

## ***Interactive comment on “Detailed budget analysis of HONO in central London reveals a missing daytime source” by J. D. Lee et al.***

### **Anonymous Referee #2**

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#### 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, HO<sub>2</sub>+NO<sub>2</sub> and heterogeneous conversion of NO<sub>2</sub> to

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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  $j(\text{NO}_2) \times \text{NO}_2$ . 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 NO<sub>2</sub>. 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. HNO<sub>3</sub> 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 NO<sub>2</sub> 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 NO<sub>2</sub> 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 NO<sub>2</sub> 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-NO<sub>2</sub> mechanisms are where modern lab and field

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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.

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 NO<sub>2</sub> to HONO on photoexcited organics can only account for a fraction of observed daytime HONO in environments where humic-like substances are modeled 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.

Secondly, the implemented mechanism for the photolysis of surface nitrate used is for

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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.

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).

3. HONO/NO<sub>x</sub> has been demonstrated in numerous recent studies to be a questionable metric for identifying the activity of daytime HONO sources due to HONO produc-

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tion not being dependent on NO<sub>2</sub>.

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; Zatkan 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 NO<sub>2</sub> takes place in the formation of NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub>, followed by reactive uptake and loss of these compounds to aerosol surfaces at night.

How do the Authors justify that the HONO/NO<sub>x</sub> analysis used represents a period of HONO production given that so much published evidence contradicts such an approach?

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 NO<sub>2</sub> 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 NO<sub>2</sub>, nitrate photolysis, acid displacement, NO<sub>2</sub>+HO<sub>2</sub>, 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

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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 NO<sub>2</sub> on organics. Given the number of surface processes that are independent of NO<sub>2</sub> 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.

The most thorough investigation of the unknown daytime HONO source dependence on light showed that total irradiance is a better predictor than  $j(\text{NO}_2)$  or other photolysis rates (Wong et al., 2012, 2013). Why have the Authors used  $j(\text{NO}_2)$  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. OHxNO<sub>2</sub>, temperature) which would be consistent with other proposed mechanisms (i.e. production, deposition, and photolysis of HNO<sub>3</sub> 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.  $j(\text{NO}_2)\times\text{NH}_4^+$ ) 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.

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).

Minor comments:

Page 2, Lines 4-7: First instance where surface processes are clearly not considered

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and should be mentioned for their implementation or lack thereof in the model.

Page 2, Line 9: The product of NO<sub>2</sub> 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 NO<sub>2</sub> and sunlight are good predictors. This needs to be revisited throughout the manuscript.

Page 3, Lines 15-17: 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.

Page 3, Line 26: 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).

Page 4, Lines 13-14: 'detailed' occurs twice in this sentence. Consider alternate phrasing.

Page 4, Line 30: 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?

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Page 5, Line 1: Remove 'a highly sensitive'. The sensitivity of the LOPAP is given explicitly by the LOD later in the paragraph.

Page 5, Lines 10-12: 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?

Page 5, Lines 14-16: 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.

Page 5, Line 26: Delete '?'

Page 5, Lines 27-30: 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?

Page 6, Line 16: Start a new paragraph at 'VOC' to help separate the different types of measurements being made.

Page 6, Line 19: 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.

Page 6, Line 28: Start new paragraph at 'non-refractory'. Also, what was the size selection of the cToF-AMS? PM<sub>1.0</sub>? 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.

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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 NO<sub>2</sub> 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.

Page 7, Line 15: There may be the possibility that NO<sub>2</sub> 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'

Page 7, Line 23: 'exception' should be plural

Page 8, Lines 3-29: HONO to NO<sub>x</sub> ratios operate on the assumption that HONO only can be produced from NO<sub>2</sub> as a precursor (see major comment above), so using this ratio to assign periods when there is unknown HONO production is biased to an NO<sub>2</sub>-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 NO<sub>2</sub> and non-NO<sub>2</sub> daytime HONO formation mechanisms.

Further, there are no error bars on the HONO/NO<sub>x</sub> figures. Are the daytime and nighttime values in HONO/NO<sub>x</sub> actually statistically different based on the variability in and accuracy of the measurements?

