MODELING OF OZONE FORMATION AT A RURAL SITE IN SOUTHERN ONTARIO

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Abstract—A one-dimensional time-dependent photochemical diffusion model has been used to simulate the chemical and vertical transport processes occurring at a rural location within Southern Ontario. The model output has been compared with the extensive measurements of several atmospheric trace gases which were made at a rural site in Southern Ontario as part of SONTOS (Southern Ontario Oxidant Study) during the summer of 1992. In particular, the measurements include various VOCs, odd nitrogen components and RO2 which have been explicitly included in the model. For the case examined, observations at the site are typical of unpolluted background conditions and the model is able to reproduce the observed variation of many of the key trace gas species observed. Though the site is remote from large population centers there appear to be important local emissions of NOx and non-methane hydrocarbons (NMHC). Modelling results suggest that for the day studied approximately 10 ppb of ozone was photochemically produced, and that the production of ozone was limited by the availability of NOx (NO + NO2). At the observed levels isoprene does not play a major role in the production of ozone. A comparison of observations and model calculations for peroxyl radical and HNO3 concentrations indicate a disagreement between the model and measurements.

Key word index: Tropospheric ozone, modelling, rural oxidants, Ontario.

INTRODUCTION

High concentrations of O3 and other photochemically produced oxidants are recognized as having negative effects on the health of people, crops, and forests (Taylor, 1969; Heck et al., 1984). A reduction of ozone concentrations in the U.S. by 40% has been estimated to yield a savings or surplus of 2.5 billion U.S. dollars due to increased production of crops such as corn and soybean (Heck et al., 1988). In Ontario high levels of ozone above the Federal Standard have an associated annual cost of about $45 M (MOE, 1989) in terms of crop loss, not to mention human and animal health effects. Southern Ontario is both the most densely populated region of Canada and the region where the Canadian National Ambient Air Quality acceptable concentration of O3 (82 ppb) is exceeded most frequently (CCME, 1991). The combination of large population and high levels of O3 make understanding the processes behind the formation of O3 in southern Ontario important. In order to further our knowledge of oxidant chemistry in this region of Canada the Southern Ontario Oxidants Study (SONTOS) was initiated.

As part of SONTOS an extensively instrumented measurement site was set up at a rural location near Hastings, Ont., within the Windsor-Quebec City Corridor, a heavily populated region of Canada running from the city of Windsor northeast to Quebec city. Measurements of trace gases, including NOx, NO2, NOy (total reactive nitrogen), PAN, C5-C10 hydrocarbons including isoprene, aldehydes and ketones, CO, and several species of organic nitrates, were conducted during the summer of 1992 and again during the summer of 1993 (Arias et al., 1994; Hastie et al., 1994; Roussel et al., 1994; O’Brien et al., 1994). A full description of the project is given by Reid et al. (1994). This paper details the use of a one-dimensional photochemical model to study local chemistry taking place at the measurement site under unpolluted conditions (NOx < 1 ppb and O3 < 45 ppb). Biogenic hydrocarbons, and isoprene in particular, can play an important role in the photochemical production of ozone (Trainor et al., 1987). However, isoprene concentrations measured during the course of this study rarely exceeded 1 ppb, and for the case modelled in this paper isoprene concentrations were not observed to rise above 0.3 ppb. In this study the effects of low concentrations of isoprene on local scale photochemistry are investigated.

†Deceased 1 April 1995.
Isoprene can be expected to significantly contribute to ozone generation only under conditions of favorable NO$_2$/NMHC ratios (Lurmann et al., 1983). Since O$_3$ production over rural areas, with NO$_x$ levels below a few ppb, are generally believed to be limited by the amount of NO$_x$ present (Liu et al., 1987), local sources of NO$_x$ will strongly influence the local photochemical generation of ozone. Studies of the NO$_2$ flux from soil have shown that over rural areas these emissions may be as large as local anthropogenic sources (e.g. Shepherd et al., 1991). Without direct measurements of the flux of NO$_x$ from the soil the modelling study presented here cannot conclusively deduce the importance of soil NO$_x$ emission relative to combustion sources. However, model results do indicate local sources of NO$_x$ are necessary to explain the observed concentrations and that the emission of NO$_x$ from soil may represent a large fraction of the local NO$_x$ emission.

During daylight periods the reaction of NO with O$_3$ forming NO$_2$ and the subsequent photolysis of NO$_2$ producing NO and O$_3$,

$$\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$$  \hspace{1cm} (1)

$$\text{NO}_2 + \text{hv} \rightarrow \text{NO} + \text{O}_3$$  \hspace{1cm} (2)

form a fast photochemical system that is near steady state. Peroxy radicals, from the atmospheric oxidation of hydrocarbons, will oxidize NO as well. The presence of peroxy radicals will perturb the NO$_x$-O$_3$ system and lead to a photochemical generation of ozone (Parrish et al., 1986). Peroxy radicals may also react with themselves and with other peroxy radicals. Such reactions will not result in the production of ozone and will become increasingly important under low NO$_x$ conditions. Direct measurements of peroxy radical concentrations were made at the Hastings site using a chemical amplifier technique (Arias et al., 1994). Peroxy radicals are extremely short lived they are little affected by horizontal transport and therefore ideally suited for study with a one-dimensional model. A direct comparison between model calculations and observations of peroxy radicals will provide an important test of our understanding of tropospheric photochemistry at the site.

