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Atmospheric chemistry and distribution of formaldehyde and several multioxygenated carbonyl compounds during the 1995 Nashville/Middle Tennessee Ozone Study

Y.-N. Lee,[1] X. Zhou,[1,2] L. I. Kleinman,[1] L. J. Nunnermacker,[1] S. R. Springston,[1] P. H. Daum,[1] L. Newman,[1] W. G. Keigley,[3] M. W. Holdren,[3] C. W. Spicer,[3] V. Young,[4,5] B. Fu,[4] D. D. Parrish,[6] J. Holloway,[6] J. Williams,[6] J. M. Roberts,[6] T. B. Ryerson,[6] and F. C. Fehsenfeld[6]

Abstract. Airborne measurements of formaldehyde (FA), glycolaldehyde (GA), glyoxal (GL), methylglyoxal (MG), and pyruvic acid (PD) were made on board instrumented aircraft platforms, the Department of Energy G1 and National Oceanic and Atmospheric Administration P3 (FA only), during the 1995 Nashville/Middle Tennessee Ozone Study. FA data determined on these two aircraft during three intercomparison flights agreed to within ~10%. The mean and median (in parentheses) concentrations observed within the boundary layer (< 2000 m) for FA, GA, GL, MG, and PD were 4.2 (3.9), 0.78 (0.70), 0.07 (0.06), 0.14 (0.10), and 0.24 (0.23), respectively (all in parts per billion by volume (ppbv)). At the observed concentrations, FA accounted for a substantial fraction of the OH reactivity, comparable to isoprene and CO. Further, it served as an important free radical precursor, contributing 25-30% of the radical production during midday and even greater during morning and late afternoon periods. Source attribution of FA was assessed using measured concentrations of hydrocarbons, their reaction kinetics with the OH radicals, and FA yields. The results showed that isoprene was the dominant source of FA, responsible for ~67%, methane and peroxyacetyl nitrate contributed equally at ~13% each, and alkanes and alkenes which are largely of anthropogenic origin accounted for only ~7%. This assessment based on reaction kinetics is consistent with the strong correlations ($r > 0.8$) observed between FA and two other isoprene products, GA and MG. Further, the magnitudes of the nonzero FA intercept exhibited in these correlation plots are found to qualitatively agree with the fraction of precursors that did not concomitantly produce GA and MG. Inspection of specific flights showed direct evidence of the dominance of isoprene as a precursor for FA, appreciable contribution of FA to CO, and negligible decay of FA overnight. Because of the dominant role isoprene plays as a precursor of FA, FA could be used as a proxy of isoprene for assessing the applicability of various versions of biogenic emission inventory.

1. Introduction

Atmospheric carbonyl compounds are primarily produced as reaction intermediates from NO_x-mediated photooxidation of volatile organic compounds (VOC) emitted into the atmosphere [*Atkinson*, 1994]. Because carbonyl compounds produce free radicals as photoproducts and react with the OH radicals, their atmospheric concentrations are required to derive reliable OH concentration fields and radical budgets in model calculations. Furthermore, carbonyls can significantly alter the distribution of NO_x by sequestering NO_2 as peroxyacyl nitrates, resulting in long-range transport of odd nitrogen compounds as well as radicals [*Singh and Hanst*, 1981]. Owing to these properties which give rise to enhanced photooxidant production among certain VOCs, concentrations and speciation of atmospheric carbonyl compounds must be determined for comparison with photochemical model predictions to test the representativeness of field measured VOC concentrations and applicability of laboratory determined mechanistic data [e.g., *Atkinson*, 1994].

Since biogenically emitted VOCs, particularly isoprene, are known to impact the photochemistry of both rural and urban environments [*Chameides et al.*, 1988], their roles in photooxidant production must be quantitatively elucidated in order to formulate effective O_3 mitigation strategies [*National Research Council* (*NRC*), 1991]. In fact, the ozone non-attainment situation facing many urban regions in the southeastern United States has been attributed to these naturally emitted VOCs [*Chameides et al.*, 1988]. The 1995 Southern Oxidants Study (SOS) in the Nashville/Middle Tennessee region permits a quantitative test of this hypothesis since isoprene emission rates are very high in

[1]Environmental Chemistry Division, Department of Applied Science, Brookhaven National Laboratory, Upton, New York

[2]Now at Wadsworth Center for Laboratories and Research, Empire State Plaza, Albany, New York.

[3]Atmospheric Science and Applied Technology, Battelle, Columbus, Ohio.

[4]Department of Chemistry, York University, Toronto, Ontario, Canada.

[5]Now at Department of Chemical Engineering, Ohio University, Athens, Ohio.

[6]Aeronomy Laboratory, NOAA, Boulder, Colorado.

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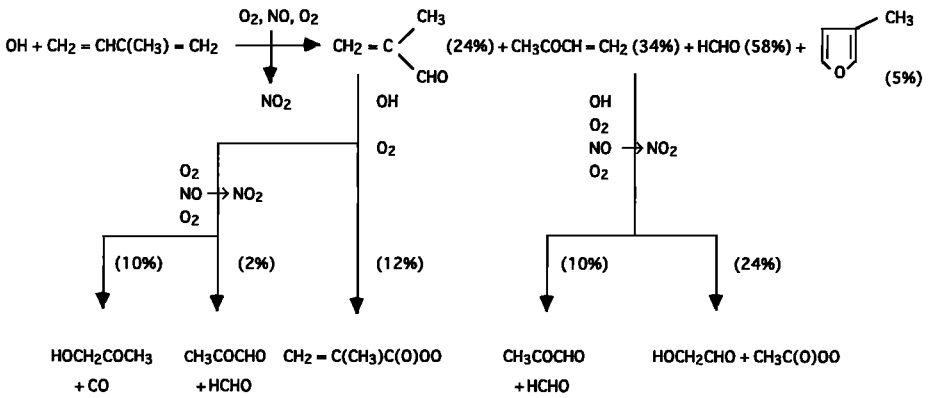

Figure 1. Mechanism of the OH-initiated oxidation of isoprene under NO_x rich conditions.

this region [*Guenther et al.*, 1994]. In this investigation, we attempted to characterize the contribution of isoprene to ozone production, utilizing airborne measurements of a number of soluble carbonyl compounds that are known products of the OH-initiated isoprene oxidation. They include formaldehyde (FA), glycolaldehyde (GA), methylglyoxal (MG), and glyoxal (GL). Pyruvic acid (PD) was also measured as it has been suggested to be produced from isoprene [*Jacob and Wofsy*, 1988]. The OH-initiated oxidation of isoprene under NO_x (=NO + NO_2) rich conditions [e.g., *Paulson and Seinfeld*, 1992; *Carter and Atkinson*, 1996] involves the formation of FA, methyl vinyl ketone (MVK), methacrolein (MACR), and 3-methylfuran as first stage products. These products react rapidly with the OH radicals to form secondary carbonyls, namely, hydroxyacetone, GA, GL, MG, as well as additional FA. Oxidation of MVK also produces peroxyacetyl radical, the precursor of peroxyacetyl nitrate (PAN). A simplified diagram showing the major isoprene oxidation products is given in Figure 1. It may be pointed out that although O_3 and NO_3 also react with isoprene, their daytime contributions are typically minor compared to the OH pathway [e.g., *Carter and Atkinson*, 1996], and are not considered in this work.

In this article, we report the observed concentrations of these carbonyls and their spatial and temporal variations. The contribution of FA to radical production will be examined and compared to that of ozone. We will also examine the relationships among these compounds and their relationships with isoprene as a precursor according to the isoprene oxidation mechanisms [*Carter*, 1996]. We will demonstrate that isoprene is the dominant source of FA and the other carbonyls measured in this work, and suggest on this basis that FA may be used as a proxy of isoprene for testing the applicability of different biogenic emission inventories. Finally, although in this article the term concentration is freely used in place of mixing ratio, readers can distinguish them by way of units; conversions always reflect pressure and temperature.

2. Experimental Section

2.1. General

A description of the major objectives, the measurement capabilities regarding chemical and meteorological parameters, and the atmospheric conditions during the Nashville intensive is found in an overview article by *Meagher et al.* [this issue]. Directly pertinent to this study are that the vegetation coverage responsible for isoprene emission, such as deciduous forest, is mainly located west of the Nashville metropolitan area [e.g., *Williams et al.*, 1997], and that the immediate NO_x sources include the urban area, the Gallatin Power Plant located 40 km northeast of downtown Nashville, the Cumberland power plant located at 80 km west of downtown, and Johnsonville Power Plant, located ~30 km southwest of the Cumberland power plant [*Meagher et al.*, this issue].

2.2. Carbonyl Compounds Measurement Technique

Continuous 5-min average concentrations of FA, GA, GL, MG, and PD were measured on the DOE G1 aircraft and continuous 3-min average concentrations of FA were measured on the NOAA P3. Details of the aircraft measurement technique for the carbonyl compounds have been previously described [*Lee et al.*, 1996]. Briefly, gaseous carbonyls are incorporated into an aqueous solution containing 0.10 mM 2,4-dinitrophenylhydrazine (DNPH) maintained at *p*H 2.50 using a 28-turn glass coil scrubber. The liquid samples containing the dissolved carbonyls were stored sequentially in septum-sealed glass vials using an autosampler (Model ISIS, Isco), the integration time being 3.0 min and 5.0 min for the P3 and the G1, respectively. After landing, the carbonyls were analyzed as respective DNPH hydrazones using high performance liquid chromatography (HPLC) equipped with a UV-vis detector [*Lee and Zhou*, 1993]. Typical gas and liquid flow rates were 2.0 standard liters per min (sLpm), which was controlled by a mass flow controller (MKS, 0-5 sLpm), and ~0.30 mL min^{-1}, which was determined gravimetrically.

The collection efficiencies of the glass coil for the highly soluble multi-oxygenated carbonyls, that is, GA, GL, MG, and PD, are 100% within experimental uncertainties [*Lee and Zhou*, 1993]. In contrast, the collection efficiency for FA is typically less than 100% under the conditions employed because of its limited Henry's law solubility, and was determined as a function of altitude upward of 7000 m using an altitude chamber. The calibration procedure used has been reported elsewhere [*Lee et al.*, 1996], and the results were found to compare reasonably well with those determined by different approaches [*Gilpin et al.*, 1997].

2.3. Instrumented Aircraft Platform

Description of the G1 and the P3 aircraft measurement capabilities regarding chemical and physical parameters are given by

Hübler et al. [this issue]. Typically, the cruise speeds of the G1 and the P3 were 190 kt at 210 kt, respectively. With repsect to spatial coverage, the P3 had a range up to 1000 km for a flight duration of ~6 hours, and the G1 had a range half that distance for a 4 hour duration. With its longer range, the P3 devoted six flights to regional studies encompassing the states of Missouri, Illinois, Indiana, Kentucky, North Carolina, and Georgia. In contrast, the G1 stayed within a more confined radius of 120 km from downtown Nashville, only occasionally venturing into southern Kentucky and northern Alabama. Regarding altitude, the P3 routinely reached a maximum height of 7 km and spent a significant portion of its flight above the boundary layer (BL). On the other hand, the G1, which had a maximum altitude of 5 km during the mission, spent a significantly greater portion of its flights within the BL.

