

Frank S. Dempsey*

Member of American Meteorological Society, Pickering, Ontario, Canada

ABSTRACT

An example of the influence of meteorological conditions on ground-level ozone concentrations is illustrated with plots of hourly measured ground-level ozone and nitrogen dioxide concentrations for three days in June, 2002 in five southern Ontario locations. In this example of a summer day followed by a cloudy, rainy day, the diurnal variation and inter-dependence of ozone and nitrogen dioxide are clearly illustrated for the urban locations, and similar ozone variations are seen for all five locations used in this case study.

This case is typical for hot summer days in southern Ontario, with daytime mixing of the atmospheric

boundary layer increasing during and following the breakup of a low-level nocturnal inversion several hours after sunrise, and with increasing ozone concentrations due to generation from photolytic reactions as well as from ozone-rich air above the boundary layer mixing down to ground level as the inversion breaks up and mixing increases. Ozone concentrations are seen to diminish during the night due to loss of generation and due to titration by nitric oxide within the stagnant layer as the nocturnal inversion strengthens and lowers, accompanied by a corresponding increase in nitrogen dioxide concentrations during the night.

INTRODUCTION

Tropospheric ozone is produced primarily from the photooxidation of volatile organic compounds in the presence of nitrogen oxides. The formation of photochemical oxidants (including ozone in particular), and other more general aspects of urban air quality, are dependent on the interaction of "precursor" pollutants emitted from various sources with complex chemical and physical processes. While natural sources contribute some of the volatile organic precursor compounds, a major component comes from anthropogenic sources that are typical in urban areas with a mixture of industrial and automotive emissions. Much of the ozone and ozone precursors are generally assumed to be transported from upwind sources, such as heavily industrialized regions of the U.S. Midwest and Ohio valley, during days when the airflow is southwesterly into southern Ontario. (Further information about ozone precursor sources for ozone in Ontario has been provided by Yap et al, 1988. A recent update on the state of the science of natural hydrocarbons that contribute to ozone formation has been provided by Fuentes et al, 2000.)

In the example presented in this study, a three day period with a hot, sunny day before and after a cool, cloudy day provided the opportunity to illustrate the

dependence of ground level ozone formation on local weather conditions. This dependence is illustrated using measurements of ozone concentrations in the southern, central and eastern Ontario locations of Hamilton, Toronto, Peterborough, Dorset and Kingston, and using measurements of nitric oxide and nitrogen dioxide for the cities of Hamilton and Toronto. The first day of this 3-day case is typical for hot summer days in southern Ontario, with daytime mixing of the atmospheric boundary layer increasing during and following the breakup of a low-level nocturnal inversion several hours after sunrise, and ground-level ozone concentrations increasing due to generation from photolytic reactions as well as from ozone-rich air above the boundary layer mixing down to ground level as the inversion breaks up and mixing increases.

The Monitoring Locations

The cities of Hamilton, Toronto and Kingston lie along the Lake Ontario shoreline, while Peterborough lies in central Ontario (Figure 1). Dorset, also in central Ontario, is in a rural environment. The five locations are generally considered to be under similar synoptic-scale meteorological conditions, and experience generally similar airmass characteristics during typical summer days.

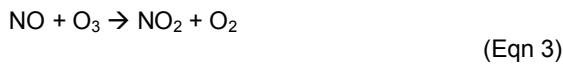
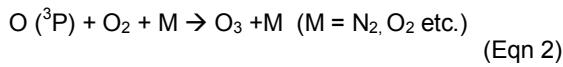
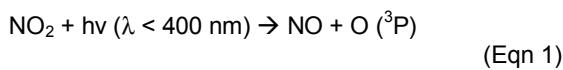
*Corresponding author address: Frank S. Dempsey, 1152 Tanzer Court, Pickering, Ontario, Canada L1W 3S6; email: Frank.Dempsey@sympatico.ca



Fig. 1 Locations of the monitoring stations in southern Ontario

A Review of Relevant Photolytic Ozone Chemistry in the Troposphere

The oxidation state of the troposphere is controlled by an interrelated group of highly reactive free radicals (mainly O^* (1D), O (3P), OH, HO_2 , and RO_2) derived from photodissociation processes of specific compounds which are in abundance in urban atmospheres. The relevant reactions for the production of tropospheric ozone and inter-relationship with oxides of nitrogen have been listed below, beginning with the photolysis of NO_2 to produce monatomic oxygen followed by combination with molecular oxygen:



The generation of radicals capable of catalytically generating more ozone requires the inclusion of OH radical generation and catalytic oxidation cycles to account for observed ozone generation. While

further significant reactions of oxy and methoxy radicals (and more generally, peroxy radicals derived from alkyl or more complex hydrocarbons) occur that contribute to ozone production, the significance of the oxidation of NO by peroxy radicals is the catalytic production of NO_2 (and subsequent ozone formation) and regeneration of the radicals capable of further oxidation. (More extensive treatments of further reaction mechanisms are available, e.g., Wayne, 2000 and Finlayson-Pitts and Pitts, 1986.)

Cloudy Day Chemistry

Under reduced sunlight, two significant results on boundary layer ozone chemistry are reduced photolytic production of radicals, and the shift of Eqn 3 toward increased NO_2 concentrations. Both processes result in lower production of ozone.

Nighttime Chemistry

After sunset, photolysis of NO_2 ends, and so Eqn 1 does not regenerate NO and O_3 . Eqn 3 proceeds to consume NO and O_3 . Without sunlight, and no production of the OH radical, nitrate (NO_3) becomes dominant as a reactive free radical. While the significance of the chemistry of the nitrate radical may extend to daytime ozone formation rates the following day (Dimitroulopoulos et al., 2002).

and Marsh, 1997), the relevant significance of nitrate, in this study of the chemistry involving measurements only of O₃, NO and NO₂, is the reduction of ozone and NO concentrations in a "closed" chemical system such as the nighttime boundary layer "capped" by a low inversion.

Relevant Meteorological Processes

Some of the meteorological factors that influence ozone chemistry in the boundary layer of the atmosphere (at and just above ground level) include:

- the amount of sunlight available (to cause reactions that proceed under solar radiation)
- temperature of the air
- dynamics of the boundary layer

- to some extent, the amount of water vapour in the air.

The depth of the mixing layer constrains the concentrations of pollutants near the ground. An example of a nocturnal inversion appears in the Buffalo NY sounding for 12Z on the morning of June 25, 2002, in Figure 2 (from University of Wyoming).

Vertical stratification of pollutant concentrations can be influenced by entrainment and fumigation processes in the convective boundary layer. The nighttime mixed layer, in particular, can be shallow enough to allow depletion of ground-level ozone; this depletion may not occur when the nocturnal inversion does not develop.

