



Challenges in the Analysis of Ammonia Collected on Phosphorous Acid-Coated Cellulose Filters for the IMPROVE NH_x Study

Eva D. Hardison, David L. Hardison,
Bryte H. Goodnight, Steven Walters

Need for NH_x Monitoring

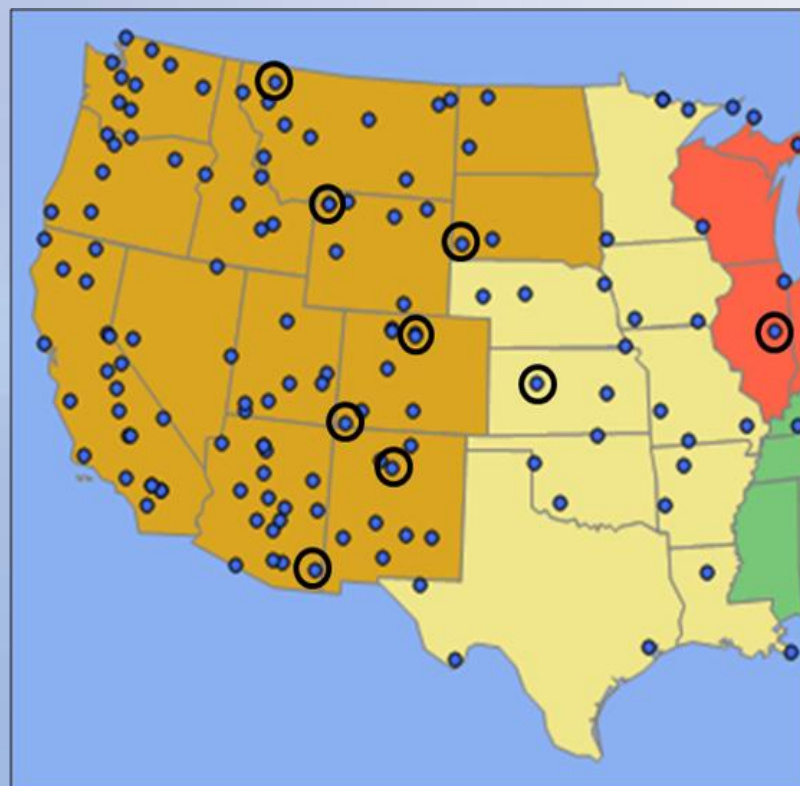
- Dry and wet deposition of NH_4^+ and dry deposition of gaseous NH_3 are important contributors to reactive N deposition throughout the U.S.
- Strong increases in deposition of these reduced N forms have been observed in recent decades, particularly in the Rocky Mountain Region.
- Current monitoring networks measure ~45% of relative reactive N species with large biases. This affects:
 - Development of critical loads
 - Source apportionment
 - Tracking trends and progress toward goals
- In addition to nitrogen deposition issues, particulate NH_4^+ is an important component of $\text{PM}_{2.5}$ aerosol at most locations in the U.S. and, consequently, an important contributor to regional haze.
- Given the role that emissions of reduced N play in particle and haze formation and N deposition, there is an urgent need to initiate efforts to measure these compounds on a routine basis.

NH_x Study Plan

- Develop an NH_x/ NH₃ measurement method that can be deployed in routine networks at sample durations from one day to a week.
- Test the methods in a controlled field test.
- Deploy the method at some IMPROVE sites.

Pilot NH_x Monitoring Study Sites

- Chiricahua, AZ
- Bandelier, NM
- Mesa Verde, CO
- Rocky Mtn, CO (collocated)
- Yellowstone, WY
- Glacier, MT
- Wind Cave, SD
- Bondville, IL (collocated)
- Cedar Bluff, KS



From: “Draft IMPROVE NH_x Study Plan “

by Jeff Collett, Doris Chen and Derek Day, CSU,
March 18, 2010; Bret Schichtel, NPS.

Site Selection

- All sites except BAND and CEBL are collocated with or located nearby CASTNet and NADP dry and wet deposition monitoring sites.
- BAND is an NADP, but not a CASTNet, site.
- BOND is a site where both NPS and LADCO special studies have previously measured gaseous NH_3 and particulate NH_4^+ .
- ROMO is collocated with ongoing measurements of gas and particle phase, reduced and oxidized nitrogen species associated with the RoMANS Study.

NHx Sample Shipment

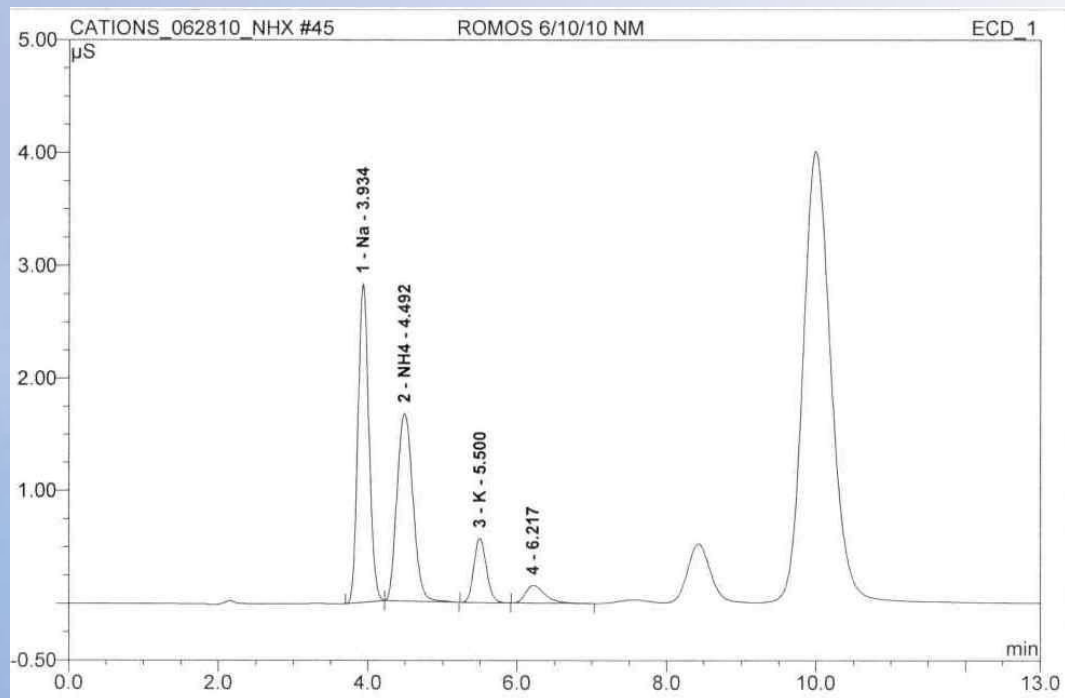


NH₃-free Glovebox



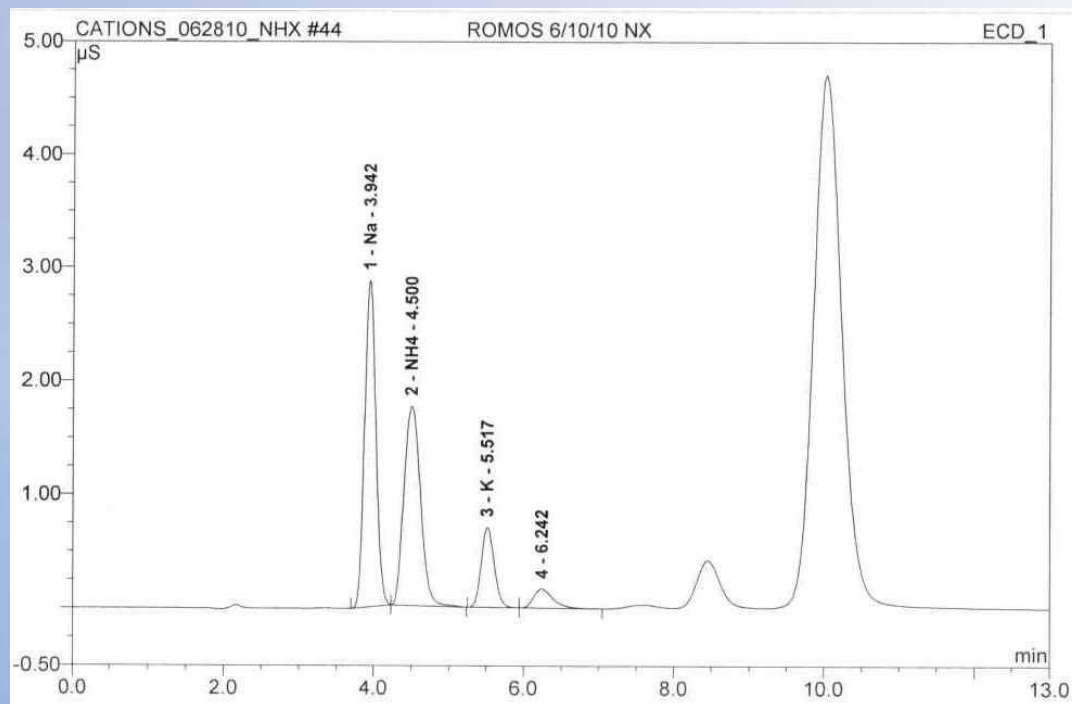
ROMOS 6/10/10 NM

- Dionex ICS-2000 Ion Chromatograph
- CS12A Cation Separator, 4-mm
- CSRS Cation Suppressor, 4-mm
- Eluent: 22 mN H₂SO₄
- Flow rate: 1 mL/min
- Sample loop size: 100 µL



