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## PHOTOCHEMISTRY OF OZONE FORMATION IN ATLANTA, GA—MODELS AND MEASUREMENTS\*

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**Abstract**—Chemical measurements made during an air pollution event in Atlanta, GA have been compared with results from several photochemical simulations. Measurements included  $O_3$ , primary reactive organic gases (ROG), aldehydes, PAN, total reactive nitrogen ( $NO_x$ ) and  $H_2O_2$ , with vertical profiles for primary ROG. Photochemical models using two different chemical representations and a range of assumptions about winds, vertical mixing and emissions were used to simulate the event. Results show that assumptions about vertical mixing can cause a variation in simulated surface concentrations of primary hydrocarbons of a factor of two or more. A tendency to underestimate isoprene was found in comparison with measured vertical profiles. The models tend to overestimate concentrations of HCHO,  $H_2O_2$  and PAN in comparison with measurements. Peak  $O_3$  and concurrent  $NO_x$  from helicopter measurements was used as a basis for evaluating individual model scenarios. Scenarios were developed with different  $O_3$ - $NO_x$ -ROG sensitivity, but only the  $NO_x$ -sensitive scenarios are consistent with measured  $O_3$ ,  $NO_x$  and isoprene.

**Key word index:** Ozone, nitrogen oxides, hydrocarbons, photochemical smog, hydrogen, peroxide.

### 1. INTRODUCTION

The photochemistry of urban areas during air pollution events is the product of complex interaction between local meteorology, emissions from individual sources and chemically active species. Urban photochemistry is routinely represented by combined dynamical/photochemical models, which are important both as a means for understanding the physical and chemical processes and as a tool for designing policies for pollution abatement. Ozone formation in urban areas shows a complex dependence on emission rates for anthropogenic and biogenic reactive organic gases (ROG) and for the oxides of nitrogen ( $NO_x$ ). Resolution of the complex scientific and policy issues associated with the ozone- $NO_x$ -ROG relationship requires the use of photochemical models and careful

evaluation of model applications against ambient measurements.

The recent field measurement program during summer, 1992 in Atlanta, GA associated with the Southern Oxidant Study provides a unique opportunity to investigate the accuracy of the current understanding of urban photochemistry. The program included surface measurements for speciated primary hydrocarbons, carbonyls, peroxides, peroxyacetyl nitrate (PAN) and total reactive nitrogen ( $NO_x$ ). The program also included measurements of hydrocarbons up to an altitude of 600 m and the use of helicopter-based measurements to identify the covariation of ozone and  $NO_x$  in urban and power plant plumes downwind from Atlanta. These vertical profiles permit an evaluation of the model performance throughout the daytime mixed layer, rather than at the surface where species concentrations may be influenced by localized emissions and dynamics. Vertical profiles for meteorological variables (wind, temperature) were also measured.

This paper presents a comparison between measured species during the Atlanta field campaign (10-11

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August 1992) and a variety of photochemical simulations for the event. The photochemical models include applications of the Urban Airshed Model (UAM-IV) (Morris and Myers, 1990) with varying emissions and meteorology and a model developed at the University of Michigan (Sillman *et al.*, 1993) with different chemistry. Results provide insights on the ability of models to represent parameters that are especially important in determining the ozone-NO<sub>x</sub>-ROG relationship in urban locations: isoprene, carbonyls, peroxides and the ozone-NO<sub>x</sub> correlation. In addition to providing specific insights about photochemistry in Atlanta, the techniques used may provide a basis for the design of future investigative studies.

## 2. MEASUREMENT TECHNIQUES

Measurements of chemically reactive species were performed in the Atlanta metropolitan area throughout the summers of 1990 and 1992, but this study focuses on the event of 10–11 August 1992. This event featured high temperatures (305 K), unusually light winds, and peak O<sub>3</sub> in excess of 140 ppb in the plume extending south from Atlanta. Results are also shown for 4 August 1990, a day with more moderate (~90 ppb) ozone. Measurements of chemical species were made at the Georgia Tech campus near downtown Atlanta, at Fort McPherson, 6 km south of downtown (Five Points), at Tucker, 19 km northeast of downtown, and at South DeKalb, 16 km southeast of downtown. Helicopter-based measurements were used to identify vertical profiles above several of the measurement sites. Meteorological measurements were made at Fernbank Science Center, 10 km east of downtown. Hydrocarbon measurements were based on canister samples and analyzed by gas chromatography using flame ionization detection (Greenberg and Zimmerman, 1984; Zimmerman *et al.*, 1988) with an automated method of sample analysis developed by Martinez (1992) and Martinez and Rodgers (1994). More detailed presentations of hydrocarbon measurements appear in Garland *et al.* (1994), Martinez and Rodgers (1994) and Stoneking *et al.* (1994). Carbonyls (formaldehyde, HCHO and acetaldehyde, CH<sub>3</sub>CHO) were measured at the Georgia Tech and South DeKalb sites by Grosjean *et al.* (1993) using liquid chromatography with ultraviolet detection (Druzik *et al.*, 1990; Grosjean, 1991). PAN was measured at South DeKalb by Hartsell *et al.* (1993) and at Georgia Tech by Williams *et al.* (1993) both using electron capture gas chromatography techniques (Williams and Grosjean, 1990). Lee *et al.* (1990, 1993, 1994) measured total and speciated peroxides at Georgia Tech on 10 August using a fluorescence technique (1990, 1994). Helicopter-based NO<sub>y</sub> measurements were made by Imhoff *et al.* (1994a, b) using a gold tube converter with CO injection (Bollinger *et al.*, 1983) which was mounted external to the helicopter in the free air stream. The NO produced was drawn through

~6 m of Teflon tubing to a Thermo Electron Instruments Model 42 Nitrogen Oxides analyzer. Tests indicated that very little O<sub>3</sub> (<3 ppb) survived the gold-tube converter and therefore no adjustment was applied for the possible reaction of NO with O<sub>3</sub> in the tubing.

Ranges of uncertainty ( $\pm 1\sigma$ ) associated with these techniques are: hydrocarbons,  $\pm 20\%$  for values greater than 3 ppbC,  $\pm 35\%$  for lower values (Bernardo-Bricker *et al.*, 1995); aldehydes,  $\pm 8\%$  (Grosjean, 1991); PAN,  $\pm 20\%$  (Williams *et al.*, 1993); peroxides,  $\pm 10\%$  (Lee *et al.*, 1993); and NO<sub>y</sub>,  $\pm 20\%$  (Fahey *et al.*, 1986).

