

## SUMMERTIME NO<sub>x</sub>, NO<sub>y</sub>, AND OZONE AT A SITE IN RURAL ONTARIO

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**Abstract**—Measurements of NO<sub>y</sub>, NO<sub>x</sub>, NO, SO<sub>2</sub>, PAN, HNO<sub>3</sub>, O<sub>3</sub>, and CO, obtained as part of SONTOS, have been examined to give a picture of the typical chemistry at this location, and for comparison with other North American sites. The total amount of odd nitrogen (NO<sub>x</sub>) at the Hastings site is less than found at other North American sites, due to the distance of the site from sources and the absence of major anthropogenic sources north west of the site. The air masses also appear younger, containing a higher fraction of NO<sub>x</sub>, although the chain length for ozone production is similar. The ozone concentrations at the site are lower than reported elsewhere, and the late afternoon maximum shows that it is typically produced elsewhere and transported to the site. A similar conclusion can be drawn from the PAN measurements. There appears to be a significant local NO<sub>x</sub> source. The flux needed to explain the observations is within the range of values from soil emissions, but a strong correlation with CO, and no correlation with SO<sub>2</sub>, suggest a mobile combustion source.

*Key word index:* Rural, ozone, production, NO<sub>x</sub>, transport.

### INTRODUCTION

As with all areas of the industrialized world, the area of Southern Ontario and Quebec usually known as the Windsor Quebec Corridor is often subjected to elevated ozone concentrations. This area is loosely defined as a 100 km wide strip starting at Windsor Ontario, stretching along the north sides of Lakes Erie and Ontario, then straddling the St Lawrence River to Quebec City. This region houses 84% of the population of Ontario, 64% of the population of Quebec and close to half of the entire population of Canada. It also includes a large amount of Canada's more productive agricultural land so that the impact of ozone is a major concern in this area. It has been estimated that crop losses in the Southern Ontario region alone, due to ozone levels above the Canadian maximum acceptable level (82 ppbv for 1 h), are in the order of \$45M per year (MOE, 1989). In a report prepared for the Canadian Council of Ministers of the Environment, the Windsor Quebec Corridor was identified as the region of Canada where the highest frequency and longest duration of ozone excursions above the maximum acceptable level occur (CCME, 1991). Typically, major urban centres within the corri-

dor experience 5–20 day<sup>-1</sup> on which the ozone air quality objective is exceeded. This has major human health and crop productivity implications, and led to the formulation of the Management Plan for Nitrogen Oxides (NO<sub>x</sub>) and Volatile Organic Compounds (VOCs) Part 1, which is aimed at "fully resolving ground level ozone problems by 2005". To achieve this will require significant advances in our understanding of the factors that influence tropospheric ozone production in this region.

The Southern Ontario Oxidant Study (SONTOS) is a multi-faceted multi-institutional study aimed at gaining a better understanding of the oxidation chemistry in the Ontario atmosphere in support of the above objectives. It combines field measurement and modelling components and involves groups from Universities, Government laboratories and the private sector.

The first major SONTOS field study took place in the summer of 1992, and involved measurements at two sites and from an aircraft. The primary intensive site was at Hastings, Ontario, roughly 150 km north-east of Toronto, with a second site at Binbrook 50 km southwest of Toronto. The aircraft made measurements upwind and downwind of the sites, performed plume studies and measured vertical profiles above each site.

In this paper we present results from the intensive measurement site at Hastings, obtained during this

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first field study. The objective is to obtain a picture of the average summertime nitrogen and ozone chemistry at the site. In particular we need to determine the similarities and differences between Hastings and the well characterized sites in North America, namely Bondville, Scotia and Egbert as described in detail in Parrish *et al.* (1993). This will provide a framework in which to use the results from these studies in SON-TOS. We compare the average concentrations of NO, NO<sub>2</sub>, NO<sub>x</sub>, HNO<sub>3</sub>, O<sub>3</sub>, PAN, SO<sub>2</sub> and CO for August 1992 and the chain length for ozone production with those at the above mentioned sites (Parish *et al.*, 1993; Trainer *et al.*, 1993). The data are also used to identify site-specific effects that may impact on the use of data from this site in addressing regional air quality issues. Companion papers (Roussel *et al.*, 1995; Reid *et al.*, 1995; Lin *et al.*, 1995) examine more specific observations than the general features addressed here.

