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# Measurements of HONO during BAQS-Met

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## Abstract

Measurements of nitrous acid (HONO) were performed as part of the 2007 Border Air Quality and Meteorology Study (BAQS-Met) at the Harrow Ontario supersite between 20 June and 10 July 2007. Nitrous acid is an important precursor of the hydroxy radical and understanding its chemistry is important to understanding daytime oxidation chemistry. The HONO measurements were made using a custom built Long Path Absorption Photometer (LOPAP). The goal of this work was to shed light on sources of daytime HONO in the border region. During the course of the campaign HONO mixing ratios consistently exceeded expected daytime values by as much as a factor of 6. Mean daytime concentrations of 61 pptv were observed. While HONO decay began at sunrise, minimum HONO values were not measured until the late afternoon. There was little difference between the daytime (mean=1.5%) and night-time (mean=1.7%) ratios of HONO/NO<sub>2</sub>. Thus there was a very strong daytime source of HONO which is consistent with other recent studies. Correlations of daytime HONO production with a variety of chemical and meteorological parameters indicate that production is dependent on UV radiation, NO<sub>2</sub> and water vapour but is not consistent with a simple gas phase process. Apparent rate constants for the production of HONO from photolytically excited NO<sub>2</sub> and water vapour vary from 2.8–7.8×10<sup>-13</sup> cm<sup>3</sup> molec<sup>-1</sup> s<sup>-1</sup>, during the campaign.

## 1 Introduction

Nitrous acid plays an important role in the atmospheric chemistry of the troposphere. Typically it follows a diurnal cycle where the concentration of HONO increases at night and is destroyed in the morning through photolysis (Reaction R1). The photolysis of HONO results in the production of the hydroxyl radical and may be the dominant early morning source of the hydroxyl radical (Alicke et al., 2002, 2003; Harris et al., 1982;

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Platt et al., 1980).



Reaction (R1) causes a morning spike in hydroxyl radical concentrations, which kick-starts the oxidation of hydrocarbons. Besides HONO photolysis, OH can be produced by photolysis of ozone and formaldehyde (followed by the reaction of HO<sub>2</sub> with NO). OH is also a secondary product of the ozonolysis of alkenes. Nitrous acid's contribution to the OH budget affects photochemistry in both urban and rural areas. In urban environments HONO mixing ratios can reach several parts per billion (ppbv) (Harris et al., 1982), while in rural or remote environments 10's to 100's of parts per trillion (pptv) appear to be common (Acker et al., 2006). A study of HONO in a forest in 2005 found that HONO contributed 33% of the integrated daytime OH budget (Kleffmann et al., 2005), surpassing all other OH formation pathways.

In recent years there has been a large amount of interest in photolytic pathways for HONO formation. Nitrous acid production from photolytically enhanced reduction of NO<sub>2</sub> on humic acid like compounds (Stemmler et al., 2006) in addition to other organic surfaces (George et al., 2005) has been observed. Production occurred when these surfaces were irradiated with light between 300–420 nm under humid condition. Conversion efficiencies of NO<sub>2</sub> to HONO between 50 and close to 100% have been reported (Stemmler et al., 2006). Photolysis of ortho-nitrophenols has also been suggested as a relevant daytime production mechanism in the urban atmosphere (Bejan et al., 2006). An excellent overview of daytime HONO chemistry examining daytime sources and sinks has been published (Kleffmann, 2007).

Here we present results of HONO Measurements from the Border Air Quality Meteorology study (BAQS-Met) at the Harrow, Ontario supersite. The mixing ratios observed were higher than anticipated during the daytime hours. Daytime HONO production rates appear to be consistent with a heterogeneous photolytically enhanced source.

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## 2 Experimental

### 2.1 Site description

During the summer of 2007 the Long Path absorption Photometer (LOPAP) was deployed as part of the Border Air Quality and Meteorological Study (BAQS-Met) at the Harrow, Ontario (Essex County) supersite (42.03418, -82.9174). BAQS-Met was a major collaborative study to help understand the effects of the transborder flow of pollutants, lake effects and gas/particle processing that often occur in Southern Ontario. There were three Supersite locations during the study; Harrow, Ontario, Ridgetown, Ontario and Bear Creek, Ontario (southwest of Wallaceburg Ontario). Measurements were also performed at two smaller sites, one on Pelee Island, the other in Windsor Ontario. Harrow is in close proximity to the metropolitan Detroit, Michigan and Windsor, Ontario areas. It is a semi rural location which is frequently affected by emissions from Detroit/Windsor as well the Ohio Valley to the South and the Sarnia, Ontario region to the North.

### 2.2 Long path absorption photometer

Nitrous acid was measured at the Harrow site using a custom built Long Path Absorption Photometer located in the middle of a grass field on the grounds of Agriculture and Agri-Food Canada's Greenhouse and Processing Crops Research Centre. The LOPAP technique has been described in detail elsewhere, (Heland et al., 2001; Kleffmann et al., 2002) and is only briefly described here. The instrument is composed of two sections, a sampling unit, and a detection unit. The sampling section is composed of two glass coils (17 cm of glass each) in series, one for each channel. A 0.06 M sulfanilamide (SA) solution is pumped to and from each coil at a flow rate of  $0.4 \text{ mL min}^{-1}$ , (HONO is sampled forming a diazonium ion). Air is pulled through the coils at a flow rate of  $1 \text{ L min}^{-1}$ . No liquid is carried from channel 1 to channel 2. The liquid is pumped from the coil to a debubbler where any small air bubbles are separated from the liquid.

