

# Gas-to-particle conversion: Observations of ammonium nitrate formation above Houston?

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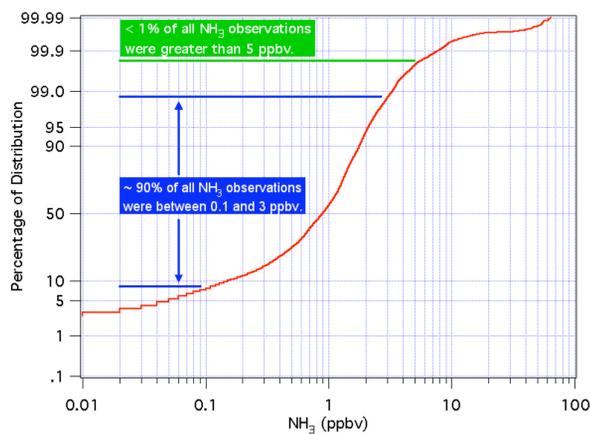
**Introduction** - The presence of fine aerosols in the troposphere affects air quality by threatening human health and lowering visibility. In some regions of the United States, secondary formation of ammonium nitrate aerosol can account for a significant fraction of particle mass and reduce visibility. Ammonium nitrate aerosol is formed from the reaction of gas-phase ammonia (NH<sub>3</sub>) and nitric acid (HNO<sub>3</sub>). Anthropogenic emissions of NH<sub>3</sub> and NO<sub>x</sub> (NO + NO<sub>2</sub>), which in sunlight is oxidized to form HNO<sub>3</sub>, can result in elevated ammonium nitrate levels. Sources of NH<sub>3</sub> in the Houston area include automobiles, industrial facilities, and outlying agricultural activity. Ammonium nitrate formation was observed from the NOAA WP-3 aircraft over Houston with fast-response measurements of NH<sub>3</sub>, HNO<sub>3</sub>, particle composition, and particle size distribution.

## Measurement Techniques

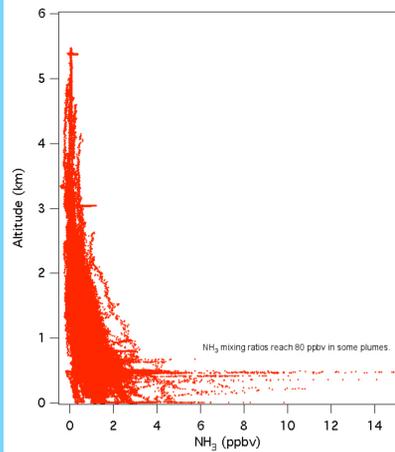
- NH<sub>3</sub> - Chemical Ionization Mass Spectrometry (CIMS) [Nowak et al., 2007]
- HNO<sub>3</sub> - Chemical Ionization Mass Spectrometry (CIMS) [Neuman et al., 2002]
- Aerosol Composition - Compact Time of Flight Aerosol Mass Spectrometer (C-ToF-AMS) [Drewnick et al., 2005]
- Aerosol Size Distributions - 5-Channel Condensation Particle Counter (CPC) Ultra-High Sensitive Aerosol Spectrometer (UHSAS) White Light Optical Particle Counter (White Light-OPC) [Brock et al., 2004]

## Summary of NH<sub>3</sub> Observations

Cumulative Probability Graph of all 1 s NH<sub>3</sub> Observations



NH<sub>3</sub> Altitude Profile - All Data



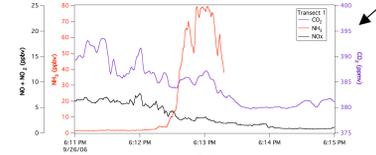
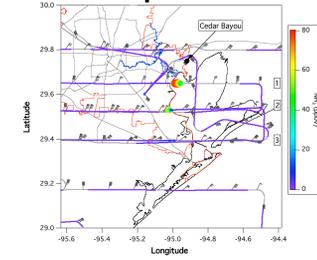
- Observed NH<sub>3</sub> mixing ratios typically ranged from 0.1 to 3 ppbv.
- As expected, NH<sub>3</sub> mixing ratios decreased with increasing altitude.
- Plumes with NH<sub>3</sub> mixing ratios greater than 5 ppbv, though infrequent, were observed below 1 km.
- **Are the plumes with high NH<sub>3</sub> mixing ratio associated with identifiable point sources?**
- **Does the high NH<sub>3</sub> mixing ratio influence aerosol formation in these plumes?**

