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

SANFORD SILLMAN,† KHALID I. AL-WALI,† FRANK J. MARSIK,†
PETER NOWACKI,† PERRY J. SAMSON,† MICHAEL O. RODGERS,‡
LESLIE J. GARLAND,‡ JOSE E. MARTINEZ,‡ CHRIS STONEKING,‡
ROBERT IMHOFF,§ JAI HOON LEE,¶ LEONARD NEWMAN,¶
JUDITH WEINSTEIN-LLOYD‖ and VINEY P. ANEJA**

† Department of Atmospheric, Oceanic and Space Sciences, University of Michigan, Ann Arbor, MI 48109-2143, U.S.A.; ‡ School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA 30332, U.S.A.; § Atmospheric Sciences, Tennessee Valley Authority, Muscle Shoals, AL 35630, U.S.A.; ¶ Department of Applied Science, Brookhaven National Laboratory, Upton, NY 11973, U.S.A.; ‖ Department of Chemistry, State University of New York/Old Westbury, Old Westbury, NY 11568, U.S.A.; ** Department of Marine, Earth and Atmospheric Sciences, North Carolina State University, Raleigh, NC 27695-8208, U.S.A.

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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_y) 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_y 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_y 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, peroxyacetylnitrate (PAN) and total reactive nitrogen (NO_y) . 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_y 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_x–ROG relationship in urban locations: isoprene, carbonyls, peroxides and the ozone–NO_y 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_3 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 ($\sim$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_3CHO) 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_y 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 $\sim$6 m of Teflon tubing to a Thermo Electron Instruments Model 42 Nitrogen Oxides analyzer. Tests indicated that very little O_3 (< 3 ppb) survived the gold-tube converter and therefore no adjustment was applied for the possible reaction of NO with O_3 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_y, $\pm 20\%$ (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 $RO_2 + HO_2$ 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_3 was set at 55 ppb based on daytime O_3 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_x, 1 ppb; HCHO, 1.75 ppb; CH_3CHO, 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 (300–500 $m^2 s^{-1}$) 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 $m^2 s^{-1}$ 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 $m^2 s^{-1}$ or 20 $m^2 s^{-1}$, 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 H_2O_2 and higher peroxides, PAN and higher-order homologues, and CH_3CHO and higher-order aldehydes. The UMICH model includes updates to Lurmann *et al.* for $RO_2 + HO_2$ 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 2.5×10^{11} molecules $cm^{-2} s^{-1}$ in suburban Atlanta and approximately half that near downtown. The equivalent emission rate at noon was 6.5×10^{11} molecules $cm^{-2} s^{-1}$ in the inventory by Pierce *et al.* used in the UAM but 1.3×10^{12} molecules $cm^{-2} s^{-1}$ 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* NO_x: A recent inventory for Atlanta (Cardelino *et al.*, 1994) has significantly higher anthropogenic NO_x emissions in comparison to the Georgia inventory used in the base case. Alternative scenarios have 25% higher anthropogenic 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_3–NO_x–ROG sensitivity

		10 August			11 August		
		Original scenario	Reduced ROG	Reduced NO_x	Original scenario	Reduced ROG	Reduced NO_x
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_x, reduced mixing	157	134	155	163	153	145
F.	Increased NO_x and isoprene, reduced mixing	193	180	171	181	174	152
G.	Increased NO_x	139	130	128	143	139	124
H.	Increased NO_x and isoprene	155	149	136	152	150	128
K.	Increased NO_x, higher wind speed	135	126	125			
L.	Increased NO_x 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_3 (ppb) is shown for each model scenario along with peak O_3 for equivalent simulations with anthropogenic ROG reduced by 35% and with NO_x 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 $m^2 s^{-1}$. 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 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.

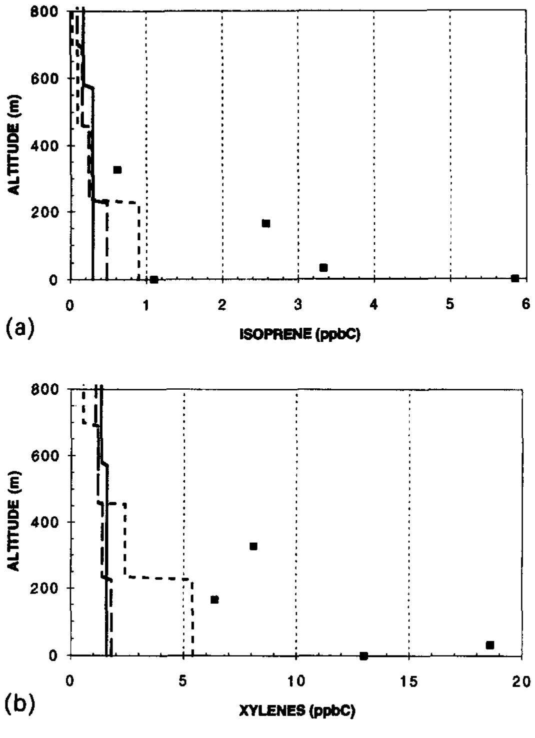

Fig. 1. Concentrations for (a) isoprene and (b) xylene (ppbC) vs height above ground (m) at 1 pm, 4 August 1990, from UAM simulations with five vertical layers (solid line), eight vertical layers and 3 m urban surface roughness (long dashed line), and eight vertical layers with vertical eddy diffusion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

