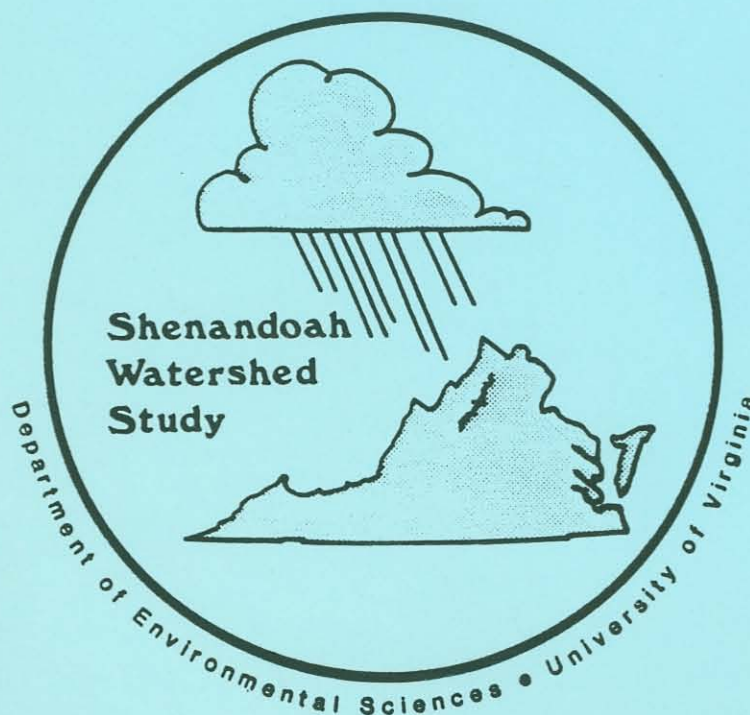


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SHENANDOAH WATERSHED STUDY

AN OVERVIEW



APRIL 20, 1989

INTRODUCTION

ACIDIC DEPOSITION

THE SHENANDOAH WATERSHED STUDY: AN OVERVIEW

THE SWAS PROJECT

PRINCIPAL SWAS

FORECAST MODELING

* * *

CONTINUING PROGRAM

SUMMARY: PROJECT

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1. Deposition watershed compared with
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3. Alkalinity relationship values

* *

4. The sensitivity function

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5. Conclusions

6. Response elevated

7. Forecasts given for

8. Distribution and potential Shenandoah

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9. Classification relationship

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INTRODUCTION

The Shenandoah Watershed Study (SWAS) was initiated in 1979 as a cooperative research and monitoring program of Shenandoah National Park (SNP) and the Department of Environmental Sciences at the University of Virginia. The objective of SWAS, in broad terms, is to understand the processes that govern biogeochemical cycles in SNP's mountain watersheds.

The primary emphasis of SWAS research and monitoring has been determined by the need to assess watershed response to the acidic deposition ("acid rain") phenomenon. SWAS research indicates a poor prognosis for aquatic ecosystems in large areas of SNP due to a combination of watershed sensitivity and elevated acidic deposition. This document provides a summary description of the SWAS program and current information concerning acidic deposition effects in SNP. A bibliography of detailed technical reports is also provided.

ACIDIC DEPOSITION IN SHENANDOAH NATIONAL PARK

SNP is located downwind of the major acidic emission regions of the nation and consequently receives one of the highest acidic deposition loads of all the national parks. The magnitude of this loading is indicated by Figure 1, which contrasts ion deposition in precipitation of SNP with that of uncontaminated precipitation from remote locations in other parts of the world.

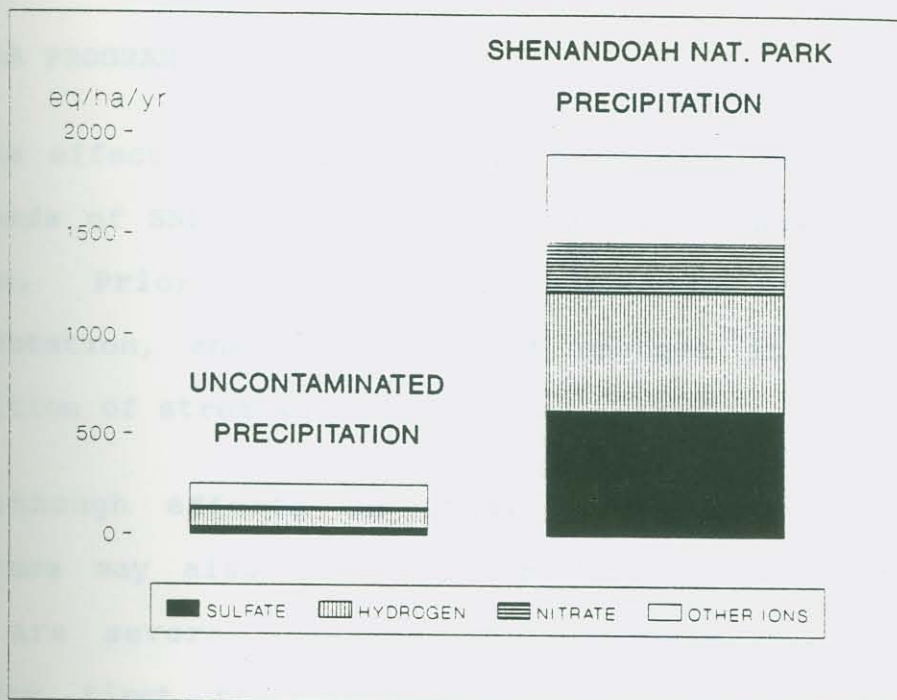


FIGURE 1

Deposition of ions in precipitation (in equivalents per hectare per year) at the White Oak Run watershed in southwestern Shenandoah National Park compared with average ion deposition for four remote locations (Poker Flat, Alaska; Katherine, Australia; Lihang, China; and Mauna Loa, Hawaii).

