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Precipitation, Throughfall, and Stemflow Chemistry in a Coastal Loblolly Pine Stand

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Abstract: Precipitation, throughfall, and stemflow quantities and chemistry were characterized over a 20-month period in a 20-year-old loblolly pine stand at North Inlet, South Carolina. Throughfall and stemflow water fluxes were 73 and 8%, respectively, of measured rainfall (178 cm) for the study period; consequently, canopy loss was calculated by difference as 19%. Site precipitation chemistry is strongly influenced by prevailing winds from the ocean or nearby industries. Sulfate, Cl, and Na were particularly responsive to air mass (i.e., high concentrations of Na and Cl were associated with winter and spring frontal storms, \( \text{SO}_4^{2-} \) with summer thunderstorms). Sulfate, Cl, Na, K, Ca, and Mg showed enrichment as water passed through the canopy. At least 26% of the cation leaching in throughfall can be accounted for by hydrogen exchange with the canopy. Nitrate-nitrite, \( \text{NH}_4^+ \), and total nitrogen showed depletion in throughfall flux while there was no change in \( \text{PO}_4 \) and total P fluxes. Dissolved inorganic constituent concentrations were higher in stemflow than throughfall except during periods of frequent storm events. Stemflow was a significant process in the delivery of nutrients to the forest floor and accounted for 13 to 20% of the total flux for all constituents except \( \text{NO}_3 \) and total P which were 4 and 8%, respectively. Analyses of temporal patterns of nutrient fluxes suggest the importance of dry deposition as a process of nutrient input to the ecosystem.

INTRODUCTION

The atmosphere is a major source of nutrients required by forest systems (Swank, 1984; Likens et al., 1977; Swank and Henderson, 1976). Atmospheric
inputs are a combination of dissolved ions, aerosols, gaseous and vapor compounds, and condensation nuclei (Charlson and Rodhe, 1982; Pehl and Ray, 1983-1984; Lindberg et al., 1986). Bulk precipitation contains atmospheric particulates, aerosols, and gases scavenged by cloud rainout, washout below the cloud, and some sedimented dry deposition (Meszaros and Szentimrei, 1985; Swank, 1984). These atmospheric inputs potentially vary with prevailing wind patterns, anthropogenic activities, and precipitation quantity and timing (Musold and Lindqvist, 1982; Lindberg, 1981; Junge and Werby, 1958). As precipitation passes through the forest canopy (throughfall) it may be enriched by surface-deposited material or nutrients leached from plant tissues, depleted by adsorption in the forest canopy, or converted to organic compounds and other ions by microbes (Reiners and Olson, 1984; Olson et al., 1981; Jordan et al., 1980). Stemflow, water transported to the forest floor via tree boles, is similarly modified. Tree species, location, stand density, age, and chemistry of incoming precipitation have variable influence on nutrient quantity and quality reaching the forest floor via throughfall and stemflow (Swank and Swank, 1981; Eaton et al., 1973; Pehl and Ray, 1983-1984).

Many studies focusing on capture and chemical alteration of meteoric inputs by forest canopies have been located in mountain or piedmont regions influenced by continental air masses. Loblolly pine (Pinus taeda L.) studies in the Southeast have likewise been located in nonmaritime locations (Switzer and Nelson, 1972; Van Lear et al., 1984; Wells et al., 1972; Wells and Jorgenson, 1975). Maritime atmospheric conditions are characterized by greater oceanic influence, differing wind and storm patterns, lower anthropogenic inputs, and substantially differing nutrient balances than continental air masses (Glass and Loucks, 1986; Richter et al., 1983; McColl et al., 1982; Sisterson et al., 1985). Many southeastern wetlands, however, occur within maritime influence. These wetlands are often surrounded by extensive natural and managed pine forests. Parker (1983) in summarizing studies conducted within maritime influence noted a clear oceanic effect on incident precipitation and for various ions in net throughfall with the influence occurring within 100 km of the ocean. No study has been conducted in a southeastern maritime forest encompassing precipitation, throughfall, and stemflow dynamics. Therefore, as part of a larger ecosystem study comparing long-term nutrient dynamics of maritime and piedmont pine forests, a study was initiated to quantify canopy alterations of maritime atmospheric inputs. Study of atmospheric processes in the maritime pine forest should provide some insights about canopy nutrient enhancement or depletion, annual nutrient deposition patterns, and oceanic influences which are applicable to maritime wetland forests. The objectives of this paper are (1) to quantify ionic composition and flux in maritime precipitation, and (2) to determine the pine canopy influence on nutrient composition and fluxes of throughfall and stemflow.

SITE DESCRIPTION

The study area is located in the Coastal Plain region, 1.6 km north of Georgetown, South Carolina. The stand is adjacent to the North Inlet estuary approximately 1.2 km from the Atlantic Ocean. The 20-year-old loblolly
pine stand selected is typical of natural regeneration found in the Coastal Plain. The 53-ha stand was established on abandoned agricultural land after 1872. A pine seed tree cut was conducted in 1956 followed by a second cut in 1965. In 1983, the 20-year-old stand contained 2200 stems per ha with a basal area of 25.5 m² per ha and a mean tree dbh of 14.5 cm. Sparse hardwood vegetation is comprised primarily of wax myrtle (*Myrica cerifera*) in the understory and occasional oaks (*Quercus* spp.) and red maples (*Acer rubrum*) in the overstory.

The soils are classified Spodosols composed of Aerie Hapludolls on the drier portions and Typic Hapludolls on the wetter areas. The organic horizons average 15 cm; the organic-mineral horizon averages 35 cm with the underlying mineral soil being composed primarily by weathered sands with intermixed shell deposits. The topographic relief of the watershed is less than 1 m per km.