2.4. Inlet Arrangement

On the G1, which was operated under unpressurized conditions, sample air was drawn into the coil scrubber from ram air ducted into the cabin via a ~100 cm long 1.0 cm ID PFA tube. The ram air flow was believed to be at least 50% isokinetic, permitting a flow ~200 L min^{-1} at the G1's cruising speed. Although the flow is expected to be turbulent, a similar arrangement employed on the G1 for a NO_y instrument indicated no appreciable loss of HNO_3. We surmise that wall losses of the present analytes which are less labile than HNO_3 are unimportant. On the P3, whose cabin was pressurized, sample air was drawn through the glass coil by way of a 0.4 cm ID FEP inlet tube (~120 cm long) housed in a rear-facing stainless steel tube. At a sampling rate of 2.0 sLpm, the residence time of sample air in the inlet tubing was fairly long, for example ~0.7 s. Accordingly, we limited our measurement on the P3 to FA only because of potential wall losses of the highly soluble multi-oxygenated carbonyls. In a recent FA intercomparison study, it was found that surface loss of FA to Teflon tubings was insignificant [*Gilpin et al.*, 1997].

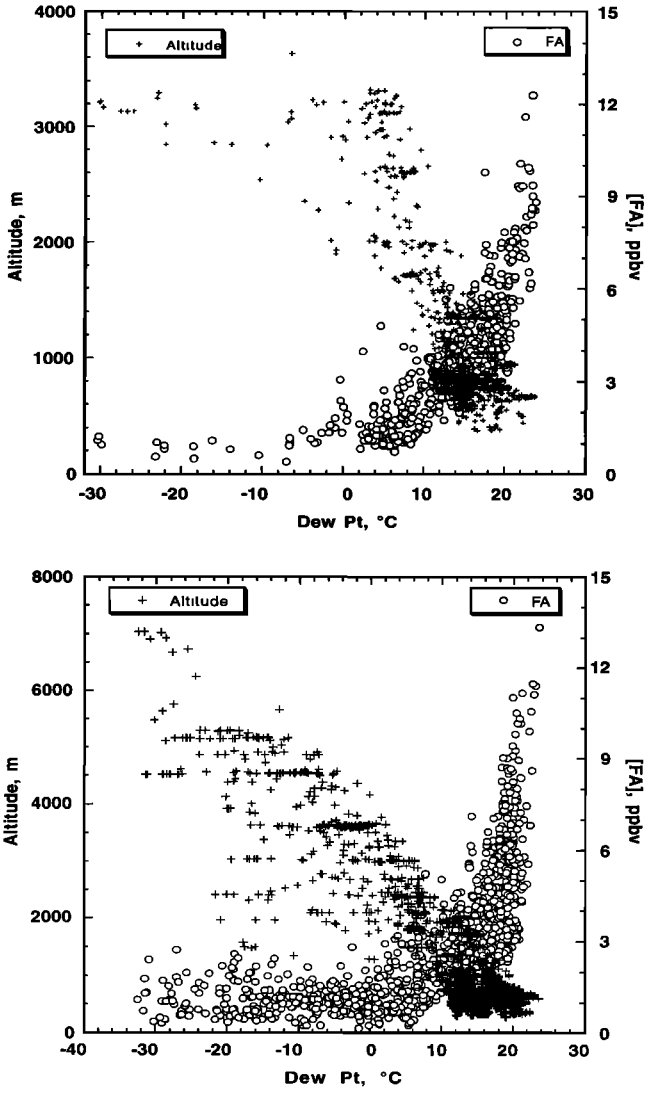

Figure 2. Altitude dependence of fomaldehyde and dew point. (top) G1; (bottom) P3.

3. Results

3.1. Overview and Statistical Summary

Concentrations of FA were determined on the P3 on 13 flights between June 29 and July 20. There were six regional flights, extending north into Illinois, Indiana, and Ohio (July 10, 11, 14, and 17), and east into North Carolina and South Carolina (July 20). Concentrations of FA, GA, GL, MG, and PD were determined on the G1 on 16 flights between June 27 and July 20.

FA concentration, along with altitude, are plotted as a function of dew point temperature (DT) in Figure 2 for both the P3 and G1. Two different relationship regimes between the FA concentration and dew point are seen: [FA] sharply increased with increasing DT for DT >10°C and remained independent of DT at low DT (i.e., <5°C). For the purpose of segregating the free tropospheric measurement data from those of the BL, we use the altitude of 1800 ~2000 m that has been measured by *McNider et al.* [this issue] as the average value of the mixing height. It is noted from Figure 2 that this altitude range corresponds to DP between 0° and 10°C, the region where the transition between the two FA-DT dependence regimes occurred, suggesting that in the BL FA is correlated with H_2O concentration (see below). However, it should be pointed out that the data in Figure 2 include those obtained on the P3 when the maximum mixing height was either not developed or deviated from the ~2000 m value. These included two early morning flights (July 3 and 19) before the nocturnal inversion was broken up and a flight (July 20) over the Great Smoky Mountain where the terrain elevation reaches ~1000 m msl.

Concentrations of FA determined in the BL are presented for each flight as box plots in Figure 3. Statistical summaries, including, mean, median, minimum, and maximum, of the carbonyls determined in the BL are tabulated in Table 1. The concentrations of FA observed on the two aircraft were comparable: the maximum concentrations were nearly identical, that is, ~13 ppbv; so were the median and mean. The slightly lower values observed on the P3 are attributed to the fact that the P3 spent a greater fraction of its time over rural regions than did the G1. The concentrations of the multi-oxygenated carbonyl compounds were much lower compared to FA, with mean concentrations all below 1 ppbv. The most abundant species amongst them is GA, which showed a maximum concentration of nearly 3 ppbv, followed by PD, MG and GL, maximum all being <1 ppbv (Table 1).

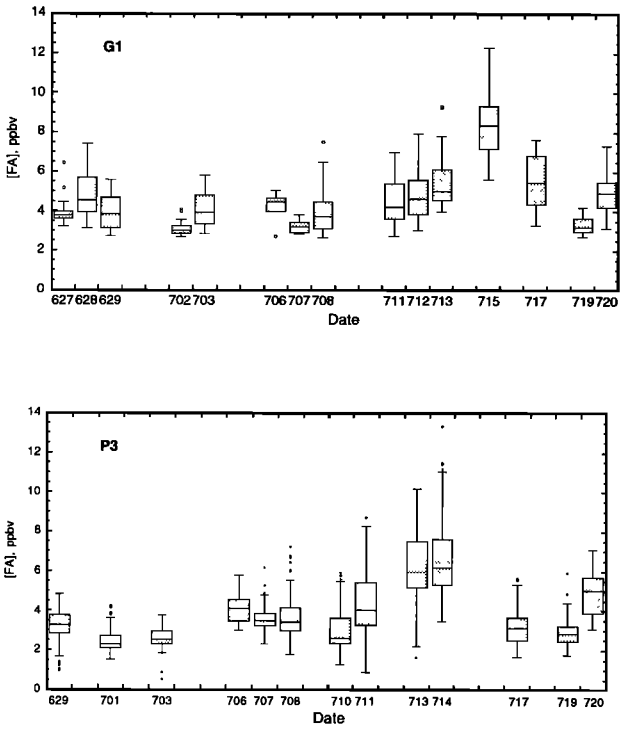

Figure 3. Box plots of FA concentrations determined in the boundary layer for individual flights. Boxes indicate center 50%; wiskers denote 100%; circles are outliers. Horizontal bars inside the boxes represent medians.

3.2. Vertical Distributions

The vertical profiles of FA obtained on the two aircraft (Figure 4) showed comparable concentration ranges and a trend of decreasing concentration with increasing altitude. Despite the negative altitude dependence, [FA] did not exhibit a sharp cut-off at the top of the BL, ~2000 m. Instead, it decreased gradually with altitude and reached a median value of ~0.7 ppbv at ~7 km, the highest altitude of the P3. The absence of a sharp concentration change at the top of the BL suggests that FA and its precursors could be mixed into the free troposphere (FT) from the BL by vertical transport processes such as cloud venting [*Lin et al.*, 1994]. This possibility is compatible with the fact that FA is relatively long-lived (2-4 hours, see below) and is not appreciably removed by cloud processing due to its limited Henry's law solubility. Similar behavior is also observed for water vapor concentration, which exhibited an altitude dependence also without an abrupt cutoff at the top of the BL.

Table 1. Statistical Summary of the Concentrations of Carbonyl Compounds Determined During the 1995 Nashvile Intensive

Variable	Count	Mean	Median	Standard Deviation	Minimum	Maximum
			Altitude < 1900 m			
FA (P3)	914	3.82	3.34	1.828	0.53	13.3
FA (G1)	498	4.21	3.90	1.780	0.72	12.3
GA	494	0.78	0.70	0.480	0	2.82
GL	538	0.067	0.06	0.040	0.01	0.29
MG	538	0.14	0.10	0.124	0	0.92
PD	539	0.24	0.23	0.085	0.09	0.94
			Altitude > 1900 m			
FA (P3)	464	1.26	1.07	0.778	0.14	5.22
FA (G1)	109	1.51	1.34	0.639	0.39	3.96
GA	86	0.15	0.12	0.098	0	0.58
GL	113	0.026	0.02	0.009	0.01	0.06
MG	113	0.021	0.02	0.010	0	0.07
PD	113	0.163	0.15	0.062	0.02	0.37

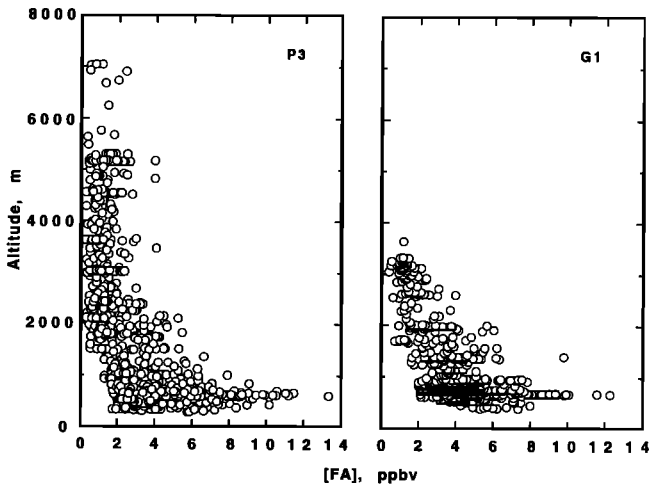

Figure 4. Vertical profiles of FA concentrations measured on the G1 and the P3 aircraft.