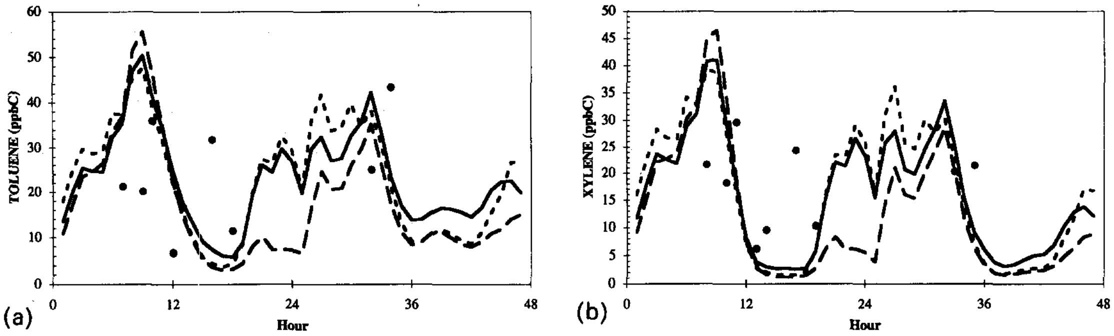

Fig. 2. Concentrations for (a) toluene and (b) xylene (ppbC) on 10–11 August 1992 at Tucker, GA, east of Atlanta, from UAM simulations with five vertical layers (dashed line), eight vertical layers (solid line) and eight layers with vertical eddy diffusion coefficient $\leqslant 20\,m^2\,s^{-1}$ (short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

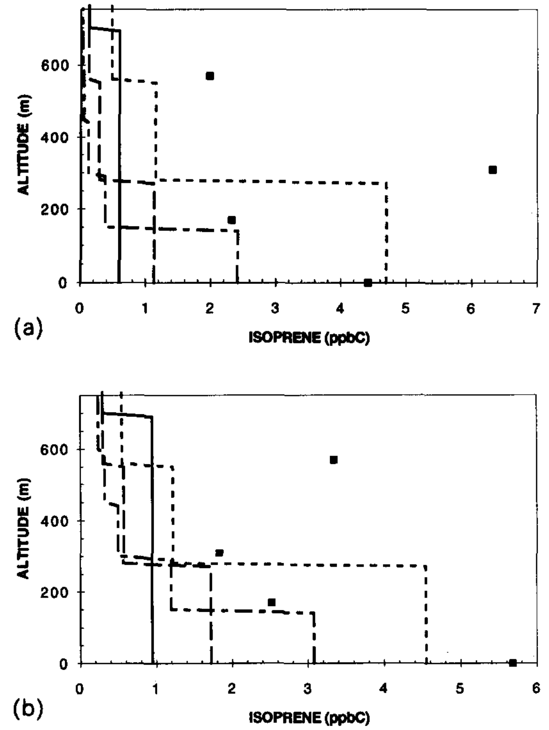

Fig. 3. Concentrations of isoprene (ppbC) vs height above ground (m) at 12 pm, 10 August 1992 at (a) Georgia Tech and (b) Tucker from UAM simulations with five vertical layers (solid line), eight vertical layers (long dashed line), eight layers with a lower mixing height (line-dash line), and eight layers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

4.2. *Carbonyls*

Figures 4 and 5 show a comparison between measured concentrations of HCHO and CH_3CHO (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 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

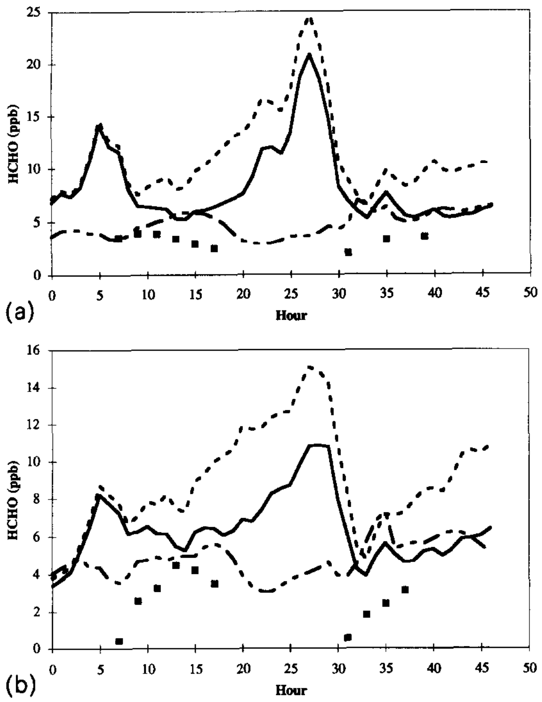

Fig. 4. Concentrations of HCHO (ppb) on 10–11 August 1992 at (a) Georgia Tech and (b) South DeKalb from the UAM simulation with eight vertical layers (solid line), UAM simulation with tripled isoprene (short dashed line) and the UMICH simulation (long dashed line) compared with measurements (points).