#### EXPERIMENTAL

##### Site

The Hastings site is located about 150 km northeast of Toronto in a lightly populated farming area, as shown in Fig. 1. The town of Hastings, population 1000, is 5 km to the southwest. The nearest major town in Peterborough, approximately 40 km to the northwest. Unlike sites within the continental United States, this site is at the northern edge of the population belt, thus it is positioned to receive both clean and polluted air masses. Air from the northwest quadrant will usually not have recently contacted major urban or

industrial centres so will be typical of a slightly contaminated continental environment, whereas air from the south west may be quite heavily impacted.

The site itself is on a hill with an average elevation above the immediately surrounding area of about 30 m, and is about 40 m above the Trent river, a largely recreational waterway. The field in which the monitoring trailers were located was ungrazed pasture, and the major crops in the area were hay, fodder corn and soy beans. A full description of the site and the experiment is given in Reid *et al.* (1995).

##### Instrumentation

The instruments for this study were mounted in three separate trailers, each with a glass inlet system which was used to pump air from more than 5 m above the ground into the trailer with a residence time of less than 2 s. Trailer 1 housed the CO, NO/NO<sub>x</sub>, Thermolectron O<sub>3</sub> and SO<sub>2</sub> instruments (see below). Air to the individual instruments was drawn from the manifold through 1/4 inch Teflon lines of less than 1 m. Trailer 2 housed the NO/NO<sub>2</sub>, and Dasibi O<sub>3</sub> instruments. Teflon lines of between 1 and 2 m connected the instruments to the manifold. Only PAN measurements were made in Trailer 3 and air was drawn through the sampling system at a flow rate of 200 ml min<sup>-1</sup> from a dedicated glass manifold. The filter packs were located at the top of a 10 m post adjacent to the trailers.

Ozone measurements were made with Dasibi model 1003-AH and Thermolectron Model 49 U.V. absorption analysers located in separate trailers. These units were calibrated by the Ontario Ministry of the Environment and Energy's audit group, before and during the study, and found to be within 5% of the NBS traceable standard. Instrument precision and detection limits are 2 ppbv. Post study intercomparison of the data showed no significant difference between the instruments.

NO and NO<sub>2</sub> were measured using a TECAN model CLD 770-AL ppt NO chemiluminescent analyser equipped with a PLC-760 photolysis converter to convert the NO<sub>2</sub> to NO,

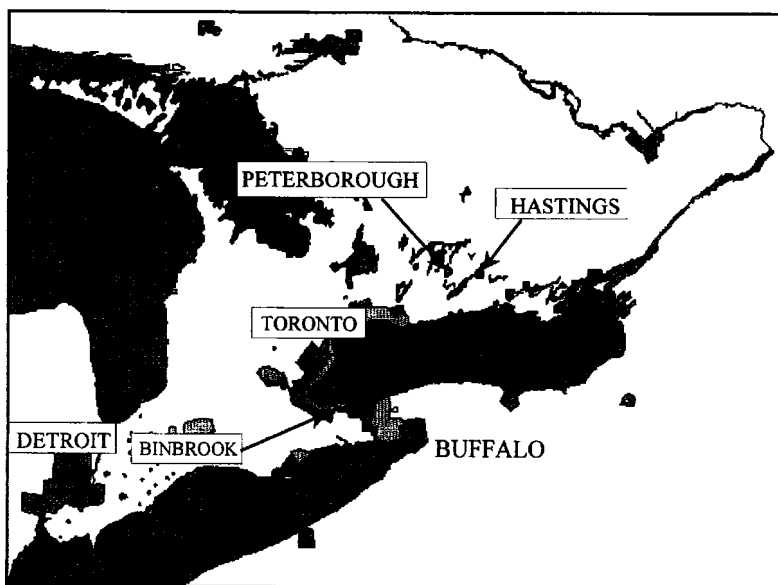


Fig. 1. Map showing the location of the sampling site.

run on a 16 min measurement cycle (4 min NO, 4 min NO<sub>2</sub>, and 8 min zero). Zero is determined by removal of NO by titration with ozone prior to reaction cell. The NO<sub>2</sub> concentration was determined from the difference between the two channels. The residence time in the instrument is < 8 s which was considered short enough that no correction for NO oxidation was included. The NO instrument was calibrated daily against a diluted standard of 6.6 ppmv NO in nitrogen supplied by Scott Specialty gases. An independent calibration, by the MOE audit group, against an NBS traceable standard was within the 10% accuracy estimated from the standard and the errors in the propagated errors. The conversion efficiency was determined by using an in house fabricated gas phase titration system which produced NO<sub>2</sub> from the NO standard by the addition of less than a stoichiometric quantity of ozone. These calibrations were performed weekly in the latter stages of the study, but more frequently earlier. The sensitivity of the NO analyser was ~800 counts/ppbv and a zero air background of ~800 counts gave a one second detection limit (2 $\sigma$ ) of 70 ppt, slightly above the quoted value of 50 pptv. However, since the data were recorded as 5 min averages, more than a 10-fold improvement in this detection limit was expected. The consistency of exceedingly low values at night suggest that this improvement in detection limit was obtained. The converter efficiency was typically 45%.

