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FACTORS AFFECTING STREAMWATER CHEMISTRY IN THE GREAT SMOKY MOUNTAINS, USA

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Abstract. The Great Smoky Mountains in the southeastern U.S. receive high total atmospheric deposition of sulphur and nitrogen (N) and contain large areas of shallow, poorly buffered soils. Results from extensive surveys conducted in October 1993 and March 1994 showed that stream pH values were near or below 5.5 and Acid Neutralizing Capacity (ANC) was below $50 \mu\text{eqL}^{-1}$ at high elevations. Mechanisms of acidification varies among stream systems in the study. We classified each study catchment into one of five water quality districts based upon within-basin elevational gradients of streamwater quality. Geologic factors, cf. the presence of calcareous or pyritic bedrock types exhibited a major influence on water quality and within-basin elevational gradients. Atmospheric deposition is an important factor affecting water quality at high elevations in all districts. Nitrate was the dominant strong acid anion in streamwater in many catchments, particularly at high elevation and especially in basins draining old growth forests. Most high elevation catchments appear to be N saturated. Continued high atmospheric loadings of N will likely spread N saturation of catchments downslope into areas where second growth forests are now maturing. Stream sulphate concentrations were lower than expected at higher elevations and may be related to the N saturation status of these systems.

Key Words: Great Smoky Mountains, Water Chemistry, Stream, Atmospheric Deposition, Nitrogen Saturation

1. Introduction

Airborne oxides of nitrogen (N) and sulphur (S) have become increasingly important sources of acidity in terrestrial and freshwater ecosystems since the industrial revolution. Results from the Integrated Forest Study of the late 1980s showed that high elevation areas of the Great Smoky Mountains National Park (GRSM) in the southeastern United States receive about $2,200 \text{ Eqha}^{-1}\text{yr}^{-1}$ of total S deposition and about $1,900 \text{ Eqha}^{-1}\text{yr}^{-1}$ of total N deposition (Lindberg and Lovett, 1992; Johnson and Lindberg, 1992), some of the highest rates of atmospheric loading in North America. A large portion of this loading is from dry and cloud deposition, efficiently collected by spruce-fir forests occurring along the ridge tops (Lindberg and Owens, 1993).

Assessing the effects of atmospheric deposition in GRSM is complicated since variation in total deposition fluxes within the complex topographic area is not fully quantified. The situation is further complicated by the myriad of factors and gradients that modify depositional inputs in GRSM, including: forest stand type and age; pedologic, topographic, and geologic factors; and disturbance histories. Each of these factors also varies between catchments. Therefore, assessing the environmental impacts to water quality in GRSM requires a focus not only on regional factors and gradients but also on catchment to catchment differences in factors that can impact water quality within the Park. The objective of this paper is to provide a preliminary assessment of the importance of major factors, including atmospheric deposition, on streamwater chemistries in the Great Smoky Mountains National Park.

2. Materials and Methods

2.1. STUDY AREA

The Great Smoky Mountains National Park occupies ~220,000 ha in southeastern North America and lies within a unit of uplifted (maximum elevation 2024 m) and metamorphosed sedimentary rock (King *et al*, 1968). Most of the bedrock is resistant to chemical and mechanical weathering with two exceptions. First, one bedrock type (Anakeesta Formation) contains pyrite which weathers to yield substantial quantities of sulphuric acid when exposed to air and water by landslides and other disturbances. Second, several “windows” of limestone and dolomite bedrock exist in the western portion of GRSM. Weathering processes in these areas result in greatly increased base cation concentrations, conductivity, and ANC in the associated stream systems.

Most of the soils in GRSM are thin, rocky, and deeply weathered with weak potential for base cation mobilization (Elwood, 1991). Although a detailed soil map is not available, the soils on high ridges have been generally classified as Inceptisols (*e.g.* Harrison *et al* 1989) while soils at lower elevations grade to weathered Ultisols (Eilers and Selle, 1991). GRSM ecosystems support diverse and complex plant communities. Plant biodiversity includes over 100 tree species. Logging and settlement disturbance prior to establishment of the National Park in 1934 has altered stand age and structure in many areas (Pyle, 1988). Nevertheless, GRSM contains some of the largest tracts of old growth forest extant in the eastern United States. These undisturbed forests drain into several of the 28 major stream systems of the Park.