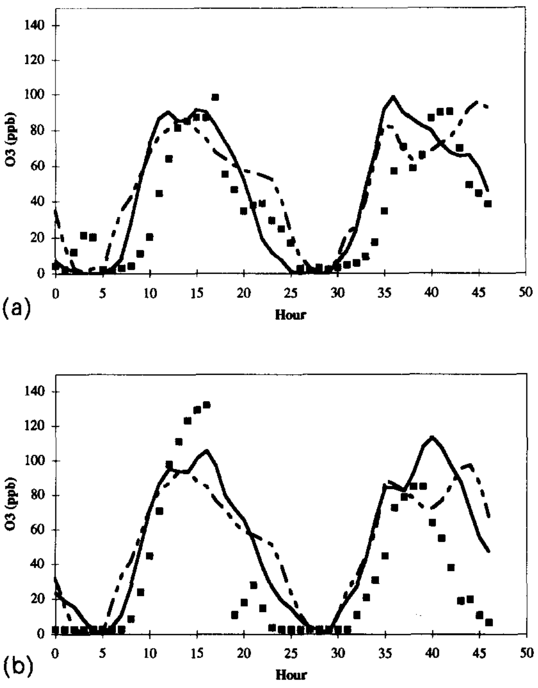

Fig. 6. Concentrations of O_3 (ppb) on 10–11 August 1992 at (a) Georgia Tech and (b) South Dekalb from UAM simulations with eight vertical layers (solid line) and from the UMICH simulation (dashed line) compared with measurements (points).

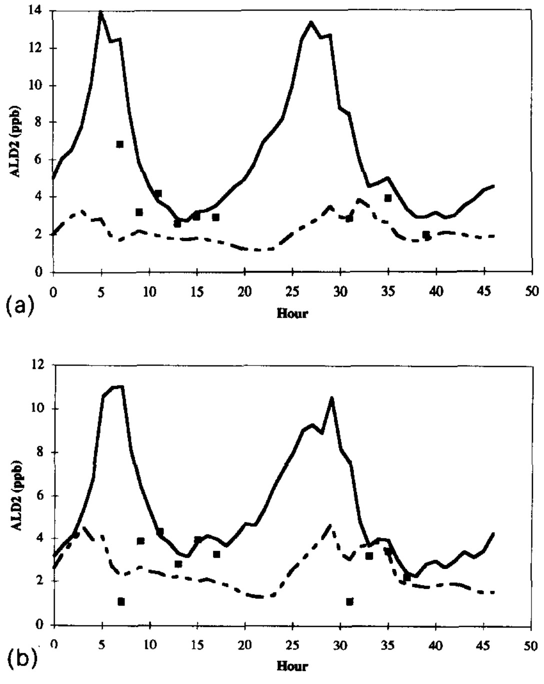

Fig. 5. Concentrations of CH_3CHO (ppb) on 10–11 August 1992 at (a) Georgia Tech and (b) South Dekalb from UAM simulations with eight vertical layers (solid line) and from the UMICH simulation (dashed line) compared with measurements (points).

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 $HCHO/CH_3CHO$ and $HCHO/O_3$ in comparison with measurements.

Comparisons between simulated and measured CH_3CHO show no clear trends. The UAM overestimates CH_3CHO but the chemical mechanism used in the UAM represents higher-order aldehydes as CH_3CHO, so that a model overestimate of up to 30% can be expected. The CB-IV mechanism also uses CH_3CHO 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_3CHO.

4.3. O_3 *and* PAN

Examination of O_3 and PAN (Figs 6 and 7) suggests that the models may overestimate production of PAN in comparison to O_3, although results are inconclusive. Both models show reasonable agreement

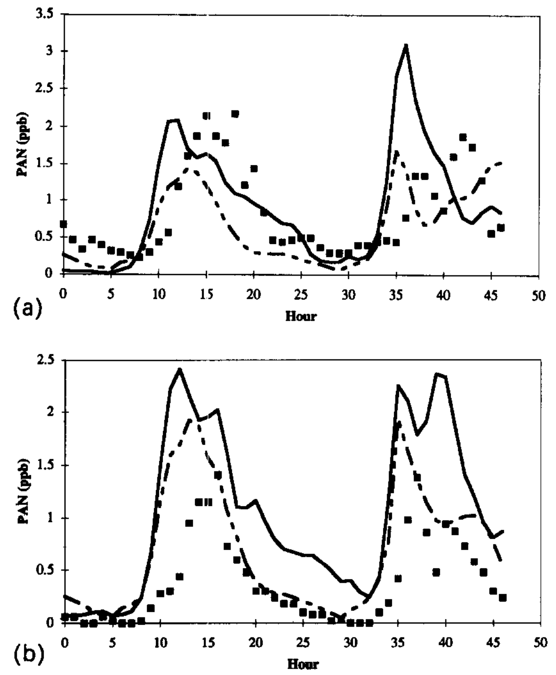

Fig. 7. Concentrations of PAN (ppb) on 10–11 August 1992 at (a) Georgia Tech and (b) South Dekalb from UAM simulations with eight vertical layers (solid line) and from the UMICH simulation (dashed line) compared with measurements (points).