## 3. SIMULATION METHODS

Simulations were developed for Atlanta based on meteorological conditions on 3–4 August 1990 and 9–11 August 1992. Temperatures, and winds were based on vertical measurements made at Fulton County Airport and at Georgia Tech (Samson and Fischer, 1993a) with spatial interpolation and adjustments for terrain effects as described in Morris and Myers (1990). Water vapor concentrations were derived from temperature and relative humidity measurements at Fulton County Airport. The height of the mixed layer was derived from vertical temperature profiles following methods described by Marsik *et al.* (1993). Emission rates for anthropogenic species were obtained from the Georgia Department of Natural Resources (1987) based on the NAPAP 1985 inventory (EPA, 1989). Emission rates for isoprene were based on Pierce *et al.* (1990). Simulations were performed using UAM-IV (Morris and Myers, 1990), a simulation based on the CB-IV photochemical mechanism (Gery *et al.*, 1989) with clear-sky photolysis rates, advection based on the method of Smolarkiewicz (1983) and vertical mixing based on eddy diffusion coefficients calculated as described by Businger *et al.* (1971) and Lamb *et al.* (1975). A recent modification of CB-IV chemistry with added RO<sub>2</sub> + HO<sub>2</sub> reactions and corrected reaction rates associated with PAN formation (Morris, Systems Applications Inc., private communication, 1993) is included. Horizontal resolution is 4 × 4 km over a 108 × 140 km domain. Initial and upwind O<sub>3</sub> was set at 55 ppb based on daytime O<sub>3</sub> observed at a rural site (Buzzard Flapper Creek) 50 km east of Atlanta. Other initial/upwind species concentrations were based on the recommendations of Morris and Myers (1990) and include the following: NO<sub>x</sub>, 1 ppb; HCHO, 1.75 ppb; CH<sub>3</sub>CHO, 0.46 ppb; CO, 200 ppb; lumped paraffins, 30 ppbC; lumped olefins, 1 ppb; isoprene, 1 ppb. The simulations were exercised for time periods beginning at least 24 h before the period of interest (e.g. 9 August in a simulation for 10 August).

Following EPA recommendations (Morris and Myers, 1990) the model was initially exercised with five vertical grids, including two grids within the

convective mixed layer, and vertical mixing rates based on surface roughness length of 3 m in urban areas. The resulting simulations have near-instantaneous mixing within the daytime mixed layer, due in part to the lack of vertical resolution and in part to high ( $300\text{--}500\text{ m}^2\text{ s}^{-1}$ ) calculated vertical diffusion coefficients. Measurements in Atlanta during 1990 (Pearson *et al.*, 1994; Garland *et al.*, 1994, see also Fig. 1) showed that concentrations of primary hydrocarbons vary significantly with height, suggesting that rates of vertical mixing are relatively slow even within the daytime mixed layer. In order to explore the impact of reduced vertical mixing in photochemical simulations the number of vertical grids was increased to eight including five grids within the convective mixed layer. The surface roughness length in the urban portion of the model domain was also reduced from 3 to 0.75 m, following the recommendations of Stull (1988) and Wieringa (1993). The reduced surface roughness causes the calculated eddy diffusion to decrease from  $300$  to  $150\text{ m}^2\text{ s}^{-1}$  in simulations for the 1992 event. The reported model results are all for eight-layer UAM simulations with 0.75 m urban surface roughness unless noted otherwise. Some additional simulations were performed with vertical diffusion coefficients restricted to a maximum value of  $50\text{ m}^2\text{ s}^{-1}$  or  $20\text{ m}^2\text{ s}^{-1}$ , based on results from meteorological simulations by Samson *et al.* (1993b). In these simulations, vertical diffusion coefficients were set equal either to the value calculated internally by the UAM or to the specified maximum value, whichever was smaller. These modifications cause some changes in simulated surface concentrations of primary hydrocarbons.

An additional simulation has been applied to Atlanta based on the University of Michigan (UMICH) model developed by Sillman *et al.* (1993) for the northeast corridor and Lake Michigan airsheds. The UMICH model was used to identify the impact of photochemical representation on species concentrations. Chemistry in the UMICH model is based on the mechanism of Lurmann *et al.* (1986), which includes over 200 species with separate representation for  $\text{H}_2\text{O}_2$  and higher peroxides, PAN and higher-order homologues, and  $\text{CH}_3\text{CHO}$  and higher-order aldehydes. The UMICH model includes updates to Lurmann *et al.* for  $\text{RO}_2 + \text{HO}_2$  reactions (Jacob and Wofsy, 1988), reaction rates (DeMore *et al.*, 1992) and isoprene (Paulson and Seinfeld, 1992). Vertical resolution and meteorological representation in the UMICH model is less detailed than in UAM (three vertical layers, wind speeds based on average mixed-layer values). Horizontal resolution (4 km) and calculation of horizontal advection (Smolarkiewicz, 1983) are similar to the UAM, and emission rates for anthropogenic species are identical to the rates used in the UAM. The diurnal schedule of isoprene emissions in the UMICH model is derived from the emissions profile identified by Jacob and Wofsy (1987) with a strong maximum near solar noon, in combination

with the sensitivity to temperature recommended by Lamb *et al.* (1985). The resulting diurnal profile differs from the one used in the UAM. Diurnally averaged emission rates in both models were  $2.5 \times 10^{11}$  molecules  $\text{cm}^{-2}\text{ s}^{-1}$  in suburban Atlanta and approximately half that near downtown. The equivalent emission rate at noon was  $6.5 \times 10^{11}$  molecules  $\text{cm}^{-2}\text{ s}^{-1}$  in the inventory by Pierce *et al.* used in the UAM but  $1.3 \times 10^{12}$  molecules  $\text{cm}^{-2}\text{ s}^{-1}$  based on the diurnal schedule used in the UMICH simulation.

Simulations were also performed to test the impact of uncertainties associated with both meteorology and emission rates. The base case UAM simulation uses eight vertical layers, reduced surface roughness, and other assumptions and methods described above. The alternative scenarios include the following specific changes from the base case:

(a) *Increased wind speed*: Winds in the base case were derived on measurements at Georgia Tech using the NCAR Cross-chain Loran Atmospheric Sounding System (CLASS) (Marsik *et al.*, 1993). Measurements made by radar wind-profiler systems at rural sites near Atlanta showed somewhat higher wind speeds. Alternative scenarios were developed with winds based on profiler measurements instead of CLASS.

(b) *Lower mixing height*: The base case used mixing heights derived from criteria developed by Marsik *et al.* (1993). The resulting mixing heights were often significantly higher than the base of the inversion from measured temperature profiles. Alternative scenarios were developed with mixing heights equal to the inversion base.

(c) *Increased isoprene*: The base case uses isoprene emissions from the inventory by Pierce *et al.* (1990). An alternative scenario has isoprene emissions increased by a factor of three as recommended by more recent inventories (Geron *et al.*, 1994).

(d) *Increased  $\text{NO}_x$* : A recent inventory for Atlanta (Cardelino *et al.*, 1994) has significantly higher anthropogenic  $\text{NO}_x$  emissions in comparison to the Georgia inventory used in the base case. Alternative scenarios have 25% higher anthropogenic  $\text{NO}_x$  than the base case.

(e) *Five-layer UAM*: The base case scenario uses eight vertical layers and modified surface roughness as described above. Simulations with five vertical layers are used as an alternative scenario.

The impact of uncertain photolysis rates represents an additional uncertainty that was not varied in any of the scenarios. Table 1 provides a concise description of the individual scenario options. The labels in Table 1 (e.g. "increased wind") all refer to the specific modifications described here.

