for aquatic organisms in central Appalachian streams that are marginally suitable for aquatic life under base-flow conditions.

Figure 2-7: *The native brook trout (Salvelinus fontinalis).*

2.3 Acid-Base Limitations on Aquatic Fauna

Although decreases in species richness with increasing acidity have been observed for fish and other aquatic fauna, multiple factors may affect biological populations in individual aquatic systems. The most important surface water constituents that directly influence biological responses to changes in acid-base chemistry are pH, inorganic monomeric aluminum, and calcium ion (Baker and Christensen, 1991). ANC is also recognized as an indicator of surface water suitability for aquatic biota.

Surface water pH has probably received the most attention with respect to effects on fish. A literature review by Baker and Christensen (1991) revealed that the pH range of 6.0-5.5 is associated with loss of fish species such as the blacknose dace (*Rhinichthys atratulus*) and the pH range of 5.0-4.5 is associated with loss of more tolerant fish species such as the brook trout. (*Salvelinus fontinalis*). Studies in the Blue Ridge mountains of Virginia have demonstrated significant mortality of brook trout fry at episodic or storm flow pH values of 5.0 (MacAvoy and Bulger, 1995) and sub-lethal effects on blacknose dace (a prevalent fish species in central Appalachian mountain streams) at chronic pH values of 6.0 (Dennis and Bulger, 1995).

Another factor that affects fish populations is the presence of elevated aluminum concentrations. As summarized by Baker et al. (1990b), the toxicity of aluminum fractions differs. Aluminum that is complexed with dissolved organics is relatively nontoxic; so waters with high organic content may contain little toxic aluminum. However, few acidic streams in the central Appalachian region contain appreciable concentrations of dissolved organics (Baker et al., 1990a). The inorganic monomeric aluminum fraction is generally regarded as the toxic component, with concentrations in the range of 30-50 μg/L (or parts per billion) associated with adverse biological effects.

Dissolved calcium has the effect of mitigating the physiological responses of fish to acidity (low pH) and dissolved aluminum (Baker et al., 1990b). Depletion of calcium, a base cation, from watershed soils thus reduces the availability of calcium both for neutralization of acidity by exchange in soil, as well as for mitigation of toxicity in surface water.

ANC criteria have also been used for evaluation of potential acidification effects on aquatic ecosystems. The utility of these criteria lies in the association between ANC and the surface water constituents that directly contribute to or ameliorate acidity-related stress on aquatic biota. Bulger et al. (2000) have developed ANC thresholds for brook trout response to acidification in forested headwater catchments in western Virginia. These criteria are presented here in Table 1 in order to provide perspective on stream water ANC concentrations described in following sections of this report. Selection of the brook trout as the basis for ANC criteria reflects its recognized recreational and aesthetic value (SAMAB, 1996). Note, however, that because the brook trout is comparatively acid tolerant, adverse effects on other fish species should be expected at relatively higher ANC values. Figure 2-8 provides examples of fish species common to streams draining forested mountain watersheds in the central Appalachian region. The fish species are in two groups based on apparent relative differences in tolerance to low pH and low ANC.

Table 2-1 – Stream water acid neutralizing capacity (ANC) categories for brook trout response (Bulger et al., 2000).

Response Category	ANC Class	ANC Range μeq/L	Brook Trout Response
Suitable	Not acidic	>50	Reproducing brook trout populations expected where habitat suitable
Indeterminate	Indeterminate	20-50	Extremely sensitive to acidification; brook trout response variable
Marginal	Episodically acidic	0-20	Sub-lethal and/or lethal effects on brook trout possible
Unsuitable	Chronically acidic	<0	Lethal effects on brook trout probable

Note: ANC range based on volume-weighted annual mean.

Figure 2-8: *Fish species associated with forested mountain watersheds in the central Appalachian region. Examples of species commonly present in streams with relatively low pH and ANC; based on data presented in Bugas et al. (1999) and Sullivan et al. (2003).*

Brook Trout *(Salvelinus fontinalis)*

Blacknose Dace *(Rhinichthys atratulus)*

Fantail Darter *(Etheostoma flabellare)*

Mottled Sculpin *(Cottus bairdi)*

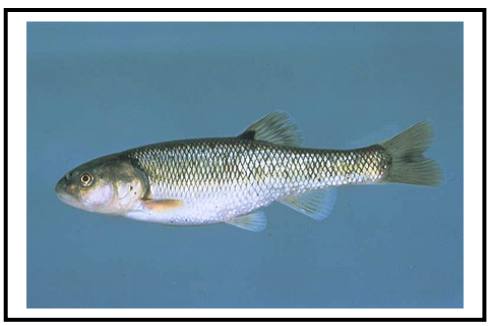
The photographs in Figure 2-8 were obtained from EFISH: The Virtual Aquarium, a website maintained by the Department of Fisheries and Wildlife Sciences at Virginia Polytechnic Institute and State University (photographers: Bob Jenkins and Noel Burkhead) (http://www.fw.vt.edu/efish/)

Figure 2-8 (continued): *Fish species associated with forested mountain watersheds in the central Appalachian region. Examples of additional species commonly present in streams with relatively high pH and ANC; based on data presented in Bugas et al. (1999) and Sullivan et al. (2003).*

Rosyside Dace *(Clinostomus funduloides)*

Torrent Sucker *(Thoburnia rhothocea)*

Longnose Dace *(Rhinichthys cataractae)*



Creek Chub *(Semotilus atromaculatus)*

3.0 Stream Water Acidification in the Central Appalachian Mountain Region

The presence of acidic and low-ANC streams associated with forested mountain watersheds in the central Appalachian region has been well documented (Webb et al., 1989; Baker et al., 1990a; Herlihy et al., 1993). The following sections describe findings for research and monitoring efforts conducted on a number of streams in the central Appalachian region that have been affected by acidic deposition.

Figure 3-1:

The Blue Ridge Mountains in Shenandoah National Park.

Note that the focus in the following sections is on streams; natural lakes are rare in the central Appalachians. Also note that the focus is primarily on relatively small headwater streams that drain ridges. Throughout the central Appalachian region there are distinct differences in ANC values between streams draining ridge versus valley topography (Baker et al., 1990a; Herlihy et al., 1993). Due to the noncarbonate composition and weathering-resistant character of the underlying bedrock, streams draining the ridges commonly have minimal ANC. In contrast, due to the carbonate (e.g., limestone) composition and more-weatherable character of the underlying bedrock, the streams located in the valleys commonly have high ANC. Relative to all the streams in the region, the streams draining the ridges thus represent a more-acidic and more-sensitive subpopulation.

The following sections describe the status of streams in Shenandoah National Park, and in Saint Marys, Otter Creek, and Dolly Sods Wildernesses, and throughout the range of the brook trout in western Virginia. Major findings of other regional-scale investigations are also provided.

3.1 Shenandoah National Park: Case Study

Shenandoah National Park (SNP) straddles a 100-km segment of the Blue Ridge Mountains in western Virginia (Figure 3-2), on the eastern edge of the central Appalachian Mountain region. Several areas in the park have been designated Wilderness.

Information concerning the status of SNP streams relative to acidic deposition has been obtained though the Shenandoah Watershed Study (SWAS), a cooperative program of the Department of Environmental Sciences at the University of Virginia and the National Park Service. The SWAS program was initiated in 1979, with the establishment of water quality monitoring on two streams. The current watershed data-collection system involves 14 primary study watersheds (Figure 3-2), including a combination of routine discharge gauging, routine quarterly and weekly water quality sampling, and high-frequency episodic, or storm-flow, sampling. In addition, a number of extensive stream quality surveys, fish population surveys, and other watershed data collection efforts have been conducted throughout SNP in support of various research objectives.

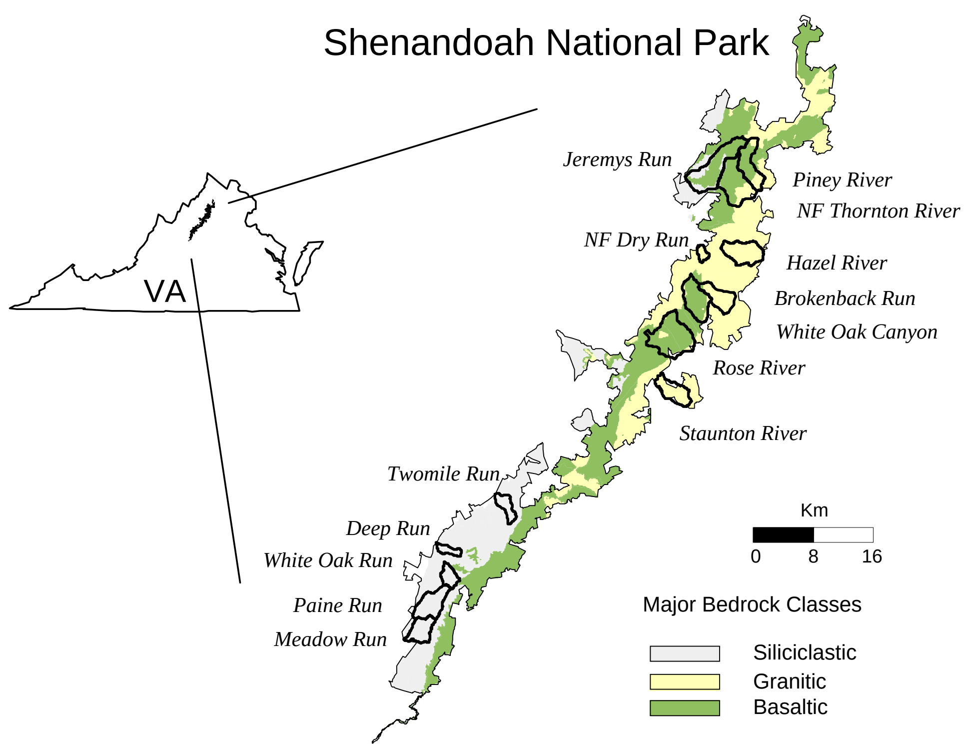


Figure 3-2: *Primary study watersheds in Shenandoah National Park shown in relation to the distribution of major bedrock. (Bedrock map based on Gathright, 1976.)*

3.1.1 Shenandoah National Park: Current Stream Water Composition

Base Flow Condition

Lynch and Dise (1985) determined that stream water ANC, pH, and base cation concentrations in SNP are strongly correlated with bedrock geology. SNP landscape includes three major bedrock types, siliciclastic (quartzite and sandstone), granitic, and basaltic. Each of these bedrock types influence about one-third of the stream miles in SNP. Table 3-1 presents descriptive statistics for ANC, pH, base-cation (the sum of calcium, magnesium, potassium, and sodium), and sulfate analyses of samples obtained in a spring 1992 sampling survey of streams draining small sub-watersheds within the primary study watersheds. The values are shown for samples associated with single bedrock types.

Relative to the brook trout response categories listed in Table 2-1, ANC concentrations for streams associated with siliciclastic bedrock are extremely low. Almost half of the sampled streams had ANC in the chronically acidic range (< 0 µeq/L) in which lethal effects on brook trout are probable. The balance of the streams associated

Table 3-1 - Range and Distribution of Stream-Water Concentrations Associated With Major SNP Bedrock Classes: Spring 1992 Synoptic Survey (Galloway et al., 1999).

	N	MINIMUM	25%	MEDIAN	75%	MAXIMUM
ANC (µeq/L)						
Siliciclastic	62	-18.1	-1.0	1.2	3.7	12.8
Granitic	46	22.0	47.2	58.7	67.0	130.4
Basaltic	14	33.7	97.0	142.9	179.0	226.7
pH						
Siliciclastic	62	4.8	5.4	5.6	5.7	6.0
Granitic	46	6.0	6.7	6.8	6.8	7.1
Basaltic	14	6.6	6.9	7.1	7.2	7.3
Sum of Base Cations (µeq/L)						
Siliciclastic	62	92.1	138.1	168.2	190.4	272.1
Granitic	46	89.5	136.7	147.7	161.3	243.5
Basaltic	14	138.0	232.0	369.5	381.1	450.9
Sulfate (µeq/L)						
Siliciclastic	62	67.2	88.5	97.2	104.8	177.8
Granitic	46	13.4	30.1	36.6	42.1	96.3
Basaltic	14	12.3	36.2	62.2	97.9	164.3

Note: 25% and 75% refer to the 25th and 75th percentile values. 50 percent of all the values are within the interquartile range, as bounded by the 25th and 75th percentile values.

Figure 3-3: *Three intensively studied watersheds in Shenandoah National Park.*

Piney River – *Associated with basaltic bedrock, relatively high pH and ANC, and twelve fish species.*

Staunton River – *Associated with granitic bedrock, intermediate pH and ANC, and five fish species.*

Paine Run – *Associated with siliciclastic bedrock (quartzite and sandstone), relatively low pH and ANC, and three fish species.*

with siliciclastic bedrock had ANC in the episodically acidic range (0-20 µeq/L) in which sub-lethal or lethal effects are possible. Many of the streams associated with the granitic bedrock type were in the extremely sensitive or indeterminate range. In contrast, the streams associated with the basaltic bedrock type have ANC values that are well within the suitable range for brook trout. Note that each of these three bedrock types influence about a third of the total stream miles in the park.

The pH values for the streams in the 1992 survey display a similar relationship with bedrock, with the most-acidic streams associated with siliciclastic bedrock and the least-acidic streams associated with basaltic bedrock. All of the streams associated with siliciclastic bedrock are in the pH range (≤6.0) identified by Baker and Christensen (1991) as too acidic for acid-sensitive fish species.

The distribution of base-cation concentrations for streams in the 1992 survey indicates that soils in much of SNP have extremely limited base-cation supplies. The base-cation concentrations for SNP's mountain streams are generally less than 25 percent of the median base-cation concentration value for the general population of all regional streams sampled in the 1986 National Stream Survey (Kaufmann et al., 1988; Sale et al., 1988). As discussed previously, the availability of base-cations in watershed soils is a primary determinant of stream response to acidic deposition. A common measure of base availability in soils is percent base saturation, which is the base-cation fraction of total exchangeable acid and base cations. Percent base-saturation values in the range of 10–20 percent have been cited as threshold values for leaching of aluminum to soil and surface waters (Reuss and Johnson 1986; Binkley et al. 1989; Cronan and Schofield, 1990). As indicated in Figure 3-4, median base saturation is less than 10 percent for SNP soils associated with siliciclastic bedrock and less than 15 percent for SNP soils associated with granitic bedrock. The present low base-cation availability in SNP soils can be

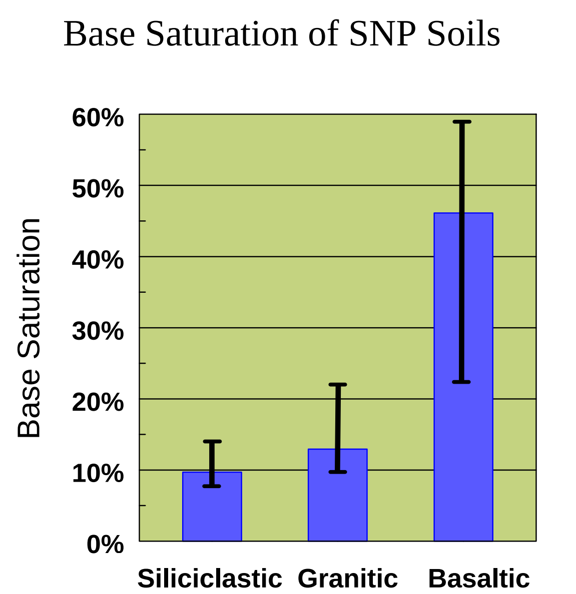


Figure 3-4: *Median percent base saturation for soils associated with SNP's three bedrock types. Brackets delimit interquartile ranges. The base saturation of soils derived from siliciclastic and granitic bedrock is too low for effective buffering of acidic deposition.*

(The data were obtained for mineral-horizon soil samples collected in the summer of 2000 at 80 geologically distributed sites in SNP; Welsch et al., 2001.)

attributed to low base-cation content of the parent bedrock and depletion by decades of accelerated leaching by acidic deposition.

Sulfate is the major strong-acid anion present in most SNP streams. Nitrate concentrations are generally negligible, except in association with forest defoliation by the gypsy moth (Webb et al., 1995). Sulfate concentrations in the streams sampled in the 1992 survey are consistent with the interpretation by Galloway et al. (1983), Elwood (1991), and others that a substantial proportion of atmospherically deposited sulfur is retained in the soils of the southeastern United States. Based on comparison with estimates of total sulfur deposition, sulfur retention in the forested mountain watersheds of western Virginia, including those in SNP, has been variously estimated to range from 45-65 percent of sulfur deposition (Webb et al., 1989; Cosby et al., 1991). The evident differences in sulfate concentrations between streams associated with the different bedrock types is probably not due to differences in deposition amounts, as sulfur deposition is relatively uniform throughout SNP (Galloway et al, 1999). Instead, the differences probably reflect variation in the sulfur retention properties of soils associated with the different bedrock types.

