A CASE STUDY OF OZONE PRODUCTION IN A RURAL AREA OF CENTRAL ONTARIO

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Abstract—An O_3 episode observed at Dorset, a rural site in central Ontario, during a stagnant high pressure period of the intensive Eulerian Model Evaluation Field Study (EMEFS), in the summer of 1988, is simulated using a photochemical box model with a two-layer treatment. In the model analysis, natural hydrocarbon chemistry is simulated based on an isoprene-only scenario. Sensitivity tests indicate that local isoprene emissions are an important contributor to local O_3 production, relative to anthropogenic hydrocarbons (AHCs), during the event.

The model calculated isoprene contribution to the local O_3 production, defined as the ratio of the O_3 amount formed in the absence of AHCs to that in the presence of AHCs, is characterized by a strong NO_x dependence. A minimum value ($\sim$50%) of the contribution was found at a NO_x level of $\sim$6 ppbv for the representative hydrocarbon composition during the episode. At this NO_x level, O_3 production was strongly influenced by the presence of AHCs. At significantly higher or lower NO_x levels, isoprene is more important than AHCs in the local O_3 production.

Key word index: Anthropogenic hydrocarbons, natural hydrocarbons, isoprene, O_3 production.

INTRODUCTION

Frequent occurrences of high O_3 concentrations in the U.S. and Canada continue to be of great concern. Multiday O_3 episodes, extending over large (> 6,000,000 km^2) areas of eastern North America are observed 5–10 times a year (Logan, 1989). The 1-h Canadian National Ambient Air Quality acceptable level for O_3 (82 ppbv) is exceeded more than 150 h per year at sites in Ontario near the lower Great Lakes (OME, 1990). Air pollution monitoring at Dorset, a rural site in central Ontario, indicates that even at sites relatively distant from anthropogenic emission sources the Canadian standard is exceeded quite frequently (121 h in 1988 and 20 h in 1983; Modelling Workgroup, 1990).

Concern over O_3 (as well as acidic deposition) prompted the development in Canada (with involvement by F.R.G. and the Electric Power Research Institute) of the Acid Deposition and Oxidant Model (ADOM) in the early 1980s (Venkatram *et al.*, 1988). At the same time, the U.S. proceeded with the development of RADM, the Regional Acid Deposition Model (Chang *et al.*, 1987). Both models are designed to assess source–receptor relationships, using an Eulerian framework and detailed description of photochemistry. One of the important steps in the development of both models involves the evaluation of the models against observations. A 2-year field study, the Eulerian Model Evaluation Field Study (EMEFS) was launched in June 1988 to provide the data required for the evaluation (Puckett *et al.*, 1991).

Included in the EMEFS project was an intensive measurement program at six highly instrumented sites in the U.S. and Canada. The program at the two Canadian sites (Egbert and Dorset, Ontario) was coordinated by the Canadian Institute for Research in Atmospheric Chemistry (CIRAC), and involved the Atmospheric Environment Service of Environment Canada, Concord Scientific Corporation, Ontario Hydro, The Ontario Ministry of the Environment, Unisearch Associates and York University. The program involved measurement of a number of key chemical species, meteorological parameters and solar radiation at the two ground stations and from aircraft flying between them. In addition to supporting the goals of EMEFS, this data set provides a unique opportunity to study the relevant atmospheric processes involved in regional and local O_3 episodes in central Ontario.

Previous studies have shown that, on a large scale, the emission of natural hydrocarbons dominates the emission of anthropogenic hydrocarbons. Zimmerman (1979) estimated that 15 Mt of isoprene and 50 Mt of monoterpenes are emitted annually in the U.S. In 1985, the total amount of hydrocarbons emitted from anthropogenic sources in the U.S. was about 22.3 Mt (Zimmerman *et al.*, 1988a). An inventory by Lamb *et al.* (1987) indicated that the total emission of natural hydrocarbons (NHCs) is as large as or larger than that of anthropogenic hydrocarbons (AHCs) on regional scales, consistent with the estimates of Zimmerman. According to their study, 63% of the total non-methane hydrocarbon (NMHC) emission in the U.S. is of natural origin. A similar situation is thought to exist in Canada, even though emission rates of NHCs are highly dependent on temperature. For example, the emission of NHCs in Ontario was estimated to be about twice that of AHCs in 1980 (OME, 1984).

NHCs are more reactive than most of the AHCs under atmospheric conditions typically encountered at rural sites. For example, at 300 K, the rate coefficient for the reaction of isoprene with OH is 9.2×10^{-11} cm^3 molecule^{-1} s^{-1} while the rate coefficients for propane, *n*-butane and propylene are 1.3×10^{-12}, 2.7×10^{-12} and 2.5×10^{-11} cm^3 molecule^{-1} s^{-1}, respectively (IUPAC, 1989). Therefore, the potential of NHCs to generate secondary pollutants, such as O_3, PAN, etc, is expected to be significant in the tropospheric photochemical system even though their concentrations may be lower than those of AHCs.

In earlier studies (Altshuller, 1983; Lurmann *et al.*, 1983, 1984), it was generally concluded that the impact of NHCs on tropospheric O_3 production was small. Altshuller (1983) found that NHCs did not contribute substantially to the formation of O_3 in ambient air, based on information on the ratios of O_3 produced to hydrocarbons consumed. In a trajectory modelling study, it was shown that NHC emission contributed little to the maximum O_3 concentration and only 2–11 ppbv (2–9%) of the predicted maximum O_3 was due to natural emissions in the Tampa/St Petersburg region of Florida (Lurmann *et al.*, 1984).

More recently, Trainer *et al.* (1987b, 1991) used a one-dimensional PBL photochemical model to successfully simulate O_3 concentrations measured at Scotia, PA, a rural site in the eastern U.S., during a high O_3 episode in the summer of 1986. They found that NHCs played a dominant role over AHCs in O_3 production during the 4-day meteorologically stagnant period. The calculated O_3 levels without AHCs accounted for more than 90% of the total O_3 predicted in the baseline run with both natural and anthropogenic emissions included. Chameides *et al.* (1988) studied the role of biogenic hydrocarbons in the Atlanta metropolitan area. Their calculations, performed with a city-specific empirical kinetics modelling approach (EKMA), indicated that, even in an urban area, natural emissions can significantly affect O_3 levels and the presence of NHCs can exert a profound influence on the effectiveness of an O_3 abatement strategy based on AHC reductions.

In the present study, simulations of measurement data, obtained at the Dorset, Ontario site of the Ontario Ministry of the Environment during an O_3 episode which occurred in the first week of August 1988, were conducted. The concurrently measured levels of primary pollutants (hydrocarbons and NO_x), temperature and solar radiation were used as inputs to a photochemical box model with a two-layer treatment. Calculated secondary pollutant concentrations (O_3 and formaldehyde) are compared with the observed values. The relative role of NHCs vs AHCs in oxidant production during the episode is investigated. Factors affecting the importance of NHCs in O_3 production at Dorset, Ontario during this episode are also discussed.

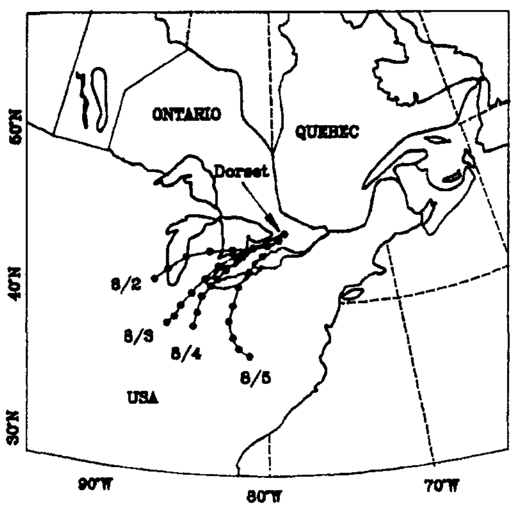

Fig. 1. Forty-eight hour back trajectories at 925 mb for 1400 h local time on 2–5 August 1988.

MEASUREMENTS AND MODEL DESCRIPTION

The Dorset site is an Acid Precipitation in Ontario Study (APIOS) monitoring site maintained by the Ontario Ministry of the Environment, located in a rural forested area of central Ontario (45°13′N; 78°55′W), elevation 320 m. A small town (Dorset), population < 1000, is located 4 km to the NE. There are no significant local point sources of AHCs or NO_x. The monitoring site is in a valley with a hill (elevation 387 m) 100 m to the SW. The site is also surrounded by hilltops ~500 m to the NW (elevation 385 m), ~500 m to the NE (elevation 401 m), and ~1000 m to the S (elevation 409 m). The local land is 88% forested (75% deciduous, 25% coniferous) and 10% water.