Assuming that precipitation at the remote locations is similar to that of SNP in preindustrial times, the total deposition of ions in precipitation has increased about six fold. Most of the change is in sulfate, hydrogen, and nitrate. Hydrogen ion concentration has increased from a preindustrial pH of 5.0 or higher to a mean pH of about 4.2. The cause of this increase is atmospheric emission of sulfur and nitrogen gases associated with fossil fuel combustion. These gases react in the atmosphere to form sulfuric and nitric acid, which occur as sulfate, nitrate and hydrogen ion when dissolved in precipitation.

THE SWAS PROGRAM

The effect of present-day acid loading on the mountain watersheds of SNP has been the principal focus of the SWAS program. Priority has been placed on detection, interpretation, and prediction of changes in the chemical composition of streamwaters.

Although effects on other components of watershed ecosystems may also be associated with acidic deposition, there are several reasons for emphasis on streamwater chemistry. First, the acid neutralization capacity of many SNP streams is extremely low; substantial stream acidification is predicted. Second, the chemical composition of streamwater represents a quantifiable synthesis of watershed inputs and processes. Whereas changes in streamwater chemistry can be precisely measured, reliable detection of changes in soil or vegetation is substantially more difficult. Finally, acidification of streamwater can directly affect the distribution and productivity of fish and other aquatic biota. Measurements of streamwater composition can thus provide a warning of pending biological effects or an explanation for past and current biological effects.

The monitoring and research components of the SWAS program are described separately on the following pages.

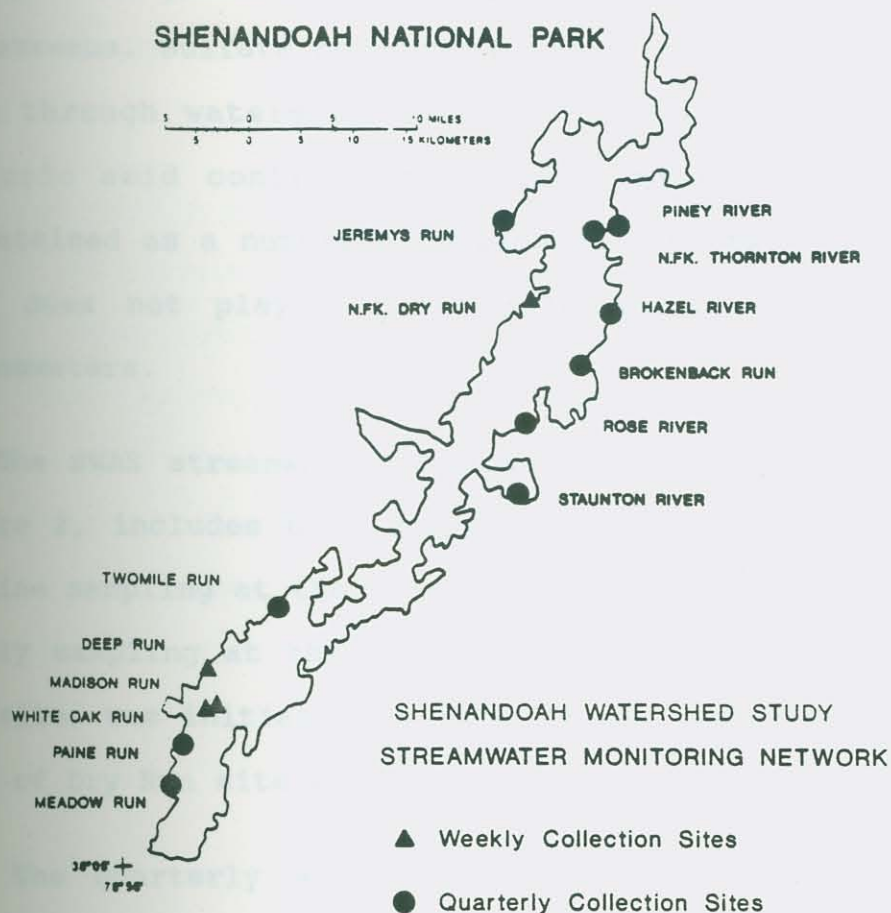


FIGURE 2

SWAS Monitoring

The principal objective of the monitoring program is early and reliable detection of changes in streamwater chemical composition that occur as a consequence of acidic deposition. Routine analyses include all the major dissolved chemical species. The concentrations of sulfate and alkalinity (acid neutralization capacity) and pH are of primary interest as measures of the effect of acidic deposition. Alkalinity and pH

indicate the present buffering capacity and acidity level of the streams. Sulfate concentrations provide a measure of acid flux through watershed systems. Although both nitric and sulfuric acid contribute to deposition acidity, nitrogen is retained as a nutrient by watershed biota, and thus nitric acid does not play a major role in acidification of SNP streamwaters.