Precipitation in the study area averages 130 cm per year (NOAA, 1985a). The climate is characteristically maritime with temperatures ranging from −4° to 36°C with an annual average of 18°C. Annual precipitation patterns are highly variable due to the episodic occurrence of tropical storms and hurricanes. Storm size and frequency for a given season are quite variable. Winter and spring are drier (20 and 21% of annual precipitation) averaging 4.8 and 4 storms per month, respectively. Fall is wetter (24% of annual precipitation) with 4 storms per month. Summer is the wettest season (35% of annual precipitation) with the greatest variation in storm frequency and size due to frequent tropical storms and hurricanes.

**METHODS**

**Field**

Gross rainfall for chemical analysis was sampled with five gages comprised of polypropylene bottles fitted with 16.5-cm-diameter funnels and located at 45° openings adjacent to the forest stand. Volumes were calibrated against standard rain gages. Throughfall was sampled by randomly locating 20 trough gages, each 1864 cm² in area, within a 0.1-ha plot. Stemflow was measured on 14 randomly selected trees within the study plot. A collar was fitted to each tree and connected to 20-l plastic containers. Gross precipitation, throughfall, and stemflow volumes were measured and samples collected for chemical analyses following each storm. Measured volumes were converted to cm depth over the study site. Conversions for rainfall and throughfall were accomplished by converting interception areas of collectors and concurrent volumes per storm to total watershed area. The relatively small and uniform size of loblolly pines in the study site showed no statistically significant relationship between dbh and stemflow volume. Therefore, total watershed stemflow volume was calculated by multiplying the average stemflow volume per tree per storm by the number of trees in the watershed.

**Laboratory**

Precipitation, throughfall, and stemflow samples were analyzed for ammonia, orthophosphate, nitrate-nitrite, total nitrogen and phosphorus, sulfate, chloride, sodium, potassium, magnesium, calcium, and pH. Ammonia,
orthophosphate and nitrate-nitrite were analyzed immediately to minimize loss due to sample storage. Aliquots for total nitrogen and phosphorus, sulfate, chloride, and cations were stored separately. All samples were maintained at 4°C until analyses. Alkalinity and pH were measured on whole samples immediately after return to the lab.

Ammonia, nitrate-nitrite, orthophosphate, sulfate, chloride, and total N and P were measured by automated colorimetric tests with a Technicon Autoanalyzer II or Orion Scientific Autoanalyzer System. Ammonia was determined by the phenate method (Technicon Industrial Method No. 154-71W), nitrate-nitrite by cadmium reduction (Technicon Industrial Method No. 158-71W), orthophosphate by ascorbic acid reduction (Technicon Industrial Method No. 155-71W), chloride by ferricyanide method (Technicon Industrial Method No. 99-70W), and sulfate by a modification of Technicon Industrial Method No. 226-72W modified by McSwain et al. (1974). Total N and P were determined using Technicon Industrial Method No. 329-74W following persulfate digestion (Gilbert et al., 1977). Cation analyses were determined by flame atomic absorption.

Statistical Methods

Data on throughfall, stemflow, and combined throughfall plus stemflow volumes were analyzed in a multiple linear regression in which the independent variables were gross rainfall, growing season and dormant season (expressed as a cosine function), and an interaction function derived by multiplying gross precipitation by the cosine value. The \( \cos^2 \) function represents the annual temperature cycle and simulates tree growth relationship. The purpose of this function is to simulate factors which might be influencing canopy-related water fluxes such as evapotranspiration (ET) during high temperature periods and determine whether a given amount of rain would produce the same amount of throughfall and stemflow at all times of the year when corrected for ET. Univariate analyses indicated the necessity to log transform all chemical data to obtain a normal distribution. Linear regression analyses were used to determine the relationship between volumes and chemical composition for precipitation, throughfall, and stemflow. Data used to calculate annual flux for \( \text{SO}_4^{2-} \), \( \text{Cl}^- \), \( \text{Na}^+ \), \( \text{Ca}^{2+} \), and \( \text{Mg}^{2+} \) in precipitation and throughfall were from 37 storms while 25 storms were available for stemflow flux calculations. Total N and P, \( \text{NO}_3^- \) plus \( \text{NO}_2^- \), \( \text{NH}_4^+ \), and \( \text{PO}_4^{3-} \) were analyzed in all components (bulk precipitation, throughfall, and stemflow) from January 1984 to January 1985 and thus anion and cation budgets were based on data during this period when all chemicals were analyzed.

RESULTS

Hydrology

Gross rainfall volumes for the time period of May 1983 to January 1985 are given in Table 1. Only storms greater than 1 cm were sampled. Numerous small storms occur during the summer months yielding little volume. Subsequent studies where all storms were collected indicated that approximately 30% of the storms were less than 1 cm, but the relative con-
TABLE 1
Seasonal Hydrologic Fluxes for the Entire Watershed*

<table>
<thead>
<tr>
<th>Season</th>
<th>Bulk</th>
<th>Throughfall</th>
<th>Stemflow</th>
<th>Interception</th>
</tr>
</thead>
<tbody>
<tr>
<td>Summer 83</td>
<td>24.38</td>
<td>15.58</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fall 83</td>
<td>27.33</td>
<td>21.59</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Winter 83</td>
<td>34.42</td>
<td>26.04</td>
<td>2.73</td>
<td>5.65</td>
</tr>
<tr>
<td>Spring 84</td>
<td>38.43</td>
<td>27.85</td>
<td>3.61</td>
<td>7.05</td>
</tr>
<tr>
<td>Summer 84</td>
<td>15.41</td>
<td>10.41</td>
<td>0.81</td>
<td>4.19</td>
</tr>
<tr>
<td>Fall 84</td>
<td>37.73</td>
<td>28.15</td>
<td>2.07</td>
<td>7.50</td>
</tr>
</tbody>
</table>

*In area cm.