From 2 to 5 August 1988 the whole of southern and central Ontario was under the influence of a stationary high pressure system. This produced daily maximum temperatures above 33°C. The air flow to Dorset, as determined from isobaric back trajectories, was from the SW throughout this period. Forty-eight hour back trajectories (925 mb) for 1400 h (local time) for these 4 days are shown in Fig. 1, which also indicates the location of the site in central Ontario.

In situ measurements were made for formaldehyde, NO_x, temperature and u.v. radiation. Formaldehyde was measured by Tunable Diode Laser Absorption Spectrometry (TDLAS) with the data reported as 30-min averages. The TDLAS formaldehyde data were in reasonable agreement with simultaneous measurements conducted by DNPH/HPLC (Shepson *et al.*, 1991). Harris *et al.* (1989) detail the procedures for sampling and calibration for an identical configuration and report an instrument accuracy of ±20%. The precision of each measurement in the data presented here was estimated, from the statistics of the routine used to extract the data, to be better than 10%. NO_x data were from a luminol-based NO_2 analyser (Unisearch/Scintrex Model LMA-3) equipped with a chromium trioxide (CrO_3) converter for NO_x measurements. These data were corrected for instrument non-linear-

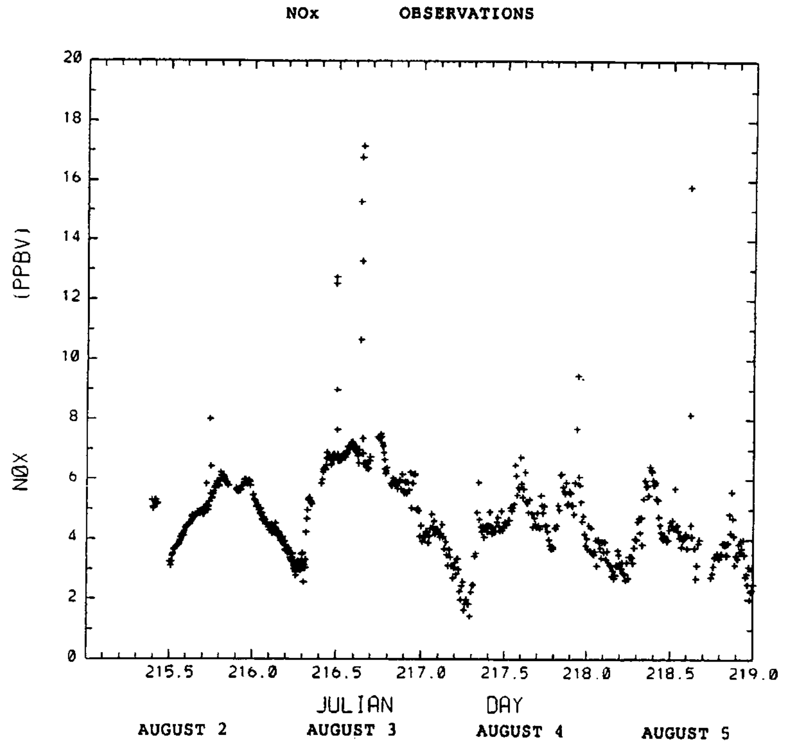

Fig. 2. Measured NO_x levels at Dorset, Ontario during 2–5 August 1988.

ity and known PAN and O_3 interferences. Since the measured NO_x levels were relatively high and PAN concentrations were quite low (~0.15 ppbv on average), these corrections were small and did not influence the measurement accuracy, which was dominated by the calibration source and was estimated at ±20%. The instrument measured NO_2 and NO_x over 5-min periods, sequentially, so the NO_x data used here are 5-min averages over a 10-min interval. Ozone was measured with a Dasibi model AH-1008 u.v. absorption analyser, for which we estimate an absolute uncertainty of ±10%. Temperature was measured with a Met-One temperature probe with an accuracy of ±1°C, and solar u.v. radiation with an Eppley radiometer which responds in the range 280–420 nm. The data from these 3 monitors were averaged over 5 min intervals. The measured NO_x, temperature and solar intensity data are presented in Figs 2 and 3.

Air samples for hydrocarbon analysis were collected 3 times daily (mid-morning, late afternoon and late evening) in stainless steel canisters pressurized to 35 psi by a stainless steel metal bellows pump and analysed by Gas Chromatography. The overall precision of the hydrocarbon measurements was estimated to be 30%. Details of the measurements have been discussed by Bottenheim *et al.* (1990).

In the daytime, NHCs are destroyed quickly through reactions with hydroxyl radicals. For example, the chemical lifetime of isoprene can be as short as 30 min, which is shorter than or comparable to the vertical diffusion time in the planetary boundary layer (PBL). NHCs are emitted into the PBL from the underlying vegetative surface. This, together with the short lifetime, leads to a rapid decrease of NHC concentrations with height (Hov *et al.*, 1983; Trainer *et al.*, 1987a). This is quite different from the vertical distributions of trace gases of anthropogenic origin, transported (advected) from other regions. For the latter, a uniform concentration throughout the PBL can be reasonably assumed. Thus, it would be improper to use a single uniform box model to represent the whole PBL if one is interested in evaluating the impacts of NHCs on the photochemistry of ambient air.

In the present study, the PBL is divided into two layers. Isoprene, which is used to represent NHCs because of the dominance of deciduous trees at the Dorset site, is treated differently in the two layers. In the lower layer, isoprene was set to the measured value while the concentration in the upper layer was set to zero to reflect the rapid decrease with height. The reasons for this treatment are as follows. Firstly, because of the valley-type topography of the Dorset site, the strong turbulence which occurs in the lower part of the PBL during sunny summer days mixes isoprene fairly well up to about 150 m. This was confirmed in a separate field study of vertical isoprene profiles conducted by Ontario Hydro at the Dorset site in August 1989 (Ontario Hydro, 1991). Isoprene concentrations were measured up to about 300 m at 4 levels using a tethered helium balloon technique, fashioned after that of Zimmerman *et al.* (1988b). Samples were collected in Teflon bags using remotely-activated pumps (~2.5 min to fill the bags) and then transferred to evacuated canisters and analysed as described by Bottenheim *et al.* (1990). For a typical strong convective case, concurrent vertical measurements of isoprene and temperature are plotted in Fig. 4, where the width of the bars represents the measurement uncertainty. It is seen that isoprene was well mixed in the lower PBL whereas its mixing ratio fell off rapidly above about 150 m. In addition, aircraft measurements conducted in the Dorset–Egbert area during the first week of August 1988 indicated that isoprene concentrations were only 0.1 ppbv at 420 m above the ground while the simultaneous ground-level concentrations were about 0.7 ppbv (Bottenheim *et al.*, 1990).

A shallow nocturnal inversion layer, with a depth of about 150 m, as indicated from acoustic sounding data, separates the air aloft from the surface. Chemical species above the inversion layer do not experience depletion due to dry