The vertical distribution of GA, GL, MG, and PD are shown in Figure 5. In contrast to FA, these carbonyls showed a relatively more pronounced decrease in concentration above the BL, suggesting that vertical transport is less efficient for these species compared to FA. This is expected in the case of cloud venting when these highly soluble species [*Betterton and Hoffmann*, 1988] are removed by cloud droplets. The concentrations of GA, GL, and MG above the BL were low, median values being 0.12, 0.02, and 0.02 ppbv, respectively, indicating that their sources are much reduced in the FT. With regard to PD, it is noted that its concentrations were distributed in a narrow range, showing an altitude dependence weaker still compared to other carbonyls. Since the photolysis of PD is rapid, time constant ~1 hr [*Grosjean*, 1983], this weak altitude dependence most likely reflects that PD is either a second or even a third generation product of isoprene. The mean [PD] of 0.24 ppbv, if maintained at steady state, suggests a production rate of this compound of ~0.12 ppbv hr^{-1}.

3.3. Intercomparison Study

Three intercomparison flights between the G1 and the P3 were conducted to examine measurement comparability on the two aircraft on June 29, July 3, and July 13. Although these studies were mainly intended for NO_x, O_3, and SO_2, they also afforded an opportunity to examine the consistency of FA measurements on the two aircraft. The [FA] determined on the two aircraft were found to agree to within ~10%. The data collected on July 13 are shown as an example in Figure 6; a good agreement was evident despite that a fairly large [FA] range was encountered which varied from less than 1 ppbv at 3000 m to ~9 ppbv at ~400 m, and that different sample integration time was used on the two aircraft. This agreement, in combination with a general agreement in the median and average concentrations observed on the two platforms over the entire intensive, provided us confidence in our measurement

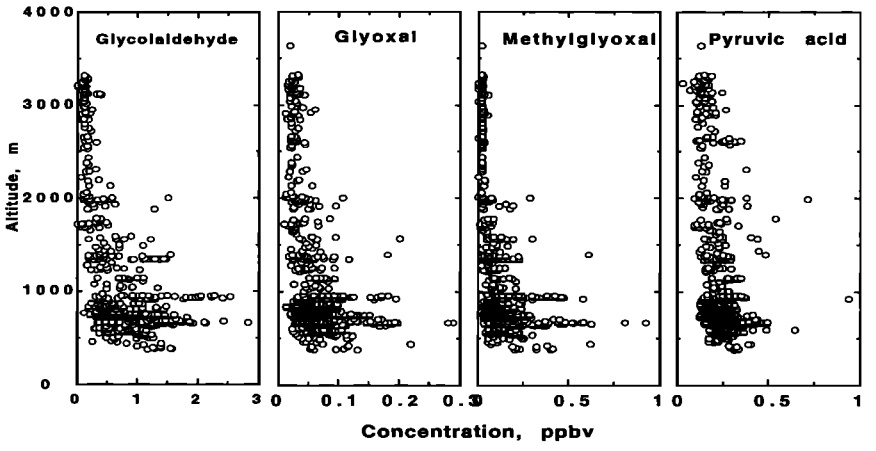

Figure 5. Vertical profiles of glycolaldehyde, glyoxal, methylglyoxal, and pyruvic acid measured on the G1.

technique. This agreement also suggests that the different inlet arrangements on the two aircraft did not give rise to appreciable biases.

4. Discussion

4.1. FA as Sink and Source of Free Radicals

A key to reliable photochemical modeling lies in the model's ability to determine the OH concentration field as the OH radical represents the most important oxidant in the atmosphere [e.g., *McKeen et al.*, 1997]. This information in turn requires as input the concentrations of all the major sink species, such as VOC, CO and NO_x, as well as those of the radical sources, namely, O_3 and carbonyls. Concerning the removal of OH, the concentrations and reactivities against the OH of all the sink species that were measured on the G1 are seen to be dominated by CH_4, CO, isoprene (Figure 7), as well as by FA (compare reactivity of ~1.0 s^{-1} based on a mean [FA] of 4.2 ppbv and a rate constant with the OH radical of $k = 1 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}). A similar conclusion was also reached from ground based measurements by *Cantrell et al.* [1992], whereby the directly measured isoprene products, MVK and MACR, were also found important.

Carbonyl compounds are important free radical sources by way of photolysis; the lifetimes for those measured in this work are listed in Table 2. Since FA represents the most important carbonyl in this regard resulting from the combination of its fast photolysis rate and large atmospheric abundance, we compare its contribution to that of O_3, the primary source of free radicals. The photolysis and radical producing channels of FA and O_3 are given below.

$$H_2CO + h\nu \rightarrow 2\,HO_2 + CO \quad (1)$$

$$H_2CO + h\nu \rightarrow H_2 + CO \quad (2)$$

$$O_3 + h\nu \rightarrow O(^1D) + O_2 \quad (3)$$

$$O(^1D) + H_2O \rightarrow 2\,OH \quad (4)$$

$$O(^1D) + M \rightarrow O(^3P) \quad (5)$$

Using time-dependent photolysis rate constants evaluated for Nashville for July 7 under clear-sky conditions and the measured concentrations of FA, O_3, H_2O, and pressure, we calculated the contribution of FA to total radical production. In Figure 8, we show the fraction of the total radical due to FA, namely, the total from both O_3 and FA, along with [FA], as a function of time of day. It is seen that this fraction is a substantial ~25% at midday, and increases toward morning and late afternoon hours, due to the slightly red-shifted absorption of FA compared to O_3. In order to properly take into account the significant contribution of FA in radical budget calculations, its conenctration must either be evaluated using reliable kinetics and mechanisms data (in the case of emission based models) or directly determined (applicable to observational based models in treating instantaneous chemistry). In this regard, model calculation results must be critically compared to measurement data for mechanistic insights as well as for validation.

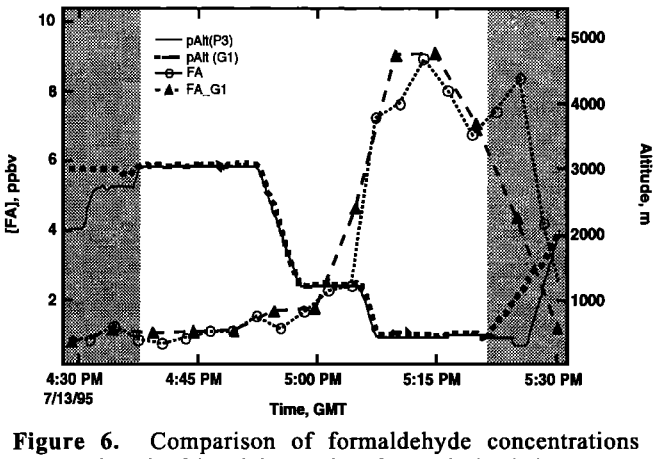

Figure 6. Comparison of formaldehyde concentrations measured on the G1 and the P3 aircraft on July 13, 1995.

4.2. Sources of FA

FA is produced at high molar yield (~0.6) from OH initiated oxidation of isoprene, and from the OH oxidation of its two major first stage products, MACR and MVK, the total yield being estimated to be 0.7 [*Carter and Atkinson*, 1996]. FA is also produced from anthropogenically emitted VOCs, but at a rate significantly smaller than that from isoprene due to a combination of relatively low concentrations, slower reaction kinetics, and small FA yields of these VOCs. Their contribu-

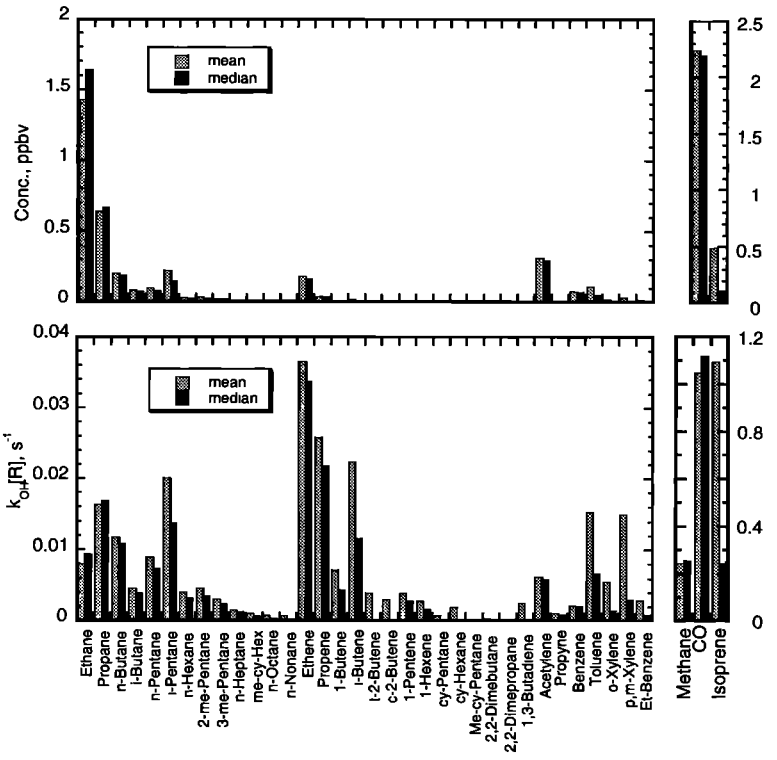

Figure 7. (top) Mean and median concentrations of VOC observed on the G1. The concentration of CO is scaled by /100. The bottom panel shows the reactivities of the measured VOCs, that is, the product of concentration and the corresponding second-order rate constant against the OH radical. Note that CH_4 is also included in this comparison and that scales are different for the right and left panels.

tions to FA production can be estimated using the OH reactivities of the VOCs measured on the G1 (Figure 7) and the corresponding FA yields. The molar FA yields of alkanes, alkenes, alkynes, and aromatics are evaluated below based on mechanistic information provided by *Atkinson* [1994].

4.2.1. Alkanes. The OH initiated oxidation of alkanes involves abstraction of H followed by addition of O_2 and reaction with NO, producing alkoxy radicals. Alkoxy radicals undergo decomposition and O_2 reaction; for carbon chain length n > 4 isomerization is also important. Among the various channels, decomposition of 2-alkoxy radicals is the main route for FA production via the formation of CH_3 radical. For straight chain terminal alkoxy radicals (n = 2 - 4) which are produced at a ~15% yield, reaction with O_2 dominates, generating corresponding aldehydes. 2-Alkoxybutane, which is produced from n-butane at a yield of ~85%, decomposes with a ~40% efficiency and reacts with O_2 at 60% efficieny to form methyl ethyl ketone. Ignoring the leaving group effect, the decomposition of 2-alkoxybutane is to result in a maximum FA yield of

Table 2. Lifetimes of the Carbonyl Compounds Against Photolyis and Reaction With OH.

