Below are the responses to the 2 reviewer comments (in blue text) followed by the revised manuscript with changes from the original ACPD version (new text in blue, deleted text stuck through in red).

We would like to thank reviewer 1 for their comments. We have tried to address the points below, along with how we have changed the manuscript.

Referee #1 comments:

The manuscript entitled, "Detailed budget analysis of HONO in central London reveals a missing daytime source" reports on measurements of nitrous acid (HONO) made during the ClearfLo 2012 campaign. The measured HONO levels exceed those of the calculated (assuming photo-stationary state and utilizing observed values of OH, jHONO and NO and parameterized deposition), indicating a "missing" HONO source. Inclusion of observed (as opposed to PSS) values into a box model results in a marked improvement in constraining observed OH mixing ratios. This daytime missing term – defined as difference between observed and PSS – is most correlated to the product of jNO2 and NO2 (as well as [NO2] × OH reactivity), possibly elucidating the production pathway. The analysis is thorough and this manuscript should be strongly considered for publication in ACP. A few questions I feel must first be addressed.

The reviewer gave page and line numbers from the original submission during the pre-review process and not for the published ACPD manuscript. To better follow the discussion we have added references to the line and page numbers of the final ACPD document.

Major:

The authors report negligible contribution from direct HONO emissions (lines 21-25 on page 3 (ACPD: page 22101 lines 7-9). This is based on the fact that HONO has a short lifetime during the day.

We actually do not say direct emissions make a negligible contribution, rather we say 'relatively small'. In our case the contribution from emissions is 5 – 10% so we have changed the text to make it clear that it can be an important contributor.

The same reasoning is invoked to justify assuming photostationary state (lines 28-31 on page 9 (ACPD: page 22106 lines 18-20)). The authors state that a 10-20 minute HONO lifetime (40-50 minutes for NOx) is for noontime conditions. Does the PSS assumption still hold in the early morning and late afternoon periods when HONO and NOx photo-lifetimes are much longer? The authors state (lines 4-6 on page 14 (ACPD: page 22113 lines 15-17).) PSS is not reliable at night. At what hour of day does the PSS assumption become valid? Even with a short (10-20 min) lifetime, close proximity of emission sources to the measurement site can test the PSS assumption. The authors note that the ClearfLo site was far downwind of sources such that PSS is established (lines 26-27 on page 9 (ACPD: page 22106 lines 15-17)).

This is an important concern. We now only consider data with J(HONO) > 4 x 10^{-4} s^{-1} and assume the PSS and MCM model simulations are only valid for these times (08:00 – 20:00 UTC). This is now stated in the manuscript (section 3.1 and 3.2). In addition, the stated time for NO_x of 40-50 min refer to the estimated average transport time of NO_x since emissions, the chemical lifetime of NO_x is much longer (some hrs). This will be also corrected in the revised manuscript.

Can you constrain the photochemical age of the airmass being sampled at each hour of day? At what (airmass photochemical age):(HONO lifetime) ratio can PSS safely be assumed?

To our understanding it is not the airmass photochemical age that is an issue, but simply the average NOx transport time to our site. If this is shorter than the photochemical lifetime of HONO then there could be a problem and as we have stated we do not believe this to be the case.

The authors note (lines 27-29 on page 8 (ACPD: page 22107 lines 12-14)) the observed daytime HONO/NOx ratio is above what has been reported in automobile exhaust, and this is evidence of secondary (likely photo-enhanced) HONO production. How does the model led NOx compare to that of the observed values? Have the authors accounted for the loss of NOx (by OH+NO2–>HNO3, NO2+HO2–>HO2NO2, NO+OH–>HONO, formation of organic nitrates, etc. following emission while being transported downwind) that can increase the HONO/NOx ratio?

We do not model the NO_x as this is beyond the capability of our model, however we believe that here the NO_x lifetime should be long enough (4-5 hours) compared to the average NO_x transport time since emission (40 – 50 minutes) so that we not have significant NO_x losses. In addition as described above, the HONO lifetime is the more important quantity here ($\tau_{HONO} << \tau_{NOx}$). HONO is emitted (together with NO_x) anywhere in central London and is transported to our site whilst going into PSS. So the contribution of HONO emissions to the HONO/NO_x ratio at the measurement site should be even lower than 0.008. Since we consider this fixed ratio here, direct emissions are even overestimated and the missing HONO source is underestimated.

The "daytime peak in HONO/NOx" (fig 2b) exhibits a different diel trend than the "missing" HONO (fig 6). How much of the observed HONO/NOx trend (fig 2b) can be explained by NOx oxidation?

We do not believe that NO_x oxidation is a major factor controlling the HONO/NO_x ratio (see argument about the relative lifetimes above). To clarify, we have changed figure 6 to show the rate of the missing HONO source [ppb hr^{-1}] rather than the magnitude of it [ppb]. This tracks the diurnal HONO/NO_x peak much better and is a better quantity to examine for this work. The concentration of the “missing HONO” is a strong function of J(HONO), and a small source in the morning will result in higher levels of missing HONO compared to noontime (short photolytic lifetime). The rate of production better describes source processes. We have updated the manuscript accordingly.

(Lines 26-30 on page 13 (ACPD: page 22113 lines 6-10)) The authors multiply measured NOx levels by 0.008 (reported HONO/NOx ratio in automobile exhaust by Kurtenbach et al. 2001) to estimate HONO from direct emissions. This approach, however, fails to account for the NOx that is lost by reaction, therefore, underestimates directly emitted HONO. Can the amount of NOx lost since emission be constrained? HONO levels during ClearfLo are strongly influenced by anthropogenics (lines 15-17 and 18-21 on page 8 (ACPD: page 22106 lines 27-29 and page 22107 lines 1-3)). Can directly emitted HONO be distinguished from that produced by secondary reaction(s) if HONO/NOx > 0.008 is entirely explained by NOx loss?

We do not believe NO_x loss to be an important factor at our site (see discussion above; $\tau_{HONO} << \tau_{NOx}$). Since the HONO loss since emission is far greater than the NO_x loss, using the initial emission ratio we believe we even overestimate the emission source in the model and thus, underestimate the extra HONO source. We have made this clear in the revised manuscript.

Minor:

Line 19, page 2 (ACPD: page 22100 lines 15-17): Reaction 2 is invoked before reaction 1. Perhaps change the order such that HONO+hv reaction is the first reaction?

Done

Lines 1-3, page 3 (ACPD: page 22103 line 20); lines 21-24, page 13 (ACPD: page 22113 lines 1-5): Instead of equal signs, arrow signs?

Done

Lines 24-27, page 5 (ACPD: page 22100 lines 15-17): There is a question mark.

Already removed in the ACPD revised version

Line 22, page 6 (ACPD: page 22104 line 23): Need a comma after 'briefly'

Done

Line 5, page 9 (ACPD: page 22107 line 23): Change 'maybe' to 'may be'

Done

Lines 26-30 on page 13 (ACPD: page 22113 lines 6-9): Authors state 60% of the observed NOx is directly emitted from automobiles. What is the source of the rest of the NOx and how much HONO is in this source?

We thank the reviewer for pointing this out – it is a good point. We have now removed the 0.6 term from our model and just use the HONO/NO_x ratio from all NO_x sources.

Figure 3a: Can you place error bars on both the observed (standard deviation or error) and calculated (accounting for uncertainty in OH, jHONO, HONO deposition) HONO values?

We have now done this.

We would like to thank reviewer 2 for their extensive comments. We have made an initial statement within the general comments as to how we have now changed the model in this study, which answers a few of the subsequent points. We also try to address all of the specific points below, along with how we have changed the manuscript.

Referee #2 comments:

General comments:

The Authors present an observationally-constrained model analysis of the unknown daytime HONO source. Measurements of HONO from an urban environment during the ClearfLo experiment are presented, showing levels similar to those observed in other urban environments. The Authors use these observations in addition to many supporting measurements to constrain the MCM to interrogate the potential source(s) of daytime HONO at this location. In particular, the Authors provide interesting commentary and analysis on the limitations of modeling this daytime source using the simple PSS approach instead of a photochemical box model such as the MCM, consistent with previous reports for urban environments (Lee et al., 2013). Mechanisms for the photolysis of o-nitrophenols, HO2+NO2 and heterogeneous conversion of NO2 to HONO on the ground and on aerosols have been added to the model to more fully represent the current state of knowledge in HONO production. The correlational analysis of a variety of collocated measurements with the modeled unknown daytime HONO source provides discussion consistent with previous reports in the literature, with a strong relationship observed with j(NO2) x NO2. The Authors then use the model to assess the impact of using observations versus model-generated HONO on the oxidative capacity of the atmosphere, finding that major discrepancies can arise.

One issue with the paper is the discussion is focused mainly on a single HONO source at the ground surface dependent on the conversion of NO2. This is done despite the clear evidence in the literature over the past 5 years that multiple mechanisms underpinning the HONO daytime source are likely at work and are variable depending on the observation location (e.g. HNO3 or particle nitrate photolysis, physisorption of HONO at mineral interfaces, soil nitrite partitioning from soil pore water, acid displacement of surface nitrite produced from deposited HONO, and microbial production of nitrite followed by soil emission of HONO). These mechanisms are all expected to have different diurnal trends and are not dependent on NO2 for the release of HONO. This suggests that correlational analyses, such as that presented, are biased from being able to identify phenomena which may have inconsistent temporal variability over the course of a day and between days.

The Authors clearly understand this limitation based on their discussion surrounding the inability to unequivocally confirm surface photoenhanced conversion of NO2 on sensitized organics with such an approach. Yet, the mechanism assigned to be the dominant daytime HONO source in discussion and in their concluding statements is the ‘photosensitized heterogeneous conversion of NO2 on organic substrates discovered in laboratory studies’, which is decidedly at odds with the current state of knowledge. Further, many variables in the correlational analysis that return moderate to strong correlations with the unknown daytime HONO source are not discussed in light of supporting mechanisms where they exist. This major issue certainly warrants discussion and, potentially, inclusion to a reasonable extent in the model analyses as these non-NO2 mechanisms are where modern lab and field measurements indicate significant daytime HONO may be generated.

In addition, the impact of vertical structure in radical reservoirs on the oxidative capacity of the atmosphere have certainly been presented in the literature, including using the MCM to assess the impact of HONO on OH levels. The lack of a 1D vertical transport component to this analysis, coupled to the use of HONO measurements made presumably within 10 m of the ground surface, mean that the impact on oxidative chemistry is biased by the proximity of the HONO measurements to the ground surface and do not apply throughout the daytime boundary layer.

Response to general comments

We are aware of also other HONO sources proposed for certain atmospheric conditions, however, our experimental data do not confirm most of them for the urban conditions in London (see discussion below). In addition, most of the sources listed by the referee were already cited in the introduction. As already stated in the text, we have not considered soil emissions here in detail, since the different postulated sources are a) still speculative b) depend on many uncertain variables (soil pH, bacterial activity, soil humidity, etc.) and c) most probably have a very minor contribution under our highly urban conditions (low soil coverage), even if the conditions would be optimal for that source (and they are often not, see e.g. Oswald et al., 2015, ACP, 15, 799). We have updated the reason for not including this in the manuscript.

The photolysis of HNO_3 using an upper limit deposition velocity and the high photolysis frequency based on several lab studies is considered in our model.

Further, we have reduced the yield of HONO from $HO_2 x H_2O$ + NO_2 to 3% in light of recent work by Ye et al. (2015) showing that this reaction is not as important as had previously been postulated.

We have reduced the effective boundary layer height in the model and the PSS calculation as we have estimated that for a HONO lifetime of 15 minutes HONO will on average only reach ~ 75 m height over ground (1/e). This “effective mixing height” is now considered for ground surface sources of HONO and also for its deposition losses.