The SWAS streamwater monitoring network, as indicated in Figure 2, includes both quarterly and weekly sampling sites. Routine sampling at the quarterly sites was initiated in 1988. Weekly sampling at the Deep Run, Madison Run, and White Oak Run sites was initiated in 1979. Weekly sampling at the North Fork of Dry Run site was initiated in 1987.

The quarterly sites provide a spatially extensive and geographically representative component of the monitoring network. The sites were selected to provide information for the range of watershed conditions and sensitivities present in SNP. The same sites have also been adopted into SNP's newly initiated Long-Term Ecological Monitoring System which will provide routine information concerning the status of stream biota. The quarterly sample collection is further coordinated with the Virginia Trout Stream Sensitivity Study (supported by the Va. Dept. of Game and Inland Fisheries and the U.S. Forest Service) for which a total of 67 headwater streams located in Virginia's mountain region are sampled on a quarterly basis. The replication and regional perspective gained by this coordination should serve to strengthen findings of the

monitoring effort in SNP. The monitoring in SNP, in turn, provides a critical component of the regional scale monitoring effort.

The weekly sampling provides the most sensitive component of the SWAS monitoring network. Like the quarterly sites, the weekly sites represent the range of watershed conditions in SNP. The temporally-intensive streamwater composition data obtained for these sites provide for better resolution of short-term variation related to seasonal and hydrologic conditions. By improving our ability to account for short-term variation in streamwater chemistry, weekly sampling improves our ability to detect long-term trends such as chronic acidification.

The benefits of weekly sampling will also extend in part to interpretation of the quarterly data, as the data obtained for the weekly sites will help define conditions for the quarterly sampling. As demonstrated by Figure 3, the perspective provided by weekly data collections may prove critical to interpretation of the quarterly data. This plot shows weekly and quarterly alkalinity values for a four year period of sampling on Deep Run. A misleading trend of increasing alkalinity is indicated based on the quarterly data alone. In contrast, the weekly data reveals the critical information that alkalinity actually reached lower values and remained acidic (alkalinity ≤ 0 $\mu\text{eq/L}$) for a longer period of time in the winter and spring of 1987 than in the previous years. Moreover, as discussed below, analysis of eight years

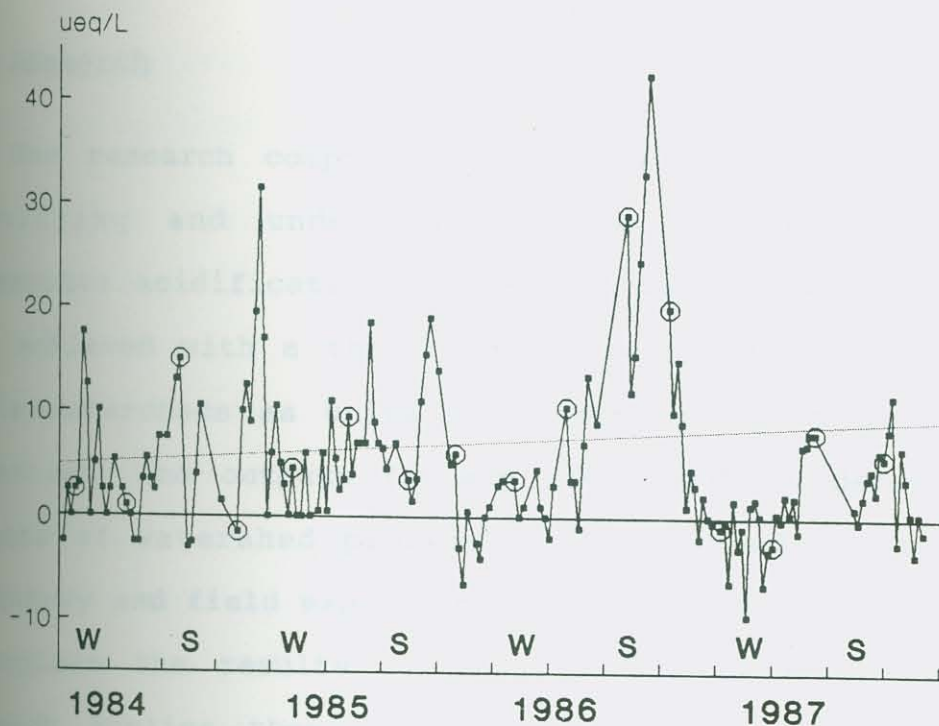


FIGURE 3

Alkalinity of streamwater in Deep Run, showing relationship between weekly values (uncircled points) and quarterly values (circled points). The upward trend for the quarterly values is indicated by the broken line.

of weekly data for this site indicates a decreasing trend in alkalinity.

The weekly stream sampling sites have also provided a focus for much of the SWAS watershed research. The watersheds for three of these streams are calibrated; routine measurements are obtained of precipitation quantity and composition, as well as streamwater composition and discharge amount. These calibrated watersheds are associated with White Oak Run and Deep Run in the Park's southern section and North Fork of Dry Run in the Park's central section.