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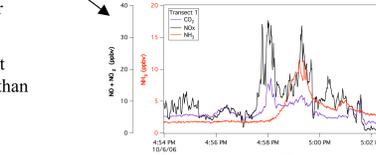
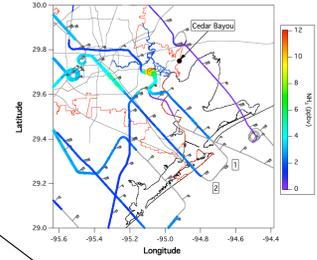
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## Plumes observed with high NH<sub>3</sub> mixing ratios over Houston

Sept. 26th

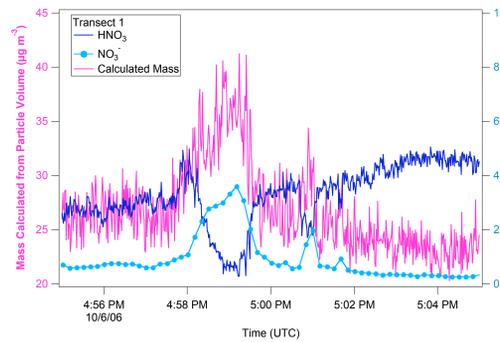
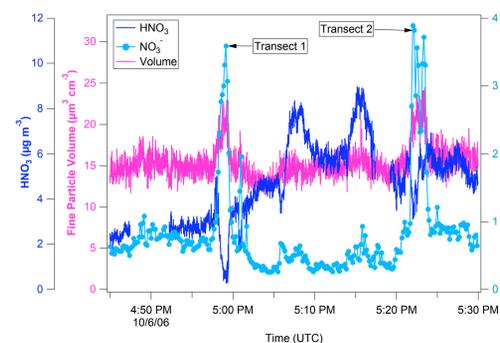
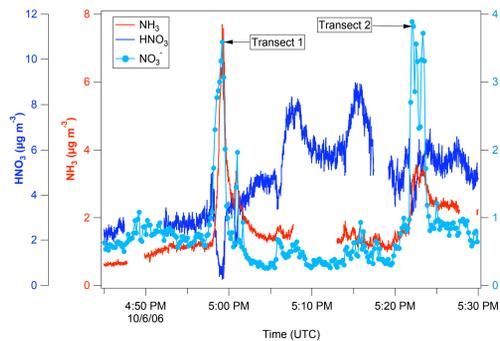
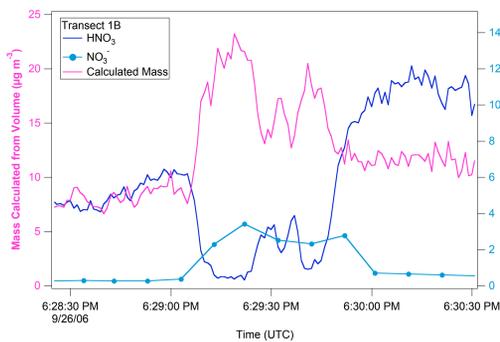
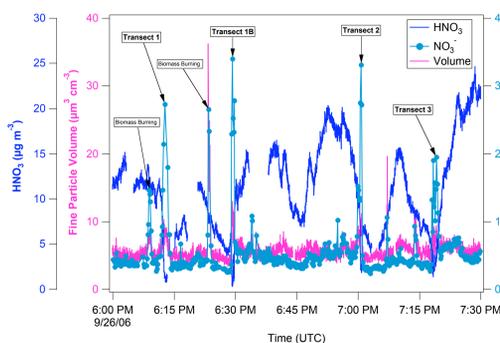
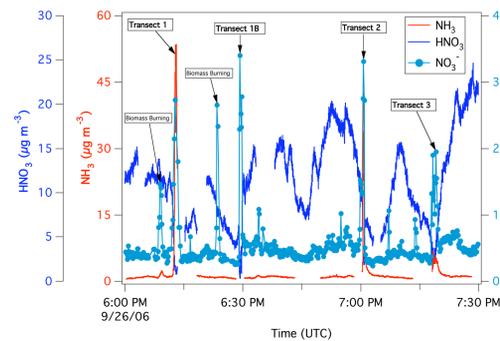


