

MONITORING AIR QUALITY AND ACIDDEPOSITION IN SOUTHERN U.S. FORESTS

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Abstract

Atmospheric monitoring capabilities were established in 1988 by the University of Florida at Duke forest, near Durham, NC; Cary forest, near Gainesville, FL; and Austin forest, near Nacogdoches, TX. Continuous (hourly averaged) measurements of air quality (ozone, nitrogen oxides and sulfur dioxide) and meteorological variables were made at these three low elevation (< 200 meters), rural locations in the southeastern U.S. for more than three years. During the same period at these sites wet and dry acid deposition samples were collected and analyzed on an event and weekly basis, respectively. The monitoring locations were selected to determine actual atmospheric exposure indices for southern pine species in support of on-site surrogate exposure chamber studies conducted by Southern Commercial Forest Research Cooperative (SCFRC) investigators.

Daily and quarterly averaged ozone maxima were higher (55 ppb) at the northernmost site in the network (Duke forest) in the second and third quarters (spring and summer seasons) and lower (35 ppb) in the first and fourth quarters (winter and fall seasons), when compared to ozone levels at the two southernmost sites (Cary and Austin forests). Seasonal ozone levels at the latter two sites were similar. Nitrogen oxides and sulfur dioxide levels were insignificant (< 5ppb) most of the time at all sites, although soil emissions of NO at two sites were found to influence nighttime ozone concentrations. Typical maximum quarterly and annual aggregate ozone exposure indices were significantly higher at Duke forest

(92.5/259 ppm-hr) than those values observed at the two southern sites (65.6/210 ppm-hr).

Acid deposition (wet and dry) components concentrations and deposition fluxes observed at the Duke forest, NC piedmont site, were generally greater, dependent on site and season, than corresponding variables measured at either of the two southern coastal plain sites (Cary and Austin forests). Acid deposition variables observed at the latter two sites were remarkably similar, both qualitatively and quantitatively, although the sites were located 1300 km apart. A comparison of deposition fluxes of elemental nitrogen (NO_3^- , NH_4^+) and sulfur (SO_4^{2-} , SO_2) components in wet and dry forms indicated that wet deposition accounts for approximately 70% of the total nitrogen and 73% of the total sulfur input on an annual equivalent basis at all sites.

Introduction

In the mid-1980s there was great concern for and speculation on the possible environmental effects of acidic deposition (primarily in the form of the strong acids, H_2SO_4 and HNO_3) on the forests of eastern North America. Much of this attention, however, was focused primarily on the northeastern U.S. and eastern Canada, where forest decline had been observed, particularly at higher elevations (>1000m). Some information on acid deposition was available for the southeastern U.S. but no long term comprehensive study of the region had been conducted to address the nature and possible effects of acid deposition on regional commercial forests (Garner et al. 1985). Likewise information was limited on rural air quality and atmospheric exposure indices for native pine trees in the region, that might indicate a major impact on the productivity of the regions principal industrial natural resource, southern pine forests. In the southwestern U.S. damage to pine trees had been attributed to exposure to high levels of ozone (> 100ppb), a phytotoxic air pollutant and major constituent of photochemical smog.

In response to these concerns, the Southern Commercial Forest Research Cooperative (SCFRC) was established in 1985, as part of the Forest Response Program (FRP) of the National Acid Precipitation Assessment Program (NAPAP), to address these issues. Controlled exposure chamber

studies were initiated by forestry researchers to study the effects of varying applications of ozone and/or simulated acid rain on the growth and health of southern pine seedlings. In support of these field studies, the Atmospheric Exposure Cooperative (AEC) branch of the FRP, sponsored by the U.S. Environmental Protection Agency (EPA), contracted with the University of Florida in 1987 to provide ambient air quality, meteorology and acid deposition monitoring support services at three of these SCFRC sites. The objectives of these proposed long-term monitoring activities were to provide reliable and representative on-site data on air quality, meteorology and wet and dry acid deposition and to identify typical and extreme exposures of trees at these sites to air quality and acid deposition variables. In addition, the monitoring data would allow SCFRC investigators to relate their exposure chamber studies and findings to realistic exposure situations.

Facilities for continuous monitoring of air quality and meteorological variables, as well as periodic collection of wet and dry acid deposition components were established by University of Florida (UF) researchers at Duke forest, near Durham, NC; Cary forest, near Gainesville, FL and Austin forest, near Nacogdoches, TX. All of these SCFRC sites were rural in nature and were low in elevation above mean sea level (amsl). Monitoring activities commenced October 1, 1987 at the North Carolina (NC) piedmont site and on July 1, 1988 at the Florida (FL) and Texas (TX) coastal plain sites. The Duke forest, NC site is the northernmost (36.02°N, 78.97°W; 152m amsl) site in the UF network, whereas the two southern sites, Cary forest, FL (29.75°N, 82.22°W; 48m amsl) and Austin forest, TX (31.52°N, 94.78°N; 70m amsl) are situated at similar latitudes, but are 1300 km apart, see Figure 1.

Air quality and meteorological variables were continuously measured and recorded by certified commercially available equipment. Certification of instruments against National Institute for Science and Technology (NIST) reference standards was provided by the manufacturers and maintained by quarterly internal auditing and annual external audits by U.S. EPA technicians or contractors. Measurement of acid deposition species involved collection of wet and dry deposition samples at the sites, preliminary on-site testing and shipment of these samples to the air pollution program laboratories at UF in Gainesville, FL, for chemical analyses. Chain of custody protocols were followed throughout. Field monitoring and air sampling data were transmitted electronically to the UF data management

center on a daily basis, where data acquisition, validation, assessment, analysis and reporting activities were carried out.

Methods

Field Techniques

A full time site operator was employed at each location to maintain, modify, calibrate and repair field equipment and collect samples for wet and dry deposition analysis. Identical equipment and instrumentation were set up at each site.

Continuous Monitoring

Ambient air was drawn through a glass manifold at 10 liters per minute (Lpm) and exhausted below the air-conditioned shelter that contained commercial air quality monitoring instrumentation. Thermo Environmental Corporation (TECo) equipment was used exclusively to continuously monitor ozone (TECo Model 49), sulfur dioxide (TECo Model 43A) and nitrogen oxides (TECo Model 14B/E). All of these analyzers sampled ambient air from the manifold at flow rates near 1 Lpm. Data from these analyzers were fed to a 16-channel data logger (Odessa Model DSM-3260) where they were processed to generate one hour average values and stored. The computer-controlled data logger system is also used to acquire, average, store and communicate data received from all continuous sensors (air quality analyzers, meteorological instruments and triple filter pack flow meters) as well as to perform a variety of equipment control functions. Daily calibration checks of the air quality instruments were performed automatically using a commercial multigas calibration system (TECo Model 146) and certified cylinder gases (SO₂/NO in N₂). Ozone standards were generated internally by the multigas calibration system. Meteorological sensors and signal processing equipment were obtained from Climatronics Inc (CI). Wind speed and direction sensors (CI Model F460) were mounted on top of a 10 m tilt-down mast. Air temperature sensors (CI Model 100093) were located inside blower units at 1 m and 8m above ground. A relative humidity sensor (CI Model 100098) was located inside the latter blower housing. Solar radiation was measured by a LiCor photovoltaic

pyranometer (CI Model 101655) and surface wetness by a Vaisala Model DRD-11 sensor, both of which were placed 1m above ground. Barometric pressure (CI Model 101458) was measured outside the shelter at 1.5 meters above ground. Precipitation was measured using a tipping-bucket rain gauge (CI Model 100097) in 0.01 inch increments. In case of power failure a battery powered back-up system was activated to service the rain gauge. Also, a mechanical Belfort weighing rain gauge provided supplemental precipitation data. Calibration checks of meteorological equipment were made using simulated signals to the meteorological signal conditioners.

Total suspended particle concentrations were determined for a 24 hour sampling period every sixth day using a high volume sampler (Anderson Model GMWS-2310) and gravimetric analysis. Some of these samples were analyzed for lead. Ambient particles in the size ranges 10-2.5 μm and < 2.5 μm were collected for 24 hours measured using a commercial dichotomous sampler (Anderson Model GMW-241) with a size selective inlet and microgravimetric analysis of the Teflon filters.

Wet deposition samples were collected on an event basis, usually >65% of the time, and less frequently on a multiple event or weekly basis. Automated wet-dry bucket collectors (Aerochem Metrics Model 301) were used for precipitation collection at all sites. Immediately following collection of rain samples, aliquots were analyzed on site for pH and conductivity using a solution analyzer (Markson Model 4603). A 250 ml aliquot of each event or weekly integrated sample was shipped under refrigeration in a cleaned high density polyethylene (HDPE) bottle with completed sampling forms to the analytical laboratory at the University of Florida.

Dry deposition samples were collected by drawing ambient air at a constant flow rate (2 Lpm) through inverted triple filter packs (TFPs) mounted inside a stainless steel hood that was attached to the top of a 10 m tilt-down mast. A triple filter pack consists of a Teflon holder, in which are mounted three 47 mm diameter filters in series that are separated by Teflon spacers. The filters in order of exposure to sampled air are: i) Teflon (Zefluor), ii) Nylon (Nylasorb) and iii) potassium carbonate-impregnated cellulose acetate (Schleicher and Schuell). Constant air flow through the filter packs was achieved by a mass flow controlled pumping system (Kurz Model 251-4A). A blank (no flow) triple filter-pack was used to determine the influence of stagnant ambient air on the sampling system over the 7 day integrated sampling period. System operational

checks are performed when filter packs are changed by the operator. Used filter packs are immediately shipped, in sealed containers with completed sampling forms, to the analytical laboratory at the University of Florida. General methods of measurement and quality control (QC) techniques followed when using commercial instrumentation in the field are described in detail elsewhere (U.S. EPA 1976-83, Allen and Sutton, 1991).

