

# **Reactive Nitrogen Monitoring**

# Some definitions

- $\text{NO}_y \equiv \text{NO} + \text{NO}_2 + \text{NO}_3 + 2x\text{N}_2\text{O}_5 + \text{HNO}_3 + \text{HONO} + \text{HO}_2\text{NO}_2 + \text{RONO}_2$  (organic nitrates such as PAN and alkyl nitrates) +  $\text{RONO}$  (organic nitrites) +  $\text{NO}_3^-$  (particulate nitrate).
- The ecology community defines “Total Reactive Nitrogen” to include  $\text{N}_2\text{O}$  which is not reactive in the sense considered here, thus we define “Total Chemically Reactive Nitrogen” to exclude  $\text{N}_2\text{O}$  and  $\text{N}_2$ .

# NEEDS

- Ecosystem health
  - Total deposition estimates (wet and dry) of all sulfur and reactive nitrogen species –
  - Critical loads
- Attribution of each species to its emission source (control measures)
- Other effects of these species (visibility, health.....)

# Issues

- Deposition is not measured but estimated from limited wind measurements.
- Some key species are not measured
- Accuracy with which some species are measured
- Time scale of measurement
  - 1 week
  - Need shorter sampling time increment for credible source apportionment (preferable hourly but not >24 hr.

# Species of interest

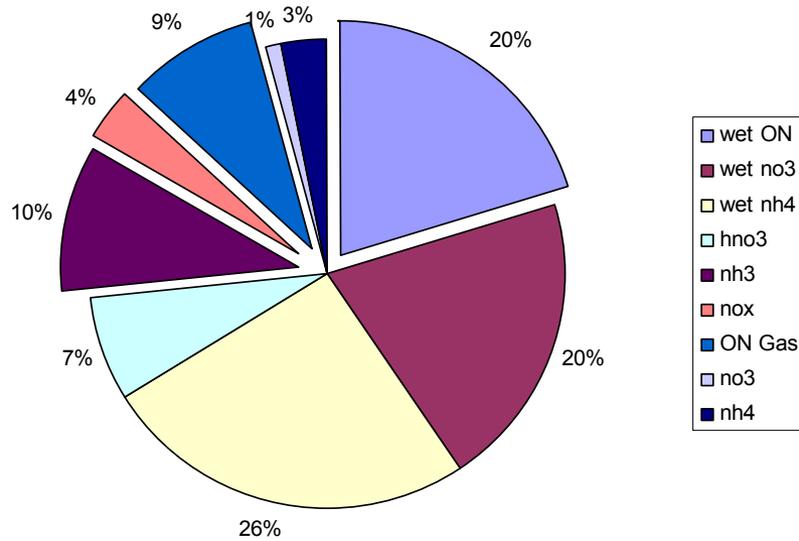
- Dry Species (Current)
  - $\text{SO}_2/\text{SO}_4$
  - $\text{HNO}_3/\text{NO}_3$
  - $\text{NH}_4$
- Dry Species (Missing)
  - $\text{NH}_3$
  - Reduced organic gases (Aliphatic amines .....
  - $\text{NO}_x$  (NO and  $\text{NO}_2$ )
  - Oxidized organic gases (PAN - alkyl nitrates ...)
  - Reduced and oxidized organic nitrogen containing particulates.

# Accuracy/Uncertainty

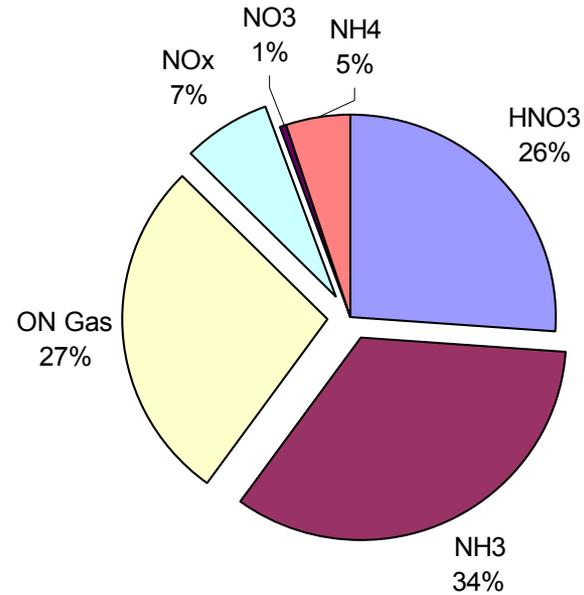
- $\text{SO}_2/\text{SO}_4$  measured reasonable well for both wet and dry
- Nitrogen is problematic across the board
  - Cut point is ill defined (coarse vs fine)
  - $\text{HNO}_3/\text{NO}_3$  split has large error
  - $\text{NH}_4$  error (underestimated) may be on order of 20-50%

# A typical dry deposition budget?

Total Deposition Budget (Spring)