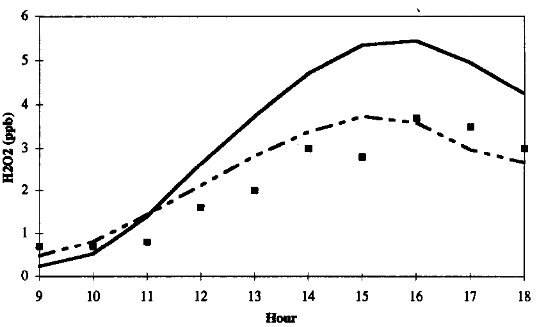

Fig. 8. Concentrations of H_2O_2 (ppb) on 10 August 1992 at Georgia Tech from UAM simulations with eight vertical layers (solid line) and from the UMICH simulation (dashed line) compared with measured total peroxides (points).

with measured O_3 although the UAM base case scenario underestimates peak O_3 for the entire domain (132 ppb vs 150 ppb in helicoptor 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 helicoptor 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 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 peroxypropionylnitrate ($C_2H_5CO_3NO_2$) and peroxymethacryloylnitrate (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 H_2O_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 H_2O_2, hydroxymethyl hydroperoxide and methyl hydroperoxide (Hellpointner and Gab, 1989; Hewitt and Kok, 1991). The discrepancy between H_2O_2 in the UAM and UMICH simulations also suggests that the odd hydrogen sink associated with $HO_2 + RO_2$ reactions in the chemistry of Lurmann *et al.* (1986) may be significantly greater than $RO_2 + HO_2$ in the CB-IV mechanism, even with recent updates to include $HO_2 + RO_2$.

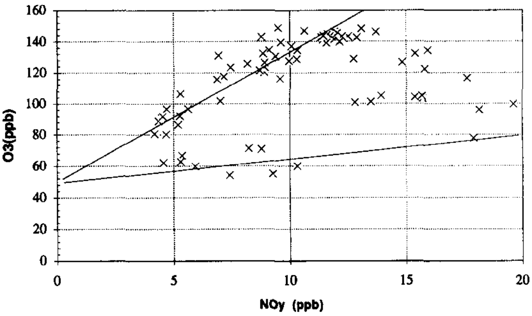

Fig. 9. Measured correlation between O_3 and NO_y (ppb) in the urban plume 10–40 km south of Atlanta at 600 m above ground, 4:00–5:20 pm, 10 August 1992 (points). Points represent 1 min average concentrations coinciding with measured NO between 0.2 and 0.75 ppb. The solid lines represent approximate O_3–NO_y slopes through two different subsets of measurements. From Imhoff and Valente (1994b).

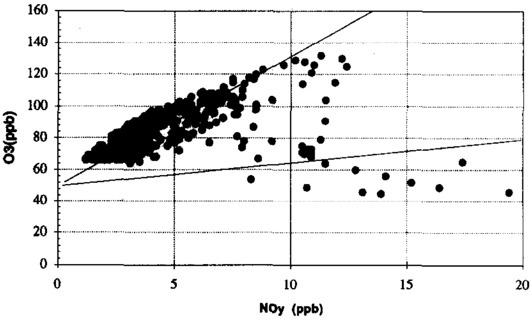

Fig. 10. Simulated correlation between O_3 and NO_y (ppb) for the Atlanta modeling domain at 5 pm, 10 August 1992, 600 m above ground (points) from the eight-layer UAM base case. The lines show approximate O_3–NO_y slopes based on measurements (Fig. 9).

4.5. O_3–NO_y *correlations*

Correlations between O_3 and total reactive nitrogen (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 O_3 and 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. O_3 and 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 O_3 increases consistently with increasing NO_y ($\Delta O_3/\Delta NO_y = 8$) as NO_y varies between 4 and 12 ppb and that O_3 remains constant or decreases with increasing NO_y when NO_y is greater than 12 ppb. Other measurements show lower O_3 and suggest a much lower rate of increase ($\Delta O_3/\Delta NO_y = 1$). A small number of measurements shows much higher NO_y (> 20 ppb) relative to the other measurements, possibly associated with a plume of fresh NO_x emissions. The measurements with low O_3/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 O_3 vs NO_y and a gradual leveling off for NO_x concentrations above 10 ppb. The model slope ($\Delta O_3/\Delta NO_y = 7$ for NO_y between 4 and 12 ppb) is lower than the measured slope and model O_3 corresponding to 8–10 ppb NO_y is consistently lower than measured O_3. The simulations also show some locations with high NO_y and low O_3, roughly equivalent to the measurements with high NO_y. However the simulated high NO_y is associated with emissions from large power plants located 40 km from Atlanta. The measured high 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 O_3 and NO_y is to examine NO_y in the vicinity of peak O_3. Helicopter measurements identified the local maximum for O_3 in the urban plume downwind from Atlanta and provided near-continuous measurements for O_3 and NO_y throughout the plume. These can be compared with peak O_3 and concurrent NO_y from the various model scenarios. Model peak 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 O_3/NO_y ratio associated with peak O_3 is also linked to model predictions for O_3–NO_x–ROG sensitivity (Sillman, 1995, see discussion below).