Despite the fact that a high percentage of the sulfur deposited in SNP watersheds does not enter the streams, sulfate is still the chemical species with the highest concentration among all the solutes in many SNP stream waters. Given the absence of significant sulfur-bearing minerals in SNP (Gathright, 1976; Webb, 1988), it is clear that most of this sulfur is derived from the atmosphere. It is also clear that without the delaying effect of sulfur retention in watershed soils, many more SNP streams would now be acidic.

High-Flow Condition

Figure 3-5 displays the general relationship between flow level and ANC for three intensively studied streams representing

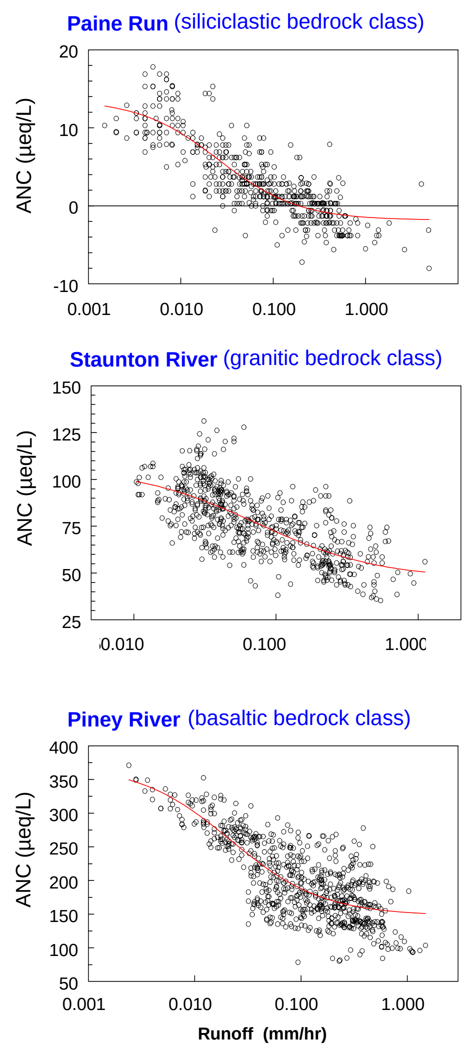


Figure 3-5: *Relationship between ANC and runoff for stream water samples collected at intensively studied sites in Shenandoah National Park.*

(The data represent samples collected during the 1992-1997 period.)

the major bedrock types in SNP. The most acidic conditions in SNP streams occur during higher streams flows, with the most extreme conditions occurring in conjunction with storm or snowmelt runoff. The response of all three streams is similar in that most of the lower ANC values occur in the upper range of flows levels. However, consistent with observations by Eshleman (1988), the minimum ANC values that occur in response to high flow are related to base-flow ANC values. Paine Run (siliciclastic bedrock) has a mean weekly ANC value of about 6 µeq/L and often has high-flow ANC values that are less than 0 µeq/L. Staunton River (granitic bedrock) has a mean weekly ANC value of about 82 µeq/L and has only a few high-flow ANC values less than 50 µeq/L. Piney River (basaltic bedrock) has a mean weekly ANC value of 217 µeq/L and no values as low as 50 µeq/L.

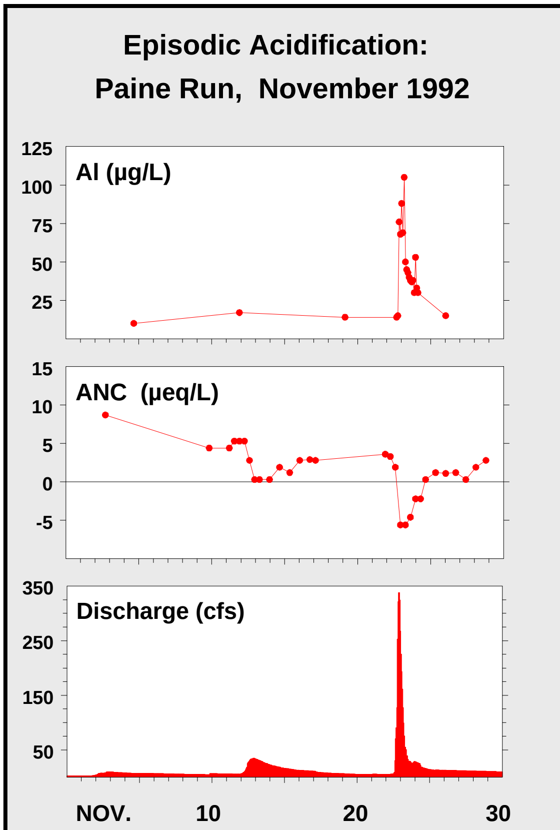


Figure 3-6: *Loss of ANC and increase in dissolved aluminum in Paine Run in response to a sharp increase in stream flow.*

Previous studies have shown that mobilization of dissolved aluminum during episodic acidification is a primary cause of fish mortality in streams that have low ANC under base-flow conditions (Wigington et al., 1993). Streams with higher ANC during base flow are less likely to become sufficiently acidic during episodic acidification to bring aluminum into solution. Figure 3-6 provides an example of changes in ANC and dissolved aluminum that occurred in Paine Run during a high-flow episode in the fall of 1992. Under base-flow conditions ANC is above 0 µeq/L and aluminum concentration is less than 20 µg/L. Stream flow levels increased dramatically around the 23rd of November, resulting in depression of ANC to less than 0 µeq/L and an increase in aluminum concentration to about 100 µg/L, well above the threshold for adverse effects on aquatic biota.

Episodic acidification in SNP streams can be attributed to a number of causes, including dilution of base cations and increased concentrations of sulfuric, nitric, and organic acids (Eshleman et al., 1995; Hyer et al., 1995). Some of these causes are not related to acidic deposition. Base-cation dilution and release of organic acids during high-flow conditions are natural processes. The contribution of nitric acid, indicated by increased nitrate concentrations, is evidently (at least for SNP streams) related to forest defoliation by the gypsy moth (Webb et al., 1995; Eshleman et al., 1998). However, significant contributions of sulfuric acid, indicated by increased sulfate concentrations, should be interpreted as an impact of atmospheric deposition (Eshleman and Hyer, 1999). Moreover, the potential for biologically significant episodic acidification is determined by base-flow ANC, which for many SNP streams is closely related to acidic deposition.

3.1.2 Shenandoah National Park: Change in Stream Water Composition

Although SNP has the longest continuous record of stream water composition in a national park and among the longest anywhere in the United States, the record only goes back to 1979. Given that stream water acidification has been occurring for many decades, the empirical record is only partial at best. Nonetheless, the available information is convincing.

Atmospherically derived sulfate has become the major dissolved ion in many of the streams in SNP, especially in the low-ANC streams associated with siliciclastic bedrock. Estimates of background or natural sulfate concentrations in low-ANC surface waters in the eastern United States range from 10-15 µeq/L (Brakke et al., 1989) to 22 µeq/L (Cosby et al., 1991). Based on the latter estimate and on comparison with median stream water sulfate concentrations observed in the 1992 survey samples, it appears that sulfate concentrations have increased by a factor of 4.4 in streams associated with siliciclastic bedrock, by a factor of 1.7 in streams associated with granitic bedrock, and by a factor of 2.8 in streams associated with basaltic bedrock (Figure 3-7). This represents a dramatic change in stream water composition –a change that can only be attributed to acidic deposition.

It is possible for a large increase in surface water sulfate concentration to occur without a loss of ANC if the watershed system is well buffered. In such a case, base-cation availability would have to be very high. That is, the watershed would have to have deep soils with a high cation-exchange capacity and a high

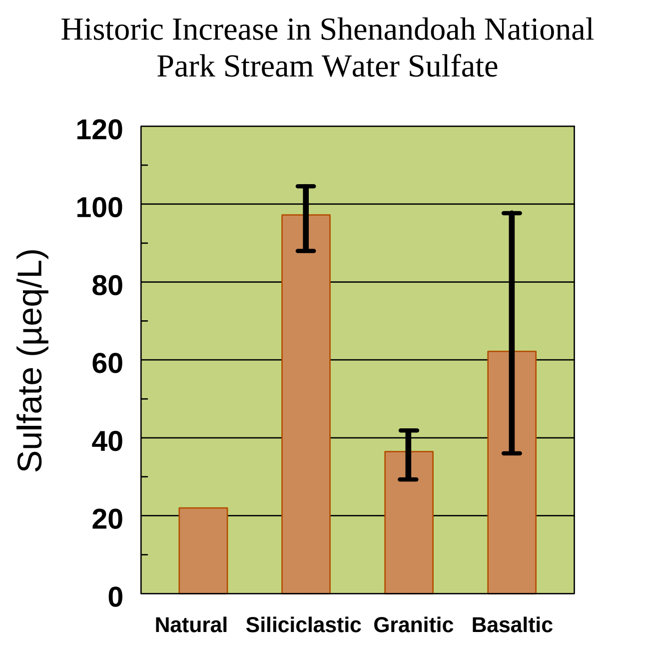


Figure 3-7: *Comparison of estimated natural and current median sulfate concentrations among streams associated with major bedrock types in Shenandoah National Park. Error bars delimit interquartile ranges. (Current concentrations based on 1992 survey data; see Table 3-1.)*

percent base saturation. Given the relatively high ANC values presently observed in streams associated with basaltic bedrock (Table 3-1), as well as the high base saturation of soils derived from that bedrock (Figure 3-4), it is possible that the degree of acidification among those streams has been minimal. In contrast, the large increase in sulfate concentrations among the streams associated with the siliciclastic bedrock provides strong evidence of acidification, given that these streams have minimal remaining ANC (Table 3-1), associated watershed soils are relatively shallow, and soil base availability is minimal (Figure 3-3). If the SNP watersheds with siliciclastic bedrock previously had the much higher base supplies needed to neutralize the acidity associated with decades of increasing sulfate, the associated surface waters would have also had much higher ANC.

The historic loss in stream water ANC in SNP has been estimated based on model analysis (Sullivan et al., 2003). The mathematical model used in the analysis was MAGIC (model of groundwater acidification in catchments), the most widely used acid-base chemistry model in the United States and Europe (Sullivan, 2000), and the principal model used by the National Acid Precipitation Assessment Program to estimate future damage to lakes and streams in the eastern United States (Thornton et al., 1990; NAPAP, 1991). The model was calibrated and applied using soils data obtained at 80 geologically distributed locations in SNP, stream water composition data obtained from the 14 long-term study streams in SNP, and interpolated deposition estimates. As indicated in Figure 3-8, losses in stream water ANC have differed between streams associated with different bedrock types, with the greatest losses occurring in the class of streams associated with siliciclastic bedrock. This is consistent with observations that base availability in soils is the least among this class of streams (see Figure 3-4) and that increases in sulfate have been the greatest among this class of streams (Figure 3-7).

The modeled estimate of historic ANC loss is consistent with the results of trend analysis conducted by Ryan et al. (1989), who examined stream composition

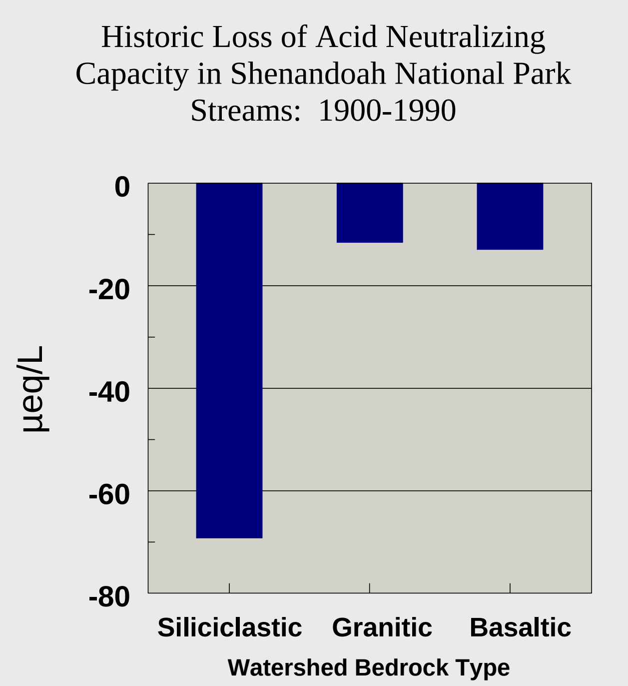


Figure 3-8: *Estimated historic loss of ANC in Shenandoah National Park stream waters classified by watershed bedrock type. Estimates are based on model hindcasts (Sullivan et al., 2003).*

data for two SNP streams associated with siliciclastic bedrock: White Oak Run and Deep Run. Their analysis was based on an examination of both weekly samples and flow-weighted annual averages for the period 1980 through 1987 (8 years). Consistent with expected changes due to acidic deposition, sulfate concentrations were shown to be significantly increasing at a rate of about 2 µeq/L per year in both streams, and ANC was significantly decreasing at a rate of about 1 µeq/L per year in Deep Run.

More recent trend analysis for the 1988-2001 period indicates that some recovery from acidification may now be occurring in the 14 SNP study streams in conjunction with regional reductions in sulfur deposition (Sullivan et al., 2003; Webb et al., 2004). This is indicated by median slope values determined by simple linear regressions of change in concentrations over time. Consistent with recovery from acidification, sulfate concentrations decreased at a rate of –0.229 µeq/L per year, and ANC increased at a rate of 0.168 µeq/L per year. For both constituents, the median slope values are statistically significant.

This observation of recovery is an encouraging indication that reductions in sulfur emissions and deposition can have beneficial results. Similar evidence for recovery of surface waters has recently been observed for other regions in the United States that have been affected by acidic deposition (Stoddard et al., 2003). However, it should be noted that the degree of apparent recovery among SNP streams is very small compared with the degree of recovery observed in most of the other regions (see description of regional trends in Section 3.4), and that other factors, such as changes forest nutrient cycling associated with insect infestation (Webb et al., 1995) or climate-driven changes in hydrologic conditions (Driscoll et al., 2003), may be partially responsible for the observed trends.

It should also be noted that the degree of apparent recovery among SNP streams for the 1988-2001 period is minor in relation to the magnitude of past acidification. Moreover, the contrast between recent recovery and historic acidification is even greater when only the more-sensitive streams associated with siliciclastic bedrock are considered.

- Whereas the median estimated historic increase in sulfate for SNP streams is 55.7 µeq/L, the median observed decrease is 3.2 µeq/L, or 5.8%.

- Whereas the median estimated historic loss in ANC for SNP streams is 20.3 µeq/L, the recent median observed increase is 2.3 µeq/L, or 11.6%.

- Whereas the median historic loss of ANC in streams associated with siliciclastic bedrock is 69.2 µeq/L (see Figure 3-6), the recent median observed increase is 2.0 µeq/L, or 2.9%.

Finally, it should be recognized that the eventual magnitude of recovery will be limited by both the magnitude of reductions in sulfur deposition and the magnitude of cumulative damage due to base-depletion in watershed soils.

3.1.3 Shenandoah National Park: Acidification Effects on Fish

Effects of stream acidification on fish in the streams of SNP were recently quantified through the Fish in Sensitive Habitats (FISH) Project (Bulger et al., 1999a). The FISH project was an integrated multi-discipline study of fish communities in the SWAS project study streams in SNP (see Figure 3-2). The research included intensive basin-wide surveys of stream habitat structure and fish species distribution, in-stream and in-laboratory bioassays, collection of fish physiological data, and investigation of spatial and temporal variation in stream water composition.

Results of the FISH project demonstrate that major effects of stream acidification on fish in SNP occur at different ecosystem levels:

1. effects on single organisms (reduced condition factor);
2. population-level effects (increased mortality);
3. community-level effects (reduced species richness).

The FISH project thus served to link water quality effects of acidic deposition to adverse effects (both lethal and sub-lethal) on fish communities in SNP streams.

Effects on Single Organisms (reduced condition factor)

Because fish may be adversely affected by acidification before conditions have deteriorated sufficiently to cause mortality, the FISH project also focused on indicators of sub-lethal stress. The blacknose dace, which is one of the more-common fish species in the central Appalachian region, was selected for study of condition factor across the acid-base gradient represented in SNP streams. Condition factor is an index used by fish physiologists to describe the relationship between a fish's weight and length. Fish with higher condition factor values are more robust than fish with lower condition factor values, and a low condition factor value is usually interpreted as a sign of low or depleted energy reserves. Condition factor values for blacknose dace collected from 11 SNP streams were positively correlated with several indicators of acid-base status. The strongest relationship was with minimum pH observed in the preceding three years (the life span of the blacknose dace). The difference in condition factor between Paine Run (low ANC) and Piney River (high ANC) was about 11 percent, a difference that has been associated with diminished survival and recruitment success in other fish species. The FISH project investigators suggested that the differences in blacknose dace condition factor among SNP streams may occur because maintenance of internal chemistry in the more-acidic streams requires energy that might otherwise be diverted to growth (Dennis and Bulger, 1999). These results indicate that acidification can adversely affect fish before dramatic changes are evident.

