Total Reactive Nitrogen Deposition Budgets in Rocky Mountain NP

Sunrise on Loch Vale
Thomas Mangan: http://www.thomasmangan.net/

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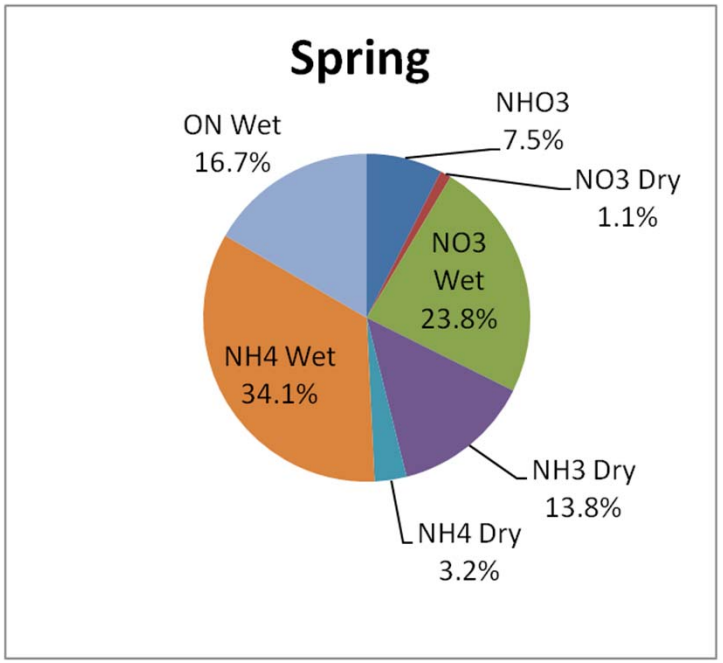
Rocky Mountain Deposition Studies

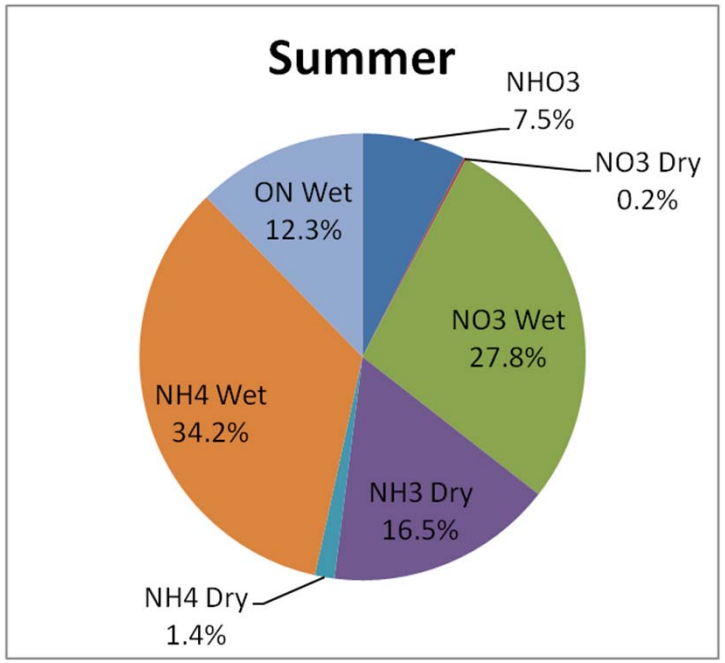
RoMANS I: 2006 – March/April (spring) and July/August (summer)
RoMANS II: November 2008-November 2009
April – September 2010

- Particle composition and gases
  - 24 hr $PM_{2.5}$ and composition
  - 15 minute $PM_{2.5}$ ions (PILS)
  - 24 hr SO_2, NH_3 and HNO_3 (URG)
  - Continuous NO_x, NO_y, NH_3, O_3, CO
  - Weekly HiVol – $PM_{2.5}$
- Wet deposition
  - Event and sub-event/hourly
  - Ion chromatography
  - Org N = TN – inorg N
- Other measurements