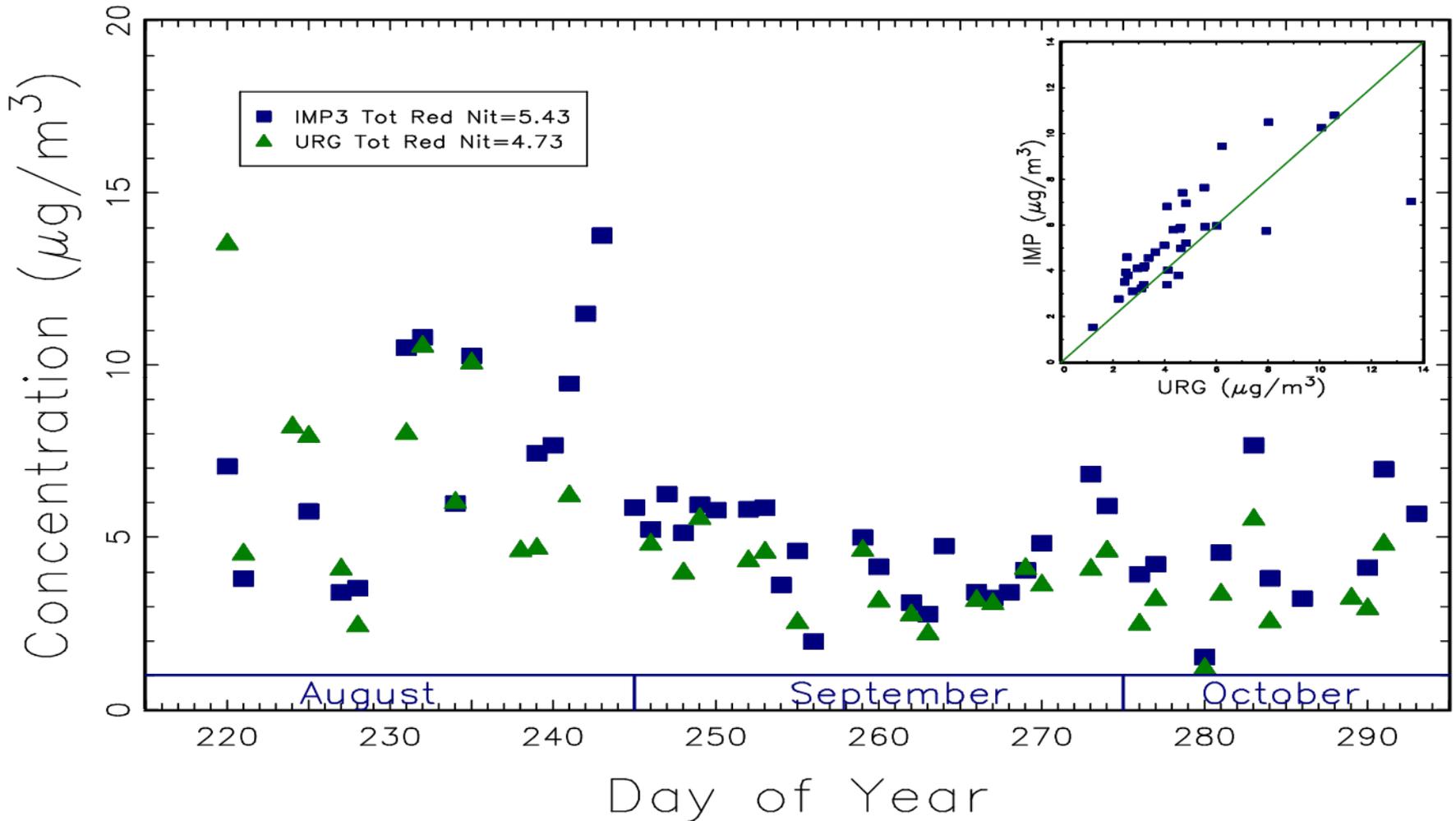


GAS CONCENTRATION BUDGET

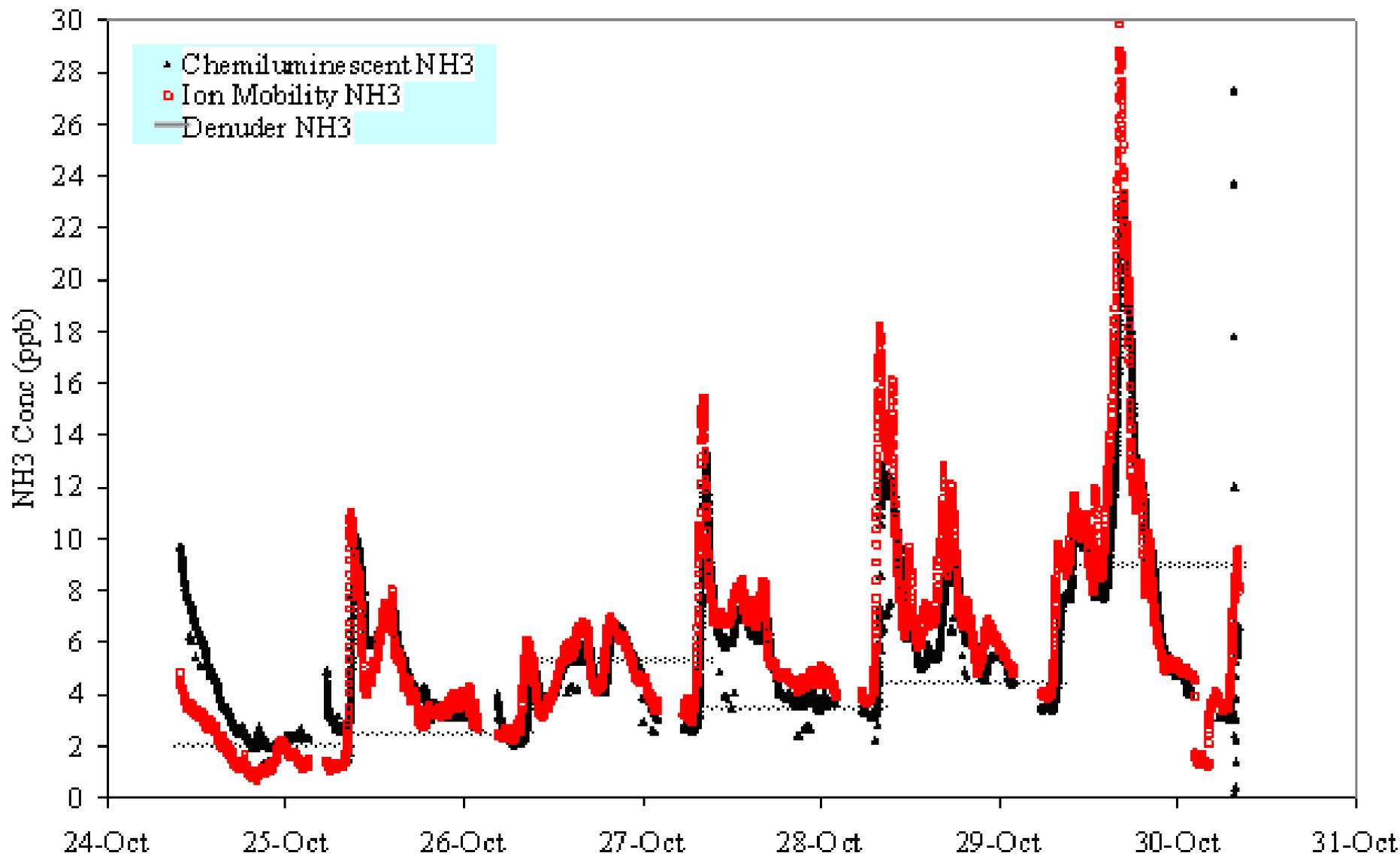


# Modified IMPROVE

Sum of Reduced Nitrogen Species ( $\text{NH}_3 + \text{NH}_4^+$ )



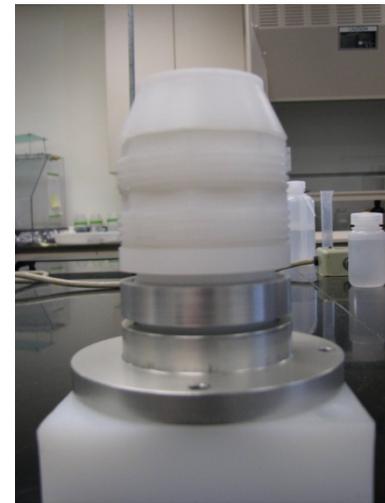
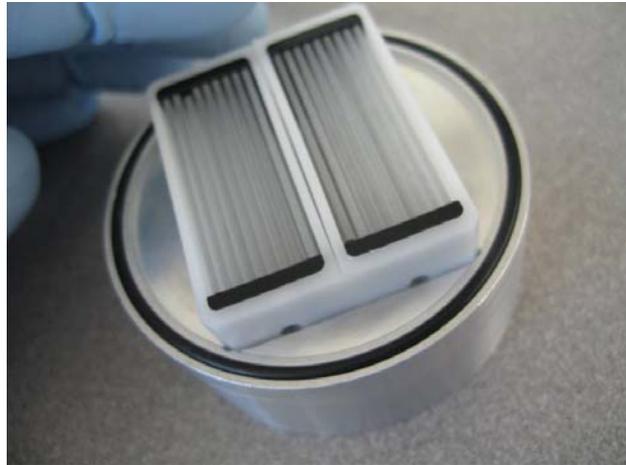
# Urban Comparison of 3 NH<sub>3</sub>



# Outline

- Motivation
- CASTNET Overview
- Sampling Setups of the Major Networks
- Proposed Sampling Trains for CASTNET and the Chemical Speciation Network
- Features of SASS Denuder Prototype 1
- SASS Testing: Experimental Design
- Results: Blanks, Collection Efficiency, Total Load Capacity
- Conclusions: Prototype 1
- Features of SASS Denuder Prototype 2
- Results: Blanks and Collection Efficiency
- Conclusions: Prototype 2