In addition to the generation of O$_3$, the reaction of NO with a peroxy radical may result in the addition of the NO resulting in the formation of an organic nitrate,

$$\text{RO}_x + \text{NO} \rightarrow \text{zRONO}_2 + (1 - a)(\text{RO} + \text{NO}_2)$$  \hspace{1cm} (3)

where $a$ is the organic nitrate yield. The formation of organic nitrates impact both the radical and NO$_x$ cycles (Carter and Atkinson, 1989) and organic nitrates may constitute a significant fraction of the total reactive nitrogen, NO$_x$ (O'Brien et al., 1994). For alkanes the organic nitrate yield is relatively well known and has been shown to increase with increasing hydrocarbon molecular weight (Atkinson, 1990). The formation of hydroxylalkyl nitrates, through the oxidation of alkenes, is not as well understood, but it is generally believed that the nitrate yields for hydroxylalkyl peroxy radicals are lower than that for the corresponding alkyl peroxy radicals (Atkinson, 1990).

The work presented here focuses on observations made on the date of 6 August 1992. Much of the day was characterized by trace gas variations that are typical of "unpolluted" background conditions at this site. For the early part of the day the winds were from the west (Fig. 3c in Reid et al., 1994). Around noon (EDT) the winds veered to the northwest and then backed to the west around 1500 EDT. The wind continued to back and at roughly 1730 EDT the concentration of many of the trace gases and meteorological variables measured at the site were observed to change rapidly (cf. Fig. 2 of Reid et al., 1994). Ozone concentrations increased from 42 to 68 ppb within 15 min and total odd nitrogen (NO$_x$) levels increased from 1.2 to 6.8 ppb during the same period. It is likely that this dramatic change in the air mass is due to a polluted plume of air that left Toronto early in the morning of 6 August. Simple geostrophic forward trajectories from Toronto on 6 August suggest that the plume travelled out over Lake Ontario, carried along by prevailing westerly winds. In the afternoon the geostrophic wind became more southwesterly. The change in wind direction, coupled with an existing land-lake breeze, transported the polluted air mass inland toward the Hastings site.

Because of the impact of the putative Toronto plume, modelling has been restricted to observations made at the site prior to the arrival of the polluted air mass in an effort to gain a greater understanding of the background conditions at this site. The variation in concentration of the major trace gases observed at the site during the "clean air" portion of 6 August are typical of the variations observed during other clean air days at this site and we therefore feel that the conclusions derived from the modelling study of 6 August 1992 apply broadly to background conditions at this site. Simple two-day geostrophic back trajectories from Hastings also suggest that the air had not passed over Toronto. However, during the middle of the day when the wind was veering there may have been some contribution from Peterborough, a town of approximately 65,000 inhabitants 40 km to the NW.

**SITE DESCRIPTION**

The Hastings field site is located in southern Ontario about 40 km north of Lake Ontario and about 130 km northeast of metropolitan Toronto, and urban area with a population of over 3 million people. The nearest settlement to the site is the town of Hastings (population 1000), 4 km to the southwest. The area within 1 km of the measurement site is predominantly farmland with heavily forested woodlots. An analysis by Ontario Hydro (Roussel and
Moroz, 1992) indicated no significant point sources for hydrocarbons or NO, near the site. As such, the air chemistry at the site is dominated by relatively clean continental background conditions (NO, < 1 ppb and O, < 40 ppb), however, the site is frequently affected by the transport of polluted air from Toronto and the surrounding area when the winds are from the southwest (Roussel and Moroz, 1992).

The main measurement site sits atop a hill that is 28 m above the Trent river, approximately 250 m to the north. There is a second measurement site, for meteorological variables, located at the bottom of the hill. The behavior of trace gases at the site during times when a stable nocturnal boundary layer is present is complicated by local dynamical effects. If the nocturnal boundary layer (NBL) is stable, preventing up slope flow, the air flow may actually be around the hill, with the resultant disconnection of the site from the surrounding area and local surface sources. Alternatively, cold air drainage down the sides of the hill at night can occur, again effectively decoupling the air at the site from the surface. This will influence the trace gas behavior that is inferred from the measurements. Those species subject to removal by dry deposition or emitted at the surface will be particularly influenced by the local air flow. A one-dimensional model could not be expected to account for these influences. Therefore the model description of the nocturnal chemistry will be relatively more qualitative.

MODEL DESCRIPTION

The time evolution of the mixing ratio for all trace gases within the model is given by the simplified continuity equation

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = \frac{\partial}{\partial x} \left( \frac{\partial \rho}{\partial x} \right) + \rho \frac{\partial}{\partial z} \left( \frac{\partial \rho}{\partial z} \right) - \nabla \cdot (\rho \mathbf{F}) - P_i/M - L_i$$  

where \( \rho \) is the mixing ratio of the species, \( M \) (cm\(^{-3}\)) is the background number density, \( P_i \) (cm\(^{-3}\) s\(^{-1}\)) is the production rate of species \( i \) and \( L_i \) (s\(^{-1}\)) is the loss frequency. The vertical flux, \( \Phi_i = -K_z \frac{\partial \rho}{\partial z} \) and \( K_z \) (cm\(^3\) s\(^{-1}\)) is the vertical eddy diffusion coefficient.

The continuity equation is solved for all species using an operator splitting technique, where the vertical diffusion and chemistry terms are solved separately for a non-uniform grid. Fluxes into or out of the model, including emissions and dry deposition, are treated as part of the chemistry term. The chemistry portion of the continuity equation is solved using a completely implicit scheme with a Newton's method solver, which is mass conserving (e.g. McConnell et al., 1991). The diffusion operator is solved by a second-order finite difference method which is not mass conservative. However, conservation is strictly enforced for the diffusion operator by scaling the mixing ratios of each species, uniformly at all heights, at each time step in order to conserve the total column mass. A timestep of 15 min has been used for convenience and speed as it is not essential for this analysis to resolve the details of the chemistry near sunrise or sunset.