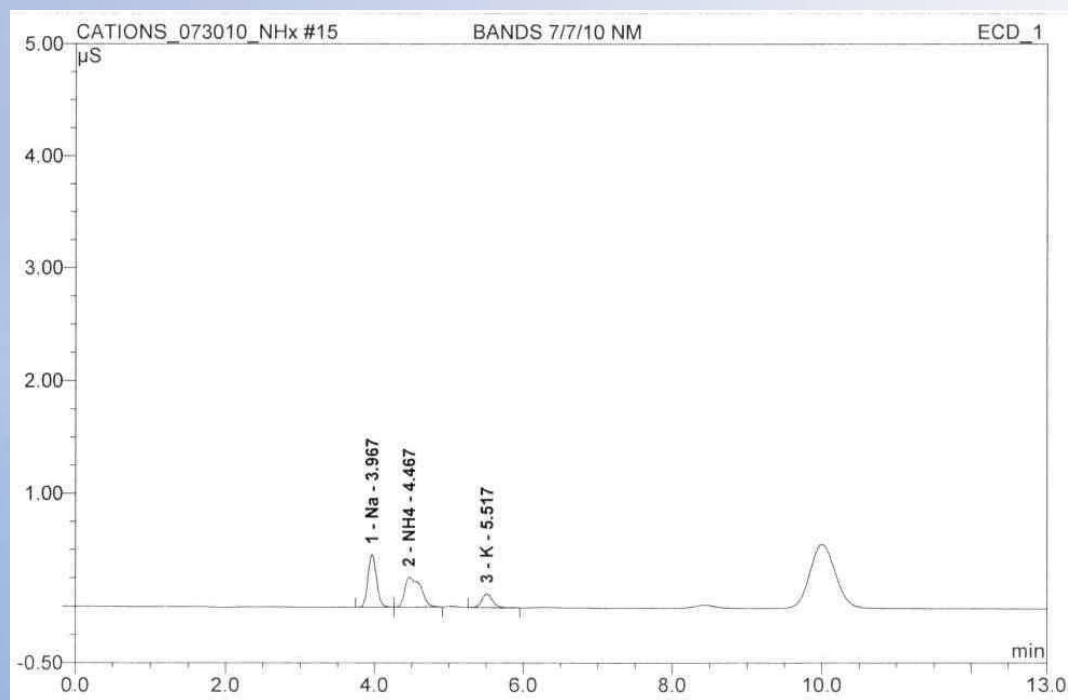
ROMOS 6/10/10 NX

- Symmetrical peaks
- Agreement between collocated samplers



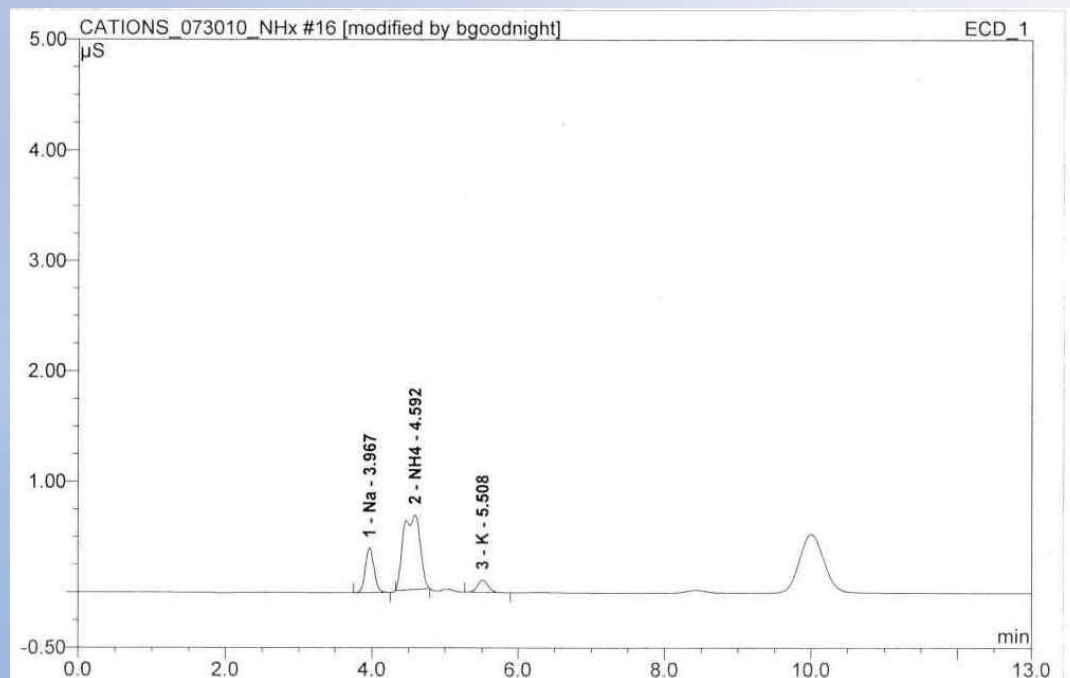
BANDS 7/7/10 NM

- Peak at ammonium ion retention time (4.47 min) is a “double peak”



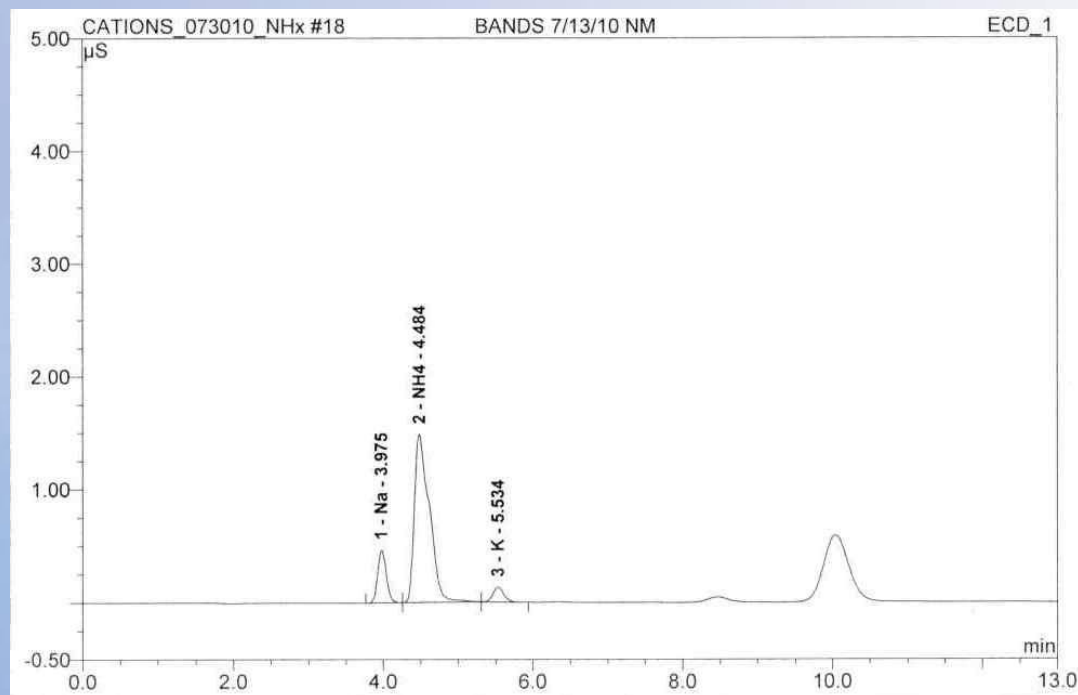
BANDS 7/10/10 NM

- Peak at ammonium ion retention time is a “double peak”
- Software chooses “second” peak (RT 4.59 min) as ammonium ion



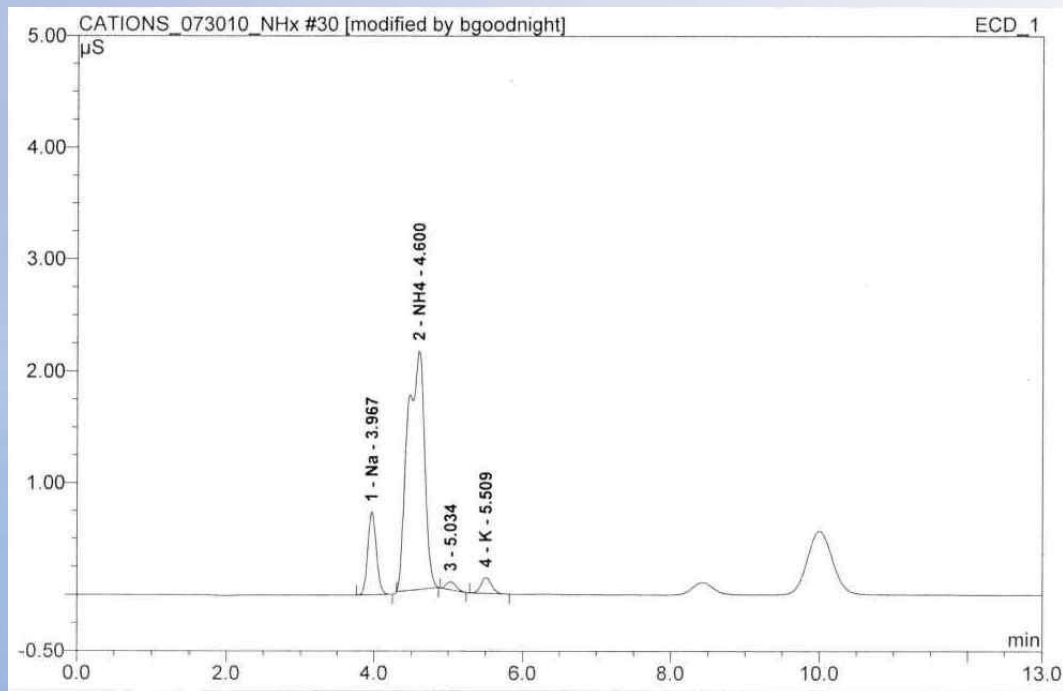
BANDS 7/13/10

- Peak at ammonium ion retention time is has a shoulder on the right



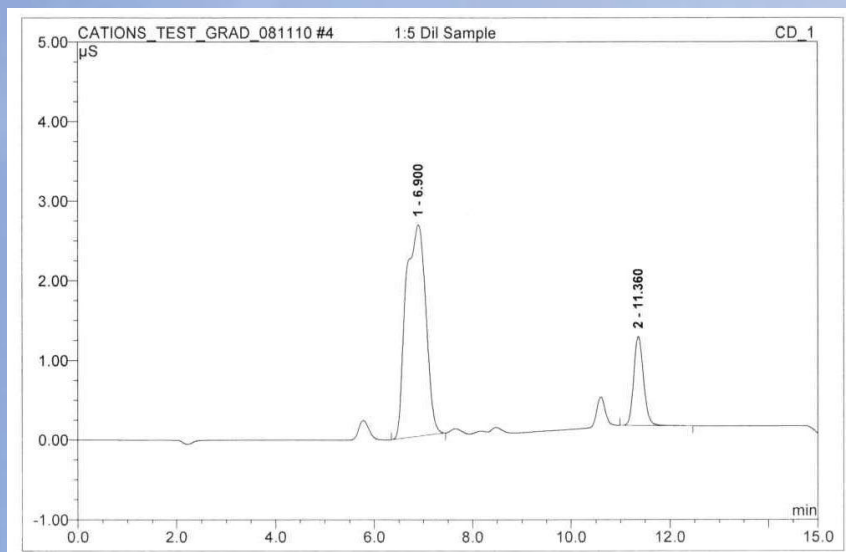
CEBLS 7/16/10 NM

- Software again chooses “second” peak (RT 4.60 min) as ammonium ion
- What is the second peak???
- Methylamine?
- Identified a Dionex method to separate the peaks on the CS12A column

