

Influence of nitrate radical on the oxidation of dimethyl sulfide in a polluted marine environment

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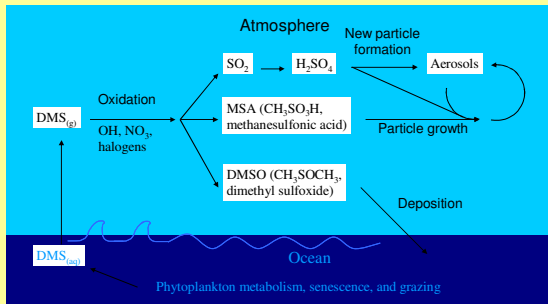
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DMS production and oxidation mechanism



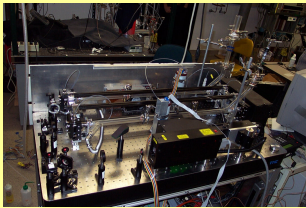
DMS is the most important (90%) contributor to biogenic atmospheric sulfur. Its contribution to total atmospheric sulfur varies, depending on anthropogenic emissions. It is a major contributor to total sulfur in the southern hemisphere. The chemical DMS oxidation mechanism determines the aerosol yield. If the H_2SO_4 yield from DMS oxidation by NO_3 is different, then NO_3 could have an influence on aerosol production.

What happens to DMS in the marine boundary layer (MBL) determines the global role of DMS and its role in the free troposphere.

- Questions: (1) Can we see a clear role of NO_3 in DMS oxidation?
 (2) What is the contribution of NO_3 to the removal of DMS from MBL?
 (3) What is the contribution of DMS to conversion of NO_3 to HNO_3 , and hence removal of NO_3 in MBL?

Simultaneous in-situ measurement of NO_3 and DMS during NEAQS helps answer these questions.

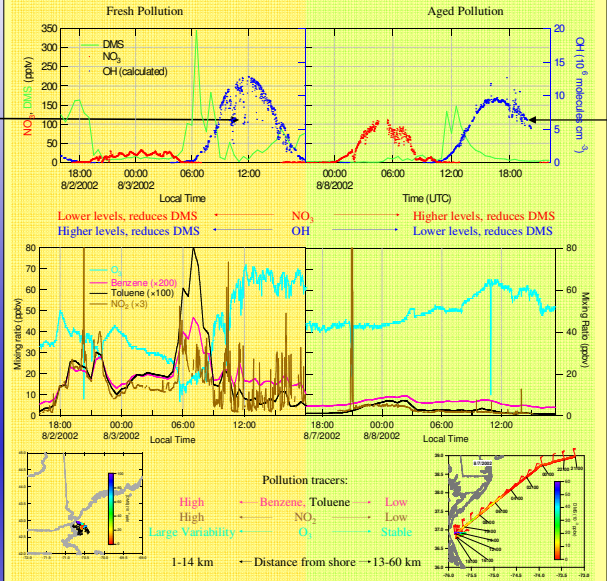
NO_3 Detection: Cavity Ringdown Spectroscopy



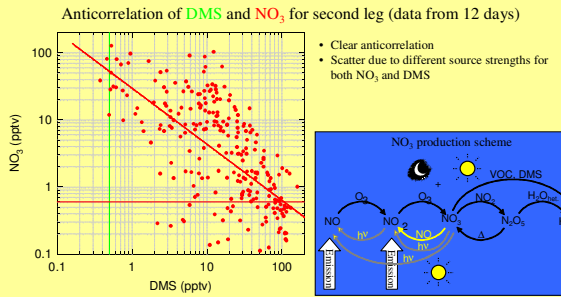
- Optical detection @ 662 nm
- Measure light decay rate from optical cavity
- Empty cavity ringdown times = 200 μ s = path length of 60 km
- Dual cell instrument for simultaneous detection of NO_3 and N_2O_5
- Sample rate = 20 Hz, averaged for 1 min data
- More details: see poster A51D-0716
- Detection limit: 1 pptv

- DMS detection:
- Gas Chromatography/Mass Spectrometry
 - 5 Minutes sampling time; repeat every 30 minutes, detection limit = 0.5 pptv

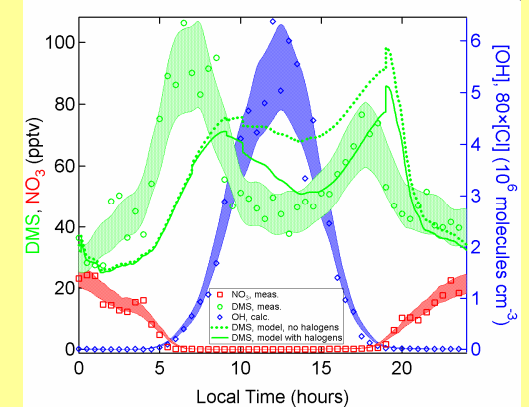
Measurements



DMS oxidation by NO_3 important, even after much of the NO_3 has been removed!



Diurnal averages of DMS, NO_3 , and OH, comparison with chemical box model



- Good agreement between modeled and measured DMS during most periods of the day
- NO_3 oxidizes \approx 80% of the available DMS in comparison to OH in the coastal region
- Inclusion of Cl as a proxy for halogens improves daytime agreement

Conclusions

- DMS and NO_3 anticorrelated, clear indication of NO_3 reaction with DMS
- DMS oxidation by NO_3 remains important well downwind of NO_3 sources
- DMS oxidation by NO_3 4 times more important than by OH during NEAQS
- DMS oxidation by NO_3 can be equal to oxidation by OH up to 3000 km downwind
- Aerosol production and growth altered by NO_3 -DMS oxidation
- The flux of DMS out of the MBL will be suppressed in NO_3 -rich regimes
- Reaction with DMS is one of the most important pathways for NO_3 removal
- DMS + NO_3 is an important contribution to nocturnal nitric acid production

These results have been recently published:



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