Detailed budget analysis of HONO in central London reveals a missing daytime source

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Abstract

Measurements of HONO were carried out at an urban background site near central London as part of the *Clean air for London* (ClearfLo) project in summer 2012. Data was collected from 22nd July – 18th August 2014, with peak values of up to 1.8 ppbV at night and non-zero values of between 0.2 and 0.6 ppbV seen during the day. A wide range of other gas phase, aerosol, radiation and meteorological measurements were made concurrently at the same site, allowing a detailed analysis of the chemistry to be carried out. The peak HONO / NO_x ratio of 0.04 is seen at ~02:00 UTC, with the presence of a second, daytime peak in HONO / NO_x of similar magnitude to the night-time peak suggesting a significant secondary daytime HONO source.

A photostationary state calculation of HONO involving formation from the reaction of OH and NO and loss from photolysis, reaction with OH and dry deposition shows a significant underestimation during the day, with calculated values being close to zero, compared to the measurement average of 0.4 ppbV at midday. The addition of further HONO sources from the literature, including dark conversion of NO_2 on surfaces, direct emission, photolysis of ortho-substituted nitro phenols, the postulated formation from the reaction of $HO_2 \times H_2O$ with NO_2, photolysis of adsorbed HNO_3 on ground and aerosols, and HONO produced by photosensitized conversion of NO_2 on the surface increases the daytime modelled HONO to 0.1 ppbV, still leaving a significant missing daytime source. The missing HONO is plotted against a series of parameters including NO_2 and OH reactivity (used as a proxy for organic material), with little correlation seen. Much better correlation is observed with the product of these species with $j(NO_2)$, in particular NO_2 and the product of NO_2 with OH reactivity. This suggests the missing HONO source is in some way related to NO_2 and also requires sunlight. Increasing the photosensitized surface conversion rate of NO_2 by a factor of 10 to a mean daytime first order loss of ~6×10^{-5} s^{-1} (but which varies as a function of $j(NO_2)$) closes the daytime HONO budget at all times (apart from the late afternoon) suggesting that urban surfaces may enhance this photosensitized source. The effect of the missing HONO to OH radical production is also investigated and it is shown that the model needs to be constrained to measured HONO in order to accurately reproduce the OH radical measurements.

1 Introduction

The hydroxyl radical (OH) is the main daytime oxidant in the troposphere, playing a key role in the chemical transformations of trace species (Levy II, 1971). A major source of OH, especially in polluted environments, is the photolysis of nitrous acid (HONO) in the near UV region (R2). It has been shown in numerous studies that HONO can actually be the dominant early morning source of OH (Ren et al., 2003; Ren et al., 2006; Dusanter et al., 2009; Michoud et al., 2012) and has often been shown to also be significant during the rest of the day (Elshorbany et al., 2009; Hofzumahaus et al., 2009; Villena et al., 2011; Michoud et al., 2014). This is mainly due to unexpectedly high levels of HONO measured during daylight hours when fast photolysis would have been expected to keep concentrations low and hence insignificant for a source of OH. As a result of these studies, it has become clear that HONO

has the ability to initiate and accelerate daytime photochemistry and hence knowledge of its formation and loss are crucial to understanding tropospheric oxidation chemistry.

Typically, HONO in the troposphere would be expected to be governed by formation by the reaction between nitric oxide (NO) and OH (R2) and losses by photolysis (R1) and oxidation by OH (R3).

$$HONO + h\nu \rightarrow OH + NO \quad (\lambda < 400\ nm) \qquad (R1)$$

$$OH + NO + M \rightarrow HONO + M \qquad (R2)$$

$$HONO + OH \rightarrow H_2O + NO_2 \qquad (R3)$$

These reactions can be used, along with measurements of concentrations of the relevant species and HONO photolysis rates, to calculate a photochemical steady state concentration of HONO. Such calculations from field studies typically show a peak of HONO at night (when there is no photolysis), with levels in the low pptv range during the day. However, measurements usually show that daytime HONO levels can reach substantially higher concentrations than this, with mixing ratios up to a few hundred pptv frequently observed (Zhou et al., 2002; Kleffmann et al., 2005; Acker et al., 2006). It is clear from these analyses that there is an extra source of HONO present, which can have a significant impact on the atmospheric oxidising capacity due to its potential to form OH. A range of reactions have been postulated during the various studies to account for the missing source of HONO, with these likely to be heterogeneous either on aerosols or the ground itself. Major ground surfaces were recently confirmed by direct flux measurements of HONO (Ren et al., 2011; Zhou et al., 2011; Zhang et al., 2012). Tower measurements (Harrison and Kitto, 1994; Kleffmann et al., 2003; Oswald et al., 2015; Sörgel et al., 2011a, 2015; Stutz et al., 2002; Vandenboer et al., 2013; Villena et al., 2011; Vogel et al., 2003; Wong et al., 2012; Young et al., 2012), and aircraft observations (Li et al., 2014; Zhang et al., 2009) have also demonstrated that major HONO sources exist at canopy or ground surfaces through the measurement of vertical gradients. It is postulated that such processes involve the conversion of nitrogen dioxide (NO_2) or nitric acid (HNO_3) to HONO on ground surfaces and are enhanced by sunlight, thus providing a daytime only source of HONO (Zhou et al., 2003; George et al., 2005). In addition, bacterial production of nitrite in soil surfaces were also proposed as additional

HONO source (Su et al., 2011, Oswald et al., 2013). It has also been shown that HONO is emitted directly from petrol and diesel vehicle exhausts (Kurtenbach et al., 2001; Li et al., 2008). At most sites, this is a relatively small contributor to HONO due to its relatively short atmospheric lifetime in the daytime (10-20 minutes), however close to major roads and especially in tunnels in can contribute greatly to the HONO present. A recent publications by Michoud et al. (2014) gives a good summary of the possible daytime HONO sources under similar conditions to this study (in Paris) and a reivew by Kleffmann (2007) also discusses daytime HONO sources in depth.

Almost all previous field studies still show a significant missing daytime HONO source, thus showing the requirement for more studies. In this work we report what are, to our knowledge, the first measurements of HONO made in London, UK, one of the largest cities in Europe. The measurements were made as part of the summer intensive operation period of the *Clean Air for London* (ClearfLo) project and, as a result, were made concurrently with a wide range of other atmospheric gas and aerosol phase species (including OH, HO_2, NO, NO_2 and photolysis rates). This has enabled us to undertake a detailed modelling study of HONO using the Master Chemical Mechanism (MCMv3.2), in which we have included a series of known sources of HONO found in the literature. We then investigate the difference between daytime measured and modelled HONO, with a simple correlation analysis against other measured parameters. The model was also used to assess the radical forming potential of the missing HONO, which can ultimately lead to increased production of secondary pollutants such as ozone (O_3) and secondary organic aerosol (SOA).

2 Experimental

The ClearfLo project had the aim of providing an integrated measurement and modelling program in order to help better understand the atmospheric processes that affect air quality (Bohnenstengel et al., 2014). As part of ClearfLo, a summer intensive operation period (IOP) took place in July and August 2012, which involved the measurement of a wide range of gas and aerosol phase species (including meteorology), which enabled a detailed study of the atmospheric chemistry of London's air to be carried out.

2.1 Site description

The main site for the IOP was an urban background site at the Sion Manning School in North Kensington, London, (51^{o} 31' 16'' N, 0^{o} 12' 48'' W), which is situated in a residential area approximately 7 km west of central London (defined here as Oxford Street). Measurements of NO, NO_2 and total reactive nitrogen (NO_y), sulphur dioxide (SO_2), O_3, carbon monoxide (CO), PM10 and total particle number concentration have been routinely made at the site since January 1996 as part of the Automatic Urban and Rural Network (AURN) and the London Air Quality Network (LAQN) (Bigi and Harrison, 2010). For the ClearfLo IOP, other instruments were installed in various shipping container laboratories in the grounds of the school, all within 20 metres of the long term measurements. A full description of the campaign, including the instruments present can be found in (Bohnenstengel et al., 2014), however details of the measurements pertinent to this work are given below. All measurements were carried out at a height of around 5 metres above ground level, within a horizontal area of 10 metres from each other.

2.2 HONO measurements

HONO was measured using a long-path absorption photometer (LOPAP) instrument from the University of Wuppertal, Germany, which is explained in detail elsewhere (Heland et al., 2001). Briefly, gaseous HONO is sampled in a stripping coil containing a mixture of sulfanilamide in a 1M HCl solution and is derivatized into an azo dye. The light absorption by the azo dye is measured in a long path absorption tube by a spectrometer at 550 nm using an optical path length of 2.4 m. The stripping coil was placed directly in the atmosphere being sampled; meaning the length of the glass inlet was only 2 cm minimizing sampling artefacts. The LOPAP has two stripping coils connected in series to correct interferences. In the first coil (channel 1), HONO is trapped quantitatively together with a small amount of the interfering substances. Assuming that these interfering species are trapped in a similar amount in the second coil (channel 2), the difference between the signals of the two channels provides an interference-free HONO signal. Zero measurements were performed every 7 hours. Calibrations of the spectrometer using a known concentration of the derivatized azo dye were carried out 3 times during the campaign. The instrument was previously successfully validated against the spectroscopic DOAS technique under urban conditions and in a smog chamber (Kleffmann et al., 2006). During the campaign a detection limit of 1 pptV (for a time resolution of 5 min), a precision of 1 % and an accuracy of 10 % were obtained.

2.3 Radical measurements

OH, HO_2 and RO_2 radical concentrations were measured using the FAGE (fluorescence assay by gas expansion) technique (Heard and Pilling, 2003). In the case of HO_2 and RO_2, the radicals were first titrated with NO to OH before FAGE detection. The current mode of operation is described in detail elsewhere (Whalley et al., 2015a). The HO_2 observations used as a constraint in the modelling studies reported in section 3.3 were made using a low flow of NO (7.5 sccm), which laboratory tests have shown minimised interferences from alkene and aromatic-derived RO_2 species (Whalley et al., 2013). Under this regime, the interference from RO_2 radicals present is estimated to contribute <3 % to the HO_2 concentration. The limit of detection (LOD) at a signal to noise ratio of three for one data acquisition cycle was ~1.3 x 10^6 molecule cm^{-3} for OH and ~6.3×10^6 molecule cm^{-3} for HO_2. The measurements were recorded with 1 s time-resolution, and the accuracy of the measurements was ~15 %.

