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ACIDIC DEPOSITION, ECOSYSTEM PROCESSES, AND NITROGEN SATURATION IN A HIGH ELEVATION SOUTHERN APPALACHIAN WATERSHED

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Abstract. High-elevation red spruce-Fraser fir forests in the Southern Appalachian mountains: 1) receive among the highest rates of atmospheric deposition measured in North America, 2) contain old-growth forests, 3) have shown declines in forest health, 4) have sustained high insect-caused fir mortality, and 5) contain poorly buffered soils and stream systems. High rates of nitrogen and sulphur deposition (~1900 and ~2200 $Eq \cdot ha^{-1} \cdot yr^{-1}$, respectively) are dominated by dry and cloud deposition processes. Large leaching fluxes of nitrate-nitrogen (100-1400 $Eq \cdot ha^{-1} \cdot yr^{-1}$) occur within the soil profile. We have expanded the study to the watershed scale with monitoring of: precipitation, throughfall, stream hydrology, and stream chemistry. Two streamlets drain the 17.4 ha Noland Divide Watershed (1676-1920m) located in the Great Smoky Mountains National Park. A network of 50 20x20 m plots is being used to assess stand structure, biomass, and soil nutrient pools. Nitrate is the predominant anion in the streamlets (weighted concentrations: 47 and 54 $\mu eq \cdot L^{-1}$ NO_3^- ; 31 and 43 $\mu eq \cdot L^{-1}$ SO_4^{2-}). Watershed nitrate export is extremely high (~1000 $Eq \cdot ha^{-1}$ yr^{-1}), facilitating significant base cation exports. Stream acid neutralizing capacity values are extremely low (–10 to 20 $\mu eq \cdot L^{-1}$) and episodic acidifications (pH declines of a full unit in days or weeks time) occur. Annual streamwater sulfate export is on the order of 770 $Eq \cdot ha^{-1} \cdot yr^{-1}$ or about one-third of total annual inputs, indicating there is net watershed sulfate retention. The system is highly nitrogen saturated (Stage 2, Stoddard, 1994) and this condition promotes both chronic and episodic stream acidification.

Key Words: atmospheric deposition, nitrogen saturation, budgets, calcium export, sulphate adsorption

1. Introduction

The Southern Appalachian spruce-fir (SASF) ecosystem, located in the eastern United States, is primarily old-growth and 60% has never been cut or burned (Lyle and Schafale, 1988; Dull *et al.*, 1988). However, even the remaining old-growth areas are undergoing severe Fraser fir (*Abies fraseri* (Pursh) Poir.) mortality due to an infestation by the balsam woolly adelgid (*Adelges piceae* Ratz.). The exotic insect was first detected in the southern Appalachians in the late 1950's (Speers, 1958). Dendroecological and plot-based data, respectively, have shown red spruce (*Picea rubens* Sarg.) radial growth decline (LeBlanc *et al.*, 1992) and canopy crown deterioration during the mid- to late 1980's (Peart *et al.*, 1992).

In the 1980's, the Integrated Forest Study (IFS) and related studies demonstrated that high-elevation SASF ecosystems receive among the highest loadings of sulphur (S) and nitrogen (N) measured in North America (Johnson and Lindberg, 1992; total N loadings: ~1900 $Eq \cdot ha^{-1} \cdot yr^{-1}$; total S loadings: ~2200 $Eq \cdot ha^{-1} \cdot yr^{-1}$). Total atmospheric loadings are dominated (~75%) by dry and cloud deposition processes. The IFS also found large soil leaching fluxes of nitrate-N (1100-1400 $Eq \cdot ha^{-1} \cdot yr^{-1}$).

We have expanded the stand-based IFS work in the SASF zone to the catchment scale through continued monitoring of: precipitation and throughfall (Shubzda *et al.*, this volume) and additional monitoring of stream hydrology, stream chemistry, and biomass and nutrient distributions. We have monitored water chemistry and hydrology of the two streamlets draining the 17.4 ha Noland Divide Watershed (NDW) since July 1991. In addition, we established a network of 50 20x20 m plots within the watershed to assess stand structure, biomass, and soil nutrient pools (Pauley *et al.*, submitted). We report here findings for the first three water-years stream-water chemistry trends and N, S, and calcium (Ca) budgets for the NDW.