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Page 8, Lines 28-29: '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.

Page 8, Line 32 to Page 9, Line 9: 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.

Page 9, Lines 9-13: This suggests even further that HONO/NO<sub>x</sub> is a poor proxy for understanding daytime HONO production.

Page 9, Lines 13-16: 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.

Page 9, Lines 23-26: 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

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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).

Page 10, Line 9: Fix reference formatting.

Page 10, Lines 10-16: 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.

Page 10, Lines 21-23: 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 ...'

Page 11, Lines 15-17: 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. NO<sub>2</sub> vs HNO<sub>3</sub>). How do the Authors justify this approach?

Page 12, Lines 3-6: There are many published reactive uptake values for NO<sub>2</sub>, 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.

Page 12, Lines 6-9: 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

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section.

Page 12, Line 9: 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.

Page 12, Line 13: Is this why nighttime HONO is not presented in Figure 3?

Page 12, Lines 19-25: The experimental data for the photolysis rates of HNO<sub>3</sub> 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 HNO<sub>3</sub> photolysis rates.

Page 12, Lines 26-32: If this is the case, then the same argument is relevant for the previous section on HNO<sub>3</sub> 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).

Page 14, Lines 4-5: 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?

Page 14, Line 8: 'significantly' Which statistical test was performed that substantiates this word choice?

Page 14, Lines 14-15: If it is possible to ballpark the daytime contributions of o-nitrophenols to the daytime HONO budget without measurements, then it does not seem unreasonable to also consider the NO<sub>2</sub>-independent surface mechanisms from the literature that have been shown to have a greater potential significance on daytime

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HONO production. Addition of aerosol conversion of NO<sub>2</sub> or photolysis of particulate HNO<sub>3</sub> would also raise the impact in testing hypotheses contrasting the different surfaces present for production of daytime HONO.

Page 14, Lines 23-25: 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?

Page 14, Lines 28-31: In urban areas of California, NO<sub>2</sub> 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 NO<sub>x</sub> emissions are greater, but not be directly dependent on NO<sub>x</sub>. Assigning the likelihood of the daytime HONO production to NO<sub>2</sub> 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.

Page 15, Lines 1-5: 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 NO<sub>2</sub> 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

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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.

Page 15, Lines 23-25: 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 HO<sub>2</sub>NO<sub>2</sub> at 15 % interference would explain the difference between measured and modeled HONO.

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).

Page 16, Lines 3-8:  $j(\text{anything}) \times \text{NO}_2$  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 NO<sub>2</sub> 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  $j(\text{NO}_2)$ ) and not dependent on NO<sub>2</sub> (Pusede et al., 2015).

Page 16, Lines 12-20: 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

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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  $r^2$  approach to account for the number of terms in the model?

Page 16, Lines 32-33: The Authors should explain how  $k(\text{OH})$  represents surface organic matter in brief here. Some expansion is certainly warranted and may reduce the speculative tone of the photolytic  $\text{NO}_2$  conversion arguments.

Page 17, 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?

Page 17, Lines 21-32: 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?

Page 18, Lines 8-10: 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.

Page 18, Lines 27-30: 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.

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Page 19, Lines 4-6: 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.

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.  $j(\text{NO}_2)*T$ ;  $j(\text{NO}_2)*\text{NH}_4^+$ ,  $j(\text{NO}_2)*k(\text{OH})$ , etc.). Certainly these warrant some expansion in the discussion since they are as important as the  $j(\text{NO}_2)*\text{NO}_2$  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  $\text{HNO}_3$ ). 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).

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  $\pm 40$  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/ $\text{NO}_x$ ? When the error is considered is there any statistically significant change in HONO between maximum and minimum HONO/ $\text{NO}_x$  average values?

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

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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/NO<sub>x</sub> from primary emissions.