Figure 11 shows the range of measured O_3 vs NO_y for locations within 4 km of the measured maximum 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 O_3 varies by $\pm 10\%$ over this distance and NO_y varies by up to 30%. Peak

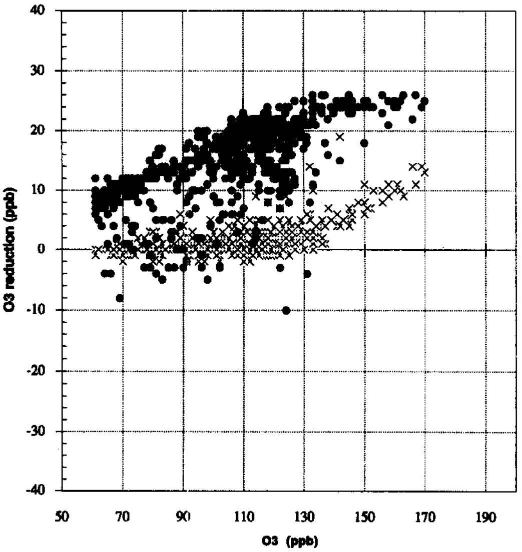

Fig. 11. Predicted reduction in peak O_3 (ppb) on 10 August 1992 resulting from a 35% reduction in emission of anthropogenic ROG (crosses) or from a 35% reduction in anthropogenic NO_x emissions (circles) plotted vs peak O_3, based on the eight-layer scenario B (reduced vertical mixing).

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*

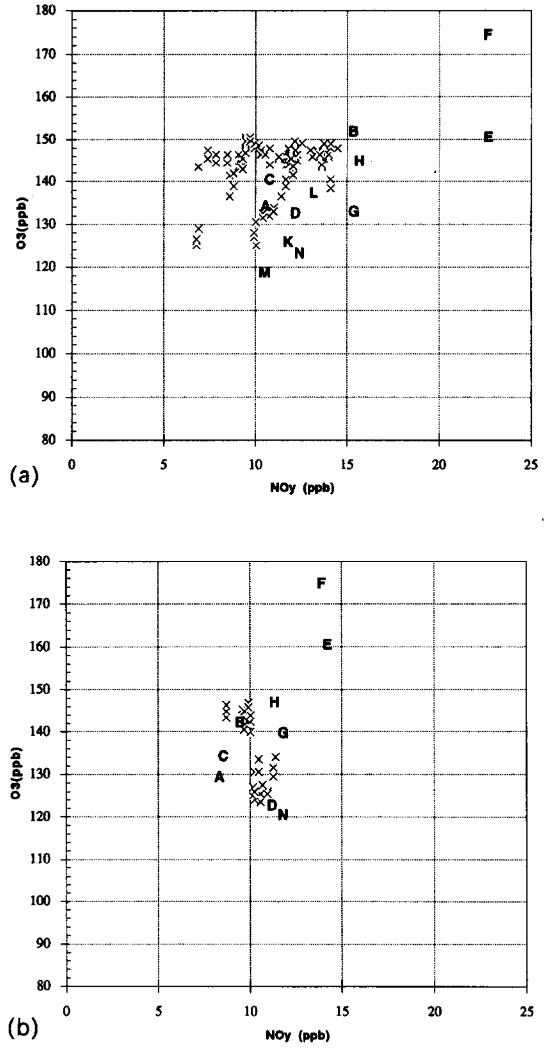

Fig. 12. Peak O_3 and concurrent NO_y (ppb) in the Atlanta urban plume, (a) 10 August 1992 and (b) 11 August 1992. The ×'s represent helicopter measurements at 600 m elevation, 4–5 pm, located within 4 km of the location of measured peak O_3. Bold letters represent domain-wide peak O_3 and concurrent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

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 communication, 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 NO_x than ROG although ROG reductions also cause a reduction in O_3. In some model scenarios (E), peak O_3 at these locations shows greater sensitivity to ROG than to NO_x, while in other scenarios (C) peak O_3 is almost totally insensitive to ROG. The sensitivity response for domain-wide peak O_3 can be used to summarize differences between model scenarios (Table 1).

As shown in Table 1, significant differences appear in model NO_x–ROG sensitivity for 10 and 11 August. Peak O_3 on 11 August is sensitive to NO_x and insensitive to ROG in all model scenarios. Peak O_3 on 10 August shows greater sensitivity to 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. NO_x from this power plant contributes to the Atlanta urban plume in simulations for 10 August, causing higher NO_x and lower ROG/NO_x ratios relative to 11 August. These differences in model behavior are also consistent with differences in measured NO_y between the two days (Fig. 10). A comparison of model scenarios for 10 August shows that predicted NO_x–ROG sensitivity is affected by changes in both emissions and meteorology. Increased NO_x emissions cause a shift from NO_x-sensitive to ROG-sensitive chemistry (B vs E), increased isoprene emissions cause a shift from ROG- to NO_x-sensitive chemistry (E vs F, G vs H), and more stagnant meteorology causes a shift from 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 O_3 and concurrent 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 O_3 and concurrent NO_y also provides a basis for accepting certain model scenarios and rejecting others.

