SHENANDOAH WATERSHED STUDY
AN OVERVIEW

Shenandoah Watershed Study

Department of Environmental Sciences • University of Virginia

JANUARY 1, 1989

THE SHENANDOAH WATERSHED STUDY: An Overview

By Rick Webb, Project Manager

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 research emphasis of SWAS has been determined by the need to assess watershed response to the acid 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 acid deposition. This document provides a summary description of the SWAS program and current information concerning acid deposition impact in SNP.

THE MAGNITUDE OF ACID 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 acid deposition loads of all the national parks. One measure of this acid loading is the amount of sulfate dissolved in precipitation. Based on comparison with remote

areas of the world, the current deposition of sulfate in SNP precipitation is conservatively estimated to be about ten times preindustrial levels. This amounts to about 25 lbs. of sulfate per acre per year in SNP. The acidity of this precipitation, as indicated by a mean pH of about 4.2, is likewise an order of magnitude greater than in uncontaminated precipitation.

THE SWAS PROGRAM

The SWAS program has focused on identification and understanding of factors controlling both aquatic and terrestrial response to the elevated acid deposition. Progress toward this goal 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 three calibrated watersheds in SNP. The quantity and chemical composition of precipitation and streamwater are measured on a routine basis for White Oak Run and Deep Run in the Park's southern section and North Fork of Dry Run in the Park's central section.

