

Aerosol chemical composition and source characterization during 2008 VOCALS REx

- **Composition and distribution**
- **Sources**
- **Chemical relationships**
- **Mixing and transport**

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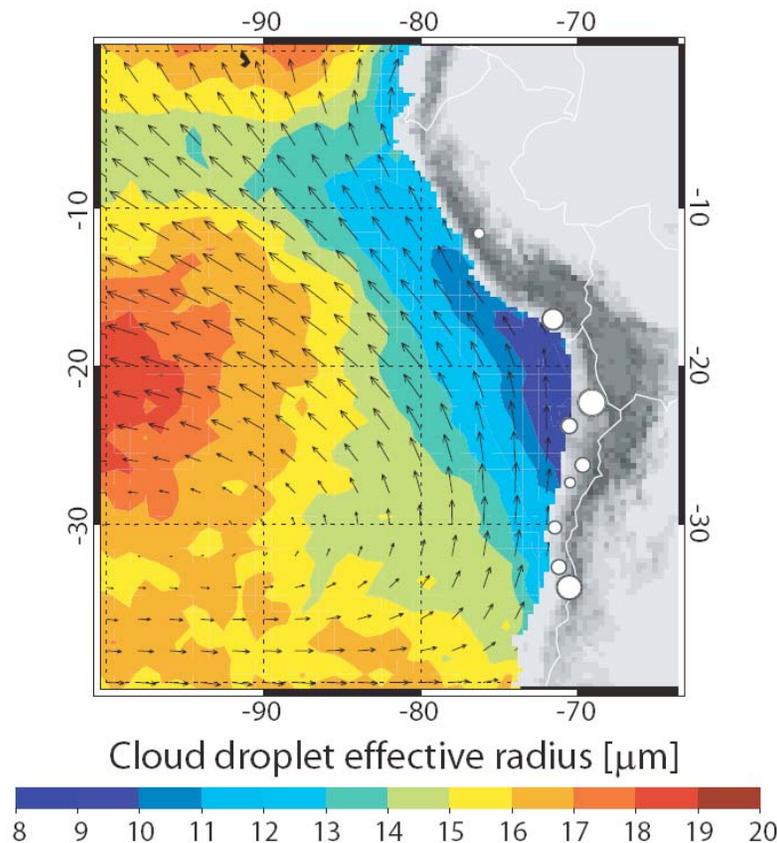
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VOCALS SEP REx: Scientific Program Overview

Hypothesis 1c: *The small effective radii measured from space over the SEP are primarily controlled by anthropogenic, rather than natural, aerosol production, and that entrainment of polluted air from the lower free-troposphere is an important source of cloud condensation nuclei (CCN).*



A first level goal:
To identify sources of aerosol particles by measuring their chemical constituents and spatial distributions

Natural sources:

- DMS
- sea-salt
- dust

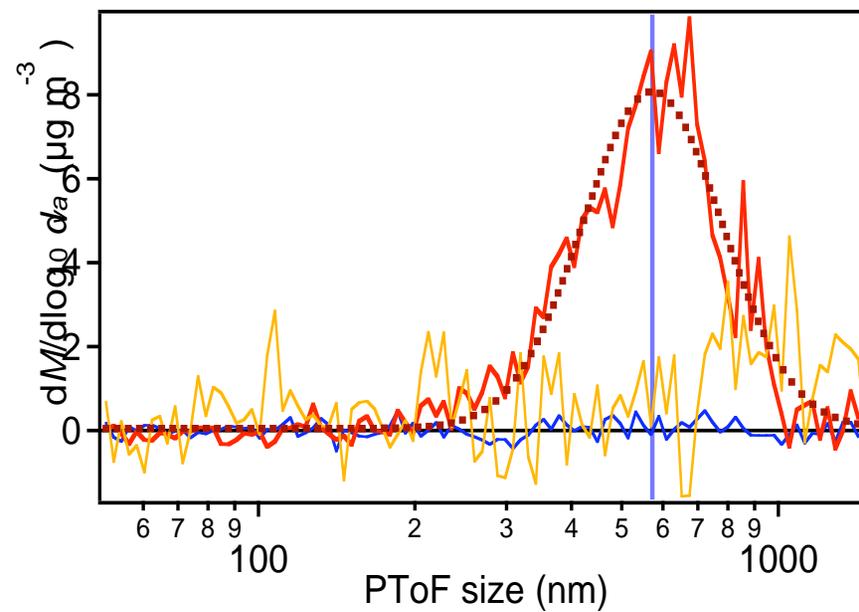
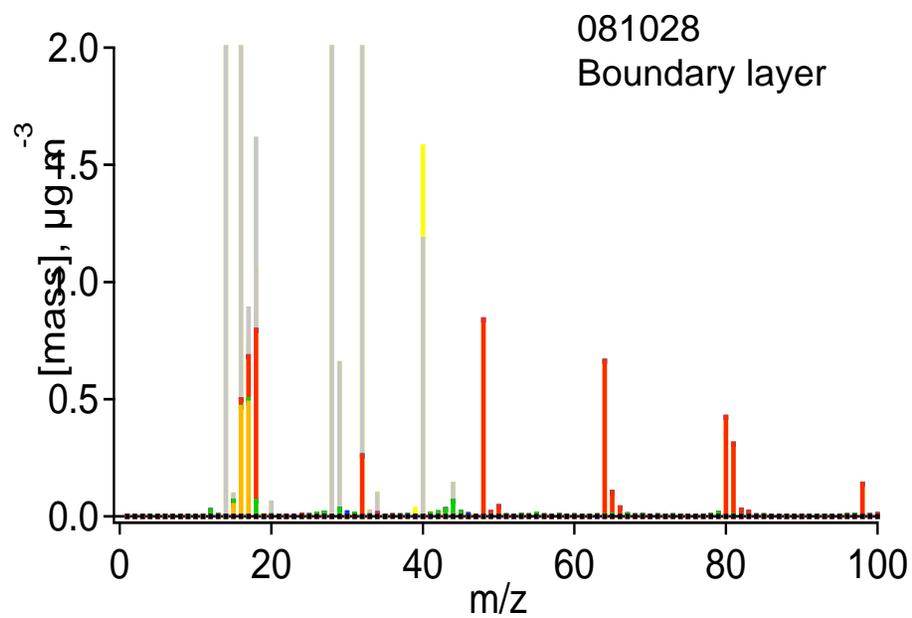
Anthropogenic sources:

