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Trace gas concentrations and emissions in downtown Nashville during the 1995 Southern Oxidants Study/Nashville intensive

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Abstract. Continuous measurements of O_3, CO, NO_y, and SO_2 and twice a day samples of hydrocarbons were made over a 40 day period in June and July 1995 at the downtown Nashville Southern Oxidants Study (SOS) site located on the rooftop of the Polk office building, 106 m above ground level, in the urban center. This site experiences elevated concentrations of VOCs, CO, and NO_y due to local emissions from the Nashville urban area. High O_3 concentrations were also observed and are discussed with reference to violations of the existing air quality standard and the much harder task of meeting the proposed 8 hour average standard. A comparison between the VOC measurements made from the Department of Energy G-1 aircraft with those measured downtown indicates a preferential loss of reactive ingredients in the samples taken outside of the city. The concentration ratios, VOC/CO (ppbC/ppb), VOC/NO_x (ppbC/ppb), and CO/NO_x (ppb/ppb) were calculated to be 0.32, 2.9, and 9.3, respectively, from morning samples. These ratios agree to within 35% with estimates from Nashville emissions.

1. Introduction

The Southern Oxidants Study (SOS) Nashville/Mid Tennessee Ozone Study had as one of its objectives an analysis of O_3 formation in the Nashville urban plume. In support of this objective trace gas and meteorology measurements were made by the Tennessee Valley Authority (TVA) from on top of the James K. Polk office building in downtown Nashville [*Meagher et al.*, 1996; K. J. Olszyna et al., unpublished manuscript, 1997]. Hydrocarbon samples were analyzed by researchers from the University of Miami. The intent of these observations was to characterize the chemical composition of the urban air mixture before extensive processing had occurred. Aircraft observations were used to determine the composition of the urban plume in later stages of its evolution [*Hübler et al.*, this issue].

In this study we are concerned with the chemical content of the air in downtown Nashville. This air, as it is advected downwind from Nashville, is subject to dilution and chemical reactions leading to the disappearance of primary pollutants and the formation of O_3. The downtown measurements provide the initial conditions for that process (L. J. Nunnermacker et al., unpublished manuscript, 1998).

A second objective of this study is to compare ratios of ambient concentrations observed downtown with the corresponding quantities determined from emission inventories. In making this comparison we take advantage of the downtown site's location in a high emission rate region. Ambient concentrations of NO_x, CO, and VOCs should thereby be dominated by recent emissions, and concentration ratios of these compounds should reflect their emission rates. Assessing the accuracy of an emission inventory is a difficult but important step in establishing the overall accuracy of models that are used to determine O_3 control strategies. A comparison between emission ratios and ambient concentration ratios in a source region is one of the few ways of making such an assessment. Similar comparisons have been conducted at other downtown sites, in adjacent urban areas, and in the confined space of highway tunnels [*Lonneman et al.*, 1986; *Fujita et al.*, 1992; *Goldan et al.*, 1995; *Pierson et al.*, 1996].

The downtown measurements included twice a day hydrocarbon samples, and continuous measurements of CO, NO_y, SO_2, O_3, and meteorological parameters. We present time series data and diurnal cycles for CO, NO_y, and O_3. We use SO_2, CO, and NO_y to distinguish between urban and power plant impacted air masses. Ratios of morning concentrations of CO, NO_y, and VOCs are compared with the corresponding ratios derived from emission estimates for the Nashville area. We have a particular interest in measurements that were made on July 3 and 18 as a well defined urban plume was encountered downwind of Nashville by the Department of Energy (DOE G-1) aircraft on those days (L. J. Nunnermacker et al., unpublished manuscript, 1998; Imre et al., unpublished manuscript, 1998). Measurements from July 3 are used to illustrate diurnal changes in pollutant concentration, and hydrocarbon data from July 18 are compared with a sample collected downwind by the G-1 on that day (analyzed by York University, 1995).

2. Experiment

Nashville is a city of 1/2 million people. It is surrounded by suburbs which make up a metropolitan area of 1 million people

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spread over 10^4 km^2 (eight county Nashville Metropolitan Statistical Area). The James K. Polk Building where atmospheric samples were obtained is in the center of downtown Nashville (corner of Fifth and Deadrick Avenues at 36.16 latitude, 86.78 longitude). The area surrounding the Polk building within a radius of about 6 km is primarily commercial, with heavy traffic that peaks in the morning and afternoon rush hours.

Sampling was done from the rooftop of the Polk Building which is 106 m above street level. Measurements were made at the southeast corner of the building from a temperature-controlled enclosure. Sample inlets were at a height of 4 m above the rooftop. This site, which we will refer to as the "downtown site" was equipped and operated by TVA [*Meagher et al.*, 1996]. The University of Miami was responsible for providing canisters for hydrocarbon samples and for the analysis of those samples [*Apel et al.*, 1995].

The downtown site was part of the Level 2 Enhanced Surface Chemistry Network which provided real-time measurements of O_3 (UV absorption), NO_y (Mo converter, placed in the air sample box at the top of the sampling tube, and O_3 chemiluminescence), CO (non-dispersive-infrared/gas-filter-correlation), and SO_2 (pulsed fluorescence) with a 5 minute time resolution (K. J. Olszyna et al., unpublished manuscript, 1997). A standard meteorological package was deployed, recording 5-min average wind speed, wind direction, temperature, relative humidity, and solar radiation. Hydrocarbon samples were collected twice a day at 0700 and at 1200 central daylight time(CDT), which we will refer to as AM and PM samples. Collection periods were 1 hour long. Samples were collected in pressurized SUMMA® canisters and analyzed for selected C_2 to C_{10} VOC compounds using gas chromatographic/flame ionization detector (GC/FID). Analysis of hydrocarbon samples was done at the Youth Incorporated Level 1 site. Further information about instrumentation at the Level 2 SOS sites and the hydrocarbon analysis procedure are given by TVA/Environmental Research Center (ERC) [1995], K. J. Olszyna et al. (unpublished manuscript, 1997), and *Apel et al.* [1995].

A subset of the hydrocarbon samples (9% of AM and 37% of PM samples) had anomalously high concentrations of one or more of the compounds; i-butane, toluene, limonene, or beta-pinene. We suspect that these samples were contaminated with cleaning solvents or other volatile emitted products that are used at the office building. It was decided to discard these samples from the analysis. Identification was based on the ratio of i-butane to n-butane with the valid samples having a ratio less than one.

In addition, there were a small number of outliers that did not follow any pattern. These were identified by examining the fractional contribution that each species makes to the total VOC concentration of that sample. Species were judged to be outliers if that fractional contribution differed by more than 4 standard deviations from the average contribution of that species over the entire experimental period. If that was the case, the outlier was replaced by a concentration which yielded an average fractional contribution. This has only a minimal effect on the results presented here; on average, it reduced the total VOC concentration by 4%, most of which was contained in several clearly spurious spikes.

