Response to referee comments on:

Night-time chemistry above London: measurements of NO_3 and N_2O_5 from the BT Tower during REPARTEE-II

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We thank both referees for their helpful and supportive comments. We have addressed each referee's comments individually below:

Responses to referee 1

Comment 1: "Zero measurements and mirror reflectivity. Because of limited instrument access, the time between successive I_0 measurements and mirror reflectivity determinations was variable. How stable was I_0 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?"

Response: This is an astute and important point and one which was identified during the data analysis but on reflection not explained in sufficient detail in the text. The following text has been added to the final paragraph of Section 2.4 "The degradation of effective mirror reflectivity between successive phase-shift calibrations was considered. In order to quantify this degradation, the spectrally derived water concentration (see Fig 3.) was compared to water concentrations derived from relative humidity (RH) measurements made at the same level on the tower (Harrison et al., 2010). There are a number of caveats involved comparing BBCEAS-derived water concentrations with relative humidity: Evaporation from aerosols can act to increase humidity and pressure needs to be accurately known in order to be able to convert RH to water concentration, water vapour absorption spectroscopy exhibits non Beer-Lambert behaviour (Langridge, 2008;Platt and Stutz, 2008) due to the highly structured spectral lines not being fully resolved. These combined uncertainties justify not using measured and derived water mixing ratios as a primary method of mirror reflectivity calibration, but enable a deterioration factor to be then applied to the effective mirror reflectivity, maintaining the correlation between BBCEAS-derived humidity and that from RH measurement. This deterioration factor was never more than 0.0004%, which corresponds to a transmission efficiency reduction from 0.9998 to 0.9994 over a period of 3 days."

Comment 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."

Response: The word "rate" has been changed to "coefficient".

The first order wall loss coefficient for NO_3 on PFA reported by Dube et al. (2006) of $0.2 \pm 0.05\ s^{-1}$ was used and that for the machined Teflon portion was assumed to be the same as this area accounts for less than 1% of the total surface area of the cell and inlet so any differences were deemed negligible. The total net TE was found to be 68±8% but it is noted that differences in geometry between this system and that of Dube et al. (2006) could introduce additional unquantifiable error.

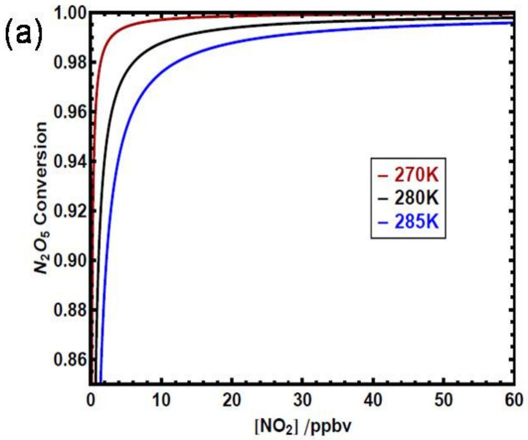
Comment 3: "Commercial NOx analyzer. The NO2 measurement was based on a heated Mo catalyst for conversion to NO. Such measurements are prone to conversion of other NOy species, so that the

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."

Response:

Chemiluminescent (CL) NO_x monitors employing heated Mo converters for NO_2 measurement are known to suffer from interferences from the conversion of other NO_y species to NO on the heated converter – for example, NO_3, N_2O_5, PAN and HNO_3. This will lead to the measured NO_2 overestimating the true value. Dunlea et al. (2007) have examined this issue extensively using data from within and around Mexico City obtained during the MCMA campaign, concluding that a significant interference signal in NO_2 levels measured by chemiluminescence / Mo conversion could be observed, peaking in the mid afternoon, and that this was likely due to a combination of HNO_3 and alkyl nitrates.

In principle similar interference would occur for the NO2 data reported here, and lead to the reported values being overestimates, and consequently the NO3/N2O5 ratio and NO_3, N_2O_5 lifetimes being underestimated (where this was calculated). Estimation of the potential interference effect is hard as this has been shown to depend upon the characteristics of the particular monitor used (Dunlea et al., 2007); however some estimate of the extent of the likely interference signal can be obtained using the abundance of other NO_y species reported: In the REPARTEE study the mean level of NO_2 during the NO_3/N_2O_5 measurement period was approximately 20 ppb. This may be compared with abundance of potential interferants: HNO_3, 0.17ppb (Nemitz et al., 2010) so taking the mean interference factor of 1.83 derived by Dunlea et al. this would suggest an NO_2 interference of ca. 0.3 ppb; NO_3 + N_2O_5 were always below 0.8 ppb, so from these species (which were identified as the major contributors in Mexico City) an interference in NO_2 of up to 5 % might be anticipated. Alkyl nitrate levels were not measured during REPARTEE, but are expected to be low at this site (altitude) at night. The most substantial contribution may arise from HONO. Splicer et al. (1994) measured an interference factor for HONO of upto 1 for similar instruments HONO was present at a mean mixing ratio of approximately 3ppbv (Fig. 7) during periods where BBCEAS measurements were also made. This leads to a total intereference of approximately 16% (assuming the maxima NO_2 and NO_y coincide. Since the effect of NO_2 on the calculation of the partitioning between NO_3 and N_2O_5 is small at the temperatures experienced during REPARTEE II, this is only likely to be significant for the very low NO_2 periods (<5ppbv). Figure 7 shows that such periods do not ever coincide with periods of high NO_3 or N_2O_5. Supplementary Figure 1 illustrates how at typical REPARTEE night-time temperatures of 270-285K a change in NO_2 of this magnitude would have little effect on the N_2O_5 conversion (=$[N_2O_5]/[NO_3+N_2O_5]$). Text has been added regarding this.