- smelters
- urban
- agricultural activities

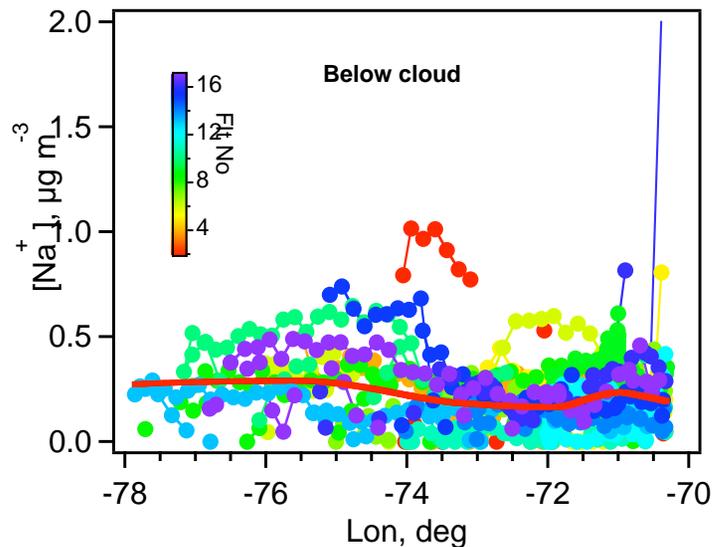
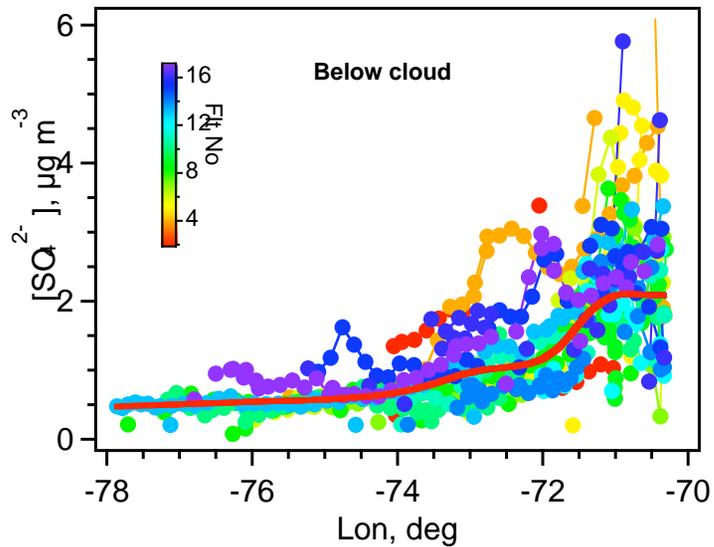
Chemical measurements on board the G-1

PILS-IC (3.0 min, bulk)	Na^+ , Cl^- , CH_3SO_3^- , Mg^{2+} NO_3^- , SO_4^{2-} , NH_4^+ K^+ , Ca^{2+}
cToF-AMS (22 sec, size resolved)	NO_3^- , SO_4^{2-} , NH_4^+ , Org
PTR-MS (30 s)	VOC, DMS
Other (10 s)	O_3 , SO_2 , CO