Species	j^a 10^5 s^{-1}	k^b x 10^{11}	τ, ^{c}hours
Formaldehyde	3.2 (r)	1.0	1.6
Formaldehyde	4.4 (m)		
Glycolaldehyde	~0.7	1.0	1.7
Glyoxal	6.0	1.1	1.6
Methylglyoxal	23	1.7	0.7
Pyruvic acid[d]	27	< 0.05	~1

The rate constants are denoted as j and k, respectively.

[a] Noontime maximum value (r, radical branch; m, molecular branch; d, day).

[b] Units of cm^3 $molecules^{-1}s^{-1}$ [*Atkinson and Lloyd*, 1984; *Atkinson et al.*, 1989].

[c] At [OH] = 1 x 10^7 molecules cm^{-3}

[d] *Grosjean* [1983].

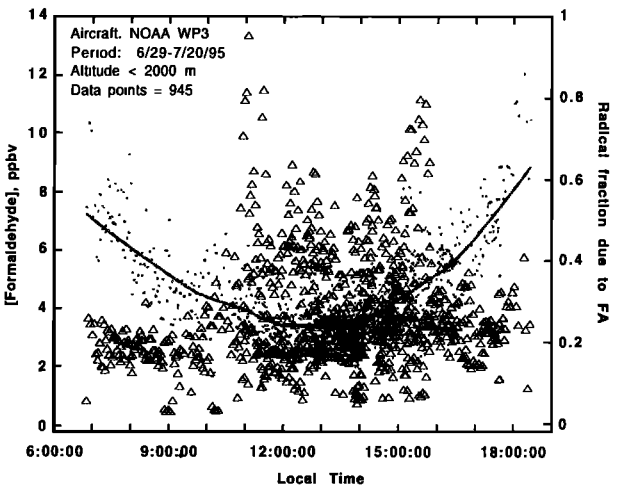

Figure 8. A composite diurnal plot of boundary layer FA concentrations (triangles) observed on the P3 for the entire intensive period. The radical production due to FA (solid circles) is expressed on the right-hand side ordinate as a fraction of the total, sum of that by FA and O_3. The solid curve represents the best fit to the radical fraction, closely resembling the median values.

50%. The total yield of FA from n-butane is therefore assigned to be 0.2. Propane is expected to behave somewhere between ethane and n-butane. Using n-butane as a model, more generous in FA yield, we derive a maximum yeild of 0.4, assuming decomposition of 2-alkoxypropane is equally important as its reaction with O_2. For higher normal alkanes, FA yields decrease compared to n-butane arising from the fact that isomerization and reaction with O_2 dominate. Branched alkanes with methyl substituent groups produce FA at higher yields than n-alkanes and we estimated values of 0.8, 0.5, 0.35, and 0.35 for isobutane, isopentane, 2-methyl-pentane, and 3-methyl-pentane, respectively, assuming H abstraction on secondary and tertiary carbons accounts for 80% of the reactions and isomerization is unimportant. We assume a FA yield of 0.3 for all higher alkanes. One notes that the most reactive product of alkanes that is known to accumulate to a substantial level in the ambient air is acetaldehyde. Longer chain aldehydes are present in much lower levels. Ketones are also produced, but their reactivities are significantly smaller compared to aldehydes.

4.2.2. Alkenes. Alkenes react with OH mainly by addition, resulting in β-hydroxy-substituted alkoxy radicals. These radicals, for n <4, primarily undergo decomposition. The FA yield of the decomposition of $HOCH_2CH_2O$ is estimated to be 1, the remaining forming GA by way of O_2 reaction. Since the alkoxy radicals from higher terminal alkenes behave analogously, the FA yield is assigned to be 1 for propene and 1-butene. For 1-petene and 1-hexene, we estimate a FA yield of 0.5, assuming that the reaction rate of the alkoxy radical with O_2 is comparable to that of their decomposition. With isomerization becoming more important for n > 6, FA yields of terminal alkenes decrease and are assumed to be 0.15 as determined for 1-octene.

4.2.3. Alkynes. First stage reaction products reported for reactions of OH with ethyne, propyne, and butyne are formic acid and GL, MG, and biacetyl, respectively. FA yields of these compounds are taken as zero.

4.2.4. Aromatics. The aromatics, dominated by benzene, toluene, ethylbenzene, and xylenes, react with OH in two pathways: (1) abstraction of an alkyl hydrogen producing a final product benzaldehyde or substituted benzaldehyde, and (2) abstraction of a benzyl hydrogen which eventually yields nitroaromatics and phenolic compounds along with MG, GL, and PAN. Again, the FA yields of aromatics are taken as zero.

Multiplying the reactivities of the VOCs by their FA yields given above, we determined the FA production efficiencies of these measured VOCs (Figure 9). The relative contributions to FA production of CH_4, alkanes, alkenes, and isoprene, calculated using mean concentrations, are 21%, 2.3%, 8%, and 69%, respectively. We point out that in this evaluation two major simplications were made. First, we only considered the first generation products. This truncation is expected to result in underestimate in the FA yields for those fast reactions whose secondary products also rapidly produce FA. Consequently, we use a combined value of 0.7 as the FA yield for isoprene to include the contributions of its secondary products, MVK and MACR. However, since we did not extend this treatment to other alkenes, we may have artificially emphasied isoprene in this analysis. Nonetheless, we note that using a FA yield of 0.6 for isoprene itself does not appreciably alter the conclusion reached here. Furthermore, by way of including PAN as a source of FA (see below), we have effectively taken acetaldehyde (an important secondary product from, e.g., prepene) into consideration, partially removing the slight bias. The second simplication deals with the assumption that NO reaction dominates the fate of RO_2 radical, producing RO. Since the mean [NO] observed on the G1 was 0.3 ppbv, signifcantly greater than the 0.05 ppbv value whereby RO_2/HO_2 self reactions can compete with NO, we consider the simplification justified.

As surface-emitted FA precursors are mixed into the BL while being removed by chemical reactions, appreciable vertical concentration gradients can result for those which react rapidly. Consequently the measured concentrations of these species at aircraft altitudes had been attenuated relating to surface to varying degrees depending on their reaction kinetics. As isoprene exhibits the fastest reaction kinetics with OH ($k = 9.7 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}), its concentration would be subject to the largest kinetic effect; at [OH] = 1×10^7 molecules cm^{-3}, the lifetime of isoprene is ~30 min. Using this reaction lifetime and a stochastic mixing time constant of ~30 min for vertical transport from the surface to the top of the BL of ~1500 m, we estimate that ~30% of the isoprene has reacted at the median sampling height of 560 m. Alkenes are in general quite reactive and have rate constants ranging from ~30-70% of that of isoprene. The magnitude of depletion of the alkenes at the median sampling height is estimated to range from 10 to 20%. In contrast, methane and alkanes show a much weaker OH reaction effected attenuation, ~5%. The percentage contributions to FA production calculated using mean concentrations corrected for OH reactions are however not significantly affected, namely, 16, 1.5, 6.9, and 76% for CH_4, alkanes, alkenes, and isoprene, respectively.

Several additional sources of FA are the O_3 oxidation of α- and β-pinenes, and the decomposition of PAN. Since both pinenes are of biogenic origin, and PAN has approximately half of its source in isoprene [*Williams et al.*, 1997], the inclusion of these sources will not affect the conclusion that biogenical VOCs (BVOC) are the dominant sources of FA. The contribution of PAN to FA cannot be directly compared to the FA production efficiency defined above because PAN produces FA by thermo-decomposition followed by reaction with NO, rather than by reaction with OH. The rate of FA production from PAN is estimated from the mean concentrations of PAN (0.90 ppbv), NO (0.30 ppbv), and NO_2 (1.21 ppbv) measured on the G1, and the rate constants corresponding to the mean temperature and

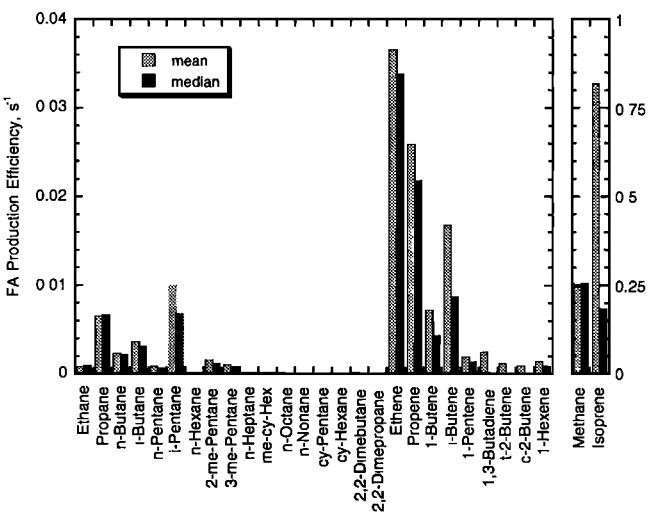

Figure 9. FA production efficiencies of individual VOCs, which are defined as the product of the reactivity given in Figure 7 and FA yield.

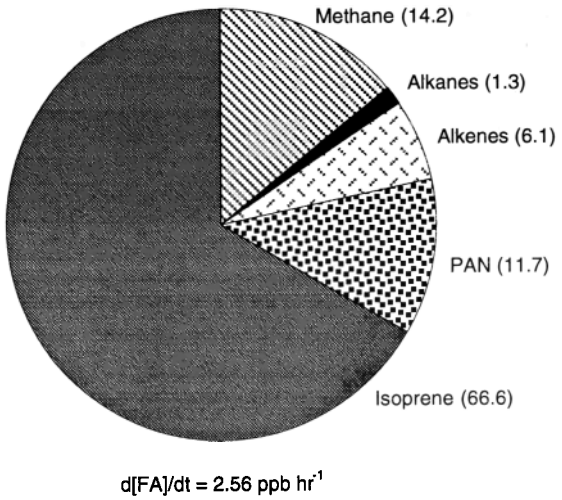

Figure 10. Relative contributions of CH_4, alkanes, alkenes, PAN, and isoprene to FA production, calculated using [OH] = 1 x 10^7 molecules cm^{-3}. Numbers shown in parentheses represent the percentages.

pressure of 293 K and 703 torr, respectively. The rate of FA production from PAN decomposition is estimated to be 0.29 ppbv h^{-1}. This contribution is compared in Figure 10 to that of the VOCs for an [OH] of 1 x 10^7 molecules cm^{-3}, a concentration which was found to be appropriate for the mean concentrations used in the context of this analysis (e.g., L. J. Nunnermacker et al., unpublished manuscript, 1998). The total FA production rate thus calculated is 2.56 ppbv h^{-1}. This evaluation shows that while isoprene remained as the dominant source of FA, PAN also contributed appreciably, comparable to CH_4. We examine below both these absolute and relative FA production rates in light of other available information.

