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

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ACPD

15, 22097–22139, 2015

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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 22 July–18 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, including postulated formation from the reaction of HO_2 with NO_2 and photolysis of HNO_3, increases the daytime modelled HONO to 0.1 ppbV, still leaving a significant extra daytime source. The missing HONO is plotted against a series of parameters including NO_2 and OH reactivity, 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. 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 (Reaction R2). It has been shown in numerous studies that HONO can actually be the dominant early morning source of OH (Ren et al., 2003, 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 (Reaction R1) and losses by photolysis (Reaction R2) and oxidation by OH (Reaction R3).

$$OH + NO + M = HONO + M \tag{R1}$$

$$HONO + h\nu = OH + NO \quad (\lambda < 400\,nm) \tag{R2}$$

$$HONO + OH = H_2O + NO_2 \tag{R3}$$

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

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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). It is postulated that such processes involve the conversion of NO_2 or HNO_3 to HONO on ground surfaces and are enhanced by sunlight, thus providing a daytime only source

5   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), although at most sites (with the exception of those adjacent to major roads or in tunnels), this is a rela-

10 tively small contributor to HONO due to its relatively short atmospheric lifetime in the daytime (10–20 min). Recent reviews of the possible daytime HONO sources are given in Kleffmann (2007) and Michoud et al. (2014).

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

15 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 un-

20 dertake a detailed modelling study of HONO using the Master Chemical Mechanism (MCMv3.2), with subsequent investigation of potential missing sources. 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).

25 ## 2   Experimental

The Clean air for London (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., 2015). 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 (as well as detailed 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°31′16″ N, 0°12′48″ W), which is situated in a residential area approximately 7 km West of central London (defined here as Oxford Street). Measurements of nitric oxide, nitrogen dioxide and total NO_y, sulphur dioxide, O_3, carbon monoxide, PM_{10} 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 m of the long term measurements. A full description of the campaign, including the instruments present can be found in Bohnenstengel et al. (2015), however details of the measurements pertinent to this work are given below.

2.2 HONO measurements

HONO was measured using a highly sensitive, 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 1 M 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 h. 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 will be described in detail elsewhere (Whalley et al., 2015). The HO_2 observations used as a constraint in the modelling studies reported in Sect. 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 one for one data acquisition cycle was $\sim 4.5 \times 10^5$ molecule cm^{-3} for OH and $\sim 2.1 \times 10^6$ molecule cm^{-3} for HO_2. The measurements were recorded with 1 s time-resolution, and the accuracy of the measurements was $\sim 15\%$.

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 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 (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

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in this case), DLL fluoresces thus allowing quantitative assay by monitoring the emitted light. Non refractory nitrate and ammonium aerosol measurements were taken using a compact time-of-flight aerosol mass spectrometer (cToF-AMS – Aerodyne Inc.), which gave data with a time resolution of 5 min (Young et al., 2015).

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 $0.1 \, \text{m}^2 \, \text{s}^{-2}$. This threshold value was perturbed by 20 %, (i.e. between 0.08 and $0.121 \, \text{m}^2 \, \text{s}^{-2}$) 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 22 July–18 August 2012 and time series of local wind speed, wind direction, NO, NO_2, O_3, HONO and the photolysis rate of HONO ($j(\text{HONO})$) are shown in Fig. 1. The majority of the measurement period was characterised by south westerly winds, with the wind speed showing a diurnal cycle of less than $1 \, \text{m s}^{-1}$ at night (the minimum measurable by the anemometer) to 4–$6 \, \text{m s}^{-1}$ in late afternoon.

These periods show NO and NO_2 with peaks of 15 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 exception to this are two periods from 24–27 July and 8–10 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 Fig. 2a and j(HONO) and the HONO/NO_x ratio in Fig. 2b. 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 LT), 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 nitro-

gen oxides. However, the morning peak of HONO is around 1 h 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 Fig. 2b. The peak HONO/NO_x of 0.04 is seen at $\sim$ 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. The presence of a second, daytime peak in HONO/NO_x of similar magnitude to the nighttime peak suggests a significant secondary and probably photo-enhanced, HONO source.