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The process in channel 2 is identical. Once the diazonium ion is formed, the solution is pumped through the debubbler and is mixed with a 0.2 mM solution of 1-naphthyl ethylenediamine dihydrochloride (NED), where it forms the azo dye. The azo dye is pumped from each channel into separate liquid core waveguides. The waveguides used were 2 m in length and purchased from World Precision Instruments (WPI LWCC, 2200). The azo dye can then be measured by photometry using a UV/VIS light source and a spectrometer as its absorption follows Beer's Law. The light source used was a Tungsten Halogen lamp (LS-1, Ocean Optics) while the detector was a 2-channel mini-CCD spectrometer (Ocean Optics S2000). All solutions are delivered using an 8-channel peristaltic pump (Ismatec). From gas phase calibrations it was determined that nitrous acid is sampled nearly quantitatively in the first channel (99%). Other slightly soluble species are sampled in both channels with the interference in the 1st channel removed by the subtraction of the signal in the 2nd channel. Interferences have been discussed at length by others (Kleffmann et al., 2002). A  $3\sigma$  detection limit of 5 pptv was determined for 5 min measurement with the LOPAP. At the Harrow site the custom built LOPAP was installed in a trailer that contained other standard instruments for measuring gas and aerosol concentrations. The sampling coil was mounted through a window of the trailer. During the campaign the instrument was calibrated using sodium nitrite ( $\text{NaNO}_2$ ) standard solutions.

### 2.3 Other measurements

Other concurrent measurements were made at the site including ozone based on UV-absorption,  $\text{NO}_x$  and meteorological parameters such as temperature, relative humidity, wind speed, wind direction, and barometric pressure. HONO photolysis frequencies ( $J_{\text{HONO}}$ ) were estimated from measurements using an Eppley total UV radiometer on the roof of the trailer. This estimation was based on a previously quantified relationship between the UV Radiometer and a HONO Chemical Actinometer (Wall et al., 2006). In that study a Heraeus Amersil Electrically Fused quartz cell was used as the photolysis cell on the roof of a building in Toronto, Ontario. The actinometer was set up so

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that known amounts of HONO could be sent through the cell to a high pressure liquid chromatograph (HPLC) detection unit or diverted directly to the HPLC detection unit. The measured difference was used to calculate values of  $J_{\text{HONO}}$ . Their estimated error in  $J_{\text{HONO}}$  values under clear sky conditions was 11% at sunrise and 4% at solar noon during the summer months. This relationship was used in order to estimate the values of  $J_{\text{HONO}}$  at the Harrow site. Based on the error in the original  $J_{\text{HONO}}$  measurement (from clear sky conditions)  $J_{\text{HONO}}$  values are estimated to be accurate within 20%. A list of instruments used is shown in Table 1.

### 3 Measurements of HONO at Harrow

Nitrous acid measurements were made between 20 June and 10 July 2007. During many nights of the campaign HONO concentrations would build up over the course of the night and begin to decrease in the morning when wind speeds increased and photolysis would begin. Minimum HONO concentrations were not reached until the late afternoon and rarely decreased below detection limits (5 pptv). The mean daytime mixing ratio of HONO was 61 pptv (maximum=473 pptv), while the mean night-time value was 102 pptv, (maximum=376 pptv). The majority of the  $\text{NO}_x$  observed was in the form of  $\text{NO}_2$ . The fraction of  $\text{NO}_x$  resulting from  $\text{NO}_2$  is likely artificially high, as a result of the 1 ppbv detection limit for NO of the  $\text{NO}_x$  monitor. Significant amounts of  $\text{O}_3$  (reaching upwards of 80 ppbv) may have helped suppress NO concentrations during the study. The NO data should however be treated with caution. During the period of 21 June to 27 June (Fig. 1), HONO mixing ratios consistently reached 300 pptv or more during the night-time. Winds during this time were generally from between 150–250°. The increases in HONO during this period were matched by increases in  $\text{NO}_2$  mixing ratio. As the sun rose concentrations would show an initial sharp decrease in the early morning which would continue more slowly throughout the day until minimum mixing ratios were reached generally late in the afternoon. As the sun set (typically not until ~21:00 EST), and wind speeds decreased, HONO and  $\text{NO}_2$  mixing ratio would

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increase. Nitrous acid mixing ratios were consistently lower between 28 June and 6 July (Fig. 3). Winds during this time were typically from the North East bringing pollution from the Sarnia, Ontario area (the location of many chemical, plastics and rubber making facilities).

5 The night of 23/24 June was of interest as HONO concentrations reached 200 pptv and remained roughly constant for the duration of the night. Since wind speeds were low that night it is not obvious why HONO concentrations would not rise for the duration of the night until the breakup of the boundary and onset of photolysis in the morning hours. This phenomenon has been observed before (Stutz et al., 2002). It was shown  
10 that NO<sub>2</sub> concentrations greater than 10 ppbv lead to HONO formation (positive HONO gradients) over grass in Milan. A compensation point in the HONO/NO<sub>2</sub> ratio of 3% was determined where HONO would begin to deposit on the grass surface under stable meteorological conditions. It was believed that NO<sub>2</sub> was hydrolyzing on the damp grass to produce the measured HONO. This is consistent with the HONO/NO<sub>2</sub> ratios  
15 observed on the night of the 23/24 when HONO/NO<sub>2</sub> ratios were between 2–4%. While NO<sub>2</sub> concentrations were not consistently greater than 10 ppbv on this night it is likely that deposition was the cause of the relatively constant HONO concentrations observed that night, with production matched by deposition.