## 4. RESULTS

### 4.1. Hydrocarbons and vertical mixing

UAM simulations include independent representation for six classes of primary hydrocarbons: lumped

Table 1. O<sub>3</sub>, NO<sub>x</sub>, ROG sensitivity

	10 August			11 August		
	Original scenario	Reduced ROG	Reduced NO <sub>x</sub>	Original scenario	Reduced ROG	Reduced NO <sub>x</sub>
A. Base case	134	128	120	134	131	114
B. Reduced mixing	166	154	144	149	143	123
C. Increased isoprene	146	142	125	140	139	116
D. Five-layer UAM	132	126	117	126	123	108
E. Increased NO <sub>x</sub> , reduced mixing	157	134	155	163	153	145
F. Increased NO <sub>x</sub> and isoprene, reduced mixing	193	180	171	181	174	152
G. Increased NO <sub>x</sub>	139	130	128	143	139	124
H. Increased NO <sub>x</sub> and isoprene	155	149	136	152	150	128
K. Increased NO <sub>x</sub> , higher wind speed	135	126	125			
L. Increased NO <sub>x</sub> and isoprene, higher wind speed	152	146	135			
M. Higher wind speed	131	125	118			
N. UMICH simulation	126	120	109	124	116	108

Note: Domain-wide peak O<sub>3</sub> (ppb) is shown for each model scenario along with peak O<sub>3</sub> for equivalent simulations with anthropogenic ROG reduced by 35% and with NO<sub>x</sub> reduced by 35%. The scenario labels refer to specific modifications in the UAM base case and are described in Section 3.

paraffins, ethylene, lumped olefins, toluene (representing all aromatics with attached single carbon chains), xylenes (representing aromatics with two or three attached carbon chains) and isoprene as an individual species. Simulated concentrations for these classes have been compared with the sum of individual measured species (including all < C10 species) associated with the class.

Figure 1 shows measured vertical profiles for isoprene and for lumped xylenes at Georgia Tech at 1 pm, 4 August 1990, compared with simulated concentrations from several versions of the UAM. The measured vertical profiles for this event, described in detail by Pearson *et al.* (1994) and Andronache *et al.* (1994), show that species concentrations vary by a factor of three or more within 300 m of the ground and that relative maxima occur at 50–100 m above ground. A similar factor-of-three variation was found between simultaneous surface measurements at two different locations on the Georgia Tech campus. As shown in Fig. 1 model species concentrations also vary by a factor of three within the lower 300 m if eight vertical layers are included and the rate of vertical diffusion is reduced to 50 m<sup>2</sup> s<sup>-1</sup>. Models cannot reproduce the maximum at 100 m above ground unless greater vertical resolution and spatial detail of emissions are added (see discussion in Andronache *et al.*, 1994). In addition, reduced vertical mixing causes the simulated surface concentrations for isoprene and lumped xylenes to increase by a factor of two or more. The impact of reduced vertical mixing is smaller for hydrocarbons with a long photochemical lifetime or for secondary species, including ozone. The UAM simulations with surface roughness recommended by Morris and Myers (1990), even with eight vertical grids, underestimate surface isoprene and lumped xylenes by an order of magnitude. The UAM with reduced vertical mixing still underestimates isoprene

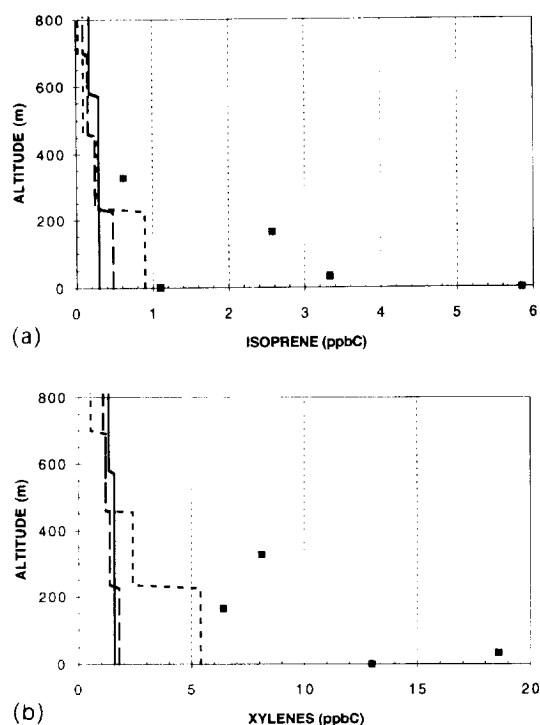


Fig. 1. Concentrations for (a) isoprene and (b) xylene (ppbC) vs height above ground (m) at 1 pm, 4 August 1990, from UAM simulations with five vertical layers (solid line), eight vertical layers and 3 m urban surface roughness (long dashed line), and eight vertical layers with vertical eddy diffusion coefficient  $\leq 50 \text{ m}^2 \text{ s}^{-1}$  (short dashed line) compared with measurements at the Georgia Tech campus (points) (Pearson *et al.*, 1994; Andronache *et al.*, 1994).

by a factor of three and tends to underestimate lumped xylenes, but the remaining underestimate for xylenes appears to lie within the range of uncertainty generated by near-surface dynamics.

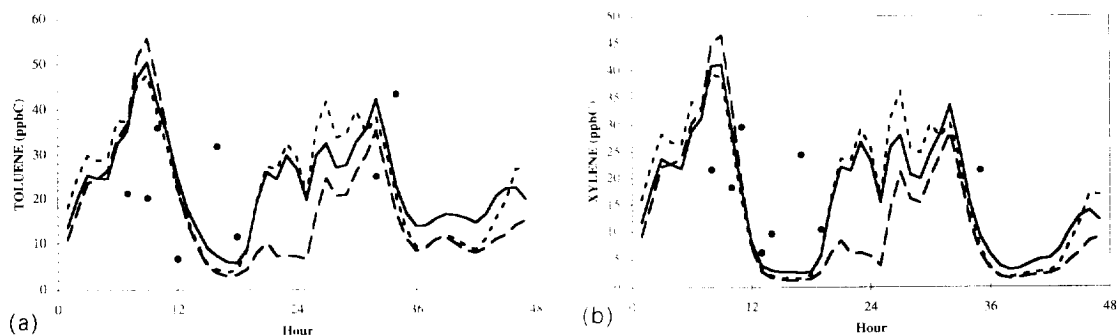


Fig. 2. Concentrations for (a) toluene and (b) xylene (ppbC) on 10–11 August 1992 at Tucker, GA, east of Atlanta, from UAM simulations with five vertical layers (dashed line), eight vertical layers (solid line) and eight layers with vertical eddy diffusion coefficient  $\leq 20 \text{ m}^2 \text{ s}^{-1}$  (short dashed line) compared with measurements (points).