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 h 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 maybe 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). Some other studies in large cities have reported even 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, b), however all of

these were at sites with much larger NO_x loading, with the resultant $HONO/NO_x$ ratio being 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 and hence a modelling study is required for gaining a full understanding of its 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 min 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 photochemical lifetime using the NO_x/NO_y ratio (using the technique described in Cappa et al., 2012) shows a lifetime since emission of 40–50 min, significantly greater than the lifetime of HONO (typically 10–20 min at noon). Thus, we consider the PSS approach still as a useful tool to quantify HONO sources during daytime.

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 Eq. (1):

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

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. 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 min 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 average daytime diurnal profiles in both easterly and westerly conditions are shown in Fig. 3. 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 virtually zero (< 0.05 ppbV) by midday and remains low throughout the rest of the daylight hours (until around 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). 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 $\sim 15\,000$ reactions and ~ 3800 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 2-D-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 $j(CH_3CHO)$) made using the spectral radiometer. A constant H_2 concentration of 500 ppbV was assumed (Forster et al., 2012). The model inputs were updated every 15 min. For species measured more frequently, data was averaged to 15 min intervals, whilst those measured at a lower time resolution were interpolated. The loss of all non-constrained, model generated, species (apart from HONO) by deposition or mixing was represented as a first order loss rate equivalent to $1\,cm\,s^{-1}$ in a 300 m boundary layer depth.

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 (22 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:

1. 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).

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2. Heterogeneous conversion of NO_2 to HONO on ground has been parameterised and included in the model taking a ground surface conversion efficiency of 0.03 (Stutz et al., 2002) and NO_2 deposition velocity of $1\,cm\,s^{-1}$ (Joyce et al., 2014) and the measured boundary layer depth. 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 in the whole BL, see Eq. (1). In contrast strong HONO gradients have been observed in night-time atmospheres (e.g. Kleffmann et al., 2003; Wong et al., 2011; VandenBoer et al., 2013) confirming the ground as the main source of HONO during nighttime. Since the measurements of the present study were performed also close to the ground surface the contribution of heterogeneous HONO formation is underestimated in the model. For the more accurate description of the night-time HONO formation, which was not the main topic of this study, models should be used which consider vertical transport.

3. 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).

4. Photolysis of HNO_3 on surfaces has been reported to produce HONO (Zhou et al., 2003, 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 a deposition velocity of HNO_3 of $2\,cm\,s^{-1}$ (Zhou et al., 2011). To assess the maximum impact of this potential HONO source, a photolysis rate of surface HNO_3 which is two orders of magnitude faster than $j(HNO_3)$ in the gas phase has been taken (Zhou et al., 2011) for which in addition a 100 % HONO yield was assumed.

We did not include photosensitized heterogeneous conversion of NO_2 on organic substrates like humic acids (George et al., 2005; Stemmler et al., 2006, 2007) into

the model, since this ground surface source cannot easily be implemented into a box model. The exact nature of organic substrates in the vicinity of the measurement site is not well known, but have a significant impact on the reactivity against NO_2 (George et al., 2005). In addition, vertical transport will strongly influence the impact of this ground surface source on modelled HONO levels for which at least a vertical 1-D transport model is recommended. We also do not include desorption of adsorbed HONO from soil (Oswald et al., 2013; VandenBoer et al., 2013) or any building surfaces as again these would be difficult to include in a box model and we do not believe them to be a significant source in an urban environment.

It has recently been suggested that a reaction between HO_2 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 $HO_2 \times H_2O$ 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., 2014). 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. Although the reaction was yet not experimentally confirmed in the laboratory and seems to be of less importance than proposed (Hofzumahaus, 2014), upper limit HONO formation by the reaction of $HO_2 \times H_2O$ with NO_2, was calculated by the MCM model. The following additional reactions were added to the basic MCM model to account for the equilibrium that exists between uncomplexed and H_2O-complexed HO_2 in the atmosphere (Reactions R4 and R5) and the major reactions of H_2O-complexed HO_2 in this urban

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environment (Reactions R6 and R7):

$$HO_2 + H_2O = HO_2 \times H_2O, \quad k = 1.0 \times 10^{-13}\,cm^{-3}\,s^{-1} \tag{R4}$$

$$HO_2 \times H_2O = HO_2 + H_2O, \quad k = 1.92 \times 10^{5}\,s^{-1} \tag{R5}$$

$$HO_2 \times H_2O + NO_2 = HONO, \quad k = 2.1 \times 10^{-12}\,cm^{-3}\,s^{-1} \tag{R6}$$

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

A direct emission source of HONO was also 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 tunnels (Kurtenbach et al., 2001) and the measured NO_x concentrations, along with a value of 60 % NO_x estimated to come from traffic emissions in London (take from the UK National Atmospheric Emissions Inventory; Bush et al., 2006). It is likely that the value we use is an upper limit of the direct emission contribution to HONO during daytime, due to the short atmospheric lifetime of HONO (10–20 min) compared to NO_x.