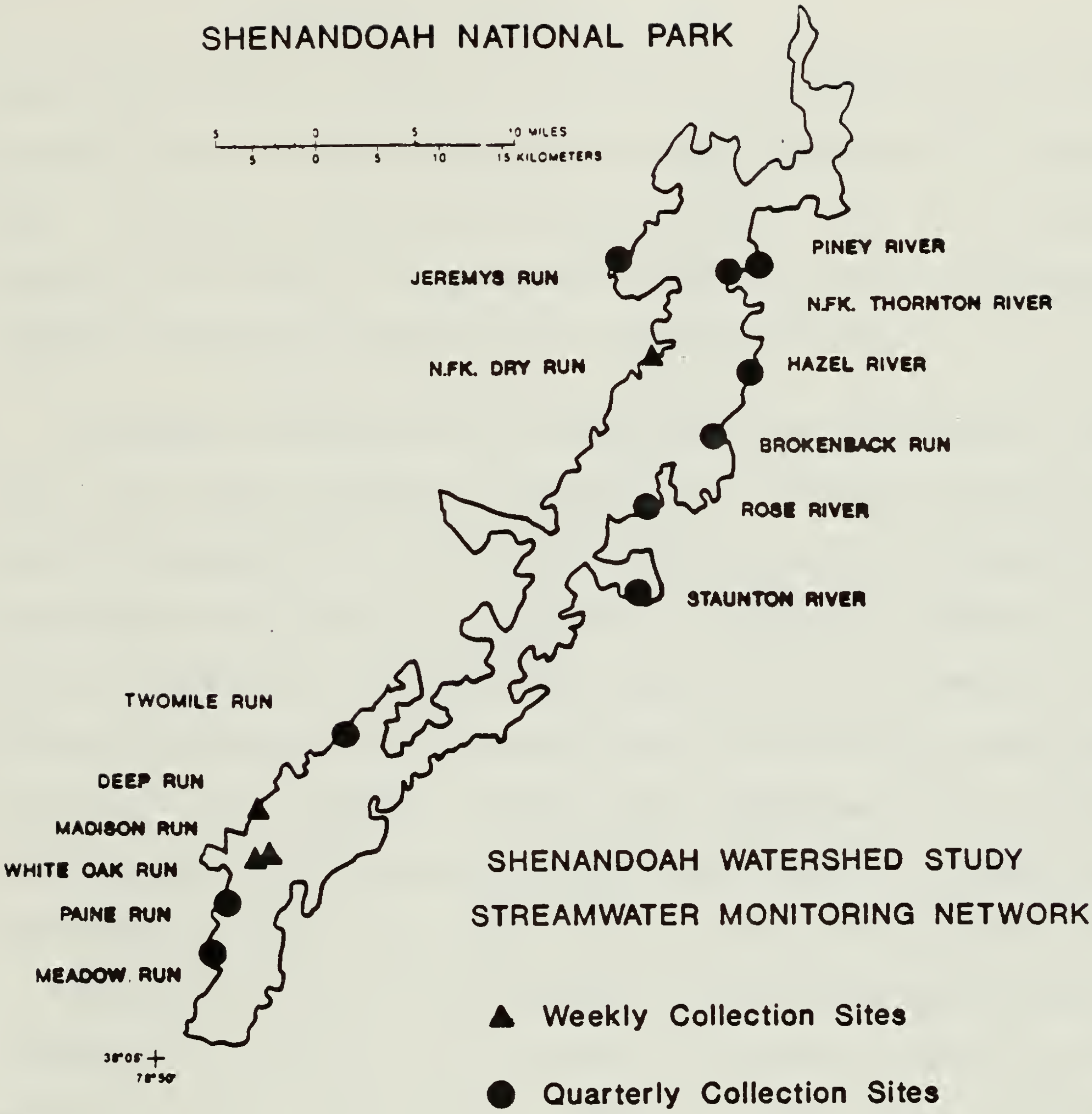

FIGURE 1

The calibrated watersheds, as indicated in Figure 1, are part of a parkwide trend monitoring system comprised of both weekly and quarterly sampling sites. The quarterly sites were selected to provide information for the range of watershed conditions and sensitivities present in SNP. These same sites have also been adopted into SNP's newly initiated Long-Term Ecological Monitoring System which will provide ongoing information concerning the status of stream biota. The SWAS

trend monitoring system 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 67 headwater streams located in Virginia's mountain region are sampled on a quarterly basis.

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. Recently the SWAS effort has expanded to include 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 intensive study of elemental transfer between the atmosphere and the watershed system.

PRINCIPLE 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. Differences in the composition and weathering properties of SNP's major bedrock

