ROcky Mountain Atmospheric Nitrogen and Sulfur study (ROMANS

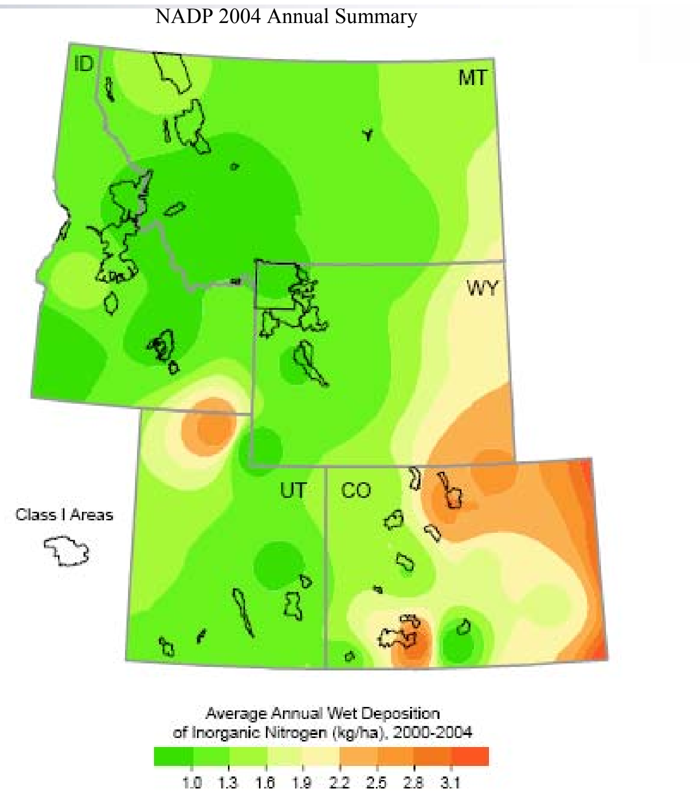
STATEMENT OF THE PROBLEM

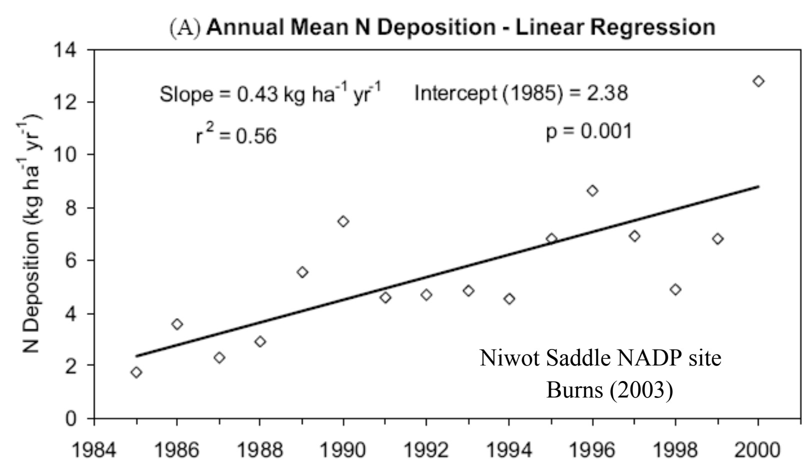
- Rocky Mountain National Park (ROMO) is experiencing a number of deleterious effects due to atmospheric nitrogen and sulfur compounds. These effects include visibility degradation, changes in ecosystem function and surface water chemistry from atmospheric deposition, and human health concerns due to elevated ozone concentrations.

- The nitrogen compounds include both oxidized and reduced nitrogen. Emissions of nitrogen compounds need to be reduced to alleviate these deleterious effects. Various regulatory programs are underway to address emission reductions, many of which will be achieved from the most easily identified contributors to oxidized nitrogen related effects at the park.

Wet deposition patterns and trends

- N deposition "hot spot" in northern Colorado Rockies
  - Current N deposition ~ 20x natural levels
- Nitrogen deposition increasing at high elevation sites
  - Ammonium deposition increasing faster than nitrate

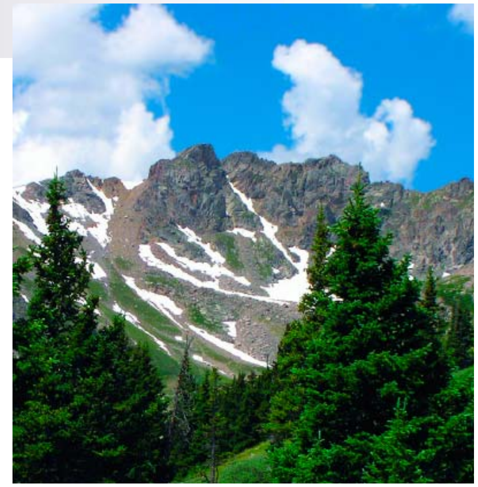




ROMANS OBJECTIVES

- **Characterize the atmospheric concentrations of sulfur and nitrogen species in gaseous, particulate and aqueous phases (precipitation and clouds) along the east and west sides of the Continental Divide (Organic Nitrogen?)**
    - GAS: NH_3, R-NH_2, NO_X(NO+NO_2), NO_Y(HNO_3, PAN, etc)
    - PARTICLE: NH_4, NO_3, ORGANICS (reduced and oxidized)?
    - WET (rain, snow, and clouds): NH_4, NO_3, ORGANICS (reduced and oxidized)?
- **Identify the relative contributions to atmospheric sulfur and nitrogen species in RMNP from within and outside of the state of Colorado.**
- **Identify the relative contributions to atmospheric sulfur and nitrogen species in RMNP from emission sources along the Colorado Front Range versus other areas within Colorado.**
- **Identify the relative contributions to atmospheric sulfur and nitrogen species from mobile sources, agricultural activities, large and small point sources within the state of Colorado.**

The urban/industrial-agricultural interface



Organic nitrogen?

+hv

$HNO_3 + NH_3 \rightarrow NH_4NO_3(p)$

NO_x VOC

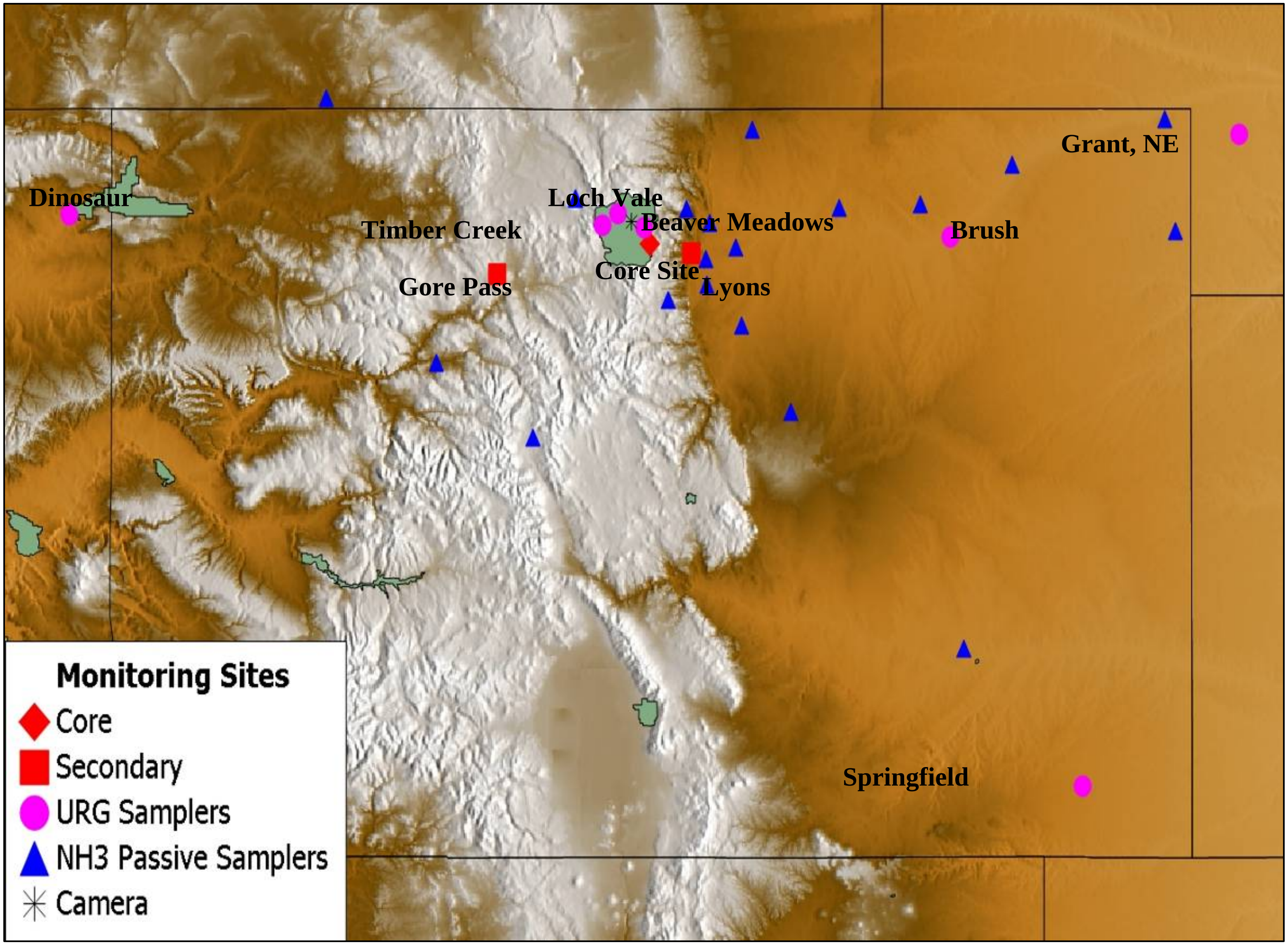
Apportionment Strategy

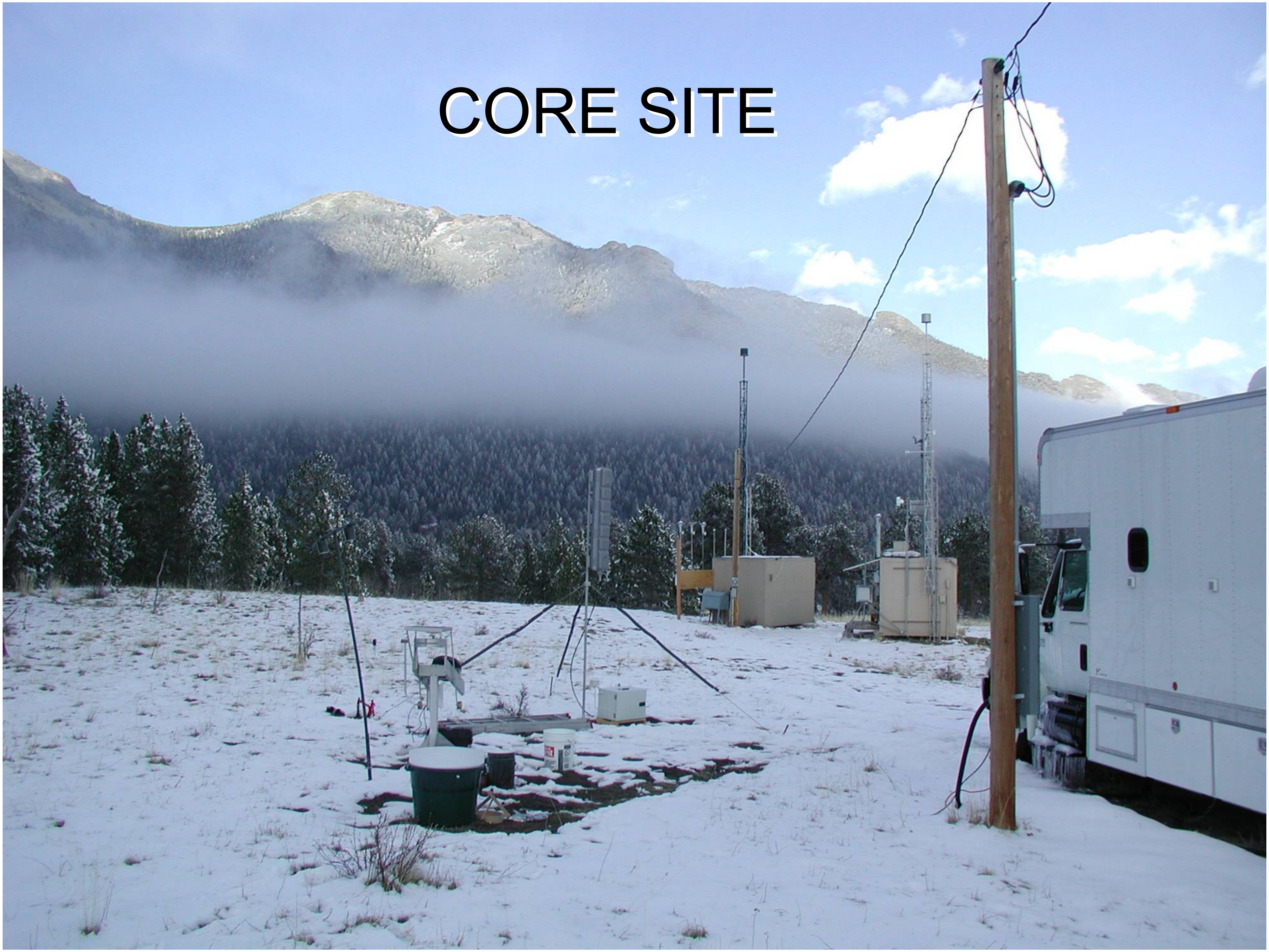
- If chemical transport models were "perfect" then all apportionment problems would best be addressed through the exercise of these models.
- BUT THEY ARE NOT! –especially when addressing species other than ozone and sulfate.