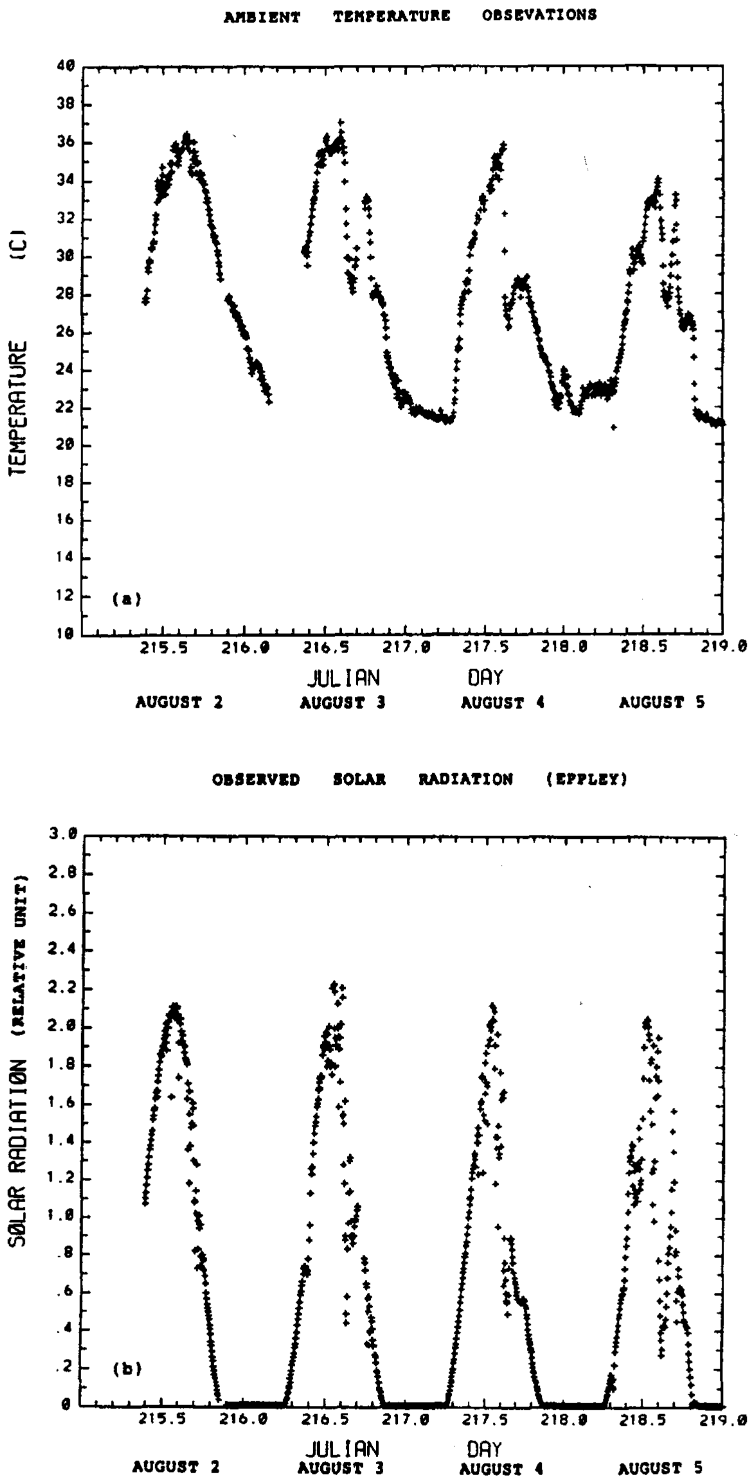

Fig. 3. (a) Measured ambient temperature at Dorset, Ontario during 2–5 August 1988.
(b) Measured solar intensity at Dorset, Ontario during 2–5 August 1988.

deposition whereas those confined to the inversion layer suffer surface losses. After sunrise, breakup of the nocturnal layer results in downward mixing of the air from above. The downward mixing is responsible for the observed increases of O_3 and other secondary pollutants in the morning hours. During the day, the PBL develops up to about 1000 m above the ground (P. Chen, pers. comm., 1989) and is followed by the formation of the radiation inversion around sunset.

Based on the above considerations, an algorithm which describes the nocturnal inversion, the variation of the depth

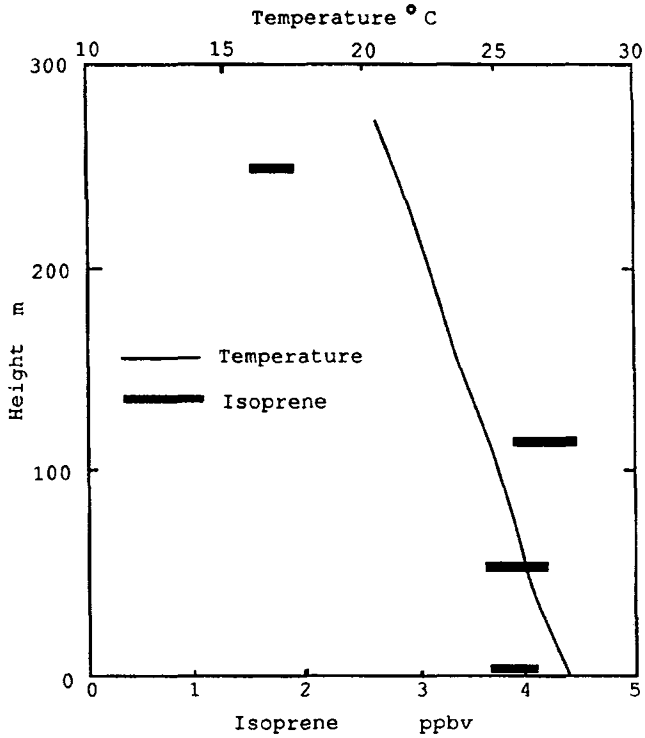

Fig. 4. Concurrent measurements of vertical profiles of isoprene and temperature at Dorset, Ontario on 1 August 1989.

of the PBL and the strong vertical gradient in isoprene concentration was designed. The diurnal variation of mixing height is presented in Fig. 5. During the night, separate boxes are applied to the nocturnal inversion layer and the air above. Calculations within the inversion layer (the lower box) include losses due to deposition to the surface while calculations for the upper box do not. In the morning, species from the two boxes are mixed as the nocturnal inversion breaks up. The mixing rate is determined by the rate of change of the mixing height. During the day, separate boxes are again imposed on the PBL, one between the surface and 150 m, and the other from 150 m up to the mixing height. The contents of the two boxes are mixed every 40 min. In all cases, the isoprene concentration was set to zero above 150 m while the measured values were used below 150 m to reflect the characteristic vertical distribution of isoprene discussed above. The concentrations of AHCs were set to the same values for both boxes.

The photochemical box model used in this study has been described in detail elsewhere (Liu *et al.*, 1987; Trainer *et al.*, 1987a; Lin *et al.*, 1988). Briefly, the model includes the chemistry of alkanes up to butane and the alkenes C_2H_4 and C_3H_6 using the reaction scheme proposed by Atkinson *et al.* (1982), and Atkinson and Lloyd (1984). In the present study, the levels of aromatics and higher anthropogenic alkanes and alkenes were very low compared with those of ethane, propane, *n*-butane, ethylene and propylene. All anthropogenic hydrocarbons with more than 3 carbon atoms were treated as *n*-butane. The reaction rate constants have been updated according to the recommendations of JPL (1990) and IUPAC (1989). The model uses isoprene as the only component of NHCs. This is justified on the basis of the predominance of deciduous trees in the local forest mix. The isoprene reaction scheme proposed by Lloyd *et al.* (1983) was used in the model.

CALCULATIONS AND RESULTS

The measured NO_x and NMHC concentrations were used as inputs to the model calculations. Since the hydrocarbons were measured at discrete times, linear interpolation was employed to extend the data set over the 4-day modelling period, as shown for selected hydrocarbons in Fig. 6. The measured solar u.v. flux was used to account for the effects of clouds on the photodissociation rate coefficients (Js). The photodissociation coefficients were calculated for 2–5 August at 45°13′N latitude for a clear sky condition. The absorption cross-sections and quantum yields given in JPL (1990) and the solar flux in NASA (1979) were used in the calculation. A column O_3 of 313 Dobson units and a surface albedo of 0.1 were assumed. The effects of Rayleigh and Mie scattering were included following the approach of Anderson and Meier (1979). 18 August 1988 was a perfectly cloud-free day suitable for calibrating the calculated photodissociation coefficients against the Eppley radiometer. For the days of the model run, where there was significant but not heavy cloud, the calculated photodissociation coefficients were then scaled from the clear sky condition by the ratio of the measured solar u.v. flux to that measured on 18 August.