Hydrocarbon concentrations are reported here in units of parts per billion of carbon (ppbC). We also make use of the OH reactivity due to a single hydrocarbon or a mixture of hydrocarbons. The OH reactivity has units of per second and is given by

$$k(VOC) = \sum k_i \, (cm^3 \text{ molecules}^{-1} \, s^{-1}) \, [VOC_i \, (\text{molecules } cm^{-3})] \quad (1)$$

where k_i is the rate constant for reaction of OH with the ith VOC, evaluated at 1 atm and 300°K for samples collected downtown, or evaluated at ambient conditions for samples collected on the G-1.

3. Observations and Discussion

Trace gas measurements were made at the downtown site over a 40 day period between June 19 and July 28. The aircraft operations period covered 30 days, starting on June 21 and ending on July 20. Weather conditions during this time period were warm to hot and usually humid. The average noon time temperature and relative humidity were 27°C and 73%, respectively. All times that are referred to in this study are central daylight time (CDT) (equal to UT -5).

3.1. Time Series

Concentrations of CO, NO_y, and O_3 during the aircraft operations period are shown in Figure 1. CO and NO_y have a very spiky appearance, with similar magnitude spikes at coincident

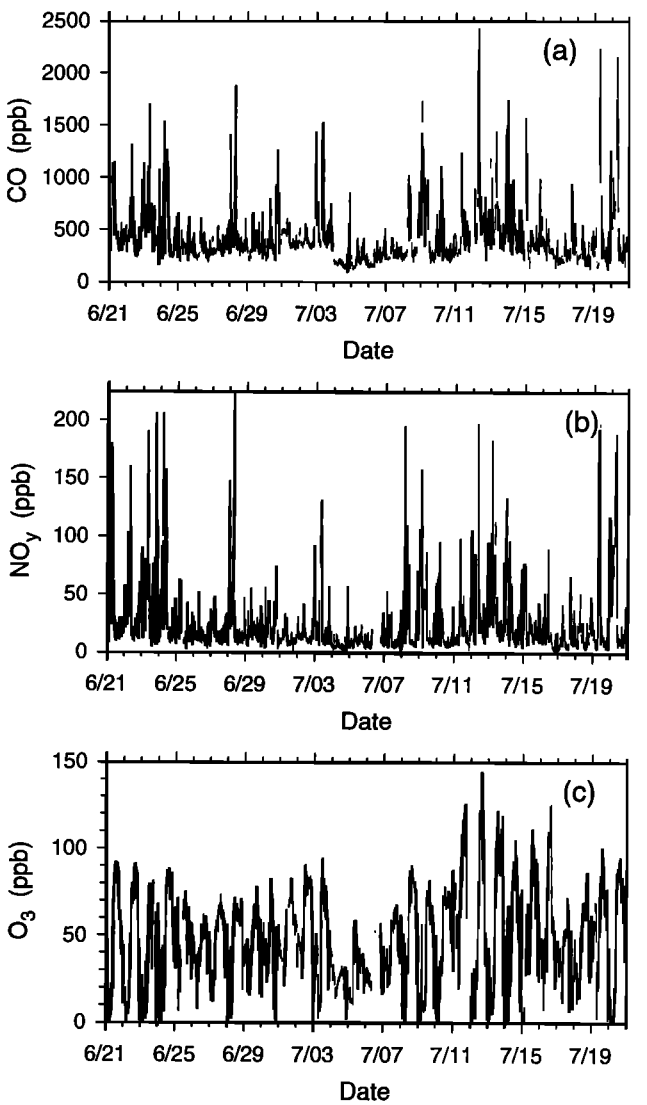

Figure 1. Time series of (a) CO, (b) NO_y, and (c) O_3 for the main aircraft operations period, June 21 to July 20.

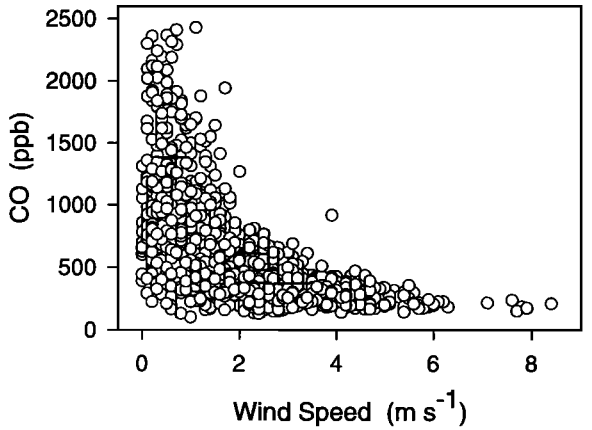

Figure 2. Observed relation between CO and wind speed for the hours between 0600 and 1000.

times. Maximum concentrations of CO and NO_y can vary by more than an order of magnitude from day to day. Figure 2 shows that the highest morning CO levels only occur when wind speeds are near zero. NO_y behaves similarly. Morning levels of O_3, in contrast, do not depend in any obvious way on wind speed.

Ozone has a prominent cyclical behavior which at higher magnification is seen to be a diurnal variation between a night-time minimum and a daytime maximum. There is also a low frequency component associated with the passage of synoptic weather patterns. Days with high O_3 levels occur in groups, most notably between July 11-13 and July 15-16 (Figure 1c). Wind speeds were low in the former period (1-2 m s^{-1} in the afternoon), and aircraft observations indicated that during this stagnation period a region of enhanced O_3 was directly over the city of Nashville [*Valente et al.*, this issue].

In Figure 3 we examine the daily maximum 1-hour and 8-hour averaged ozone concentrations measured downtown. These two averaging times form the basis of the current and proposed National Ambient Air Quality Standard for O_3. Aside from an allowance for a specified number of exceedances, the current standard requires that 1-hour average O_3 be less than 120 ppb; the proposed standard requires that an 8-hour average be less than 80 ppb. We note that the Polk building is not an official monitoring site and that there may be systematic differences between it and the official sites which are located at ground level. We also note that exceedances are determined for

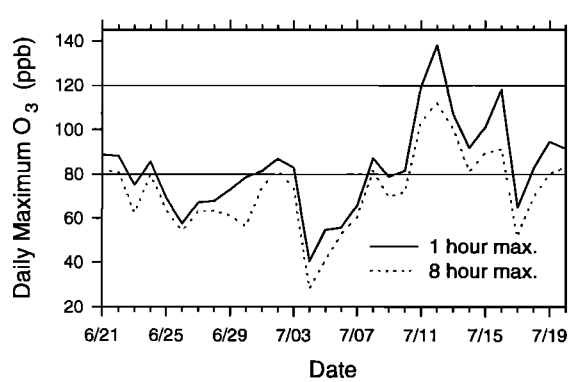

Figure 3. Daily maximum O_3 concentration for a 1 hour and 8 hour averaging period. Horizontal lines indicate the current 1 hour national air quality standard of 120 ppb and the proposed 8 hour standard of 80 ppb.

time periods that start and stop on the hour, while our daily maxima are calculated for time periods that can start at any point in the day. With these caveats in mind, there was one violation of the current standard occurring on July 12. Ozone exceeded 120 ppb on that day for a 3 hour period with a maximum 1-hour average of 138 ppb. The proposed 8 hour standard was exceeded on 12 out of 30 days. In Nashville the 8-hour standard will be much more difficult to meet than the existing 1-hour regulation; the proposed standard drops the allowable O_3 level by 40 ppb, while the actual average drop in O_3 in going from a 1 hour to 8 hour averaging period is only 10 ppb.