#### References:

Anastasio, C. and Liang, C.: Photochemistry of nitrous acid (HONO) and nitrous acidium ion (H<sub>2</sub>ONO<sup>+</sup>) in aqueous solution and ice, *Environ. Sci. Technol.*, 43(4), 1108–1114, doi:10.1021/es802579a, 2009.

Baergen, A. M. and Donaldson, D. J.: Photochemical renoxification of nitric acid on real urban grime, *Environ. Sci. Technol.*, 47(2), 815–820, doi:10.1021/es3037862, 2013.

Bröske, R., Kleffmann, J. and Wiesen, P.: Heterogeneous conversion of NO<sub>2</sub> on secondary organic aerosol surfaces: A possible source of nitrous acid (HONO) in the atmosphere?, *Atmos. Chem. Phys.*, 3, 469–474, doi:10.5194/acp-3-469-2003, 2003.

Donaldson, M. A., Bish, D. L. and Raff, J. D.: Soil surface acidity plays a determining role in the atmospheric-terrestrial exchange of nitrous acid., *Proc. Natl. Acad. Sci. U. S. A.*, 1–6, doi:10.1073/pnas.1418545112, 2014.

Harrison, R. M. and Kitto, A. M. N.: Evidence for a surface source of atmospheric nitrous acid, *Atmos. Environ.*, 28(6), 1089–1094, doi:10.1016/1352-2310(94)90286-0, 1994.

Honrath, R. E., Lu, Y., Peterson, M. C., Dibb, J. E., Arsenault, M. A., Cullen, N. J. and Steffen, K.: Vertical fluxes of NO<sub>x</sub>, HONO, and HNO<sub>3</sub> above the snowpack at Summit, Greenland, *Atmos. Environ.*, 36(15-16), 2629–2640, doi:10.1016/S1352-2310(02)00132-2, 2002.

Kebede, M. A., Scharko, N. K., Appelt, L. E. and Raff, J. D.: Formation of nitrous acid during ammonia photooxidation on TiO<sub>2</sub> under atmospherically relevant conditions, *J. Phys. Chem. Lett.*, 4(16), 2618–2623, doi:10.1021/jz401250k, 2013.

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Kim, S., Vandenboer, T. C., Young, C. J., Riedel, T. P., Thornton, J. A., Swarthout, B., Sive, B., Lerner, B., Gilman, J. B., Warneke, C., Roberts, J. M., Guenther, A. B., Wagner, N. L., Dubé, W. P., Williams, E. and Brown, S. S.: The primary and recycling sources of OH during the NACHT-2011 campaign: HONO as an important OH primary source in the wintertime, *J. Geophys. Res.*, 119, 6886–6896, doi:10.1002/2013JD020225. Received, 2014.

Kleffmann, J. and Wiesen, P.: Technical Note: Quantification of interferences of wet chemical HONO measurements under simulated polar conditions, *Atmos. Chem. Phys.*, 8, 6813–6822, doi:10.5194/acp-8-6813-2008, 2008.

Kleffmann, J., Kurtenbach, R., Lörzer, J., Wiesen, P., Kalthoff, N., Vogel, B. and Vogel, H.: Measured and simulated vertical profiles of nitrous acid - Part I: Field measurements, *Atmos. Environ.*, 37(21), 2949–2955, doi:10.1016/S1352-2310(03)00242-5, 2003.

Kleffmann, J., Lörzer, J. C., Wiesen, P., Kern, C., Trick, S., Volkamer, R., Rodenas, M. and Wirtz, K.: Intercomparison of the DOAS and LOPAP techniques for the detection of nitrous acid (HONO), *Atmos. Environ.*, 40(20), 3640–3652, doi:10.1016/j.atmosenv.2006.03.027, 2006.

Lee, B. H., Wood, E. C., Herndon, S. C., Lefer, B. L., Luke, W. T., Brune, W. H., Nelson, D. D., Zahniser, M. S. and Munger, J. W.: Urban measurements of atmospheric nitrous acid: A caveat on the interpretation of the HONO photostationary state, *J. Geophys. Res. Atmos.*, 118(21), 12274–12281, doi:10.1002/2013JD020341, 2013.

