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MEASUREMENTS AND ANALYSIS OF REACTIVE NITROGEN SPECIES IN THE RURAL TROPOSPHERE OF SOUTHEAST UNITED STATES: SOUTHERN OXIDANT STUDY SITE SONIA

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Abstract—Ambient concentrations of reactive nitrogen compounds as well as total NO_x were measured during June and early July 1992 at a rural site, site SONIA, in the central Piedmont region of North Carolina as a part of the Southern Oxidants Study. The measurements of reactive nitrogen species were made in an effort to provide a comprehensive understanding of nitrogen chemistry and to investigate the total nitrogen budget at the site. NO_y, NO₂ and NO showed diurnal variations with maxima in the morning between 0600 and 0900 EST. The maximum NO_y concentration reached was ~14.5 ppbv, and the maximum concentrations of NO and NO₂ were 5.4 and 7.8 ppbv, respectively. The mean NO_y mixing ratio was found to be 2.88 ± 1.58 ppbv (*n* = 743) with an average daily maximum of 3.6 ppbv. The mean mixing ratios of NO and NO₂ were found to be 0.15 ± 0.29 ppbv (*n* = 785) and 1.31 ± 0.99 ppbv (*n* = 769). Average daily maxima of NO and NO₂ were 0.4 and 2.0 ppbv, respectively. HNO₃ and PAN showed diurnal variation with maxima in the afternoon and minimum in the night, and mean mixing ratios were found to be 0.67 ± 0.33 ppbv (*n* = 250) and 0.40 ± 0.24 ppbv (*n* = 578). The fractions of individual reactive nitrogen species to total NO_y were investigated and contrasted to the results from a remote marine site and rural continental sites. As in two other rural continental sites in the U.S., NO_x was found to be the most abundant constituent (~45%) of NO_y; while HNO₃ was the most abundant compound in NO_y measured at a remote marine site. The discrepancy between the NO_x partitioning at site SONIA and the marine site is attributed to the influence of local and regional anthropogenic sources of NO_x and the continental origin of the majority of air masses encountered at the site. The NO_x/NO_y ratio and NO₂ (= NO_y – NO_x) were used as an indicator of the chemical age of airmasses. The NO_x/NO_y ratio showed strong positive correlations with the photochemical oxidants HNO₃ (*r* = 0.76), PAN (*r* = 0.68) and O₃ (*r* = 0.79) measured at the site. Positive correlations were found between surface wind direction and both the magnitude of NO_y and the NO_x/NO_y ratio. These correlations suggest that synoptic meteorological conditions and transport of NO_y are important in the distribution of NO_y and its relationship with photochemical oxidants at the site. The ozone production efficiency was illustrated by correlation of O₃ and NO₂ and compared with other published measurements made in the Southeast U.S., and published results from a 3D Eulerian model simulation.

Key word index: Reactive nitrogen species, atmospheric budget, ozone, oxidants, modeling.

INTRODUCTION

Recent experiments and model calculations indicate that reactive species of oxides of nitrogen, NO_x (NO_x = NO + NO₂), play an important role in the photochemistry of the troposphere. They participate not only in the acidification of precipitation but also in the formation of tropospheric ozone.

Throughout these reactions, the concentration of NO_x plays an important role in the distribution of O₃ and the radical balance in the troposphere. The primary pollutant, NO, is ultimately oxidized to HNO₃ which is removed from the atmosphere by wet

and dry deposition. Organic peroxy and hydroperoxy radicals are responsible for much of the oxidation of NO to NO₂. In the lower troposphere, O₃ is formed by photochemical processes involving the oxidation of nonmethane hydrocarbons (NMHCs) in the presence of NO_x. While the NMHCs are consumed in these processes, NO_x acts as a catalyst. The only known photochemical reaction in the troposphere that produces ozone is the photolysis of NO₂ yielding atomic oxygen (O(³P)), and its subsequent combination with O₂ to produce NO and ozone. For net ozone production to occur, the NO₂ has to be produced from NO by species other than ozone itself. Thus, the oxidation of NO by ozone and the photolysis of the resultant NO₂ yields no net change in ozone, i.e. the photostationary state. However, the peroxy

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radicals (i.e. HO₂ and/or RO₂) produced as intermediates in hydrocarbon oxidation also can oxidize NO to NO₂ and yield net ozone production. Thus, the characterization of the levels of NO_x is essential to the understanding of tropospheric photochemistry in NO_x limited environments.

In the lower atmosphere, oxides of nitrogen are emitted primarily from anthropogenic processes such as combustion of fossil fuels and biomass burning (Logan, 1983). In rural/remote areas, however, natural processes that exhibit spatial and temporal variability such as soil emission (Slemr and Seiler, 1984; Williams *et al.*, 1987; Johansson and Sanhueza, 1988; Kim *et al.*, 1994), and lightning strikes (Borucki and Chameides, 1984) may be significant sources for atmospheric NO_x. Anthropogenic sources are generally confined to small geographic areas and can be well defined. On the other hand, natural sources of NO_x are more widespread and less intense, making quantitative estimation much more difficult (Williams *et al.*, 1992).

NO_x lifetime in the troposphere ranges from less than a day in summer at mid-latitudes to several days in the absence of active photochemistry (Logan, 1983; Liu *et al.*, 1987). NO_x is converted into other organic and inorganic nitrogen species such as nitric acid (HNO₃), peroxyacetyl nitrate (PAN), other organic nitrates, nitrate radical (NO₃[·]), and particulate nitrate (NO₃⁻) via photochemistry in the atmosphere. These odd-nitrogen species have relatively longer lifetimes than NO_x and some may eventually regenerate NO_x in the troposphere by thermal decomposition or photolytic reaction. Interconversion of NO_x into other odd-nitrogen species, therefore, can be an effective mechanism for the long-range transport of reactive oxidized nitrogen to remote regions (Crutzen, 1979; Singh and Hanst, 1981).

Most of the tropospheric nitrogen species are assumed to be present as NO, NO₂, HNO₃, PAN, and NO₃⁻ (Atlas *et al.*, 1992; Ridley, 1991; Fahey *et al.*, 1986). Measurements of these species in rural and remote environments have, however, indicated the presence of an odd-nitrogen deficit (Aneja *et al.*, 1994). That is, the sum of the concentrations of the individually measured species do not add up to the concentration of NO_y (= NO_x + HNO₃ + PAN + HNO₂ + NO₃⁻ + organic nitrates) measured by total NO_y instruments. It has been suggested that unidentified odd-nitrogen species, organic nitrates, for instance, may be present in significant enough quantities to account for the odd-nitrogen deficit. For example, Fahey *et al.* (1986) measured individual NO_y species and total reactive nitrogen, NO_y, at a high elevation remote site. The sum of the five individual species (NO, NO₂, HNO₃, PAN, NO₃⁻) accounted for only 55% of the total NO_y during the summer months. The odd-nitrogen shortfall also showed seasonal variations displaying a minimum during the fall months and a maximum during the summer months. NO_y measurements during the Mauna Loa Observatory Photochemistry Experiment showed the mass contri-

bution of the individual NO_y species measured accounted for ~75% of the total NO_y (Atlas *et al.*, 1992), and contribution of the individual species to total NO_y at other rural/remote sites have ranged from 58% to 93% (Fahey *et al.*, 1986; Buhr *et al.*, 1990; Ridley, 1991; Hübner *et al.*, 1992).