Besides these modifications, we disagree with the statement that the photosensitized conversion of NO_2 “decidedly at odds with the current state of knowledge” for the following reasons:

a) There are several lab studies on different organic substrates now available confirming the first studies by George et al. (2005) and Stemmler et al. (2006). We feel that they are certainly important sources in the atmosphere, due to their fast uptake kinetics.
b) There are now several field studies available (including flux measurements, and detailed budget analysis studies) where similar findings (HONO source correlates with NO_2 x radiation, see below) confirm our proposed major source mechanism.
c) Results from recent papers mentioned below by the referee in which other sources were proposed based on field measurements are still under discussion. For example

> the results from the study of Pusede et al. (see below) can be easily explained by the well-known non-linear HONO formation by NO_2 conversion on different substrates. Laboratory studies show that HONO/NO_x is higher at low NO_x levels (Langmuir-Hinshelwood type kinetics). In addition, many field studies also confirm these lab observation (HONO/NO_x(rural): typically 10-20 %, much higher compared to HONO/NO_x(urban): only ca. 3-5 %). These observations are however not in contrast with NO_2 being a HONO precursor, for further details on other proposed reactions, see discussion below.

We have now added a parameterisation of light induced conversion of NO2 to HONO on aerosol surfaces in our model.

We have described all the extra HONO sources in our model point by point (section 3.3), which should now better describe exactly what we have included.

We also now carry out a sensitivity study into light induced conversion of NO2 to HONO on the ground surface and its effect on the 'missing' HONO source (section 4.2 of the revised manuscript), which shows that a first order conversion of $6x10^{-5}$ s^{-1} allows the HONO budget to be closed at all times other than late afternoon. We have introduced an extra figure (9) to show the effect of this on the HONO budget and comparison to the measurement.

In addition, also in contrast to the statement by the referee we have discussed some other correlations besides that with NO_2 x J(NO_2), (e.g. k(OH)), However, we have added a few more discussions on some other correlations in the revised manuscript (section 4.2).

The discussion in section 4.3 has been updated to reflect the changes to the model and how this in turn effects the modelled OH. Figures 9 and 10 now become 10 and 11 due to the addition of the extra figure 9 described above. The effect of 'missing' HONO is reduced from our original analysis due to the extra sources included in the model, however we still show that the effect of 'missing' HONO is important for OH production (adding around 20%) and hence for accurately predicting OH (as shown in figure 11). We do not include the effect of changing the light induced conversion of NO2 to HONO on the ground surfaces in this discussion as we feel this is speculative.

The missing 1D vertical model analysis would be indeed a preferable approach when ground surface processes are studied and when the whole boundary layer should be considered. In contrast, the results presented here describe only the radical budget at the measurements site (no vertical resolved measurement data available in the present study). This will be further clarified in the revised manuscript.

We now respond to each point in turn with details of how we have updated the manuscript.

Overall, a number of major revisions should be made prior to this manuscript being considered for publication in Atmospheric Chemistry and Physics.

Major comments:

1. Surface processes considered in the model and discussion are not comprehensive and should be updated.

Firstly, Sörgel and coauthors have demonstrated on a number of occasions that surface conversion of NO2 to HONO on photoexcited organics can only account for a fraction of observed daytime HONO in environments where humic-like substances are modelled to cover the entire ground surface (Sörgel et al., 2011a, 2015). In built environments such as London, other surface processes (e.g. nitrate photolysis in aqueous solution (Scharko et al., 2014), metal/mineral surface sorption (Donaldson et al., 2014), reduction of nitrate on organic aerosols (Rutter et al., 2014; Ziemba et al., 2010), photolysis of nitrate in urban grime (Baergen and Donaldson, 2013) and acid displacement of nitrite (VandenBoer et al., 2015)) should be considered plausible and included in the model if possible. These mechanisms and their potential importance must be presented in the discussion even if they cannot be explicitly represented in the model as they provide much needed context.

We thank the reviewer for the comprehensive listing of HONO sources, however we did not intend this paper to be a review concerning all HONO source studies related to any atmospheric conditions, but mainly only major studies related to the urban environment in this study were referred to in the introduction. However, we will add some more postulated HONO sources to the introduction in the revised manuscript.

We do not say here that the photosensitized conversion only takes place on humic like substrates. Other organic substrates like organic grime typically prevailing in urban environments may be important. However, the exact identification of the organics adsorbed on the urban surfaces is out of the scope of the present study. We just say, the source correlates with $J(NO_2)xNO_2$ (along with other things) and postulate the photosensitized conversion of NO_2 on a generic organic substrate (based on the only available known lab studies explaining that observation). In addition, in Sörgel et al. 2011, it was only 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 much faster compared to the artificial surfaces studied in the lab. Detailed lab 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 our study.

In addition, aqueous solutions (Scharko et al., 2014) in which HONO yields from nitrate photolysis may be enhanced by organics will be not important for the present field site, since there are no aqueous surfaces in the surrounding. Besides, the low photolysis frequency of aqueous nitrate (ca. $4x10^{-7}$ s^{-1}, 0° SZA) was not enhanced in Scharko et al. (2014) making that source less important independent on any HONO yield. Finally, the much faster photolysis of HNO_3 adsorbed on surfaces (10^{-5} s^{-1}) with a 100 % upper limit HONO yield is already included in our model. However even this fast source is contradicted by its small contribution in the model and by the correlation analysis (correlation of the missing HONO source with HNO_3(ads) or HNO_3(ads)$xJ(NO_2)$ is weaker compared to $NO_2xJ(NO_2)$).

In the study of Donaldson et al. (2014), only HONO adsorption/desorption on soil substrates as a function of the pH is studied, independent on the HONO source active. Thus, we feel these results are not in contrast to our proposed mechanism. In addition, since the pH and composition of the surrounding surfaces are not known, any parameterization of these pH-dependent physical soil processes would be completely speculative and cannot be considered here.

In contrast to the statement by the referee, in the study of Rutter et al. (2014), HNO_3 reduction on organic aerosols was explicitly excluded and a gas phase reaction was proposed. However, since the conditions of that lab study were far away from any atmospheric relevant situation (reaction in the presence of a saturated steam of a high molecular motor oil, ca. 200 ppb), we have not considered this source for the analysis of our field study. In addition, this is a dark reaction, while we have mainly considered the more important daytime HONO chemistry in the present manuscript caused by the discrepancy between known HONO sources and measurements only during daytime.

In the study of Ziemba et al. (2010) indeed a conversion of HNO_3 on organic aerosols was proposed based solely on field observations (which actually could be alternatively explained by air mass changes). However, HONO formation was only observed in the dark in that study, which is out of the scope of the present study (see above). In addition the completely absent correlation of the missing HONO source with aerosol nitrate (0.0006) also does not support this mechanism.

The lab study by Baergen and Donaldson is on the renoxification by HNO_3 on organic grime surfaces, in which however HONO was not detected. Thus, we might introduce that as a loss process for surface HNO_3, but not as a HONO source (HONO yield would be completely speculative). In addition, this source is not supported by our analysis for London (correlation of the missing HONO source with HNO_3(ads) or HNO_3(ads)x$J(NO_2)$ is much weaker compared to NO_2x$J(NO_2)$) even if HONO would be a product in this reaction.

In VandenBoer et al. (2015) a so called “acid displacement mechanism” is presented, which is based on the more than 100 years old inorganic chemistry rule that a “weak acid (here HONO) is displaced by a strong acid (e.g. HNO_3)”. They studied this for soil and similar substrates and also discuss the source for urban surfaces like concrete, which could be of importance for the field conditions in London. However, the “acid displacement efficiencies” were found to be highly substrate dependent (average 9% of adsorbed HONO was displaced) and accordingly, this source would be highly uncertain for London. Also, true “acid displacement efficiencies” in the real atmosphere will be by definition much lower than those determined in the clean lab experiments of VandenBoer et al. since nitrite (NO_2^-) is a very unstable salt, which is a) oxidized by any surface oxidant (O_2, O_3, H_2O_2, OH) and b) photolyzes to NO in the daytime atmosphere. These loss processes were not considered in VandenBoer et al. leading to expected “acid displacement efficiencies” much lower than 9% in the real atmosphere. VandenBoer et al. also calculated theoretical HONO fluxes based on their mechanism and compared these results with measured HONO fluxes during the CalNex campaign (Ren et al., 2011). While the magnitudes of the theoretical fluxes (which will likely be lower in reality - see above) were on the same order like the measured fluxes, the diurnal behaviour of the two fluxes was completely different (see their Fig. 4 c). Reasons for this are:

a) In Ren et al. the HONO flux correlated perfectly with NO_2 x radiation (in excellent agreement with our results), leading to an asymmetric shape of the flux with higher values in the morning compared to the afternoon (higher NO_2 in the morning).

b) In contrast, calculated fluxes by the “acid displacement mechanism” will maximize in the afternoon caused by the delayed formation of HNO_3 by NO_2+OH during daytime (HNO_3 is highest in the afternoon…) and subsequent acid deposition.

Thus, the different temporal shapes of measured and speculated fluxes clearly demonstrate that the “acid displacement mechanism” had no significant impact on HONO formation during CalNex and is also not supported by the experimental data of the present study. Here, the correlation of the missing HONO source with HNO_3(ads) is much weaker (0.096) compared to NO_2xJ(NO_2) (0.696).

Because of the high uncertainty of the “acid displacement efficiencies” and the contradiction of the propose mechanism to field data we have not included this mechanism in our model. The recent paper by VandenBoer et al. (2015) will be added to the references cited in the revised manuscript.

We have now added brief discussions on these other potential HONO sources to the manuscript (section 4.2).

Secondly, the implemented mechanism for the photolysis of surface nitrate used is for leaf surfaces using rates that have not formally been published. There are a number of recent literature reports that probe this mechanism specifically for surfaces more representative of urban environments, along with rates, and the analysis and discussion should be modified to reflect the current state of knowledge (Baergen and Donaldson, 2013; Ma et al., 2013; Nanayakkara et al., 2014; Scharko et al., 2014). Assumption of 100 % HONO yield is also not consistent with reports of product ratios in this literature and the citations within.

In contrast to the statement of the referee, the values which we used for the photolysis of adsorbed HNO_3 in our model (daytime maximum used is 1.2 x 10^{-5} s^{-1}) is not based on the unpublished lab results for leaf surfaces from the group of Xianliang Zhou, but is based on several of their former studies in which this photolysis frequency was determined on glass surfaces (e.g. Zhou et al., 2003). Using this photolysis frequency, atmospheric HONO levels (Zhou et al. 2003) and HONO fluxes (Zhou et al., 2011) could be explained for rural environments.

In contrast, a much higher photolysis frequency (10^{-3} s^{-1}) of HNO_3 adsorbed on urban grime was determined in Baergen and Donaldson (2013). However, they not measured HONO in their study (see above). Also, based on calculations by Zhou et al. (2003, 2011) in which good agreement with measurements was obtained for J(HNO_3=>HONO) = 10^{-5} s^{-1}, it is expected that such fast photolysis would strongly overestimated HONO near to the ground surface. Thus, we not include this highly uncertain HONO source in the model.

The paper of Ma et al. is a review, which we do not feel should be the basis of a photolysis frequency that we use in our model.

In Nanayakkara et al. (2014) no photolysis frequencies of HNO_3 are specified and thus, can also not be considered here.

In the study of Scharko et al. (2014) the photolysis was studied in the liquid phase. Besides the fact that there are no significant liquid surfaces near the field site, the small photolysis frequencies of nitrate in the liquid phase (4x10^{-7} s^{-1} at 0° SZA) were considered there, too low to be of importance even if the HONO yield was increased by the addition of organics. Thus, we also not considered this source.

And finally, in the studies of Zhou et al. HONO was a major product in the HNO_3 photolysis on glass surfaces and the photolysis frequency used (J(HNO_3=>HONO)) reflects only the

HONO formation (here the yield is 100 % per definition). Any lower yield would even reduce the significance of this reaction. In the manuscript we already stated that the 100 % yield was used as upper limit and even with this upper limit the contribution was found to be minor.

We have made it clearer in the manuscript what photolysis frequency was used and that our model will be an upper limit for this source.