During the night of 28/29 June HONO and NO<sub>2</sub> were also highly correlated (Fig. 4).  
20 Winds were consistently from the North East and decreased from 10 to <5 km hr<sup>-1</sup> in the early part of the evening. Two decreases in concentration of HONO, NO<sub>2</sub> and NO were observed. The first minima occurred at 01:00, while the second occurred at 04:00 (both local time). These minima correspond with increases in O<sub>3</sub> concentration. Ratios of HONO/NO<sub>2</sub> varied between 0.5–2 percent on this night. The increase in O<sub>3</sub> concentration during both minima in HONO and NO<sub>x</sub> is likely due to entrainment of fresh air  
25 from above the boundary diluting the HONO and NO<sub>x</sub> rich air below the boundary layer and decreasing concentrations of both. It is also possible that small changes in wind direction contributed to the decreases in NO<sub>x</sub> and HONO concentration. Mixing ratios of HONO and NO<sub>2</sub> began to decrease on the morning of the 29th (~06:00 local time)

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as O<sub>3</sub> concentrations increased, prior to the onset of photolysis.

### 3.1 Variations in HONO/NO<sub>2</sub> ratio during the BAQS-Met study

The ratios of HONO/NO<sub>x</sub> and HONO/NO<sub>2</sub> over the course of the study were also examined. The ratios of HONO/NO<sub>x</sub> ranged from 0.05–10.1% (mean=1.6%) while those from HONO/NO<sub>2</sub> were between 0.06–12% (mean=1.5%).

The HONO/NO<sub>2</sub> ratio can be used as an indicator of the extent of HONO production from NO<sub>2</sub> (Kleffmann et al., 2003). Using the HONO/NO<sub>2</sub> ratio on a night when meteorological conditions were stable, a conversion efficiency of NO<sub>2</sub> to HONO could be calculated. On the night of the 23rd/24th the HONO/NO<sub>2</sub> ratio increased from 0.5–4% over the course of a four hour period (20:00–00:00 local time) (Fig. 5). This corresponds to a first order conversion rate of  $2.43 \times 10^{-6} \text{ s}^{-1}$ . This value of the rate of HONO formation is also comparable to values calculated from data in polluted urban sites such as Berlin ( $3.3 \times 10^{-6} \text{ s}^{-1}$ ) and Milan ( $5.8 \times 10^{-6} \text{ s}^{-1}$ ) (Alicke et al., 2002, 2003).

On average the ratio of HONO/NO<sub>2</sub> did not vary greatly from the day (mean=1.5%) to the night (mean=1.7%) implying that a daytime source converting NO<sub>2</sub> to HONO would have to be significantly more rapid than the night-time hydrolysis of NO<sub>2</sub> since the photolytic lifetime of HONO at midday is only 10–15 min.

### 3.2 HONO/NO<sub>2</sub> ratio as a function of wind direction

To determine if increases in the HONO/NO<sub>2</sub> ratio were related to the direction of wind impacting the site the ratios of HONO/NO<sub>2</sub> were examined as function of wind direction during the day and night. Polar plots (Fig. 6) showing HONO/NO<sub>2</sub> ratios as a function of wind direction for both day and night-time with wind speeds less than  $5 \text{ km h}^{-1}$  were removed due to unclear wind direction during low wind conditions. Shown on these plots is the approximate direction of the nearest, major industrial centres. During the daytime period the highest ratios are observed when winds are from between 180–270°. In both cases air masses would have to travel over Lake Erie in order to reach

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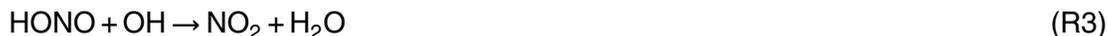


the Harrow site. Ratios during the daytime when winds were from either the North East or South East are also lower than during the night-time hours. The night-time ratio plot shows HONO/NO<sub>2</sub> ratios >5% coming from the South and South-west. This is not observed in the daytime data. Ratios greater than 3% are not often observed when winds are from 270–90° during either the day or the night. It may be that increased humidity from air travelling over the lake may increase the conversion of NO<sub>2</sub>-HONO.

### 3.3 Daytime production of HONO

Daytime production of HONO was examined closely since HONO mixing ratios remained well above zero during the daytime for the duration of the study. This cannot be explained by the first order conversion rate determined in the previous section ( $2.43 \times 10^{-6} \text{ s}^{-1}$ ), as that is roughly two orders of magnitude smaller than HONO photolysis at midday. It is not believed that there any large emission sources of HONO in the area of the Harrow site. There was minimal vehicle traffic passing the site, and no large NO<sub>x</sub> emission sources in the immediate vicinity which could account for the high daytime concentrations.

In order to determine the amount of HONO present that could not be accounted for during the daytime hours, a gas phase photo stationary state (PSS) of HONO was assumed, in order to calculate a background of HONO. The PSS is calculated from (Reaction R1), the reaction of NO with OH to form HONO (Reaction R2), the loss of HONO by reaction with OH (Reaction R3)



As well as a heterogeneous formation rate (taken to be the night-time conversion rate of NO<sub>2</sub> to HONO) to give

$$[\text{HONO}]_{\text{PSS}} = \frac{(k_2[\text{NO}][\text{OH}] + \text{heterogeneous HONO})}{J_{(\text{HONO})} + k_3[\text{OH}]} \quad (1)$$

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Since OH measurements were not available an approximation was made. A noontime OH value of  $1 \times 10^6$  molec  $\text{cm}^{-3}$  was used and mixing ratios were estimated by using a diurnal variation (noontime maximum, zero at sunrise and sunset) given by a  $\cos^3$  (SZA) function (where SZA is the solar zenith angle). A  $\cos^3$  function was chosen since its shape closely matches the profile of  $\text{O}^1\text{D}$  production from  $\text{O}_3$  photolysis. Using these estimated OH values in addition to measured NO and derived  $J_{\text{HONO}}$  values, a HONO PSS was calculated. While there is uncertainty in the OH concentration, the calculated PSS values are so small that this is not likely to be significant. Thus the uncertainty in the HONO produced by identified sources mostly arises from the “dark” HONO formed and in the loss from photolysis, whose uncertainty is taken to be 20%. The calculated  $[\text{HONO}]_{\text{PSS}}$  values were found to be only a few parts per trillion indicating that virtually all of the actually observed daytime HONO present was formed through other sources. This background HONO is subtracted from the measured total.