2.4 Other supporting measurements

The NO and NO_2 data used in this work were taken using an Air Quality Design Inc. custom built high sensitivity chemiluminescence analyser with LED based blue light NO_2 converter. The instrument consists of two channels measuring NO by reaction with excess O_3 to form excited state NO_2 followed by the detection of the resultant chemiluminescence (Drummond et al., 1985; Lee et al., 2009). The air flow in one of the channels first passes through a photolytic converter where light at 395 nm from an array of LEDs photolyses NO_2 to NO. The 395 nm wavelength has a specific affinity for NO_2 photolytic conversion to NO, giving high analyte selectivity within the channel and there is a low probability of other species (such as HONO) being photolysed (Pollack et al., 2010). This makes this measurement a significant improvement over the high temperature catalytic NO_2 conversion used for the long term measurement at the North Kensington site (Steinbacher et al., 2007; Villena et al., 2012). Calibration of the instrument was carried out every 2 days using 5 ppm NO in nitrogen (BOC – certified to NPL scale) - diluted to ~20 ppb using high purity zero air (BOC BTCA 178). The NO_2 conversion efficiency (ca. 40%) was calibrated using gas phase titration of the NO standard by O_3. NO_y data were taken using a TEI 42i TL NO analyser with Molybdenum converter.

VOC measurements were obtained using two gas chromatography (GC) instruments. The volatile fraction of VOCs (C_2-C_7 hydrocarbons, with a small selection of OVOCs) was measured using a dual channel (DC)-GC-FID (flame ionization detector) (Hopkins et al., 2003), while a comprehensive two dimensional GC (GC×GC-FID) measured the less volatile fraction (C_6-C_{13}, with a large group of OVOCs) (Lidster et al., 2014).

Measurements of HCHO were made using an Aerolaser 4021 analyser (Salmon et al., 2008). Briefly, gaseous formaldehyde is scrubbed into the liquid phase via a stripping coil containing dilute sulphuric acid. This is followed by reaction with Hantzsch reagent, a dilute solution made with acetyl acetone, acetic acid, and ammonium acetate. Aqueous phase formaldehyde reacts with this reagent via the 'Hantzsch reaction' to produce 3,5-diacetyl-1,4-dihydrolutidine (DDL). Once excited by an appropriate wavelength (400 nm in this case), DLL fluoresces thus allowing quantitative assay by monitoring the emitted light.

Non-refractory PM1.0 nitrate, sulphate, organic matter, chloride and ammonium were quantified using a compact time-of-flight aerosol mass spectrometer (cToF-AMS - Aerodyne Inc.), which gave data with a time resolution of 5 minutes (Young et al., 2015). Ammonium is reflective of the overall ammonium nitrate because ammonium nitrate is both non-refractory and tends to be in the submicron fraction. While there is supermicron nitrate, it is overwhelmingly in the form of sodium nitrate, which is refractory and not measured by the AMS. It is specifically the nitrate measurement that is of interest here because it pertains to the working hypothesis.

Total aerosol surface area was calculated using data from an aerodynamic particle sizer (APS) instrument (TSI Inc, model 3321). The mean diameter of particles in each size bin (assume spherical) multiplied number of particles in that bin. In total there were 53 size bins ranging from 0.53 to 21.29 μm. Actinic fluxes of solar radiation were measured using a spectral radiometer, which consisted of an Ocean Optics high resolution spectrometer (QE65000), couple via fibre optic to a 2π quartz collection dome. These measurements were then used to calculate the photolysis frequencies of a number of >50 trace gases, including NO_2, HONO and O_3 ($j(O^1D)$) (Kraus and Hofzumahaus, 1998; Edwards and Monks, 2003). Wind speed and direction, temperature and relatively humidity were measured using a Davis Vantage Vue met station. Mixing heights estimation was based on the vertical profiles of the hourly vertical velocity variance (Barlow et al., 2011). The vertical velocity variance was measured with a Doppler Lidar (Halo-Photonics scanning Doppler lidar) located at the North Kensington site

with a gate resolution of 18 m; the un-sampled portion of the vertical velocity variance is calculated with the spectral correction technique described in (Barlow et al., 2015). The mixing height is defined as the height up to which the vertical velocity variance is higher than 0.1 m^2 s^{-2}. This threshold value was perturbed by 20%, (i.e. between 0.08 m^2 s^{-2} and 0.121 m^2 s^{-2}) and the median of the estimated values was taken as the hourly mixing height.

3 Results

3.1 Overview of data

Data were collected from 22nd July – 18th August 2012 and time series of local wind speed, wind direction, NO, NO_2, O_3, HONO and the photolysis rate of HONO (*j(HONO)*) are shown in figure 1. The majority of the measurement period was characterised by south westerly winds, with the wind speed showing a diurnal cycle of less than 1 m s^{-1} at night (the minimum measurable by the anemometer) to 4 – 6 m s^{-1} in late afternoon. These periods show NO and NO_2 with peaks of 15 ppbV and 10 ppbV respectively, typically at ~07:30 UTC, the peak of the morning rush hour. O_3 shows a diurnal cycle with a typical maximum of 40 – 45 ppbV at ~16:00 UTC and minima of <20 ppbV at night. The exceptions to this are two periods from 24th – 27th July and 8th – 10th August, during which the site was subjected to generally easterly flow, with lower wind speed. Due to central London being to the East of the site, these periods are characterised by higher levels of NO_x (up to 60 ppbV of NO and 50 ppbV of NO_2), which has its source mainly from traffic exhaust. O_3 is also higher during these periods, due to a combination of the higher primary pollution levels (NO_x and VOCs) and low wind speeds causing a build-up of this secondary pollutant during the 3-4 day period. Peak daytime levels of O_3 of 60 – 100 ppbV are observed during these more polluted periods. HONO concentrations show peak values at night throughout the campaign (up to 1.8 ppbV during the easterly periods and up to 0.7 ppbV during the rest of the campaign), with non-zero values seen during the day (0.3 – 0.6 ppbV).

This behaviour is better visualised using the average diurnal cycle, which is shown for HONO and NO_x in figure 2(a) and *j(HONO)* and the HONO / NO_x ratio in figure 2(b). As well as the total campaign average, diurnal cycles are shown for the easterly and westerly time periods described above. NO_x follows an expected profile, with a peak of 29 ppbV on average during the morning rush hour at ~05:30 UTC (06:30 local time), followed by a decrease during the day, due largely to increasing boundary layer depth and hence dilution. After ~16:00 UTC,

the NO_x levels begin to rise from a minimum of 8.5 ppbV, due to a combination of increased emissions during the evening rush hour and the reduction of the boundary layer depth into the night. Concentrations reach ~18 ppbV by midnight and remain reasonably constant throughout the rest of the night. Diurnal averages in the easterly and westerly conditions follow the same pattern as for the total data series, with significantly higher NO_x during the easterly period. During the morning peak, NO_x is a factor of 3 higher during easterly flow compared to westerly and 15 - 20 % higher during the daytime. HONO appears to follow a similar diurnal profile to NO_x, which is not unexpected since the main known HONO sources involve nitrogen oxides. However, the morning peak of HONO is around 1 hour earlier compared to NO_x (at around 04:30) due to the onset of HONO photolysis at sunrise. HONO concentrations are also higher under easterly flow conditions compared to westerly, with the early morning peak being a factor of around 2 higher and the daytime average around 25% higher. The behaviour of HONO is perhaps better described by looking at the HONO / NO_x ratio and the average diurnal cycle of HONO / NO_x and *j(HONO)* is shown in figure 2b. The peak HONO / NO_x of 0.04 is seen at ~02:00 UTC, due to the lack of photolysis (the major loss route for HONO), direct HONO emissions and heterogeneous HONO formation at the surface during the night, into a relatively shallow boundary layer. After this (and before sunrise), the ratio begins to decrease due to the onset of fresh NO_x emissions and continues to decrease during the morning due to the increase of HONO photolysis. If the HONO sources which are active during night-time are the only active sources also during daytime, the HONO/NO_x ratio should show a deep minimum around noon. In contrast, in figure 2 a maximum is observed, which is a hint to an additional daytime source. In addition, the maximum of HONO/NO_x correlates well with the radiation, which is again a hint for a photochemical process.

The HONO levels measured in London are within the range of data published from other urban sites, although there is a wide range of concentrations reported in the literature. Michoud et al., 2014 reported daytime levels of 0.11 ppbV (averaged for 3 hours around local solar noon) at a site near Paris, France, which is lower than our value of 0.44 ppbV. However the site was 14 km from the centre of Paris (upwind), significantly further away from the major emission sources than the London site. As a result, NO_x was lower in Paris, with a daytime campaign average of 5.3 ppbV compared to our value of 13.9 ppbV, giving a daytime HONO / NO_x ratio of 0.020 compared to our value of 0.031, although this may be partially explained by the lower *j(HONO)* values in London compared to Paris. The fact that the

London site is closer to emission sources will most likely also influence this, as direct emission of HONO from traffic exhaust is potentially a significant proportion of HONO in large cities (Kurtenbach et al., 2001). Kleffmann et al, 2006, reported daytime HONO levels of between 0.2 – 0.3 ppbv in Milan, Italy. They also compared data from a LOPAP instrument (similar to that used in this study) and a Differential Optical Absorption Spectroscopy (DOAS) instrument and showed excellent agreement. The resultant HONO / NO_x ratio reported was 0.046. Wong et al., 2012, reported daytime HONO mixing ratios averting 0.1 ppbv in Houston, USA, with corresponding average daytime NO_x of 10 ppbv, giving a HONO / NO_x ratio of 0.03. Some other studies in large cities have reported larger daytime HONO concentrations, e.g. Santiago, Chile (1.5 ppbV) (Elshorbany et al., 2009), Guangzhou, China (2.0 ppbV) (Qin et al., 2009) and Xinken, China (0.80 ppbV) (Su et al., 2008a; Su et al., 2008b), however, all of these were at sites with much larger NO_x loading and so the resultant HONO / NO_x ratio is similar to the measurements in London. The range of ambient HONO values reported in the literature suggest that the specific conditions at a particular site are key to the HONO levels, in particular the prevalence of different levels of NO_x during daylight hours. Thus a modelling study including a range of known HONO sources and sinks is required to fully understand the observed behaviour.