SWAS Research

The research component of SWAS has largely focused on identifying and understanding the factors controlling streamwater acidification. Progress toward this objective has been achieved with a threefold approach. The first approach treats watersheds as units by measuring inputs (atmospheric deposition) and outputs (stream discharge) to determine net effects of watershed processes. The second approach uses laboratory and field experiments to test hypotheses formulated to explain the results of input-output studies. The third approach applies these results and explanations to create models that may be used for prediction of watershed response and impacts.

Input-output budgets are calculated for the three calibrated watersheds maintained by SWAS. As indicated previously, measurements of the quantity and chemical composition of precipitation and streamwater are obtained on a routine basis for these watersheds.

Individual research projects associated with SWAS during the last nine years have ranged in scale from parkwide surveys of stream chemistry to laboratory studies of soil properties. Investigations have been mounted to determine controls on stream chemistry; these investigations have examined the effects of bedrock, soil, vegetation, and watershed hydrology. In support of predictive modeling efforts, a special emphasis has been placed on an understanding of factors controlling the

flux of atmospheric sulfate and the generation of alkalinity or acid neutralization capacity within watersheds.

The SWAS effort has also included establishment of permanent terrestrial sites for soil and vegetation studies. This work, in the North Fork Dry Run area, is coordinated with the Mountain Cloud Chemistry Project (supported by the U.S. Environmental Protection Agency) which maintains three above-canopy towers to facilitate study of elemental transfer between the atmosphere and the watershed system.

PRINCIPAL SWAS FINDINGS

- * Streamwaters in large areas of Shenandoah National Park are poorly buffered against acidification.

The sensitivity of SNP streamwaters to acid deposition is primarily a function of watershed bedrock (Figure 4). Differences in the composition and weathering properties of SNP's major bedrock types have produced a range of soils with differing development and acid buffering capacities. These differences are in turn reflected in the acid buffering capacity or alkalinity of associated streamwaters.

Surface waters with alkalinity concentrations of less than 200 $\mu\text{eq/L}$ are commonly classified as acid sensitive. Relative to this value, the SNP streams associated with basaltic bedrock are classified as marginally sensitive. The streams associated with granitic bedrock are classified as sensitive, while the streams associated with silico-clastic

SHENANDOAH NATIONAL PARK

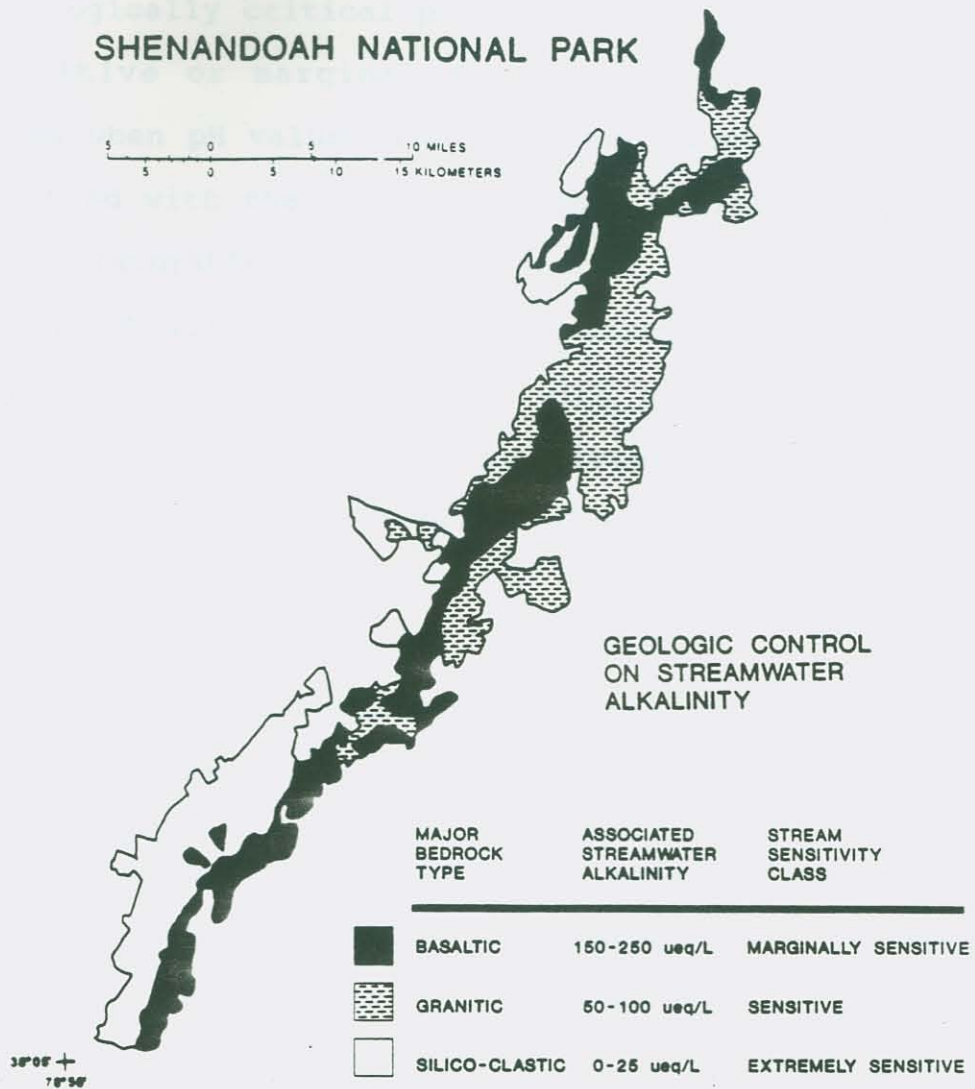


FIGURE 4

bedrock (quartzite, sandstone, phyllitic shale) can be classified as extremely sensitive.

