OBSERVATIONS OF OZONE AND PRECURSOR LEVELS AT TWO SITES AROUND TORONTO, ONTARIO, DURING SONTOS 92

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Abstract—Characteristic air quality features observed at two ground level air quality monitoring stations operated during the Southern Ontario Oxidant Study field campaign (SONTOS 92) are described. The two sites, Binbrook and Hastings, are located 60 km SSW and 140 km NE of Metropolitan Toronto, respectively. The analysis of 5-min average concentrations in relation with local wind directions suggests that a strong contrast exists between conditions of northerly clean air and polluted southwesterly flows at both locations. This contrast is shown to deeply influence the shape and amplitude of the diurnal cycles of O_3, NO and NO_x. The analysis indicates that the downward transport of either clean or polluted background air during the first part of the day, as the boundary layer develops, is responsible for the alteration of the diurnal patterns with the prevailing wind direction between 08:00 and 10:00 (EDT). At Hastings, NMHC/NO_x ratios are found to be relatively elevated (> 8 ppbC ppb^{-1}) and highly variable for both the clean northerly and the southwesterly polluted regimes. At this site and for the polluted southwesterly flow, an average of 11.2 molecules of O_3 appear to be formed for each molecule of NO_x oxidized. Estimated values for "background" ozone levels associated with the different sectors, as well as for the contribution of major urban centres in the region are discussed.

Key word index: Oxidant monitoring, tropospheric photochemistry, diurnal cycles.

1. INTRODUCTION

Emission of anthropogenic ozone precursors from urban and industrialized areas can result in an enhancement of ozone concentrations in suburban and rural areas downwind (see for example NRC, 1992, for a recent review of this topic). During southwesterly flow, emissions from local sources distributed along the Lake Erie and Lake Ontario shorelines in the southwestern part of the Windsor-Quebec City Corridor (WQCC, Fig. 1) are diluted into an incoming background air mass containing ozone and its precursors from the Ohio River Valley and the Lake Michigan Region (Yap *et al.*, 1988, 1991). The Southern Ontario Oxidant Study (SONTOS), under the coordination of the Canadian Institute for Research in Atmospheric Chemistry (CIRAC), was designed to address the problem of oxidant formation in this part of the WQCC. During the summer of 1992, a 6-week intensive field monitoring campaign, consisting of a variety of surface measurements, was carried out at two rural surface sites (Binbrook and Hastings) in the southwestern part of the WQCC by several research groups (York University, the Ontario Ministry of Environment and Energy (MOEE), Atmospheric Environment Service, Ontario Hydro and Unisearch Associates). Aircraft monitoring of the Toronto plume and of the surrounding background was also carried out on selected days. Separate papers in this issue are dealing with different subjects related to SONTOS 92 (Hastie *et al.*, 1994; Lin *et al.*, 1994; McLaren *et al.*, 1994; Plummer *et al.*, 1994; Poissant *et al.*, 1994; Reid *et al.*, 1994). In this paper, the influence of wind direction and planetary boundary layer (PBL) dynamics on the averaged levels and diurnal cycles of O_3, NO_z, NO, and NO_y at the two stations are

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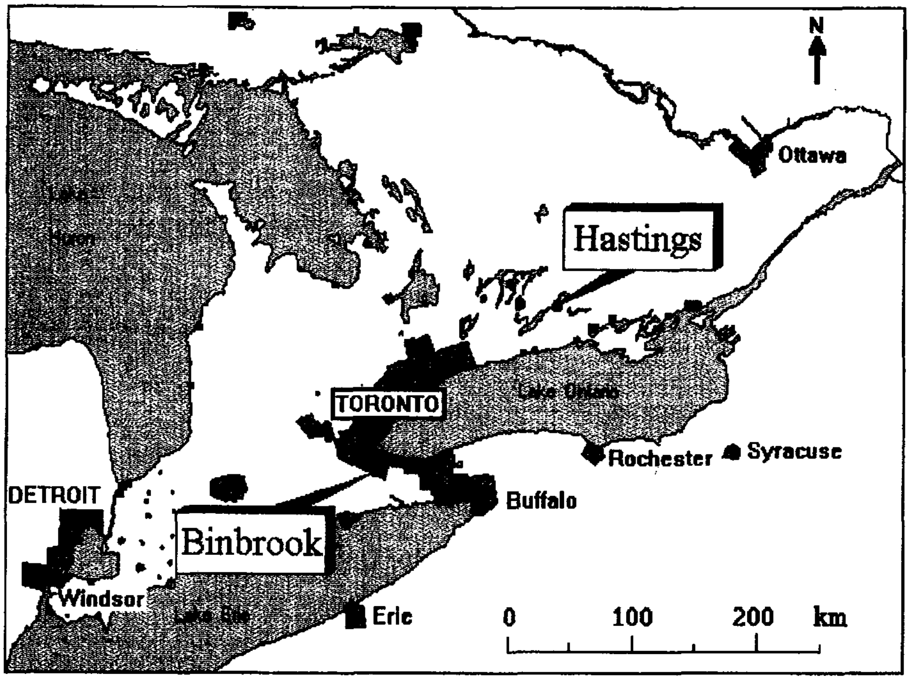

Fig. 1. Location of the two ground level monitoring stations for the SONTOS 92 study in the Southwestern part of the Windsor-Quebec City Corridor.

discussed for the 6-week period. A first approximation of two important parameters related to the formation of ozone (measured local NMHC/NO_x ratios and O_3–NO_z relationship) are presented for the Hastings station.