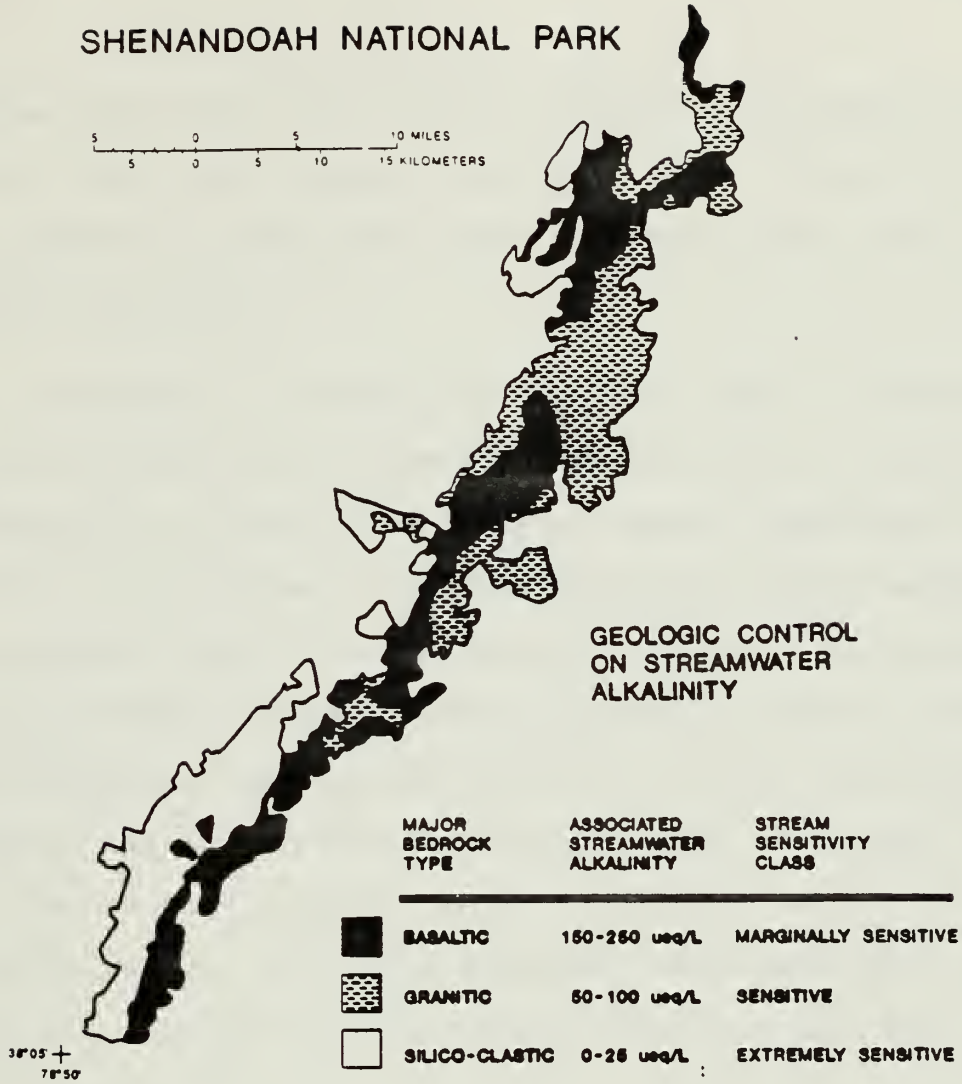

FIGURE 2

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 (Figure 2).

Surface waters with alkalinity concentrations of less than 200 ueq/L (10 mg/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 bedrock (quartzite, sandstone, phyllitic shale) are 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 Deep Run, one of several SNP streams which have been intensively monitored since 1980. Deep Run, which represents the most sensitive class of SNP streams, is located in an area dominated by silico-clastic bedrock. It has an alkalinity concentration of only about 5 ueq/L (flow-weighted annual mean). The current rate of acidification for Deep Run, as indicated by the increase in streamwater sulfate concentration, is 2-3 ueq/L/yr. About 20% of this sulfate increase is matched by a direct reduction in alkalinity (streamwater acidification). The other 80% of the sulfate increase is matched by a rise in the rate of base cation removal from watershed soils (soil acidification).

For Deep Run, the observed acidification trend represents

a state of ecological deterioration. The acidity level in Deep Run streamwater, which has pH values ranging from 5.1 to 5.5, is already well within the biologically critical range. Furthermore, when pH values are this low, additional pH reductions can be relatively large for small additional alkalinity losses.

It is also important to note that surface water acidification can be chronic or episodic. Chronic, or long-term acidification, as described for Deep Run, is indicated by a gradual increase in the mean concentration of sulfate and a decrease in the mean concentration of alkalinity. Episodic, or short-term acidification refers to periods of elevated sulfate and reduced alkalinity that occur during high flow as buffering processes in watershed soils are overwhelmed. Periods of episodic acidification are superimposed on chronic acidification trends and appear to be more likely in streams that have lower mean alkalinities. SNP streams such as Deep Run, which have minimal streamwater alkalinity and weak buffering capacity in watershed soils, are likely subject to both chronic and episodic acidification.

FORECAST MODELING

An important integrating factor for SWAS research and monitoring has been the development of MAGIC, a model that incorporates present understanding of the most important controls on watershed response to acid deposition. MAGIC can

be applied to explain current soil and streamwater chemistry, and to predict future changes under a range of future acid 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. White Oak Run is similar to Deep Run with respect to watershed bedrock and soil type. Based on streamwater alkalinity, however, White Oak Run is relatively less sensitive to acidification than Deep Run. White Oak Run alkalinity is currently about 20 ueq/L (flow-weighted annual mean). While no strong acidification trend has been observed for White Oak Run over the period of record, application of the MAGIC model suggests that this will change. As indicated in Figure 3, the model predicts that sulfate concentrations in White Oak Run will increase several-fold over a period of about 100 years if the present-day sulfate deposition level is maintained. Given the predicted rate of increase in streamwater sulfate concentration, the model further predicts that complete alkalinity loss will occur over a period of several decades.