Distribution to the total annual volume was less than 9% for rainfall and throughfall and less than 0.4% for stemflow. Therefore, the measured storms of less than 1 cm in this study represent by far the majority of the hydrologic fluxes. Gross rainfall during the study period averaged 12% above the 30-year mean, with winter and fall showing normal seasonal variation. Spring 1984 was 10% above the 30-year average while both summers were (21 and 7%, respectively) below average. During the study period storm frequency was similar to the 30-year average for fall and spring with both summers below average and winter 60% above the 30-year average.

Linear regression analysis showed that gross rainfall accounted for 90% of the variability in throughfall. The gross rainfall-cosine interaction contributed little to improve the regression for throughfall and stemflow. Gross rainfall accounted for 55% of the variation in stemflow. Throughfall and stemflow volumes were smaller for high intensity storms.

Equations for estimating throughfall, stemflow, and throughfall plus stemflow for a 20-year-old pine stand are given in Table 2. The equations are consistent with equations developed for pine stands in the piedmont of South Carolina (Swank et al., 1972). Throughfall measured during the study period averaged 73% of gross rainfall. The predicted throughfall volume for the 30-year average rainfall is 72.6%. Measured stemflow quantities averaged 8% of gross precipitation. The amount of rainfall reaching the forest floor can be estimated from the throughfall plus stemflow equation and averages 109.25 cm (84%) of gross precipitation, slightly higher than measured quantities during this study period. Storm interception loss was calculated

TABLE 2
Throughfall (THF), Stemflow (SF), and Throughfall Plus Stemflow (THF+SF) Regressions Calculated from Precipitation (PPT)*

<table>
<thead>
<tr>
<th></th>
<th>R2</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>THF</td>
<td>-0.055 + 0.757(PPT)</td>
<td>0.88</td>
</tr>
<tr>
<td>SF</td>
<td>0.021 + 0.063(PPT)</td>
<td>0.55</td>
</tr>
<tr>
<td>THF+SF</td>
<td>-0.034 + 0.820(PPT)</td>
<td>0.90</td>
</tr>
</tbody>
</table>

*In area cm.
by subtracting throughfall and stemflow from gross precipitation for each storm, then totalled for the period. Interception loss was 19% of gross precipitation. Since throughfall and stemflow relationships were consistent for North Inlet and the piedmont pine forest, it is no surprise that interception loss in the coastal region is similar to losses reported for loblolly in the piedmont 20-year-old stand (Swank et al., 1972).

**Chemistry**

Bulk precipitation (wet plus some dry deposition) on the South Carolina coast is highly acidic, dominated by hydrogen and chloride ions. The mean weighted hydrogen ion concentration was 47 µeq/l yielding a mean pH of 4.3 (Table 3). Anionic components of rainfall in order of equivalent acid concent-

<table>
<thead>
<tr>
<th>Ion</th>
<th>North Inlet Bulk</th>
<th>Throughfall</th>
<th>Stemflow</th>
<th>Santee* Bulk</th>
</tr>
</thead>
<tbody>
<tr>
<td>H⁺</td>
<td>47.00†</td>
<td>27.68†</td>
<td>141.42†</td>
<td>50.00</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>0.96</td>
<td>0.53</td>
<td>0.99</td>
<td>4.65</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>15.48†</td>
<td>31.23</td>
<td>45.47</td>
<td>22.44</td>
</tr>
<tr>
<td>Na⁺</td>
<td>39.46†</td>
<td>90.07†</td>
<td>148.43†</td>
<td>18.72</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>10.53</td>
<td>34.30</td>
<td>61.37</td>
<td>10.99</td>
</tr>
<tr>
<td>K⁺</td>
<td>3.94†</td>
<td>28.79†</td>
<td>50.93†</td>
<td>1.78</td>
</tr>
<tr>
<td>Total</td>
<td>115.49</td>
<td>212.60</td>
<td>448.61</td>
<td>108.28</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>41.23†</td>
<td>68.87†</td>
<td>191.62†</td>
<td>114.1</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>1.27</td>
<td>1.35</td>
<td>0.45</td>
<td>9.63</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>58.39†</td>
<td>119.26</td>
<td>202.78†</td>
<td>30.46</td>
</tr>
<tr>
<td>PO₄³⁻</td>
<td>0.126</td>
<td>0.09</td>
<td>0.19</td>
<td>0.28</td>
</tr>
<tr>
<td>Total</td>
<td>101.016</td>
<td>189.57</td>
<td>395.04</td>
<td>51.78</td>
</tr>
</tbody>
</table>

*Richter et al., 1983.
†Indicates significant differences at $P = .001$. 

Concentration are $Cl^- > SO_4^{2-} > NO_3^- > NO_2^- > PO_4^{3-}$. Chloride accounts for 58.5%, $SO_4^{2-}$ for 41.3%, $NO_3^- > NO_2^-$ for 1.3%, and $PO_4^{3-}$ 0.1% of total equivalent anionic components. The order of cation equivalent concentrations in bulk precipitation are $H^+ > Na^+ > Ca^{2+} > Mg^{2+} > K^+ > NH_4^+$. The respective contributions to the cationic components are 41%, 34%, 13%, 9%, 3%, and 0.8%. North Inlet bulk precipitation has higher concentrations of ocean-originated constituents ($Na^+, Mg^{2+}, Cl^-$, and $SO_4^{2-}$) than found in piedmont or mountain regions of South Carolina. All constituent concentrations were negatively correlated with gross precipitation amount. Bulk precipitation for the Santee Experimental Forest located 25 km west of the Atlantic Ocean and 100 km south of Georgetown, South Carolina, has similarly high levels of
ocean-derived constituents (Table 3). Annually approximately 55.5 kg/ha of dissolved inorganic constituents were deposited as bulk precipitation. Sulfate, Cl\(^-\), Na\(^+\), and Ca\(^{2+}\) accounted for 95% of measured ion input. Inputs of NO\(_3^-\)-NO\(_2^-\), Mg\(^{2+}\), K\(^+\), NH\(_4^+\), H\(^+\), and PO\(_4^{3-}\) were less than 2.8 kg/ha/yr.