In contrast to the 1990 event, measurements during 10–11 August 1991 show less variation with height. Significant variation with height was found for hydrocarbons during the morning hours and for isoprene throughout the event, but concentrations for anthropogenic hydrocarbons showed little variation with height at downwind locations during the afternoon hours (Imhoff and Valente, 1994b). Models also show little variation with height at downwind locations for species other than isoprene. A comparison between modeled and measured surface concentrations at the Tucker and Fort McPherson sites south and east (downwind) from Atlanta (Fig. 2) shows reasonable agreement for anthropogenic hydrocarbons. However the models seriously underestimate isoprene (Fig. 3). The model-measurement comparison for isoprene during the 10–11 August even demonstrates that surface measurements alone are often inadequate for evaluating model performance. Models sharply underestimate surface isoprene in comparison with measurements, but surface isoprene varies by at least a factor of five among models with different vertical structure and meteorology. The poor model performance could be associated with errors in either emissions or dynamics near the surface. By contrast, comparison with measurements at 300–500 m above ground shows a serious underestimate for isoprene that cannot be corrected by dynamical changes. These aloft measurements confirm the increase in emission rates for isoprene recommended by Geron *et al.* (1994). Simulations with isoprene emissions tripled from the base case show better agreement with measured isoprene (see Fig. 3).

#### 4.2. Carbonyls

Figures 4 and 5 show a comparison between measured concentrations of HCHO and CH<sub>3</sub>CHO (Grosjean *et al.*, 1993) and results of UAM and UMICH simulations for 10–11 August 1992. The most important result for this intercomparison is the tendency for

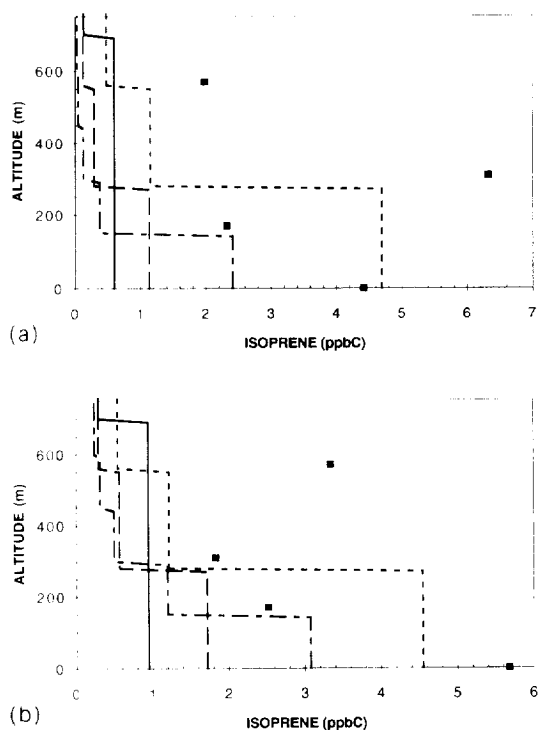


Fig. 3. Concentrations of isoprene (ppbC) vs height above ground (m) at 12 pm, 10 August 1992 at (a) Georgia Tech and (b) Tucker from UAM simulations with five vertical layers (solid line), eight vertical layers (long dashed line), eight layers with a lower mixing height (line-dash line), and eight layers with tripled isoprene emissions (short dashed line) compared with measurements (points).

both models to overestimate HCHO in comparison with measured daytime concentrations. Nighttime and early morning concentrations are determined by combination of transport, emissions and vertical mixing near the surface, and conditions at these times are largely an artifact of surface mixing and local emissions. Simulated concentrations between 10 am and 6 pm are more likely determined by photochemical

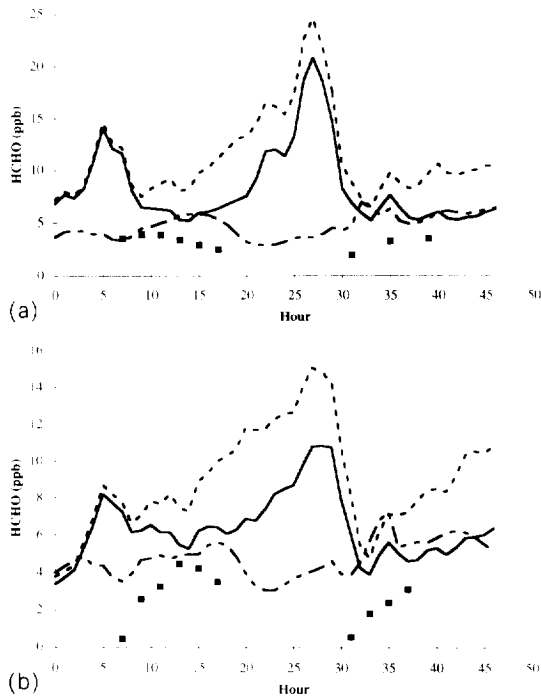


Fig. 4. Concentrations of HCHO (ppb) on 10–11 August 1992 at (a) Georgia Tech and (b) South DeKalb from the UAM simulation with eight vertical layers (solid line), UAM simulation with tripled isoprene (short dashed line) and the UMICH simulation (long dashed line) compared with measurements (points).

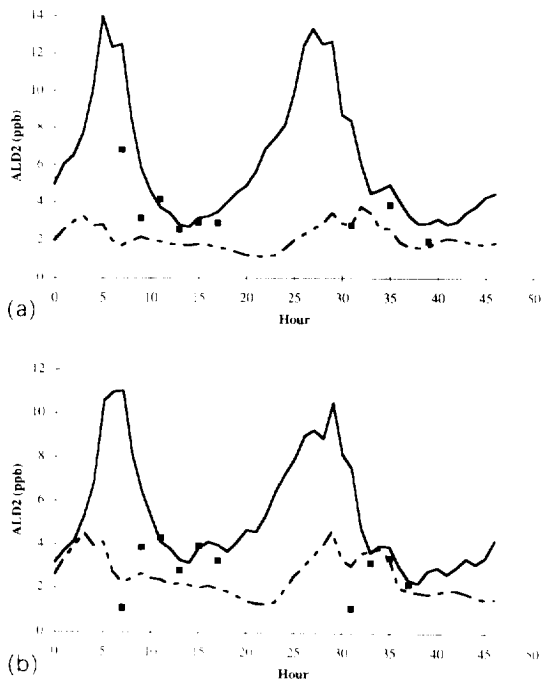


Fig. 5. Concentrations of CH<sub>3</sub>CHO (ppb) on 10–11 August 1992 at (a) Georgia Tech and (b) South DeKalb from UAM simulations with eight vertical layers (solid line) and from the UMICH simulation (dashed line) compared with measurements (points).