Laboratory Operations

Upon receipt of wet deposition samples at the UF analytical laboratory, aliquots of solution were taken for measurement of pH and conductivity. The remainder of the sample is filtered (0.45 μm pore Nalgene) and the filtrate stored at 4°C for later analysis. Conductivity and pH measurements were performed with a solution analyzer (Markson Model 4603). Flame and furnace atomic absorption measurements of alkali and alkaline earth metal ions (Na^+ , K^+ , Ca^{2+} , Mg^{2+}) and lead (Pb^{++}) were made with an automated commercial atomic absorption spectrophotometer (Perkin Elmer Mode 5100). Separation and quantitative analyses of inorganic anions (Cl^- , NO_3^- , SO_4^{2-} , HPO_4^{2-}) and selected inorganic cations (Na^+ , K^+ , NH_4^+) was achieved using an automated commercial micromembrane-suppressed ion chromatograph (Dionex Model 4000i) equipped with separate eluents and columns for anion and cation analyses using conductivity detection.

Dry deposition samplers received at the UF analytical laboratory were carefully dismantled and the separated filters were individually sonicated with either distilled water or ion chromatograph eluent solution ($\text{K}_2\text{CO}_3/\text{KHCO}_3$). The extracts were analyzed for SO_4^{2-} and NO_3^- anions using ion chromatography. General methods and QC protocols followed at the UF analytical laboratory for the detailed chemical analysis of precipitation and triple filter pack samples are described elsewhere (Allen and Sutton, 1991; Peden et al., 1986). Other laboratory activities included: providing cleaned and checked sample shipping containers, field standard and check solutions for field site pH and conductivity measurements, as well as preparing and shipping clean TFP samplers to each of the field sites.

Data Management

Data management center activities at the University of Florida consisted

of three principal operations: data acquisition, validation and reporting. Data acquisition procedures incorporated several levels of redundancy in order to minimize data loss. Validation of data consisted of a detailed review of site operator logs, on-site inspection forms, field calibration results, instrument zero/span checks, internal and external audits. In addition, a series of parameter specific range and consistency checks of the data were made and out-of-range or inconsistent data were noted for further inspection. The air quality and meteorological data bases were formatted into one page monthly summaries of hourly averages for each variable measured, see Tables 1 and 2. Wet deposition data were summarized on a monthly basis by precipitation events, collection efficiency, chemical analyses and estimates of wet deposition fluxes, see Table 3. Dry deposition reports consisted of calendar quarterly summaries of weekly averages of air flow, chemical analyses of filters and ambient acidic component concentration estimates, see Table 4.

Results and Discussion

Air Quality

Continuous measurements were made of the air pollutants ozone (O_3), nitrogen oxides (NO_x) and sulfur dioxide (SO_2) and meteorological variables using commercial instruments at Duke forest, NC commencing October, 1987 and at Cary forest, FL and Austin forest, TX sites commencing July 1988. Monitoring was terminated at Duke forest, NC and Austin forest, TX sites in June, 1990 and at the Cary forest, FL site in June, 1991. These data are reported as hourly averages. Monthly summaries of the data are available in Appendices Volumes I and II in the final report to U.S. EPA (Allen and Sutton, 1991).

Significant exposures to ozone were observed at all three rural monitoring locations. Daily average and daily maximum ozone concentrations for Duke forest, NC in 1988 and 1989 and Cary Forest, FL and Austin Forest, TX monitoring sites in 1989 are shown in Figure 2. The data obtained for each site exhibit the typical diurnal and seasonal cycles for ozone observations, see Figure 3. Daily and seasonally averaged hourly ozone concentrations at all three sites showed large diurnal fluctuations, from a nighttime low to a daytime high. Unlike urban and

high-elevation site O₃ concentration profiles, however, the leading edge of these rural O₃ profiles rises very rapidly after sunrise and reached a maximum value near 13:00 hours local standard time (LST), i.e. the maximum O₃ level occurred earlier in the day than in typical urban environments. In addition, a major fraction (>75%) of the maximum ozone generated daily was routinely attained by about 10:00 hours LST, when only 20% of the total daily solar radiation had been received. Previous observations of vertical ozone profiles (Cavender and Allen, 1991) in a north central Florida forest suggested that the early morning ozone increase in a rural setting is a result of downward vertical mixing and advection following break-up of an overnight surface radiation inversion layer, see Figure 4. Disruption of the stable surface layer is indicated by the onset of winds in excess of 1 m s⁻¹ and rapid air and delta temperature changes after sunrise. Thus, less than 25% of the total daily ozone observed at these rural sites may be a result of local photochemistry.

High levels of nitric oxide (NO) were occasionally observed at night at two sites (Duke forest, NC; Cary forest, FL) when O₃ concentrations were depleted below 2 ppb during nighttime boundary layer inversions. A systematic examination of all possible local anthropogenic sources, including site activities and mobile sources, led to the conclusion that NO was emitted from the soil at these locations. This conclusion was subsequently substantiated (Kardono, 1990) by measurements made at Cary forest, FL in the summer of 1990, that showed typical soil emissions of the order 4 kgNO/ha-yr. during a three month summer study. These continuous emissions could rapidly reduce nighttime O₃ levels in the stable inversion layer, that are normally depleted by diffusion to surfaces.

Seasonal variations in hourly ozone averages at SCFRC sites, as shown in Figure 3, indicate that the highest seasonal values (55 ppb) for O₃ occurred during the second calendar quarter (spring season) at the more northerly piedmont site (Duke forest, NC), and the lowest values were observed also at Duke forest, in the fourth and first quarters (fall and winter seasons). Seasonally averaged O₃ values for Cary forest, FL and Austin forest, TX, however, were quite similar. The latter rural coastal plain sites are located at about the same latitude (30°N) but are separated by 1300 km. Furthermore, the largest seasonal differences in hourly averaged O₃ values were observed at the Duke forest, NC site. Both the Cary forest, FL and Austin forest, TX sites showed only small differences in seasonal diurnal

averages from winter to spring seasons and much lower seasonal average ozone values than those observed at the northern site in the second and third quarters (spring and summer seasons) despite higher average seasonal temperatures and similar solar radiation intensities.

Forest effects researchers are particularly interested in aggregate ozone exposures values at rural forest sites. Such values have been reported as annual and 'growing' season 24-hour (total), 12-hour (daytime: 07:00 to 18:59 hours LST) and 7-hour (optimum daylight: 09:00 to 15:59 hours LST) aggregate values. The latter parameters may be more important because the mode of attack of ozone on trees probably occurs through stomatal conductance, which is enhanced by solar radiation. Knowledge of 24-hour average and aggregate O₃ values is probably of greater value in photochemical modeling applications than in estimating pollutant stress on trees. Statistical analyses of ozone data for 24-hour, 12-hour and 7-hour quarterly and annual averages and aggregate exposure values for the three sites are presented in Table 5.

Concurrent air quality monitoring of ambient nitrogen oxides and sulfur dioxide have shown conclusively that exposure to these pollutants at the rural locations studied pose no threat or stress to trees or vegetation at the concentration levels observed. Sulfur dioxide concentrations were equal to or less than 2 ppb (the instrument detection limit) more than 95% of the time and nitrogen dioxide (NO₂) concentrations were less than 10 ppb more than 90% of the time. The former observations were confirmed by TFP measurements, that indicated annual average SO₂ concentrations of 1.4, 0.5 and 0.3 ppb at the Duke, Cary and Austin forest sites, respectively.

Quarterly and annual averaged concentration estimates of total suspended particles (< 50 μm diam.) and size-fractionated particles (2.5 to 10 μm and < 2.5 μm diam.) are presented in Table 6, together with estimates of airborne lead associated with total suspended particulate matter. Note that lower concentrations of particles are observed in 1989 than in 1988 at Duke forest, NC corresponding to increased precipitation in 1989.

Wet Deposition

One of the primary objectives in establishing the atmospheric exposure monitoring network was to generate long term data on wet deposition fluxes at these rural forest monitoring sites in the southeastern U.S. Of particular

interest were the seasonal and annual fluxes of hydrogen (H^+), ammonium (NH_4^+), sulfate (SO_4^{2-}) and nitrate (NO_3^-) ions. Wet deposition fluxes in equivalents per hectare (eq/ha) were determined from estimates of volume-weighted average concentrations in micrograms per liter ($\mu g/L$), total wet deposition in decimeters (dm) for the averaging period of observation and the equivalent weights of the ions in micrograms per microequivalent ($\mu g/\mu eq$).

It was evident from the precipitation data obtained that, on an event basis, the highest ion concentrations were associated with the smallest quantities of precipitation, particularly, but not necessarily always, after a long dry period. This observation confirms previous reports (Sisterson et al., 1990) that most of the ion deposition occurs in the early stages of an event from "rain-out" of acidic cloud water; and that volume-weighting between precipitation samples is necessary in order to account for dilution of cloud water components in larger precipitation events. Quarterly (seasonal) and annual summaries of volume-weighted wet deposition ion concentrations are presented in Table 7 for the three SCFRC sites and corresponding seasonal and annual wet deposition flux data are presented in Table 8.

The higher concentrations of components in precipitation at Duke Forest, NC in 1988 relative to 1989 were a reflection of the much larger precipitation amounts received in 1989 (61.3 in.) versus 1988 (37.9 in.). It is interesting to note, however, that despite the lower annual average concentrations found in 1989 compared to 1988, higher ion deposition fluxes were found in 1989 compared to 1988, due to the much greater amount (62% greater) of precipitation in 1989, which more than offset the lower volume-weighted concentrations observed that year.

Annual average values for H^+ were highest at the Duke forest site (46 $\mu eq/L$, 2 yr average), but were similar at the Cary forest, FL and Austin forest, TX sites (33 $\mu eq/L$, 2 site average). Also, it is interesting to note that the annual average H^+ concentration was 25% higher in 1988 (51.1 $\mu eq/L$) than for 1989 (41.3 $\mu eq/L$) at the Duke forest site. Similar differences (25%) for annual NO_3^- and SO_4^{2-} concentrations were observed at the latter site when 1988 and 1989 data were compared. The highest seasonal concentration values for H^+ , SO_4^{2-} and NO_3^- at Duke forest occurred in the second quarter (April, May, June) of 1988 ($H^+ = 90.5$; $NO_3^- = 43.0$ and $SO_4^{2-} = 98.7 \mu eq/L$). However, the highest seasonal concentrations of H^+ ($\sim 40 \mu eq/L$) observed at the southern sites of the

network in Florida and Texas occurred in the third quarter (July, August, September), but this was not necessarily the case for both NO_3^- and SO_4^{2-} concentrations. Such observations suggest that the absolute seasonal quantities of H^+ , NO_3^- and SO_4^{2-} wet deposited at all of these sites were a strong function of the quantity of precipitation received at the site.

