Reactive nitrogen fate in the southeastern U.S.: Preliminary results from the SOAS campaign

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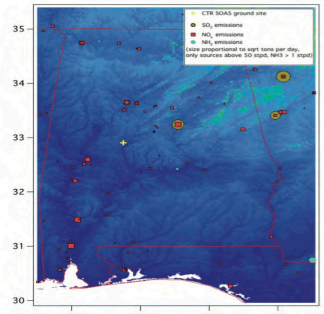
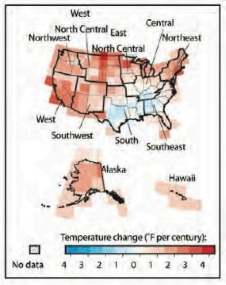
Goals

- Analyze composition of aerosols responsible for a localized cooling effect over Alabama
- Investigate interaction between anthropogenic emissions and naturally-emitted volatile organic compounds (VOCs)
- Determine sources and composition of aerosol NO_3^-
- Model gas-aerosol partitioning of reactive nitrogen
- Quantify NO_3 radical production and reactivity with biogenic VOCs
- Validate N_2O_5 steady state

Field Site: Centreville, AL



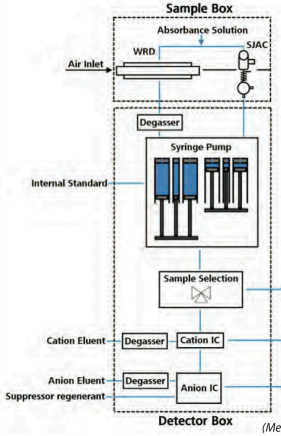


Alabama is representative of the chemistry of the southeastern U.S., which exhibits an overall cooling trend thought to be caused by regional aerosol.

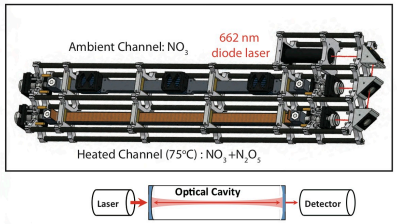
(Figure courtesy of U.S. EPA, data courtesy of NOAA's National Climatic Data Center)

The field campaign took place from June 1 to July 15, 2013 in Centreville, Alabama (yellow) as part of the Southern Oxidant and Aerosol Study (SOAS), a collaborative effort to characterize aerosol in the southeastern US. Centreville was chosen because it is a rural site influenced by nearby anthropogenic emission point sources, such as SO_2 (green), NO_x (red) and NH_3 (aqua).

Instrumentation: MARGA & CRDS



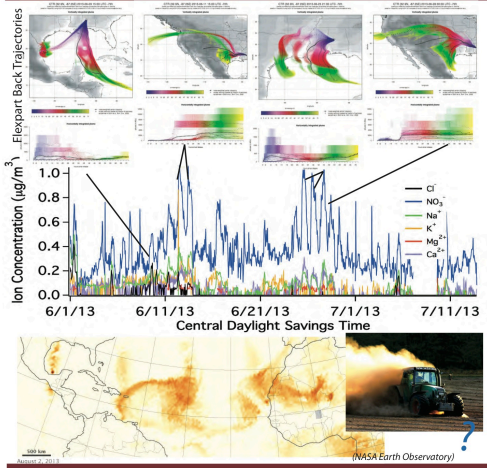
(Metrohm, MARGA guide)



RONALD: Cavity Ringdown Spectroscopy (CRDS) of N_2O_5 and NO_3 radicals in the atmosphere. The resonant absorption of 662 nm light by NO_3 radical results in observation of a ringdown decay, which can be used to determine absolute concentration at high sensitivity.

The Monitor of AeRosols and GAses (MARGA) is an ion chromatography based instrument that samples ambient air to quantitatively measure aqueous phase Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, NH_4^+ and SO_4^{2-} and gas phase HCl, HNO_3, HNO_2, SO_2, and NH_3.

Mineral Dust Influence



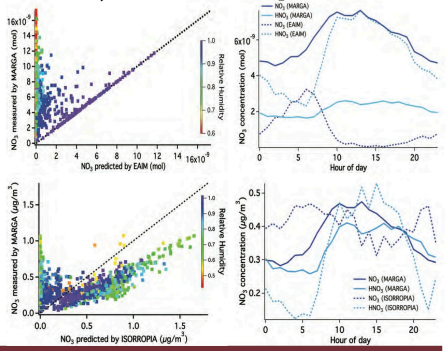
During the campaign, two separate events occurred in which high concentrations of both $NO_{3\ (aero)}$ and minerals were observed. These events are attributed to coarse mode nitrate, e.g. $NaNO_3$ and $Ca(NO_3)_2$, forming as wind passes in a low altitude over regions of the United States. [1] The elemental composition of these plumes, which exhibit high K^+ and Ca^{2+} in addition to Na^+, futher suggests a mineral dust source rather than an oceanic source. Ongoing work seeks to determine whether the origin of this dust is from long-range (transcontinental or transatlantic) transport, or a local phenomenon.