Since FA is relatively short-lived, its concentration is expected to be either at or near steady state, that is, the production rate approximates its destruction rate. The destruction of FA is by photolysis and by reaction with OH radicals (Table 2). Using the solar noon j values appropriate for Nashville on July 7 and the mean total UV irradiance of 75% of the maximum, we derived a mean j_{FA} = 5.5 x 10^{-5} s^{-1}. At [OH] = 1 x 10^7 molecules cm^{-3} as before, we estimate a decay rate constant for FA k_d = 1.50 x 10^{-4} s^{-1}, or 0.54 h^{-1}. At the mean [FA] of 4.2 ppbv, the rate of FA decomposition is calculated to be 2.3 ppbv h^{-1}, in close agreement to the estimated production rate of 2.56 ppbv h^{-1}, suggesting that the calculated FA production rate is representative. At this juncture, it may be noted that the rate of CO production from FA decomposition is also 2.3 ppbv h^{-1}. Assuming an upper limit of isoprene emission rate of 1 x 10^{16} molecules m^{-2} s^{-1} and a BL height of 1500 m, this CO production corresponds to a CO yield from isoprene of ~2.3, comparable to the value of ~3 reported by *Miyoshi et al.* [1994] evaluated for NO_x rich conditions.

It is interesting to note that GA, GL, and MG are produced from isoprene oxidation along with FA, but not from the remaining two major FA precursors, that is, CH_4, and PAN. The strong correlations observed among GA, GL, MG, and FA (r values ranging from 0.84 to 0.92, Figure 11) are consistent with a scenario that these compounds are dominated by a common precursor, that is, isoprene. Given this observation, it is instructive to compare the correlations observed among the carbonyls measured in this work to that observed at a rural ground site

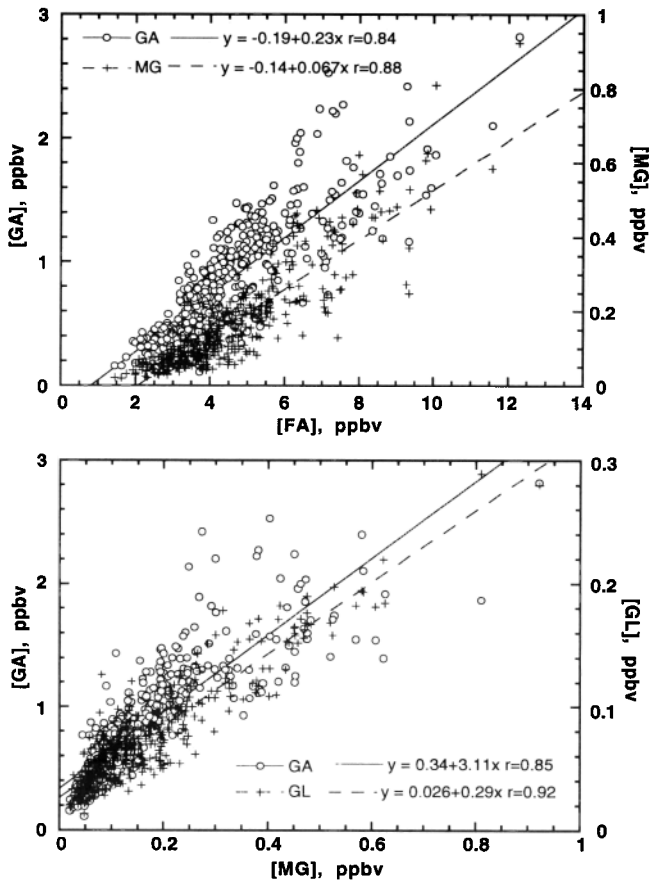

Figure 11. Correlations among FA, and multioxygenated carbonyls, GA, MG, GL.

during an earlier SOS study at Metter, Georgia, in 1992 [*Lee et al.*, 1995]. It is striking to see (Table 3) that the values observed during these two field studies were identical for GA/FA and MG/FA. Since the ground measurement site at Metter is away from major urban areas or emission sources and is located in a region of strong BVOC emission [*Guenther et al.*, 1996], isoprene was found to be the dominant reactive HC [*Cantrell et al.*, 1992] responsible for the observed carbonyls. The constancy of the ratios lends further support to the conclusion that during the Nashville/Middle Tennessee Ozone Study isoprene was also the dominant VOC as far as the production of these carbonyls are concerned. However, the ratios of GL to MG were different in these two studies; the greater value at Metter suggests the presence of GL precursors that are less important in the present work. Judging from a small yield of GL from isoprene oxidation [*Paulson and Seinfeld*, 1992], we estimated that the ratio of GL to MG to be <0.3, a magnitude consistent with the present value of 0.29.

Table 3. Ratios of Daytime Concentrations of Several Carbonyl Compounds.

Ratios	Metter, Georgia, 1992	This Work
GA/FA	0.23	0.23
MG/FA	0.067	0.067
GL/MG	0.70	0.29

Finally, we note that the intercepts of the least squares fits of the correlation plots of GA and GL against MG tended to pass through the origin. However, the fits of the plots of GA and MG against FA indicated a nonzero intercept of [FA] ~1 to 2 ppbv. The former observation can be interpreted as these carbonyl compounds are coproduced either from a common precursor or precursors that have common origins. The latter, on the other hand, suggests that there exist FA precursors that do not concomitantly produce GA and MG. Noting that ~30% of the FA production was attributed to CH_4 and PAN (Figure 10) which do not produce GA, GL, or MG upon oxidation, we consider the observed nonzero intercepts to be in qualitative agreement with the source attribution analysis. Since the least squares fits in Figure 11 represent a statistical analysis based on mean concentrations, we calculate a [FA] that is unrelated to GA and MG, and therefore to isoprene, to be 4.2 x 0.3 = 1.3 ppbv (4.2 ppbv being the mean [FA]). That this estimate is in qualitative agreement with the intercept values of ~1 and ~2 ppbv observed in plots of GA vs FA and MG vs FA, respectively (Figure 11), corroborates the FA source attribution analysis given above. Since GA has a yield of ~0.5 in ethene oxidation, this pathway may contribute to the slight positive deviation in the GA-MG plot, and a smaller FA intercept in the GA-FA plot (Figure 11).

4.3. Observations from Individual Flights

Several interesting observations obtained during the intensive which may provide useful insights into the sources of FA and isoprene and their influences on photooxidants formation are described below.

4.3.1. July 20 - Regional orographic. This P3 flight which spanned 6 hours between 1000 and 1600 LT extended eastward into the Great Smoky Mountains in the Carolinas over an area of dense vegetative coverage. Although it is apparent that both FA

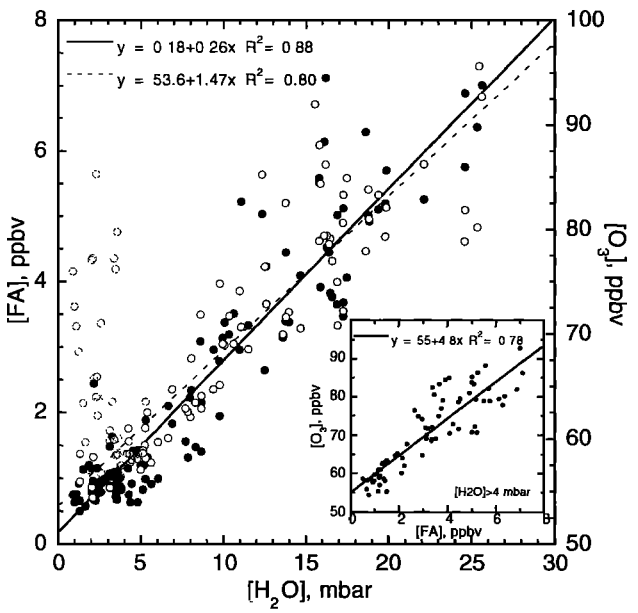

Figure 12. Plot of FA and O_3 against H_2O vapor observed on a P3 regional flight on July 20, 1995. Regressions between FA and H_2O (solid line) and between O_3 and H_2O (dashed line) are for $[H_2O] > 4$ mbar only. Inset shows the regression between O_3 and FA.

Table 4. Correlation Coefficients of Several Key Photochemical Species Observed on July 20, 1995, at Altitude <2500 m

	MPAN	PAN	NO_y	FA
PAN	0.79			
NO_y	0.83	0.90		
FA	0.74	0.79	0.75	
O_3	0.73	0.86	0.83	0.78

and O_3 were strongly correlated with H_2O vapor pressure (Figure 12) for $[H_2O] > 4$ mbar, the correlation between O_3 and H_2O disappeared for $[H_2O] < 4$ mbar. Accompanied by high O_3 concentrations (Figure 12), these dry air mass data points are assigned to be of free tropospheric origin and not included in the regression calculations. While we note that $[H_2O] < 4$ mbar was associated with a mean sea level altitude of 2500 m or greater, the ground level elevation can be reduced by as much as 900 m in this mountainous terrain.

Since FA is predominately derived from isoprene and is significantly longer-lived than isoprene (compare lifetime of ~3 hours versus 0.5 hour), it can be treated as a proxy for isoprene. Given this premise, we therefore take the strong correlation between FA and H_2O as evidence of concomitant surface emissions of isoprene and H_2O. The fact that FA and O_3 were also fairly strongly correlated ($r^2 = 0.78$, inset of Figure 12) suggests that isoprene was the principal VOC responsible for O_3 production in the BL. Two conditions that would favor the chance of observing such a correlation are (1) a somewhat homogeneous vegetation coverage in terms of species composition, providing a relatively constant emission characteristic regarding H_2O and BVOC, and (2) a fairly uniform meteorological condition so that the oxidation rates as well as the emission rates of the BVOC are not drastically variant. Regarding the former, this rural region has a uniform forest coverage with a substantial BVOC emission estimated to range between 8 and 12 mg C m^{-2} h^{-1} (under full Sun and a leaf temperature at 30°C [*Geron et al.*, 1994] With respect to the latter, the weather pattern of the region on July 20, including Tennessee, Georgia, and the Carolinas, was sunny and warm (in the low 30s) with only scattered clouds and mild southwesterly winds (R. Clymer, personal communications, 1997), conducive for active biogenic emissions [*Lamb et al.*, 1986].