Supplementary Figure 1 – The effect of varying $[NO_2]$ on the conversion of N_2O_5 to NO_3 at a range of temperatures encountered in REPARTEE-II (Benton, 2010).

Comment 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?”

Response: This filter was applied to display more clearly the LOD on the plot with the purpose of differentiating both between differing values of the LOD and also times when no data was retrieved. We have changed Figs 4 and 5 so that the values of NO_3+N_2O_5 display the whole baseline below the LOD.

Comment 5: “there appears to be a general lack of recognition that reaction of NO_3 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 NO_3 in the presence of NO is attributed to reduction in the NO_3 source strength via titration of O_3 by NO rather than the very rapid direct reaction of NO_3 with NO. There are several other instances in which the anticorrelation of NO_3+N_2O_5 against NO is identified, but the direct reaction of NO_3 with NO is not discussed.”

Response: Although this was mentioned in section 3.1 we agree there was not much emphasis on this as a dominant route for NO_3 loss. Discussion of this with reference to figure 8 has been included in section 3. In addition, the text on page 14359 has been amended to include reference to the most likely loss through reaction of NO_3 with NO.

Comment 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.”

Response: Agreed. A statement to this effect has been added at the end of Section 3.4.

Comment 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.

Response: Noted. “but is most likely due to the approximations made in assuming a steady state for calculation of $\tau_{ss}(N_2O_5)$ (see Fig. 10.),” has been added.

Comment 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?

Response: The text has been changed to “As HNO_3 mixing ratio measurements averaged approximately 0.17 ppbv during this night (Nemitz et al., 2010), calculated $[HNO_3]_{total}$ represents a very small fraction of the total step-function integration of the measured mean mixing ratio, -of the order of 0.001%. HNO_3 is more likely to be formed once the air mass has travelled further from emissions sources than at this site, as longer transport and reaction times may be required for this to become a more dominant HNO_3 formation pathway.”

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

Response: Agreed, figure axes and data points in Figures 4, 5, 7 and 8 have been made larger and clearer.

Responses to referee 2

In response to referee 2's general comments, we have described further how this work contributes a new dataset to our understanding of urban night-time chemistry and shows that urban nitrate levels are highly variable and are contributed towards through both physical (aerosol) and chemical properties to a degree of variability not previously observed. We have also contributed estimates for HNO_3 formation from this route. This study demonstrates the inappropriateness to assume a steady state under such conditions with the example of different lifetime calculations obtained. These points have been specified more rigidly in the discussion section.

The term "the night-time analogue" has been amended to "its reactivity to some VOCs can be considered the night-time analogue".

We agree that the NO_x removal pathway provided by reactions of NO_3 and N_2O_5 is the predominant subject of this paper and therefore have amended the text in the introduction to concentrate on this.

Comment: "Note that there is also evidence for a gas-phase reaction between N_2O_5 and H_2O to produce HNO_3, which the authors do not discuss although the rate may be around 0.1 min-1, comparable to the bottom end of the estimated aerosol removal rates in Fig. 11."

Response: This is noted briefly on page 14350 line 14 and indirectly in Fig. 1. A statement to this effect will be added in section 3.5.

Comment: "An upper limit to the night-time production rate of HNO_3 (in aerosol and the gas phase) is simply given by the rate of $NO_2 + O_3$. In fact, the only reason that the rate would be below this limit in moderately polluted air is if the NO_3 reacted significantly with unsaturated organics by addition rather than production of HNO_3; or if the aerosol surface area was very small so that uptake was rate-limiting. "

Response: This was identified in table 2, where the production rates calculated by both methods are compared. These differences serve to illustrate the shortcomings of a steady-state approximation in this instance. Text to this effect has been added in section 3.5. Figure 11 shows that aerosol surface area is unlikely to limit this rate.

Comment: "I am confused by the discussion at the top of page 14366. It seems that far more HNO_3 was estimated to be made than was actually measured, so how was this a "very small fraction".

Response: Our comparison of the overall integrated night-time production (Table 2) with mean amounts (Fig. 7 (e)) was confusing. In Eq. 9. *$[HNO_3]$* has been changed to *$[HNO_3]_{total}$* to clarify that this is a night-integrated total amount. In addition the following text has been added ""As HNO_3 mixing ratio measurements averaged approximately 0.17 ppbv during this night (Nemitz et al., 2010), calculated $[HNO_3]_{total}$ represents a very small fraction of the total step-function integration of the measured mean mixing ratio, -of the order of 0.001%. HNO_3 is more likely to be formed once the air mass has travelled further from emissions sources than at this site, as longer transport and reaction times may be required for this to become a more dominant HNO_3 formation pathway."

Comment: "The authors describe some unexpectedly low NO_3/N_2O_5 levels on occasion. Unfortunately there were not enough measurements of other compounds - particularly organic species (?) - to investigate these episodes more deeply."

Response: Unfortunately there weren't any organic measurements available to the authors. However, a more general summary of the REPARTEE campaign was will shortly be submitted to this special issue (Harrison et al., 2010).

Minor specific points:

Comment 1: "Is the title really appropriate? REPARTEE-II may mean a lot to the participants of the field study, but might the significance of the work be better exhibited with a more general title?

Response: "during REPARTEE-II" has been removed.

Comment 2: “some of the figures need much larger tick and axis labels.”

Response: Agreed, figure axes and data points in Figures 4, 5, 7 and 8 have been made larger and clearer.

References

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