Population-Level Effects (increased mortality)

Another component of the FISH project examined the survival of brook trout eggs and fry in three intensively studied streams representing the acidification gradient and different bedrock types present in SNP. These streams were Paine Run, Staunton River, and Piney River. Six 1-3 month-long bioassays were conducted on each stream during which brook trout eggs were placed into artificial gravel nests which could be withdrawn periodically to determine rates of mortality. Brook trout eggs (and hatching fry) were selected for study because they represent the most-sensitive life stages of the brook trout. In four of the bioassays, differential mortality could only be attributed to ANC differences between the three streams. In each of these four bioassays, the trout eggs and fry in Piney River (high ANC) showed higher survival rates than in Paine Run (low ANC). Results for Staunton River (intermediate ANC) were mixed. Bulger et al. (1999b) concluded that both chronic and episodic acid water chemistry, including elevated acidity and aluminum concentrations, reduced survivorship in the low-ANC stream. It is difficult to separate episodic effects from chronic effects in terms of their importance for fish, because low-ANC streams, as discussed previously, are more prone to extreme acid episodes. However, storm flows that occurred simultaneously in all three streams during two of the bioassays resulted in differential mortality among the three streams. Survivorship for the two bioassays was 5 and 0 percent in Paine Run, 4 and 85 percent in Staunton River, and 80 and 85 percent in Piney River. These results suggest that episodic acidification may be the principal mode of acidification impact on fish populations in SNP's low-ANC streams.

Figure 3-9: *University of Virginia environmental science students, Joe Krawczel and Adam Humphreys, conducting in-situ bioassays on Meadow Run, an acidic stream in Shenandoah National Park, to determine the relative sensitivity of park fish.*

Community-Level Effects (reduced species richness)

Perhaps the most import finding of the FISH project is the strong dependence of fish species richness on the acid-base status of stream water (Figure 3-10). Although acidification has been shown to reduce species richness (the number of species in a defined area) by eliminating sensitive species from fish communities (Baker and Christensen, 1991), complete fish community records for SNP streams are too recent (begun in the 1990s) to demonstrate historic loss of species from streams. However, there is a strong statistical relationship between the number of fish species present in streams now and stream acid-base status. Streams with low ANC host fewer species. This relationship suggests that the more-sensitive fish species have disappeared in the past from acidifying SNP streams and that additional species will disappear in the future unless effective steps are taken to prevent further stream acidification.

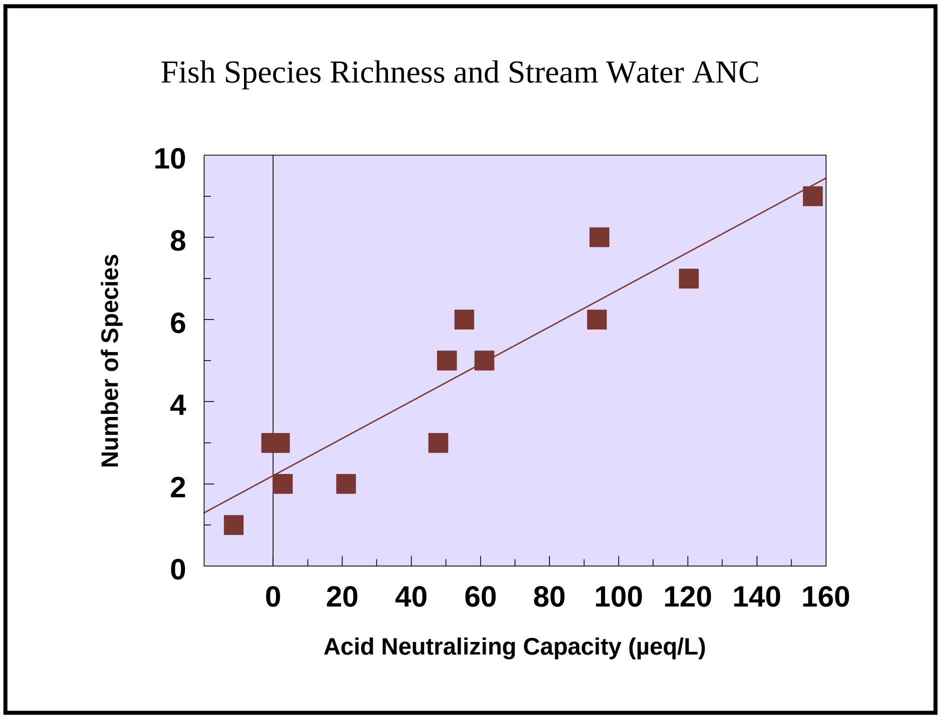


Figure 3-10: *Relationship between number of fish species and minimum ANC recorded in Shenandoah National Park streams (from Bulger et al., 1999b).*

3.2 Saint Marys River: Case Study

The Saint Marys River is among the most well known and well studied of the upland streams in the central Appalachian region that have been affected by deposition of acidity from the atmosphere.

The Saint Marys River drains the western slope of the Blue Ridge Mountains in the George Washington National Forest. The physiographic setting of the Saint Marys River watershed is similar to that of other areas in the central Appalachian Mountain region where acidification-related changes have been observed in stream water composition and aquatic biota. The watershed is almost entirely underlain by the siliciclastic bedrock types associated with acidified streams and acidification-sensitive landscape throughout the central Appalachian region.

Figure 3-11:

Saint Marys Wilderness.

The Saint Marys River was previously recognized as one of Virginia's premier wild trout streams. This quality was acknowledged in its management as a special regulation trout fishery and by federal designation of its watershed and adjacent areas as Wilderness. Today the Saint Marys River is recognized as one of Virginia's most acidification-impaired streams.

The historic effects of acidification on the aquatic ecosystem of Saint Marys River have been documented with water quality, fisheries, and benthic macroinvertebrate data. The most extensive water quality data have been provided by the Virginia Trout Stream Sensitivity Study (VTSSS), which conducts routine water quality sampling for native

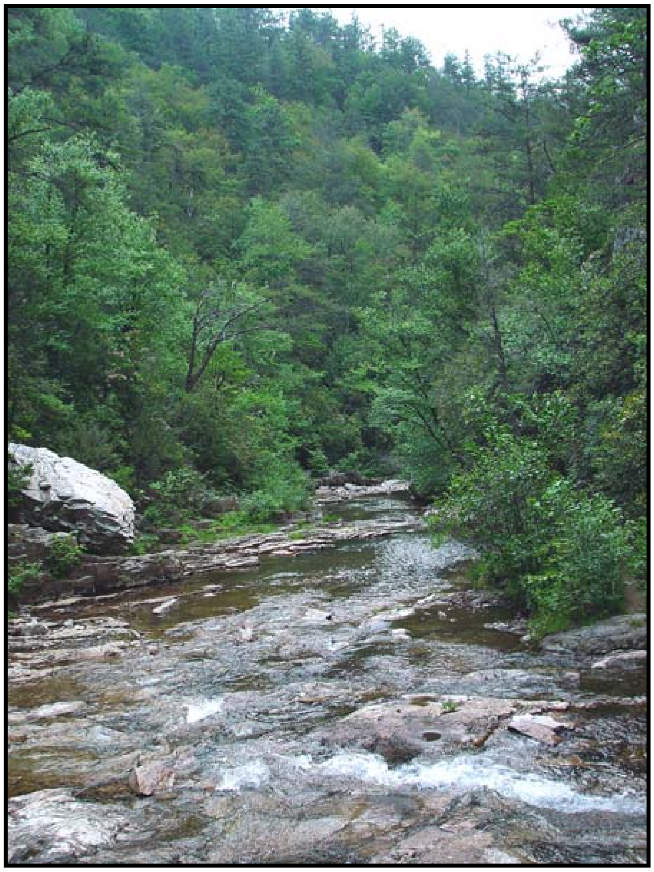


Figure 3-12:

Saint Marys River.

brook trout streams throughout western Virginia (see Section 3.4). As described by Webb and Deviney (1999), the VTSSS program has provided uninterrupted seasonal water quality data for a site on Saint Marys River near the Wilderness boundary since 1987. In addition, the VTSSS program has provided sample data for multiple sites within the watershed. Fish and macroinvertebrate community data have been provided by the Virginia Department of Game and Inland Fisheries (VDGIF) which first conducted fish and macroinvertebrate sampling in 1976, followed by biennial sampling beginning in 1986 (Kauffman et al., 1999; Bugas et al., 1999). Earlier macroinvertebrate data were obtained during a two-year investigation conducted in the 1930s (Surber, 1951). Few, if any, streams in the central Appalachian Mountain region have comparable data for examination of ecosystem response to acidification.

3.2.1 Saint Marys River: Stream Water Acidification

Stream water sampling sites in the Saint Marys River watershed are identified in relation to mapped geologic formations in Figure 3-13. Color-coding of the sample-site symbols indicates spatial variation in ANC on March 28, 1992. Based on the ANC categories for brook trout response to acidification (see Table 2-1) most of the drainage network provides poor brook trout habitat. The lower section of the main stem is well within the 0-20 μeq/L ANC range, or marginal category, in which sub-lethal or lethal

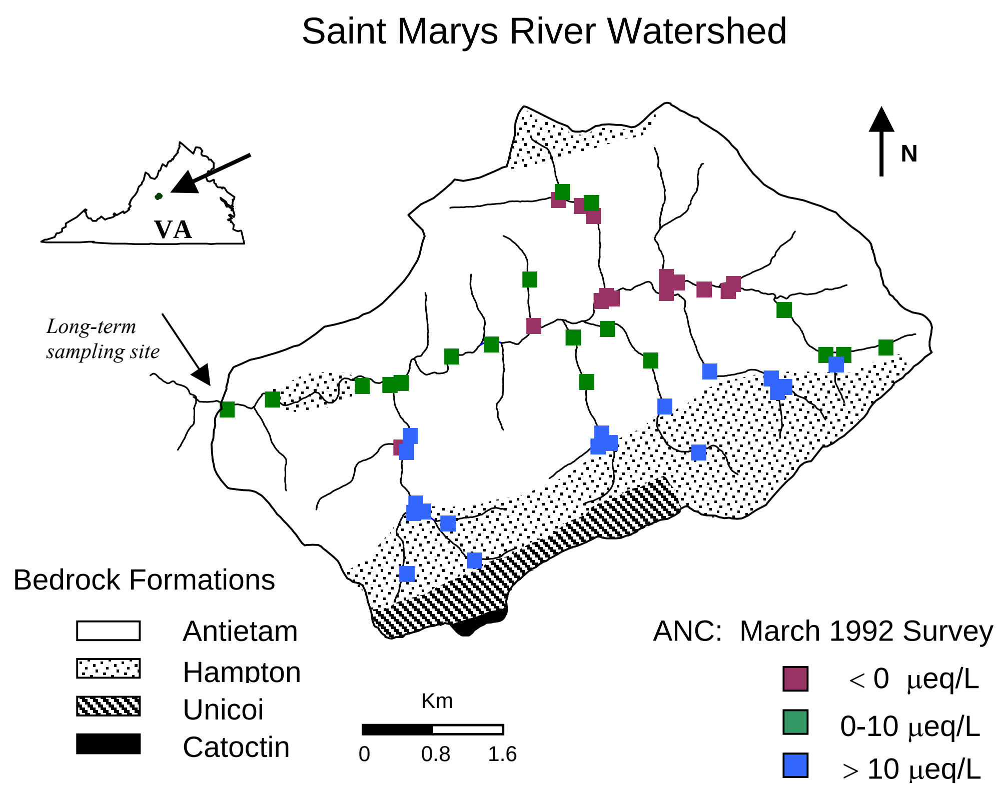


Figure 3-13: *Stream water sampling sites in the Saint Marys River watershed in relation to bedrock (based on Werner, 1966). The Antietam, Hampton, and Unicoi Formations are siliciclastic; the Catoctin Formation is basaltic.*

effects on brook trout are possible. The upper part of the main stem is within the less than 0 µeq/L ANC range, or unsuitable category, in which lethal effects on brook trout are probable.

The spatial variation in ANC on the main stem, as well as among the tributaries, can be explained by the distribution of bedrock in the watershed. Consistent with relationships observed in Shenandoah National Park (Dise and Lynch; 1985; Bulger et al., 1999a), ANC values for stream waters draining the geologic formations present in the Saint Marys River watershed generally decrease in the following order: Catoctin > Unicoi > Hampton > Antietam. Both the Antietam and Hampton formations are primarily comprised of quartzites, which are notably deficient in the base cations required for buffering acidic inputs.

The most intensive stream water composition data for Saint Marys River have been obtained at the downstream long-term sampling site shown in Figure 3-13. The median sulfate concentration for quarterly samples collected at this site during the 1988-1997 period was 62 μeq/L, a three to six-fold increase over estimated background sulfate concentrations (Brakke et al., 1989; Cosby et al., 1991). This is a dramatic change in stream water composition that can only be attributed to acidic deposition. As discussed in Section 3.1.2, elevated sulfate concentrations provide strong evidence of acidification in surface waters with low ANC and base-poor watersheds.

The median ANC for quarterly samples collected at the long-term site on Saint Marys River during the 1988-1997 period was only 4.4 μeq/L. Given the nonlinear relationship between pH and ANC, stream waters with ANC values in this range are highly susceptible to rapid declines in pH and associated increases in concentrations of toxic aluminum. This relationship between pH and ANC is clearly evident in Figure 3-14, which provides a plot of median pH and ANC for Virginia trout streams sampled quarterly in 1988-1997. The downstream sampling site on Saint Marys River falls on the part of the curve where even small changes in ANC result in large changes in pH

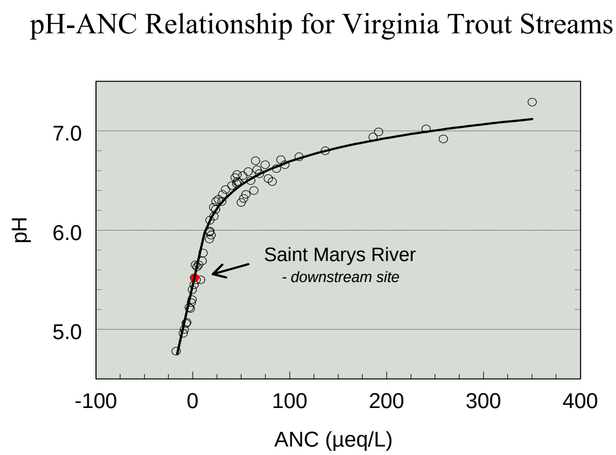


Figure 3-14: *pH and ANC for brook trout streams sampled quarterly through the Virginia Trout Stream Sensitivity Study. The plotted values are medians for samples collected in the 1988-1997 period.*

The ANC values for all quarterly and weekly samples collected at the long-term site on Saint Marys River are plotted in Figure 3-15. Several components of change in ANC are evident. As commonly observed for upland surface waters (Baker et al., 1990b), cold season ANC values are generally lower than warm season values. Superimposed on this seasonal pattern is variation related to changes in discharge. Although discharge measurements are not available to allow direct examination of the flow-concentration relationship at this site, investigations in similar areas (see Section 2.2.3) have shown that the lowest stream water ANC values occur on an episodic basis in association with high-discharge conditions. As indicated by multiple-year trend analysis, the observed short-term variation in the ANC of Saint Marys River occurred in a context of long-term or chronic change in ANC.

A trend analysis using 10 years (1987-1997) of quarterly data was performed in two steps using simple linear regression (Webb and Deviney, 1999). Step one involved removal of background variation or "noise" related to discharge. Although the Saint Marys River is not gauged for discharge, discharge data from U.S. Geological Survey (USGS) stream gauging stations within 80 kilometers were used to interpolate daily discharge for the Saint Marys River on days that samples were collected. As a preliminary step, it was determined that there was no trend in estimated runoff during the 10-year period. Regression analysis was then applied to test the association between ANC and the estimated runoff values. This test was significant at $\rho<0.001$.

Step two in the analysis was performed by testing the association between time and the residuals of step one (interpreted as variation in ANC in addition to variation caused by changes in runoff). This test was significant at $\rho<0.01$, with an estimated slope of -0.50 μeq/L per year (Figure 3-16). Additional tests were performed on the remaining residuals to confirm normality and constant error variance.

Based on the described trend analysis, the ANC of the long-term sampling site on Saint Marys River effectively declined 5 μeq/L during the period of 1988-1997. This change is substantial in relation to the median ANC value of 4.4 μeq/L for the 10-year period and in relation to the ANC thresholds for brook trout response to acidification (see Table 2-1). This change is also consistent with the impaired status of the fish and macroinvertebrate communities as described in the following sections.