NO and NO<sub>2</sub> were measured using an unmodified Thermolectron model 42S high sensitivity chemiluminescent analyser equipped with a molybdenum reduction converter. The detection limit and noise are quoted as 50 and 25 pptv, respectively, for a time constant greater than 120 s, which is much shorter than the 30 min averaging used here. However, the nighttime NO values measured by this instrument were higher than those measured by the TECAN instrument suggesting a bias at low concentrations. Thus we have not used data from this instrument for concentrations below 200 pptv. The converter was not placed external to the instrument, so there may be some question as to the inlets ability to pass nitric acid. The residence time in the manifold and the instrument inlet are short so the losses of nitric acid are assumed negligible. This instrument was calibrated before, during and after the study against the NBS NO standard mentioned above and the converter efficiency tested against NO<sub>2</sub> produced by a gas phase titration of the NO standard. The instrument zero and span were checked daily from midnight to 0030 h.

The two NO instruments agreed well with the common NBS standard and this agreement continued throughout the measurement campaign for concentrations greater than 200 pptv, the functional detection limit of the NO<sub>2</sub> analyser as used in this study. Since the TECAN instrument had a significant down time, a composite NO data set was constructed where the nighttime and low concentration data were generated by the TECAN instrument, otherwise the data from the Thermolectron instrument were used. The NO<sub>x</sub> quoted in this paper is the sum of this NO and the NO<sub>2</sub> from the TECAN instrument, even though the NO<sub>2</sub> was always derived by difference using the TECAN measured NO.

CO was measured using an unmodified Thermolectron model 48 non-dispersive infrared gas filter correlation spectrometer. The detection limit and the precision of the instrument are quoted as 100 ppbv with a noise of 50 ppbv. These instruments are known to show a water and temperature variation in the zero baseline (Parrish *et al.*, 1991). This instrument was calibrated daily (from midnight to 0030) against a certified CO standard diluted with dry zero air. The use of dry zero air for calibration would provide an offset in the absolute CO concentration. However, as the diurnal water concentration typically changed by less than 10% and the instrument temperature variation was small, the data obtained could still be used to measure changes in CO concentration. The instrument zero and span were checked

daily against zero air and a diluted NBS CO standard from midnight to 0030 h.

SO<sub>2</sub> was measured by a Thermolectron model 46 fluorescence analyser. This has a detection limit of 100 pptv and a precision of the larger of 1% or 1 ppbv. The instrument zero and span were checked daily, from midnight to 0030 h, against zero air and a standard obtained by dilution of the output from a permeation tube, which was calibrated gravimetrically.

PAN was measured using a gas chromatograph with electron capture detection. Air was drawn through a 5  $\mu$ m Teflon filter to remove particulate matter. Separation was achieved using a glass column (6.3 mm o.d., 105 cm length) packed with 10% Carbowax on Chromosorb G-AW with 5% CH<sub>4</sub> in argon at a flow rate of 65 cm<sup>3</sup> min<sup>-1</sup> as the carrier gas. The column was maintained at 35°C and the Valco model 140BN ECD detector at 50°C. Injections of 5 ml air samples were made every hour. The PAN retention time was  $\approx$ 4 min and the peaks integrated by a HP3390 integrator. Calibrations were conducted using known concentration dynamically produced PAN/air samples, generated by bubbling N<sub>2</sub> through a solution of PAN in dodecane and quantified using a chemiluminescence NO<sub>x</sub> monitor as described in Blanchard *et al.* (1990). The estimated uncertainty in the concentrations reported here is  $\pm$  20% for measurements more than three times the detection limit of 0.01 ppbv.

Nitric acid was measured using a filter pack system similar to that described in Anlauf *et al.* (1985). The pack consists of a Teflon particulate filter followed by a nylon filter to absorb nitric acid, and finally a citric acid impregnated filter for ammonia determination. Two sets of filters were collected. A 6 h set sampled 0800–1400, 1400–2000, 2000–0200, 0200–0800 daily. In addition an integrated 24 h sample was collected. Only the 6 h nitric acid data were reported here.