Additionally, the correlations among several key photochemical products measured during this flight, namely, O_3, NO_y, PAN, MPAN, and FA were also strong (Table 4), consistent with a photooxidant production catalyzed by NO_x and fueled by isoprene. The strong correlation between O_3 and NO_y (Figure 13) is widely used as the basis upon which the dependence on NO_y of O_3 production is interpreted (e.g., L. J. Nunnermacker et al., unpublished manuscript, 1998). The correlation between O_3 and FA (Figure 12, inset) and between FA and NO_y (Figure 13) demonstrate that like O_3, FA is also produced as a NO_x mediated photochemical product. Using FA as a proxy for isoprene, which is produced at a yield of 0.75, and the correlation between O_3 and FA, we estimate an O_3 production efficiency of ~3.5 O_3 molecules for each isoprene molecule oxidized. It is interesting to point out since FA is not nearly as rapidly removed by dry deposition as HNO_3 (the major component of NO_y), the analysis of the FA-O_3 relationship is subject to less uncertain compared to that of O_3-NO_y.

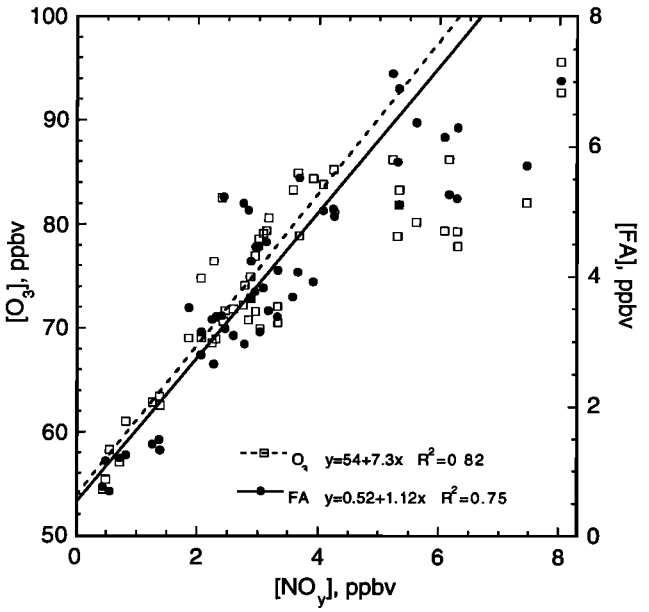

Figure 13. Dependence of O_3 and FA on NO_y observed on July 20, 1995.

4.3.2. July 7-Western Tennessee. On this P3 subregional flight a series of six southwest-northeast traverses in the BL was made (Figure 14). The winds were mostly northwesterly, between 300° and 340°; the wind speed was variable, ranging from 3 to 7 m s^{-1}. The concentrations of FA, O_3, CO, SO_2, and H_2O measured on these transects are plotted along a coordinate perpendicular to the wind direction (Figure 15) with the southwesternmost point reached by the P3 as the origin (x = 0 km). Because of the variability in wind speed and, to some extent, direction, a Lagrangian type of analysis of the chemical evolution of emissions from the embedded sources (i.e., Paradise, Cumberland, Johnsonville, and the Gallatin power plants, and the Nashville urban area) is expected to be uncertain. In fact, slight adjustments in the distance coordinate were necessary for the SO_2 peaks to be reasonably aligned (Figure 15, bottom).

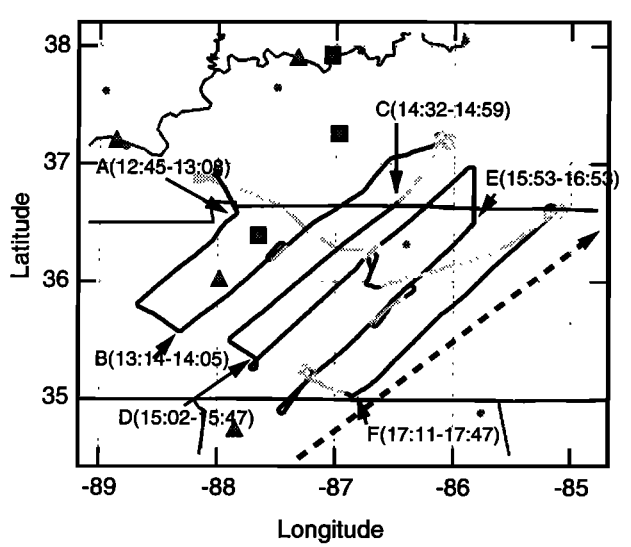

Figure 14. Flight track of a P3 subregional flight on July 7, 1995. The dashed line represents a cross wind coordinate. Flight transects are identified by uppercase letters.

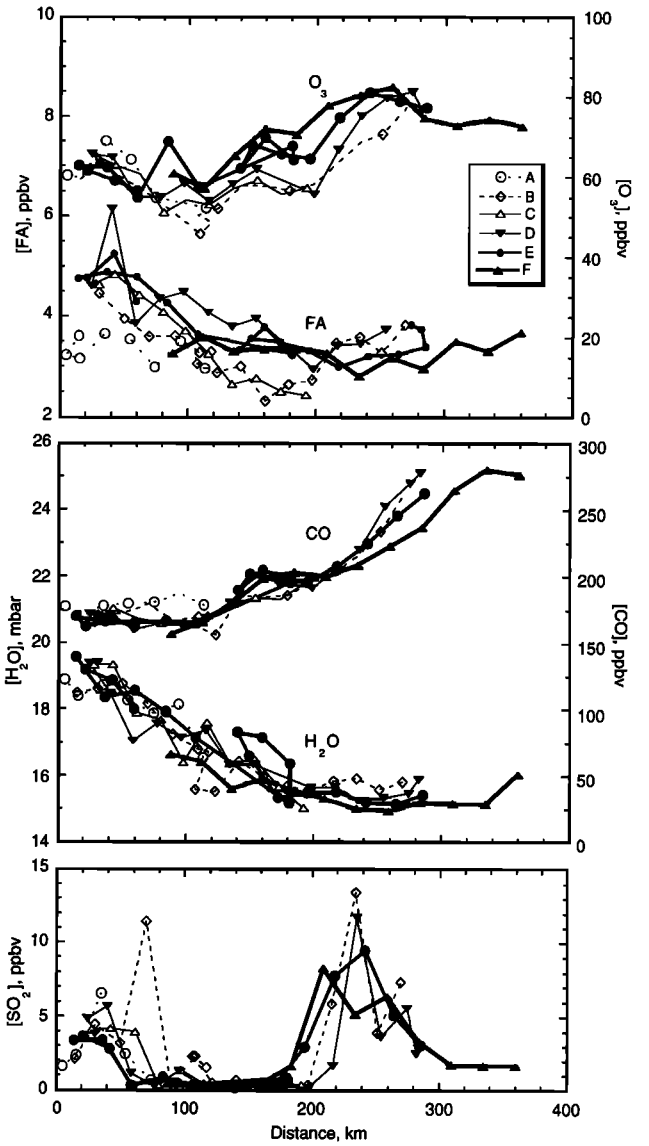

Figure 15. Concentrations of FA, O_3, CO, SO_2, and H_2O observed on cross wind transects during a P3 flight on July 7, 1995. The different symbols correspond to different flight tracks defined in Figure 14.

Despite this limitation, we observed several interesting photochemical features which we qualitatively examine below.

Transect B (diamonds connected by dotted line) intercepted the plumes from Johnsonville (x~35 km), Cumberland (x~100 km), and Paradise (x~230 km), and transects E and F intercepted the Gallatin plume at the ~240 km point. An apparent O_3 increase of ~25 ppbv (x~250 km) was observed in the Paradise plume along transect B using the lowest O_3 level observed along track B at x~100 km to be the background O_3 value of the air flowing into the region. The transport time from the Paradise plant to transect B was ~3 hours. Using transect D as background, an O_3 increase on an order of ~20 ppbv was observed on transect F at x~200 km, corresponding to an area downwind of the region between downtown Nashville (x~170 km) and the Gallatin power plant. The time elapsed between downtown and transect F was roughly 4 hours. These observations demonstrate that NO_x emissions from power plant plumes and urban plumes are responsible for O_3 production within a few hours. The rate

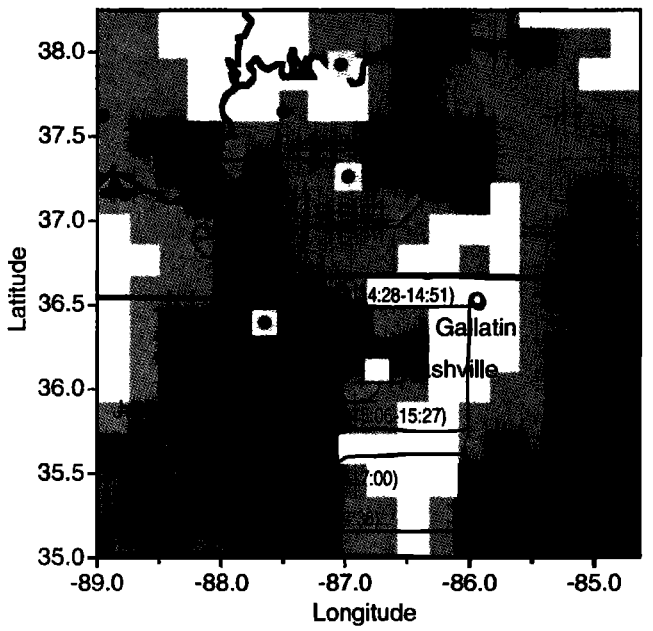

Plate 1. Flight track of the P3 on July 1, 1995: traverses within the boundary layer are in black with local time given in parentheses; segments above the boundary layer are in blue. Isoprene emission rates, in units of 10^{14} molecules m^{-2} s^{-1} [*Williams et al.*, 1997], are coded in color: dark green, green, yellow-green, yellow, and light yellow, represent 80-120, 40-80, 20-40, 10-20, and 5-10, respectively. Power plants are identified according to annual NO_x emissions (in 10^6 tons): red square, blue triangle, and black dot denote >200, >100, and >50, respectively.

of O_3 production and its efficiency with respect to NO_x level were found to be in qualitative agreement with that reported by L. J. Nunnermacker et al. (unpublished manuscript, 1998) based on data collected on the G1.

FA concentrations showed a progressive increase from ~2.5 to 5 ppbv along the wind flow in the southwestern edge of the domain, and a general trend of increasing concentration with decreasing distance along the cross wind coordinate. The latter is seen to coincide with that prominently shown by the H_2O vapor concentration, suggesting that the sources of H_2O and isoprene, precursor of FA, are highly correlated. This observation is consistent with the fact that the southwestern edges of these transects are located in an area of high isoprene emission (Plate 1). The much greater scatter in FA concentration than that in H_2O can be interpreted to reflect a variable isoprene emission rate or, more plausibly, the fact that the oxidation of isoprene to produce FA is being governed by, among other factors, the concentration of NO_x.