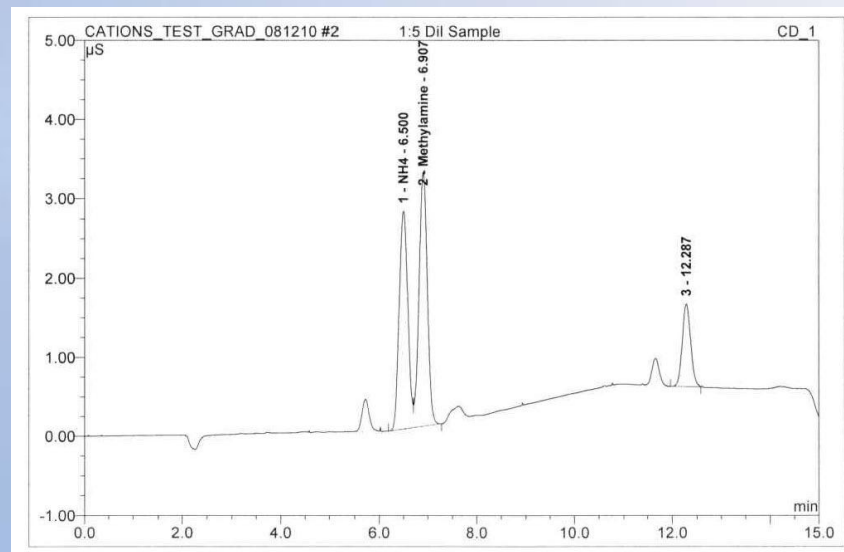


CEBSLS 7/16/10 NM

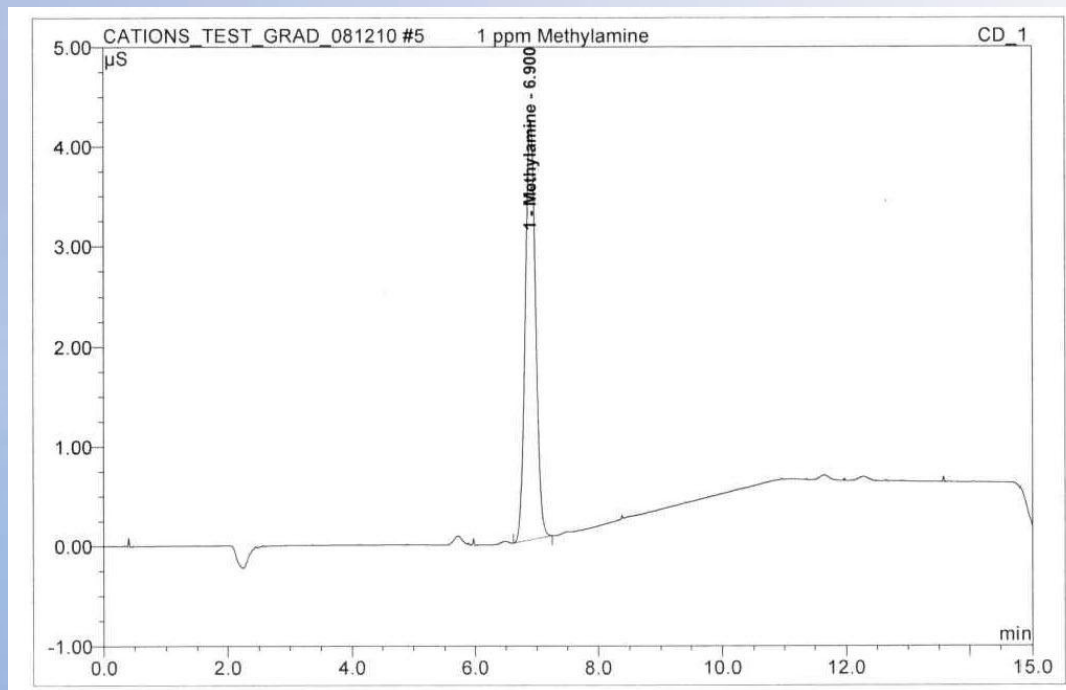
Dionex ICS-3000 IC
CS12A column, Gradient elution



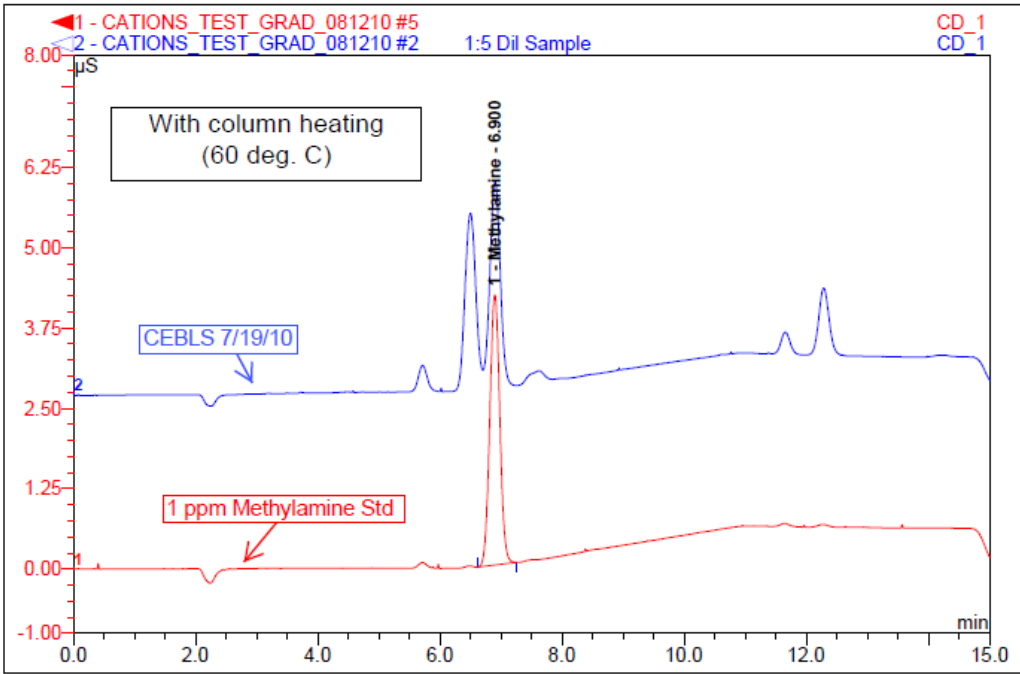
CS12A column, Gradient elution
Heated column (60°C)



1.0 ppm methylammonium (MEA⁺) standard



MEA⁺ Std/Sample Overlay



No.	Ret.Time min	Peak Name	Height μS	Area μS*min	Plates(EP)	Amount ppb	Type
1	6.90	Methylamine	4.205	0.796	8419	0.915	BMB
Total:			4.205	0.796	8419.00	0.915	

Questions/Observations

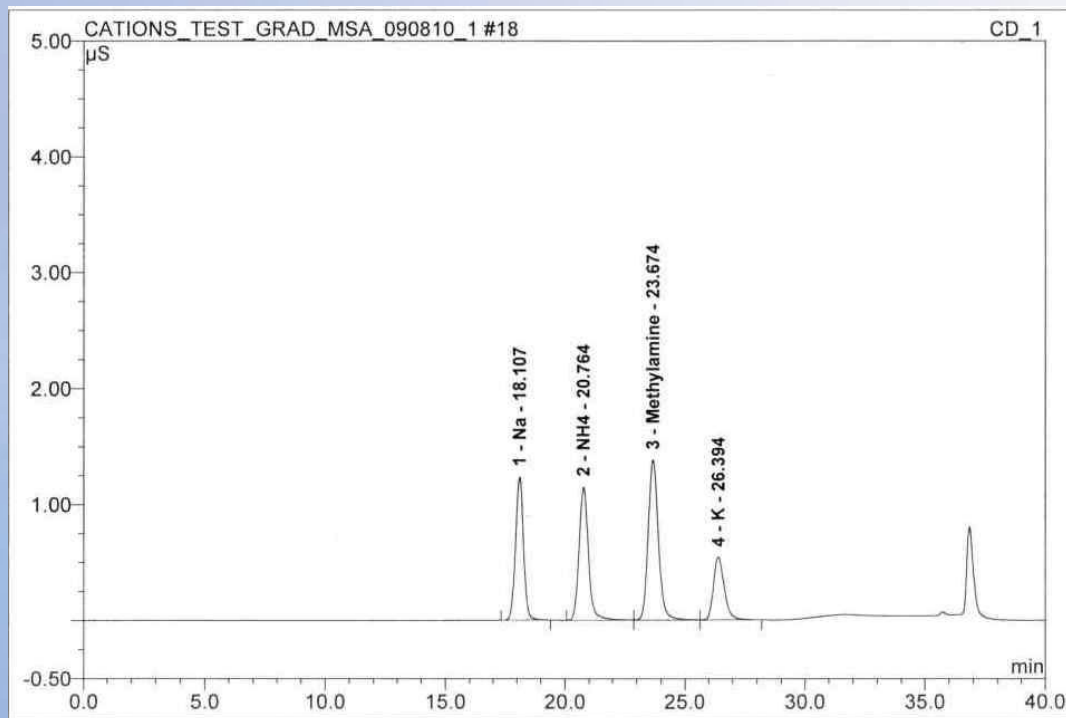
- Are we really seeing methylamine? If not, what is the unidentified peak?
- ✓ RTI confirmed that the IC retention time for an MEA+ standard on a CS12A column matches that of the unidentified peak.
- ✓ CSU confirmed the presence of methylamine in the RTI extracts by both IC (CS18 column) and electrospray time-of-flight mass spectrometry.
- CSU observed that the cellulose filters initially contain “a fair amount” of ethanolamine which is mostly removed by washing prior to use. There is sometimes a very small ethanolamine peak in the chromatograms of the sample extracts, likely from the filter.