3.2. Diurnal Cycles

Figure 4 shows composite diurnal cycles for CO, NO_y, and O_3. The emitted substances, CO and NO_y, are seen to have their highest concentrations in the morning between 0600 and 1000 CDT. The day to day variability during this time period is larger than at any other time of the day and is responsible for most of the spikes seen in Figure 1. There is a second, smaller, buildup in concentration during the late evening hours. Ozone has a very different time sequence, with a broad maximum occurring between 1200 and 1600.

The composite cycles are averages over many different meteorological conditions and consequently do not show the abrupt concentration changes that often occurred, particularly in the morning. This behavior is illustrated in Figure 5, which contains a time series for O_3, CO, NO_y, and wind speed on July 3. Concentrations on this day were at the high end of the observed range as indicated by a comparison with the composite cycles in Figure 4.

NO_y and CO on July 3 have an abrupt increase between 0600 and 0700 and then an abrupt decrease between 0930 and 1030. The decrease occurring at 0930 is coincident with a steep increase in O_3. The timing of the high primary pollutant peak coincides with a drop in wind speed from 2-3 m s^{-1} before 0600 to 0.5 m s^{-1} between 0600 and 0930. At 0930 wind speed increases to 3 m s^{-1}. There is a broad maximum in O_3 between 1030 and 1600. At this time, NO_y and CO concentrations are at or near their minimum values. The primary pollutants have a late night maximum at 0000 (between July 2 and 3) and at 2000. At both points there is an anticorrelation between O_3 and NO_y.

This time pattern is similar to that observed on other days and can be qualitatively explained in terms of the diurnal dependence of emissions, chemistry, and vertical mixing. The following scenario is based on observational and calculational studies at other sites and is consistent with the major features seen in Figure 5.

We start at 0000, at which point the peak in NO_y and CO suggests that there is still upward mixing of surface level emissions to the 100 m height of the downtown observation site. The concentration of O_3 is near zero at this time, which we ascribe to titration by NO. The decrease in primary pollutants at 0100 can be explained by a decrease in the height of the nocturnal boundary layer to below 100 m, thus cutting off the observation site from the surface. Sunrise is at 0600 which is also near the start of the morning rush hour. In response to increased emission rates and increased atmospheric mixing that accompanies the lifting of the inversion to above 100 m, concentrations of CO and NO_y experience a large and abrupt increase. Coincident with the increase in CO and NO_y is a decrease in wind speed probably due to the mixing of low momentum air from near the surface to the height of the observation site. Ozone at this time is removed by titration with fresh NO_x emissions.

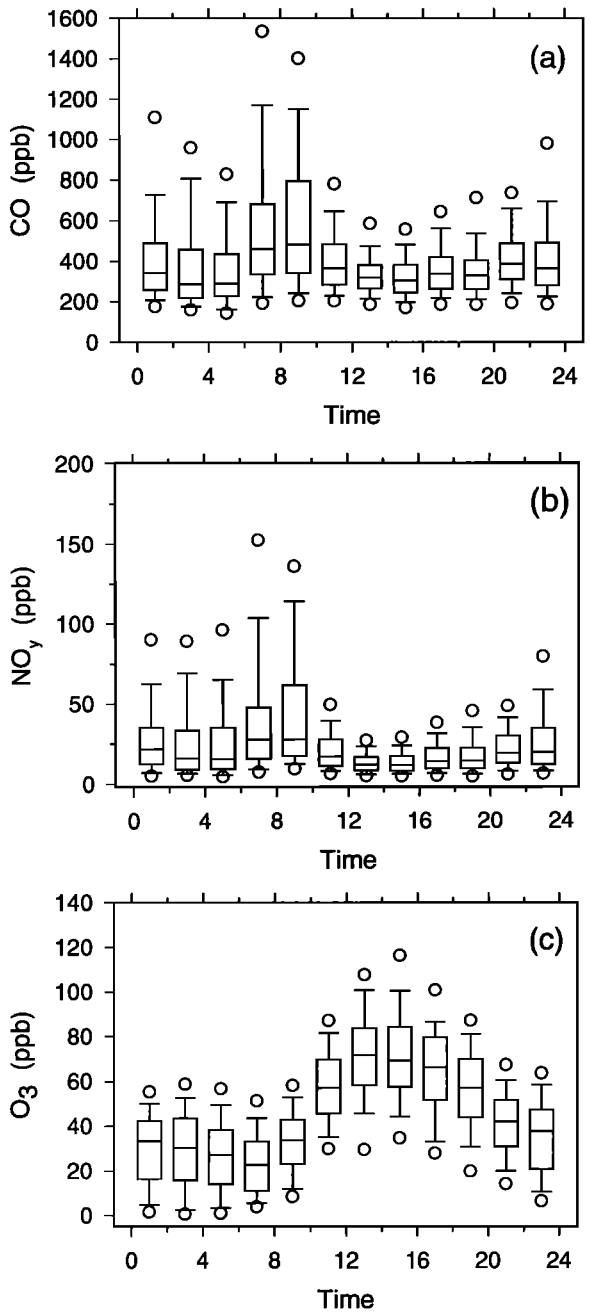

Figure 4. Composite diurnal cycle for (a) CO, (b) NO_y, and (c) O_3. Box plots show the percentile distribution of trace gases for 2 hour time intervals. Circles show 5 and 95 percentile values; whiskers show 10 and 90 percentile values. Box covers interquartile range, between 25 and 75 percentiles. Line in box is median.

