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Chemical Composition and Spatial Variation of Bulk Precipitation at a Coastal Plain Watershed in South Carolina

DANIEL D. RICHTER[1] AND CHARLES W. RALSTON

School of Forestry and Environmental Studies, Duke University
Durham, North Carolina 27706

WILLIAM R. HARMS

Southeastern Forest Experiment Station, Forestry Sciences Laboratory
Charleston, South Carolina 29407

Bulk precipitation was collected for analysis of ionic constituents at eight rainfall stations over a 4-year period at a 500-ha watershed in the Lower Coastal Plain of South Carolina. Mean annual deposition rates of ions in greatest supply, Cl^-, SO_4^{2-}-S, Ca^{2+}, and Na^+, were respectively 14.2, 7.51, 5.69, and 5.66 kg/ha. Annual deposition rate for total inorganic N (NH_4^+-N plus NO_3^--N) was about 2.6 kg/ha and for orthophosphate-P about 0.12 kg/ha. Spatial variation of annual depositions to the eight rainfall stations was smallest for SO_4^{2-}, NO_3^-, and Ca^{2+}, with coefficients of variation (CV) less than 10%. Variation of annual inputs to the eight collectors was intermediate for Mg^{2+}, Cl^-, H^+, and Na^+ with CV ranging between 13.9 and 21.5%, whereas the CV for annual inputs of NH_4^+, PO_4^{3-}, and K^+ exceeded 30%. Sample size estimates for this 500-ha watershed indicated that 19 collectors should provide estimates of the annual bulk precipitation inputs within 10% of true means for 7 of 10 ions (SO_4^{2-}, NO_3^-, Ca^{2+}, Mg^{2+}, Cl^-, H^+, and Na^+) and that more than 35 collectors would be necessary to provide similar confidence intervals for annual inputs of NH_4^+, PO_4^{3-}, and K^+ ($\pm$ 10% at $P < 0.05$). Although estimates of annual bulk precipitation inputs may be quite variable over local areas, control of sampling errors can be gained by increasing the number of collectors.

INTRODUCTION

The contribution of nutrients in rainwater to soil nutrient supplies was the incentive for many early studies of precipitation chemistry with the result that by the beginning of the twentieth century, chemical analyses of precipitation had been reported on six continents [*Miller*, 1905; *Wilson*, 1921; *MacIntire and Young*, 1922]. Although the reliability of these early studies has been questioned, they revealed that rainwater was a dilute solution of a variety of substances of natural and anthropic origin and that its composition was highly variable at different geographic locations as well as at the same location at different sampling times.

Atmospheric deposition processes are inherently variable, causing considerable variation in precipitation composition over regional and local areas [*Hem*, 1970]. Spatial variation in chemical composition of rain has been documented over large regional areas for some time [*Junge and Werby*, 1958; *Gambell and Fisher*, 1966; *Granat*, 1972; *Gatz*, 1978]. However, information on local variations of rainwater constituents is much more limited. Although local variability in the composition of precipitation has been examined by several investigators, these studies usually have emphasized differences between rural and urban/industrial environments [*Andersson*, 1969; *Boyce and Butcher*, 1976] or have been investigations of short duration [*Huff*, 1965; *Galloway and Likens*, 1976].

Research described in this report was undertaken to measure ionic constituents in bulk precipitation at a forested watershed in the Lower Coastal Plain of South Carolina. The measurements were taken to provide estimates of annual additions of nutrient elements to this forest ecosystem from atmospheric sources. Particular attention was given to spatial variations of ionic deposition to evaluate sampling errors of annual inputs of elements as measured by bulk precipitation.

METHODS

Collection Site

Bulk precipitation was collected on a 500-ha watershed at the Santee Experimental Forest located in the Francis Marion National Forest in the coastal flatwoods of South Carolina (33°N, 80°W). The experimental watershed (composed of U.S. Forest Service watersheds 77, 79, and 80) is near the village of Huger, about 50 km north-northeast of Charleston and 25 km west of the Atlantic Ocean (Figure 1).

The climate of the Santee Forest is classified as humid subtropical [*Trewartha*, 1954] with long, hot summers and short, mild winters. Since 1946, mean annual precipitation at the Santee Headquarters gaging station has been about 135 cm. Over the last 34 years, the wettest months have been July and August with precipitation averages of 19.6 and 18.2 cm, respectively; the driest months have been April and November with means of 6.7 and 6.5 cm.