Questions/Observations, continued

- Methylamine shows up on the coated filters and not on the nylon filters, consistent with expectation that methylamine should be present in the atmosphere mostly in the gas phase.
- RTI does not detect methylamine in the field blank filters

0.5 ppm Na⁺, NH₄⁺, K⁺
1.0 ppm MEA⁺

- Dionex ICS-3000 Ion Chromatograph
- CS18 Cation Separator, 2 mm
- CSRS-Ultra II Cation Suppressor, 2 mm
- Eluent: 0.05 methanesulfonic acid (MSA)
- Flow rate: gradient
- Sample loop size: 25 µL



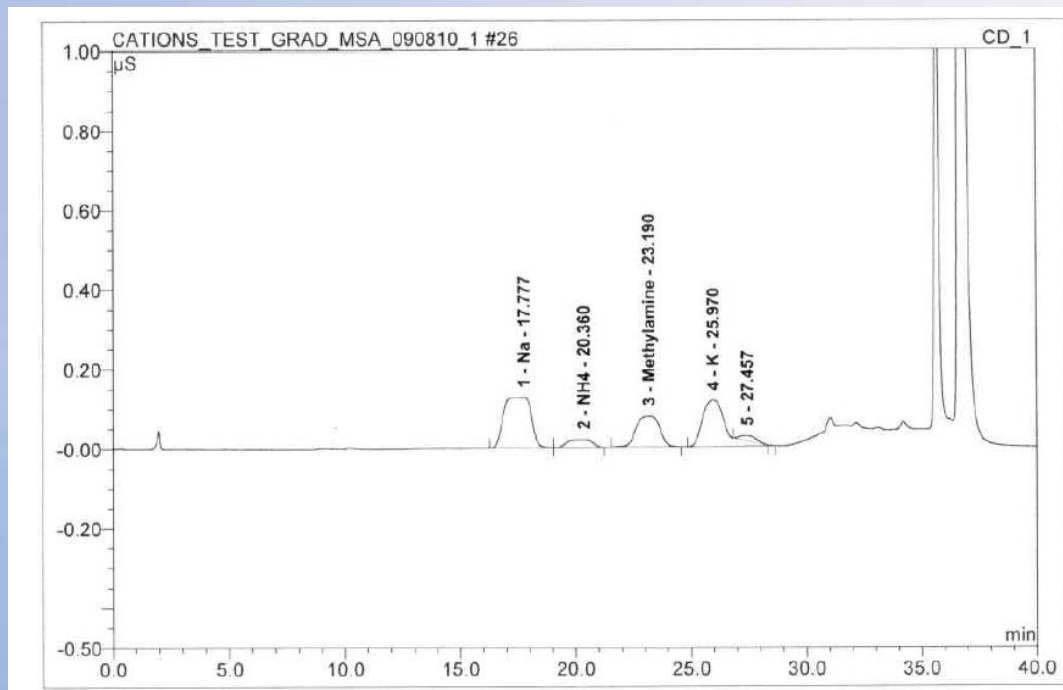
Dionex ICS-3000 – Ready for Analyses



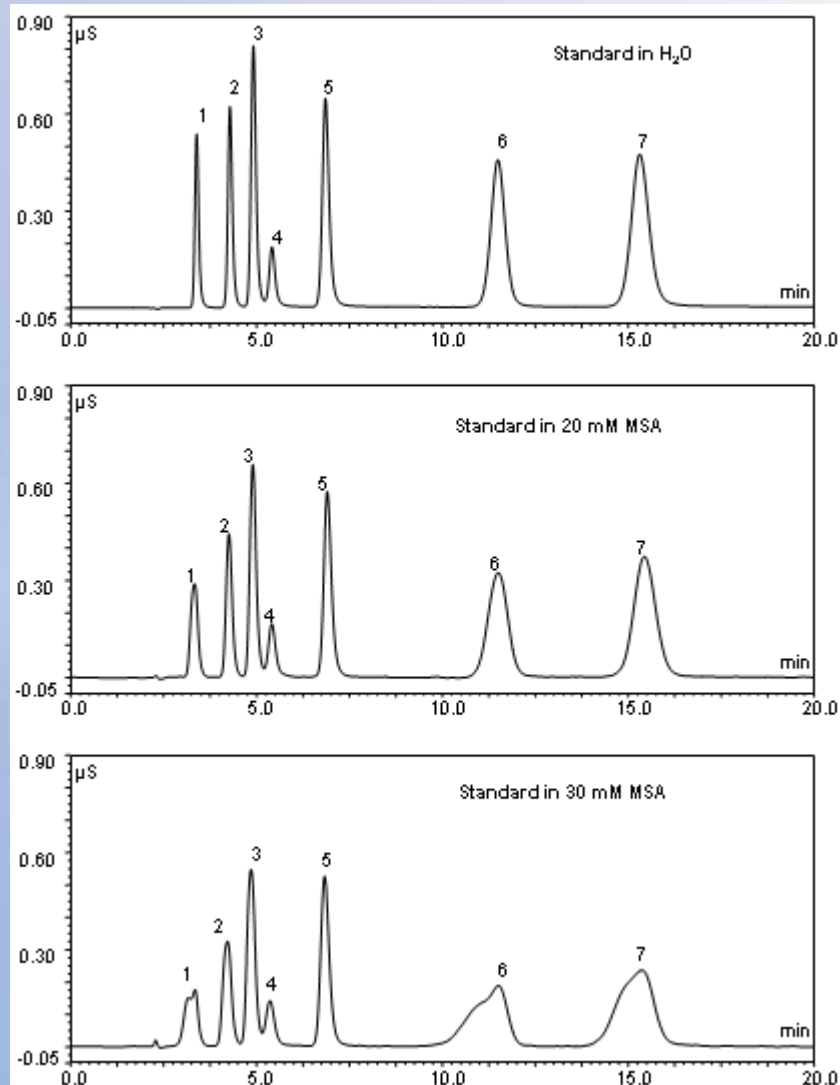
WICAS 7/1/10

10.0 mL extract, undiluted

- Yet another challenge -- peaks from undiluted extracts are asymmetrical
- Back to the Dionex literature!



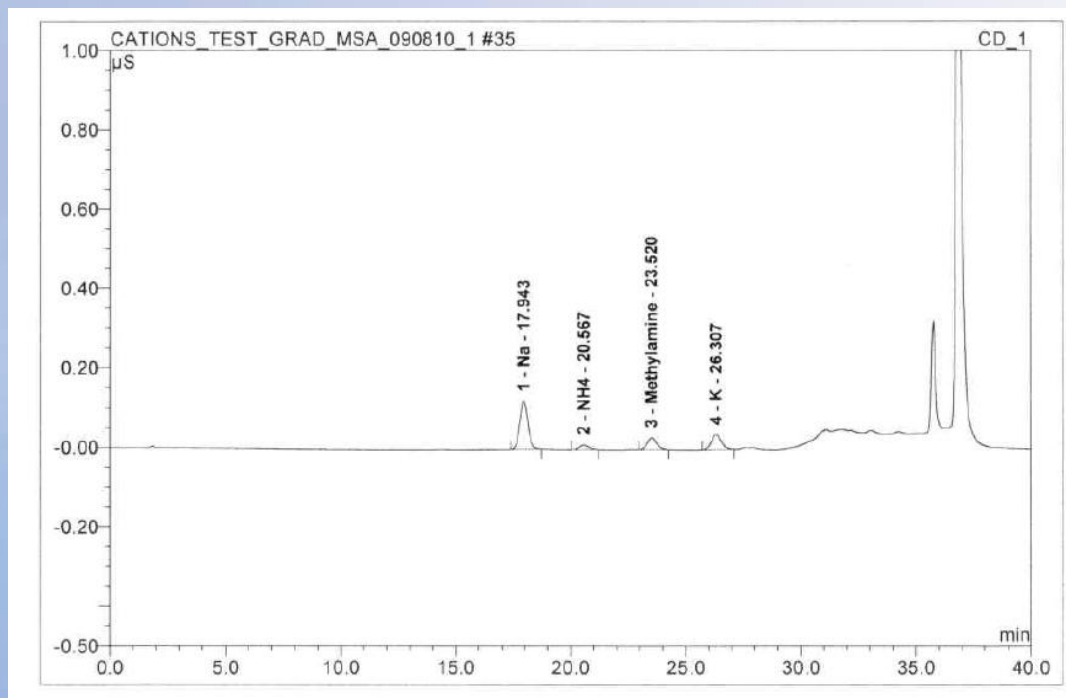
Effect of pH on Peakshape Dionex CS18 Column