The large and abrupt decrease in CO and NO_y at 0930 is at a point in the diurnal cycle where the height of the mixed layer typically experiences rapid growth. This dilutes the concentrated mixture of near-surface primary pollutants with faster moving upper altitude air. Since the air aloft has high O_3 from the previous day, entrainment causes O_3 at the 100 m height to increase. Chemical production of O_3 could contribute to the late morning increase, but judging from the near temporal coincidence between O_3 increase and primary pollutant decrease, it

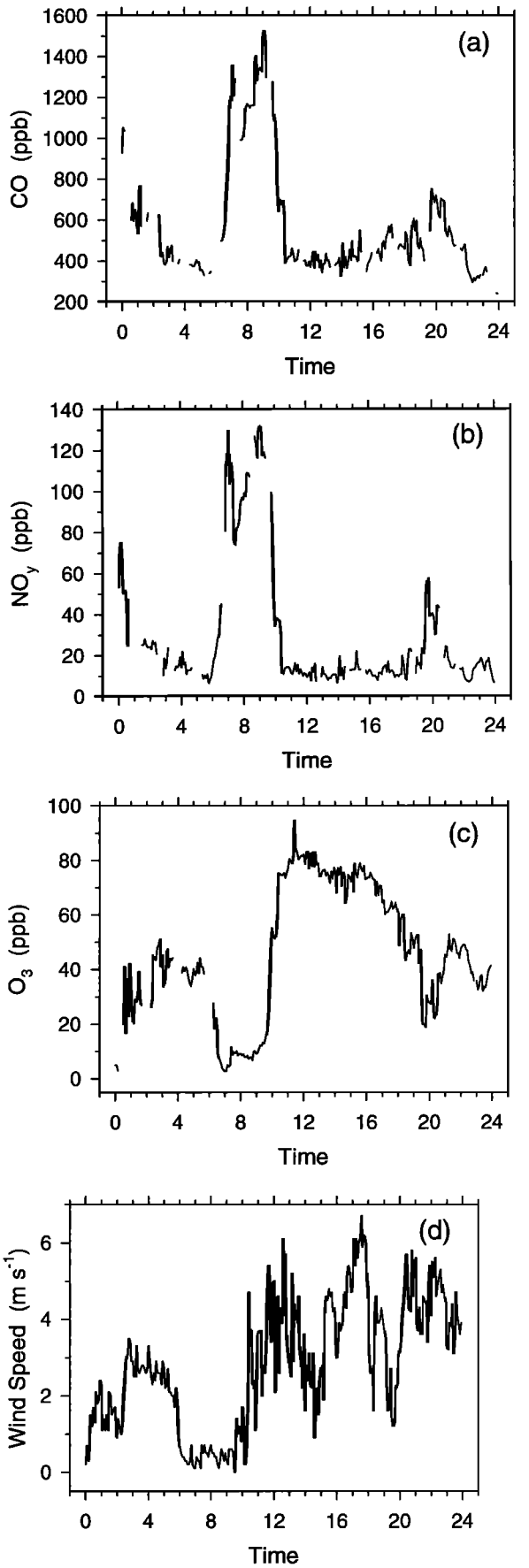

Figure 5. Diurnal cycle for (a) CO, (b) NO_y, (c) O_3, and(d) wind speed on July 3.

appears that on this day the major factor is entrainment. Mixing during the midday period from 1030 to 1600 is evidently efficient in keeping concentrations of NO_y and CO at low values. A shallow nocturnal inversion is again established in the evening. At 2000, the peak in CO and NO_y suggests that the inversion height is still above 100 m, but not so high that surface level emissions are extensively diluted. A decrease in O_3 at 2000 due to titration is coincident with a peak in NO_y.

On July 3 the Nashville urban plume was encountered by the G-1 between 1400 and 1500, about 5 hours and 50 km downwind of Nashville (L. J. Nunnermacker et al., unpublished manuscript, 1998). According to this time difference the air that the G-1 sampled was over Nashville at about the time of the inversion breakup. As discussed above, we believe that the majority of the boundary layer had an O_3 concentration similar to the air that is entrained downward after the inversion breakup. With that assumption, the 115 ppb O_3 observed from the G-1 represents about a 35 ppb net increase over downtown levels.

3.3. Hydrocarbon Composition

Table 1 provides the median concentrations and OH reactivities of anthropogenic VOCs and isoprene at the two primary sampling periods; 0700-0800 and 1200-1300. These downtown observations are compared with low-altitude measurements from the G-1 aircraft taken outside of the city center. The G-1 samples were collected between 1100 and 1400, a time period centered on the downtown "PM" collection time. Percentile distributions for the downtown concentrations are shown in Figure 6.

As with the other primary pollutants, median anthropogenic hydrocarbon concentrations are higher in the morning (97 ppb C) than in the afternoon (45 ppb C). Reactivity per ppb of anthropogenic carbon does not vary indicating that the hydrocarbon mix observed in the afternoon is not any more aged than that observed in the morning. Effects of aging are clearly seen in the G-1 samples. According to Table 1 the median anthropogenic hydrocarbon concentration observed from the G-1 is a factor of 3.5 lower than downtown; but the median OH reactivity is a factor of 7 lower.

The median isoprene concentration does not change much from morning (1.10 ppbC) to afternoon (0.96 ppbC), although, as might be expected by the 2 order of magnitude range in concentration, there can be large differences between AM and PM on any given day. Because anthropogenic VOCs decrease in concentration in the afternoon while isoprene remains constant, we find that the contribution that isoprene makes to total OH-VOC reactivity is about a factor of 2 greater in the afternoon as compared with the morning. Although isoprene is usually a minor contributor to the total reactivity, there are a few occasions in the afternoon when it is the dominant reactive hydrocarbon. Isoprene levels observed from the G-1 are similar to those observed downtown. We believe that this is due to two opposing effects; namely, an increase in isoprene emission rate outside of the urban area and a decrease in isoprene concentration with altitude that reflects a very short atmospheric lifetime. Because the reactivity of the anthropogenic hydrocarbons decreases outside of the urban area, isoprene becomes, on average, the largest measured contributor to VOC-OH reactivity. Our analysis does not include daughter oxidation products which in the case of isoprene are quite reactive. We might therefore be underestimating the contribution that isoprene makes to OH reactivity. Biogenic reactivity is also underestimated by not including terpenes.