2.2. STREAM MONITORING PROGRAM

We have implemented a comprehensive water quality monitoring program for GRSM that utilizes a nested design to provide a range of monitoring scales from intensive (15 minute hydrologic) data on a small watershed (Nodvin *et al*, this volume) to biannual sampling over the entire GRSM. In this paper we report results from the first two biannual sampling events conducted in October 1993 and in March 1994. October and March were selected because they are the normal months of least and greatest stream discharge, respectively (McMaster and Hubbard, 1970). The sampling design allowed for an analysis of elevational gradients in main channel chemistries for each stream system. Chemistries of select tributaries were also evaluated to provide a distribution of samples from each stream order over the entire range of elevations.

Streamwater grab samples were taken at each site using 250 mL polyethylene bottles. Samples were analyzed for pH (Radiometer autotitrator) and conductance (Jenway meter) within 24 hours of collection. Within one week of collection, samples were analyzed for ANC, anions and cations (Dionex DX100 Ion Chromatograph), and silica and aluminum (Skalar autoanalyzer utilizing colorimetric techniques). Quality assurance followed US Environmental Protection Agency guidelines (Raulsen *et al*, 1988).

3. Results and Discussion

October water levels were relatively low while March levels were considerably above normal (USGS, 1995). Relative to March, October nitrate and sulphate levels were low while base cations were somewhat elevated. ANC values ranged from $-25 \mu\text{eq L}^{-1}$ to

about 150 μeqL^{-1} in October in streams without limestone influence and decreased by about 25 μeqL^{-1} at each site in March.

3.1. WATER QUALITY DISTRICTS

Classification of stream systems into categories was accomplished by examining maximum and minimum values for six chemical criteria (Table I) and by cross referencing the classification system with Geographic Information System (GIS) coverages of catchment surficial geology, vegetation type, and disturbance history. Our classification system is comprised of five major water quality districts, each containing stream systems with similar modes of biogeochemical regulation of stream water chemistries (Figure 1). Most stream systems with ANC values above 100 μeqL^{-1} are probably influenced by limestone weathering and are located in the West District. Streams systems with minimum pH values below 5.0, minimum ANC below 0, and maximum sulphate concentrations greater than $\sim 65\mu\text{eqL}^{-1}$ are likely influenced by Anakeesta weathering and are located in the Anakeesta District (Ana).

TABLE I
Criteria used to classify stream systems into water quality districts. ()Concentrations are μeqL^{-1} .

Stream System [†]	#	Dis- trict	N	Min pH	Min ANC	Max ANC	Max SO_4^{2-}	Max NO_3^-	LEMax NO_3^-
Abrams Creek	10	West	17	5.72	18.43	749.1	64.71	30.00	4.63
Parsons Branch	14	West	5	6.40	43.81	138.2	45.90	4.01	0.00
M. Pr. Little Pigeon	3	Ana	22	4.45	-28.39	65.06	66.76	69.35	29.96
LeConte/Roaring F.	4	Ana	15	4.86	-11.24	75.30	79.74	43.92	19.13
W. Pr. Little Pigeon	5	Ana	21	4.64	-20.65	82.55	121.3	61.42	32.20
Cosby Creek	1	EU	5	5.51	-0.98	30.82	57.96	36.81	31.65
Indian Camp Creek	2	EU	6	5.55	0.04	49.66	67.78	80.70	17.72
Raven/Straight F.	24- 25	EU	11	4.58	-25.05	62.19	23.55	86.04	17.97
Little River	6	WC	5	4.88	-0.72	53.54	51.13	100.6	4.14
Mid. Pr. Little River	7	WC	9	6.22	19.99	39.08	32.76	17.29	10.19
Twentymile Creek	15	WC	5	6.44	40.23	60.07	30.36	8.02	0.00
Eagle Creek	16	WC	15	5.54	0.69	83.44	29.12	21.67	2.72
Hazel Creek	17	WC	8	5.25	9.83	84.12	51.98	87.89	4.27
Forney Creek	19	WC	8	6.11	13.62	77.36	35.44	29.07	3.74
Noland Creek	20	WC	7	5.48	-0.02	72.92	47.72	47.75	3.66
Deep Creek	21	WC	10	6.41	45.81	64.98	16.42	45.56	8.02
Oconaluftee River	22	East	27	5.68	1.63	61.46	51.54	31.22	3.96
Cataloochee Creek	27	East	25	4.71	-20.30	83.77	53.84	73.05	7.99
Big Creek	28	East	16	6.20	23.20	49.07	45.41	28.79	2.30

