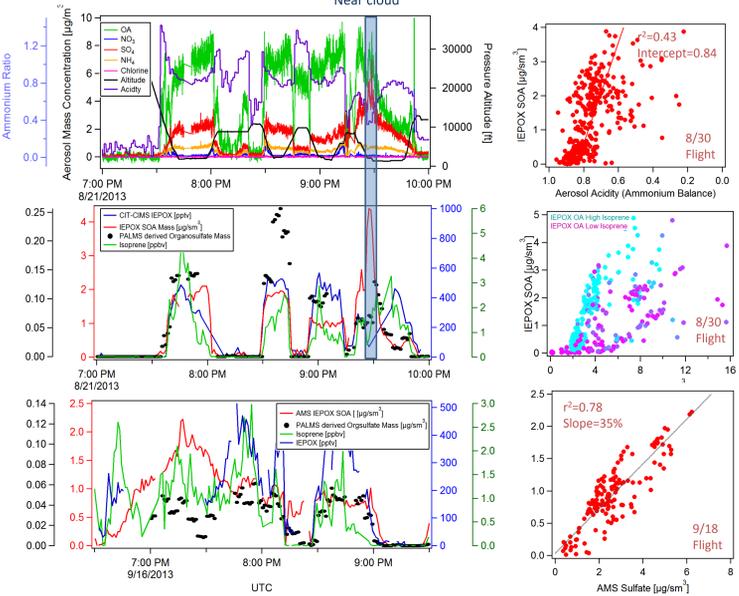


Quantification of IEPOX SOA in the SEUS

IEPOX (isoprene dihydroxy epoxide) has been identified in both chamber and field studies as the critical intermediate in the formation of SOA from isoprene under low-NO_x conditions. Uptake of IEPOX into acidic aerosols leads to the formation of SOA and organosulfates with low enough volatility to partition to the aerosol phase.

Robinson et al (2011) first identified the C₉H₁₆O⁺ ion in AMS spectra as a marker for IEPOX derived SOA. During the SOAS ground study, our group was able to confirm that not only did the C₉H₁₆O⁺ highly correlate with one of the SOA Factors retrieved by PMF, but also independent, real time measurements of 2-methyl-tetrols, a common marker of IEPOX SOA in the aerosol phase.

SEAC4RS provided a unique opportunity to test further the AMS quantification of IEPOX-SOA under a much wider range of conditions in terms of isoprene and IEPOX concentrations, acidities, and sulfate concentrations. Moreover, comparison of the AMS with the organosulfate fraction of the PALMS (or mass, once scaled with AMS OA) in this changing environment is possible as well.



SEAC4RS SEUS Averages

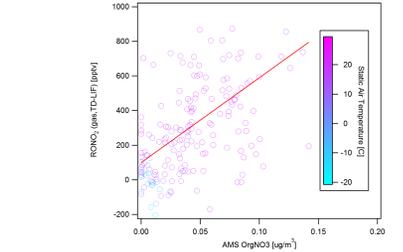
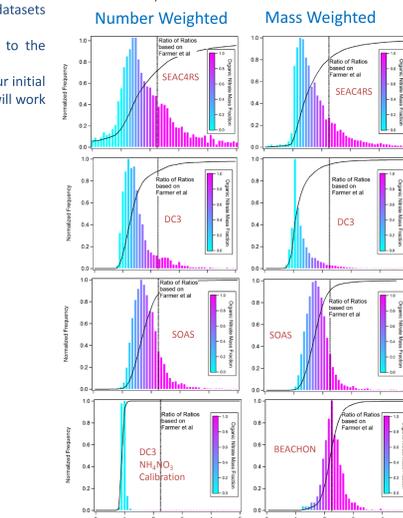
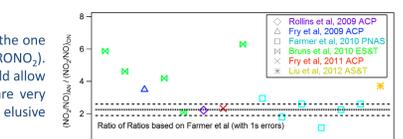
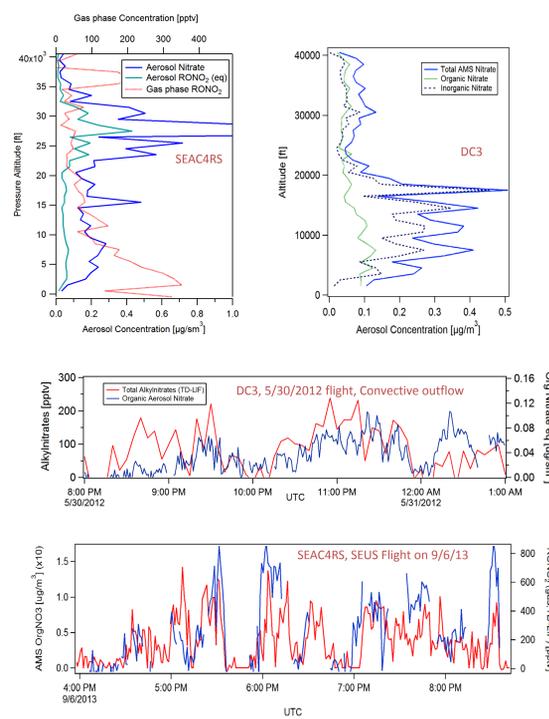
Please contact Pedro.CampuzanoJost-1@colorado.edu or Jose.Jimenez@colorado.edu for these plots