In this paper, the partitioning of the major nitrogen species to total NO_y and the balance between the primary nitrogen species, NO_x, and total reactive nitrogen are investigated at a Southern Oxidant Study (SOS), Southeastern Regional Oxidant Network (SERON), enhanced chemistry site SONIA (Southeast Oxidants and Nitrogen Intensive Analysis). This is a rural site near Candor, NC, which is located in the central Piedmont region of North Carolina.

These observational results are important because the regional distribution of NO_y within the rural South is relatively unknown (SOS Report, 1994), and modeling results seem to suggest that in rural areas of the South production of ozone in the planetary boundary layer is NO_x limited.

The temporal variation in the composition of NO_y is also examined and compared to that reported for other measurement sites, and published results from a 3D Eulerian model simulation. Additionally, an observational based analysis is performed to explore the relationship between the composition of NO_y with both photochemistry and meteorology. Because site SONIA is indicative of a typical rural setting throughout much of the Southeast U.S. (being colocated to a National Dry Deposition Network (NDDN) site which is designated as rural), it is hoped that the analysis and discussion of the NO_y measurements made at site SONIA may shed light on the regional characteristics of reactive nitrogen species in the Southeast U.S.

EXPERIMENTAL

Air Quality group of North Carolina State University operates an enhanced chemistry site, site SONIA in the central Piedmont region of North Carolina (32.26°N, 79.84°W, ~170 m MSL). Measurements of a number of species, i.e. NO, total NO_y, SO₂, CO, O₃, particulates, and meteorological data were measured year round at the site or at the adjacent NDDN site. From 6 June to 7 July 1992, an intensive measurement period was operated where NO₂, PAN, H₂O₂, HNO₃, and speciated NMHCs were also monitored. Figure 1 shows a map of the site area and the surrounding region. The sampling site is in an open field (area ~1200 m²) which was previously used to grow soybeans (~10 years ago) and is surrounded by mixed deciduous and coniferous forest. The site is located on the eastern border of the Uwharrie National Forest. Four large urban areas of North Carolina are within a 150 km radius of the sampling site. These sources of anthropogenic pollution, Raleigh–Durham, Greensboro, and Winston–Salem as well as the junction between two busy interstate highways, I-40 and I-85, are situated to the north and northeast of the site (Fig. 1) and were upwind approximately 35% of the sampling period. Charlotte is nearly due west of the site and is relatively close but was upwind only approximately 10% of the sampling period. When the prevailing wind direction is

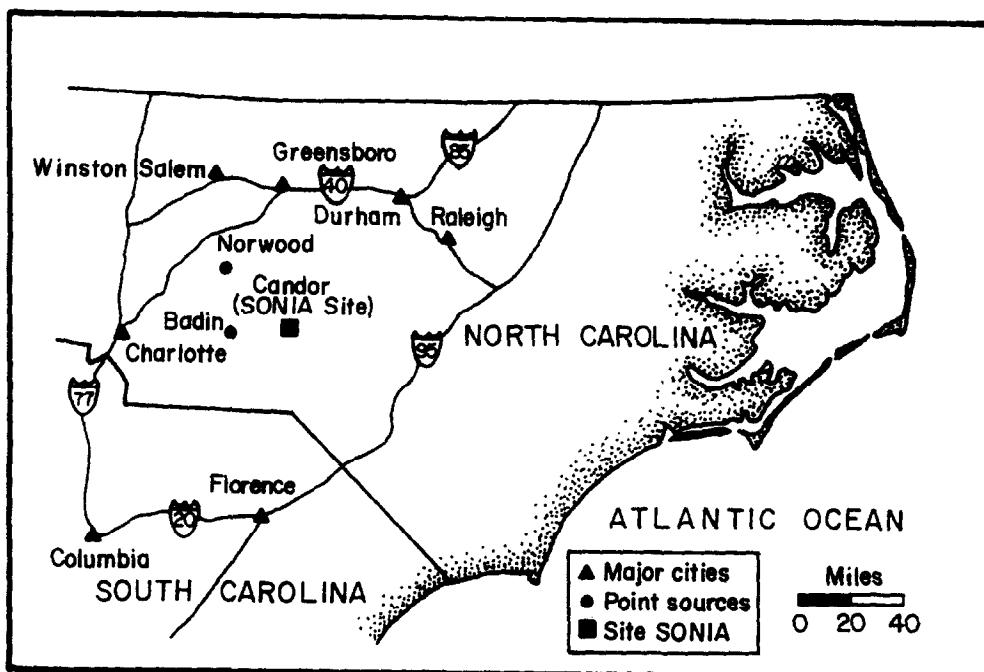


Fig. 1. Map of sampling site SONIA near Candor, NC.

from the west, north, or northeast, the site can be impacted by the more polluted air masses emanating from or crossing over these urban areas.

SETUP

Sampling tower. The ambient air was drawn from a height of 10 m through a 76.2 mm ID glass sampling tower by a blower. The air flow rate through the glass sampling tower was $31,148 \text{ l min}^{-1}$ resulting in a residence time of gases to the base of the tower of ~ 0.25 s. A 16 port glass manifold was installed at the base of the glass sampling tower above the blower to permit sampling access. All species, with the exception of total NO_y , HNO_3 , and particulate NO_3^- , were sampled from the manifold via 3 m lengths of 6.4 mm OD Teflon tubing. To maximize the efficiency of NO_y conversion for the total NO_y measurement, a heated molybdenum converter was mounted at the top of the 10 m tower. The NO_y sample, now converted to NO and less susceptible to loss in the sampling line, was transferred to the high sensitivity NO monitor by a 10 m length and 6.4 mm OD Teflon tube.

NO and NO_y . Ambient NO and NO_y were measured with a single instrument, the TECO 42S (Thermo Environmental Instruments Inc.) chemiluminescent high sensitivity analyzer. For this experiment, as mentioned above, a heated ($\sim 325^\circ\text{C}$) molybdenum converter was mounted at the top of the 10 m tower and all calibrations were made through the converter. Recent preliminary results from the SOS-MTS sponsored 1994 NO_y intercomparison in Nashville, TN, have shown that the careful operation of this instrument with its converter mounted externally and using a minimal inlet configuration leads to results that compare favorably with research grade instrumentation (Williams, 1995). For the laboratory operating conditions, the instrument detection limit is 50 parts per trillion volume (pptv) for both NO and NO_y (Thermo Environmental Instruments, Inc., 1992).

Periodic multipoint calibrations were performed using TECO 146 Multi Gas Calibrator during the measurement period. NO and NO_y calibration sources were certified master gas of 0.109 ppmv of NO and 0.114 ppmv of NO_x in N_2 gas (Scott Specialty Gases), respectively. During the

measurement period, system and performance audits were performed twice: one was an external audit performed by the North Carolina Department of Environment, Health and Natural Resources, and the other was an internal audit performed by the Fleming Group in NY. Data accuracy determined from the calibration lines for NO and NO_2 were 10% and 20%, respectively. To examine the conversion efficiency NO_y to NO for the molybdenum converter, NIST traceable NO_2 in N_2 standard was used to calibrate the response of the instrument. Conversion efficiency of NO_2 was calculated to be $> 98\%$ for the entire field study.