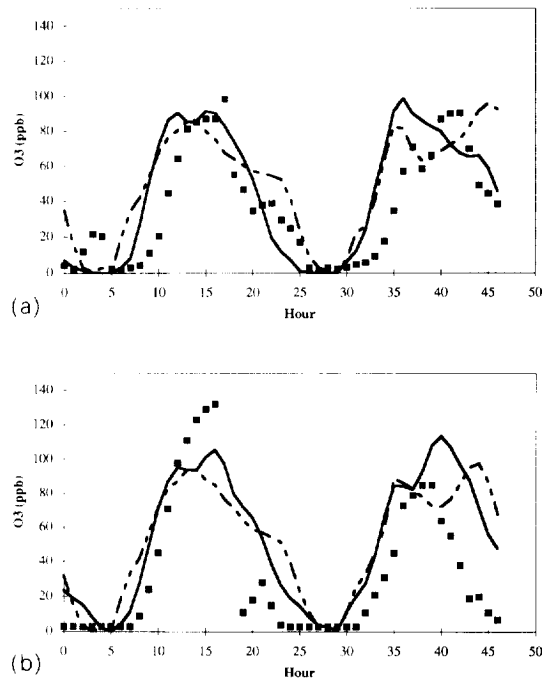


Fig. 6. Concentrations of O<sub>3</sub> (ppb) on 10–11 August 1992 at (a) Georgia Tech and (b) South DeKalb from UAM simulations with eight vertical layers (solid line) and from the UMICH simulation (dashed line) compared with measurements (points).

production rather than emissions and therefore provide an indication of the accuracy of model chemistry. Results show that the simulations overestimate HCHO by ~50%. This finding is especially important because the simulations show no tendency to overestimate other primary ROG species and they significantly underestimate isoprene, a major source of HCHO. Model scenarios with increased isoprene overestimate HCHO by a factor of two. The models also overestimate the ratios HCHO/CH<sub>3</sub>CHO and HCHO/O<sub>3</sub> in comparison with measurements.

Comparisons between simulated and measured CH<sub>3</sub>CHO show no clear trends. The UAM overestimates CH<sub>3</sub>CHO but the chemical mechanism used in the UAM represents higher-order aldehydes as CH<sub>3</sub>CHO, so that a model overestimate of up to 30% can be expected. The CB-IV mechanism also uses CH<sub>3</sub>CHO to represent emission of internal alkenes, causing an overestimate in comparison with measurements during the morning hours. The UMICH simulation, which includes separate representation for higher aldehydes, slightly underestimates CH<sub>3</sub>CHO.

#### 4.3. O<sub>3</sub> and PAN

Examination of O<sub>3</sub> and PAN (Figs 6 and 7) suggests that the models may overestimate production of PAN in comparison to O<sub>3</sub>, although results are inconclusive. Both models show reasonable agreement

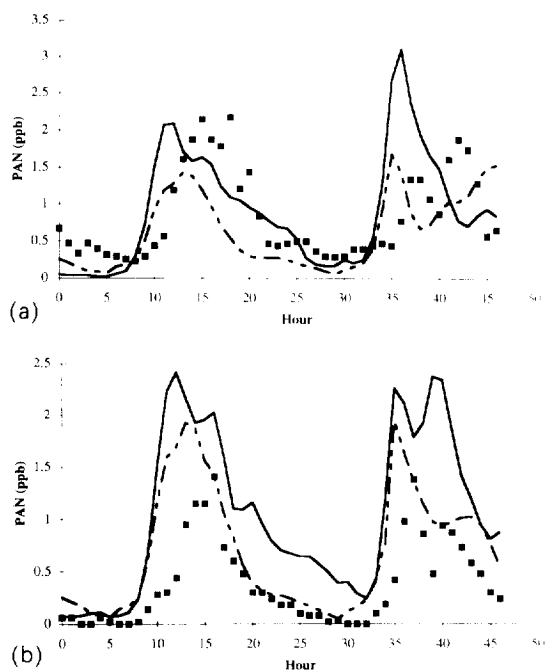


Fig. 7. Concentrations of PAN (ppb) on 10-11 August 1992 at (a) Georgia Tech and (b) South DeKalb from UAM simulations with eight vertical layers (solid line) and from the UMICH simulation (dashed line) compared with measurements (points).

with measured  $O_3$  although the UAM base case scenario underestimates peak  $O_3$  for the entire domain (132 ppb vs 150 ppb in helicopter measurements on 10 August). The simulated peak  $O_3$  occurs significantly further downwind than the observed peak on 10 August (40 km south of downtown Atlanta vs 20 km south of downtown in helicopter measurements). Simulated peak  $O_3$  on 11 August was 50 km northeast of downtown, while the observed peak was 50 km ENE from downtown. A more serious difference between models and measurements appears for PAN, where simulated concentrations exceed measurements by up to a factor of two. There are also important discrepancies in the ratio  $O_3$ /PAN in comparison with afternoon measurements. The models underestimate  $O_3$ /PAN between noon and 4 pm at South DeKalb, south of Atlanta (90-110 measured, 40-50 modeled) but not at Georgia Tech near downtown (40-50 measured, 45-60 modeled).

UAM simulations give higher PAN than the UMICH simulation, but the chemistry used in the UMICH simulation includes higher-order homologues of PAN that are not included in the UAM. These higher-order PANs have a combined concentration in the UMICH simulation equal to roughly half the concentration of PAN proper, and the sum of PAN and higher-order PANs in the UMICH simulation is comparable to the simulated concentration of PAN alone in the UAM. Therefore it may be appro-

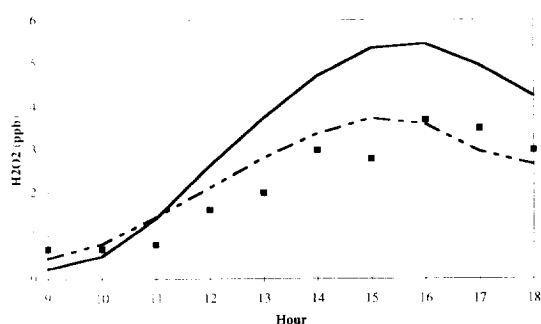


Fig. 8. Concentrations of  $H_2O_2$  (ppb) on 10 August 1992 at Georgia Tech from UAM simulations with eight vertical layers (solid line) and from the UMICH simulation (dashed line) compared with measured total peroxides (points).

appropriate to interpret PAN in the UAM simulations as a lumped species representing the sum of PAN and higher-order homologues. Measurements by Parrish *et al.* (1993) failed to verify that the higher-order homologues of PAN exist in the atmosphere in significant quantities but recent measurements by Williams *et al.* (1993) in Atlanta during July and August 1992 found concentrations of peroxypropionyl nitrate ( $C_2H_5CO_3NO_2$ ) and peroxyacetyl nitrate (MPAN,  $CH_2=C(CH_3)CO_3NO_2$ , associated with isoprene products) in significant amounts relative to PAN (11% and 14%, respectively). These correspond to proportions of 20% and 7%, respectively in the UMICH simulation. The overestimate for PAN in the UAM simulation may be partially explained if simulated PAN is interpreted as the sum of PAN and higher-order homologues.

