Impacts of Sea Salt, Acidity, Organic Nitrates & Sulfates on AMS NH$_4^+$ balance (& NO$_2^+$ /NO$^+$ Ratio)

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(with data from Karl Froyd @ NOAA as well as Yongjing Zhao & Steven Cliff @UC-Davis)

Hayes et al., JGR 2012, submitted

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Ammonium Balance
1. Effect of acidity

- When there is a lot of acidic sulfate, impact on ammonium balance can be obvious
- (This is UMR Q-AMS data)
A Note on Ammonium Balance

2. Effect of Organic nitrates

BEACHON-RoMBAS Forest: P. Campuzano-Jost in Fry et al. (2012 in prep.)

- Organic nitrates, sulfates (amines) are correlated with pollution, subtle effect on the NH$_4$ balance
- Need HR balance & careful quantification of RIE$_{NH4}$
- Again, subtle effect on slope, not on R$^2$
- One CANNOT use ambient data to measure RIE$_{NH4}$

A Note on Ammonium Balance

3. Effect of Organic nitrates, sulfates (amines)

Riverside: Docherty et al. (ACP 2011)

- Organic nitrates, sulfates (amines) are correlated with pollution, they have a more subtle effect on the ammonium balance
- Need HR balance & careful quantification of RIE$_{NH4}$ (also RIE$_{SO4}$ -> James)
Scope of particle-phase instrumentation:
1. HR-ToF-AMS (Jimenez Group)
2. PAM
3. SMPS
4. UHSAS
5. SO4 Monitor
6. EC/OC
7. WSOC
8. PILS + ion chromatography + CIMS
9. TAG-AMS
10. 2-D TAG
11. HR-PTR-TOF-MS
12. CRDS/Integrating Sphere Nephelometry
13. Aethalometer
14. PASS
15. SP2
16. CAPS
17. ASTER
18. PALMS (K. Froyd, NOAA)
19. NAMS
20. CCN Counter
21. MOVi-ToF-CIMS
22. SP-AMS
23. Synchrotron XRF (Y. Zhao & S. Cliff, UC-Davis)

CalNex Campaign and Pasadena Ground Site

Pasadena
Riverside
Downtown LA

PM Composition during CalNex

- Red box indicates period of higher marine influence as indicated by the presence of refractory chloride and sea particles identified by the PALMS instrument.
- Sea salt is mostly reacted (e.g. converted from NaCl to NaNO₃).
- Note: Sampled air is dried before the AMS measurement (to approx. 20 – 30% RH)
Dependence of nitrate TD evaporation on sea salt

![Graph showing the dependence of nitrate TD evaporation on sea salt](image)

Na mass estimated from PALMS measurements

Ammonium Balance and Dependence on Na⁺, Part 1

![Graph showing ammonium balance and dependence on Na⁺](image)

Apparent correlation between refractory chloride and deviations in measured-to-predicted ammonium ratio
Ammonium Balance and Dependence on Na⁺, Part 2

- ‘NH₄⁺ Predicted’ is the sum of the molar concentrations of nitrate, sulfate, and ammonium.
- Sodium mass concentration is estimated from the PALMS measurement of sea salt particle type volume concentration.
- Na⁺ from Sea Salt is balancing the electrostatic charge of ammonium.

Impact of Sea Salt on Nitrate Fragment Ratios measured by AMS

Sea salt mass estimated from PALMS measurements
**Conclusions**

- AMS is detecting sea salt in some form, either ‘fresh’ NaCl and/or ‘processed’ NaNO$_3$.

- High degree of sea salt processing during CalNex. Chloride depletion calculated to be approximately 90%, on average, during the campaign.

- Thus, detection of NaCl from sea salt is not conclusive, but detection of NaNO$_3$ seems certain.

- In cases when sea salt concentrations are substantial, then the ammonium balance may not be a good indicator of particle acidity.

- When processed sea salt is present the NO$_2^+$/NO$^+$ ratio will **NOT** be a good indicator of organo-nitrates.