HNO_3 and NO_3^- . HNO_3 and particulate nitrate (NO_3^-) were measured at 10 m using the filter pack method (Goldan *et al.*, 1983). Sampling air flow rate was maintained at 24 l min^{-1} and was checked each time new filters were installed in the filter pack. The collected filters were later desorbed into a buffer solution in an ultrasonic bath, and the solution was analyzed with an ion chromatograph to determine the nitrate ion content. The total mass of nitrate was corrected for "blank" nitrate (from loaded but unexposed filters). The detection limits for both HNO_3 and NO_3^- are ~ 30 pptv.

NO_2 . Ambient NO_2 was measured directly with the LMA-3 Scintrex Luminol based NO_2 analyzer that utilizes a chemiluminescent analytical technique.

Multipoint calibrations were conducted every week during the study period using a certified master gas of 0.116 ppm of NO_2 in N_2 gas (Scott Specialty Gases) and calibrated mass flow controllers, and daily zero-span checks were performed. An O_3 scrubber which was supplied from Scintrex was installed to remove O_3 interference. The scrubber was tested to remove 99.5% of O_3 at 50 ppbv. Typically, 85–95% of NO_2 is passed. Any NO_2 loss was accounted for by calibrating through the O_3 scrubber. There was about 20% PAN interference in LMA3. The uncertainty of NO_2 measurement during the study period, when we assume 20% PAN interference (PAN average at Site SONIA; ~ 0.4 ppbv), was less than 10% of NO_2 measured. We did not perform a field intercomparison on the LMA3.

PAN. Calibration of the PAN GC was carried out during and following the field measurements. A bag of high

(~15 ppmv) concentration PAN was synthesized by irradiating a Tedlar bag containing acetaldehyde, chlorine, and nitric oxide with ultraviolet radiation (Gay *et al.*, 1976). The concentration of the bag was then quantified by infrared spectrophotometry (Shimadzu IR6) with a 6.92 m path length multiple pass cell and known absorptivity (Stephens, 1969). The standard preparation and quantification was performed at the EPA Environmental Research Laboratory in Research Triangle Park (RTP), NC. The high concentration bag of PAN was then transported two hours to site SONIA in an air conditioned car. A multipoint calibration was then performed on the GC system by syringe injection of aliquots of the high concentration PAN mixture into bags containing metered volumes of zero grade air. Prepared PAN concentrations of 0.5, 1, 2, and 5 ppbv were used for system calibration. After GC calibration, the high concentration PAN bag was returned to the EPA lab in RTP and reanalyzed by the IR Spectrophotometer. No loss or decomposition of the high concentration PAN sample was observed. The response factors from the two calibrations were 26.7 ± 0.9 mm (peak height) per ppbv and 24.8 ± 1.6 mm per ppbv. Thus, the precision of the measurements based on the two calibrations was the average of the two standard deviations or 4.9%.

A comparison between this PAN analyzer and other PAN analyzer provided by Daniel Grosjean and Associates (DGA) was carried out during the 1992 Atlanta Intensive component of the Southern Oxidants Study. The two analyzers were colocated on the GIT campus and sampled ambient air through identical lengths of Teflon line. The DGA analyzer had been calibrated by chemiluminescent detection of a PAN sample obtained from the diffusion of liquid PAN sample into purified air. The comparison showed close agreement between the two instruments with a linear regression of the data yielding the following results. $NCSU_{PAN} = 1.33$ DGA_{PAN} - 0.04 ppbv; $R^2 = 0.95$ and $n = 54$. Daily checks of detector response and retention time were performed by sampling through methyl nitrate impregnated filter. The instrument response and retention were found to be consistent within $\pm 20\%$.

All of the instruments were calibrated at the site and quality assurance of data was assessed according to the Quality Assurance Plan for the Southern Oxidant Study (The Fleming Group, 1993). Accuracy objectives for each measurement were 10% for NO, 20% for NO₂ and NO_y. Internal and external system audits of the site were performed by the QA office (The Fleming Group, 1993) and NC Dept of Environmental Health and Natural Resources, respectively.

RESULTS AND DISCUSSION

Diurnal variations of nitrogen species and O₃

Figure 2 illustrates the composite diurnal profiles of nitrogen species and O₃ for the entire measurement period. Total NO_y and NO₂ show consistent maxima in the early morning hours between 0600 and 0900 EST. The mechanism hypothesized for the morning peaks of NO₂ and NO_y is regional transport of polluted air masses above the nocturnal boundary layer (NBL) (Trainer *et al.*, 1987) along with local biogenic source emissions from the soil. At sunrise, when increased solar insolation triggers the breakup of the low NBL, a period of downward mixing brings the relatively undepleted polluted air mass aloft to the surface. However, Kim *et al.* (1994) have also suggested the possibility of enhanced biogenic emissions of NO_x from the soils during morning as contributing to morning peaks of NO₂ and NO_y.

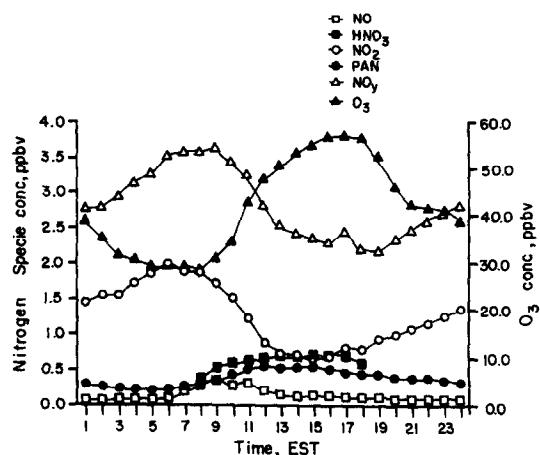


Fig. 2. Composite diurnal profiles of nitrogen species and ozone.

The diurnal profile of NO₂ reached a minimum during the early afternoon after the peak in solar insolation was reached. During the daytime, NO₂ is thought to be depleted due to its conversion to other NO_y species like HNO₃, PAN, and other higher-order organic nitrates (reactions R6 and R7, Table 3). Increase of daytime mixing height also causes a decrease in NO₂ by diluting it. The NO₂ mixing ratio then gradually increases throughout the night until the rapid early morning rise to the daily maximum.

An alternative hypothesis for the nighttime buildup of NO₂ is that the increase may be due to natural emissions of nitrogen species from the local soils. A dynamic flux chamber experiment to measure nitrogen compound flux was conducted on several different days during the measurement period (Kim *et al.*, 1994). There was a significant level of NO flux from the soil at night, i.e. typically about $2.4 \text{ ng N m}^{-2} \text{ s}^{-1}$. Levels of O₃ overnight are typically near 30 ppbv and are sufficient to immediately titrate any NO from the soil to NO₂ (reaction R3, Table 3). Assuming a nocturnal boundary layer (NBL) depth of 100 m, and the $2.4 \text{ ng N m}^{-2} \text{ s}^{-1}$ NO emission rate, the rate of increase in NO₂ would be approximately 0.1 ppbv h^{-1} . The observed rate of increase in NO₂ during nighttime is quite consistent to the estimated rate of increase in NO₂ ($\sim 0.1 \text{ ppbv h}^{-1}$). These results suggest that the soil emission of NO may be an important source of nighttime NO_x buildup at the site.