Apportionment Strategy (Weight of Evidence)

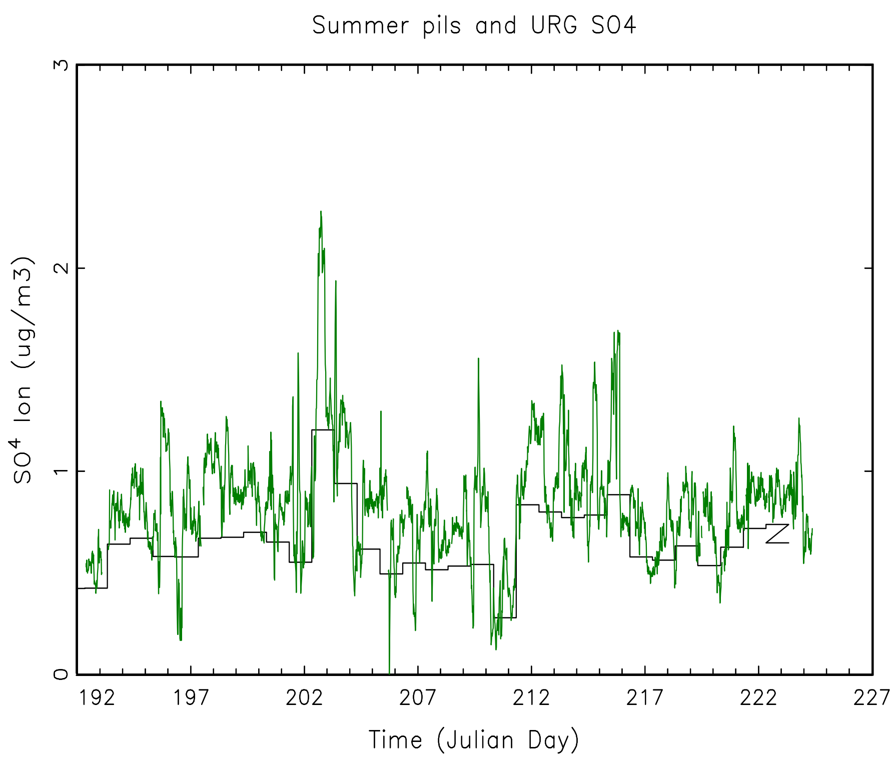
- Concentration gradients.
- Which way is the wind coming from?
- Simple back trajectories.
- Frequency with which the air mass passes over source areas before it arrives at the receptor -residence time analysis.
- Trajectory receptor models.
- Receptor models.
- Chemical transport models.
- Hybrid Models.

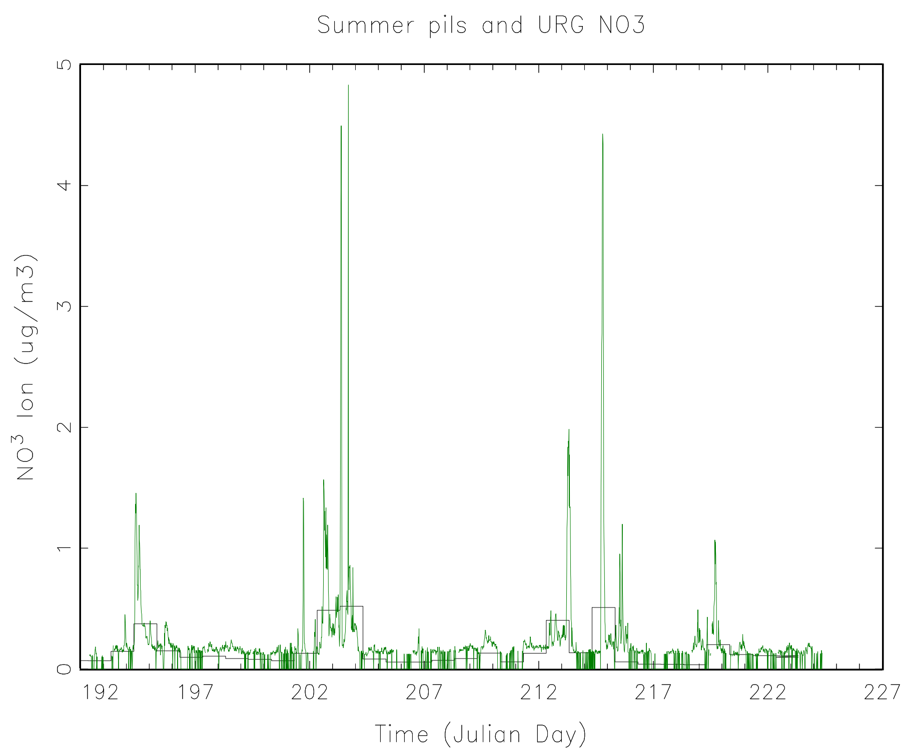
STUDY DESIGN



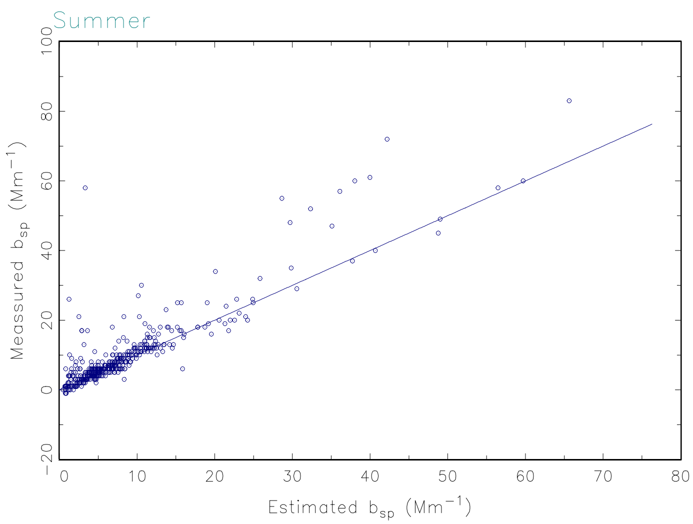

CORE SITE

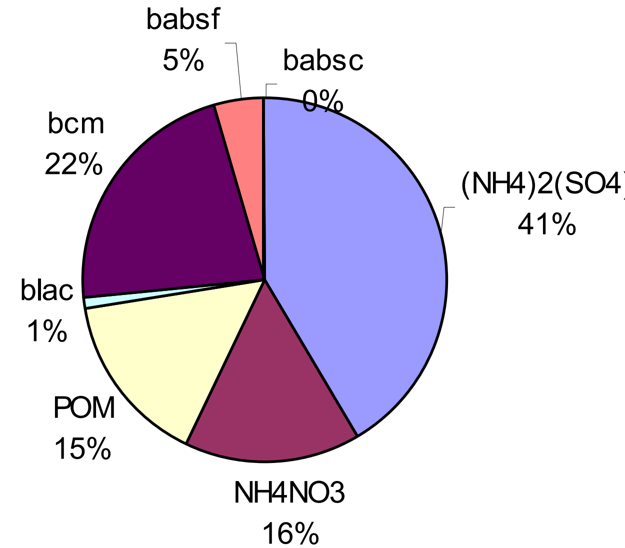
Time series of PILS and IMPROVE sulfate and nitrate

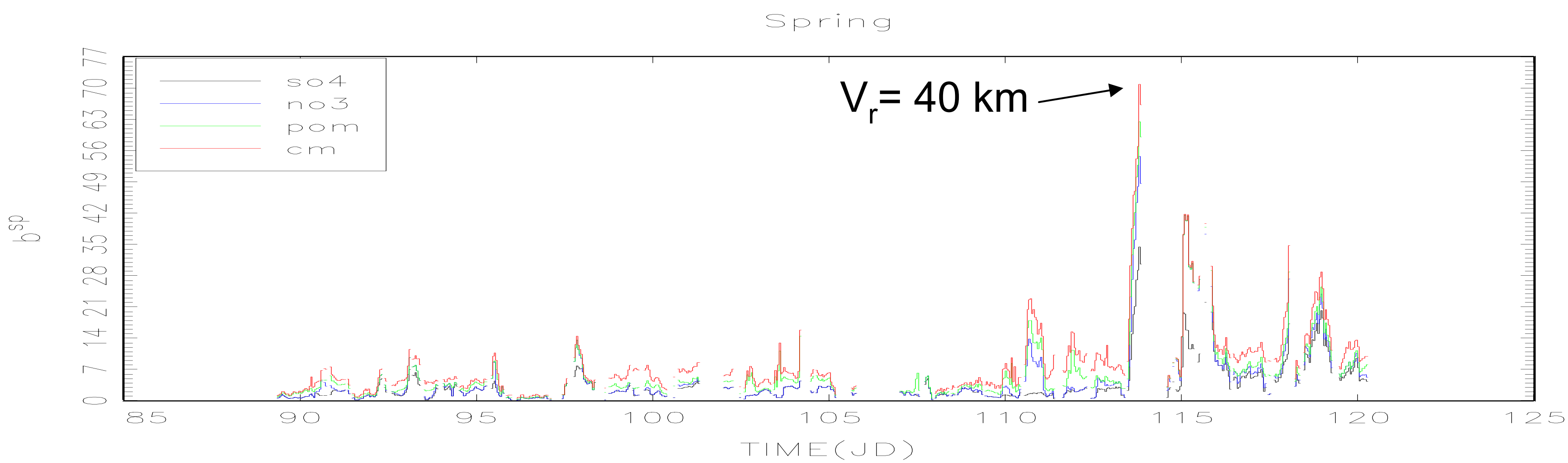




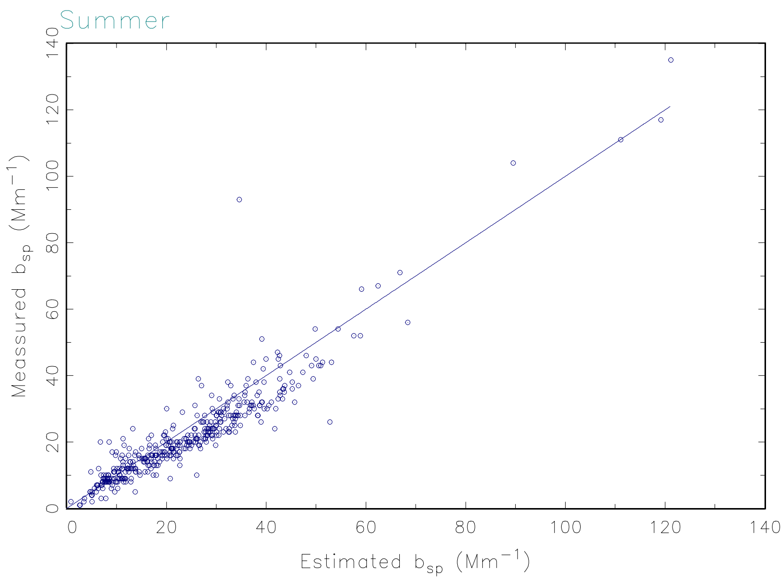
Spring atmospheric scattering estimations