The intensive field campaign ran from 15 July to 31 August 1992 with the data presented here being for the month of August. For nitric acid the four daily data points were linearly interpolated to give apparent 1 h data. The PAN measurements were used as the instantaneous measurements each hour. For the other species the 5 min data were averaged up to 30 min. These data were averaged over the month of August to give the average diurnal variation for each parameter.

## OBSERVATIONS AND DISCUSSION

### General observations

The summer of 1992 was, in Southern Ontario, an atypically cool and cloudy season. As a result there were no identified ozone exceedences in the Windsor Quebec corridor. Figure 2 shows the time series of ozone measurements made at the site for the month of August. This shows that only on one day did the ozone concentration approach the Canadian maximum acceptable level of 82 ppbv, and only on 10 of the 31 days did it exceed 60 ppbv. Thus the analysis of these data are likely biased towards lightly photochemically impacted air masses and their major use may be as a baseline against which to examine measurements during ozone "events".

### Ozone

The average diurnal variation of ozone throughout the month of August is shown in Fig. 3. Ozone exhibits the characteristic diurnal variation of a "flatland" site in which the formation and breakup of the

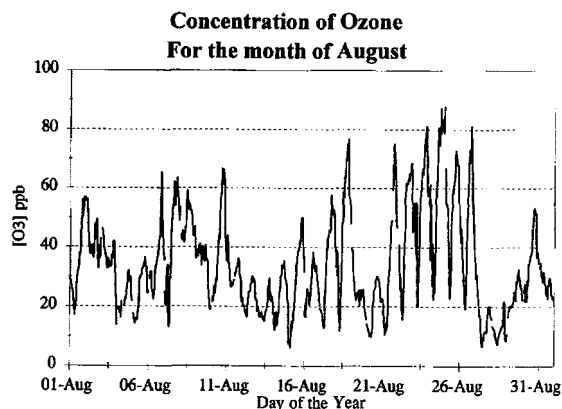


Fig. 2. Time series of ozone concentrations measured at the Hastings site for the month of August 1992.

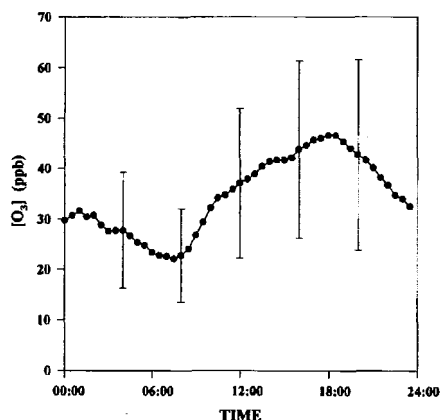


Fig. 3. The diurnal variation of the average ozone for the month of August 1992. One standard deviation of the means of the measurements are indicated.

nocturnal boundary layer (NBL) has a major impact (see for example Hastie *et al.*, 1993; Parrish *et al.*, 1993).

The ozone concentration decreases from onset of the nocturnal inversion ( $\sim 1800$  h) and throughout the night, due to surface deposition and titration with NO emitted from the soil or combustion processes within the inversion layer. The concentration rises quickly upon breakup of the nocturnal inversion (at  $\sim 0900$  h) as air from aloft, that has not been subjected to the same loss processes, is mixed downward. Early afternoon ozone profile measurements, taken from the aircraft in the vicinity of the site, show almost no vertical variation in the ozone concentration from the surface to 1 km, indicating that the effects of the

nocturnal inversion have dissipated by that time (Mackay and Drummond, Unisearch Associates, Unpublished data). From 1100 to 1800 h there is a slow increase in the ozone concentration which is attributed to photochemical production.

While the shape of the profile is similar to that found for other sites, it is quantitatively somewhat different. Compared to the Bondville and Scotia sites, as described in Parrish *et al.* (1993), the morning minimum is less pronounced. This indicates that the nocturnal inversion is less well developed at this site, and/or that there are weaker sources of NO. Both of these possibilities are likely. The site is on the top of a hill close to a river, so there is a large amount of drainage flow that would give a weaker nocturnal inversion than in the valley sites. This is consistent with individual nighttime ozone measurements that often show intermittent increases as the NBL is disturbed. Also the low population density in the area would give lower anthropogenic NO emissions. The maximum daytime concentration is lower than found at the other sites. This can be explained in part by the impact, on the mean, of cleaner air parcels from the northwest quadrant. However, this is not the complete story as the time of the maximum ozone concentration is 1800 h, almost 5 h after solar noon and 2-3 h later than reported for other sites. While the daytime increase in ozone is attributed to photochemical production, the late afternoon maximum is totally inconsistent with local ozone production. It is more in keeping with the measured ozone having been produced earlier in the day, somewhere with higher solar irradiance, and transported to the site. The diurnal ozone profile observed here is similar to those reported for the other Ontario sites, i.e. Egbert (Parrish *et al.*, 1993) and Dorset (Hastie *et al.*, 1993), which are also impacted by clean air masses and transported ozone.