3.2 HONO photostationary state approach

In order to initially assess HONO concentrations and in particular the impact of any potential extra sources during this campaign, a photostationary state (PSS) calculation has been carried out. In this approach, the sources and sinks of the species in question are assumed to balance each other and is thus only suitable for species with a short lifetime, such as free radicals. However, it has been widely used to study the daytime HONO budget, despite its lifetime being in the range of 10 – 20 minutes during the day (Alicke et al., 2002; Wong et al., 2012), resulting in significant uncertainties, especially for measurements close to emission sources (Lee et al., 2013). However, the measurement site in this study is described as an urban background site and thus is relatively free from the influence of major roads or point sources. Calculation of the transport time since emission using the NO_x / NO_y ratio (using the technique described in (Cappa et al., 2012)) shows a lifetime since emission of 40-50 minutes, significantly greater than the photochemical lifetime of HONO (typically 10 - 20 minutes at noon). Thus, we consider the PSS approach still as a useful tool to quantify HONO sources

during daytime. HONO is expected to be in photostationary state due to its formation by the reaction between OH and NO, and its sinks by rapid photolysis (to reform OH and NO), its reaction with OH and its dry deposition. Combining these terms, the concentration $[HONO]_{PSS}$ can be calculated using the following equation (1):

$$HONO_{PSS} = \frac{k_{OH+NO}[OH][NO]}{k_{OH+HONO}[OH] + j(HONO) + \frac{v_{HONO}}{h}} \quad (1)$$

Measured data were used for OH, NO and *j(HONO)*, with the relevant pressure and temperature dependant rate constants for $k_{OH + NO}$ and $k_{OH + HONO}$ taken from (Atkinson et al., 2004). v_{HONO} is the deposition velocity of HONO, set at an upper limit of 3.0 cm s^{-1}, and *h* is the boundary layer height. We use an effective HONO boundary layer height (BL) of 75 m, calculated using typical Eddy diffusion coefficients and j(HONO), as the likely height to which HONO will reach, given a daytime lifetime of 15 minutes. This method will strongly underestimate HONO deposition because the boundary layer height will be considerably larger than the height at which HONO will actually be transported to, due to its short lifetime (10-20 minutes during the day). This effect is partly compensated for by using 3.0 cm s^{-1} for the deposition velocity, which is at the upper end of the ranges quoted in the literature (Harrison and Kitto, 1994; Stutz et al., 2002; Trebs et al., 2006); however it does mean there are considerable errors in this approach. The PSS analysis also does not consider vertical structure, thus the magnitude of any unknown source inferred from the analysis will be dependent on the height above the ground surface that the measurements are being made. The average daytime diurnal profiles in both easterly and westerly conditions are shown in figure 3. We do not consider night time data as the PSS approach would not be valid at night. We only consider data from 08:00 UTC (j(HONO) $>4 \times 10^{-4} s^{-1}$), a time at which all HONO produced during the night will have been lost due to photolysis after sunrise. It is clear that the PSS calculation cannot replicate the measured HONO during daylight hours (08:00 – 20:00 UTC). The PSS does appear to reproduce the daylight cycle of HONO, with high concentrations during the morning peak between 06:00 and 09:00, due to the increase in NO and OH at the morning rush hour. However, after this morning peak, $HONO_{PSS}$ rapidly decreases to <0.05 ppbV by midday, followed by a gradual decrease during the afternoon reaching a minimum of 0.007 ppbv at 19.30. This is due to the rapid photolysis of HONO,

which occurs in the near UV region, and occurs significantly faster than the only production route in the PSS calculation (OH + NO), especially during the later part of the day when NO is low. $HONO_{PSS}$ during the day shows similar levels in both easterly and westerly conditions, despite measured HONO being significantly higher in the more polluted easterly regime. The PSS treatment of HONO is clearly incomplete, with significant missing source terms.

3.3 HONO box model approach

In order to assess the importance of other potential HONO sources in our study, we use a photochemical model based on the Master Chemical Mechanism (MCMv3.2) (Jenkin et al., 2012). Complete details of the kinetic and photochemical data used in the mechanism are available at the MCM website (http://mcm.leeds.ac.uk/MCM/home). The model was run with a sub-set of the MCM and treated the degradation of simultaneously measured trace VOCs, CH_4 and CO following oxidation by OH, O_3 and NO_3 and included ~15,000 reactions and ~3,800 species. The model was constrained to measurements of NO, NO_2, O_3, CO, CH_4, 62 individual VOC species measured by GC-FID and also 2D-GC, PAN, HCHO, HNO_3, HO_2, water vapour, temperature and pressure. The model was constrained with the measured photolysis rates (including $j(O^1D)$, $j(NO_2)$, $j(HONO)$, $j(HCHO)$, $j(CH_3COCH_3)$ and $j(CH_3CHO)$). A constant H_2 concentration of 500 ppbV was assumed (Forster et al., 2012). The model inputs were updated every 15 minutes. For species measured more frequently, data was averaged to 15 minute intervals, whilst those measured at a lower time resolution were interpolated. The loss of all non-constrained, model generated, species by a wind speed dependent deposition (ν) was calculated by summing the resistances $1/R_a$, $1/R_b$ and $1/R_c$, for which R_a describes turbulent convective transport, R_b the laminar diffusion near the surface and R_c the surface resistance. The inverse of the surface resistances ($1/R_c$) assumed are 3 cm s^{-1} for HNO_3 and 2 cm s^{-1} for HONO and 1 cm s^{-1} for NO_2 (and all other non-constrained model species). For the campaign average wind speed of 1.6 m s^{-1}, ν_{HNO_3}, ν_{HONO} and ν_{NO_2} equal 0.52, 0.48 and 0.38 cm s^{-1} respectively. As with the steady state approach, we use an effective HONO boundary layer height (BL) of 75 m in the model. This assumption leads to a campaign average first order loss of HONO (at a mean wind speed of 1.6 m s^{-1}) of ν_{HONO}/BL = 6.4×10^{-5} s^{-1}. The model was run for the entirety of the campaign in overlapping 7 day segments. To allow all the unmeasured, model generated intermediate species time to reach steady state concentrations, the model was initialised with inputs from the first measurement

day (22nd July) for 5 days before comparison to measurements were made. Comparison of these 5 spin up days demonstrated that the concentration of model generated species rapidly converged and there was less than a 1% difference in (for example) modelled OH or HONO concentration by the second spin up day. As a result of this, the model segments were run so as to overlap for 2 days only to reduce the computing time. The model was run unconstrained to HONO (for the results presented in this paper) for comparison with measured HONO concentration.

A number of HONO sources in addition to the gas phase source from the reaction of hydroxyl radicals with NO have been included in the model. These include:

a.) A direct emission source of HONO was added to the model, using a ratio of HONO:NO_x of 0.008 reported previously from tailpipe emission studies of NO_x and HONO in a tunnel (Kurtenbach et al., 2001) and the measured NO_x concentrations. It is likely that the used value represents an upper limit of the direct emission contribution to HONO during daytime, due to the short atmospheric lifetime of HONO (10-20 minutes) compared to NO_x.

b.) It has been suggested that a reaction between $HO_2 \times H_2O$ and NO_2 could produce HONO at a sufficiently fast rate to be a significant source in the troposphere (Li et al., 2014). It had previously been shown in laboratory studies that this reaction produces negligible HONO yields under dry conditions (Tyndall et al., 1995; Dransfield et al., 2001). However, in the lower troposphere, around 30% of HO_2 is suggested to be present as an $HO_2 \cdot H_2O$ complex, and hence may show different chemical behaviour. Kinetic measurements of the self reaction $HO_2 + HO_2$ have revealed the chaperone effect of water vapour enhancing the rate coefficient (Stone et al., 2005). It has also been shown that the rate coefficient of the reaction $HO_2 + NO_2$ increase by 50% from dry to humid atmospheric conditions (Sander and Peterson, 1984). In the Li et al. study it was postulated that the reaction converts NO_2 to HONO with a yield of 100% and this allowed a model to reproduce the observed levels of HONO, albeit under free tropospheric conditions away from surfaces. Inclusion of this reaction also improved the agreement between the model and measured levels of HO_2 and NO_x. However, recent field data has shown that in fact, this reaction produces only a 3% yield of HONO (Ye et al., 2015), thus greatly reducing the impact of the reaction on HONO production. Nevertheless, the following additional reactions were included in our MCM model to account for the equilibrium that exists between uncomplexed and H_2O-

complexed HO_2 in the atmosphere (R4 & R5) and the major reactions of H_2O-complexed HO_2 in this urban environment (R6 and R7):

$$HO_2 + H_2O \rightarrow HO_2{\cdot}H_2O\ , \qquad k = 1.0 \times 10^{-13}\ cm^{-3}\ s^{-1} \qquad (R4)$$

$$HO_2{\cdot}H_2O \rightarrow HO_2 + H_2O, \qquad k = 1.92 \times 10^{5}\ s^{-1} \qquad (R5)$$

$$HO_2{\cdot}H_2O + NO_2 \rightarrow HONO\ , \qquad k = 2.1\times 10^{-12}\ cm^{-3}\ s^{-1} \qquad (R6)$$

$$HO_2{\cdot}H_2O + NO \rightarrow OH + NO_2\ , \qquad k = 3.60 \times 10^{-12}\ (e^{(270/T)})\ cm^{-3}\ s^{-1} \qquad (R7)$$

c.) Light induced heterogeneous conversion of NO_2 to HONO on aerosol surfaces was also considered assuming an uptake coefficient of 10^{-6} (Kleffmann et al., 1999; Arens et al., 2001; Monge et al., 2010).

d.) Heterogeneous conversion of NO_2 to HONO on ground surfaces at a rate equal to $\sim 2\times10^{-8}$ s^{-1} has been included in the model which is consistent with laboratory studies, which put an upper limit on dark surface source of $<10^{-7}$, e.g. Stemmler et al. (2007). This was parameterised in the model by taking the wind-speed dependent v_{NO_2} and assuming instantaneous mixing of surface emitted HONO up to a height of 75 m. This leads to a first order loss of NO_2 to the ground at a rate of 4×10^{-5} s^{-1} on average. This rate was scaled down by a factor of 2000 to represent the dark surface conversion of NO_2 to HONO reported in laboratory studies. However, it has to be stressed, that the present calculation strongly underestimates the contribution of heterogeneous HONO formation on ground surfaces, especially during night-time at the measurement height, caused by the assumption of an instantaneous mixing up to a height of 75 m, see Eq 1.

e.) A daytime source from the photolysis of ortho nitro phenols which were not measured during the campaign but have been estimated to be present at an upper limit constant concentration of 1 ppbV and which photolyse at a rate of $\sim 3 \times 10^{-5}$ s^{-1} at midday (Bejan et al., 2006).

f.) Photolysis of adsorbed HNO_3 on ground surfaces has been reported to produce HONO (Zhou et al., 2003; Zhou et al. 2011). We have estimated the concentration of HNO_3 deposited to the ground surface from the gas-phase HNO_3 concentration that was measured during ClearfLo and from the wind speed dependent v_{HNO_3} (Zhou et al., 2011). To assess

the maximum impact of this potential HONO source, a noon photolysis rate of surface HNO_3 of 6×10^{-5} s^{-1}, two orders of magnitude faster than $j(HNO_3)_g$ ($j(HNO_3)_{0°SZA} = 6 \times 10^{-7}$ s^{-1}) in the gas phase, has been taken (Zhou et al., 2011) and a 100 % HONO yield was assumed.

g.) Photolysis of nitrate aerosols. To assess the maximum impact of this potential HONO source, a noon photolysis rate of aerosol NO_3^- of 6×10^{-5} s^{-1} and a 100 % HONO yield was again assumed.

h.) Photosensitised heterogeneous conversion of NO_2 to HONO on ground surfaces has been parameterised and included in the model by taking a ground surface conversion, which correlates with NO_2 photolysis. A wind speed dependent NO_2 deposition velocity calculated using $1/R_c = 1$ cm s^{-1} (Joyce et al., 2014) in 75 m BL leads to a first order loss of NO_2 to the ground at a rate of 4×10^{-5} s^{-1} on average, this is multiplied by a scaling factor equal to 0.25 × $j(NO_2)$ which leads to an overall photosensitized conversion of NO_2 → HONO of ~5.6×10^{-6} s^{-1} during the day on average; consistent with the light induced conversion of NO_2 to HONO observed in laboratory studies on humic acid surfaces (Stemmler et al 2007).