Dry deposition of the species with significant surface deposition velocities was included. In the study, a deposition velocity of $0.5\ cm\ s^{-1}$ was used for the

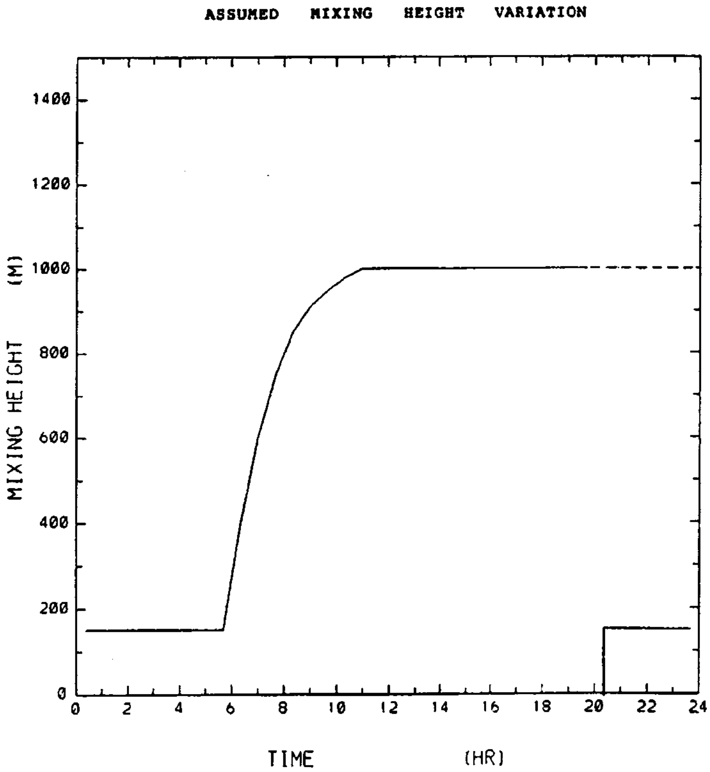

Fig. 5. Assumed diurnal variation of mixing height at Dorset, Ontario.

deposition of O_3. This value is consistent with the measurements made by Lenschow *et al.* (1982) and Colbeck and Harrison (1985). A deposition velocity of $1\ cm\ s^{-1}$ was adopted for HNO_3 based on the measurements of Huebert and Robert (1985). Deposition velocities for several other secondary products were set as follows: $0.3\ cm\ s^{-1}$ for PAN (Garland and Penkett, 1976; McRae and Russell, 1984); $0.5\ cm\ s^{-1}$ for H_2O_2 and CH_3OOH and $0.75\ cm\ s^{-1}$ for aldehydes (Wesely, 1989). Background levels of CO and CH_4 were assumed to be 200 ppbv and 1600 ppbv, respectively.

The model was initialized with a 4-day run. The calibrated photolysis rates and the observed diurnal variations of temperature, NO_x and NMHCs of 2 August 1988 were used as inputs for the 4-day period. Steady diurnal variations of chemical species were established by the end of the 4-day period. Input variables were then set according to their actual variations from 3 to 5 August. Modelled results from the 4th to the 7th model day were extracted and compared with measurements of O_3 and CH_2O made during the O_3 episode, 2–5 August 1988.

Calculated and measured O_3 concentrations are plotted against time for the 4-day episode in Fig. 7. It is apparent that the model calculation reproduced the main features of the observed O_3 episode. That is, the general diurnal pattern and the peak concentrations, ranging from 75 to 105 ppbv with the highest values at the beginning of the episode, were reasonably well simulated. A similar comparison for formaldehyde is presented in Fig. 8. It is seen that on average the model slightly underpredicted formaldehyde concentrations. During the first 2 days, differences between the predicted and the observed daily maxima are as high as 50%, although there is considerable scatter in the data. In general, the results from the current model calculation show reasonable agreement with the observed O_3 and formaldehyde variations for this episode.

The sensitivity of the O_3 and formaldehyde levels to the uncertainties in the measured NO_x and hydrocarbon concentrations were tested by changing these values in the model calculations. When a 20% change (the upper limit of the uncertainty) was applied to NO_x, the daily maxima of O_3 and formaldehyde changed by less than 10%. When a 30% uncertainty was assumed for hydrocarbon measurements, a change in concentration of this magnitude resulted in about the same percentage changes of the daily maxima of O_3 and formaldehyde. This was consistent with the fact that the O_3 production was hydrocarbon limited during the episode as we will discuss in the following section.

DISCUSSION

Variation of total hydrocarbon reactivity

Both the observed and model-predicted O_3 variations during the 4-day episode show a clear descend-

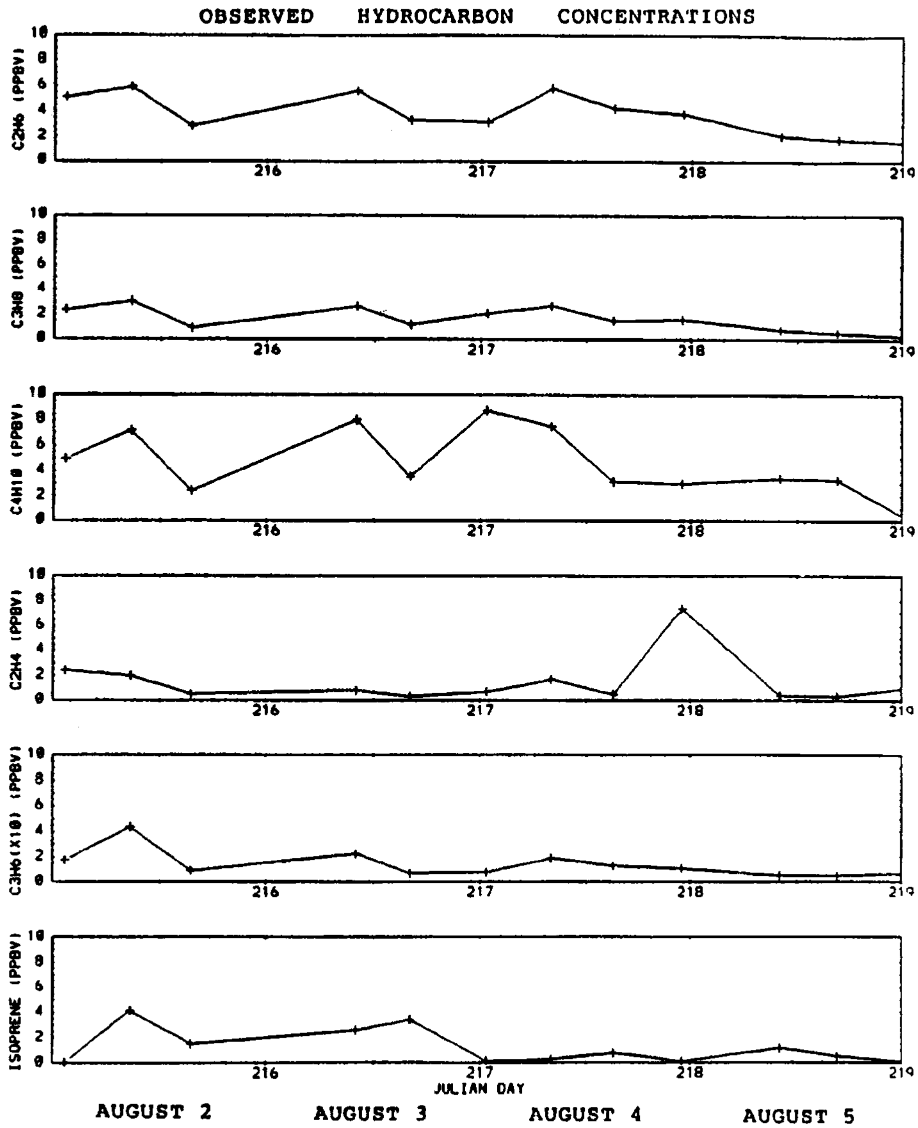

Fig. 6. Linearly interpolated hydrocarbon concentrations used as inputs to model calculations. Cross marks indicate the measurements.

ing trend of the O_3 daily maximum. This can be explained from the levels of O_3 precursors. Since NO_x fluctuated around the 5 ppbv level during the 4 days, O_3 variations were mainly controlled by the levels of hydrocarbons as will be discussed below. To illustrate the variation of the O_3 production potential of the hydrocarbons (Uno *et al.*, 1985), the reactivity of the hydrocarbon mixture was calculated for the 4 days. The reactivity of the hydrocarbon mixture was defined as

$$\sum_i k_{OH,i} \cdot C_i$$

where $k_{OH,i}$ denotes the reaction rate coefficient of the ith hydrocarbon with OH and C_i represents the concentration of the ith hydrocarbon in carbon units. Both measured AHCs and isoprene were included in the calculation. All the AHCs with carbon number greater than 3 were treated as *n*-butane in the reactivity calculation to be consistent with the model calculations mentioned earlier. The variation of hydrocarbon reactivity during the 4 days is plotted in Fig. 9. The plot reveals a substantial decrease in the reactivity from the first day to the third day of the episode followed by a small increase on the fourth day due mainly to the increase of C_2H_4. This increase in C_2H_4 has a significant impact on formaldehyde concentrations as shown in Fig. 8. Since the upper part of the PBL serves as a large reservoir for the secondary pollutants, the longer lifetime of O_3 in the upper layer