Aerosol was dominated by SO_4^{2-} during VOCALS



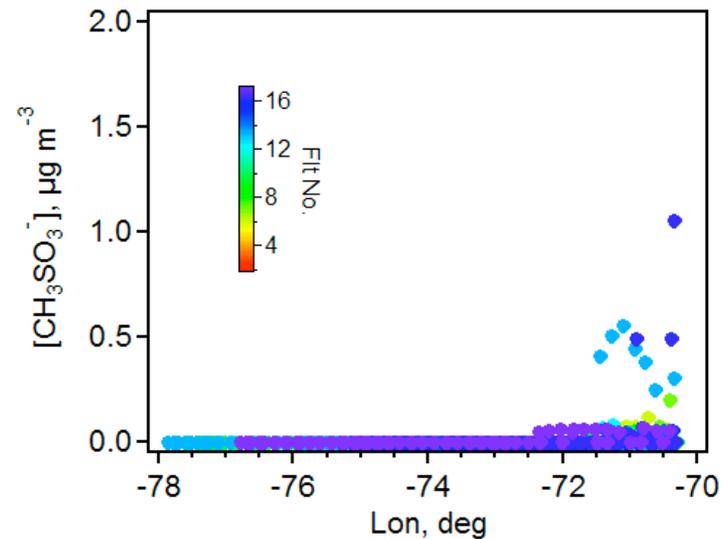
Hypothesis 1c: The small effective radii measured from space over the SEP are primarily controlled by anthropogenic, rather than natural, aerosol production, and that entrainment of polluted air from the lower free-troposphere is an important source of cloud condensation nuclei.



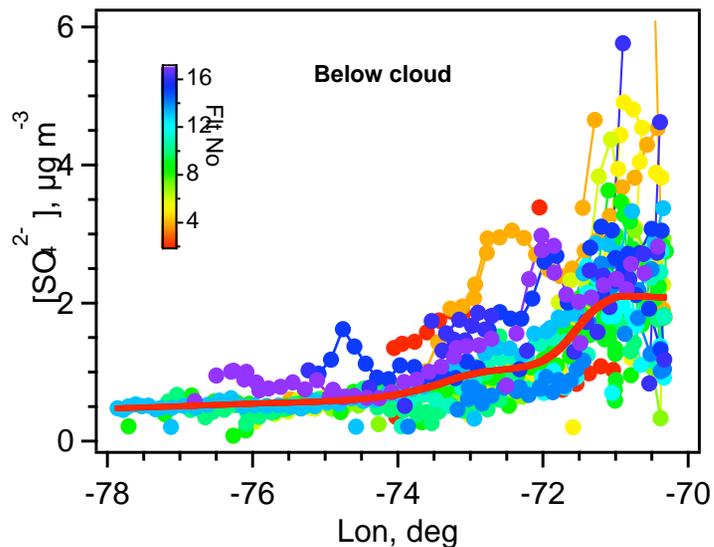
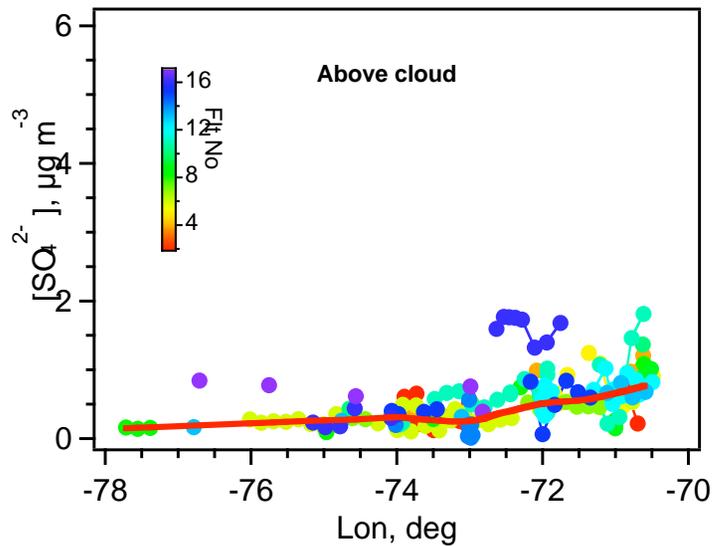
The first part of the hypothesis is supported by the observation that the coastal aerosol was dominated by anthropogenic SO_4^{2-} *.

- strong land-to-sea SO_4^{2-} gradient, consistent with terrestrial origin
- Insignificant DMS contribution
- Small sea-salt SO_4^{2-}

*Thick red lines in graphs represent weighted average



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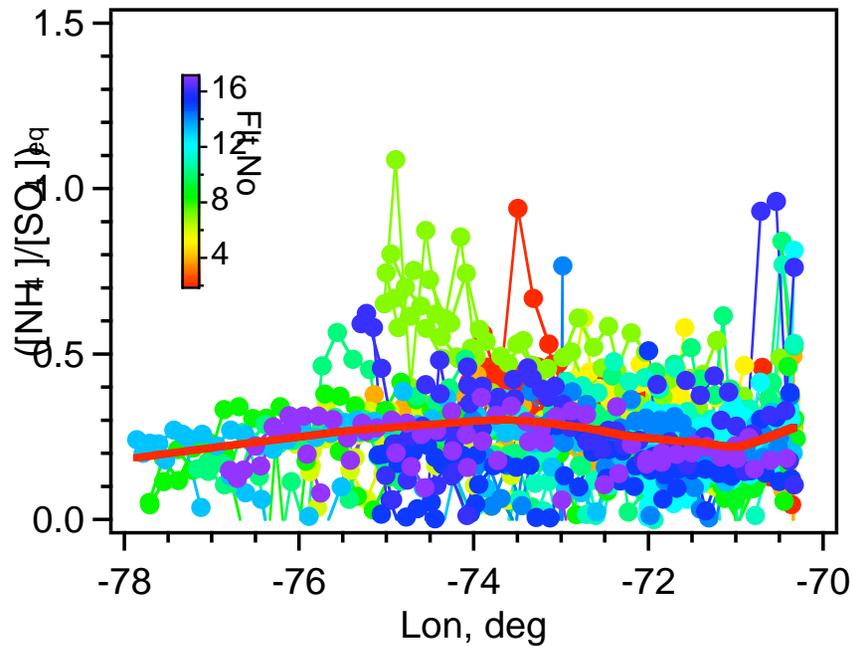


The second part of the hypothesis is not supported by G1 observations*.