PROGNOSIS FOR SHENANDOAH NATIONAL PARK STREAMS

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

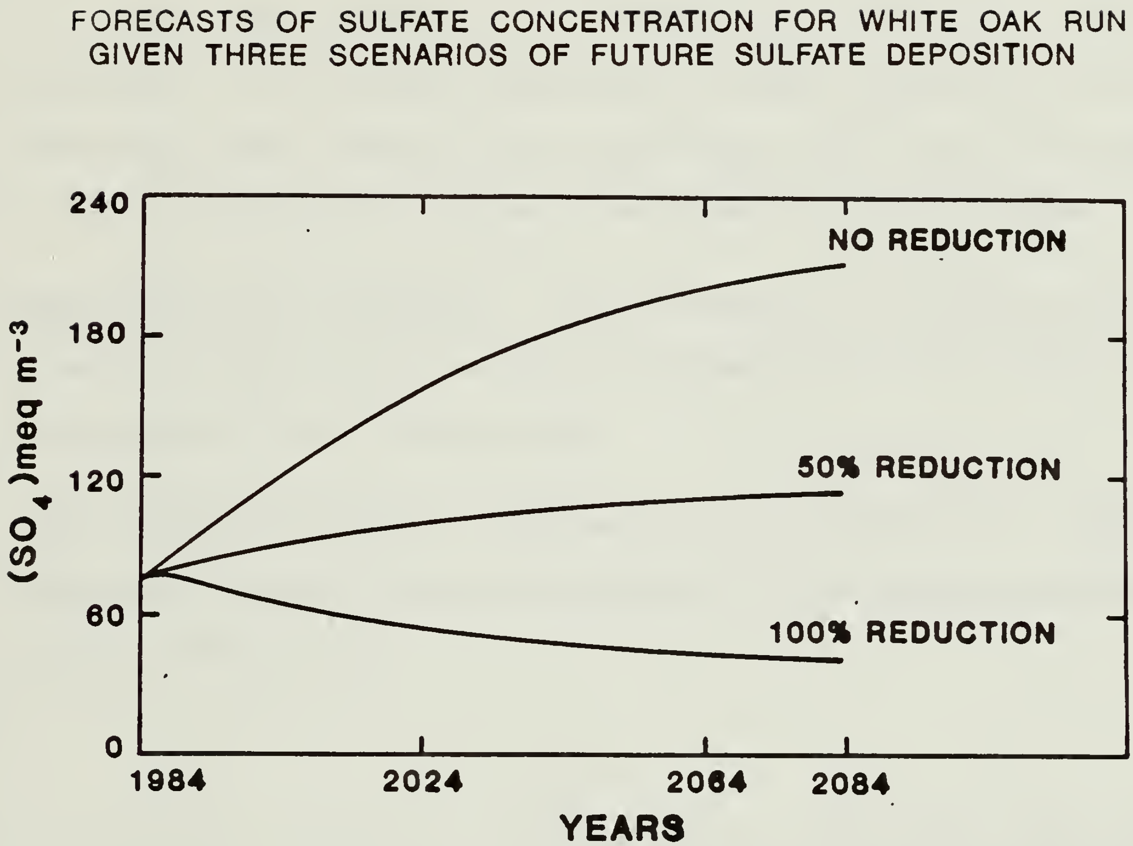

FIGURE 3

watershed soil declines. This sulfate increase will either be matched by direct alkalinity reduction or by an increase in streamwater base cation concentrations. For the SNP streams associated with base-poor soils and bedrock types, alkalinity reductions may have already occurred and further reductions are expected. As 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.