72528 BUF Buffalo Int

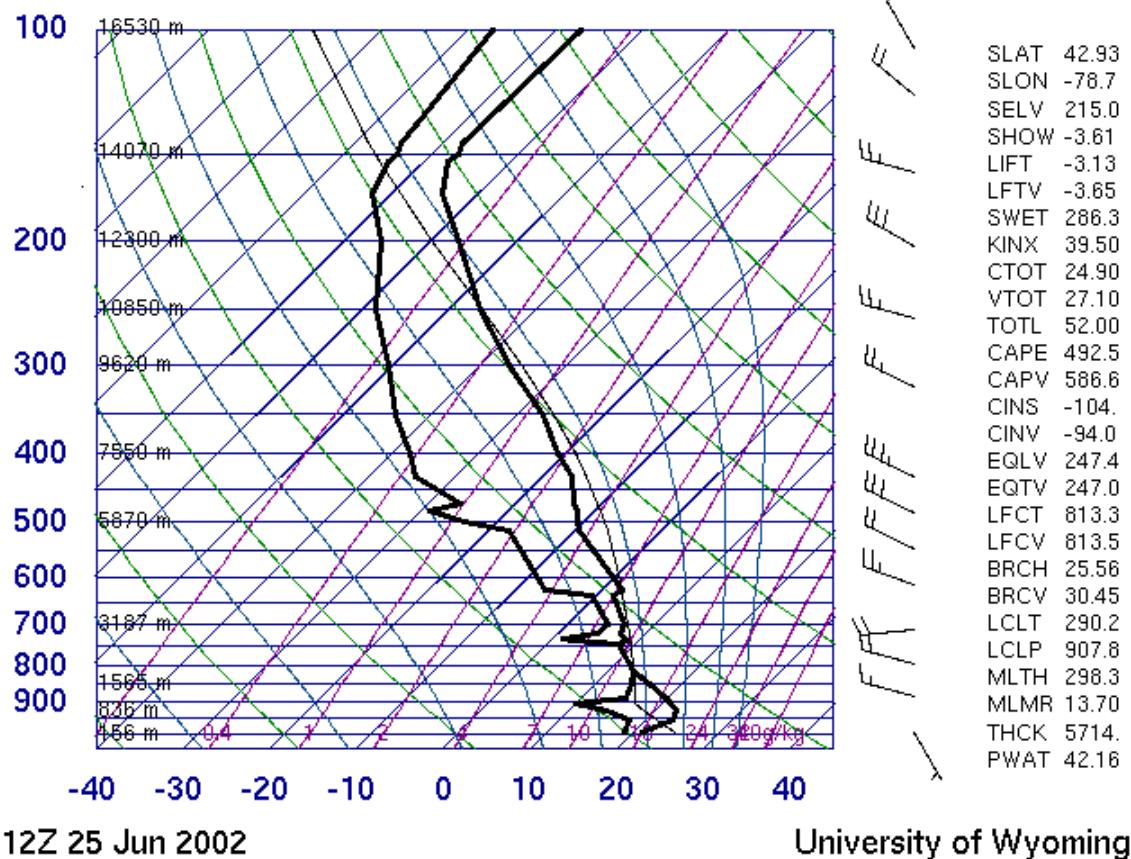


Fig. 2. Upper air sounding from Buffalo NY for 12Z, June 25, 2002 illustrating nocturnal inversion above surface.

Overview of Weather Patterns During June 23-25, 2002

On June 23, a high pressure region over the northeastern USA and a low pressure region over the US Midwest caused a southwesterly flow of

warm air across the Great Lakes area, including over southern Ontario. A high pressure region over northern Ontario moved eastward to lie over western Quebec by the morning of June 24. A weak, nearly stationary surface frontal boundary, associated with a mid-atmospheric level

disturbance, stretched across southern and central Ontario on June 23, with the Toronto area under a warm, hazy and humid airmass. By the evening of June 23, the front was over Toronto. During the morning of June 24, with a high pressure region over Quebec, the front was moving southward as a weak cold front to lie mainly over New York State, allowing a flow, from the northeast, of cooler air with cloudiness and moisture over the Toronto region. During the morning of June 25, the frontal boundary was moving northward again as a weak warm front, followed by a southerly flow of humid, warm air and allowing increasing sunshine over Hamilton, Toronto, and Peterborough but not over the meteorological stations at Trenton and Kingston.

While the general features associated with a frontal boundary include cloudiness, precipitation to some extent and a shift in wind direction, the main significance in this case was that the front was a boundary between a cool airmass to the north and a hot, humid airmass to the south. Maps showing the upper-level (500 mb) pattern, and surface pressure patterns, over the Great Lakes region for the evenings of June 23 and June 24, appear in Figures 3 and 4. In both cases, the upper air pattern

features a warm ridge over southern Ontario while the significant features of the surface pattern include a nearly stationary high pressure region centered over West Virginia and another high pressure region near James Bay on June 23 and over Quebec on June 24. Maps of the surface air temperatures (actually, 2 m above surface temperatures) at 14:00 EDT on the afternoons of June 23, 24 and 25 appear in Figures 5-7. The significant feature of June 23 is the very warm air across all of southern and central Ontario. On the afternoon of June 24, the same region was under a uniformly cool airmass. In Figure 7, the frontal boundary during June 25 is indicated by the strong temperature gradient between an axis of warmth (extending from the west end of Lake Ontario northeastward to Peterborough) and cooler conditions remaining closer to eastern Lake Ontario (including the meteorological stations at Trenton and Kingston).

A satellite image showing the cloud cover over western Lake Ontario along the frontal boundary at 10:45 am EDT on the morning of June 24 appears in Figure 8 (from NOAA, which also shows unrelated smoke over the US mid-Atlantic region).



NOAA Air Resources Laboratory

This product was produced by an Internet user on the NOAA Air Resources Laboratory's web site. See the disclaimer for further information (<http://www.arl.noaa.gov/ready/disclaim.html>).

METEOROLOGICAL DATASET INFORMATION
Initialization time: 00 UTC 24 JUN 2002

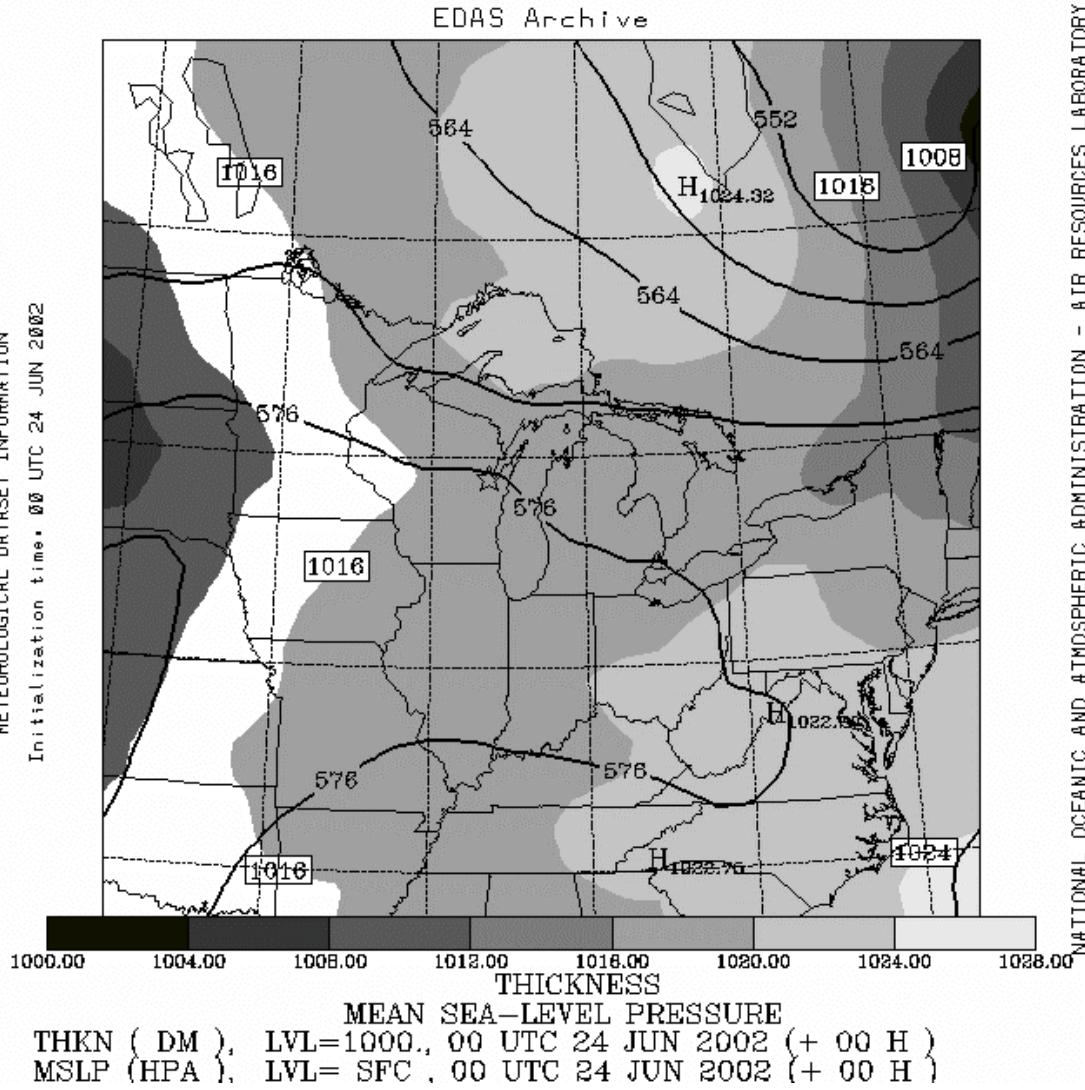


Fig. 3. Upper (500 mb-1000 mb thickness contours) and surface (isobars) chart for evening of June 23, 2002.



NOAA Air Resources Laboratory

This product was produced by an Internet user on the NOAA Air Resources Laboratory's web site. See the disclaimer for further information (<http://www.arl.noaa.gov/ready/disclaim.html>).