Ammonium (NH_4^+) concentrations observed at Duke forest were approximately 40% higher than those found at the Cary forest, FL site and 10% higher than at the Austin forest, TX site, in 1989. A significantly higher annual average NH_4^+ concentration was observed at Duke forest, NC in 1988 than in 1989. The highest seasonal concentrations of NH_4^+ were observed at all sites in the second quarter (April, May, June) and could be a result of enhanced biological activity, nitrogen and fertilizer application to soils and/or animal waste decomposition during this period.

Higher annual average concentrations of Na^+ and Cl^- were found at the two southern coastal plain sites in Florida and Texas, than at the northernmost piedmont site in North Carolina. However, annual average K^+ concentrations were similar but small at all sites. The highest seasonal concentrations of Na^+ and Cl^- were found during the first quarter (January, February, March) at the Cary forest, FL site and during the second quarter (April, May, June) at the Austin forest, TX site. These observations suggest that there was a significant marine contribution to precipitation at these locations during those periods. In most cases the Na^+/Cl^- annual equivalence ratio varied from 1.5 at the Duke and Cary forest sites to 0.8 at the Austin forest site. The latter site was influenced by unusually high values for Na^+ and Cl^- during the spring (second quarter) of 1989 and generally higher annual average concentrations than at the other sites, suggesting a strong maritime influence from the Gulf of Mexico.

Absolute annual equivalent ratios of Ca^{2+} and Mg^{2+} varied with season and location but the equivalence ratios $\text{Ca}^{2+}/\text{Mg}^{2+}$ (2.27, std. dev. \pm 0.16) were essentially constant and independent of the observing site. Because these ions are presumably soil derived, such observations might be expected.

Poor correlations were found between total anion and total cation equivalents, if all ions were taken into account, at all sites. However good correlations were obtained if the sum of the cations H^+ , NH_4^+ , Na^+ and K^+ were compared with the sum of the anions NO_3^- , Cl^- and SO_4^{2-} . Exclusion of Mg^{2+} and Ca^{2+} from ion balances suggests that these components may have been inadvertently measured by atomic absorption spectrophotometry as

soluble ions although they may have existed in particulate form. Significant quantities of the organic acid anions, formate ($20 \mu\text{eq/L}$) and acetate ($10 \mu\text{eq/L}$) were found in precipitation samples analyzed specifically for these species. Inclusion of the latter species in material balance estimates reduced total ion balance discrepancies to less than 10%.

Dry Deposition

Previous investigations (Edgerton et al., 1991) of dry deposition have indicated that the input of acidic components from the atmosphere to lithosphere/hydrosphere systems by this mechanisms occurs at a rate which is comparable to that for wet deposition. As a consequence dry deposition monitoring was carried out at the three SCFRC sites in conjunction with wet deposition, air quality and meteorological observations.

The triple filters packs (TFPs) used for dry deposition sampling in this study were identical to those employed in the U.S. EPA-sponsored National Dry Deposition Network (NDDN), except that ambient air was sampled at 2.0 standard liters per minute (SLpm). Ambient air sampling at flow rates up to 10 Lpm does not appear to affect dry deposition results (Kim and Allen, 1996). Nitrate (NO_3^-) and Sulfate (SO_4^{2-}) quantities found in Teflon filter extracts were assumed to result from water soluble components of fine particles ($< 5 \mu\text{m}$) collected by the filter and are referred to as particulate nitrate (p- NO_3^-) and particulate sulfate (p- SO_4^{2-}). Similarly, NO_3^- and SO_4^{2-} in aqueous extracts from the Nylon filter were attributed to accumulation of HNO_3 vapor and SO_2 on the filter, respectively. Extracts of K_2CO_3 impregnated cellulose acetate filters containing SO_4^{2-} and NO_3^- were assumed to result from accumulation of SO_2 and NO -respectively on the treated filter. Weekly averaged, concentration estimates of dry deposition species in ambient air were obtained from these chemical analyses and the total volume of air sampled. In order to estimate dry deposition fluxes from concentration measurements it was necessary to identify suitable deposition velocities for the species of interest. In this study deposition velocities of 0.2 cm s^{-1} for p- SO_4^{2-} and p- NO_3^- ; 0.4 cm s^{-1} for SO_2 and NO_2 and 2.0 cm s^{-1} for HNO_3 were arbitrarily selected after reviewing the literature. Seasonally and annually averaged concentrations of dry deposition components observed in ambient air at the three sites in the network are presented in Table 9. Corresponding estimates of dry acid deposition component fluxes are shown

in Table 10.

The highest levels of sulfur components ($p\text{-SO}_4$ and SO_2) in the ambient air were observed at the northernmost site, Duke forest, NC. This result coupled with wet deposition and air quality observations suggested an important influence of local sources as well as regional long range transport and transformation of sulfur compounds from industrialized and heavily populated regions of the mid western U.S. Also, the highest $p\text{-SO}_4/\text{SO}_2$ ratios at the Duke forest site occurred in the third quarter of 1988 (4.4) and the lowest (0.48) in the fourth quarter of 1989. These observations suggest that enhanced conversion of SO_2 to $p\text{-SO}_4$ occurred during the higher temperatures and solar radiation intensities available during the summer months. The higher annual dry deposited sulfur in 1989 did not reflect the much higher precipitation, but similar solar radiation, amounts received at the site in 1989 relative to 1988. At neither of the southern sites in the network did the $p\text{-SO}_4/\text{SO}_2$ ratio fall below unity, although maximum values were observed in the third quarter (summer season) of the year. It is also interesting to note that $p\text{-NO}_3$ concentrations found at Duke forest, NC were significantly lower than those observed at the southern sites, although HNO_3 concentrations were at least 40% greater at the former site. It is possible that total atmospheric particulate nitrate may have been underestimated at all sites, because $p\text{-NO}_3$ is presumably associated with larger particles that would not have been collected efficiently by the invested filter packs at the low flowrates employed.

Conclusions

Air Quality

Continuous measurements of ozone, nitrogen oxides and sulfur dioxide have been made at three rural forest sites in the southeastern U.S. Significant exposures (≥ 24 ppb) to ozone were observed at all sites. At one site, Duke forest, NC several exceedances of the National Ambient Air Quality Standard (120 ppb) were observed in the summer of 1988 that could be attributed to the occurrence of a stagnating high pressure system over the eastern U.S. A detailed discussion of air quality variables in the southeastern U.S. is available elsewhere (Allen and Gholz, 1995). Concentrations of nitrogen oxides (NO or NO_2) exceeded 10 ppb less than

10% of the time. Also, SO₂ concentrations exceeded 2 ppb, the instrument detection limit, less than 5% of the time. These measurements were confirmed by triple filter pack measurements that indicated annual average SO₂ concentrations of 1.4, 0.5 and 0.3 ppb at Duke, Cary and Austin forest sites, respectively, and annual average NO₂ concentrations in the range from 0.3 to 0.5 ppb at all sites.

Wet Deposition

Wet deposition ion fluxes have been determined for three rural forest sites in the southeastern U.S, although the wet deposition data obtained may not be representative of a typical year at these sites. Annual volume-weighted average concentrations for major cations and anions were similar (within 20%) for 1988 and 1989, yet precipitation amounts i.e. at Duke forest, NC, were much less in 1988 than 1989. Thus, we conclude that wet deposition fluxes at these locations are mainly a function of the annual quantity of precipitation rather than being due to large changes in individual ion concentrations.

At all sites, sulfate (SO₄²⁻) ion concentrations alone could account for hydrogen (H⁺) ion concentrations observed in wet deposition. Also, concentrations of ammonium (NH₄⁺) ions were similar to equivalent concentrations of nitrate (NO₃⁻) ions. The equivalence ratio of SO₄²⁻/NO₃⁻ was approximately 2.2. In general, it appears that the annual wet deposition fluxes of hydrogen ions and the major anions (NO₃⁻ and SO₄²⁻) at Duke forest, NC were approximately 90 and 75% greater, respectively, than corresponding values observed at the two southern sites in the network, indicating that a more polluted atmosphere exists at the former location. Annual volume-weighted concentrations and wet deposition fluxes of these species at the latter sites were remarkably similar and could be typical of the region, with the fluxes depending mainly upon the quantity of precipitation received at a specific location.

Dry Deposition

Dry deposition fluxes have been estimated for particulate sulfate (p-SO₄), particulate nitrate (p-NO₃), nitric acid vapor (HNO₃) and sulfur dioxide (SO₂) using standardized procedures for collecting dry deposition

components. Concentrations of the dry acid deposition components p-SO₄, HNO₃ and NO₂ at the Duke forest, NC site were at least 40% greater than those observed at the Cary forest, FL and Austin forest, TX sites in 1989. These dry deposition measurements, in conjunction with much higher sulfate levels found in wet deposition, suggest that the airshed of the northernmost site in the network was influenced more by local and regional industrial and population sources than those for the two southern sites.

Ratios of p-SO₄/SO₂ and total airborne sulfur compounds observed at network sites suggested rapid conversion of SO₂ to p-SO₄ during the summer months but increased energy use in the region of the northernmost site in winter, in contrast to the summer for the two southern sites. The former could be a result of winter heating requirements whereas the latter is possibly a consequence of seasonal cooling demands.

Estimates of the relative contributions of wet and dry deposition components at the three monitoring sites are presented in Table 11. Based on the deposition velocities used, the largest contribution to dry deposition of nitrogen components is that by nitric acid vapor, whereas particulate sulfate and sulfur dioxide make approximately equal and significant contributions to the annual dry deposition of sulfur components. A comparison of the deposition fluxes of elemental nitrogen (NO₃) and sulfur (SO₄²⁻, SO₂) components in wet and dry forms indicated that wet deposition accounts for approximately 53% (70% including NH₄⁺) of the total nitrogen and 73% of the total sulfur components on an annual equivalent basis at all sites in 1989.