The ecological significance of these differing sensitivity or alkalinity ranges is best revealed by reference

to biologically critical pH or acidity levels. Conditions are prohibitive or marginal for many fish and other aquatic species when pH values are less than about 6.0. SNP streams associated with the basaltic bedrock typically have pH values in the favorable range of about 7.0 to 7.2. For streams associated with the granitic bedrock, the pH values are slightly lower (more acidic), with a range of about 6.5 to 6.8. The extremely sensitive streams associated with the silico-clastic bedrock have pH values in the critical range of about 5.1 to 6.2.

*** Acidification of Shenandoah National Park streams is delayed by sulfate retention in watershed soils.**

Consistent with observations made for other streams in the southeastern U.S., a large proportion of the sulfate deposited in SNP is not appearing in streamwaters. Approximately 60-70% of the sulfate deposited in SNP watersheds is being adsorbed by watershed soils. This differs from conditions observed for acidified surface waters in the northeastern U.S. and Canada where soils adsorb less sulfate and most of the sulfate deposited in watersheds is transported away by surface water.

Sulfate adsorption in watershed soils helps explain why severe surface water acidification has not been observed in SNP. Adsorption, however, is a capacity-limited mechanism which provides only a temporary delay in the acidification process. As the adsorption capacities of watershed soils are

exhausted, the sulfate concentrations and acidity levels in SNP streams will rise.

*** Acidification of Shenandoah National Park streams is an ongoing process.**

Chronic acidification has been documented for both Deep Run and White Oak Run, two SNP streams which have been intensively monitored since 1979. These streams are located in an area dominated by quartzites, sandstones, and shales. They represent the most sensitive class of SNP streams. Changes in the annual volume-weighted mean concentrations of sulfate, alkalinity, and hydrogen ion for these two streams are indicated in Figure 5. Over the eight year period, the sulfate concentrations in both streams have risen about 2 $\mu\text{eq/L}$ per year and alkalinity has declined 0.5 to 0.75 $\mu\text{eq/L}$ per year. For Deep Run, the stream with least buffering capacity, hydrogen ion has increased about 0.4 $\mu\text{eq/L}$ per year. In pH units, Deep Run has declined from about 5.6 to 5.3 over the eight year period. White Oak Run, which has more buffering capacity, has shown less increase in hydrogen ion. White Oak Run pH has declined from about 6.1 to 6.0. For both of these streams, the observed acidification indicates a state of ecological deterioration. The acidity level of White Oak Run is entering the biologically critical range, while the acidity of Deep Run is already well within the critical range.

