

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 ClearLo 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 jNO<sub>2</sub> and NO<sub>2</sub> (as well as [NO<sub>2</sub>] × 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 NO<sub>x</sub>) is for noontime conditions. Does the PSS assumption still hold in the early morning and late afternoon periods when HONO and NO<sub>x</sub> 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 ClearLo 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  $J(\text{HONO}) > 4 \times 10^{-4} \text{ s}^{-1}$  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<sub>x</sub> of 40-50 min refer to the estimated average transport time of NO<sub>x</sub> since emissions, the chemical lifetime of NO<sub>x</sub> is much longer (some hrs). This will be also corrected in the revised manuscript.

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

To our understanding it is not the air mass photochemical age that is an issue, but simply the average NO<sub>x</sub> 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/NO<sub>x</sub> 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 NO<sub>x</sub> compare to that of the observed values? Have the authors accounted for the loss of NO<sub>x</sub> (by OH+NO<sub>2</sub>→HNO<sub>3</sub>, NO<sub>2</sub>+HO<sub>2</sub>→HO<sub>2</sub>NO<sub>2</sub>, NO+OH→HONO, formation of organic nitrates, etc. following emission while being transported downwind) that can increase the HONO/NO<sub>x</sub> ratio?

We do not model the NO<sub>x</sub> as this is beyond the capability of our model, however we believe that here the NO<sub>x</sub> lifetime should be long enough (4-5 hours) compared to the average NO<sub>x</sub> transport time since emission (40 – 50 minutes) so that we not have significant NO<sub>x</sub> losses. In addition as described above, the HONO lifetime is the more important quantity here ( $\tau_{\text{HONO}} \ll \tau_{\text{NO}_x}$ ). HONO is emitted (together with NO<sub>x</sub>) anywhere in central London and is transported to our site whilst going into PSS. So the contribution of HONO emissions to the HONO/NO<sub>x</sub> 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/NO<sub>x</sub>" (fig 2b) exhibits a different diel trend than the "missing" HONO (fig 6). How much of the observed HONO/NO<sub>x</sub> trend (fig 2b) can be explained by NO<sub>x</sub> oxidation?

We do not believe that NO<sub>x</sub> oxidation is a major factor controlling the HONO/NO<sub>x</sub> 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<sup>-1</sup>] rather than the magnitude of it [ppb]. This tracks the diurnal HONO/NO<sub>x</sub> 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 NO<sub>x</sub> levels by 0.008 (reported HONO/NO<sub>x</sub> ratio in automobile exhaust by Kurtenbach et al. 2001) to estimate HONO from direct emissions. This approach, however, fails to account for the NO<sub>x</sub> that is lost by reaction, therefore, underestimates directly emitted HONO. Can the amount of NO<sub>x</sub> lost since emission be constrained? HONO levels during ClearLo 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/NO<sub>x</sub> > 0.008 is entirely explained by NO<sub>x</sub> loss?

We do not believe NO<sub>x</sub> loss to be an important factor at our site (see discussion above;  $\tau_{\text{HONO}} \ll \tau_{\text{NO}_x}$ ). Since the HONO loss since emission is far greater than the NO<sub>x</sub> 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 NO<sub>x</sub> is directly emitted from automobiles. What is the source of the rest of the NO<sub>x</sub> 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<sub>x</sub> ratio from all NO<sub>x</sub> 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.