# Developing and Testing Prototype Compact Denuders for Ambient Air Sampling Applications

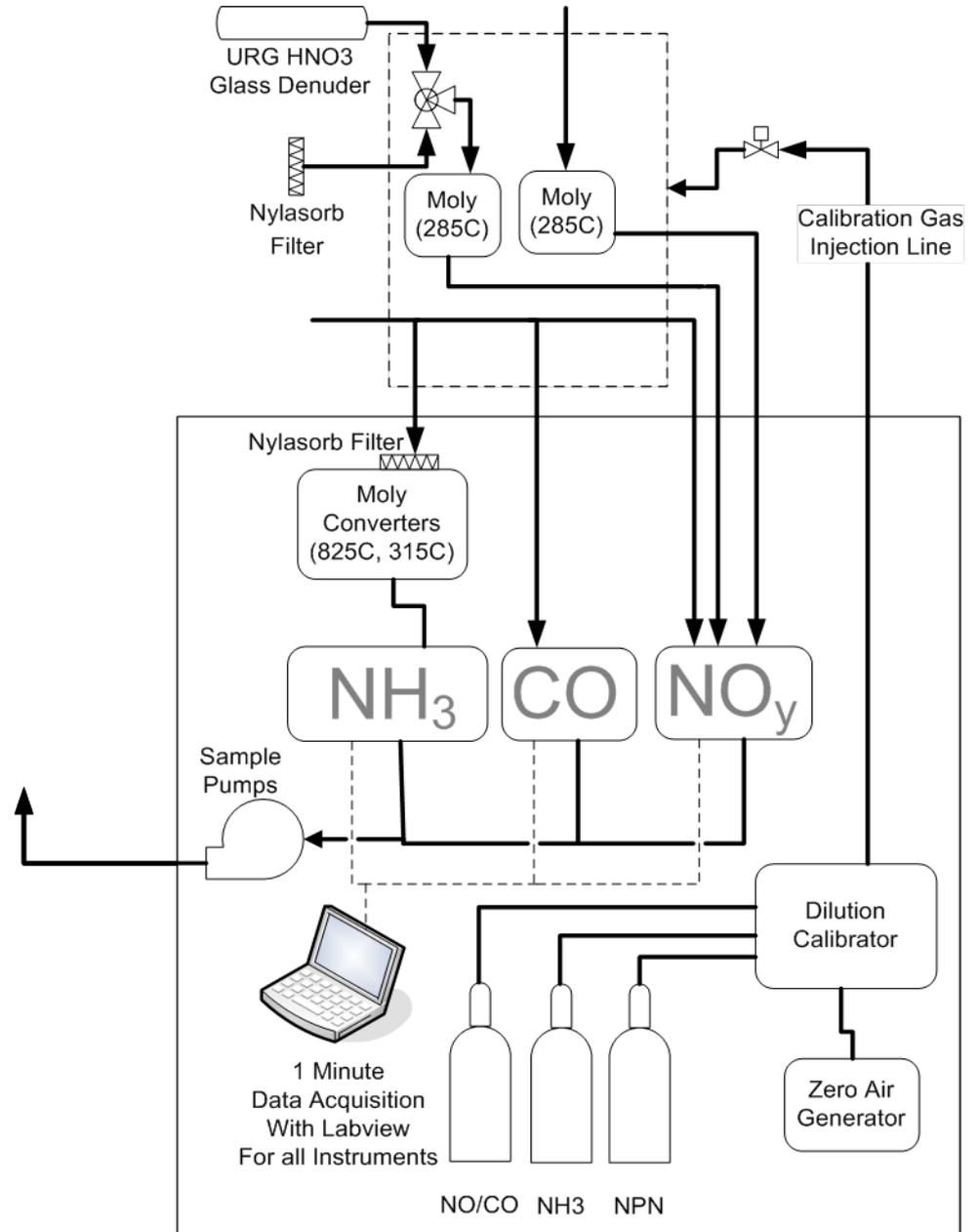


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# Dry gas and particle ON

- Can get estimates of oxidized ON both in gas and particle phase using catalytic converters and  $\text{NO}_x$  boxes on a near real time basis

# Trace Gas Samplers (off the shelf and custom)



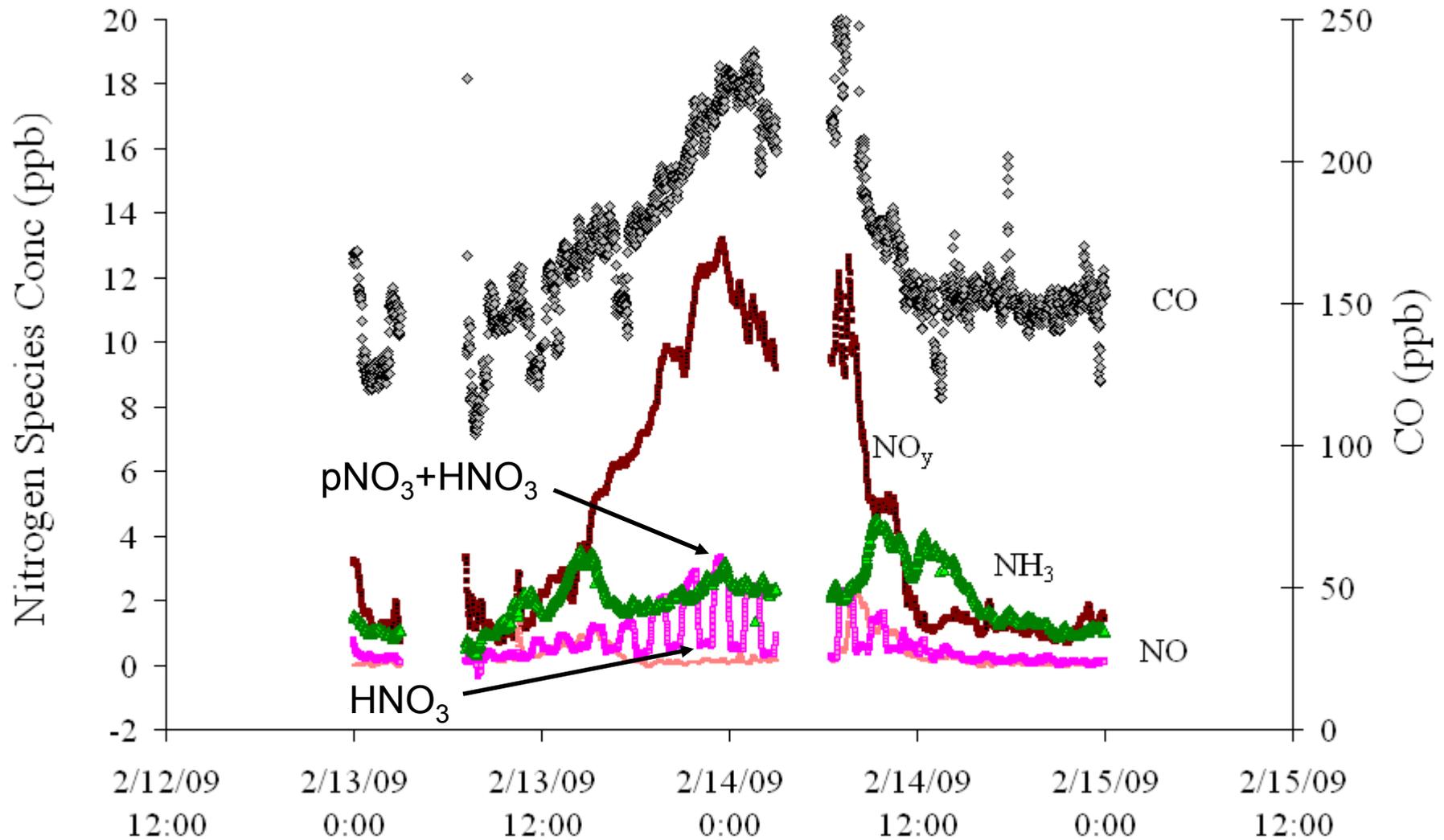
# Online N measurements: Two 3 Channel Instruments