L. J. Nunnermacker et al. (unpublished manuscript, 1998) have compared the hydrocarbon composition measured downtown on the morning of July 18 with the composition measured from the G-1 [*York University*, 1995] later in the day in a downwind location. By using CO as a conservative tracer to account for dilution, they were able to derive an average OH concentration experienced by the air parcel as it was advected from downtown to the G-1 located 25 km from the urban center. Figure 7a shows the concentrations of a select group of alkanes, alkenes, and aromatics, from the downtown July 18 AM and July 18 G-1 samples that were analyzed by Nunnermacker et al.. We have adjusted the scales on the vertical axes so that the two concentration plots coincide at iso-pentane. The total concentrations, including compounds not explicitly shown in Figure 7a are

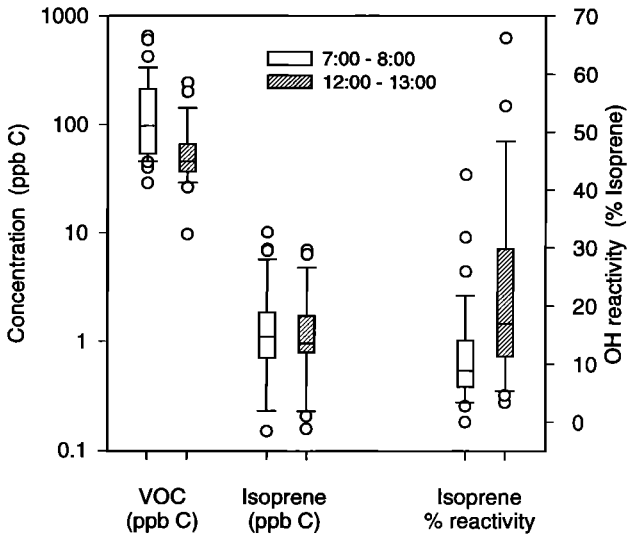

Figure 6. Percentile distributions of total VOC (ppb C), isoprene (ppb C), and percent contribution of isoprene to total OH reactivity. Box covers interquartile range, between 25 and 75 percentiles. Whiskers are at 10 and 90 percentile. Line in box is median. Data are given at the two primary measurement times, 0700-0800 and 1200-1300. Morning data is from 30 hydrocarbon samples, noon data are from 20 samples. Percentile distribution for morning isoprene does not include two samples with isoprene lower than detection limit.

Table 1. Median Hydrocarbon Concentration and VOC-OH Reactivity at the Downtown Site and in the Boundary Layer Outside of Nashville

Location	Anthropogenic[a]		Isoprene	
	Concentration, ppb C	Reactivity, s^{-1}	Concentration, ppb C	Reactivity, s^{-1}
Downtown AM[b]	97	4.48	1.10	0.51
Downtown PM[b]	45	2.06	0.96	0.45
G-1[c]	13.2	0.29	0.92	0.41

[a]All compounds except isoprene and terpenes.

[b]There were 30 samples in AM and 20 samples in PM, same data as used for Figure 6.

[c]Includes 62 samples, 300-1000 m altitude at a median distance of 55 km from the urban center. Average altitude equal to 550 m. G-1 samples collected from 1100-1400.

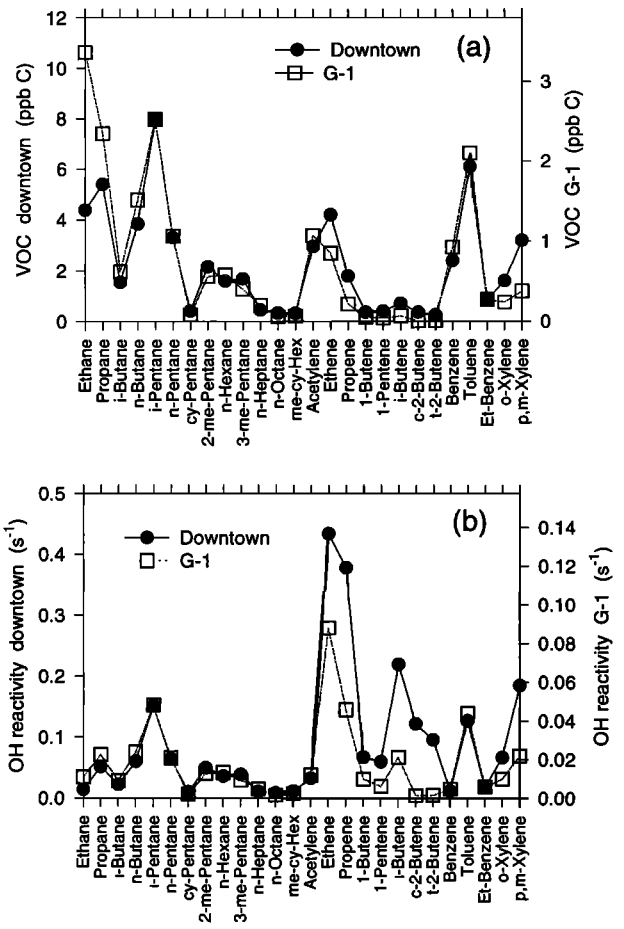

Figure 7. Comparison of hydrocarbon samples observed downtown on July 18 AM and downwind on July 18 from the G-1. Vertical scales have been adjusted so that plots coincide at iso-pentane. Compounds are arranged by category (i.e., alkanes, C_2H_2, olefins, and aromatics) and within a category by OH reaction rate constant. (a) Concentration (ppb C); (b) OH-VOC reactivity as defined in equation (1) (s^{-1}).

approximately a factor of 3 greater downtown as compared with the downwind measurement on the G-1. Differences between the downtown and G-1 samples are not all that apparent in Figure 7a because most of the high concentration species have a similar relative abundance at both sites.

Figure 7b shows OH reactivities. Again, the vertical scales are adjusted so that the downtown and G-1 plots coincide at iso-pentane. The first two compounds, ethane and propane, have an appreciable background which is proportionately more important in the G-1 sample. Most of the alkanes do not react appreciably in the 2 hours that L. J. Nunnermacker et al.(unpublished manuscript, 1998) estimate for a travel time to the G-1, and therefore the two reactivity curves almost coincide. The G-1 samples show a preferential removal of the more reactive olefins and aromatics. Internally bonded olefins with OH rate constants of order 10^{-11} (cm^3 $molecules^{-1}$ s^{-1}) have very low concentrations and reactivities in the G-1 sample. The reactivity per unit VOC is some 40% lower in the G-1 sample compared with the downtown sample.

4. Comparison With Emission Inventories

In this section we compare concentration and reactivity ratios determined from the downtown observations with the corresponding quantities determined from estimates of local emission rates. This comparison is performed to assess the accuracy of emission information.

There are two major categories of emission sources that could impact the downtown site; namely, the urban area in which the downtown site is located and the power plants located outside of the city. Table 2 contains emission estimates for these sources. Power plant emission estimates are from TVA (N. Gillani, personal communication, 1998) and are provided for the four large plants closest to Nashville. Paradise and Cumberland are among the largest NO_x sources in the United States [*Environmental Protection Agency (EPA)*, 1993a]. Urban area emission estimates were obtained from the 1995 SOS emission inventory. This emission inventory is an update of the 1990 Middle Tennessee Emission Inventory [*Davis et al.*, 1993]. Emission data collected during the 1995 SOS Ozone Field Study was used to modify and to update the 1990 inventory to 1995 values [*Cardelino et al.*, 1996]. Table 2 provides an emission estimate for Davidson County which contains the city of Nashville. The downtown site is located approximately in the center of the county. Emissions in the five county O_3 nonattainment region, which includes Davidson, Rutherford, Sumner, Williamson, and Wilson counties is approximately double that of Davidson by itself. Table 2 indicates that NO_x emissions from the Nashville metropolitan area are significantly smaller than that from the surrounding power plants. The three larger power plants, however, are located 80 or more km from the city center, so it is not a priori evident which source will contribute the most NO_x to the Nashville urban area.

