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Atmospheric
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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 #2

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This paper focuses on measurements of NO3 and N2O5, with ancillary measurements of NO2,NO O3, and aerosol surface area, during a 1-month campaign from a tower 160 m above central London. The NO3/N2O5 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

study) at a height in the boundary layer where the immediate impact of fresh emissions of NOx 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 "analague" 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 NOx from the troposhere 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 NOx can match the daytime removal by OH. 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. 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 $NO_2 + O_3$ 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 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. 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.