The full time series of the modelled HONO using the MCM, along with the measured values for the entire measurement campaign are shown in Fig. 4. Due to the difficulties of predicting nighttime chemistry with a photochemical model (such as the MCM), we only consider here the daytime (06:00–20:00). 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 significantly lower than the measurement on all days. 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 Fig. 5. From just after sunrise (06:00), the contribution to HONO of the reaction between OH and NO decreases quickly due to the increasing j(HONO) throughout the morning. During this time, the HONO sources from direct emissions and the $HO_2 \times H_2O + NO_2$ reaction are roughly similar in magnitude to the OH+ NO reaction). 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. However, as explained above most probably the $HO_2 \times H_2O + NO_2$ reaction is overes-

timated here, while the heterogeneous conversion of NO_2 on ground surfaces is underestimated by the simplified box model approach. 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 3 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, and average diurnal daytime profile of this is plotted in Fig. 6. The amount of missing HONO begins to increase at 06:30 and reaches a maximum at 08:00 of ~ 0.35 ppbV. 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 significantly 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) except the photosensitized conversion of NO_2 on organic ground surfaces (which cannot easily be including in a zero dimensional box model) 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, it would mean levels of HO_2NO_2 would need to be up to 2 ppbV to account for all of the missing HONO, which 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. In addition, 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" – Fig. 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: $j(NO_2)$, 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). The correlation plots are shown in the Supplement (Fig. 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, and seem to favour the products of $j(NO_2) \times NO_2$ ($r^2 = 0.66$) and $j(NO_2) \times k(OH)$ ($r^2 = 0.75$). A plot of the missing HONO source against the combined product ($NO_2 \times k(OH) \times j(NO_2)$) gives an r^2 of 0.79. In order to investigate the day-to-day variation in the potential HONO source, correlation plots were made of the daytime average (06:00–18:00) missing HONO source against NO_2 and the product of $j(NO_2)$ with NO_2, $k(OH)$ and $NO_2 \times k(OH)$ (Fig. 8). These show that there is some correlation for all species, with the products of the species with $j(NO_2)$ ($r^2 = 0.72$, 0.73 and 0.77 for NO_2, $k(OH)$ and $NO_2 \times k(OH)$ respectively) being significantly higher than with NO_2 alone ($r^2 = 0.52$). We therefore suggest that the process or processes responsible for the unknown source of HONO in this particular study are connected with light, NO_2 and organic matter (represented by $k(OH)$), as described in Stemmler et al. (2006, 2007). Other processes are potentially at work, as shown by the

weaker correlation with $HNO_{3\,ads.}$ and $NO_{3\,aero.}^-$, but these are likely of less importance here. It is, however, clear that at the present urban background site close to central London a significant missing source of HONO is active when compared to the output of a box model containing most known sources.

4.3 HONO contribution to atmospheric oxidation

HONO is known to be an important initiation source of OH radicals (Ren et al., 2003, 2006; Dusanter et al., 2009; Elshorbany et al., 2009; Hofzumahaus et al., 2009; Villena et al., 2011; Michoud et al., 2012, 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. For this analysis, the ROPA output was plotted for all OH radical sources and the diurnal average for these is shown in Fig. 9. 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 when constraining the model to measured HONO, with the most important time being just before solar noon. Here, the OH production rate increases from 1.9×10^7 molecule cm^{-3} s^{-1} to 2.9×10^7 molecule cm^{-3} s^{-1}, an increase of 65 %. This result shows the crucial importance of the missing HONO in the model to HO$_x$ radical production, 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 Fig. 10. If the model is run with PSS calculated HONO, there is a significant under prediction of OH levels ($\sim$ 60 % during daytime). When the known or postulated HONO sources are included in the model, the predicted OH is increased by a factor of around 1.8. However predicted OH is still 30 % lower at noon compared to the measurement, suggesting a missing OH source. It is only when the model is constrained to measured HONO the agreement between measured and modelled OH becomes excellent (< 5 % discrepancy at midday) and within the experimental error of the measurements ($\sim$ 15 %). This clearly demonstrates the need for models to include accurate HONO measurements for further investigation on the missing HONO source to be carried out so that HONO is better characterised by the model.