Seasonal patterns of air mass trajectories have important implications for the character and composition of precipitation at the Santee Forest. In winter, polar air masses push into the southeastern United States, and cyclonic systems tend to move northeastward parallel to the Atlantic coastline. Many of these frontal storms are intense and bring increases in landward transport of seawater constituents. In summer, moist air tends to move across the warm, south-

[1] Now at Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830.

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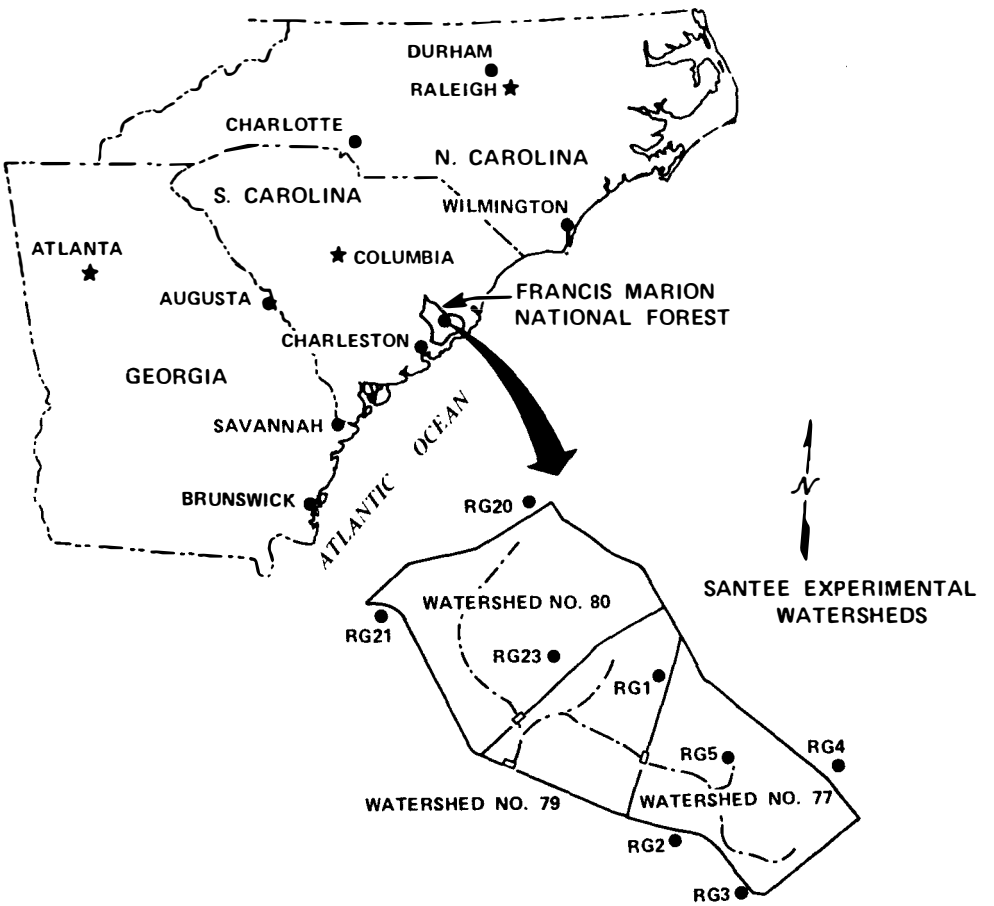

Fig. 1. Map showing the location of the Francis Marion National Forest and the locations of the eight rainfall stations at the Santee Experimental Watersheds.

eastern landmass under the influence of the Bermuda High. Convective thunderstorms form, which usually supply large amounts of precipitation. November and April, typically the driest months of the year, represent transition periods in this winter-summer cycle. In November, the polar front has not yet pushed into the southeast, but convective thunderstorm activity has diminished. Similarly, in April the polar front has retreated to the north, and convective processes are not strong enough to form many thunderstorms.