## DIRECT

## BY DIFFERENCE

NO <sub>y</sub> analyzer	{	1.	NO <sub>y</sub> (inlet moly 285C)	1.	Total
		2.	NO <sub>y</sub> '(denuded inlet)	2.	HNO <sub>3</sub>
		3.	NO <sub>y</sub> ''(filtered inlet)	3.	pNO <sub>3</sub> +HNO <sub>3</sub>
NH <sub>3</sub> analyzer	{	1.	'Total' Gas Phase Nitrogen (moly 815C)	1.	'NH <sub>3</sub> '
		2.	'Traditional' NO <sub>x</sub> (moly 315C)	2.	'NO <sub>2</sub> '
		3.	NO		

# Winter Overnight $\text{NO}_y$ Event



- Dominated by  $\text{NO}_y$  plus smaller contributions of  $\text{NH}_3$  and particulate  $\text{NO}_3^-$
- Low  $\text{NO}$ : not a locally driven event

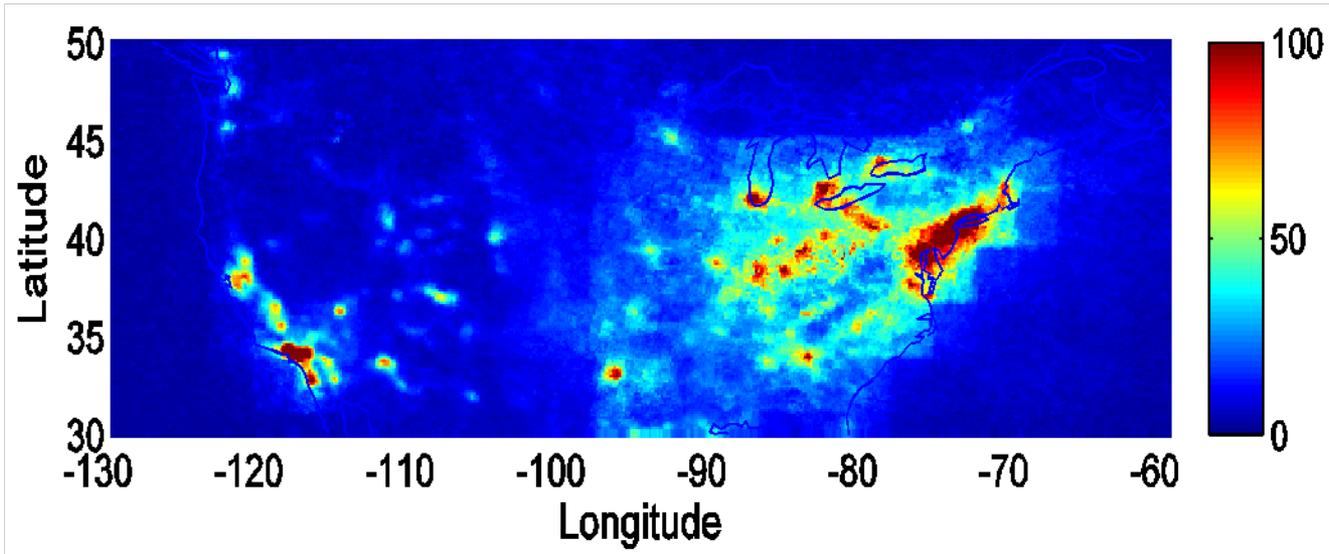
# Questions

- Are current procedures for estimating dry deposition meaningful? (high time resolution met data combined with 1 wk average concentrations measurements)
- What needs to be measured that isn't currently being measured?
- Is split between various species important
  - $\text{SO}_2/\text{SO}_4$ ,  $\text{HNO}_3/\text{NO}_3$ ,  $\text{NH}_3/\text{NH}_4$ , etc or is total sulfur, or total gas/particle phase reactive nitrogen adequate?
    - For ecosystem response may not be so important?
    - For attribution and model assessment it is critical!
- Can defensible critical loads be set without a knowledge of total nitrogen?
- What sampling frequency/duration is acceptable – both in time and space?