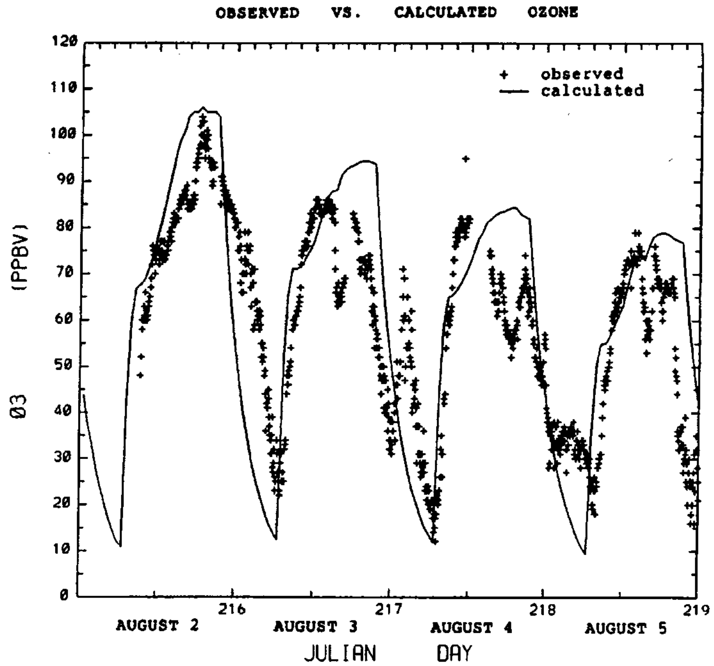

Fig. 7. Calculated O_3 variation vs measured O_3 variation at Dorset, Ontario from 2 to 5 August 1988.

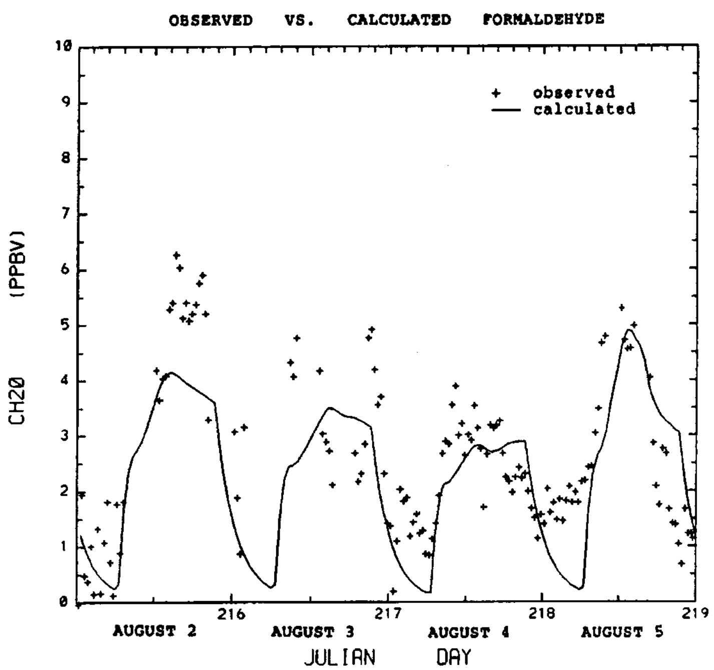

Fig. 8. Calculated CH_2O variation vs measured CH_2O variation at Dorset, Ontario from 2 to 5 August 1988.

of the PBL resulted in a relatively gradual decrease of daily maximum O_3 over the 4-day period.

To investigate the relative importance of NHCs vs AHCs in local O_3 production at the Dorset site during the O_3 episode, calculations were conducted for two scenarios. In the first scenario, the parameter values discussed above were used except that the AHC concentrations were set to zero, whereas only the

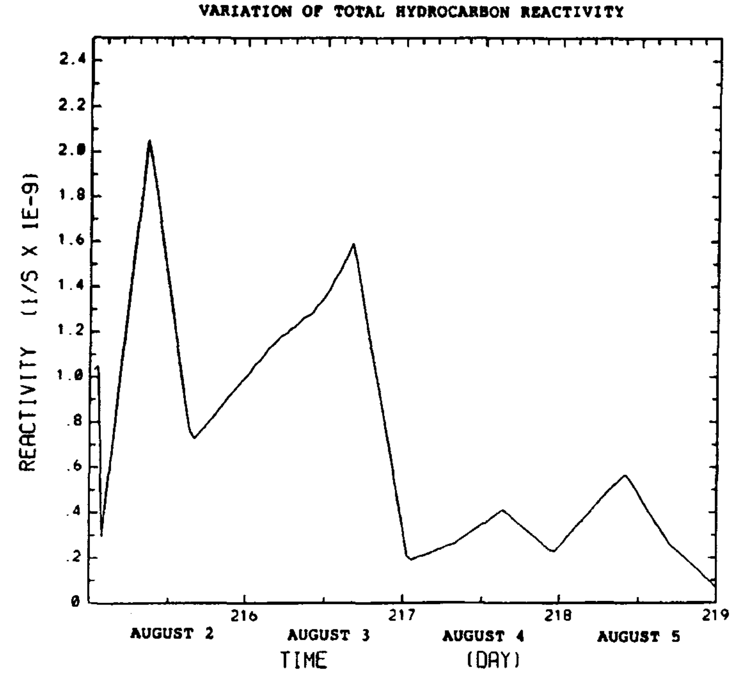

Fig. 9. Variation of the reactivity of the hydrocarbon mixture at Dorset, Ontario for the period of 2–5 August 1988.

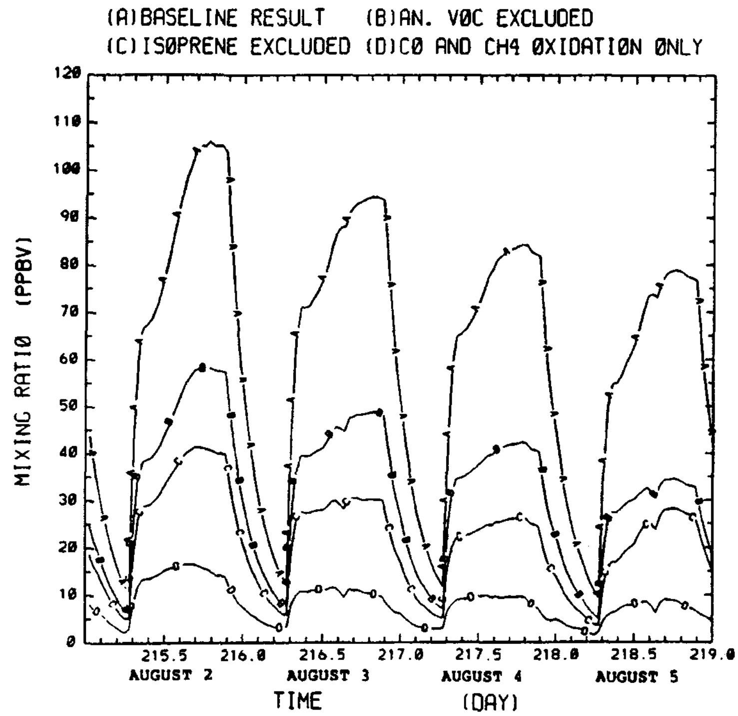

Fig. 10. Relative importance of isoprene, AHCs and $CO+CH_4$ in total O_3 production during the modelled episode.

concentration of isoprene was set to zero in the second scenario. The calculated O_3 variation from these two scenarios, together with the results from the baseline run and a run for only CO and CH_4 chemistry, are presented in Fig. 10. From the results, one can observe the following. First, CO and CH_4 chemistry contributed an insignificant part to local O_3 production. Secondly, isoprene played a more important role in local O_3 production than AHCs during the episode studied. Finally, contributions to the O_3 production from these two types of hydrocarbons were not additive, simply due to the non-linearity of the photochemical system. Neither the isoprene nor the AHCs contributed more than 55% to the total O_3 production during the episode.