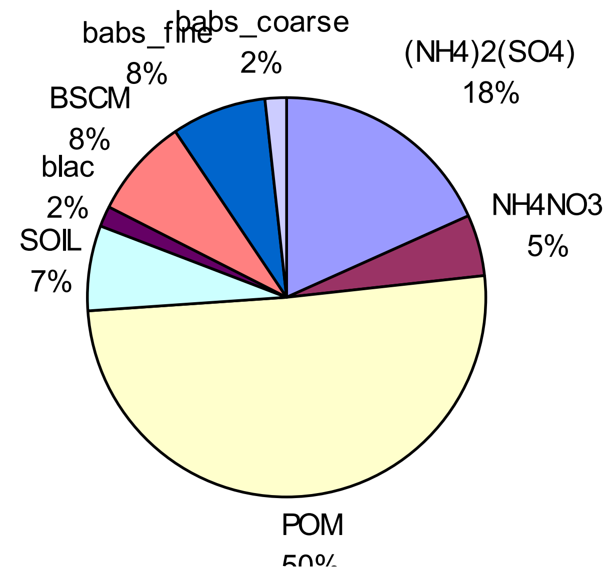


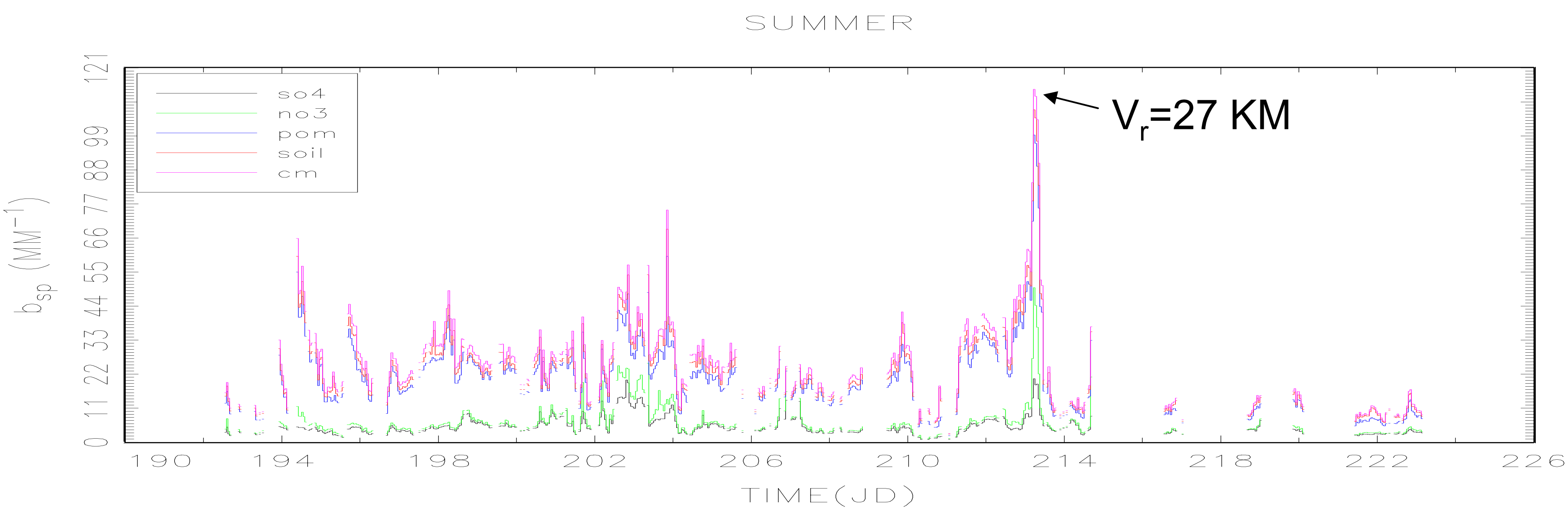




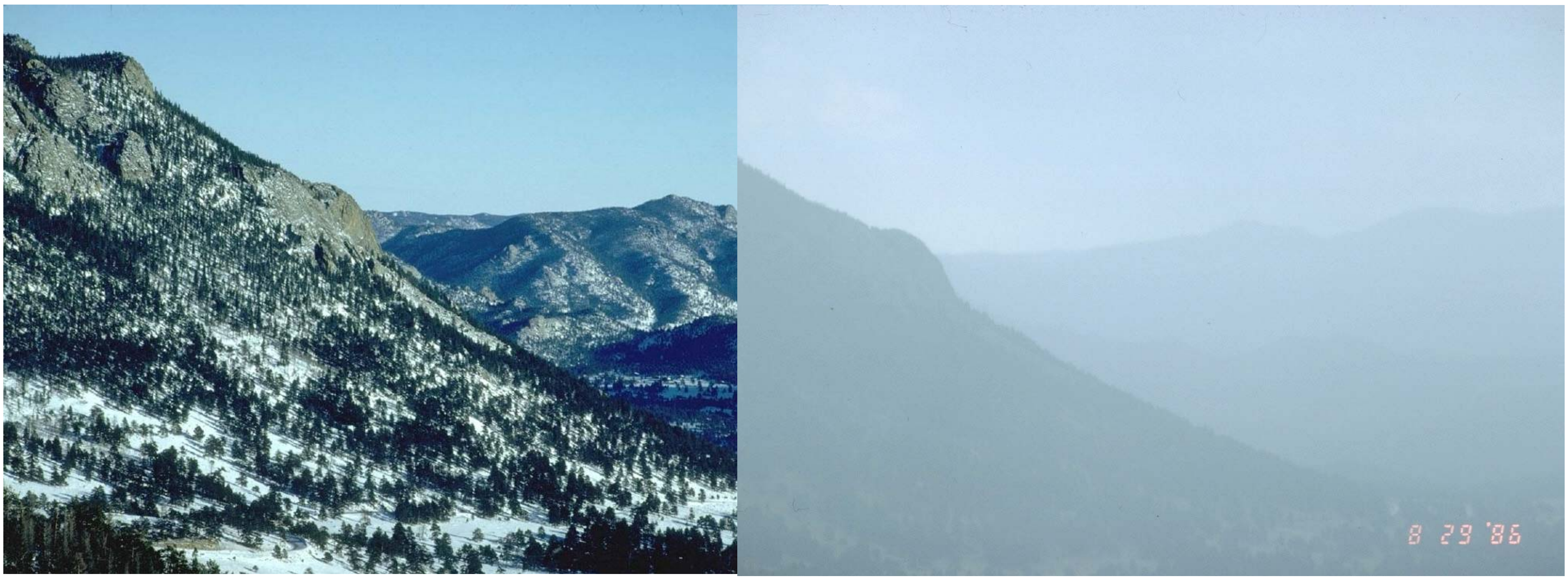
Summer atmospheric scattering estimations



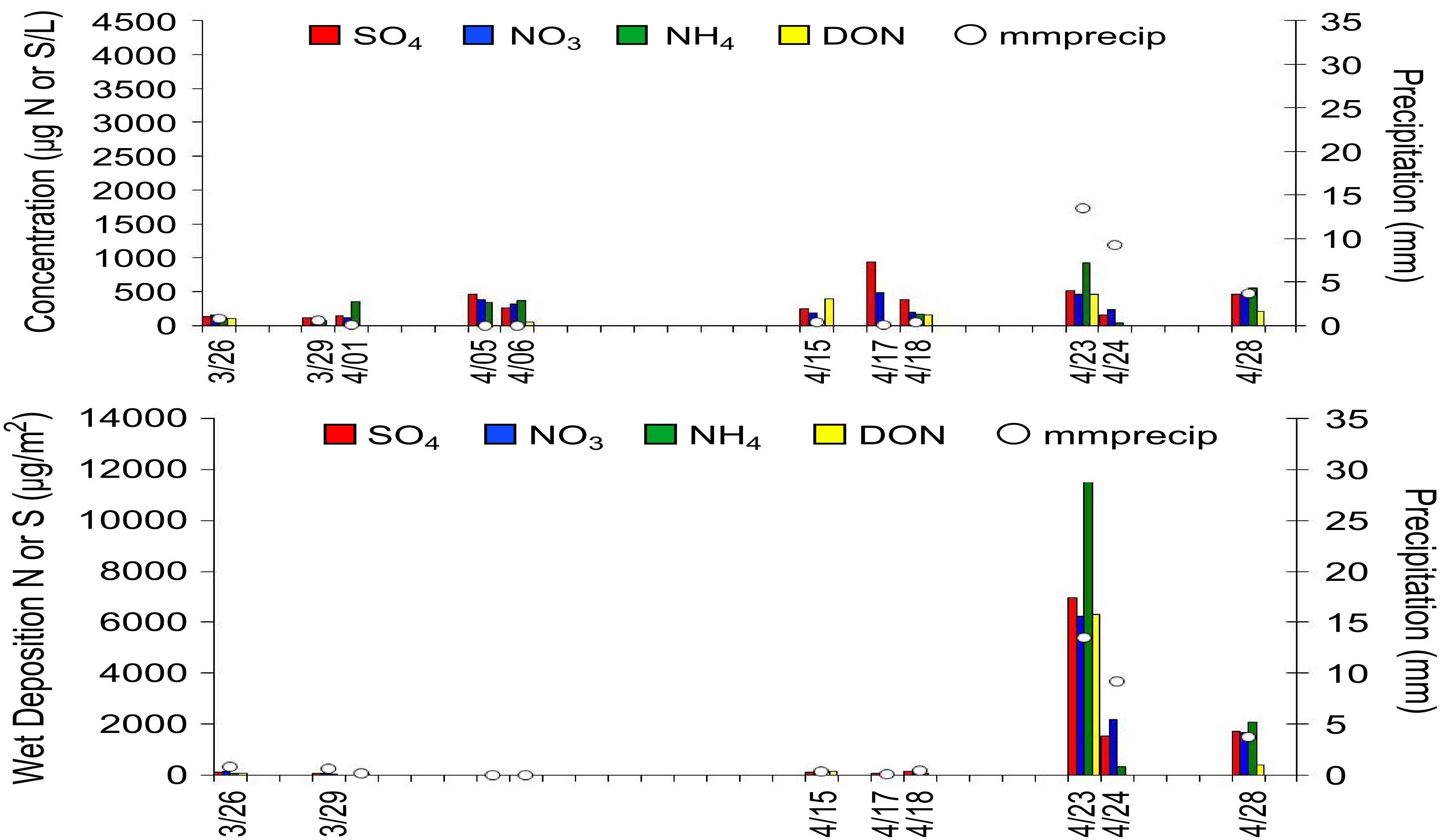




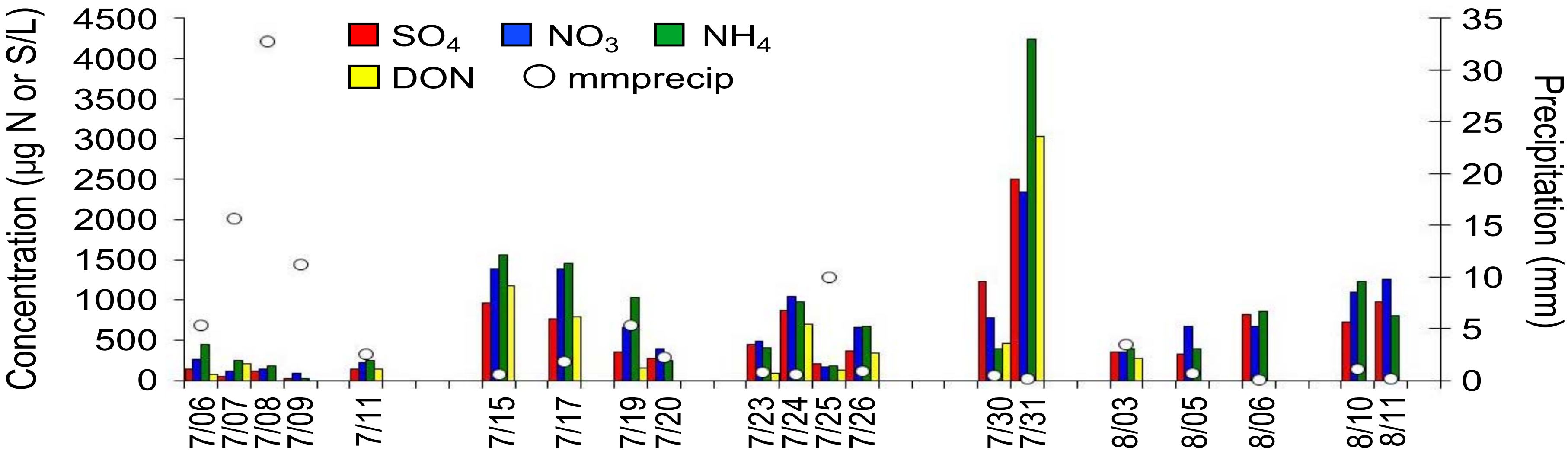
Comparison of visibility on clear day and a day with V_r=25 km

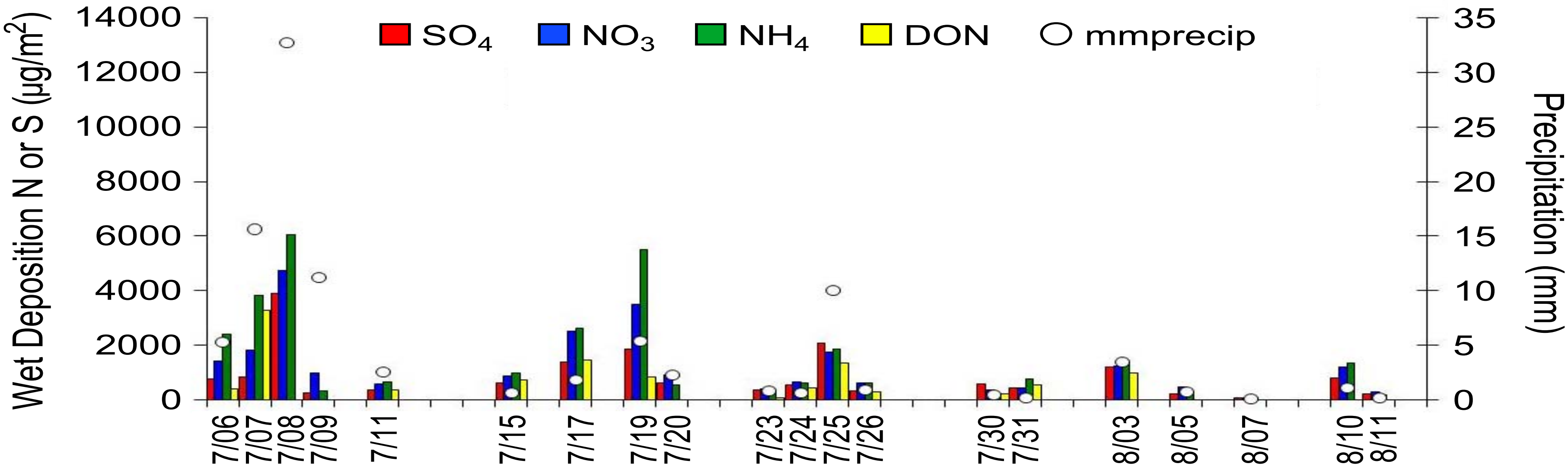


Wet Concentration and Deposition (Spring)

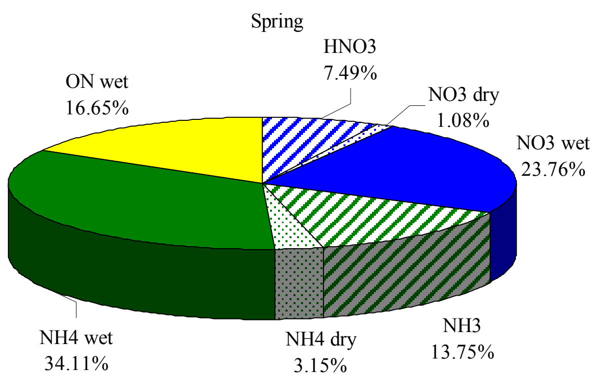


Wet Concentration and Deposition (Summer)