In Fig. 2, NO shows a morning maximum between 0700 and 0900 EST. The morning NO increase is likely the combined effect of local NO_x emissions, photolysis of available NO₂, and an increase in NO flux from the soil. The NO peak occasionally coincided with the NO_y and NO₂ peaks but often followed the NO₂ peak by 1–2 h.

Gaseous HNO₃ concentrations were measured during the daytime between 0800 and 1800 EST. The HNO₃ diurnal profile exhibits a steady increase in concentration from its morning minimum to a maximum occurring at ~ 1500 EST followed by a steady

decrease to nighttime lows. HNO_3 is primarily produced through the reaction of NO_2 with OH during the daytime (reaction R6, Table 3). HNO_3 typically starts to increase at the same time NO_2 mixing ratios begin to decline, and the HNO_3 maximum corresponds with the NO_2 minimum in the middle afternoon (Fig. 2). Statistically, there was found to be a negative correlation ($[\text{HNO}_3] = -0.14 [\text{NO}_2] + 0.86, r = -0.6$) between diurnal profiles of NO_2 and HNO_3 in our data.

PAN exhibits a diurnal profile similar in shape and magnitude to profiles observed by Singh and Salas (1989) for Northeastern U.S. cities. The magnitude of PAN concentrations also agree well with PAN concentrations reported from rural Alabama where PAN concentrations were usually between the detection limit and $\sim 1 \text{ ppbv}$, with concentrations rarely exceeding 1.5 ppbv (Cantrell *et al.*, 1992). The nighttime minimum in PAN concentration is the result of enhanced dry deposition at the surface beneath the subsiding NBL. The early morning increase in PAN concentration accompanied by a rapid increase in O_3 is likely due to downward mixing of PAN from the undepleted residual layer aloft (Hartsell *et al.*, 1994).

Continued PAN production throughout the morning and into the early afternoon, however, is considered to be the result of photochemical production of PAN in the region. Evidence supporting this hypothesis is the correlation of PAN concentrations to solar radiation which suggests that local photochemical production of PAN may be important at the site (Shepson *et al.*, 1992). A regression of PAN on solar radiation showed a strong positive correlation with $R^2 = 0.73$. In addition, the other pollutants which are mixed down from aloft, NO_2 and NO, reach their maximum concentrations shortly after sunrise, while PAN concentrations continue to build throughout the morning and into the early afternoon. The night-

time minimum of PAN is attributed to deposition under the nocturnal boundary layer. PAN concentrations never dropped below the detection limit of the instrument (50 pptv), however, and often remain as high as 300 pptv throughout the night. A more detailed analysis of PAN at site SONIA is published elsewhere (Hartsell *et al.*, 1994).

Relationships between NO_y and its constituent species

Table 1 presents statistical summaries of the average, daytime, and nighttime mixing ratios of individual odd-nitrogen compounds and total NO_y measured at the site. Daytime is defined as 0700–1700 EST and nighttime as 2000–0400 EST. All mixing ratios reported in this table are based on hourly averages integrated over the measurement period except for nitric acid which is a 2 h average and was measured only during the daytime. Median concentrations of daytime NO and O_3 are found to be similar to those observed at a high elevation site (1100 m) in the Shenandoah National Park (SNP) in rural Virginia (Doddridge *et al.*, 1992) but the NO_y was about 25% higher at this site. NO_y concentrations were found to be similar to those observed in Bondville, Illinois, and Scotia, Pennsylvania (Parrish *et al.*, 1993). The partitioning of NO_y among individual odd-nitrogen compounds for all data are given in Table 2. The fractional contributions of each odd-nitrogen compound measured recently at several different sites in the U.S. are also presented in Table 2.

Comparison of the fractions of HNO_3 and NO_x for the remote marine site and continental sites in Table 2 shows that the fraction contribution of HNO_3 to NO_y (0.43) is significantly higher than the contribution of NO_x to NO_y (0.14) at a remote marine site, Mauna Loa. In contrast, for the rural continental sites (Niwot Ridge, Scotia, and site SONIA), NO_x is the primary contributor to total NO_y (NO_x/NO_y ratio 0.32–0.59).

Table 1. Statistical summaries of the average, daytime, and nighttime mixing ratios of individual odd-nitrogen compounds and total NO_y measured at site, SONIA

Species	Data set	n	Max.	Mean	Med.	St. dev.
NO	Day	357	1.46	0.22	0.14	0.23
	Night	299	5.41	0.09	0.04	0.33
	All	785	5.41	0.15	0.07	0.29
NO_2	Day	336	5.06	1.19	0.91	0.96
	Night	302	7.84	1.38	1.25	0.91
	All	769	7.84	1.31	1.06	0.99
PAN	Day	267	1.17	0.48	0.46	0.27
	Night	216	0.86	0.33	0.32	0.17
	All	578	1.17	0.40	0.36	0.24
HNO_3	Day	250	1.76	0.67	0.66	0.33
NO_y	Day	333	9.31	2.97	2.78	1.49
	Night	291	14.47	2.77	2.68	1.59
	All	743	14.47	2.88	2.70	1.58
Sum NO_{yi}	Day	148	5.55	2.38	2.25	1.04

Table 2. Partitioning of NO_y among individual odd-nitrogen compounds at site SONIA and recent results from other rural sites in the U.S.

Species	<i>n</i>	Max.	Mean	Med.	St. dev.	Scotia, PA	Niwot ridge, CO	Mauna Loa, HI
NO/NO_y	568	0.38	0.05	0.03	0.05	—	—	—
NO_2/NO_y	577	1.02	0.41	0.38	0.22	—	—	—
NO_x/NO_y	568	1.40	0.45	0.41	0.27	0.59	0.32	0.14
PAN/ NO_y	488	0.64	0.13	0.12	0.08	0.14	0.24	0.05
HNO_3/NO_y	180	0.64	0.21	0.19	0.11	0.16	0.13	0.43
Sum $\text{NO}_{yi}/\text{NO}_y$	180	—	0.80	0.72	—	0.93	0.73	0.75

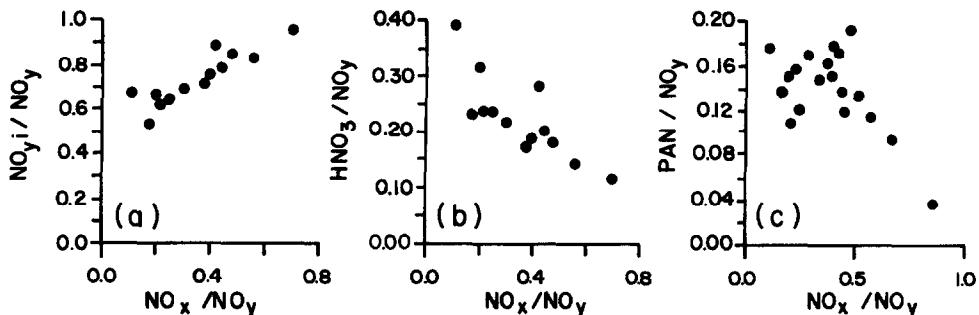


Fig. 3. Variations of (a) the fraction $\sum \text{NO}_{yi}$, (b) HNO_3 , and (c) PAN to total NO_y vs the ratio of NO_x/NO_y . Each cell represents 20 data points and the cells are sorted in ascending order of NO_x/NO_y .