2. EXPERIMENTAL

2.1. *Measurements*

Two ground level monitoring stations were operated 60 km SSW and 140 km NE of Toronto, at Binbrook, Ont., and Hastings, Ont., respectively. The Binbrook site is located in a flat, suburban, agricultural area while the Hastings station is established near the top of a 40 m hill overlooking the Trent River, in a rural area. The location of the two stations in Southwestern Ontario is shown on Fig. 1. The two sites were equipped with identical instrumentation to measure O_3 (Dasibi 1003, UV absorption), NO and NO_y (TECO 42S, Mo/325°C, chemiluminescence) and SO_2 (ML 8850S, UV Fluorescence) in a continuous mode. Five-minute averages were logged on Campbell Scientific data loggers (Model 21X and CR7X). Preliminary data analysis indicated that the "NO_x" signal from the TECO 42S was consistently within 10% of the sum of the major NO_y species (NO, NO_2, HNO_3, NO_3^- and PAN) measured individually at Hastings despite the presence of a 5 μm, 47 mm diam., Teflon® filter, on the sample inlet. Furthermore, Fehsenfeld *et al.* (1987) showed that a heated Mo converter unit is adequate for the reduction of all NO_y species, provided concentrations do not remain above 100 ppb for extended periods (several hours). For these reasons, in the following, we will refer to the "NO_x" signal from the TECO 42S instrument as a measure of NO_y. At the Hastings station only, NO_2 was measured individually by photolytic conversion, together with NO (TECAN unit). The NO levels were taken from the TECO 42S, above 0.2 ppb, and from the TECAN unit below this threshold (mostly nighttime values). During the month of August, simultaneous NO levels (5-min avg.) from the TECO 42S and TECAN were shown to be in reasonable agreement between 0.2 and 0.5 ppb ($NO_{TECAN} = 1.13 \times NO_{TECO\,42S} - 0.44$ ppb, $R^2 = 0.50$, $N = 4857$). Speciated concentrations of volatile non-methane hydrocarbons (NMHC) were measured through grab samples of ambient air collected once to six times a day in evacuated canisters; a list of the measured NMHC species is provided in Table 1. (See Niki *et al.* (1993) and Niki (1994) for a complete description of the hydrocarbon measurements.) All chemical analysers were audited by the MOEE before and after the monitoring campaign (Table 2); when needed, the instruments were calibrated against MOEE reference gas mixtures during the "pre-study" audit (the MOEE gas mixtures are themselves calibrated against NIST standards, except for SO_2, generated with a permeation device calibrated gravimetrically by the MOEE). The results of the post-study audit revealed an overall excellent stability of the chemical analysers at both locations throughout the study period. The largest deterioration in instrumental response occurred on the TECO 42S at Binbrook (− 15.9% relative to the MOEE/NBS standard) but no data correction was attempted to account for this drift because of its small magnitude.

At both sites, wind speed and direction were recorded from a Young 05103 anemometer installed at the top of

Table 1. List of hydrocarbon species analysed by GC from the canister grab samples

Ethane	Propane	Butane and C > 4 paraffins	Acetylene	Ethene	Propene and C > 3 olefins	Isoprene	Xylene and other aromatics
Ethane	Propane	*n*-Butane	Acetylene	Ethene	Propene	Isoprene	*o*-Xylene
		i-Butane			1-Butene		*p*,*m*-Xylene
		n-Pentane			*i*-Butene		Ethyl-benzene
		i-Pentane			1-Pentene		Benzene
		n-Hexane			1,3-Butadiene		Toluene
		2-Methyl-pentane			Propyne		
		3-Methyl-pentane			*t*-2-Butene		
		n-Heptane			*c*-2-Butene		
		Methyl-cyclo-hexane			1-Hexene		
		n-Octane					
		n-Nonane					
		Cyclo-pentane					
		Cyclo-hexane					
		Methyl-cyclo-pentane					
		2,2-Dimethyl-butane					

Note. Species have been grouped under main classes headed by one representative compound, as used in the C.B. IV chemistry module of the Regional Oxidant Model and the associated emission inventory.

Table 2. Audit results for the trace gas analysers

	O_3		NO		NO_x		SO_2	
Station	Pre	Post	Pre	Post	Pre	Post	Pre	Post
Binbrook	+ 0.6	+ 3.0	0.0[a]	− 3.3	0.0[a]	− 5.8	0.0[a]	+ 6.9
Hastings	− 2.0	+ 5.0	0.0[a]	+ 3.4	0.0[a]	− 15.9	− 4.9	− 2.4

Note. Maximum deviations in response (%) during MOEE standard span tests on the pre- and post-study audits (15 July and 23 September 1992)

[a] Instrument calibrated against MOEE standard.

a 10 m meteorological tower. Temperature gradients between 1 and 9 m above the surface were recorded using thermocouples fitted in radiation shields installed on the 10 m tower. Mixing heights were measured with acoustic radars (Aerovironment Inc. Model 300C, range ≈600 m, resolution ≈30 m).

2.2. *Data analysis*

The statistical analysis described hereafter was performed using SAS®. Pollutant roses and diurnal cycles were constructed from median concentrations isolated for each 10° wind direction and "hour of day" bins, respectively. To selectively address the effect of the direction of transport on the level of the measured pollutants and to limit the "noise" associated with stagnant conditions, we only retained measurements for which the wind speed was higher than $1\ \mathrm{m\,s^{-1}}$. Furthermore, the pollutant roses were constructed from data collected between 10:00 and 18:00 (EDT, as for all hours referred to in the text unless otherwise specified) in order to characterize well mixed air masses only. The 25 and 75% quartiles for the pollution roses and diurnal cycles were found to typically lie between 15 and 40% of the median value. At Hastings, where NO_x (= NO + NO_2) was available, the quantity NO_z, which represents the photochemical products containing nitrogen (primarily HNO_3, PAN and NO_3^-), was approximated by NO_y–NO_x.