We do not include desorption of adsorbed HONO from soil (Oswald et al., 2013, 2015; VandenBoer et al., 2013) as they are still largely speculative, depend on many uncertain variables (soil pH, bacterial activity, soil humidity) and most probably have a very minor contribution under our highly urban conditions (low soil coverage, different expected diurnal contribution).

The full time series of the modelled HONO using the MCM, along with the measured values for the entire measurement campaign are shown in figure 4. Due to the difficulties of predicting nighttime chemistry with a photochemical model (such as the MCM), we only consider here the daytime (08:00 – 20:00). The time series show that predicted daytime HONO using the full model is higher than from the simple PSS calculation, however, it can be seen that the predicted daytime HONO is still lower than the measurement on all days and falls outside the 10% error of the LOPAP instrument. The average daytime diurnal cycle of the measured and modelled HONO, along with the contribution of the different sources in the

model is shown in figure 5. From just after sunrise (08:00), the contribution to HONO of the reaction between OH and NO decreases quickly due to the increasing *j(HONO)* and decreasing NO levels throughout the morningThe largest contribution throughout the day comes from the photolyiss of adsorbed HNO_3, contributing around 50% of the HONO source at midday. There are small contributions during the day and from heterogeneous conversion of NO_2 (on both aerosol and ground surfaces) and the photolysis of ortho-nitro-phenol. Examining the total HONO predicted by the model compared to the measurement shows a significant underestimation of the modelled HONO compared to the measurement. They do both follow a similar diurnal cycle, with a decrease in HONO until around 16:00, followed by an increase into the evening, however the modelled HONO is up to a factor of around 2 lower than the measurement throughout the day. Subtracting the modelled from the measured HONO gives us a quantity that can be described as 'missing' HONO source, and average diurnal daytime profile of this is plotted in figure 6. The amount of the missing HONO source begins to increase at 08:00 and reaches a maximum at 12:00 of ~2.8 ppbV hr^{-1}, exhibiting a similar diurnal trend to that of the HONO / NO_x ratio (see figure 2). It then starts to decrease throughout the afternoon and into the evening. Further analysis can be carried out by examining the diurnal profiles in the easterly and westerly flow conditions described earlier. Both conditions show broadly the same diurnal profile, however the daytime peak in missing HONO is greater in the more polluted easterly flow (up to 0.6 ppbV). This suggests that any missing source of HONO is related in some way to the pollution loading, most likely the amount of NO_2. This will be discussed further in later sections.

It is clear from this data, that neither a photostationary state calculation nor a more complete photochemical model containing currently known and postulated sources of HONO (that are relevant for this environment) can reproduce the daytime levels measured in London during this study. This is potentially significant, as HONO can be a large source of free radicals in such an urban environment, and any missing source in models can lead to an underestimation of the oxidising capacity of the atmosphere, and hence its ability to produce O_3. Therefore it is worth considering where the 'missing' HONO may come from and the importance of any extra source to the atmospheric oxidation capacity.

4 Discussion

4.1 Instrument interference

It is first worth considering the effect of possible instrument interferences on the HONO measurements made in this study. As described earlier, the LOPAP technique is not direct rather it measures HONO by conversion to a coloured azo dye which is then detected by absorption spectroscopy. However, it has been postulated that HO_2NO_2 could interfere with the conversion reaction, leading to erroneous HONO measurements. A recent study by (Legrand et al., 2014), using an identical instrument to the one described here and investigating apparently high measurements of HONO in Antarctica, showed in laboratory experiments that the instrument does have an interference with HO_2NO_2. Their work indicated that up to 15% of HO_2NO_2 was converted to the azo dye in the instrument and detected as HONO. For this study, 2 ppbv of HO_2NO_2 would explain the difference between measured and modelled HONO, however this seems unrealistic in an urban environment in summer (Dentener et al., 2002). In fact, the box model used here shows HO_2NO_2 levels to only be between 2 – 10 pptv, therefore we feel that this instrument interference can be discounted here. For submicrometer particles we exclude any interferences by particle nitrite, since their sampling efficiency is <2 % in the very short stripping coil (4 coil sampler). Even if that increased to values of 10 % for larger coarse particles, such interference would be almost perfectly corrected for by the two channel approach. For much larger fog particles (which actually were not present during the campaign during daytime) interferences would be only expected in the case of high fog pH vales of >5. For lower pH, expected for the urban conditions in London, the effective solubility of HONO (HONO + nitrite) would be too low to significantly influence the HONO data, even for high uptake efficiency of fog particles. Accordingly, we do not consider particle interferences as an important issue. Finally, the LOPAP was successfully inter-compared to the spectroscopic DOAS technique under urban background conditions similar to the present study (Kleffmann et al., 2006).

4.2 Missing HONO source

The ClearfLo IOP campaign involved a wide range of measurements, thus enabling the relationship between the apparent missing HONO and various other species to be investigated. Initially, daytime diurnal average profiles were plotted for NO_2 and the product $NO_2 \times j(NO_2)$, along with the extra rate of production of HONO required for the model to reproduce the measurements (termed ‘missing HONO source’ - figure 7). The plots show that, whilst there is little correlation between the NO_2 on its own with the missing HONO, there

appears to be a reasonable correlation with the product of NO_2 and $j(NO_2)$, hence pointing towards a photolytic source.

To further investigate any potential correlation, the full data series of the missing HONO source and different input data are normalised to 1 and correlated against each other. The normalised missing HONO source data are then correlated with the normalised products of all possible combinations of the input data. The datasets are then filtered to determine if inclusion of an extra dataset has led to a genuine increase in the correlation coefficient. For inclusion in the filtered output, the correlation coefficient for the product must be greater than the correlation coefficient for each of the individual components in the product. Additionally, inclusion of an additional dataset in a product must lead to an increase in the correlation coefficient for the new product when compared to the correlation coefficient without that new dataset. Datasets included are: $j(NO_2)$ (used as a proxy for radiation), water vapour, NO, NO_2, temperature, adsorbed HNO_3 ($HNO_{3\ ads.}$), OH, HO_2, RO_2, OH reactivity ($k(OH)$), nitrate aerosol ($NO_3^-{}_{aero.}$), ammonium aerosol ($NH_4^+{}_{aero.}$) and aerosol surface area (SA). We use $k(OH)$ as a proxy for organic substances as it has been shown by Whalley et al., 2015b, that $k(OH)$ is largely controlled by VOCs during the measurement period (typically 80% during daytime). The correlation plots are shown in the supplementary information (figure S1), with the correlation coefficients of the different combinations presented in table 1. The data shows that several product combinations are significantly higher than those of the individual components. For instance, the correlation coefficient with NO_2 alone is virtually zero, whereas for the product of $j(NO_2) \times NO_2$ the r^2 is 0.696, for $j(NO_2) \times k(OH)$ it is 0.678 and for $NO_2 \times k(OH) \times j(NO_2)$ the r^2 is 0.659. Thus, if gaseous VOCs (represented here by $k(OH)$) are precursors for VOCs adsorbed onto surfaces, then this is an indication that the photosensitised reaction of NO_2 on surfaces containing organics as a source of HONO may currently be under-estimated in the model. We also see high correlation coefficients with $j(NO_2) \times T$ (0.628), however this can be explained by radiation and temperature following a similar diurnal pattern, albeit with a slight (1 - 2 hours) time lag. The product of $j(NO_2)$ and ammonium aerosol (NH_4^+) is 0.583, suggesting this may play a role in the missing HONO, although any possible mechanisms for this are unclear.

In order to investigate the day-to-day variation in the potential HONO source, correlation plots were made of the daytime average (08:00 – 20:00) missing HONO source against NO_2 and the product of $j(NO_2)$ with NO_2, $k(OH)$ and $NO_2 \times k(OH)$ (figure 8). These show that

there is some correlation for all species, with the products of the species with *j(NO2)* (r^2 = 0.64, 0.55 and 0.71 for NO_2, *k(OH)* and NO_2 × *k(OH)* respectively) being significantly higher than with NO_2 alone (r^2 0.33).

Based on the correlational analysis we propose here an enhancement in the photosensitized conversion of NO_2 on organic substrates to explain the missing HONO source. In contrast, other recently proposed HONO sources will have a minor contribution. Aqueous solutions in which HONO yields from nitrate photolysis may be enhanced by organics (Scharko et al., 2014) will be not important for the urban conditions investigated in this study as there are no aqueous surfaces in the surrounding area. Or recently, in the study of Rutter et al. (2014), a gas phase reduction of HNO_3 by VOCs to HONO was proposed. However, since the conditions of that laboratory study were not atmospherically relevant (reaction in the presence of ca. 200 ppb of a high molecular weight motor oil), we have not considered this source for this analysis. In addition, this is a dark reaction, while we have mainly considered the more important daytime HONO chemistry in the present manuscript. In the study of Ziemba et al. (2010) a conversion of HNO_3 on organic aerosols was proposed based on field observations. However, HONO formation was only observed in the dark, which again is out of the scope of this study. In addition the very low correlation coefficient of the missing HONO source with aerosol nitrate does not support this mechanism. Formation of HONO by soil sources (Oswald et al., 2013, 2015) are also expected to be of minor importance for London, due to low soil surface coverage.