2. Materials and Methods

2.1. STUDY AREA

NDW (35°34'N, 83°28'W) is located between 1676 and 1920m within the Great Smoky Mountains National Park, on the North Carolina and Tennessee border. Overstory vegetation of is dominated by red spruce and interspersed patches of standing dead Fraser fir. Yellow birch (*Betula alleghaniensis* Britt.) serves as a co-dominant in the lower elevations of the watershed. Within the last decade, much of the mature Fraser fir in NDW suffered mortality due to the balsam woolly adelgid infestation (Pauley *et al.*, submitted). The understory consists of regenerating spruce and fir saplings mixed with blackberry (*Rubus canadensis* L.), hobblebush (*Viburnum alnifolium* Marsh.), mountain-ash (*Sorbus americana* Marsh.), and various mosses and ferns.

The watershed is underlain by the Thunderhead Sandstone of the Great Smoky Group (Upper Proterozoic), composed principally of quartz and potassic feldspar (King *et al.*, 1968). The soils are primarily shallow Inceptisols formed from the bedrock or colluvium, in the upper and lower parts of the watershed (Johnson *et al.*, 1991).

2.2. WATERSHED MONITORING

Five monitoring stations are maintained at NDW: two atmospheric deposition stations at 1740 and 1920m (established 1986 and 1993, respectively), a soil solution collection system at 1740m (soil depths of 10, 20 and 50cm), and two stream monitoring sites (monitoring discharge continuously with H-flumes mounted to the bedrock and weekly chemistry by manual collection) at each streamlet draining NDW. Each deposition monitoring station contains two subsites: 1) an "open site", for wet-only deposition, and 2) a throughfall site (Shubzda *et al.*, this volume).

All water samples are analyzed for pH, conductance, major cations and anions (ion chromatography), acid neutralizing capacity (ANC - Gran titration), silica and aluminum (colorimetric) at the Environmental Sciences Laboratory at The University of Tennessee. Methodology for collecting wet deposition, throughfall, and soil solution chemistry follow protocols developed for the IFS (Lindberg *et al.*, 1989) and for collecting stream water samples, measuring hydrology, performing water chemistry analyses, and for maintaining Quality Assurance/Quality Control procedures are detailed elsewhere (Nodvin *et al.*, submitted). Nutrient and water budgets for NDW are based upon water years from 1 August through 31 July.

2.3. WATERSHED AREA and TOPOGRAPHY

A high-resolution survey of the watershed topography was completed to 1) determine watershed area, 2) determine area-elevation relationships (hypsography), and 3) establish an accurate reference coordinate system for the watershed. In November 1992, six highly accurate Global Positioning System (GPS) survey units were stationed within or near the NDW for an eight hour period. High resolution aerial stereo photographs were taken less than a week after the GPS data were collected and were georectified using flagged locations of the ground survey points. Using the stereo photographs, UTM and elevational coordinates were determined manually at visible ground at approximately 30 m distances throughout and surrounding the watershed.

3. Results and Discussion

3.1. STREAM TRENDS

Nitrate was the predominant anion in NDW streamwaters during most of the study period (Figure 1). Concentrations ranged between 40-80 $\mu eq \cdot L^{-1}$ and showed some seasonal variation with maximum values tending to occur in the winter. Sulphate concentrations were surprisingly low (~20-60 $\mu eq \cdot L^{-1}$) given the large loadings of S (>2000 $Eq \cdot ha^{-1} \cdot yr^{-1}$) to NDW. Chloride values were ~10 to 20 $\mu eq \cdot L^{-1}$. Calcium was the predominant cation (~40-80 $\mu eq \cdot L^{-1}$), with magnesium and sodium in the 20-30 $\mu eq \cdot L^{-1}$ range, potassium ~10 $\mu eq \cdot L^{-1}$, and only trace amounts of ammonium. Streamwater Ca concentrations and annual exports increased over the study period. Streamwater chemistries at NDW are consistent in what we have found in other streams in the Great Smoky Mountains spruce-fir zone (Flum and Nodvin, this volume).

