Nighttime NO_{3y} chemistry: *In situ* Observation of the Various Removal Pathways of NO_3 and N_2O_5 around the UK

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NO_{3y} chemical processes

$NO_2 + O_3 \rightarrow NO_3 \leftrightarrow N_2O_5$

N_2O_5 + cloud / ice (4) → HNO_3 (mainly)

N_2O_5 + VOCs (1) → Products

NO_3 + RO_2 / HO_2 (2) → NO_2 + RO/OH

N_2O_5 + aerosol (3) → HNO_3 + $ClNO_2$

Measurement techniques:

$NO_2/NO_3/N_2O_5$: broadband cavity enhanced absorption spectroscopy (Cambridge);

Aerosol composition / size distribution: aerosol mass spectrometer / SMPS (**Manchester**);

HO_2: laser induced fluorescence (**Leeds**); Aerosol scattering: nephelomter (**FAAM**);
VOCs: gas chromatography + flame ionization detector, (**York**);
O_3/CO: UV absorption (**FAAM**); Liquid & total water content: Nevzorov probe (**FAAM**);

Analysis metrics based on steady-state approximation:

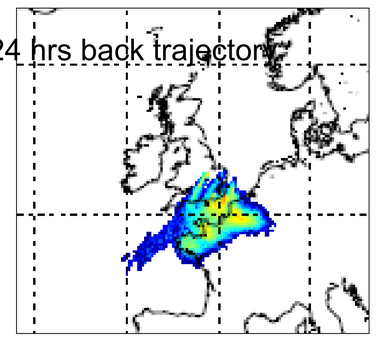
$$(\tau_{NO_3})^{-1} = \frac{k_1[NO_2][O_3]}{[NO_3]} = k_x + k_y K_{eq}[NO_2]$$

$$(\tau_{sum})^{-1} = \frac{k_1[NO_2][O_3]}{([NO_3]+[N_2O_5])} = \frac{k_x}{1+K_{eq}[NO_2]} + \frac{k_y K_{eq}[NO_2]}{1+K_{eq}[NO_2]}$$

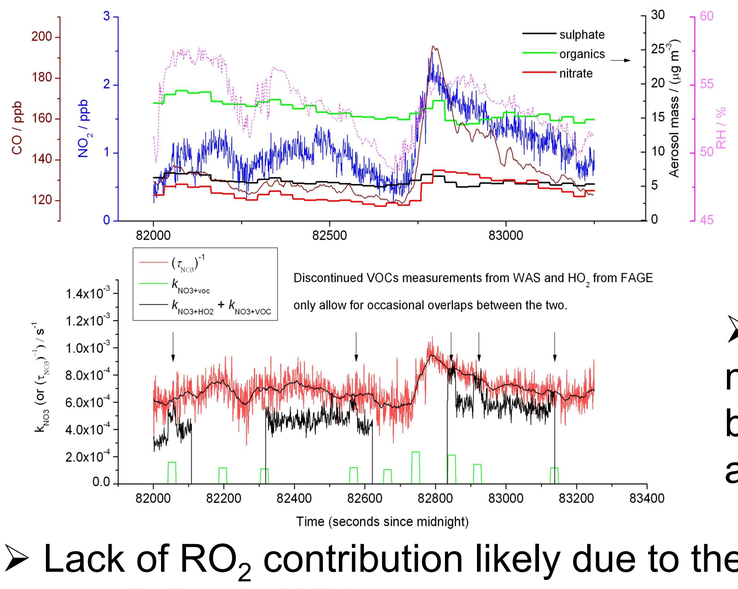
k_1: reaction rate constant between NO_2 and O_3;
k_x: loss rate of NO_3 due to gas-phase NO_3 reactions;
k_y: loss rate of N_2O_5 due to heterogeneous reactive uptake;

- **$(\tau_{sum})^{-1}$** is the *weighted average* of the loss rates of NO_3 and N_2O_5 – its magnitude is inversely proportionaly to the lifetime of NO_{3y}, and dictates the time required for NO_{3y} to reach steady-state;
- **$(\tau_{sum})^{-1}$** controlled by NO_3 loss when $K_{eq}[NO_2]$ is small, and by N_2O_5 loss when $K_{eq}[NO_2]$ is large, i.e. shifts depending on the N_2O_5 / NO_3 partitioning.