#### 4.4. Peroxides

A comparison between measured total peroxides on 10 August and simulated  $H_2O_2$  is shown in Fig. 8. Evaluation of simulated peroxide concentrations is especially important because peroxides in combination with  $HNO_3$  act as an indicator for ROG-sensitive vs  $NO_x$ -sensitive ozone formation (Sillman, 1995). Measurements made in Atlanta on 3 August 1992 (Lee *et al.*, 1994) showed that  $H_2O_2$ ,  $CH_3OOH$  and  $HOCH_2OOH$  were all present with concentrations between 1 and 3 ppb.  $H_2O_2$  accounted for approximately half of the three-species total but partitioning between the three species varied greatly. Other measurements with the same technique (Lee *et al.*, 1993) similarly showed that  $H_2O_2$  accounted for 50-70% of the total peroxide measurement. The UMICH simulation includes  $CH_3OOH$  and other organic peroxides (but not  $HOCH_2OOH$ ) with  $H_2O_2$  typically representing 60% of total peroxides. The UAM includes no peroxides other than  $H_2O_2$ . Figure 8 shows that simulated  $H_2O_2$  is ~50% higher in the UAM relative to the UMICH simulation. However the measurements suggest that both simulation

significantly overestimate total peroxides. Total peroxides in the UMICH simulation is roughly comparable to  $\text{H}_2\text{O}_2$  alone in the UAM and represents a significant overestimate. It is unlikely that the overestimate results from failure to measure significant organic peroxides, as HPLC measurements show negligible concentrations of peroxides other than  $\text{H}_2\text{O}_2$ , hydroxymethyl hydroperoxide and methyl hydroperoxide (Hellpointner and Gab, 1989; Hewitt and Kok, 1991). The discrepancy between  $\text{H}_2\text{O}_2$  in the UAM and UMICH simulations also suggests that the odd hydrogen sink associated with  $\text{HO}_2 + \text{RO}_2$  reactions in the chemistry of Lurmann *et al.* (1986) may be significantly greater than  $\text{RO}_2 + \text{HO}_2$  in the CB-IV mechanism, even with recent updates to include  $\text{HO}_2 + \text{RO}_2$ .

#### 4.5. $\text{O}_3$ - $\text{NO}_y$ correlations

Correlations between  $\text{O}_3$  and total reactive nitrogen ( $\text{NO}_y$ ) at times of high photochemical activity have been used routinely to diagnose the accuracy of model chemistry in rural locations (Fahey *et al.*, 1986; Trainer *et al.*, 1993). The simultaneous measurement of  $\text{O}_3$  and  $\text{NO}_y$  by Imhoff and Valente (1994b) in the urban plume downwind from Atlanta on 10–11 August 1992 (Fig. 9) provides an opportunity to do a similar evaluation in an urban environment.  $\text{O}_3$  and  $\text{NO}_y$  were measured along transects through the urban plume at locations ranging from 10 to 40 km from the center of Atlanta between 4:00 and 5:20 pm at 600 m above ground. The majority of measurements shows that  $\text{O}_3$  increases consistently with increasing  $\text{NO}_y$  ( $\Delta\text{O}_3/\Delta\text{NO}_y = 8$ ) as  $\text{NO}_y$  varies between 4 and 12 ppb and that  $\text{O}_3$  remains constant or decreases with increasing  $\text{NO}_y$  when  $\text{NO}_y$  is greater than 12 ppb. Other measurements show lower  $\text{O}_3$  and suggest a much lower rate of increase ( $\Delta\text{O}_3/\Delta\text{NO}_y = 1$ ). A small number of measurements shows much higher  $\text{NO}_y$  ( $> 20$  ppb) relative to the other measurements, possibly associated with a plume of fresh  $\text{NO}_x$  emissions. The measurements with low  $\text{O}_3/\text{NO}_y$  ratios generally represent locations closest to the center of Atlanta.

Model results for the same time period (Fig. 10) show a similar pattern with initially increasing  $\text{O}_3$  vs  $\text{NO}_y$  and a gradual leveling off for  $\text{NO}_x$  concentrations above 10 ppb. The model slope ( $\Delta\text{O}_3/\Delta\text{NO}_y = 7$  for  $\text{NO}_y$  between 4 and 12 ppb) is lower than the measured slope and model  $\text{O}_3$  corresponding to 8–10 ppb  $\text{NO}_y$  is consistently lower than measured  $\text{O}_3$ . The simulations also show some locations with high  $\text{NO}_y$  and low  $\text{O}_3$ , roughly equivalent to the measurements with high  $\text{NO}_y$ . However the simulated high  $\text{NO}_y$  is associated with emissions from large power plants located 40 km from Atlanta. The measured high  $\text{NO}_y$  was found south of Atlanta and may represent a narrow (1 km) plume from a local source that could not be represented within the model horizontal grid structure. A useful way to interpret simulated and measured  $\text{O}_3$  and  $\text{NO}_y$  is to examine

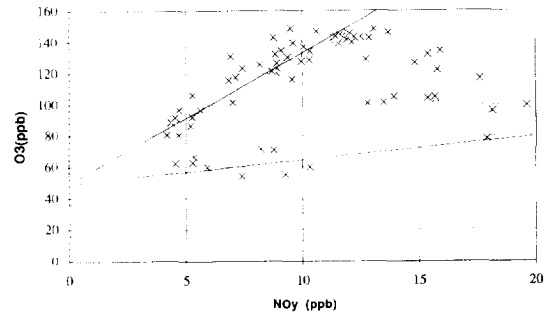


Fig. 9. Measured correlation between  $\text{O}_3$  and  $\text{NO}_y$  (ppb) in the urban plume 10–40 km south of Atlanta at 600 m above ground, 4:00–5:20 pm, 10 August 1992 (points). Points represent 1 min average concentrations coinciding with measured  $\text{NO}$  between 0.2 and 0.75 ppb. The solid lines represent approximate  $\text{O}_3$ - $\text{NO}_y$  slopes through two different subsets of measurements. From Imhoff and Valente (1994b).

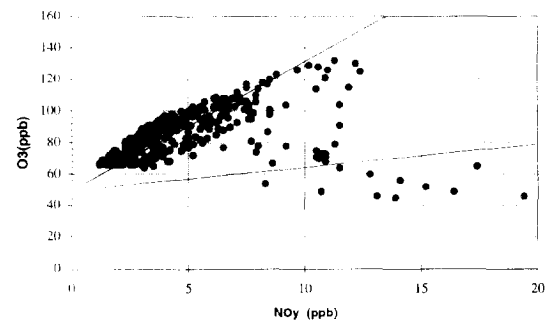


Fig. 10. Simulated correlation between  $\text{O}_3$  and  $\text{NO}_y$  (ppb) for the Atlanta modeling domain at 5 pm, 10 August 1992, 600 m above ground (points) from the eight-layer UAM base case. The lines show approximate  $\text{O}_3$ - $\text{NO}_y$  slopes based on measurements (Fig. 9).