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Table I. Typical summary reporting form for one month of hourly averaged ozone (air quality) data.

DAY	1-HOUR DATA LISTING																								DAILY MEAN	NO.	
	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23			
1	16	15	13	12	10	10	9	10	10	11	10	12	15	19	20	20	22	25	25	28	28	24	21	27	23	17	24
2	29	21	14	11	10	7	9	10	13	18	23	27	37	44	42	37	29	23	15	13	9	10	11	20	24	20	24
3	11	10	9	7	8	9	9	10	13	21	22	23	25	27	28	35	37	33	14	7	5	4	9	10	16	24	
4	10	11	10	6	3	2	4	8	17	25	36	40	39	39	43	45	46	49	34	30	33	29	22	16	25	24	
5	10	4	1	1	1	1	3	10	16	19	21	23	24	24	25	29	32	34	25	12	27	32	20	17	24	24	
6	8	3	1	1	1	1	1	6	11	15	20	23	27	29	29	28	26	21	9	4	1	0	0	0	11	24	
7	18	33	22	16	10	14	18	24	31	28	30	28	42	60	54	43	35	30	28	20	17	15	18	28	24	28	24
8	23	21	20	22	23	23	22	25	34	41	47	52	61	69	49	56	56	55	35	20	12	9	17	21	33	24	
9	18	17	11	5	2	1	1	11	36	55	65	68	69	69	66	65	65	60	34	18	16	12	8	4	32	24	
10	2	2	1	1	1	1	1	6	29	57	68	69	68	75	75	55	48	33	22	13	10	13	10	9	28	24	
11	9	8	9	6	4	5	14	28	41	53	63	66	69	68	71	72	68	48	28	18	19	13	6	3	33	24	
12	2	2	2	2	2	2	2	10	33	49	57	56	57	57	55	47	30	22	16	14	13	10	8	25	24	24	
13	5	3	3	2	2	2	2	9	34	51	59	60	61	61	61	59	54	38	25	12	8	6	6	6	26	24	
14	3	4	3	2	2	2	3	7	9	29	52	65	71	68	59	53	54	55	51	30	15	8	3	2	27	24	
15	2	2	1	1	1	1	1	5	16	31	45	53	50	46	42	34	32	40	24	14	11	11	6	2	20	24	
16	1	1	1	3	2	3	2	11	27	47	63	66	69	68	72	76	65	47	23	17	19	16	10	6	30	24	
17	5	2	1	1	1	1	1	10	21	34	38	45	53	43	44	40	42	30	20	12	4	2	2	3	19	24	
18	2	1	1	1	1	1	2	9	16	26	40	43	45	50	53	52	41	28	14	16	16	13	6	3	21	24	
19	1	1	1	1	1	1	1	8	15	21	29	33	38	46	50	49	45	36	21	13	15	18	21	15	20	24	
20	9	4	5	3	2	1	1	5	14	20	26	36	39	33	35	42	50	36	16	8	3	3	5	7	17	24	
21	6	6	5	2	1	1	1	7	21	36	41	43	46	49	52	55	55	35	20	8	5	5	3	4	21	24	
22	4	2	1	1	1	1	1	7	26	34	44	49	45	43	44	40	28	15	29	21	15	8	4	1	19	24	
23	1	1	1	1	1	1	1	1	26	28	26	44	44	44	44	44	44	39	29	16	14	16	16	17	22	22	
24	22	19	9	4	2	1	1	6	13	19	26	29	25	28	27	26	24	18	12	4	3	4	2	1	14	24	
25	4	6	2	2	3	3	2	6	16	25	32	40	42	44	42	40	38	33	19	12	11	6	3	3	18	24	
26	1	2	1	1	1	0	1	6	16	43	56	64	56	54	56	43	30	19	10	4	3	1	0	1	20	24	
27	1	1	1	1	1	1	1	6	23	31	38	47	48	50	53	52	35	21	12	7	8	6	3	3	21	24	
28	2	2	1	1	1	1	1	11	20	24	34	45	54	59	83	55	51	36	23	13	7	8	14	22	24	24	
29	14	12	7	4	1	1	1	6	12	18	26	38	43	51	56	56	41	29	19	22	13	9	9	8	22	23	
30	15	12	10	1	1	1	1	11	25	36	48	55	56	56	59	68	71	55	28	21	13	14	10	5	29	23	
31	3	2	1	1	1	1	1	7	17	25	30	35	38	45	52	54	46	29	13	12	16	25	18	21	24	24	
AVG.	8	7	5	4	3	3	4	10	21	31	40	44	46	48	49	48	45	36	24	15	12	11	10	9	22	740	
NO.	31	31	30	31	31	31	31	31	31	31	31	31	31	31	31	31	31	31	31	31	31	31	31	31	31	740	
MAX	29	33	22	23	23	22	28	41	57	68	69	71	75	83	76	71	60	51	30	33	29	32	27	83	0	0	
MIN	1	1	1	1	1	0	1	5	9	15	20	23	24	24	25	26	24	15	9	4	1	0	0	0	0	0	0

State: Texas
 County: Macopdoches
 Site Name: Austin Forest
 Location: Macopdoches, TX 85U
 Operation: University of Florida
 Funding: USEPA
 Network: AEC/SCFRC/FRP

OZONE CONCENTRATION IN PARTS PER BILLION
 INSTRUMENTAL - U. V. PHOTOMETRIC
 DURING : August 1989

Site Number: 48-34-7-0003
 Observer: PBM
 Latitude: 31:30:30 N
 Longitude: 94:46:27 W
 Elevation: 70 m amsl
 Date Printed: July 25, 1990

Table 2. Typical summary reporting form for one month of hourly averaged air temperature (meteorology) data