The deposition velocities used within the model are given in Table 1 while details of the emissions used in the model are described below. The top of the model is in the free troposphere at a height of 1.85 km and, on the time scales of a few days, we have assumed that the fluxes in and out of the upper boundary are zero. The bottom nine layers of the model stretch from 3 to 250 m with increasing spacing between layers. Above 250 m a constant spacing of 200 m is maintained up to 1.85 km.

The diurnal behavior of the planetary boundary layer is parameterized to reproduce the main features of a typical diurnal cycle as described in Stull (1988). At night \( K_z \) is fixed at 1.0 \( \times 10^5 \) cm\(^2\) s\(^{-1}\) within the bottom 100 m. Between 100 m and the maximum height of the daytime mixed layer \( K_z \) is set to 1.0 \( \times 10^2 \) cm\(^2\) s\(^{-1}\), to simulate a residual layer. The nighttime profile for \( K_z \) is maintained until 830 EDT to reproduce the observed variation of the boundary layer as evidenced by the behavior of \( O_3 \) and other trace gases that are strongly depleted from within the NBL. The behavior of the boundary layer during the daytime is parameterized using the time-dependent function for \( K_z \) and the height of the planetary boundary layer given by Singh et al. (1993). The original function for \( K_z \) given by Singh et al. is independent of height and is modified for the purpose of this paper to include an exponential height dependence for \( K_z \). The height of the mixed layer increases from 100 m at 830 EDT to a maximum height of 1.25 km at 1200 EDT. Above 1.25 km \( K_z \) is kept constant at 1.0 \( \times 10^4 \) cm\(^2\) s\(^{-1}\). The eddy diffusion coefficient switches from a daytime well mixed profile to a stable nighttime profile at 1930 EDT, about one hour before sunset.

The model run is started at midnight of 6 August and continued for 24 h. The surface initial conditions

| Table 1. Species deposition velocities (cm s\(^{-1}\)) used in the clean air case |
|-----------------|-----------------|
| Species         | \( \nu_d \) (cm s\(^{-1}\)) |
| O_3             | 0.3             |
| NO_2            | 0.2             |
| HNO_2           | 0.6             |
| H_2O_2          | 0.6             |
| HCHO            | 0.75            |
| ALD_2           | 0.75            |
| PAN and PAN analogs | 0.60          |
| HAC             | 0.75            |
| HNIT            | 1.0             |
| ISO-NIT         | 1.0             |
| MVK-NIT         | 1.0             |
| MAC-NIT         | 1.0             |

ALD_2, C_2 and greater aldehyde; HAC, hydroxymethylacetaldehyde; HNIT, hydroxymethyl nitrate; ISO-NIT, isoprene nitrate; MVK-NIT, methyl vinyl ketone nitrate; MAC-NIT, methacrolein nitrate.

*Hastie et al. (1993).
for NO$_x$, ozone, and CO are based on the measurements (cf. Reid et al., 1994). Since there are no measurements relating to the variation of the species with height, as required by the model, we have used the measurements taken at 1000 EDT as approximate indicators of the nighttime mixing ratios in the residual layer above the NBL. This is particularly the case for O$_3$ and NO$_x$. For the alkanes and alkenes we have assumed that the early morning measurements can be applied to the midnight starting values and also that these same conditions are independent of height. The initial concentration of nitric acid and all of the organic nitrate species are assumed to be zero. The initial concentrations of the short-lived species e.g. PAN, HCHO, isoprene and many of its oxidation products, are derived from a five-day initialization run performed using identical boundary conditions as those used in the standard model run.

**CHEMICAL MECHANISM**

The chemical reaction mechanism used in the model is largely based on the work of Lurmann et al. (1986), with the additions suggested by Jacob and Wofsy (1988). The reaction

$$
\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2
$$

(5)

has been added to the original mechanism, as has a more complete treatment of organic nitrates. The loss of organic nitrates by photolysis and reaction with OH has been added. All loss mechanisms for organic nitrates are assumed to yield stable products. For isoprene the organic nitrate yield has been set to 12% (Tuazon and Atkinson, 1990). The reaction of OH with the isoprene derived nitrate is assumed to occur at the same rate as OH attack on the lumped alkene species used within the mechanism (4.1 x 10$^{-12}$ s$^{-1}$). This assumption is reasonable given that the isoprene nitrate will still contain a carbon-carbon double bond.

The model calculates the photolysis rates allowing for Rayleigh scattering, O$_3$ absorption, and a surface albedo using the approach of Henderson et al. (1990). The surface albedo was set to 0.15 and the total column ozone was 310 Dobson units. The photolysis reactions and model calculated local noon J-values are given in Table 2.

The non-methane hydrocarbons are treated using both a lumped molecule and surrogate species approach. The C$_2$ smaller alkanes and ethene are treated explicitly within the mechanism. The C$_3$ and larger alkanes are lumped together as one hydrocarbon while the C$_2$ and larger alkenes are treated as the surrogate propene-like alkene. Formaldehyde is treated separately though higher aldehydes, except methacrolein, are lumped together as a single aldehyde species. With the exception of methyl vinyl ketone all ketones are lumped together as one species.