Throughfall and stemflow mean concentrations (volume weighted) of all chemicals were, in general, enriched over bulk precipitation. The exceptions were depletions in NH\(_4^+\) in throughfall and NO\(_3^-\)-NO\(_2^-\) in stemflow. Enrichment ranged from 12 for total P to 9.5 for K\(^+\) in throughfall and 1.1 for total P to 16.7 for K\(^+\) in stemflow. Concentrations were negatively correlated with throughfall and stemflow volumes.

Throughfall SO\(_4^{2-}\), Cl\(^-\), Na\(^+\), Ca\(^{2+}\), and Mg\(^{2+}\) flux exceeded bulk precipitation by an average factor of 1.8 and stemflow by an average of 5.7. Potassium was substantially enriched in throughfall averaging 7.2 times greater than precipitation and stemflow. Throughfall fluxes of total N and P, NO\(_3^-\)-NO\(_2^-\), and NH\(_4^+\) were 18 to 54% lower than incoming precipitation indicating depletion by the canopy. Orthophosphate interactions with the canopy were negligible. Although stemflow fluxes were significantly less than throughfall, the percentage of these constituents contributed to the forest floor by stemflow, however, is significant (13% for Ca\(^{2+}\) to 20% for SO\(_4^{2-}\)).

Seasonal fluxes varied with hydrologic component and chemical constituent (Fig. 1). By comparing the percent change from one season to the
next of both hydrologic and chemical flux, one can determine which ions are primarily influenced by water volume and those influenced by other processes. Seasonal precipitation, throughfall, and stemflow chemical fluxes of Cl⁻, NH₄⁺, TP, Ca²⁺, Mg²⁺, and Na⁺ exhibited similar seasonal patterns and reflect hydrologic variation. Throughfall fluxes of Ca²⁺, K⁺, and SO₄²⁻ in the summer are enriched relative to changes attributable to hydrologic variation when examining the changes from spring to summer. Throughfall water volume decreased by 63% while Ca²⁺ and SO₄²⁻ decreased by only 46%, 44%, and 41%, respectively. From the summer to fall Cl⁻ flux increased 202% while throughfall water volume increased 170%. Seasonal flux patterns of K⁺ and NO₃⁻-NO₂⁻ differed substantially from hydrologic seasonal patterns (averaging 154% for rainfall, throughfall, and stemflow) with an 83%, 120%, and 186% increase in K⁺ fluxes occurring in the fall for precipitation, throughfall, and stemflow and throughfall NO₃⁻-NO₂⁻ fluxes (28%). An order of magnitude increase from spring to summer in precipitation NO₃⁻-NO₂⁻ flux was not reflected in throughfall and stemflow fluxes. Stemflow NO₃⁻-NO₂⁻ fluxes decreased by 46% from the spring to summer season.

DISCUSSION

Hydrology

The amount of throughfall and stemflow measured agreed with amounts measured for similar aged loblolly stands in the South Carolina Piedmont (Swank et al., 1972). The coastal pine stand had a higher stocking (over 270 stems per ha greater), however, the lower basal area may have offset potential differences between study sites. In addition, loblolly pine frequently reaches a maximum foliage density at 20 years of age. Net rainfall may be more a function of the quantity of intercepting plant surfaces rather than simply basal area of stand density (Waring et al., 1980). Thus, throughfall characteristics of loblolly within a given region may be more a function of foliage density and only slightly influenced by differences in storm size or frequency.

Stemflow is a significant component of the interception process in coastal pine stands. In the coastal region, with a 30-year average annual rainfall of 130 cm, interception loss would be overestimated by 9.7 cm if stemflow was not included. Stemflow volumes were similar to quantities (9%) reported by Swank et al. (1972). In contrast, Pehl and Ray (1983-1984) reported stemflow quantities equaling 11% of incoming precipitation (131 cm in 62 storms) for maritime loblolly pine in eastern Texas. Although lower stocking density potentially contributed to reduced stemflow volumes, interregional differences in storm size, intensity, and seasonal distribution may have greater influence. Rainfall was uniformly distributed throughout the year in east Texas. Storms were predominantly under 2 cm creating greater opportunity for evaporative losses to be important. Therefore, care should be taken when extrapolating estimates of potential stemflow in maritime forests over large geographic regions.
CHEMISTRY

Precipitation

Coastal precipitation anion constituents are dominated by oceanic chloride (58% of anions for North Inlet and Santee Forest) (this study; Richter et al., 1983). Southeastern Piedmont precipitation averages 30 to 34% chloride, while continental precipitation chloride comprises only 5% of the anion budget (Jones and Suarez, 1985; Glass and Loucks, 1986). Sulfate is frequently the dominant anion in Piedmont (54%) and continental (61%) precipitation (Jones and Suarez, 1985; Glass and Loucks, 1986). Concentrations and relative importance of NO$_3^-$--NO$_2^-$ increases from the coast (1.27 μeq/l, 1%), Santee Forest (2.08 μeq/l, 4%) to the Piedmont (Clemson, South Carolina 3.82 μeq/l, 13%) (Richter et al., 1983; Jones and Suarez, 1985). Continental precipitation contains a substantially higher proportion of NO$_3^-$--NO$_2^-$ (18.7 μeq/l, 35%) than coastal precipitation (Glass and Loucks, 1986). Phosphate is present in such small quantities (0.004 mg/l North Inlet, 0.009 mg/l Santee Forest) that it contributes less than 1% to the overall anion budget.

