Atmos. Chem. Phys. Discuss., 15, C7336–C7338, 2015
www.atmos-chem-phys-discuss.net/15/C7336/2015/

Atmospheric Chemistry and Physics Discussions

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

Anonymous Referee #1

Received and published: 28 September 2015

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] $\times$ 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.

Major The authors report negligible contribution from direct HONO emissions (lines 21-25 on page 3). This is based on the fact that HONO has a short lifetime during the day. The same reasoning is invoked to justify assuming photostationary state (lines 28-31 on page 9). 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) 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). 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?

The authors note (lines 27-29 on page 8) 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 modeled 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?

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?

(Lines 26-30 on page 13) 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). Can directly emitted HONO be distinguished from that produced by secondary reaction(s) if HONO/NOx > 0.008 is entirely explained by NOx loss?

Minor (line 19, page 2) Reaction 2 is invoked before reaction 1. Perhaps change the order such that HONO+hv reaction is the first reaction?

(lines 1-3, page 3; lines 21-24, page 13) Instead of equal signs, arrow signs?

(lines 24-27, page 5) There is a question mark.

(line 22, page 6) Need a comma after 'briefly'

(line 5, page 9) Change 'maybe' to 'may be'

(lines 26-30 on page 13) 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?

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?

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 22097, 2015.