2. Model is constrained by or compared to HONO measured at an unspecified height near the ground surface, but applied throughout the depth of the PBL.

The model simulations of the unknown daytime source and nighttime production are using HONO measured from a height not presented in the manuscript. Presumably this measurement was made within 10 m of the ground surface? Numerous measurements demonstrate that near-surface vertical structure in HONO can be significant at night and during the day (Oswald et al., 2015; Stutz et al., 2002; Villena et al., 2011; Wong et al., 2012; Young et al., 2012; Zhang et al., 2009) and that a model using a near-surface value distributed throughout the PBL or into a stable nocturnal boundary layer produces results inconsistent with observations (Kim et al., 2014; Sörgel et al., 2015; Vandenboer et al., 2013; Wong et al., 2013). 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.

The influence of vertical structure in radical reservoirs has also been demonstrated to have similar impact on collocated production of atmospheric oxidants (Young et al., 2012). In particular, the MCM has previously been shown to underestimate HONO contributions to OH production when the observation heights have not been confined to the same atmospheric layer (Kim et al., 2014).

This is indeed a good point and a 1D model would be clearly preferable when vertical transport is considered. Thus, our model results only represent the contribution of different HONO sources at the measurement height of all instruments (OH, HONO, NO_x) of ca. 5 m (now stated in the manuscript in section 2.1) and should not be used for the whole boundary layer. This is now clarified in the revised manuscript (section 4.1). However, since we have no information of the vertical structure of important trace species and of the vertical mixing for the present field campaign, 1D model calculations are out of the scope of the present study.

3. HONO/NOx has been demonstrated in numerous recent studies to be a questionable metric for identifying the activity of daytime HONO sources due to HONO production not being dependent on NO2.

Examples include: nitrate photolysis in aqueous solution (Scharko et al., 2014), on urban grime (Baergen and Donaldson, 2013), and on solid/frozen substrates (Anastasio and Liang, 2009; Honrath et al., 2002; Zatko et al., 2015), acid displacement (VandenBoer et al., 2015), mineral/metal sorption (Donaldson et al., 2014), soil nitrite pore water partitioning (Su et al., 2011), microbial production and emission (Maljanen et al., 2013; Oswald et al., 2013), and through weekend-weekday analyses (Pusede et al., 2015)).

Urban environments also pose a reasonable possibility that a significant loss of NO2 takes place in the formation of NO3 and N2O5, followed by reactive uptake and loss of these compounds to aerosol surfaces at night.

How do the Authors justify that the HONO/NOx analysis used represents a period of HONO production given that so much published evidence contradicts such an approach?

Although the HONO/NO_x ratio is indeed depending on many variables (e.g. WS, BLH, general pollution level: urban/rural/remote) it can nicely indicate the daytime HONO production for a single field site (see maxima in Fig. 2). In addition, by the increase of the HONO/NO_x ratio during all the night (until morning when NO_x emissions and photolysis start) night-time formation by NO_2 conversion can also be nicely demonstrated (see Fig 2 and also the discussion on Fig. 5 in Kleffmann et al., 2002). Thus, we disagree with the statement by the referee that HONO production is not dependant on NO_2. The NO_2 and irradiance dependence of the daytime HONO formation was for example confirmed by the above cited flux measurements by Ren et al. (2011). Flux measurements over irradiated surfaces are the most direct method to prove a surface source mechanism in the atmosphere. These results were also confirmed by recent flux measurements over soil surfaces of one of the co-authors here (Kleffmann) in the German/French PHOTONA project (manuscript in preparation). A light and NO_2 dependent HONO formation was also proposed in many other field studies from urban to remote conditions (e.g. Wong et al., 2012; Sörgel et al., 2011; Villena et al., 2011) and should definitely be considered. We do not say that other mechanisms as identified by lab studies are not important under certain conditions, but the experimental data of the present study do not confirm most of them for the field conditions in London.

Short comments to the cited references in the reviewer comment:

Scharko et al. (2014): aqueous nitrate photolysis, not important here (see above).

Baergen and Donaldson (2013): no HONO detected, not confirmed as a major source in London based on the correlation analysis (see above).

References to the frozen samples: We had no snow or ice during the field campaigns in London. Besides that, even over polar snow surfaces, the daytime source of HONO nicely correlated with NO_2 x $J(NO_2)$ in Villena at al., 2011.

VandenBoer et al. (2015): acid displacement not confirmed by present and other field data, see detailed answer above.

Donaldson et al. (2014): see above, not in contradiction with the present study.

References to the soil mechanisms: not considered here (urban field site).

Pusede et al. (2015): see above - results are not in contradiction with the proposed photosensitized NO_2 conversion.

Finally, with respect to the losses of NO_x and its impact on the HONO/NO_x ratio, the losses of HONO by photolysis are much faster than the chemical losses of NO_x. Thus, this ratio is not expected to be significantly affected by NO_x losses during daytime. For the nighttime this certainly has to be considered, but the night-time chemistry was not the focus of the present study.

Thus, for these reasons we believe our discussion using the HONO / NO_x ratio should remain in the manuscript.

4. Given that many hypothesized daytime HONO sources are present in the literature, the Authors' decision in making the assignment of a single daytime HONO source as the only one that matters based on a correlational analysis is questionable. The choosing of the photoexcited organic reduction of NO2 mechanism as the dominant daytime HONO source is biased by the chosen analysis.

The correlation approach taken by the Authors and others (e.g. (Michoud et al., 2014)) between HONO and other co-located measurements relies on the assumption that there is a single source responsible for the majority of the unknown daytime HONO source. This is inconsistent with the literature where up to six separate mechanisms (photoenhanced NO2, nitrate photolysis, acid displacement, NO2+HO2, soil partitioning, microbial production) have been presented that may account for more than 10 % of the unknown daytime HONO source. The Authors should be clear in that their approach is looking for the source(s) that have HONO production terms that most closely match the sum of the mechanisms and may allow for a tentative identification of mechanisms that have a more important role to play in this observational dataset. A correlational analysis throughout the daytime will only identify HONO production mechanisms that have a consistent diel cycle, such as the photoenhanced conversion of NO2 on organics.

Given the number of surface processes that are independent of NO2 in their production of HONO, it seems plausible that multiple mechanisms may be contributing to the HONO daytime source, but at different times of day and with differences between days (e.g. microbial activity, and evaporation of surface or soil water) and the discussion of this work should more appropriately reflect this.

Again, we do not say that other mechanisms than the photosensitized conversion of NO2 could not be important under certain conditions (e.g. HNO3 photolysis under rural conditions, see studies by Zhou et al.) but are expected to be of minor importance for the field site in London by the following reasons.

a) nitrate photolysis: This source is included in the model with upper limit kinetics, but is not significant. In addition, much lower correlations of the missing HONO source with HNO_3 and HNO_3 x radiation compared to analogue correlations with NO_2 are observed.

b) Acid displacement: see long discussion above; completely different diurnal profile expected for that source compared to the experimental data. In addition, much lower acid displacement efficiencies are expected in the atmosphere compared to the lab results caused by additional nitrite losses.

c) NO_2+HO_2: Reaction is included in the model. In addition to that, it turned out that even this source (which was speculated solely based on field data, not confirmed by any lab experiments) is not of importance in the atmosphere (Ye et al., 2015) and that HONO yields are much lower (<3 %) compared to the unity yield proposed in Li et al. (2014). These recent findings will be implemented in the revised manuscript, making this source completely unimportant for the present field site.

d) Microbial production: will be not important for the present field site (minor soil coverage).

In conclusion, we feel that our postulated source mechanism is the most reasonable one for the present field site and is confirmed by the correlation analysis. We have added to our discussion the above mechanisms along with reasons for not including them in our analysis (section 4.2).

The most thorough investigation of the unknown daytime HONO source dependence on light showed that total irradiance is a better predictor than j(NO2) or other photolysis rates (Wong et al., 2012, 2013). Why have the Authors used j(NO2) as their proxy in the correlational investigation? There are also other multiple or single parameter terms with significant correlation coefficients in Table 1 that are not discussed (e.g. OHxNO2, temperature) which would be consistent with other proposed mechanisms (i.e. production, deposition, and photolysis of HNO3 or displacement of HONO from a reservoir at the surface; soil emissions by bacterial processes or temperature-driven partitioning from surface water films after nocturnal deposition). Other strong correlation coefficients (e.g. j(NO2)xNH4+) are also not discussed and demonstrate that such relationships may be spurious or that unexpected mechanisms (Kebede et al., 2013) may be identified in urban environments.

We agree with the referee, that the two studies by Wong et al. are very nice pieces of work, especially since the vertical structure of the atmosphere was considered (1D approach). Unfortunately, this was not possible in the present study (see above).

In addition, the irradiance was used in Wong et al. instead of J(NO_2) (the latter is a measure for the actinic flux) to parameterize the photosensitized NO_2 conversion. However, we used here J(NO_2) for two reasons:

a) there were simply no UV-irradiance measurements available during the campaign and any conversion of actinic fluxes to the irradiance are highly uncertain, especially in the case of cloud coverage;

b) when considering the photochemistry on surfaces, only for completely horizontal, flat surfaces, the irradiance is a correct measure to describe the photons flux densities. However, for the highly urban situation in London, with surfaces orientated in all upwards directions (vertical walls, tilted roof tops, etc.) on which photosensitized HONO formation is expected, the 180° measured actinic flux is still considered as a reasonable measure for parameterization. In addition, the long-wavelength UV J(NO_2) was used instead of e.g J(O^1D), since this was shown to be a good measure to describe the photosensitized conversion of NO_2 on organic substrates in lab experiments (Stemmler et al., 2007) in agreement with field studies, see e.g. Elshorbany et al. (2009).

In the revised manuscript we have added further discussions on other (weaker) correlations observed, e.g. with temperature and OH. However, we do not expect significant contribution of the photocatalytic conversion of NH_3 into HONO on TiO_2 containing urban surfaces (Kebede et al., 2013), caused by the still very limited use of this air remediation technique in the urban atmosphere.

5. Referencing throughout the introduction and results and discussion should provide a more comprehensive survey of the recent literature. Citations provided do not represent first, best or most recent examples in many cases (see references provided above and in the following minor comments).

We have added some more references of importance for the present urban field and model study in the introduction and discussion to the revised manuscript. However, this is not a review on all postulated HONO sources and thus, e.g. studies on snow or liquid surface are not considered here. Finally, we also think it is difficult to judge what is the ‘best’ example of the work done as this is quite a subjective term.

Minor comments:

Unfortunately, it appears the reviewer gave page and line numbers from the original submission during the pre-review process and not for the published ACPD manuscript. To better follow the discussion we have added references to the line and page numbers of the final ACPD document.

Page 2, Lines 4-7 (ACPD: page 22099, lines 14-17): First instance where surface processes are clearly not considered and should be mentioned for their implementation or lack thereof in the model.

We have added the most important surface processes for the urban field site in London to our model (dark conversion of NO_2 on surfaces, photosensitised conversion of NO_2, HNO_3(ad) photolysis on ground and aerosol surfaces, HONO deposition). Because information on surfaces types in London is lacking, we will run a sensitivity analyses (varying the rate of photosensitised conversion of NO2 by an order of magnitude)- to assess how photosensitised NO2 conversion on ground surfaces can impact modelled HONO. Others sources were not considered for the reasons discussed above. We do now discuss the reasons for not including them in the discussion.

Page 2, Line 9 (ACPD: page 22099, lines 18-20): The product of NO2 with OH reactivity is essentially a proxy for the production and deposition rates of nitric acid. There are surface mechanisms in the literature that would support such a correlation, yet the Authors conclude that only NO2 and sunlight are good predictors. This needs to be revisited throughout the manuscript.