[†]LE MAX = Lower Elevation Maximum; Stream Drainage labels (#) follow Figure 1. District abbreviations are defined in the text. Data from isolated sites are not shown

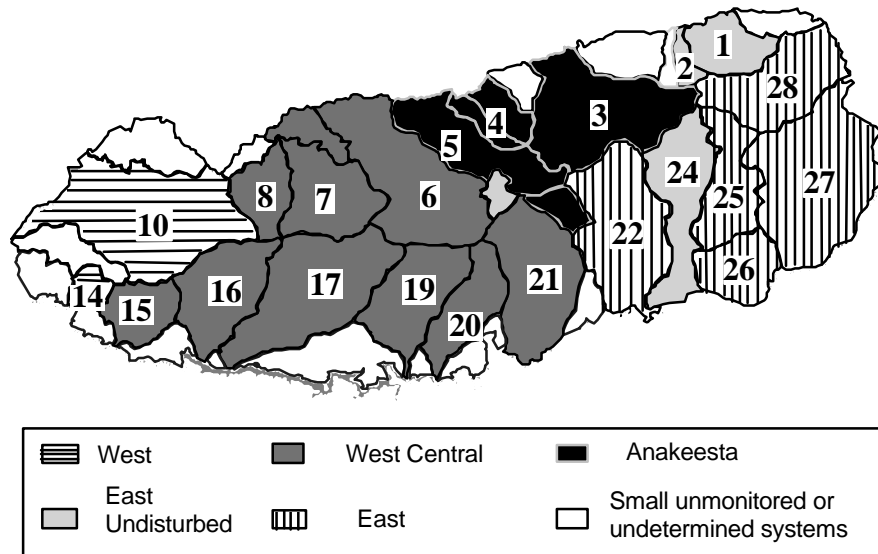


Figure 1. Categorized water quality districts of the Great Smoky Mountain Drainages indexed in Table I).

In all systems above 1500m, where old growth spruce-fir forests predominate, nitrate concentrations were greater than $50\mu\text{eqL}^{-1}$. However, stream systems draining low-elevation old growth forests also exhibited relatively high nitrate levels. The Anakeesta-influenced systems were predominantly old growth and also showed this pattern. High nitrate stream systems draining old growth forests but not influenced by Anakeesta were categorized as being within the East Undisturbed District (EU). Stream systems draining predominantly second growth and exhibiting lower nitrate levels at low elevations were located in either the East District or the West Central (WC) District.

3.2. ELEVATIONAL GRADIENTS

Within each water quality district, means of measured parameters within successive 150m elevational bands were evaluated against the entire elevational gradient (Figure 2). An overall pattern of decreasing pH (Figure 2A) and ANC (Figure 2B) with increasing elevation was apparent in all Districts. Streams in the Anakeesta District had the lowest pH and ANC values and those in the West District had the highest. Given the high sulphate loadings in GRSM, sulphate levels were remarkably low in all high-elevation streams except for those within the Anakeesta District (Figure 2C). Net catchment retention of sulphate is known to be high in some high elevation basins at GRSM (Nodvin *et al*, this volume). Soil sulphate adsorption is likely maintaining the lower than expected sulphate concentrations in the high-elevation streams (Elwood, 1991). The N saturation status of the high-elevation catchments may be facilitating sulphate retention in these systems (Nodvin *et al*, 1988).

3.3. IMPLICATIONS FOR NITROGEN SATURATION

Stream nitrate levels were highest at high elevation and low stream order (Figure 2D). The high levels of nitrate observed in both October and March suggest that many systems are reaching an advanced stage of N saturation (Stoddard, 1994).