In order to maximize the likelihood that the observations are capturing fresh emissions, we have limited the comparison to data collected between 0600 and 1000. This is a period of high emission rates due to morning rush hour traffic. Vertical mixing is limited during this period resulting in high concentrations, which overwhelm the dilute mixture of pollutants carried over from the previous day. Contributions from power plants are minimized because fumigation of elevated plumes does not generally occur until later in the day [*Duncan et al.*, 1995]. Reactive losses are also minimized. NO and NO_2 were not successfully measured, so a direct comparison between emitted and observed NO_x is not possible. However, NO_y can be used instead. This has the advantage that loss of emitted NO_x from reaction is accounted for because the products are measured as part of NO_y. We expect NO and NO_2 to make up most of the NO_y, especially for the high concentration conditions occurring in the morning. An NO_y instrument intercomparison conducted in Nashville in 1994, indicated high detection efficiencies under these conditions [*Williams et al.*, this issue]. There are 30 hydrocarbon samples suitable for this analysis, all of which were collected over 1-hour long periods extending from 0700 to 0800.

Table 2. Emission Rates

Emission Source	Distance From Nashville, km	Emissions, kton yr^{-1}			
		CO	VOCs	NO_x	SO_2
Power Plant[a]					
Gallatin	38			12	98
Cumberland	82			118	26
Johnsonville	110			20	115
Paradise	124			132	192
Urban area[b]					
Davidson County	---	187	50	40	

[a]Annual average rates.
[b]Summertime average rate.

According to Table 2 the urban area and power plants have very different emission characteristics. Power plant emissions contain NO_x and SO_2, but essentially no CO or hydrocarbons. Urban emissions in contrast have high NO_x, CO, and hydrocarbons, but low SO_2. These signatures can be used to identify the primary emission source impacting the downtown site [*Parrish et al.*, 1991; *Poulida et al.*, 1994]. Figure 8a shows SO_2 as a function of NO_y at the downtown site. Straight lines on this figure indicate the SO_2 to NO_x emission ratios for the four power plants listed in Table 2. We do not expect that air masses influenced by power plant emissions will correspond quantitatively to any of the curves because the urban area could still be supplying most of the NO_y. However, the SO_2 observations do indicate only a minor impact from power plants with plume-like excursions of high SO_2 occurring less than 5% of the time. This view is confirmed in Figure 8b which shows the close association between CO and NO_y in the downtown observations. Taken together these figures indicate that there are almost no points that simultaneously have high SO_2, high NO_y, and low CO. Accordingly, the downtown observations will be compared only with urban area emissions.

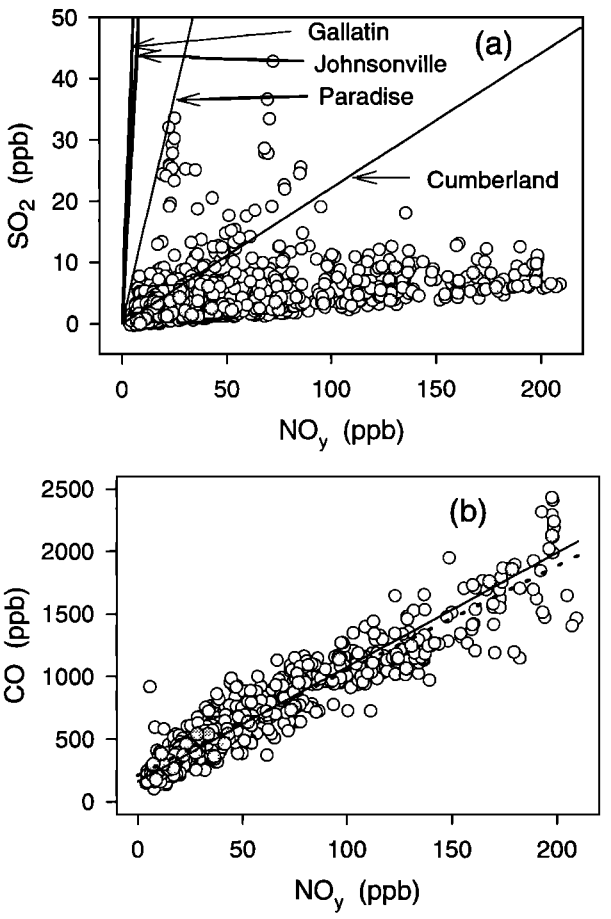

Figure 8. Correlations between SO_2, CO, and NO_y observed downtown in the morning. Each open data point is a 5 minute average between 0600 and 1000. Solid symbols indicate 1 hour average concentrations during the 0700-0800 time period in which hydrocarbon samples were collected. (a) SO_2 versus NO_y. Straight lines indicate emission ratios of SO_2 to NO_y from the Gallatin, Johnsonville, Paradise, and Cumberland power plants; (b) CO versus NO_y. Solid straight line is a linear regression fit to the data points coincident with the hydrocarbon samples. Broken line is a linear regression fit to the 5 minute average data.

Table 3. Comparison of Observed Concentration and Reactivity Ratios With Corresponding Quantities From Emission Estimates

Ratio	Observations	Emissions	
		1990 NAPAP[a]	1995 SOS
VOC[b]/CO, ppb C/ppb	0.32	0.46	0.42
VOC/NO_x, ppb C/ppb	2.9	4.1	2.9
CO/NO_x, ppb/ppb	9.3	9.1	6.9
k(VOC)[c]/VOC, cm^3 $molecules^{-1}$ s^{-1}	2.13e-12[d]	1.64e-12	

[a]Encompasses 40 by 40 km region that includes the city of Nashville. Emission rates are for a summer weekday with maximum and minimum temperatures of 29.4° and 18.3°C.
[b]VOC does not include CH_4 or biogenics.
[c]The term k(VOC) defined in equation (1).
[d]Read 2.13e-12 as 2.13×10^{-12}.