Although direct emissions were already considered in the model, we carried out a sensitivity analysis into the direct emission of HONO, to study potential errors within our model. We found that increasing direct emissions by a factor of 2 (even though we think our estimate is already an upper limit), only results in a 4% increase in the modelled HONO. Hence we do not believe direct emissions to be the source of the missing HONO. We have also run a sensitivity analysis on the heterogeneous photosensitized conversion of NO_2 on ground surfaces by increasing the conversion rate by up to a factor of 10 to assess the impact of enhanced reactive uptake of NO_2 on other surfaces, for example urban grime. We find that a reactive conversion rate of ~6×10^{-5} s^{-1} (but which varies as a function of $j(NO_2)$) closes the daytime HONO budget at all times (apart from the late afternoon). This is shown in figure 9, demonstrating that with an increased conversion rate, the heterogeneous photosensitized conversion of NO_2 on ground surfaces becomes the largest HONO source throughout the day.

Based on this sensitivity study and on the high correlation of the missing HONO source with the product $j(NO_2)\times NO_2$ and $j(NO_2)\times NO_2\times k(OH)$ enhanced photosensitized conversion of NO_2 on organic surfaces is proposed here as a major HONO source in London. However, the exact identification of the organics adsorbed on the urban surfaces (humic acids, organic grime, etc.) is out of the scope of the present study. In Sörgel et al. 2011b, it was shown that the results presented by Stemmler et al., 2007 on an artificial humic acid are not able to describe their field observation. The heterogeneous NO_2 uptake kinetics and HONO yields of real urban organic substrates are not known and maybe different compared to the artificial surfaces studied in the laboratory. Detailed laboratory studies on real surfaces collected from the surrounding of the field site in London would be necessary, which is again out of the scope of this study.

It should also be pointed out that our model only represents the situation at the measurement height of HONO and the supporting species (5 m) and is not used to attempt to describe the entire boundary layer. Numerous measurements demonstrate that near-surface vertical structure in HONO can be significant at night and during the day (Stutz et al., 2002; Kleffmann, 2003; 2007; Zhang et al., 2009; Villena et al., 2011; Wong et al., 2012; Young et al., 2012; Oswald et al., 2015) and that a model using a near-surface source distributed throughout the boundary layer produces results inconsistent with observations (Vandenboer et al., 2013; Wong et al., 2013; Kim et al., 2014; Sörgel et al., 2015). Thus, some of the discrepancy between the model and measurements, particularly in the early morning when thermal inversions can persist, could be ascribed to biases from vertical stratification in HONO. It is, however, clear that at the present urban background site close to central London and within 5 meters of the surface, a significant missing source of HONO is active when compared to the output of a box model containing most known sources. We suggest from our analysis of the supporting data that processes responsible for the unknown source of HONO in this particular study are at least partially connected with light, NO_2 and organic matter (represented by $k(OH)$), in agreement with the source described in Stemmler et al. (2006; 2007).

4.3 HONO contribution to atmospheric oxidation

HONO is known to be an important initiation source of OH radicals (Ren et al., 2003; Ren et al., 2006; Dusanter et al., 2009; Elshorbany et al., 2009; Hofzumahaus et al., 2009; Villena et al., 2011; Michoud et al., 2012; Michoud et al., 2014), so any extra source that is not well understood or defined in models could have a potentially important impact on atmospheric oxidation capacity and hence O_3 and secondary organic aerosol (SOA) production. The model described above was used to produce a rate of production analysis (ROPA) for OH radicals during the measurements campaign, with a view to assessing the importance of HONO and in particular the missing HONO source. It should again be pointed out here that any conclusions drawn from this analysis are only valid for this particular measurement site (i.e. close to the surface). The model is only being used to understand OH production at the HONO measurement height even though the chemistry is taking place in a dynamic boundary layer. For the analysis of the vertical structure of the HONO contribution to the OH initiation, our measurement data is not sufficient and further gradient studies would be necessary. We also do not include the enhanced reactive conversion of NO_2 on other surfaces nor increased direct emissions described in the sensitivity analysis in this investigation.

For this analysis, the ROPA output was plotted for all OH radical sources and the diurnal average for these is shown in figure 10. Initially ignoring the missing HONO source, it can be seen that in the early morning shortly after sunrise, HONO is a significant OH source (30 – 40% of the total, second only to the propagation source of NO + HO_2). This is due to the build-up of HONO concentrations overnight, followed by its rapid photolysis after sunrise. Then, approaching solar noon, whilst the absolute production rate from HONO photolysis remains relatively constant, the dominant OH source becomes the HO_2 + NO reaction. At solar noon, HONO unconstrained in the model accounts for around 40% of the total OH radical sources and 57% of the HO_x initiation sources. During the late afternoon and evening approaching sunset, OH from HONO photolysis again becomes comparable to HO_2 + NO. The photolysis of O_3 is only a minor component of the total OH radical sources throughout the day, peaking at around 10% in early afternoon. The same holds for the ozonolysis of alkenes which is caused, at least in part, by the low levels of measured alkenes. With the model constrained to the measured HONO, it was possible to add on the effect of the missing HONO source to OH radical production rate to the diurnal profile. It can clearly be seen that the OH production rate is significantly increased during the daytime, especially during the

afternoon when constraining the model to measured HONO,. where the OH production rate increases by around 20%. This result shows that, even when all currently known sources of HONO are added to a box model, missing HONO sources are still crucial to HO_x radical production at the surface, which is directly relevant to atmospheric oxidation capacity and O_3 formation.

This importance is also shown when the model is used to calculate OH concentrations, as shown in figure 11. If the model is run with PSS calculated HONO (i.e. only OH + NO as a source), there is a significant under prediction of OH levels (~40% during daytime). When the known or postulated HONO sources are included in the model, the predicted OH is increased by a factor of 1.4 – 1.6 during the day. However, during the afternoon, predicted OH is still 20 – 30% lower than modelled , suggesting a missing OH source. It is only when the model is constrained to measured HONO the agreement between measured and modelled OH becomes good (<5% discrepancy at midday and during most of the afternoon) and within the experimental error of the measurements (~15%). This clearly demonstrates the need for models to include accurate HONO data (either from measurements or a model containing all HONO sources and sinks) and thus shows the need for further investigation on the missing HONO source to be carried out.

5 Summary and Conclusions

In this study a month long time series of HONO levels at an urban background site in London was measured, with average mixing ratios showing a peak in the early morning of ~0.6 ppbV and a minimum during early afternoon of ~0.18 ppbV. Analysis of the HONO / NO_x ratio showed a significant secondary peak during daytime, suggesting additional sources of HONO other than the reaction between NO and OH. The presence of a large range of other atmospheric gas and aerosol measurements (including OH and HO_2 radicals), allowed a detailed study of known and postulated production routes of HONO to be undertaken, using both a simple PSS analysis and a box model based on the MCMv3.2. The calculated HONO shows a daytime underestimation of ~0.2 ppbV on average, even when recently suggested sources such as the reaction of $HO_2 \times H_2O$ with NO_2 to produce HONO, photolysis of adsorbed HNO_3, photo-enhanced conversion of NO_2 on ground and aerosol surfaces and direct traffic emissions are included, again suggesting a significant missing HONO source. Correlation plots of the missing HONO production rate against various other species measured at the site show a reasonable correlation with the product of $j(NO_2)$ with NO_2 and $k(OH)$, suggesting

that the proposed photosensitized heterogeneous conversion of NO_2 to HONO on organic substrates as observed in laboratory studies may be enhanced under these urban conditions.

The effect of the missing source of HONO to the oxidising capacity of the urban background atmosphere has been investigating using radical rate of production analyses. These show that OH radical production during the day increases by over 20% if measured HONO is used in the model as compared to allowing the model to run unconstrained to HONO, even with known and postulated HONO sources included. In addition, modelled OH only reproduces the measurement when HONO was constrained in the model. Whilst our results are only valid at the surface due to the likely HONO gradients, it is still an important result and demonstrates the need of a full understanding of the HONO production processes in an urban area such as London in, for example, air quality prediction models. The results presented here provide further evidence that unknown sources of HONO are present in the urban environment, and they are probably a function of NO_x and sunlight. It is not possible to conclude exactly the origin of the source from this work, hence further field measurements and, probably more crucially, laboratory studies are needed to investigate these important processes further.

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Table 1. Correlation coefficients (r^2) for plots between various species measured during ClearfLo (and their products), using *j(NO_2)* as a proxy for radiation, and the missing HONO source from the model (using the model with all additional sources). The species used were chosen using the method described in the text. SA = total aerosol surface area. See supplementary material figure S1 for plots.

Species	r^2 for correlation vs missing HONO
$j(NO_2)$	0.5394
H_2O	0.0004
NO	0.0270
NO_2	0.0001
Temp	0.3557
$HNO_{3\ ads.}$	0.0966
OH	0.2745
HO_2	0.1925
RO_2	0.2763
k(OH)	0.0001
$NO_3^-{}_{aero.}$	0.0006
$NH_4^-{}_{aero.}$	0.0007
aerosol surface area (SA)	0.0001
$j(NO_2) \times H_2O$	0.5981
$j(NO_2) \times NO_2$	0.6960
$j(NO_2) \times T$	0.6276
$j(NO_2) \times k(OH)$	0.6781
$j(NO_2) \times NH_4^+$	0.5829
$j(NO_2) \times HNO_{3\ ads.}$	0.4356
$H_2O \times HNO_{3\ ads.}$	0.1044
$H_2O \times OH$	0.3378
$H_2O \times RO_2$	0.2899
$H_2O \times NO_3^-{}_{aero.}$	0.0006
$NO \times HNO_3$	0.1276
$NO \times OH$	0.2791
$NO \times HO_2$	0.2580
$NO_2 \times OH$	0.3867
temp × OH	0.3952
$OH \times k(OH)$	0.3497
$OH \times NH_4^+{}_{aero.}$	0.3888
$HO_2 \times k(OH)$	0.1941
$RO_2 \times k(OH)$	0.2819
$j(NO_2) \times NO_2 \times T$	0.7262
$j(NO_2) \times T \times k(OH)$	0.7069
$j(NO_2) \times NO_2 \times k(OH)$	0.6594
$NO \times HNO_{3\ ads.} \times OH$	0.4085
$NO \times HNO_{3\ ads.} \times HO_2$	0.2916
$NO \times HNO_{3\ ads.} \times RO_2$	0.3198
$j(NO_2) \times H_2O \times T \times k(OH)$	0.7280