NDW streams were very poorly buffered (pH < 6 and ANC < 40 $\mu eq \cdot L^{-1}$) and showed seasonal variation with pH and ANC values tending to be highest in summer (Figure 1). The streams were susceptible to episodic acidification. For example, in late November and early December 1991, two 18-20 cm storms, resulted pH declines up to one unit and the near or complete consumption of ANC in the streamlets.

3.2. NUTRIENT BUDGETS

Sulphate flux in throughfall can be utilized as a good estimator of total S deposition (Lindberg and Lovett, 1992) while N flux in throughfall is a poor indicator of total N deposition due to uptake of N in the forest canopy (Lovett and Lindberg, 1993; Shubzda *et al.*, this volume), and Ca flux in throughfall is a poor indicator of total Ca deposition due to net leaching from the vegetation (Johnson and Lindberg, 1992).

S throughfall fluxes at 1740m were consistent with IFS total deposition estimates of ~2200 $Eq \cdot ha^{-1} \cdot yr^{-1}$ (Table 1). However, S throughfall flux at 1920m was much greater (~3500 $Eq \cdot ha^{-1} \cdot yr^{-1}$; see Shubzda *et al.* this volume). With watershed S exports at ~800, NDW is retaining between 1400 and 2700 $Eq \cdot ha^{-1} \cdot yr^{-1}$. NDW showed a net retention of N, given total (IFS) N loadings of ~1900 and an enormous annual stream N export of ~1090 $Eq \cdot ha^{-1} \cdot yr^{-1}$. Ca export (~1300) was a major counter balance to strong acid anion losses. NDW showed net losses of calcium of ~200-300 $Eq \cdot ha^{-1} \cdot yr^{-1}$.

3.3. NITROGEN SATURATION IN NDW

Nitrogen saturation occurs when N inputs to a system are in excess of the N retention capacity of that system (Aber *et al.*, 1989). A result can be NO_3^- export to

Table 1. Water (cm) and Ion (Eq $\cdot ha^{-1} \cdot yr^{-1}$)Fluxes from the NDW by water-year

Water-Year	Water	Ca	N	S
	Wet Deposition 1740 m			
1991-92	219	81	511	719
1992-93	233	57	348	525
1993-94	295	85	477	739
	Throughfall flux 1740 m			
1991-92	210	695	677	1927
1992-93	236	637	729	2174
1993-94	286	908	1535	2479
	Watershed Export (Both streamlets)			
1991-92	207	1088	1005	805
1992-93	210	1164	1052	772
1993-94	253	1626	1218	960

stream water. In an N saturated system nitrate may be an equal or greater agent of soil and water acidification than sulfate and may play a critical role in episodic acidification of streams (Kahl *et al.*, 1992; Murdoch and Stoddard, 1992; Wigington *et al.*, 1993).

N saturation stages can be delineated based on the magnitude and temporal variability of biological retention (e.g. plant uptake and microbial immobilization) relative to N inputs (from the atmosphere or mineralization). Stoddard (1994) developed a ranking system for N saturation based upon annual N budgets and seasonal streamwater nitrate trends. A stage 0 system is N-deficient, showing little or no NO_3^- loss regardless of the levels of input N. With increasing N loading, stage 1 can occur whereby NO_3^- peaks appear in stream water during the winter dormant period while low values persist when vegetation is active. Further N input leads to stage 2, marked by declining N retention and elevated NO_3^- concentrations in streams throughout the year. Stage 3 is reached when the terrestrial system becomes a net source of N as NO_3^- to the aquatic system as outputs exceed inputs and biological control on streamwater NO_3^- concentration is essentially absent (Aber *et al.*, 1989; Stoddard, 1994).

NDW is Stage 2 nitrogen saturated, contributing to both chronic and episodic streamwater acidification and net catchment export of Ca. Episodes of accelerated nitrification in NDW soils have resulted in the elevation of soil solution aluminum concentrations to values known to cause inhibition of calcium uptake in red spruce (Johnson *et al.*, 1991). Nutritional concerns in red spruce in NDW could be associated with high NO_3^- leaching rates (Van Miegroet *et al.*, 1993).

When catchment nitrification rates were accelerated, as a result of disturbance (Nodvin *et al.*, 1988) or enhanced N loadings (Moldan *et al.*, 1995), the resultant soil acidification enhanced catchment S retention through enhanced sulphate adsorption. Therefore reduced sulphate export in NDW may, in fact, be a function of N saturation status. Were it not for the significant catchment retention of sulphate, thereby reducing the total export of acidic anions, chronic and episodic streamwater acidification and Ca export would be even greater than what we are currently observing in NDW.