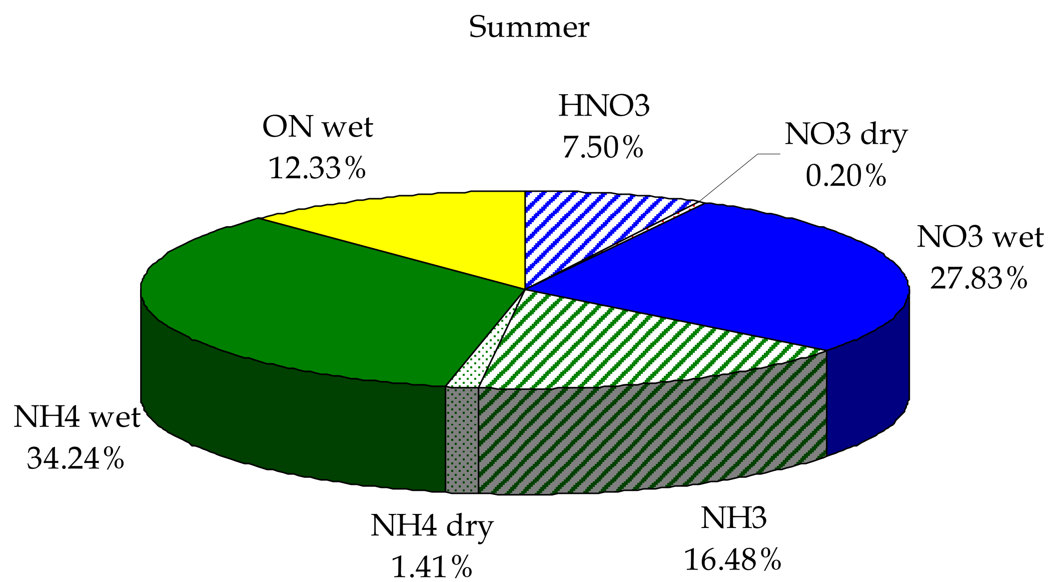




Relative contributions of individual N deposition pathways to total measured N deposition



SPRING
Total Dep=3326 ug/m2

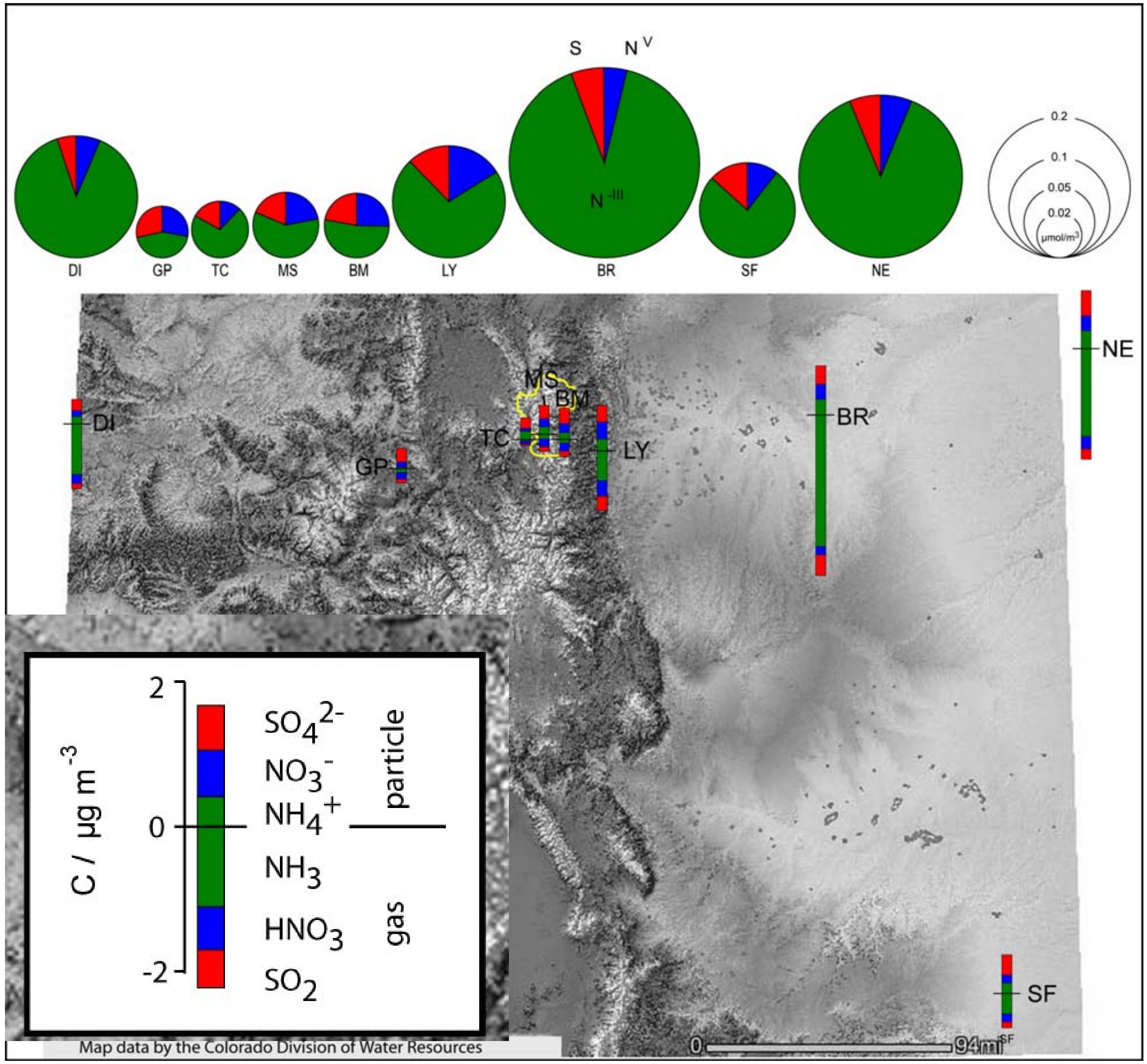


SUMMER
Total Dep = 6228 ug/m2

Concentration Gradients

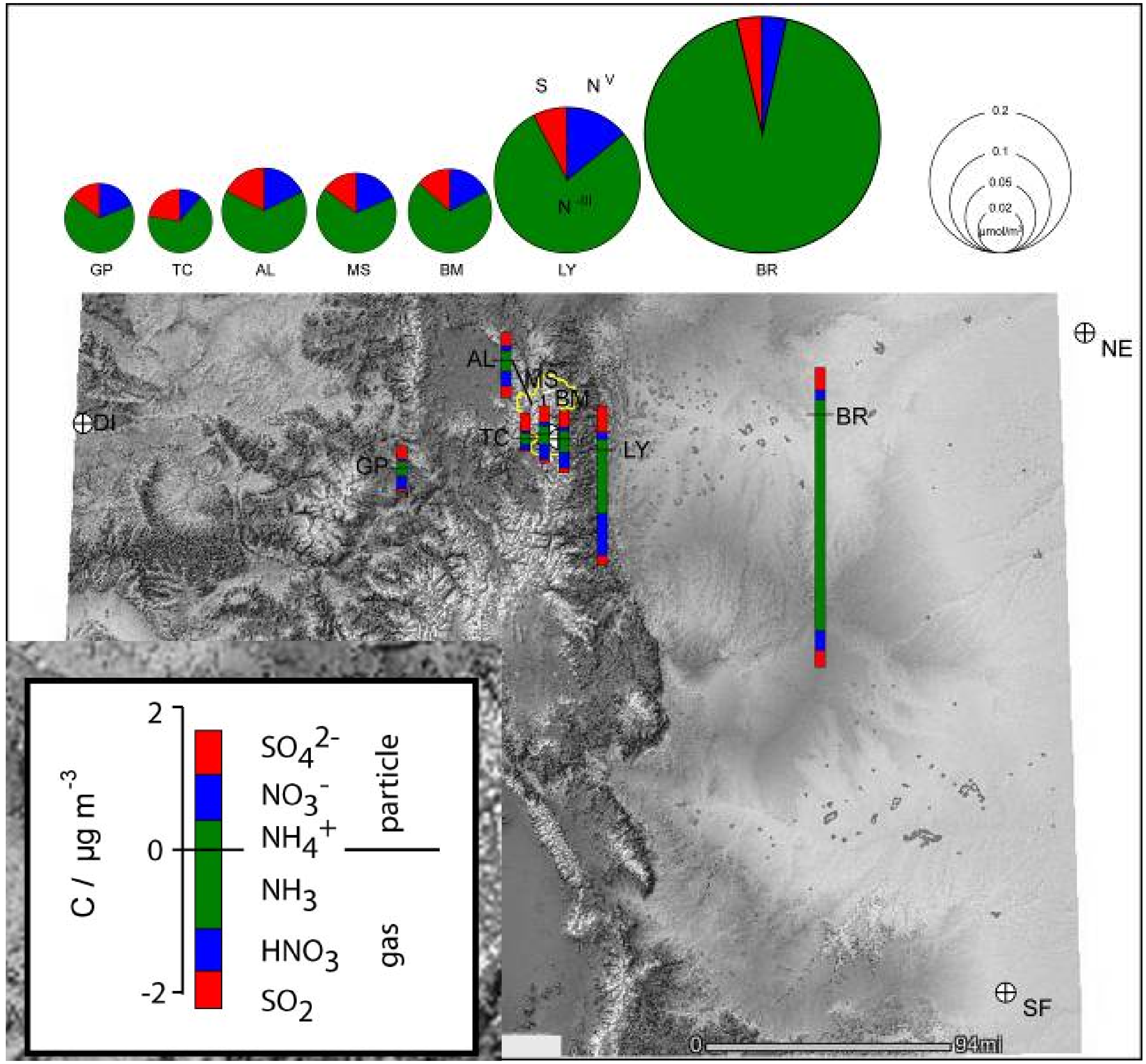
Spring overview

- Concentrations lower in mountains
- Gases dominate at eastern and western sites
  - Highest ammonia at Brush in NE Colorado
- Particles dominate in mountains