Sample Collection and Analysis

Weekly samples were taken for 4 years at eight rainfall collection stations located in large openings in the forest watershed (1976–1979). The surrounding forest canopy was sufficiently distant to prevent contamination of precipitation samples by crownwash. Precipitation volumes were measured in standard U.S. Weather Bureau nonrecording gages. Two polyethylene samplers (funnel diameter 16 cm) also were located at each station for collecting bulk precipitation for *p*H and conductance measurements and for other chemical analyses. Samples for chemical analysis were preserved with phenylmercuric acetate (PMA) (2 ml per weekly sample) and frozen until shipment to the Forest Soils Laboratory at Duke University, where they were stored at 4°C. Tests of PMA as a preservative indicated that the agent was consistently effective in inhibiting microbial activity in rainwater solutions.

Because collectors were continuously open, they collected a certain amount of dry deposition. Rainfall solutions sampled from continuously open collectors have been defined as bulk precipitation [*Whitehead and Feth*, 1964] and have been extensively used to estimate atmospheric inputs to ecosystems. However, total atmospheric depositions to ecosystems may also include inputs by aerosol impaction on vegetative surfaces and gaseous adsorption by vegetation and soils. These inputs are not efficiently sampled by bulk precipitation collectors [*Galloway and Likens*, 1976].

Bulk precipitation solutions were analyzed for *p*H and specific conductance within a few hours of collection. H-ion concentrations were calculated from the *p*H measurements. Solution concentrations of Ca^{2+}, Mg^{2+}, K^+, and Na^+ were measured by atomic absorption spectrophotometry with LaCl additions to mask interferences in Ca^{2+} and Mg^{2+} determinations [*Isaac and Kerber*, 1971]. Concentrations of NH_4^+ were determined by dichloroisocyanurate colorimetry [*Reardon et al.*, 1966], NO_3^- by cadmium reduction and azo-dye colorimetry [*American Public Health Association*, (APHA), 1976], Kjeldahl-N by Kjeldahl digestion and dichloroisocyanurate colorimetry [*Crooke and Simpson*, 1971], SO_4^{2-} by methylthymol-blue colorimetry [*McSwain et al.*, 1974], Cl^- by ferric-thiocyanate colorimetry [*Technicon Industrial Systems*, 1971], and ortho-PO_4^{3-} by molybdenum-blue colorimetry [*APHA*, 1976]. All colorimetric analyses were performed on a Technicon Auto Analyzer I. Instrument detection limits were 0.001, 0.005, 0.01, 0.02, 0.05, 0.05, 0.05, 0.1, and 0.2 mg/l for PO_4^{3-}-P, NO_3^--N,

NH_4^+-N, Mg^{2+}, K^+, Na^+, SO_4^{2-}-S, Cl^-, and Ca^{2+}, respectively. Accurate determinations of these constituents were consistently attained for U.S. Environmental Protection Agency (EPA) quality control samples that were randomly included in routine analyses.

Annual bulk precipitation inputs were estimated from 4 years of sampling, from 1976 to 1979. Annual inputs to the watershed in 1976 were estimated from the annual sum of the products of mean weekly volume and concentrations, as 1976 data were recorded only as mean weekly inputs to the eight collectors. Annual inputs at each rain station were calculated from 1977 to 1979 data by

$$t_j = \sum_{i=1}^{n} x_{ij}\, y_{ij} \tag{1}$$

where t_j is the annual ion input at collector j, n is the number of collections per year, x_{ij} is the rainfall volume in week i at collector j, and y_{ij} is the ion concentration in a sample in week i at collector j. Thus annual ion inputs to the watershed (T) were estimated for 1977–1979 data by

$$T = \left(\sum_{j=1}^{8} t_j \right) \Big/ 8 \tag{2}$$

a calculation that provides a comparable annual input estimate as that used to estimate 1976 inputs.

Coefficients of variation (CV) were estimated from the variances of annual inputs to the eight collectors (t_j in (1)) for each of three annual periods. Variances of the input estimates for 1977, 1978, and 1979 were pooled, and a coefficient of variation calculated from the quotient of the pooled standard deviation and the 3-year mean annual input:

$$\mathrm{CV} = \left(\sum_{i=1}^{3} S_i^2/3 \right)^{1/2} \Big/ \bar{T} \tag{3}$$

where S_i^2 is the variance of annual input for year i and $\bar{T}$ is the mean annual input for the 3 years.