## NO<sub>y</sub> and NO<sub>x</sub>

The August average NO<sub>y</sub> concentration variation is shown in Fig. 4. As with ozone, the NO<sub>y</sub> diurnal variation resembles that for a "flatland" site, most notably Egbert, Ontario (Parrish *et al.*, 1993). The daytime value of around 2.5 ppbv is lower than the U.S. flatland sites, and the NO<sub>y</sub> concentration reaches a maximum around midnight indicating a local surface source under the NBL, but one which is smaller than that observed at Bondville or that implied by the morning peak at Scotia (Parrish *et al.*, 1993).

An interesting feature is the local maximum at around 0900 h. There appears to be insufficient local traffic to generate a morning "rush hour" peak. Parrish *et al.* (1993) report a similar effect at Scotia which they attribute to the valley site being isolated from the local sources. The emissions that accumulate under the NBL are then transported to the site as the NBL breaks up. This explanation cannot apply to Hastings as the site is on a hilltop although still well within the NBL. The stable stratification within the NBL coupled with the drainage flow off the hill may serve to keep some of the nocturnal surface emissions below the level of the measurement site. As the NBL breaks up in the morning the enhanced mixing brings the higher surface concentrations to the site. This effect would be short lived as the mixing of air from above the inversion would ultimately dilute the nighttime accumulations, as observed.

Figure 5 shows the NO<sub>x</sub> variation. It has the same shape as the NO<sub>y</sub> in Fig. 4, and examination of the magnitudes of the changes in NO<sub>y</sub> discussed above shows they are almost entirely due to changes in NO<sub>x</sub>. There is clearly a NO<sub>x</sub> source under the NBL driving the NO<sub>y</sub> variability. Although emission from soil is likely to be a significant source of this NO<sub>x</sub>, there appears to be a combustion component, as discussed below.

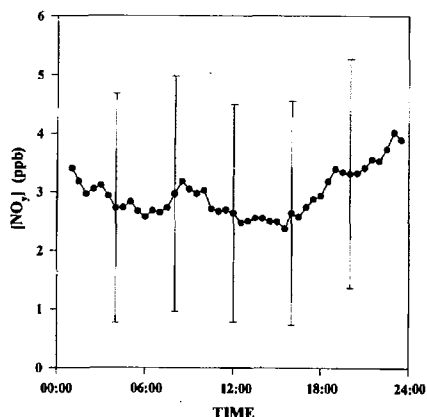


Fig. 4. The diurnal variation of the average NO<sub>y</sub> for the month of August 1992. One standard deviation of the means of the measurements are indicated.

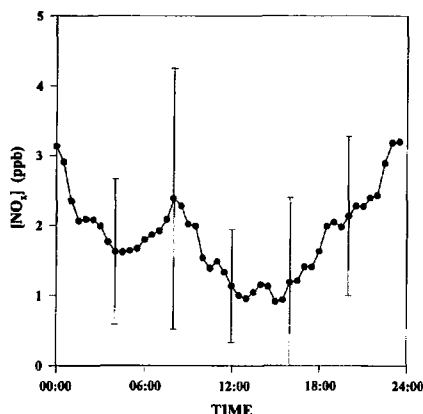


Fig. 5. The diurnal variation of the average NO<sub>x</sub> for the month of August 1992. One standard deviation of the means of the measurements are indicated.

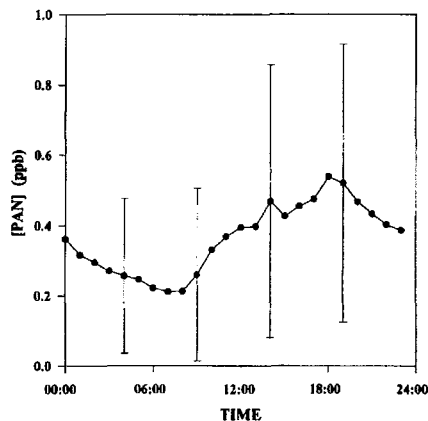


Fig. 6. The diurnal variation of the average PAN for the month of August 1992. One standard deviation of the means of the measurements are indicated.