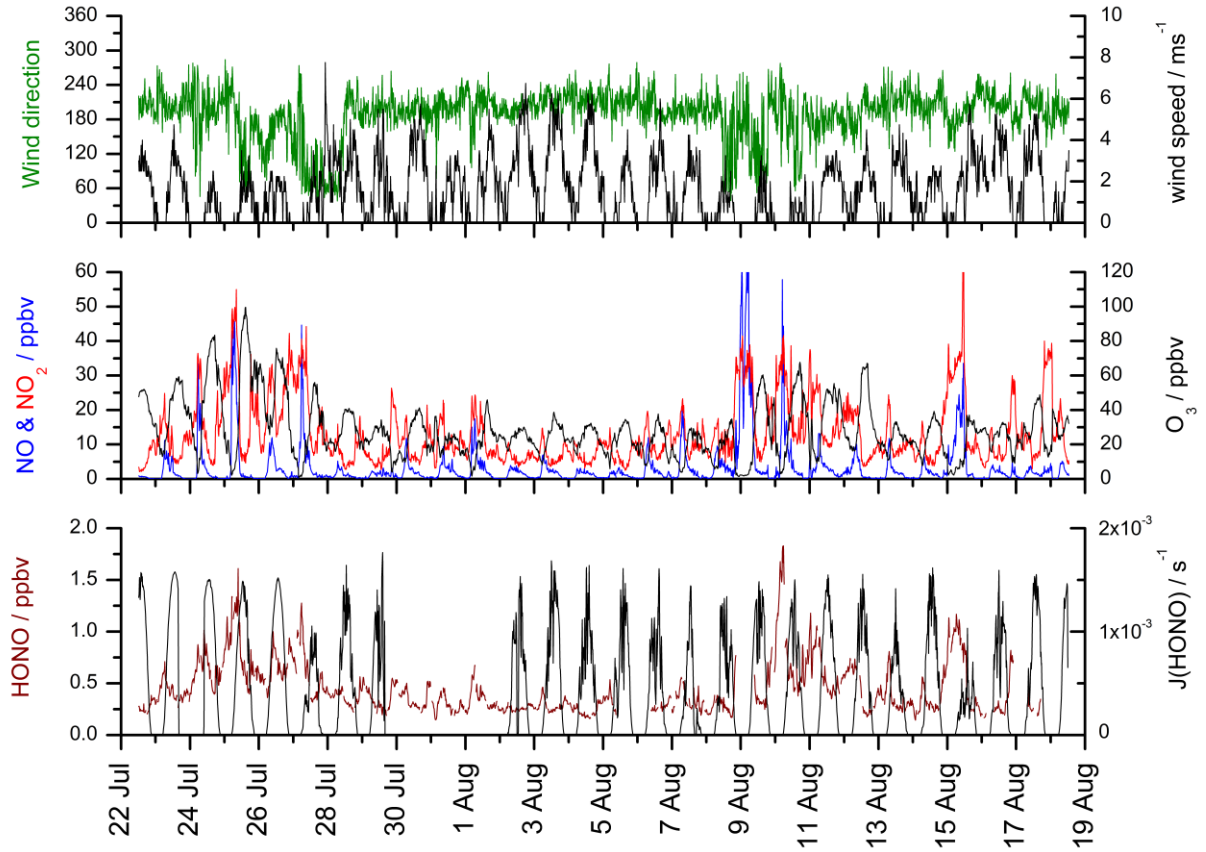


Figure 1. Time series of selected data from the ClearfLo intensive operation period (July and August 2012). The top panel shows wind speed (black) and wind direction (green); the middle panel shows NO (blue), NO_2 (red) and O_3 (black); and the bottom panel shows HONO (dark red) and j(HONO) (black). All data is 15 minute averaged and plotted as UTC (local time - 1 hour).

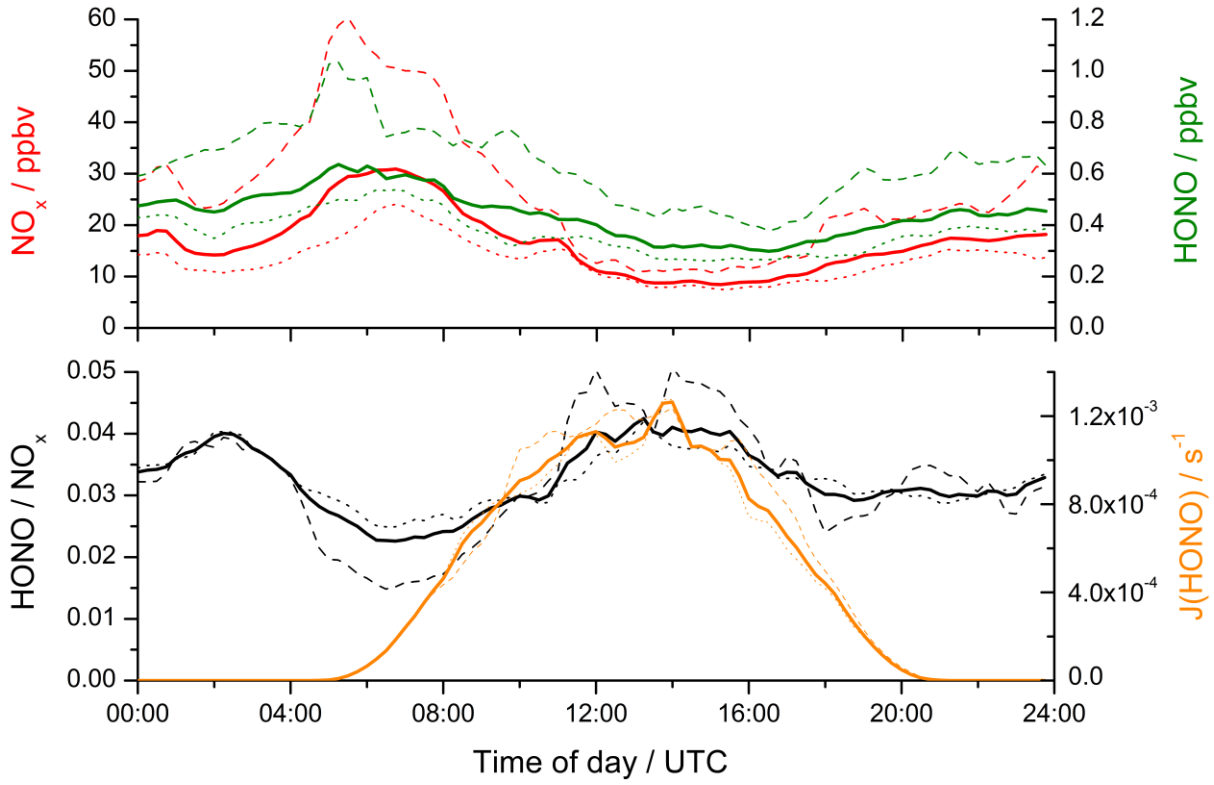


Figure 2. Average diurnal profiles of selected data from the IOP. The top panel shows total NO_x (red) and HONO (green) and the bottom panel shows *j(HONO)* (orange) and the HONO / NO_x ratio (black). Profiles were generated by binning all data in a 15 minute time period together. For each, the solid line is the total of all days, the dashed line is data from easterly conditions and the dotted line data from westerly conditions (see text for dates).

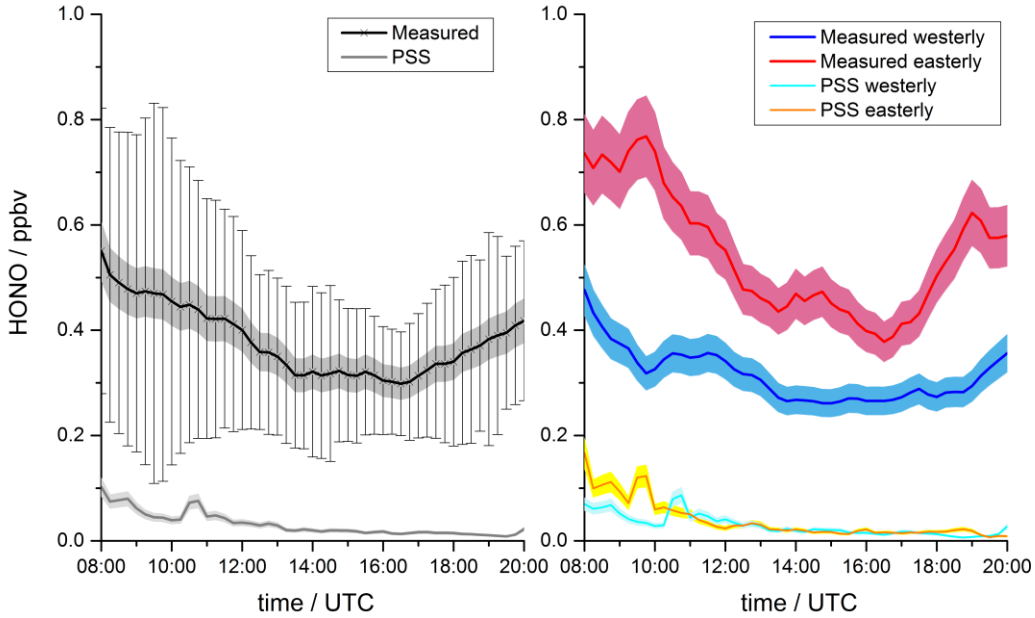


Figure 3. Averaged diurnal profiles (daylight hours) of measured (black) and photostationary state (PSS) calculated (grey) HONO (left panel). The shaded area represents instrumental (±10%) and model (±17%) error, the bars represent the standard deviation of the measurements. The right panel shows avaged dirunal profiles of measured and PSS HONO divded into easterly (red / orange) and westerly (blue / cyan) conditions. The shaded area represents the measurement (±10%) and PSS (±17%) error.