Using the HONO sinks (photolysis and reaction with OH) and the measured HONO amounts, a daytime production rate for the unknown source could be calculated by replacing ( $k_3[\text{NO}][\text{OH}] + \text{heterogeneous chemistry}$ ) with the unknown HONO source and rearranging (Eq. 1).

Correlations between HONO production rates and various gas, aerosol and meteorological parameters were examined. The  $R^2$  values for these correlations are shown in Table 2. The strongest correlations found were with  $J_{\text{HONO}}$ ,  $J_{\text{HONO}}[\text{NO}_2]$  and  $J_{\text{HONO}}[\text{NO}_2][\text{H}_2\text{O}]$ . It was expected that a correlation with  $J_{\text{HONO}}$  would be present, however this correlation is strengthened by the inclusion of  $\text{NO}_2$  and  $\text{H}_2\text{O}$  mixing ratios. The correlation between HONO production and particle surface area density alone ( $R^2 = 0.31$ ) was not strong. The surface area density was determined from the particle size distribution measured with a fast mobility particle sizer using the assumption of a spherical particle shape. Particles measured by the instrument were in the range of 5.5 to 560 nm. While it is likely that HONO production on aerosol surface is still important it appears likely that the majority of production occurred on the ground (e.g. grass or soil), or conceivably that production is occurring homogeneously in the gas phase as

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has been previously suggested (Li et al., 2008).

## 4 Comparison with laboratory studies

### 4.1 Survey of laboratory studies

There have been conflicting reports as to the significance of the photo enhanced reaction of  $\text{NO}_2$  with water vapour



In a study conducted in 1997 (Crowley and Carl, 1997),  $\text{NO}_2$  was excited using radiation between 430–450 nm as well as 532 nm. OH was generated by the reaction of  $\text{NO}_2^*$  with  $\text{H}_2\text{O}$  were excited using an OH resonance lamp to promote the OH ( ${}^2\Sigma^+$ )  $\leftarrow$  OH ( ${}^2\Pi$ ) transition at 309 nm. An upper limit for the rate constant of  $1.2 \times 10^{-14} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$  was determined.

A second study performed in 2008 (Li et al., 2008) studied the photo-enhancement using radiation at longer wavelengths, 565, 590 and 612.5 nm and determined a rate constant of  $1.2 \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ . The OH generated from R5 was monitored using laser induced fluorescence (LIF).

Attempts to replicate the 2008 results (Carr et al., 2009) using only unfocused laser light, as used by Crowley and Carl (1997) failed to observe any OH production and an upper limit of that study was a factor of 17 smaller than that of 2008 results and in agreement with the initial study (Crowley and Carl, 1997). The difference in the measured rate constants is as yet unresolved. This reaction was examined as a potential source of HONO at the Harrow site.

In order for a comparison with our chemical HONO production rate to be performed, our estimates of  $J_{\text{HONO}}$  were converted to estimates of  $J_{\text{NO}_2}^*$ . This is a two step process.

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$J_{\text{NO}_2}$  can be derived from  $J_{\text{HONO}}$  using a known relationship (Kraus and Hofzumahaus, 1998).

$$J_{(\text{HONO})} = 0.189 \times J_{(\text{NO}_2)} + 8.483 \times 10^{-2} J_{(\text{NO}_2)}^2 \quad (2)$$

$J_{\text{NO}_2}^*$  is taken to be 5 times the rate of  $\text{NO}_2$  photolysis based on the overall  $\text{NO}_2$  cross section and the UV/VIS spectrum of sunlight (Crowley and Carl, 1997). While  $J_{\text{NO}_2}^*$  is not a true photolysis rate, (it is the rate constant of the excitation of  $\text{NO}_2 \rightarrow \text{NO}_2^*$ ), the  $J_{\text{NO}_2}^*$  nomenclature is retained to remain consistent with the literature. This calculated HONO production rate from the possible reaction can be compared with the HONO production rates for the Harrow data set which is estimated based on the measured daytime HONO concentrations and the known daytime losses (photolysis and reaction with OH).

## 4.2 Apparent rate constants derived from BAQS-Met

Four time periods were chosen for examination. The time periods were chosen based on the relatively constant concentrations of HONO present and consistency of air mass. The apparent rate constants for the chosen periods are shown in Table 3. The rate constant plots are shown in Figs. 7–10. The error value associated with the rate constant represents 1 standard deviation of the apparent rate constant value. In each case the  $k$  value is different. The dominant wind directions were different each day (Table 3), and therefore the sources of  $\text{NO}_2$  and “fetch” varied accordingly. Air mass origins during the four periods were further examined by using NOAA’s HYSPLIT model to compute back trajectories (<http://www.arl.noaa.gov/ready/hysplit4.html>). During the afternoon of June 21 winds were from the North West, the direction of Detroit/Windsor and several electricity generating and chemical manufacturing plants. A larger apparent  $k$  value was calculated for the afternoon of 24 June when winds from the South West brought air from the general direction of Toledo, Ohio. There are several electricity generating units on the United States side of the border ranging from the South