## PAN

The PAN concentration, shown in Fig. 6, shows an almost identical diurnal variation to that of ozone (Fig. 3). This indicates the importance of deposition and reactive loss of PAN under the NBL, and daytime photochemical production. Since O<sub>3</sub> and PAN are produced simultaneously through NMHC/NO<sub>x</sub> chemistry, one would expect these two species to be well correlated if local scale chemistry is important. However PAN, like ozone, peaks late in the afternoon showing it is made elsewhere and transported to the site. Since the average temperature was approximately 26°C, the lifetime of PAN is on the order of a few hours, so the PAN observed at Hastings was, on

average, produced within ~100 km. Thus oxidant sources more distant than this are not responsible for the oxidant increases at this site. The values observed here are similar to those reported for summertime measurements at other locations in Southern Ontario (Shepson *et al.*, 1992).

The average nighttime loss of PAN is 63% whereas that of ozone is only 54%. If this loss is attributed entirely to surface deposition, the nighttime deposition velocity of PAN at this site is slightly greater than that of ozone. This is consistent with the previous observations of Shepson *et al.* (1992a) at rural Canadian sites.

#### CO

The CO data are presented in Fig. 7. The concentrations appear to be higher than reported elsewhere (Parrish *et al.*, 1991; Poulida, 1991), which is probably due to the systematic offset induced by the dry air calibration. Thus, as described above, only relative changes in the carbon monoxide are considered. The diurnal variation in carbon monoxide correlates extremely well with  $\text{NO}_x$ , particularly the morning peak, the afternoon minimum and the nighttime maxima. Thus the  $\text{NO}_x$  and CO appear to be from a single source, likely fossil fuel combustion. The  $\text{SO}_2$  data can be used to distinguish between  $\text{NO}_x$  and CO from mobile sources and those from stationary sources, as the latter have much higher  $\text{SO}_2$  to  $\text{NO}_x$  ratios. The  $\text{SO}_2$  data are shown in Fig. 8. They show an increase similar to  $\text{NO}_x$  and CO, as a result of downward mixing of high concentrations from aloft as the NBL breaks up. However, they have little in common with the  $\text{NO}_x$  or CO during the day and in the evening. This lack of correlation with  $\text{SO}_2$  shows that the CO and at least some of the  $\text{NO}_x$  appear to be from mobile sources rather than stationary sources.

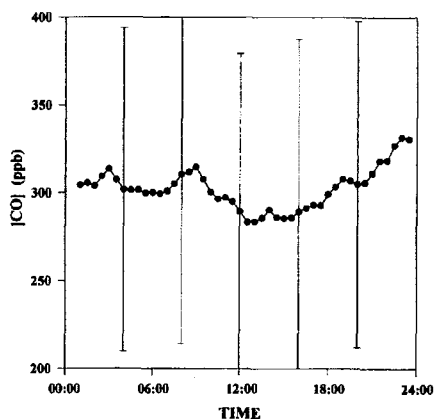


Fig. 7. The diurnal variation of the average CO for the month of August 1992. One standard deviation of the means of the measurements are indicated.

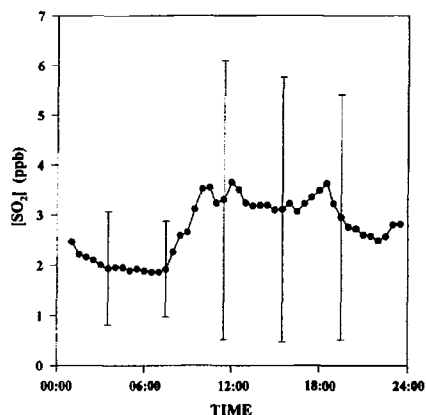


Fig. 8. The diurnal variation of the average  $\text{SO}_2$  for the month of August 1992. One standard deviation of the means of the measurements are indicated.

#### Distribution of nitrogen species

The ratio of individual nitrogen species of  $\text{NO}_x$  can be used to examine the age of the air masses being sampled.