We do not think this statement is correct, since:

a) At this site NO_2 x k(OH) is not a good proxy for the production of HNO_3, since VOCs play an important role to describe k(OH). Whalley et al., ACPD, 15, 31247–31286, 2015, show that only around 20% of k(OH) is due to reaction with NO_2 during daytime during this study. This is now stated in the discussion section of the revised manuscript.

b) Even if NO_2 completely controlled k(OH), this would be only a good proxy for the production rate of HNO_3, but not for its concentration, which shows a maximum completely different to NO_2 (HNO_3: early afternoon, NO_2: morning). That is the reason for the much worse correlations of the missing HONO source with HNO_3 compared to NO_2 (see also the flux study by Ren et al., 2011), by which any HNO_3 dependent sources are highly unreasonable as major contributors to the daytime HONO formation in London. We definitely not say here that HNO_3 could not be a minor contributor in London (see also the HNO_3 photolysis included in the model) or a major contributor at other field sites.

Page 3, Lines 15-17 (ACPD: page 22101 lines 1-3): Tower or similar gradient measurements (Harrison and Kitto, 1994; Kleffmann et al., 2003; Oswald et al., 2015; Sörgel et al., 2011b, 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 (Li et al., 2014; Zhang et al., 2009) observations also have demonstrated that major HONO sources exist at canopy or ground surfaces through the measurement of vertical gradients. They should be mentioned here and cited appropriately.

Since the aim of the present study was not the description of the vertical structure of HONO sources, we only added here references to direct surface flux studies, by which potential source reactions can be best identified. Simple gradient studies are much more indirect and can only qualitatively describe source processes. Nevertheless, we have added some references to the gradient studies mentioned, which actually partially confirm our results (photosensitized conversion of NO_2 is a ground surface HONO source).

Page 3, Line 26 (ACPD: page 22101 line 12): The observations made in France (Michoud et al., 2014) do not constitute a review of the daytime sources. More comprehensive surveys of the literature include: (Ma et al., 2013; Pöschl and Shiraiwa, 2015; Spataro and Ianniello, 2014).

Although the paper Michoud et al., 2014 is not a direct review, we found that their introduction nicely covered almost all aspects of the daytime formation of HONO, even more precise compared to some reviews. It also described measurements in a city likely to have similar composition to London (no comparable study in London itself is available), so we felt it was important for it to be a prominent reference in the introduction. The review by Pöschl and Shiraiwa (2015), although highly complex and detailed (18 pages of references) focuses mostly on the interaction with the biosphere, which was thus not considered for the highly urban conditions of the present study. We also believe the use of references (when hundreds are available) is the subjective choice of the authors of a manuscript. We have changed the text so we don't describe the Michoud paper as a review.

Page 4, Lines 13-14 (ACPD: page 22102 lines 3-4): 'detailed' occurs twice in this sentence. Consider alternate phrasing.

Corrected.

Page 4, Line 30 (ACPD: page 22101 line 18): At what height above ground level is the HONO measurement made? What about all the supporting measurements used to constrain the MCM model? These missing details influence the subsequent ability to assess how the model may be limited in addressing the issue of daytime HONO formation. For example, how would vertical gradients in any of these species, particularly HONO in the early morning when stable surface layers can persist, bias the model results? What assurances can the Authors provide that the data they are using in their model runs is consistent with the assumptions being made between the model and the variety of measurements constraining it?

The sampling height of most measured species was around 5 m above the ground. In addition, due to the missing vertical resolved measurement data, the results of the present study reflect only the situation at the sampling height and should not be used to describe the chemistry at higher altitudes. This is now clarified in the revised manuscript.

Page 5, Line 1 (ACPD: page 22102 line 20): Remove ‘a highly sensitive’. The sensitivity of the LOPAP is given explicitly by the LOD later in the paragraph.

Done

Page 5, Lines 10-12 (ACPD: page 22102 lines 3-5): There is a potential for particulate matter to interfere with the tandem stripping coil setup used by the LOPAP. What if artifact nitrite was present in coarse particles that were stripped in the primary channel, but not in the secondary (Bröske et al., 2003; Kleffmann et al., 2006)? This has been demonstrated to be a problem, particularly with fog droplets (Sörgel et al., 2011b), which may have been present during this observation time period. Have such possibilities been considered and removed from the data used to drive the model?

For submicrometer particles we can definitely exclude any interferences by particle nitrite, since their sampling efficiency is <2 % in the very short stripping coil (4 coil sampler), see e.g. the cited study by Bröske et al. And even if that increased to values of 10 % for larger coarse particles, such an interference would be almost perfectly corrected for by the two channel approach (=> 10 % interference in the first coil = 9 % interferences in the second coil => error by an incomplete interference correction = 1%, in addition typically: [nitrite] < [HONO]…). However, for much larger fog particles (which 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, which is confirmed by excellent intercomparison exercises of the instrument with the DOAS technique (Kleffmann et al., 2006). We have stated this in the revised manuscript (section 4.1)

Page 5, Lines 14-16 (ACPD: page 22103 line 8-10): An intercomparison was not made during this campaign, and it is well documented that interferences are location-dependent, so it seems unnecessary to validate the performance of the LOPAP in this way. Suggest removing this sentence.

First, interferences are not location-dependent, since they depend only on the interfering trace species and not on the location. Second, the LOPAP instrument used here was intercompared several times to the DOAS technique and to a PTRMS covering a wide range of conditions, from smog chambers (pure and complex mixtures including photosmog experiments in the presence of soot particles) over semi-urban conditions, to a highly urban situation (Milan). Caused by the similarity of the latter to London (high NO_x conditions), there is no reason to expect any significant interferences for the present field conditions. Reasons for former successful intercomparisons are:

a) the used external sampling unit (no sampling lines used for the LOPAP);

b) the extremely short gas/liquid contact time of only ca. 10 ms,

c) the acidic sampling conditions (most known interferences are important under alkaline conditions (e.g. NO_2+SO_2, NO_2+phenols, PAN, …) and

d) the two-channel concept of the instrument (correction of interferences).

The reliability of the HONO data is of high importance here, and thus we would like to leave that sentence.

Page 5, Line 26 (ACPD: page 22103 line 20): Delete '?'

Already done in the ACPD version.

Page 5, Lines 27-30 (ACPD: page 22103 line 23-25): A detection limit is usually defined as three times the signal to noise for a data acquisition cycle, at minimum. This should be corrected here unless there is precedent for this approach?

This has been changed in the revised manuscript.

Page 6, Line 16 (ACPD: page 22104 line 18): Start a new paragraph at 'VOC' to help separate the different types of measurements being made.

Done.

Page 6, Line 19 (ACPD: page 22101 line 21): FID is not yet defined in the manuscript. Page 6, Line 21: Start new paragraph at 'measurements' again to help separate different classes of measurements.

Done.

Page 6, Line 28 (ACPD: page 22105 line 2): Start new paragraph at ‘non-refractory’. Also, what was the size selection of the cToF-AMS? PM1.0? Were sulfate and organics measured as well? If so, consider alternative phrasing here to reflect: the full suite of non-refractory compounds that were measured, what particle size the instrument cut off its measurements at, and mention what compounds in particular were useful for this work.

The size selection of the inlet is approximately PM1.0 (Zhang et al., 2004), sulphate and organics were measured as well (Young et al., 2015) and it is specifically nitrate that is of interest here because it pertains to the working hypothesis.

This has been updated in the manuscript.

Non-refractory PM1.0 nitrate, sulphate, organic matter, chloride and ammonium were quantified. This 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 (see Young et al., 2015),

Were there any particle number and size distribution measurements available to include in the data analysis? A correlation coefficient is presented in Table 1, so the source of this data should be included. There is extensive precedent showing that aerosols of atmospherically relevant composition, particularly those found in urban environments, are capable of converting NO2 to HONO. Is there any ability in this work to constrain such mechanisms against a ground surface source? Such comparisons have been limited and would be of great utility in guiding the focus of future field measurements.

We calculate total surface area using data from an aerodynamic particle sizer (APS) instrument by using the mean diameter of particles in each size bin (assume spherical) multiplied by the number of particles in that bin. In total there were 53 size bins ranging from 0.53 to 21.29 µm. Details of this have been added to the manuscript.

The discrimination between heterogeneous HONO formation on ground vs. particle surfaces in field campaigns needs gradient measurements not only of HONO, but also of all precursors and the particle surface area (for discussion, see Kleffmann et al., 2003), which was out of the scope of the present study. However, at least up to now, no heterogeneous reaction on particle surfaces have been identified which would be fast enough to explain near ground HONO levels in the urban atmosphere, the reason being the much higher S/V(ground) compared to S/V(particles) and the similar uptake kinetics on ground an particle surfaces (e.g. humic, organic, aqueous, soot, surfaces, etc.). This would be also in agreement with the low correlation with the particle surface in Table 1.

Page 7, Line 15 (ACPD: page 22105 line 13): There may be the possibility that NO2 from London is being transported over the open ocean to form HONO at night, only to be returned the following day with the sea to land breeze. Such formation has been shown before (Wojtal et al., 2011) and suggested that the surface layer of the ocean could act as a reservoir for HONO. Is there any evidence here that such partitioning and transport processes may contribute to the unknown daytime HONO source? Also, from here forward the referral to figures should be capitalized as 'Figure'

We do not believe this to be a source of HONO in London. Sea breeze effect observed in central London are very rare and the distance from the ocean to the measurement site is significant (~60 miles), so any HONO produced would not live long enough to be a significant source at this site.

Page 7, Line 23 (ACPD: page 22106 line 4): 'exception' should be plural

done

Page 8, Lines 3-29 (ACPD: page 22106 line 15 onwards): HONO to NOx ratios operate on the assumption that HONO only can be produced from NO2 as a precursor (see major comment above), so using this ratio to assign periods when there is unknown HONO production is biased to an NO2-centric hypothesis. The Authors should be clear that their approach is biased or consider removing this part of their analysis from the manuscript and replacing it with a more representative analysis of NO2 and non-NO2 daytime HONO formation mechanisms. Further, there are no error bars on the HONO/NOx figures. Are the daytime and nighttime values in HONO/NOx actually statistically different based on the variability in and accuracy of the measurements?

We feel that the presentation of error bars in Fig. 2 would completely overload at least the top figure (6 data lines). For the significance of the day and nightime data only the precision errors and not the accuracy matters. This is due to the low precision errors of the HONO and NO_x data and thus we do consider the difference to be significant.

Although the HONO/NO_x ratio is indeed dependant on many variables (e.g. WS, BLH, general pollution level: urban/rural/remote) it can nicely show the daytime HONO production for a single field site (see max. in Fig. 2). By the increase of the HONO/NO_x ratio throughout the night (until morning NO_x emissions and photolysis start) also night-time formation by NO_2 conversion can be nicely demonstrated (see Fig 2 and cf. also discussion on Fig. 5 in Kleffmann et al., 2002). In contrast HONO levels often stagnate to the end of the night, caused by decreasing precursor (NO_2) levels (cf. Fig. 4 and 5 in Kleffmann et al., 2002). Thus, we disagree to the reviewer's statement that NO_2 is not a precursor of HONO (see also discussion above). If that would be the case, why are the HONO/NO_x ratios (a few % in urban regions) so constant all over the world? For the reasons presented above, we do not feel we should remove the discussion and presentation on the HONO/NO_x ratio.

Page 8, Lines 28-29 (ACPD: page 22107 lines 12-14): 'suggests a significant secondary and probably photo-enhanced, HONO source'. This statement is unjustified speculation and should be removed. While it is a valid consideration, such an assertion that one mechanism is the dominant daytime HONO source before the model results are presented is premature. The data subsequently demonstrate a variety of mechanisms may be at work. Caution in revising conclusions after all revisions are made should be taken.

We agree with the reviewer that it is too early in the manuscript to make such a statement. We have changed the manuscript so that it now presents more of a discussion, stating:

“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 clear hint to an additional daytime source. In addition, the maximum of HONO/NO_x during daytime coincidences well with the one for radiation, which is again a hint for a photochemical process.”