WICAS 7/1/10

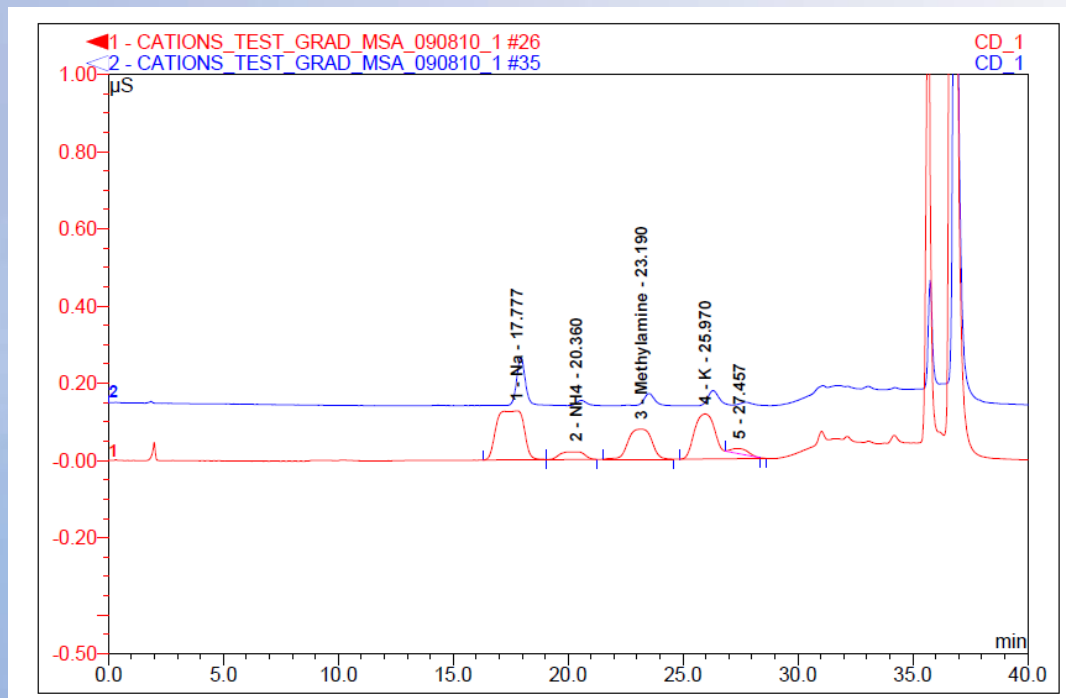
10.0 mL extract, 5-fold
dilution

- Symmetrical peaks!