These tables also indicate that the site has an odd-nitrogen deficit of 20% which is comparable to that found in recent field experiments conducted at Niwot Ridge, Colorado; Scotia, Pennsylvania; and Mauna Loa, Hawaii (Fahey *et al.*, 1986; Buhr *et al.*, 1990; Atlas *et al.*, 1992). Daily deficits varied from an actual excess of odd-nitrogen compounds, that is the sum of the individual species exceeded the total NO_y measurement, to a deficit as large as 40%. Instrument uncertainty at low pollutant concentrations could account for a portion of such a deficit but some NO_y species, especially organic nitrate species such as higher-order peroxyacetyl nitrates and alkyl nitrates, were probably detected by the NO_y instrument and not measured independently.

The consistency of the deficit from experiment to experiment and from day to day in our own measurements does, however, suggest that there are some species which are either being underestimated due to measurement technique limitations or are simply not being detected at all. Contenders for undetected species are higher-order peroxyacetyl nitrates (i.e. PPN, MPAN, PBZN) and alkyl nitrates (i.e. RONO₂). The PAN GC has detected both PPN and MPAN in another field study but did not detect those compounds at site SONIA. However, most organic nitrates cannot be quantitatively measured by conventional PAN GC techniques. PPN, in particular, is often reported as having mixing ratios that are ~10% of the mixing ratio of PAN. To ensure that there was no problem with the PAN GC that was preventing the detection of higher-order organic nitrates, PPN, PnBN, PBZN, MPAN, and methyl nitrate were all synthesized and injected onto the GC in the laborat-

ory following the experiment. All of the species were detected by the GC at ppb level concentrations but might not have been detected in the field if they were present at low pptv levels.

Figure 3a shows that the nitrogen deficit is largest when the relative contribution of NO_x to NO_y is smallest. These results agree with those published in other field study (Atlas *et al.*, 1992). This trend suggests that the deficit consists of NO_y species other than NO and NO_2 . Organic nitrates certainly fall in this category. HNO_3 also falls in this category and an underestimation of HNO_3 could also be part of the nitrogen deficit. The existence of a nitrogen deficit at several sites is a vexing one, and more research needs to be conducted in this area.

Ratio of NO_x/NO_y

NO_x is the most abundant portion of NO_y , 46% on average, at site SONIA during the measurement period. While there are natural sources of NO_x in the atmosphere, the magnitude of the NO_x/NO_y ratio at site SONIA suggests a relatively strong impact of local NO_x emissions at the site.

The NO_x/NO_y ratio was variable at the site with a standard deviation of 27%. If one considers the case where there are no physical losses of NO_y species, then the total quantity of NO_y would be conserved. The lifetime of NO_x , however, can be limited to as little as one day or less because of physical (dry deposition) and chemical (Table 3) processes in the atmosphere (Spicer, 1977). Various chemical reactions in the atmosphere serve to rapidly convert NO_x into other NO_y species, notably PAN and HNO_3 (reactions R6, R7). Thus, if one makes the assumption of minimal

dry deposition, the relative abundance of NO_x in the atmosphere expressed as the ratio of NO_x to NO_y , can be used as an indication of the photochemical age of an air mass (Ridley, 1991; Atlas 1992; Trainer *et al.*, 1993). The NO_x/NO_y ratio would be near unity near sources of NO_x emissions and would decrease towards zero as an air mass aged and NO_x was converted to other NO_y species. Measurements of NO_x/NO_y ratio at other sites have shown that the ratio tends to be lower in areas with less local emissions of NO_x (0.11 at a remote marine site in the free troposphere, Mauna Loa; Atlas *et al.*, 1992) and higher in areas with more significant impact from local NO_x emissions (0.59 at Scotia, PA; Ridley, 1991). The variability of the NO_x/NO_y ratio measured at site SONIA provides an opportunity to investigate how the partitioning of individual NO_y constituents as well as the concentration of O_3 varies in an aging air mass at site SONIA.

Figure 3b and c illustrate how the proportion of NO_y attributed to HNO_3 and PAN varied with increasing air mass age as indicated by the NO_x/NO_y ratio. In both cases, there is considerable scatter in the data but an indication that the proportion of NO_y made up of both HNO_3 and PAN increases as the air

mass age increases. This relationship is as expected from the fact that both HNO_3 and PAN are formed chemically in the atmosphere from available NO_x . In the case of PAN, however, the relationship is substantially unclear at NO_x/NO_y ratios less than 0.5 perhaps indicating the dependence of PAN on the availability of specific VOC precursors for its formation whereas HNO_3 has no such specificity of precursors. Similar trends have been observed elsewhere in the troposphere (Ridley, 1991).

Figure 4 illustrates the relationship at site SONIA between the absolute concentration of PAN and O_3 vs the ratio of NO_x/NO_y . O_3 concentrations clearly increase with increasing air mass age. O_3 accumulates when the oxidation of VOC releases radicals which more efficiently compete for NO molecules than O_3 does. The same oxidation of VOC also provides the pathways for the formation of other NO_y species from NO_x such as PAN and HNO_3 . Therefore, it is expected that the accumulation of O_3 would be positively correlated with the production of other NO_y species from NO_x as indicated by the decreasing NO_x/NO_y ratio. PAN, however, shows a more complex relationship to NO_x/NO_y ratio than does O_3 at site SONIA. From values of 1 to 0.6, PAN concentrations appear to increase with decreasing NO_x/NO_y . In the range of 0.4–0.6, there is no clear relationship, while at ratios less than 0.4 PAN concentrations seem to decrease with decreasing NO_x/NO_y . It is hypothesized that between NO_x/NO_y of ~0.6 to 1.0, PAN concentrations increase with decreasing NO_x/NO_y for the same reasons that O_3 does. The range of 0.4–0.6 may be a regime where PAN can be formed efficiently where there is the availability of appropriate VOC precursor. PAN perhaps decreases along with decreasing NO_x/NO_y at NO_x/NO_y ratios less than 0.4 because loss mechanisms for PAN have depleted the air mass of the appropriate VOC precursors for PAN formation, i.e. destruction of PAN dominates over production. This hypothesis is highly conjectural, however, and needs to be substantiated by more detailed research.