Oct. 6th



### Are these plumes from Cedar Bayou?

- WP-3 flight tracks colored and sized by 1 s NH<sub>3</sub> measurements with 2 min. average wind barbs and labeled transects.
- The only significant NH<sub>3</sub> point source listed in the NEI99v3 upwind of the observed NH<sub>3</sub> enhancements was Cedar Bayou [Frost et al., 2006].
- Times series of NH<sub>3</sub>, NO<sub>x</sub>, and CO<sub>2</sub> on the 1st transect
- On Sept. 26th, a small CO<sub>2</sub> enhancement and lack of CO enhancement (not shown) suggests this is not Cedar Bayou.
- On Oct. 6th, the high NO<sub>x</sub> values suggest this is not Cedar Bayou and that the source is likely different than the plume sample on Sept. 26th.
- Further source identification work is needed.



- Time series of NH<sub>3</sub>, HNO<sub>3</sub>, and aerosol NO<sub>3</sub><sup>-</sup> concentrations (μg m<sup>-3</sup>) during the transects shown above on Sept. 26th and Oct. 6th.
- Aerosol NO<sub>3</sub><sup>-</sup> concentrations increase when the concentrations of NH<sub>3</sub> increase and HNO<sub>3</sub> decrease suggesting the formation of ammonium nitrate from the gas-phase precursors.
- On Sept. 26th, some NO<sub>3</sub><sup>-</sup> enhancements are not correlated with NH<sub>3</sub> and HNO<sub>3</sub> but correlated with acetonitrile and CO (not shown) and are likely associated with biomass burning.

- Similarly, fine particle volume also increases in the high NH<sub>3</sub> plumes.
- The largest increases in fine particle volume on Sept. 26th are also likely associated with biomass burning plume.

### Is there quantitative agreement?

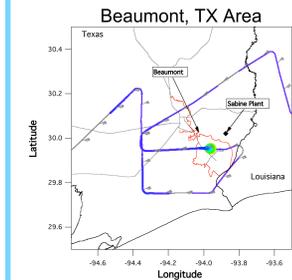
- Assume the change in volume is only from ammonium nitrate formation and calculate Δ mass from volume using the density of ammonium nitrate, 1.8 g cm<sup>-3</sup>.
- Sept. 26th example (left),  
Δ(Calculated Mass) ~14 μg m<sup>-3</sup>  
ΔHNO<sub>3</sub> ~ -5 μg m<sup>-3</sup>  
ΔNO<sub>3</sub><sup>-</sup> ~ 3.5 μg m<sup>-3</sup>
- Oct. 6th example (right),  
Δ(Calculated Mass) ~ 4-6 μg m<sup>-3</sup>  
ΔHNO<sub>3</sub> ~ -1.5 μg m<sup>-3</sup>  
ΔNO<sub>3</sub><sup>-</sup> ~ 2.5 μg m<sup>-3</sup>
- ΔHNO<sub>3</sub> and ΔNO<sub>3</sub><sup>-</sup> agree within a factor of 2.
- The difference between ΔHNO<sub>3</sub> and calculated mass along with observations of other aerosol composition species (not shown) indicate ammonium nitrate formation accounts for only part of the observed increase in aerosol volume.

## References

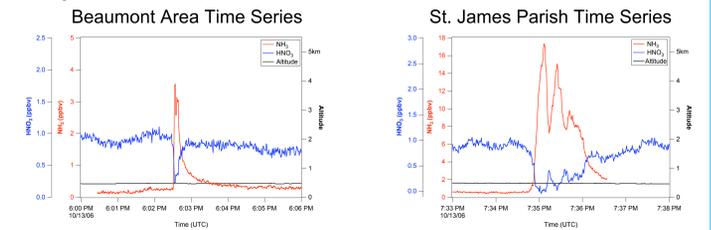
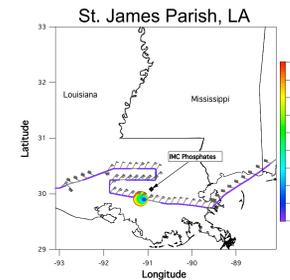
Brock, C. A., et al. (2004), Particle characteristics following cloud-modified transport from Asia to North America, *J. Geophys. Res.*, 109, D23S26, doi:10.1029/2003JD004198.  
Drewnick, F., et al. (2005), A New Time-of-Flight Aerosol Mass Spectrometer (TOF-AMS) - Instrument Description and First Field Deployment, *Aerosol Sci. Technol.*, 39(7), 637-658.  
Frost, G. J., et al. (2006), Effects of changing power plant NO<sub>x</sub> emissions on ozone in the eastern United States: Proof of concept, *J. Geophys. Res.*, 111, D12306, doi:10.1029/2005JD006354.  
Neuman, J. A., et al. (2002), Fast-response airborne in situ measurements of HNO<sub>3</sub> during the Texas 2000 Air Quality Study, *J. Geophys. Res.*, 107(D20), 4436, doi:10.1029/2001JD001437.  
Nowak, J. B., et al. (2007), A chemical ionization mass spectrometry technique for airborne measurements of ammonia, *J. Geophys. Res.*, 112, D10S02, doi:10.1029/2006JD00075