DAY	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	DAILY MEAN	NO.
1	6.0	5.8	5.7	5.7	5.8	6.0	6.5	7.6	10.0	13.0	15.4	16.2	16.3	16.6	16.4	16.3	15.7	14.1	13.1	12.2	11.8	11.3	10.8	10.3	11.2	24
2	9.6	9.5	9.3	8.7	8.6	9.1	8.7	8.9	10.1	11.6	12.8	14.0	15.2	15.7	15.8	15.8	14.9	12.6	9.4	8.5	8.7	8.7	7.6	5.6	10.8	24
3	4.2	3.1	2.4	1.5	0.9	0.3	0.0	1.1	5.2	8.8	12.0	14.0	15.4	16.4	16.7	16.8	14.9	11.4	10.0	8.6	7.4	6.7	6.1	5.9	7.9	24
4	5.6	5.4	5.2	4.6	4.3	5.0	6.0	7.4	10.3	13.3	17.1	18.7	19.0	18.5	17.7	16.7	16.4	15.9	15.8	15.3	16.0	17.1	17.4	12.7	24	
5	17.8	18.5	19.0	19.3	19.8	19.8	20.1	20.4	21.0	21.7	22.6	23.7	24.0	24.8	23.6	23.3	23.4	23.7	22.8	22.4	21.8	20.2	20.5	20.5	21.4	24
6	20.9	21.3	21.5	21.4	21.3	20.9	20.0	20.0	21.8	23.5	24.8	26.2	27.9	28.8	28.5	28.1	27.2	25.4	23.1	21.7	21.2	21.4	21.6	21.6	23.3	24
7	21.5	21.7	21.8	22.0	22.1	22.1	22.4	22.4	22.7	23.3	24.2	24.8	25.3	26.0	26.3	26.2	24.9	23.1	22.0	21.9	22.0	22.4	23.1	22.8	23.2	24
8	22.4	22.6	22.7	22.9	22.8	22.4	21.4	21.5	23.4	25.0	26.8	27.2	29.0	29.6	28.5	26.6	23.6	21.4	20.3	19.1	17.8	16.7	14.7	12.1	23.3	24
9	11.8	9.2	7.7	6.7	6.0	4.3	3.2	3.9	8.8	13.7	16.8	18.8	20.4	21.8	22.6	21.6	16.3	12.8	10.6	8.9	7.8	7.1	6.3	12.1	24	
10	5.5	4.7	4.2	3.6	3.3	3.0	2.9	4.0	8.3	11.4	16.6	20.7	25.1	25.3	25.5	22.4	17.8	15.1	14.3	12.6	11.0	9.9	9.3	12.5	24	
11	8.4	7.9	7.3	6.4	5.8	5.1	4.7	5.1	9.2	16.0	19.9	22.8	23.5	25.3	25.6	25.7	23.1	17.9	15.9	14.1	12.4	12.0	11.2	10.4	14.0	24
12	10.3	10.0	9.1	8.4	8.0	8.7	9.8	10.6	12.0	15.2	20.6	23.6	24.3	24.6	24.8	24.8	23.5	19.7	17.8	17.0	16.6	16.4	14.8	14.3	16.0	24
13	14.2	13.4	13.9	14.9	15.4	15.6	15.8	16.3	17.0	17.5	19.3	20.9	22.8	24.3	24.6	23.9	23.1	21.6	19.7	18.4	17.7	17.1	16.7	16.6	18.4	24
14	16.5	16.9	17.1	17.4	18.0	18.5	19.0	19.6	20.8	22.8	24.5	26.5	27.0	28.2	28.5	28.5	27.5	25.5	22.5	21.1	21.5	22.2	22.1	22.6	22.3	24
15	22.8	22.6	21.7	21.6	21.6	21.8	22.0	22.2	22.6	20.7	19.4	19.7	19.8	19.4	19.0	19.0	15.0	13.9	12.9	12.4	11.6	10.2	9.0	16.3	22	
16	7.6	6.2	5.9	3.5	2.2	3.2	4.7	4.8	6.2	7.0	7.6	8.8	9.8	10.2	10.8	10.5	9.7	6.4	3.9	2.3	0.9	-0.2	-1.1	-1.8	5.4	24
17	2.0	-2.4	-2.2	-1.9	-1.4	-1.2	0.0	2.4	4.9	7.0	8.6	9.2	9.6	10.0	9.8	9.2	8.6	8.5	8.5	8.6	8.9	8.4	7.8	4.9	24	
18	6.7	6.3	6.0	6.0	6.3	6.6	6.9	7.2	7.7	8.6	9.8	10.7	11.3	11.6	11.8	11.7	11.2	10.5	9.8	9.5	9.8	9.4	8.2	7.8	8.8	24
19	7.4	6.9	6.2	6.0	6.0	6.3	7.0	7.6	10.1	11.8	13.4	15.1	15.9	16.6	16.8	16.5	16.4	15.4	14.6	14.5	13.5	12.7	12.8	12.9	11.8	24
20	13.1	13.4	13.5	13.7	13.8	13.7	13.7	14.0	14.6	15.9	17.0	17.8	18.8	19.8	19.8	19.9	19.9	19.7	18.9	18.2	17.9	17.7	17.6	17.6	16.6	24
21	17.6	17.5	17.5	17.4	17.4	17.5	17.7	17.8	18.2	18.3	19.0	19.9	21.2	21.6	21.4	21.2	20.3	19.3	18.9	18.6	18.5	18.4	18.4	18.2	18.8	24
22	18.4	18.5	18.8	18.6	18.4	18.6	18.8	18.7	18.5	18.4	18.3	18.1	17.9	17.5	14.4	12.9	12.7	11.9	10.6	9.3	8.2	7.1	6.5	5.5	14.9	24
23	4.3	3.4	2.6	1.8	0.9	0.3	0.0	0.4	2.6	4.6	6.1	7.2	8.5	9.8	10.4	10.7	9.6	6.0	3.9	2.5	1.6	1.0	0.5	0.4	4.1	24
24	-0.3	-0.6	-0.4	-0.4	-0.5	-0.4	-0.3	0.4	3.1	7.1	10.7	12.8	14.4	15.7	16.6	16.6	15.6	14.2	12.7	12.2	12.8	13.3	13.6	13.8	8.4	24
25	13.8	13.8	13.6	13.5	13.5	13.6	13.7	14.1	14.8	16.5	19.6	21.1	22.1	22.9	23.2	23.1	22.2	19.8	19.5	20.2	20.2	19.9	19.4	18.6	18.0	24
26	17.8	17.6	17.8	18.2	18.1	18.2	18.3	18.4	19.5	21.2	23.2	24.8	26.2	26.1	26.6	26.4	25.1	21.9	20.4	19.4	18.8	18.6	19.2	19.7	20.9	24
27	20.2	20.2	20.2	20.1	20.0	19.8	19.9	19.7	20.8	22.3	23.4	24.8	25.9	26.8	26.2	25.8	24.3	21.0	17.7	16.5	15.2	16.7	17.1	21.0	24	
28	16.0	14.4	13.3	12.2	11.2	10.4	9.1	8.4	8.9	9.9	11.0	12.2	13.2	13.8	14.1	13.2	12.5	11.3	10.4	9.9	9.5	8.6	7.8	7.3	11.2	24
29	6.9	6.8	6.7	6.6	6.4	5.9	5.3	5.0	5.3	6.0	7.2	8.1	8.4	8.9	8.7	8.5	8.0	6.0	4.1	3.7	3.5	3.0	2.3	1.8	6.0	24
30	0.9	0.0	-0.5	-1.5	-2.0	-2.2	-1.9	-0.8	1.6	3.6	5.8	6.7	7.1	7.6	7.9	7.8	6.7	5.4	4.9	4.9	5.0	5.0	5.2	5.1	3.4	24
AVG.	11.5	11.2	10.9	10.6	10.5	10.4	10.5	10.9	12.6	14.5	16.4	17.8	18.8	19.4	19.5	19.2	18.2	16.0	14.5	13.7	13.2	12.7	12.4	12.0	14.0	718
NO.	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	29	30	30	30	30	30	30	30	30	30
MAX	22.8	22.6	22.7	22.9	22.8	22.4	22.1	22.4	23.4	25.0	26.8	27.2	29.0	29.6	28.5	27.5	25.5	23.1	22.4	22.0	22.4	22.0	22.4	23.1	22.8	29.6
MIN	-2.0	-2.4	-2.2	-2.2	-2.0	-2.2	-1.9	-0.8	1.6	3.6	5.8	6.7	7.1	7.6	7.9	7.8	6.7	5.4	3.9	2.3	0.9	-0.2	-1.1	-1.8	-2.4	

1-HOUR DATA LISTING

State: Texas
 County: Nacogdoches
 Site Name: Austin Forest
 Location: Nacogdoches, TX BSU
 Operation: University of Florida
 Funding: USEPA
 Network: AEC/SCFRC/FRP

TEMPERATURE
 CONCENTRATION IN DEGREES CELSIUS
 INSTRUMENTAL - THERMISTOR
 DURING : November 1989

Site Number: 48-347-0003
 Observer: PBM
 Latitude: 31:30:30 N
 Longitude: 94:46:27 W
 Elevation: 70 m asl
 Date Printed: October 23, 1990

Table 3. Typical summary reporting form for one month of precipitation collection and analysis data.

Atmospheric Exposure Cooperative Precipitation Chemistry Data
Southern Commercial Forest Research Cooperative, Forest Response Program
Month: July 1988

State:	North Carolina	Number:	37-063-9001
County:	Durham	Observer:	RDP
Site:	Duke Forest, SC-1	Latitude:	36:01:30 N
Location:	Durham, NC SWNW	Longitude:	78:58:30 W
Operation:	University of Florida	Elevation:	152 m amsl
Funding:	USEPA	CAL Code:	12-030-K
Network:	AEC/SCFRC/FRP	Date Printed:	December 17, 1990

SAMPLING															
----- Event ----- Collection -----															
Event No.	Start Date	Stop Date	Precip (in)	On Date	On Time	Off Date	Off Time	Vol L	Depth cm	Rain Gage cm	Coll Eff	Field Obs. Code	Lab Type	Notes	
				07/01	13:00	07/08	14:00	--	--	--	--	000000		NO EVENT	
1	07/10 17:00	07/10 19:00	0.08	07/08	15:00	07/11	12:57	0.165	0.25	0.20	1.24	010000	w	SC-33-39 (046)	
2	07/12 14:00	07/13 00:00	0.75	07/11	13:30	07/13	18:10	1.366	2.08	1.91	1.09	010000	w	SC-33-40 (048)	
3	07/21 09:30	07/22 05:00	0.58	07/13	09:30	07/22	12:25	1.089	1.66	1.47	1.13	010000	w	SC-33-41 (057)	
4	07/22 13:00	07/22 14:00	0.03	07/22	12:30										
5	07/23 13:00	07/23 15:00	0.07			07/25	12:30	0.189	0.29	0.25	1.13	010000	w	SC-33-42 (058)	
6	07/25 14:00	07/25 15:00	0.02	07/25	12:45	07/26	09:35	0.047	0.07	0.05	1.41	010400	w	SC-33-43 (060)	
7	07/26 19:00	07/27 01:00	0.44	07/26	10:00	07/27	08:00	0.769	1.17	1.12	1.05	010000	w	SC-33-44 (061)	
8	07/27 14:00	07/28 08:10	0.62*	07/27	08:15	07/28	08:10	1.012	1.54	1.57	0.98	010000	w	SC-33-45 (062)	

Total Events = 8 Total Precip = 2.59 Sample Totals = 4.637 7.07 6.58 1.08 No. Samples = 7
 * EST from Belfort (power fail)
 Precip. Fraction Analyzed (%) = 100.0

Sample ID No.	pH			Conductivity			ANALYSIS									
	Lab	Field	Check	Lab	Field	Check	Ca	Mg	K	Na	NH4	NO3	Cl	SO4	HPO4	H
SC-33-39	3.30	3.27	4.28	240.0	237.0	25.5	5.030	0.900	0.100	1.020	2.783	9.248	1.380	25.320	BDL	0.501
SC-33-40	4.27	4.24	4.50	27.1	30.2	15.0	0.696	0.171	0.009	0.387	0.319	1.254	0.224	2.767	0.042	0.054
SC-33-41	4.29	4.30	4.51	25.6	26.9	14.9	0.757	0.190	0.018	0.406	0.178	1.191	0.237	1.339	0.019	0.051
SC-33-42	3.93	3.91	4.50	57.8	55.6	15.0	2.082	0.531	0.050	1.142	BDL	2.063	0.582	3.660	0.027	0.117
SC-33-43	SAMPLE TOO SMALL						NONE CONDUCTED									
SC-33-44	3.86	3.86	4.50	66.7	71.7	15.0	0.892	0.222	0.051	0.432	0.738	2.246	0.385	6.304	0.028	0.138
SC-33-45	4.24	4.17	4.50	27.6	34.3	15.1	0.599	0.160	0.028	0.338	0.186	0.872	0.169	2.801	0.018	0.058

Monthly Volume Weighted Average Concentration (mg/L) : 0.935 0.223 0.027 0.442 0.402 1.642 0.298 3.876 0.027 0.087

Monthly Wet Deposition (Kg/ha) : 0.593 0.141 0.017 0.281 0.255 1.042 0.189 2.459 0.017 0.055

Cumulative Monthly Wet Deposition (Kg/ha) : 4.489 1.089 0.353 2.237 2.609 11.084 2.216 20.074 0.550 0.388

N S P M

Monthly Wet Deposition (Kg/ha) : 0.434 0.820 0.005 0.069

Cumulative Monthly Wet Deposition (Kg/ha) : 4.557 6.687 0.177 0.530

Table 4. Typical summary reporting form for one calendar quarter of dry deposition collection and analysis data.