3. RESULTS AND DISCUSSION

3.1. *Contrasting regimes*

At the Hastings site, all trace gas mixing ratios (except NO, due to its short lifetime), reflect the overall influence of a polluted SW sector (Figs 2 and 3). The N sector at Hastings appears to be generally associated with cleaner air masses, carrying less than half the levels encountered in the SW sector for O_3, SO_2, NO_y and NO_z. At this location, NO average levels stay low (0.1–0.2 ppb range) throughout the whole wind rose. In order to estimate the importance of local sources (within 50 km of the site) vs the long range transport of pollutants in the SW sector it is useful to perform a crude dispersion estimate based on the MOEE emission inventory. For NO_x, the source strength for the Greater Toronto area alone is ≅100,000 tonnes per year. The same emission inventory indicates that the combined NO_x emissions within 50 km of the Hastings site in the SW sector amounts for less than 200 tonnes per year. Using simple Gaussian plume dispersion calculations, for neutral conditions (sigma-*y* and sigma-*z* from standard Pasquill–Gilford curves), it can be estimated that the impact of the Greater Toronto area NO_x emissions at the Hastings site is 10 times larger than the impact from local sources in the SW sector. A similar figure can be obtained regarding the impact from remote and local SO_2 emissions. Consequently, the maxima observed in the SW sector at this site can be regarded, mainly, as a result of consistent long range transport of pollutants from major urban and industrial centres located upwind in the SW direction.

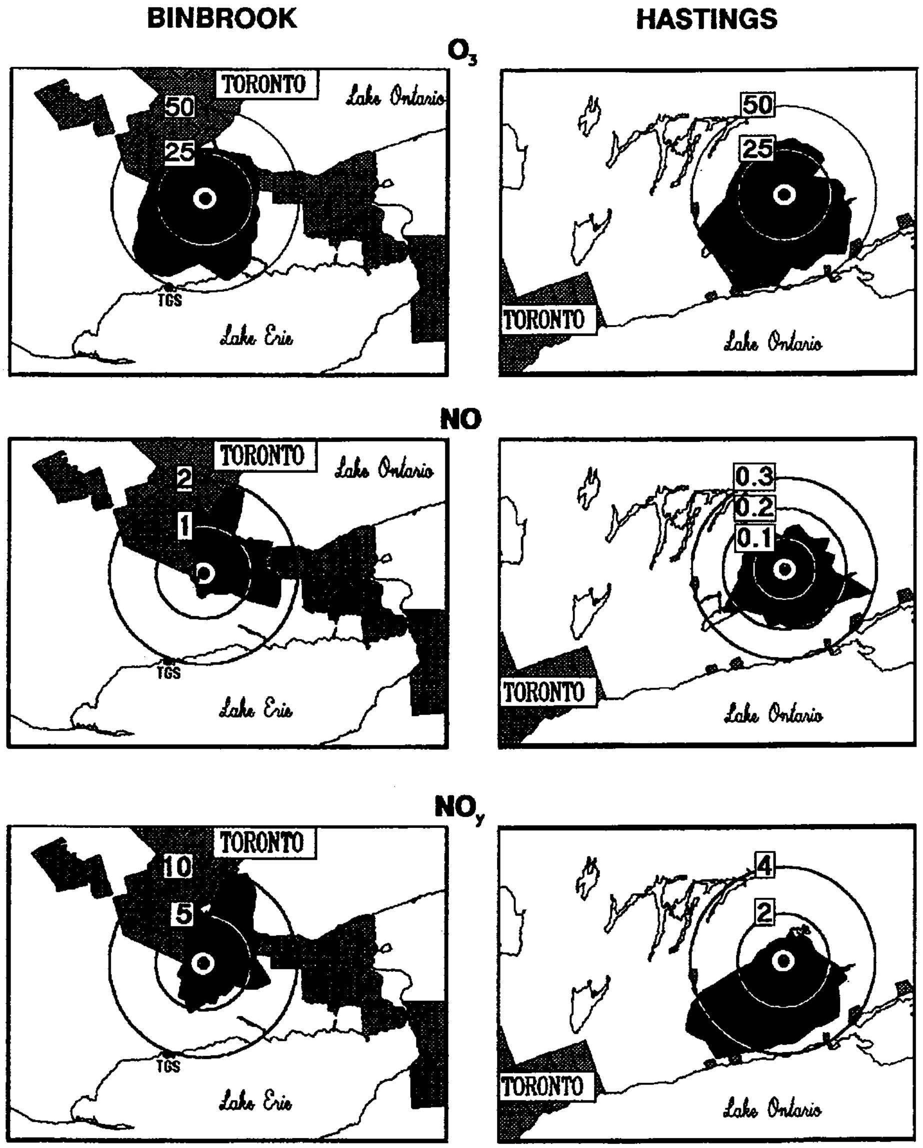

Fig. 2. Pollution roses for O_3, NO and NO_y at the Binbrook and Hastings stations. (Median concentrations in ppb for the 6-week study were derived for each 10° wind direction bin and between 10:00 and 18:00 EDT.) Note the different scales between Binbrook and Hastings for NO and NO_y.