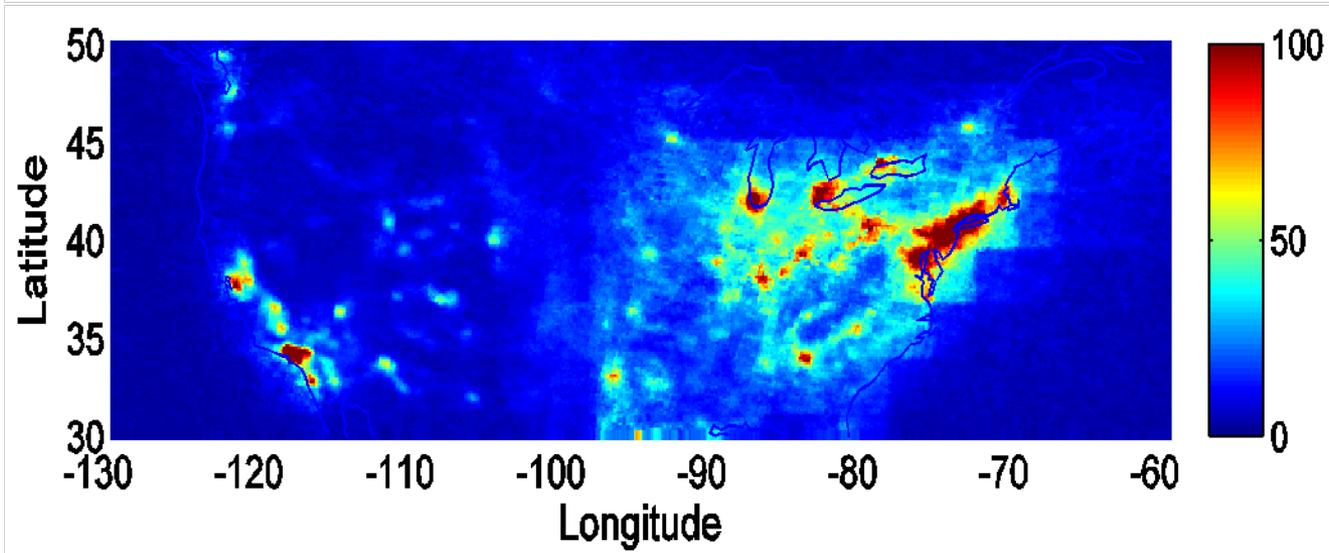
# Some Possible Changes

- Eliminate met monitoring if it isn't being used for other purposes.
- At a minimum add an impregnated filter to the existing filter pack to measure  $\text{NH}_3$ .
- Replace current filter pack with similar filter pack (including  $\text{NH}_3$ ) that operates automatically for time intervals of
  - Everyday or
  - Every third day.
- Add  $\text{NH}_3$  and  $\text{HNO}_3$  to the IMPROVE system.
- Measure total ON gas/particles at some sites.
  - Speciate ON at some basic level