## Other high NH<sub>3</sub> mixing ratios plumes

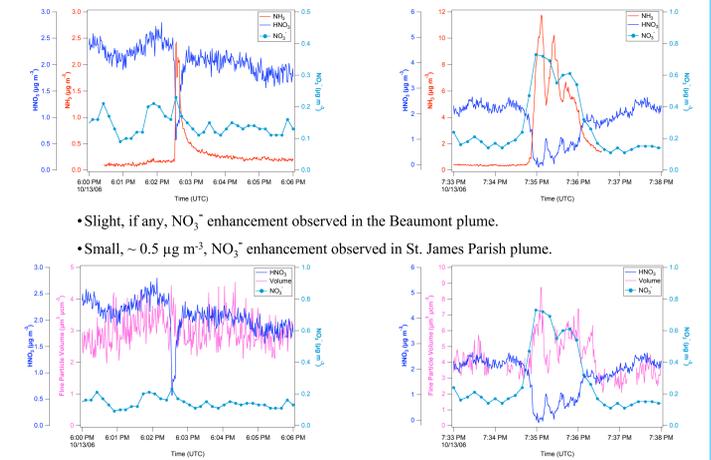
Oct. 13th - Transit to Tampa, FL



- WP-3 flight track shown colored and sized by NH<sub>3</sub> mixing ratio with 2 min. average wind barbs.
- Enhancement in NH<sub>3</sub> mixing ratio is observed downwind of two different NEI99v3 point sources, but analysis to pinpoint the source(s) using other tracers is still ongoing.
- The Sabine plant is a power generation facility, 148 tons/year [Frost et al., 2006].
- IMC Phosphates and others are a collocated group of fertilizer manufacturers, > 3688 tons/year [Frost et al., 2006].



- NH<sub>3</sub> enhancement greater downwind of the larger source(s), the fertilizer facilities.
- In both plumes a sharp decrease in HNO<sub>3</sub> is observed coincident to NH<sub>3</sub> enhancement.



- Slight, if any, NO<sub>3</sub><sup>-</sup> enhancement observed in the Beaumont plume.
- Small, ~ 0.5 μg m<sup>-3</sup>, NO<sub>3</sub><sup>-</sup> enhancement observed in St. James Parish plume.

- Similar to NO<sub>3</sub><sup>-</sup>, an enhancement in fine particle volume is only observed in St. James Parish plume.

## Summary and Future Work

- Observed NH<sub>3</sub> mixing ratios typically ranged from 0.1 to 3 ppbv, though a few plumes with NH<sub>3</sub> mixing ratios greater than 5 ppbv were also sampled.
- Though these high NH<sub>3</sub> plumes were downwind of NEI99v3 point sources, other gas-phase species, suggest different sources highlighting the need for updated inventories.
- In these plumes, coincident decreases in HNO<sub>3</sub> mixing ratio and increases in aerosol NO<sub>3</sub><sup>-</sup> and fine particle volume indicating ammonium nitrate formation.
- On Sept. 26th and Oct. 6th, the magnitude of the observed HNO<sub>3</sub> lost and NO<sub>3</sub><sup>-</sup> formed is consistent with ammonium nitrate formation within a factor of 2.
- Further analysis of the particle size distribution and aerosol composition data is needed to fully assess the quantitative agreement between the gas-phase and aerosol observations.

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