At Binbrook, an ozone maximum is found in the SW direction. This apparently indicates the influence of the polluted background air in the SW. However, at this location, emissions from the Greater Toronto area exert considerable effects in the NNE sector where SO_2, NO and NO_y present noticeable maxima. Another well defined maximum for NO_y and SO_2 is found in the 195° direction. A separated analysis of individual events in the neighborhood of this direction revealed well defined episodes with high concentrations of these species. The NO_y/SO_2 ratios associated with these episodes remain within a narrow range (0.5–0.8 ppb ppb^{-1}). This suggests a single source as the cause of these events. Ontario Hydro's

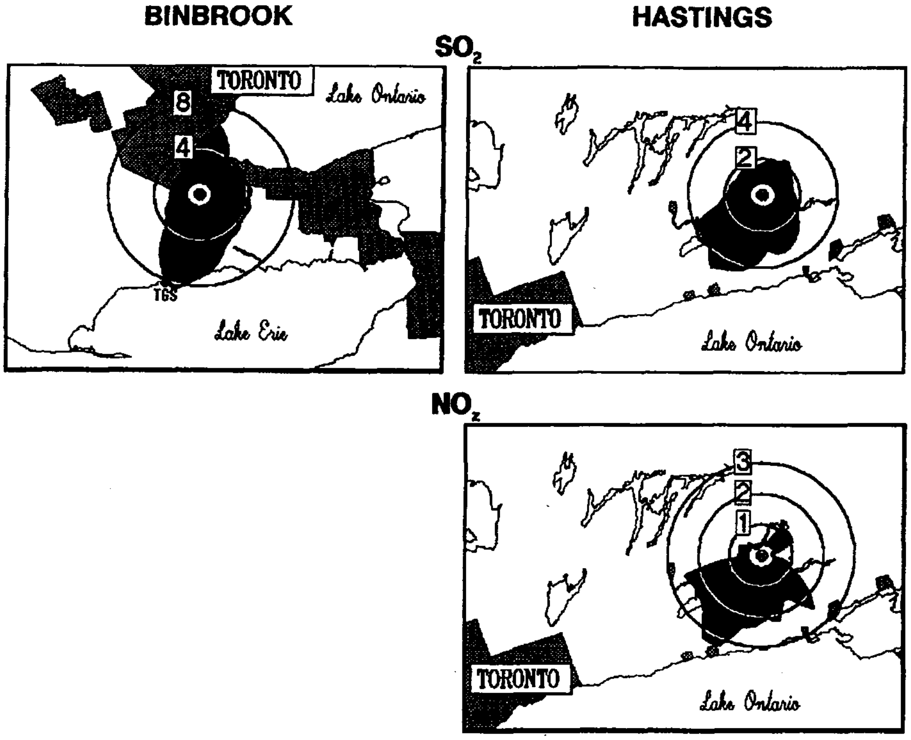

Fig. 3. Same as Fig. 2. for SO_2 and NO_z. Note the different scales between Binbrook and Hastings for SO_2.

Nanticoke Thermal Generating Station, a 4000 MW coal-fired power plant located 204° and 40 km upwind of the site, is likely responsible for these maxima. Indeed, a NO_y/SO_2 ratio of 0.8 can be derived for this power plant, using the annual emission factors (15,800 Mg for NO and 40,500 Mg for SO_2).

The similarity of the median O_3 levels observed at the two sites in the NE sector suggests that the Greater Toronto Area emissions do not systematically induce an increase in ozone levels at Binbrook. It is assumed that air masses arriving in the NE sector at Hastings and Toronto have similar content. This assumption is justified by the emission inventory in this region showing no major difference between the two locations in this sector (Saeger *et al.*, 1989). Relatively short transport times for Toronto urban plumes to reach Binbrook (approximately 2 h with a wind speed of $3\ \mathrm{m\,s^{-1}}$) do not allow for substantial photochemical ozone production after the initial titration of the incoming background ozone by NO emitted in the urban area. This observation and our interpretation are supported by model calculations done for the Toronto urban plume diluting into clean background air. Under this condition, only 2 to 3 ppb of additional ozone are expected to be formed at the downwind distance of 60 km (Lin *et al.*, 1994). At Hastings, the statistical effect of the Greater Toronto Area emissions is far more difficult to evaluate. During southwesterly flows, these emissions are likely to be superimposed on an already "polluted" southwesterly background when reaching the Hastings station (Yap *et al.*, 1988, 1991). A detailed trajectory analysis with a fine spatial resolution could help to distinguish between air masses travelling in the SW direction with and without additional emissions from the Greater Toronto Area. Unfortunately, such trajectory calculations are not available at present because of the limitation of the meteorological measurement network.

Since two contrasting broad sectors of influence were identified at both locations it was decided to investigate whether diurnal variations, $NMHC/NO_x$ ratios and the O_3–NO_z relationship would show any significant difference between the two sectors. For that purpose, two wind sectors, N and S, were defined at each location as detailed in Table 3. This classification was based on the obvious differences in pollutant levels observed on the pollution roses previously discussed. No other criteria were used to delineate the sectors.

Table 3. Classification of the SONTOS 92 database into two wind sectors at the Binbrook and Hastings ground level monitoring stations

	N sector		S sector	
Station	WD[a]	Data base fraction	WD[a]	Data base fraction
Binbrook	310–130°	36%	130–270°	47.5%
Hastings	270–40°	32%	150–250°	30%

[a]Local wind direction as measured from the 10 m meteorological tower.

3.2. *Diurnal cycles*

It is known that the dissipation and establishment of the nocturnal inversion and, therefore, the local topography and elevation of a surface monitoring site and its situation within the local vertical temperature gradient, have a large influence on the shape of the ozone diurnal cycles measured at rural surface locations (NRC, 1992; Fehsenfeld *et al.*, 1983; Wolff *et al.*, 1987; Casado *et al.*, 1994; Loibl *et al.*, 1994). For sites remaining within the nocturnal boundary layer, the O_3 levels usually drop at night due to dry deposition and titration with NO (if any is present). The break-up of the nocturnal inversion and the re-establishment of vertical mixing during the morning hours then induces a rapid increase in surface O_3 due to a downward transport from O_3 rich layers aloft.