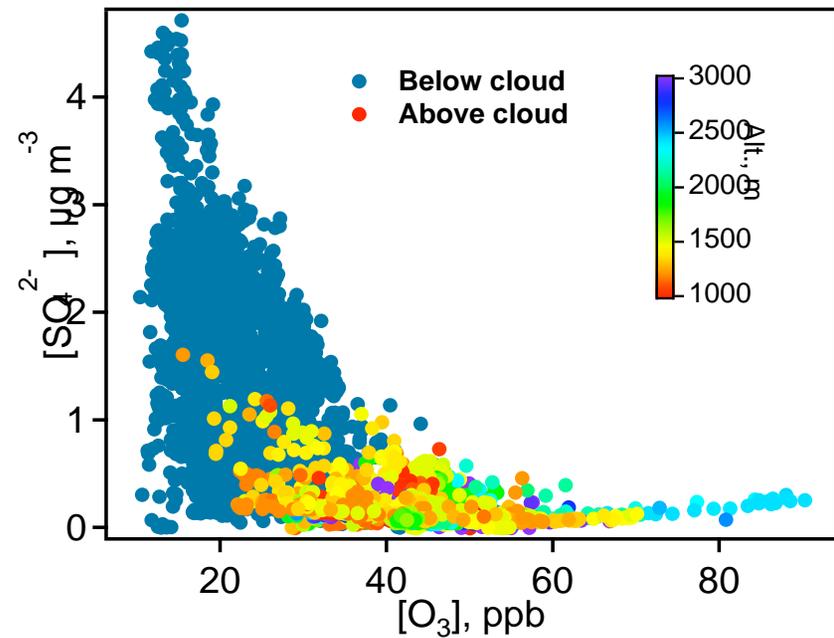
- MBL SO_4^{2-} concentration was greater than that of the lower troposphere
- A relatively smooth land-to-sea SO_4^{2-} concentration gradient suggests advection of terrestrial sources into MBL is important