Co-located with IMPROVE & CASTNet monitors

ROMANS I (2006) Reactive N Deposition Budget

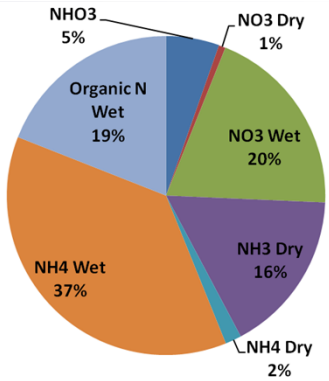


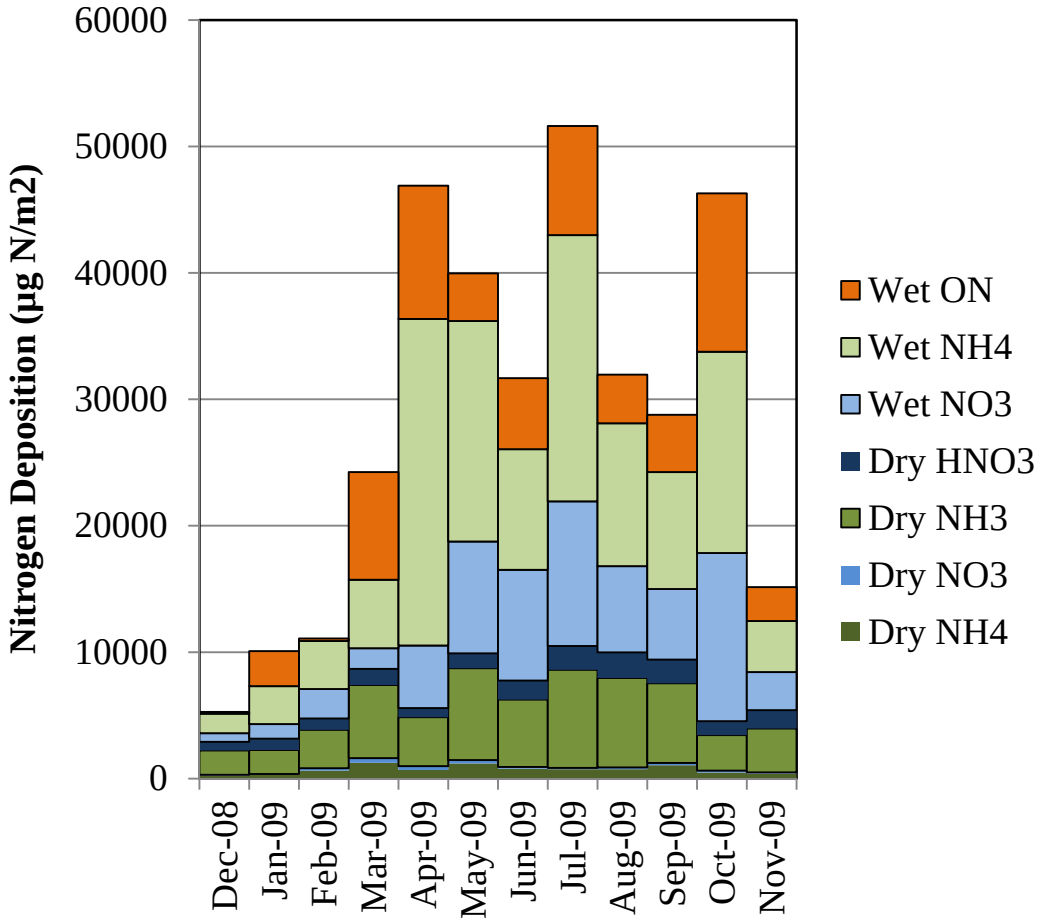


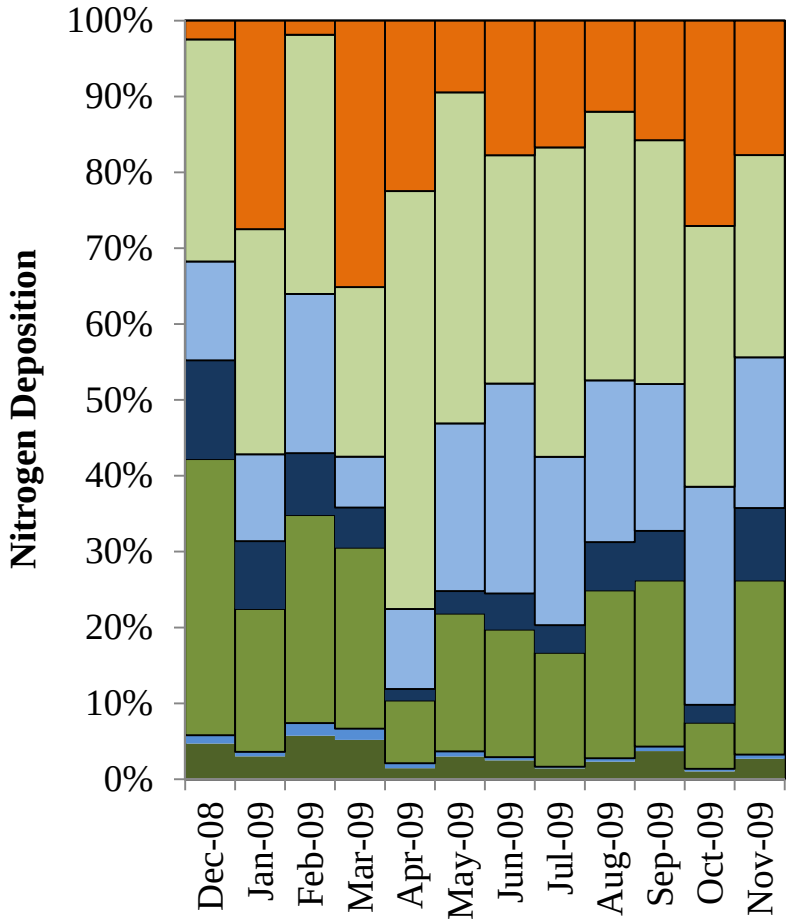
- N Deposition is ~2/3 wet (rain and snow) and 1/3 dry (particles and gases).
- ~1/2 of N deposition is due to reduced N; 1/3 oxidized; and 15% wet dep ON
- Over 30% of N deposition is not being measured in the current monitoring programs (NADP & CASTNET).
- Dry deposition of reduced and oxidized organic N is still missing

Annual N dep=3.4 kg/ha/yr

ROMANS II (2009) Reactive N Deposition Budget







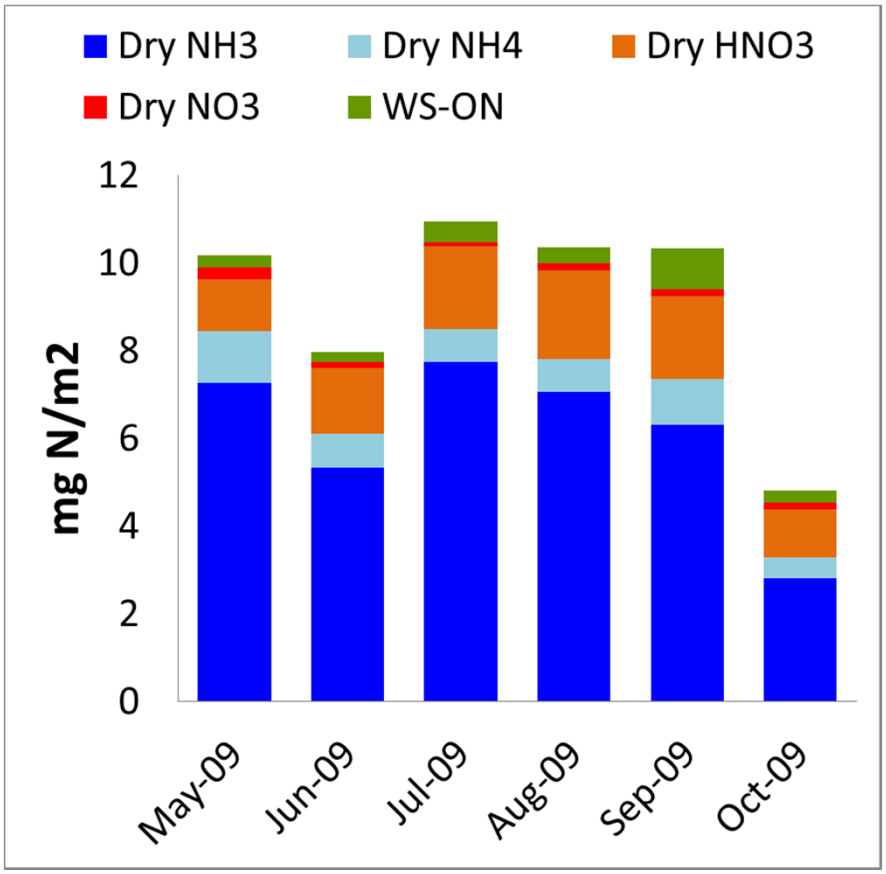
Total Water Soluble Particulate Organic nitrogen

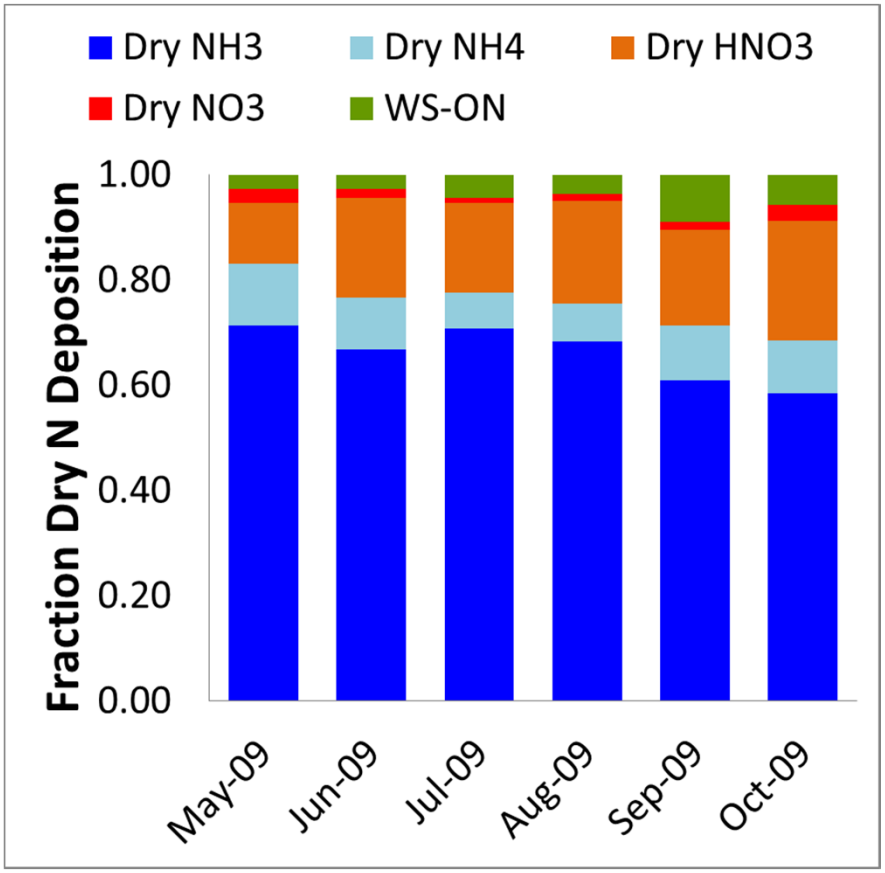
- WSON = TN – (NO_2^- + NO_3^- + NH_4^+)
- Total water soluble N
  - Shimadzu TOC V_{CSH} total organic carbon analyzer with a total nitrogen module
- NO_2^-, NO_3^-, NH_4^+
  - ion chromatography
- Individual organic nitrogen compounds
  - Liquid Chromatography with Time of Flight Mass Spectrometry using electrospray ionization