Organic Aerosol Nitrate

In the absence of dust and sea salt, a deviation of the observed NO₂⁻/NO⁺ ratio in the AMS from the one found in ammonium nitrate has long been recognized as being associated with organic nitrates (RONO₂). In theory, a linear interpolation between the characteristic ratio for inorganic vs organic ratio would allow quantification of the contribution of organic nitrates to total aerosol. However, these ratios are very dependent on the tuning of the instrument, and hence quantification of organic nitrates seemed elusive since in-field calibrations with organic nitrates are not really practical.

Our group (Fry et al. ACP 2013) proposed to overcome this problem by normalizing the laboratory RONO₂ calibration by the ratio of the inorganic calibration. Using a "ratio of ratios" of 2.25 based on Farmer et al (2010) the particulate RONO₂ quantified by the AMS instrument matched the results of the collocated TD-LIF instrument (0.91 Slope, 0.77 r²). We have applied this technique now a variety of datasets (different instrument/locations/tunings) and have found that:

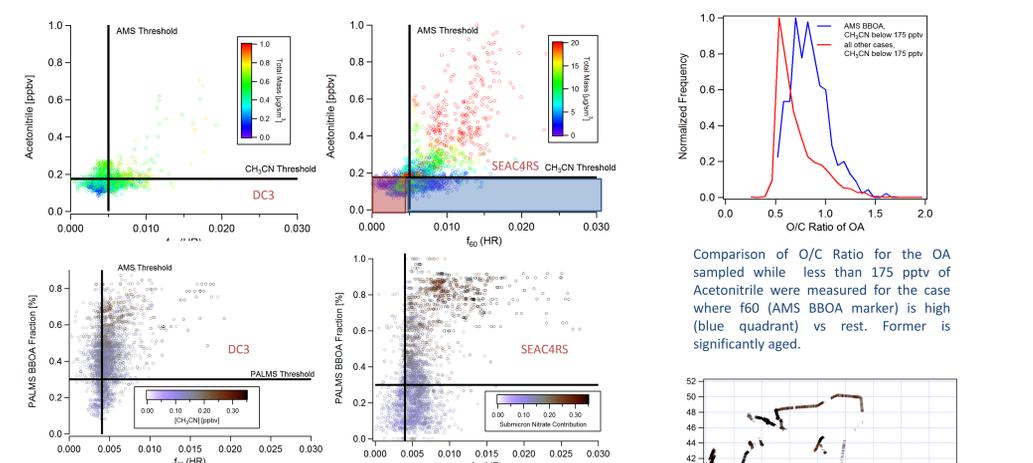
- Particulate RONO₂ is fairly ubiquitous and in the absence of strong plumes contributed to the majority of total AMS nitrate.
- The range of normalized NO₂⁻/NO⁺ ratios we see in the field are roughly in agreement with our initial estimate, likely a slightly higher ratio (closer to the average of the chamber measurements) will work better.