Page 8, Line 32 to Page 9, Line 9 (ACPD: page 22107 line 15): The Authors should summarize the range of urban HONO values from the literature and cite the appropriate references. The four following sentences is an inappropriate comparison without knowing the vertical structure of HONO near the surface. HONO mixing ratios can vary by differences greater than those discussed within a few tens of meters of the ground surface at a single location. Furthermore, there are data spanning decades which are more comprehensive (i.e. greater instrumental diversity for HONO measurement and intercomparison) urban observations of HONO for Los Angeles and Houston that would likely provide better contrasts to the presented dataset.

In the original manuscript, we used references to very different urban conditions ranging from Santiago/Chile, Paris/France to two urban Chinese locations. We agree that this is probably insufficient and so have added a couple more references, also including urban DOAS observations in Milan, Italy (Kleffmann et al., 2006); and Houston, US (Wong et al., 2011). However, it is not a review of all HONO studies so we feel that comparing to a few relevant other measurements is sufficient.

Page 9, Lines 9-13 (ACPD: page 22107 line 26): This suggests even further that HONO/NOx is a poor proxy for understanding daytime HONO production.

We do not understand this comment. The similar HONO/NO_x ratios for very different urban conditions and very different daytime HONO levels are clear indication for NO_x being precursor of HONO (cf. again also Fig. 4 and 5 in Kleffmann et al., 2002).

Page 9, Lines 13-16 (ACPD: page 22108 line 2): It seems amiss to say that the range of HONO mixing ratios is the motivation for this modeling study. The consistent identification of daytime HONO above levels predicted from easily modeled mechanisms seems to be the true reason based on the work presented. The Authors should rework this transition to reflect exactly what the purpose of comparing the MCM to a PSS approach is.

We agree and have reworded this sentence in the revised manuscript.

Page 9, Lines 23-26 (ACPD: page 22108 lines 14-18): This is a fair critique, but misses the fact that vertical structure is also often not considered in unknown daytime HONO PSS calculations, with the exception of (Wong et al., 2012). The magnitude of the unknown source, in an environment where there is vertical structure in HONO through part or all of a day, is therefore dependent on the height above the ground surface that the measurements are being made. Further, the issue of using PSS for HONO has been raised previously and should be used as a comparison for this work (Lee et al., 2013).

We already cite the study of Lee et al. (2013) as an example of the issues surrounding the use of the PSS. We now mention the vertical structure in the text, however our work does not include any vertical structure data (see previous comments).

Page 10, Line 9 (ACPD: page 22109 line 3): Fix reference formatting.

Already done in the ACPD version.

Page 10, Lines 10-16 (ACPD: page 22110 lines 6-11): This is some nice commentary that is also consistent with the observational constraints of HONO vertical structure that the MCM would otherwise not capture. It would improve the argument here and the Authors should consider adding a sentence with this context.

Certainly, a 1D model approach would be preferable, however not possible caused by the missing experimental data (see above). Thus, here we only tried to account for the vertical transport, whenever this was important for the description of the near ground surface HONO concentration and its contribution to the OH chemistry at the measurement site. We now state this throughout the revised manuscript.

In contrast to the statement by the referee we addressed that issue also elsewhere in the document (e.g. for the NO_2 conversion on ground surfaces, see page 22111, lines 4-15). In addition, in the revised manuscript, we also stress that issue for the HNO_3 source description (see major issue point 4).

Page 10, Lines 21-23 (ACPD: page 22109 line 16): This value is not ‘virtually zero’. It is 50 times the LOPAP detection limit, which is determined at three times the signal to noise (i.e. S/N = 150). Consider rewording this sentence to ‘. . . decreases to < 0.05 ppbV by midday.’

We agree and now specify the lower boarder HONO PSS levels during daytime more exactly in the revised manuscript.

Page 11, Lines 15-17 (ACPD: page 22110 lines 12-13): This value for deposition velocity is three times less than what was used for HONO (unless the HONO deposition velocity was for a boundary layer of different depth?). This blanket approach likely isn't representative of the suite of compounds in the model that are central to the chemistry being probed (e.g. NO2 vs HNO3). How do the Authors justify this approach?

We agree that this was not a good approach. We now use surface deposition velocities (1/Rc) of 3 cm s^{-1} for HNO_3 and 2 cm s^{-1} for HONO and 1 cm s^{-1} for NO_2. For the total deposition velocities used in the model parameterization of the turbulent (Ra) and diffusive (Rb) mixing with the wind speed were used (VDI 3782, 2006). In addition, in order to better describe HONO source and sink prosses on ground surfaces, we now use an effective HONO mixing layer height of 75 m, calculated as the likely height to which HONO will reach (1/e), given a daytime lifetime of 15 minutes. The deposition velocity of all other species will not affect the results of the present study (HONO chemistry) to a significant extent. The model description has been updated in the manuscript.

Page 12, Lines 3-6 (ACPD: page 22111 lines 1-4): There are many published reactive uptake values for NO2, most are smaller than 0.03. How do the Authors justify using this value? Presumably this produces the best match of the modeled HONO to that observed at night, but the argument is not made and the data is not shown.

The value specified is not a "reactive uptake value", but the effective HONO yield of the dark NO_2 conversion on ground surface. We have used an effective yield measured directly in the atmosphere, which is in contrast to lab studies on pure substrates for which higher yields have been observed. Certainly - and as already discussed in that section – the number is highly uncertain, but will not affect our daytime results (the topic of the manuscript) to any significant extent, caused by the slow uptake kinetics of the dark uptake vs. the photoenhanced uptake (minimum one order of magnitude difference). So even with a 100 % HONO yield, the dark reaction would be not significant during daytime. In the revised manuscript we have in addition scaled the effective HONO yield to better describe nighttime formation of HONO, since the literature value (0.03) was determined over grass land, which is not representative for our field site.

Page 12, Lines 6-9 (ACPD: page 22111 lines 4-7): There is certainly a lot of uncertainty in this assumption since the model is trying to match HONO mixing ratios observed at the surface, while immediately diluting them throughout the boundary layer. If the HONO mixing ratios at the surface can be matched, then the sources of daytime HONO are over-represented by the difference in the HONO vertical gradient between the measurement height and the top of the mixed layer. Similar issues arise when investigating the influence of

HONO on the local OH production, which should be discussed in more detail in the appropriate section.

The point by the referee is already discussed in detail below this (ACPD: page 22111 line 9). Again a 1D model would be preferable, but it is not possible here.

Page 12, Line 9 (ACPD: page 22111 line 8): Delete ‘in contrast’ and start the sentence with ‘Strong HONO’. This sentence presents information that is consistent with the consequence of the prior assumption. It is not a contrast.

Done.

Page 12, Line 13 (ACPD: page 22110 lines 12-13): Is this why nighttime HONO is not presented in Figure 3?

The PSS approach would not work at night and so this is why we confined this study to the daytime. This is now made clear in the manuscript (see sections 3.1 and 3.2).

Page 12, Lines 19-25 (ACPD: page 22111 lines 19-26): The experimental data for the photolysis rates of HNO3 on leaf surfaces, to the knowledge of this Reviewer, have still not been published. In any case, leaf surfaces are not truly representative of urban environments and lab studies using better urban proxies have demonstrated that the HONO yield is not 100 % (Baergen and Donaldson, 2013; Nanayakkara et al., 2014; Scharko et al., 2014). The Authors should revisit the literature to constrain these model runs with more realistic HONO yields and HNO3 photolysis rates.

See answer above, the statement is not correct and we feel that we do use realistic values.

Page 12, Lines 26-32 (ACPD: page 22111 line 27 – page 22112 line 9): If this is the case, then the same argument is relevant for the previous section on HNO3 photolysis. Approximations of this have been presented and should be implemented in the model runs presented (Oswald et al., 2015; Sörgel et al., 2011a, 2015).

The approach used by the mentioned former studies were already applied here for the ground surfaces sources used in our model (homogeneous mixed surface layer), resulting only in a minor contribution to the measured HONO levels. From the difference to the measured HONO a major extra source was quantified, which correlates with NO_2 x J(NO_2) and the photosensitized conversion of NO_2 was inferred based on known lab studies. Because information on surfaces types in London is uncertain and NO_2 uptake kinetics on different surface types e.g. urban grime is also uncertain, we have run a sensitivity analyses (varying the reactive uptake of NO_2) to assess how photosensitised NO_2 conversion on ground surfaces can impact modelled HONO which shows that a reactive uptake coefficient of 10^{-5} allows the HONO budget to be closed (section 4.2). In contrast, the kinetics of an artificial humic acid (Aldrich), see Stemmler et al. (2006; 2007), as used in other studies, is not expected to represent the reality for an urban measurement site. Thus, our results give only an indication for the missing daytime source and further studies on real urban grime (etc.) surfaces are necessary for the future. Only based on such kinetic results could the photosensitized conversion of NO_2 be implemented correctly into a model.

Page 14, Lines 4-5 (ACPD: page 22113 lines 15-17): What is the implication of this statement? If the model cannot reproduce nighttime HONO, then how is it initializing each daytime calculation when not constrained to HONO? How does this affect the performance of the model with respect to daytime HONO chemistry?

We agree that it is not clear what we have done. We have now removed the statement about nighttime chemistry and state that we only consider what is happening during the day. We now only consider data from 08:00 UTC, a time at which all HONO produced during the night will have been lost. This has now been explicitly stated in the manuscript.

Page 14, Line 8 (ACPD: page 22113 line 19): ‘significantly’ Which statistical test was performed that substantiates this word choice?

We have removed the word ‘statistical’ as we did not carry out a full statistical analysis. We do now state that the discrepancy is outside the 10% error of the LOPAP instrument.

Page 14, Lines 14-15 (ACPD: page 22113 lines 26-27): If it is possible to ballpark the daytime contributions of onitrophenols to the daytime HONO budget without measurements, then it does not seem unreasonable to also consider the NO2-independent surface mechanisms from the literature that have been shown to have a greater potential significance on daytime HONO production. Addition of aerosol conversion of NO2 or photolysis of particulate HNO3 would also raise the impact in testing hypotheses contrasting the different surfaces present for production of daytime HONO.

The considered HONO source by nitroaromatics certainly represents an upper limit, and will be not important even if the description is erroneous. For the other NO_2 independent sources, not used in the model and not expected to be a significant importance for the present measurement site, see extended discussion above. In contrast to the statement by the referee an NO_2 conversion on aerosols was used in the model, see page 22111, point 3. In addition, we have added HNO_3 photolysis in the particle phase to the model and this is now discussed in the model description and shown on the figure.

Page 14, Lines 23-25 (ACPD: page 22114 lines 7-9): This term is dependent on the measurement height which has already been stated as having bias. Daytime HONO gradients have been reported previously (Vandenboer et al., 2013; Wong et al., 2012, 2013), so is this further analysis truly giving new insight into daytime HONO production?

While the magnitude of the missing HONO daytime source may be indeed depending on possible vertical gradients, its correlation with potential precursors will be not affected. In addition also the major contribution of HONO as a daytime source of OH radicals near to ground surfaces will be also not affected. Thus, we consider the results still important, although we are aware of the shortcomings compared to a 1D model analysis.

Page 14, Lines 28-31 (ACPD: page 22114 lines 13-15): In urban areas of California, NO2 dependence has been recently shown to not underlie daytime HONO production by using statistical analyses of weekend and weekday data from the CalNex campaigns (Pusede et al., 2015). Photolysis of nitrate deposited the previous day (Zhou et al., 2011) could also be consistent with the production of HONO from urban areas where NOx emissions are greater, but not be directly dependent on NOx. Assigning the likelihood of the daytime HONO production to NO2 is not unreasonable, but without putting the assertion in the context of other hypotheses is neglecting a large body of recent literature.

The term ‘significantly’ is used here again and should be addressed as with previous instances of this word choice.