PM2.5 Hivol samplers

Benedict et al., 2011

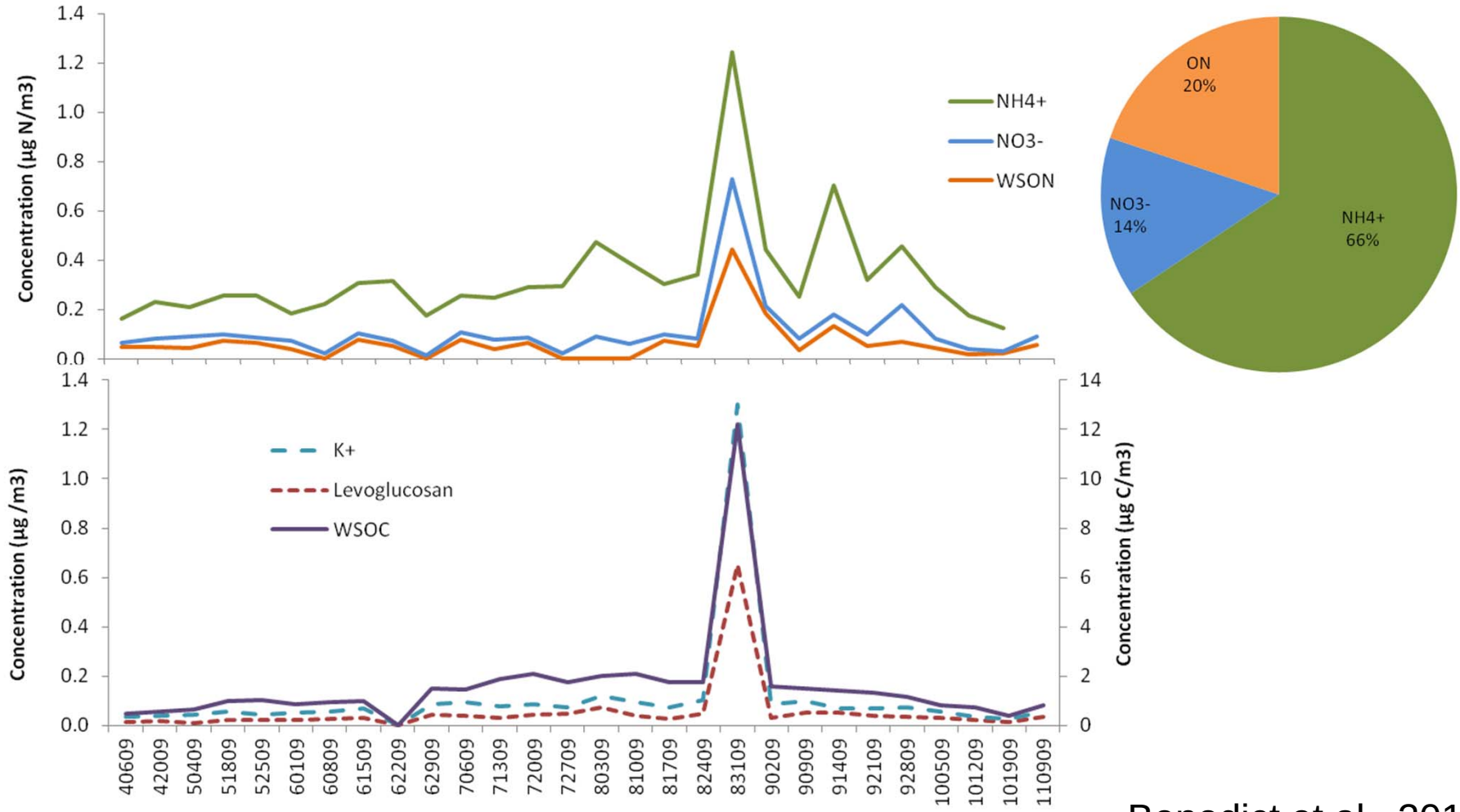
Dry Deposition
Water Soluble Particulate Organic N





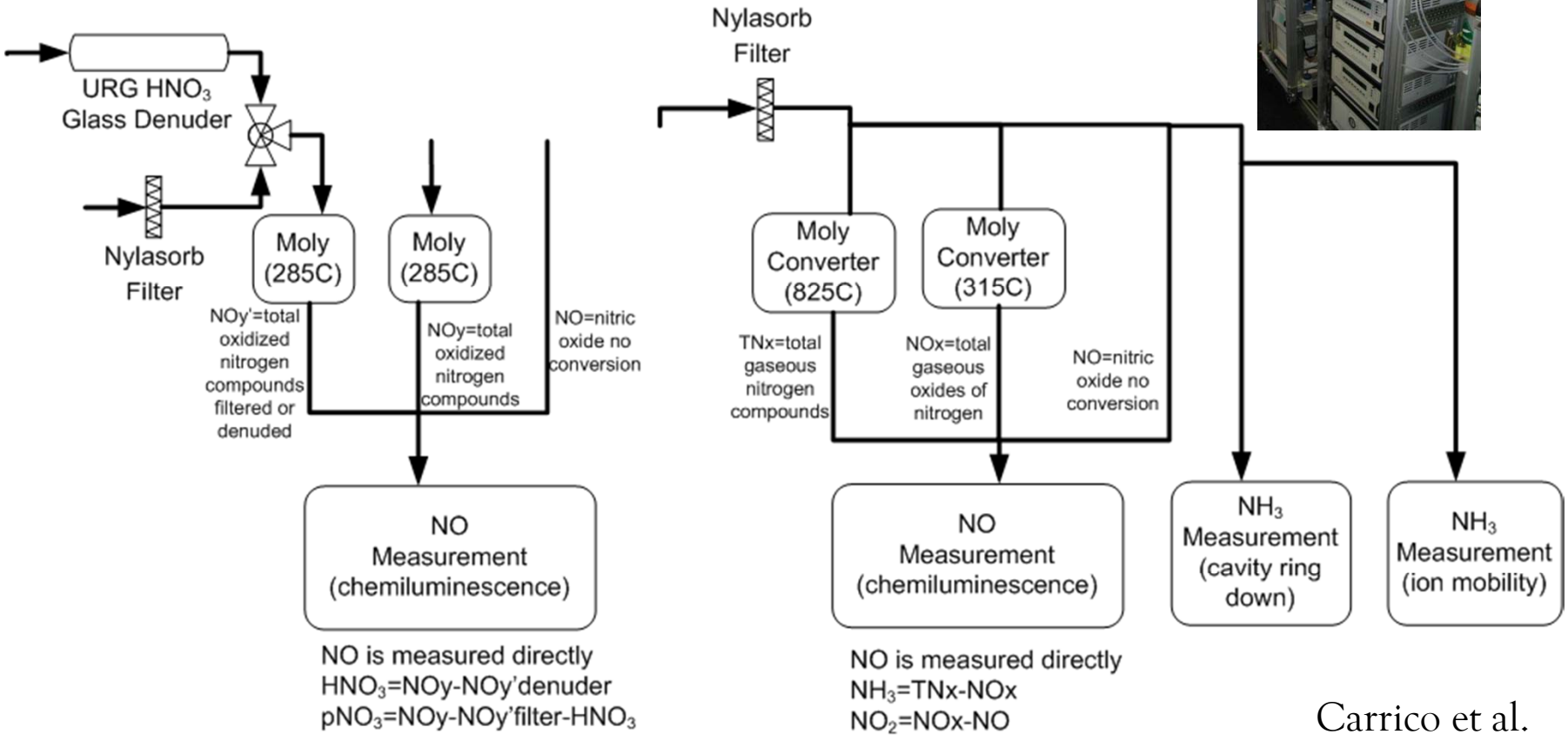
- Weekly Hi-Vol samples, April 20 – Nov 2.
- Extracted particulate sample in water and calculated total N

Total Water Soluble Particulate Organic N and Biomass Burning Markers



Benedict et al., 2011

Continuous Nitrogen Measurements



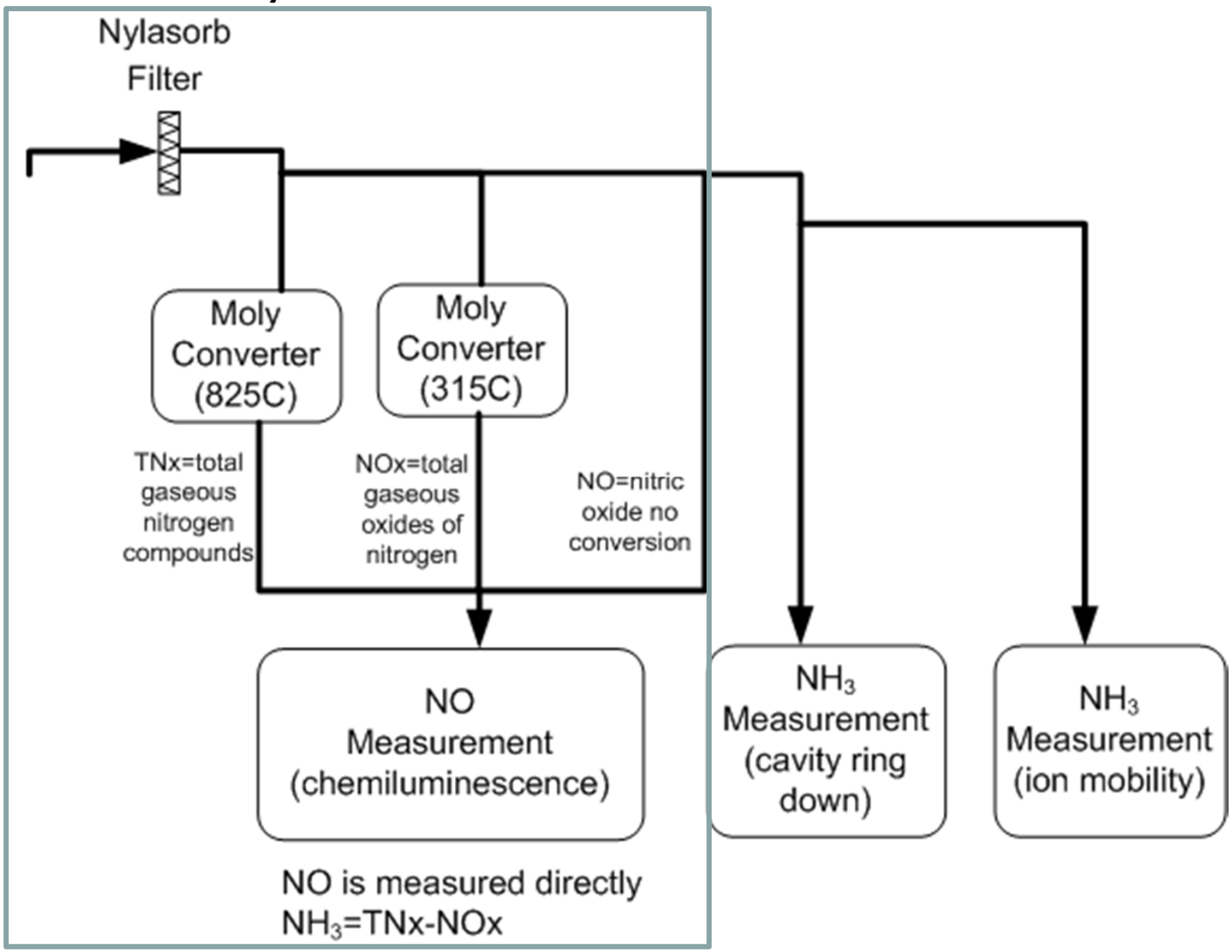
Carrico et al.