Table 3. Chemical reactions of major reactive nitrogen species in the atmosphere

<i>Photostationary state (NO, NO_2 and O_3)</i>	
$\text{NO}_2 + h\nu (\lambda \leq 420 \text{ nm}) \rightarrow \text{NO} + \text{O} (^3\text{P})$	(R1)
$\text{O}_2 + \text{O} (^3\text{P}) \xrightarrow{\text{M}} \text{O}_3$	(R2)
$\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$	(R3)
<i>Peroxy radical disruption of photostationary state</i>	
$\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH}$	(R4)
$\text{NO} + \text{RO}_2 \rightarrow \text{NO}_2 + \text{RO}$	(R5)
<i>Daytime formation of HNO</i>	
$\text{NO}_2 + \text{OH} \xrightarrow{\text{M}} \text{HNO}_3$	(R6)
<i>Formation and thermal decomposition of PAN, and loss of PAN with NO</i>	
$\text{CH}_3\text{CO}_3 + \text{NO}_2 \leftrightarrow \rightleftharpoons \text{O}_3 \dots \text{O}_2$	(R7)
$\text{CH}_3\text{CO}_3 + \text{NO} \rightarrow \text{CH}_3 + \text{CO}_2 + \text{NO}_2$	(R8)

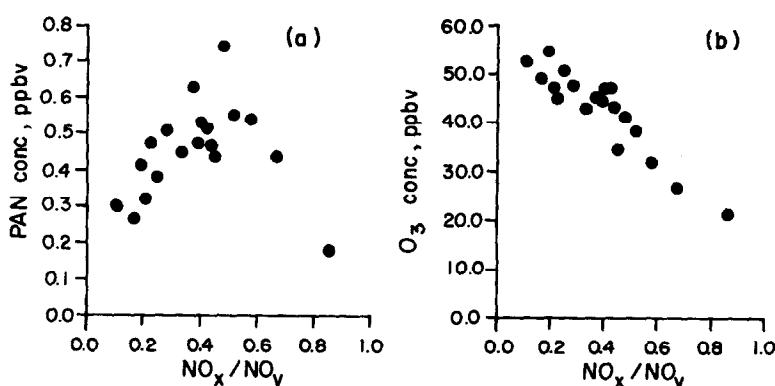


Fig. 4. Variation of (a) PAN and (b) O_3 to the ratio of NO_x/NO_y . Each cell represents 20 data points and the cells are sorted in ascending order of NO_x/NO_y .

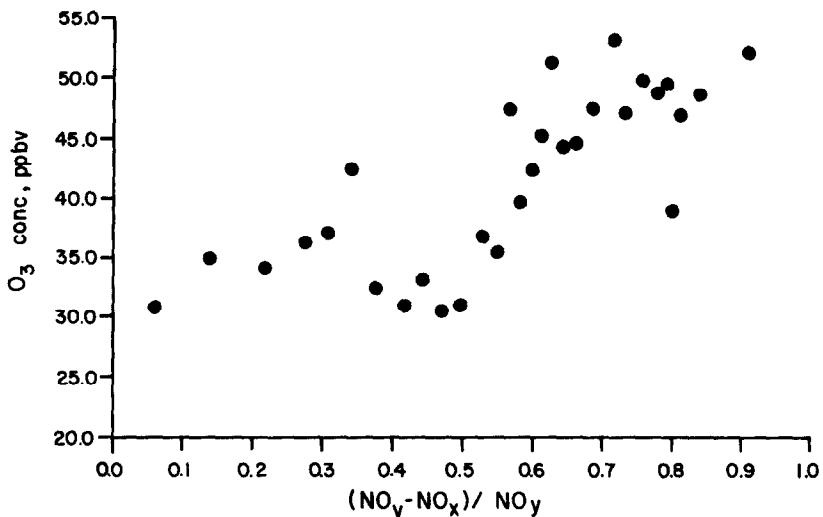


Fig. 5. Variation of O₃ vs the ratio of (NO_y - NO_x)/NO_y.

The relationship of O₃ to NO_x/NO_y is similar to the relationship between HNO₃/NO_y and NO_x/NO_y (Fig. 3b). O₃ accumulates (O₃ is formed via reactions R1, R2 in Table 3) when peroxy radicals formed from the oxidation of VOC shift the steady state to a higher NO₂/NO ratio by reacting with NO formed from the photolysis of NO₂ more rapidly than O₃ does. Unlike PAN, O₃ continues to increase with decreasing NO_x/NO_y, because O₃ requires only RO₂ radical to continue forming, while PAN requires specifically the peroxyacetyl radical which is ultimately depleted by PAN loss processes. The relationship for both PAN and O₃ to NO_x/NO_y may also be explained by examination of the local photochemical and transport process. The NO_x/NO_y ratio is typically at its maximum early in the morning when NO_x is mixed downward at the breakup of the NBL. At this time, PAN and O₃ concentrations are typically near their minimum. O₃ is plotted against (NO_y - NO_x)/NO_y in Fig. 5. This plot shows the relationship between O₃ and the degree of conversion of NO_x to reservoir NO_y species. As expected, O₃ increases as the degree of photochemical conversion of NO_x to reservoir NO_y species increases. O₃ concentrations are expected to be low in young air masses because in the troposphere O₃ is mainly formed by the same photochemical processes that lead to the conversion of NO_x into reservoir species such as PAN and HNO₃. Thus, as the ratio increases, indicating a more aged air mass and more complete photochemical conversion of NO_x to reservoir species of NO_y, the concentration of O₃ also increases. Results from the measurements show that O₃ increases with increasing photochemical age of the air mass and then remains constant as the age of parameter increases beyond 0.70 indicating that ozone is NO_x-limited at this rural site (Hess *et al.*, 1992; Olszyna *et al.*, 1994). A linear regression of O₃ on (NO_y - NO_x)/NO_y yields [O₃] = 25.8 ×

(NO_y - NO_x)/NO_y + 27, $R^2 = 0.58$). Such a statistical relationship may have temporal and spatial variations due to the complexity of the formation of O₃ that involves VOC and NO_x precursors (Trainer *et al.*, 1993) in a particular region. However, regional homogeneity in the factors that lead to O₃ formation may allow the use of such a statistical relationship. The similarity of the relationships in regional homogeneity may skip the complex chemistry in the lower troposphere associated with the formation of O₃ in that specific environment.

The dependence of ozone production efficiency on NO_y can also be illustrated by the correlation of O₃ with NO₂ (= NO_y - NO_x), the oxidation products of NO_x (Trainer *et al.*, 1993; Olszyna *et al.*, 1994). This dependence is illustrated by the results shown in Fig. 6 for the period 1000–1700 local time that shows a plot of ozone concentration vs NO₂ (SOS Report, 1994). Results from measurements made by other SOS investigators at Kinterbish, Alabama; Metter, Georgia; and Giles County, Tennessee; for the same time period are also included to offer an intercomparison of results between the different rural sites in the Southeast U.S. together with the results of a 3D Eulerian model simulation (SOS Report, 1994). The slope ranges from ~8.5 at Candor site to ~12 at the Giles County site and an intercept of ~25 ppbv of O₃ at the Metter site to ~40 ppbv O₃ at the Giles County site. The slope of the curve suggests that ~8.5 molecules of ozone are produced for every molecule of NO_x oxidized to its oxidative products, i.e. NO_x → 8.5 O₃ + NO₂. The intercept represents the nominal regional background O₃ concentration in air not directly influenced by anthropogenic emissions. This regional background at Site SONIA in Candor, NC is ~27 ppbv. The O₃ production efficiency at site SONIA is similar to the value of 8.5 reported by Trainer *et al.* (1993) for Scotia, PA, but less than the