Flight No. B537 – Jul 20, 2010, NO_3-dominated loss (via reaction with anthropogenic alkenes and HO_2)

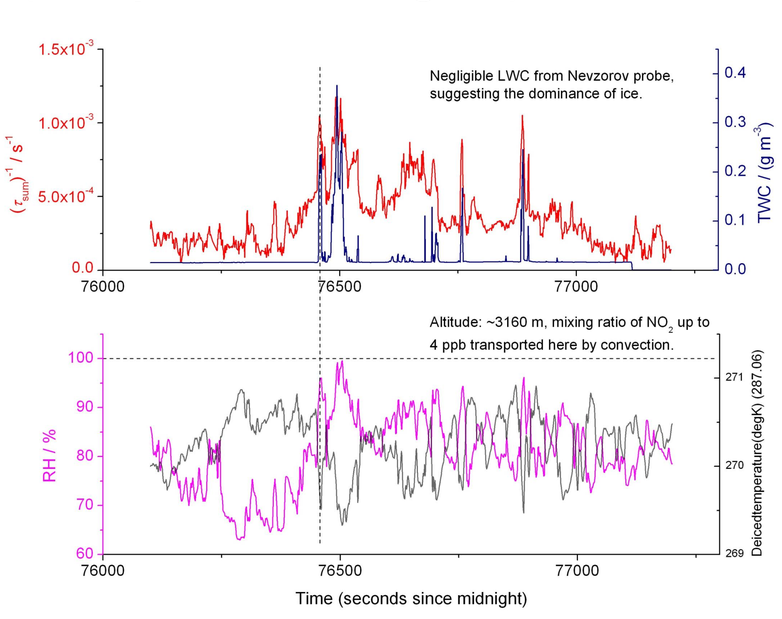


- Back trajectory and synoptic wind suggest air mass originated from the European continent;
- High aerosol organics in this aged plume outflow (suggested by high CO/NO_2), high T ($NO_3 \leftrightarrow N_2O_5$ equilibrium favoured NO_3) and relatively low RH all disfavour N_2O_5 reactive uptake to aerosol particles;



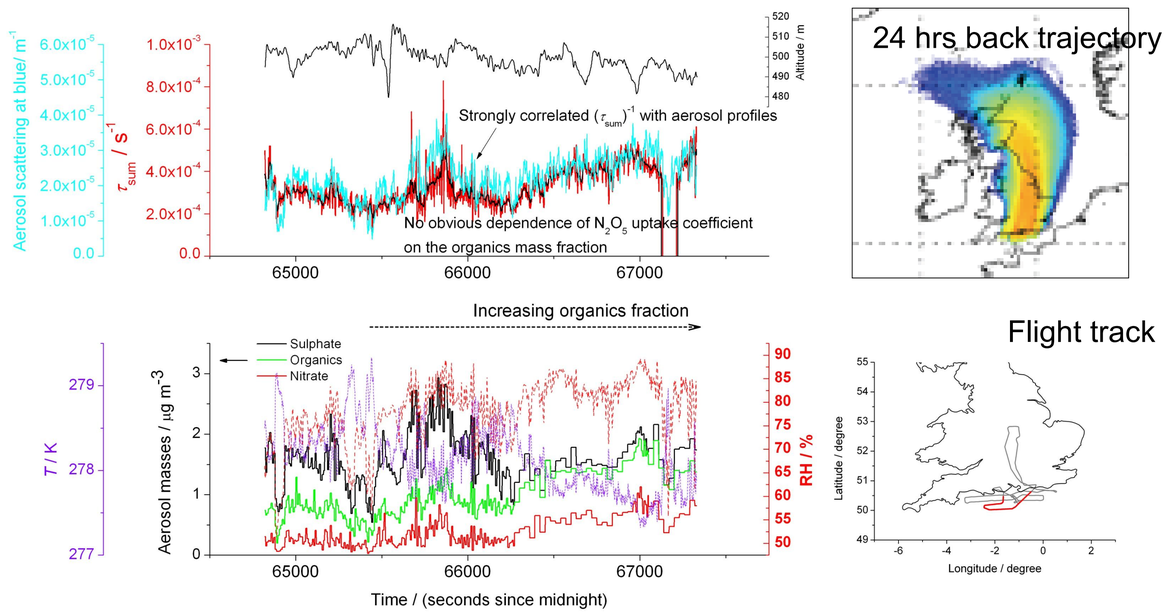
- Observed loss of NO_{3y} nearly fully accounted for by the NO_3 reactions with alkenes and HO_2;
- Lack of RO_2 contribution likely due to the sum of measurement uncertainties (~40%);
- Very **efficient NO_2 recycling** due to the regeneration of NO_2 from NO_3 via $NO_3 + HO_2/RO_2 \rightarrow NO_2$ and NO_3 + alkene reactions (which for short-chain anthropogenic usually have small organic nitrate yield);
- Transformation of $NO_2 \rightarrow NO_3^-$ / HNO_3 (i.e. a more permanent reservoir of NO_x very slow and predominantly relied on NO_2 + nocturnal OH (and potentially also partially on NO_3 + HCHO), due to the suppressed N_2O_5 heterogeneous uptake pathway;