CONTINUING PROGRAM OBJECTIVES

Given the potential for significant ecological impact, assessment of watershed response to acid deposition is the continuing SWAS emphasis. The principle SWAS objectives apply to the monitoring and research components of the program.

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

SWAS Research Objective: Refinement of predictive modeling capability through improved evaluation of factors controlling stream acidification.

* * *

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

BIBLIOGRAPHY

THESES

1982 Burns, D. The aqueous aluminum chemistry of White Oak Run.

1983 Vreeland, J.L. The role of shallow groundwater in the hydrogeochemical response of White Oak Run, Shenandoah National Park, Virginia.

1984 Dise, N. Potential impact of acid precipitation on surface water quality of Shenandoah National Park, Virginia.

1984 Haelen, T. Hydrological and solution chemistry responses of a tributary valley in the White Oak Run catchment, Shenandoah National Park, Virginia.

1985 Feldman, R. The influence of alkalinity on stream invertebrates in the Shenandoah National Park: implications of acid deposition.

1986 Cozzarelli, I. A two-water model of aluminum mobilization in a natural soil system.

1986 Castelle, A. Carbon dioxide dynamics and base cation leaching from acid forest soils in the White Oak Run catchment, Shenandoah National Park, Virginia.

1987 Harrison, E. A simulation model of forest succession in Shaver Hollow.

1987 Tenbus, F. Hydrological characteristics of the alluvial infill at the White Oak Run catchment, Shenandoah National Park.

1988 Webb, R. Retention of atmospheric sulfate by catchments in Shenandoah National Park, Virginia.

In Prog Miller, D. Base cation release from an acid forest soil of the Shenandoah National Park.

In Prog Lessard, L. The variability of acidic gas particle composition and deposition rates in a Virginia deciduous forest.

In Prog Shaffer, P.W., Acid Precipitation: Sulfate dynamics and the role of sulfate on cation mobility in White Oak Run Watershed, Shenandoah National Park, Virginia.

ARTICLES

1982 Shaffer, P.W., and J.N. Galloway, Acid precipitation: the impact on two headwater streams in Shenandoah National Park, Virginia. International Symposium on Hydrometeorology, American Water Resources Association. pp 11.

1983 Galloway, J.N., S.A. Norton, and M.R. Church, Freshwater acidification from atmospheric deposition of sulfuric acid: A conceptual model. Environmental Science and Technology. 17: 541A-545A.

1985 Cosby, B. J., Hornberger, G. M., Galloway, J. N. and R. F. Wright. Modeling the effects of acid deposition: Assessment of a lumped-parameter model of soil water and streamwater chemistry. Wat. Resour. Res. 21: 51-63.

1985 Cosby, B. J., Wright, R. F., Hornberger, G. M. and J. N. Galloway. Modeling the effects of acid deposition: estimation of long-term water quality responses in a small forested catchment. Wat. Resour. Res., 21:1591-1601.

1985 Cosby, B. J., Hornberger, G. M., Galloway, J. N. and R. F. Wright. Freshwater acidification from atmospheric deposition of sulfuric acid: a quantitative model. Env. Sci. and Tech., 19:1145-1149.

1985 Hornberger, G. M., Beven, K. J., Cosby, B. J. and D. E. Sappington. Shenandoah Watershed Study: Calibration of a topography-based, variable contributing area model to a small forested catchment. Wat. Resour. Res.,21:1841-1850.

1985 Hornberger, G. M. and B. J. Cosby. Selection of parameter values in environmental models using sparse data: a case study. Applied Math. and Comp.,17:335-355.

1986 Cosby, B.J. Modelling the reversibility of acidification with mathematical models. In: Proceedings of the Workshop on Reversibility of Acidification. Grimstad, Norway, June, 1986. Commission of the European Communities, Directorate-General for Science, Research and Development, Brussels, Belgium. pp. 137-148.