$$NO + O_3 \longrightarrow NO_2^* + O_2$$

$$NO_2^* \longrightarrow NO_2 + h\nu$$

- Combination of NOx and NOy converters, filters, denuders to speciate N compounds
- 3 independent continuous measures of NH_3

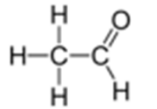
Teledyne NH3 Chemiluminescent Analyzer

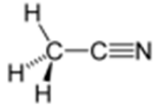


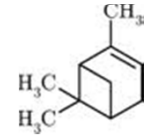
❖ NH3 = TNx – NOx, But TNx contains reduced organic and other compounds

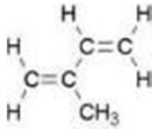
Sensitivity to non-NH_3 Gas Species

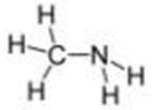
(Permeation Tube Lab Tests)





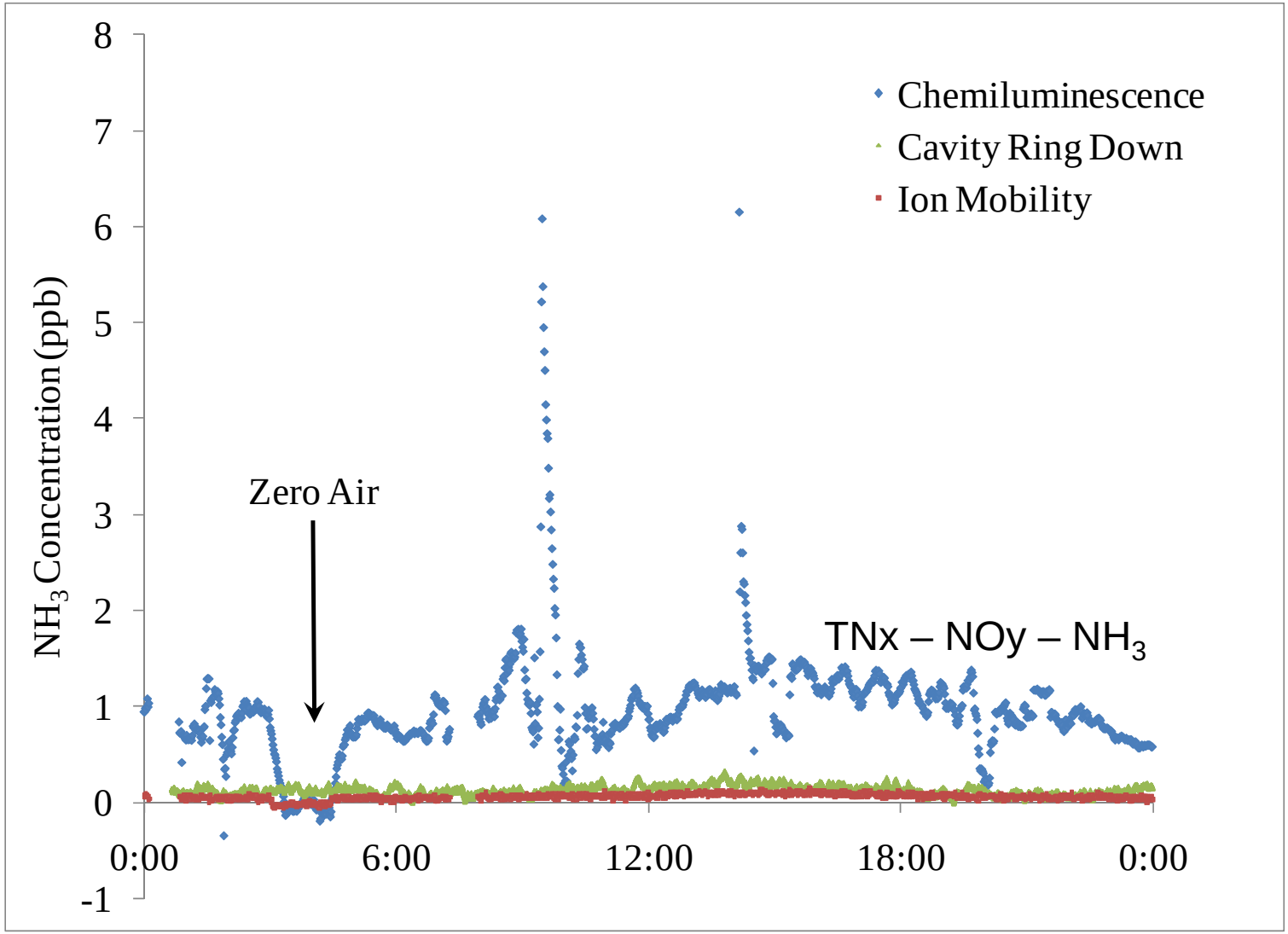






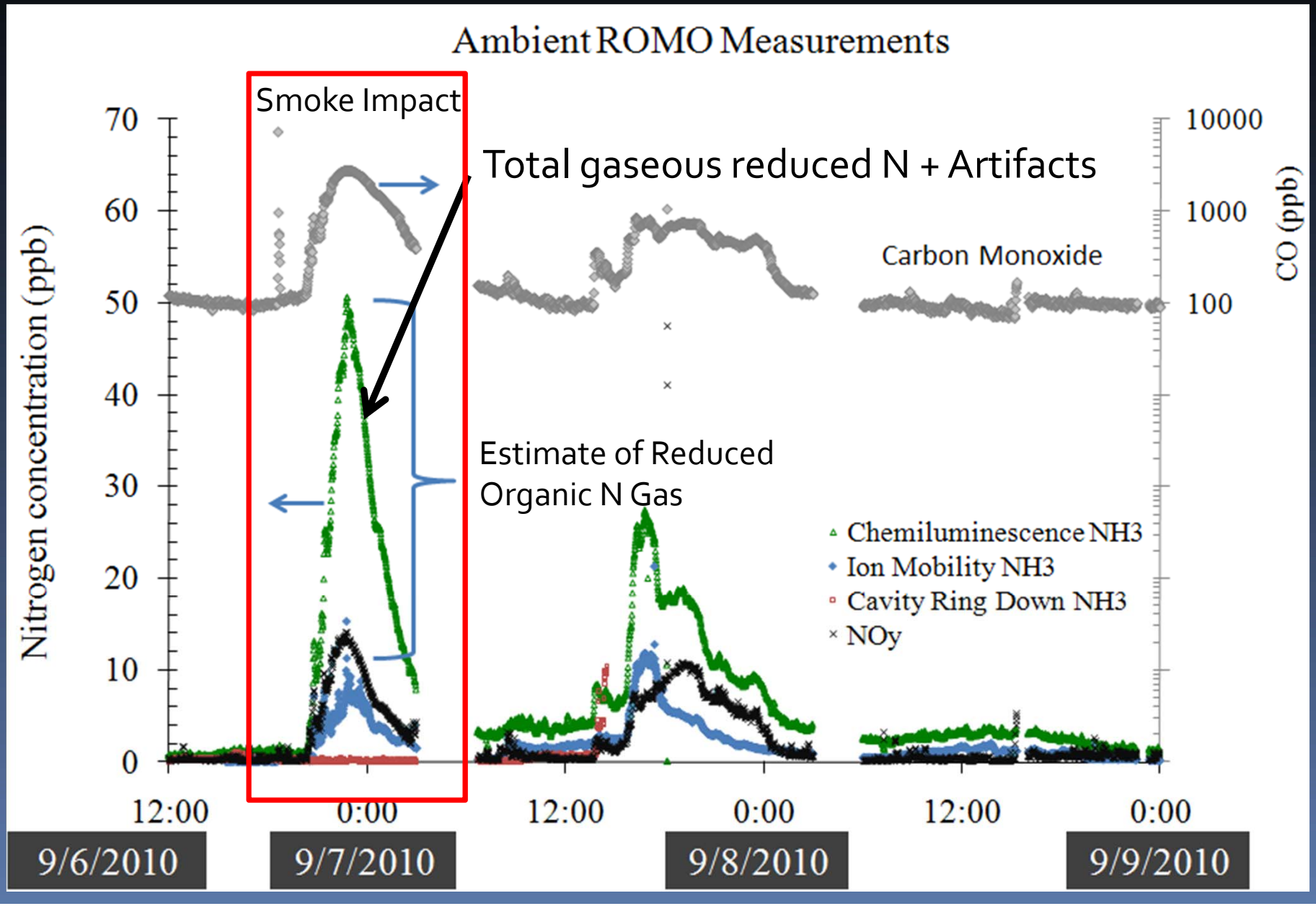
	Fractional Sensitivity of Instrument*			
	Importance	Chemiluminescence	Ion Mobility	Cavity Ring Down
Acetaldehyde	Biogenic Chemiluminescent Compound [Marley and	0.4%	0.1%	-0.1%
Acetonitrile 1	Biomass Burning Emissions	77.6%	0.2%	1.1%
Acetonitrile 2	[Yokelson et al., 2009]	63.1%	0.0%	-0.2%
Alpha-Pinene	Biogenic Emissions (Coniferous)	0.9%	0.0%	-0.1%
Isoprene	Biogenic Emissions (Deciduous)	3.5%	0.2%	0.9%
Methylamine 1	Primary Amine	69.2%	77.0%	5.5%
Methylamine 2	Ammonia-like, Particle and Gas phase	74.2%	84.8%	3.2%
Methylamine 3	[Ge et al., 2011]	86.8%	84.9%	5.6%
*using a 67 ppb input concentration generated with a permeation tube				
Sensitivity:	**Negligible**	**Slight**	**High**	