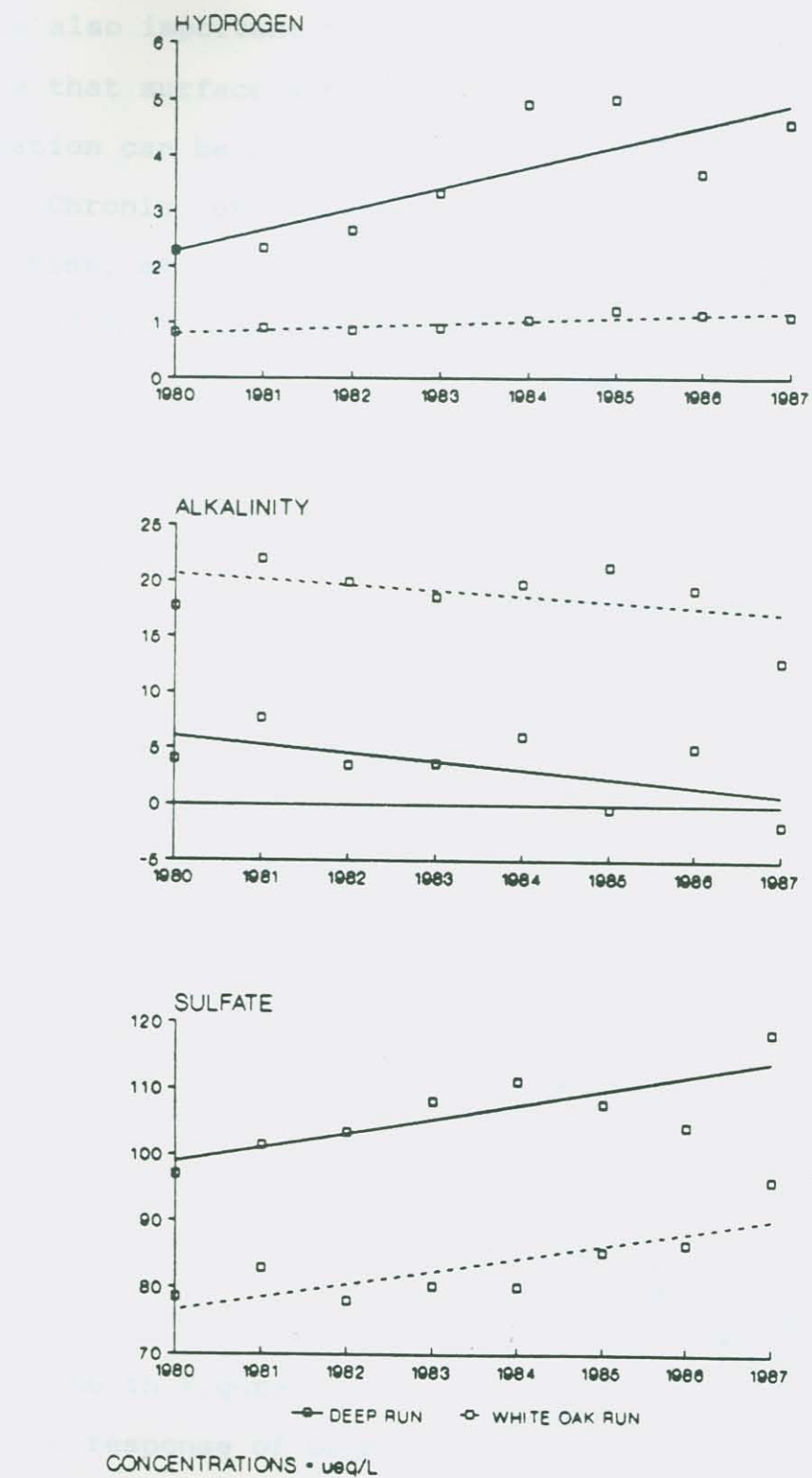


FIGURE 5

Trends in sulfate, alkalinity, and hydrogen ion concentrations (volume-weighted annual means) for Deep Run and White Oak Run.

The period of greatest precipitation and runoff occurred in the month of April. Concentrations of sulfate increased sharply in all three streams. Alkalinity reductions also occurred in all three streams. A sharp increase in hydrogen ion or acidity, however, occurred only in Deep Run, the stream with the least alkalinity. The increase in acidity in Deep Run corresponded to a pH depression of 0.3 units, from 5.4 to 5.1. The effect of this type of acidification episode on stream biota is not well known.

FORECAST MODELING

An important integrating factor for SWAS research and monitoring has been the development of the Model of Acidification of Groundwater in Catchments (MAGIC), a model that incorporates present understanding of the most important controls on watershed response to acidic deposition. MAGIC can be applied to explain current soil and streamwater chemistry, and to predict changes under a range of future deposition scenarios.

MAGIC was first developed and calibrated for the White Oak Run watershed, for which the requisite input-output budgets and soils information were available. Predictions of future change in the sulfate concentration of White Oak Run are indicated in Figure 7 for no reduction, 50% reduction, and 100% reduction in sulfate deposition. Assuming no reduction in sulfate deposition, the MAGIC model further predicts that complete alkalinity loss will occur in the next

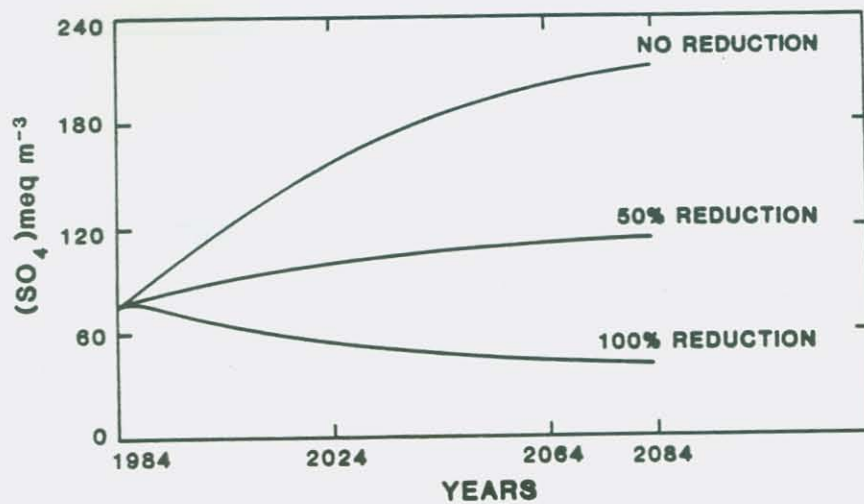


FIGURE 7

Forecasts of sulfate concentration for White Oak Run given three scenarios of future sulfate deposition.

25 years. This rate of alkalinity loss is consistent with the acidification trend observed for White Oak Run for the period 1980 to 1987.