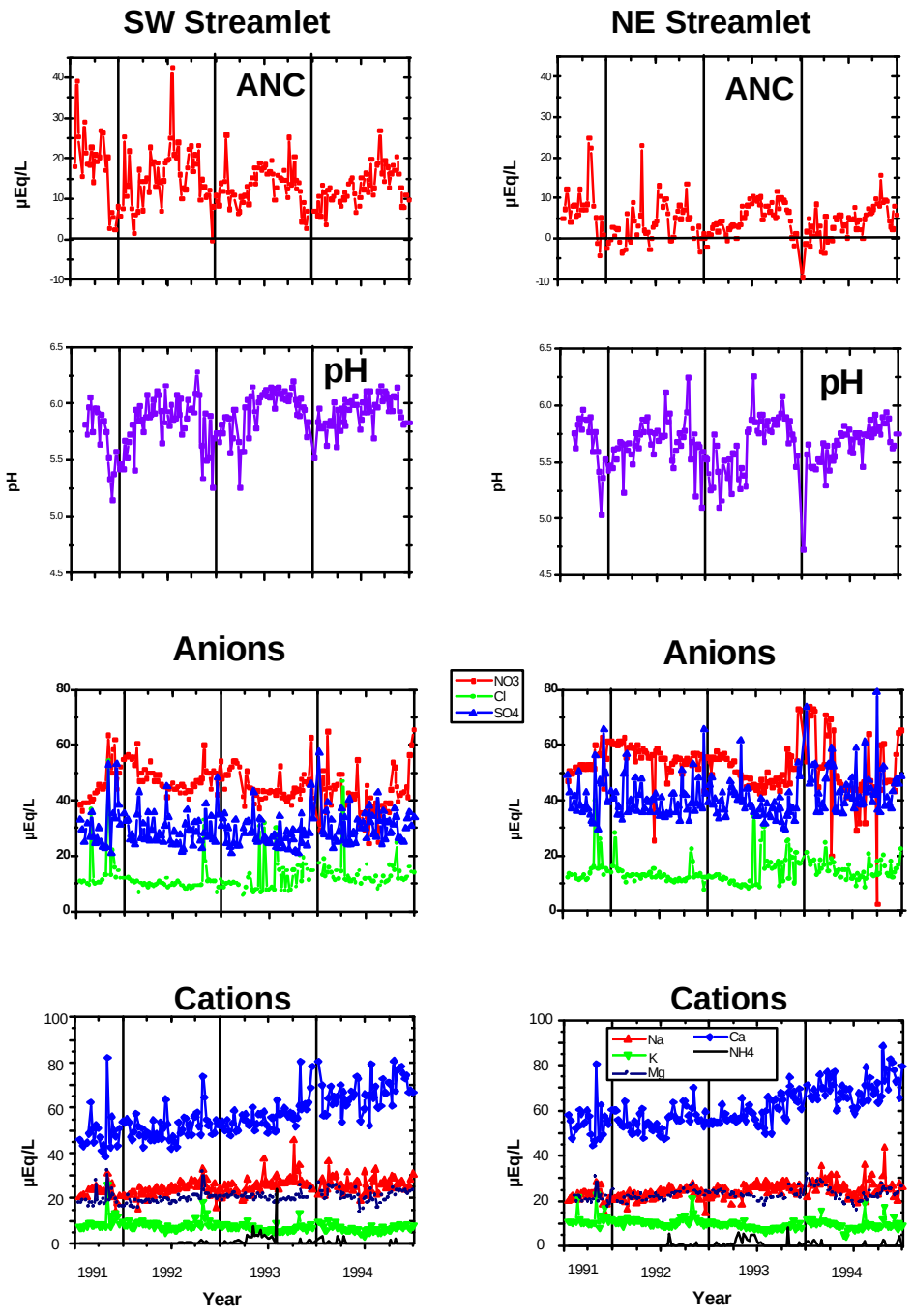

Figure 1. Water Chemistry Trends in NDW Streams from July 1991 through December 1994

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