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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 #2

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This paper focuses on measurements of NO_3 and N_2O_5 , with ancillary measurements of NO_2 , NO , O_3 , and aerosol surface area, during a 1-month campaign from a tower 160 m above central London. The $\text{NO}_3/\text{N}_2\text{O}_5$ measurements were made using a broadband cavity enhanced absorption system which seems to have worked well. This technique is now becoming quite well established as an alternative to the long-path DOAS method, and the results reported here have been carried out to a high standard. The paper is very well written and appropriately illustrated.

In this review I would like to concentrate on the science. This study is potentially important because it provides a relatively long-term set of observations (cf. an aircraft

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study) at a height in the boundary layer where the immediate impact of fresh emissions of NO_x is removed. However, the paper needs to explain more clearly to the reader how this study has furthered our understanding of night-time NO₃/N₂O₅ chemistry. To be specific, the DOAS work on NO₃ in the 1990s together with laboratory work on NO₃ kinetics, the NO₃-N₂O₅ equilibrium, and N₂O₅ uptake on aerosols, established the current understanding of NO₃ chemistry. The very nice work of Steve Brown and colleagues in the last decade or so, where N₂O₅ was measured for the first time, then confirmed what was already in atmospheric chemistry models which included the role of different types of aerosol in N₂O₅ uptake.

These models showed that NO₃ chemistry is quite constrained: it is not really the "analogue" of the daytime OH radical, as stated on the first page of the paper. The reason is that there is only one way to make NO₃, from the slow reaction between NO₂ and O₃ (decomposition of N₂O₅ does not make "new" NO₃). When NO₃ reacts with unsaturated hydrocarbons and dimethyl sulphide, there are no known chain-propagating steps which regenerate it. Thus the rate of oxidation of these organic molecules is determined by the rate of the NO₂ + O₃ reaction, and the NO₃ concentration is controlled by the reactive organics, unlike the non-linear OH system. Apart from the NO₃ + DMS reaction in the marine atmosphere, I am not aware of evidence that NO₃ is a more important oxidant than OH (or O₃) of any other organic molecules. What is important and different about NO₃ is that the reactions with some unsaturated compounds (e.g. dienes) lead to bi-functional organic nitrates, some of which are harmful compounds.

The second important role of NO₃, which is really the subject of this paper, is the role of NO₃-N₂O₅ in removing NO_x from the troposphere through uptake on aerosols. Note that there is also evidence for a gas-phase reaction between N₂O₅ and H₂O to produce HNO₃, 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.

Several studies in the past have pointed out that the night-time removal rate of NO_x can match the daytime removal by OH. An upper limit to the night-time production rate

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of HNO_3 (in aerosol and the gas phase) is simply given by the rate of $\text{NO}_2 + \text{O}_3$. 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. 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". It would be very useful to know whether the $\text{NO}_2 + \text{O}_3$ rate is generally a good estimate of the HNO_3 production rate, since this would make large GCM modelling of the impact of night-time chemistry much faster.

The authors describe some unexpectedly low $\text{NO}_3/\text{N}_2\text{O}_5$ levels on occasion. Unfortunately there were not enough measurements of other compounds - particularly organic species (?) - to investigate these episodes more deeply. Nevertheless, overall this is a very nice study which should be published in ACP.

A couple of minor points:

- 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?
- 2) some of the figures need much larger tick and axis labels.

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

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