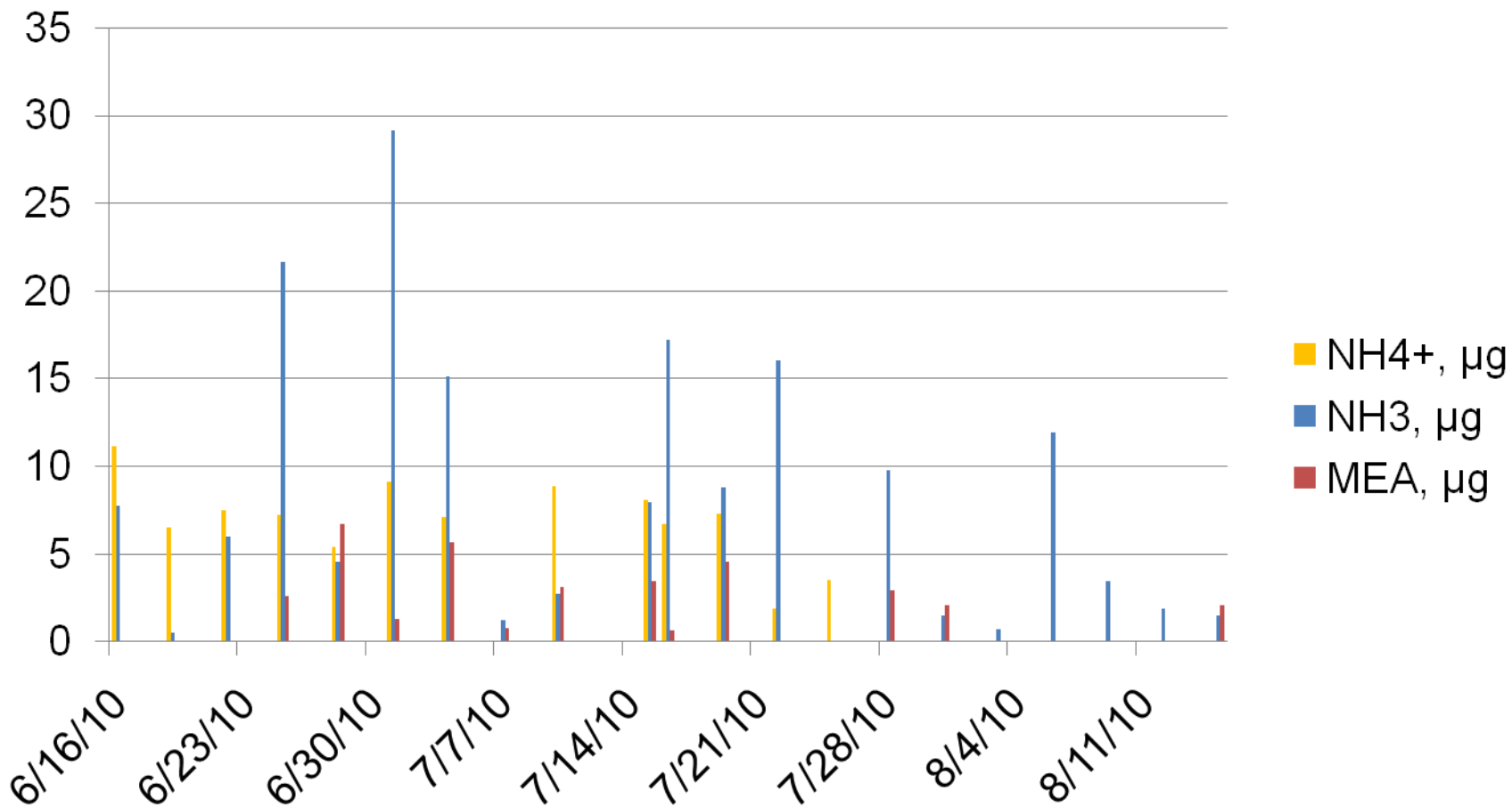


WICAS 7/1/10

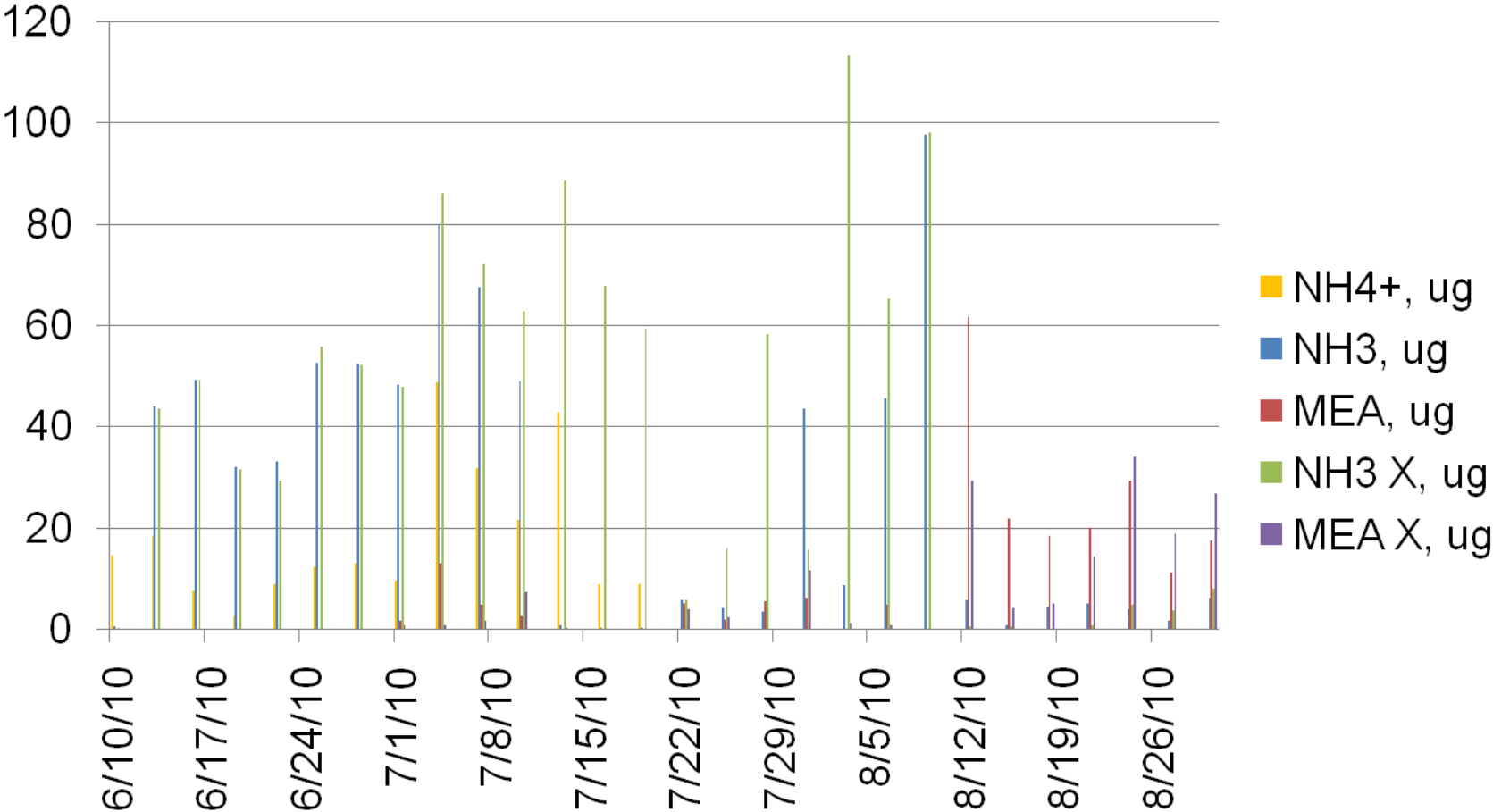
Diluted vs. undiluted



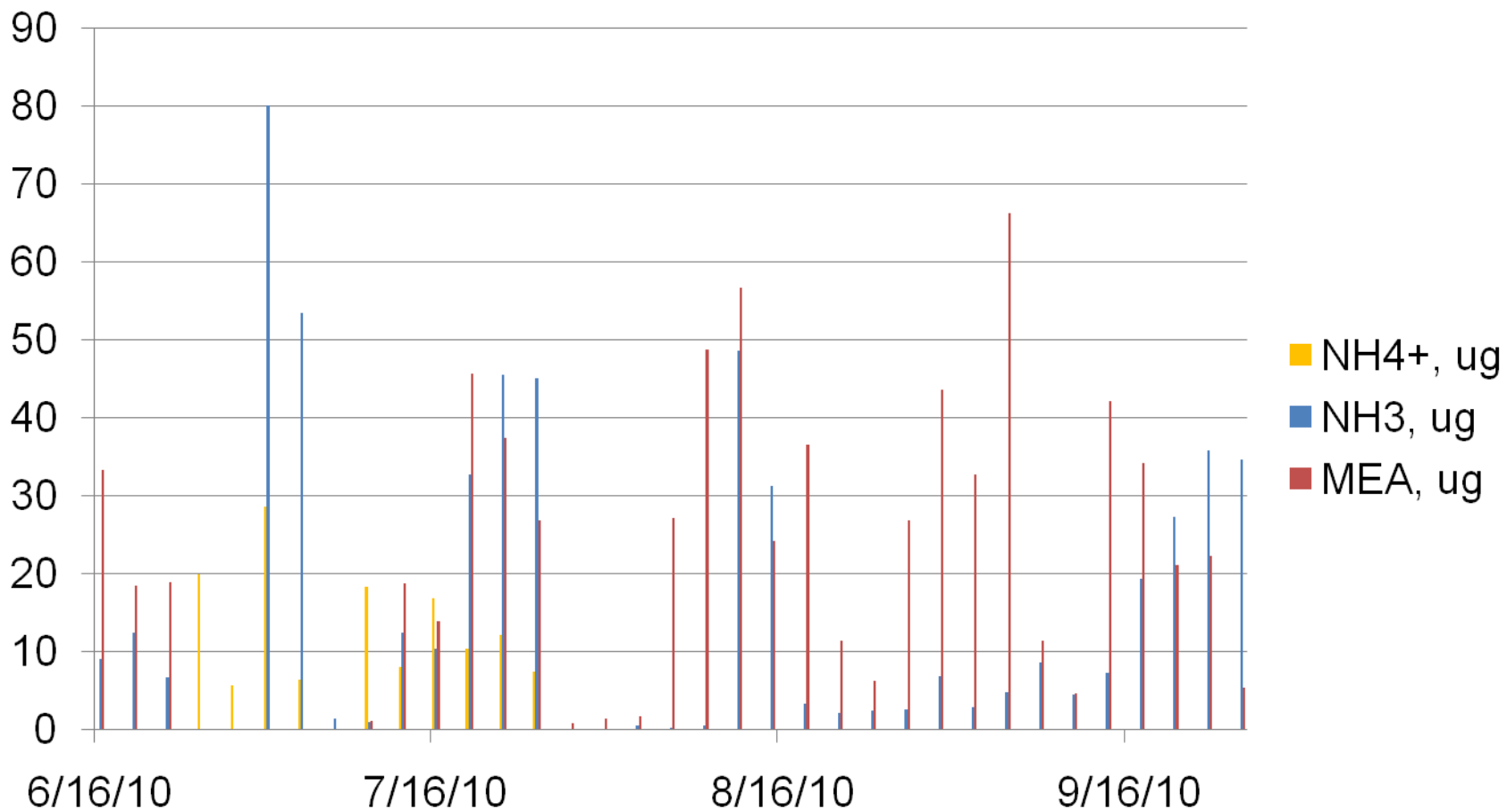
BAND



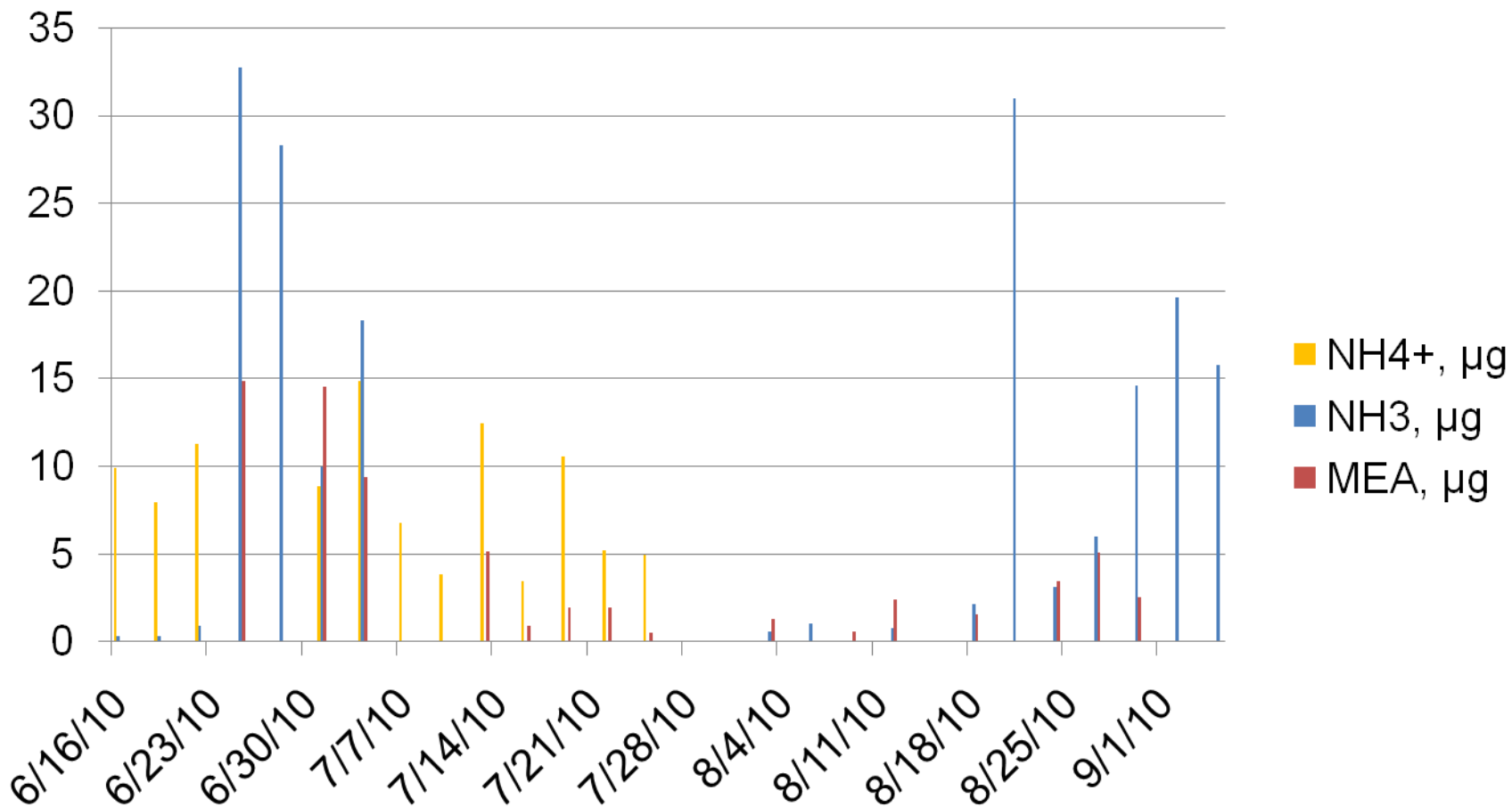
BOND



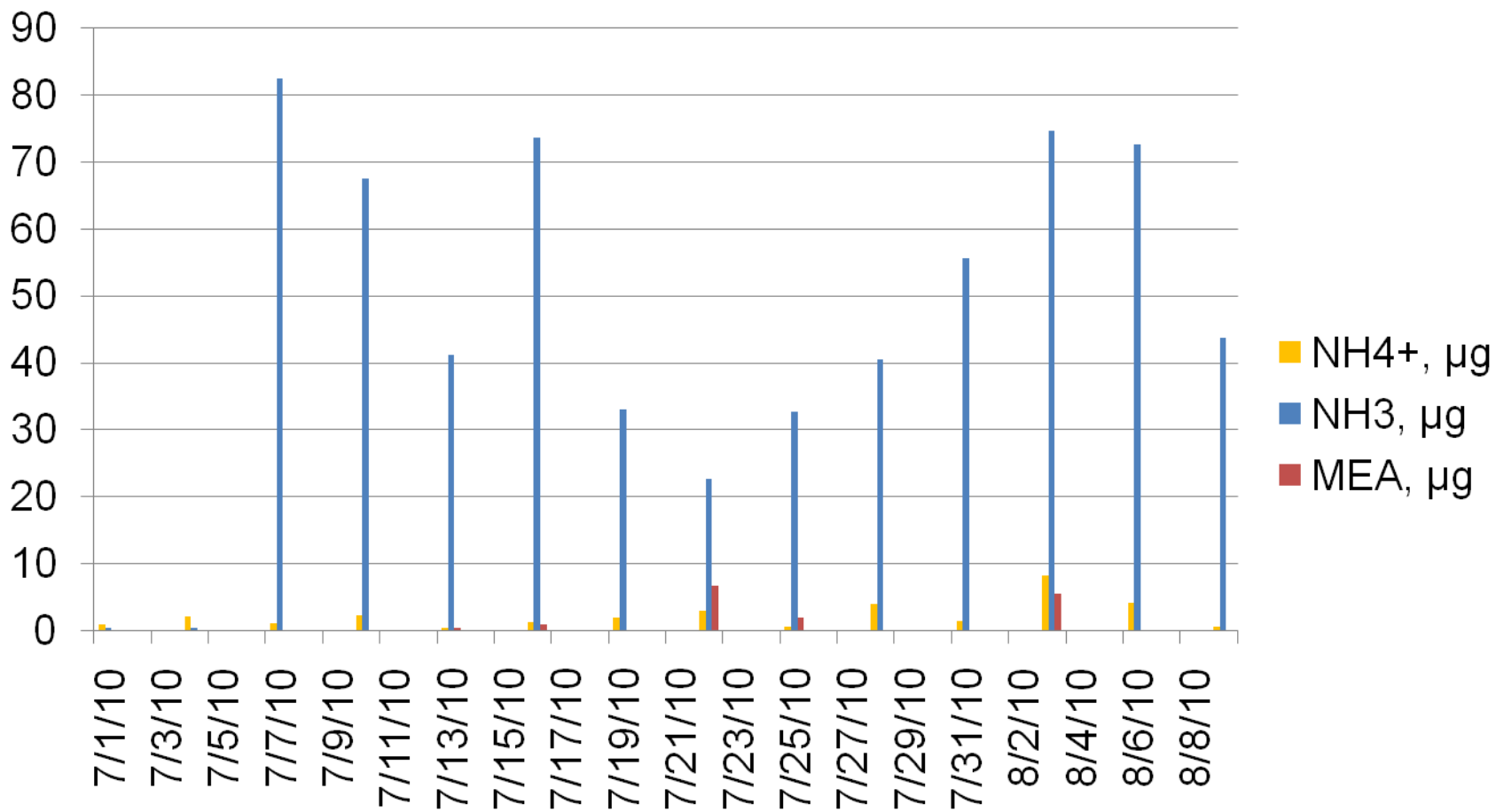
CEBL



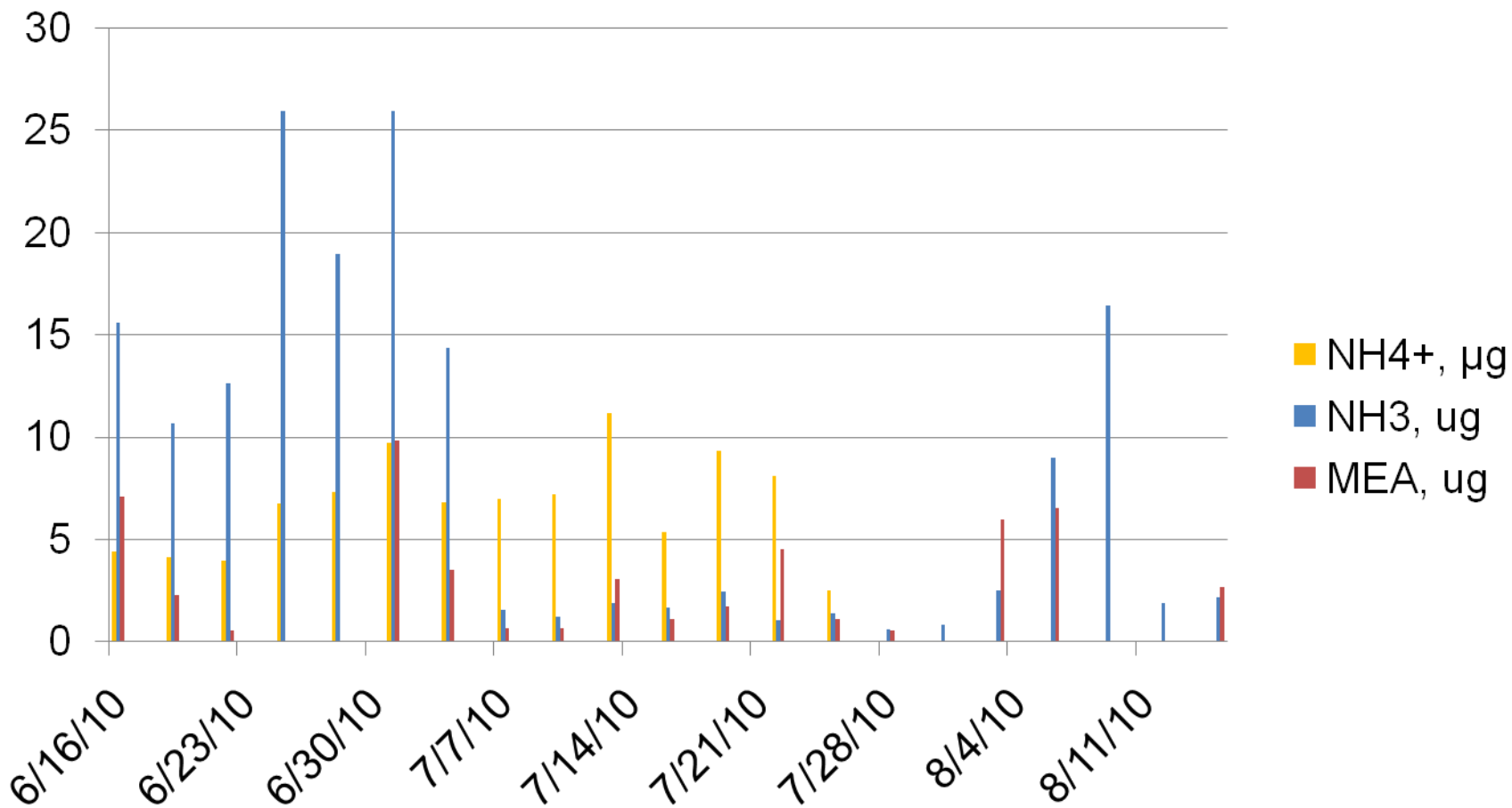
CHIR



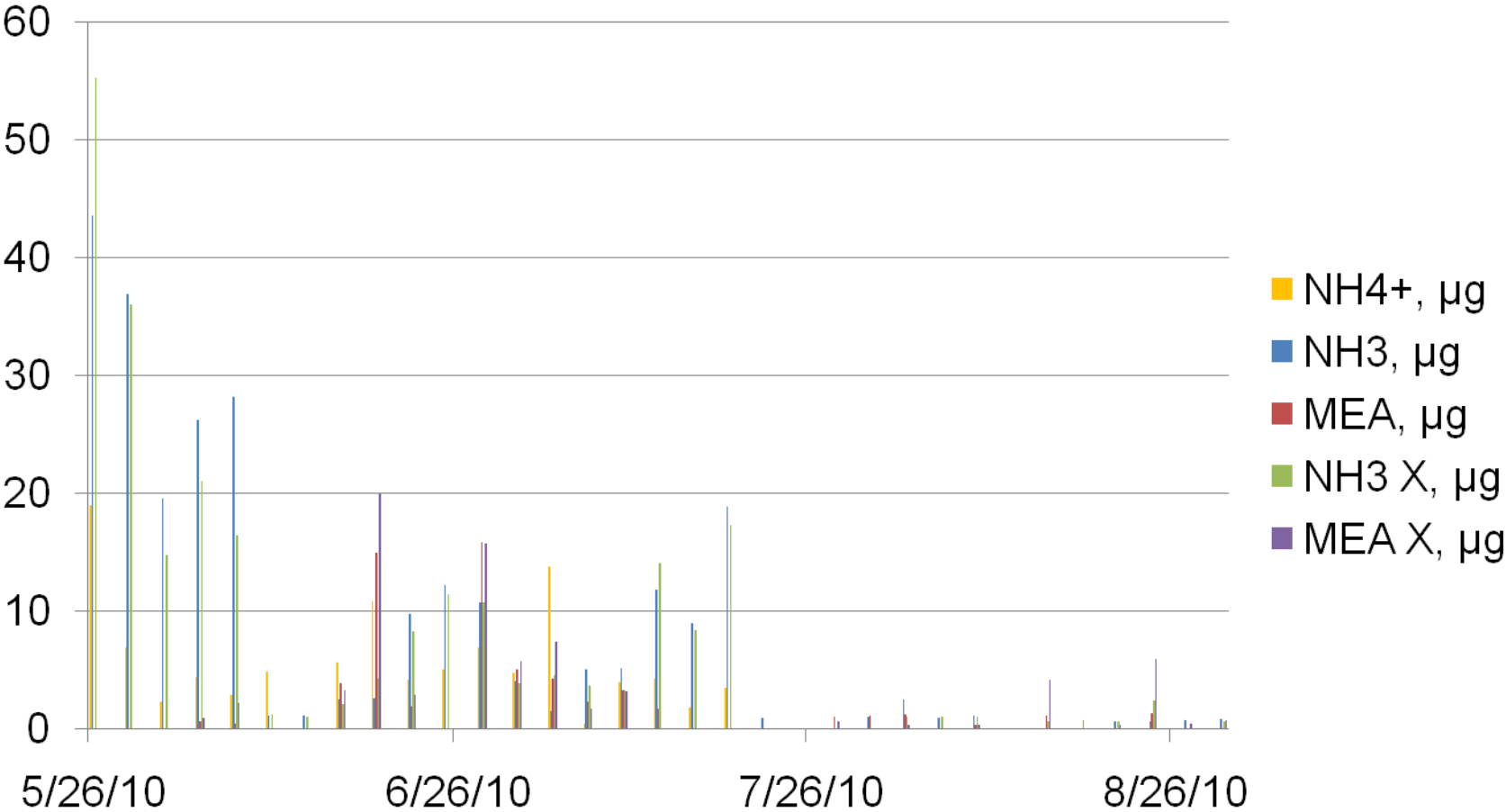
GLAC



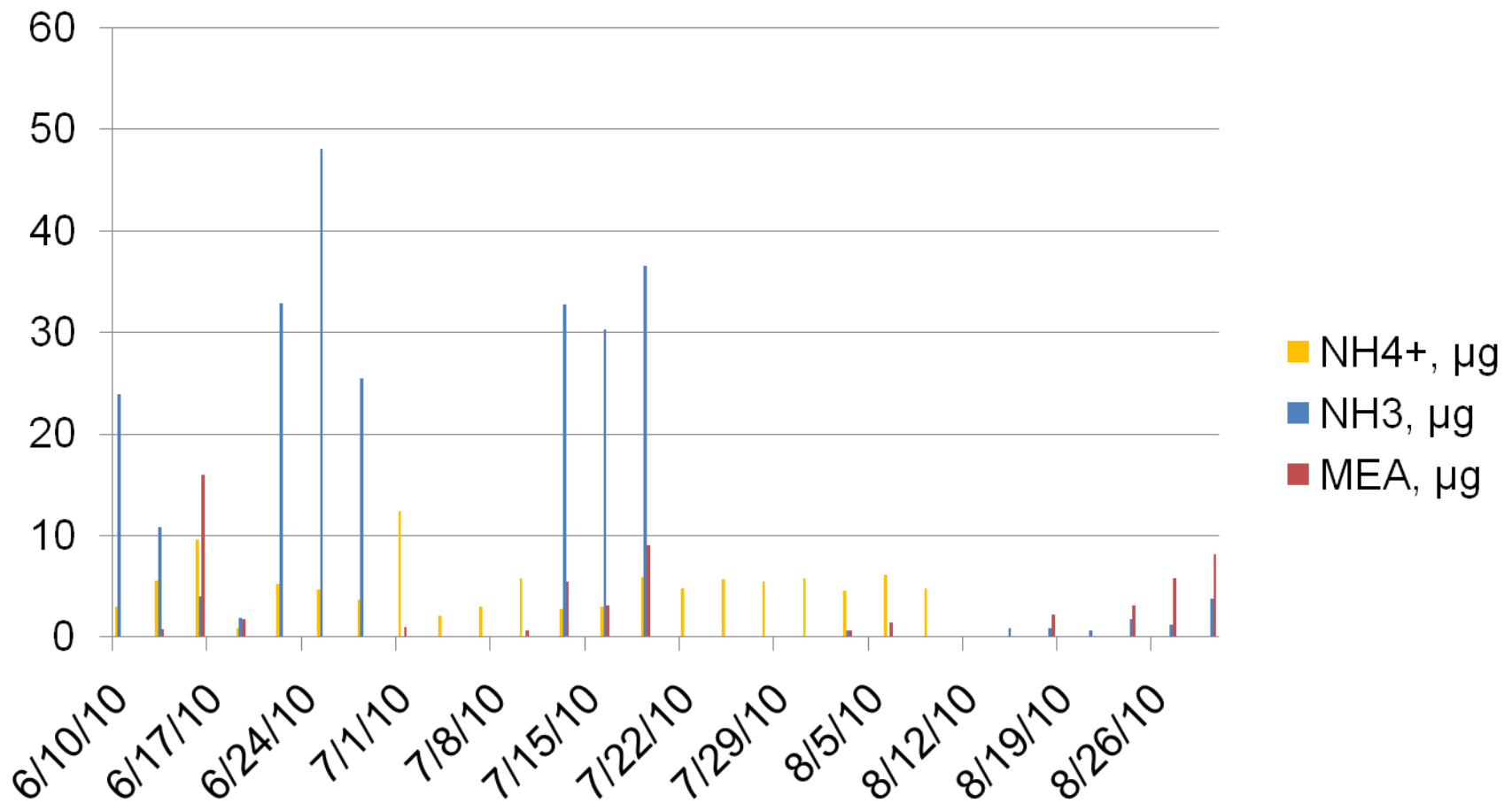
MEVE



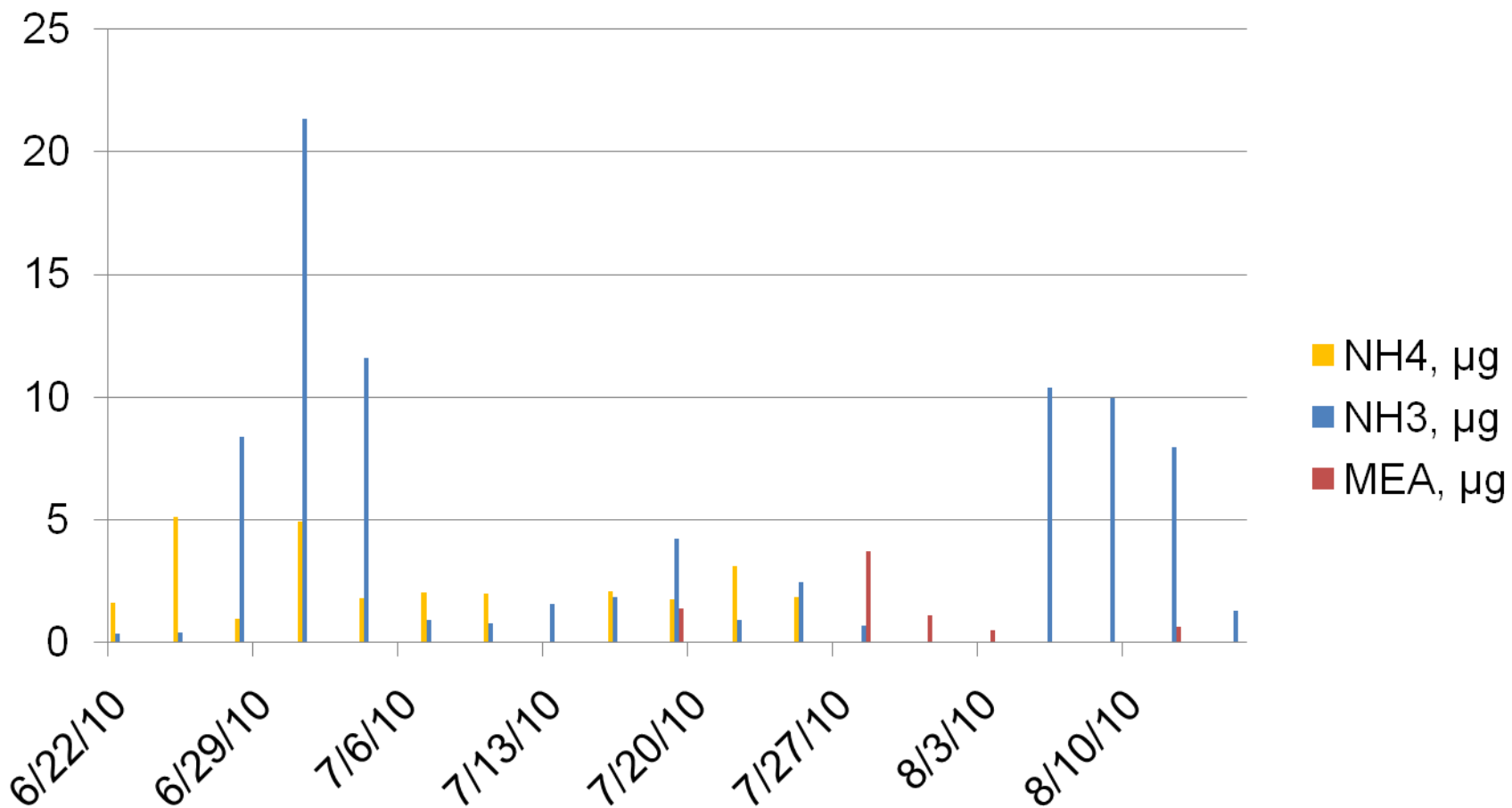
ROMO



WICA



YELL



Additional Experiments/Observations

- Is the MEA in the atmosphere, or is it an artifact of sampling/handling?
- CSU analyzed a URG sample collected in parallel at ROMO on July 7 when the IMPROVE NHx filter was found to contain MEA. Neither the URG acid-coated ammonia denuder (coated with phosphorous acid like the IMPROVE NHx filter) nor the nylasorb particle collection filter samples contained MEA.
- CSU also looked at some summertime URG denuder samples from Brush (big agricultural region in NE Colorado) with IC using the CS18 column and did not see MEA.

Additional Experiments/Observations, cont.

- CSU exposed some IMPROVE filter cartridges to a solution of phosphorous acid and NH_4^+ to see if MEA could be generated by reaction of degraded Delrin polymer with NH_4^+ in acid solution). They saw no evidence of this.