RESULTS

Annual rainfall during the 4-year study ranged from 113 cm (1978) to 146 (1979) and averaged 132.5 cm, about 2% less than the 34-year mean of 135.6 cm. Variability of weekly rainfall catches among the eight collectors depended on seasonal effects (Figure 2). Seasonal differences in spatial variability were evaluated from weekly CV for rain volumes collected in winter and summer. Average CV was 6.4% for winter weeks in contrast with 20.9% for summer weeks, despite a larger weekly rainfall volume during the summer. This seasonal pattern of spatial variation is explained by seasonal patterns of weather systems, as winter precipitation is chiefly from frontal storms that blanket large areas with rain, whereas summer precipitation is often from localized thundershowers. Over annual periods, however, rainfall was evenly distributed to the eight collectors with a CV of 3.9%.

On the basis of volume-weighted concentration data expressed in mg/l (Table 1), calcium was the most abundant cation in Santee precipitation. However, on an equivalent-weight basis, hydrogen accounted for about 46% of the total cations, followed by calcium (21%), sodium (17%), magnesium (10%), ammonium (4.2%), and potassium (1.7%). Dissolved anionic equivalents were primarily sulfates, which

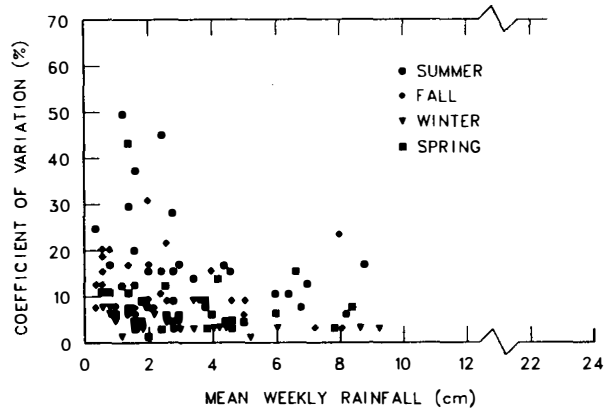

Fig. 2. Relationship between mean weekly rainfall and sample coefficient of variation at the Santee Experimental Forest, South Carolina (1977–1979).

contributed about 47% of the total anionic constituents. The remaining anions in order of abundance were chloride (40%), nitrate (12%), and phosphate (1%).

Annually, a total of about 40 kg/ha of these elements were deposited as bulk precipitation (Table 1). Elements in greatest supply on a mass basis were Cl^-, SO_4^{2-}-S, Ca^{2+}, and Na^+, which together accounted for about 85% of the measured ion input. Lesser amounts of NO_3^--N, Mg^{2+}, K^+, NH_4^+-N, H^+, and PO_4^{3-}-P were deposited, with inputs of each of these ions less than 1.8 kg ha^{-1} yr^{-1}.

Large differences were observed in the spatial variation of ion depositions (Table 2). Greatest spatial variation as measured by the CV was observed for annual inputs of K^+, PO_4^{3-}, and NH_4^+ and the least for SO_4^{2-}. The three ions in lowest concentration on an equivalent-weight basis (K^+, PO_4^{3-}, and NH_4^+) were the ions with the most variable depositions among the eight collectors (CV > 30%). Spatial variation was small for annual inputs of SO_4^{2-}, NO_3^-, and Ca^{2+} (CV < 10%) when compared with that for the other seven ions.

Spatial variation in annual rainfall volume (CV = 3.9%) was considerably less than that for inputs of most ions (Table 2). Therefore the major source of sampling error for ion deposition was attributable to the variability of ion concentrations, with smaller errors contributed by volumetric measurements.

TABLE 1. Mean Volume-Weighted Concentrations and Annual Inputs of Ions in Bulk Precipitation at the Santee Experimental Watershed in South Carolina, 1976–1979

Ion	Volume-Weighted Concentration, mg/l	Mean Annual Input, kg/ha	Annual Input CV, %
H^+*	0.050	0.64	34
Ca^{2+}*	0.45	5.69	22
Na^+	0.43	5.66	47
Mg^{2+}	0.13	1.68	20
NH_4^+-N	0.063	0.83	36
K^+	0.070	0.94	35
SO_4^{2-}-S	0.57	7.51	28
Cl^-	1.08	14.2	24
NO_3^--N	0.129	1.76	22
PO_4^{3-}-P	0.009	0.12	20

Coefficients of variation (CV) calculated from variations in four annual input estimates; annual rainfall averaged 132.5 cm with a CV of 7.7% during this period.