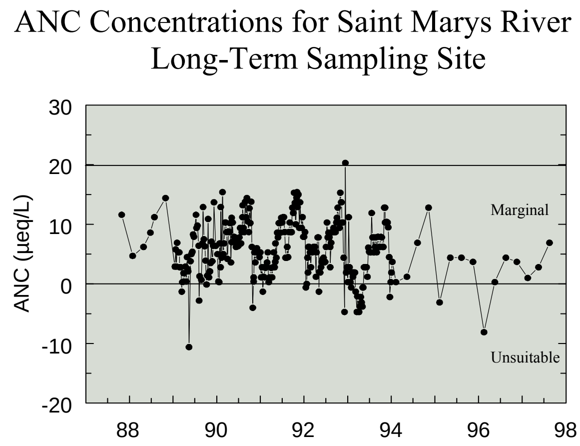


Figure 3-15: *ANC for Saint Marys River in relation to ANC thresholds for brook trout response to acidification (see Table2-1). Quarterly sample collection began in 1987. Weekly samples were collected in the 1988-1993 period.*

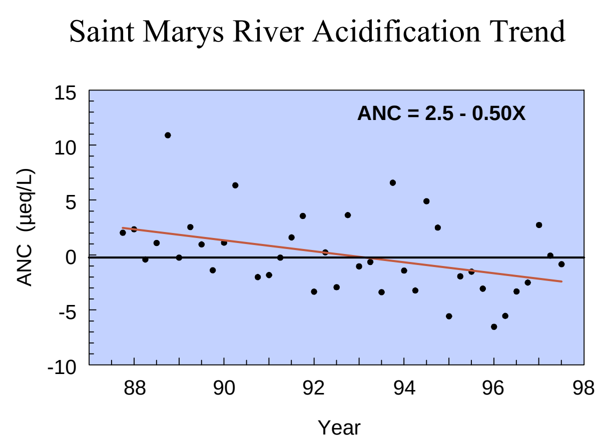


Figure 3-16: *Change in flow-adjusted ANC concentration of Saint Marys River (long-term site) during the period of 1988-1997. The trend is significant at $\rho<0.01$.*

Figure 3-17:

Aquatic biologists collecting data on Saint Marys River.

Information on benthic fauna was first collected in the 1930s.

Information on the fish community has been collected since the 1970s.

3.2.2 Saint Marys River: Effects of Acidification on Benthic Fauna

The benthic community includes aquatic insects and other macroinvertebrate fauna that spend all or part of their life cycle among the rocks, gravel, and other material that comprise the stream-bottom substrate. These organisms serve as a primary food source for fish that live in forest streams, and their diversity and numbers can serve as useful indicators for assessment of aquatic ecosystem status and trends. However, due to a lack of historic data, there has been limited documentation of acidification-related changes in benthic communities of acidified streams in the central Appalachian region. Saint Marys River is an exception. As described by Kauffman et al. (1999), the record for Saint Marys River provides a unique opportunity to compare reliable macroinvertebrate data on an acidified stream over a 60-year time span.

Surber (1951) collected the earliest benthic data for Saint Marys River. Starting in August of 1935, and continuing for two years, he collected 20 samples per month from the river's main stem. Subsequent data were collected by the VDGIF in 1976 and then biennially beginning in 1986 (Kauffman et al., 1999) using methods comparable to those used for the 1930s collections. The VDGIF data were collected at six evenly spaced locations extending the length of the main stem above the Wilderness boundary. The later collections were made in June, and only June data are used in the following comparisons.

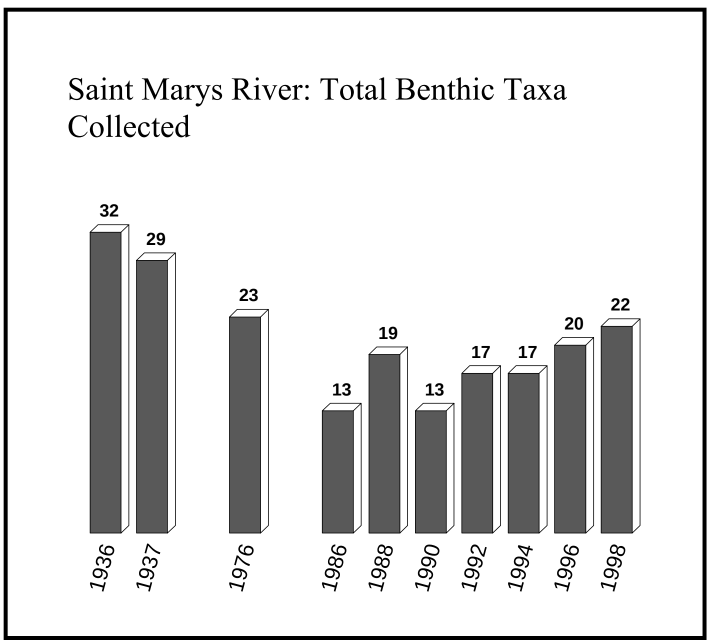


Figure 3-18: *Change over time in stream invertebrates of Saint Marys River, indicated as the number of taxa collected.*

Changes in the Saint Marys River benthic community are consistent with stream water acidification. Whereas 29-32 benthic taxa were documented in the 1930s, no more than 22 taxa were observed in the 1990s (Figure 3-18). Acid-sensitive taxa (e.g., mayflies and caddisflies) have declined in abundance and some may have been extirpated. In contrast, certain acid-tolerant taxa have increased in abundance, apparently due to less competition from acid-sensitive taxa.

The total abundance of mayfly (Ephemeroptera) larva has dramatically decreased over the 60-year period (Figure 3-19a), and two of the mayflies, *Paraleptophlebia* and *Epeorus*, were last collected in 1976. The mayflies are known to decline in species abundance and richness with increasing acidity (Peterson and Van Eeckhautz, 1992; Kobuszewski and Perry, 1993).

The total abundance of caddisfly (Trichoptera) larva has also declined dramatically over the 60-year period (Figure 3-19b). Baker et al. (1990b) indicate that caddisflies exhibit a wide range of response to acidity, with some species affected by even moderate acidity levels.

The total abundance of the larva of *Leuctra/Alloperla*, a stonefly (Plecoptera), has dramatically increased over the 60-year period (Figure 3-19c). Increased abundance of this stonefly in acidified waters has been well documented (Kimmel and Murphy, 1985).

Another organism that has prospered in Saint Marys River is the midge (Chironomidae), whose larval population has increased ten fold since the 1930s collections (Figure 3-19d). Increased midge abundance in acidified waters has also been well documented (Kimmel and Murphy, 1985; Baker et al., 1990b).

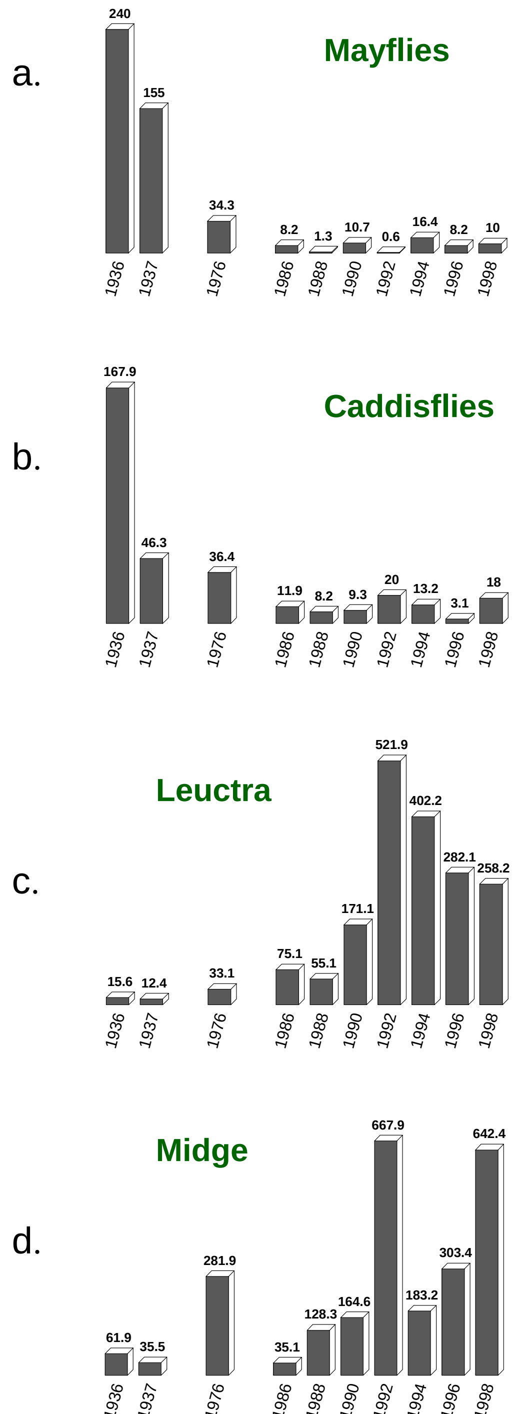


Figure 3-19: *Change over time in stream invertebrates of Saint Marys River, indicated as the number of individuals collected per square meter.*

3.2.3 Saint Marys River: Effects of Acidification on Fish

Fisheries surveys were conducted on Saint Marys River beginning in 1976 (Bugas et al., 1999). Fish were collected by three-pass electrofishing at six evenly spaced sampling sites (76-171 m reaches) extending the length of the main stem above the Wilderness boundary. All sampling was conducted in June. Results are summarized here for collections at the three sites indicated in Figure 3-20. The data for these three sites (the lower, middle, and upper sites) are sufficient to summarize the changes in fish status over the period of record.

As described by Bugas et al. (1999), fish abundance, diversity, and distribution patterns in Saint Marys River have been dramatically altered since 1976. Changes in these patterns reflect both the spatial and temporal variation of stream water acidity in the watershed.

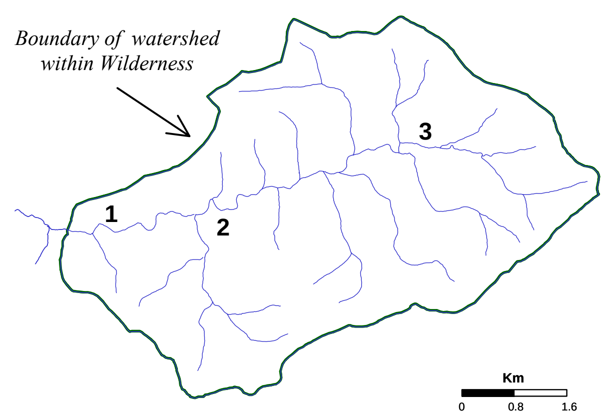


Figure 3-20: *Fisheries survey sites sampled in 1976 and biennially beginning in 1986.*

In 1998, only four fish species were collected in the river: brook trout (*Salvelinus fontinalis*), blacknose dace (*Rhinichthys atratulus*), fantail darter (*Etheostoma flabellare*), and mottled sculpin (*Cottus bairdi*). In contrast, 12 species of fish were collected in 1976. The indigenous fish that disappeared included: rosyside dace (*Clinostomus funduloides*), longnose dace (*Rhinichthys cataractae*), and torrent sucker (*Moxostoma rhothoecum*). As indicated in Figure 3-21, the number of fish species observed at the sampling sites has reflected the acidity gradient in the river, with the number of fish always greater at the downstream, less-acidic site. Throughout the period of record, the upstream, more-acidic site had only one species, the brook trout. The number of species observed at the middle site declined from six species in 1976 to only one, the brook trout, by 1994.

It is notable that three of the four species that remained at the downstream site in 1998, the brook trout, the blacknose dace, and the fantail darter, are typically the only species present in streams with similar acidity levels in Shenandoah National Park (Bulger et al., 1999a).

It is also notable that the brook trout, which remained in the more acidic sections of the river after all other species had disappeared, is generally considered among the most acid-tolerant fish species (Bulger et al., 1999a; Bugas et al., 1999).

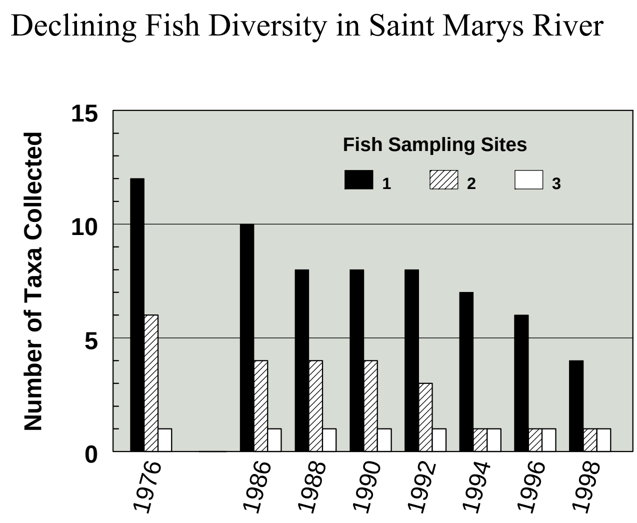


Figure 3-21: *Number of fish species collected at survey sites identified in Figure 3-20. The number of species declined from 12 in 1976 to 4 in 1998. By 1994, the only species at sites 2 and 3 was the brook trout.*

Fish distribution patterns within the Saint Marys River watershed in the 1976-1998 period were altered for all species except the brook trout. By 1998, the future of even the brook trout was in question due to repeated reproductive failure. The most-sensitive period for the brook trout is the early life stage when eggs and fry are present in stream gravel. As demonstrated by Bulger et al. (1999a), episodic exposure to the more-acidic water associated with high-flow conditions can result in mortality of eggs and fry. Brook trout in streams with minimal ANC are at risk of extirpation due to reproductive failure associated with episodic acidification. Bugas et al. (1999) reported that successful brook trout reproduction in Saint Marys River occurred only one year out of four in the 1995-1998 period.

3.2.2 Saint Marys River: Mitigation Effort

By the 1990s, the available chemical and biological data for Saint Marys River clearly indicated that the Saint Marys River ecosystem was severely impacted, and at risk of additional impact, due to acidic deposition. In response to wilderness management directives to maintain or achieve naturally functioning ecosystems, the U.S. Forest Service proposed an "aquatic ecosystem restoration" project in the Saint Marys River within the Saint Marys Wilderness (Damon, 1997). This project was initiated in 1999. It involved the addition of 140 tons of limestone sand by helicopter delivery to the main stem of the river and five tributaries. The objective of this project was to neutralize acidity and thereby improve aquatic ecosystem health and biodiversity. It was acknowledged as a temporary measure that would have to be repeated in 5-10 years.

The initial results of the mitigation project are positive, with large improvements in stream water quality and an increase the diversity of the aquatic biological community. As determined through the VTSSS program, ANC at the downstream site on Saint Marys River increased from 0.3 μeq/L in January of 1999 to 35.4 μeq/L in January of 2000. Between June of 1998 and June of 2001, the number of benthic macroinvertebrate taxa observed in the river increased from 22 to 34, and the number of fish species increased from 4 to 6 (Paul Bugas, VDGIF, Verona, VA, pers. comm. 2002).

Although the chemical and biological responses to the liming project are encouraging, it should not be described as ecosystem restoration. A meaningful consideration of aquatic ecosystem function cannot ignore the linkages between the terrestrial and aquatic components of the system. For most naturally functioning forested mountain watersheds, the primary source of acid neutralization is the accumulated supply of exchangeable base cations in the soil (see Section 2.2.2). Variation in the acid-base status of streams receiving similar inputs of acidic deposition is due, in large part, to variations in base-cation availability in watershed soils, which in turn is initially determined by the properties of the rocks from which the soils are derived. For streams such as Saint Marys River, low ANC is associated with low base supplies in soils, both due to low initial supplies and due to leeching of base cations caused by exposure to acidic deposition over time.

Although repeated liming of streams like Saint Marys River may temporarily improve conditions in the streams, the loss of base cations from watershed soils will continue as long as elevated acidic deposition continues. The loss of base neutralization capacity from watershed soils should properly be considered the fundamental, long-term impact of acidic deposition on watershed ecosystems. This is an impact that can only be mitigated by reducing acidic deposition.

3.3 Otter Creek and Dolly Sods Wildernesses: Case Study

Surface waters of Otter Creek Wilderness (OCW) and Dolly Sods Wilderness (DSW) are severely acidified as a consequence of acidic deposition.

OCW and DSW are located in the Monongahela National Forest in north-central West Virginia, an area with among the highest sulfate deposition levels of the areas described in this report (see Figure 2-1). The watershed of Otter Creek occupies most of OCW. The watershed of Red Creek occupies all of DSW. The upper areas of both the Otter Creek and Red Creek watersheds are underlain by base-poor siliciclastic bedrock. In contrast, the lower areas of both watersheds are underlain by carbonate bedrock.