UF/AEC/SCFRC DRY DEPOSITION CHEMISTRY DATA SUMMARY
 FOURTH QUARTER OF 1989
 (FROM OCT. 04, 1989 TO JAN. 03, 1990)

State: North Carolina
 County: Durham
 Site Name: Duke Forest, SC-1
 Location: Durham, NC SWNW
 Operation: University of Florida
 Funding: USEPA
 Network: AEC/SCFRC/FRP

Site Number: 37-063-9001
 Observer: DA
 Latitude: 36:01:30 N
 Longitude: 78:58:30 W
 Elevation: 152 m
 CAL. CODE: 12-030-K
 Date Printed: NOV. 10, 1990

FILTER PACK ID #	DATE/TIME DATE/TIME OFF	TRIPLE TFP OPERATION			TEFLON				NYLON				WHATMAN				NOTES
		MEAN (1pm)	VALID (hrs)	TOTAL (m3)	ANALYSIS (CONCEN.) (ug) (ug)		ANALYSIS (CONCEN.) (ug) (ug)		ANALYSIS (CONCEN.) (ug) (ug)		ANALYSIS (CONCEN.) (ug) (ug)						
BB-33-1-83	100489 15:27	0.00	168.8	0.00	BDL	28.39	NA	NA	4.70	3.43	NA	NA	5.38	BDL	NA	NA	*
	101189 16:15																
DD-33-1-83	100489 15:27	2.02	168.8	20.41	BDL	83.02	BDL	4.07	41.25	17.35	2.02	0.85	9.90	125.9	0.49	6.17	
	101189 16:15																
DN-33-1-83	100489 15:27	0.00	168.8	0.00	BDL	BDL	NA	NA	5.23	3.10	NA	NA	5.15	BDL	NA	NA	**
	101189 16:15																
BB-33-1-84	101189 16:19	0.00	167.0	0.00	BDL	BDL	NA	NA	4.78	1.58	NA	NA	6.35	BDL	NA	NA	*
	101889 15:11																
DD-33-1-84	101189 16:19	2.01	167.0	20.11	8.02	129.3	0.40	6.43	44.65	16.73	2.22	0.83	10.83	8.78	0.54	0.44	
	101889 15:11																
DN-33-1-84	101189 16:19	0.00	167.0	0.00	BDL	1.82	NA	NA	5.15	0.25	NA	NA	5.33	BDL	NA	NA	**
	101889 15:11																
BB-33-1-85	101889 15:14	0.00	167.2	0.00	BDL	BDL	NA	NA	3.90	1.78	NA	NA	BDL	BDL	NA	NA	*
	102589 14:23																
DD-33-1-85	101889 15:14	2.02	167.2	20.31	BDL	36.09	BDL	1.78	22.80	12.25	1.12	0.60	10.25	49.00	0.50	2.41	
	102589 14:23																
DN-33-1-85	101889 15:14	0.00	167.2	0.00	BDL	BDL	NA	NA	4.55	2.15	NA	NA	BDL	BDL	NA	NA	**
	102589 14:23																
BB-33-1-86	102589 14:25	0.00	169.1	0.00	BDL	0.46	NA	NA	5.88	3.05	NA	NA	6.08	BDL	NA	NA	*
	110189 15:30																
DD-33-1-86	102589 14:25	2.02	169.1	20.46	6.97	137.9	0.34	6.74	48.55	18.35	2.37	0.90	11.58	52.98	0.57	2.59	
	110189 15:30																
DN-33-1-86	102589 14:25	0.00	169.1	0.00	BDL	0.57	NA	NA	6.13	3.10	NA	NA	5.10	BDL	NA	NA	**
	110189 15:30																
BB-33-1-87	110189 15:35	0.00	169.3	0.00	BDL	0.17	NA	NA	4.95	1.75	NA	NA	5.18	BDL	NA	NA	*
	110889 16:55																
DD-33-1-87	110189 15:35	2.01	169.3	20.37	BDL	103.4	BDL	5.08	49.95	15.63	2.45	0.77	11.33	114.3	0.56	5.61	
	110889 16:55																
DN-33-1-87	110189 15:35	0.00	169.3	0.00	BDL	25.48	NA	NA	5.23	2.68	NA	NA	BDL	BDL	NA	NA	**
	110889 16:55																

NOTE :
 BDL= Below Detection-Limit
 NA= Not Applicable
 * 1 Week Blank
 ** 24 hr Day (DD) Filter Sampling Only

Table 5. Summary of ozone exposure statistics at three UF/SCFRC sites in 1987-89.

Site	Quarter/Year	24-Hour		12-Hour		7-Hour	
		Average (ppb)	Aggregate (ppm-hr)	Average (ppb)	Aggregate (ppm-hr)	Average (ppb)	Aggregate (ppm-hr)
Duke Forest, NC	4/87	21	45.6	27	29.7	33	21.5
	1/88	24	52.4	30	32.8	33	20.8
	2/88	42	92.5	57	61.9	62	39.5
	3/88	34	75.2	49	53.9	55	35.7
	4/88	18	38.9	24	26.1	29	18.7
	Annual 1988	30	259	40	175	45	115
	1/89	22	48.1	26	28.9	29	18.7
	2/89	37	81.6	50	54.2	54	34.6
	3/89	29	64.9	41	45.4	47	30.3
	4/89	20	44.9	27	29.5	32	20.6
Annual 1989	27	240	36	158	41	104	
Cary Forest, FL	3/88	20	43.5	30	32.8	33	21.3
	4/88	21	45.6	30	33.1	36	23.4
	1/89	23	49.7	31	33.8	35	22.2
	2/89	30	65.6	43	47.4	48	30.4
	3/89	22	49.3	35	38.3	39	25.4
	4/89	20	45.0	29	32.4	35	22.3
	Annual 1989	24	210	35	152	39	100
	Austin Forest, TX	3/88	24	52.3	35	38.7	30
4/88		21	47.1	29	32.0	33	21.0
1/89		24	52.7	29	31.7	31	19.6
2/89		27	58.2	37	40.4	40	25.7
3/89		22	47.8	35	38.2	40	26.0
4/89		23	50.1	31	34.3	36	23.2
Annual 1989		24	209	33	145	37	95

12-Hour values from 07:00 to 18:59 hours (LST)

7-Hour values from 09:00 to 15:59 hours (LST)

Aggregates - Sum of hourly averaged concentrations in exposed period

- Quarter - Meteorological season -
1. January, February, March
 2. April, May, June
 3. July, August, September
 4. October, November, December

Table 6. Quarterly and annual averages for total suspended particles (TSP), size fractionated particles (SFP) and airborne lead concentrations at two UF/SCFRC sites in 1987-89.

Site	Qtr/Yr	TSP $\mu\text{g}/\text{m}^3$	SFP ($\mu\text{g}/\text{m}^3$)		Lead $\mu\text{g}/\text{m}^3$
			Coarse	Fine	
Duke, NC	4/87	27.4	---	---	0.025
	1/88	28.0	14.1	21.7	0.028
	2/88	46.6	17.8	19.6	0.024
	3/88	45.1	11.1	19.1	0.023
	4/88	25.0	10.0	14.6	0.020
	Annual	1988	36.2	13.3	18.8
Duke, NC	1/89	26.3	4.3	9.2	0.020
	2/89	22.0	10.7	15.8	0.019
	3/89	32.0	6.7	13.1	0.026
	4/89	19.1	6.8	10.6	0.022
	Annual	1989	24.4	7.1	12.2
Cary, Fl	4/88	22.3	11.9	14.7	0.021
	1/89	25.6	8.2	9.9	0.022
	2/89	23.9	9.5	12.3	0.018
	3/89	25.2	7.7	10.6	0.022
	4/89	16.9	6.9	10.3	0.023
	Annual	1989	22.9	8.1	10.8

Note: Qtr/Yr - Quarter/Year
 Quarter = Meteorological season - 1. January, February, March
 2. April, May, June
 3. July, August, September
 4. October, November, December

TSP - Total suspended particulate matter

SFP - Size fractionated particles

Coarse - Particles having aerodynamic diameters in range 2.5 to 10 micrometers

Fine - Particles having aerodynamic diameters less than 2.5 micrometers

$\mu\text{g}/\text{m}^3$ - Micrograms per cubic meter

Table 7. Summary of quarterly and annual volume-weighted wet deposition components concentrations at three UF/SCFRC sites in 1987-89.

Site	(Qtr/Yr) ²	Precip (cm)	Specie Concentration (mg/L) ¹						
			Na ⁺	NH ₄ ⁺	H ⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	
Duke Forest, NC	4/87	23.1	0.51	0.14	0.014	0.71	0.71	1.31	
	1/88	14.5	0.61	0.37	0.046	0.68	1.50	2.56	
	2/88	27.9	0.38	0.63	0.091	0.36	2.67	4.74	
	3/88	32.0	0.50	0.26	0.039	0.42	0.89	2.02	
	4/88	21.6	0.21	0.10	0.025	0.29	0.79	1.09	
	Annual	1988	96.0	0.42	0.34	0.051	0.42	1.44	2.64
Duke Forest, NC	1/89	36.8	0.35	0.28	0.034	0.52	1.17	1.98	
	2/89	41.4	0.38	0.39	0.052	0.39	1.38	2.55	
	3/89	44.2	0.48	0.24	0.047	0.30	1.22	2.21	
	4/89	33.3	0.37	0.15	0.029	0.29	0.86	1.63	
	Annual	1989	155.7	0.40	0.27	0.041	0.38	1.17	2.12
Cary Forest, FL	3/88	73.7	0.52	0.11	0.021	0.35	0.62	1.16	
	4/88	14.7	0.37	0.07	0.020	0.67	0.48	1.16	
	1/89	10.2	0.87	0.23	0.025	1.08	0.86	1.80	
	2/89	37.1	0.42	0.30	0.029	0.59	1.13	1.79	
	3/89	46.7	0.46	0.16	0.038	0.33	1.02	1.58	
	4/89	15.7	0.44	0.07	0.013	0.64	0.39	0.90	
	Annual	1989	109.7	0.49	0.20	0.030	0.53	0.93	1.55
	Austin Forest, TX	3/88	21.3	0.54	0.16	0.023	0.41	1.03	1.39
4/88		32.3	0.48	0.25	0.025	0.68	0.63	1.12	
1/89		44.7	0.43	0.20	0.028	0.63	0.78	1.58	
2/89		52.3	0.55	0.28	0.024	0.66	0.89	1.38	
3/89		17.0	0.41	0.16	0.043	0.79	0.78	1.73	
4/89		13.7	0.41	0.24	0.025	0.51	0.69	1.47	
Annual		1989	127.7	0.48	0.23	0.028	0.65	0.82	1.51

¹ mg/L = milligrams per liter

² Qtr/Yr = Quarter/ Year

Quarter = Meteorological season - 1. January, February, March

2. April, May, June

3. July, August, September

4. October, November, December

Table 8. Summary of quarterly and annual averaged deposition fluxes of major ions in precipitation at three UF/SCFRC sites in 1987-89.