Although additional data are being obtained, the application of MAGIC requires more data than are presently available for most watersheds in SNP. As an alternate approach to predicting chronic acidification on a parkwide basis, a simpler, but less informative, watershed-titration model can be applied. As demonstrated in Figure 8, this model can be applied to estimate future as well as past streamwater

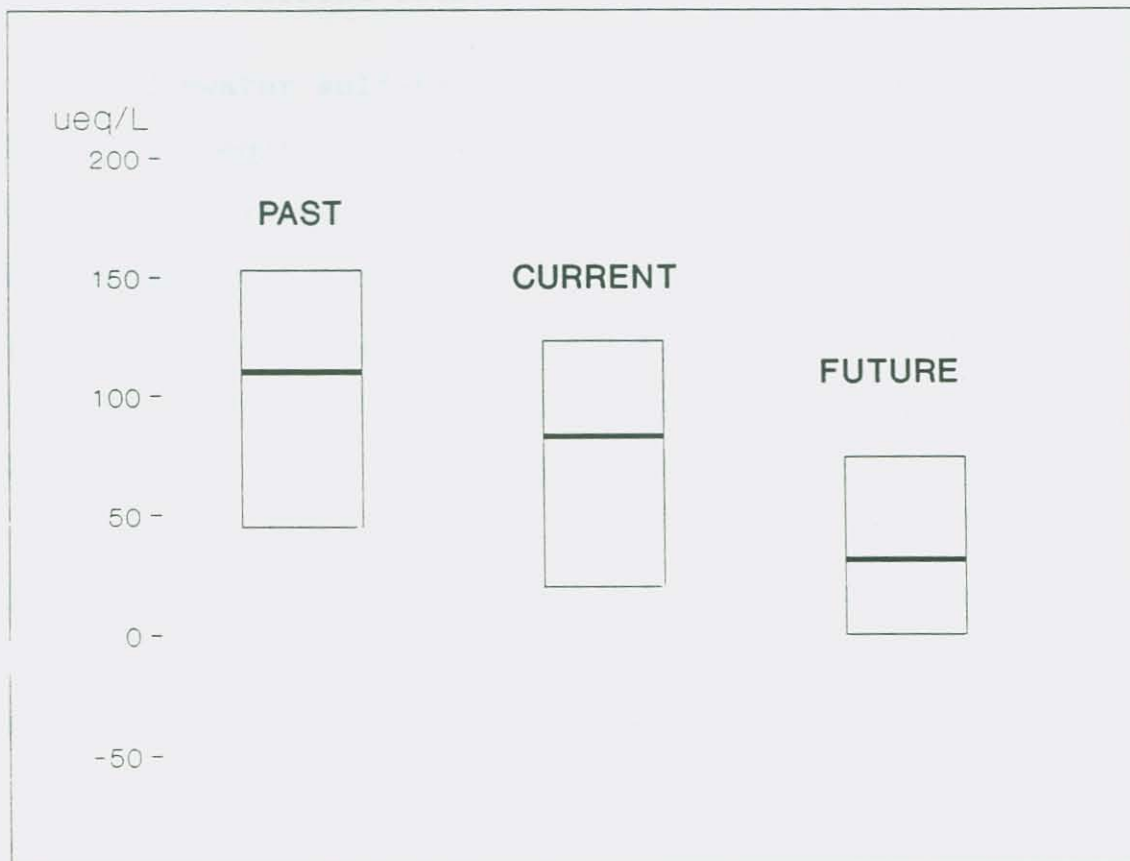


FIGURE 8

Distributions of estimated original, measured current, and potential future alkalinity concentrations for Shenandoah National Park Streams ($n = 47$). The darkened lines indicate median values; 1st and 3rd quartile values are indicated by the boxes. The cation increase factor is estimated to be 0.4.

alkalinity concentrations. Median alkalinity values of SNP streams are estimated to have declined from 108 $\mu\text{eq/L}$ in the

past to the current median of 82 $\mu\text{eq/L}$. The median alkalinity of these streams is predicted to further decline to about 29 $\mu\text{eq/L}$ under current rates of acidic deposition.

Streamwater sulfate concentrations are expected to rise to about 220 $\mu\text{eq/L}$ as sulfate adsorption capacities in watershed soils are exhausted. The preindustrial concentrations are estimated to be about one-tenth this level, or about 22 $\mu\text{eq/L}$. Based on the trends presently observed for Deep Run and White Oak Run, the loss of alkalinity (streamwater acidification) is estimated to equal about 60% of the increase in sulfate. The other 40% of the increase in sulfate is matched by a rise in the rate of base cation removal from watershed soils. Our use of the titration model assumes that these conditions apply reasonably well to all SNP watersheds.

The significance of these estimated changes in streamwater alkalinity are again best interpreted relative to biologically critical pH values. As stated previously, pH 6.0 is an approximate threshold value for biological effects in streamwaters. Another value of significance is pH 4.7, an approximate minimum for the eastern brook trout. Although no SNP streams presently have pH values below 4.7; about 25% are predicted to have pH values less than 4.7 in the future.

Figure 9 indicates the estimated past, measured present, and predicted future proportion of SNP streams in classes defined by the cited biologically critical pH values. It is apparent that changes in the biological status of SNP streams

may have occurred in the past, and that substantial changes can be expected in the future.

Our application of the titration model provides perspective concerning the potential magnitude of streamwater acidification. However, it provides no information concerning the time period over which acidification will occur. As discussed above, the observed trends, as well as application of the MAGIC model, suggest that SNP streams similar to White Oak Run are losing alkalinity at a rate of about $0.5 \mu\text{eq/L}$ per year. The observed rate of acidification in Deep Run is somewhat faster ($0.75 \mu\text{eq/L}$ per year). More information concerning rates of acidification for a broader population of SNP streams will be obtained as data are collected through the trend monitoring program.