1986 Cosby, B. J., Hornberger, G. M., Wright, R. F., and J. N. Galloway. Modeling the effects of acid deposition: control of long-term sulfate dynamics by soil sulfate adsorption. Water Resour. Res.,22: 1283-1291.

1986 Cosby, B. J., Hornberger, G. M., Wright, R. F., Rastetter, E. B. and J. N. Galloway. Estimating catchment water quality response to acid deposition using mathematical models of soil ion exchange processes. Geoderma, 38:77-95.

1986 Hornberger, G. M., Cosby, B. J. and J. N. Galloway. Modeling the effects of acid deposition: uncertainty and spatial variability in estimation of long-term responses of regions to atmospheric deposition of sulfate. Water Resour. Res.,22:1293-1302.

1987 Burns, D., Speciation and equilibrium modelling of soluble aluminum in a headwater stream at baseflow and during rain events. Submitted to Water Resour. Res.

1987 Cozzarelli, I.M., Herman, J.S., and R.A.Parnell 1987. The mobilization of aluminum in a natural soil system: effects of hydrologic pathways. Water Resour. Res. 23:859-874.

1987 Reuss, J.O., B.J. Cosby and R.F. Wright. Chemical processes governing soil and water acidification. (Review Article) Nature 329: 27-32.

1987 Sigmon, J.T. and M.J. Estes. Comparisons of Chemical Compositions of Mountain Stratiform Clouds and Valley Fog in the Shenandoah National Park. Sixth Symposium on Meteorological Observations and Instrumentation, pp 59-60. American Meteorological Society.

1988 Ryan,P.F., Hornberger,G.M., Cosby,B.J., Galloway,J.N., Webb,J.R. and E.B.Rastetter. Seasonal and interannual variation in the chemical composition of streamwater in two catchments impacted by acidic deposition. Submitted to Water Resour. Res.

1988 Sigmon, J.T., D.O. Krovetz, M.A. Reiter, and F.S. Gilliam Assembly and Field Testing of a Ground-Based Presence of Cloud Detector. Journal of Atmospheric and Oceanic Technology. 5: 579-581.

1988 Sigmon, J.T., D.O. Krovetz and M.A. Reiter An Inexpensive Thermocouple Probe-Amplifier and its Response to Rapid Temperature Fluctuations in a Mountain Forest. Journal of Atmospheric and Oceanic Technology. In Press.

1988 Sigmon, F.S. Gilliam, M.A. Reiter, and D.O. Krovetz. Elevational and Spatial Variation in Daytime Ozone Concentrations in the Virginia Blue Ridge Mountains: Implications for Forest Exposure. Canadian Journal of Forest Research. In Press

1988 Sigmon, J.T., D.O. Drovetz, M.A. Reiter, and L.H. Lessard. An Automated System for Air Sampling with Annular Denuders at a Remote Site. Environmental Pollution. In Press.

1988 Sigmon, J.T., F.S. Gilliam, and M.E. Partin. Precipitation and Throughfall Chemistry for a Montane Hardwood Forest Ecosystem: Potential Contributions from Cloud Water. Submitted to Canadian Journal of Forest Research.

1988 Sigmon, J.T., D.O Krovetz and M.A. Reiter. A Model for Estimating Cloud Water Deposition to a Hardwood Forest. Submitted to Atmospheric Environment.

1988 Sigmon, J.T. and C.E. Murphy Dry Deposition of Sulfur and Nitrogen Oxide Gases to Forest Vegetation. Submitted to Advances in Environmental Sciences.

1988 Webb,J.R., Cosby,B.J., Galloway,J.N. and G.M.Hornberger Acidification of native brook trout streams in Virginia. Submitted to Water Resour. Res.

PAPERS PRESENTED AT MAJOR CONFERENCES

1980 Beven, K., Shaffer, P., Lees, S., Hornberger, G. M., Galloway, J. and K. Nordstrom. Components of stormflow from catchments in Shenandoah National Park. AGU Chapman Conference, October 1980.