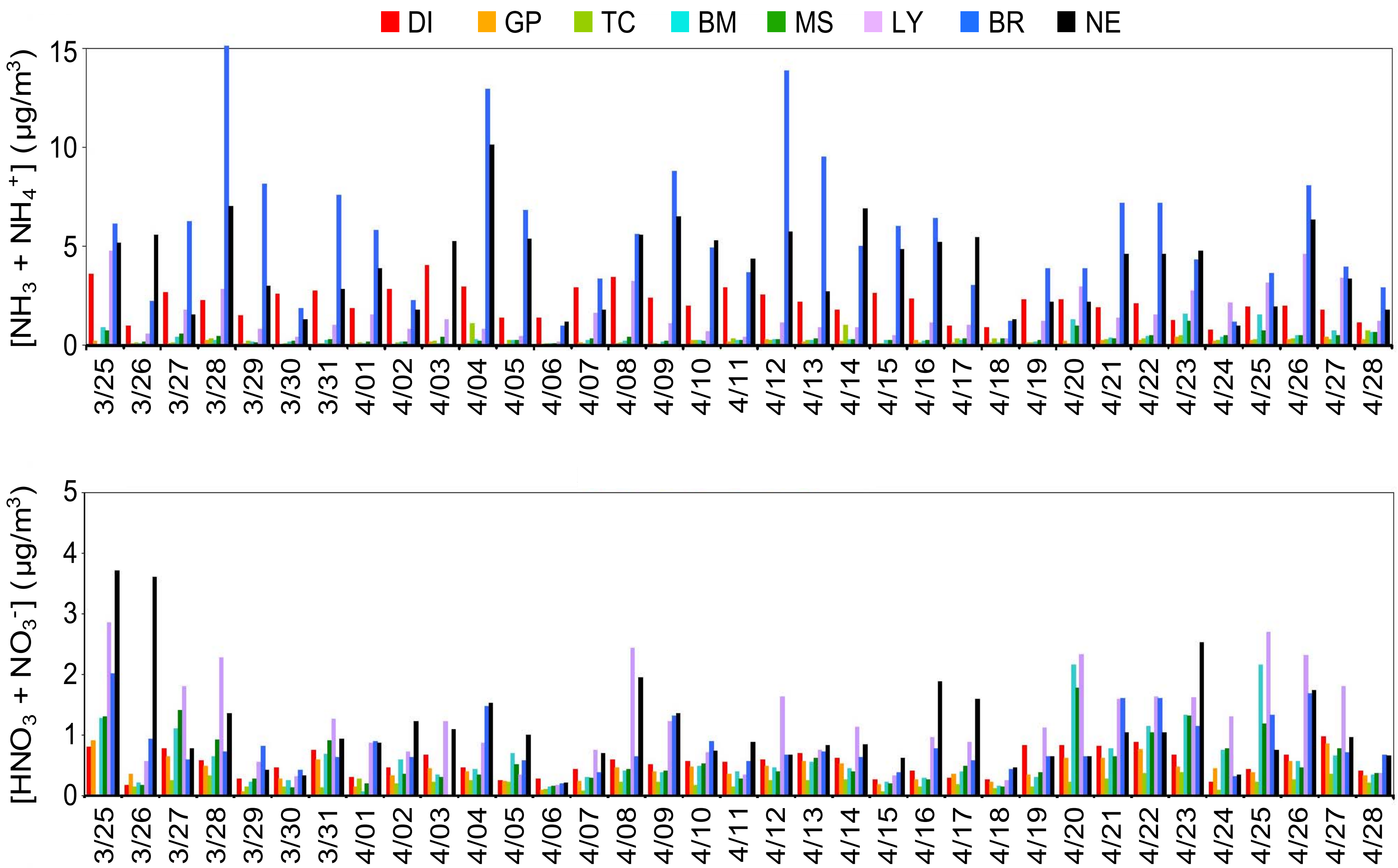


Summer overview

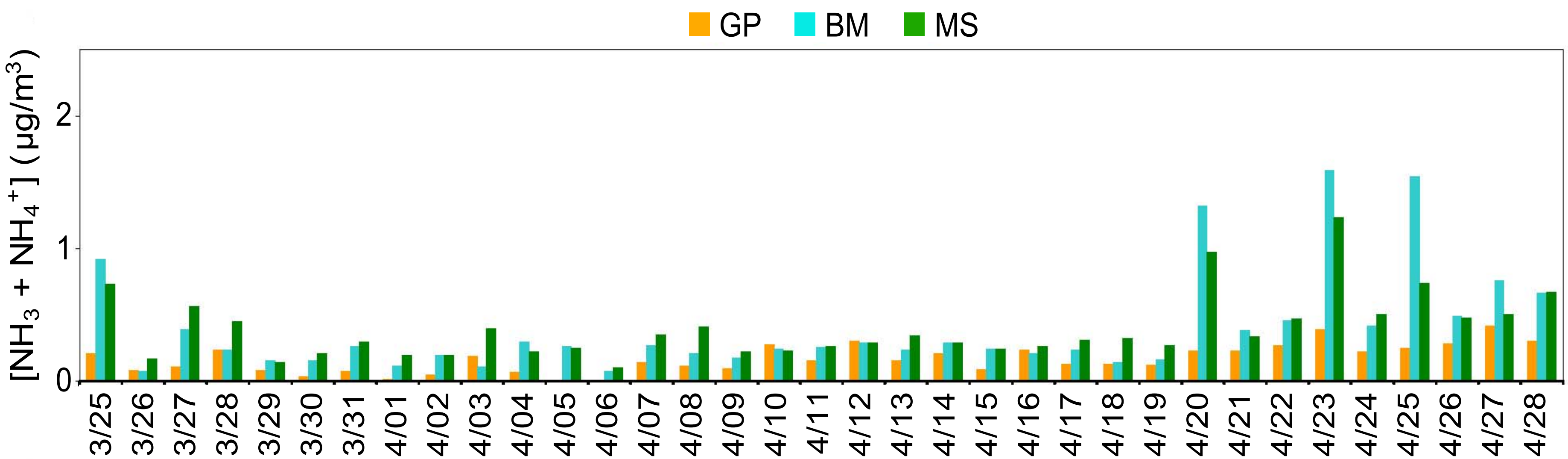
- Concentrations higher than in spring
- Highest concentrations again east of RMNP
- Increasing N gas importance in mountains

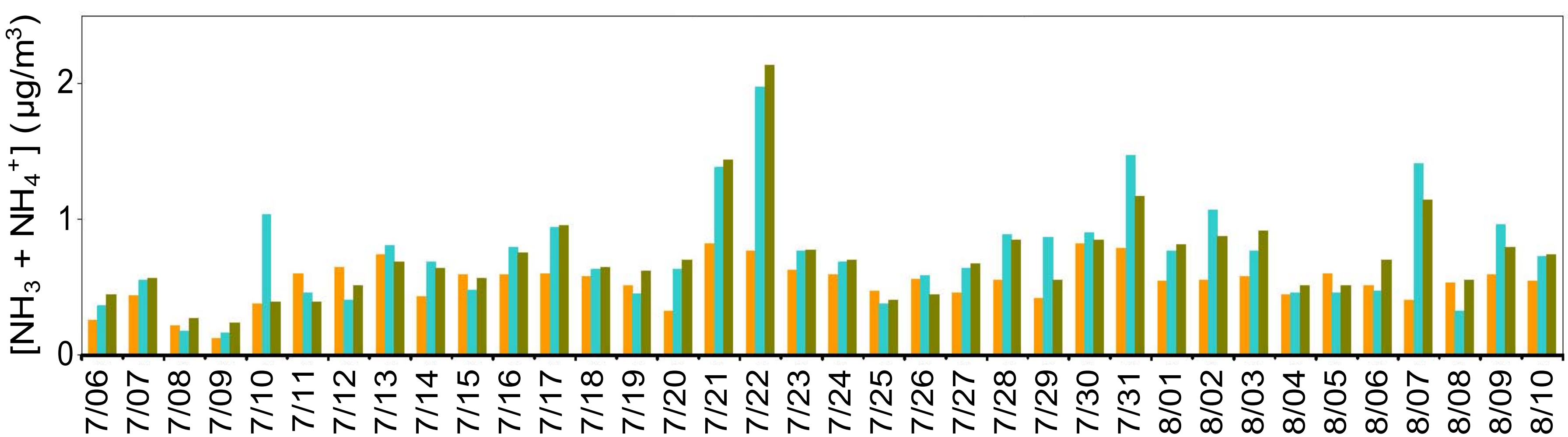


Concentration Gradient Across Monitoring Network

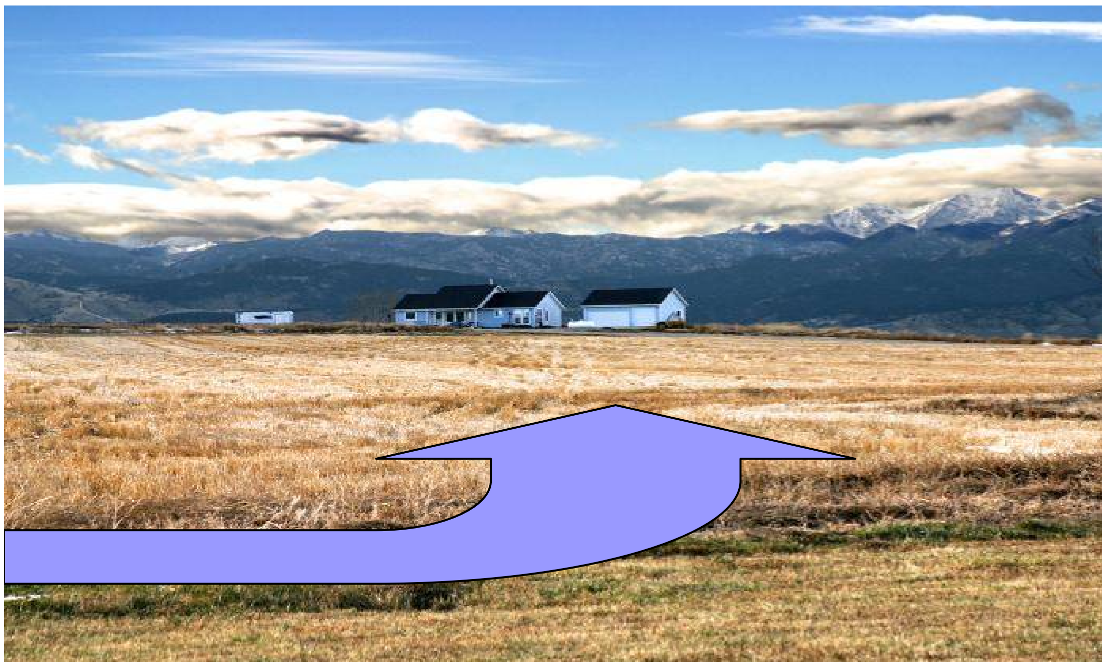


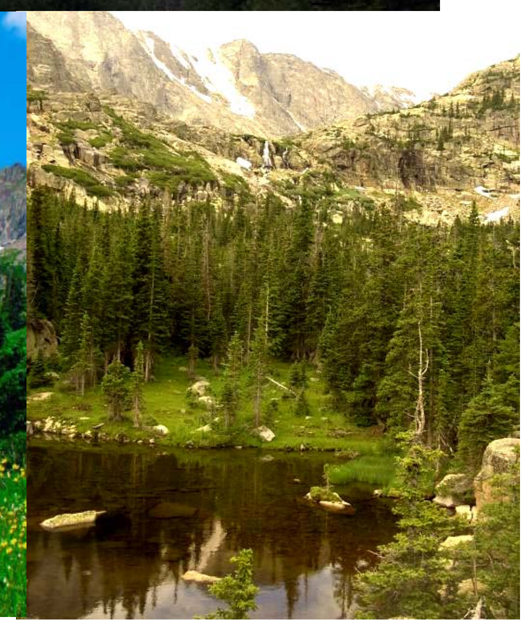
Concentration Gradient Across Rocky Mt NP





Colorado Front Range Upslope Events

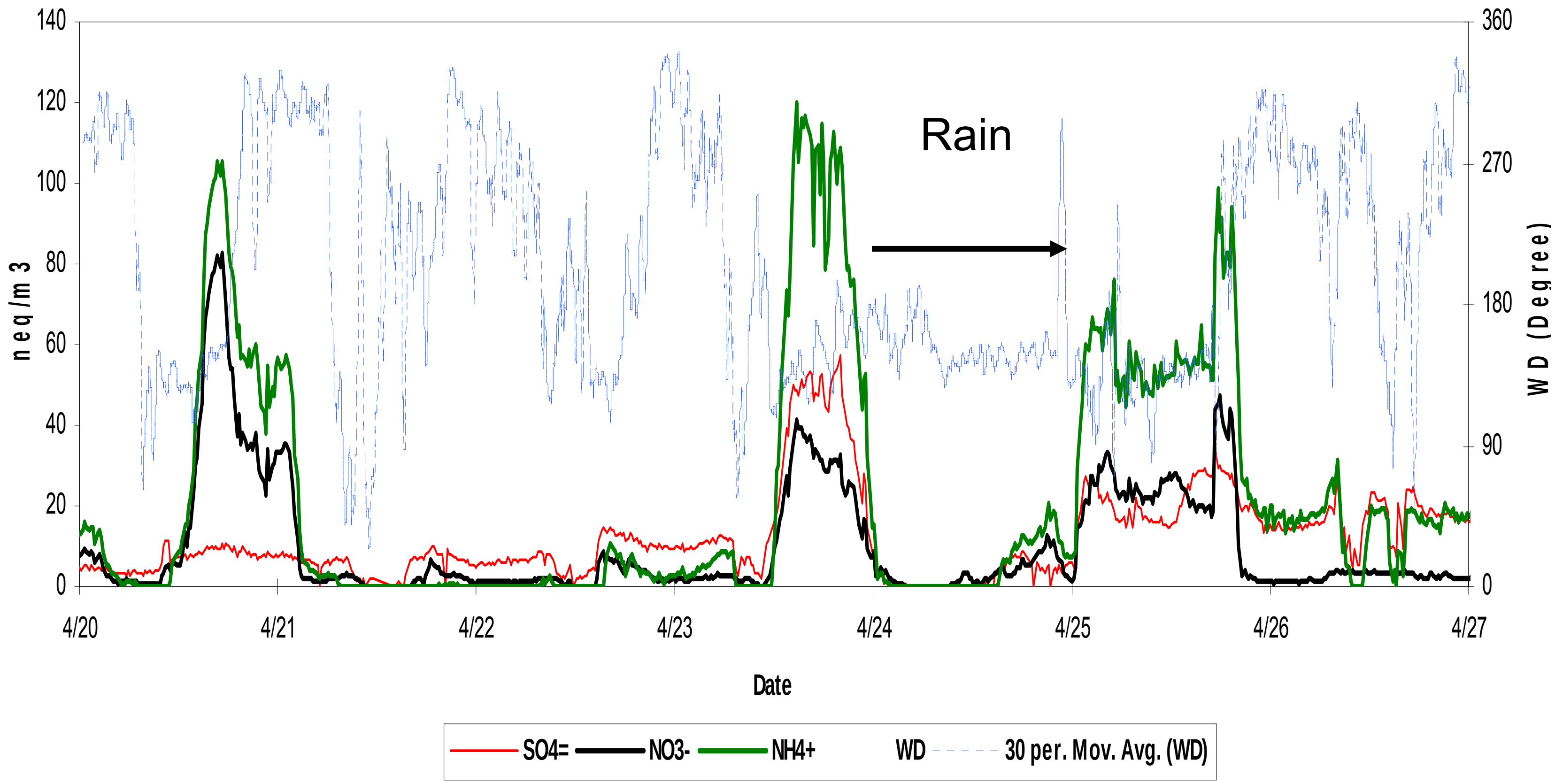




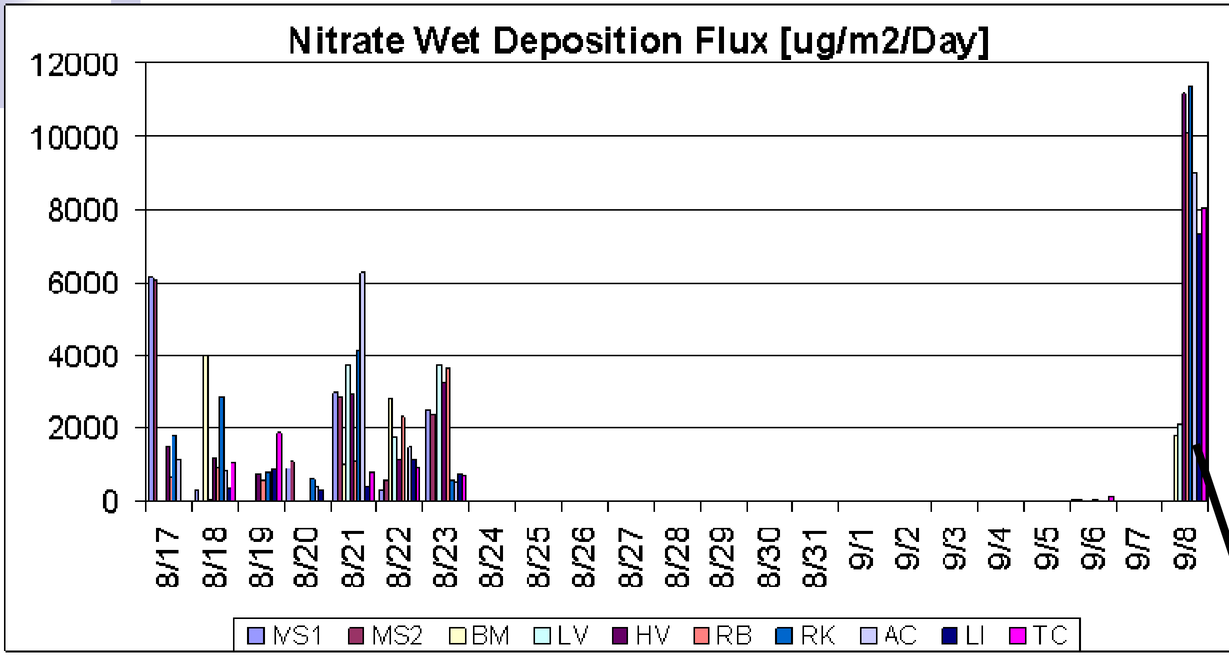
- Easterly Winds Transport Airmasses from Front Range and Further East to Rocky Mountain