3.2.1. *PBL dynamics*. Our meteorological measurements can help us to identify the main characteristics of the PBL dynamics encountered during the morning hours at each site. The acoustic sounder signals indicate that, at both locations, the well-mixed layer usually started to develop between 07:30 and 08:00 and its top was still detected until around 10:00. The acoustic sounder data also indicate that the nocturnal inversion was generally deeper at Binbrook (100–200 m) than at Hastings (50–150 m). These observations are consistent with the measurements of temperature gradients near the surface.

The diurnal cycles of these temperature gradients, averaged over the 6-week period, are shown on Fig. 4. This plot clearly confirms the onset of the PBL development around 7:00, at both sites, and reveals a stronger gradient at Binbrook throughout the 24 h. *T*-test conducted at each hour of the day on the two populations of gradients in the N and S sectors ($N \approx 18$ and $N \approx 30$, respectively), lead to *P*-values higher than 0.30 for both locations. This result suggests that at Binbrook and Hastings, the diurnal variations of the PBL are not significantly different between the N and S sectors. The diurnal cycles of O_3, NO_z, NO and NO_y will be discussed in the light of these local meteorological characteristics. As mentioned previously, stagnant conditions (wind speed $< 1\ \mathrm{m\,s^{-1}}$), where significant temperature stratification within the nocturnal boundary layer and isolation of the Hastings site from lower levels in the river valley could occur, were not included in the analysis that follows (see a discussion of this effect in Hastie *et al.* (1994)).

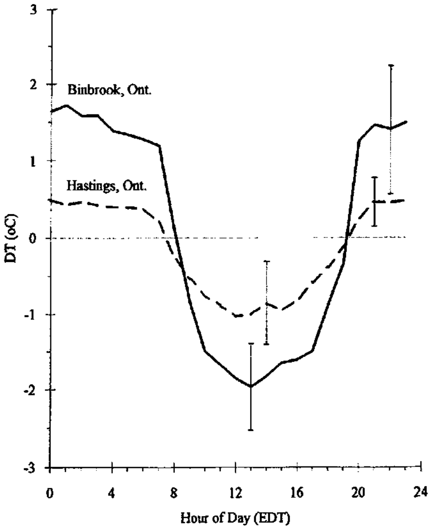

Fig. 4. Diurnal cycles of the temperature gradients measured near the surface ($T_{9m} - T_{1m}$) at the Binbrook and Hastings stations averaged over the 6-week study period. Variation bars are one standard deviation.

3.2.2. O_3 *diurnal cycles*. The afternoon ozone maxima found at both sites in the S sector are, on average, 1.7 to 1.8 times higher than the ones associated with the N sectors (Fig. 5). At the hill-top station (Hastings), the ozone levels do not drop as low as at Binbrook during the night (reaction with NO, but mainly dry deposition). This indicates a relatively more effective input from the O_3-rich free troposphere due to a thinner nocturnal inversion layer at Hastings.

The ozone daily maxima for the N sector at Binbrook and the S sector at Hastings occur later in the afternoon (17:00 and 18:00, respectively) as compared with the other sectors (16:00 for both Binbrook (S) and Hastings (N)). This delay may be caused by the Greater Toronto urban emissions that are likely to be present in the air masses associated with the N sector

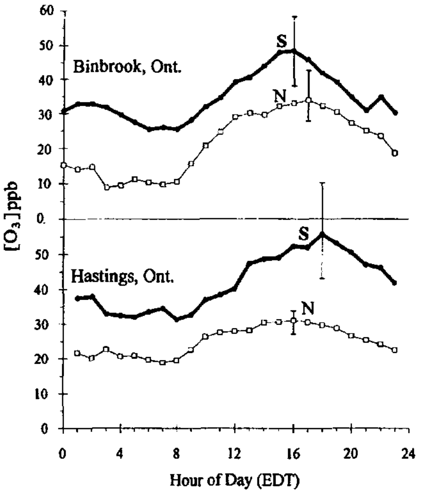

Fig. 5. Diurnal cycles for O_3 at Binbrook and Hastings, for the N and S sectors as defined in text, averaged over the 6-week study period. Variation bars for lower and upper quartiles.

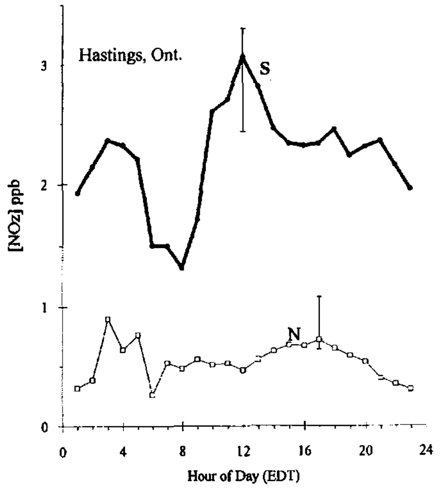

Fig. 6. Diurnal cycles for NO_z at Hastings, for the N and S sectors as defined in text, averaged over the 6-week study period. Variation bars for lower and upper quartiles.

at Binbrook and the S sector at Hastings. In other words, this feature may indicate that fresh emissions tend to sustain the photochemical production of ozone in the later afternoon.

About 7 ppb additional ozone are formed in the S sector at Hastings as compared with the maximum level observed in the same sector at Binbrook. This difference may be due to the effects of the Greater Toronto Area emissions on air masses travelling in the SW direction. The present analysis, however, does not allow us to draw a conclusive statement regarding this aspect. Case study analysis will be a more appropriate way to investigate these effects (see the treatment of the 6 August episode, when the Toronto urban plume apparently impacted the Hasting site, by Lin *et al.* (1994) and Reid *et al.* (1994)).