- In late September, CSU collected samples at Cedar Bluffs (CEBL) in parallel with the Delrin and new stainless steel filter holders. Analysis of these samples by IC showed no evidence of MEA for either cartridge type.
- RTI's analyses of the two regular IMPROVE NH_x samples from the same sampling period (CEBLS 9/23/10 and 9/26/10) revealed filter loadings of 22 and 5 mg MEA, respectively.

Additional Experiments/Observations, cont.

- CSU's analyses of some extra samples collected in parallel in Colorado, and stored a few weeks in Delrin holders, did reveal some MEA that was not seen in the parallel samples extracted and analyzed right away.
- CSU observed that the total nitrogen decreased in the stored samples (i.e. the sum of ammonium and MEA was less than the ammonium in the parallel sample analyzed right away).

Extract Stability (Reanalyses by RTI)

Sample ID	Analysis Date	Diluted Extract Conc, ppb		Filter loading, μg		% Diff	
		NH_4^+	MEA ⁺	NH_3	MEA	NH_3	MEA
CEBLS 7/19/10 NM	9/17/10	692	944	32.663	45.738		
CEBLS 7/19/10 NM RR	10/8/10	683	897	32.265	43.425	-1.2%	-5.1%
CEBLS 9/5/10 NM	9/21/10	102	1369	4.822	66.318		
CEBLS 9/5/10 NM RR	10/8/10	114	1360	5.358	65.880	11.1%	-0.7%
BONDS 7/28/10 NM	10/1/10	74	117	3.474	5.658		
BONDS 7/28/10 NM RR	10/8/10	73	116	3.437	5.631	-1.1%	-0.5%
BONDS 7/28/10 NX	10/1/10	1212	0	57.231	0.000		
BONDS 7/28/10 NX RR	10/8/10	1240	0	58.556	0.000	2.3%	0.0%