*Thick red lines in graphs represent weighted average

Aerosol acidity and vertical distribution

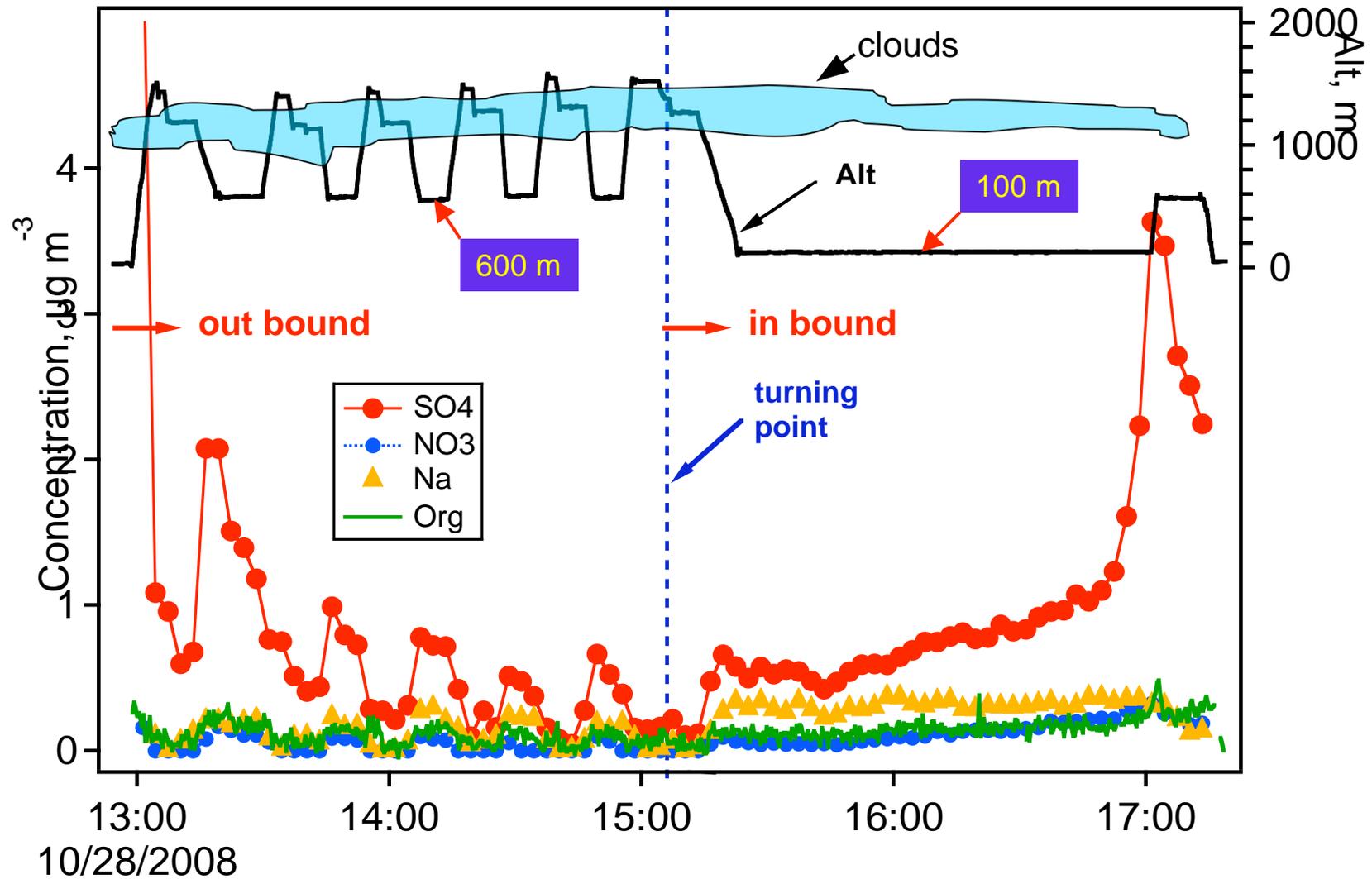


- on average, ~25% SO_4^{2-} neutralized by NH_3

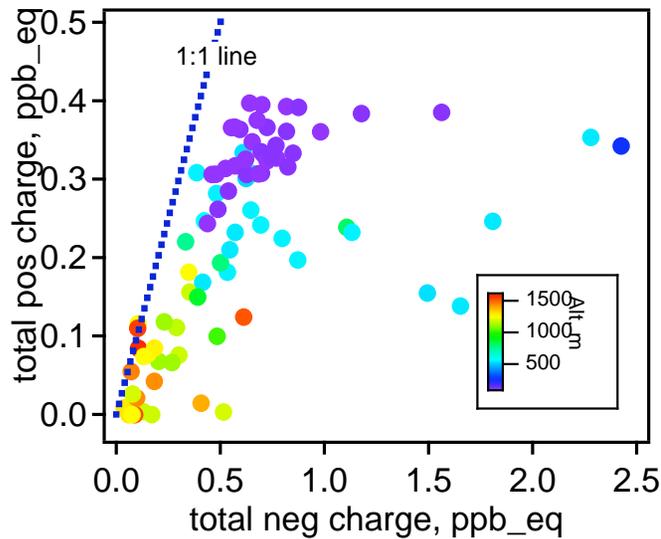


- Above-cloud SO_4^{2-} appreciable, but smaller than below-cloud levels
- Net O_3 loss in SO_2 plumes accompanying $NO \rightarrow HNO_3$

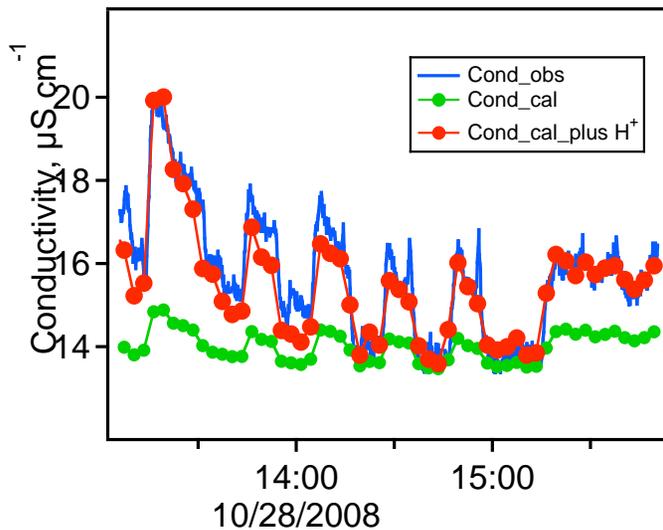
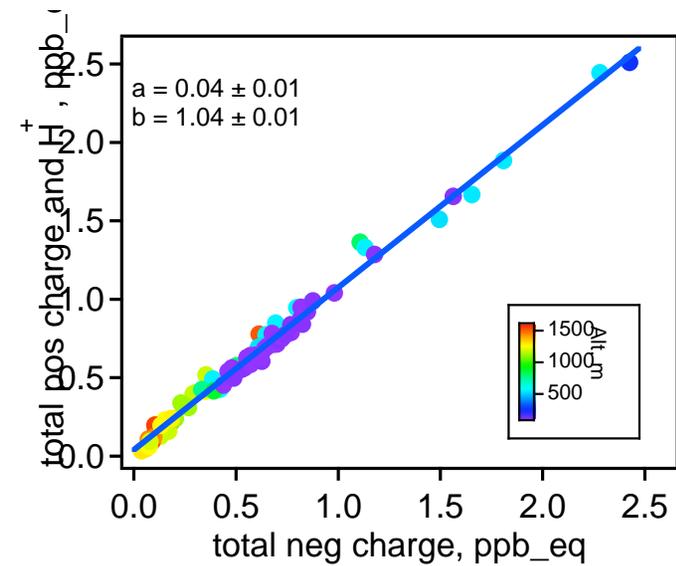
A detailed look of 10/28/08 flight