We note that [FA] showed an increase along transect D in both the Johnsonville (x~40 km) and Cumberland (x~100 km) plumes compared to that observed on transect B. In contrast, the Nashville urban plume, located at x ~160 km as indicated by the ~20 ppbv CO increase on track E, FA showed little change downwind of the urban center, reinforcing an earlier conclusion that anthropogenic HCs contribute weakly to FA formation. It is noted that an increase of ~1.3 ppb in [FA] was observed between the background values of transects B and transect D immediate upwind of the urban center, suggesting that isoprene played a major role as a precursor. Finally, it must be pointed out that the cross wind CO profiles along the wind flow remained nearly unchanged (Figure 15), indicating limited dilution during sampling. Consequently, concentration changes observed from one traverse to another are mainly due to chemistry.

4.3.3. July 1 - Kentucky and Tennessee. The P3 took off at 1200 LT, flew northwest at high altitude (>3 km) to the Kentucky-Illinois border, and made six successive east-west BL traverses southward between 500 and 700 m in altitudes (Plate 1). These traverses are shown in solid black and designated by letters A to F, with time identified in parentheses. The wind directions were quite constant, from between 320° and 350°, the wind speed was mild, varying between 4 to 6 m s^{-1}. The isoprene emission rate [*Williams et al.*, 1997] is variable in the immediate vicinity of Nashville, but very strong in an area west and southwest of Nashville where the Johnsonville and Cumberland power plants are located (Plate 1). The in situ HC measurements made on the P3 showed that the concentrations of some anthropogenic HC were fairly constant throughout the six transects: ethyne, 0.4-0.6; ethene, 0.12-0.15; propane, 0.6-1.0, and *i*-butane, 0.08-0.11, all in ppbv. In contrast, isoprene was much more variable, ranging from 0.1 to 0.3 ppbv during transects A-C, and from 0.15 to 1.1 ppbv during transects D-F.

The FA concentrations observed during these transects range between 1.8 and 4.3 ppbv (Figure 16). The three transects upwind of Nashville showed [FA] in the range 1.9 to 2.9 ppbv. The three transects downwind of Nashville found similar levels of FA in the region east of the western boundary of the urban area (i.e., -87° longitude). However, in the region between -87.5° and -88.0° longitude, a significant production of FA, ~2.2 ppbv, was observed on track E, directly downwind of the Cumberland and Johnsonville power plants. Since these power plant plumes traveled through a high isoprene emission region, this increase in FA was ascribed to isoprene oxidation. We examine below whether this secenario is consistent with other experimental data.

Using a decay rate constant of 0.4 h^{-1} for FA (calculated using [OH] = 7 x 10^6 molecules cm^{-3} and a j value appropriate for 5 pm), the observed [FA] of 4.2 ppbv corresponds to a total decay rate of FA of ~4.2 x 0.4 = 1.68 ppbv h^{-1}. This decay rate should approximate the production rate if FA is at steady state. The contribution of isoprene is estimated using an emission rate

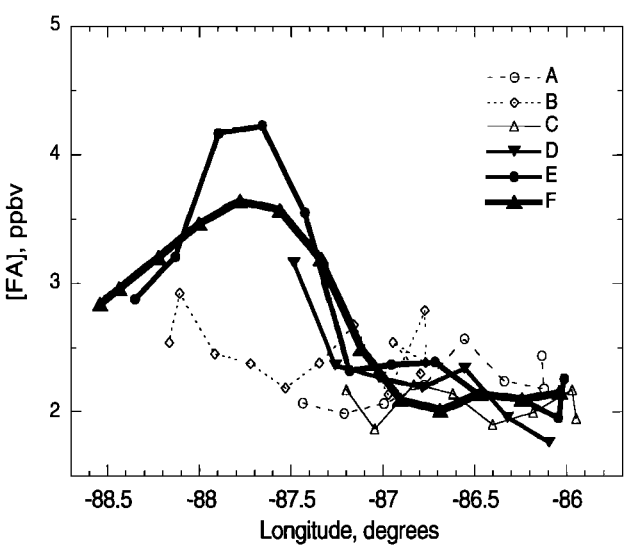

Figure 16. FA concentrations observed along the six BL transects of a P3 subregional flight on July 1, 1995.

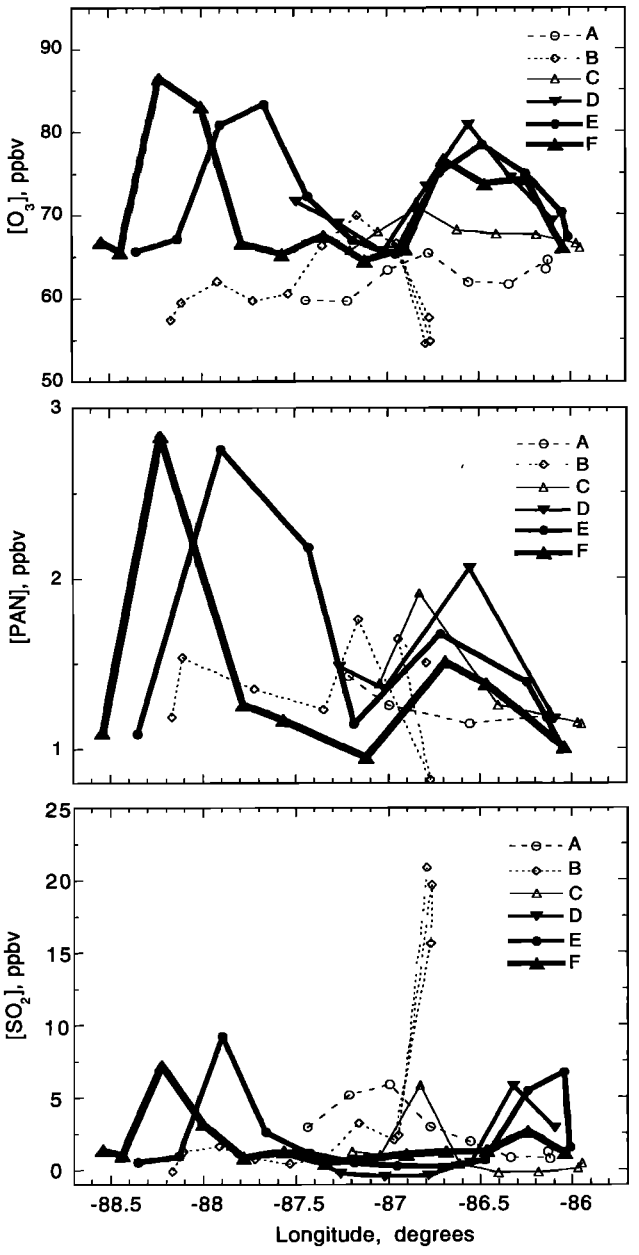

Figure 17. Concentrations of O_3, PAN, and SO_2 observed along the six BL transects of a P3 subregional flight on July 1, 1995.

of 80-120 x 10^{14} molecules m^{-2} s^{-1}, and a rapid oxidation leading to FA production (at [OH] = 7 x 10^6 molecules cm^{-3}, the time constant is 0.4 h). The FA thus produced was mixed into a boundary layer height of ~1500 m. Based on this scenario, a total isoprene consumption was estimated to be ~1 ppbv hr^{-1} (at 100 x10^{14} molec m^{-2} s^{-1}), and a FA production rate of 0.75 ppbv hr^{-1} (FA yield being 0.75). The rate of FA production from methane is estimated to be 0.25 ppbv hr^{-1} using $[CH_4]$ = 1.70 ppm, and [OH] = 7 x 10^6 molecules cm^{-3}. The contribution from PAN decomposition is estimated from the observed concentration of ~2.5 ppbv (Figure 17) and a $[NO_2]/[NO]$ ratio of 5, which led to a FA production rate of 0.72 ppbv h^{-1}. The total FA production rate was therefore 1.72 ppbv h^{-1}, nearly identical to the estimated decay rate of 1.68 ppbv h^{-1}.

Judging from the above analysis, it is evident that PAN plays an important role in FA production. PAN is produced from both anthropogenic and natural hydrocarbons [e.g., *Williams et al.*, 1997]. In the case of isoprene oxidation, PAN is produced through the intermediate MVK at an yield of 70% [*Carter and Atkinson*, 1996], which in turn is produced from isoprene at 34%. A 1 ppbv h^{-1} isoprene oxidation rate estimated above would therefore result in a 0.24 ppbv h^{-1} production of PAN. This rate however accounts for only 1/3 of decomposition. The equilibrium time constant is controlled by the thermo-decompsition of PAN and the association of peroxyacetyl radical with NO_2,

$$\tau_{PAN} = (k_d + k_a[NO_2])^{-1} \quad (6)$$

and is fairly rapid at $[NO_2]$ >0.5 ppbv, namely, ~10 min. Therefore we found that the rate of PAN production was smaller than its decomposition rate and was not sufficient to maintain the PAN peak concentrations observed in the power plant plumes. However, since isoprene was logically the only reactive HC in this forested environment, we find it difficult to reconcile this difference unless the production rate is significantly greater than 0.24 ppb h^{-1} . This suggests that the PAN production rate of 0.24 ppbv h^{-1} based on isoprene mechanism represents an underestimate by a factor of 2 or more. It may be pointed out that a discrepancy of smaller magnitude, ~40%, has also been observed by *Carter and Atkinson* [1996] in their comparison of the isoprene mechanism with chamber experiment data. Finally, we point out that because PAN was measured as a point concentration integrated over only a few seconds every 5 min, considerable discrepancy may result when compared to data of vastly different time integration. The analysis given above therefore should be viewed as highly qualitative.

4.3.4. July 3 - Early morning flight. Nighttime chemistry of photochemical species in the air above the nocturnal inversion has been an area of uncertainty for gaining a complete description of the fate and impact of emissions. One potentially important reaction in this regard is the NO_3 mediated oxidation [e.g., *Wayne et al.*, 1991]. Although FA is not expected to be greately affected by NO_3 judged from their slow kinetics, k = 6 x 10^{-16} cm^3 $molecules^{-1}$ s^{-1} at 298 K [e.g., *Cantrell et al.*, 1985] and a small $[NO_3]$ (significantly smaller than the daytime mean $[NO_2]$ of 0.7 ppbv due to fast reactions between NO_3 and other trace species such as substituted olefins), experimental data are needed to assess whether FA undergoes important nighttime transformations. Short of direct nighttime measurements, one might only be able to infer the importance of these hypothesized reactions from changes observed in the morning from that of the previous day.

As pointed out by *McNider et al.* [this issue], BL air is often subject to low-level jets and gets dispersed during the night, resulting in substantial dilution. Consequently, one must make certain that the air mass being examined is unaffected by such processes before attributing concentration changes to chemical reactions. In this context, it was found that during a mini-episode period, July 1-July 3, the air mass over the Nashville urban center and the surrounding area was moving in a clockwise direction, dispersing the urban derived pollution rather uniformly in the region [*McNider et al.*, this issue, Figure 2]. It was further found that the winds were very mild during afternoon hours on July 2 when the G1 had its flight mission southeast of the city. Overnight the air mass was pushed by a moderate low-level jet toward southwest of the city where the P3 made its first leg of sampling on early morning July 3.