Li, X., Rohrer, F., Hofzumahaus, A., Brauers, T., Häseler, R., Bohn, B., Broch, S., Fuchs, H., Gomm, S., Holland, F., Jäger, J., Kaiser, J., Keutsch, F. N., Lohse, I., Lu, K., Tillmann, R., Wegener, R., Wolfe, G. M., Mentel, T. F., Kiendler-Scharr, A. and Wahner, A.: Missing gas-phase source of HONO inferred from Zeppelin measurements in the troposphere., *Science*, 344(6181), 292–6, doi:10.1126/science.1248999, 2014.

C8499

Ma, J., Liu, Y., Han, C., Ma, Q., Liu, C. and He, H.: Review of heterogeneous photochemical reactions of NO<sub>y</sub> on aerosol - A possible daytime source of nitrous acid (HONO) in the atmosphere, *J. Environ. Sci. (China)*, 25(2), 326–334, doi:10.1016/S1001-0742(12)60093-X, 2013.

Maljanen, M., Yli-Pirilä, P., Hytönen, J., Joutsensaari, J. and Martikainen, P. J.: Acidic northern soils as sources of atmospheric nitrous acid (HONO), *Soil Biol. Biochem.*, 67(August), 94–97, doi:10.1016/j.soilbio.2013.08.013, 2013.

Michoud, V., Colomb, A., Borbon, A., Miet, K., Beekmann, M., Camredon, M., Aumont, B., Perrier, S., Zapf, P., Siour, G., Ait-Helal, W., Afif, C., Kukui, A., Furger, M., Dupont, J. C., Haeffelin, M. and Doussin, J. F.: Study of the unknown HONO daytime source at a European suburban site during the MEGAPOLI summer and winter field campaigns, *Atmos. Chem. Phys.*, 14(6), 2805–2822, doi:10.5194/acp-14-2805-2014, 2014.

Nanayakkara, C. E., Jayaweera, P. M., Rubasinghege, G., Baltrusaitis, J. and Grassian, V. H.: Surface photochemistry of adsorbed nitrate: The role of adsorbed water in the formation of reduced nitrogen species on  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particle surfaces, *J. Phys. Chem. A*, 118(1), 158–166, doi:10.1021/jp409017m, 2014.

Oswald, R., Behrendt, T., Ermel, M., Wu, D., Su, H., Cheng, Y., Breuninger, C., Moravek, a, Mougin, E., Delon, C., Loubet, B., Pommerening-Röser, a, Sörgel, M., Pöschl, U., Hoffmann, T., Andreae, M. O., Meixner, F. X. and Trebs, I.: HONO emissions from soil bacteria as a major source of atmospheric reactive nitrogen., *Science*, 341(6151), 1233–5, doi:10.1126/science.1242266, 2013.

Oswald, R., Ermel, M., Hens, K., Novelli, A., Ouwersloot, H. G., Paasonen, P., Petäjä, T., Sipilä, M., Keronen, P., Bäck, J., Königstedt, R., Hosaynali Beygi, Z., Fischer, H., Bohn, B., Kubistin, D., Harder, H., Martinez, M., Williams, J., Hoffmann, T., Trebs, I. and Sörgel, M.: Comparison of HONO budgets for two measurement heights at a field station within the boreal forest (SMEAR II – HUMPPA-COPEC 2010), *Atmos. Chem. Phys.*, 15, 799–813, doi:10.5194/acp-15-799-2015, 2015.

C8500

Pöschl, U. and Shiraiwa, M.: Multiphase Chemistry at the Atmosphere–Biosphere Interface Influencing Climate and Public Health in the Anthropocene, *Chem. Rev.*, 150409151510004, doi:10.1021/cr500487s, 2015.