In coastal environments marine salts dominate the cation concentrations just as they do for the anion constituents. Oceanic salts are primarily Na$^+$ and Mg$^{2+}$ with a Mg$^{2+}$-Na$^+$ seawater ratio (by weight) of 0.12. The Mg$^{2+}$-Na$^+$ ratio for North Inlet precipitation is 0.14 indicating oceanic dominance. Sodium concentrations in rainfall are highest along the coast and rapidly decrease inland. Santee Forest and Clemson, South Carolina, Na$^+$ inputs were 63% and 24% of North Inlet precipitation. Seasonal trends of Na$^+$ and Mg$^{2+}$ are similarly characterized by high and variable concentrations during the winter and spring and low concentrations during the summer (Fig. 2). A similar pattern at the Santee Forest was attributed to seasonal patterns in air mass trajectories. Winter and spring air masses are predominantly from the west to southwest due to frequent passage of frontal storms while summer convectional storms are derived from easterly to northeasterly air masses.

The annual Ca$^{2+}$ and K$^+$ inputs are 2.9 and 1.2 kg per ha and comprised 13% and 3%, respectively, of the cation budget. Atmospheric Ca$^{2+}$ is primarily particulate and its temporal variation is related to agricultural activities (Gambell and Fischer, 1966). Increased ionic contribution from oceanic to inland precipitation is attributable to Ca$^{2+}$’s originating from terrestrial dust. The ratios of Ca$^{2+}$-Mg$^{2+}$ (2.62) and Ca$^{2+}$-K$^+$ (3.28) are substantially higher than the concurrent seawater ratios (0.196, 0.95) indicating that the higher inputs at North Inlet were not solely from oceanic sources. Approximately 54% of the coastal roads in Georgetown County and approximately 80% of the roads within the 38,000 acres surrounding the site are unpaved or surfaced with crushed limestone contributing additional calcic material to local atmosphere (South Carolina Statistical Abstracts, 1983; Georgetown Planning Commission, 1985). Much higher Ca$^{2+}$ concentrations (22 μeq/l) were found by Richter et al. (1983). They attributed the higher calcium concentrations to limestone surfaced roads prevalent throughout the Francis Marion National Forest where their study site is located, therefore supporting this hypothesis. Seasonal variation in K$^+$ and Ca$^{2+}$ inputs at North Inlet are influenced more by rainfall quantity than air mass trajectory. No con-
Fig. 2 Storm event concentrations (mg/l) of SO$_4^{2-}$, and Na$^+$ in precipitation from May 23, 1983, to January 1, 1985. Solid line is SO$_4^{2-}$ and dashed line is Na$^+$.

Persistent changes in Ca$^{2+}$ and K$^+$ flux were observed with air mass trajectory, and highest Ca$^{2+}$ and K$^+$ inputs occurred during the winter and spring periods of high bulk precipitation volume (Fig. 1).

Atmospheric sulfur occurs in a variety of gaseous and particulate forms emitted from biogenic, oceanic, and anthropogenic processes. These atmospheric sulfur compounds can be oxidized by a number of chemical reactions. Bulk precipitation contains both particulate and oxidized sulfur forms. Annual input via bulk precipitation (Table 4) is similar to data reported for Clemson, South Carolina, and Experiment, Georgia, and approximately 84%
of inputs for Coweeta, North Carolina (Jones and Suarez, 1985). Levels at the Santee Forest were comparable with relatively homogeneous concentrations throughout the year. The homogeneous levels were attributed to regional background deposition.

Proximity to the ocean might suggest oceanic sources of sulfate. Correlation analysis revealed weak inverse association of Cl\(^{-}\) and SO\(_{4}^{2-}\) (r = -0.16) suggesting other sources, e.g., anthropogenic or biogenic sulfur sources. Utilizing the SO\(_{4}^{2-}\)-Cl\(^{-}\) seawater ratio (0.047) only 7% (1.55 kg/ha) of the annual SO\(_{4}^{2-}\) input could be attributed to oceanic sources. On a storm basis, oceanic contribution varied from less than 1 to 24%, depending on prevailing storm direction. Anthropogenic SO\(_{4}\) emissions for South Carolina are estimated at 15 kg/ha SO\(_{4}\) (U. S. EPA, 1979, in Richter et al., 1983). If all the oceanic and South Carolina anthropogenic SO\(_{4}\) were deposited as sulfate, it would still account for only 75% of the measured sulfate inputs. Therefore, other sources must be contributing to the observed SO\(_{4}^{2-}\) concentrations.

Salt marshes are significant sources of H\(_{2}\)S, which can be rapidly oxidized to SO\(_{4}^{2-}\) in humid environments (Eatough et al., 1984). Relative humidity at North Inlet averages 90 to 95% from June to November, often exceeding 97% (NOAA, 1985b). Adams et al. (1981) measured H\(_{2}\)S emissions for the North Inlet marsh. Approximate annual H\(_{2}\)S emissions for the 2630-ha marsh are 2104 kg H\(_{2}\)S. When converted to an areal annual flux for the forest, this represents a potential sulfate contribution of 3.96 kg/ha. Local industry may be contributing the remaining 1.59 kg/ha of SO\(_{4}^{2-}\).

Seasonal trends in SO\(_{4}^{2-}\) concentrations and quantities were not evident (seasonal fluxes Fig. 1; concentrations by storm Fig. 2). Generally, the higher concentrations occur during the summer, but there is substantial storm to storm variation. Lower inputs which occurred in the summer are attributable in part to lower water volumes. Winter, spring, and fall inputs were comparable. Single episodic events contribute 10 to 14% of the annual input. Sulfur variability may be strongly influenced by variation in storm origin and variable emissions in anthropogenic, biogenic, and oceanic sources.