During DC3, while sampling the fresh outflow of an MCS system, new particle formation was observed. The composition of this growth mode (as opposed to the ammonium bisulfate background that stayed constant) as measured by the AMS showed the new particle to be OA and organic nitrate. Given that the AMS only quantifies the NO₂ group in RONO₂, it is unclear if all the organic measured was pure RONO₂ SOA. In any case, the organic group was heavily oxidized with an average O/C ratio of 1.2

During SEAC4RS, we sampled the aged outflow of an MCS on the 8/19/2013 flight. Again, only OA and organic nitrate was seen (this time up to 0.8 µg/sm³) and the OA was even more oxidized than before (O/C 1.4)

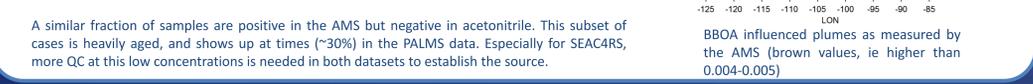
Detecting very aged BBOA



Plenty of fire influenced air masses were sampled both during DC3 and SEAC4RS, a significant number of them in the FT and UT. In many cases the signals were weak enough to get close to the "classification thresholds" of the different gas and particle instruments.

While the PALMS marker should be more robust for the particle phase than the AMS for very aged plumes, especially during SEAC4RS there is a significant fraction (~10%) where the AMS showed positives where the PALMS did not. The exact reason for this discrepancy is under investigation.

A similar fraction of samples are positive in the AMS but negative in acetonitrile. This subset of cases is heavily aged, and shows up at times (~30%) in the PALMS data. Especially for SEAC4RS, more QC at this low concentrations is needed in both datasets to establish the source.



References

N. H. Robinson et al., Evidence for a significant proportion of Secondary Organic Aerosol from isoprene above a maritime tropical forest, *Atmos. Chem. Phys.* 11, 1039–1050, (2011)
 J.L. Fry, et al. Observations of gas- and aerosol-phase organic nitrates at BEACHON-RoMBAS 2011. *ACPD*, 13, 1979–2034, doi:10.5194/acpd-13-1979-2013, 2013.
 D. K. Farmer et al., Response of an aerosol mass spectrometer to organonitrates and organosulfates and implications for atmospheric chemistry, *Proc. Natl. Acad. Sci. U. S. A.* 107, 6670–6675 (2010)
 A. W. Rollins, J. D. Smith, K. R. Wilson, R. C. Cohen, Real time in situ detection of organic nitrates in atmospheric aerosols, *Environ. Sci. Technol.* 44, 5540–5 (2010).

Acknowledgments

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New sulfur compound in Western fire plumes?

Unlike the nitrate case, the ratio of SO₄²⁻ ions is normally very constant in the AMS (with slight deviations for sulfuric acid). However, sampling BBOA at DC3 and SEAC4RS showed an altered pattern in the ratio of these ions. At the same time, the SAGA instrument measured significantly lower total sulfate. This is consistent with observations of test burns from FLAME-3 at the Missoula fire lab where certain fuels did produce "AMS Sulfate" that upon further analysis was completely devoid of SO₄²⁻ and higher ions.

During SEAC4RS, some Western BBOA plumes showed the same pattern (mostly the Rimfire plume). This would be consistent with the fuels identified during FLAME-3, which are mostly found West of the Continental Divide. Hence, if an SO₂ carrying species (not sulfate) is assumed to be present in these specific plumes and subtracted from the AMS "Sulfate" in BBOA, agreement with SAGA improves markedly. The ratio of "SulfurX" to Sulfate in these plumes is consistent as well with the observed in the FLAME-3 data. A potential SO₂ carrying species would be sulfones (SO₂R₂), and several calibrations have been conducted, but while the SO₄²⁻ ions ratio is reproducible with the AMS, parallel calibrations with the PALMS have so far not been able to arrive at similar contributions of these species to BBOA plumes.