Isoprene contribution to local O_3 production

The importance of isoprene in local O_3 production can be examined in a variety of ways. Here, AHC inputs will be treated as perturbations superimposed on the natural background. An isoprene contribution to local O_3 production will be defined by dividing the O_3 concentrations calculated in the absence of AHCs by those with AHCs and isoprene present. The results of the calculation thus indicate the extent to which O_3 production is due to isoprene chemistry under the conditions of the model runs. The model can then be run over wide ranges of both AHC and isoprene levels. For these calculations, the mix of AHCs was set as the average one measured in the 4-day episode and the total concentration was varied; temperature and solar intensity varied according to their mean diurnal variations for the 4-day period. O_3 concentrations at 6 PM, when the O_3 concentration is close to its daily maximum value, were obtained and were then used to derive the isoprene contributions as defined above. In Figs 11a and 11b, the calculated isoprene contributions, in units of percentage, are presented as isopleth lines as a function of isoprene and AHCs for NO_x levels fixed at 1 ppbv and 5 ppbv, respectively. It is apparent that, for NO_x at 1 ppbv, the isoprene contribution increases with increasing isoprene and with decreasing AHCs, as expected. For NO_x at 5 ppbv, the isoprene contribution is virtually independent of the level of isoprene as the reactivity of the mixture of AHCs and isoprene, defined previously, is low. When the hydrocarbon reactivity is above a certain level, the isoprene contribution increases with isoprene concentration. The hydrocarbon reactivity level separating two regions associated with different behaviours of the isoprene contribution, can be visualized as a zone running from high NHC and low AHC to low NHC and high AHC in Fig. 11b. In addition, comparison between Figs 11a and 11b indicates an overall increase in the isoprene contribution as NO_x drops from 5 ppbv to 1 ppbv.

Variations of the calculated isoprene contribution to O_3 production can be explained through an analysis of the chemical system. It is well known that O_3 formation responds to levels of hydrocarbons in a non-linear way (e.g. Lurmann *et al.*, 1984). The non-linearity of the O_3 production depends strongly on the amount of NO_x available (Dimitriades and Dodge, 1983). When the NO_x level is low, O_3 formation is limited by the available NO_x. Thus, a relatively large increase in the reactivity of hydrocarbons (e.g. adding AHCs to isoprene in this case) results in a small increase in O_3. The fractional increase in O_3, which is due to the addition of AHCs to the reference isoprene, becomes smaller as the level of isoprene increases. By recalling the definition of the isoprene contribution (the ratio of the O_3 level produced from isoprene chemistry alone divided by the O_3 level associated with isoprene plus AHCs), it can be concluded that an increase in isoprene concentration results in an increase in isoprene contribution. As the NO_x level is elevated, say to 3–6 ppbv, O_3 production becomes hydrocarbon limited. Now, a relatively small fractional increase in the reactivity of hydrocarbons leads to a large fractional change in O_3. It implies that the isoprene contribution appears to be almost independent of the level of isoprene. However, as the ratio of hydrocarbons to NO_x increases and NO_x becomes the rate limiting factor, the isoprene contribution increases again with isoprene concentration as shown in Fig. 11b.

The dependence of the isoprene contribution to O_3 production on the NO_x concentration is illustrated in Fig. 12a. In this figure the calculated O_3 concentration at 1800 h is plotted against NO_x concentration ranging between 0.1 and 25 ppbv. For each calculation, the NO_x level was kept constant. The calculations were conducted for an average hydrocarbon mixture and average diurnal variations of temperature and solar intensity for the 4-day episode. Ten ppbC of isoprene and 35 ppbC of AHCs (representative concentrations for the 4-day period) were assumed in the calculations. The two solid curves represent a normal run and a run without AHCs, while the dashed curve represents the isoprene contribution to O_3 production, i.e. the ratio of the values of curve B to those of curve A. The results indicate that, for NO_x levels below 1 ppbv, isoprene could be responsible for more than 85% of the O_3 production. When NO_x increases, the contribution of isoprene to O_3 production decreases. However, as NO_x increases beyond 10 ppbv, the contribution of isoprene starts to increase with increasing NO_x. It is seen that there exists a maximum O_3 concentration (at 1800 h) for a NO_x level somewhere between 2 and 4 ppbv, and that the NO_x level associated with the maximum O_3 shifts towards higher values as the hydrocarbon mixture changes from one without AHCs to one with AHCs. The NO_x level associated with the maximum O_3 for a mixture of AHCs and isoprene will be referred to as the critical NO_x level. By recalling the definition of the isoprene contribution, the above implies that a minimum value of the isoprene contribution occurs at a NO_x level that is located slightly on the high side of the critical NO_x level (at ~ 6 ppbv) as shown by the dashed curve. This is within the typical range of NO_x concentration (3–6 ppbv) of the episode. Under these conditions AHCs have a relatively large impact on local O_3 production.

For the case of the O_3 episode studied, the average NO_x mixing ratio was about 5 ppbv. The levels of isoprene were at or below about 10 ppbC. Applying

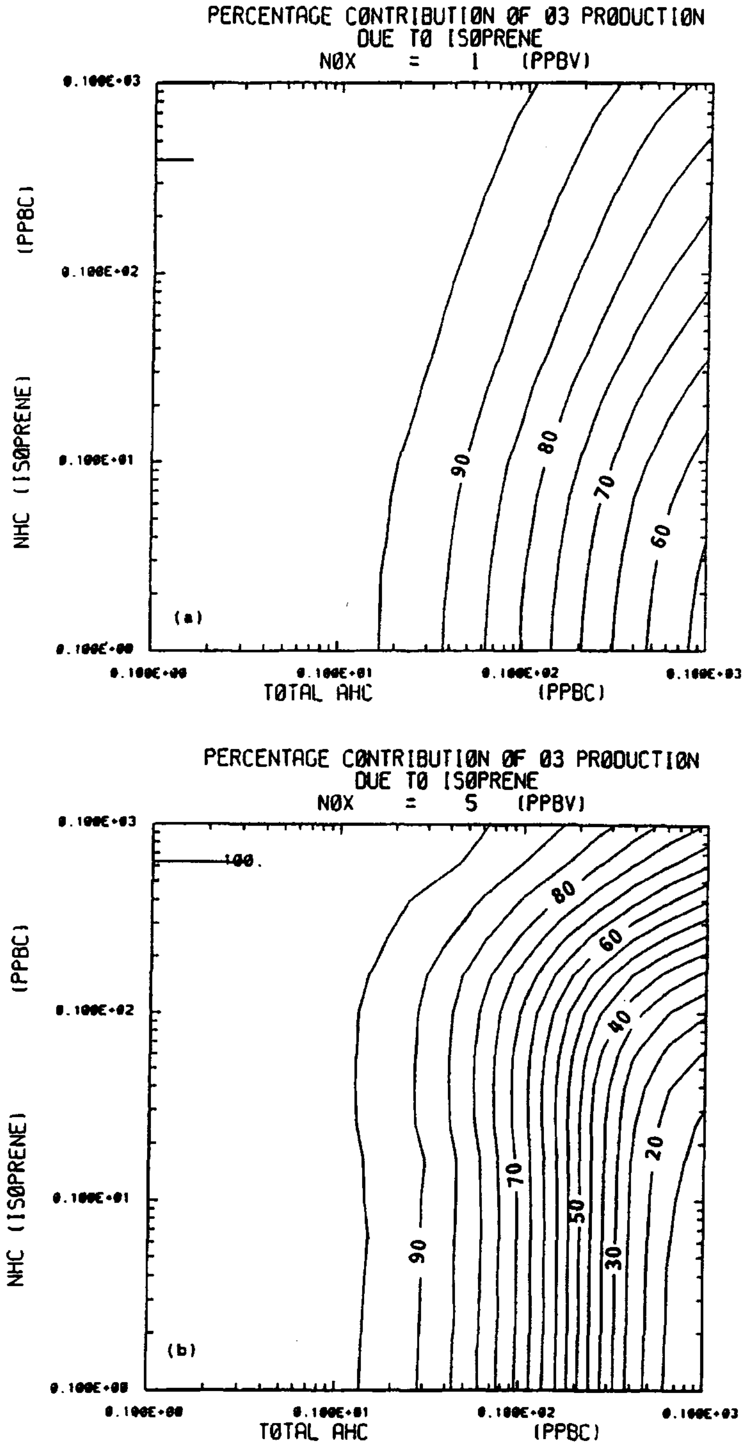

Fig. 11. (a) Calculated isoprene contributions to O_3 production, in unit of %, for NO_x at 1 ppbv. (b) Same as (a), but for NO_x at 5 ppbv.

5 ppbv of NO_x in Fig. 12a, one finds that the isoprene contribution could have been 49%. This number is consistent with the results of the sensitivity tests shown in Fig. 10.