**EMISSIONS**

Emissions of NO$_x$ into the model have been separated into two components: a constant flux, meant to be representative of the emission of NO$_x$ from the soil, and a diurnally varying anthropogenic flux. For the latter, we have used as a template the temporal behavior of the NO anthropogenic flux taken from the Acid

<table>
<thead>
<tr>
<th>Photolysis reaction</th>
<th>Rate (s$^{-1}$)</th>
</tr>
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<tbody>
<tr>
<td>1. NO$_2$ + hv $\rightarrow$ NO + O$_2$</td>
<td>1.22 x 10$^{-2}$</td>
</tr>
<tr>
<td>2. NO$_2$ + hv $\rightarrow$ 0.13(NO + O$_3$) 0.83(NO$_2$ + O$_3$)</td>
<td>4.01 x 10$^{-5}$</td>
</tr>
<tr>
<td>3. O$_3$ + hv $\rightarrow$ O$_2$D + O$_2$</td>
<td>3.91 x 10$^{-6}$</td>
</tr>
<tr>
<td>4. HOONO + hv $\rightarrow$ NO + OH</td>
<td>2.72 x 10$^{-3}$</td>
</tr>
<tr>
<td>5. HNO$_2$ + hv $\rightarrow$ NO$_2$ + OH</td>
<td>1.40 x 10$^{-4}$</td>
</tr>
<tr>
<td>6. H$_2$O$_2$ + hv $\rightarrow$ 2OH</td>
<td>1.10 x 10$^{-5}$</td>
</tr>
<tr>
<td>7. HNO$_4$ + hv $\rightarrow$ NO$_3$ + HO$_2$</td>
<td>6.84 x 10$^{-6}$</td>
</tr>
<tr>
<td>8. HCHO + hv $\rightarrow$ 2H$_2$O + CO</td>
<td>4.34 x 10$^{-4}$</td>
</tr>
<tr>
<td>9. HCHO + hv $\rightarrow$ CO + H$_2$</td>
<td>3.51 x 10$^{-5}$</td>
</tr>
<tr>
<td>10. ALD$_2$ + hv $\rightarrow$ MO$_2$ + HO$_2$ + CO</td>
<td>4.84 x 10$^{-4}$</td>
</tr>
<tr>
<td>11. ALD$_3$ + hv $\rightarrow$ CH$_4$ + CO</td>
<td>3.12 x 10$^{-4}$</td>
</tr>
<tr>
<td>12. KET + hv $\rightarrow$ MCO$_2$ + ETO$_2$ + H$_2$O</td>
<td>1.01 x 10$^{-5}$</td>
</tr>
<tr>
<td>13. GLYX + hv $\rightarrow$ PROD</td>
<td>9.76 x 10$^{-5}$</td>
</tr>
<tr>
<td>14. MGLY + hv $\rightarrow$ MCO$_2$ + HO$_2$ + CO</td>
<td>2.32 x 10$^{-4}$</td>
</tr>
<tr>
<td>15. DIAL + hv $\rightarrow$ 0.98 HO$_2$ + 0.02 MCO$_2$ + TCO$_3$</td>
<td>1.35 x 10$^{-3}$</td>
</tr>
<tr>
<td>16. HAC + hv $\rightarrow$ HCHO + HO$_2$</td>
<td>1.35 x 10$^{-5}$</td>
</tr>
<tr>
<td>17. MGGY + hv $\rightarrow$ MCO$_2$ + HO$_2$</td>
<td>1.35 x 10$^{-5}$</td>
</tr>
<tr>
<td>18. RONO$_2$ + hv $\rightarrow$ PROD</td>
<td>1.22 x 10$^{-4}$</td>
</tr>
</tbody>
</table>

ALD$_2$, C$_2$ and greater aldehydes; MO$_2$, CH$_2$O$_2$, KET, lumped ketone; MCO$_2$, CH$_3$COO$_2$, ETO$_2$, C$_3$H$_6$O$_2$; GLYX, glyoxal; PROD, stable product; MGLY, methyl glyoxal; DIAL, diacetyl; TCO$_3$, CHOCH = CHCO$_2$; HAC, hydroxycetyledehyde; MGGY, α-diacetyl; RONO$_2$, organic nitrates.
Deposition and Oxidants Model, a regional scale model used by the Ontario Ministry of the Environment (Wong, 1993). Scaling the emission to match the midday NO flux measurements, we obtain a peak NO flux of $3.0 \times 10^{10}$ molecules cm$^{-2}$ s$^{-1}$ at 1400 EDT. The average NO flux over the day is $1.7 \times 10^{10}$ molecules cm$^{-2}$ s$^{-1}$, which is within the range of NO flux reported by the Ontario Ministry of the Environment in a 1987 emissions inventory for the Hastings area (Roussel and Moroz, 1992). Figure 1 indicates the standard NO flux that was used in the model. This emission profile does not yield a sufficiently large input during the nighttime period and we have thus added a constant NO flux of $1.5 \times 10^{10}$ molecules cm$^{-2}$ s$^{-1}$ into the bottom layer of the model. We rationalize this second flux by assuming that it may be a result of emission of NO from the soil. The magnitude of the flux is within the range of soil NO flux reported for southern Ontario (e.g. Shepherd et al., 1991). The soil NO flux is emitted into the bottom layer of the model while the anthropogenic component of the NO flux is spread evenly over the bottom 100 m of the model. This spreading is to simulate mixing that will take place before the NO reaches the site. During the day the exact height range over which the NO flux is mixed is less important due to the rapid rate of vertical mixing. At night the flux is contained within the NBL as would be expected of local emissions beneath a strong inversion.

Emissions of anthropogenic hydrocarbons are scaled to the anthropogenic NO flux and applied equally over the bottom 100 m of the model in the same way as NO flux emissions. The emission of hydrocarbons, as a fraction of NO flux (mol/mol), were as follows: C$_2$H$_6$, 0.24; C$_3$H$_8$, 0.16; C$_4$ alkane, 0.50; C$_5$H$_{12}$, 0.05; propene, 0.60; aromatic hydrocarbons, 0.06. These hydrocarbon/NO ratios were taken from aircraft borne simultaneous measurements of NO and hydrocarbons above Toronto (McLaren et al., 1994). The one exception was propene which was measured as 0.09 NO during the aircraft flight. Using the measured hydrocarbon to NO emission ratio for propene, the model greatly under predicted the observed concentration of propene, and a propene emission equivalent to 0.60 NO was necessary to give reasonable agreement between model predictions and observations. The total emission of anthropogenic hydrocarbons used in the model was 6.0 ppb C/ppb NO by volume.