1982 Beven, K. J. and G. M. Hornberger. Calibration of a Hydrograph Simulation Model for a Catchment in Shenandoah National Park. AGU Fall Meeting, San Francisco, December.

1984 Cosby, B.J., J.N. Galloway, G.M. Hornberger, P. Shaffer, R.F. Wright. The effect of acid deposition on the streams of Shenandoah National Park: past, present and future. 8th Shenandoah National Park Symposium. National Park Service (Invited paper).

1984 Cosby, B. J., G. M. Hornberger, R. F. Wright and J. N. Galloway. A simple Model of Dissolved Sulfate Dynamics in Soils. AGU Spring Mtg., Cincinnati.

1984 Cosby, B.J., R.F. Wright, G.M. Hornberger and J.N. Galloway. Assessment of an equilibrium model of soil and streamwater chemistry. Workshop on Predicting Soils and Water Acidification. Knoxville, Tennessee. Oak Ridge National Laboratory (Invited paper).

1985 Cosby, B. J., Hornberger, G. M., Wright, R. F., Rastetter, E. B. and J. N. Galloway. Estimating catchment water quality response to acid deposition using mathematical models of soil ion exchange processes. Workshop on Mechanisms of Ion Transport in Soils, Weiss Fed. Inst. of Tech.

1985 Cosby, B. J., Wright, R. F., Hornberger, G. M. and J. N. Galloway. Acidic deposition and weathering: a modeling approach. Internat. Conf. on Acid Precip., Muskoka, Canada.

1985 Cosby, B. J., Hornberger, G. M., Rastetter, E. B. and J. N. Galloway. Forecasting long-term changes in water chemistry in two streams in Shenandoah National Park. AGU Fall Meeting, San Francisco.

1985 Cosby, B.J., G.M. Hornberger, R.F. Wright, E.B. Rastetter and J.N. Galloway. Estimating catchment water quality response to acid deposition using mathematical models of soil ion exchange processes. Workshop on Mechanisms of Ion Transport in Soils. Swiss Federal Institute of Technology. May, 1985, Zurich, Switzerland.

1985 Hornberger, G. M. and B. J. Cosby. Evaluation of a model describing the long-term dynamic response of catchments to deposition of atmospheric sulfate. Proc. 7th IFAC Symposium on Identification and System Parameter Estimation, Pergamon Press, pp 229-234.

1985 Hornberger, G. M., Galloway, J. N., Rastetter, E. B. and B.J. Cosby. Long-term streamwater chemistry responses of catchments in Shenandoah National Park to acidic deposition. AGU Fall Meeting, San Francisco.

1985 Rastetter, E. B., Hornberger, G. M. and B. J. Cosby. Examination of short-term dynamic responses of catchments to acid deposition using linear transfer function models. AGU Fall Meeting, San Francisco.

1986 Cosby, B.J. and R.F. Wright. Modelling the reversibility of acidification with mathematical models. Commission of the European Communities, Workshop on Reversibility of Acidification, Grimstad, Norway. (Invited paper).

1986 Galloway, J.N., G.M. Hornberger and B.J. Cosby. The influence of acid deposition on streamwater composition for two forested catchments in Shenandoah National Park, Virginia. 1986 Spring Meeting, American Geophysical Union. (Invited paper).

1986 Hornberger, G.M., B.J. Cosby and J.N. Galloway. Modelling the regional influence of acid deposition on streams in Shenandoah National Park. 1986 Spring Meeting, American Geophysical Union. (Invited paper).

1986 Hornberger, G. M., Cosby, B. J. and E. B. Rastetter Regionalization of predictions of effects of atmospheric acidic deposition on surface waters. Proc. Internat. Conf. on Water Quality Modelling in the Inland Natural Environ., Bournemouth, England, pp 535-550.