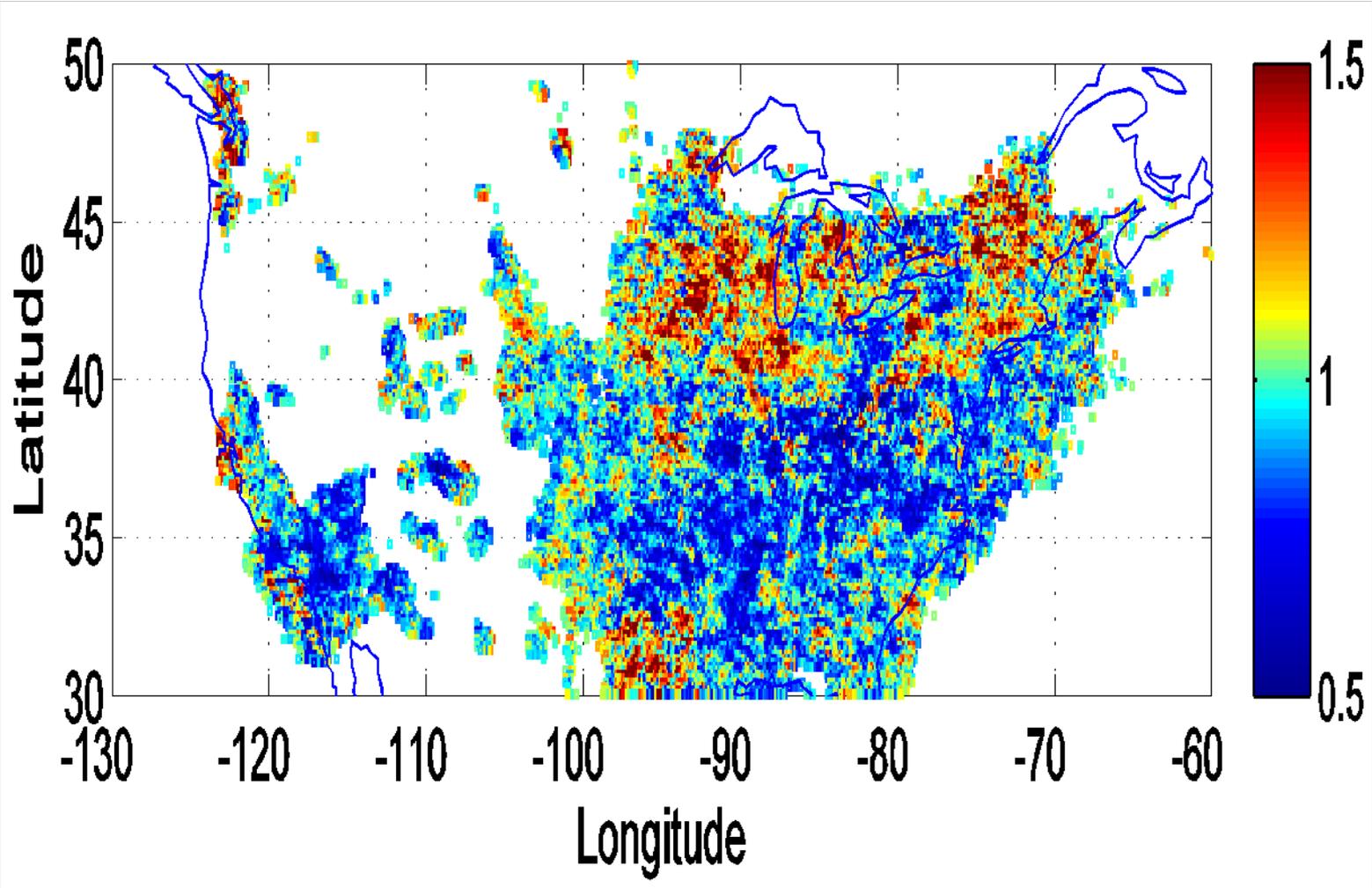
2007



2008



Notes: Average 2007 and 2008 annual NO<sub>2</sub> from SCIAMACHY satellite. The factor on colorbar is 1.0E+14 molecules per cm<sup>2</sup>. The resolution of the data is 0.125 deg x 0.125 deg. Each pixel contain the median of monthly data.



Notes: The ratio of average NO<sub>2</sub> for year 2008 to the year 2007 (i.e.  $\text{NO}_{2\_year2008} / \text{NO}_{2\_year2007}$ ) annual NO<sub>2</sub> from SCIAMACHY satellite. The low NO<sub>2</sub> concentration data ( $\text{NO}_2 < 10^{15}$ ) are not considered here. The resolution of the data is 0.125 x 0.125. Each pixel is derived from the median of 2007 and 2007 months data.