$\text{NO}_y$  in the vicinity of peak  $\text{O}_3$ . Helicopter measurements identified the local maximum for  $\text{O}_3$  in the urban plume downwind from Atlanta and provided near-continuous measurements for  $\text{O}_3$  and  $\text{NO}_y$  throughout the plume. These can be compared with peak  $\text{O}_3$  and concurrent  $\text{NO}_y$  from the various model scenarios. Model peak  $\text{O}_3$  represents the simulated maximum at the same time (5 pm) and vertical elevation (600 m) as the observed maximum, but not necessarily at the same location. This type of comparison is important because the  $\text{O}_3/\text{NO}_y$  ratio associated with peak  $\text{O}_3$  is also linked to model predictions for  $\text{O}_3$ - $\text{NO}_x$ - $\text{ROG}$  sensitivity (Sillman, 1995, see discussion below).

Figure 11 shows the range of measured  $\text{O}_3$  vs  $\text{NO}_y$  for locations within 4 km of the measured maximum  $\text{O}_3$ . The 4 km horizontal distance is equal to the horizontal resolution in simulations and provides a reasonable range of uncertainty for model-measurement comparisons. Measured  $\text{O}_3$  varies by  $\pm 10\%$  over this distance and  $\text{NO}_y$  varies by up to 30%. Peak



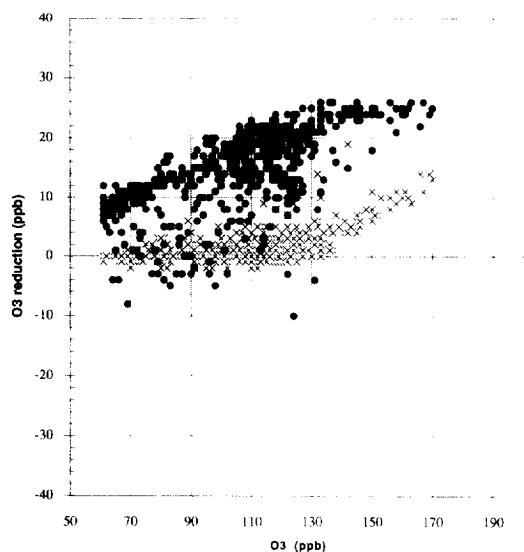


Fig. 11. Predicted reduction in peak  $O_3$  (ppb) on 10 August 1992 resulting from a 35% reduction in emission of anthropogenic ROG (crosses) or from a 35% reduction in anthropogenic  $NO_x$  emissions (circles) plotted vs peak  $O_3$ , based on the eight-layer scenario B (reduced vertical mixing).

$O_3$  and concurrent  $NO_y$  for various model scenarios are also shown in Fig. 11 (see Table 1 for a description of scenarios). Results show that some model scenarios (e.g. C) compare well with measured values on both 10 and 11 August, while other scenarios (E, F) show poor agreement on both days. Changes in wind speed are associated with a 10% change in simulated peak  $O_3$  and a 15% change in concurrent  $NO_y$ . Changed vertical mixing is associated with a 15% change in peak  $O_3$  and a 25% change in  $NO_y$ . Within limits, the uncertain meteorology can be used to create a model scenario that shows reasonable agreement with measured  $O_3$  and  $NO_y$ . For example, scenarios with high  $NO_x$  emissions and stagnant meteorology (E, F) tend to overestimate  $NO_y$ , but scenarios with high  $NO_x$  emissions and greater dispersion (G, H, K, L) perform better in comparison with measurements. The scenarios with high  $NO_x$  emissions (E, G, K) all underestimate the  $O_3/NO_y$  ratio, but scenarios with both high  $NO_x$  and high isoprene emissions (F, H, L) have  $O_3/NO_y$  ratios closer to measured values.

#### 4.6. $O_3$ - $NO_x$ -ROG sensitivity

A discussion of  $O_3$ - $NO_x$ -ROG sensitivity must begin with a warning about inherent uncertainties in this type of model prediction. Previous photochemical simulations for Atlanta have predicted that peak  $O_3$  shows greater sensitivity to  $NO_x$  than to ROG, largely due to the influence of isoprene (Chameides *et al.*, 1988; Scheffe, 1990). However some simulations with updated emission inventories predict ROG-sensitive behavior (Cardelino *et al.*, 1994; C. Cardelino, Georgia Institute of Technology, private communica-

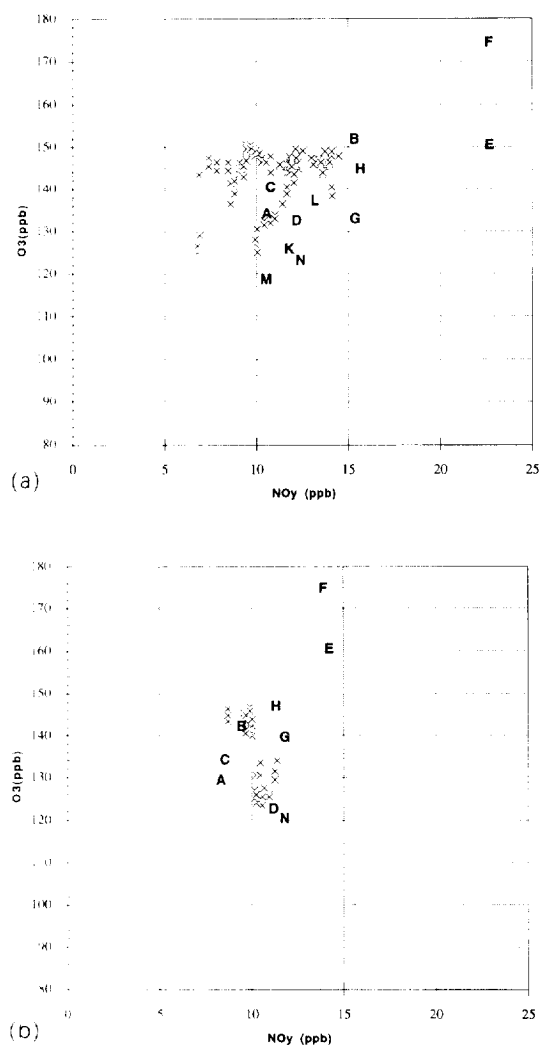


Fig. 12. Peak  $O_3$  and concurrent  $NO_y$  (ppb) in the Atlanta urban plume. (a) 10 August 1992 and (b) 11 August 1992. The  $\times$ 's represent helicopter measurements at 600 m elevation, 4–5 pm, located within 4 km of the location of measured peak  $O_3$ . Bold letters represent domain-wide peak  $O_3$  and concurrent  $NO_y$  at 600 m elevation, 4–5 pm for the model scenarios identified in Table 1.

tion, 1994). In this study the base case showed  $NO_x$ -sensitive behavior but alternative scenarios with ROG-sensitive behavior (e.g. scenario E) were intentionally created.  $O_3$ - $NO_x$ -ROG sensitivity was assessed by repeating each model scenario with a 35% reduction in anthropogenic ROG emissions and a 35% reduction in anthropogenic  $NO_x$ . Results are summarized in Fig. 12 and Table 1.

