NO$_y$ fate at SOAS 2013: Organonitrate Formation via NO$_3$ + BVOC and Inorganic Nitrte Formation via Heterogeneous Uptake of HNO$_3$


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Figure 4 - VOC concentrations over the SOAS campaign

**What we learned**

- Sum of individual components of NO$_y$ and measured NO$_y$ match within 8%.
- Steady state predicted NO$_2$ and measured NO$_2$ correlate well. Steady state NO$_2$ was used in rate calculations due to ambient concentrations being below the detection limit of the instrument (Cavity Ring Down, CRD).
- NO$_3$ + BVOC reactions account for almost 50% of NO$_y$ loss during the day.
- Predicted NO$_3$ + BVOC losses correlate with aerosol mass spectrometry (AMS) peak data provide a molar yield of 25% NO$_2$ reaction to aerosol phase organics.
- Chemical Ionization Mass Spectrometry (CIMS) coupled to a FIGAERO analyzer allows measurements of gas and aerosol phases:
  - Correlations against predicted NO$_y$ + isoprene show only aerosol NH$_3$NO$_3$ formation;
  - Steady state against NO$_3$ + monoterpenes show products from the reaction with C$_4$H$_9$NO$_3$ partition to the aerosol phase.
- Inorganic NO$_y$ analysis by ion chromatography shows dust events catalyze heterogeneous uptake of HNO$_3$.

Figure 1 - Regional map of SOAS site

Figure 2 - NO$_y$ concentration: marked spikes show that sum of individual NO$_y$ components match measured NO$_y$.

Central Alabama is a humid subtropical environment with an average daily high temperature of 26.4°C. Emissions of SO$_2$ and NO$_x$ come from regional power plants in Alabama and Georgia. The Garrison Plant emits 19.5 square tons of SO$_2$ and 6.5 square tons of NO$_x$ per day (Figure 1).

- Total NO$_3$ measured by Thermal Desorption: Laser Induced Fluorescence, NO$_3$ by cavity ring down spectroscopy and HNO$_3$, HNO$_2$ and NO$_2$ by Monitor of Aflatoxin and Gas Analyzer (MAGA).
- The individual NO$_y$ compounds show that NO$_3$ can alkyl nitrates and sum-pentanoyl nitrate are the main contributors to NO$_y$ (Figure 2).
- Organometallics make a substantial contribution to the NO$_y$ budget (Figure 2).
- Relatively constant contributions of NO$_2$ come from HNO$_3$ and HONO.

Figure 3 - Comparison of steady state and measured NO$_y$ correlation well.

N$_2$O$_5$ and NO$_3$ were measured using a cavity ring down spectrometer for nitrate radical (RONALD, NOAA-ESRL). Steady state NO$_y$ (NO$_3$/HONO) was calculated using NO$_3$ production and loss rates to NO, BVOC and photolysis. Steady state loss rates of NO$_y$ (NO$_2$) was calculated using NO$_3$ production and loss rates to NO, BVOC and photolysis. NO$_2$ loss to BVOC can be calculated from this data. NO$_2$ loss to SOAS, shown in which of the aerosol phase as seen in TD-LIF (Figure 5).

Figure 5 - Comparison of steady state and measured NO$_2$ correlation well.

AMS NO$_3$ mass fraction correlated with RONO$_2$ and RONO$_3$, calculated with BOND, shows a slope of 1.00 with a correlation coefficient of 0.995 (Figure 8).

Gas phase NO$_3$ correlates well with NO$_3$ loss to isoprene (Figure 9).

Aerosol NO$_3$ mass fraction correlated with RONO$_2$ shows products which are products from NO$_3$ radical reaction and which are not (NO$_3$ + NO) using the steady state NO$_3$/NO$_2$ ratio. Gas phase is not well correlated suggesting another type of reaction in taking place.

Aerosol phase shows C$_4$H$_9$NO$_3$ appears to be a product of NO$_3$ reaction with an R value of 0.674.

Figure 6 - NO$_y$ fate at SOAS 2013: Organonitrate Formation via NO$_3$ + BVOC and Inorganic Nitrte Formation via Heterogeneous Uptake of HNO$_3$

**Correlations of MS Products with RONO$_2$ Cumulative**

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**Predicted NO$_3$ + BVOC**

- NO$_3$ loss during the day is due to photolysis, reaction with NO and reaction with BVOC.
- Almost 25% of daytime NO$_3$ loss is from C$_3$- BVOC.
- Almost 15% of nighttime NO$_3$ loss is from isoprene.
- Almost 5% of nighttime NO$_3$ loss comes from isoprene.
- Total photolysis is normalized to solar radiation and cloud liquid water phase.
- Predicted NO$_3$ loss is calculated using published NO$_3$, BVOC and HNO$_3$ loss.

**Heterogeneous uptake of HNO$_3$, On Dust**

- Two observed periods of high NO$_y$ are correlated to high PM$_2.5$ aerosol mass loading.
- High NO$_y$ is also correlated with high sea salt and non-sea salt minerals.
- Elemental analysis of the high sea salt events shows higher NO$_y$, NO$_3$, and isoprene.
- The second dust event shows no NO$_y$ as well as higher CO and SO$_2$.
- Wind trajectory modeling shows wind coming from the Gulf of Mexico during some dust event could explain the high CO content.

**Inorganic and Organic NO$_y$ fate**

- Rate of NO$_y$ uptake is driven by PM$_2.5$ via heterogeneous uptake of HNO$_3$ onto the surface of mineral aerosols.
- An average value of 10% (predicted) for HNO$_3$ uptake was used to calculate the rate of uptake.
- Rate = $\frac{\text{rate}}{\text{PM}_2.5}$ (units of HNO$_3$).
- Organic and inorganic rates are comparable in magnitude with different peak times over the SOAS campaign.
- Inorganic NO$_y$ magnitudes are also comparable to alkyl nitrate magnitudes over the SOAS campaign.
- Organic rates calculated using (NO$_3$ + BVOC) loss and also using NO$_3$ only and then (predicted NO$_3$ + BVOC).

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