Ambient Urban Air with NH_3Denuder In-line

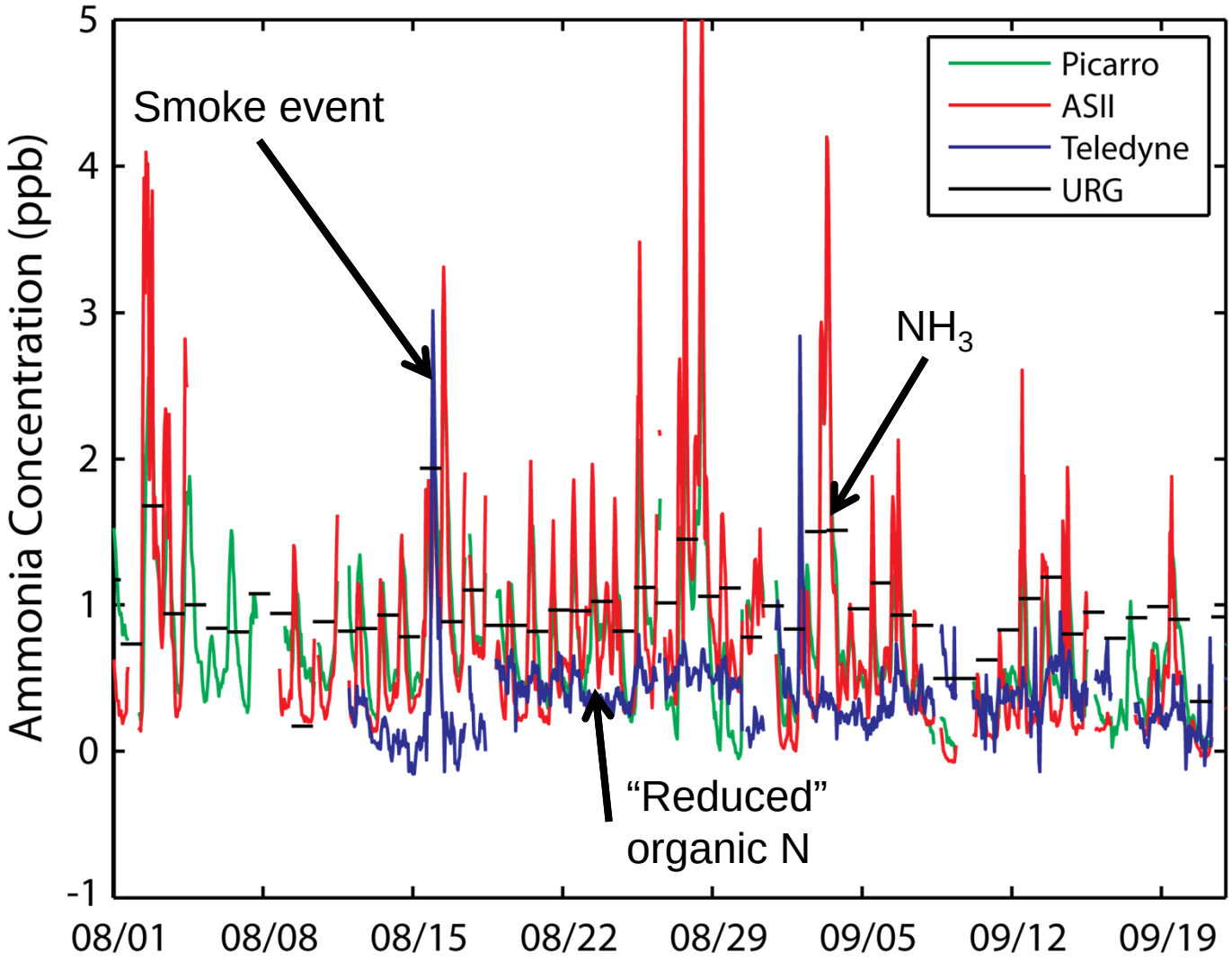


❖Chemiluminescence clearly has some non-NH_3 interferences

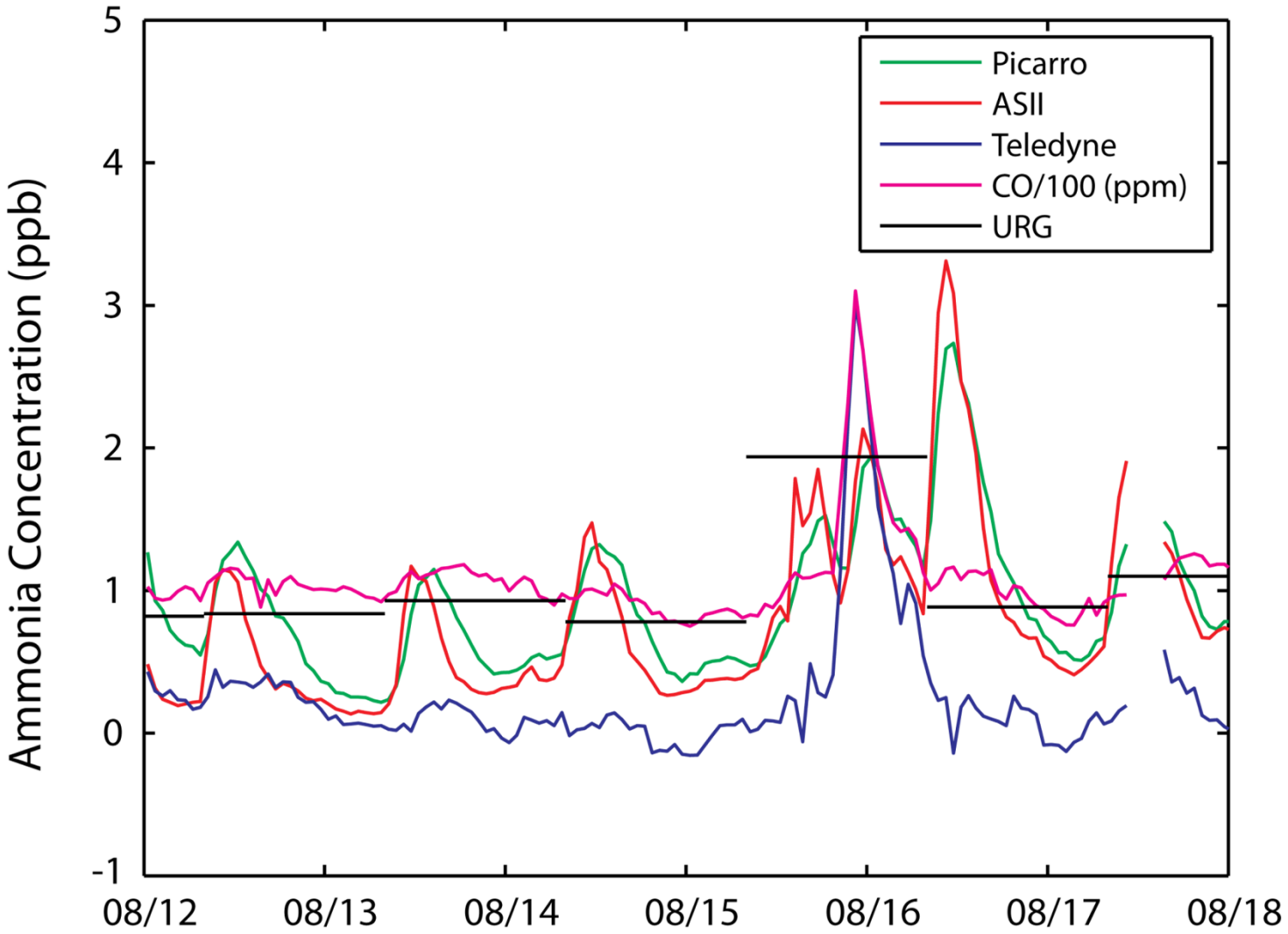
Boulder, CO Smoke Impacts



Ammonia Concentration (1 hr avg)



Ammonia + CO (1 hr avg)

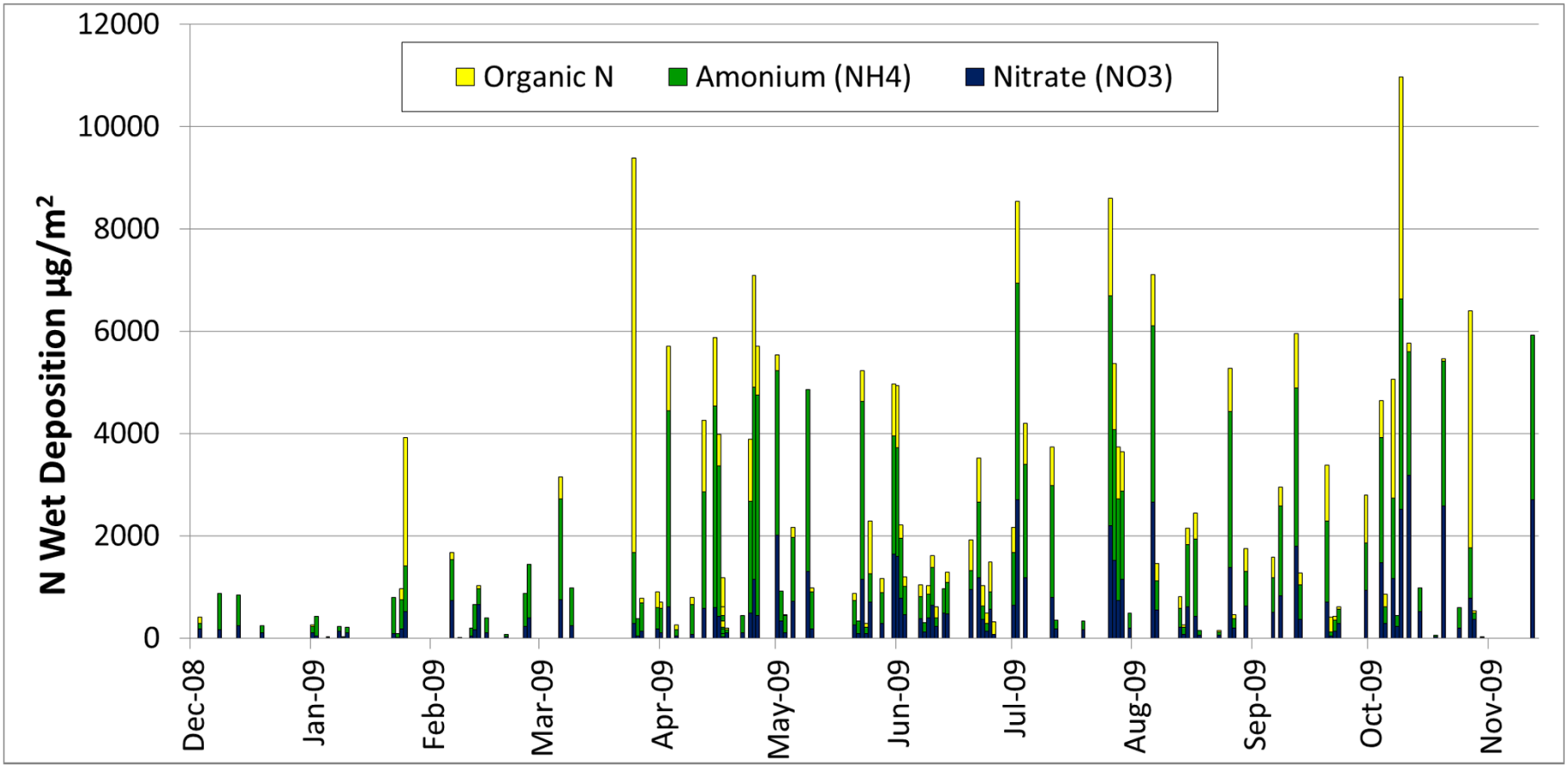


Summary