The results by the study of Pusede et al. (2015) can be explained by the non-linear kinetics of heterogeneous NO_2 conversion reactions (NO_2+H_2O, NO_2+ organics, NO2+TiO2), which was not considered in that study (see also answer above: HONO/NO_x is expected to be higher on weekend, with low NO_x levels compared to weekdays. This is not a contrast to the proposed photosensitized conversion of NO_2). In addition, Ren et al. (2011) showed a high correlation of measured HONO fluxes with NO_2 x radiation for the CalNex campaign. Flux measurements are the most direct way to identify a ground surface source mechanism, much better than any statistical analysis.

Nitrate photolysis by deposited HNO_3 was considered in the model and is not able to describe measured HONO levels.

We have left this section unchanged as it is merely pointing to the potential source of the missing HONO, however our updated discussion section (see earlier comments) now more fully discusses other sources in the literature.

We again remove the word ‘significantly’.

Page 15, Lines 1-5 (ACPD: page 22114 lines 18-21): Is the photochemical model really more complete than the PSS for understanding daytime HONO production? PSS models can capture the underlying nighttime formation mechanisms of HONO fairly well and the magnitude of the unknown daytime source. The photochemical model does not have any vertical resolution or transport processes and this was used despite the fact that HONO is well documented to be formed from surface chemistry. Further to this point, statements here about the postulated HONO sources are simply not true as per the comments made in the major comments above, specifically for surface NO2 conversion on photosensitized surfaces (Sörgel et al., 2015). It seems that the point of using the MCM here is to get at the impact of near-surface HONO on radical reservoirs, since this would be the major reason for including all of the supporting measurements mentioned, but the issue is not presented clearly between the stated objectives at the outset of the manuscript, nor in the discussion.

If the major HONO source is missing, neither a PSS nor the MCM model can describe HONO daytime levels properly. Since the missing source correlates with NO_2 x $J(NO_2)$ a photosensitized NO_2 conversion – as identified in the lab – is proposed here. To the uncertain description of this source in other models, see answers above (nobody knows the kinetics for the urban surfaces of London). We have updated the manuscript introduction to make clearer the objectives of using the MCM study.

Page 15, Lines 23-25 (ACPD: page 22115 lines 12-15): This sentence is confusing. This seems to be saying that the LOPAP is not measuring all of the HONO, but if that was the case then the bias would be a higher HONO signal. Maybe rephrase to be clear that 2 ppb HO2NO2 at 15 % interference would explain the difference between measured and modeled HONO.

We agree and have updated the sentence accordingly.

Page 15, Lines 27-29: An intercomparison was not done during the ClearfLo study though, so this statement has marginal relevance. Consider removing. More suitable to the discussion would be statements summarizing the known maximum error in the LOPAP measurements of HONO from the literature, specifically those that cannot be easily corrected for, such as coarse particulate matter that is collected with bias in the measurement channel over the background channel (Bröske et al., 2003; Kleffmann and Wiesen, 2008; Sörgel et al., 2011b).

We feel this sentence is important, since we do not expect any other interferences in London compared to the similar urban conditions in Milan. All identified interferences are marginal including particle matter. For further details see answer above.

Page 16, Lines 3-8 (ACPD: page 22115 lines 22-24): j(anything) x NO2 that is relevant in the troposphere will give this relationship. Irradiance has been shown to be the best measure of unknown daytime HONO production through correlational analysis (Wong et al., 2012, 2013). This style of analysis may indicate that NO2 conversion on photoexcited organics is taking place, but should not be constrained to that interpretation as the production could equally be interpreted as any process related to photochemistry (e.g. Table 1 shows a stronger correlation with OH than with j(NO2)) and not dependent on NO2 (Pusede et al., 2015).

The use of irradiance would have been a better parameter to describe photolytic surface reactions for perfectly flat and horizontal surfaces, which we however do not have at our field site. In addition, we did not have such data available and calculating it from actinic fluxes has potentially large errors. So we use $J(NO_2)$ as a ‘proxy’ for radiation and now state this in the manuscript. However we do not feel this changes our conclusions. The correlations with

$J(NO_2)$ (0.539) is smaller than when NO_2 is included ($J(NO_2)xNO_2$: 0.696) in contrast to the inclusion of HNO_3 ($J(NO_2)xHNO_3$(ads): 0.435). All these results support our proposed mechanism. For answers to the statement that the source is not NO_2 dependent and to the Pusede et al. study, see above.

Page 16, Lines 12-20 (ACPD: page 22116 lines 6-14): This is, in effect, confirming that additional degrees of freedom allow for higher explanatory power in the variance of daytime HONO production. Maybe explain why such an approach is technically sound for isolating mechanisms of HONO production and how the variables explored may cause bias. Can this approach be used to soundly assign the dominant daytime HONO source? What about sources that have a more spurious, yet significant, nature within or between days? How does the error in the product of the two term investigations get taken into account when performing linear regression? Are the linear regressions weighted by the error in all measurements and/or the propagated error where two measurements are being combined? Is the regression utilizing an adjusted rˆ2 approach to account for the number of terms in the model?

All we can say about this analysis is that if r^2 increases when adding another precursor parameter it is likely that the source is more relevant. We do not attempt a full statistical analysis of this, it is merely to suggest potential parameters that may have an influence on HONO production that are not currently in our model.

Page 16, Lines 32-33 (ACPD: page 22116 lines 28-29): The Authors should explain how k(OH) represents surface organic matter in brief here. Some expansion is certainly warranted and may reduce the speculative tone of the photolytic NO2 conversion arguments.

If organic matter results from the uptake of semivolatile organics on surfaces, than it is reasonable that the postulated source correlates with k(OH) which represent, at least in part, VOC levels in the atmosphere. Whalley et al. (2015) showed that k(OH) was dominated by VOCs during the daytime at the measurement site (~80%). We have added this statement to the manuscript.

Page 17, Section 4.3 (ACPD: section 4.3): Vertical gradients in measured radical reservoirs have been demonstrated in the literature (Kim et al., 2014; Young et al., 2012) and, like HONO, not accounting for this vertical structure in a photochemical model may lead to biases. How might these previous studies affect the interpretation of the MCM results in this work?

We stress again, that the results of the present study are strictly only valid for the measurement site, i.e. close to the ground surfaces. For the analysis of the vertical structure of the HONO contribution to the OH initiation, our measurement data is not sufficient. Here further gradient studies would be necessary. We now state this in the revised manuscript.

Page 17, Lines 21-32 (ACPD: page 22117 lines 21-28): If the photochemical model is diluting the surface HONO throughout the boundary layer, but the HONO measured at the surface is part of a vertical gradient due to surface production and subsequent transport, would constraining the model to surface HONO measurements be appropriate for assessing HONO impacts on boundary layer OH production rates? Would it be more accurate to say that the model is being used to understand OH production at the HONO measurement height even though it is doing the chemistry in a dynamic boundary layer?

We agree with this and the manuscript has been updated accordingly.

Page 18, Lines 8-10 (ACPD: page 22118 lines 13-15): As with the previous comment, the vertical structure in HONO and radical reservoirs means that the model is heavily biased to the surface observations and that reproduction of observed OH is only valid near the measurement heights of the HONO and OH instrumentation, and not throughout the boundary layer. This should be clearly stated.

We agree with this and the manuscript has been updated accordingly.

Page 18, Lines 27-30 (ACPD: page 22119 lines 4-5): The result is still only a correlation, not a confirmation. Maybe if this gave the only high correlation value, but that is not the case.

We agree with this and have updated the text in the revised manuscript accordingly.

Page 19, Lines 4-6 (ACPD: page 22119 lines 14-16): The significance of these results is certainly that models need to get HONO formation chemistry and number densities right to understand OH production. However, vertical structure is not captured by this model and so the results only apply to the measurement height and caution should be used in the breadth of the conclusions.

We agree with this and have updated the text in the revised manuscript accordingly.

Table 1: There are a number of ‘species’ here that have published ‘mechanisms’ where correlations greater than 0.3 have been found, but are not discussed (e.g. j(NO2)*T; j(NO2)*NH4+, j(NO2)*k(OH), etc.). Certainly these warrant some expansion in the discussion since they are as important as the j(NO2)*NO2 finding and were included in this table for a reason. There are a number of other variables that were explored, that returned correlations greater than 0.3 that are consistent with other hypotheses presented for surface processes (e.g. photochemistry, partitioning from soil pore water as a function of temperature, production of HNO3). Further, this approach is looking only for a persistent daytime production mechanism and would miss any HONO production that has temporal variability

that is not captured by the included terms (e.g. soil microbial activity, changes in surface acidity and/or water leading to release of HONO).

We have added some discussion to other correlations in the revised manuscript.

Figure 2: Error bars in the measurements here would be useful in justifying the separation of easterly and westerly flows for further analysis. The LOPAP accuracy at 400 pptV is ±40 pptV, so are the daytime HONO values between the two transport conditions actually statistically different? If so, is it possible to exclude known LOPAP interferences from direct bias in these air masses (e.g. aerosols (Bröske et al., 2003), fog (Sörgel et al., 2011b))

What is the error in HONO/NOx? When the error is considered is there any statistically significant change in HONO between maximum and minimum HONO/NOx average values?

For the error analysis discussed by the referee only the precision errors and not the accuracy has to be considered. For example, the main contribution to the accuracy errors of the LOPAP results from the calibration (pipettes, flasks, standard, etc.). However, these errors are independent e.g. on the wind direction. Precision errors of the instruments used are much lower than stated here (e.g. only 1-2 % for the LOPAP and NOx at these concentrations). Since we also do not consider interferences to be of significant importance for the highly urban conditions in London (see above), differences between the data traces are significant. We feel that error bars on the figure would make it overly busy and would not add to the discussion for the reasons described above.

Figure 6: What explanatory power would an error of a factor of 2 in direct emissions of HONO have on this figure? Is the current data available on this satisfactory or is there a need for greater constraints so that better estimates of the unknown daytime source can be made? It would be interesting to see how the missing HONO term changes by constraining the model to the upper and lower limits of HONO/NOx from primary emissions.

We believe we have already overestimated the emissions as stated in the MCM model description text (there is significant HONO photolysis since emission of HONO/NOx but we used a constant emission ratio). We have now carried out a sensitivity analysis in the model by increasing the direct emissions by a factor of 2 and we see a 4% increase in the modelled HONO. Hence we do not believe direct emissions to be the source of the missing HONO. We now stated this in the text (section 4.2).

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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 x 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 (~~R1~~R2) and losses by photolysis (~~R2~~R1) and oxidation by OH (R3).

$HONO + h\nu \rightarrow OH + NO$ (λ <400 nm) (R1)

$OH + NO + M$ ~~=~~$\rightarrow$ $HONO + M$ (~~R1)~~

~~$HONO + h\nu = OH + NO$ (λ < 400 nm) (~~R2)

$HONO + OH$ ~~=~~$\rightarrow$ $H_2O + NO_2$ (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). ~~It is postulated that such processes involve the conversion of NO_2 or HNO_3~~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~~), although at most sites (with the exception of those adjacent to major roads or in tunnels),~~). At most sites, this is a relatively small contributor to HONO due to its relatively short atmospheric lifetime in the daytime (10-20 minutes~~). Recent reviews~~), 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 ~~are given in~~ under similar conditions to this study (in Paris) and a reivew by Kleffmann (2007) ~~and Michoud et al. (2014).~~ 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), ~~with subsequent investigation of potential missing sources.~~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 ~~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., 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° 31' 16'' N, 0° 12' 48'' W), which is situated in a residential area approximately 7 km ~~West~~ west of central London (defined here as Oxford Street). Measurements of ~~nitric oxide~~NO, ~~nitrogen dioxide~~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 ~~will be~~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 ~~one~~ for one data acquisition cycle was $\sim 1.3 \text{ x } 10^6$ ~~$\sim 4.5\times10^5$~~ molecule cm^{-3} for OH and $\sim 6.3\times10^6$ ~~$\sim 2.1\times10^6$~~ 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’~~ 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 aerodyn~~ma~~amic 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~~ 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 ~~photochemical lifetime~~ 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.