METEOROLOGICAL DATASET INFORMATION
Initialization time: 00 UTC 25 JUN 2002

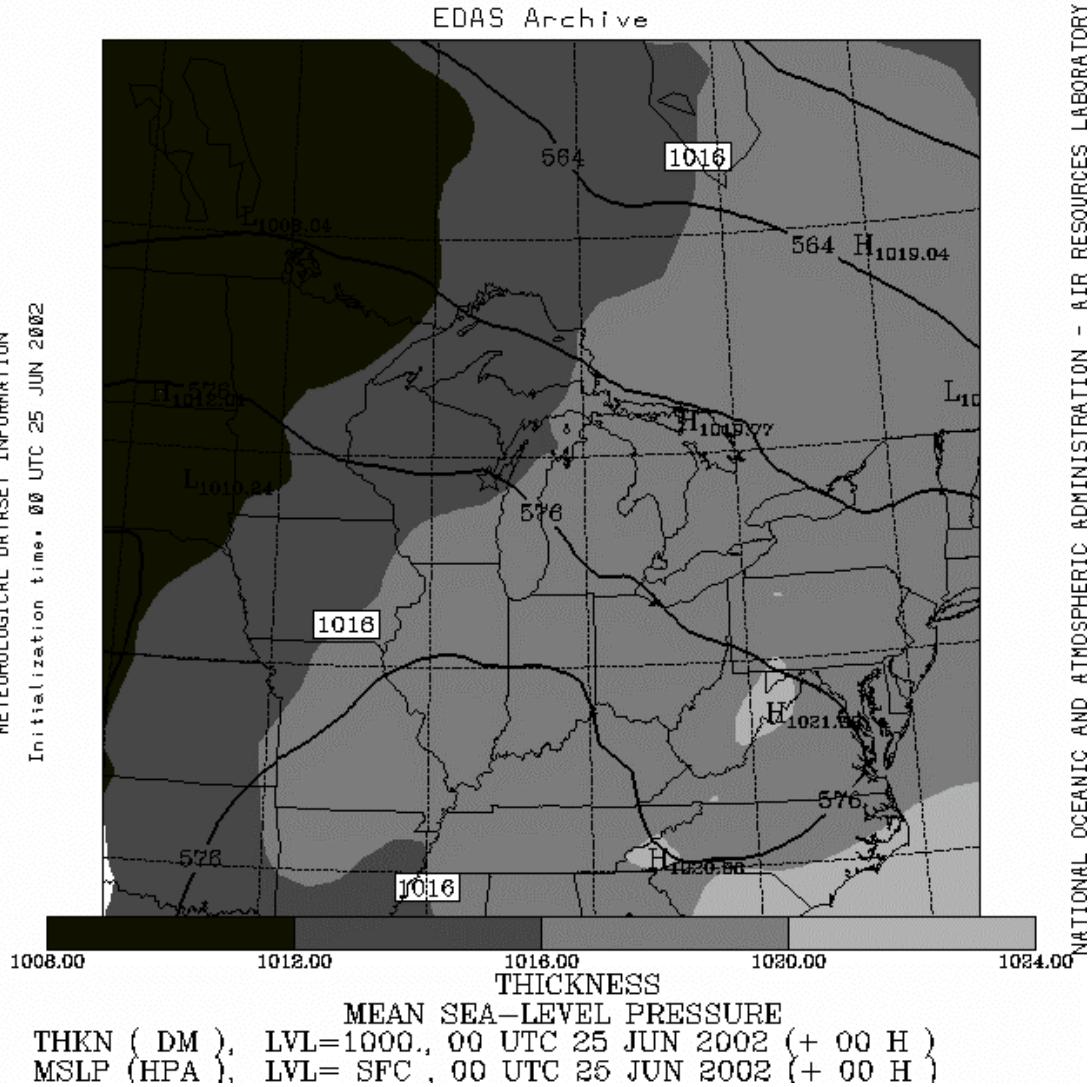


Fig. 4. Upper (500 mb-1000 mb thickness contours) and surface (isobars) chart for evening of June 24, 2002.

NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION - AIR RESOURCES LABORATORY



NOAA Air Resources Laboratory

This product was produced by an Internet user on the NOAA Air Resources Laboratory's web site. See the disclaimer for further information (<http://www.arl.noaa.gov/ready/disclaim.html>).

METEOROLOGICAL DATASET INFORMATION
Initialization time: 18 UTC 23 JUN 2002

EDAS Archive

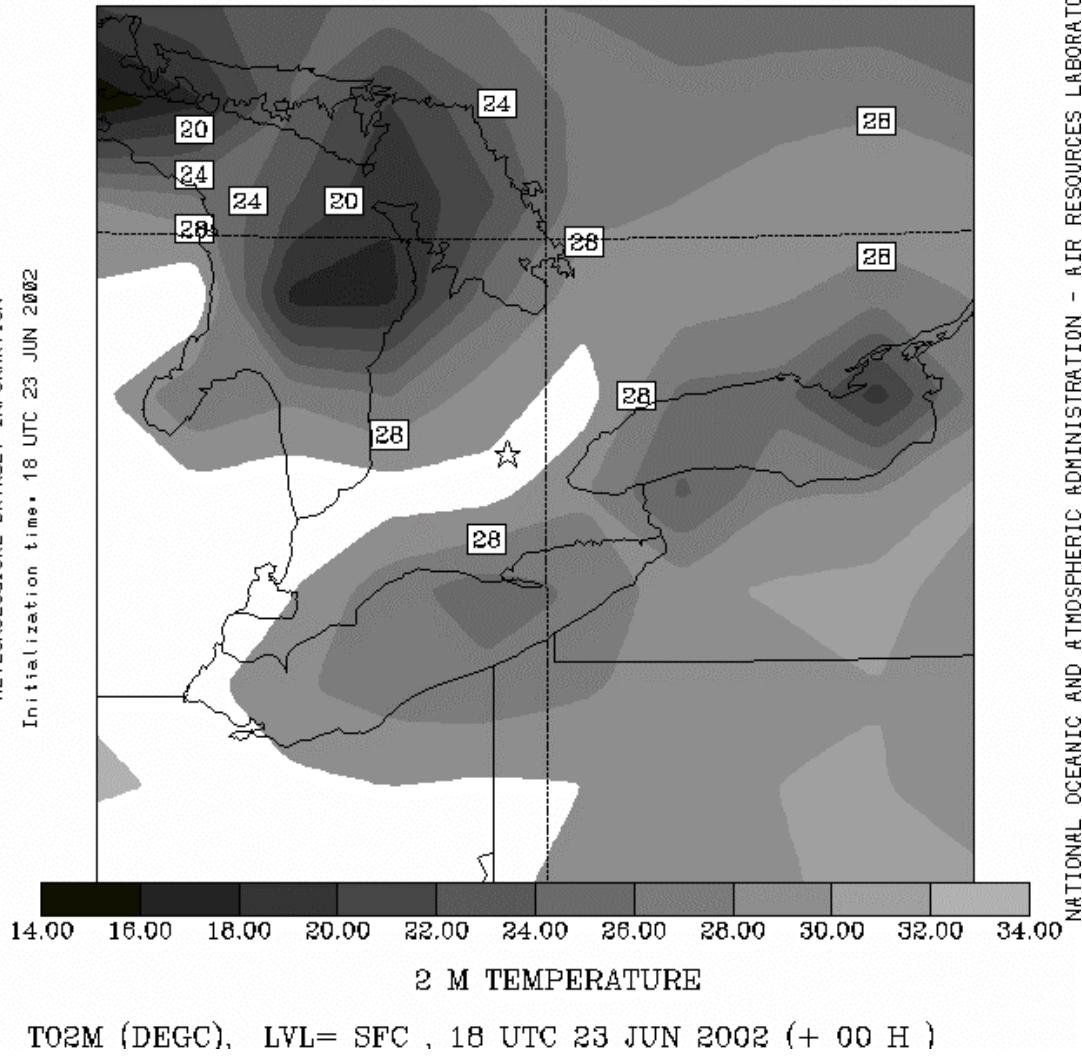


Fig. 5. Air temperatures (deg. C) over the Great Lakes region afternoon of June 23, 2002.



NOAA Air Resources Laboratory

This product was produced by an Internet user on the NOAA Air Resources Laboratory's web site. See the disclaimer for further information (<http://www.arl.noaa.gov/ready/disclaim.html>).

