# Observations of Methanesulfonic Acid in Tropical Tropospheric Aerosol

**Karl D. Froyd**[*1,2], T. Sanford[1,2], D.S. Thomson[1,2], J. Schreiner[3], and D.M. Murphy[1]

[1]*NOAA Earth System Research Lab, Boulder, CO* [2]*Cooperative Institute for Research in Environmental Science, University of Colorado, Boulder, CO*

[3]*Max-Planck-Insitut fur Kernphysik, Heidelberg, Germany*

*Karl.Froyd@noaa.gov

## INTRODUCTION

### CR-AVE Mission

The Costa Rica Aura Validation Experiment (CR-AVE) took place in San Jose, Costa Rica from Jan-Feb 2006. A principal goal of the mission was to validate data from the Aura satellite, part of NASA's Earth Observing System.

Over 25 remote sensing and in situ instruments took measurements aboard the NASA WB-57 aircraft within the tropical tropopause layer (TTL) and the lower stratosphere.

The PALMS instrument measured aerosol chemical composition. Common particle types observed during CR-AVE were sulfate/organic mixtures, meteoric debris, mineral dust, sea salt, soot, biomass burning remnants, and industrial pollution.

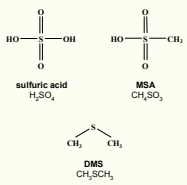
This poster describes elevated MSA:nss-$SO_4^=$ ratios detected by PALMS in the tropical free troposphere.

### Particulate Sulfur Species

In the remote marine atmosphere, the principal source of sulfuric acid and methanesulfonic acid (MSA) is oxidation of dimethyl sulfide (DMS), a biogenic compound emitted from the ocean's surface.

The low vapor pressures of sulfuric acid and methanesulfonic acid cause them to partition effectively to the particle phase, where they exist as sulfate and methanesulfonate. Particulate sulfate is ubiquitous throughout the atmosphere, whereas MSA is typically found at very low levels outside the boundary layer.

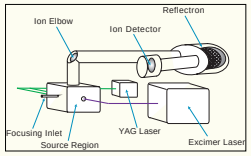
The ratio of particulate MSA to non-sea salt sulfate (**MSA:nss-$SO_4^=$**) has historically been used as a measure of relative biogenic influence. During CR-AVE, PALMS frequently observed MSA/sulfate particles with high relative MSA.




## INSTRUMENT

### Particle Analysis by Laser Mass Spectrometry

The NOAA PALMS instrument measures single particle size and chemical composition




1. ambient particles sampled through aerodynamic focusing inlet
2. detect particles by light scattering: YAG laser
3. evaporation & ionization: UV Excimer laser
4. time-of-flight MS gives chemical composition

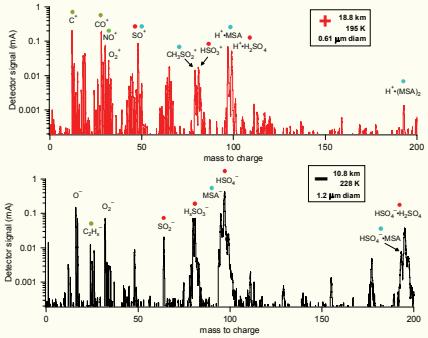
- 1 mass spectrum (+ or –) per particle
- aerodynamic particle sizes (~0.3 – 5 μm)
- data rate ≤ 10Hz


The WB-57 has a range of 2500 miles and a ceiling of >60 kft (20 km).

PALMS has flown aboard the WB-57 during 6 campaigns.

65,000 particle spectra were acquired during CR-AVE.

### Single Particle Mass Spectra




## RESULTS

### CR-AVE Flight 12 – Feb 07

Initial flight segment along tropopause (16.5 km).

Dive to 10 km at ~18:00.

**Sulfate**

Low at the tropopause, increases during dive, dominates in stratosphere.

**MSA**

**Increases by x10** during dive and final descent.

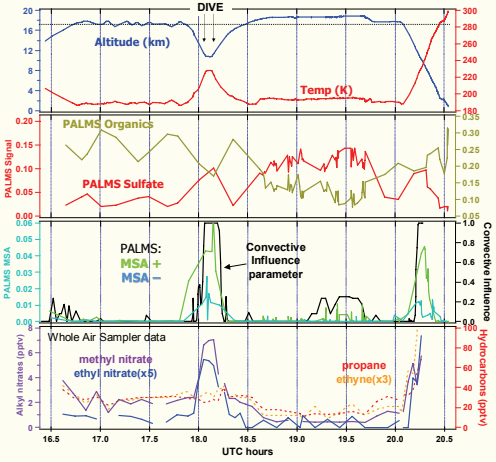
Back trajectory analysis shows correlation with Convectively Influenced air.