*Data from 1977 to 1979 only.

TABLE 2. Mean Annual Inputs and Spatial Variation (CV) for Ions in Bulk Precipitation at the Santee Experimental Watershed

Ion	Mean input, kg ha^{-1} yr^{-1}	CV, %	Minimum Input, kg ha^{-1} yr^{-1}	Maximum Input, kg ha^{-1} yr^{-1}
SO_4^{2-}-S	7.41	7.1	6.83	8.10
NO_3^--N	1.52	8.4	1.37	1.67
Ca^{2+}	5.69	9.5	5.23	6.70
Mg^{2+}	1.54	13.9	1.37	1.77
Cl^-	13.5	15.2	12.0	16.0
H^+	0.64	17.0	0.50	0.72
Na^+	5.45	21.5	4.83	6.87
NH_4^+-N	0.79	30	0.59	0.95
PO_4^{3-}-P	0.126	31	0.080	0.170
K^+	0.95	35	0.71	1.38

Annual means estimated from inputs to eight rain collectors in three annual periods, 1977–1979. CV estimated from pooled variances of inputs to eight collectors for three annual periods. Minimum and maximum inputs represent range in mean annual inputs over 3 years to individual rain collectors. Mean annual rainfall during this period was 127.7 cm with a CV of 3.9%. The range in annual rainfall collected at individual rain gages over 3 years was 123 and 136 cm.

DISCUSSION

Bulk Precipitation pH

Volume-weighted mean *p*H, as calculated from H^+ activities, was 4.3. No consistent time trend was evident between 1976 and 1980. Correlation coefficients for concentrations of H^+ with SO_4^{2-}, NO_3^-, and Cl^- were calculated to evaluate possible sources of acidity in bulk precipitation at the study site. This analysis indicated significant positive correlations of H^+ with SO_4^{2-} and NO_3^- in all storm size classes (Table 3). Concentrations of H^+ and Cl^- were not highly correlated, but high correlations of Na^+ and Mg^{2+} with Cl^- suggested that Cl^- in Santee rain solutions was associated with marine aerosols rather than rain acidity.

In recent years, several studies have shown that the *p*H of precipitation is low in several areas of the southeastern United States. On Sapelo Island in Georgia, *Haines* [1976] reported acidity in coastal precipitation ranging among storms from *p*H 4.0 to 7.5. At five locations in Florida, *Brezonik et al.* [1980] reported the annual volume-weighted bulk rainfall *p*H to range from 4.6 to 5.2. Historical records are lacking to substantiate a hypothesis of increased rain acidification in this region, although results of *MacIntire and Young* [1922] and *Gambell and Fisher* [1966] appear to support this hypothesis. The latter study showed that annual rainfall *p*H averaged about 5.0 over eastern North Carolina and southeastern Virginia between August 1962 and July 1963 (arithmetic average of 27 locations). However, *p*H of bulk rainfall in the Gambell and Fisher study was determined from monthly samples, a procedure that experimentally and theoretically has been shown to result in higher *p*H values than those from comparable weekly collections if appreciable volumes of rainfall are buffered by bicarbonate [*Hornbeck et al.*, 1977; *Reuss*, 1977].

Oceanic Salts

Oceanic salts in precipitation are primarily Na^+ and Cl^- together with smaller quantities of Mg^{2+} and SO_4^{2-}. The dominant role of marine salts in maritime environments is clearly shown in the work of *Junge and Werby* [1958] and *Gambell and Fisher* [1966] with Na^+ and Cl^- concentrations in rainfall highest along the coast and rapidly decreasing inland. At the Santee Forest, mean volume-weighted concentrations of Na^+ and Cl^- were 0.42 and 1.06 mg/l, respectively, with bulk precipitation inputs averaging 5.7 and 14.2 kg ha^{-1} yr^{-1}. In general, seasonal trends for Na^+ and Cl^- were characterized by high concentrations during winter months and low concentrations in summer months [*Richter*, 1980], a trend that follows seasonal changes in air mass trajectories. The importance of hurricanes in supplying large quantities of oceanic salts to coastal environments was shown by Hurricane David in 1979, the rainfall of which was laden with 30–40% of annual Cl^- and Na^+ inputs based on 1976–1979 averages. This amounted to about 4.7 kg/ha of Cl^- and 2.5 kg/ha of Na^+.