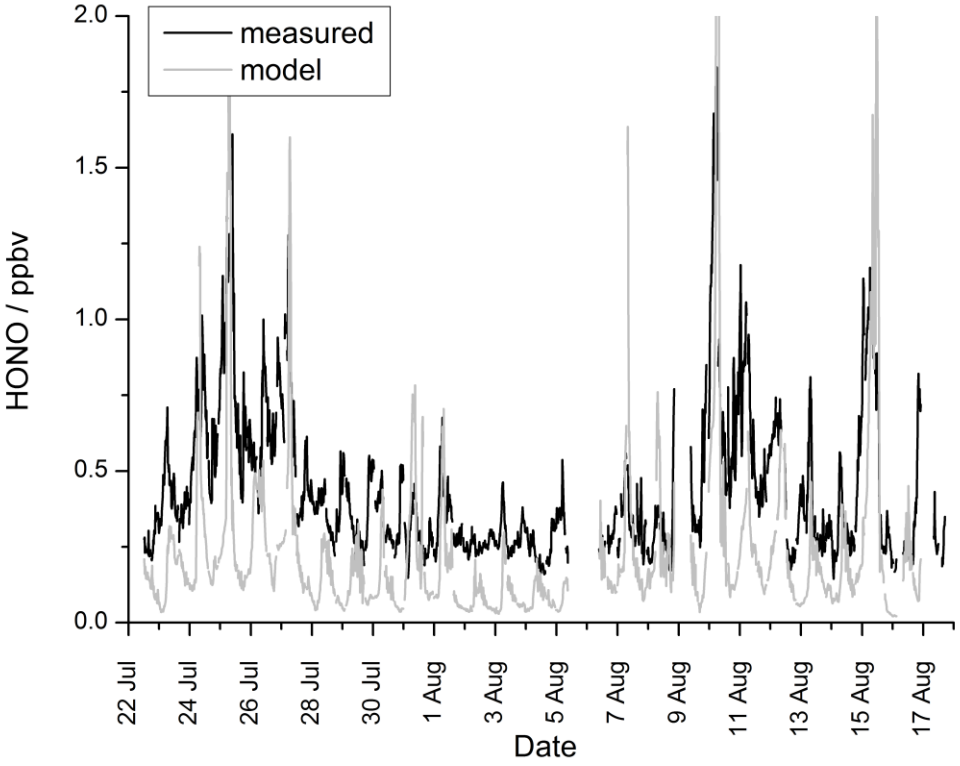
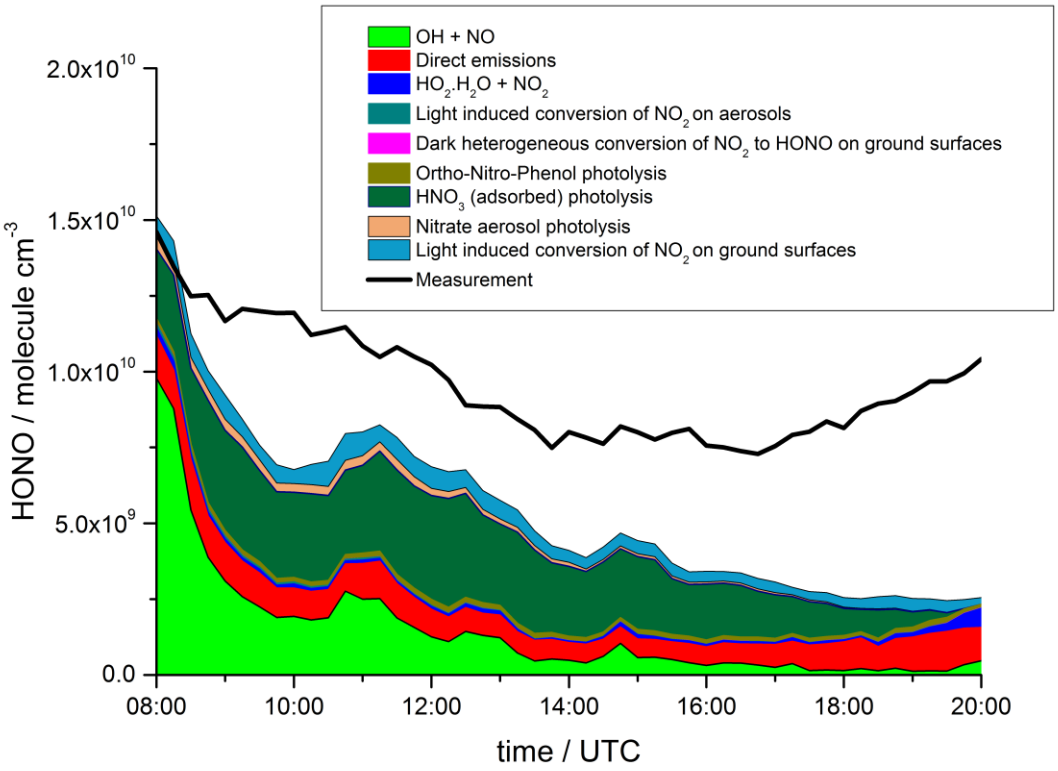


Figure 4. Time series of measured (black) and model calculated (grey) HONO during the IOP. The model was based on the Master Chemical Mechniasm (MCM v3.2), see text for details.



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2 Figure 5. Average daytime dirunal profile of the modelled HONO from different sources
3 shown as a compound area plot, as described in section 3.3 of the text. Also plotted (black
4 trace) is the measured HONO.

5

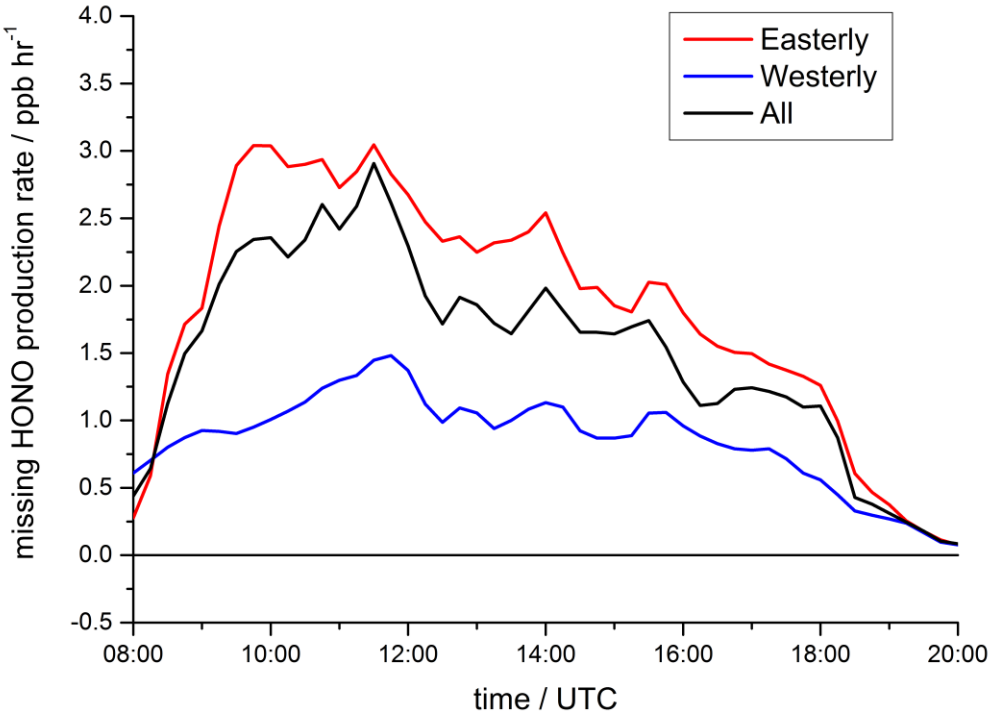


Figure 6. Average daytime dirunal profile of the 'missing' HONO production rate (in ppb hr^{-1}), defined as the rate of HONO production required to reproduce the measurements in the model. The black trace shows average of all data, the red trace shows the average of data from easterly conditions and the blue trace shows the avergae of data from westerly conditions.

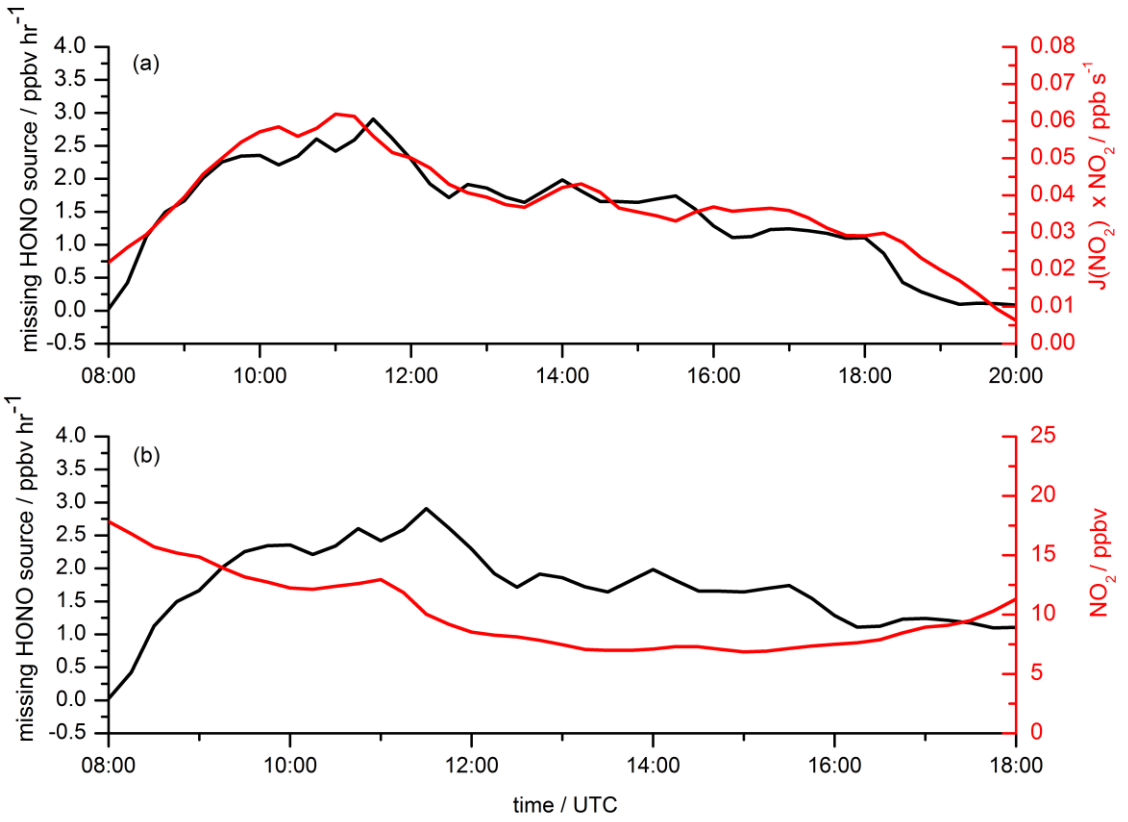
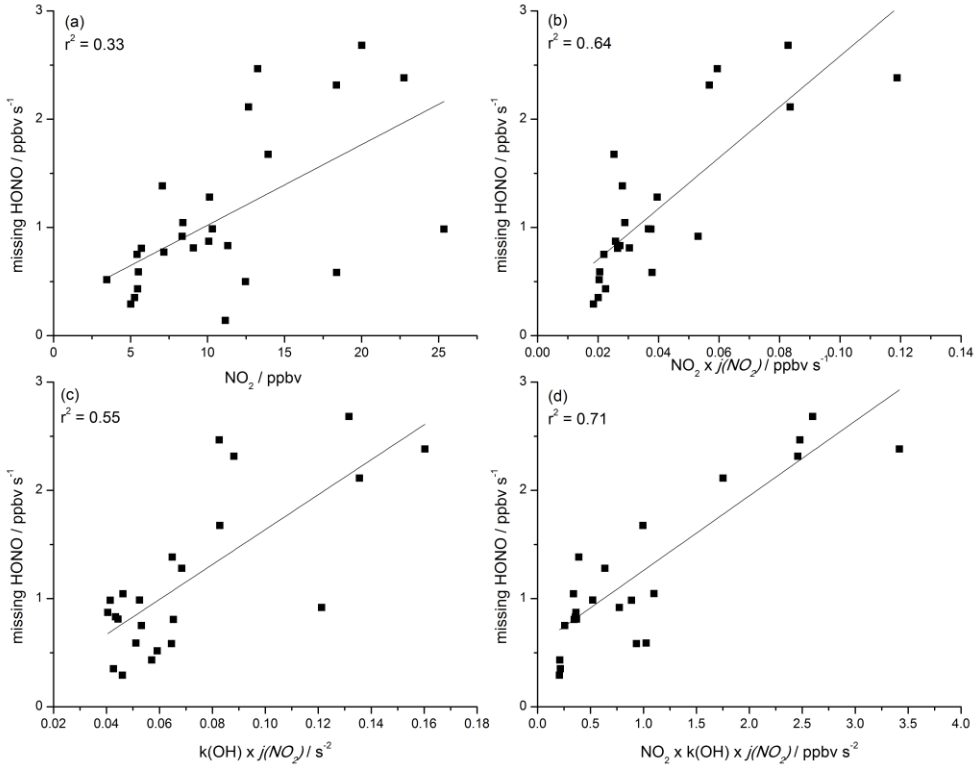