3.2.3. NO_z *diurnal cycles.* The averaged NO_z diurnal variations were derived from $NO_y - (NO_2 + NO)$ at Hastings and are shown in Fig. 6. The contrasts between the two sectors—concentration differing by one order of magnitude and different shapes—suggest some interesting mechanisms and, therefore, deserve some discussions.

From Fig. 6 it is seen that a sharp increase from 1.2 to 3 ppb exists in the S sector between 08:00 to 10:00 whereas a flattened profile is evident during the same period in the N sector. The NO_z species are produced photochemically but this process is far from being instantaneous. An upper limit of 0.33 ppb has been calculated for the combined local photochemical production of PAN and HNO_3 (the main NO_z species) between 08:00 and 10:00 (the details of the photochemical model used for these calculations can be found in Lin *et al.* (1994)). Furthermore, we also know that none of the NO_z species are emitted locally at Hastings (either anthropogenically or naturally). Therefore, we propose that the sharp increase in NO_z concentration in the S sector at Hastings is due mainly to the downward mixing of upper air containing significant amount of NO_z species after the inversion break-up. The observation in the N sector does not conflict with the proposed mechanism since the downward transport of clean upper air (virtually NO_z free) is not expected to induce any increase in surface concentration. As the PBL height continues to expand and vertical mixing dominates, NO_z levels eventually decline after 12:00 in the S sector. Horizontal transport and photochemical production maintain the levels at nearly 2.5 ppb throughout the afternoon period.

Both the N and S sectors display a nighttime maximum at 03:00 followed by a rapid decrease to reach the daily minimum between 06:00 and 08:00. The nighttime maximum could be a result of the formation of HNO_3 by heterogeneous reactions involving NO_3 and N_2O_5. Our database is inadequate to test such a hypothesis.

3.2.4 NO *diurnal cycles.* The short-lived nitric oxide species is a good indicator of local vehicle emissions. NO levels start to increase at both sites between 06:00 and 08:00, two hours earlier than the increase in ozone concentration (Fig. 7). This early peak, with

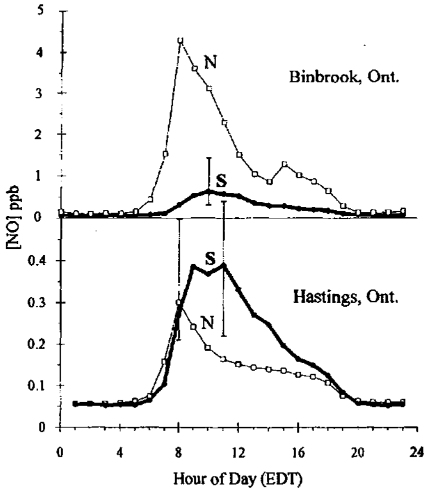

Fig. 7. Diurnal cycles for NO at Binbrook and Hastings, for the N and S sectors as defined in text, averaged over the 6-week study period. Variation bars for lower and upper quartiles.

an onset appearing well before the break-up of the nocturnal inversion, points to an impact from local traffic. The source strength of the local traffic is expected to be a determining factor for the rate of increase of NO levels during this period. At Binbrook, fresh emissions of NO from the Greater Toronto area clearly enhanced the slope and maximum value observed in the N sector during the morning hours (06:00 to 08:00). On the contrary, at Hastings, NO levels in the N and S sectors rise at similar rates during this rush-hour period, because of the absence of a major urban centre within 100 km of the site in either of the two sectors (Roussel and Moroz, 1992).

After the rush-hour traffic and at both locations, NO levels continue to increase for another two hours (between 08:00 and 10:00) in the S sector whereas they fall abruptly in the N sector. The downward transport of upper air is probably responsible for the observed difference. We explain the delayed peaks of NO in the S sectors observed at both sites as follows. The polluted air masses, usually associated with the S sector, retain a relatively large quantity of photochemical products which are preserved above the nocturnal inversion during the night. While these "reservoir species" are transported down to the surface in the S sector following the break-up of the nocturnal inversion, some species, such as PAN, will be prone to release NO_2 as thermal decomposition becomes more and more efficient with an increase in the air temperature. Subsequently, NO is rapidly produced through NO_2 photolysis until a photostationary state is achieved between O_3, NO_2 and NO. This temporary source of NO overcompensates the dilution effect associated with the simultaneous development of the boundary layer and leads to, at both locations, a later maximum for NO in the S sector. This mechanism is consistent with the diurnal pattern of NO_z discussed above. On the contrary, in the N sector, the dilution of the traffic emissions into the clean air aloft results in the observed sharp decrease of NO levels, starting at 08:00, at both locations.

3.2.5. NO_y *diurnal cycles.* The observations previously made for NO are consistent with the observed patterns for NO_y (Fig. 8) and the same interpretations hold at both locations. At Binbrook, NO_y cycles display an early morning increase (06:00 to 08:00), caused by local traffic emission (mostly NO), with a strong influence from the emissions from the Greater Toronto area in the N sector. Here, again, we propose that the dilution into clean upper air in the N sector induces an abrupt decline of the NO_y levels (maxima at 08:00 at Binbrook and Hastings) whereas the downward mixing of nitrogen containing species in the S sector counteracts the dilution process and tends to induce a later maximum (11:00 at Binbrook, 9:00 at Hastings).

