

Aerosol organosulfates measurements by PALMS during DC3

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Introduction

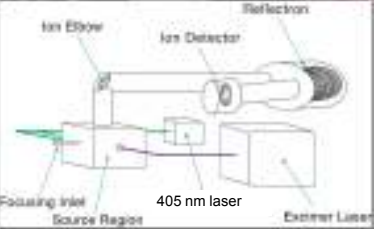
Atmospheric aerosols have an important impact on climate change and human health. Organic and sulfur are major constituents of tropospheric fine aerosols [Zhang et al. GRL, 2007 ; Froyd et al; ACP, 2009]. Secondary organic aerosol (SOA) accounts for a significant fraction of organic aerosols [Kroll and Seinfeld, AE, 2008]. The formation mechanism, chemical composition and properties of SOA are not well understood and remain one of the current aerosol research focuses [Hallquist et al., ACP, 2009].

Organosulfates can be an important class of SOA. Organosulfates have been identified in laboratory generated SOA produced from oxidation of biogenic volatile organic compounds (e.g. isoprene) [e.g. Surratt et al., JPCA, 2008] with acidity seed aerosols. Organosulfates have also been detected in field study [e.g. Froyd et al., PNAS, 2010; Zhang et al., EST, 2012]. Organosulfates can comprise up to 5-10% of organic aerosol mass over the continental U.S [Tolocka and Turpin, EST, 2012].

Here we report the organosulfates including H-IEPOX-SO₄ and C₂H₃O₂-SO₄ measurements by Particle analysis by laser mass spectrometry during DC3.

Methods

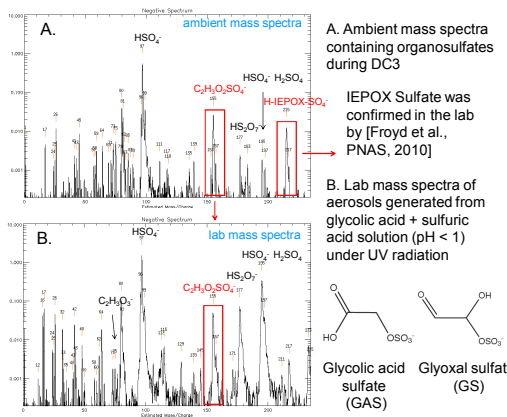
Particle Analysis by Laser Mass Spectrometry (PALMS)



The NOAA PALMS instrument measures the chemical composition of individual aerosol particles using laser absorption ionization technique [Murphy and Thomas, AST, 1995]. Particles with diameter larger than ~200 nm can be sized by a continuous laser beam (405 nm), ionized by an excimer laser (193 nm) and detected by the time of flight mass spectrometer. [Murphy, Mass Spectrom. Rev., 2007].

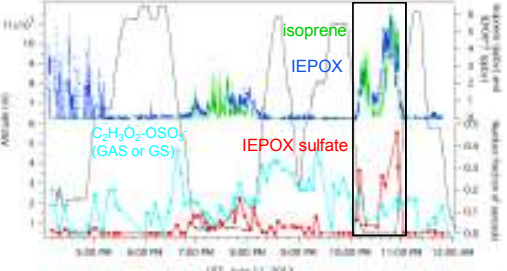
PALMS instrument is capable to detect inorganic (e.g. potassium, sulfate, metals) and organic compounds. Most of the organic compounds get fragmented with excimer laser ionization. However, Froyd et al. found that isoprene derived organosulfate IEPOX sulfate can be detected as H-IEPOX-SO₄ by PALMS. The fragmentation is reduced and the sensitivity of PALMS to IEPOX sulfate increases with reduced laser power. PALMS instrument has the potential to detect organosulfates in the ambient aerosols.

Organosulfates mass spectra by PALMS



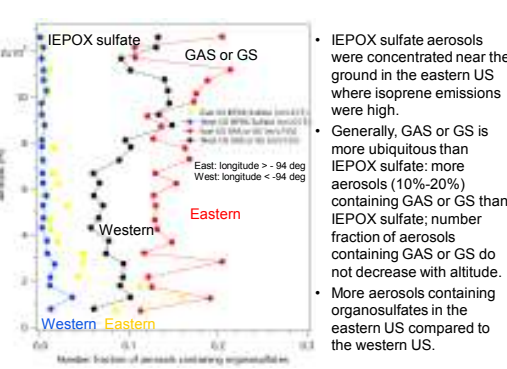
Organosulfates and isoprene chemistry

Case study: June 11 flight to Mississippi, Alabama and Tennessee



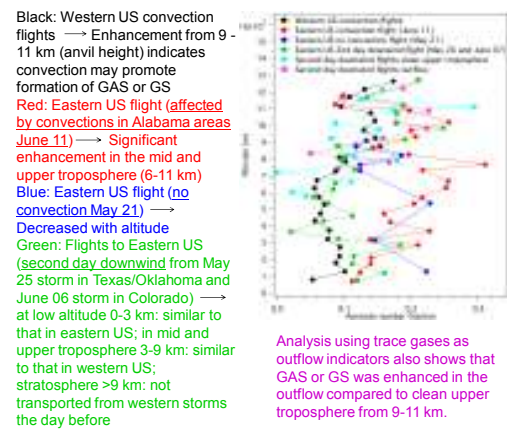
- IEPOX sulfate consistent with isoprene chemistry
- Significant fraction of aerosols contained GAS/GS in upper troposphere where isoprene and its oxidation products levels were low