Missing cation was H^+ , confirming H_2SO_4 aerosols

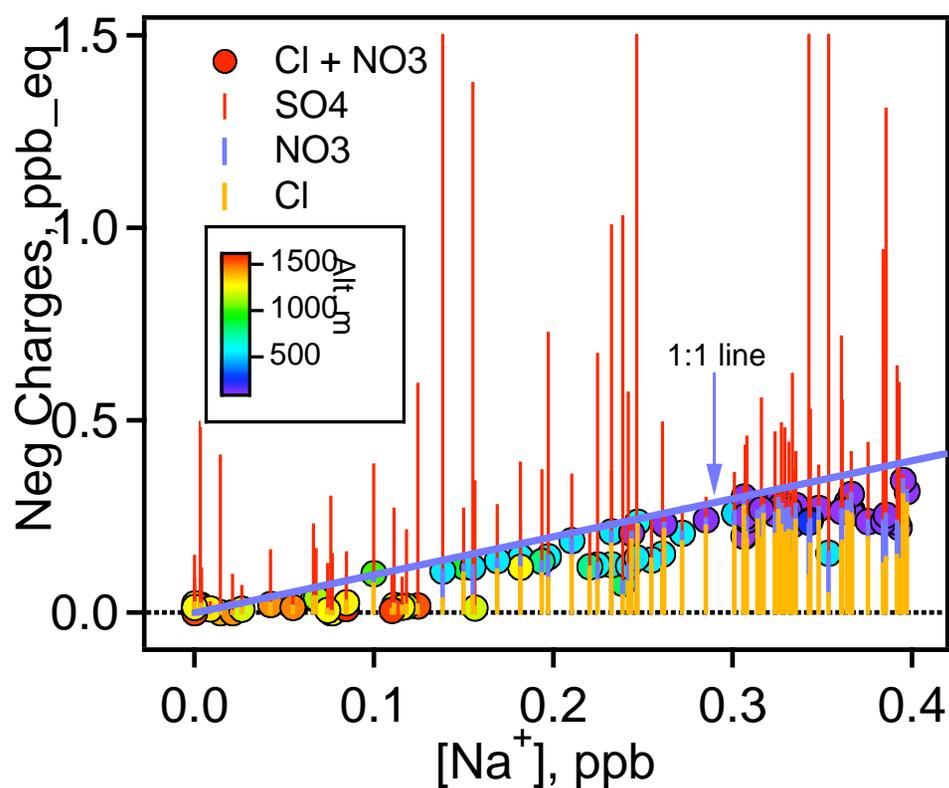


Add
 $2 \times \text{nss}[\text{SO}_4^{2-}] -$
 $[\text{NH}_4^+]$
in ppb to ordinate



- *Missing cations were associated with excess nss-SO_4^{2-}*
- *The missing ion is identified to be the hydronium ion by conductivity measurement*

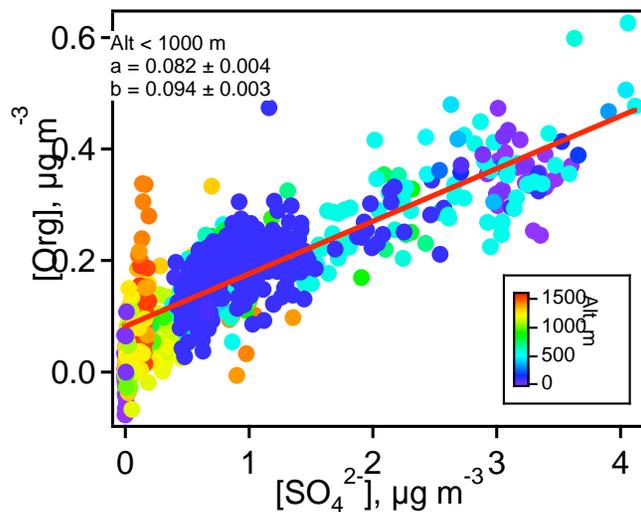
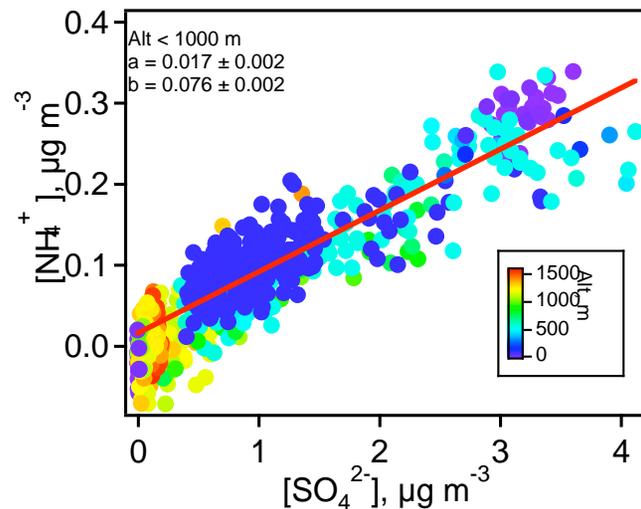
H_2SO_4 aerosols were externally mixed with modified sea-salt particles