METEOROLOGICAL DATASET INFORMATION
Initialization time: 18 UTC 24 JUN 2002

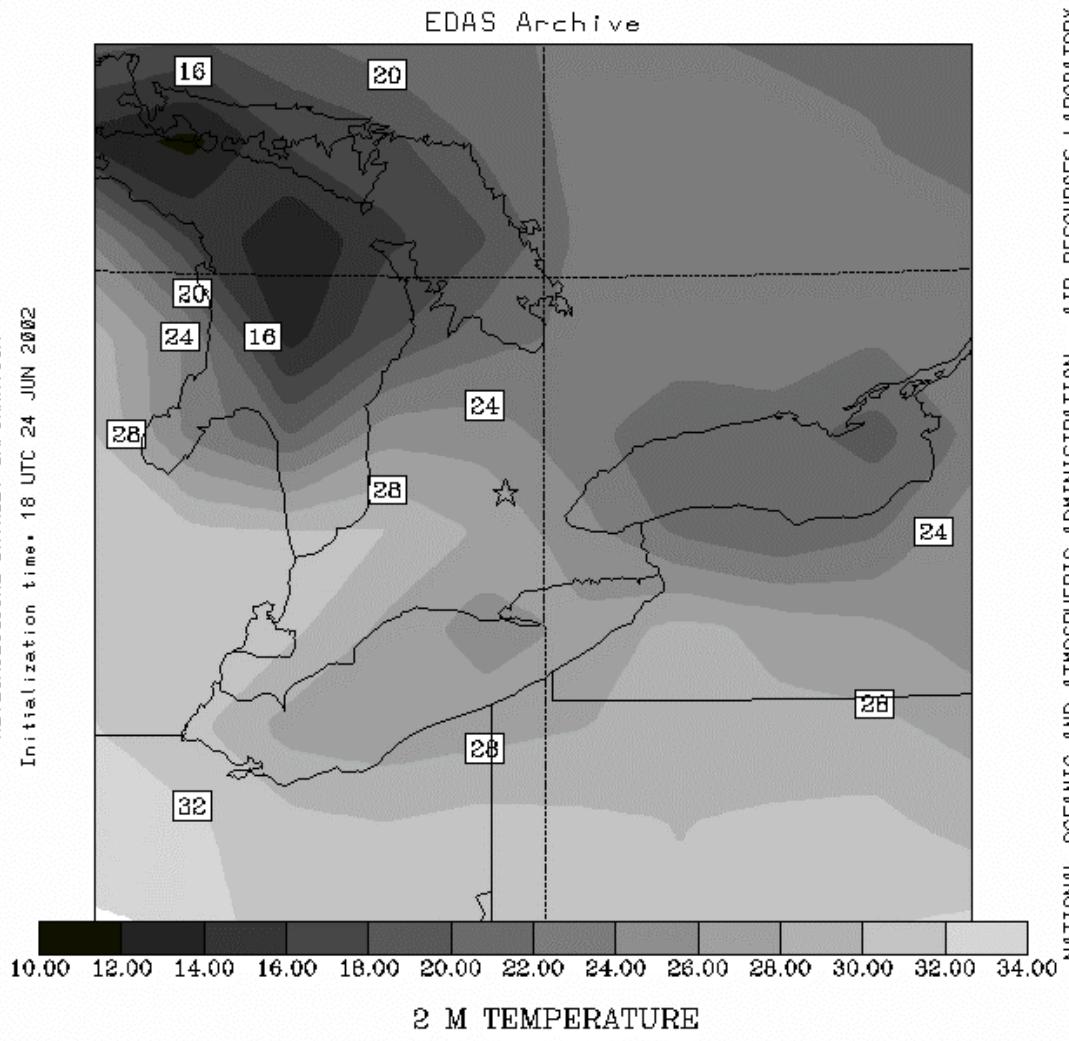


Fig. 6. Air temperatures (deg. C) over the Great Lakes region afternoon of June 24, 2002.



NOAA Air Resources Laboratory

This product was produced by an Internet user on the NOAA Air Resources Laboratory's web site. See the disclaimer for further information (<http://www.arl.noaa.gov/ready/disclaim.html>).

METEOROLOGICAL DATASET INFORMATION
Initialization time: 18 UTC 25 JUN 2002

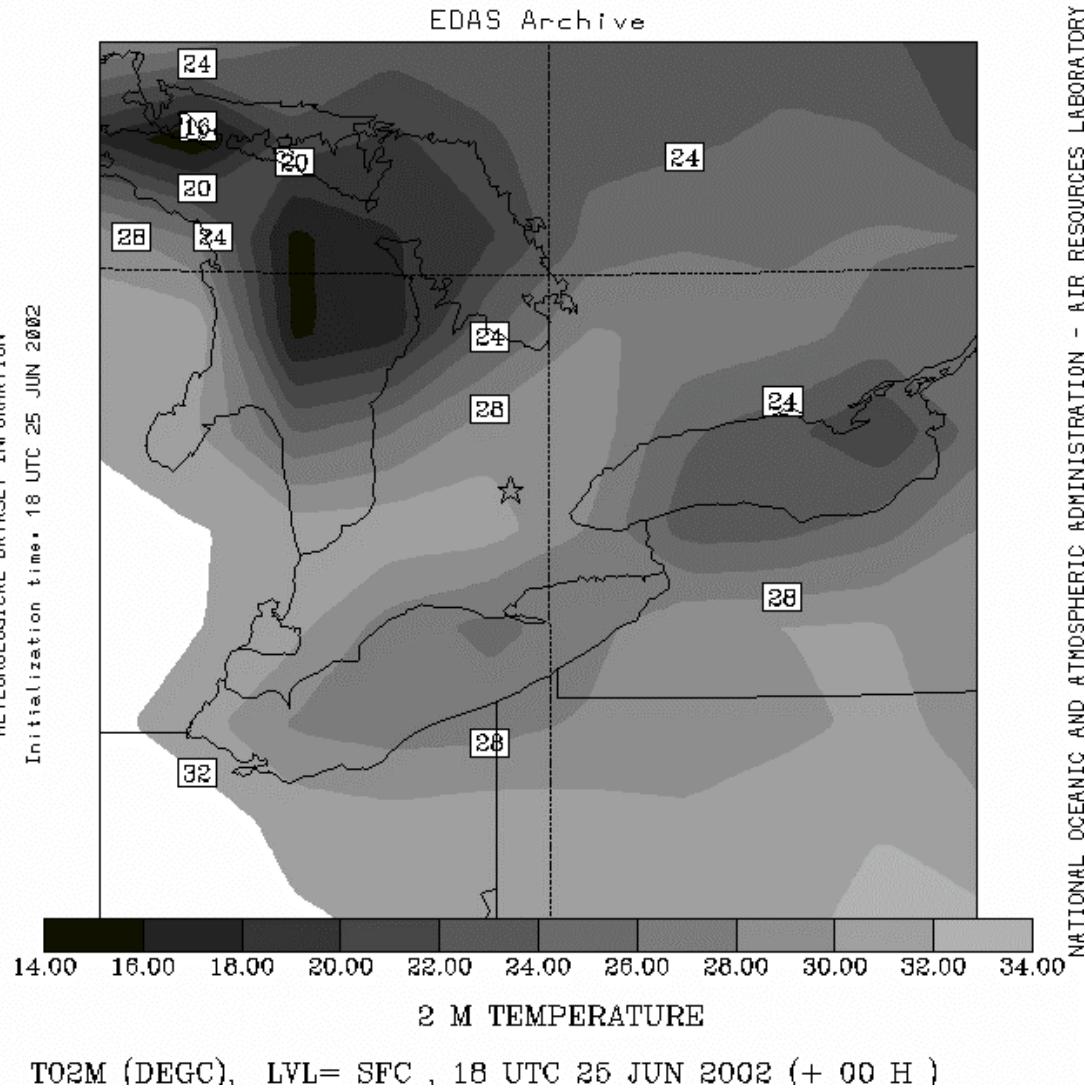


Fig. 7. Air temperatures (deg. C) over the Great Lakes region afternoon of June 25, 2002.