There is an important connection between peak O_3 and concurrent NO_y in model scenarios and model predictions for O_3–NO_x–ROG sensitivity. O_3/NO_y ratios have been linked to predicted O_3–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, O_3/NO_y greater than 7 is associated with NO_x-sensitive chemistry and lower O_3/NO_y is associated with ROG-sensitive chemistry. Measurements in the vicinity of peak O_3 (Fig. 10) show $O_3/NO_y > 10$ on both 10 and 11 August, which is consistent with NO_x-sensitive chemistry. A cross-comparison between Fig. 10 and Table 1 shows that the NO_x-sensitive model scenarios are consistent with measured O_3 and NO_y while the ROG-sensitive scenario (E) underestimates O_3/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 O_3 generally agrees with measurements. Evidence for excess reactivity includes model overprediction of HCHO, H_2O_2 and PAN and the fact that peak O_3 occurs closer to the center of Atlanta in model calculations relative to the helicopter measurements. The overprediction for H_2O_2 is especially significant because H_2O_2 reflects the availability of odd hydrogen radicals which drive most daytime chemistry. Alternatively, overestimation of HCHO and H_2O_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, H_2O_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 O_3, NO_y, primary and secondary hydrocarbons, and H_2O_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, H_2O_2 and PAN. Despite these errors, model peak O_3 and O_3–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 NO_x-sensitive chemistry. These scenarios have been evaluated by comparing domain-wide peak O_3 and concurrent NO_y with peak O_3 and NO_y identified from helicopter measurements. The ROG- and NO_x-sensitive scenarios are both able to reproduce observed peak O_3, but the ROG-sensitive scenario overpredicts NO_y and underpredicts O_3/NO_y. The O_3/NO_y ratio provides a more rigorous test for model performance than just O_3. Because NO_x-sensitive and ROG-sensitive simulations give different results for O_3/NO_y, 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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REFERENCES

Andronache C., Chameides W. L., Rodgers M. O., Martinez J.E., Zimmerman P. and Greenberg J. (1994) Vertical distribution of isoprene in the lower boundary layer of the rural and urban southern United States. *J. geophys. Res.* (submitted).

Bernardo-Bricker A., Farmer C., Milne P., Riemer D., Zika R. and Stoneking C. (1995) Validation of speciated nonmethane hydrocarbon compound data collected during the 1992 Atlanta intensive as part of the Southern Oxidant Study (SOS). *J. Air Waste Man. Ass.* (in press).

Bollinger M. J., Sievers R. E., Fahey D. W. and Fehsenfeld F. C. (1983) Conversion of nitrogen dioxide, nitric acid and *n*-propyl nitrate to nitric oxide by gold-catalyzed reduction with carbon monoxide. *Analyt. Chem.* **55,** 1980–1986.

Businger J. A., Wyngaard J. C., Izumi Y. and Bradley E. F. (1971) Flux-profile relationships in the atmospheric boundary layer. *J. atmos. Sci.* **28,** 181–191.

Cardelino C., Chang W.-L. and Chang M. E. (1994) Comparison of emissions inventory estimates and ambient concentrations of ozone precursors in Atlanta, Georgia. Presented at the Air and Waste Management Asso. Int. Conf. on the Emission Inventory: Applications and Improvement, Raleigh, North Carolina, 1–3 November.

Chameides W. L., Lindsay R. W., Richardson J. and Kiang C. S. (1988) The role of biogenic hydrocarbons in urban photochemical smog: Atlanta as a case study. *Science* **241,** 1473–1474.

DeMore W. B., Sander S. P., Golden D. M., Hampson R.F., Kurylo M. J., Howard C. J., Ravishankara A. R., Kolb C. E. and Molina M. J. (1992) Chemical kinetics and photochemical data for use in stratospheric modeling. JPL 92-20, Jet Propulsion Laboratory, NASA.

Druzik C., Grosjean D., Van Neste A. and Parmar S. S. (1990) Sampling of ambient carbonyls with DNPH-coated cartridges and liquid chromatography analysis with diode array detection. *Int. J. Envir. Anal. Chem.* **38,** 495.

Enders G., Dlugi R., Steinbrecher R., Clement B., Daiber R., Eijk J. V., Gab S., Haziza M., Helas G., Herrmann U., Kessell M., Kesselmeier J., Kotzias D., Kourtidis K., Kurth H.-H., McMillen R. T., Roider G., Schurmann W., Teichmann U. and Torres L. (1992) Biosphere/atmosphere interactions: integrated research in a European coniferous forest ecosystem. *Atmospheric Environment* **26A,** 171–189.

Environmental Protection Agency (EPA) (1989) The 1985 NAPAP emissions inventory (version 2): development of the annual data and modelers' tapes. EPA-600/7-89-012a, Environmental Protection Agency, Research Triangle Park, North Carolina.

Fahey D. W., Hubler G., Parrish D. D., Williams E. J., Norton R. B., Ridley B. A., Singh H. B., Liu S. C. and Fehsenfeld F. C. (1986) Reactive nitrogen species in the troposphere: Measurement of NO, NO_2, HNO_3, particulate nitrate, peroxyacetylnitrate (PAN), O_3 and total reactive nitrogen (NO_y) at Niwot Ridge, Colorado. *J. geophys. Res.* **91,** 9781–9793.