Wind Direction for a Major Episode

WIND DIRECTION AND PARTICLE CONCENTRATIONS

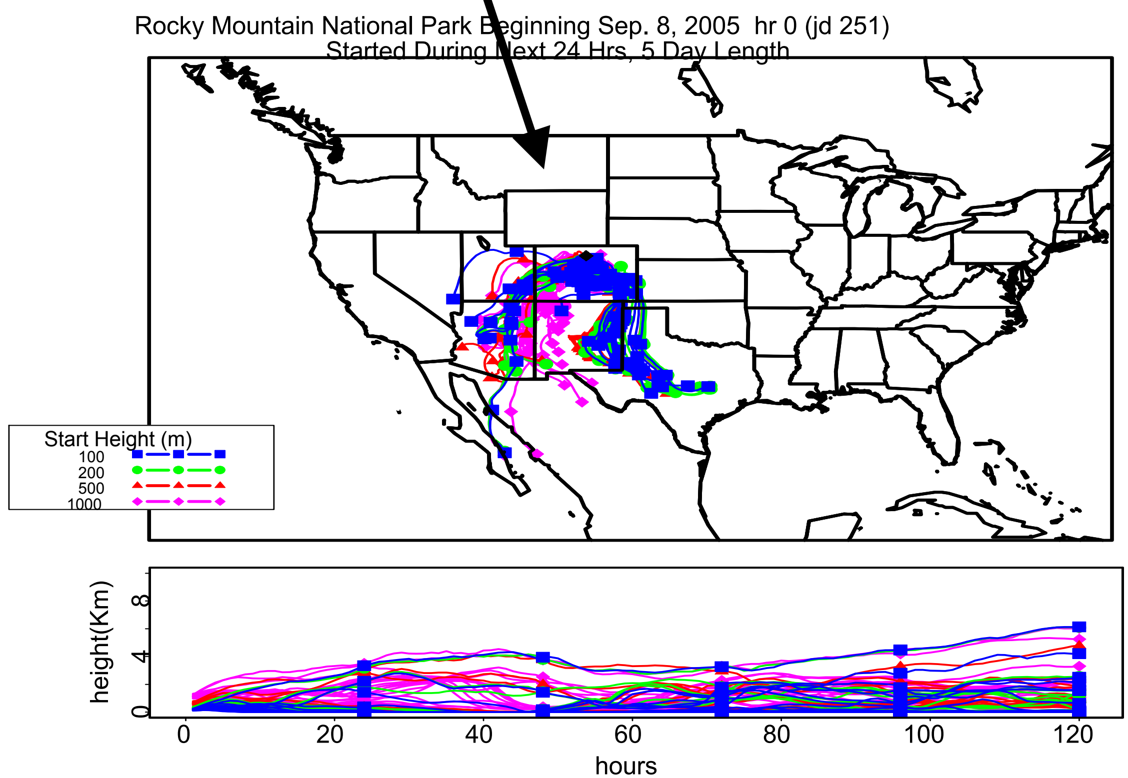


Simple Trajectory Analysis

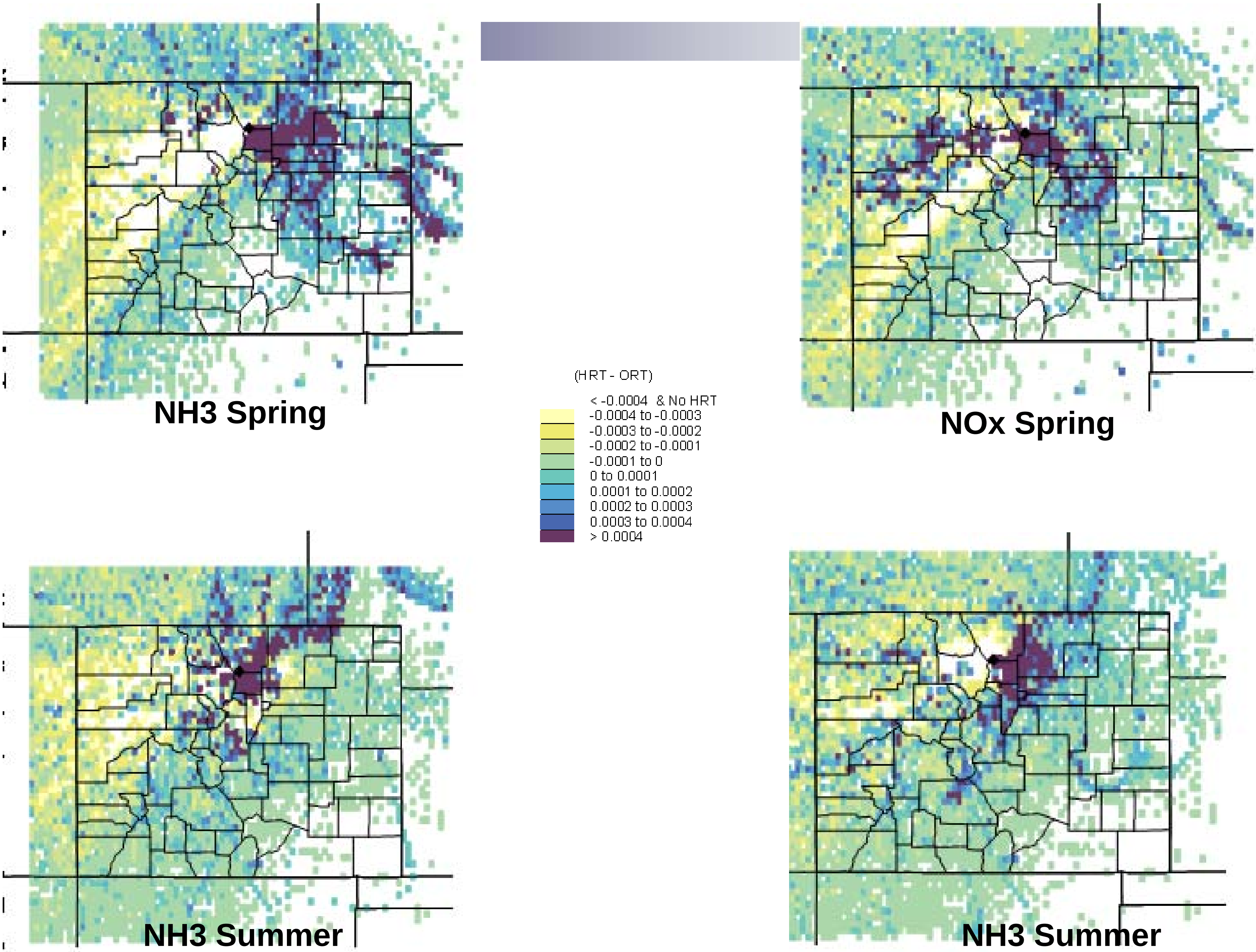


However, most of the upslope events were associated with precipitation events – accounts for between 80-90% of the deposition.

Upslope trajectories occurred: Aug 20-22, Sept 2-3, 6, 8

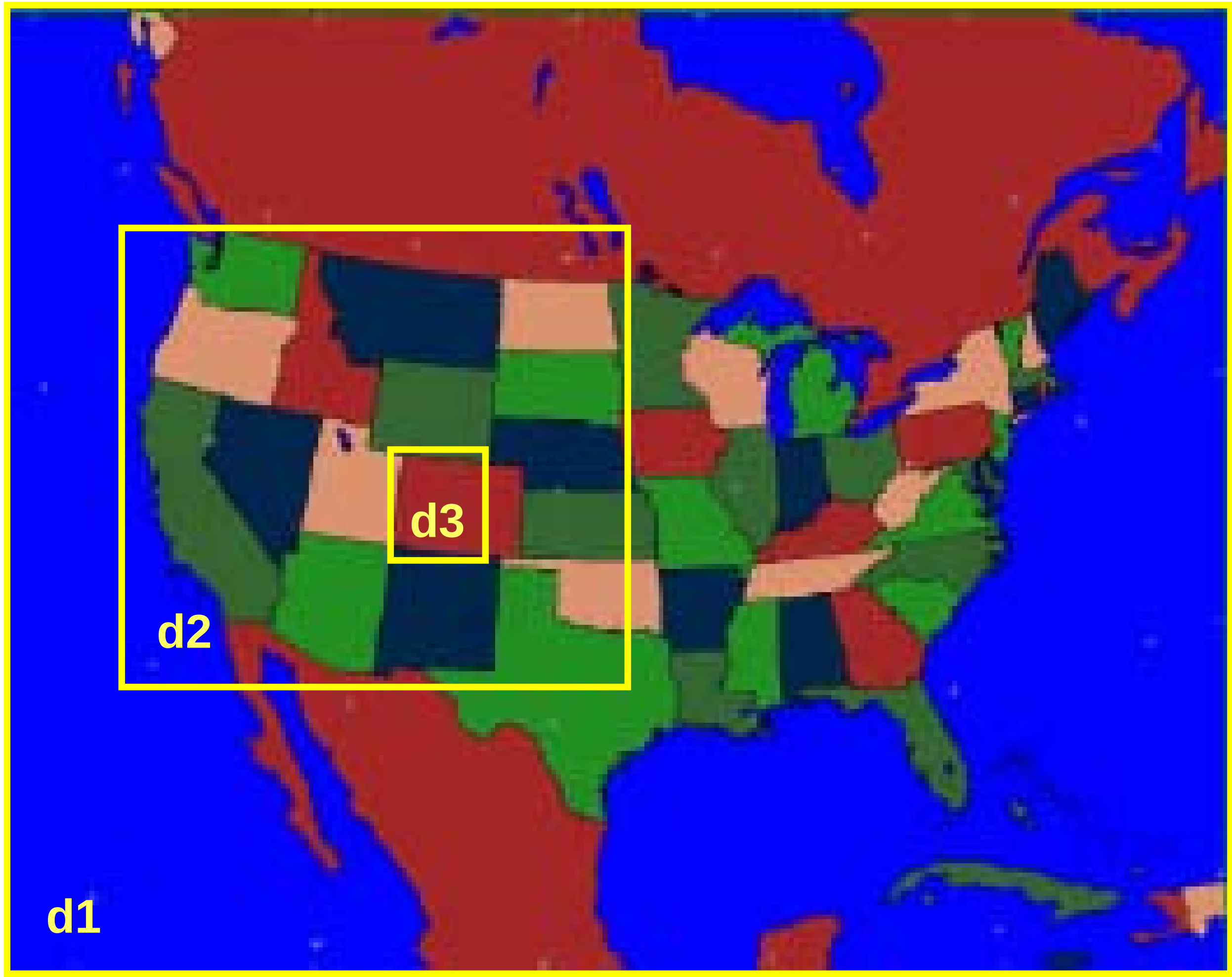


Statistical Analysis of Many Trajectories (Residence Time)

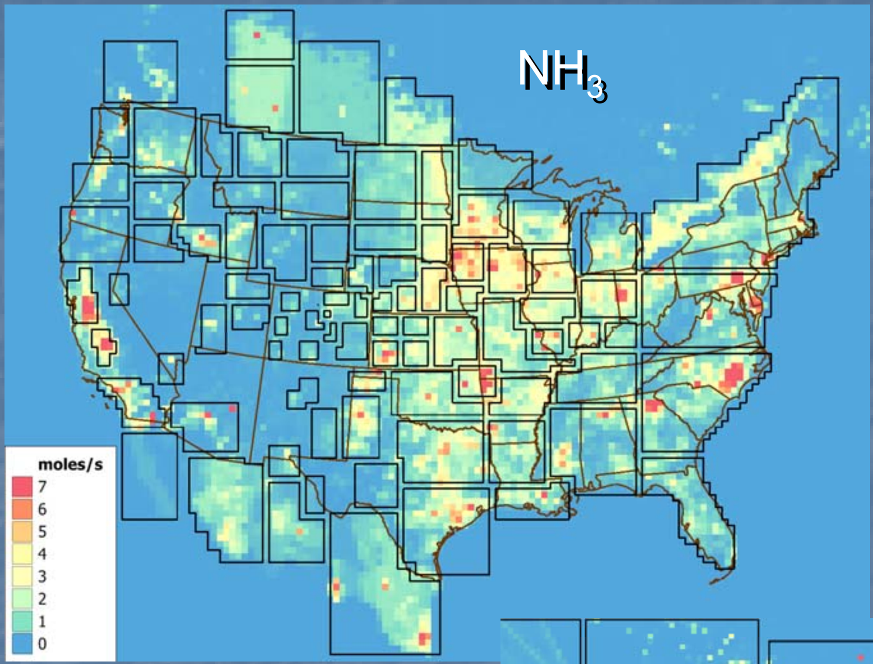

NH3 Spring
NOx Spring
(HRT - ORT)
< -0.0004 & No HRT
-0.0004 to -0.0003
-0.0003 to -0.0002
-0.0002 to -0.0001
-0.0001 to 0
0 to 0.0001
0.0001 to 0.0002
0.0002 to 0.0003
0.0003 to 0.0004
> 0.0004
NH3 Summer
NH3 Summer