### Table 4

Annual Flux (kg/ha/yr) of Anions and Cations in Precipitation, Throughfall, and Stemflow for North Inlet, South Carolina

<table>
<thead>
<tr>
<th>Ion</th>
<th>Bulk</th>
<th>Throughfall</th>
<th>Stemflow</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH(_{4}^{+})</td>
<td>0.11</td>
<td>0.05</td>
<td>0.01</td>
</tr>
<tr>
<td>Ca(^{2+})</td>
<td>3.93</td>
<td>5.00</td>
<td>0.74</td>
</tr>
<tr>
<td>Na(^{+})</td>
<td>8.60</td>
<td>16.30</td>
<td>2.84</td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td>1.50</td>
<td>3.50</td>
<td>0.58</td>
</tr>
<tr>
<td>K(^{+})</td>
<td>1.20</td>
<td>8.60</td>
<td>1.58</td>
</tr>
<tr>
<td>SO(_{4}^{2-})</td>
<td>22.10</td>
<td>29.40</td>
<td>7.50</td>
</tr>
<tr>
<td>NO(_{3}^{-})</td>
<td>0.18</td>
<td>0.13</td>
<td>0.005</td>
</tr>
<tr>
<td>Cl(^{-})</td>
<td>18.00</td>
<td>33.70</td>
<td>5.90</td>
</tr>
<tr>
<td>PO(_{4}^{3-})</td>
<td>0.03</td>
<td>0.02</td>
<td>0.005</td>
</tr>
<tr>
<td>TN</td>
<td>2.45</td>
<td>2.02</td>
<td>0.35</td>
</tr>
<tr>
<td>TP</td>
<td>0.14</td>
<td>0.015</td>
<td>0.011</td>
</tr>
</tbody>
</table>
Nitrate plus nitrite deposition was substantially greater in summer, exceeding the combined deposition for all other seasons (Fig. 1). The annual \( \text{NO}_3^- \) plus \( \text{NO}_2^- \) deposition in precipitation was 8 to 10% of the values reported for Santee Forest or piedmont locations. Potentially lower fossil fuel combustion, lower agricultural activities, and resultant biogenic processes along this portion of the coast may contribute to these lower concentrations. Nitrate plus nitrite contributes only 7% to the overall bulk precipitation nitrogen inputs to North Inlet. Nitrogen in precipitation is predominantly organic and accounts for an additional 88% or 2.16 kg/ha. Total nitrogen inputs are similar to Santee Forest but between those of Coweeta, North Carolina, (8.8 kg/ha) and Hubbard Brook, New Hampshire (0.82 kg/ha).

Hydrogen ion concentration at North Inlet, although potentially influenced by proximate sources (e.g., oceanic, local industry), reflects a more regional phenomenon. Bulk precipitation pH (4.3) is similar to Santee Forest and data reported by Jones and Suarez (1985) for Clemson, South Carolina. The relative contribution of \( \text{H}^+ \) to the ionic balance was 41%, 46%, and 56% for North Inlet, Santee Forest, and Clemson Forest precipitation, respectively. Correlation coefficients were calculated for \( \text{H}^+ \) with \( \text{SO}_4^{2-}, \text{NO}_3^- \) plus \( \text{NO}_2^- \) and \( \text{Cl}^- \) to assess potential sources of acidity in bulk precipitation. Hydrogen was positively correlated with \( \text{SO}_4^{2-} \) \((r = 0.42)\) and \( \text{NO}_3^- \) \((r = 0.53)\) but only weakly correlated with \( \text{Cl}^- \) \((r = -0.11)\). High correlation of \( \text{Na}^+ \) \((r = 0.97)\) with \( \text{Cl}^- \) suggests that \( \text{Cl}^- \) in bulk precipitation was associated with marine aerosols rather than rain acidity.

Ammonia is a minor component of coastal precipitation, accounting for less than 4% of the ionic balance. This differs substantially from southeastern piedmont or continental bulk precipitation where \( \text{NH}_4^+ \) is the dominant cation after \( \text{H}^+ \). Piedmont and continental \( \text{NH}_4^+ \) precipitation inputs are higher in the spring and summer due to volatilization of anhydrous \( \text{NH}_4^+ \) used extensively in field fertilizer applications (Jones and Suarez, 1985; Glass and Loucks, 1986). Ammonia vapor is highly soluble in raindrops and can account for a significant portion of dissolved \( \text{NH}_4^+ \) in precipitation (Lindberg et al., 1986). Seasonal \( \text{NH}_4^+ \) input patterns for this site differ from piedmont and continental seasonal patterns: highest inputs occur during the winter consistent with more frequent frontal storms. In coastal areas with low agricultural activity (silviculture is the dominant land use), it appears that the ammonia is not predominantly from proximate sources but being transported from areas of higher agricultural activity with the frontal storms. Tjepkea et al. (1981) suggest that dry deposition of particulate \( \text{NH}_4^+ \) on pine leaf surfaces may be a significant input of atmospheric \( \text{NH}_4^+ \). Lower ammonia concentrations in throughfall than precipitation do not indicate that this source is important at North Inlet.

**Throughfall**

Canopy chemical constituents originate from a variety of sources. In maritime pine forests, sources may include (1) bulk precipitation (rainout, constituents incorporated from cloud droplets and washout, atmospheric constituents removed by falling precipitation); (2) dry deposition (sedimentation,
aerosol impaction, and gaseous sorption); and (3) leaching or ion exchange of chemicals from canopy tissues. Additional modification can occur through exchanges with canopy lichens, mosses, and microbial populations (Lindberg et al., 1986; Eaton et al., 1973; Olson et al., 1981; Reiners and Olson, 1984; Swank, 1984; Carroll, 1980).