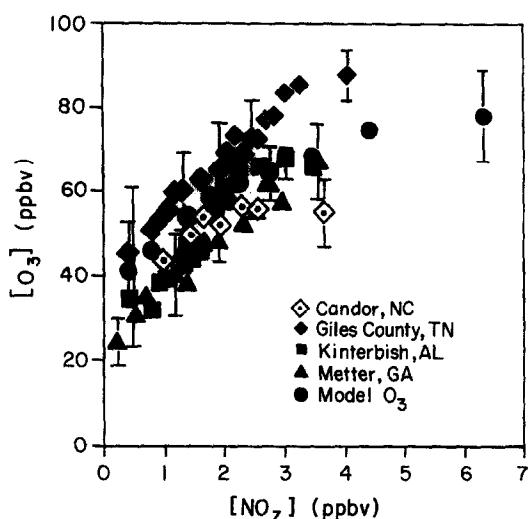


Fig. 6. Variation of concentrations of O_3 vs NO_x ($= NO_y - NO_x$) at the various SOS sites during summer 1992 and published results from a 3D Eulerian model simulation (Source: SOS Report, 1994).

value of 12 reported by Olszyna *et al.* for Giles County, TN. This difference can be attributed to the differences in the VOC/ NO_x ratio and the hydrocarbon composition of the air masses impacting the sites, and generally varies from 5 to 13 (Liu *et al.*, 1987; Trainer *et al.*, 1993). These results suggest that NO_x is a reasonable diagnostic for estimating rural O_3 concentrations on regional scales, thus providing a tool for predicting O_3 concentration in ambient air.

SUMMARY AND CONCLUSIONS

Reactive odd-nitrogen compounds as well as total NO_y were measured at a rural site, site SONIA, in the central Piedmont region of North Carolina as a part of the Southern Oxidants Study. The measurements of reactive nitrogen species were made in an effort to provide a comprehensive understanding of nitrogen chemistry and to investigate the total nitrogen budget at the site. Other trace gases and meteorological data were also collected. The diurnal variation of each NO_y species was discussed and the relationship between NO_x and total NO_y was explored on the basis of air mass origin and age. The relationship between NO_x and NO_y was also used to determine the extent of chemical processing among the nitrogen species in an air mass and the relationship of that chemical processing among the nitrogen species in an air mass and the relationship of that chemical processing to photochemical oxidants (O_3 , HNO_3 , and PAN), and results compared with published results from a 3D Eulerian model, similar measurements were made in the Southeast U.S.

The mean NO_y mixing ratio was found to be 2.88 ppbv (median 2.70 ppbv). The mean mixing ratios of NO , NO_2 , HNO_3 and PAN were found to be

0.15, 1.31, 0.67, and 0.40 ppbv, respectively (Table 1). Each species showed diurnal variations (Fig. 2). NO_y , NO and NO_2 maxima occurred in the morning between 0500 and 0900 EST. The NO_y and NO_2 maxima typically occurred around 0700 EST. It is likely that the NO_x was mixed down to the surface during the morning breakup of the NBL along with local biogenic emissions from the soil. The NO peak at the site could also be supplied by downward mixing of polluted air masses but the short lifetime of NO and the lack of strong correlation between the NO_2 and NO peak suggest other mechanisms may be at work. Possible other mechanisms responsible for the NO peak at 0900 EST are conversion of NO_2 to NO by photolysis and peroxy radicals available at the time in the morning or natural NO flux from the soil. A flux experiment conducted over the measurement period showed elevated morning flux of NO in 30% of the samples. PAN , HNO_3 and O_3 diurnal variation were quite similar suggesting they might share a common source, probably mesoscale photochemical production from transported and locally produced precursor species.

NO_x was the most abundant of NO_y species accounting for ~45% of total NO_y (Table 2). These results are significantly different than those obtained from a remote marine site but were comparable with recent results from two other rural continental sites (Niwot Ridge, CO and Scotia, PA) in the United States. The discrepancy between the NO_y partitioning at site SONIA and the marine site is attributed to the influence of regional anthropogenic sources of NO_y and the continental origin of the majority of air masses encountered at the site.

The dependence of ozone production efficiency on NO_y was examined by the correlation of O_3 with various combinations of NO_y species (Figs 3, 5 and 6). An ozone background of ~27 ppbv and ozone production efficiency of 8.6, i.e. 8.6 molecules of O_3 formed per molecule of NO_x oxidized products, were obtained for site SONIA. Air masses, with photochemical ages greater than 0.7, were found to be in a NO_x -limited regime.

In conclusion, while this study has shed some light on the behavior of reactive odd-nitrogen compounds in the Southeast U.S., it is clear that more comprehensive research into the role of naturally produced nitrogen species and its characteristics and the behavior of photochemical oxidants is needed to enhance our understanding of the chemical climatology of the Southeast U.S. Such knowledge will be required if an accurate photochemical model to research atmospheric chemistry in this area or region is to be developed. The understanding gained from field research and future chemical models developed based on data collected in field research are of great importance to the formation of basic pollution control policy for the Southeast U.S.