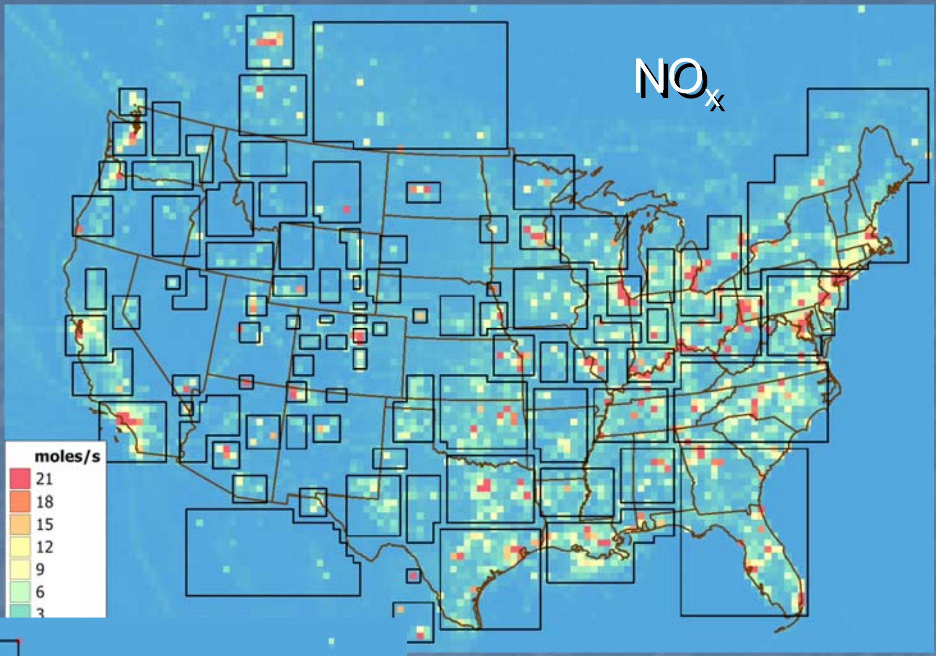
Apportionment of Gas/Particle Species Using Modeled Tracer

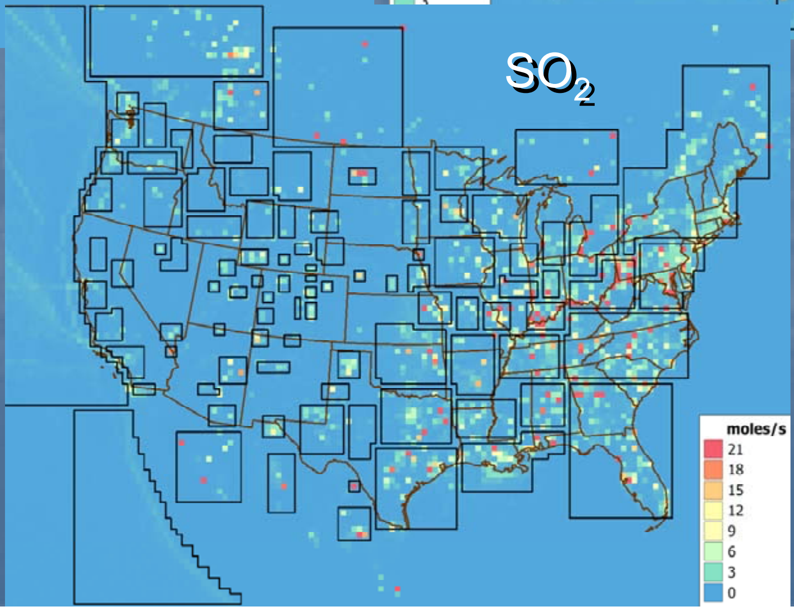
Existing CAMx 36 km and 12 km nested grids, and approximate location of 4 km grid



SOURCE REGIONS for CAMX RUNS







The receptor model

$$C_{ki} = \sum_{j} a_{kj} S_{ji} + \varepsilon_{ik}$$

Where

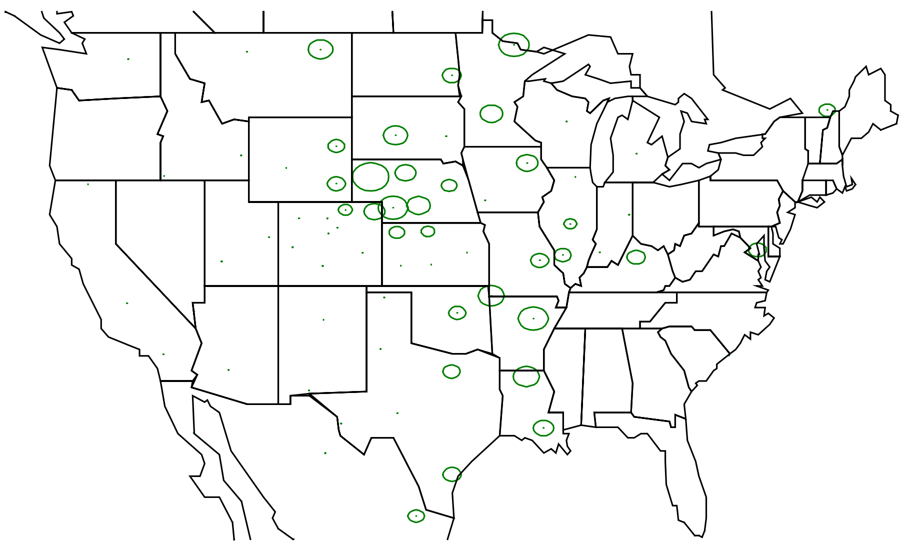
k = 1 ... m, the number of observations,
i = 1 ... n, the number of sources contributing to receptor,
j = 1 ... N, the number of source region vectors,
C_{ki} = concentrations of ammonia from source i for time period k,
a_{kj} = time weighting functions, and
S_{ji} = source vectors.
ε_{ik} = error term including random and lack of fit error.

$$(C)_k = \sum_{j} \alpha_{jk} \Phi_{jk}$$

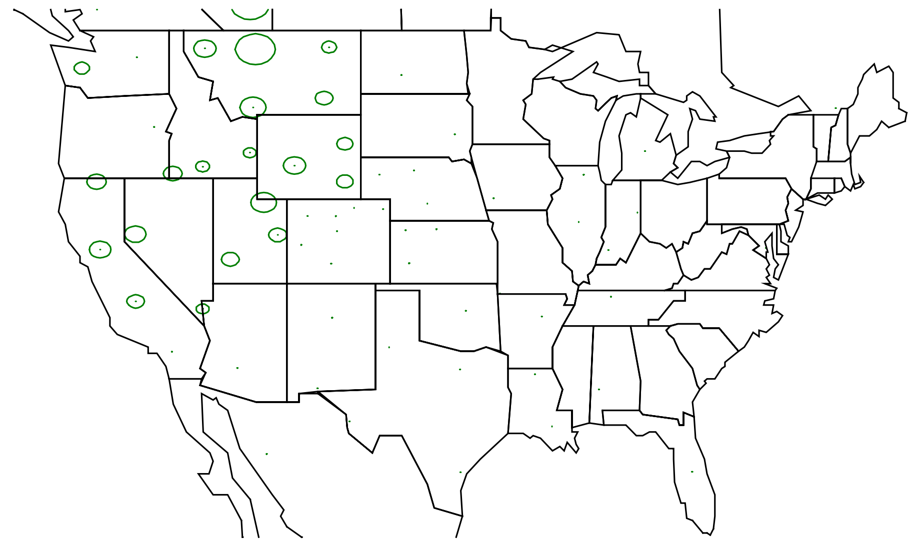
C_k = the measured hourly aerosol concentrations
A_{jk} = the regression coefficients
Φ_{jk} = the average of modeled concentrations arriving at the receptor from sources areas grouped according to eigenvectors, *v*