Bulk precipitation measurements give the combined input of rain and sedimentation. Wetfall and dryfall were not measured directly, but estimates can be drawn from ratios of bulk precipitation and throughfall input. Bulk precipitation was an important input for PO43-, NO3-, plus NO2-, and SO42- (150%, 130%, and 75%, respectively, of throughfall quantities). Throughfall Ca2+, Cl-, Na+, Mg2+, and K+ had significant sources within the canopy with lower contributions from precipitation (58%, 56%, 53%, 43%, and 11%, respectively). Relative to the total atmospheric input, bulk precipitation was less important at Walker Branch, Tennessee, for Ca2+ (27%), SO42- (43%), NO3- (37%), NH4+ (67%), and PO43- (11%) but more important for K+ (40%) in mixed hardwoods (Lindberg et al., 1986). Bulk precipitation's contribution to total atmospheric input at Coweeta, North Carolina, was substantial for Ca2+ (80%), K+ (68%), NO3- (93%), NH4+ (79%), and PO43- (89%) in mixed hardwoods (Swank and Swank, 1981). Site differences are due to the nature and source of atmospheric constituents associated with land use differences, prevailing wind patterns, canopy leaching potential, and other canopy interactions. Frontal winter and spring storms at North Inlet contain substantial amounts of long range transported constituents of potential terrestrial or anthropogenic origin (Richter et al., 1983). The relative importance of bulk precipitation for Na+, Mg2+, Cl-, and SO42- was higher during the winter and spring and for K+ and Ca2+ in the winter. During the summer and fall localized thunderstorms which have lower concentrations of many ions and the dominance of oceanic breezes contribute to lower precipitation ion contribution and greater dryfall inputs, thereby reducing the overall annual bulk precipitation influence.

Aerosol impaction and gaseous absorption can be an important source of chemical inputs to the pine canopy. Needles are more efficient aerosol collectors than most leaves suggesting pine forests are an efficient vegetation cover for trapping aerosols (White and Turner, 1970). Sources other than bulk precipitation contribute 42% Ca2+, 47% Na+, and 44% Cl- in throughfall. Chloride and Na+ have the same ionic enrichment in throughfall (2.0 to 2.3), therefore suggesting originating from sea salt aerosols. Contributions from sources other than precipitation are higher in the summer and fall than winter and spring. Summer sea breeze predominance in wind patterns and longer interstorm periods contribute to higher aerosol inputs in the summer and fall of 1984.

Ionic Ca2+ enrichment in throughfall at this site was 1.27 indicating a source different from that for Na+ and Cl-. The dry deposition contribution to the total Ca2+ flux at Walker Branch, Tennessee, was 60 to 70%. Fifty-five percent of the airborne Ca2+ was associated with particles greater than 3 μm in diameter indicating the ultimate source was resuspended soil and road dust (Lindberg et al., 1986).

Bulk precipitation sulfate input was 75% of measured throughfall. Dry deposition of sulfur oxides is generally thought to be primarily aerosol
impacted \( \text{SO}_2 \) and fine particle \( \text{SO}_2^- \) (Lindberg et al., 1986). The mean annual concentration of \( \text{SO}_2 \) at this site is 3.98 (SCDHEC, 1983). The deposition velocity for \( \text{SO}_2 \) in a South Carolina loblolly pine forest is 0.72 cm/sec (Lorenz and Murphy, 1985). Assuming a mean canopy height of 11.7 m yields an annual flux of 2.93 kg/ha. The remaining is likely being deposited as particulate \( \text{SO}_2^- \). A conservative oxidation rate of \( \text{SO}_2 \) to \( \text{SO}_4^{2-} \) in the atmosphere is 1% per hour and with a deposition velocity for particulate \( \text{SO}_4^{2-} \) of 0.4 cm/sec, \( \text{SO}_4^{2-} \) inputs from \( \text{SO}_2 \) conversion are an additional 1.39 kg/ha (Ragland and Wilkening, 1982). Based on the ratio of sea salt \( \text{SO}_4^{2-} - \text{Cl}^- \) and \( \text{Cl}^- \) concentrations in throughfall, 1.38 kg/ha potentially comes from oceanic origin. The remaining 0.55 kg/ha may be particulates of anthropogenic origin. These calculations are tentative because they are based on numerous assumptions about rates, conversions, and similarity in micrometeorological factors between our site and published data. The analysis is useful, however, in suggesting priorities for future research on partitioning sulfur input measurements.

Canopy leaching or ion exchange represents internal recycling rather than new inputs to the ecosystem (Likens et al., 1977). These processes can greatly influence canopy inputs to the forest floor. Hydrogen ion exchange is an important mechanism in leaching cations in the canopy (Eaton et al., 1973). It is not clear whether the leaching mechanism is due to hydrogen being transferred from water to exchange sites, hydrogen combining with soluble Bronsted bases, or association with weak organic acids. Simple cation exchange models were insufficient to explain behavior of hydrogen in fir canopies (Reiners and Olson, 1984). The net result, however, is an increase in acidity and cation concentration in throughfall over bulk precipitation. Based on equivalents/ha, hydrogen ions make up 41% of the cation budget in precipitation and only 13% in throughfall. The net cation loss from the canopy was 0.73 eq/ha. At least 26% of the total cation leaching which occurred in throughfall, therefore, can be accounted for by hydrogen ion exchange in the canopy. Similar cation leaching by hydrogen exchange (27%) measured in white pine and mixed hardwoods in Virginia suggests that there may be factors (i.e., exchange rates) which limit the total quantity potentially leached by this mechanism (Parker, 1982; Eaton et al., 1973).

Bulk precipitation was a minor input for \( \text{Mg}^{2+} \) (28%) and \( \text{K}^+ \) (11%), but the ionic enrichment of precipitation to throughfall ratio \( \text{Mg}^{2+} \) (3.25) and \( \text{K}^+ \) (9.47) was much higher than \( \text{Na}^+ \) (2.28) indicating within canopy enrichment. Luxmore et al. (1981) obtained significant amounts of \( \text{Mg}^{2+}, \text{K}^+, \text{Ca}^{2+}, \) and \( \text{Na}^+ \) from loblolly pine foliage. Absolute amounts vary with concentration gradient between plant tissue and overlying water, relative ionic mobility or leachability, and storm duration (Reiners and Olson, 1984). To separate crown leaching from the aerosol component in nutrient gain, regressions were derived for \( \text{Mg}^{2+} \) and \( \text{K}^+ \) inputs in throughfall versus the amount in gross rainfall. The regression intercept on the y axis may be taken as an estimate of each element’s contribution through crown leaching (Miller et al., 1976). On this basis, crown leaching accounted for 0.25 kg/ha or 22% of total \( \text{K}^+ \) flux and 0.12 kg/ha (32%) of total \( \text{Mg}^{2+} \) flux. The potassium flux via crown leaching is lower than ranges (60 to 90%) summarized by Parker (1983). Substantially more magnesium comes from crown leaching at this
site than quantities obtained in other maritime forests (0 to 8%). Deposition sources for magnesium (78%), however, still dominate this site when compared to more inland sites (54 to 59% Mg from crown leaching or 41 to 46% via deposition).

