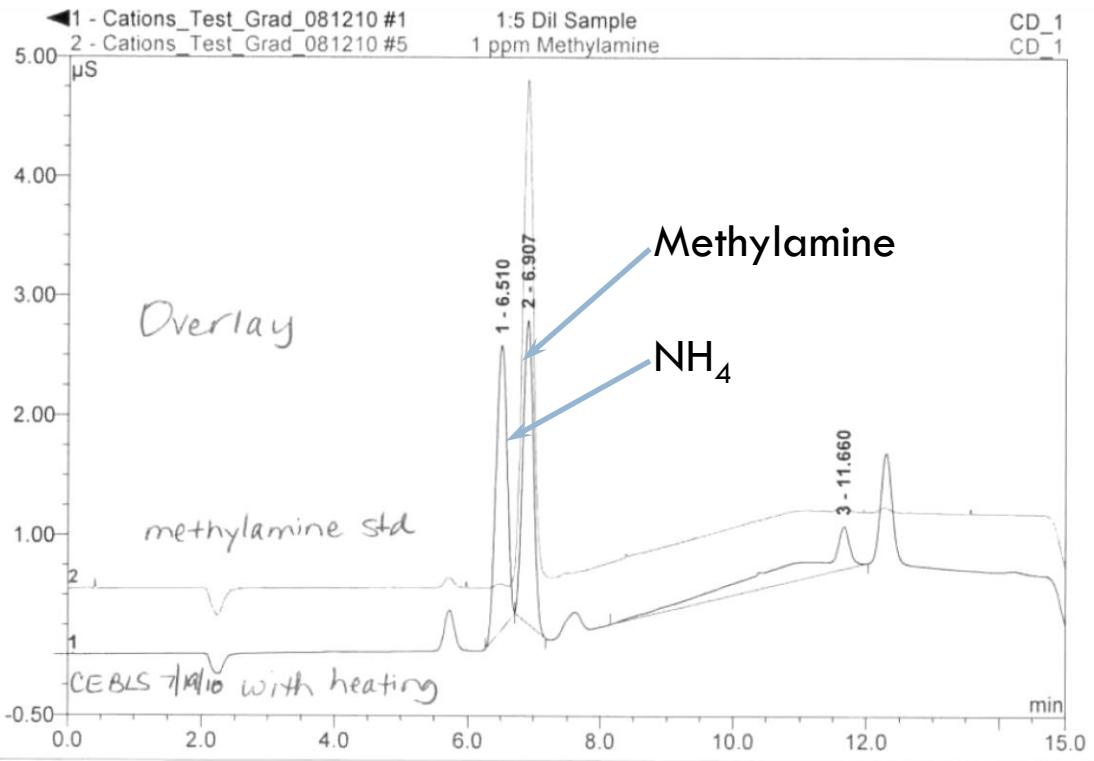


# IS THE METHYLAMINE IN THE ATMOSPHERE OR A SAMPLING ARTIFACT?

Doris Chen, Derek Day, and may others

# RTI's Startling Discovery – Methylamines on Acid Impregnated Filters



- RTI successfully separated the two peaks and the mystery peak matched the methylamine standard

No.	Ret.Time min	Peak Name	Height μS	Area μS*min	Rel.Area %	Amount ppb	Type
1	6.51	n.a.	2.370	0.456	36.00	n.a.	BMb
2	6.91	n.a.	2.533	0.469	36.98	n.a.	bMB
3	11.66	n.a.	0.355	0.343	27.02	n.a.	BMB
Total:			5.258	1.268	100.00	0.000	

# Is the Methylamine on the Filters Real?

- RTI sent samples to CSU (Doris Chen, Jeff Collet, et al.,) to try to replicate the results
- After modifying the CSU IC system they were able to replicate the RTI results
- Samples were also analyzed using the time-of-flight mass spectrometry to validate that the compound measured by IC were actually methylamine
- The methylamines on the filters are real

# Etching of Filter Cartridges by Phosphorus Acid on Filters



- Filter cartridges after repeated use with acid impregnated filters used in initial CSU field study
- Filter cartridges made from Polyoxymethylene plastic, i.e. Delrin

# Is methylamine real or a sampling artifact?

- At Rocky Mountain NP, CSU has been conducting on going sample of nitrogen species include using a URG sampler to measure NH<sub>3</sub> and NH<sub>4</sub>
  - URG uses glass denuders and has been extensively used to measure NH<sub>x</sub>
- One of the IMPROVE NH<sub>x</sub> samples that RTI found methylamines on corresponded with a URG sample
- CSU reanalyzed the ROMO URG denuder and nylasorb samples using the revised IC system and found no methylamines.