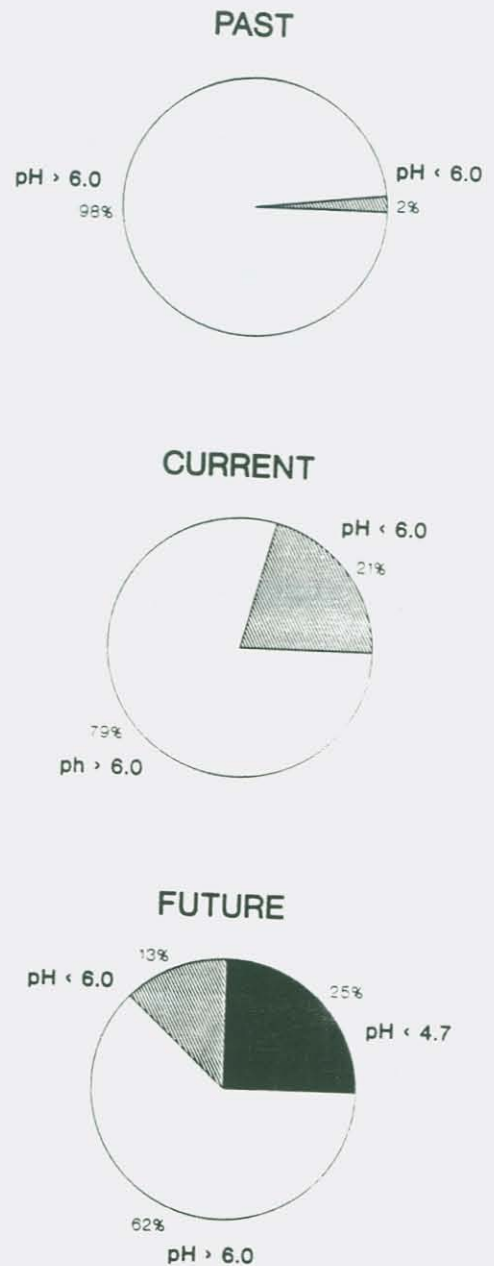


FIGURE 9

Classification of Shenandoah National Park streams relative to biologically critical pH values. Past and future conditions are estimated based on application of the watershed titration model.

CONTINUING PROGRAM OBJECTIVES

Given the potential for significant ecological impact, assessment of watershed response to acidic deposition is the continuing SWAS emphasis. The principal SWAS objectives apply to the monitoring and research components of the program. These objectives are restated as follows, together with a brief discussion of current work under each objective.

SWAS Monitoring Objective: Early detection of changes in the chemical composition of SNP streamwaters that occur as a consequence of acidic deposition.

A systematic effort has been initiated to quantify sources of variation in the composition of streams included in SWAS monitoring program. The intention of this undertaking, which is coordinated on a regional scale with the Va. Trout Stream Sensitivity Study, is to improve detection of long-term trends by accounting for short-term trends. A secondary objective is to clarify the role and significance of storm-related episodic acidification.

As a means to meet these objectives, an empirical model will be developed to explain streamwater chemistry for each of the collection sites given variable seasons and hydrologic conditions. Development of this model requires information on geology, soil, and topography for each watershed. Additional data requirements include quarterly streamwater composition, and antecedent precipitation and stream discharge. Evaluation

and refinement of this model will be obtained as the model is tested and recalibrated on a continuing basis.

SWAS Research Objective: Improved evaluation of factors controlling stream and watershed acidification.

A number of individual research projects are now underway that will contribute to reduction of uncertainty in predictive modeling. Current efforts address hydrologic control of sulfate mobility in hillslope soils, the exchange of water between stream channels and temporary storage zones in alluvial areas, and the generation of acid neutralization capacity through weathering processes in watershed rocks and soils. Additional projects are investigating the importance of sulfur gas evolution from soil and the deposition of sulfur in cloud water and aerosol forms. Plans have also been made to apply the MAGIC model for prediction of watershed acidification on a parkwide basis as critical factors are quantified.

SUMMARY: PROGNOSIS FOR SHENANDOAH NATIONAL PARK STREAMS

Results from monitoring at weekly sampling sites indicate that acidification is ongoing in at least some SNP streams; streamwater concentrations of sulfate are increasing, alkalinity is decreasing, and hydrogen ion is increasing. Assuming no change in the present-day level of acid deposition, large changes in both the chemical and biological

composition of SNP streams are expected. Sulfate, which has already become the major dissolved anion in most SNP streams, will further increase in streamwaters as sulfate retention in watershed soil declines. This sulfate increase will result in a reduction in streamwater alkalinity and pH. For those SNP streams associated with base-poor soils and bedrock types, substantial reductions in streamwater alkalinity and pH may have already occurred and further reductions are expected. As further alkalinity is lost in these streams, pH values will decline to critical levels for many of the fish and other aquatic species which are now present.

* * *

For further information concerning the Shenandoah Watershed Study contact: Rick Webb, Project Manager, SWAS, Department of Environmental Sciences, Clark Hall, University of Virginia, Charlottesville, Virginia 22903.

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