**Alkyl nitrates**

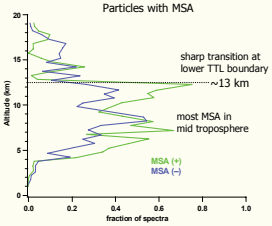
Spikes during dive and descent suggest air originated in marine boundary layer.[1]

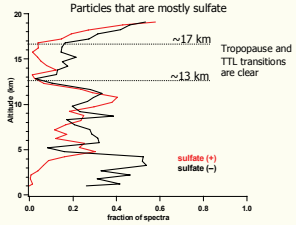
**Short-lived hydrocarbons**

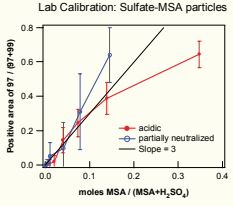
Constant , indicating minimal continental influence during dive.



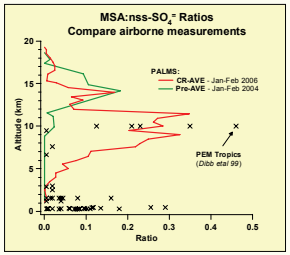

### CR-AVE Mission averages




*Calculate MSA:nss-$SO_4^=$ ratio*




*Typical MSA:nss-$SO_4^=$ Ratios*

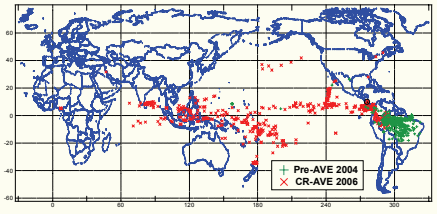
| Region | Method | Ratio | Ref |
|---|---|---|---|
| Tropical Pacific BL | | | |
| < 2 km | airborne bulk filter | ≤ 0.20 | 2 |
| Fanning Isld | bulk filter | 0.07 | 3 |
| Fanning Isld | global 3D model | 0.16 | 3 |
| Antarctic BL | | | |
| Palmer | bulk filter | 0.5 - 0.6 | 3 |
| | global 3D model | 0.45 - 0.85 | 3 |
| Halley | bulk filter | 0.30 | 3 |
| | global 3D model | 0.72 | 3 |
| Tropical Free Trop. | | | |
| 2-11 km | airborne bulk filter | 0.1 - 0.5 | 2 (ITCZ) |
| | | ≤0.02 | 2 |
| 6-12 km | single particle MS | 0.1 - 0.3 | CR-AVE |
| | | ≤0.02 | Pre-AVE |
| free trop avg | global 3D model | 0.8 - 1.0 | 3 |

- Mid and upper tropospheric ratios higher than typical MBL ratios
- MSA enhancement is more pronounced during CR-AVE
- Enhanced MSA:nssSO4 observed previously during PEM Tropics by Dibb etal '99 (×), but only near ITCZ

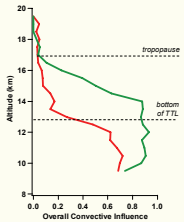
## COMPARE COSTA RICA MISSIONS

***Convectively influenced air encountered by the WB-57:***

### Origins of convection




### Average Profiles

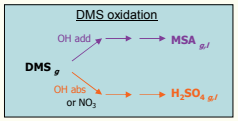



CR-AVE: Convection lofts marine air, stopping short of the TTL

Pre-AVE: Continental convection over Amazon lofts air into the TTL. Lack of marine convection is consistent with less overall MSA.

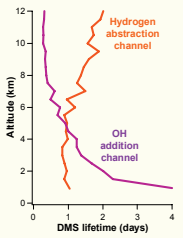
## MSA MECHANISM

### Why is particulate MSA enhanced in the free troposphere?

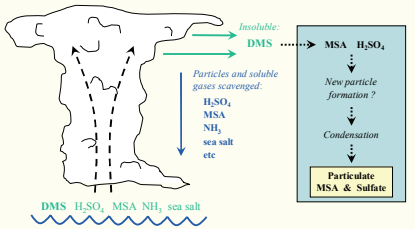



- MSA is only produced from oxidation of DMS
- Highly complex – numerous aqueous steps
- Can only yield MSA from OH addition channel
- OH addition dominates above lower troposphere

**DMS lifetime due to OH calculated for the tropical troposphere[4,5]**




**Lofted DMS is more efficiently converted to MSA**




## SUMMARY

- The first single particle composition measurements in the tropical troposphere show overall MSA:nss-$SO_4$ ratios as high as 0.3.
- Marine tracers and convective influence calculations confirm that the observed MSA is of marine origin.
- Particle chemistry is consistent with the hypothesis that DMS is lofted by wet tropical convection and then converted to MSA with high relative efficiency.
- Mechanistic descriptions are limited without gas phase sulfur or oxidant measurements aboard the WB-57.
- We have proposed to fly PALMS aboard the **NASA DC-8** (0-12km) for the upcoming **TC4 Costa Rica Campaign 2007** to further investigate tropospheric sulfate and MSA.

### Acknowledgements

We thank Elliot Atlas for the Whole Air Sampler data and Lenny Pfister for providing Convective Influence calculations. The diligence and dedication of the CR-AVE mission coordinators and the crew of the NASA WB-57 are also gratefully acknowledged.

### References

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3. Gondwe etal. *GlobBioGeoChem* 2004
4. Tan etal. *J Geophys Res* 2004
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