Figure 3-22: *Sandstone outcrop in Otter Creek Wilderness.*

Although the phenomenon of acidic deposition only received substantial attention in the last few decades, the presence of acidic streams, in addition to those affected by acid mine drainage, was noted in certain areas of the central Appalachian Mountains as early the 1930s. McGavok and Davis (1935) described a group of nearly fishless acidic streams located in an "acid belt" in the north-central section of West Virginia that includes OCW and DSW. They reported that streams in this area had become acidic since 1930. They suggested that this change was due to the then-prevalent drought conditions and the recent loss of forest cover in the area. They further suggested that if their explanation was correct, conditions should improve with forest growth and increased rainfall. This has not happened. Seventy years later the forest has returned and the drought conditions of the 1930s have passed. However, these streams are still acidic.

More recent water quality and fisheries information for OCW and DSW was summarized by Adams et al. (1991), who described information needs concerning effects

Figure 3-23: *Dolly Sods Wilderness.*

Figure 3-24: *Red Creek drains the Dolly Sods Wilderness. Most of Red Creek and its tributaries are too acidic to support fish.*

Figure 3-25: *A limestone treatment system in the upper reach of Otter Creek. The system is designed to regulate the addition of crushed limestone to the stream to maintain pH levels in a range suitable for fish. Without treatment, most of Otter Creek would be too acidic to support fish.*

of air pollution on certain Wildernesses in the Forest Service Eastern Region. They reported that most of the streams in OCW and DSW remain too acidic to maintain fish populations and that acidity levels in both areas are closely related to bedrock geology. They suggested that the acidity might be derived from a combination of anthropogenic and natural sources, including atmospheric deposition and oxidation of pyritic material in watershed bedrock. They also noted that streams of both OCW and DSW contain organic acids associated with wetland areas.

Subsequent investigations and analysis, including a detailed water quality survey (Webb et al., 1997), have served to further clarify the factors that determine the acid-base status of surface waters in OCW and DSW. As described in following sections, the acidic condition of these surface waters is due to relatively high atmospheric deposition of sulfur and minimal release of base cations from watershed rocks and soil. Any contribution to the acidity by natural mineral or organic sources appears to be minimal.

3.3.1 OCW and DSW: Stream Water Acidification

Figures 3-26 and 3-27 indicate the locations and ANC ranges for surface waters sampled in both OCW and DSW on May 23, 1994. Most of the surface waters in both

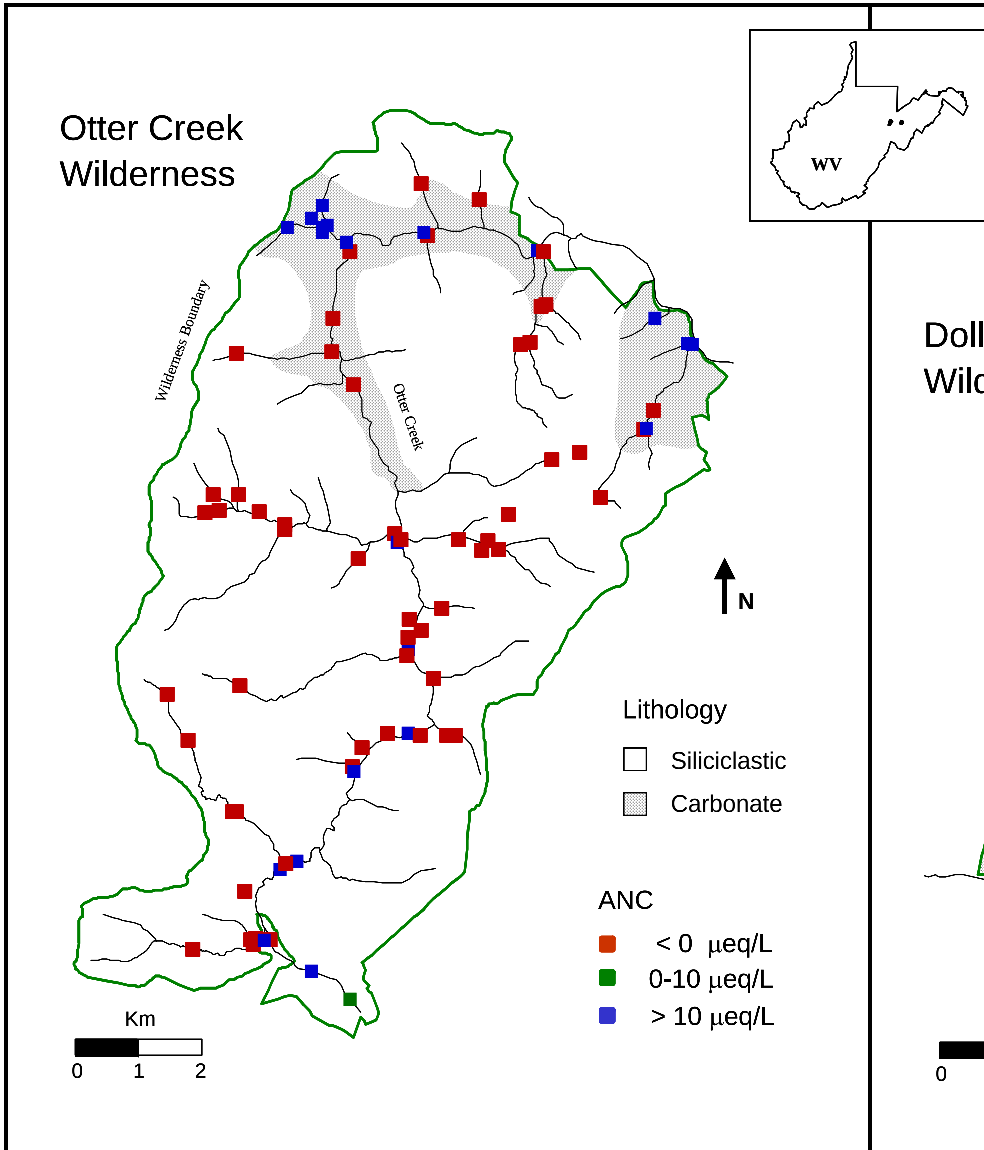


Figure 3-26: *Sampling sites in Otter Creek Wilderness*

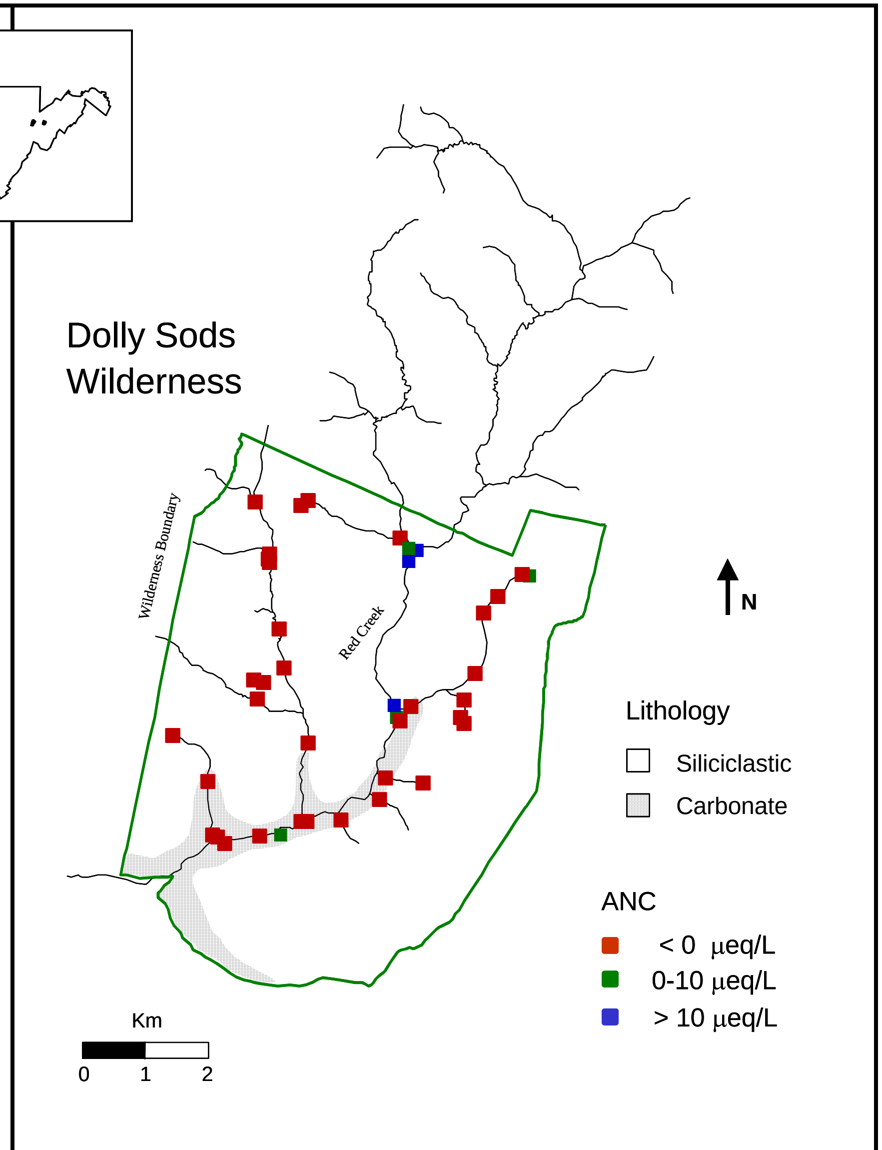


Figure 3-27: *Sampling sites in Dolly Sods Wilderness*

watersheds have ANC less than 0 µeq/L, values that are unsuitable for brook trout and other less-tolerant fish (see Table 2-1). Somewhat higher ANC values are present in areas associated with carbonate bedrock. The main stem on Otter Creek is also influenced by a continuous-dosing limestone treatment facility located in the upper part of the watershed (see Figure 3-25). On the day of the sampling survey, the neutralizing affect of this station was sufficient to maintain ANC values greater than 0 µeq/L for about 8 km on the main stem below the treatment facility.

Although stream waters with ANC less than 0 µeq/L have been defined as unsuitable for most fish, vestigial brook trout populations may still survive with ANC values in this range. This was made evident by the presence of brook trout in the upper Saint Marys River, even prior to liming (see Section 3.2.3). However, except for areas influenced by carbonate bedrock or limestone treatment, there are no fish in the streams of OCW and DSW (Adams et al., 1991). As indicated by the plots of pH with ANC in Figure 3-28, the ANC of most of the surface water in OCW and DSW is substantially less than 0 µeq/L and pH levels are correspondingly low. A literature review by Baker et al. (1990b) revealed that the pH range of 6.0-5.5 is associated with loss of intolerant fish species (e.g., the blacknose dace), and the pH range of 5.0 to 4.5 is associated with the loss of the most-tolerant fish species (e.g., the brook trout). Most of the pH values in stream waters of OCW and DSW are less than 5.0 and many are less than 4.5.

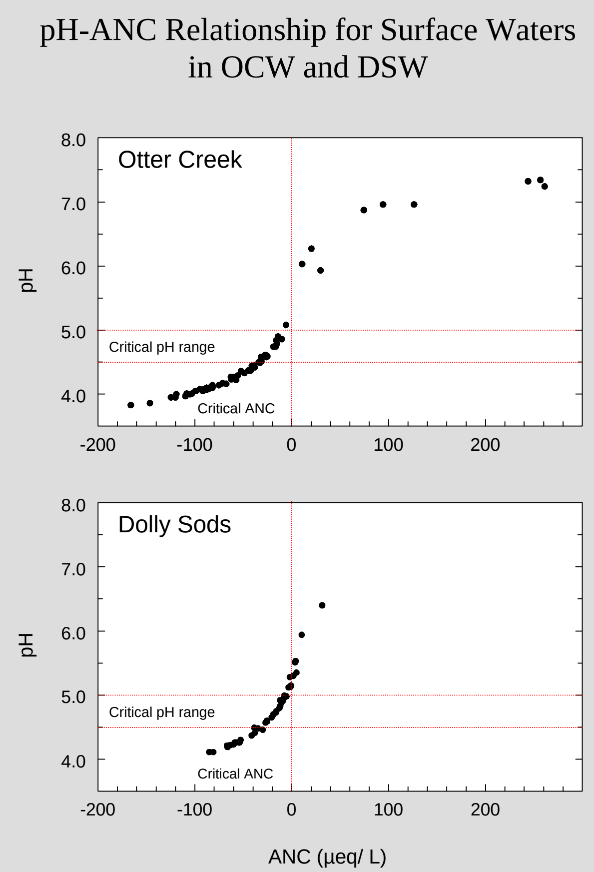


Figure 3-28: *pH and ANC for surface waters in OCW and DSW (excluding sites below limestone treatment) shown in relationship to critical values. The critical pH range is the range for loss of brook trout.*

3.3.2 OCW and DSW: Sources of the Acidity

ANC in most surface waters is determined by the difference between the sum of base cations and the sum of strong acid anions. Surface water acidification, defined as the loss of ANC, occurs when concentrations of strong-acid anions increase relative to concentrations of base cations (see Section 2.2). The strong-acid anions of importance in most upland surface waters include sulfate, nitrate, chloride, and strong-acid organic anions (Kaufmann et al. 1988; Baker et al., 1990a). With the exception of some organic acids, the acids and neutral salts associated with these anions are completely dissociated in the pH range of most natural waters. Thus, surface water acidity cannot be attributed to specific acids based simply on the strong-acid anions in solution. However, ratios or differences between strong-acid anions and the sum of base cations (calcium, magnesium, potassium, and sodium) do indicate the relative potential importance of the individual strong acids in determining ANC (Baker et al., 1991; Munson and Gherini, 1991).

For stream waters in both OCW and DSW, the ratio of sulfate to base cations is distinctly greater than the ratio of the other strong-acid anions to base cations (Figure 3-29). The median ratios of sulfate to base cations were greater than 1.0 for both areas; the median ratios of the other strong-acid anions to base cations were less than 0.25 for both areas. This provides strong evidence that sulfuric acid is the dominant acidifying agent in OCW and DSW.

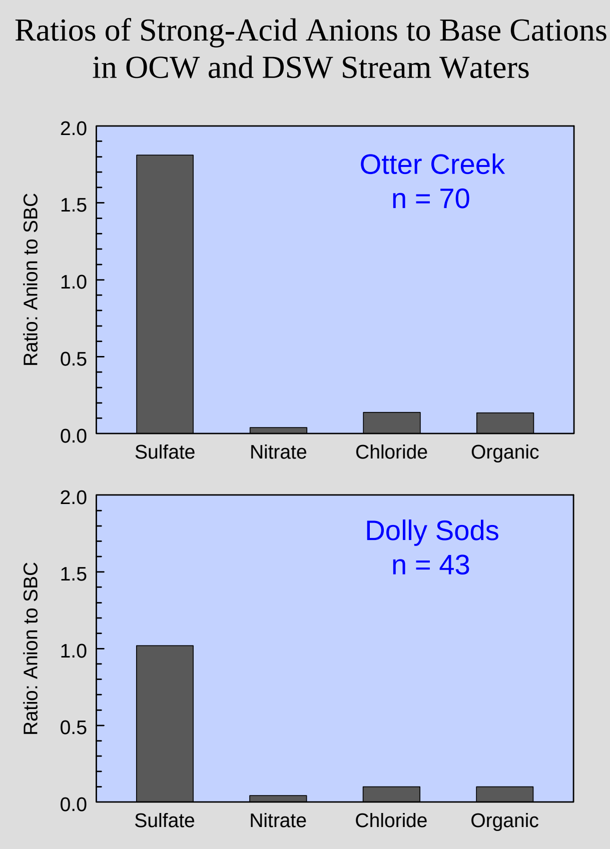


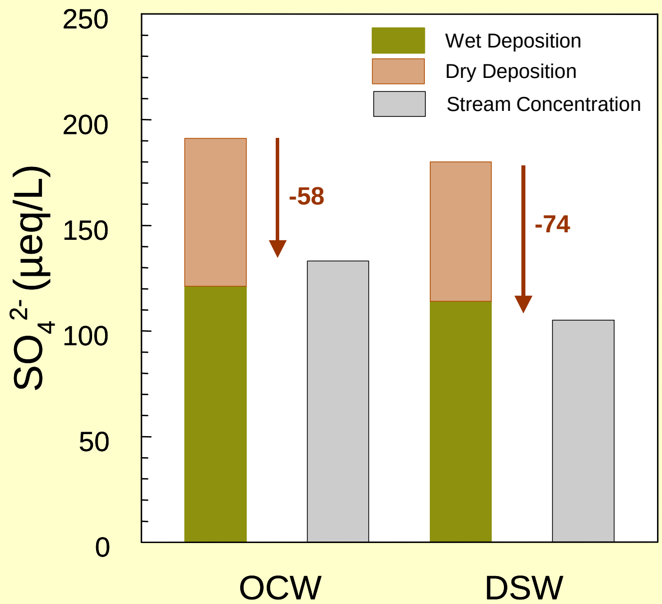
Figure 3-29: *Ratios of strong-acid anions to the sum of base cations (SBC = Ca^{2+} + Mg^{2+} + Na^{+} + K^{+}) in stream waters of OCW and DSW. The bars indicate median values.*

The relative importance of sulfate in determining the acid-base status of surface waters in OCW and DSW suggests that any variation in sulfur inputs to watersheds in these areas will contribute to changes in the acid-base status of the associated surface waters. Although this has implications for assessment of acidic deposition effects, additional analysis is needed to determine the relative importance of atmospheric and internal watershed sources of sulfate. One approach, involving ion-enrichment analysis, indicates that present-day atmospheric deposition of sulfur is more than sufficient to account for all of the sulfate in the study area surface waters.