Seasonal $K^+$ and $Mg^{2+}$ throughfall inputs were highest during the spring and fall (Fig. 1). Fall throughfall enrichment was 329% for $Mg^{2+}$ and 791% for $K^+$ of bulk precipitation. These seasonal trends may be partially due to greater leaching during the autumn when leaf cuticles are well-weathered and cracked (Henderson and Harris, 1975). Reiners and Olson (1984) also reported greater leaching of cations from older balsam fir leaves than from newer leaves. Elevated spring inputs are associated with periods of high pollen release.

**Stemflow**

Loblolly pine stemflow was more acid (pH 3.84) and enriched (with exception of NO$_3^-$ plus NO$_2^-$) relative to throughfall (Table 3). Similar stemflow enhancement has been demonstrated for a variety of hardwood, conifer, and mixed conifer-hardwood forests in the Northeast, East Texas, and Southeast (Olson et al., 1981; Eaton et al., 1973; Pehl and Ray, 1983-1984). The enrichment varies with species, stand age, dominant air mass, and proximity to anthropogenic and oceanic sources.

The sum of cation and anion equivalent concentrations in stemflow are over twice that for throughfall. The increase in ions is due in part to longer contact time of water moving over the bark surface than in throughfall. When bulk precipitation passes down the tree there is a shift in the relative ion abundance. The shift for this site is from $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ in bulk precipitation to $Na^+ > Mg^{2+} > K^+ > Ca^{2+}$ in stemflow. The continued dominance by $Na^+$ and increased importance in $Mg^{2+}$ demonstrated the influence of impaction by sea salt aerosols in maritime forests over leaching or ion exchange with the bark for these particular ions. The rough texture of pine bark provides an effective surface for trapping aerosols. In nonmarine forests the shift in stemflow cations ($K^+ > Ca^{2+} > Mg^{2+} > Na^+$) is dominated by leaching or relative mobility of the ions (Eaton et al., 1973). The high $K^+$ enrichment results from high $K^+$ tissue concentrations, $K^+$'s presence in ionic form, and concurrent high leachability (Olson et al., 1981).

Enrichment of both $H^+$ (5.1) and SO$_4^{2-}$ (2.7) in stemflow relative to throughfall was greater than $Na^+$ and Cl$^-$ (1.7). Increased acidity in stemflow could result from dry deposition of SO$_2^-$ from the atmosphere or organic acids leached from the bark (Hoffman et al., 1980). The rough bark surfaces may provide increased trapping of SO$_2$ or nonmarine SO$_4^{2-}$. Stemflow at this site was highly colored which suggests enrichment with organic acids. Reiners and Olson (1984) measured a net $H^+$ ion efflux from leaching associated with balsam fir bark.

High storm frequency from March to May 1984 reduced $Na^+$ concentration differences between throughfall and stemflow. For several storms stemflow $Na^+$ concentrations were lower than throughfall suggesting a washing of surface deposited particulates. During the entire study stemflow SO$_4^{2-}$
concentrations were greater than throughfall suggesting some potential leaching of sulfate or trapping of nonmarine sulfate. Sulfate leaching from tree boles was not detected by Reiners and Olson (1984). Although a majority of the sulfate may originate as deposition, the consistently higher concentrations suggest some decomposition of the bark may be occurring, releasing organic acids and sulfur containing compounds which are easily oxidized to $\text{SO}_4^{2-}$.

Nitrate plus nitrite and $\text{NH}_4^+$ were the only ions that showed a depletion as water passed through the canopy. On an annual basis $\text{NH}_4^+$ equivalent concentrations were depleted 45% in throughfall relative to precipitation. Similar equivalent concentration depletions in $\text{NH}_4^+$ (49%) and even greater depletions in $\text{NO}_3^-$ plus $\text{NO}_2^-$ (65%) relative to precipitation were observed in stemflow. The fate of inorganic nitrogen in the canopy is complex. Inorganic N may be taken up directly by higher plant foliage or epiphytes or leached from the apoplasm of conifer foliage (Reiners and Olson, 1984). Variations in foliar leaching and absorption strongly influence seasonal changes in inorganic nitrogen. Throughfall $\text{NH}_4^+$ depletions occurred during the winter and summer whereas deletions were detected only during the summer. Miller et al. (1976) found foliar absorption in Corsican pine to be the dominant process affecting inorganic nitrogen during the summer and winter. Higher winter levels in throughfall from this site may be due to nitrification of $\text{NH}_4^+$ by microepiphytes which coat canopy surfaces (Carroll, 1980). Summer bulk precipitation $\text{NH}_4^+$ flux was 3.75 times greater than throughfall $\text{NH}_4^+$, however, throughfall flux was enhanced 3.4 times over bulk precipitation.

Inorganic nitrogen decreased relative to organic nitrogen as rainwater passed through the canopy. The ratios of inorganic-organic nitrogen were 1:7.8 bulk, 1:11.1 throughfall, and 1:21.8 stemflow. Throughfall seasonal variation in inorganic-organic nitrogen ratios reflect precipitation ratios except during the summer. Summer stemflow enrichment in organic nitrogen over precipitation is concurrent with stemflow $\text{NO}_3^-$ plus $\text{NO}_2^-$ depletion (46% eq/ha of precipitation). These transformations are potentially a function of epiphytic coverage and their release of organic nitrogen concurrent with their uptake of inorganic nitrogen (Reiners and Olson, 1981). Another source of organic nitrogen in stemflow solutions may be bark decomposition.

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