# Stainless Steel Filter Cartridges

- To test if the Delrin filter cartridges are the source of the methylamines, UCD made 8 cartridges out of stainless steel



# Is methylamine real or a sampling artifact?



- Three sets of IMPROVE samplers, 2 with Delrin and 1 with SS cartridges were deployed at Brush Colorado for 4 days

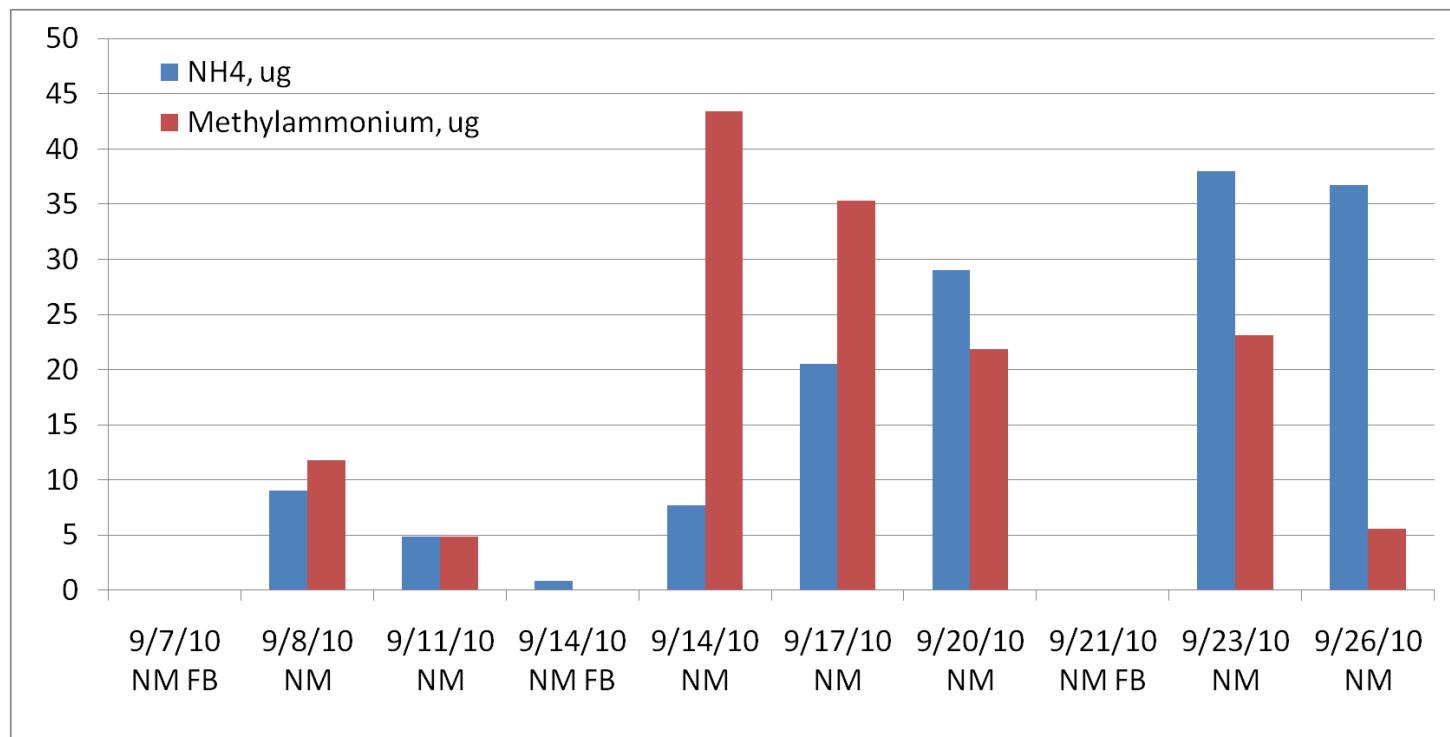
- One Delrin and SS set was immediately extracted, the second Delrin set was kept in ziploc bag with acid paper towel for 2 weeks at room temp.
- No methylamine measured on “young” extracted samples
- Methylamines measured on aged samples
  - Total nitrogen (sum of ammonium and methylamine ) was less than the NH<sub>4</sub> from the young samples (~50% left).
- Acid etching was evident on the Delrin cartridges