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 $\sim$ 0.6 ppbV and a minimum during early afternoon of $\sim$ 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 significant daytime underestimation of ~ 0.2 ppbV on average, even when recently suggested sources such as the reaction of HO_2 with NO_2 to produce HONO and a direct source from traffic 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 on organic substrates discovered in laboratory studies is a source of HONO 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 100 % if measured HONO is used in the model as compared to allowing the model to run unconstrained to HONO. In addition, modelled OH only agreed to the measurements when HONO was constrained to the measurements in the model. This is a significant result and demonstrates the potential importance 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.

The Supplement related to this article is available online at doi:10.5194/acpd-15-22097-2015-supplement.

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Table 1. Correlation coefficients (r^2) for plots between various species measured during ClearfLo (and their products) 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 Supplement Fig. S1 for plots.

Species	r^2 for correlation vs. missing HONO
$j(NO_2)$	0.3046
H_2O	0.0049
NO	0.0008
NO_2	0.0009
temp	0.3241
$HNO_{3\,ads.}$	0.0914
OH	0.3139
HO_2	0.0984
RO_2	0.3132
$k(OH)$	0.0020
$NO_{3\,aero.}^-$	0.0001
$NH_{4\,aero.}^+$	0.0112
aerosol surface area (SA)	0.0001
$j(NO_2) \times NO_2$	0.6571
$j(NO_2) \times$ temp	0.6496
$j(NO_2) \times HNO_{3\,ads.}$	0.3082
$j(NO_2) \times k(OH)$	0.7479
$j(NO_2) \times NH_4^+$	0.5960
$H_2O \times HNO_{3\,ads.}$	0.0929
$NO \times HO_2$	0.1090
$NO_2 \times OH$	0.3782
temp $\times OH$	0.3660
$OH \times k(OH)$	0.3718
$OH \times NH_{4\,aero.}^+$	0.3910
$HO_2 \times k(OH)$	0.1180
$HO_2 \times NH_4^+$	0.1083
$RO_2 \times k(OH)$	0.3386

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 min averaged and plotted as UTC (LT −1 h).

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 min 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).
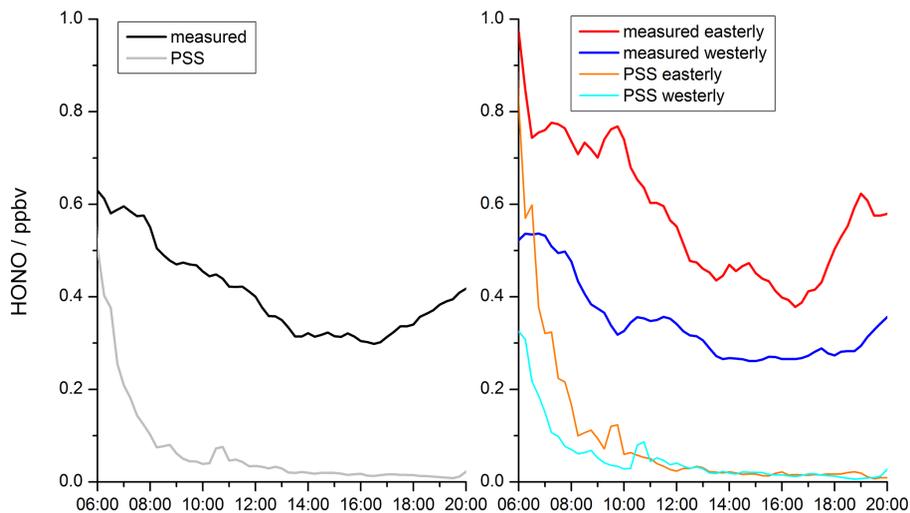
Figure 3. Average diurnal profiles (daylight hours) of measured (black) and photostationary state (PSS) calculated (grey) HONO (left panel). The right panel shows avaged dirunal profiles of measured and PSS HONO divded into easterly (red/orange) and westerly (blue/cyan) conditions.