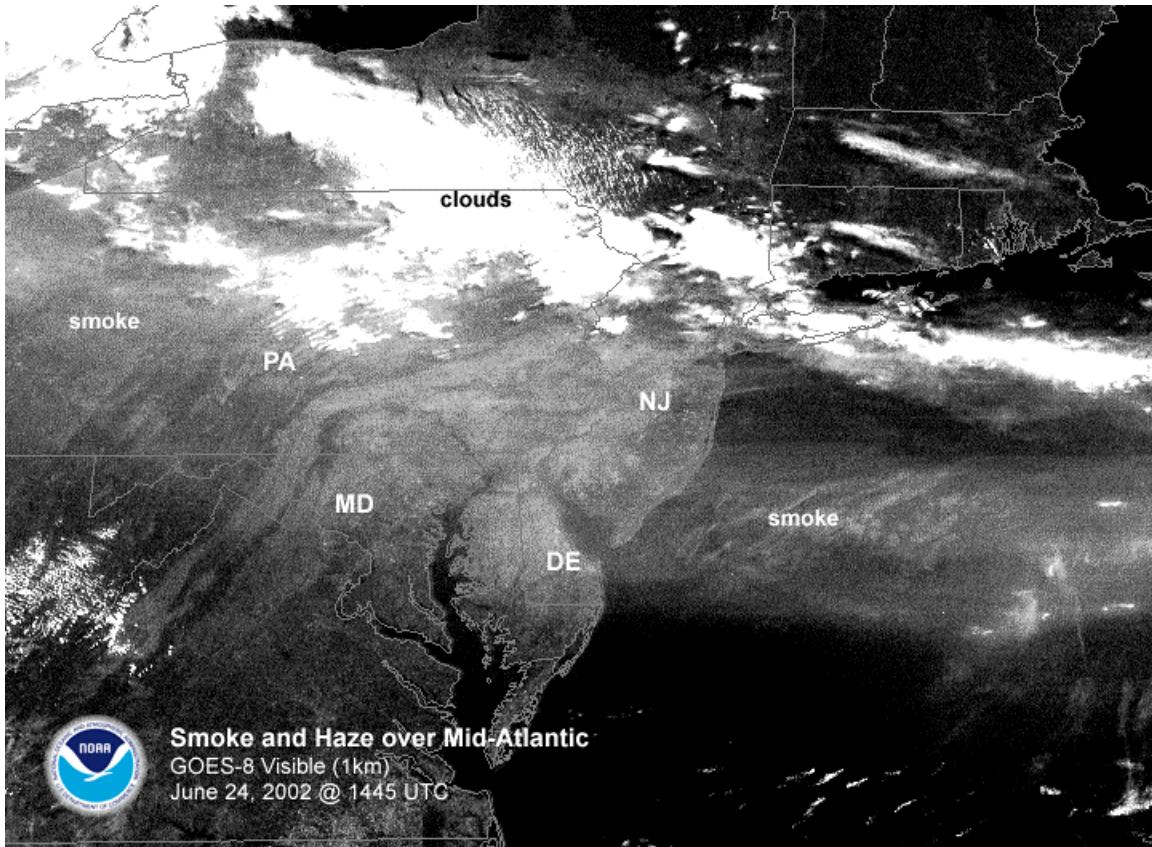


Fig. 8. Visible satellite image of cloud band across western Lake Ontario mid-morning June 24, 2002.

DATA AND DISCUSSION

Measured hourly concentrations of ozone (measured by the Environmental Monitoring and Reporting Branch of the Ontario Ministry of Environment) for the period June 23-25, 2002 for the locations of Hamilton, Toronto, Peterborough, Kingston and Dorset have been plotted vs. time in Figure 10. Hourly concentrations of NO and NO_2 have been plotted for the locations of Hamilton and Toronto to illustrate diurnal trends and differences between "sunny day" and "cloudy day" ground level ozone chemistry in Figures 11-13, following some notes about the chemistry and relevant meteorology.

June 23 Ozone and NO_x Trends:

-in the urban locations of Hamilton and Toronto, NO_2 concentrations during the morning generally reached maxima near the time of minimum O_3 concentration and then decreased as O_3 concentrations increased (Figure 11). Here, NO (primarily from local emissions) reacted with O_3 as in Eqn 3, producing NO_2 which then dissociated in

the afternoon sunlight (Eqn 1) to produce NO and O_3 (Eqn 2), allowing O_3 production to dominate the equilibrium cycle of Eqns 1, 2 and 3.

June 23 Meteorology:

-following a hazy morning, the afternoon became mostly sunny with surface temperatures measured at Toronto (YYZ) reaching 29.6°C at noon and then increasing to a high of 31.7°C at 15:00 EDT. Similar warmth was experienced across the southern and central Ontario region (Figure 5).
 -air parcel back trajectory analysis indicated that air parcels reaching Toronto on the afternoon of June 23 originated during the previous 2 days over northern Illinois and central Michigan (Figure 9, from Draxler, R.R. and Rolph, G.D., 2003). An ozone-rich layer above the nocturnal boundary layer likely provided a source of ozone that mixed downward to the surface as morning convection commenced; this effect accounted for some component of the sharp increase in O_3 concentrations during mid-morning.

NOAA HYSPLIT MODEL
 Backward trajectories ending at 18 UTC 23 Jun 02
 EDAS Meteorological Data

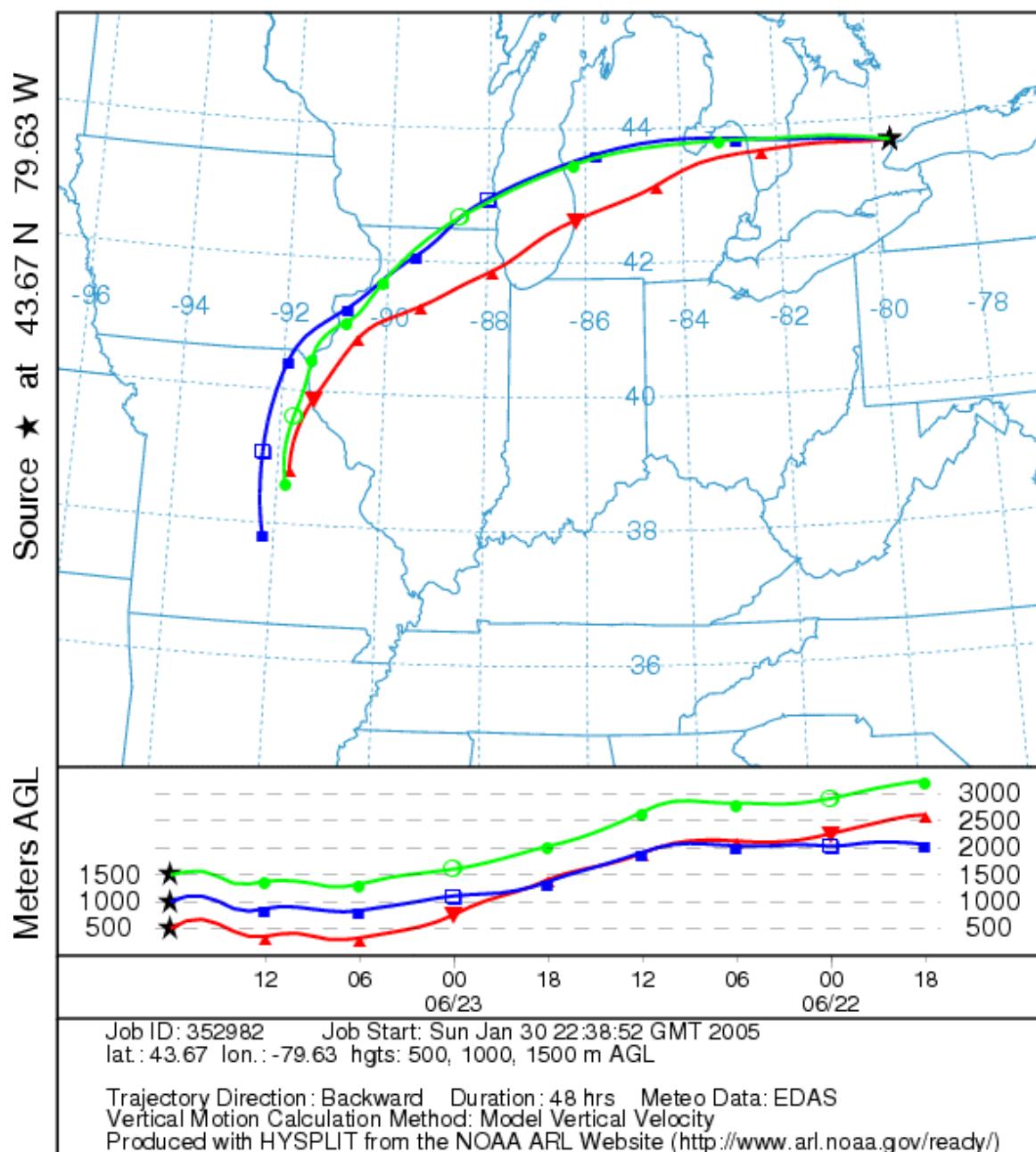


Fig. 9. 48-hr Back trajectory analysis of air parcels arriving at Toronto, June 24, 2002.