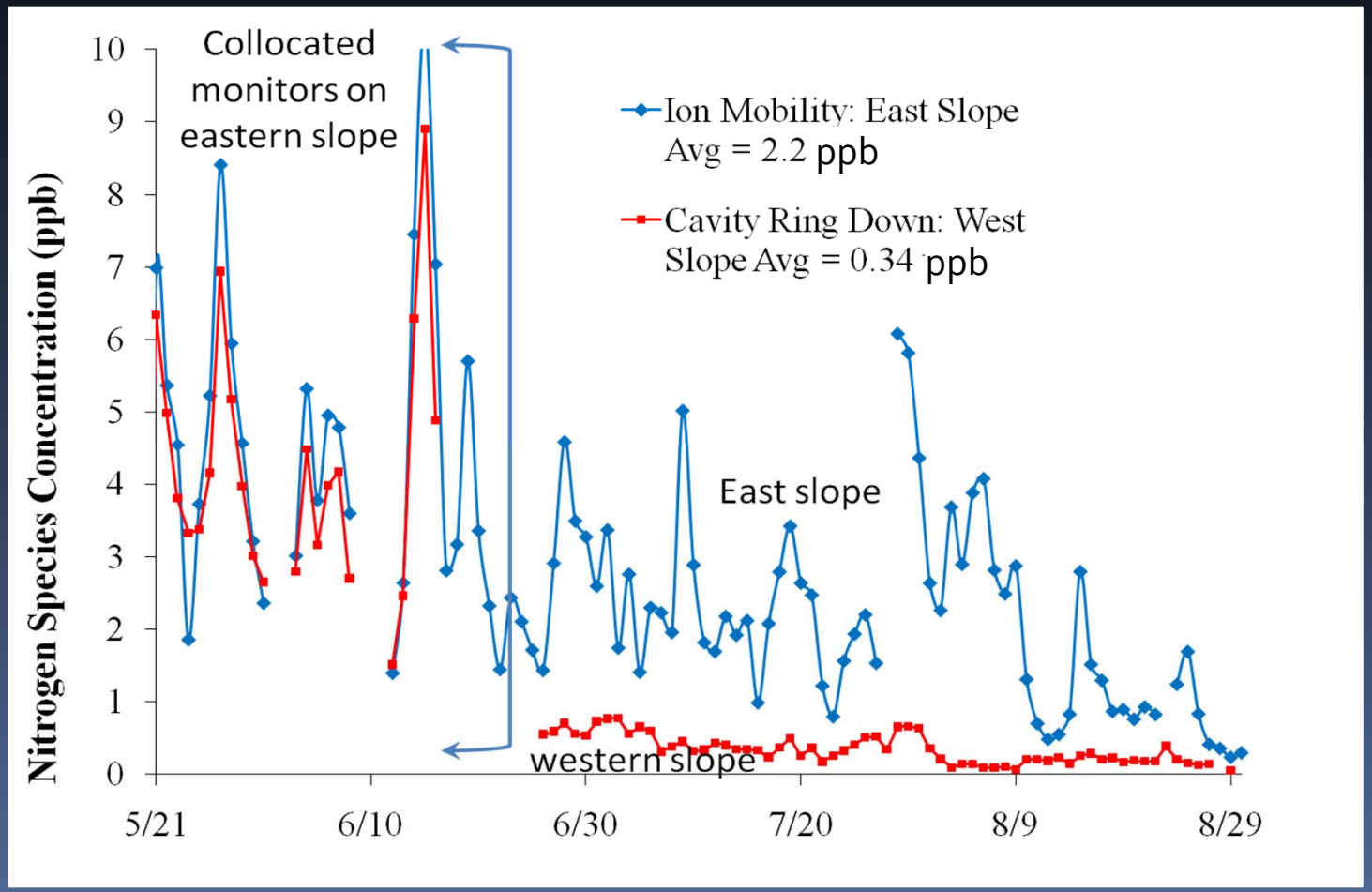
- Total Nr deposition at Rocky Mountain NP
  - Organic N wet deposition ~20%
  - NH_3 dry deposition ~15%
- Dry organic N deposition
  - Water soluble particulate ON > particulate NO_3
  - Evidence for large ambient concentrations of reduced organic N
  - Biomass burning source of organic N