Pusede, S. E., VandenBoer, T. C., Murphy, J. G., Markovic, M. Z., Young, C. J., Veres, P., Roberts, J. M., Washenfelder, R. A., Brown, S. S., Ren, X., Tsai, C., Stutz, J., Brune, W. H., Browne, E. C., Wooldridge, P., Graham, A. R., Weber, R., Goldstein, A. H., Dusanter, S., Griffith, S., Stevens, P. S., Lefer, B. and Cohen, R. C.: An Atmospheric Constraint on the NO<sub>2</sub> Dependence of Daytime Near-Surface Nitrous Acid (HONO), *Environ. Sci. Technol.*, xx(xx), 8, doi:10.1021/acs.est.5b02511, 2015.

Rutter, a. P., Malloy, Q. G. J., Leong, Y. J., Gutierrez, C. V., Calzada, M., Scheuer, E., Dibb, J. E. and Griffin, R. J.: The reduction of HNO<sub>3</sub> by volatile organic compounds emitted by motor vehicles, *Atmos. Environ.*, 87(x), 200–206, doi:10.1016/j.atmosenv.2014.01.056, 2014.

Scharko, N. K., Berke, A. E. and Raff, J. D.: Release of Nitrous Acid and Nitrogen Dioxide from Nitrate Photolysis in Acidic Aqueous Solutions, *Environ. Sci. Technol.*, doi:10.1021/es503088x, 2014.

Sörgel, M., Regelin, E., Bozem, H., Diesch, J. M., Drewnick, F., Fischer, H., Harder, H., Held, A., Hosaynali-Beygi, Z., Martinez, M. and Zetzsch, C.: Quantification of the unknown HONO daytime source and its relation to NO<sub>2</sub>, *Atmos. Chem. Phys.*, 11(20), 10433–10447, doi:10.5194/acp-11-10433-2011, 2011a.

Sörgel, M., Trebs, I., Serafimovich, A., Moravek, A., Held, A. and Zetzsch, C.: Simultaneous HONO measurements in and above a forest canopy: Influence of turbulent exchange on mixing ratio differences, *Atmos. Chem. Phys.*, 11(2), 841–855, doi:10.5194/acp-11-841-2011, 2011b.

Sörgel, M., Trebs, I., Wu, D. and Held, A.: A comparison of measured HONO uptake and release with calculated source strengths in a heterogeneous forest environment,

C8501

Atmos. Chem. Phys., 15(16), 9237–9251, doi:10.5194/acp-15-9237-2015, 2015.

Spataro, F. and Ianniello, A.: Sources of atmospheric nitrous acid: State of the science, current research needs, and future prospects, *J. Air Waste Manage. Assoc.*, 64(11), 1232–1250, doi:10.1080/10962247.2014.952846, 2014.

Stutz, J., Alicke, B. and Neftel, A.: Nitrous acid formation in the urban atmosphere: Gradient measurements of NO<sub>2</sub> and HONO over grass in Milan, Italy, *J. Geophys. Res. Atmos.*, 107(22), doi:10.1029/2001JD000390, 2002.

Su, H., Cheng, Y., Oswald, R., Behrendt, T., Trebs, I., Meixner, F. X., Andreae, M. O., Cheng, P., Zhang, Y. and Pöschl, U.: Soil nitrite as a source of atmospheric HONO and OH radicals., *Science*, 333(6049), 1616–1618, doi:10.1126/science.1207687, 2011.

Vandenboer, T. C., Brown, S. S., Murphy, J. G., Keene, W. C., Young, C. J., Pszenny, A. A. P., Kim, S., Warneke, C., De Gouw, J. A., Maben, J. R., Wagner, N. L., Riedel, T. P., Thornton, J. A., Wolfe, D. E., Dubé, W. P., Öztürk, F., Brock, C. A., Grossberg, N., Lefer, B., Lerner, B., Middlebrook, A. M. and Roberts, J. M.: Understanding the role of the ground surface in HONO vertical structure: High resolution vertical profiles during NACHTT-11, *J. Geophys. Res. Atmos.*, 118(17), 10155–10171, doi:10.1002/jgrd.50721, 2013.

VandenBoer, T. C., Young, C. J., Talukdar, R. K., Markovic, M. Z., Brown, S. S., Roberts, J. M. and Murphy, J. G.: Nocturnal loss and daytime source of nitrous acid through reactive uptake and displacement, *Nat. Geosci.*, 8(1), 55–60, doi:10.1038/ngeo2298, 2015.