June 24 Ozone and NO_x Trends:

-ozone concentrations decreased after midnight to minimum values during the morning and then increased to generally steady values in the range of 20-30 ppb during the afternoon, and then began declining from shortly before sunset until midnight (Figure 10).

-concentrations of NO remained at or below 10 ppb at Hamilton during the day and overnight period while at Toronto, NO concentrations increased to a mid-morning maximum of 43 ppb, decreased to a range of 9-13 ppb during the early afternoon, and then increased to an early evening maximum of 33 ppb, before settling to the range of 20-40 ppb until the following morning.

-NO₂ concentrations in Hamilton decreased to a late-morning minimum of 6 ppb and remained less than 30 ppb until increasing during early evening. At Toronto, NO₂ concentrations increased to a late-morning local maximum of 27 ppb and then remained less than 30 ppb until increasing during early evening. NO₂ concentrations in both locations then remained in the 30-50 ppb range during the night and the following morning.

-here, the NO- NO₂- O₃ equilibrium cycle of Eqns 1, 2 and 3 favoured much lower O₃ concentrations than during the sunny day of June 23, and the reduced solar insolation allowed Eqns 1 and 2 to maintain more NO₂ and less O₃ production. Local emissions of NO (particularly in Toronto) allowed scavenging of O₃ (Eqn 3) to increase concentrations of NO₂.

June 24 Meteorology:

-a mainly cloudy day was recorded, with moderate intensity rain reported at 16:00 EDT (mid-afternoon) with the front over New York State by mid-afternoon. Following a nearly steady overnight temperature at Toronto of 21°C, temperatures decreased gradually to a low temperature of 16°C. The cloudiness and cooler temperatures were observed across the Hamilton-Toronto-Kingston-Peterborough region during the day. Figure 6 shows contoured surface temperatures plotted for

14:00 EDT. The band of cloudiness across western Lake Ontario can be clearly seen in the satellite image in Figure 8 at 10:45 EDT on June 24.

June 25 Ozone and NO_x Trends:

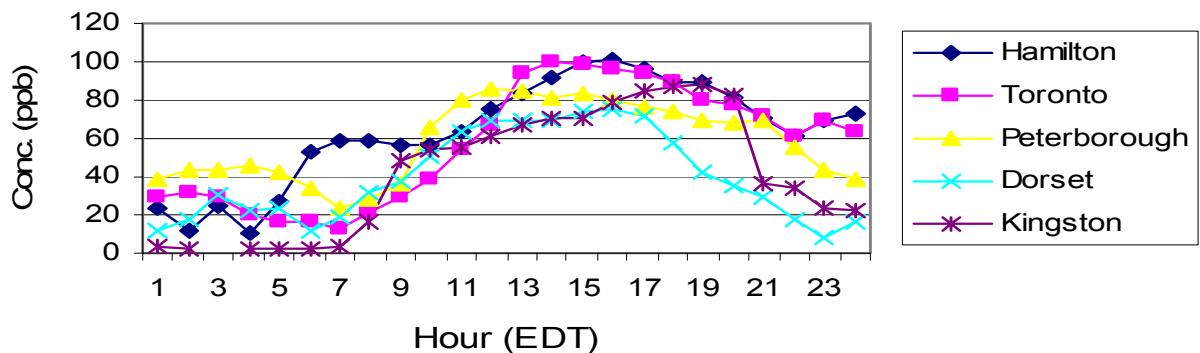
-ozone concentrations reached minimum values during the early morning or just after sunrise at all five locations and then began a gradual increase to maximum values in the range of 89-113 ppb at four of the locations, and a lower maximum of 73 ppb at Kingston was eventually reached an hour before sunset (Figure 10). The afternoon O₃ concentrations increased generally to the high values observed during June 23 but with the trend of increasing ozone concentrations occurring several hours later in the afternoon.

-concentrations of NO increased sharply, beginning at 06:00 EDT in Toronto and at 08:00 EDT in Hamilton, and then decreased to minimum concentrations by mid-afternoon. Generally, NO₂ concentrations at both locations decreased and NO concentrations disappeared almost completely to the 2-3 ppb range as O₃ concentrations reached maxima by mid- to late afternoon and the concentrations of NO, NO₂ and O₃ returned to the equilibrium cycle observed during the sunny day of June 23. After sunset, NO₂ concentrations increased as O₃ concentrations decreased (Figure 13).

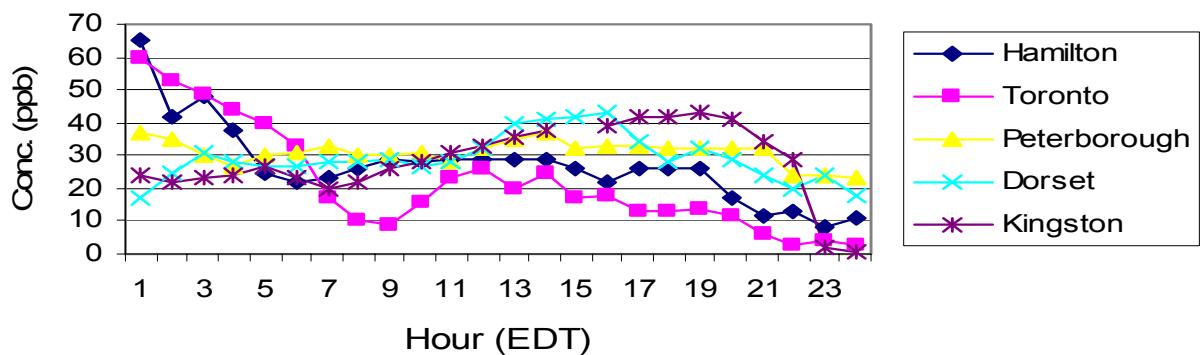
June 25 Meteorology:

-at Toronto, following mostly cloudy conditions overnight, generally sunny conditions were experienced during the morning and afternoon. While hot, sunny conditions returned to Hamilton, Toronto and Peterborough, cloudiness remained over Trenton and Kingston as the warm front moved northeastward from Toronto but not across Trenton or Kingston until later during the evening. Figure 7 shows contoured surface temperatures plotted for 14:00 EDT, clearly indicating the sharp northwest-southeast temperature gradient from a Toronto-Peterborough line to a Trenton-Kingston-Ottawa line.

June 23 2002 Ozone Concentrations



June 24 2002 Ozone Concentrations



June 25 2002 Ozone Concentrations

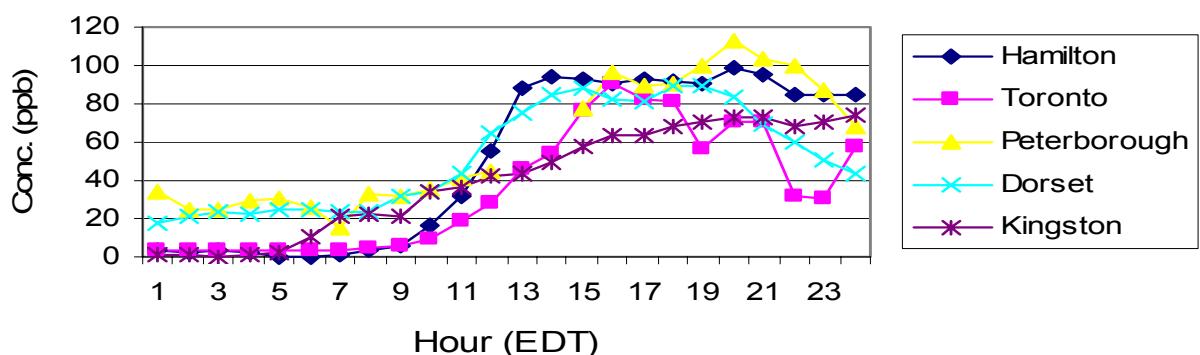


Fig. 10. Hourly concentrations of O_3 during June 23, 24 and 25, 2002.