BONDS 7/31/10 NM	10/1/10	922	130	43.532	6.276		
BONDS 7/31/10 NM RR	10/8/10	944	131	44.565	6.358	2.4%	1.3%
BONDS 7/31/10 NX	10/1/10	336	243	15.856	11.766		
BONDS 7/31/10 NX RR	10/8/10	338	242	15.974	11.729	0.7%	-0.3%

Sample Collection/Handling Considerations

- Unexposed samples are usually loaded and shipped the same day to the sites about one week before the first cartridge is deployed in the field.
- The cartridge for the 2nd week sits for another week, and the cartridge for the 3rd week sits for another two weeks, before being deployed.
- The exposed filter in the 1st cartridge sits in the field for 2 weeks before being shipped to RTI.
- Filters that are stored for 2 or more weeks after collection become very brittle, as observed by both CSU and RTI.

CSU Experiments with Results Pending

- CSU is performing experiments to examine conditions that could result in the formation of methylamine(ie. methanol from the paper towel+ NH_x collected on the filter + some collected species that might serve as catalyst).
- CSU has collected samples and stored them under different conditions. The filters will be analyzed and results reported around the last week in October.

More Information

Eva D. Hardison

Sr. Manager

Environmental Chemistry Department

919-541-5926

eva@rti.org

David L. Hardison

Manager

Ion Analysis Section

919-541-5922

davidh@rti.org