~~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 $[\mathrm{HONO}]_{\mathrm{PSS}}$ can be calculated using the following equation (1):

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

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 × $10^{-4}s^{-1}$), 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 $j(CH_3CHO)$)~~ 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 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, ~~W~~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 $\nu_{HONO}/BL = 6.4\times10^{-5}$ s^{-1}.

~~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 75 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 (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):

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

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

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

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

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 ~2×10^{-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 ν_{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 x 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 ~3 × 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 ν_{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 × 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 $NO_2 \rightarrow$ 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).

~~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 ~3 × 10-5 s-1 at midday (Bejan et al., 2006).~~

~~Heterogeneous conversion of NO2 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 NO2 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.~~

~~Heterogeneous conversion of NO2 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).~~

~~Photolysis of HNO3 on surfaces has been reported to produce HONO (Zhou et al., 2003; Zhou et al. 2011). We have estimated the concentration of HNO3 deposited to the ground surface from the gas phase HNO3 concentration that was measured during ClearfLo and a deposition velocity of HNO3 of 2 cm s-1 (Zhou et al. 2011). To assess the maximum impact of this potential HONO source, a photolysis rate of surface HNO3 which is two orders of magnitude faster than j(HNO3) 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 NO2 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 NO2 (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 1D transport model is recommended. We also 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 diurnal contribution).~~

~~It has been suggested that a reaction between HO2 and NO2 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 HO2 is suggested to be present as an HO2·H2O complex, and hence may show different chemical behaviour. Kinetic measurements of the self reaction HO2 + HO2 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 HO2+NO2 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 NO2 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 HO2 and NOx. However, recent laboratory work has shown that in fact, this reaction produces only a 3% yield of HOHO (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 H2O-complexed HO2 in the atmosphere (R4 & R5) and the major reactions of H2O-complexed HO2 in this urban environment (R6 and R7):~~

~~HO2 + H2O = HO2·H2O , k = 1.0 × 10-13 cm-3 s-1 (R4)~~

~~HO2·H2O = HO2 + H2O, k = 1.92 × 105 s-1 (R5)~~

~~HO2·H2O + NO2 = HONO , k = 2.1× 10-12 cm-3 s-1 (R6)~~

~~HO2·H2O + NO = OH + NO2 , k = 3.60 × 10-12 (e(270/T)) cm-3 s-1 (R7)~~

~~A direct emission source of HONO was also added to the model, using a ratio of HONO:NOx of 0.008 reported previously from tailpipe emission studies of NOx and HONO in tunnels (Kurtenbach et al., 2001) and the measured NOx concentrations, 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 minutes) compared to NOx.~~

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 (~~06~~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 (~~06~~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 morning~~. During this time, the HONO sources from direct emissions and the HO_2·H_2O + NO_2 reaction are roughly similar in magnitude to the OH + NO reaction).~~ The 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. ~~However, as explained above most probably the HO_2·H_2O + NO_2 reaction is overestimated 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 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 $NO_2 \times k(OH)$ 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 x 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).

~~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, 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 $NO_2 \times k(OH)$ (figure 8). These show that there is some correlation for all species, with the products of the species with $j(NO2)$ ($r^2 = 0.72$, 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; 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 ~~9~~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,~~ with the most important time being just before solar noon~~. ~~Here, ~~where 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%~~by around 20%. This result shows that, even when all currently known sources of HONO are added to a box model, ~~the crucial importance of the ~~missing HONO sources are still crucial ~~in the model ~~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 ~~10~~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 (~~~6~~40% during daytime). When the known or postulated HONO sources are included in the model, the predicted OH is increased by a factor of ~~around ~~1.4 – 1.6 during the day~~1.8~~. However, during the afternoon, predicted OH is still 20 – 30% lower than modelled ~~ 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 ~~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.~~ so that HONO OH radical production 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 ~~~-~~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 ~~a~~ direct ~~source from~~ 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 ~~100~~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. ~~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.

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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 ~~the photolysis term~~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.

Commented [AF1]: The table has been updated to show the new correlation coefficients following the new model runs.

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

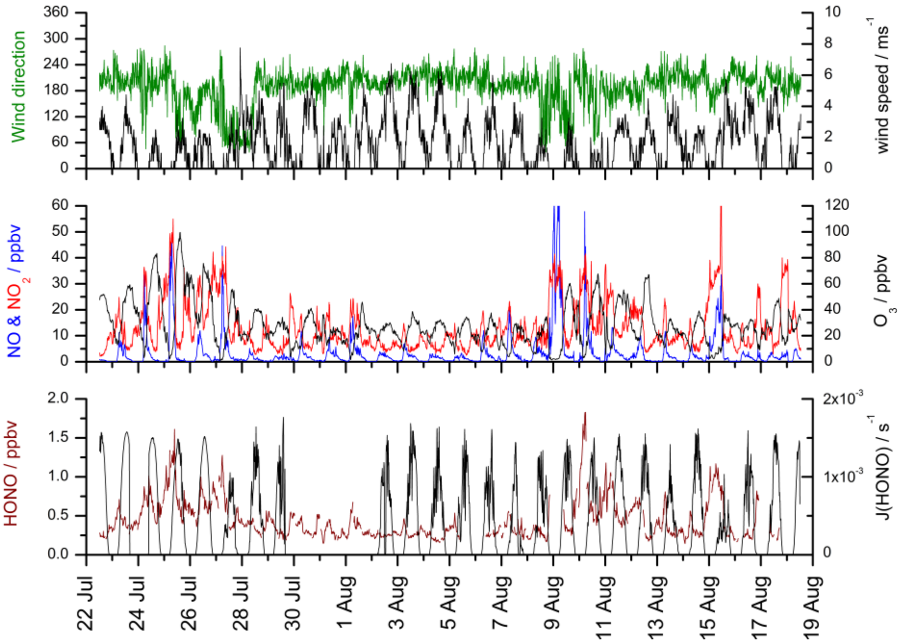

Figure 1. Time series of selected data from the ClearfLo intensive operation period (July and August 2012). The top panel shows wind speed (black) and wind direction (green); the middle panel shows NO (blue), NO_2 (red) and O_3 (black); and the bottom panel shows HONO (dark red) and j(HONO) (black).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

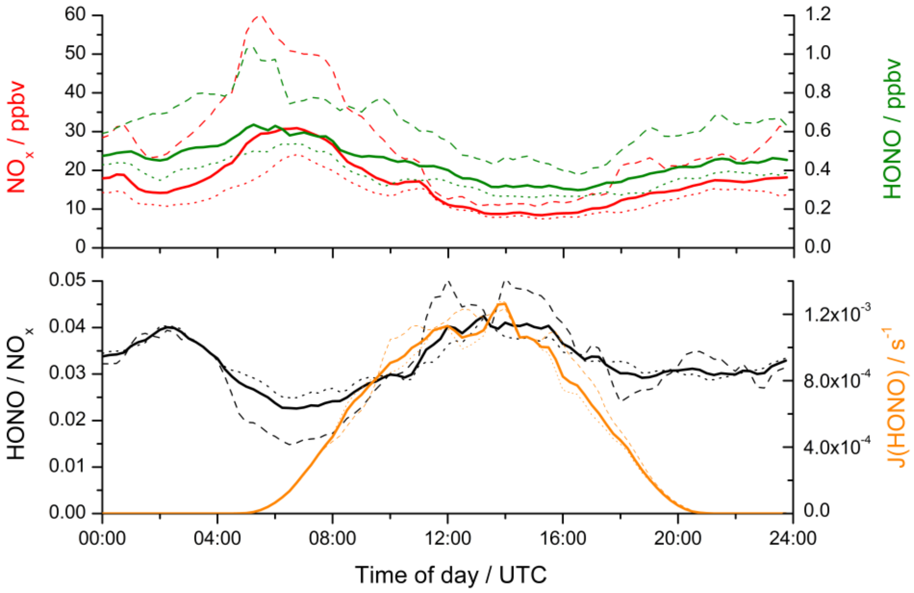

Figure 2. Average diurnal profiles of selected data from the IOP. The top panel shows total NO_x (red) and HONO (green) and the bottom panel shows *j(HONO)* (orange) and the HONO / NO_x ratio (black). Profiles were generated by binning all data in a 15 minute time period together. For each, the solid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

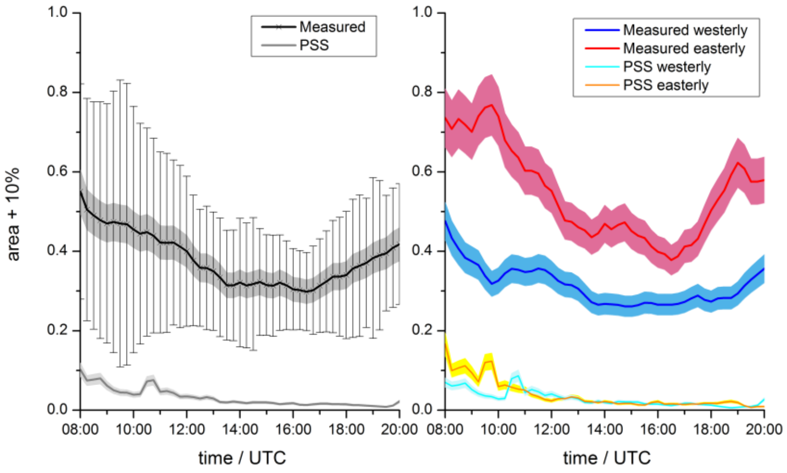

Figure 3. Average diurnal profiles (daylight hours) of measured (black) and photostationary state (PSS) calculated (grey) HONO (left panel). The shaded area represents instrumental (±10%) and model (±17%) error, the bars represent the standard deviation of the measurements. The right panel shows avaged 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.

Commented [JDL2]: This figure has been updated to show errors for the measurement and the PSS calculation, as well as the standard deviation for all the measurements that make up the average diurnal profile.

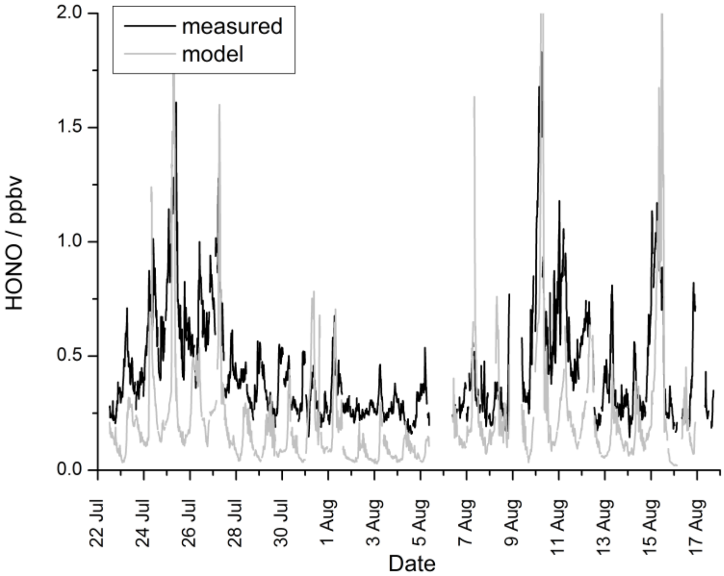

Figure 4. Time series of measured (black) and model calculated (grey) HONO during the IOP. The model was based on the Master Chemical Mechniasm (MCM v3.2), see text for details.

Commented [JDL3]: This figure has been updated to show the new model results.