Garland L. J., Stoneking C., Martinez J. E., Smyth S., Gatti D., Strekowski R., Manly M. and Rodgers M. O. (1994) Speciated hydrocarbon measurements in Atlanta, Georgia: comparison of 1990, 1991 and 1992 results. *Atmospheric Environment* (submitted).

Georgia Department of Natural Resources (1987) *Georgia's State Implementation Plan for Ozone in the Atlanta Area,* Air Protection Branch.

Geron C. D., Guenther A. B. and Pierce T. E. (1994) An improved model for estimating emissions of volatile organic compounds from forests in the eastern United States. *J. geophys. Res.* **99,** 12,773–12,791.

Gery M. W., Whitten G. Z., Killus J. P. and Dodge M. C. (1989) A photochemical kinetics mechanism for urban and regional computer modeling. *J. geophys. Res.* **94,** 12,925–12,956.

Greenberg J. P. and Zimmerman P. R. (1984) Nonmethane hydrocarbons in remote tropical, continental and marine atmospheres. *J. geophys. Res.* **89,** 4767–4778.

Grosjean D. (1991) Ambient levels of formaldehyde, acetaldehyde and formic acid in southern California: results of a one-year baseline study. *Envir. Sci. Technol.* **25,** 710.

Grosjean E., Williams E. L. II and Grosjean D. (1993) Ambient levels of formaldehyde and acetaldehyde in Atlanta, Georgia. *J. Air Waste Man. Ass.* **43,** 469–474.

Hall B. D., Claiborn C. S., Baldocci D. B. and Howard H. (1994) Deposition of gas phase peroxides: measurements in a deciduous forest. In Proc. 74th American Meteorological Soc., Nashville, Tennessee.

Hartsell B. E., Aneja V. P. and Grosjean D. (1993) Peroxyacetyl nitrate in Atlanta, GA: comparison and analysis of ambient data for suburban and downtown locations. *Atmospheric Environment* (submitted).

Hellpointner and Gab S. (1989) Detection of methyl, hydroxymethyl and hydroxyethyl hydroperoxides in air and precipitation. *Nature* **337,** 631–634.

Hewitt C. N. and Kok G. L. (1991) Formation and occurrence of organic hydroperoxides in the troposphere: laboratory and field observations. *J. atmos. Chem.* **12,** 181–194.

Imhoff R. E. and Valente R. J. (1994a) Spatial variability of ozone and its precursors during the Atlanta ozone intensive. *J. geophys. Res.* (submitted).

Imhoff R. E., Valente R. J., Meagher J. F. and Luria M. (1994b) The production of O_3 in and urban plume: airborne sampling of the Atlanta urban plume. *Atmospheric Environment* **29,** 2349–2358.

Jacob D. J. and Wofsy S. C. (1988) Photochemistry of biogenic emissions over the Amazon forest. *J. geophys. Res.* **93,** 1477–1486.

Lamb R. G., Chen W. H. and Seinfeld J. H. (1975) Numerico-empirical analyses of atmospheric diffusion theories. *J. atmos. Sci.* **32,** 1794–1807.

Lamb B., Westberg H., Allwine G. and Quarles T. (1985) Biogenic hydrocarbon emissions from deciduous and coniferous trees in the United States. *J. geophys. Res.* **90,** 2380.

Lee J. H., Tang I. N. and Weinstein-Lloyd J. B. (1990) Nonenzymatic method for the determination of hydrogen peroxide in atmospheric samples. *Analyt. Chem.* **62,** 2381–2384.

Lee J. H., Leehy D. F., Tang I. N. and Newman L. (1993) Measurement and speciation of gas phase peroxides in the atmosphere. *J. geophys. Res.* **98,** 2911–2915.

Lee J. H., Tang I. N., Weinstein-Lloyd J. B. and Halper E. B. (1994) An improved nonenzymatic method for the determination of gas-phase peroxides. *Environ. Sci. Tech.* **28,** 1180–1185.

Lurmann F. W., Lloyd A. C. and Atkinson R. (1986) A chemical mechanism for use in long-range transport/acid deposition computer modeling. *J. geophys. Res.* **91,** 10,905–10,936.

Madronich S. (1987) Photodissociation in the atmosphere: 1. Actinic flux and the effect of ground reflections and clouds. *J. geophys. Res.* **92,** 9740–9752.

Marsik F. M., Fischer K., McDonald T. D. and Samson P. J. (1993) Comparison of methods for estimating mixing height used during the 1992 Atlanta field intensive. In Proc. Int. Conf. on Regional Photochemical Measurement and Modeling Studies, Air and Waste Man. Ass., 8–12 November.

Martinez J. E. (1992) Impact of natural and anthropogenic hydrocarbons on tropospheric ozone production: results from automated gas chromatography. Ph.D. thesis, Georgia Institute of Technology.

Martinez J. E. and Rodgers M. O. (1994) Continuous atmospheric hydrocarbon measurements during the 1992 Southern Oxidant Study Atlanta intensive: Results from the urban superchemistry site. *Atmospheric Environment* (submitted).