![Fig. 1. The standard diurnal anthropogenic NO flux used in the model and input into the bottom 100 m. The details are given in the text.](image-url)
Previous studies have shown that isoprene is often the dominant non-methane hydrocarbon involved in the local photochemical production of O_3 at rural sites (e.g. Trainer et al., 1987). In this model, to describe the emission of isoprene from vegetation, we adopt the expression of Guenther et al. (1993) for isoprene emission from a single leaf. This expression is then extrapolated to a canopy following the approach of Jacob and Wofsy (1988). The emission of isoprene predicted by the model begins to saturate with respect to light levels between 400 and 600 \mu mol cm^{-2} s^{-1}; a light level which is attained relatively early in the morning. Thus for our conditions isoprene will be controlled by temperature for most of the day. For the clean air simulation of 6 August 1992 the model isoprene flux peaks at 3:00 PM EDT and 25°C at 7.1 x 10^{10} molecules cm^{-2} s^{-1}. This value represents an average emission over the farmland and woodlots surrounding the site. As the magnitude of the isoprene emission used in the model has been scaled to reproduce the observed concentration of isoprene, the rate of isoprene emission will be sensitive to the values of K_v used. Larger values of K_v would result in a faster rate of transport of isoprene away from the surface and, consequently, a larger rate of isoprene emission would be required to achieve the same near surface isoprene concentration. The emission of isoprene was distributed evenly over the lowest 11 m of the model. The temporal variation of the model isoprene emission and the observed temperature are shown in Fig. 2.

RESULTS AND DISCUSSION

As noted above the focus of this study is on the understanding of background chemistry conditions at the Hastings site, and the behavior of the short-lived species in particular. Here we present a comparison between model calculations and observations for several of the important trace gas species.

NO and NO_2

In Fig. 3 we present the diel behavior for NO, NO_2, NO_3, HNO_3, NO, and the NO_2/NO ratio from the model together with the measurements of Roussel et al. (1994) and Hastie et al. (1994) for 6 August. As noted above, the behavior of NO and NO_2 at night is complicated by local dynamical effects. However, the model is still able to reproduce the major features of the variation. During the nighttime the fraction of NO_2 in the form of NO_3 is greater than 70%. A large

![Fig. 2](image_url)
Fig. 3a and b.
Fig. 3c and d.
Fig. 3. The diurnal variation of model mixing ratios for several nitrogen species at 11, 45, and 850 m. (a) NO, (b) NO₂, (c) NO₃, (d) HNO₃, (e) NO, and (f) NOₓ/NO. The measurements are also shown for NO, NO₂, NO₃ (Hastie et al., 1994); NO (Roussel et al., 1994); and HNO₃ (Reid et al., 1994).
fraction of NO₂ as NO₃ indicates that the NO₂ has not undergone a great deal of photochemical processing since the time of emission, and suggests the sources of the NO₂ being observed at night are of local origin. It is noteworthy that to maintain a NO₂ abundance of approximately 1 ppbv in the NBL (Fig. 3b) a surface emission of \( \sim 1 \times 10^{19} \) molecules \( \text{cm}^{-2} \text{s}^{-1} \) is required. Since this is typical of emission rates from soils (e.g. Shepherd et al., 1991), we believe that at night the dominant source of NO₂ is from the soil. Once the NO is emitted it is quickly oxidized to NO₂ by reaction with O₃. The NO₂ produced, is removed from the NBL both directly and indirectly: directly by dry deposition (with a time constant of \( \sim 14 \) h) and indirectly by conversion of NO₂ to N₂O₅ (rate limited by the conversion to NO₃ with a time constant \( \sim 6 \) h), followed by the heterogeneous reaction of N₂O₅ with liquid water to form HNO₃ which then deposits. The result of the soil NO flux is an increase in NO₂ within the NBL. The actual observations are much more complex reflecting local micrometeorological effects as discussed above. NO₃ concentrations, which were greater than 2 ppb at midnight of 6 August, drop rapidly to nearly 1 ppb within 3 h. The model is unable to reproduce this feature using chemical and reasonable deposition losses for NO₂. At night the dominant source of NO₂ will be emission from the soil, and with slow vertical mixing NO₂ can be expected to possess a strong vertical gradient, with concentration dropping rapidly with height. Such a feature is predicted by the model (Fig. 4). If, as hypothesized, between 000 and 300 EDT the air sampled at the hilltop measurement site originated above the surrounding countryside, the concentrations of NO₂ within this air would have been considerably lower than in air originating closer to the surface. The decoupling of air at the measurement site from the surface may be responsible for the rapid decrease in NO₂ concentrations between 000 and 300 EDT, though a change in air mass cannot be ruled out.

At sunrise photolysis of NO₂ leads to a rapid increase in NO concentrations (Fig. 3a), as the NO₂ remains trapped near the ground until the breakup of the nocturnal inversion (Fig. 3c). Between sunrise and the breakup of the nocturnal inversion NO₂ concentrations are observed to increase at the surface. Model runs conducted with a constant soil NO flux and no anthropogenic flux gave a rise in NO, though both the magnitude of the increase and the halfwidth of the peak were much smaller than that observed. The increase in NO₃ concentrations, despite a constant NO₂ input, is related to the rate of NO₃ loss by dry deposition. The fraction of NO₃ present as NO₂ dur-

![Fig. 4. Vertical distribution of NO₂ at 0700, 1000, and 1300 EDT.](image)
ing daylight periods will be comparatively smaller than the fraction of NOx in the form of NO2 during the nighttime periods. As a result, the rate of NOx loss by dry deposition will decrease after sunrise. Observations indicate an increase in NO2 concentrations after sunrise nearly three times larger than that predicted by the model with only a constant NOx flux. With the addition of a diurnally varying anthropogenic NO flux (Fig. 1), which increases in magnitude rapidly after 500 EDT, the model predicted rise in NO2 after sunrise is in much better agreement with observations.

