Nighttime NO$_3^-$ chemistry: In situ Observation of the Various Removal Pathways of NO$_3$ and N$_2$O$_5$ around the UK

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**NO$_3^-$ chemical processes**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO$_2$ + O$_3$</td>
<td>NO$_3$ + O$_2$</td>
</tr>
<tr>
<td>NO$_2$ + RO/ OH</td>
<td>HNO$_3$ + H</td>
</tr>
<tr>
<td>+ cloud / ice</td>
<td>HNO$_3$ (mainly)</td>
</tr>
</tbody>
</table>

**Measurement techniques**

- NO$_2$/NO/NO$_2$: broadband cavity enhanced absorption spectroscopy (Cambridge)
- Aerosol composition / size distribution: aerosol mass spectrometer / SMPS (Manchester)
- H$_2$O: laser induced fluorescence (Leeds)
- VOCs: gas chromatography + flame ionization detector, (York)
- O$_3$/O: UV absorption (FAAM)
- Liquid & total water content: Nevzorov probe (FAAM)

**Analysis metrics based on steady-state approximation:**

- $k_1$: reaction rate constant between NO$_2$ and O$_2$
- $k_2$: loss rate of NO$_2$ due to gas-phase NO$_2$ reactions
- $k_3$: loss rate of N$_2$O$_5$ due to heterogeneous reactive uptake

- $(r_{no3}^-)$ is the weighted average of the loss rates of NO$_2$ and N$_2$O$_5$ – its magnitude is inversely proportional to the lifetime of NO$_3^-$ and dictates the time required for NO$_3^-$ to reach steady-state
- $(r_{no3}^-)$ controlled by NO$_2$ loss when $K_{eq}[NO_2]$ is small, and by N$_2$O$_5$ loss when $K_{eq}[NO_2]$ is large, i.e. shifts depending on the N$_2$O$_5$/NO$_2$ partitioning.

**Flight No. B537 – Jul 20, 2010, NO$_3^-$-dominated loss**

- Back trajectory and synoptic wind suggest air mass originated from the European continent;
- High aerosol organics in this aged plume outflow (suggested by high CO/NO$_2$), high T (NO$_2$ ↔ N$_2$O$_5$, equilibrium favoured NO$_3^-$ and relatively low RH all disfavour N$_2$O$_5$ reactive uptake to aerosol particles;
- Observed loss of NO$_3^-$ nearly fully accounted for by the NO$_3^-$ reactions with alkenes and HO$_2$
- Lack of RO$_2$ contribution likely due to the sum of measurement uncertainties (~40%);
- Very efficient NO$_3^-$ recycling due to the regeneration of NO$_3$ from NO$_3$ via NO$_3$ + HO$_2$/RO$_2$ → NO$_3$ and NO$_3$ + alkene reactions (which for short-chain anthropogenic usually have small organic nitrate yield);
- Transformation of NO$_2$ → NO$_3$ / HNO$_3$ (i.e. a more permanent reservoir of NO$_3$ very slow and predominantly relied on NO$_3$ + nocturnal OH (and potentially also partially on NO$_3$ + HCHO), due to the suppressed N$_2$O$_5$ heterogeneous uptake pathway;

**Flight No. B570 – Jan 23, 2011, N$_2$O$_5$-dominated loss**

- The strongly correlated profile as well as large $K_{eq}[NO_2]$ value (>10, winter) for the entire period suggest that the heterogeneous reactive uptake of N$_2$O$_5$ by aerosol particles is the dominant NO$_3^-$ loss pathway for the period shown;

**Flight No. B538 – Jul 22, 2010, N$_2$O$_5$-dominated loss**

- The graph on the left shows a typical scenario when urban emitted NO$_2$ was transported to > 3 km, forming N$_2$O$_5$ which was then removed by falling ice particles formed at higher altitude;
- Uptake of N$_2$O$_5$ to cloud droplets and to falling ice were frequently observed (even though days with forecast precipitation were deliberately avoided in flight planning) and constitute a significant loss pathways of N$_2$O$_5$ around the UK;

**Flight track**

- 24 hrs back trajectory
- Flight track
- Flight track

**Flight track**

- Flight No. B537 – Jul 20, 2010, NO$_3^-$-dominated loss (via reaction with anthropogenic alkenes and HO$_2$)
- Flight No. B570 – Jan 23, 2011, N$_2$O$_5$-dominated loss (via uptake to internally-mixed ambient aerosols)
- Flight No. B569 – Jan 20, 2011, complicated N$_2$O$_5$ uptake behaviour (the important role of aerosol organics)

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