Milford J., Gao D., Sillman S., Blossey P. and Russell A. G. (1994) Total reactive nitrogen (NO_y) as an indicator for the sensitivity of ozone to NO_x and hydrocarbons. *J. geophys. Res.* **99,** 3533–3542.

Morris R. E. and Myers T. C. (1990) User's guide for the urban airshed model, Vol. I–V. EPA-450/4-90-007A–E.

Parrish D. D., Buhr M. P., Trainer M., Norton R. B., Shimshock P., Fehsenfeld F. C., Anlauf K. G., Bottenheim J. W., Tang Y. Z., Wiebe H. A., Roberts J. M., Tanner R. L., Newman L., Bowersox V. C., Olszyna K. J., Bailey E. M., Rodgers M. O., Wang T., Berresheim H., Roychowdhury U. K. and Demerjian K. L. (1993) The total reactive oxidized nitrogen levels and the partitioning between the individual species at six rural sites in eastern North America. *J. geophys. Res.* **98,** 2927–2939.

Paulson S. E. and Seinfeld J. H. (1992) Development and evaluation of a photooxidation mechanism for isoprene. *J. geophys. Res.* **97,** 20,703–20,715.

Pearson J. R., Stoneking C., Smyth S., Goggin P., Eversmann J., Montieth R. and Rodgers M. O. (1994) Non-methane hydrocarbon vertical profiles in Atlanta, Georgia: Tethered balloon observations. *J. geophys. Res.* (submitted).

Pierce T. E., Lamb B. K. and Van meter A. R. (1990) Development of a biogenic emissions inventory system for regional scale air pollution models. Presented at the 83rd Air Waste Man. Ass. Ann. Meeting, Pittsburgh, Pennsylvania, Paper No. 90-94.3, 24–29 June.

Rao S. T., Sistla G., Ku J. Y., Zhou N. and Hao W. (1994) Sensitivity of the Urban Airshed Model to mixing height profiles. Presented at the 8th Joint Conf. on the Applications of Air Pollution Meteorology and the Air Waste Man. Ass., Nashville, Tennessee.

Samson P. J. and Fischer K. (1993a) Lidar observations of winds and aerosols above Atlanta. In Proc. Int. Conf. on Regional Photochemical Measurement and Modeling Studies, Air Waste Man. Ass., 8–12 November.

Samson P. J., Al-Wali K. and Marshik F. (1993b) Evidence for reduced vertical mixing over Atlanta. In Proc. Int. Conf. on Regional Photochemical Measurement and Modeling Studies, Air and Waste Man. Ass., 8–12 November.

Scheffe R. D. (1990) Urban Airshed Model Study of Five Cities. EPA 450/2-90-006a. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina.

Sillman S. (1995) The use of NO_y, H_2O_2 and HNO_3 as indicators for ozone–NO_x–ROG sensitivity in urban locations. *J. geophys. Res.* (in press).

Sillman S., Logan J. A. and Wofsy S. C. (1990) The sensitivity of ozone to nitrogen oxides and hydrocarbons in regional ozone episodes. *J. geophys. Res.* **95,** 1837–1851.

Sillman S., Samson P. J. and Masters J. M. (1993) Ozone production in urban plumes transported over water: photochemical model and case studies in the northeastern and midwestern U. S. *J. geophys. Res.* **98,** 12,687–12,699.

Smolarkiewicz P. K. (1983) A simple positive definite advection scheme with small implicit diffusion. *Mon. Weath. Rev.* **111,** 479–486.

Stoneking C., Pearson J. R., Wang T., Hayes A., Grodzinski G., Zhao J.-Z., Melin D., Norman S. and Rodgers M. O. (1994) Spatial analysis of ozone and ozone precursors during the August 9–11, 1992 ozone episode of the Southern Oxidant Study Atlanta intensive. *Atmospheric Environment* (submitted).

Stull R. B. (1988) *An Introduction to Boundary Layer Meteorology.* Kluwer Academic Publishers, Dordrecht.

Trainer M., Parrish D. D., Buhr M. P., Norton R. B., Fehsenfeld F. C., Anlauf K. G., Bottenheim J. W., Tang Y. Z., Widbe H. A., Roberts J. M., Tanner R. L., Newman L., Bowersox V. C., Maugher J. M., Olszyna K. J., Rodgers M. O., Wang T., Berresheim H. and Demerjian K. (1993) Correlation of ozone with NO_y is photochemically aged air. *J. geophys. Res.* **98,** 2917–2926.

Weiringa J. (1993) Representative roughness parameters for homogeneous terrain. *Boundary-Layer Met.* **63,** 323–364.

Williams E. L. II and Grosjean D. (1990) Southern California Air Quality Study: Peroxyacetyl nitrate. *Atmospheric Environment* **24A,** 2369.

Williams E. L. II, Grosjean E. and Grosjean D. (1993) Ambient levels of the peroxyacyl nitrates PAN, PPN and MPAN in Atlanta, Georgia. *J. Air Waste Man. Ass.* **43,** 873–879.

Zimmerman P. R., Greenberg J. P. and Westberg C. (1988) Measurements of atmospheric hydrocarbons and biogenic emission fluxes. *J. geophys. Res.* **93,** 1407–1416.