# Is methylamine real or a sampling artifact?

- New Delrin and stainless steel cartridges in IMPROVE samplers were deployed at Ceder Bluff, KS, 9/22/10-9/28/10
- No methylamine was measured in either set of cartridges analyzed soon after sample was collected
- To age the samples, one set was stored in zip bag with acid paper towel at under room temperature for 2 weeks
- No methylamine was found on aged samples
- NHx concentrations for young and aged samples agreed well.
- No evidence of acid etching was observed on cartridges

# However,

- Analysis of Ceder Bluff, 9/22/10-9/28/10 filters from the standard IMPROVE NH<sub>x</sub> samplers using older, acid etched Delrin cartridges and “naturally” aged during storage and shipping did show methylamines.

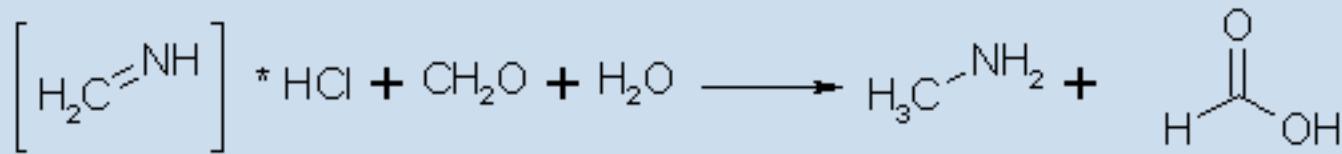
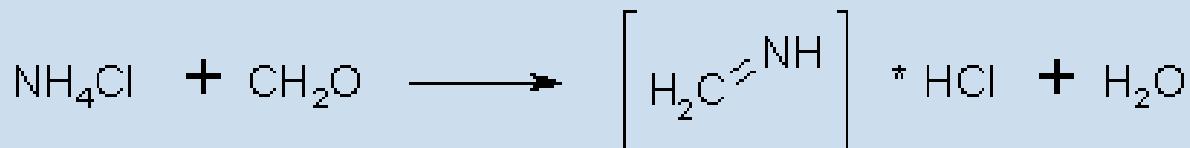


# Sampling artifact

- ❑ No evidence of methylamine in freshly collected and processed samples; even at Cedar Bluff, the site where highest methylamine concentrations were reported by RTI
- ❑ These findings support that methylamine is formed as sampling artifact during cartridge

# Possible methylamine formation pathways

From reaction of  $\text{NH}_4^+$  with formaldehyde



Formaldehyde could be formed from acid degradation of Delrin cartridges under high temperature.

# Lab experiments to reproduce methylamine

- Spike NH<sub>4</sub>Cl solution to unexposed phosphorous acid coated filters, ~500µg NH<sub>4</sub>Cl per filter;
- Loaded spiked filters to cartridges, both cartridges (2 sets) with/without evident acid etching used to compare;
- One set of cartridges were kept in oven at temp ~45°C, another set was kept under room temp ~22°C;
- Cartridges kept for 24hrs before IC analysis.

# Lab experiments to reproduce methylamine

Temperature	45°C	22°C
Cartridge conditions		
Evident acid etching	Methylamine+ $\text{NH}_4^+$ *	$\text{NH}_4^+$
NO evident acid etching	$\text{NH}_4^+$	$\text{NH}_4^+$

\* Only about 6% of N left under high temp for 24hrs in acid-etched cartridges; other conditions,  $\text{NH}_4^+$  concentrations agree with the amount spiked .

# Methylamine formation pathways

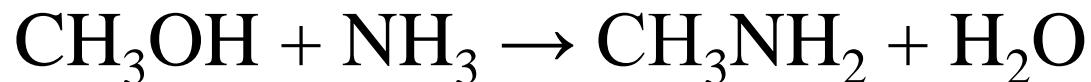
- Based on our lab experiments, most likely, methylamine is formed through reaction of  $\text{NH}_4^+$  + formaldehyde
- Temperatures and duration of filters inside cartridges determine to what extent methylamine is formed and  $\text{NH}_4^+$  depleted.

# Next Steps

- New cartridges will be made from a non reactive plastic with phosphorus acid
- Candidate plastics include
  - polycarbonate (Lexan)
  - Noryl
- UCD is making sample cartridges for testing

# Possible methylamine formation pathways

From reaction of methanol with NH<sub>3</sub> in the presence of silicoaluminate (SiO<sub>2</sub> · Al<sub>2</sub>O<sub>3</sub>) as catalyst



Acid paper towel contains methanol.