Questions?

Daily Wet N Deposition Budget



Continuous NH_3 monitoring on RMNP east slope and remote west slope.

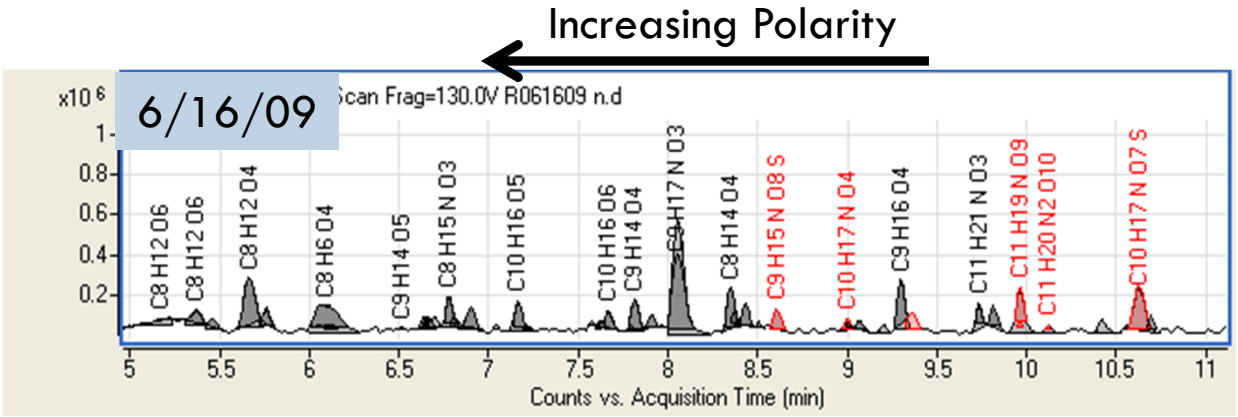


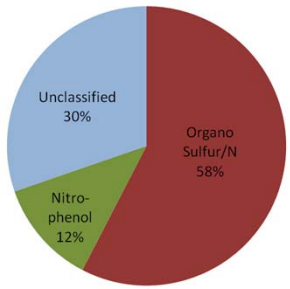
Carrico et al.,

- West Slope NH3 primarily due to natural sources and sources to the west of RMNP

Experimental procedure for identification of organic nitrogen compounds

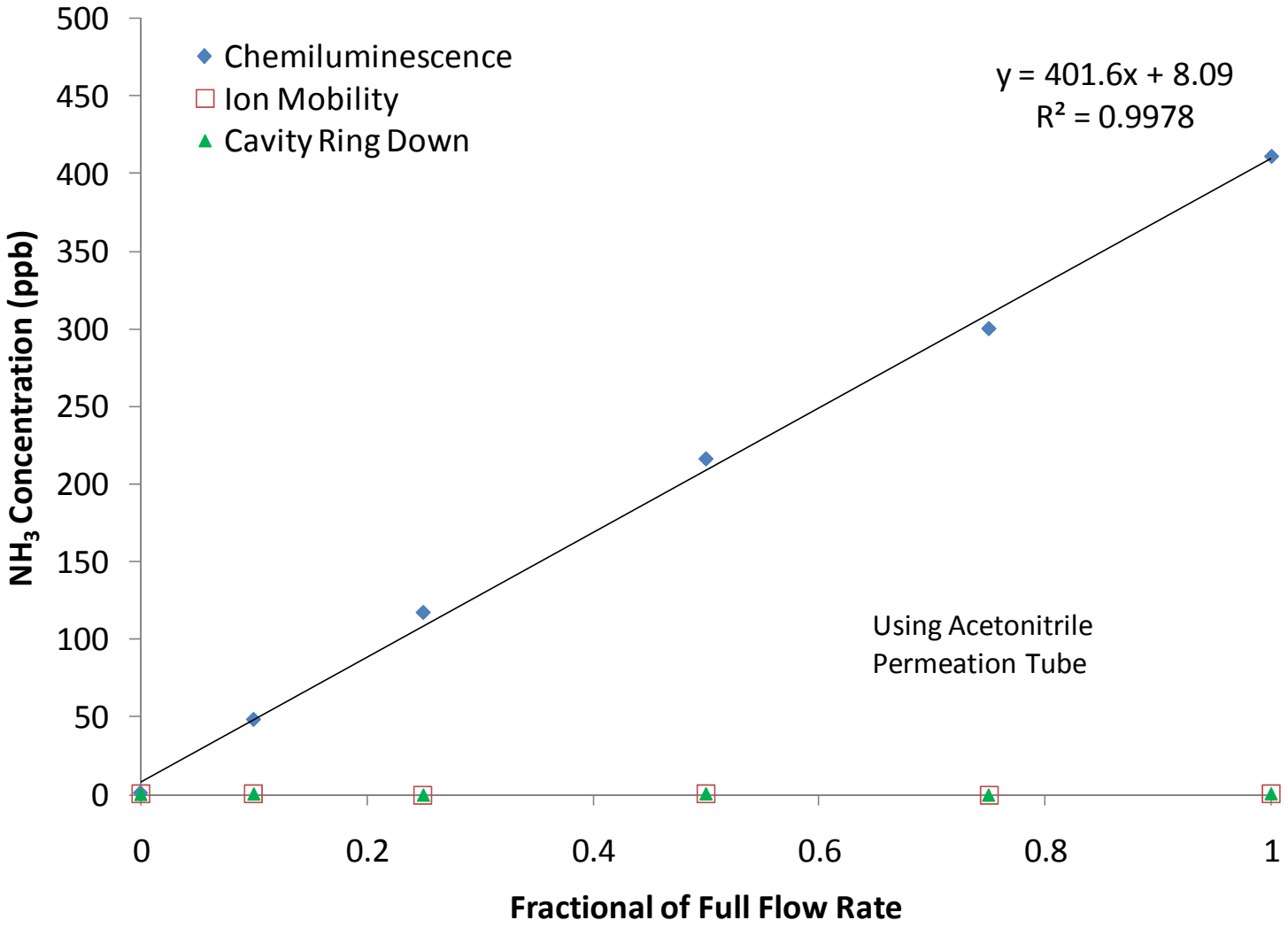
- Analyzed by Liquid Chromatography with Time of Flight Mass Spectrometry using electrospray ionization
  - Improves accuracy for complex mixtures, allows to distinguish isotopes
  - Soft ionization results in parent molecules, sometimes clusters and adducts
  - High mass accuracy helps determine elemental composition
  - Separated on C18 column with mixture of water and methanol. Initially mainly water in mobile phase with change to methanol throughout separation. (Polar to non-polar)