Chemical concentrations of rainfall commonly follow an inverse relationship between volume and concentration that can be described by negative exponential functions [*Gatz and Dingle*, 1971; *Lindberg*, 1981]. Concentrations of all 10 ions measured in bulk precipitation decreased with increasing weekly rainfall volume in patterns similar to that shown for conductivity and storm size in Figure 3. However, the Santee Forest receives substantial rainfall from both continental and marine air masses, and concentration-volume relationships for Na^+ and Cl^- and other ions may be modified by storm origin and history. For example, Hurricane David, which tracked inland near Charleston, South Carolina [*National Oceanic and Atmospheric Administration*, 1979] supplied about 23 cm of rainfall to the Santee Forest. Despite this large volume of rainfall, Na^+ and Cl^- concentrations averaged about 2-fold greater than annual volume-weighted mean concentrations. Concentrations of other ions, however, were very dilute in these samples compared with volume-weighted averages.

Concentrations of Cl^- were positively correlated with Na^+ and Mg^{2+} in all storm size classes (Table 3). Although the ocean is frequently cited as a source of SO_4^{2-} in rain solutions, correlation analysis revealed only weak association of Cl^- and SO_4^{2-}, probably because anthropic and

TABLE 3. Pearson Product-Moment Correlation Coefficients for Mean Weekly Concentrations of Selected Pairs of Ions in Bulk Precipitation at the Santee Experimental Watershed, 1977–1979

Weekly Storm Size Class, cm	H^+:SO_4^{2-}	H^+:NO_3^-	H^+:Cl^-	Cl^-:Na^+	Cl^-:Mg^{2+}	Cl^-:SO_4^{2-}	Sample Size, weeks
0.7–2	0.43*	0.53*	−0.11	0.95*	0.94*	0.41*	47
2–4	0.68*	0.65*	−0.22	0.75*	0.60*	−0.16	39
4–6	0.83*	0.72*	0.16	0.98*	0.92*	0.20	18
>6	0.66*	0.68*	−0.30	0.83*	0.71*	−0.22	17
All volumes	0.56*	0.59*	−0.01	0.95*	0.93*	0.42*	121

*Significance level at $P < 0.01$.

nonoccanic natural sources of S greatly exceeded contributions from the sea. On the basis of a SO_4^{2-}-S/Cl^- ratio of 0.047 for seawater [*Hem*, 1970], only 9% (0.67 kg/ha) of annual SO_4^{2-}-S inputs to the Santee may be attributed to oceanic sources.

Despite the large quantities of oceanic salts found in Santee rainfall, annual deposition of Na^+ and Cl^- to the eight rain collectors was quite variable (Table 2). This spatial variation may be attributable to the proximate ocean (25 km) and to incomplete mixing of marine aerosols at this distance from the coast. In fact, depositions of Na^+ and Cl^- that resulted from Hurricane David varied among collectors by a factor of 4.

Sulfate

Sulfur is emitted to the atmosphere in gaseous and particulate forms by natural and anthropic processes and can be oxidized to SO_4^{2-} by a number of chemical reactions [*Newman*, 1980]. Anthropic SO_x emissions in South Carolina for 1976 were estimated from U.S. EPA data to be about 15 kg/ha of S, an emission rate lower than other southeastern states with the exception of Mississippi [*U.S. EPA*, 1979; *Richter*, 1980]. However, only about half of these anthropic emissions for South Carolina on a unit area basis were recovered as SO_4^{2-}-S in bulk precipitation at the Santee Forest (7.5 kg ha^{-1} yr^{-1}).

Bulk precipitation inputs of SO_4^{2-} to the Santee Forest watershed exhibited the least spatial variability of the ions measured (Table 2). The Santee is distant from point pollution sources and relatively homogenous collections of SO_4^{2-} from the bulk precipitation network suggest regional background deposition. This is supported by SO_4^{2-} data from other recent bulk precipitation studies in the southeast, which have reported SO_4^{2-} inputs to rural areas similar to those reported here. For example, annual SO_4^{2-}-S inputs were reported to be 8.3 kg/ha by *Jones et al.* [1979] in rural South Carolina and to be 9.1 kg/ha in northern Florida by *Hendry and Brezonik* [1980].