# Climate Change

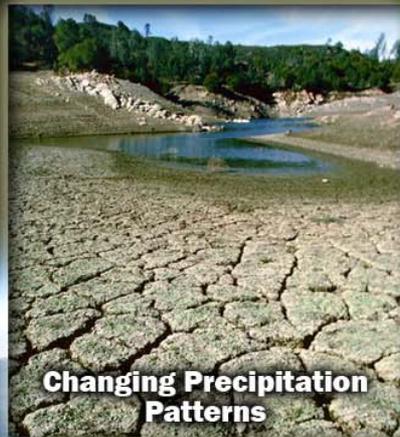
**Effects of  
Climate  
Change**

**Radiation  
Balance**

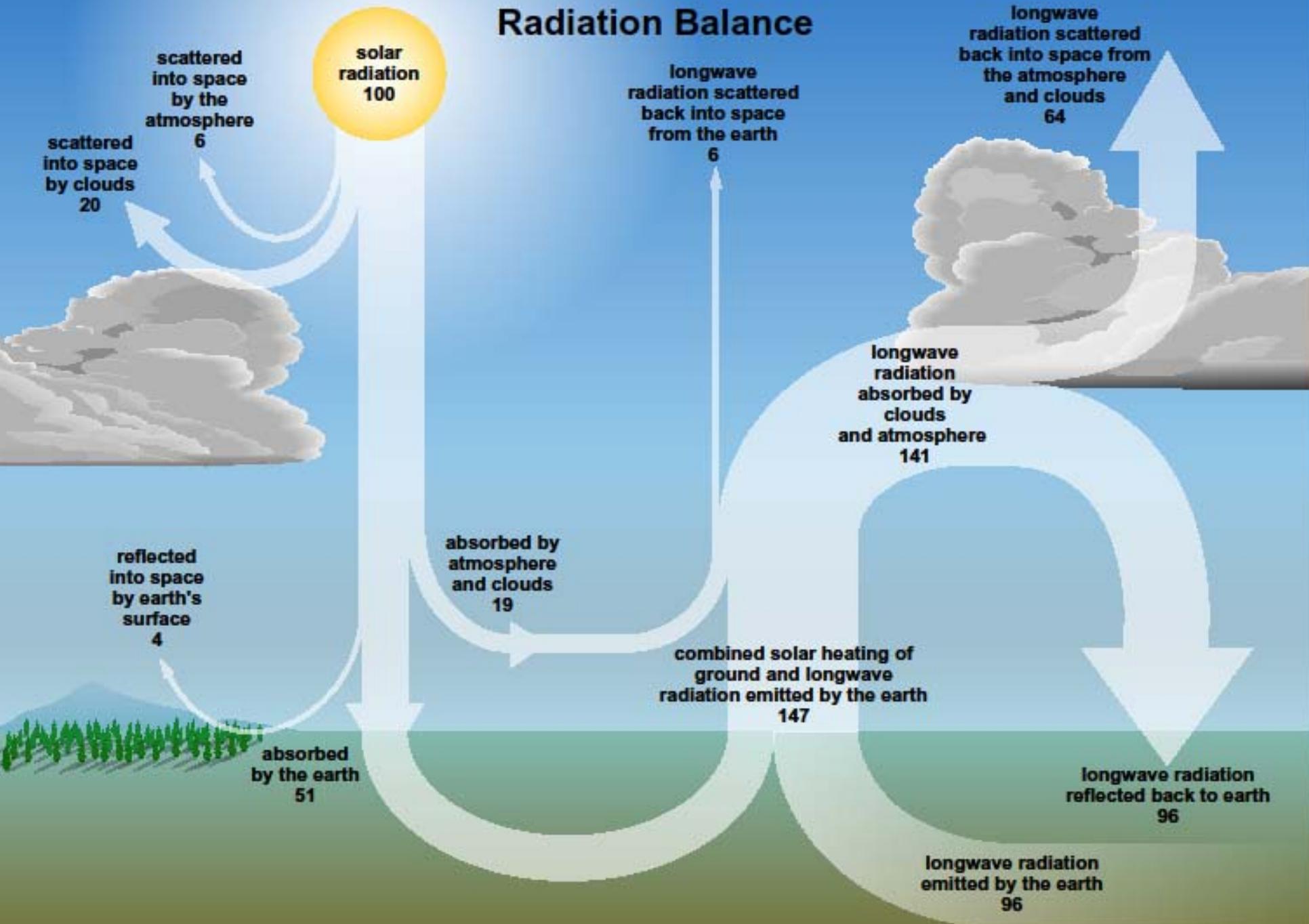
**Carbon  
Feedbacks**

**Greenhouse  
Gas  
Contributors**

**What Can  
Be Done?**



# Radiation Balance



solar radiation  
100

scattered into space by the atmosphere  
6

scattered into space by clouds  
20

longwave radiation scattered back into space from the earth  
6

longwave radiation scattered back into space from the atmosphere and clouds  
64

longwave radiation absorbed by clouds and atmosphere  
141

reflected into space by earth's surface  
4

absorbed by atmosphere and clouds  
19

combined solar heating of ground and longwave radiation emitted by the earth  
147

absorbed by the earth  
51

longwave radiation reflected back to earth  
96

longwave radiation emitted by the earth  
96



**END**

# Other Recommendations from EPA NOX/SOX review

- We recommend monitoring a suite of reactive nitrogen species the sum of which is “Total Chemically Reactive Nitrogen” defined as the sum of all oxidized species except  $N_2O$  and the sum of ammonia and ammonium.
- Total Chemically Reactive Nitrogen =  $NO_y + NH_x$
- **Species Method**  $NO_y$  (total oxidized nitrogen) Reduction to NO followed by chemiluminescence  $NO_3^-$  (particulate nitrate) Denuder/filter sampling followed by ion chromatography  $HNO_3$  (nitric acid vapor) Filter/denuder and followed by ion chromatography.  $NH_3$  (ammonia) Filter/denuder followed by colorimetry or ion chromatography  $NH_4^+$  (ammonium) Denuder/filter followed by colorimetry or ion chromatography

# WHAT WE REALLY NEED TO MEASURE

	WET	GAS	PARTICLE	Temporal scale (gas/particle)
$\text{SO}_2/\text{SO}_4^{-2}$	*****	****	*****	Min/hr/day/week
$\text{NO}_2/\text{HNO}_3^-$ $/\text{NO}_3^-$	****	****(***)CASTNET)	****(***)CASTNET)	Min/hr/day/week
$\text{NH}_3/\text{NH}_4^-$	***	***	***	Min/hr/day/week
<b>Total ON</b>	***	*	*	Integrated sample/event based
$\text{ON}_r$	* (markers)	*	* (markers)	?
$\text{ON}_o$	* (markers)	***	***	Min/hr/day/week (gas/part) Event for markers
$\text{ON}_b$	* (markers)	**	*	Integrated samples

\*\*\*\*\* Measure with high degree of accuracy

\*\*\*\* Measure with reasonable accuracy

\*\*\* Measure with low accuracy

\*\* Research monitoring

\* Currently cannot do

Note: measurements should be event based for wet deposition and gases and particles measured at least on a 24 hr schedule.

# Next Steps

- Establish/examine need for ON measurements at x number of sites?
- Develop denuders to do  $\text{NH}_3$ ,  $\text{NH}_4$ , and  $\text{HNO}_3/\text{NO}_3$  split (within 6 months – year)
- Test filter based measurements for gas/particle phase oxidized ON measurements (1+ years)
- Develop marker technology/methodology for apportioning ON in wet deposition (2+ years ?)
- Do the same for reduced gas/particles (time ?)
- Implementation schedule (Funding??)

# Nitrogen Monitoring

- Wet ON at a number of regionally representative sites
- Develop method for apportioning wet ON to reduced, oxidized, biological
- NH<sub>x</sub> at a number of regionally representative sites
- NO<sub>y</sub> at a number regionally representative sites
- How to measure total reduced ON gas and/or particle phase?
- Supplemental measurements in ROMO – east/west – additional species – temporally representative

# Wet DON

- Can measure TON
- Can't directly measure reduced, oxidized, or biological ON – important to make these distinctions from an apportionment perspective because sources are distinctive
- Can use receptor type models to apportion DON if one has reliable chemical markers
  - Measure reduced OC markers such as amines and urea for reduced DOC
  - Measure oxidized OC markers such as alkyl nitrates, nitrophenols, and other nitroaromatic
  - Measure biological markers such as amino acids and peptides
  - Apply simple regression models or more sophisticated models such as PMF and UNMIX.

# How important is AON?

- 51 studies in North America have DON at  $38 \pm 19\%$  of TON (Wet)
- As much as 30% of particulate OC is nitrogen containing
- Gas % of TON ?

# What isn't measured?

- $\text{NH}_3$
- Organic nitrogen either in wet or dry (gas and particle phase) or its reduced, oxidized or biological forms
  - $\text{NO}_2$ , peroxyacetyl nitrate (PAN) and related alkyl nitrates
  - Aliphatic amines
  - Proteins, amino acids, etc

# Tabular summary

Species	Method
NO <sub>y</sub> (total oxidized nitrogen)	Reduction to NO followed by chemiluminescence
NO <sub>3</sub> <sup>-</sup> (particulate nitrate)	Denuder/filter sampling followed by ion chromatography
HNO <sub>3</sub> (nitric acid vapor)	Filter/denuder and followed by ion chromatography.
NH <sub>3</sub> (ammonia)	Filter/denuder followed by colorimetry or ion chromatography
NH <sub>4</sub> <sup>+</sup> (ammonium)	Denuder/filter followed by colorimetry or ion chromatography

WHAT'S MISSING: ORGANIC NITROGEN