Ion-enrichment analysis, as described by Baker et al. (1991), involves determination of a watershed enrichment factor (EF) based on the difference between observed surface water ion concentrations and concentrations that are expected based on atmospheric deposition (Figure 3-30). For any given ion, a positive enrichment factor indicates that the watershed acts as a net source; a negative enrichment factor indicates that the watershed acts as a net sink.

The estimated median watershed EF values for sulfate in OCW and DSW are –58 and –74, indicating that watersheds in both areas are net sinks for sulfate. Sulfate in OCW streams can account for only 70% of deposition, and sulfate in DSW streams can account for only 58% of deposition. Although this result does not rule out the possibility of watershed sources of sulfate, the importance of any such sources to the sulfate budgets of the two areas must be relatively minor compared to atmospheric deposition.

Ion-Enrichment Analysis for Sulfate in Stream Waters of OCW and DSW



– Wet deposition concentrations (mean annual values for 1989-1993) based on the deposition model of Grimm and Lynch (1997).
– Dry deposition concentrations based on annual dry:wet sulfur deposition ratios determined for Parsons, WV (CASTNet, 1998; NADP, 1998).
– Effective deposition concentrations based on wet and dry deposition concentrations divided by the 40-year mean yield (0.439) for Watershed 4 at Fernow Experimental Forest (Adams et al., 1993).
– Stream water sulfate concentrations indicated as median values for the May 24, 1994 surveys.

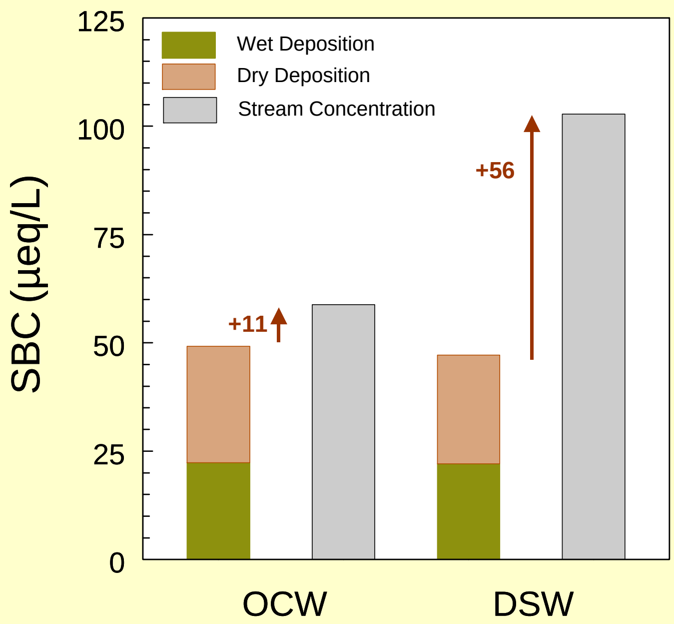
Figure 3-30*:* *Ion-enrichment analysis for sulfate, indicating that OCW and DSW watersheds act as sinks for sulfate input from atmospheric deposition.*

3.3.3 OCW and DSW: Base-Cation Availability

The other factor contributing to the degree of stream water acidification in OCW and DSW is the low availability of base-cations in watershed soils and rocks. This interpretation is supported by application of ion-enrichment analysis to base-cation concentrations in surface waters of OCW and DSW. Due to the release of base cations from watershed sources, base-cation concentrations in most upland surface waters greatly exceed the concentrations that would be expected from atmospheric deposition alone (Reuss and Johnson, 1986; Baker et al., 1991). However, ion-enrichment analysis indicates little release of base cations from watersheds in OCW and DSW (Figure 3-31). The estimated median EF values for base cations in OCW and DSW are only 11 and 56 μeq/ L. In contrast, EF values for base cations in surface waters of several regions of the northeastern U.S. have been estimated to range between 115 and 144 μeq/L (Baker et al., 1991).

The present low availability of base-cations in OCW and DSW is probably a result of both low initial base supplies and extended exposure to the leaching effect of acidic deposition. For the extremely acidic stream waters in OCW and DSW, the effect is clear. Present base-cation availability is insufficient to buffer the acidity associated with the present sulfate deposition level.

Ion-Enrichment Analysis for Base Cations in Stream Waters of OCW and DSW



- Wet deposition concentrations (mean annual values for 1989-1993) based on the deposition model of Grimm and Lynch (1997).
- Dry deposition concentration based on regional dry:wet deposition ratios (Baker et al., 1991).
- Effective deposition concentrations based on wet and dry deposition concentrations divided by the 40-year mean yield (0.439) for Watershed 4 at Fernow Experimental Forest (Adams et al., 1993).
- Stream water base-cation concentrations indicated as median values for the May 24, 1994 surveys.

Figure 3-31: *Ion-enrichment analysis for base cations (SBC = Ca^{2+} + Mg^{2+} + Na^{+} + K^{+}) in stream waters of OCW and DSW, indicating relatively low input from watershed sources.*

3.4 Virginia's Native Brook Trout Streams: Case Study

Because of its requirements for cool and clean water, the streams that provide viable habitat for Virginia's native brook trout are essentially restricted to relatively undisturbed forested mountain watersheds. Thus, the native brook trout is closely associated with the subpopulation of regional streams that is most susceptible to the effects of acidic deposition. The number of Virginia streams that support naturally reproducing populations of native brook trout is about 450 (Mohn and Bugas, 1980). Most are located on lands managed as national forest or national park (Figure 3-33).

Figure 3-32: *Ramseys Draft, one of 60 native brook trout streams included in the VTSSS long-term water quality monitoring program.*

Information concerning the status of Virginia's native brook trout streams has been obtained through the Virginia Trout Stream Sensitivity Study (VTSSS), a regional component of the SWAS program conducted by the Department of Environmental Sciences at the University of Virginia and a number of federal and state agencies with resource management responsibilities. The VTSSS program was initiated in 1987, with a stream sampling survey that included about 80 percent (n=344) of the state's identified native brook trout streams. Following the 1987 survey, a physiographically representative subset of streams was selected for long-term water-quality monitoring. The VTSSS long-term monitoring program presently includes 60 streams that are sampled on a quarterly basis for analysis of major acid-base constituents. The distribution of the VTSSS long-term monitoring streams is indicated in Figure 3-33. Note that the depicted sites include the SWAS program study streams in Shenandoah National Park (see Section 3.1).

Much of what is known about acidic deposition effects on native brook trout streams in SNP also applies to brook trout streams throughout the western Virginia region. As described by Webb et al. (1989) and Cosby et al. (1991):

- Many of region's brook trout streams are either acidic or sensitive to acidification. Of the 344 native brook trout streams sampled in the initial 1987 VTSSS survey, 10 percent had ANC less than 0 µeq/L and 49 percent had ANC less than 50 µeq/L. Base-cation concentrations are much lower than among the larger population of all regional streams. Variation in acid-base status among the region's brook trout streams is related to differences in watershed bedrock.

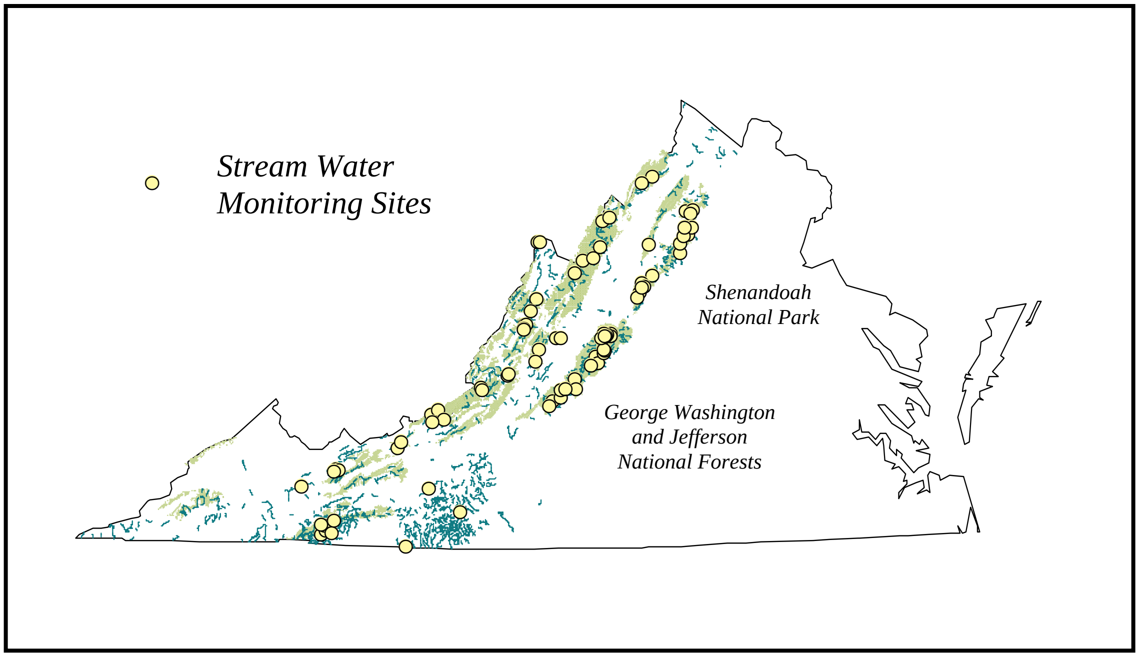


Figure 3-33: *The distribution of VTSSS long-term stream water monitoring sites in the mountains of western Virginia. Native brook trout streams are shown as blue lines. Shaded areas indicate national forest and national park lands.*

- As a result of acidic deposition, sulfate has become the major solute in most of the region's brook trout streams. The median sulfate concentration for streams sampled in the 1987 VTSSS survey was 71 µeq/L, higher than any other dissolved ion and more than 3 times the estimated natural background concentration.
- A substantial fraction of sulfur deposition in the region's forested mountain watersheds is retained in watershed soils. This protects the region's brook trout streams from the full potential effect of sulfur deposition. However, sulfur retention capacity in soil diminishes in time. Thus it delays but does not prevent the acidifying effect of sulfur deposition.

The VTSSS data set provides an opportunity to observe and better-understand regional-scale changes in the acid-base status of sensitive aquatic systems that occur in response to continuing or changing levels of acidic deposition. As described in the following sections:

- Analysis of water quality trends indicates that Virginia's brook trout streams continued to acidify during the past decade.
- Application of a predictive model indicates that unless substantial additional reductions in acidic deposition levels are achieved, biologically significant acidification will continue for decades into the future.

3.4.1 Virginia's Native Brook Trout Streams: Observed Change

A recent U. S. Environmental Protection Agency report, **Response of Surface Water Chemistry to the Clean Air Act Amendments of 1990** (Stoddard et al., 2003), examined trends in surface water acid-base composition for five eastern and northern United States regions containing surface waters affected by acidic deposition. As indicated in Figure 3-34, surface waters in four of the regions showed evidence of recovery from acidification, including decreasing concentrations of sulfate and increasing ANC. However, the observed trends for the Western Virginia region provided no evidence of recovery. Trend analysis for the Western Virginia region, designated the Blue Ridge/Ridge region in the Stoddard et al. (2003) report, was based on data obtained for the SWAS and VTSSS long-term stream monitoring sites in Shenandoah National Park (SNP) and the western Virginia mountains.

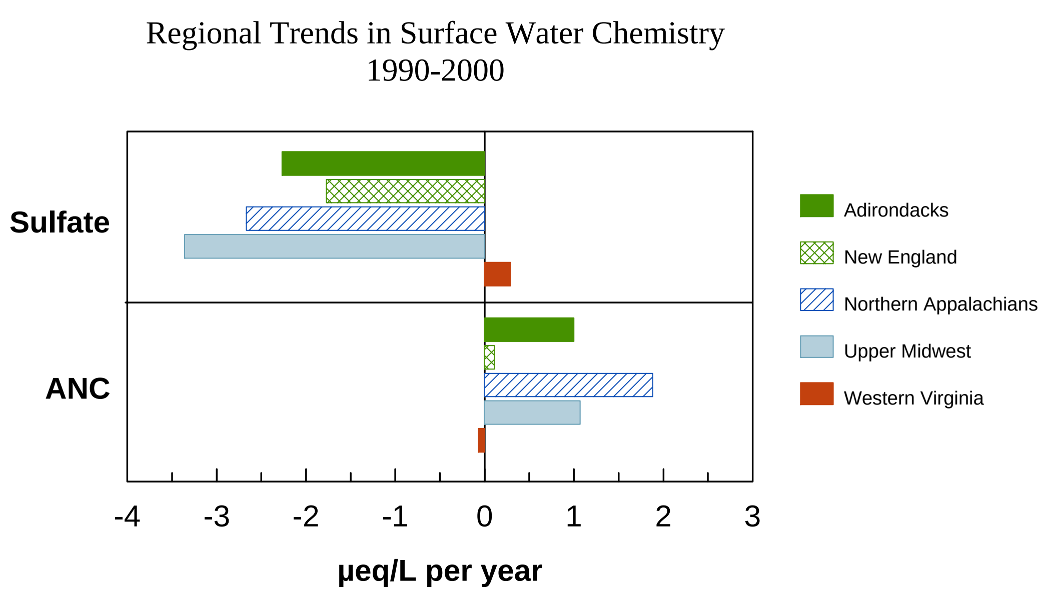


Figure 3-34: *Regional trends in sulfate and ANC concentrations in surface waters. Trends are given as median slope values obtained by regressions of concentrations with time for multiple sites within each region. (Based on Stoddard et al., 2003).*

Stoddard et al. (2003) attributed the increase in stream water sulfate concentrations in the Western Virginia region to the adsorption property of soils in this region, which has the effect of both decoupling trends in deposition and surface waters and lowering concentrations below those found in deposition. This is consistent with current understanding of sulfur retention dynamics as described in Section 2.2 of this report. Given the positive median trend in sulfate concentrations, it is evident that reductions in emissions of sulfur have not been sufficient to reduce the sulfur deposition equivalent to levels below the current sulfate concentrations of most streams in the region. As depicted in Figure 2-4, sulfate concentrations in stream water will continue to increase until the sulfur deposition equivalent is attained.

Although evidence for recovery is lacking for most of the VTSSS long-term monitoring streams, there is some evidence for recovery in some of the streams. Trend analysis for the subset of streams in SNP, for example, indicates decreasing sulfate and increasing ANC (see Section 3.1). Examination of trends for individual study streams throughout western Virginia suggests that these observed differences in sulfate trends and resulting differences in ANC trends can also be explained as a consequence of sulfur retention dynamics. Those streams with the largest negative trends in sulfate concentration, including many in SNP, are generally those with the higher median sulfate concentrations (Sullivan et al., 2003; Webb et al., 2004). Apparently for these streams, the reductions in emissions of sulfur have been sufficient to reduce the sulfur deposition equivalent to levels below current sulfate concentrations.

As stated previously, any evidence for a decrease in stream water sulfate concentrations in response to reductions in sulfur emissions and deposition is encouraging and suggests that expectations for some recovery is warranted. However, as also stated previously, the degree of eventual recovery will be limited by both the magnitude of reductions in sulfur deposition and the magnitude of cumulative damage due to base-depletion in watershed soils.

3.4.2 Virginia's Native Brook Trout Streams: Predicted Change

Bulger et al. (2000) reported results of model analysis conducted to assess the current status, reconstruct the past status, and project the future responses to acidic deposition of brook trout streams in Virginia. The mathematical model used in the analysis was MAGIC (see Section 3.1).

The model was calibrated and applied using available soils data, interpolated deposition estimates, and stream water composition data obtained from 60 of the long-term study streams maintained through the VTSSS and SWAS programs. Through the use of a geology-based landscape classification scheme, modeling results for the 60 streams were weighted and collectively scaled-up to represent about 70 percent of the regional population of brook trout streams. The biological significance of the modeling results was expressed by reference to the ANC thresholds for brook trout response to acidic conditions listed in Table 2-1 of this report.

Model Results: Past and Current Conditions

The model reconstruction of past conditions indicates that 82 percent of the brook trout streams were in the not acidic (ANC > 50 µeq/ L) category in 1852, or prior to the advent of acidic deposition. By 1991 the number of brook trout streams in this category had decreased to 50 percent. Whereas in 1851 there were no streams in the chronically acidic category (ANC < 0 µeq/ L), 6 percent of the streams were in this category by 1991 (see Figure 3-35a).