Seasonal trends of monthly SO_4^{2-} concentrations and contents in the bulk precipitation solutions were not evident from the 4 years of data. Variable contributions of sulfur emissions from anthropic, biogenic, and oceanic sources were probably important in obscuring monthly trends.

Nitrogen

Considerable amounts of reactive nitrogenous compounds are emitted to the atmosphere by fossil fuel combustion, natural biogenic processes, and agricultural activities [*Kramer*, 1978]. At the Santee Forest, concentrations of NH_4^+ and NO_3^- in bulk precipitation were in the lower range of values than those reported for forested areas [*Likens et al.*, 1977]. Mean volume-weighted concentrations of NO_3^--N and NH_4^+-N were 0.129 and 0.063 mg/l, respectively, amounting to inputs of 1.76 and 0.83 kg ha^{-1} yr^{-1} of N. Kjeldahl digestion of composited samples collected in 1977 and 1978 indicated that N in Santee bulk precipitation may be predominantly in organic form, amounting to an additional 2.5 kg ha^{-1} yr^{-1}. Little information exists for comparison with this organic N estimate, although *Hendry and Brezonik* [1980] in Florida and *Henderson and Harris* [1975] in Tennessee reported measurable quantities of organic N in bulk precipitation (5.7 and 3.7 kg ha^{-1} yr^{-1}, respectively).

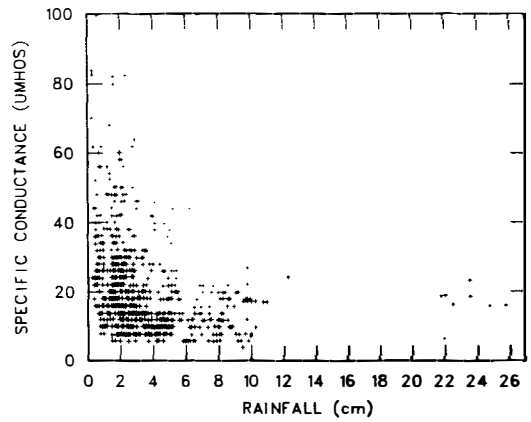

Fig. 3. Relationship between specific conductance and weekly rainfall at eight bulk precipitation collectors at the Santee Experimental Forest, South Carolina (1977–1979).

Calcium

Calcium in bulk precipitation has been attributed to terrestrial dust particulates and industrial fly ash, and its temporal variation has been related with agricultural activities during the growing season [*Gambell and Fisher*, 1966]. In the Francis Marion National Forest, unpaved roads commonly are surfaced with crushed limestone that supplies additional calcic particulates to the local atmosphere. Annual Ca^{2+} inputs averaged about 5.7 kg/ha over the 1977–1979 period. Monthly amounts of Ca^{2+} in bulk rainfall followed distinctly seasonal patterns with Ca^{2+} concentrations and inputs highest in summer months and lowest in winter months [*Richter*, 1980]. This pattern probably reflects the seasonal cycle of agricultural activity, the convectional characteristics of summer air masses, and also the low Ca^{2+} concentrations in winter storms from oceanic sources. Increased traffic on unpaved Forest Service roads in summer months may be an additional factor contributing to Ca^{2+} increases in this season. A major portion of Ca^{2+} in bulk precipitation solutions was probably from particulate fallout rather than from rainout or washout processes [*Hendry and Brezonik*, 1980], although deposition to the eight rain collectors at the Santee Forest were not related to distance from unpaved roads.

Potassium and Phosphate

Potassium and phosphate in bulk rain solutions are generally attributed to soil-derived particulates. Both were present in Santee bulk precipitation in low concentrations. Four-year volume-weighted concentrations of K^+ and PO_4^{3-}-P were 0.07 and 0.009 mg/l, respectively. Thus rainfall at the Santee Forest supplies minor quantities of these nutrients (0.94 and 0.12 kg ha^{-1} yr^{-1} of K^+ and PO_4^{3-}-P, respectively), a result in agreement with other studies in the eastern United States [*Likens et al.*, 1977; *Ralston*, 1978].