Site	(Qtr/Yr) ³	Na ⁺	Wet Deposition (kg/ha-qr) ²				
			NH ₄ ⁺	H ⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻
Duke Forest, NC	4/87	1.11	0.30	0.033	1.57	1.60	2.96
	1/88	0.89	0.53	0.067	1.00	2.18	3.74
	2/88	1.07	1.81	0.265	1.03	7.86	13.86
	3/88	1.70	0.87	0.123	1.41	2.96	6.73
	4/88	0.50	0.20	0.051	0.67	1.62	2.33
Annual (kg/ha-yr)	1988	4.16	3.41	0.506	4.11	14.6	26.7
Duke Forest, NC	1/89	1.29	1.04	0.125	1.94	4.31	7.33
	2/89	1.56	1.61	0.212	1.60	5.77	10.61
	3/89	2.18	1.08	0.208	1.34	5.39	9.74
	4/89	1.21	0.51	0.084	0.99	2.88	5.43
Annual (kg/ha-yr)	1989	6.24	4.24	0.629	5.87	18.4	33.1
Cary Forest, FL	3/88	3.87	0.78	0.155	2.59	4.58	8.59
	4/88	0.54	0.11	0.103	0.99	0.71	1.69
	1/89	0.90	0.23	0.025	1.09	0.87	1.83
	2/89	1.57	1.12	0.108	2.20	4.21	6.67
	3/89	2.16	0.77	0.176	1.55	4.79	7.40
	4/89	0.69	0.11	0.021	1.01	0.62	1.42
Annual (kg/ha-yr)	1989	5.32	2.23	0.330	5.85	10.5	17.3
Austin Forest, TX	3/88	1.16	0.35	0.049	0.89	2.24	3.00
	4/88	1.56	0.82	0.087	2.27	2.05	3.67
	1/89	1.93	0.90	0.126	2.83	3.50	7.04
	2/89	2.89	1.47	0.126	3.47	4.68	7.25
	3/89	0.70	0.27	0.072	1.35	1.35	2.97
	4/89	0.56	0.33	0.034	0.70	0.95	1.99
Annual (kg/ha-yr)	1989	6.08	2.97	0.358	8.35	10.5	19.3

¹ kg/ha-qr = kilograms per hectare per quarter

² kg/ha-yr = kilograms per hectare per year

³ Qtr Yr = Quarter/Year

Quarter = Meteorological season - 1. January, February, March

2. April, May, June

3. July, August, September

4. October, November, December

Table 9. Summary of quarterly and annual averaged concentrations of dry acid deposition components concentrations in ambient air at three UF/SCFRC sites in 1987-89.

Site	(Qtr/Yr) ²	Concentration ($\mu\text{g}/\text{m}^3$) ¹					
		p-SO ₄	p-NO ₃	HNO ₃	SO ₂	NO ₂	
Duke Forest, NC	1/88	2.40	0.46	1.74	4.14	0.16	
	2/88	5.38	0.39	3.26	2.86	0.57	
	3/88	6.95	0.33	2.88	1.58	0.93	
	4/88	2.15	0.28	1.30	2.48	0.27	
	Annual 1988	4.22	0.37	2.30	2.77	0.48	
Duke Forest, NC	1/89	4.02	0.19	3.35	6.79	0.35	
	2/89	6.31	0.09	2.47	2.18	0.50	
	3/89	5.97	0.17	1.87	1.24	0.58	
	4/89	3.87	0.27	2.18	8.07	0.25	
	Annual 1989	5.04	0.18	2.47	4.57	0.42	
Cary Forest, FL	3/88	2.70	0.59	1.29	1.86	0.46	
	4/88	3.16	0.89	1.85	1.03	0.31	
	1/89	3.31	1.12	2.01	1.11	0.30	
	2/89	3.93	0.96	1.67	1.27	0.38	
	3/89	3.88	0.48	1.35	1.00	0.34	
	4/89	2.67	0.74	1.29	1.44	0.27	
	Annual 1989	3.45	0.83	1.58	1.21	0.32	
	Austin Forest, TX	3/88	4.72	0.36	2.15	1.68	0.85
		4/88	2.48	0.52	2.10	0.92	0.34
1/89		3.22	0.69	2.27	0.63	0.27	
2/89		3.84	0.84	1.87	0.62	0.27	
3/89		4.84	0.40	1.35	0.50	0.36	
4/89		3.21	0.56	1.48	1.53	0.26	
Annual 1989		3.78	0.62	1.74	0.82	0.30	

¹ $\mu\text{g}/\text{m}^3$ = micrograms per cubic meter

² Qtr/Yr = Quarter/ Year

Quarter = Meteorological season -

1. January, February, March
2. April, May, June
3. July, August, September
4. October, November, December

Table 10. Summary of estimated annual average fluxes of dry acid deposition components at three UF/SCFRC sites in 1988-89.

Site	Year	Deposition Flux (kg/ha-yr)				
		p-SO ₄	p-NO ₃	HNO ₃	SO ₂	NO ₂
Duke Forest, NC	1988	1.17	0.10	8.63	6.91	1.19
	1989	1.40	0.05	9.40	11.4	1.05
Cary Forest, FL	*1988	0.41	0.10	2.91	1.80	0.48
	1989	0.95	0.24	6.25	3.02	0.85
Austin Forest, TX	*1988	0.50	0.06	3.95	1.62	0.74
	1989	1.01	0.17	7.14	2.04	0.87

¹ kg/ha-yr = kilograms per hectare per year

² * = 6 month (July - December) deposition

³ p-SO₄ = particulate sulfate

⁴ p-NO₃ = particulate nitrate

⁵ HNO₃ = nitric acid vapor

⁶ SO₂ = sulfur dioxide

⁷ NO₂ = nitrogen dioxide

Table 11. Comparison of sulfur (kg S/ha-yr) and nitrogen (kg N/ha-yr) wet and dry deposition flux estimates to a grass surface at three UF/SCFRC sites in 1988-89.

Year	Site	Wet Deposition		Dry Deposition		Total Deposition kg/ha-yr	
		kg/ha-yr	(% Total)	kg/ha-yr	(% Total)		
1988	Duke Forest - S	8.90	(70%)	3.85	(30%)	12.75	
	- N	5.95	(72%)	2.30	(28%)	8.25	
	*Cary Forest - S	3.43	(77%)	1.04	(23%)	4.47	
	- N	1.89	(70%)	0.80	(30%)	2.69	
	*Austin Forest - S	2.22	(69%)	0.98	(31%)	3.20	
	- N	1.88	(63%)	1.12	(37%)	3.00	
	1989	Duke Forest - S	11.0	(64%)	6.17	(36%)	17.20
		- N	7.45	(75%)	2.42	(25%)	9.87
Cary Forest - S		5.77	(76%)	1.83	(24%)	7.60	
- N		4.10	(71%)	1.24	(29%)	5.80	
Austin Forest - S		6.43	(83%)	1.36	(17%)	7.79	
- N		4.68	(71%)	1.88	(29%)	6.57	

¹ kg/ha-yr = kilograms per hectare per year

² * = 6 month (July - December) deposition

³ S wet = SO_4^{2-}

⁴ S dry = p- SO_4 + SO_2

⁵ N wet = NO_3^- + NH_4^+

⁶ N dry = p- NO_3 + HNO_3 + NO_2

SO_4^{2-} - Sulfate ion (wet only)

p- SO_4 - particulate sulfates

SO_2 - sulfur dioxide

NO_3^- - nitrate ion (wet only)

p- NO_3 - particulate nitrate

HNO_3 - nitric acid vapor

NO_2 - nitrogen dioxide

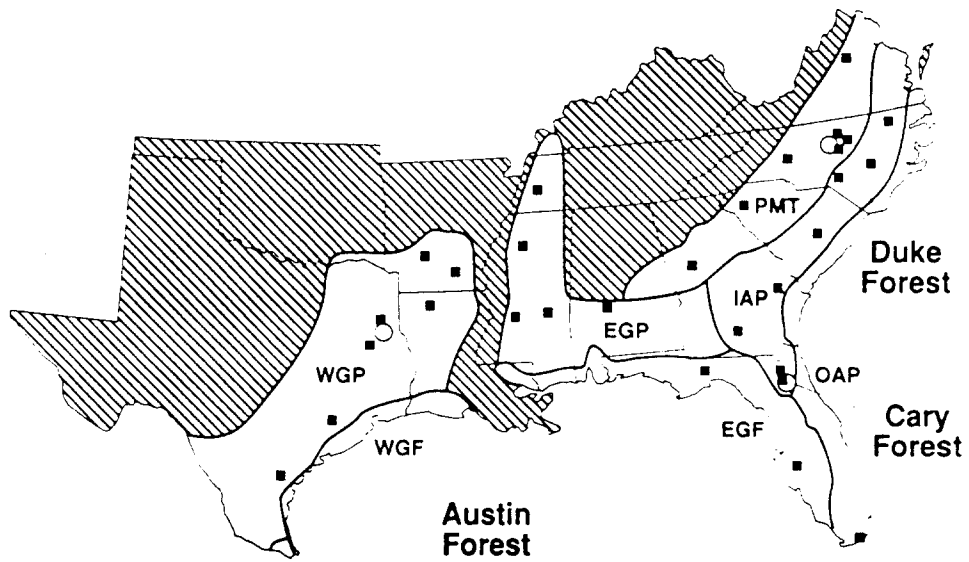


Figure 1. Map showing physiographic regions and locations of three UF/SCFRC monitoring sites.