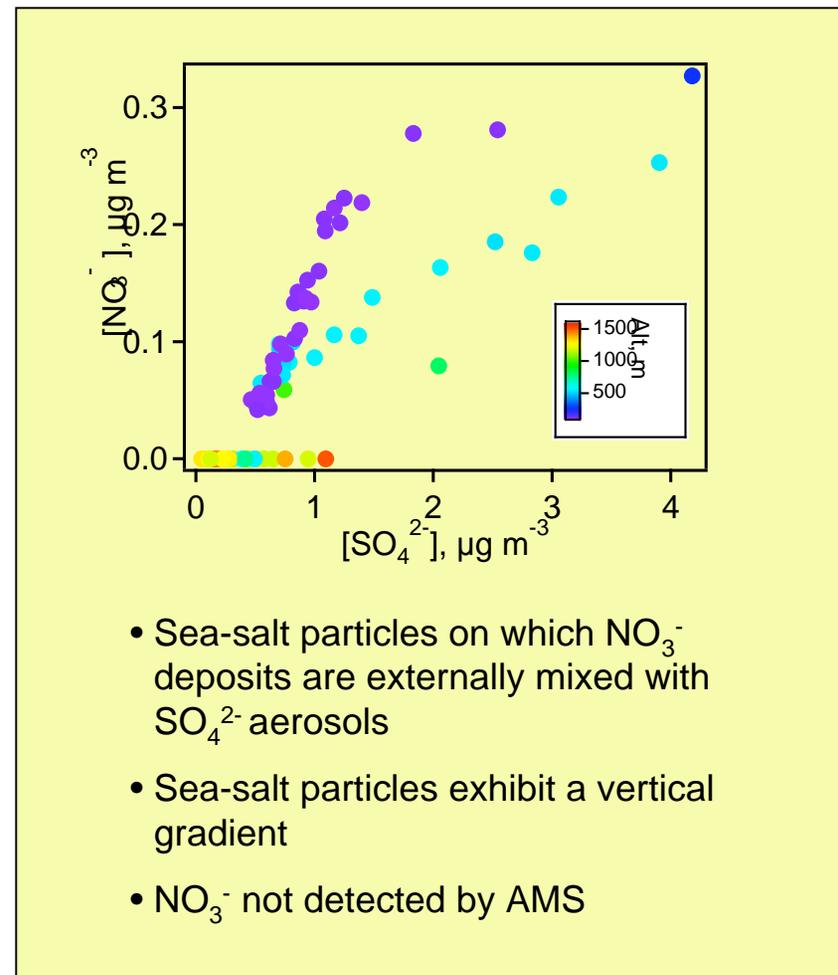
- Cl^- deficit of ~20% was evident
- mostly due to uptake of gaseous HNO_3
- partly due to H_2SO_4 via
 - gas phase?
 - cloud phase?

Org, NH_4^+ , and NO_3^- were correlated with SO_4^{2-} , suggesting common source attributes and terrestrial origin

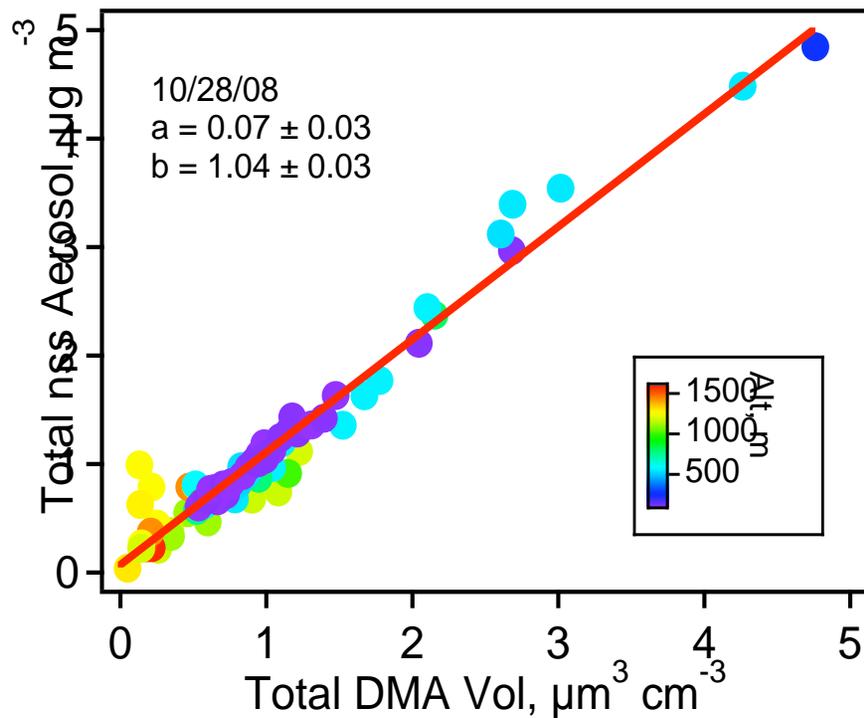
Org, NH_4^+ , SO_4^{2-} well mixed in MBL