3.3. *NMHC and* NO_x *at Hastings*

A summed concentration of selected hydrocarbons (in units of ppbC) was derived from the speciation analysis of the NMHC grab samples collected at Hastings. The volatile organic compounds containing oxygen and/or nitrogen, referred to VOCs in the literature, are not included in this NMHC sum. Results from Dann (1994) indicate that the NMHC sum typically accounts for about 70–80% of the total VOC load in

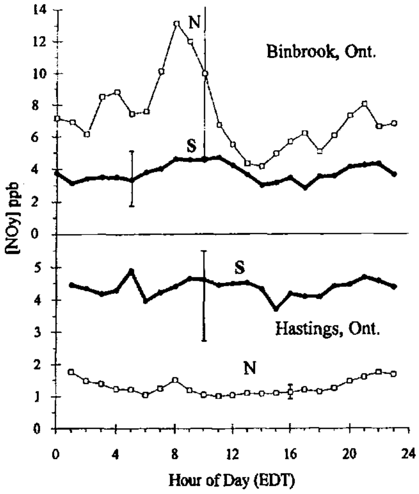

Fig. 8. Diurnal cycles for NO_y at Binbrook and Hastings, for the N and S sectors as defined in text, averaged over the 6-week study period. Variation bars for lower and upper quartiles.

the study area. NO_x was available at Hastings only, where NO_2 and NO were measured individually. Only NMHC and NO_x measurements recorded in the afternoon were retained for the analysis in an attempt to characterize the vertically well-mixed conditions. The analysis of these data shows that, from the N sector to the S sector, NMHC average levels increase from 9.4 to 13.1 ppb (a factor of 1.4) while NO_x average levels rise from 1.6 to 3.8 ppb (a factor of 2.4). Both increases are obviously due to anthropogenic emissions upwind of the site in the S sector. The difference in increase may result from the shorter residence time of the NO_x species as compared with NMHC. Furthermore, the anthropogenic fraction of the total emission is much higher for NO_x than for NMHC, making NO_x a better indicator of relatively "young" polluted air masses than NMHCs. This holds for transport shorter than a couple of days or so for which NO_x is not completely depleted by the photochemical processes. This should therefore be true for air masses passing over the Detroit, Cleveland and Greater Toronto areas, which are 25.6, 24.3 and 8 h away, respectively, from Hastings (with a typical advective wind speed of 5 $m\,s^{-1}$ and assuming a straight trajectory). A co-factor could be that a stronger biogenic component in the largely forested N sector matches, to some degree, the anthropogenic input of NMHC in the S sector, resulting in a smaller difference of NMHC levels between the two sectors than the one observed for NO_x. However, the NMHC speciation analysis revealed no significant difference in the fraction of isoprene, the main biogenic hydrocarbon, between the N and S sectors (Niki *et al.*, 1993). Consequently, this second mechanism cannot be retained to explain the difference reported above.

The VOCs/NO_x ratio of a given air mass is known to be an important parameter that greatly influences the potential for ozone production (NRC, 1992). The averaged NMHC/NO_x ratios were found at 14.5 and 8.7 ppbC ppb^{-1} for the N and S sectors, respectively, at the Hastings site. Both ratios exhibit a large variability (> 50%). Moreover, the NMHC total concentration is a lower limit for the VOCs level and therefore, the reported NMHC/NO_x ratios should be regarded as a lower limit for the VOCs/NO_x ratios in this area. The relatively high values for both sectors may indicate a predominance of a NO_x-limited ozone production at Hastings, regardless of the direction of transport.

3.4. *Ozone vs nitrogen products at Hastings*

Surface ozone levels have been shown to exhibit a significant correlation with NO_z concentrations at several surface sites in North America (e.g. Trainer *et al.*, 1993). We have examined the relationship between O_3 and NO_z levels at Hastings for the N and S sectors. Since ozone maxima occurred quite late in the afternoon, especially for the S sector (see Section 3.2.2.), we focused on the period between 13:00 and 20:00. As before, we selected data corresponding to non-stagnant conditions only (wind speed > 1 $m\,s^{-1}$). The NO_z levels were classified in 10 bins of equal population (41 data per bin for the N sector, 74 data per bin for the S sector). An averaged ozone level was derived for each NO_z bin and plotted against the bin-averaged NO_z level (Fig. 9). For the whole population of the N sector ($[NO_z] < 3.3$ ppb), a least squares regression analysis gives

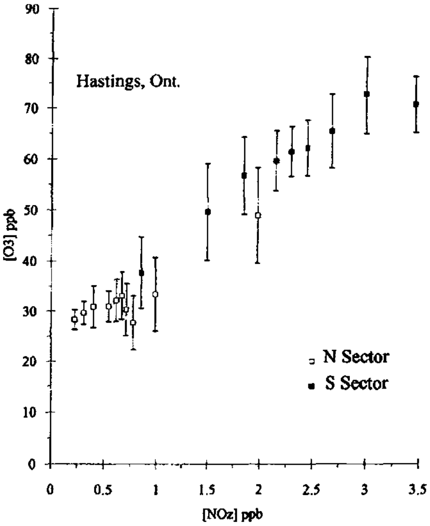

Fig. 9. O_3 vs NO_z at Hastings ($NO_z = NO_y - NO_x$), between 12:00 and 19:00 EST, for the N and S sectors as defined in text (wind speed > 1 $m\,s^{-1}$). Individual points are averaged levels within each equi-populated NO_z bin for the 6-week study period. Error bars are one standard deviation.

$$[O_3]_N = 10.7 \times [NO_z]_N + 24.7 \text{ ppb},$$

$$(R^2 = 0.51, N = 415).$$

A regression analysis for the S sector, where a larger range of NO_z levels is available ($0.3 < NO_z < 4.9$) leads to

$$[O_3]_S = 11.2 \times [NO_z]_S + 33.9 \text{ ppb}$$

$$(R^2 = 0.69, N = 746).$$

The results are summarized in Table 4, together with those from other previous studies in North America for comparison. Our results regarding the slope obtained for the S sector at Hastings (11.2) is in good agreement with the results from Kleinman *et al.* (1994) at Metter, GA (11.4) and is slightly larger than the one derived from the Egbert (Ont.) and Scotia (PA) data sets (8.9 and 8.5, respectively).

