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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Night-time chemistry above London: measurements of NO_3 and N_2O_5 from the BT Tower during REPARTEE-II" *by* A. K. Benton et al.

Anonymous Referee #1

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This paper describes new measurements of the sum of the nighttime nitrogen oxides, NO3 + N2O5, from a tower above London during the fall season. The measurements took place over a 1 month time period. As the introduction to the paper describes, these particular measurements are unusual in several respects. First, and most important, they are at an elevation of 160 m over a major urban area (described as a "developed megacity"). Nighttime measurements in near-source regions within this altitude range are uncommon but also very important to understanding nighttime chemistry, since upward mixing of surface level emissions can be less efficient and / or more variable at night than during daytime. Second, the instrument was a broadband cavity enhanced spectrometer, BBCEAS, used here for the first time in a sustained field

deployment. There is a relatively small set of ancillary measurements to support the BBCEAS NO3+N2O5 data, but it is sufficient for interpretation of the measurements. Of particular importance were measurements of vertical wind velocities and their variance, an important parameter for understanding turbulent mixing. For these reasons I recommend publication of results in ACP. The authors should consider the following comments prior to publication.

1. Zero measurements and mirror reflectivity. Because of limited instrument access, the time between successive I0 measurements and mirror reflectivity determinations was variable. How stable was I0 between successive measurements, and how was variability in this quantity handled? Similarly, was the 50% (typical) deterioration in mirror reflectivity assumed to be linear over the interval between measurements?

2. NO3 + N2O5 transmission. A wall loss rate coefficient (note, it should be specified as a coefficient, not a rate) of 0.2±0.05 s 1 was used based on the work of Dubé et. al. This rate coefficient is for a specific diameter of PFA tubing and may vary for different flow geometries. While the rate coefficient is may not be very different from this nominal value, the authors may wish to make note of the difference in cell diameters and consider larger error limits on the transmission efficiency. Also, losses on machined Teflon are generally larger than those on molded PFA, so it is also worth noting that the potential loss on the machined Teflon block that joins the flow to the axis of the cell is not quantified in this work. Presumably this is a small surface area relative to the rest of the flow system.

3. Commercial NOx analyzer. The NO2 measurement was based on a heated Mo catalyst for conversion to NO. Such measurements are prone to conversion of other NOy species, so that the NO2 values used here may be larger than actual NO2. The potential effect of over-estimation of NO2 on, for example, prediction of the N2O5 to NO3 ratio later in the paper should be noted. If possible, the authors should give the uncertainty associated with the use of this type of NO2 measurement. There is mention later in the paper of the potential for conversion of N2O5 itself on the Mo catalyst, but

no consideration (that I found) of other species such as HNO3 or PAN. Possibly this is a small effect if, as suggested later, HNO3 is a small fraction of NOy at this site.

4. Data in Figure 4 and elsewhere have been filtered to exclude values below the limit of detection. It is not clear why this is necessary, since one normally displays the scatter of the data about zero for values that fall below detection limits. Is it possible to display the baseline while still excluding large outliers?

5. Reaction of NO3 with NO. In section 3 and elsewhere, there appears to be a general lack of recognition that reaction of NO3 with directly emitted NO at night is a very rapid sink. This reaction is shown in Figure 1, but is less clear in the discussion in the text. For example, on page 14359, lines 5-12, the absence of NO3 in the presence of NO is attributed to reduction in the NO3 source strength via titration of O3 by NO rather than the very rapid direct reaction of NO3 with NO. There are several other instances in which the anticorrelation of NO3+N2O5 against NO is identified, but the direct reaction of NO3 with NO is not discussed.

6. Deposition losses of NO3+N2O5. Following on the above, it seems likely that if NO3+N2O5 is smaller during periods of higher turbulence, that the NO3+NO reaction may be a more important factor than deposition losses. If NO emissions occur at surface level and are mixed more rapidly to the tower height during periods of turbulence, then the presence of these fresh emissions at tower altitude would effectively prevent NO3 formation. It seems less likely (though not impossible) that NO3+N2O5 is first formed, then lost to deposition, since the deposition sink is likely slower than the NO3+NO sink. This point is captured to some extent at the top of page 14363 in the statement that enhanced NO3+N2O5 aloft occurs during the most stable conditions that decouple the air aloft from surface level emissions – i.e., chemistry can proceed according to the NO2 + O3 reaction clock if not interrupted by mixing of fresh NO from surface level.

7. NO3+N2O5 lifetimes. The authors point out correctly that a steady state is not likely

achieved for NO3+N2O5 for the high NOx, cold temperatures of this study, and that the steady state analyses neglect transport effect. Based on the correlation of NO3+N2O5 with stability (and anticorrelation with turbulence), it seems likely that transport is the most important factor influencing NO3+N2O5 levels at this site.

8. Page 14365, line 11: Reaction of NO3 with alkenes does not produce HNO3, though reaction with some other VOCs, such as aldehydes, does. This point seems to be understood correctly later in the same paragraph and is shown correctly in Figure 1.

9. Page 14365, line 21-25: Differences here seem much less likely due to inlet artifacts and much more likely in the steady state assumption.

10. HNO3 production. That there seems to be a large discrepancy between measured and predicted HNO3 formation does not seem very surprising. The predicted HNO3 would likely form during the transport of air masses away from this near-source site. The small observed HNO3 may be due to the short transport times and the short reaction times for any observation made this close to a source region. The text should distinguish between these regimes. Also, it is not clear how 0.17 ppbv HNO3 (avg) is only 0.001% of the "integrated mixing ratio for the night", given earlier as 8.6 ppbv?

11. Figures 4, 5, 7 (especially), 8: Font sizes on axes are almost too small to read and should be increased.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 14347, 2010.