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West to North West presumably producing large amounts of  $\text{NO}_x$ . The afternoon of 24 June yielded the largest apparent  $k$  value. During the morning of 30 June the wind directions were from the North East and gave the smallest apparent  $k$  value. Winds were from the South West during the morning of 4 July yielding an apparent  $k$  value of  $(4.4 \pm 0.06) \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ . These winds correspond to the Toledo, Ohio region (South West). The variation in apparent rate constants for formation of daytime HONO is inconsistent with a gas phase formation mechanism, but could possibly be explained by a surface reaction (or variety of surface reactions) as has been suggested in the literature (George et al., 2005a; Ndour et al., 2008; Stemmler et al., 2006, 2007). As the measurement site is several kilometres away from the lake in either direction it is unlikely that the measured HONO was produced over the lake at midday when  $J_{\text{HONO}}$  is highest. With wind speeds as high as  $10 \text{ km hr}^{-1}$  HONO could not be brought to the site within its midday lifetime of 10 to 20 min. This would mean that during midday the HONO was produced between the measurement site and the shoreline over ground surfaces. If the homogeneous rate constant of  $1.2 \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$  was assumed for this period, it could still not account alone for the excess HONO produced as the calculated production rate is more than a factor of 2 larger. This means that greater than 50% of the HONO observed would have to be a result of surface reactions.

## 5 Conclusions

A custom long path absorption photometer (LOPAP) was successfully deployed to measure HONO in Southern Ontario. The instrument provided excellent sensitivity (3 $\sigma$  detection limit=5 pptv) and response time (5 min) for making high quality HONO measurements. The measurements of HONO at the Harrow site during BAQS-Met show high concentrations of daytime HONO present with a mean value of 61 pptv. These larger than anticipated daytime concentrations imply that HONO may play a larger role in the midday OH budget than originally thought. A night-time compensation point for

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heterogenous production and deposition of HONO consistent with the work of Stutz et al. (2002) was also observed during the night-time when stable meteorological conditions were present. Since the slopes of the correlations between chemical HONO production and the calculated HONO production are changing it is very unlikely that the observed HONO is produced solely through a simple gas phase process. Days featuring similar wind direction, 24 June and 4 July, showed apparent rate constants which varied by nearly a factor of two. Many laboratory studies have suggested efficient heterogeneous conversion of NO<sub>2</sub> on surfaces, enhanced by photo-excitation, which appears to be more consistent with the Harrow data than a homogeneous process.

*Acknowledgements.* The authors would like to thank Greg Evans from the University of Toronto and Nick Karellas from the Ontario Ministry of the Environment for providing measurements of particle surface area densities, meteorological data, and measurements of O<sub>3</sub> and NO<sub>x</sub> from the Harrow site as well as Agriculture and Agri-Food Canada for the use of the site.

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**Table 1.** List of Instrumentation at Harrow Supersite.

Species	Instrument	Affiliation
HONO	LOPAP	York University
NO <sub>x</sub>	NO <sub>x</sub> analyser (Thermo-Scientific)	Ontario Ministry of the Environment
O <sub>3</sub>	O <sub>3</sub> monitor (Thermo-Scientific)	Ontario Ministry of the Environment
<i>J</i> <sub>HONO</sub> (estimate)	Total UV Radiometer (Eppley Labs)	York University
Particle Size Distribution	FMPS (TSI)	University of Toronto

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**Table 2.** Tabulated  $R^2$  values for HONO production correlations.

Correlation Parameter	$R^2$
$\text{NO}_x$	0.12
$\text{NO}_2$	0.04
NO	0.32
$J_{\text{HONO}}$	0.62
$J_{\text{HONO}}[\text{NO}_2]$	0.70
$J_{\text{HONO}}[\text{NO}_2][\text{H}_2\text{O}]$	0.76
$\text{O}_3$	0.16
Particle Surface area Density	0.31
$J_{\text{HONO}}[\text{NO}_2](\text{Particle Surface Area Density})$	0.61
Relative Humidity	0.14
Wind Speed	0.21
Temperature	0.25

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**Table 3.** List of apparent rate constants and dominant wind directions during selected periods of the Harrow study.

Time Period	$k$ ( $\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ )	$R^2$	Dominant Wind Direction
All daytime data	$(4.5 \pm 3.5) \times 10^{-13}$	0.75	–
21 July 2007 (12:00–18:00 EST)	$(6.1 \pm 0.3) \times 10^{-13}$	0.82	North West
24 July 2007 (12:00–18:00 EST)	$(7.8 \pm 0.3) \times 10^{-13}$	0.80	South West
30 June 2007 (06:00–12:00 EST)	$(2.9 \pm 0.07) \times 10^{-13}$	0.90	North East
4 July 2007 (06:00–12:00 EST)	$(4.4 \pm 0.06) \times 10^{-13}$	0.97	South West