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REFERENCES

- Aneja V. P., Das M., Kim D. S. and Hartsell B. E. (1994) Measurements and analysis of photochemical oxidants and trace gases in the rural troposphere of the Southeast United States. *Israel J. Chem.* **34**, 387–401.
- Atlas E. L., Ridley B. A., Hubler G., Walega J. G., Carroll M. A., Montzka D. D., Huebert B. J., Norton R. B., Grahek F. E. and Schauffler S. (1992) Partitioning and budget of NO_x species during the Mauna Loa Observatory Photochemistry Experiment. *J. geophys. Res.* **97**, 10,449–10,462.
- Borucki W. and Chameides W. (1984) Lightning: Estimates of the rates of energy dissipation and nitrogen fixation. *Rev. Geophys. Space Phys.* **22**, 363–372.
- Buhr M. P., Parrish D. D., Norton R. B., Fehsenfeld F. C., Sievers R. E. and Roberts J. M. (1990) Contribution of organic nitrates to the total odd nitrogen budget at a rural eastern U.S. site. *J. geophys. Res.* **95**, 9809–9816.
- Cantrell C. A., Lind J. A., Shettler R. E., Calvert J. G., Golden P. D., Kuster W., Fehsenfeld F. C., Montzka S. A., Parrish D. D., Williams E. J., Buhr M. P., Westberg H. H., Allwine G. and McAin R. (1992) Peroxy radicals in the ROSE experiment: Measurement and theory. *J. geophys. Res.* **97**, 20,671–20,686.
- Crutzen P. J. (1979) The role of NO and NO₂ in the chemistry of the troposphere and stratosphere. *Ann. Rev. Earth Planet Sci.* **7**, 443–472.
- Dodderidge B. G., Dickerson R. R., Wardell R. G., Civerolo K. L. and Nunnermacker L. J. (1992) Trace gas concentrations and meteorology in rural Virginia, 2, Reactive nitrogen compounds. *J. geophys. Res.* **97**, 20,631–20,646.
- Fahey D. W., Hubler G., Parrish D. D., Williams E. J., Norton R. B., Ridley B. A., Singh H. B., Liu S. C. and Fehsenfeld F. C. (1986) Reactive nitrogen species in the troposphere: Measurements of NO, NO₂, HNO₃, particulate nitrate, peroxyacetyl nitrate (PAN), O₃, and total reactive nitrogen (NO_x) at Niwot Ridge, Colorado. *J. geophys. Res.* **91**, 9781–9793.
- Finlayson-Pitts B. J. and Pitts J. N. Jr (1986) *Atmospheric Chemistry: Fundamentals and Experimental Techniques*, pp. 526–528. Wiley, New York.
- Fleming Group (1993) Quality Assurance Project Plan for the Southern Oxidant Study, SCION Network, G. Momberger, SOS QA Officer, Albany, NY 12,206.
- Gay B. W., Noonan R. C., Bufalini J. J. and Hanst P. L. (1976) Photochemical synthesis of peroxyacetyl nitrates in gas phase via chlorine-aldehyde reaction. *Environ. Sci. Technol.* **10**, 82.
- Goldan P. D., Kuster W. C., Albritton D. L., Fehsenfeld F. C., Connell P. S., Norton R. B. and Huebert B. J. (1983) Calibration and tests of the filter-collection methods for measuring clean-air, ambient levels of nitric acid. *Atmospheric Environment* **17**, 1355–1364.
- Hartsell B. E., Aneja V. P. and Lonneman W. A. (1994) Relationships between peroxyacetyl nitrate (PAN), O₃, and NO_x at the rural Southern Oxidants Study Site in Central Piedmont North Carolina, Site SONIA. *J. geophys. Res.* **99**, 21,033–21,041.
- Hess G. D., Carnovale F., Cope M. E. and Johnson G. M. (1992) The evaluation of some photochemical smog reaction mechanisms. I. Temperature and initial composition effects. *Atmospheric Environment* **26A**, 625–641.
- Hübner G., Fahey D. and Ridley B. A. (1992) Airborne measurements of total reactive odd nitrogen NO_x. *J. geophys. Res.* **97**, 9833–9850.
- Instruction Manual Model 42(S), Chemiluminescence NO-NO₂-NO_x analyzer, Designated reference method number RFNA-1289-074, 1992. Thermo Environmental Instruments Inc., Franklin, Massachusetts.
- Johansson C. and Sanhueza E. (1988) Emission of NO from savanna soils during rainy season. *J. geophys. Res.* **93**, 14,193–14,198.
- Kim D. S., Aneja V. P. and Robarge W. P. (1994) Characterization of nitrogen oxides fluxes from soil of a fallow field in the Central Piedmont of North Carolina. *Atmospheric Environment* **28**, 1129–1137.
- Liu S., Trainer M., Fehsenfeld F. C., Parrish D. D., Williams E. J., Fahey D. W., Hubler G. and Murphy P. C. (1987) Ozone production in the rural troposphere and the implication for regional and global ozone distributions. *J. geophys. Res.* **92**, 4191–4207.
- LMA-3 LUMINOX Operation Manual (1987) SCINTREX/UNISEARCH, Concord, Ontario, Canada.
- Logan J. A. (1983) Nitrogen oxides in the troposphere: Global and regional budgets. *J. geophys. Res.* **88**, 10,785–10,807.
- Madronich S. (1987) Intercomparison of NO₂ photodissociation and U.V. radiometer measurements. *Atmospheric Environment* **21**, 569–578. Environmental Management/Air Quality Section, 1989 Ambient Air Quality Report, May 1991.
- North Carolina Dept of Environment, Health, and Natural Resources (1991) Environmental Management/Air Quality Section, May.
- Olszyna K. J., Bailey E. M., Simonaitis R. and Meagher J. F. (1994) O₃ and NO_x relationships at a rural site. *J. geophys. Res.* **99**, 14,557–14,563.
- Parrish D. D., Trainer M., Buhr M. P., Watkins B. A. and Fehsenfeld F. C. (1993) The total reactive oxidized nitrogen levels and the partitioning between the individual species at six rural sites in eastern North America. *J. geophys. Res.* **98**, 2927–2940.
- Ridley B. A. (1991) Recent measurements of oxidized nitrogen compounds in the measurements. *Atmospheric Environment* **21**, 569–578.
- Ridley B. A. and Robinson E. (1992) The Mauna Loa Observatory Photochemistry Experiment. *J. geophys. Res.* **97**, 10,285–10,290.
- Shepson P. B., Hastie D. R., So K. W., Schiff H. I. and Wong P. (1992) Relationship between PAN, PPN and O₃ at urban and rural sites in Ontario. *Atmospheric Environment* **26A**, 1259–1270.
- Singh H. B. and Hanst P. L. (1981) Peroxyacetyl nitrate (PAN) in the unpolluted atmosphere; an important reservoir for nitrogen oxides. *Geophys. Res. Lett.* **8**, 941–944.
- Singh H. B. and Salas L. J. (1989) Measurements of peroxyacetyl nitrate (PAN) and peroxypropionyl nitrate (PPN) at selected urban, rural and remote sites. *Atmospheric Environment* **23**, 231–238.

- Slemr F. and Sciler W. (1984) Field measurements of NO and NO₂ emissions from fertilized and unfertilized soils. *J. atmos. Chem.* **2**, 1–24.
- SOS Report (1994) *Southern Oxidants Study 1993 Data Analysis Workshop Report* (edited by Fehsenfeld F., Meagher J. and Cowling E.), p. 92. North Carolina State University, Raleigh, North Carolina, 27695.
- Spicer C. W. (1977) The fate of nitrogen oxides in the atmosphere. In *Advances in Environmental Science and Technology* (edited by Pitts J. N. Jr, and Metcalf R. L.), Vol. 7, pp. 182–197. Wiley, New York.
- Stephens E. R. (1969) The formation, reactions, and properties of peroxyacetyl nitrates, PANs, in photochemical air pollution. *Ad. Environ. Sci. Technol.* **1**, 119–146.
- Trainer M., Williams E. J., Parrish D. D., Buhr M. P., Allwine E. J., Westberg H. H., Fehsenfeld F. C. and Liu S. C. (1987) Models and observations of the impact of natural hydrocarbons on rural ozone. *Nature* **329**, 705–707.
- Trainor M., Parrish D. D., Buhr M. P., Norton R. B., Fehsenfeld F. C., Anlauf K. G., Bottenheim J. W., Tang Y. Z., Wiebe H. A., Roberts J. M., Tanner R. L., Newman L., Bowersox V. C., Meagher J. F., Olszyna K. J., Rodgers M. O., Wang T., Berresheim H., Demerjian K. L. and Roychowdhury U.K. (1993) Correlation of ozone with NO_x in photochemically aged air. *J. geophys. Res.* **98**, 2917–2925.
- Williams E. (1995) NO_x Intercomparison Study, Southern Oxidants Study 1995 Data Analysis Workshop and Annual Meeting, Raleigh, North Carolina.
- Williams E. J., Parrish D. D. and Fehsenfeld F. C. (1987) Determination of nitrogen oxide emission from soils; results from a grassland site in Colorado, United States. *J. geophys. Res.* **92**, 2173–2179.
- Williams E. J., Guenther A. and Fehsenfeld F. C. (1992) An inventory of nitric oxide emissions from soils in the United States. *J. geophys. Res.* **97**, 7511–7519.