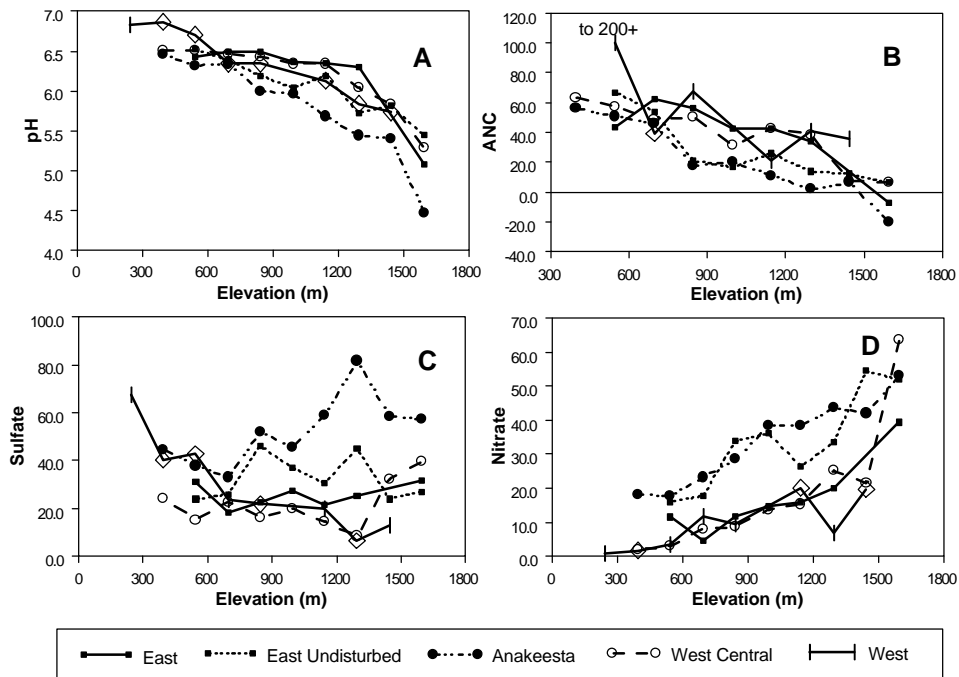


Figure 2. Mean changes in water quality with elevation for March 1994. Concentrations are $\mu\text{mol L}^{-1}$.

Intensive sampling in a high-elevation watershed in GRSM supports this conclusion (Nodvin *et al.*, this volume). Declining nitrate levels downstream may reflect: 1) elevational gradients in N deposition, 2) terrestrial alterations including plant uptake, or 3) in-stream processes. The downstream decrease in nitrate levels much more precipitous in districts where high-elevation old-growth forests grade to low-elevation second growth forests (WC and East) than in districts where old-growth forests are present at both high and lower elevations (Ana and EU).

The observation of higher stream concentrations and exports of nitrate from older terrestrial systems supports the hypothesis that ecosystem maturation leads to decreased N retention (Vitousek and Reiners, 1975). As forests mature, the atmospheric input of N tends to exceed the biological demand, a condition defined as N saturation (Abert *et al.* 1989). Therefore, as lower-elevation, second growth forests mature in GRSM, it is likely that N saturation will spread downslope within the Park. Continuing loading of atmospheric N is likely to exacerbate the downslope expansion of N saturated catchment areas. Since most GRSM soils are naturally acidic, enhanced export of nitrate (a mobile acid anion) from N saturated soils in GRSM would likely facilitate the acidification of adjacent stream systems (Reuss and Johnson, 1986). The effect could be somewhat self-limiting since soil acidification by N mineralization can enhance sulphate adsorption and thus reducing the mobility of this second strong acid anion and its leaching to streams (Nodvin *et al.* 1986).

4. Conclusions

Although rates of atmospheric deposition for both S and N are very high in GRSM, it is N loading that appears to have the most effect on stream water chemistry since catchment S retention is high. N saturation has reached advanced stages at high elevations and may progress more rapidly in catchments with old growth forests. Since high N loadings are likely to continue, N saturation may extend further downslope in old growth areas and into second growth catchments as they mature. The interaction between N and S and sulphate adsorption complicates quantitative forecasting of stream acidification in GRSM but expanding streamwater acidification seems assured.

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