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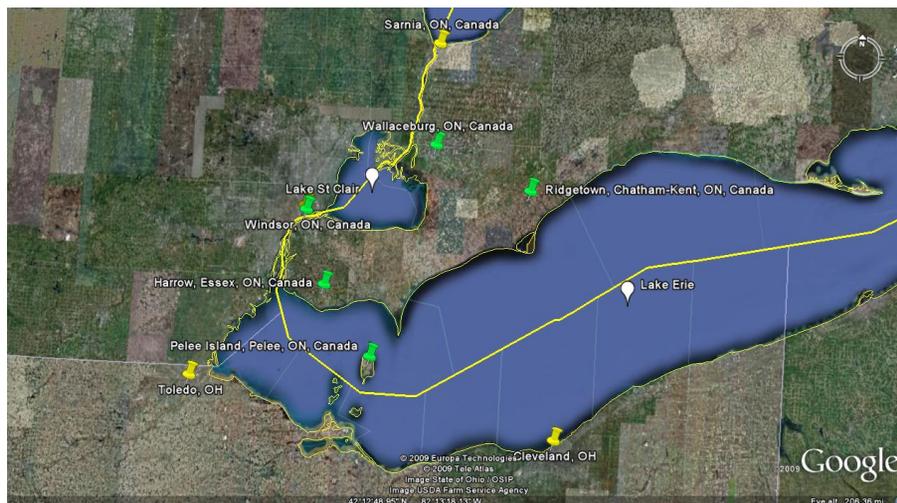
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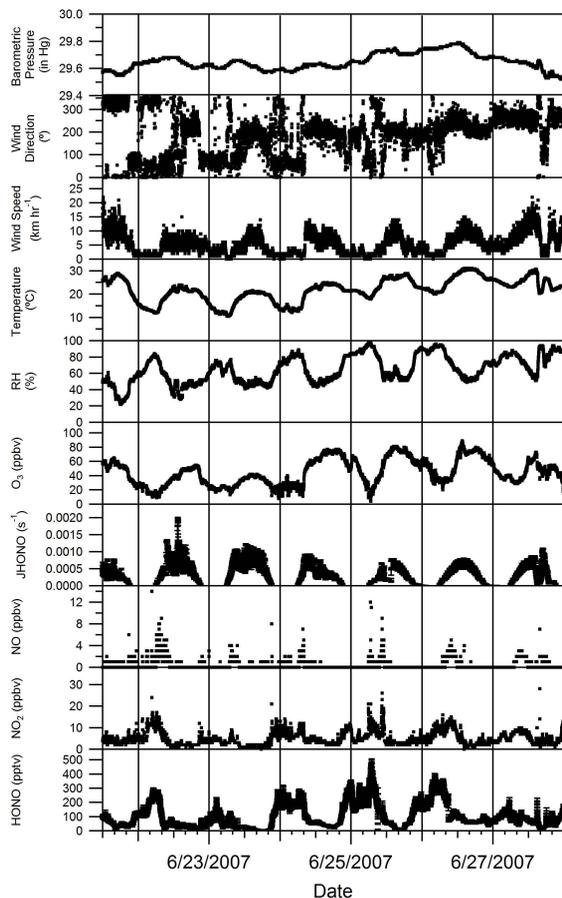
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**Fig. 1.** Map South Western Ontario showing BAQS-Met measurement sites in green and industrial towns in the Lake Erie area (courtesy of Google Earth).



**Fig. 2.** Time series of the measurements of HONO, NO<sub>2</sub>, NO,  $J_{\text{HONO}}$ , O<sub>3</sub>, relative humidity, temperature, wind speed, wind direction and barometric pressure at the Harrow measurement site from 21 June–27 June 2007.

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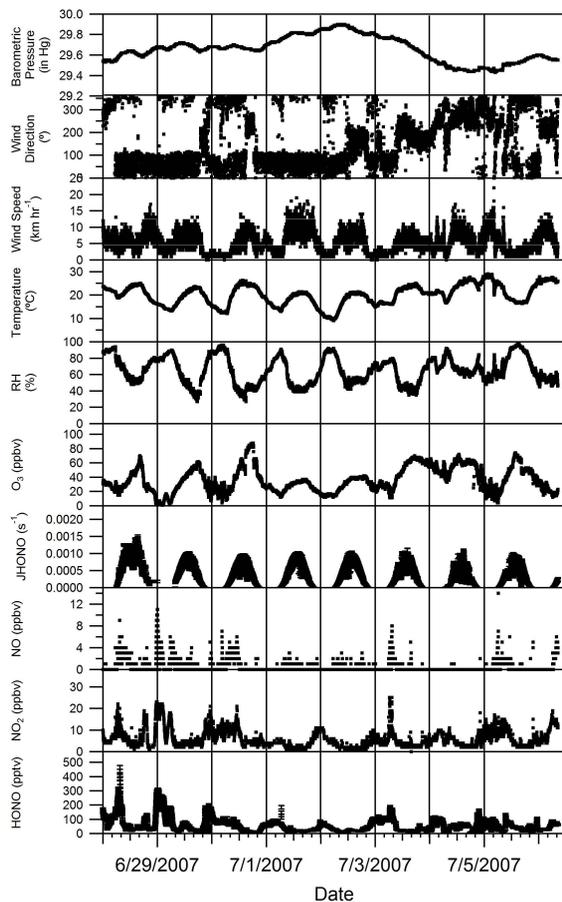
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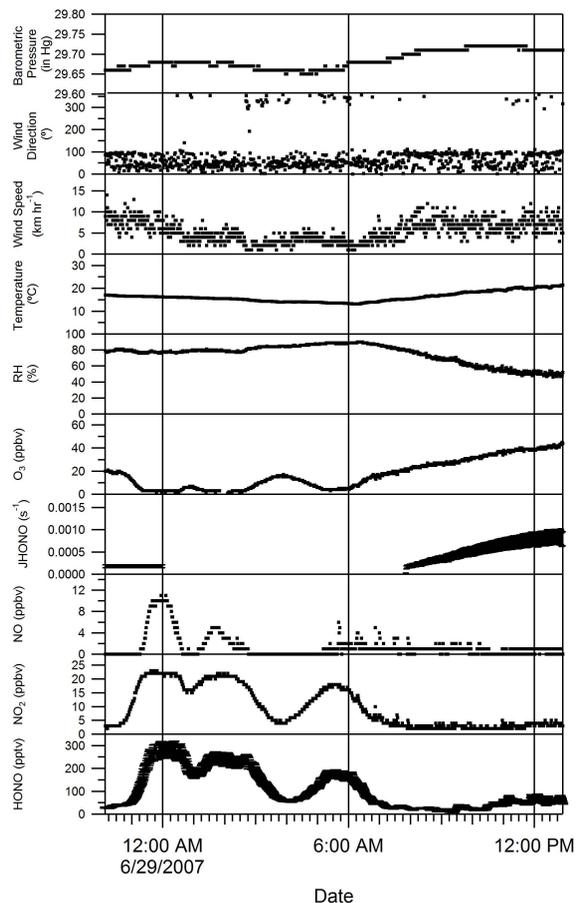
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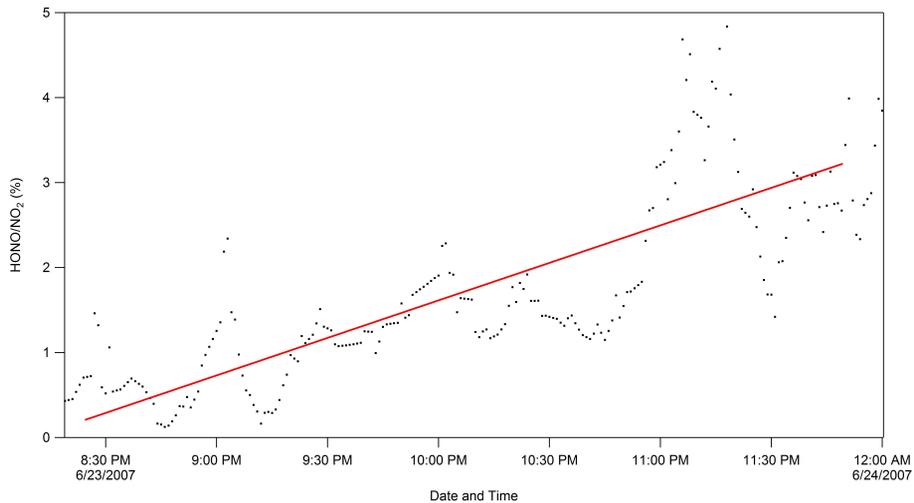