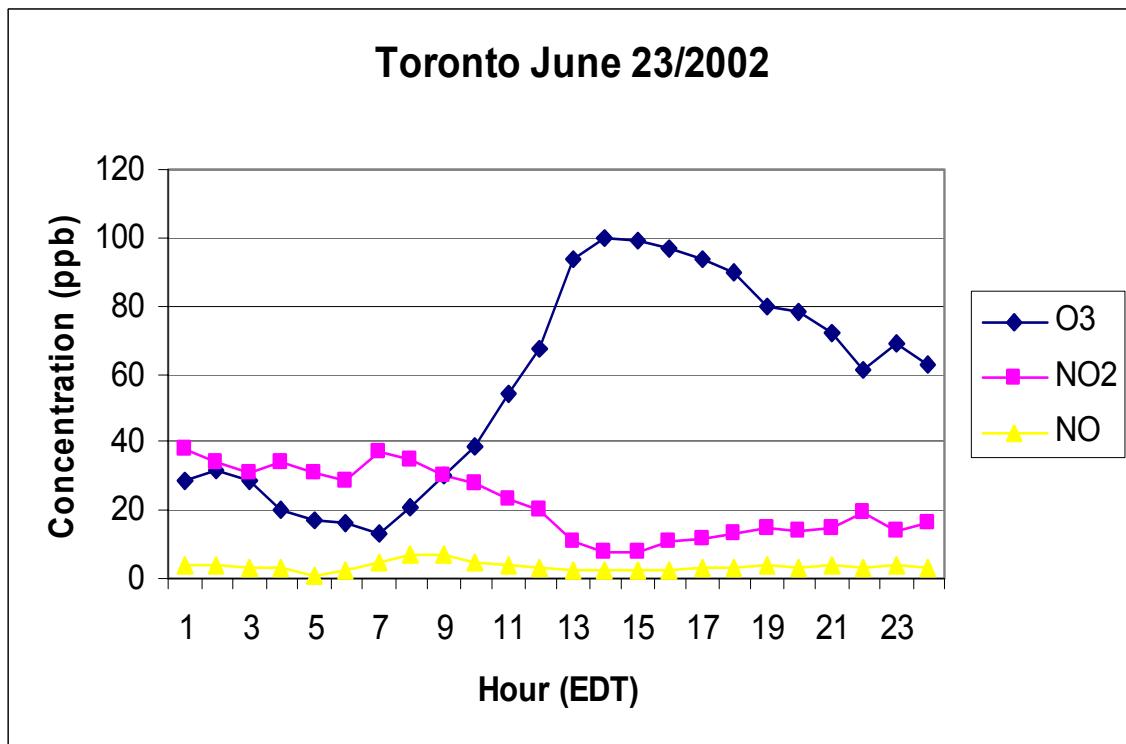
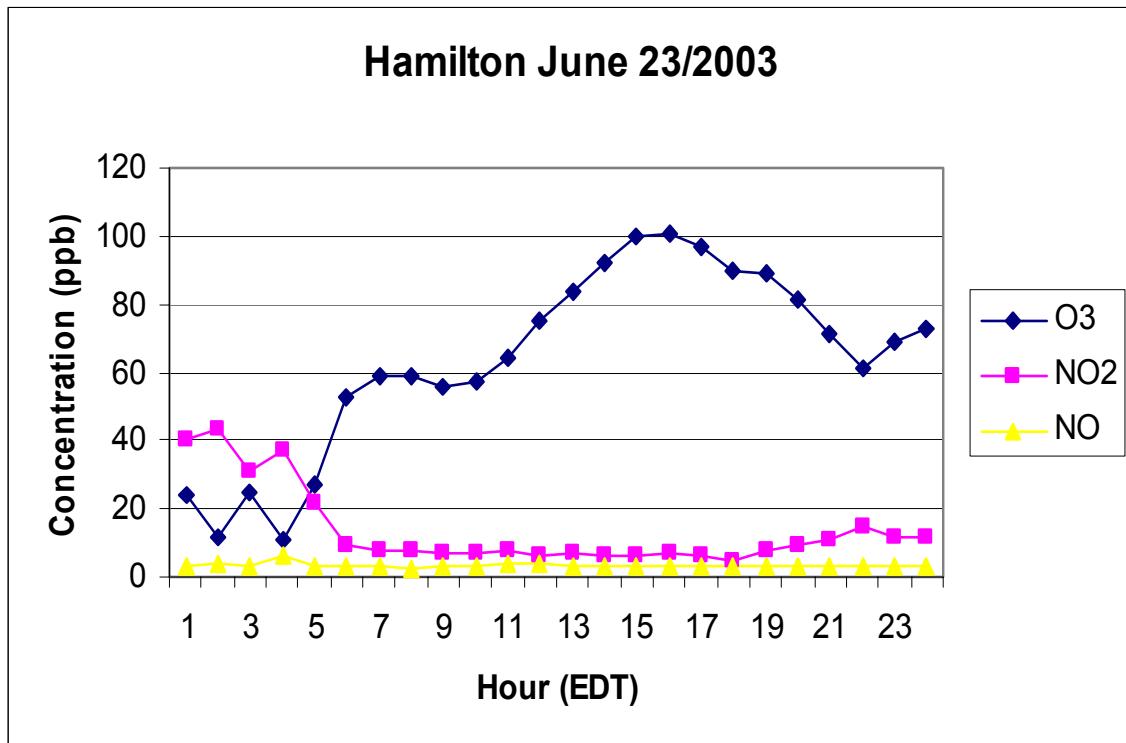


Fig. 11. Hourly concentrations of O₃, NO and NO₂ during June 23, 2002.

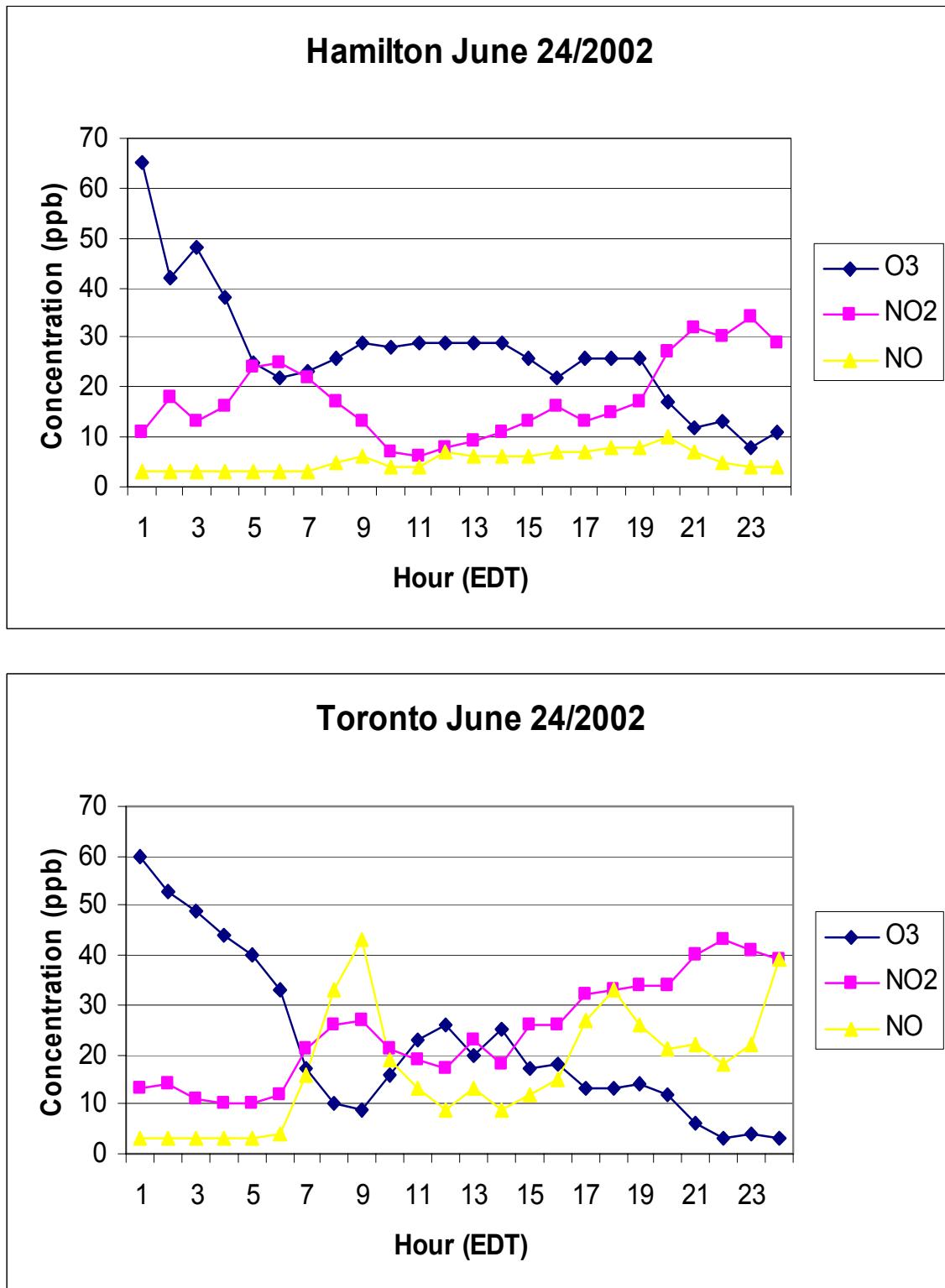


Fig. 12. Hourly concentrations of O₃, NO and NO₂ during June 24, 2002.