As indicated in Table 3, the comparison between observations and emissions is carried out for the concentration ratios CO/NO_y, VOC/NO_y, and VOC/CO, and also for a measure of hydrocarbon reactivity, k(VOC)/VOC. The term k(VOC) is defined in (1) as the OH reactivity of a hydrocarbon mixture and k(VOC)/VOC is thereby the average rate constant for reaction of that mixture with OH. Emission ratios are determined from the 1995 SOS inventory used in Table 2 and also from a gridded version of the National Acid Precipitation Assessment Program (NAPAP) 1990 [*EPA*, 1993a] that was provided to us by S. Sillman (personal communication, 1998). This inventory was used by *Sillman et al.* [this issue] for photochemical model calculations of the Nashville/Mid Tennessee region. Reactivity calculations were carried out only for the 1990 NAPAP inventory. For both inventories we used a temporal weighting factor to account for the diurnal dependence of emission rates. The fraction of emissions in the downtown area that occur between 0600 and 10:00 for NO_x, VOCs, and CO are taken to be 0.214, 0.171, and 0.192, respectively. The fraction of mobile emissions were computed using traffic counter data [*Cardelino et al.*, 1996], while the other categories, area, mobile nonroad, and point emissions were computed using default values within the emissions model EPS2 [*EPA*, 1993b]. Urban area SO_2 emissions were not available from the 1995 SOS inventory. The 1990 NAPAP inventory does include SO_2 but it appears to be several-fold higher than is consistent with the observed SO_2 to NO_y ratio (3.2%).

In order to minimize the effects of background concentration, the observed ratios in Table 3 have been determined as the slope of a linear least squares regression between the two quantities that make up the ratio. In performing the regressions we assume that both variables have equal "errors" [*Imre et al.*, 1996]. This assumption applies when the departure from a perfect correlation reflects a real atmospheric variability. The equal error regression slope so obtained is the geometric mean between the slopes that are calculated by considering one and then the other variable as independent. Measurements errors for CO, NO_y, and VOCs are estimated to be in the range 10-20% depending on absolute concentration. As the slopes in Table 3 depend more on the higher concentration observations, the lower error estimate is more appropriate. The propagated error in the ratios is thereby approximately 15-20%.

Regression fits to the concentration data are shown in Figures 8b, 9a, and 9b for CO/NO_y, VOC/CO, and CO/NO_y,

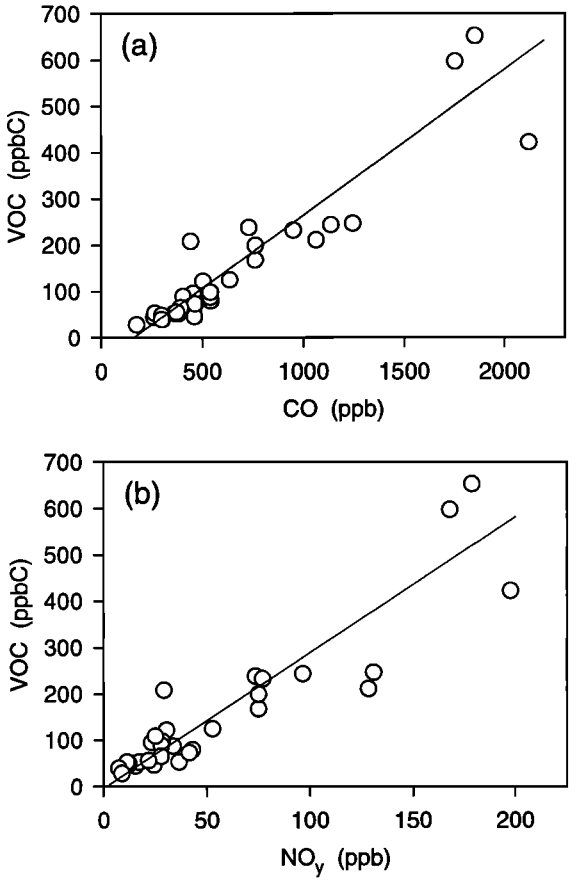

Figure 9. Correlation between VOC, CO, and NO_y observed downtown between 0700 and 0800. Solid lines are linear least squares regression fits, the slope of which is the observed ratio in Table 3. (a) VOC versus CO; (b) VOC versus NO_y.

respectively. The ratio, CO/NO_y, that is in Table 3 was determined from CO and NO_y measurements that coincide with the times of the hydrocarbon samples; these are the shaded points in Figure 8b. This figure shows two almost identical regression fits, which indicates that there is only a small difference between the CO to NO_y ratio determined from the measurements coincident with the VOC samples and those determined from the entire 0600-1000 data set.

According to Table 3 the observations reproduce the CO/NO_x ratio in the 1990 NAPAP inventory and the VOC/NO_x ratio in the 1995 SOS inventory. The problem of deducing errors in emission rates (assuming observations are accurate) is underdetermined, leaving us with a family of possible solutions. The simplest way to proceed is to assume that the two correct ratios imply that emissions of CO and NO_x are correctly given by the 1990 inventory and that VOCs and NO_x are correctly given in the 1995 inventory. This agrees with the perception that emission inventories are more accurate for NO_x than for VOCs or CO [*Fujita et al.*, 1992]. The remaining ratios can be brought into agreement with observations if the 1990 NAPAP VOC emission rate is decreased by 30% and the 1995 SOS CO emission rate is increased by about 35% (i.e., the 1990 VOC emissions are high, and the 1995 CO emissions are low). Although the VOCs in the 1990 inventory are 30% higher than suggested by observation, we note that the OH reaction rate constant is 77% of observed, which leaves the 1990 VOC mixture only slightly less reactive than the observed VOC mixture.

Compared with some earlier attempts to reconcile emissions and ambient concentrations, the comparisons in Table 3 are very encouraging. Similar to the observations by *Goldan et al.* [199]) in Boulder, Colorado, we do not find any evidence that emission inventories are underpredicting CO and VOCs by factors 2 or more as was deduced for several sites from CO/NO_x and VOC/NO_x ratios [*Morris*, 1990; *Fujita et al.*, 1992] (for a review of prior measurements, see *National Research Council (NRC)* [1991]).

5. Conclusions

Trace gas measurements from the Polk office building in downtown Nashville show elevated concentrations of CO, NO_y, and VOCs characteristic of urban area emissions. Peak levels occur in the morning when vertical mixing is limited and emissions are high due to rush hour traffic. High O_3 concentrations were measured later in the afternoon. During the 30 day aircraft intensive period, there was one occasion when O_3 exceeded the current 1-hour average, 120 ppb standard. In downtown Nashville the daily maximum 8-hour average O_3 is, on average, only 10 ppb lower than the daily maximum 1-hour average O_3. As a consequence, changing the standard to 80 ppb averaged over 8 hours would cause the number of potential violations to increase to 12.