Model Results: Forecasts

The forecast modeling involved 50-year projections: 1991 to 2041. By 2041, given a 40 percent reduction from 1991 sulfur deposition levels (about the reduction that the 1990 CAAA will achieve), the number of streams in the not acidic category will decrease by 5 percent and the number of streams in the chronically acidic categories will increase by 16 percent (Figure 3-35b).

By 2041, given a 70 percent reduction from 1991 sulfur deposition levels, the number of streams in the not acidic category will stay about the same (Figure 3-35c). However, the number of chronically acidic streams will increase from 6 to 11 percent.

The results of the modeling indicate that the percentage of acidification-impacted brook trout streams will increase despite anticipated reductions in sulfur deposition, and that even with a much larger (70 percent) reduction, there will be little improvement and some additional acidification among the more-acidic streams.

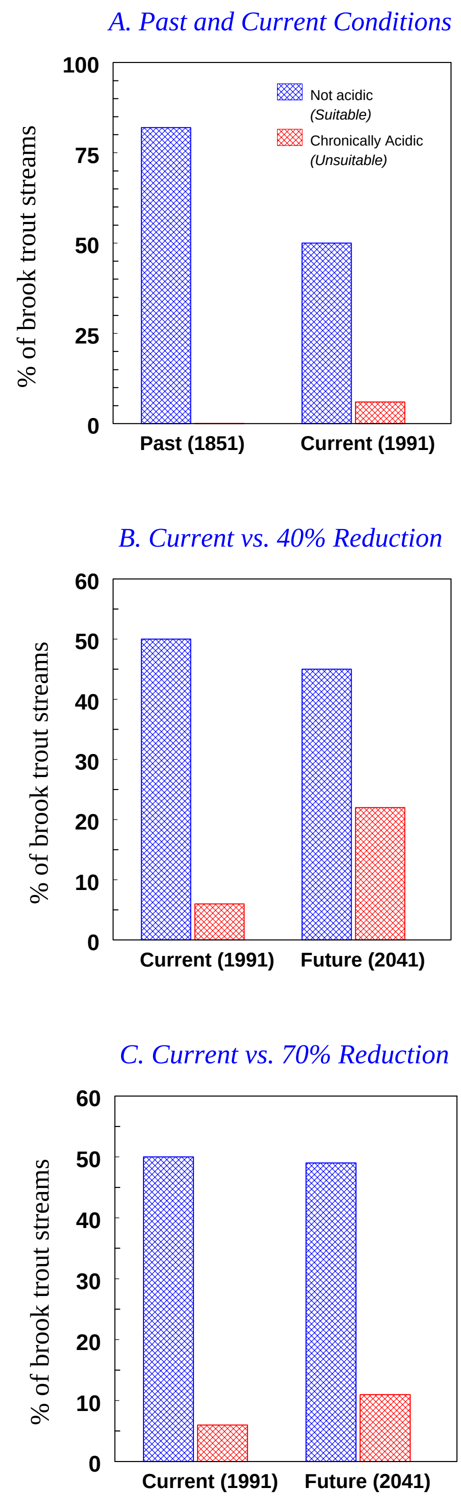


Figure 3-35: *Modeled change in brook trout stream status relative to changes in sulfur deposition.*

3.5 Other Regional Investigations

The central Appalachian mountain region contains surface waters that are among the most severely affected by acidic deposition (Baker et al., 1991) and among the most likely to experience additional acidification in the future (Church et al., 1992). This perspective is supported by scientific investigation conducted over the last 25 years, including surface water investigations associated with the case study areas described in the preceding sections of this report. This section summarizes findings of two other important regional investigations.

3.5.1 The National Stream Survey

The National Stream Survey (NSS) (Kauffman et al., 1988; Baker et al., 1990a) was conducted as part of the Congressionally mandated National Acid Precipitation Assessment Program (NAPAP), an interagency study of acidic deposition and other effects of sulfur and nitrogen emissions. The NSS was a probability-based sampling survey designed to allow quantitative characterization of regional stream conditions. NSS data for the mid-Appalachian region, a combination of upland areas in Pennsylvania, Maryland, West Virginia, and Virginia defined by Baker et al. (1990a) and Herlihy et al. (1993), includes most of the area defined in the present report as the central Appalachian mountain region. The NSS served to establish the widespread distribution of acidic and low ANC streams in the region.

Key NSS finding included:

- The central Appalachian mountain region is one of the two areas of the United States that appear to be most affected by atmospheric deposition. (The other is the southwest Adirondacks.)
- Among the region's acidic streams (ANC $\leq$ 0 μeq/L), 57% have inorganic monomeric aluminum concentrations greater than 100 μg/L, a value associated with harm to aquatic fauna.
- The highest percentages of acidic streams (ANC $\leq$ 0 μeq/L) and highly sensitive streams (ANC $\leq$ 50 μeq/L) in the region are associated with forested mountain ridges (see Figure 3-36).
- The most important factor controlling the ANC of surface waters in the region is the amount of base cation mobilization in watersheds.
- Sulfate, derived from atmospheric deposition, is the dominant (most concentrated) dissolved ion in the region's acidic and highly sensitive streams.
- Variation in sulfur retention exists in the region, with the most retention occurring in the Valley and Ridge areas and the least occurring in the Appalachian Plateau areas.

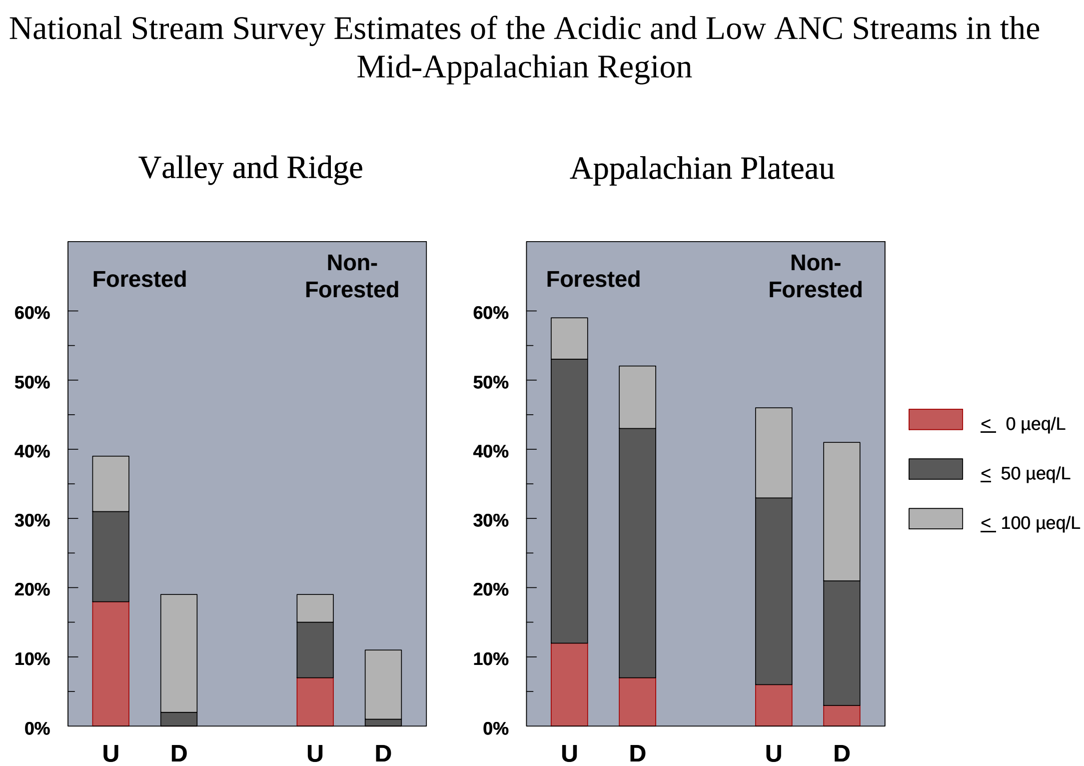


Figure 3-36: *Percentages of acidic and low ANC streams in the mid-Appalachian region: classified by physiographic province, forested and nonforested watersheds, and upstream (U) and downstream (D) sampling sites for NSS sample reaches, and (based on analysis of Herlihy et al., 1993).*

3.5.2 The Southern Appalachian Mountain Initiative

Recognition of the regional scope of environmental problems related to air pollution led to the formation in the early 1990s of the Southern Appalachian Mountain Initiative (SAMI), a multi-party effort involving state and federal resource agencies, industry, and other stakeholders to find solutions to regional air quality problems. The geographic region of SAMI interest included the mountainous physiographic provinces of eight southeastern states and overlapped (in Virginia and West Virginia) with the area designated for purposes of this report as the central Appalachian mountain region. SAMI undertook assessments of environmental effects related to air pollution in the region, including the effects of acidic deposition on aquatic resources (Sullivan et al., (2002).

In addition to examining the current condition of regional streams, modeling was conducted to predict the future condition of regional streams given implementation of emission control strategies ranging from On-The-Way (OTW) to Bold-With-Constraints (BWC) and Beyond-Bold (BYB). The OTW strategy represented emission reductions expected for promulgated and relatively certain controls on acid-precursor emissions, including the Clean Air Act Amendments of 1990. BWC and BYB strategies assumed progressively larger emission reductions. Predicted decreases in sulfur deposition for the SAMI region between 1995 and 2040 were smallest for the OTW strategy (mean -57%), intermediate for BWC (mean -67%), and largest for BYB (mean -73%).

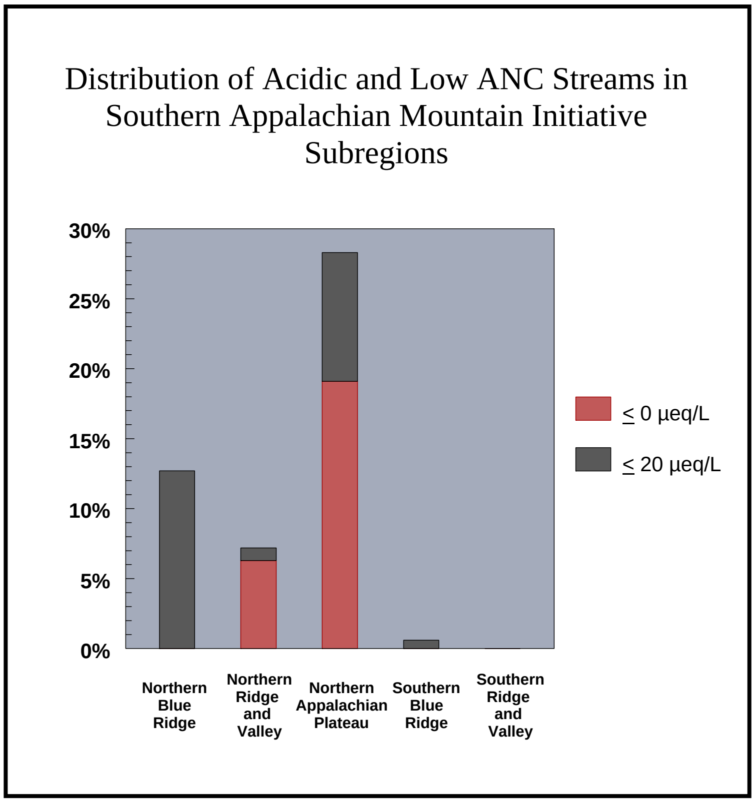
The SAMI region analysis of current stream conditions and projection of future stream conditions relied on existing available stream and soil data, including much of the data described in preceding sections of this report. For purposes of the SAMI assessment, the biological significance of current and projected stream conditions was evaluated in relation to ANC thresholds for brook trout response (see Table 2-1). It should again be noted that brook trout are relatively tolerant to acidification and that other aquatic fauna are harmed by conditions that are less acidic.

SAMI findings related to the central Appalachian mountain region, include:

- Estimates for 1995 indicate that 6.7% of all SAMI region stream reaches have ANC ≤ 0 μeq/L (unsuitable for brook trout). Almost all of these reaches are located in the northern SAMI subregions (i.e., Virginia and West Virginia). See Figure 3-37).

Figure 3-37:

Estimated 1995 percentages of acidic and low ANC stream reaches (determined for upper reach ends) for different subregions within the Southern Appalachian Mountain Initiative (SAMI). The central Appalachian mountain region, addressed in this report, encompasses the northern SAMI subregions.



- Estimates for 1995 indicate that 11.2% of SAMI region stream reaches have ANC $\leq$ 20 μeq/L (marginal for brook trout). All of these reaches are located in the northern SAMI subregions, (i.e., Virginia and West Virginia). See Figure 3-37.

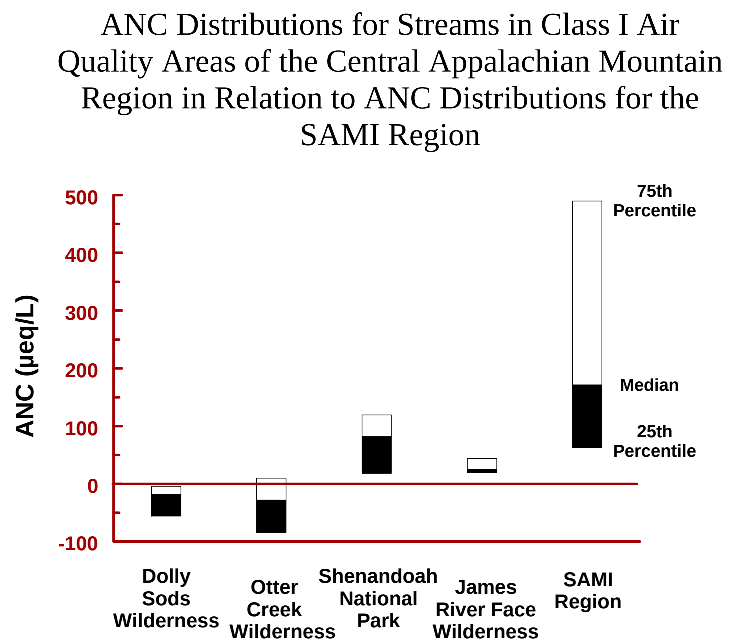


Figure 3-38: *Median and interquartile range of ANC values for stream waters in Class I areas of the central Appalachian region compared with all streams in the SAMI region.*

- Within the SAMI region, stream waters in Class I areas (i.e., those areas designated for the highest level of protection under the Clean Air Act), are disproportionately acidic or sensitive to acidification. The estimated median ANC for 1995 for all SAMI region streams is 172 μeq/L. In contrast, the median ANC values for streams in the Class I areas of Virginia and West Virginia is much lower, ranging from –28 to 82 μeq/L (Figure 3-38).

- Model projections for 2040 based on the three emission control strategies indicate that significant recovery will not occur in the northern SAMI subregions. The distribution of stream reaches relative to biologically defined ANC classes will either not improve or the percentages of streams in unsuitable or marginal classes will increase (Figure 3-39).

- The lack of significant recovery projected for northern SAMI subregions under all three of the emission control strategies can be attributed to depletion of base-cation supplies in watershed soils.

Predicted Percentages of Acidic and Low ANC Streams in Northern SAMI Subregions For 2040 For Three Emission Control Strategies Compared With Estimated 1995 Percentages

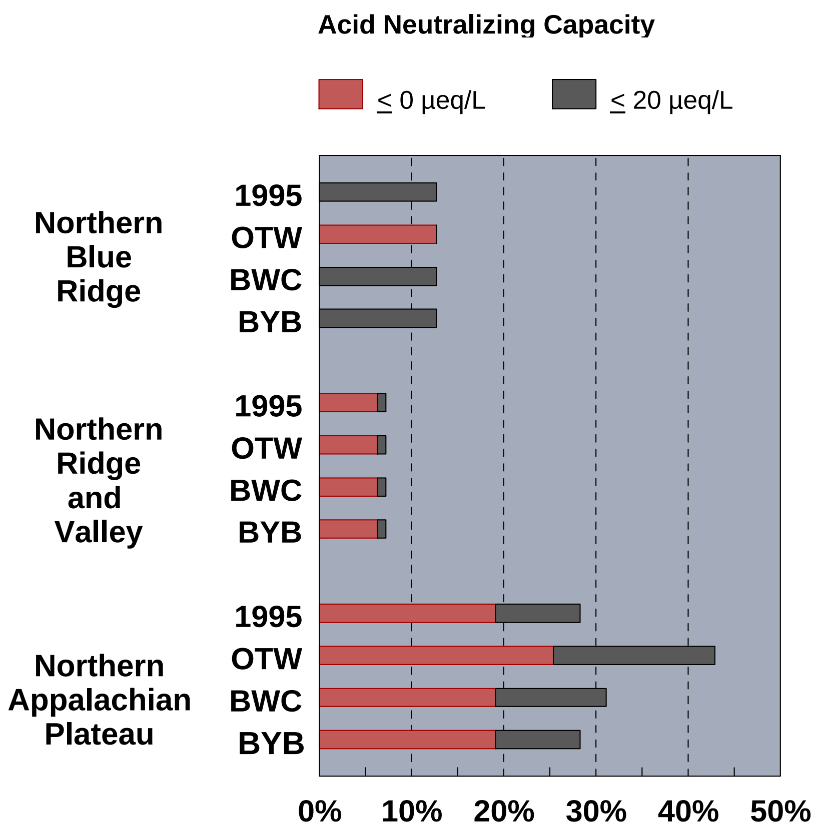


Figure 3-39: *Predicted percentages of acidic and low ANC streams (determined for upstream reach ends) for SAMI subregions in the central Appalachian mountain region. Estimates for 1995 are compared with predicted percentages for 2040 given implementation of three emission control strategies.*

The three emission control strategies and estimated median reductions in sulfur deposition (from 1990 levels) for the SAMI region are:

On-The-Way (OTW): -57%

Bold-With-Constraints (BWC): -67%

Beyond-Bold (BYB): -73%

4.0 Recovery and Mitigation

As described in the preceding sections, the chemical and biological evidence for harm to aquatic ecosystems due to acidic deposition in the central Appalachian Mountain region is both coherent and compelling. Although public policy analysis is outside the purview of this report, it is clear that continued acidification of surface waters and the attendant extirpation of fish and other aquatic species are inconsistent with the intent of our nation’s environmental protection laws and public land management programs. This section addresses the prospects for recovery and the options for mitigation.