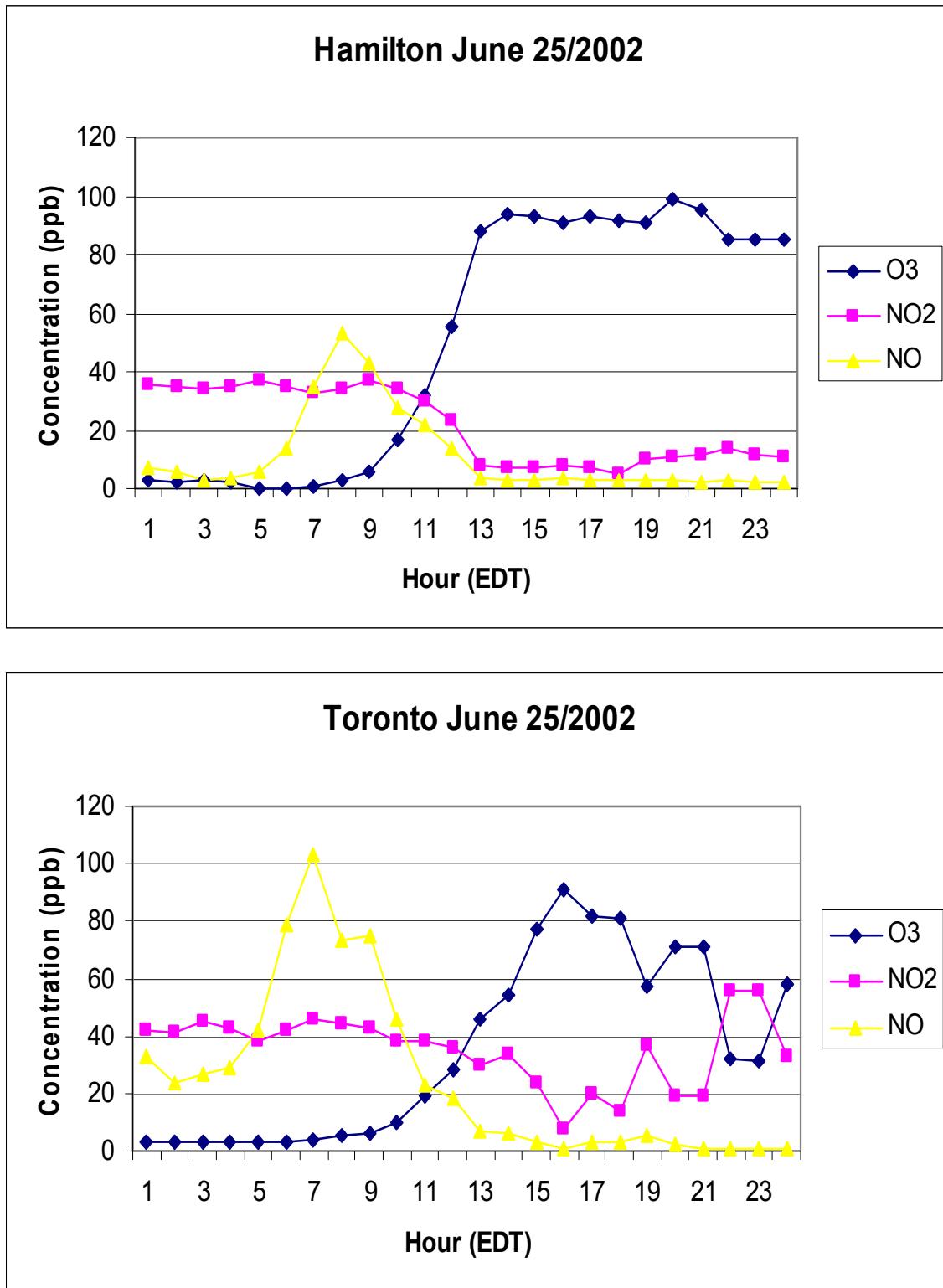


Figure 13. Hourly concentrations of O₃, NO and NO₂ during June 25, 2002.

SUMMARY

The effects on measured concentrations of O_3 and NO_x , caused by local variations of temperature, winds, and cloudiness, have been highlighted for the 3-day period June 23-25, 2002 during which a frontal boundary drifted south of southern Ontario as a cold front and then northward across southern Ontario as a warm front, allowing examples of sunny-day and cloudy-day ozone chemistry to be displayed.

Sunny day photolytic ozone chemistry in the boundary layer was illustrated by the trends of O_3 at all five locations used in this study and of NO and NO_2 at Hamilton and Toronto during June 23. Ozone concentrations increased in mid-morning and decreased during late afternoon and during the overnight period until reaching a minimum at about sunrise of June 24.

The chemistry of a cloudy day was illustrated during June 24, with O_3 , NO and NO_2 concentrations reaching a general equilibrium lasting most of the day at Hamilton and Toronto and with ozone concentrations in all five locations significantly lower than they were during the previous day.

Day 3 (June 25) showed a return to sunny day chemistry at Hamilton and Toronto along with the return of sunny and hot conditions to southern and central Ontario, and with O_3 concentrations increasing to the high values observed during June 23 but with the trend of increasing ozone concentrations occurring several hours later in the afternoon than during June 23. Kingston remained under cloud during most of June 25, and O_3 concentrations increased to values that were significantly lower than at the other locations, as well as significantly lower than those reached during June 23 at Kingston.

The maxima in NO_x concentrations several hours after the increase of morning vehicle traffic could be seen in data from each of the three days in Hamilton and Toronto, but is most clearly indicated on the data of June 25, and a late-afternoon NO_x maximum was also displayed in the data of June 24.

Overall, ozone concentrations were significantly higher during June 23 and June 25 than during the cloudy day of June 24 at all five locations used in this study, and concentrations of oxides of nitrogen at the urban cities illustrated the chemistry of an urban boundary layer.

ACKNOWLEDGEMENTS

The author gratefully acknowledges the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT transport and dispersion model and/or READY website (<http://www.arl.noaa.gov/ready.html>) used in this publication.

The author gratefully acknowledges the helpful comments provided by staff of the Air Monitoring Section of the Environmental Monitoring and Reporting Branch of the Ontario Ministry of Environment.

REFERENCES

Dimitroulopoulou, C. and Marsh, A. (1997): Modelling studies of NO_3 nighttime chemistry and its effects on subsequent ozone formation, *Atmos. Environ.*, 31, 3041-3057.

Draxler, R.R. and Rolph, G.D., 2003. HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website (<http://www.arl.noaa.gov/ready/hysplit4.html>). NOAA Air Resources Laboratory, Silver Spring, MD.

Finlayson-Pitts, B. J. and J. N. Pitts Jr. (1986): *Atmospheric Chemistry: Fundamentals and Experimental Techniques*, Wiley-Interscience, New York.

NOAA (National Oceanic and Atmospheric Administration), <http://rapidfire.sci.gsfc.nasa.gov/gallery>

University of Wyoming website, <http://weather.uwyo.edu/upperair/sounding.html>

Wayne, R. (2000): *Chemistry of Atmospheres: An Introduction to the Chemistry of the Atmospheres of Earth, the Planets, and their Satellites*, Oxford University Press UK.

Yap, D., Ning, D. and Dong, W. (1988): An assessment of source contributions to the ozone concentrations in southern Ontario 1979-1985, *Atmos. Environ.*, 22, 1161-1168.