At 900 EDT, with the breakup of the nocturnal inversion, the high concentrations of NO2 near the surface mix upward and are diluted with less NO2 rich air above. The result is a sharp decrease in NO and NO2 concentrations in the lowest 100 m of the model after 900 EDT (cf. Fig. 3). The model predicted concentrations of NO and NO2 follow observations made at the site on 6 August 1992 reasonably well until 1800 EDT, when the rapid change in air mass is observed to occur. Of course, the midday agreement is not too surprising since the surface emissions were adjusted to fit the daytime observations. However, our calculations do indicate that a source of anthropogenic NO is required to maintain the observed NO2 concentrations over the course of the day.

Figure 3d shows the model calculated gas phase HNO3 mixing ratio vs time and the filter data of Reid et al. (1994) collected over six-hour integration periods. There is reasonable agreement during the early part of the morning, though the agreement during this time is due to the HNO3 concentration used to initialize the model. By noon the model is overpredicting HNO3 by more than a factor of three. At sunrise, 0600 EDT, the HNO3 concentration, averaged over the bottom 1250 m of the model, is calculated to be 0.14 ppb. At 1400 EDT the nitric acid concentration is calculated to be approximately 0.45 ppb, averaged over the depth of the PBL. Therefore, it is clear that much of the NOx conversion to HNO3 is being calculated to occur during the daytime, predominately through the reaction of NO2 with OH. It is possible that some of the HNO3 that has been formed in the model should have been converted to NO3, reducing the model HNO3 to some extent this may be accounted for by adding the measured NO2 to the measured HNO3. Even accounting for possible NO3 formation, there still remains considerable discrepancy between model predictions and observations of HNO3 and NO2. We do note, however, that serious problems are known to exist with the consistency of HNO3 measurement at concentrations below 1 ppb (Crosley, 1994), and the possibility that the model does not adequately account for the loss of HNO3 by dry deposition remains.

The total odd nitrogen, NOx, calculated by the model and observed, is shown in Fig. 3e. There is reasonable agreement between model calculations and observations from 0600 until the end of the comparison at 1700 EDT. The agreement between the modelled and observed concentration of NOx during the afternoon is surprising, given that the model appears to be overpredicting the concentration of HNO3 during this time. Between the hours of 1300 and 1500 EDT the NOx concentration is at its lowest value of the day and, at the same time, model agreement with the observed NOx concentration is good. Looking more closely at the daytime partitioning of odd nitrogen, in particular for 1400 EDT and the 11 m grid point, the model predicts the following concentrations: NOx 0.41 ppb; HNO3 0.45 ppb; PAN, 0.15 ppb; and NO2 1.12 ppb. The species given above account for 90% of the total NOx predicted by the model, with the remaining NOx comprised of PAN analogues (3% NOx), organic nitrates (6% NOx), HONO, and HN03. Observations of the nitrogen species give the following concentrations: NOx 0.39 ppb; HNO3 0.11 ppb; NO2 0.09 ppb; PAN, 0.19 ppb; and NO2 1.02 ppb. Including the measured organic nitrates (see below), the measurements of the individual NOx components fail to account for 0.24 ppb of the total measured NOx. The inability to account for all of the measured NOx by measurements of the component species has been observed before (Fahey et al., 1986; Buhr et al., 1990, for example). The measurements and the model agree quite well for NOx, PAN, and total NOx, while the model partitions the NOx missing from the individual measurements as HNO3. Given the known difficulties with HNO3 measurements at concentrations below 1.0 ppb (Crosley, 1994), the model results suggest that the HNO3 measurements are not capturing all of the HNO3 present. At this point, however, the problem of the partitioning of NOx remains unsolved and warrants continued attention.

Figure 3f shows the HNO3/NO2 ratio which, as previously mentioned, provides an important measure of the photochemical age of the air mass. Both the measurements and model indicate nighttime odd nitrogen was relatively "fresh". During the day the NOx/NO2 ratio decreases indicating increased chemical oxidation. Overall, model calculations and observations of the NOx/NO2 ratio are in good agreement over much of the day.

Isoprene

Figure 5 shows the modelled isoprene mixing ratios at 11, 45 and 850 m for the standard emission case. Also shown are the measurements taken at the site. The sharp rise in isoprene concentration predicted by the model just after dawn reflects the emission of isoprene into the shallow NBL. The rapid decrease in near surface concentration after 900 EDT reflects the breakup of the NBL and the dilution of the isoprene emission into a greater volume. The fact the measurements do not show evidence of a sharp early morning peak in isoprene concentration may be related to the frequency of the measurements. The timing of the breakup of the nocturnal inversion within the model...
will also be critical to the development of the early morning peak in surface isoprene concentrations.

The midday peak isoprene concentration predicted by the model occurs late in the afternoon, about 3 h after the peak in the measurements. This is a reflection of the strong dependence of the model isoprene emission on temperature, which peaks around 1500 EDT (Fig. 2). Part of the reason for the disagreement in timing of the peak isoprene concentration may be due to the limited nature of a one-dimensional model. The model isoprene emission varies with temperature and light level but does not, because of the nature of a one-dimensional model, vary with location. Over the course of the day, the wind direction at Hastings was observed to change from the northwest to the southwest. The air arriving at the measurement site would have been exposed to different isoprene sources, with different emission strengths, as the wind direction changed, and this effect may partly account for the difference in timing between the observed peak isoprene concentration and that calculated by the model.