Comparison with other studies

It is instructive to compare the above results with similar calculations based on data obtained at other rural sites. The levels of isoprene during the episode

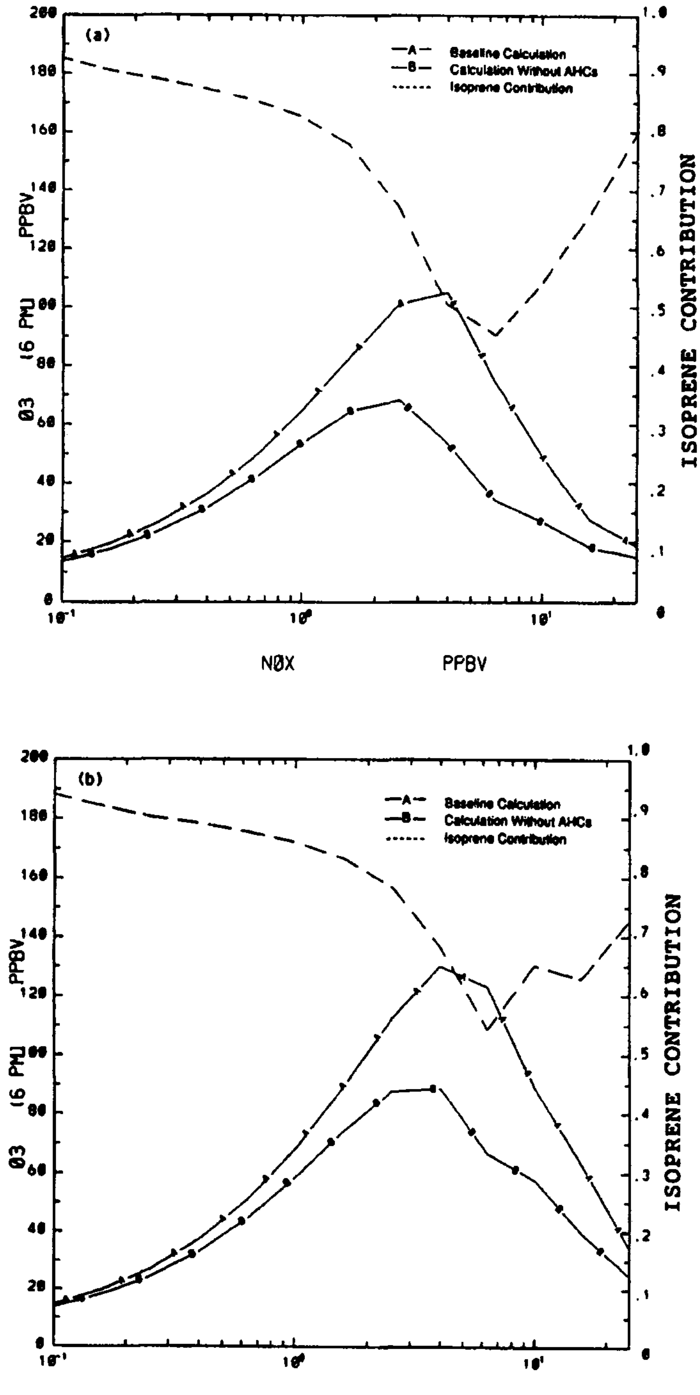

Fig. 12. (a) Calculated non-linear response of O_3 to hydrocarbons and NO_x for AHCs at 35 ppbC and isoprene at 10 ppbC. Curves A and B represent a normal run and a run without AHCs, respectively. The dashed curve represents isoprene contributions to O_3 production. (b) Same as (a), but for isoprene at 20 ppbC.

were not as high as those observed at more southerly rural sites (Trainer *et al.*, 1987b, 1991; Yokouchi and Ambe, 1988; Niki *et al.*, 1991) or even those measured on other occasions at the same site. On the other hand, the levels of NO_x during the episode were fairly high. The typical range of NO_x concentrations was 3–6 ppbv for the 4-day period. Median afternoon concentrations of NO_x measured at Scotia, PA, a rural site in the eastern U.S., were about 0.6 ppbv (Hubler *et al.*, 1987). Even for an O_3 episode under stagnant meteorological conditions, NO_x at Scotia varied around the 2 ppbv level (Trainer *et al.*, 1987b, 1991). During that episode, the concentrations of isoprene were about 20 ppbC. To enable comparison of our results from Dorset with those from Scotia, the calculations that yielded Fig. 12a, were repeated with an isoprene level of 20 ppbC. Results from the calculations are plotted in Fig. 12b and show similar characteristics to the ones in Fig. 12a, e.g. the O_3 maxima appear around NO_x concentrations of 2–4 ppbv. The relative importance of isoprene vs AHCs, however, becomes greater since more isoprene is available. For a NO_x level of 5 ppbv, the isoprene contribution accounts for 62% of the total O_3. If the NO_x level drops to 2 ppbv, the isoprene contribution is further enhanced to 81%. This is similar to the findings of Trainer *et al.* (1987b) in a case study for the Scotia, PA site.

There were limitations in the present modelling study. We were using measured NO_x and hydrocarbon levels as inputs into the calculations instead of adjusting fluxes to match the measured levels of the precursors. Our choice was based on the consideration that a flux treatment would introduce more uncertainties into the calculated results within the current box model framework. Thus, the present treatment prohibited us from rigorously testing the sensitivity of O_3 formation to changes in emissions of precursors. In our calculations, the vertical dilution effect was represented, to some extent, by using multiple boxes. However, no effect of long-range transport was explicitly included. The Dorset site is downwind of the anthropogenic source regions in the midwestern U.S. and southern Ontario under the condition of a southwesterly flow. Since the transport time of an air parcel from the source area to the rural site is of the order of a day, there should be a significant amount of secondary oxidants accumulated in the air mass. Thus, these species might be somewhat underpredicted by the model.

CONCLUSIONS

In the present paper, an O_3 episode under stagnant meteorological conditions at the Dorset site in central Ontario during 2–5 August 1988 was simulated with a photochemical box model with a two-layer treatment utilizing observed concentrations of NO_x and hydrocarbons. The calculated results from model runs showed satisfactory agreement with the observed O_3 and formaldehyde data. The sensitivity runs with either AHCs or isoprene absent indicated that isoprene played an important role relative to AHCs in the local O_3 production during this event.

The isoprene contribution to the local O_3 production was defined by dividing the O_3 amount formed in the absence of AHCs by the one in the presence of AHCs. Model calculations indicated that the isoprene contribution is characterized by a strong NO_x dependence. A minimum value of the contribution occurs usually at a NO_x level of ~6 ppbv. The NO_x dependence can be explained by the non-linearity of the photochemical system. Around the NO_x level associated with the minimum value of the isoprene contribution, AHCs have a relatively large impact on O_3 formation while, beyond this region, the level of NO_x gradually becomes the limiting factor in O_3 production. However, it is worth noting that O_3 levels are usually low when NO_x levels are either very low or very high. For the episode studied here, the representative range of NO_x levels was about 3–6 ppbv. Therefore, the O_3 production was significantly influenced by the presence of AHCs.

The present study was performed under the conditions of a specific O_3 episode. It should be noted that the episode was characterized by relatively high NO_x and relatively low isoprene levels compared to measurements made by others (e.g. Trainer *et al.*, 1987b, 1991). As more data for central Ontario become available, further work is planned to improve our understanding of the role played by NHCs in the O_3 budget of the region.

Acknowledgements—The authors would like to thank R. Berman for data acquisition and analysis, and to acknowledge the contributions of K. Puckett, C. Francis, J. Jones, J. P. Varto, C. Blair, D. Morris, S. Malle, B. Zhang, H. Malle, L. Toth and B. Kieser for their assistance in all areas of operation. D. R. Hastie acknowledges support from the Ontario Ministry of the Environment. H. Niki and P. B. Shepson acknowledge support from the Atmospheric Environment Service. This is a CIRAC contribution, #90-3.

REFERENCES

Altshuller A. P. (1983) Review: natural volatile organic substances and their effect on air quality in the United States. *Atmospheric Environment* **17**, 2131–2165.

Anderson D. E. and Meier R. R. (1979) Effects of anisotropic multiple scattering on solar radiation in the troposphere and stratosphere. *Appl. Opt.* **18**, 1955–1960.

Atkinson R. and Lloyd A. C. (1984) Evaluation of kinetic and mechanistic data for modelling of photochemical smog. *J. phys. Chem. Ref. Data* **13**, 315–444.