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.
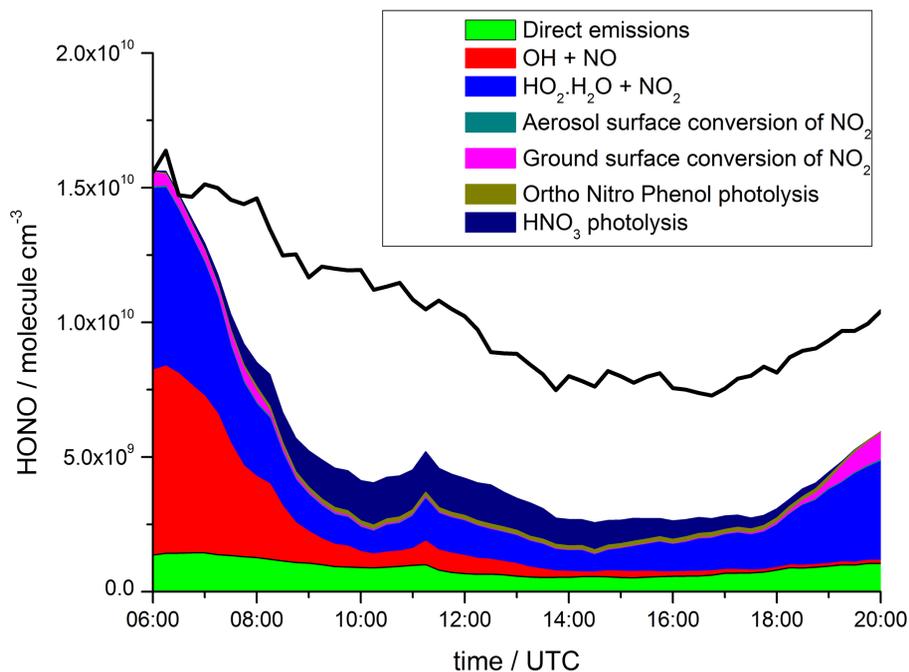
Figure 5. Average daytime dirunal profile of the modelled HONO from different sources shown as a compound area plot. Also plotted (black trace) is the measured HONO.
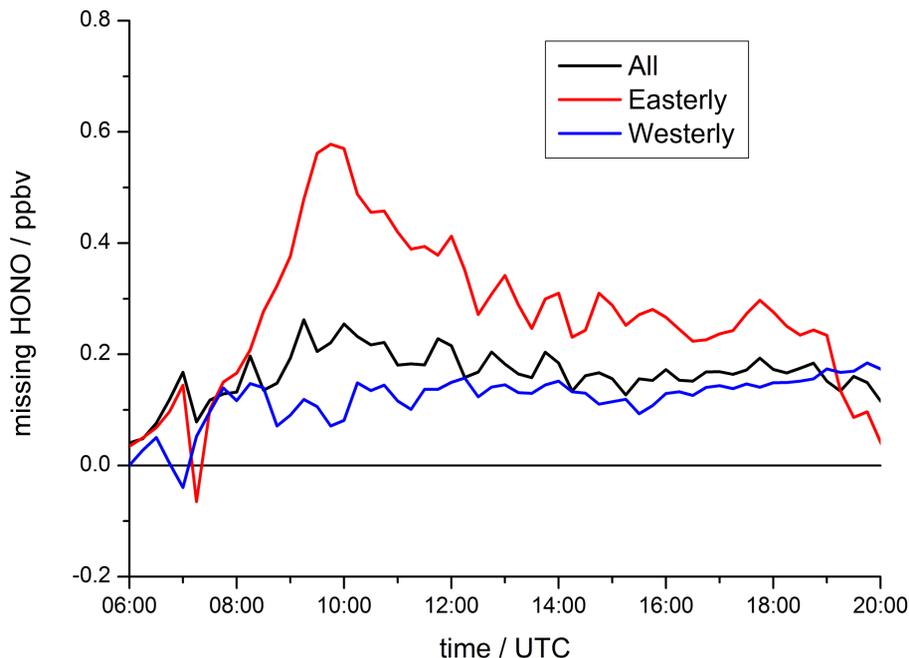
Figure 6. Average daytime dirunal profile of the "missing" HONO, defined as the difference between the measurement and model calculated HONO concentration. The black trace shows average of all data, the red trace shows the average of data from easterly conditions and the blue trace shows the avergae of data from westerly conditions.