Ozone

The model predictions and the surface observations for O₃ are shown in Fig. 6. During the nighttime there is no detailed agreement; however, there is qualitative agreement given the limitations of the model's representation of the meteorological situation at the site. The measured O₃ remains elevated until about 0330 EDT, when it begins to decrease, while the model O₃ decreases throughout this period. Sounder acoustic data and vertical temperature gradients near the surface show evidence of a stable inversion over the site during the early morning hours of 6 August 1992. Thus, we would expect O₃ to deposit during the night with a concomitant decrease in mixing ratios within the NBL, as produced by the model and as observed, for example, in the measurements at Dorset, Ontario (Hastie et al., 1993). Local micrometeorological effects, as noted above, obviously strongly impact the behavior of O₃ during the night.

After the early morning breakup of the nocturnal inversion, higher concentrations of O₃ from above the nocturnal inversion are mixed down to the surface. The result is a sharp rise in O₃ concentrations shortly after 0900 EDT. As expected the model reproduces this feature well. During the remainder of the morning and into the middle of the afternoon the model and measured O₃ concentrations are in reasonable accord. Thus the rate of local photochemical O₃ production and transport calculated by the model closely matches
that which was observed. After 1500 EDT the O$_3$ concentrations calculated by the model begins to level off while observations show O$_3$ concentrations increasing steadily until 1700 EDT (Fig. 6). A steady increase in concentration through the late afternoon hours is a typical feature of the diurnal variation of O$_3$ observed at this site. It is believed that the advection of higher concentrations of O$_3$ produced elsewhere, is responsible for the late afternoon rise in O$_3$ (Hastie et al., 1996). Such an effect is also suggested by the observations of C$_2$Cl$_4$ (cf. Reid et al., 1994), a distinctive tracer of anthropogenic air, which displayed a steady increase in concentration during the afternoon.

Ozone production

As noted above, during the day the dominant chemical source of O$_3$ is the oxidation of NO to NO$_2$ by peroxy radicals, as shown by reaction (3), followed by the photolysis of NO$_2$. Figure 7 shows the rate of O$_3$ production from the reaction of NO with HO$_2$ and several species of peroxy radicals at two model levels, 20 and 850 m. At both levels the main source of O$_3$ production is clearly due to HO$_2$ and CH$_3$O$_2$. The largest single source of HO$_2$ was the reaction of OH with CO, which accounted for 48% of the total HO$_2$ production at 20 m and 1300 EDT and nearly 60% of the total HO$_2$ production at 850 m and 1300 EDT. Methane oxidation accounted for 68% of the CH$_3$O$_2$ radical and 18% of the HO$_2$ at the 20 m grid point and 1300 EDT, while at 850 m methane oxidation was responsible for the production of 74% of the CH$_3$O$_2$ and 22% of the HO$_2$ at 1300 EDT. Isoprene oxidation, reflecting the strong height dependence of the isoprene concentration, accounted for 13% of the HO$_2$ production at 20 m, and only 2% of the HO$_2$ at 850 m. For the 20 m point isoprene is quite clearly the dominant non-methane hydrocarbon (NMHC) O$_3$ source followed by our generic alkane. At 850 m within the model the contribution to O$_3$ production by isoprene, relative to other non-methane hydrocarbons, is much less. This effect is due to the strong vertical gradient of isoprene concentrations calculated by the model. The effect of isoprene on the local photochemical production of O$_3$ at greater heights is further minimized by the near total depletion of isoprene within the boundary layer overnight by reaction with O$_3$ and NO$_3$. Isoprene does not begin to appreciably participate in the oxidation of NO, at 850 m within the model, until fresh emissions of isoprene reach that height with the growth of the boundary layer through the morning. A similar effect can be seen for all levels above the height of the
Fig. 7. Ozone production rates from NO + HO₂ and NO + RO₂ for CH₄ and several NMHC species at (a) 20 m and (b) 850 m.
The initial concentration of PAN was taken from elsewhere, followed by transport to the Hastings site. The observed NO2/NO ratio show a large degree of agreement with the calculated NO2/NO ratio. As explained above, NO2 and NO form a fast photochemical system during daylight periods, where the photolysis of NO2 to NO is balanced by the conversion of NO back to NO2 by reaction with O3 and peroxy radicals. As such, the ratio of NO3 to NO will be dependent upon the NO3 photolysis rate, the ozone concentration, and the peroxy radical concentration. Based on the model calculation for the NO3 photolysis rate, the NO3/NO ratio would have been approximately 1.5, if there had been no effects from peroxy radicals, while the midday NO3/NO ratio calculated by the model was closer to 2.1. As can be seen, the expected effect of peroxy radicals on the NO3/NO ratio will be small, and given the error and scatter in the measured NO3/NO ratio, and the expected uncertainty in the photolysis rate for NO3, the effect of peroxy radicals will not be significant. As a result, no definite conclusions can be reached about the modelled peroxy radical concentration.
Fig. 8. (a) PAN model mixing ratios vs time at 11, 45, and 850 m are presented. Also shown are the surface PAN measurements (Shepson, 1993). (b) Model calculated PAN/NO$_2$ ratio at 11, 45, and 850 m vs time and the surface measurements.
Fig. 9. (a) Model calculated (HO$_x$ + RO$_x$) mixing ratios at 11 m vs time. Also shown are the RO$_x$ = HO$_x$ + RO$_x$ measurements of Arias et al. (1994). (b) The model calculations for the NO$_2$/NO ratio at 11, 45, and 850 m. Also shown are the surface observations of the NO$_2$/NO ratio (Hastie, 1993).
in relation to the actual peroxy radical concentration, from the NO$_2$/NO ratio.

At this point we cannot definitively account for the disparity between the measurements and the model results for the peroxy radical concentrations.