**Fig. 3.** Time series of the measurements of HONO, NO<sub>2</sub>, NO,  $J_{\text{HONO}}$ , O<sub>3</sub>, relative humidity, temperature, wind speed, wind direction and barometric pressure at the Harrow measurement site from 28 June–6 July 2007.



**Fig. 4.** Measurements of HONO, NO<sub>2</sub>, NO,  $J_{\text{HONO}}$ , O<sub>3</sub>, relative humidity, temperature, wind speed, wind direction and barometric pressure at the Harrow measurement site from 28 June–29 June 2007.



**Fig. 5.** Increase in HONO/NO<sub>2</sub> over the course of the evening of 23 June 2007.

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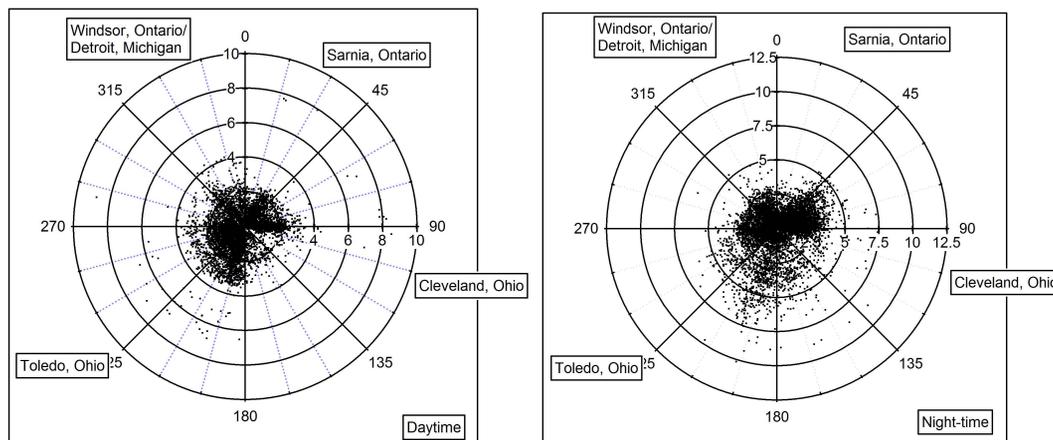
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**Fig. 6.** Polar plots of HONO/NO<sub>2</sub> (%) as a function of wind direction. The daytime ratios are in the top plot, the night-time ratios are in the bottom plot. Points where wind speeds are below 5 km/hr have been removed.

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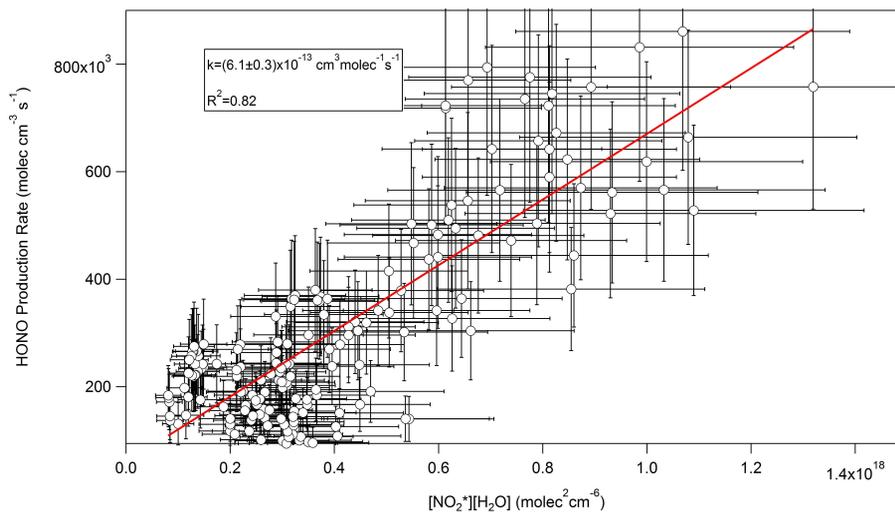
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**Fig. 7.** Plot of measured HONO production rate with the calculated HONO production rate for the afternoon of 21 June 2007.