It should be noted that the NO_z and O_3 levels in the N sector are poorly correlated ($R^2 = 0.51$). The NO_z atmospheric lifetime, mostly governed by the dry de-

Table 4. Linear regression analysis of the correlation between O_3 and NO_z surface measurements performed during this study and as reported at three other rural sites in North America

Site		NO_z range (ppb)	Time (EST)	O_3/NO_z (linear regression)				Refs
				Slope	Intercept	R^2	N	
Hastings, Ont.	N sector	[0, 1]	12:00–19:00	N.A.	N.A.	0.006	356	This study
	N sector	[0, 3.3]	12:00–19:00	10.7	24.7	0.51	415	
	S sector	[0.3, 4.9]	12:00–19:00	11.2	33.9	0.69	746	
	S&N sector	[0, 4.9]	12:00–19:00	13.8	25.6	0.83	1161	
Egbert, Ont.		[0, 5]	13:00–17:00	8.9	31	N.A.	N.A.	Trainer *et al.* (1993) Anlauf (1994)
Scotia, PA		[0, 15]	13:00–17:00	8.5	35	0.67	N.A.	Trainer *et al.* (1993)
Metter, GA		[0, 6.5]	13:00–17:00	11.4	27	0.78	N.A.	Kleinman *et al.* (1994)

position of HNO_3 and PAN and the thermal decomposition of PAN is of the order of 1 d during the summer months. This is much less than the ozone lifetime in the troposphere, which ranges between 4.5 and 12 d during the summer months, depending on the NO_x mixing ratio (Liu *et al.*, 1987). For the N sector, there are no major NO_x sources within multiple days of transport. Thus, NO_z produced concurrently with ozone, is depleted to a large extent through dry and wet deposition before reaching the Hastings site. In fact, in the N sector, the 86% of the $[NO_z]$ data which were below 1 ppb showed no correlation between O_3 and NO_z levels: R^2 is 0.006 ($N = 356$). These results indicate that, at the Hastings site, surface O_3 concentrations were correlated to simultaneous NO_z levels provided that significant NO_x sources were within a relatively short transport distance to the site (1–2 d travelling time), which is the case for the S sector influenced by Cleveland, Detroit, the Greater Toronto area and other urban and industrial sources in the Lower Great Lakes basin.

Physically, the intercepts of the two regression lines shown on Fig. 9 can be interpreted as the ozone maxima that would be observed at Hastings if a given air mass was completely depleted from all NO_z species during its transport to the site. This would be the case for a travelling air mass for which all NO_x sources would have been "shut off" at a certain upwind distance, corresponding to a particular transport time, from the site. This transport time would have to be the minimum time required to completely deplete the air mass from the NO_z species, while no NO_x is being added. Since NO_z species will continue to be produced from the photooxidation of NO_x initially present in the air mass, the time required to deplete the air mass from its NO_z content stems from the NO_z sink and production rates for a given set of initial NO_x and NO_z concentrations. For the N sector the extrapolated ozone level, ≈ 25 ppb, can be regarded as the incoming clean background air since no major sources exist upwind of the site in this direction. For the S sector, our results suggest that an average O_3 maxima of ≈ 34 ppb would be observed in the absence of the major sources upwind of Hastings (Cleveland, Detroit, Toronto, etc.). This O_3 level is still higher than the one derived from the measurements for the N sector by 9 ppb. Moreover, since the O_3 median maxima actually observed at Hastings in the S sector is 56 ppb (see Section 3.2.2.), a contribution of ≈ 22 ppb of O_3 may be specifically attributed to the combined effects of the emissions from these and other major urban areas.

4. SUMMARY AND CONCLUSION

Our analysis of a 6-week data set collected during the summer of 1992 at two surface sites in southwestern Ontario lead to the following conclusions.

(1) The median levels of O_3, SO_2, NO, NO_y and NO_z are shown to differ markedly between two contrasting sectors (S and N) at each location. The maximum median ozone mixing ratio associated with the S sector was higher than its counterpart in the N sector by 20–25 ppb at both sites. During the 6-week study the emissions from the Greater Toronto area did not induce a measurable variation in the average ozone levels measured at 60 km downwind during northeasterly winds.

(2) The diurnal cycles of O_3, NO and NO_z differ substantially between the two sectors because of the downward transport of upper air of radically different pollutant content after the inversion break-up, between 08:00 and 10:00. In the case of NO, local traffic induced an early increase in nitric oxide levels between 06:00 and 8:00. For the S sector, the production of NO from the decomposition of reservoir species, transported down from higher levels, counteracted the onset of dilution of the vehicle emissions between 08:00 and 10:00.

(3) The data suggest that the input of fresh urban emissions into a travelling air mass tends to shift the appearance of the afternoon ozone maximum from around 16:00 to 17:00–18:00.

(4) A first measure of the NMHC/NO_x ratio at the Hastings station, higher than 8 for both the N and S sectors, suggests a predominance of a NO_x-limited

production of ozone measured at this site regardless of the wind sector. However, the NMHC/NO_x ratios display a large variability and should be interpreted with caution at this stage.

(5) At Hastings, O_3 and NO_z levels are found to correlate in the S sector with an average of 11.2 molecules of O_3 formed for each molecule of NO_x being oxidized. From the regression analysis, a 22 ppb increment in ozone may be attributed to urban areas within 2 d of transport to Hastings in the S sector. In the N sector the correlation between O_3 and NO_z levels is poor due to in-transport loss of most of the NO_z species.

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