*Non-methane hydrocarbons*

Figure 10 compares the measurements (Niki, 1993) and calculations for C$_2$H$_6$, C$_3$H$_8$ and our generic alkane for several heights for the 6 August period. The C$_2$H$_6$ comparison shown in Fig. 10a is more by way of a consistency check since the C$_2$H$_6$ chemical time constant is much greater than one day. It is only the period around 6 a.m. that suggests a signature of a local C$_2$H$_6$ source. The C$_3$H$_8$ comparison shown in Fig. 10b is more problematical: the model suggests that we should not expect a substantial signature due to local sources except perhaps in the early morning before the NBL breaks up. In addition, given that the site may be coming under the influence of more polluted air later in the day (cf. the C$_2$Cl$_4$ measurements in Fig. 1 of Reid et al., 1994), we might expect the C$_3$H$_8$ to be increasing with time. In fact, the measurements indicate C$_3$H$_8$ decreasing with time. Possibly, the air from the west may have sampled a C$_3$H$_8$ source or there may be problems with the C$_3$H$_8$ measurements. The disparity between the model and measurements will not seriously impact O$_3$ or radical generation. To compare our generic alkane model results shown in Fig. 10c we have added the C$_4$ and higher alkanes from Niki (1993). The results indicate a reasonable agreement between the measurements and model, except for what appears to be a local pollution spike that registers in the C$_{>4}$ alkanes and propene but not in ethane, propane or ethene.

The chemical time constants for the alkenes are such that any alkenes originating from Toronto will be oxidized before reaching the Hastings site. Thus, a comparison of the measured alkenes with the model results should be more indicative of local sources than is the case for the alkanes. Figure 11 shows the model results for several heights for C$_2$H$_4$ (panel a) and our generic (propene-like) alkene (panel b). As noted earlier the lumped alkene emissions have been adjusted to give better agreement with the measurements. Nevertheless, the temporal agreement for C$_2$H$_4$ is good and certainly suggests that there is substantial local emission. The comparison of the measurements with our generic alkene shown in Fig. 11b suggests that our alkene source is still too small by at least a factor of two, in spite of the enhanced source ratio noted in the previous emission section.

An important radical generator with a potential local impact is HCHO. Figure 12 shows the measurements (Hastie, 1993) and the model mixing ratios. The
Fig. 10. Alkane mixing ratios vs time for 2 altitudes, 11 and 850 m. (a) C₂H₆, (b) C₃H₈ and (c) generic alkane. The measurements from Niki (1993) are also shown.
Fig. 11. Alkene mixing ratios vs times for 11 and 850 m. (a) C$_2$H$_4$ and (b) generic alkene. The measurements from Niki (1993) are also shown.
observations are quite noisy and the mean value appears to be about a factor of two larger than the model results, although the model results are just within a standard deviation. The nighttime model results indicate the effects of deposition, but ameliorated by generation of HCHO via NO₃ reactions. The effects of deposition are not apparent in the measurements.

As discussed above organic nitrates may represent a significant fraction of the total reactive nitrogen. Our modelling results indicate a production of 35 ppt of nitrates from C₃H₆, the model lumped alkane, and the lumped alkene over the course of the day. This compares with the measurements of the corresponding organic nitrates which indicate between 10 and 20 ppt nitrates. The lumped alkane accounts for approximately 26 ppt of the above nitrates and, while the models over-prediction of organic nitrates may indicate an overestimation of hydrocarbon oxidation, the discrepancy most probably arises as a result of attempting to assign a single nitrate yield to a lumped hydrocarbon species. In addition to the above nitrates, the model also predicts the production of 34 ppt of organic nitrates from the OH reaction with isoprene, methyl vinyl ketone and methacrolein, where nearly 60% of these are in the form of isoprene nitrate. Overall organic nitrates are predicted to account for 5.9% of the total reactive nitrogen by the end of the model run.

SUMMARY

This paper presents a comparison between measurements and a one-dimensional model at the Hastings site for relatively unpolluted background conditions. There is agreement between many of the key trace gas observations made at the Hastings site on 6 August 1992 and the model calculations presented here. The model calculates 10 ppb of net local ozone production during the course of the day which agrees with observations, though after 1500 EDT the advection of ozone produced elsewhere appears to have an influence on ozone concentrations at the site. For the background conditions, methane plays a major role in the production of ozone, although among the NMHCs isoprene plays an important role near the surface. Since the photochemical production of ozone is strongly limited by the availability of NOₓ, local anthropogenic and biogenic sources are important and have been shown to strongly influence the local chemistry.
The modelling suggests that there are local sources of alkene and NOx, and that there are likely nocturnal emissions of NOx, that are certainly similar in magnitude to measured soil emissions. However, the measured NOx mixing ratios are more than a factor of two less than the noon-time model values and, as yet, we have no explanation, though heterogeneous reactions may be responsible.

As evidenced by observations, the transport of polluted air masses, possibly influenced by lake breezes, will occasionally affect the Hastings site. A more detailed study of this effect using a three-dimensional model is in progress.

Acknowledgements—This is a Scientific Contribution number 94-10 of the Canadian Institute for Research in Atmospheric Chemistry (CIRAC). The work described herein was undertaken as part of the CIRAC SONTOS project.

The authors wish to thank the Ontario Ministry of the Environment for support through a RAC grant, the Natural Science and Engineering Research Council of Canada, and the Atmospheric Environment Service of Canada for continuing support. We also wish to thank Drs X. Lin and P. Taylor for useful discussions, and the reviewers of the paper for their input.

REFERENCES


Shepherd M. F., Barzetti S. and Hastie D. R. (1991) The production of atmospheric NOx and N2O from a fertilized
Modeling of ozone formation