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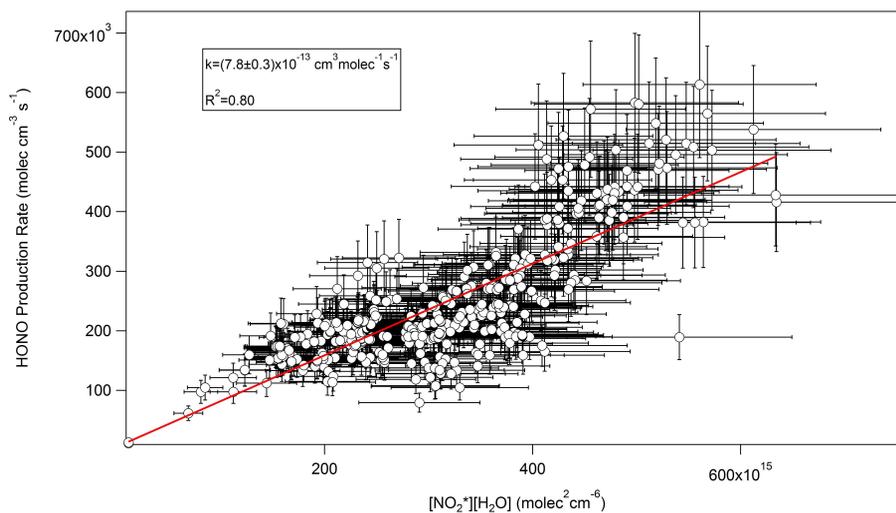
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**Fig. 8.** Plot of measured HONO production rate with the calculated HONO production rate for the afternoon of 24 June 2007.

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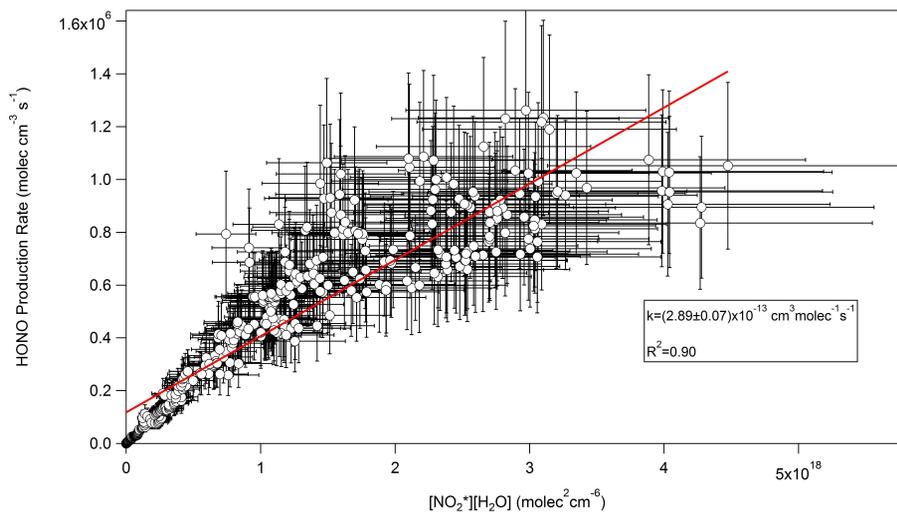
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**Fig. 9.** Plot of measured HONO production rate with calculated HONO production rate for the morning 30 June 2007.

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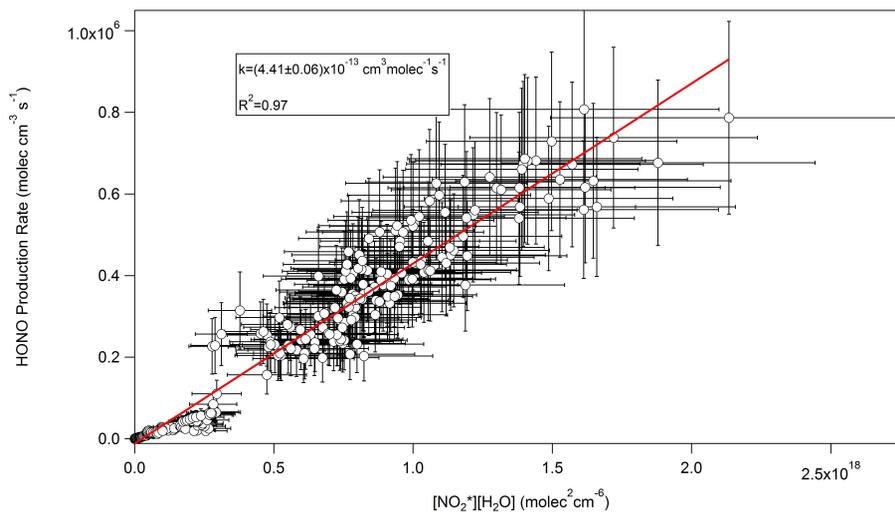
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**Fig. 10.** Plot of measured HONO production rate with the calculated HONO production rate for 4 July 2007.

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