Figure 9 shows the fraction of the  $\text{NO}_y$  present as  $\text{NO}_x$ . At night the  $\text{NO}_x$  source under the nocturnal inversion increases the  $\text{NO}_x/\text{NO}_y$  ratio to a maximum of 80%. The source of this  $\text{NO}_x$  will be discussed later. During the day this value drops to be approximately constant at ~40%. This is a higher fraction than reported for the flatland sites of Scotia and Bondville, (< 30%) but comparable to that for Egbert (Parrish *et al.*, 1993). Since  $\text{NO}_x$  is the emitted form of  $\text{NO}_y$ , this shows that there has been less nitrogen oxidation in these air masses than in the sites further south. Figure 9 also shows the fractions of the other measured nitrogen species to  $\text{NO}_y$ . The afternoon NO to  $\text{NO}_y$  ratio is higher than for all sites other than Bondville. This is consistent with the higher  $\text{NO}_x$  fraction and the lower ozone concentration at Hastings, which enhances NO relative to  $\text{NO}_2$ . The  $\text{HNO}_3/\text{NO}_y$  ratio is comparable to that observed at Egbert and Scotia, although the combination of the 6 h  $\text{HNO}_3$  data with the 1 h  $\text{NO}_y$  data means that the variation in the ratio is due mostly to NO, and this makes detailed comparisons difficult. The contribution of PAN, the other major oxidized nitrogen species, to  $\text{NO}_y$  is less than observed at Scotia. This is in spite of the fact that the mean temperature at Hastings is slightly lower than at Scotia (26 cf 28°C) so the thermal stability of PAN would be greater. Hence the production of PAN must be much lower in the Hastings region than at Scotia. Egbert, which has a similar temperature, ozone concentration and NO to  $\text{NO}_y$  ratio also has a similar PAN to  $\text{NO}_y$  ratio (Parrish *et al.*, 1993). When compared to other rural North American sites, the differences in the distribution among the different odd

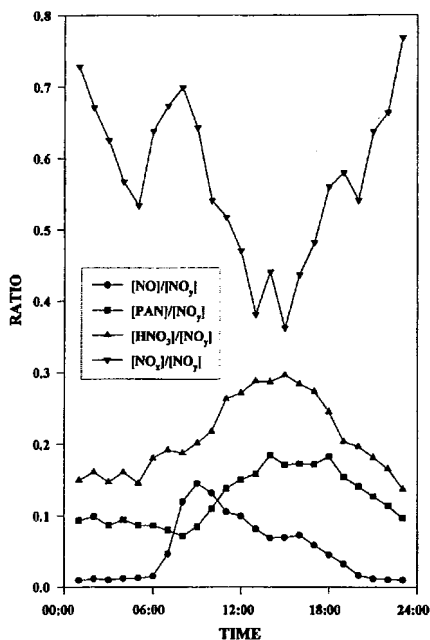


Fig. 9. The diurnal variation of the average ratios of  $\text{NO}_x$ , NO, PAN and  $\text{HNO}_3$  to  $\text{NO}_x$  for the month of August 1992. One standard deviation of the means of the measurements are indicated.

nitrogen compounds are consistent with a lower degree of nitrogen oxidation but with no other major discrepancies. This indicates that, despite the cleaner environment, the nitrogen chemistry being observed at the Hastings site is not markedly different from that at the other sites.

#### The source of the $\text{NO}_x$

The  $\text{NO}_x/\text{NO}_y$  ratios found here show that there is a relatively high fraction of  $\text{NO}_x$  at this site. If all the  $\text{NO}_y$  comes from a source well upwind of the site, the high  $\text{NO}_x$  must be due to a lower air mass reactivity giving a longer  $\text{NO}_x$  lifetime than the 8 h generally accepted (as calculated for an HO concentration of  $10^6 \text{ cm}^{-3}$ ). However the increase in  $\text{NO}_x$  at night shows that the high  $\text{NO}_x$  could be due to a local  $\text{NO}_x$  source, soil emission and/or combustion being the most likely. The local  $\text{NO}_x$  source strength necessary can be estimated from the accumulation of  $\text{NO}_x$  under the NBL. Taking the data from 1800-midnight and assuming the  $\text{NO}_x$  is dispersed into a layer 150 m deep, indicates a  $\text{NO}_x$  source strength of  $2.7 \times 10^{10} \text{ molecules cm}^{-2} \text{ s}^{-1}$ . This is consistent with emissions measured from ammonium nitrate fertilized fields in Southwestern Ontario by Shepherd *et al.* (1991), and with the upstate New York values in Williams *et al.* (1992). The farms surrounding the site were cropping corn, and local ammonium nitrate and liquid ammonia applications for corn are high (W. Moroz, personal communication). Thus it is reasonable that soil emissions could be the  $\text{NO}_x$  source. However, the strong correlation between CO and  $\text{NO}_x$  points towards an additional contribution from combustion sources. Examining the increase of the  $\text{NO}_x$  and CO under the NBL gives a CO/ $\text{NO}_x$  ratio of around 20. Emission inventories and measurements in Colorado (Parrish *et al.*, 1991) suggest a CO/ $\text{NO}_x$  ratio of 10 is indicative of fresh combustion emissions. However, Fujita *et al.* (1992) measured values in the Los Angeles area of around 20 for fresh combustion emissions. Hence we cannot say anything definitive about the age of the air masses giving rise to the high  $\text{NO}_x$  levels until the CO/ $\text{NO}_x$  ratio for fresh emissions in this region is determined. Thus there are contribu-