Flight No. B538 – Jul 22, 2010, N_2O_5-dominated loss (via uptake to falling ice)



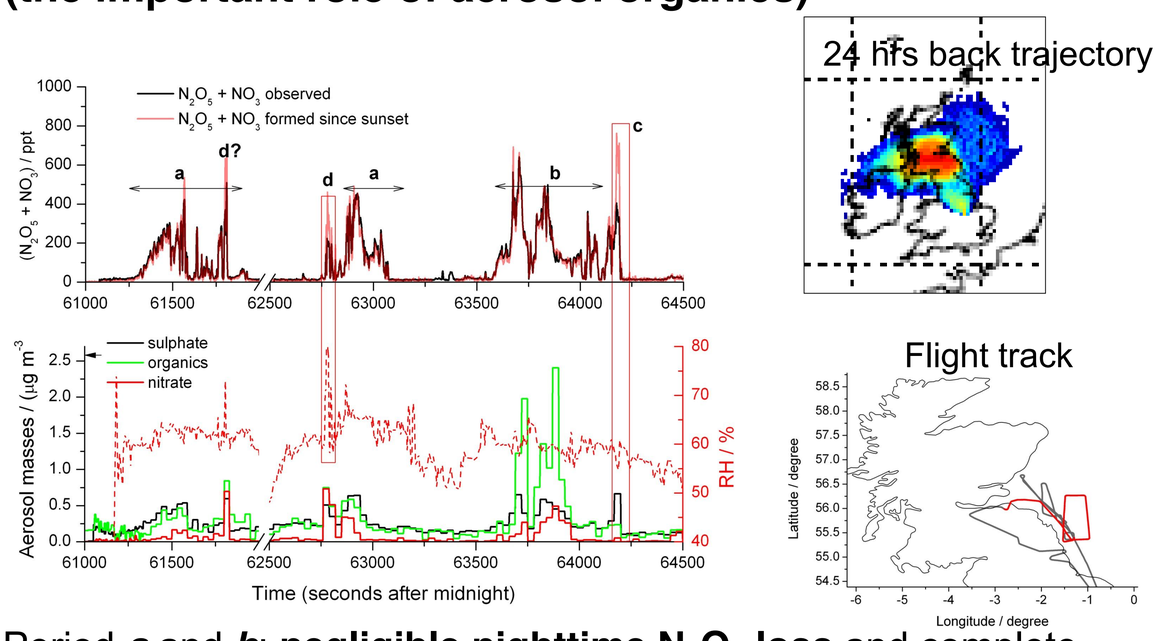
- The graph on the left shows a typical scenario when urban emitted NO_2 was transported to > 3 km, forming N_2O_5 which was then removed by falling ice particles formed at higher altitude;
- Uptake of N_2O_5 to cloud droplets and to falling ice were frequently observed (even though days with forecast precipitation were deliberately avoided in flight planning) and constitute a significant loss pathways of N_2O_5 around the UK;

Flight No. B570 – Jan 23, 2011, N_2O_5-dominated loss (via uptake to internally-mixed ambient aerosols)



- 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_2O_5 by aerosol particles is the dominant NO_{3y} loss pathway for the period shown;

Flight No. B569 – Jan 20, 2011, complicated N_2O_5 uptake behaviour (the important role of aerosol organics)



- Period ***a*** and ***b***: **negligible nighttime N_2O_5 loss** and complete inhibition of N_2O_5 uptake to aerosol particles, as suggested by the nearly equal amount of observed sum of NO_3 and N_2O_5 and that could be formed since sunset; the large change in organics mass fraction (~0.3 to ~0.5 from period ***a*** to ***d***) does not seem to matter;
- Period ***c***: **Significant N_2O_5 loss observed**, coincident with peak in aerosol sulphate – indicative of externally mixed sulphate and organics aerosols, or inefficient inhibition on N_2O_5 uptake by organics due to the relatively low organics mass fraction (~0.2)?
- Period ***d***: **Significant N_2O_5 loss observed**, coincident with sharp rise in RH; possibly due to disappearance of segregation of aerosol inorganic and organics (disappearance of coating), but a more likely cause is the "earlier" scavenging of N_2O_5 by precipitation (rain or ice);

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