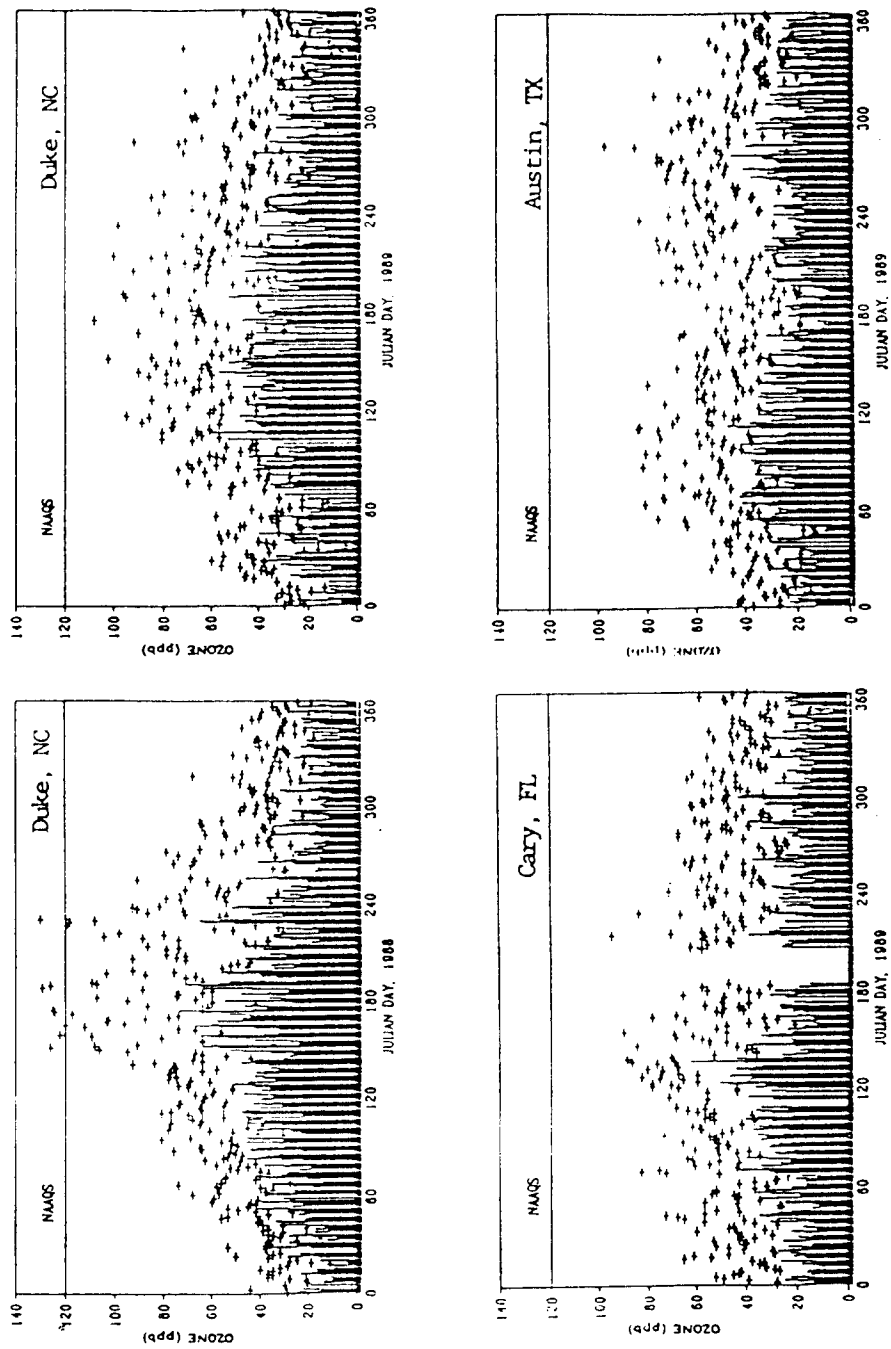


Figure 2. Daily ozone averages (bars) and maximum (crosses) at three UF/SCFRC sites in 1988-89.

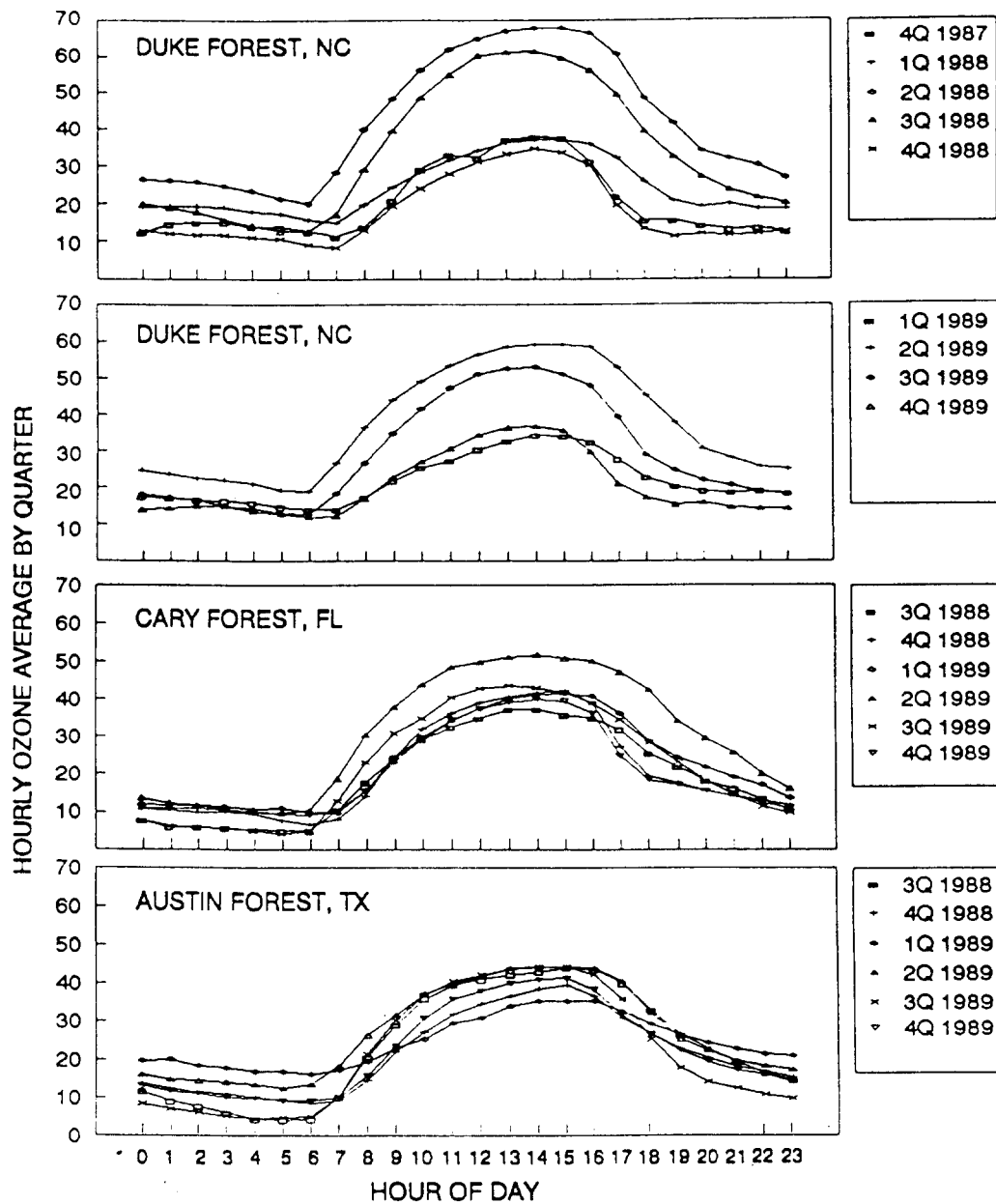


Figure 3. Seasonal (quarterly) averaged diurnal distributions of hourly ozone values at three UF/SCFRC sites in 1988-89.

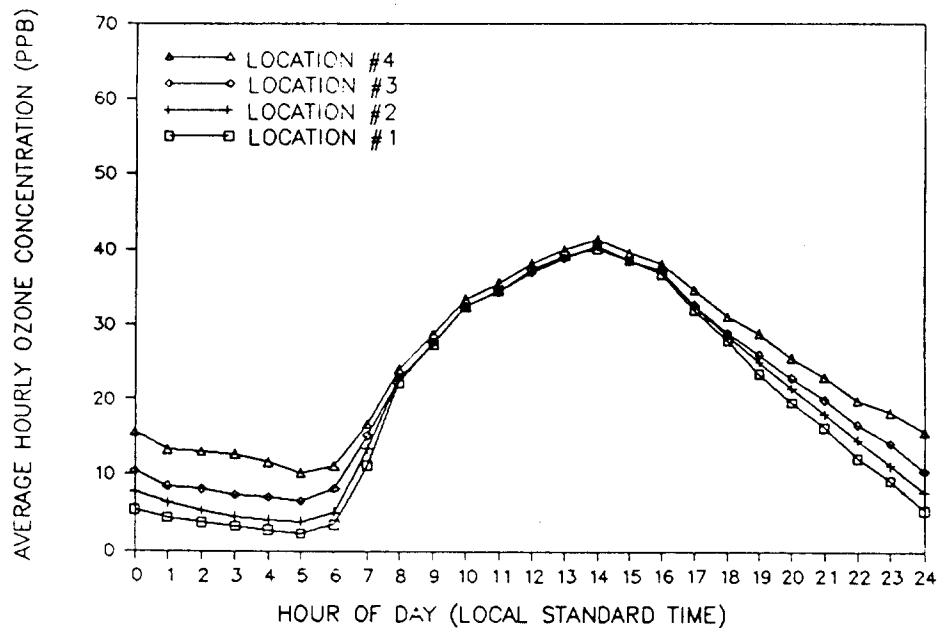


Figure 4. Simultaneously measured vertical profiles of monthly averaged ozone concentrations at Cary forest, FL in July 1988 at (1) 3m above ground, (2) 10m above ground, bottom of canopy; (3) 17m above ground, top of canopy; and (4) 27m above ground, 10m above canopy.