#### CORRELATION BETWEEN [O3] & [NO<sub>y</sub>]-[NO<sub>x</sub>] AT HASTINGS IN AUGUST 1992

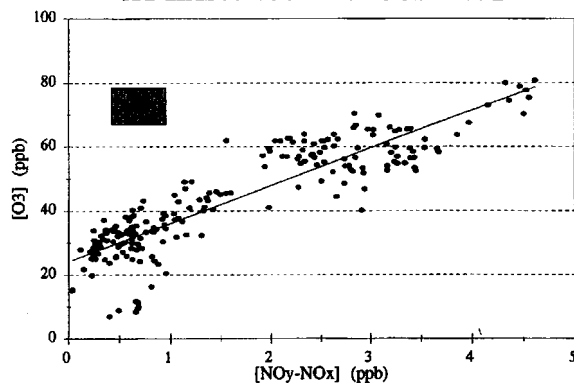


Fig. 10. Individual half hour averaged ozone concentration plotted against the concentrations difference  $\text{NO}_y - \text{NO}_x$ . Only data between 1000 and 1600 are plotted.

tions from both  $\text{NO}_x$  sources which need to be considered at this site and more detail on the combustion input is required.

#### OZONE-NITROGEN RELATIONSHIP

Trainer *et al.* (1993) have shown that the number of ozone molecules that are produced for every  $\text{NO}_x$  that is oxidized, i.e. the chain length for the production of ozone in the atmosphere, can be obtained from a plot of the ozone concentration against the difference between  $\text{NO}_y$  and  $\text{NO}_x$ , and that the intercept gives the regional background ozone level before the air masses are impacted with additional  $\text{NO}_x$ . They found that such a plot is linear, and report a chain length of about 8.5 for a site in rural Pennsylvania. Other groups have reported values of 12.3 in Tennessee (Olszyna *et al.*, 1994), and 11.4 in Georgia (Kleinman *et al.*, 1994). Figure 10 shows that in the daytime there is also a linear relationship at this site with an average chain length of 12, consistent with the results from other rural North American sites. This shows that ozone production at all sites is driven by the same chemistry, and that the lower ozone observed at the Hastings site is due to the lower availability of  $\text{NO}_x$ . However, it should be noted that the  $\text{NO}_x/\text{NO}_y$  ratio is higher than at the other sites (see Fig. 9 and discussion above), implying a "younger" or less photochemically processed air mass than seen at these sites. Thus there is still ample  $\text{NO}_x$  to make ozone in the air masses being sampled at Hastings. The background ozone, as determined from the intercept of this plot, is 24 ppbv, similar to that observed in Georgia, but less than the 35 and 42 observed in Scotia and Tennessee respectively (Trainer, 1993; Kleinman *et al.*, 1994; Olszyna *et al.*, 1994). Thus, not only is there less impact of the recent  $\text{NO}_x$  inputs, but the background regional ozone concentration in this part of North America is lower.

#### CONCLUSIONS

A study of the data obtained during August 1992, as part of the SONTOS program, has shown that the average ozone and  $\text{NO}_y$  concentrations, at the Hastings site, are lower than found at other North American sites. This is due to the distance of the site from sources and the limited number of anthropogenic sources northwest of the site, so cleaner air is sampled from this direction. The air masses contain a higher fraction of the  $\text{NO}_y$  as  $\text{NO}_x$  than observed elsewhere showing the air masses have not undergone as much photochemical processing as those seen elsewhere. However, the chain length for ozone production is similar to that found in locations where there has been more photochemical activity, implying these air masses could still produce more ozone. The late afternoon maximum in ozone and PAN concentrations shows

that the bulk of these oxidants are made elsewhere and transported to the site.

The increase in  $\text{NO}_x$  at night suggests a local  $\text{NO}_x$  source. The flux needed to explain the observations is within the range of values from soil emissions, but the strong correlation with CO suggests a mobile combustion source. Both sources need to be examined in more detail.

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