We consider that the data collected during these two aircraft missions had a high probability of characterizing roughly the

same air mass and therefore are suitable for a comparison to discern possible nighttime chemistry of FA. The last stretch of BL measurement made on July 2 between 1510 and 1550 LT, southeast of the city, after a spiral showed mean concentrations of O_3 and FA to be, in ppbv, 59 ± 1 and 2.6 ± 0.5, respectively. The corresponding values determined on the P3 between 0650 and 0740 on July 3 were 68 ± 4 and 3.1 ± 0.4 ppbv, respectively, both being essentially unchanged overnight. We take this as evidence that FA is not significantly affected by nighttime chemistry and therefore can serve as a radical source in early morning hours.

5. Conclusions

Airborne measurement of FA was made on the NOAA P3 and DOE G1 aircraft during the 1995 Nashville/Middle Tennessee Ozone Study. FA, GL, MG, and PD were also measured on the G1. FA concentrations were high, the mean and median in the BL being 4.2 and 3.9 ppbv, respectively. The BL mean and median (in parentheses) concentrations of GA, GL, MG, and PD were 0.78 (0.70), 0.07 (0.06), 0.14 (0.10), and 0.24 (0.23), respectively. At the observed levels, FA contributed significantly to the OH reactions, comparable to isoprene and CO, and served as an important radical source, responsible for ~1/2 of that produced by O_3. A source attribution analysis based on measured concentrations of VOCs and their reaction kinetics and mechanisms with the OH radicals showed that isoprene contributed to ~67% of FA. PAN and CH_4 contributed ~13% each. Other VOCs were found to of minor importance. This analysis is corroborated by the strong correlation observed between FA and other isorpene oxidation products, namely, GA, MG, and GL. The nonzero FA intercept values observed in these correlation plots were also consistent with the ~30% of FA source that does not coproduce these multioxygenated carbonyls. Individual flight data obtained under farily uniform wind flow conditions also demonstrated that FA was mainely produced from NO_x mediated photooxidation of isoprene. Because of the strong precursor-product relationship between isoprene and FA, FA can be used a complementary tracer for assessing the emission inventory of isoprene in the Middle Tennessee region. Although biogenic emission rates can in principle be verified by direct field measurements, the rapid reactions of these compounds, for example, isoprene, coupled to inhomogeniety in surface vegetation coverage and complex atmospheric structures, would typically hamper such approach [*Andronache et al.*, 1994]. While using FA as a proxy to assess biogenic emission rates requires well established VOCs oxidation mechanisms affecting FA production, one recognizes that by the same token the model calculated concentrations of FA are similarly governed by the same mechansitic data, affecting the validity of model predictions in many key photochemical aspects discussed here. Clearly, oxidation mechanisms of VOCs built into models, particularly relating to FA production, are of critical importance and must be intercompared with and validated by field measured data.

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References

Andronache, C., W. L. Chameides, M. O. Rodgers, J. Martinez, P. Zimmerman, and J. Greenberg, Vertical distribution of isoprene in the lower boundary layer of the rural and urban southern United States, *J. Geophys. Res.*, *99*, 16989-16999, 1994.

Atkinson, R. Gas-phase troposphere chemistry of organic compounds, *J. Phys. Chem. Ref. Data Mono. 2*, 1-126, 1994.

Atkinson, R. and A. C. Lloyd, Evaluation of kinetic and mechanistic data for modeling of photochemical smog, *J. Phys. Chem. Ref. Data, 13*, 315-444, 1984.

Atkinson, R., D. L. Baulch, R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, and J. Troe, Evaluated kinetic and photochemical data for atmospheric chemistry: Supplement III, *J. Phys. Chem. Ref. Data, 18*, 881-1097, 1989.

Betterton, E. A., and M. R. Hoffmann, Henry's law constants of some environmentally important aldehydes, *Enivron. Sci. Technol., 22*, 1415-1418, 1988.

Cantrell, C. A., W. R. Stockwell, L. G. Anderson, K. L. Busarow, D. Perner, A. Schmeltekoph, J. G. Calvert, and H. S. Johnston, Kinetic study of the NO_3-CH_2O reaction and its possible role in night-time tropospheric chemistry, *J. Phys. Chem., 89*, 139-146, 1985.

Cantrell, C. A., et al., Peroxy radicals in the ROSE experiment: Measurement and theory, *J. Geophys. Res.*, *97*, 20671-20686, 1992.

Carter, W. P. L., Condensed atmospheric photooxidation mechanisms for isoprene, *Atmos. Environ.*, *30*, 4275-4290, 1996.

Carter, W. P. L., and R. Atkinson, Development and evaluation of a detailed mechanism for the atmospheric reactions of isoprene and NO_x, *Int. J. Chem. Kinet.*, *28*, 497-530, 1996.

Chamedies, W. L., R. W. Lindsay, J. Richardson, and C. S. Kiang, The role of biogenic hydrocarbons in urban photochemical smog: Atlanta as a case study, *Science, 241*, 1473-1475, 1988

Geron, C. D., A. B. Guenther, and T. E. Pierce, An improved model for estimating emissions of volatile organic compounds from forests in the eastern United States, *J. Geophys. Res.*, *99*, 12773-12791, 1994.

Gilpin, T., et al., Intercomparison of six ambient [CH_2O] measurement techniques, *J. Geophys. Res.*, *102*, 21161-21188, 1997.

Grosjean, D., Atmospheric reactions of pyruvic acid, *Atmos. Envrion.*, *17*, 2379-2382, 1983.

Guenther, A., P. Zimmerman, and M. Wildermuth, Natural volatile organic compound emission rate estimates for U.S. woodland landscapes, *Atmos. Envrion*, *28*, 1197-1210, 1994.

Guenther, A., P. Zimmerman, L. Klinger, J. Greenberg, C. Ennis, K. Davis, W. Pollock, H. Westberg, A. Allwine, and C. Geron, Estimates of regional natural volatile organic compound fluxes from enclosure and ambient concentration measurements, *J. Geophys. Res.*, *101*, 1345-1359, 1996.

Hübler, G., R. Alvarez, P. Daum, N. Gillani, L. Kleinman, W. Luke, J. Meagher, D. Rider, M. Trainer, and R. Valente, An overview of the airborne activities during the SOS 1995 Nashville/Middle Tennessee Ozone Study, *J. Geophys. Res.*, this issue.

Jacob, D. J., and S. C. Wofsy, Photochemistry of biogenic emissions over the Amazon forest, *J. Geophys. Res.*, *93*, 1477-1486, 1988.

Lamb B., H. Westberg, and G. Allwine, Isoprene emission fluxes determined by an atmospheric tracer technique, *Atmos. Environ.*, *20*, 1-8, 1986.

Lee, Y.-N., and X. Zhou, A method for the determination of some soluble atmospheric carbonyl compounds, *Environ. Sci. Technol.*, *27*, 749-756, 1993.

Lee, Y.-N., X. Zhou, and K. Hallock, Atmospheric carbonyl compounds at a rural southeastern U.S. site, *J. Geophys. Res.*, *100*, 25933-25944, 1995.

Lee, Y.-N., X. Zhou, W. R. Leaitch, and C. M. Banic, An aircraft measurement technique for formaldehyde and soluble carbonyl compounds, *J. Geophys. Res.*, *101*, 29075-29080, 1996.

Lin, X., B. A. Ridley, J. Walega, G. F. Hübler, S. A. McKeen, E.-Y. Hsie, M. Trainer, F. C. Fehsenfeld, and S. C. Liu, Parameterization of subgrid scale convective cloud transport in a mesoscale regional chemistry model, *J. Geophys. Res.*, *99*, 25615-25630, 1994.

McKeen, S., et al., Photochemical modeling of hydroxyl and its relationship to other species during the Tropospheric OH Photochemistry Experiment, *J. Geophys. Res.*, *102*, 6467-6493, 1997.

McNider, R. T., W. B. Norris, A. J. Song, R. L. Clymer, S. Gupta, R. M. Banta, R. J. Zamora, and M. Trainer, Meteorological conditions during the 1995 SOS Nashville/Middle Tennessee field intensive, *J. Geophys. Res.*, this issue.

Meagher, J. F., E. B. Cowling, F. C. Fehsenfeld, and W. J. Parkhurst, Ozone formation and transport in the southeastern United States: An overview of the SOS Nashville/Middle Tennessee Ozone Study, *J. Geophys. Res.*, this issue.

Miyoshi, A., S. Hatakeyama, and N. Washida, OH radical-initiated photooxidation of isoprene: An esitmate of global CO production, *J. Geophys. Res., 99*, 18779-18787, 1994.

National Research Council (NRC), Committee on Tropospheric Ozone Formation and Measurement, Rethinking the ozone problem in urban and regional air pollution, Natl. Acad. Press, Washington, D.C., 1991.

Paulson, S. E., and J. H. Seinfeld, Development and evaluation of a photooxidation mechanism for isoprene, *J. Geophys. Res., 97*, 20703-20715, 1992.

Singh, H. B., and P. L. Hanst, Peroxyacetyl nitrate (PAN) in the unpolluted atmosphere: An important reservoir for nitrogen species, *Geophys. Res. Lett., 8*, 941-944, 1981.

Wayne, R. P., et al., The nitrate radical: Physics, chemistry, and the atmosphere., *Atmos. Environ., 25*, Part A, 1-206, 1991.

Williams, J., et al.., Regional ozone from biogenic hydrocarbons deduced from airborne measurements of PAN, PPN, and MPAN, *Geophys. Res. Lett., 24*, 1099-1102, 1997.

P. H. Daum, L. I. Kleinman, Y.-N. Lee, L. Newman, L. J. Nunnermacker, and S. R. Springston, Environmental Chemistry Division, Department of Applied Science, Brookhaven National Laboratory, Upton, NY 11973. (email: ynlee@bnl.gov)

F. C. Fehsenfeld, J. Holloway, D. D. Parrish, J. M. Roberts, T. B. Ryerson, and J. Williams, Aeronomy Laboratory, NOAA, Boulder, CO 80303.

B. Fu, Department of Chemistry, York University, Toronto, Ontario, Canada M3J 1P3.

M. W. Holdren, W. G. Keigley, and C. W. Spicer, Atmospheric Science and Applied Technology, Battelle, Columbus, OH 43201.

V. Young, Department of Chemical Engineering, Ohio University, Athens, OH 45701.

X. Zhou, Wadsworth Center for Laboratories and Research, Empire State Plaza, Albany, NY 12201-0509.

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