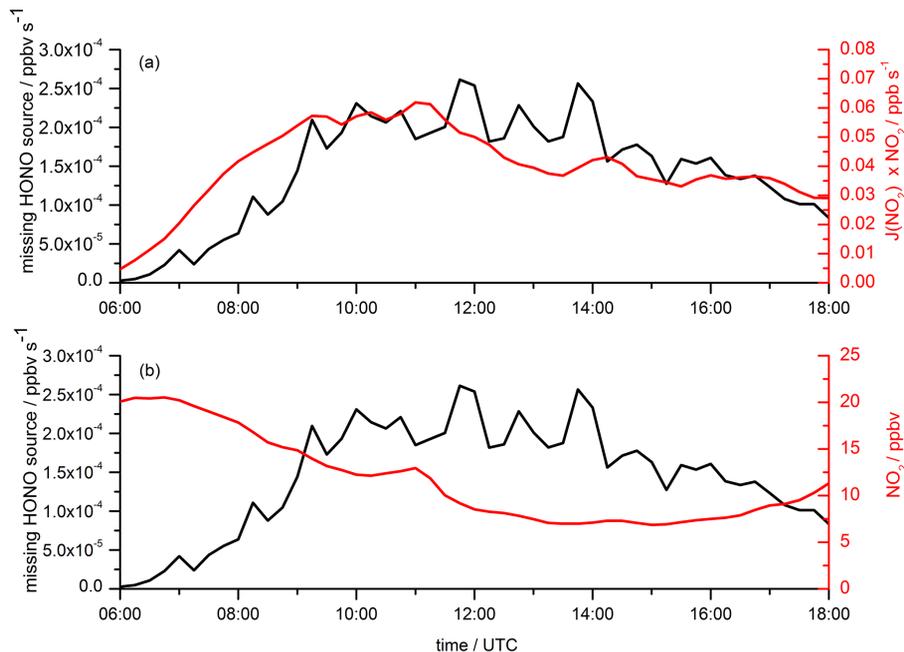
Figure 7. Average dirunal profiles of the missing HONO source (black traces) plotted with (as red traces) **(a)** $NO_2 \times j(NO_2)$ and **(b)** NO_2.
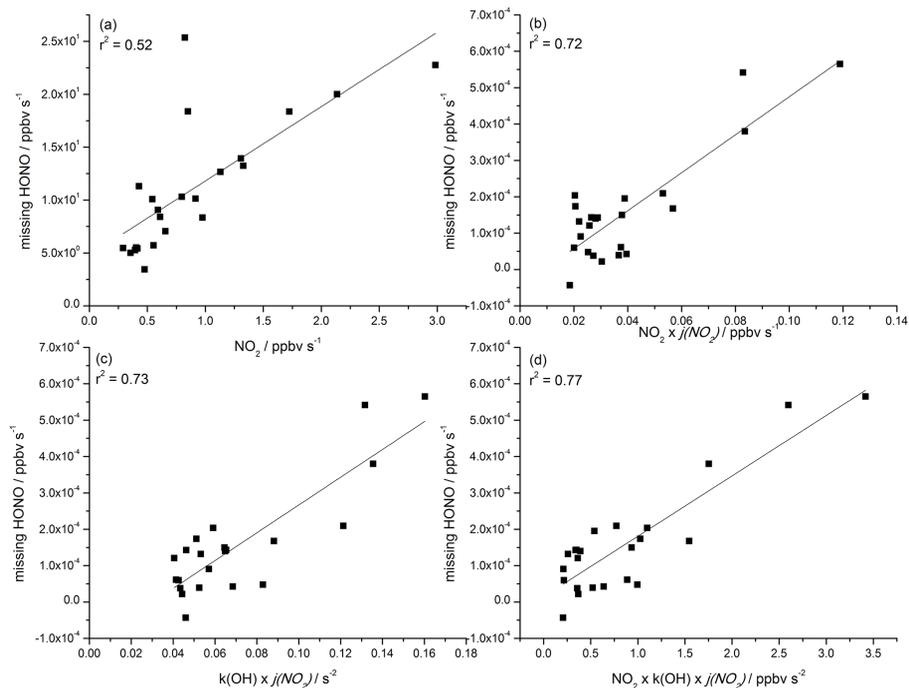
Figure 8. Daytime averaged (07:00–19:00) missing HONO source plotted against **(a)** NO_2, **(b)** $NO_2 \times j(NO_2)$, **(c)** $k(OH) \times j(NO_2)$, **(d)** $NO_2 \times k(OH) \times j(NO_2)$.
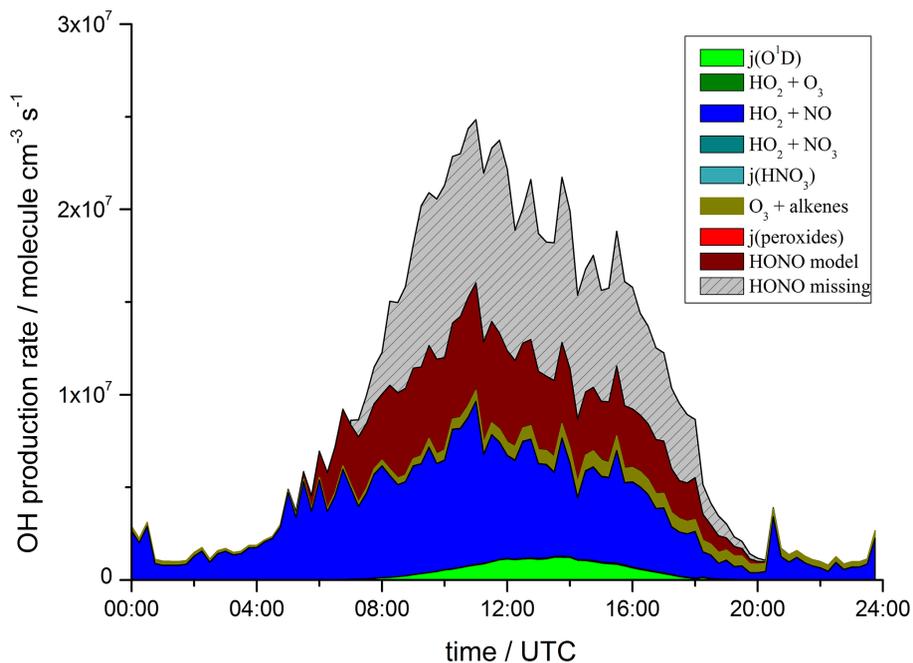
Figure 9. Average dirunal profile of gross OH production rates from different initiation and propagation sources calculated by the model.