Modeling Inorganic Nitrate Partitioning

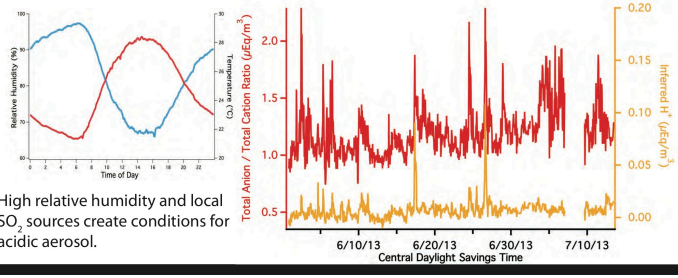
Two thermodynamic models that calculate gas/liquid/solid partitioning of inorganic gas and aerosol phase components were run using input data of temperature, relative humidity, and inorganic species collected during the campaign. These were the Extended Aerosol Inorganics Model (E-AIM), [2] which uses a Na^+ - NH_3/NH_4^+ - H_2SO_4/SO_4^{2-} - HNO_3/NO_3^- - HCl/Cl^- - H_2O system, and ISORROPIA II, [3] which addionally includes K^+, Ca^{2+}, and Mg^{2+}.

E-AIM:
- Gas-aerosol partitioning of NO_3^- strongly depends on relative humidity
- Most NO_3^- is partitioned into the gas phase as $HNO_{3\ (g)}$

ISORROPIA:
- Gas-aerosol partitioning of NO_3^- shows weak dependance on relative humidity
- Partitioning between NO_3^- and $HNO_{3\ (g)}$ varies diurnally

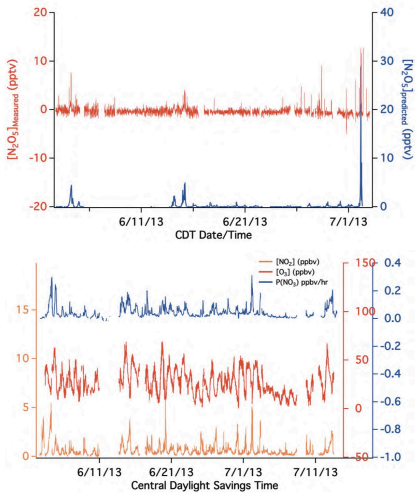


Aerosol Acidity



High relative humidity and local SO_2 sources create conditions for acidic aerosol.

Role of Nitrate Radical

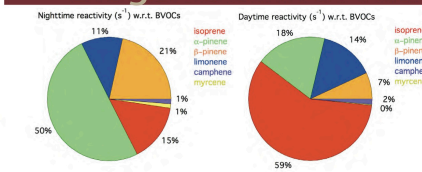


Calculations using $[NO_2]$ and $[O_3]$ can be used to predict the amount of N_2O_5 produced in the atmosphere. This is verified by CRDS. The resulting thermal breakdown of N_2O_5 into NO_3 radical allows reaction with BVOCs leading to SOA production. [BVOC] and rate constants (k_x) [4] can then be used to calculate nitrate lifetime (τ), production rate ($P(NO_3)$) and steady state approximation [5] of nighttime nitrate concentration.

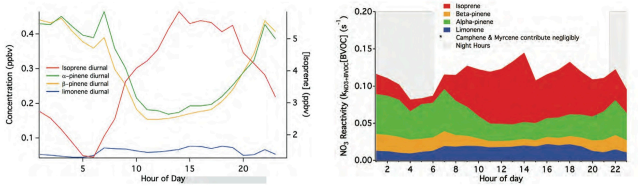
$$NO_2 + O_3 \rightleftharpoons NO_3 + O_2$$
$$NO_3 + NO_2 \rightleftharpoons N_2O_5$$

$$\tau_{NO_3,BVOC} = 1 / \Sigma(k_{NO_3+BVOC}[BVOC])$$
$$P(NO_3) = k[NO_2][O_3]$$
$$[NO_3]_{SS} = P(NO_3) \times \tau_{NO_3,BVOC}$$

Biogenic Sink of Nitrate Radical



Daytime NO_3 reaction is dominated by isoprene, however α-pinene, β-pinene and limonene make up more than 75% of NO_3 reactivity at night. Reactive lifetimes of BVOCs show a regular diurnal cycle of isoprene and the terpene uptake of nitrate. Daytime photolysis proceeds at 0.5 sec^{-1}. [6]



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A special thank you Ann Marie Carlton, Jim Moore, and all of the folks who made SOAS possible.

1. Lee et al. (2008) Observations of fine and coarse mode particulate nitrate at several rurual locations in the United States, *Atmos. Environ.*, *42* (11), 2720-2732.
2. E-AIM can be found at *http://www.aim.env.uea.ac.uk/aim/aim.php*
3. ISORROPIA can be found at *http://www.isorropia.eas.gatech.edu*
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6. Stark et al. (2007) Atmospheric in situ measurement of nitrate radical (NO_3) and other photolysis rates using spectroradiometry and filter radiometry, *J. Geophys. Res.*, *112*, D10504.