Villena, G., Kleffmann, J., Kurtenbach, R., Wiesen, P., Lissi, E., Rubio, M. A., Croxatto, G. and Rappenglück, B.: Vertical gradients of HONO, NO<sub>x</sub> and O<sub>3</sub> in Santiago de Chile, *Atmos. Environ.*, 45(23), 3867–3873, doi:10.1016/j.atmosenv.2011.01.073, 2011.

Vogel, B., Vogel, H., Kleffmann, J. and Kurtenbach, R.: Measured and simulated ver-

C8502

tical profiles of nitrous acid - Part II. Model simulations and indications for a photolytic source, *Atmos. Environ.*, 37(21), 2957–2966, doi:10.1016/S1352-2310(03)00243-7, 2003.

Wojtal, P., Halla, J. D. and McLaren, R.: Pseudo steady states of HONO measured in the nocturnal marine boundary layer: A conceptual model for HONO formation on aqueous surfaces, *Atmos. Chem. Phys.*, 11(7), 3243–3261, doi:10.5194/acp-11-3243-2011, 2011.

Wong, K. W., Tsai, C., Lefer, B., Haman, C., Grossberg, N., Brune, W. H., Ren, X., Luke, W. and Stutz, J.: Daytime HONO vertical gradients during SHARP 2009 in Houston, TX, *Atmos. Chem. Phys.*, 12(2), 635–652, doi:10.5194/acp-12-635-2012, 2012.

Wong, K. W., Tsai, C., Lefer, B., Grossberg, N. and Stutz, J.: Modeling of daytime HONO vertical gradients during SHARP 2009, *Atmos. Chem. Phys.*, 13(7), 3587–3601, doi:10.5194/acp-13-3587-2013, 2013.

Young, C. J., Washenfelder, R. a., Roberts, J. M., Mielke, L. H., Osthoff, H. D., Tsai, C., Pikelnaya, O., Stutz, J., Veres, P. R., Cochran, A. K., Vandenboer, T. C., Flynn, J., Grossberg, N., Haman, C. L., Lefer, B., Stark, H., Graus, M., De Gouw, J., Gilman, J. B., Kuster, W. C. and Brown, S. S.: Vertically resolved measurements of nighttime radical reservoirs in los angeles and their contribution to the urban radical budget, *Environ. Sci. Technol.*, 46(20), 10965–10973, doi:10.1021/es302206a, 2012.

Zatko, M. C., Geng, L., Alexander, B., Sofen, E. D. and Klein, K.: The impact of snow nitrate photolysis on boundary layer chemistry and the recycling and redistribution of reactive nitrogen across Antarctica in a global chemical transport model, *Atmos. Chem. Phys. Discuss.*, 15(13), 18963–19015, doi:10.5194/acpd-15-18963-2015, 2015.

Zhang, N., Zhou, X., Shepson, P. B., Gao, H., Alaghmand, M. and Stirm, B.: Aircraft measurement of HONO vertical profiles over a forested region, *Geophys. Res. Lett.*, 36(15), doi:10.1029/2009GL038999, 2009.

C8503

Zhou, X., Zhang, N., TerAvest, M., Tang, D., Hou, J., Bertman, S., Alaghmand, M., Shepson, P. B., Carroll, M. A., Griffith, S., Dusanter, S. and Stevens, P. S.: Nitric acid photolysis on forest canopy surface as a source for tropospheric nitrous acid, *Nat. Geosci.*, 4(7), 440–443, doi:10.1038/ngeo1164, 2011.

Ziemba, L. D., Dibb, J. E., Griffin, R. J., Anderson, C. H., Whitlow, S. I., Lefer, B. L., Rappenglück, B. and Flynn, J.: Heterogeneous conversion of nitric acid to nitrous acid on the surface of primary organic aerosol in an urban atmosphere, *Atmos. Environ.*, 44(33), 4081–4089, doi:10.1016/j.atmosenv.2008.12.024, 2010.

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