Figure 7. Average diurnal profiles of the missing HONO source (black traces) plotted with (as red traces) (a) $NO_2 \times j(NO_2)$ and (b) NO_2.



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2 Figure 8. Daytime averaged (08:00 – 19:00) missing HONO source plotted against (a) NO_2,
3 (b) $NO_2 \times j(NO_2)$, (c) $k(OH) \times j(NO_2)$, (d) $NO_2 \times k(OH) \times j(NO_2)$.

4

5

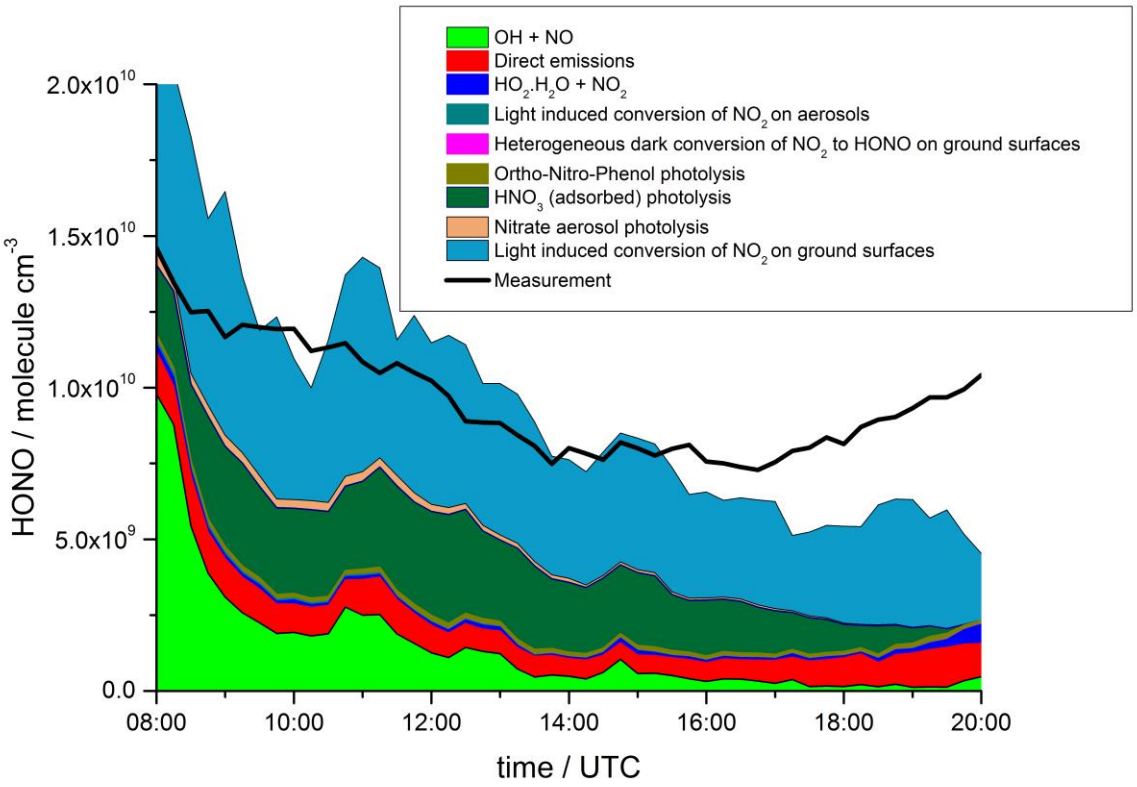

Figure 9. Average daytime dirunal profile of the modelled HONO from different sources shown as a compound area plot, as described in section 3.3 of the text, showing the result of increasing the reactive uptake coefficient of the light enhanced conversion of NO2 on ground surfaces (see text for details). Also plotted (black trace) is the measured HONO.

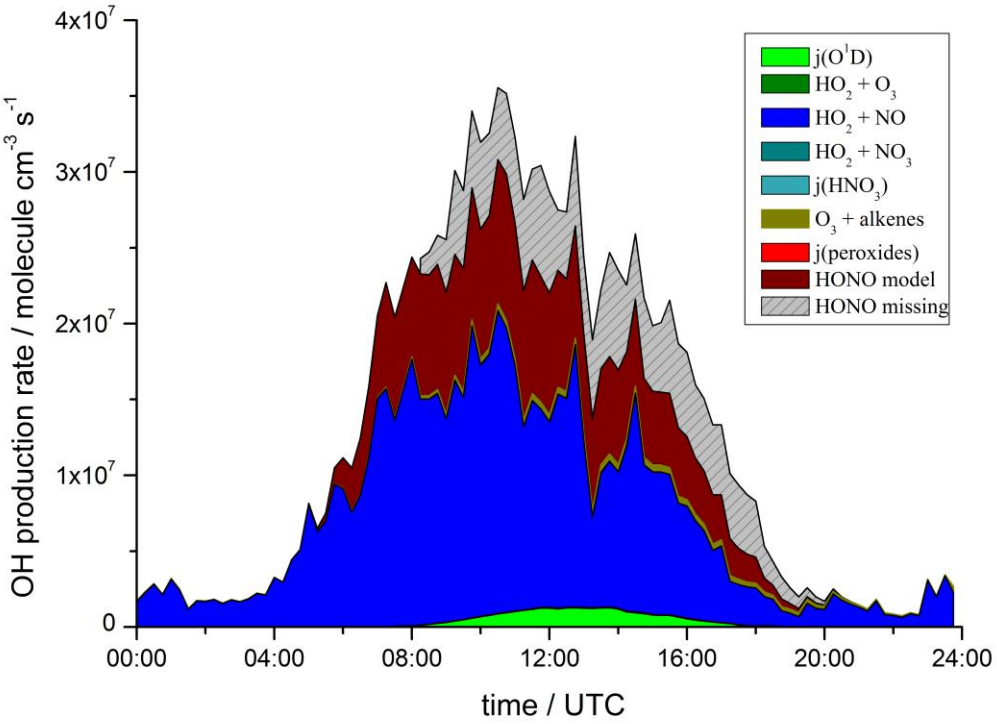

Figure 10. Average dirunal profile of gross OH production rates from different initiation and propagation sources calculated by the model.

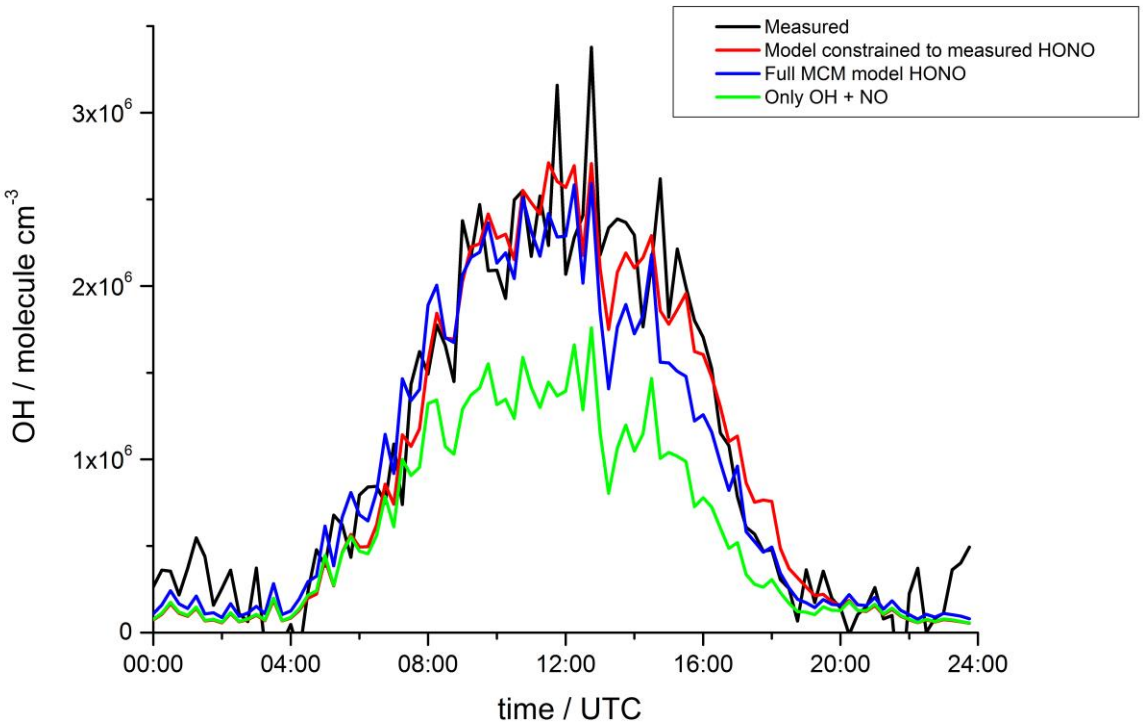

Figure 11. Average diurnal profile of OH, showing measured (black), modelled unconstrained to HONO with only NO + OH as a HONO sources (green), modelled unconstrainted to HONO including additional HONO sources (blue – see text for details) and model constrained to measured HONO (red).