Sensitivity to Acetonitrile

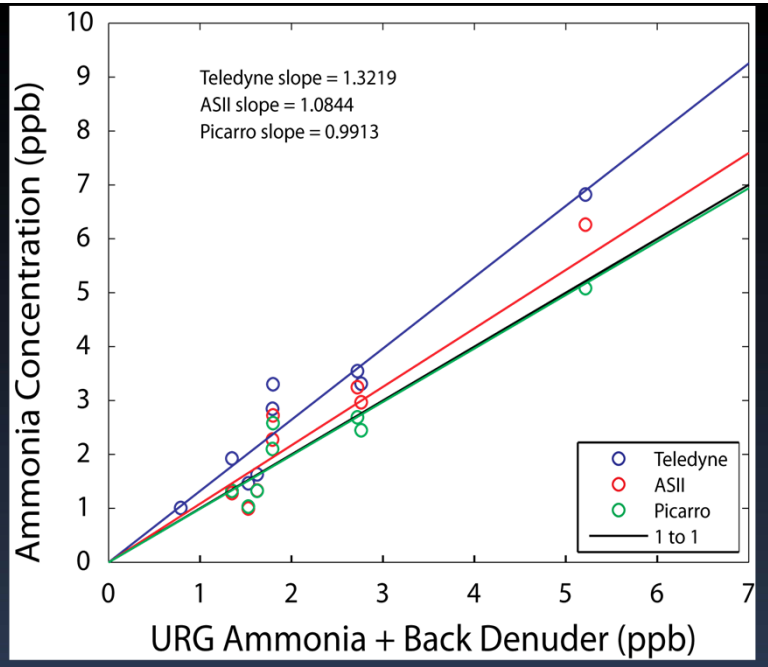
(beyond rated output of permeation tube)

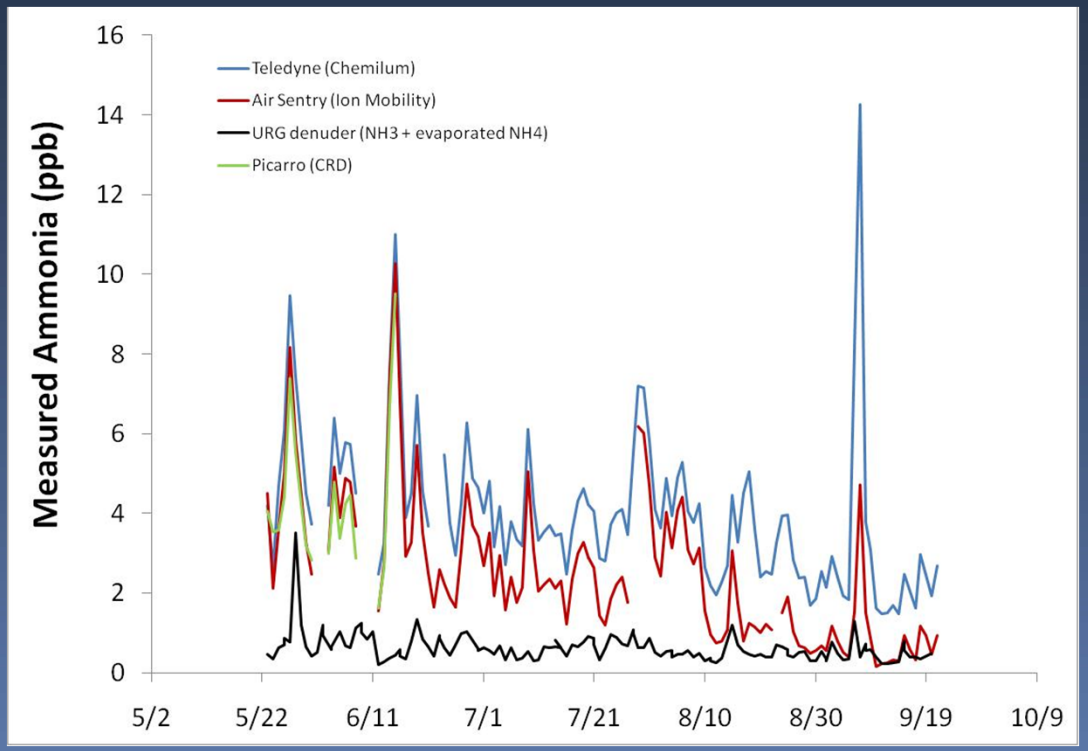


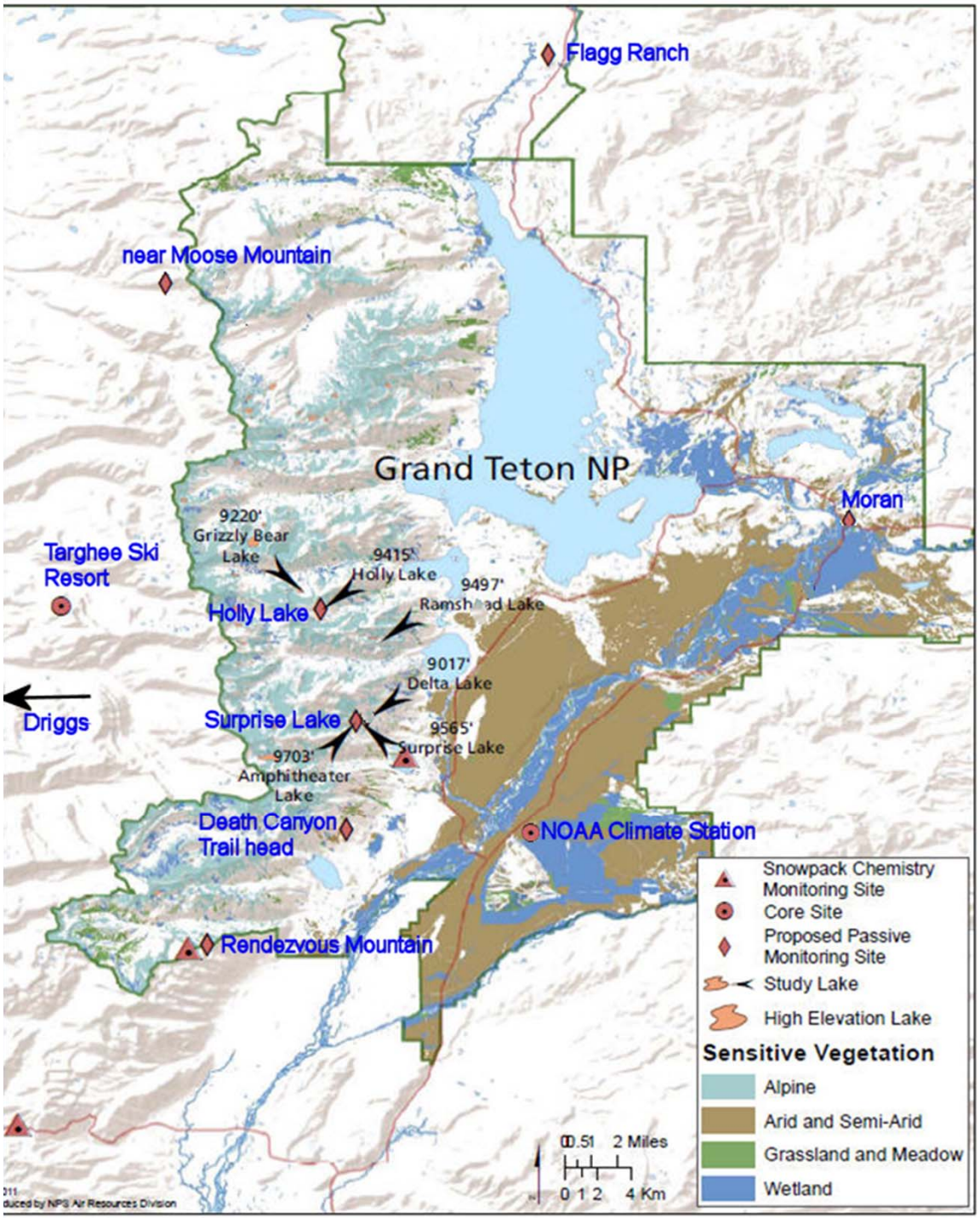
❖ Chemiluminescence is strongly sensitive to acetonitrile

Continued Evaluation of NH3 and R-NHx measurements

- Reducing artifacts
  - Overhaul instruments
  - Changed field procedures
  - Change calibration procedures
  - lab contamination e.g. biogenic VOCs







Monitoring Site Locations

- 2 Core sites
  - Targhee Ski Resort
  - NOAA Climate Station
  - Intensive monitoring of aerosol, gas and wet deposition data
  - Detailed N deposition budgets
- 7 Satellite Sites
  - Capture spatial patterns
  - Bulk measurements of inorganic nitrogen and wet deposition
- Preliminary monitoring at Driggs begins April, 2011
- Intensive monitoring: July 1 – August 31, 2011