Large spatial variability, as given by coefficients of variation, was observed for inputs of PO_4^{3-} and K^+ (Table 2). Variation in ion inputs reflects local, spatial variability in deposition but is also affected by magnitudes of ionic concentrations in relation to bulk precipitation sampling errors and errors related to chemical analysis. Analytical sensitivity and reproducibility are especially critical for ions in lowest concentrations (e.g., K^+, PO_4^{3-}, and NH_4^+). For example, the arithmetic mean concentration of K^+ (0.10

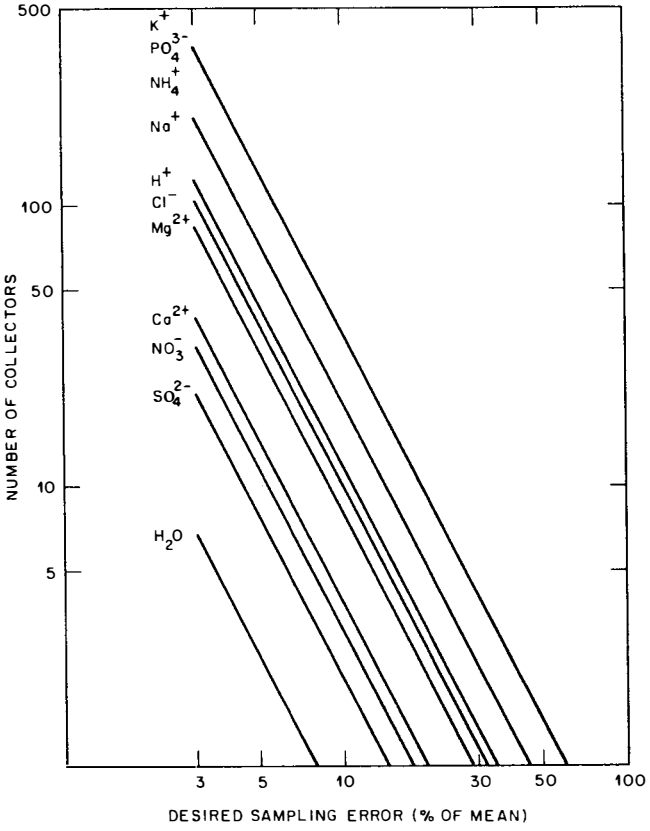

Fig. 4. Number of bulk precipitation collectors for sampling to given percentages of mean annual rainfall and ion input to a 500-ha watershed in the Santee Experimental Forest, South Carolina.

mg/l) was only twice the instrumental detection limit of 0.05 mg/l.

Control of Sampling Errors

The number of rainfall collectors required to make the width of 95% confidence intervals equal to various percentages of annual bulk precipitation inputs was calculated for the 10 ions. Sample size requirements were based on variation in annual inputs to the eight collectors (Table 2). The sample size equation is given by *Cochran* [1977] as

$$n = [tS/r\bar{Y}]^2 \quad (4)$$

where n is the required number of rain collectors, t is Student's t (usually taken as 2 for $\alpha = 0.05$), S is the estimated standard deviation, $\bar{Y}$ is the estimated mean input, and r is the desired relative error. Since $S/\bar{Y}$ is the coefficient of variation, i.e., sampling error as a proportion of the mean, the sample size equation used in this report is

$$n = \frac{t^2\, CV^2}{r^2} \quad (5)$$

Applying (5) to annual input estimates in Table 2 shows that the variability of certain ions is so large that it is necessary to accept broad confidence intervals for estimates of annual inputs to this 500-ha watershed. Using SO_4^{2-} and PO_4^{3-} data to illustrate ions with small and large sampling errors, five collectors should provide annual input estimates within confidence limits of about ±6.4 and ±28% of sample means for these nutrients, respectively ($P < 0.05$). Since quadrupling the sample size should reduce sampling errors by one half, a network of 20 collectors should narrow confidence limits for inputs of SO_4^{2-} and PO_4^{3-} to ±3.2 and ±14% of sample means, respectively. Figure 4 illustrates estimated sample size characteristics for the measured ions. Nineteen collectors should estimate annual bulk precipitation inputs for 7 of 10 ions within about ±10% of true inputs ($P < 0.05$). The other three ions (NH_4^+, PO_4^{3-}, and K^+) would require over 35 collectors to provide estimates of similar precision for this watershed.

It can be concluded that multicollector networks are necessary for even modestly precise estimates of bulk precipitation composition and that interpretations of bulk precipitation chemistry that are based on only a few collectors should be formulated cautiously. Because of the importance attributed to anthropic influences on atmospheric chemistry, greater consideration should be given to local variations in atmospheric depositions and their sampling errors.

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