All the model scenarios conform to the general pattern of  $O_3$ - $NO_x$ -ROG sensitivity shown in Fig. 12. Peak  $O_3$  is sensitive to  $NO_x$  and shows little sensitivity to ROG for most of the model domain. However the locations downwind from Atlanta, characterized by the highest peak  $O_3$ , can also include ROG-sensitive chemistry. For the scenario shown in Fig. 12, the locations with the highest  $O_3$  show greater

sensitivity to  $\text{NO}_x$  than ROG although ROG reductions also cause a reduction in  $\text{O}_3$ . In some model scenarios (E), peak  $\text{O}_3$  at these locations shows greater sensitivity to ROG than to  $\text{NO}_x$ , while in other scenarios (C) peak  $\text{O}_3$  is almost totally insensitive to ROG. The sensitivity response for domain-wide peak  $\text{O}_3$  can be used to summarize differences between model scenarios (Table 1).

As shown in Table 1, significant differences appear in model  $\text{NO}_x$ -ROG sensitivity for 10 and 11 August. Peak  $\text{O}_3$  on 11 August is sensitive to  $\text{NO}_x$  and insensitive to ROG in all model scenarios. Peak  $\text{O}_3$  on 10 August shows greater sensitivity to  $\text{NO}_x$  than to ROG in the base case but some scenarios (E, G, K) show equal or greater sensitivity to ROG. The difference in model behavior for 10 August vs 11 August is associated with emissions from the McDonough power plant 10 km west of Atlanta.  $\text{NO}_x$  from this power plant contributes to the Atlanta urban plume in simulations for 10 August, causing higher  $\text{NO}_x$  and lower ROG/ $\text{NO}_x$  ratios relative to 11 August. These differences in model behavior are also consistent with differences in measured  $\text{NO}_y$  between the two days (Fig. 10). A comparison of model scenarios for 10 August shows that predicted  $\text{NO}_x$ -ROG sensitivity is affected by changes in both emissions and meteorology. Increased  $\text{NO}_x$  emissions cause a shift from  $\text{NO}_x$ -sensitive to ROG-sensitive chemistry (B vs E), increased isoprene emissions cause a shift from ROG- to  $\text{NO}_x$ -sensitive chemistry (E vs F, G vs H), and more stagnant meteorology causes a shift from  $\text{NO}_x$ - to ROG-sensitive chemistry (G vs E). These results are consistent with previous findings (Chameides *et al.*, 1988; Milford *et al.*, 1994; Rao *et al.*, 1994).

## 5. DISCUSSION

Model-measurement comparisons for isoprene, peak  $\text{O}_3$  and concurrent  $\text{NO}_y$  are especially useful for evaluating the performance of individual model scenarios. The isoprene measurements provide evidence that the initial emission estimate for isoprene was too low. This largely confirms the results of Geron *et al.* (1994). Peak  $\text{O}_3$  and concurrent  $\text{NO}_y$  also provides a basis for accepting certain model scenarios and rejecting others.

There is an important connection between peak  $\text{O}_3$  and concurrent  $\text{NO}_y$  in model scenarios and model predictions for  $\text{O}_3$ - $\text{NO}_x$ -ROG sensitivity.  $\text{O}_3/\text{NO}_y$  ratios have been linked to predicted  $\text{O}_3$ - $\text{NO}_x$ -ROG sensitivity in models for the northeast corridor and Lake Michigan regions (Sillman, 1995; see also Milford *et al.*, 1994). For the Atlanta simulations described here,  $\text{O}_3/\text{NO}_y$  greater than 7 is associated with  $\text{NO}_x$ -sensitive chemistry and lower  $\text{O}_3/\text{NO}_y$  is associated with ROG-sensitive chemistry. Measurements in the vicinity of peak  $\text{O}_3$  (Fig. 10) show  $\text{O}_3/\text{NO}_y > 10$  on both 10 and 11 August, which is consistent with  $\text{NO}_x$ -sensitive chemistry. A cross-

comparison between Fig. 10 and Table 1 shows that the  $\text{NO}_x$ -sensitive model scenarios are consistent with measured  $\text{O}_3$  and  $\text{NO}_y$ , while the ROG-sensitive scenario (E) underestimates  $\text{O}_3/\text{NO}_y$  by a factor of two in comparison with measurements.

Model-measurement comparisons for other species provide some evidence that model reactivity is too high, although simulated  $\text{O}_3$  generally agrees with measurements. Evidence for excess reactivity includes model overprediction of HCHO,  $\text{H}_2\text{O}_2$  and PAN and the fact that peak  $\text{O}_3$  occurs closer to the center of Atlanta in model calculations relative to the helicopter measurements. The overprediction for  $\text{H}_2\text{O}_2$  is especially significant because  $\text{H}_2\text{O}_2$  reflects the availability of odd hydrogen radicals which drive most daytime chemistry. Alternatively, overestimation of HCHO and  $\text{H}_2\text{O}_2$  in the models may arise from incorrect treatment of deposition velocities of these two soluble species. There have been few field measurements of vertical profiles for hydrogen and organic peroxides (Enders *et al.*, 1992; Hall *et al.*, 1994). Until more measurements have been compared with model calculations, deposition velocities must be considered tentative. The model overprediction of HCHO,  $\text{H}_2\text{O}_2$  and PAN must also be viewed as tentative unless it is confirmed by more extensive field measurements in urban locations.

## 6. CONCLUSION

Measurements of  $\text{O}_3$ ,  $\text{NO}_y$ , primary and secondary hydrocarbons, and  $\text{H}_2\text{O}_2$  have been used to evaluate the performance of photochemical simulations during a recent air pollution event in Atlanta. Results show the importance of assumed daytime vertical mixing and vertical profiles for species within the daytime convective layer. Model assumptions about vertical mixing can create uncertainties in simulated surface concentrations for chemically active primary species, especially isoprene, and vertical profiles for primary organic species are important for evaluating model accuracy. Model results show a serious underestimate in the simulated concentration of isoprene in comparison with measurements. Models also overestimate the concentrations of several reaction products, including HCHO,  $\text{H}_2\text{O}_2$  and PAN. Despite these errors, model peak  $\text{O}_3$  and  $\text{O}_3$ - $\text{NO}_y$  correlations show good agreement with measured values.

Model scenarios have been created with alternative emissions and meteorology, including scenarios with both ROG- and  $\text{NO}_x$ -sensitive chemistry. These scenarios have been evaluated by comparing domain-wide peak  $\text{O}_3$  and concurrent  $\text{NO}_y$  with peak  $\text{O}_3$  and  $\text{NO}_y$  identified from helicopter measurements. The ROG- and  $\text{NO}_x$ -sensitive scenarios are both able to reproduce observed peak  $\text{O}_3$ , but the ROG-sensitive scenario overpredicts  $\text{NO}_y$  and underpredicts  $\text{O}_3/\text{NO}_y$ . The  $\text{O}_3/\text{NO}_y$  ratio provides a more rigorous test for model performance than just  $\text{O}_3$ . Because  $\text{NO}_x$ -sensi-

tive and ROG-sensitive simulations give different results for  $O_3$ - $NO_x$  model measurement comparisons for this ratio are especially important for establishing the ability of models to accurately predict  $O_3$ - $NO_x$ -ROG sensitivity.

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