Most of the downtown VOC samples indicate that isoprene makes only a small contribution to OH reactivity (median contribution is 9 and 17% in the AM and PM, respectively), in contrast to what is found in samples taken outside of the city from the DOE G-1 aircraft. A comparison of a sample taken downtown on July 18 with a sample taken later in that day downwind of the city shows that there is a preferential loss of reactive alkenes and xylenes in the downwind sample.

Correlations between CO, NO_y, and SO_2 were used to establish the relatively minor influence of the nearby power plants on the downtown air. Because the downtown site is located in a high emission rate region, we are able to assess the accuracy of the Nashville urban area emission inventories by comparing emission ratios with the corresponding observed morning concentration ratios. The observed morning ratios were VOC/CO equal to 0.32 (ppbC/ppb), VOC/NO_x equal to 2.9 (ppbC/ppb), and CO/NO_x equal to 9.3 (ppb/ppb). The 1990 NAPAP emission estimates can be brought into agreement with these values if the VOC emission rate is decreased by 30%. The 1995 SOS inventory will agree if the CO emission rate is increased by about 35%. In contrast to comparisons that have been made in other locations, we do not find any evidence for large (i.e., factor of 2 or greater) underpredictions of CO or VOCs in the inventories.

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References

Apel, E.C., J.G. Calvert, R. Zika, M.O. Rodgers, V.P. Aneja, J.F. Meagher, and W.A. Lonneman, Hydrocarbon measurements during the 1992 Southern Oxidants Study Atlanta Intensive: Protocol and quality assurance, *J. Air Waste Manage. Assoc.*, *45*, 521-528, 1995.

Cardelino, C., W.L. Chang, and M.E. Chang, Daily variability of motor vehicles emissions during the 1995 SOS Nashville/Middle Tennessee Ozone Field Study, Paper presented at AWMA International Conference on the Emission Inventory, Air and Waste Manage. Assoc., New Orleans, La., Sept. 1996.

Davis, W.T., T.L. Miller, and A. Chatterjee, 1993, SIP base year 1990 emissions inventories for precursors of ozone for the Nashville nonattainment area and middle Tennessee modeling domain, University of Tenn., Knoxville, July 1993.

Duncan, B.N., A.W. Stelson, and C.S. Kiang, Estimated contributions of power plants to ambient nitrogen oxides measured in Atlanta, Georgia in August 1992, *Atmos. Environ.*, *29*, 3043-3054, 1995.

Environmental Protection Agency (EPA), Regional interim emission inventories (1987-1991), vols. 1 and 2, *EPA-454/R93-021a and b*, Research Triangle Park, N. C., 1993a.

Environmental Protection Agency (EPA), User's guide for urban airshed model. vol. 4, User's manual for the Emissions Preprocessor System 2.0, *EPA-450/4-90-007D(R)*, Research Triangle Park, 1993b.

Fujita, E.M., B.E. Croes, C.L. Bennett, D.R. Lawson, F.W. Lurmann, and H.H. Main, Comparison of emission inventory and ambient concentration ratios of CO, NMOG, and NO_x in California's South Coast Air Basin, *J. Air Waste Manage., Assoc.*, *42*, 264-276, 1992.

Goldan, P D., M. Trainer, W.C. Kuster, D.D. Parrish, J. Carpenter, J.M. Roberts, J.E. Yee, and F.C. Fehsenfeld, Measurements of hydrocarbons, oxygenated hydrocarbons, carbon monoxide, and nitrogen oxides in an urban basin in Colorado. Implications for emission inventories, *J Geophys Res.*, *100*, 22,771-22,783, 1995.

Hübler, G., R., et al., An overview of the airborne activities during the SOS 1995 Nashville-Middle Tennessee Ozone Study, *J. Geophy., Res.*, this issue.

Imre, D.G., E.H. Abramson, and P.H. Daum, Quantifying cloud-induced shortwave absorption: An examination of uncertainties and of recent arguments for large excess absorption, *J. Appl. Meteorol.*, *35*, 1991-2010, 1996.

Lonneman, W.A., R.L. Seila, and S.A. Meeks, Non-methane organic composition in the Lincoln Tunnel, *Environ. Sci. Technol*, *20*, 790-796, 1986.

Meagher, J.F., W.J. Parkhurst, and J.L. Christ, The SOS Nashville/Middle Tennessee Ozone Field Study data base, Environ. Res. Cent., Tenn. Val. Auth., Muscle Shoals, Ala., 1996.

Morris, R., Selection of cities for assessing the effects of test fuels on air quality, Sys. Appl. Int., Inc., San Rafael, Calif., 1990.

National Research Council, *Rethinking the Ozone Problem in Urban and Regional Air Pollution*, edited by J. Seinfeld, Natl. Acad. Press, Washington, D. C., 1991.

Parrish, D.D., M. Trainer, M.P. Buhr, B.A. Watkins, and F.C. Fehsenfeld, Carbon monoxide concentrations and their relation to total reactive nitrogen concentrations at two rural U.S. sites, *J. Geophys, Res.*, *96*, 9302-9309, 1991.

Pierson, W.R., A.W. Gertler, N.F. Robinson. J.C. Sagebiel, B. Zielinska, G.A. Bishop, D.H. Stedman, R.B. Zweidinger, and W.D. Ray, Real-world automotive emissions - Summary of studies in the Fort McHenry and Tuscarora mountain tunnels, *Atmos. Environ.*, *30*, 2233-2256, 1996.

Poulida, O., K.L. Civerolo, and R.R. Dickerson, Observations and tropospheric photochemistry in central North Carolina, *J. Geophys. Res.*, *99*, 10,553-10,563, 1994.

Sillman, S., D. He, M. Pippin, P.H. Daum, D.G. Imre, J.H. Lee, L. Kleinman, and J. Weinstein-Lloyd, Model correlations for ozone, reactive nitrogen and peroxides for Nashville in comparison with measurements: Implication for O_3-NO_x-hydrocarbon chemistry, *J. Geophys. Res*, this issue.

Tennessee Valley Authority Environmental Research Center (TVA/ERC), 1995 Nashville/Middle Tennessee Ozone Study, vol. 2, Level 2 network operations manual, Muscle Shoals, Ala., 1995.

Valente, R.J., R.E. Imhoff, R.L. Tanner, J.F. Meagher, P.H. Daum, R.M. Hardesty, R.M. Banta, R.J. Alvarez, R. McNider, and N. Gillani, Ozone production during an urban air stagnation episode over Nashville, Tennessee, *J. Geophys, Res.*, this issue.

Williams, E.J., et al., Intercomparison of NO_y measurement techniques, *J. Geophys. Res.*, this issue.

York University, Hydrocarbon analysis for "Southern Oxidant Study 1995" canister samples collected by Brookhaven National Laboratory, Cent. for Atmos. Chem., North York, Ontario, Canada, 1995.

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