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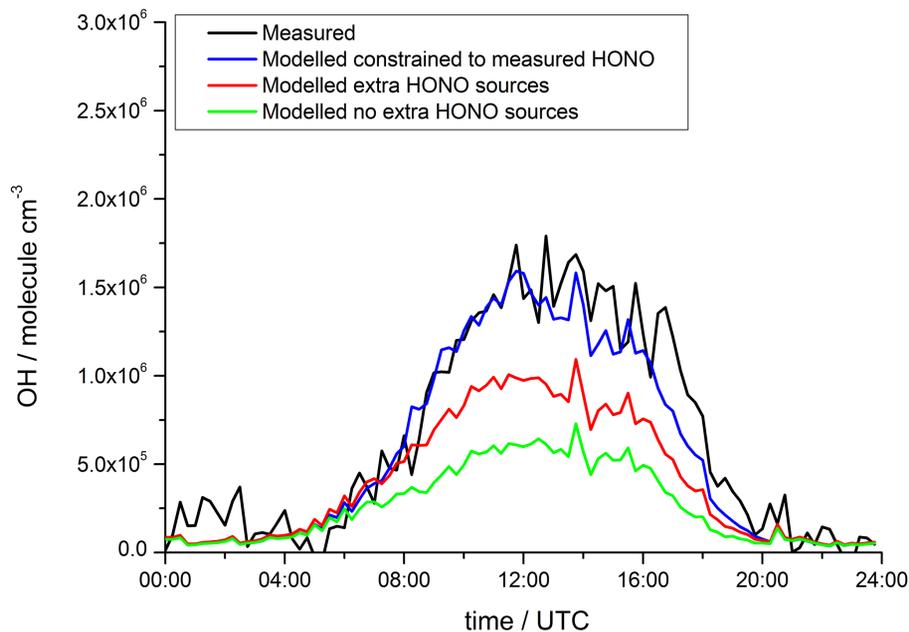
Figure 10. Average diurnal profile of OH, showing measured (black), modelled unconstrained to HONO with only NO + OH as a HONO soruces (green), modelled unconstrainted to HONO including additional HONO sources (red – see text for details) and model constrained to measured HONO (blue).