Vertical profiles of organosulfates

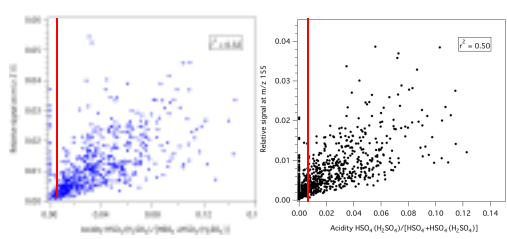


- IEPOX sulfate aerosols were concentrated near the ground in the eastern US where isoprene emissions were high.
- Generally, GAS or GS is more ubiquitous than IEPOX sulfate; more aerosols (10%-20%) containing GAS or GS than IEPOX sulfate; number fraction of aerosols containing GAS or GS do not decrease with altitude.
- More aerosols containing organosulfates in the eastern US compared to the western US.

Convection influence on GAS or GS



Organosulfates and acidity

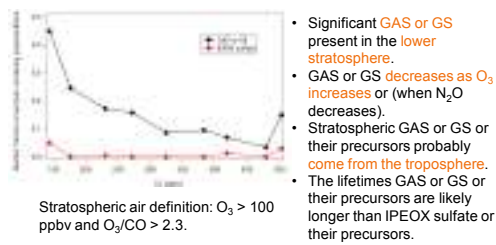


- Cluster ion HSO₄(H₂SO₄) at peak 195 m/z from PALMS negative mass spectra only appears for acidic aerosols [Froyd et al., ACP, 2009] and can be used as aerosol acidity indicator.
- PALMS acidity HSO₄(H₂SO₄)/(HSO₄+HSO₄(H₂SO₄)) was calibrated to PILS measurements [Froyd et al., ACP, 2009]. When PILS NH₄⁺ : SO₄²⁻ ≤ 1 or PALMS acidity > 0.007, pH can be lower than 1 assuming aerosol composition is similar to ammonia and sulfuric acid solution.
- The organosulfate levels above PALMS detection limit correlated with acidity in single particles near the ground (0-1000 m).
- Consistent with the previous lab experiments [e.g. Surratt et al., JPCA, 2008] that acidic seed aerosols are needed for organosulfate formation.
- Indicates that formation of organosulfates may be limited by acidity near the ground for most particles.

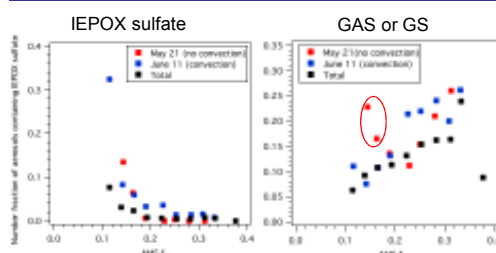
Acknowledgements

We would like to thank Dan Law, Chuck Brock and Justin Langridge for their help to operate PALMS instrument when we did not fly during the campaign. We appreciate the DC3 aerosol sampling inlet from NASA LARGE group and the Hi-CAS inlet from Chuck Brock at NOAA. We also would like to thank James Burkholder and Andy Neuman for lending us the mercury lamp and LEDs to do lab experiment. This work is supported by NASA grant NNN12AT291.

Stratospheric organosulfates



Organosulfates and aerosol aging



- Significant GAS or GS present in the lower stratosphere.
 - GAS or GS decreases as O₃ increases or (when N₂O decreases).
 - Stratospheric GAS or GS or their precursors probably come from the troposphere.
 - The lifetimes GAS or GS or their precursors are likely longer than IEPOX sulfate or their precursors.
- Aerosols sampled during DC3 are OOA (AMS f₄₄ > 0.1) [Ng et al., ACP, 2011].
 - Relatively less aged or oxidized OOA contain more IEPOX sulfate. Consistent with— IEPOX sulfate and its precursors are not very long lived and concentrated near the source region.
 - Generally, more aerosols contain GAS or GS when they are more aged/oxidized during DC3. This is more evident for flights when convection storms were present.
 - High fraction (20%) of aerosols contain GAS or GS near the biogenic emission source region even the aerosols were not highly oxidized/aged.

Summary

1. Organosulfates IEPOX sulfate and GAS or GS were detected by NOAA PALMS aboard on DC8 during the DC3 campaign.
2. Lab experiment confirmed that GAS or GS can be detected by PALMS at m/z 155.
3. IEPOX sulfate were concentrated near the ground in the eastern US, consistent with isoprene chemistry.
4. GAS or GS are present in more ambient aerosols and more ubiquitous in spatial distribution.
5. Convection may promote formation of GAS or GS in the upper troposphere or even to the lower stratosphere.
6. Acidity favors formation of IEPOX sulfate and GAS or GS. The formation of GAS or GS and IEPOX sulfate is probably limited by acidity near the ground.
7. GAS or GS detected in the lower stratosphere decreased as O₃ increased. This indicates that stratospheric GAS or GS or their precursors probably origin from the troposphere and have a relatively long lifetime.
8. IEPOX sulfate decreased when the aerosols were more oxidized during DC3 while GAS or GS generally increased when the aerosols were more oxidized during DC3.