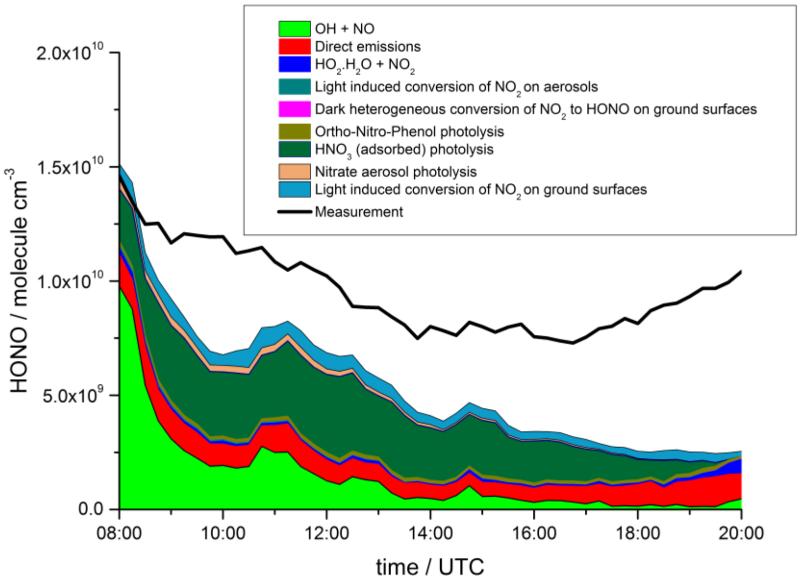

Figure 5. Average daytime dirunal profile of the modelled HONO from different sources shown as a compound area plot, as described in section 3.3 of the text. Also plotted (black trace) is the measured HONO.

Commented [JDL4]: This figure has been updated to show the new model results, including 2 new sources not previously included (nitrate aerosol photolysis and ground NO2 photolysis). We have also reduced the HO2.H2O + NO2 yield to 3% and changed the direct emissions (see details in text).

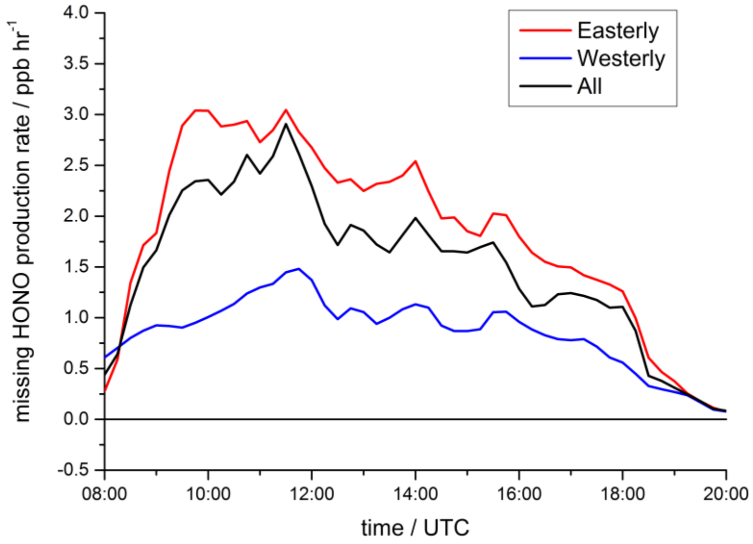

Figure 6. Average daytime dirunal profile of the ‘missing’ HONO production rate (in ppb hr^{-1}), defined as the rate of HONO production required to reproduce the measurements in the model. The black trace shows average of all data, the red trace shows the average of data from easterly conditions and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

Commented [JDL5]: Figure changed so it now shows missing HONO production rather than mixing ratio.

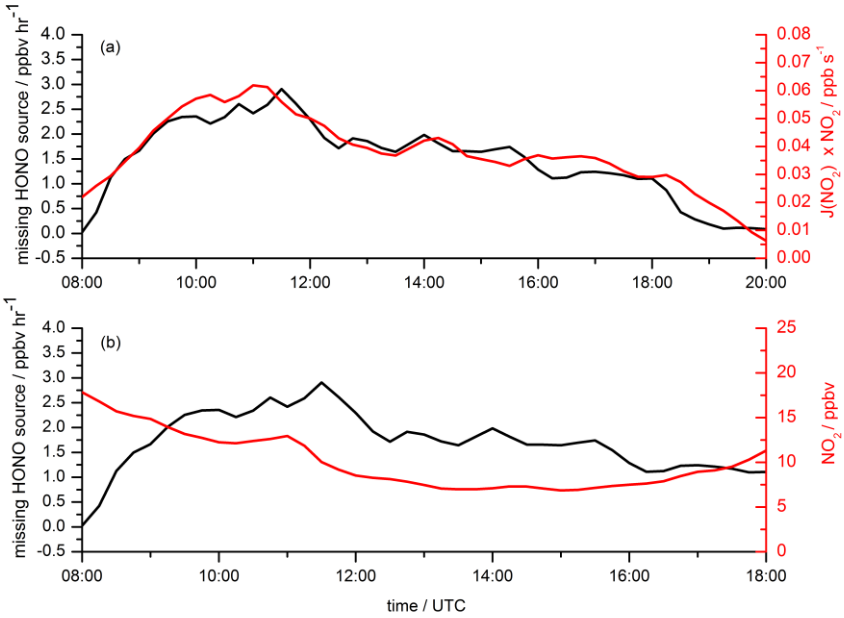

Figure 7. Average dirunal profiles of the missing HONO source (black traces) plotted with (as red traces) (a) NO_2 × $j(NO_2)$ and (b) NO_2.

Commented [JDL6]: Figure changed to show the updated model data.

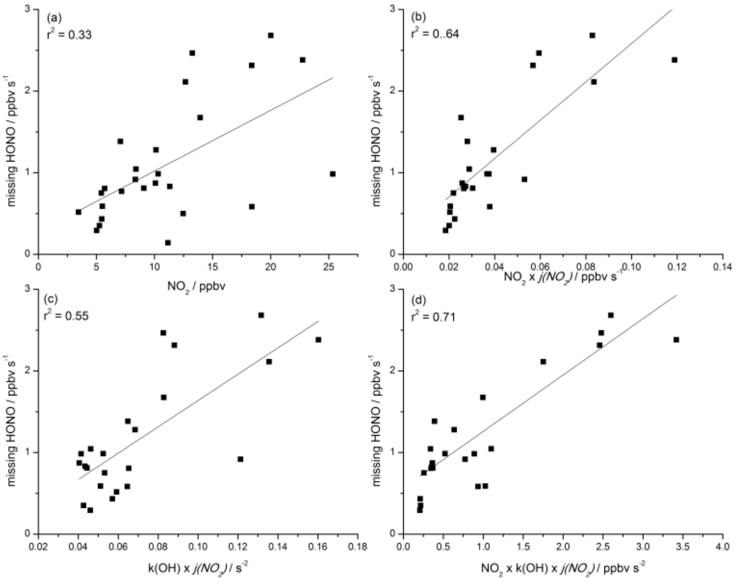

Figure 8. Daytime averaged (08:00 – 19:00) missing HONO source plotted against (a) NO_2, (b) NO_2 × *j*(NO_2), (c) *k(OH)* × *j*(NO_2), (d) NO_2 × *k(OH)* × *j*(NO_2).

Commented [JDL7]: Figure changed to show the updated model data.

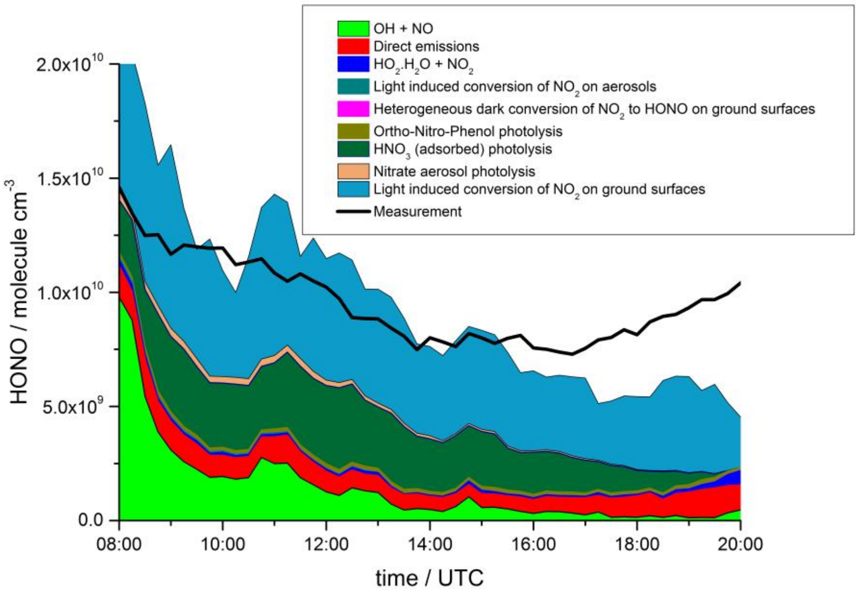

Figure 9. Average daytime dirunal profile of the modelled HONO from different sources shown as a compound area plot, as described in section 3.3 of the text, showing the result of increasing the reactive uptake coefficient of the light enhanced conversion of NO2 on ground surfaces (see text for details).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

Commented [JDL8]: This is a new figure showing the result of increasing the reactive uptake coefficient of the light enhanced conversion of NO2 on ground surfaces (see details in text).

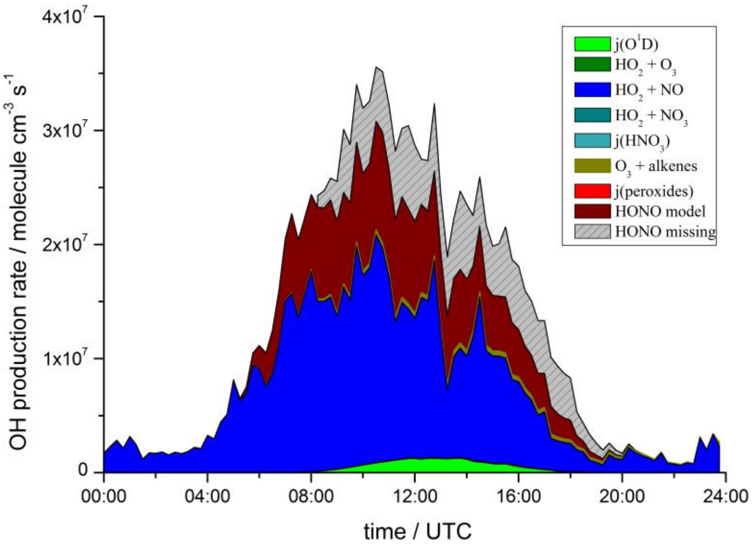

Figure 10. Average dirunal profile of gross OH production rates from different initiation and propagation sources calculated by the model.

Commented [JDL9]: Figure changed to show the updated model data. This was the old figure 9 in the ACPD submission

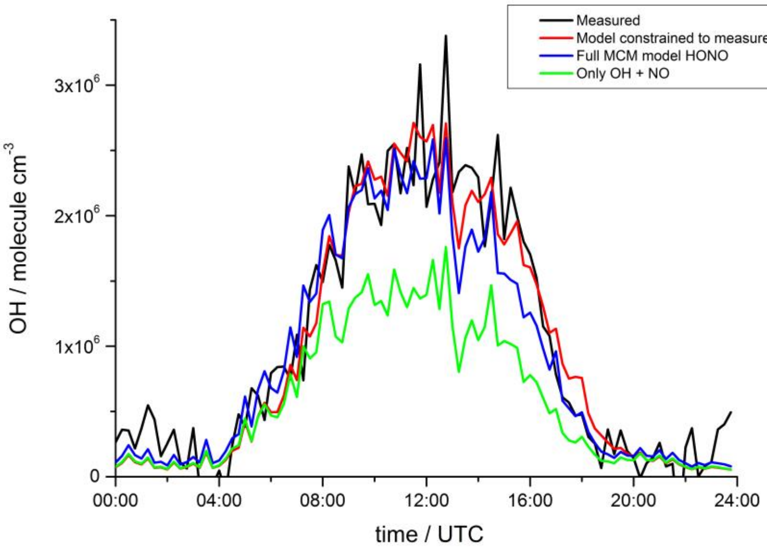

Figure 11. Average diurnal profile of OH, showing measured (black), modelled unconstrained to HONO with only NO + OH as a HONO sources (green), modelled unconstrainted to HONO including additional HONO sources (blue – see text for details) and model constrained to measured HONO (red).

Commented [JDL10]: Figure changed to show the updated model data)