However, not NO_3^-



Effects of hygroscopicity of H_2SO_4

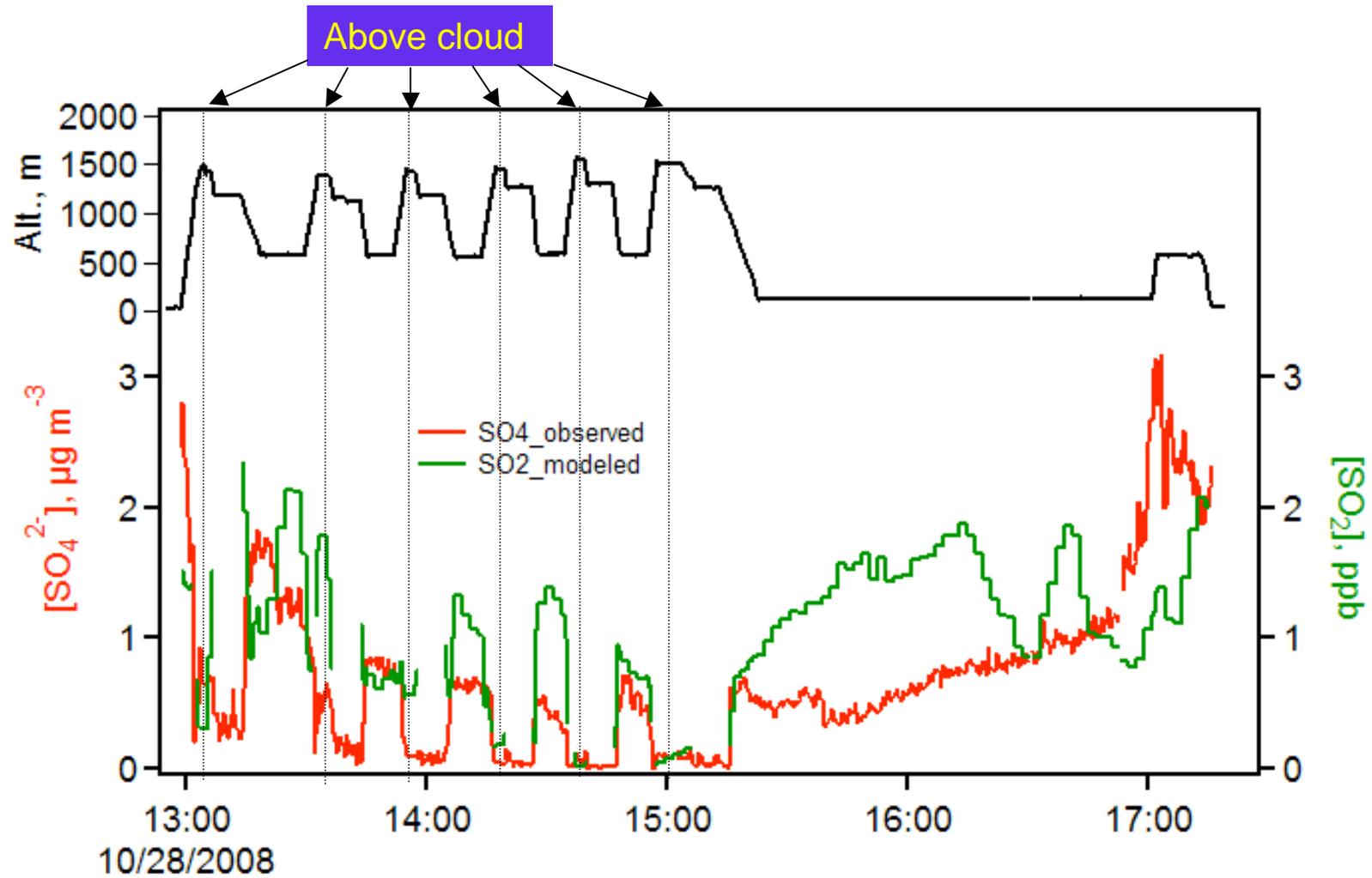


- *Direct radiative effect*
- *CCN properties*

Example: aerosol mass vs DMA volume:

- The near unity slope indicates DMA volume included the water present in SA aerosols (cf. DMA RH = ~13-16%, and H_2SO_4 growth factor is ~1.2).

Comparison of observed and calculated $[\text{SO}_4^{2-}]$



Conclusions

- Coastal MBL aerosols were dominated by externally mixed H_2SO_4 and sea-salt particles.
- Sea-salt particles were modified by HNO_3 as well as by H_2SO_4
- H_2SO_4 aerosols are anthropogenic:
 - a strong land-ocean gradient
 - known emission sources
 - good correlations with organics and NO_3^-
 - insignificant contributions from DMS
- Entrainment into MBL from lower free troposphere as an CCN source may be less important than model predictions