Atkinson R., Lloyd A. C. and Winges L. (1982) An updated chemical mechanism for hydrocarbon/NO_x/SO_2 photooxidations suitable for inclusion in atmospheric simulation models. *Atmospheric Environment* **16**, 1341–1355.

Bottenheim J. W., Brice K. A., Wang D., Handy B., Singer E. and Niki H. (1990) Measurements of light molecular weight hydrocarbons at Egbert, Dorset and aloft (DC-3 and Twin Otter) during EMEFS—summer 1988: method and results. Report ARD-90-004, Atmospheric Research Division, Atmospheric Environment Service, Downsview, Ontario, Canada.

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**, 1473–1475.

Chang J. S., Brost R. A., Isaksen I. S. A., Madronich S., Middleton P., Stockwell W. R. and Walcek C. J. (1987) A three-dimensional Eulerian acid deposition model:

physical concepts and formulation. *J. geophys. Res.* **92,** 14,681–14,700.
Colbeck I. and Harrison R. M. (1985) Dry deposition of ozone: some measurements of deposition velocity and of vertical profiles to 100 meters. *Atmospheric Environment* **19,** 1807–1818.
Dimitriades B. and Dodge M. (1983) (editors) Proceedings of the empirical kinetic modeling approach (EKMA) validation workshop, EPA Report No. EPA-600/9-83-014.
Garland J. and Penkett S. A. (1976) Absorption of peroxyacetylnitrate and ozone by natural surfaces. *Atmospheric Environment* **10,** 1127–1131.
Harris G. W., Mackay G. I., Iguchi T., Mayne L. K. and Schiff H. I. (1989) Measurements of formaldehyde in the troposphere by Tunable Diode Laser Absorption Spectroscopy. *J. atmos. Chem.* **8,** 119–137.
Hov O., Schjoldager J. and Wathne B. M. (1983) Measurement and modelling of the concentrations of terpenes in coniferous forest air. *J. geophys. Res.* **88,** 10,679–10,688.
Hubler G. *et al.* (1987) Partitioning of reactive odd nitrogen species in the tropospheric boundary layer. Paper presented at the *6th Int. Symp. Commission on Atmospheric Chemistry and Global Pollution.* Int. Ass. of Met. and Atmos. Phys., Peterborough, Ontario, Canada, 23–29 August.
Huebert B. J. and Robert C. H. (1985) The dry deposition of nitric acid to grass. *J. geophys. Res.* **90,** 2085–2090.
IUPAC (1989) Evaluated photochemical data for atmospheric chemistry: supplement III. *J. phys. Chem. Ref. Data* **89,** 881–1097.
JPL (1990) Jet Propulsion Laboratory, Chemical kinetics and photochemical data for use in stratospheric modelling. Evaluation Number 9. Calif. Inst. of Technol., Pasadena.
Lamb B., Guenther A., Gay D. and Westberg H. (1987) A national inventory of biogenic hydrocarbon emissions. *Atmospheric Environment* **21,** 1695–1705.
Lenschow D. H., Pearson R., Jr and Stankor B. B. (1982) Measurements of ozone vertical flux to ocean and forest. *J. geophys. Res.* **87,** 8833–8837.
Logan J. (1989) Ozone in rural areas of the United States. *J. geophys. Res.* **94,** 8511–8532.
Lin X., Trainer M. and Liu S. C. (1988) On the nonlinearity of the tropospheric ozone production. *J. geophys. Res.* **93,** 15,879–15,888.
Liu S. C., Trainer M., Fehsenfeld F. C., Parrish D. D., Williams E. J., Fahey D. W., Hubler G. and Murphy P. C. (1987) Ozone production in the rural troposphere and the implications for regional and global ozone distributions. *J. geophys. Res.* **92,** 4191–4207.
Lloyd A. C., Atkinson R., Lurmann F. W. and Nitta B. (1983) Modelling potential ozone impacts from natural hydrocarbons—I. Development and testing of a chemical mechanism for the NO_x–air photooxidations of isoprene and α-pinene under ambient conditions. *Atmospheric Environment* **17,** 1931–1950.
Lurmann F. W., Lloyd A. C. and Nitta B. (1983) Modelling potential ozone impacts from natural hydrocarbons—II. Hypothetical biogenic HC emission scenario modelling. *Atmospheric Environment* **17,** 1951–1963.
Lurmann F. W., Nitta B., Ganesan K. and Lloyd A. C. (1984) Modelling potential ozone impacts from natural sources—III. Ozone modelling in Tampa/St. Petersburg, Florida. *Atmospheric Environment* **18,** 1133–1143.
McRae G. J. and Russell A. G. (1984) Dry deposition of nitrogen-containing species. In *Deposition Both Wet and Dry* (edited by Hicks B. B.), chapter 9, pp. 153–193. Acid Precipitation Series. (series edited by Teasley J. I.). Butterworth, Boston.
Modelling Workgroup (1990) Modelling Workgroup Final Report. Prepared for the Federal/Provincial Long Range Transport of Air Pollutants (LRTAP) Steering Committee and Canadian Council of Ministers of the Environment (CCME).
NASA (1979) The stratosphere: present and future. Ref. Publ. 1049.
Niki H. *et al.* (1991) A comparison of speciated non-methane hydrocarbon concentrations at four rural sites in eastern North America (in preparation.)
OME (1984) Ontario Ministry of the Environment, 1980 Ontario VOC emission inventory: Summary Report. ARB-183-85-AQM, November.
OME (1990) Ontario Ministry of the Environment, Air quality in Ontario 1988. ISSN-0840-9366.
Ontario Hydro (1991) Vertical profiles of VOCs at Dorset, Ontario. Research Division Report (in preparation.)
Puckett K. J. *et al.* (1991) Some results from the Spring and Summer Intensive Measurement Periods of the Eulerian Model Evaluation Field Study (EMEFS) (in preparation.)
Shepson P. B, Hastie D. R., Schiff H. I., Polizzi M., Bottenheim J. W., Anlauf K. G., Mackay G. I. and Karecki D. R. (1991) Atmospheric concentrations and temporal variations of C_1–C_3 carbonyl compounds at two rural sites in central Ontario. *Atmospheric Environment* **25A,** 2001–2015.
Trainer M., Hsie E. Y., Mckeen S. A., Tallamraju R., Parrish D. D., Fehsenfeld F. C. and Liu S. C. (1987a) Impact of natural hydrocarbons on hydroxyl and peroxy radicals at a remote site. *J. geophys. Res.* **92,** 11,879–11,894.
Trainer M., Williams E. J., Parrish D. D., Buhr M. P., Allwine E. J., Westberg H. H., Fehsenfeld F. C. and Liu S. C. (1987b) Models and observations of the impact of natural hydrocarbons on rural ozone. *Nature* **329,** 705–707.
Trainer M., Buhr M. P., Curran C. M., Fehsenfeld F. C., Hsie E. Y., Liu S. C., Norton R. B., Parrish D. D. and Williams E. J. (1991) Observations and modeling of reactive nitrogen photochemistry at a rural site. *J. geophys. Res.* **96,** 3045–3063.
Uno I., Wakamatsu S., Wadden R. A., Konno S. and Koshio H. (1985) Evaluation of hydrocarbon reactivity in urban air. *Atmospheric Environment* **19,** 1283–1293.
Venkatram A., Karamachandani P. K. and Misra P. K. (1988) Testing a comprehensive acid deposition model. *Atmospheric Environment* **22,** 737–747.
Wesely M. L. (1989) Parameterization of surface resistances to gaseous dry deposition in regional-scale numerical models. *Atmospheric Environment* **23,** 1293–1304.
Yokouchi Y. and Ambe Y. (1988) Diurnal variations of atmospheric isoprene and monoterpene hydrocarbons in an agricultural area in summertime. *J. geophys. Res.* **93,** 3751–3759.
Zimmerman P. R. (1979) Testing for hydrocarbon emissions from vegetation leaf litter and aquatic surfaces, and development of a methodology for compiling biogenic emission inventories. EPA Report 450/4-4-79-004.
Zimmerman D., Tax W., Smith M., Demmy J. and Battye R. (1988a) Anthropogenic emission data for the 1985 NAPAP inventory. EPA-600/7-88-022.
Zimmerman P. R., Greenberg J. P. and Westberg C. E. (1988b) Measurements of atmospheric hydrocarbons and biogenic emission fluxes in the Amazon boundary layer. *J. geophys. Res.* **93,** 1407–1416.