4.1 Limitations on Recovery

As demonstrated by recent trends in surface water concentrations of sulfate and acid neutralizing capacity (ANC), reductions in emissions and deposition of sulfur can be expected to achieve some degree of recovery from surface water acidification. This is indicated by observations for surface waters in the northern and eastern United States (see Stoddard et al., 2003) and to a lesser extent by observations for streams in Shenandoah National Park (see Section 3.1 in this report). However, not all surface waters have shown signs of recovery and the magnitude of recovery is generally much less than the magnitude of historic acidification impact.

There are two basic problems that limit recovery from surface water acidification, despite recent reductions in sulfur emissions and deposition.

First, reductions are insufficient to offset historic increases in sulfur emissions and deposition. Even with recent and anticipated reductions, sulfur emissions in the United States will remain many times greater than background or natural levels (see Section 2.1 and Figure 2-2 in this report).

Second, aquatic and terrestrial ecosystems have suffered harm that is essentially irreversible due to depletion of base-cation supplies (particularly available calcium) in watershed soils as a consequence of prolonged exposure to acidic deposition. As described in Section 2.2 of this report, base cations provide acid neutralization through soil exchange and serve as critical nutrients for aquatic fauna and terrestrial vegetation.

The first problem can be solved by reductions in sulfur emissions that are substantially greater than will be attained by current control programs. However, it remains to be seen how quickly and to what extent additional reductions will occur. Delays in reductions will result in more harm to biological resources and more damage to base-cation supplies in watershed soils.

The second problem admits no easy solution. Natural replenishment of base-cation supplies in watershed soils is a slow process. Acidification and recovery occur on different time scales. Although loss of exchangeable base cations in soils results from exposure to sulfur deposition over many years, replacement by mineral weathering takes even longer. Base-cation capital, which can only build-up in conjunction with soil development over very long periods of time, has been lost as a consequence of acidic deposition in a relatively short period of time. As stated previously in this report (Section 3.2), the depletion of base-cations supplies in watershed soils should properly be considered the fundamental, long-term impact of acidic deposition on watershed ecosystems.

4.2 Options for Mitigation

In addition to obtaining additional reductions in sulfur emissions and deposition, several watershed-level options for mitigation of past and ongoing damage are available.

1. Neutralization of surface water acidity by direct application of limestone.
2. Watershed-scale application of limestone or other base material.
3. Incorporation of base-cation conservation strategies in forest management.

4.2.1 Surface Water Limestone Treatment

Limestone treatment of streams and lakes has a history of generally successful results in many areas that have been affected by acidic deposition, including the central Appalachian region. Methods of limestone application for streams include installation of mechanically controlled dosing systems and direct application to streambeds.

As described in this report (Section 3.2), direct liming of tributaries of the Saint Marys River has resulted in increased numbers of both fish and aquatic macroinvertebrate taxa. Increased productivity of aquatic fauna has also been obtained for an additional small number of other western Virginia streams that are presently limed (Larry Mohn, Virginia Department of Game and Inland Fisheries, Verona, VA, pers. comm., 2003). In West Virginia, 26 streams and several lakes are limed with positive results for fish productivity (Mike Shingleton, West Virginia Division of Wildlife Resources, Elkins, WV, pers. comm., 2003). Liming programs have also been conducted in both Maryland (Price and Morgan, 1993) and Pennsylvania (Janicki and Greening, 1988). As summarized by Olem (1990), the majority of liming studies report successful reproduction and increased biomass of acid-sensitive fish species

The extent of limestone treatment of impaired surface waters has been limited by the cost, although relatively low-cost methods have been developed (Downey et al., 1994). Other limitations include the probability that liming will not result in the restoration of the original preacidification biological communities (Olem, 1990). There have also been instances where liming has caused mortality due to increased aluminum toxicity (Rossland et al., 1992). In addition, limestone treatment of surface waters provides only a temporary solution; limestone must be continuously or periodically applied if reacidification is to be prevented. More importantly, adding limestone to surface waters only addresses the most obvious aspect of the acidification problem.

Although limestone treatment can improve chemical and biological conditions in a stream, the loss of base cations from watershed soils will continue as long as elevated acidic deposition continues.

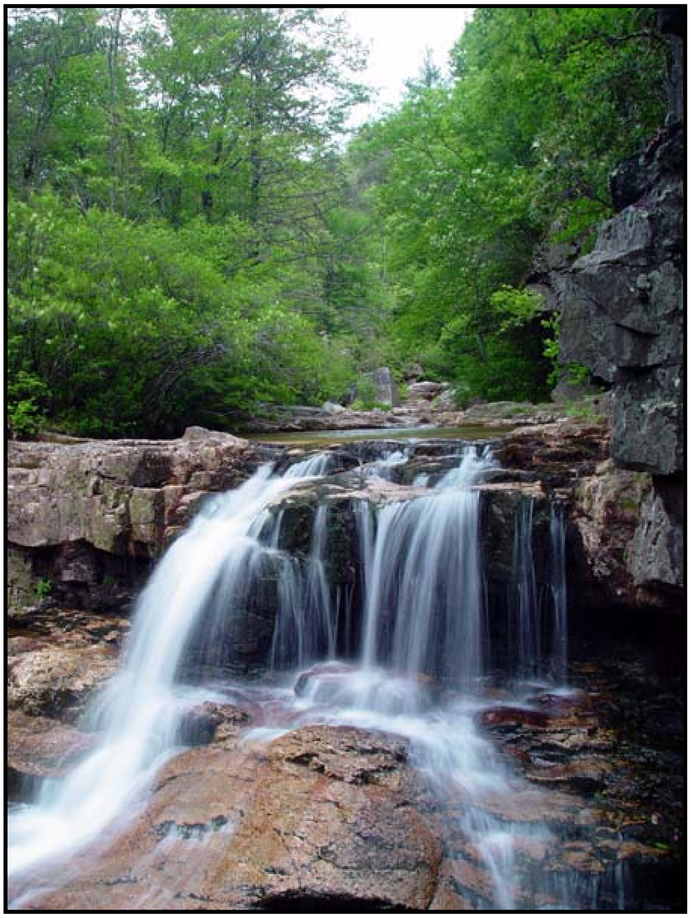


Figure 4-1:

Direct liming of acidified streams, such as Virginia's Saint Marys River, has resulted in greatly improved chemical and biological conditions. However, direct liming of streams does not address acidification of watershed soils.

4.2.2 Watershed-Scale Limestone Treatment

Watershed-scale application of limestone offers the potential for more-complete restoration of watershed ecosystems. It also offers the possibility of long-term benefits. A review of forest liming studies by Johnson et al. (1995) suggests that positive soil responses, including elevation of base saturation, can persist for decades after limestone application. It also appears that by comparison with direct surface water treatment, watershed liming can moderate hydrologically driven episodic acidification and minimize the potential for abrupt treatment failure (Driscoll et al., 1996).

However, actual watershed-scale liming is rarely, if ever, undertaken. This is evidently due to logistical difficulties and cost. The objective of most watershed-scale treatment programs is to achieve stream or lake neutralization, rather than watershed-scale soil treatment. Thus, limestone is often only applied to identified wetland areas or other hydrologically important areas, not to the entire watershed. For example, the Western Maryland Watershed Liming Study involved application of pelletized limestone in a 61-meter band on either side of the main stream course of Alexander Run, an area amounting to about 14% of the total watershed area (Price and Morgan, 1993). Similarly, the Experimental Watershed Liming Pilot Study in the Adirondacks region of New York involved treatment of Woods Lake by application of pelletized limestone to two subcatchments comprising about 50% of the watershed (Driscoll et al., 1996).

It also appears that short-term success of watershed-scale liming is limited by problems with dissolution and incorporation of limestone into forest soils. Limestone that is applied to forest soils may fail to contribute to either surface water neutralization or improved base status in deeper soil horizons. The only significant neutralization of the stream following the above mentioned Alexander Run watershed liming project was provided by limestone pellets that were deposited in the stream during the application, and the only significant increase in soil base supply was limited to the upper, shallow soil layer (Price and Morgan, 1993). Similarly, most of the increase in surface water ANC during above mentioned Woods lake watershed liming was derived from direct limestone application to wetlands; relatively little was derived from application to freely draining upland soils (Driscoll et al., 1996). In both of these cases, the pelletized limestone that was applied to soil rather than stream or wetland areas remained largely undissolved during the 1-3 year course of the studies. Experience with forest soil liming, however, suggests that watershed liming can provide long-term benefits (Johnson et al., 1995).

Another problem with watershed liming is the potential for unintended ecosystem effects (Price and Morgan, 1993). For example, there are some concerns about the effects of watershed liming on acid-tolerant biological communities. In addition to affects on acid-tolerant plants, there may be an increase in the rate of decomposition of the peat and organic substances that physically support bog wetlands.

4.2.3 Conservative Forest Management

Base cations, especially calcium and magnesium, can be removed from soils by plant uptake as well as by leaching associated with sulfuric acid deposition. As indicated by Figure 2-4 in this report, increasing movement of sulfate through forest soils results in increased export of base cations in surface water. Base cations that are taken up as nutrients by vegetation are depicted as cycling back to the soil (through litter fall and decomposition). However, this equilibrium between uptake and recycling is not maintained in forests that are managed for timber production. Instead, the base cations that have been incorporated in trees are exported from the watershed system when the trees are harvested. Subsequent regrowth then results in additional removal of base cations from the available soil supply.

A number of investigators have addressed the link between depletion of base cations in soil and both acid deposition and timber harvest. A study by Federer et al.,

Figure 4-2:

Depletion of calcium and other base-cations in watershed soils is the fundamental, long-term impact of acidic deposition on watershed ecosystems.

(1989) showed that leaching associated with acidic deposition and removal of above-ground biomass by timber harvest contribute equally to net loss of calcium from six eastern United States forests. An assessment of calcium budgets at southeastern United States forested sites by Lawrence and Huntington (1999) showed that depletion of calcium in soils is common, that acid deposition and forest growth are both factors that contribute to calcium depletion, and that calcium availability will be further lowered by forest harvesting at sites currently low in calcium.

Recommendations for conservation of base-cation capital on base-poor and base-depleted sites have been proposed. Hornbeck et al. (1990) and Hornbeck (1992), for example, suggested avoiding whole tree harvest, avoiding harvest during the growing season or insuring that leaves remain on site, and otherwise decreasing the intensity of harvest. Federer et al. (1989) suggested that three measures are possible to mitigate calcium depletion in a context of timber production, including reduction of acidic deposition to preindustrial levels, restrictions on short-rotation whole-tree harvest, and large-scale liming of forest areas.

5.0 Summary of Findings

- The central Appalachian Mountain region, defined as the mountainous area of Virginia and West Virginia, is exposed to among the highest acidic deposition loads in the United States.

- Implementation of the 1990 Clean Air Act Amendments has achieved, and should achieve more, reduction in acidic deposition levels, especially reductions in the sulfur component. However, acidic deposition levels will remain high because anthropogenic emissions of sulfur will continue to greatly exceed natural background emission levels.

- Sulfate concentrations in central Appalachian mountain streams have increased dramatically as a consequence of acidic deposition, and sulfate concentrations in many streams will increase further as sulfur retention capacity in watershed soils is exhausted. Sulfate has become the dominant solute in many streams–a major change in the chemical environment.

- The increase in sulfate concentrations in western Virginia mountain streams has had a dramatic effect on acid-base status and aquatic fauna. The evident elevation of sulfate concentrations in stream water, the presently low acid neutralizing capacity (ANC) in stream water, and the base-poor status of watershed soil and bedrock, provides strong evidence of historic acidification (loss of ANC) in a substantial portion of these streams.

- The close correlation between ANC and fish diversity in Shenandoah National Park indicates that acidification-related species losses have occurred and that more losses will occur if acidification continues.

- Despite recent declines in acidic deposition and encouraging evidence for initial recovery of some streams in the central Appalachian region, the degree of recovery has been minor in relation to historic acidification, and many streams continue to acidify.

- The eventual magnitude of potential recovery will be limited by both the magnitude of reductions in sulfur deposition and the magnitude of cumulative long-term damage due to base-depletion in watershed soils.

- Options for mitigation include direct stream liming, watershed-scale liming, and conservative forest management. Stream liming can result in dramatic biological and water quality improvements. However, only the second two options address the fundamental long-term problem of base-cation depletion in watershed soils.

6.0 Definitions

Acid anion – a negatively charged ion that does not react with hydrogen ion in the pH range of most natural waters, e.g., sulfate, and nitrate.

Acid cation – hydrogen ion or metal ion that can react in water to produce hydrogen ions, e.g., aluminum.

Acidic deposition – transfer of acids and acidifying compounds from the atmosphere to terrestrial and aquatic environments via rain, snow, hail, cloud droplets, particles, and gas exchange.

Acidification – the decrease in acid neutralization capacity in surface water or base saturation in soil.

Acid neutralization capacity (ANC) – the capacity of a solution to neutralize strong acids.

Anion – a negatively charged ion.

Basaltic – a defined bedrock class, including extrusive igneous rocks, commonly composed of minerals with high concentrations of base cations.

Base cation – a nonacidic positively charged ion, e.g., calcium, magnesium, sodium, and potassium ions.

Base saturation – the proportion of total soil cation exchange capacity that is occupied by exchangeable base cations.

Bedrock – solid rock exposed at the earth surface or overlain by unconsolidated surficial material, e.g., soil and sapprolite.

Benthic – refers in this report to the stream bottom.

Cation – a positively charged ion.

Cation exchange in soil – the interchange between a cation in solution and another cation on the surface of soil particles.

Chronic acidification – long-term acidification.

Delayed response – refers in this report to delayed acidification due to sulfur retention in watersheds.

Episodic acidification – short-term acidification usually associated with high-flow conditions.

Granitic – a defined bedrock class, including intrusive igneous rocks, commonly composed of minerals with intermediate to low concentrations of base cations.

Macroinvertebrate – an organism without a backbone that is visible without magnification, e.g., an insect.

Micro equivalent per liter (µeq/L) – An ionic concentration unit; one millionth of an equivalent per liter of water, where an equivalent is a mole of charge.

Micrograms per liter (µg/L) – a mass concentration unit; one millionth of a gram per liter of water or one part per billion.

Monomeric aluminum – aluminum that occurs as a free ion or as a simple inorganic or organic complex, but not in polymeric forms.

Nitrate – the fully oxidized nitrogen species, the form of dissolved nitrogen most prevalent in surface waters.

pH – a measure of acidity; specifically the negative log of the hydrogen ion activity or concentration. pH is represented on a scale of 1-14, where 7 is neutral, lower values are more acidic, and each pH unit indicates a ten-fold change in hydrogen ion activity.

Siliciclastic – a defined bedrock class of sedimentary origin, commonly composed of minerals with low concentrations of base cations.

Strong acids – acids with a high tendency to donate hydrogen ions or to completely dissociate in natural waters, e.g., sulfuric acid and nitric acid.

Sulfate – the fully oxidized sulfur species, the form of dissolved sulfur most prevalent in surface waters.

Sulfur retention – the process by which sulfur or sulfate in watersheds is retained or prevented from reaching receiving surface waters.

Sulfur deposition equivalent – refers in this report to the surface water sulfate concentration that occurs when atmospherically deposited sulfur is not retained in watersheds or watershed sulfur retention capacity is exhausted.

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