1986 Hornberger, G.M., Cosby, B.J. and R.F. Wright 1986. Regional application of a conceptual surface water acidification model. AGU Fall Meeting, San Francisco, December 1986. (Invited paper).

1986 Ryan, P.F., B.J. Cosby, G.M. Hornberger, R.F. Wright and P.G. Whitehead. Long-term pH changes inferred using a hydrochemical model of catchment soils. 50th Annual Meeting, American Society of Limnology and Oceanography.

1986 Ryan, P.F., Hornberger, G.M. and B.J. Cosby 1986. Differences between sulfate concentration/discharge relationships in "replicate" catchments in an acid deposition study. AGU Fall Meeting, San Francisco.

1986 Wolock, D.M., Hornberger, G.M., Cosby, B.J. and T.A. King. The influence of catchment hydrological characteristics on the likelihood of episodic stream pH depression. AGU Fall Meeting, San Francisco, December 1986.

1987 Cosby, B.J. and G.M. Hornberger. Analysis of surface water acidification in Shenandoah National Park, VA, using a regionalized conceptual model (MAGIC). Symposium session of the International Society for Ecological Modelling, 38th AIBS Annual Meeting, 9 - 13 August, 1987, Ohio State University, Columbus, Ohio. (Invited Paper).

1987 Galloway, J.N., Hornberger, G.M., Ryan, P.F., Cosby, B.J. and J.R. Webb. The cycling of S,N, and Cl through two forest catchments in Shenandoah National Park, VA. AGU Spring Meeting. Baltimore. (Invited paper).

1987 Miller, D. and J.N. Galloway. Base cation leaching from an acid forest soil, Shenandoah National Park, Virginia. AGU Spring Meeting, Baltimore.

1987 Ryan, P.F., J.N. Galloway, B.J. Cosby and C. Gold. Elevational differences in bulk precipitation chemistry in Shenandoah National Park, VA. 1987 Spring Meeting, American Geophysical Union.

1987 Sigmon, J.T. and L.H. Lessard. Measurements of Concentrations of Some Reactive Atmospheric Gases and Fine Primary Particulates with Annular Denuder Atmospheric Samplers. Sixth Symposium on Meteorological Observations and Instrumentation, pp 60-62. American Meteorological Society.

1987 Sigmon, J.T. and F.S. Gilliam. Relationships Between Throughfall Chemistry and the Chemical Fluxes in Dry Deposition and Mountain Clouds. Sixth Symposium on Meteorological Observations and Instrumentation, pp 63-65. American Meteorological Society

1987 Sigmon, J.T., K.R. Knoerr, D. Krovetz and T. Schneider. An Inexpensive Fine Wire Thermocouple Probe and Amplifier for Rapid Temperature Fluctuation Measurements. Sixth Symposium on Meteorological Observations and Instrumentation, pp 229-230. American Meteorological Society.

1987 Tenbus, F.J. and G.M.Hornberger. The role of heterogeneous hydraulic conductivity in calculation of subsurface discharge from an upland catchment. AGU Spring Meeting. Baltimore.

1987 Webb, J.R., Galloway, J.N., Cosby, B.J. and G.M. Hornberger 1987. Spatial variability of alkalinity and sulfate in the streams of Shenandoah National Park, VA. AGU Spring Meeting, Baltimore.

1988 Mathews, N. and G.M. Hornberger. Hydrological interactions between stream and stream bed in an upland catchment. AGU Fall Meeting, San Francisco.

1988 Sigmon, J.T. and M.J. Estes. Relationship Between Cloud Chemistry and Meteorology in Central Virginia: A Preliminary Study. Preprints of the 81st Annual Meeting of the Air Pollution Control Association.

1988 Webb, J.R., Potential for Streamwater Acidification in the Virginia Mountains: Coordination of the Shenandoah Watershed Study and the Virginia Trout Stream Sensitivity Study. Tenth Shenandoah Research Symposium. Shenandoah National Park.