Grouping of Source Regions

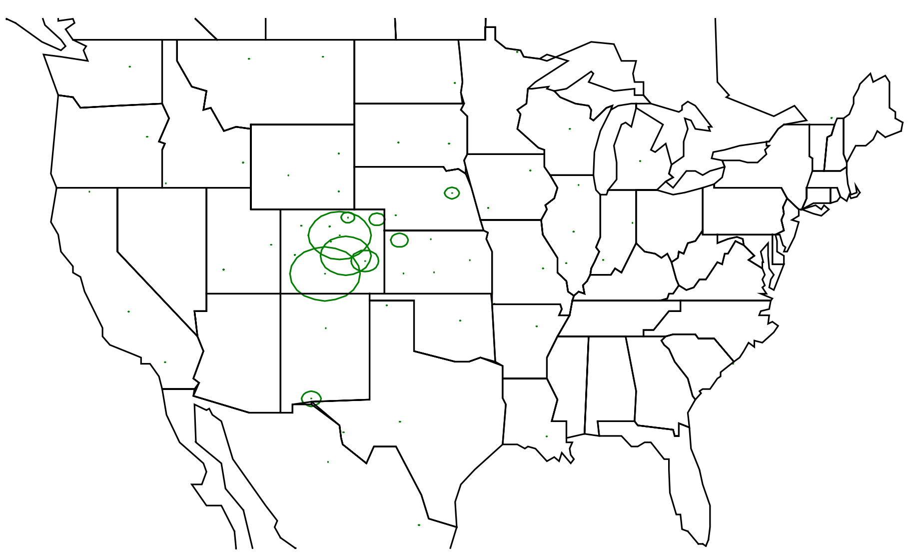
Spring NH_3/NH_4 Northeast Region



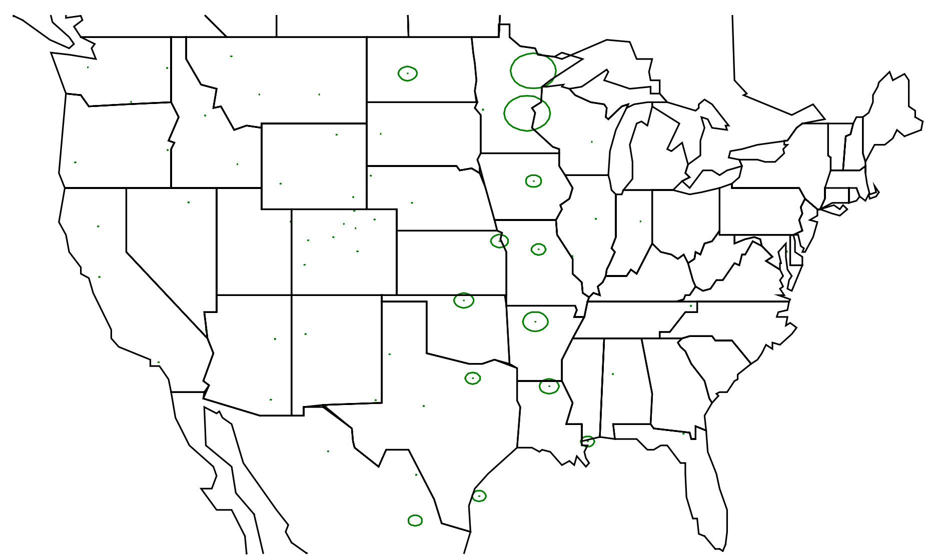
Spring NH_4 Region 7



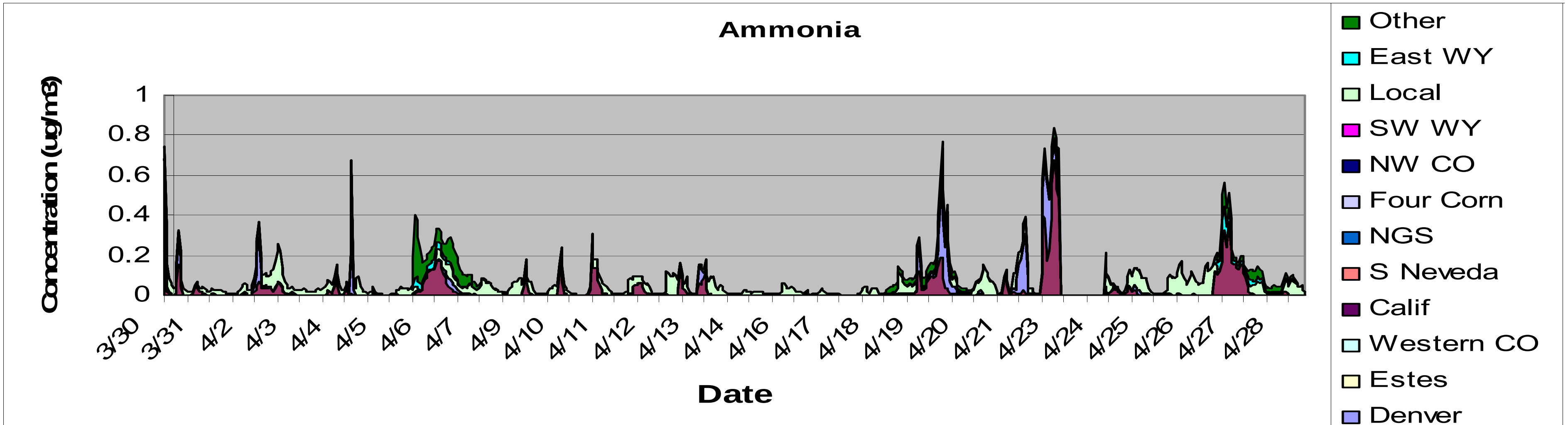
Spring NH_3/NH_4 Region 8

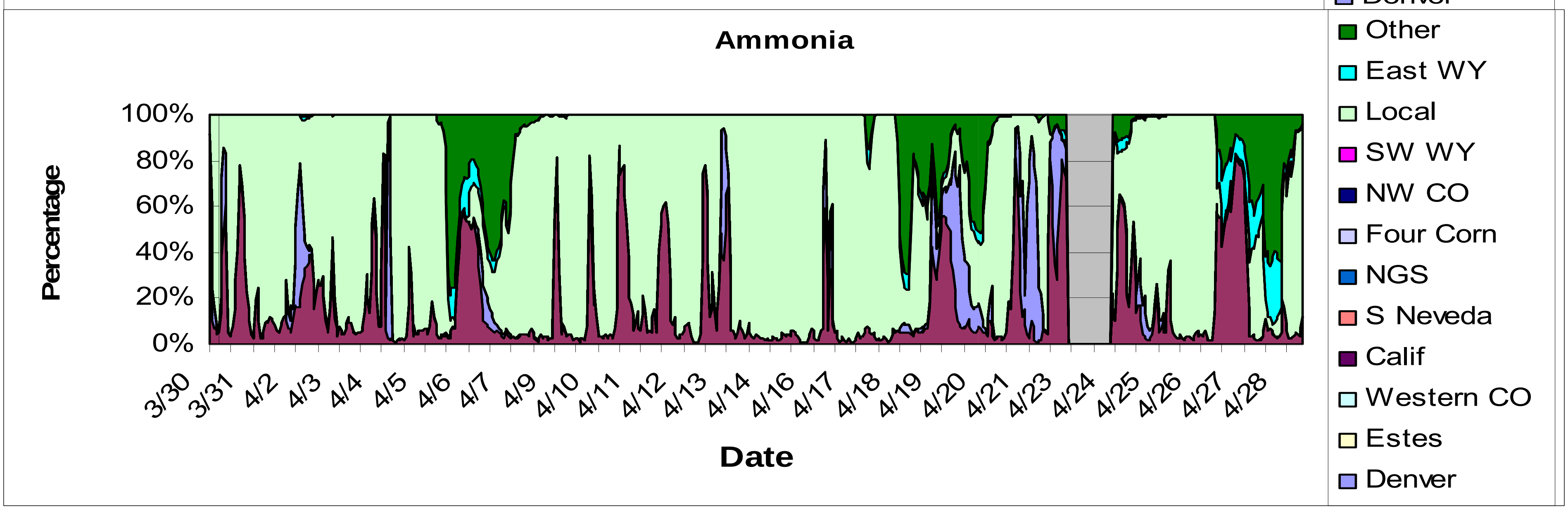


Spring NO_X Region 2

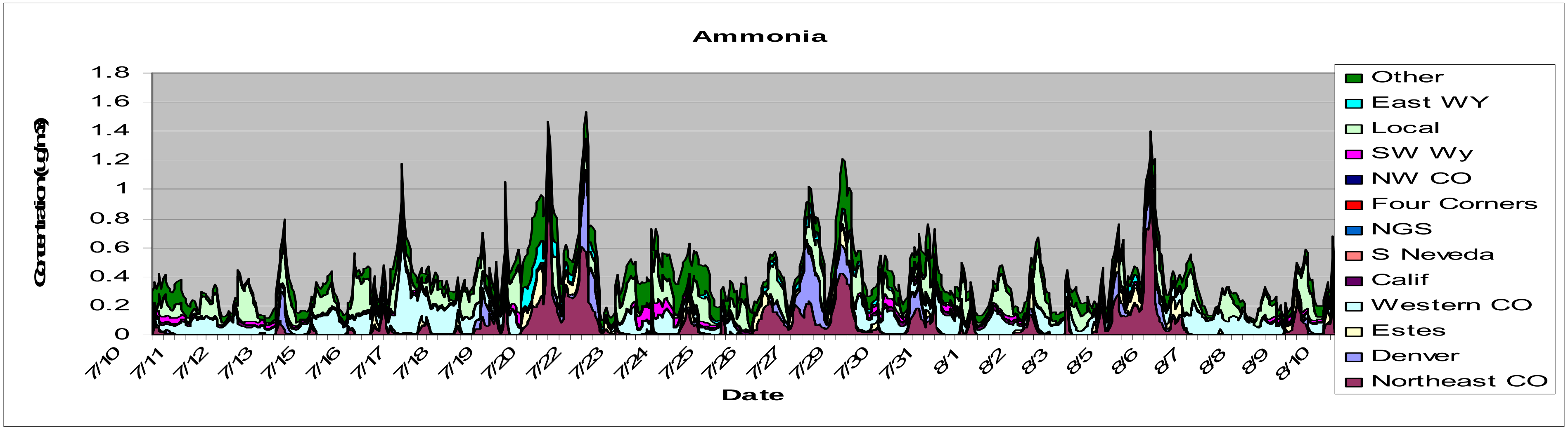


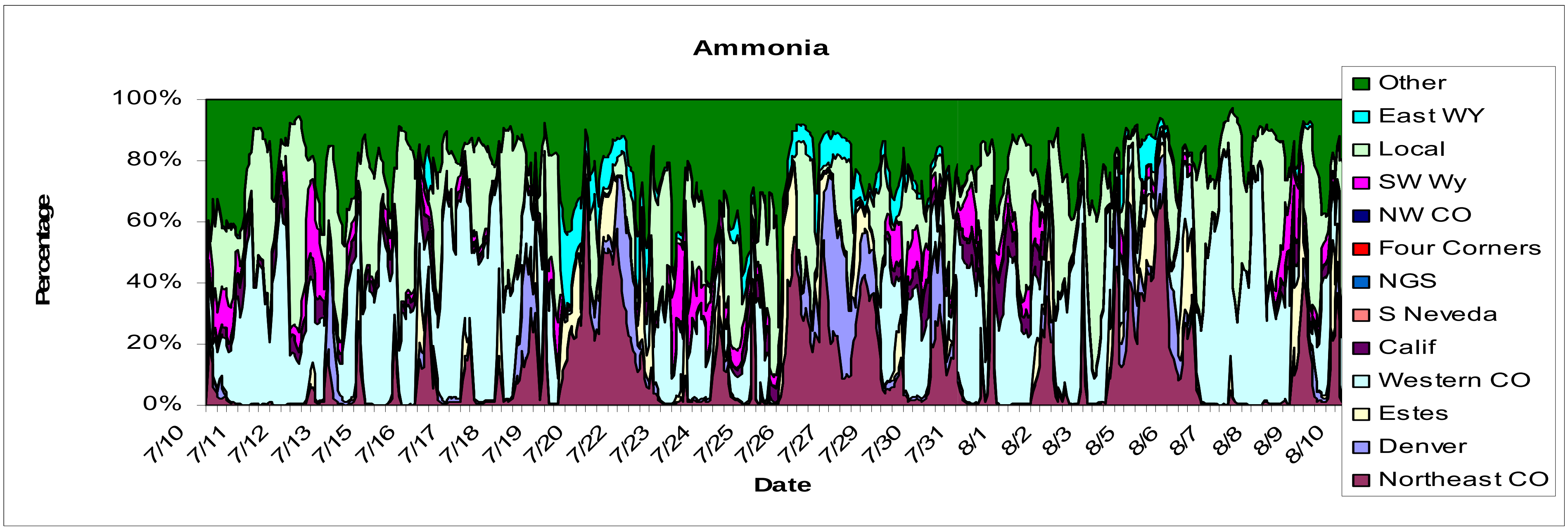
APPORTIONMENT TO SOURCE REGIONS (NH_3 SPRING)



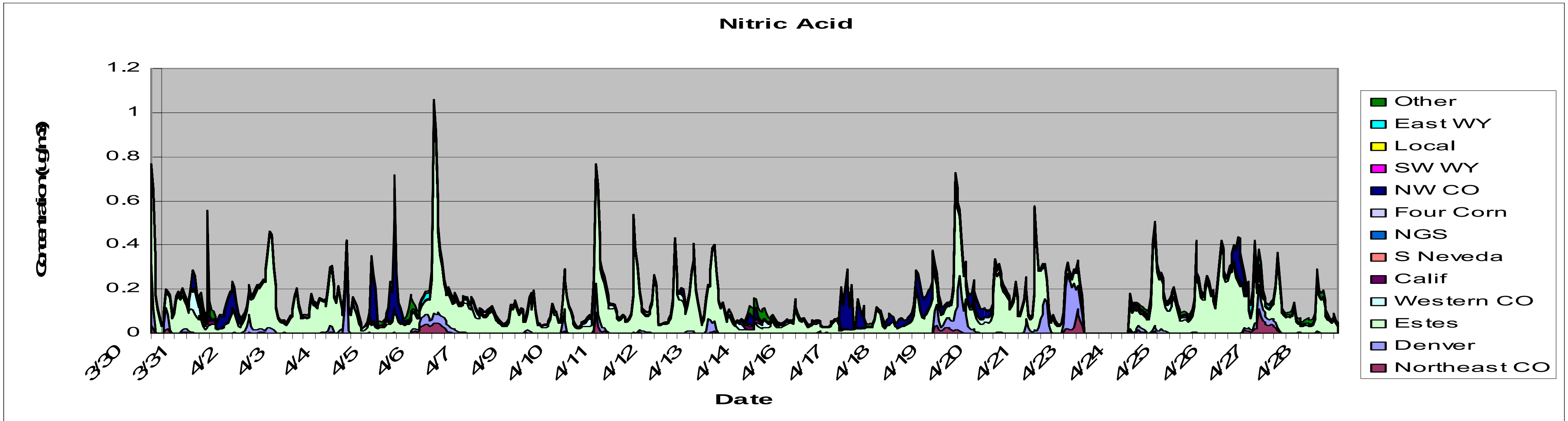


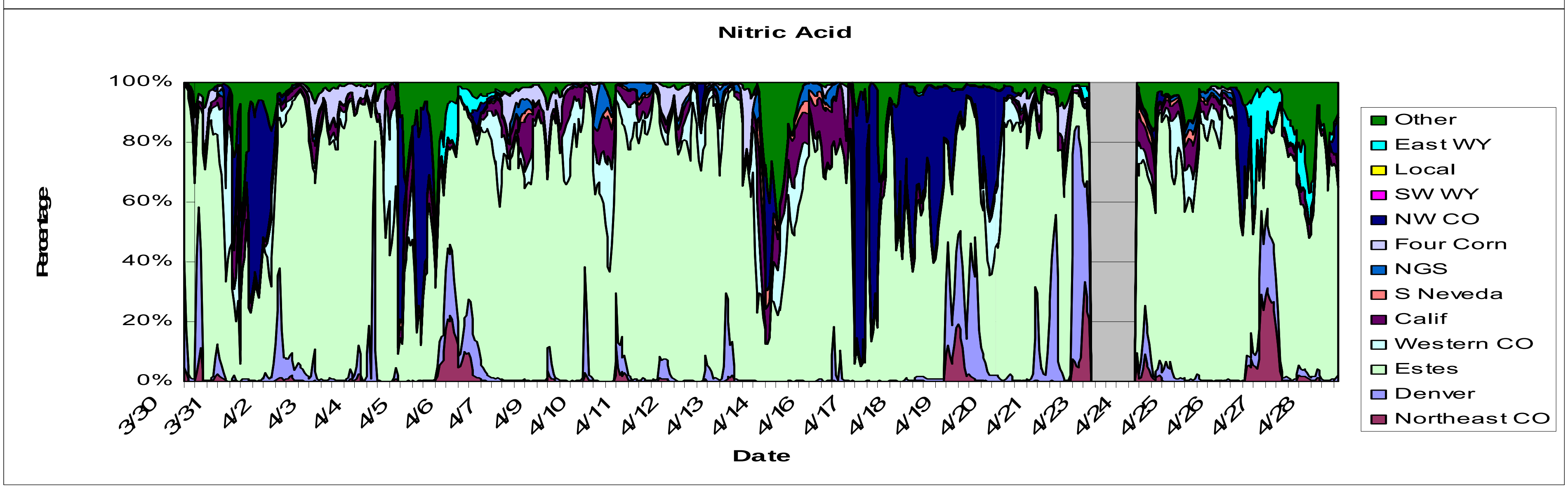
APPORTIONMENT TO SOURCE REGIONS (NH_3 SUMMER)



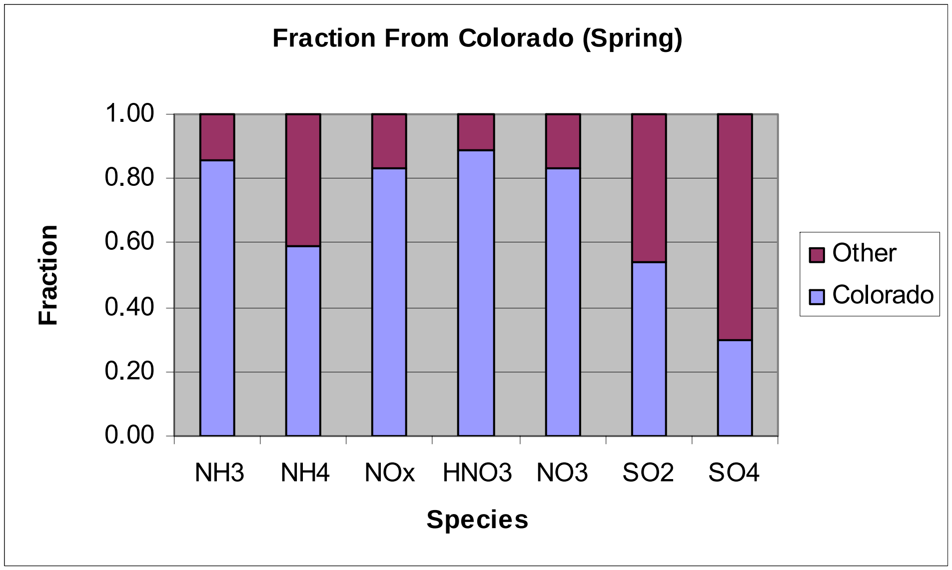


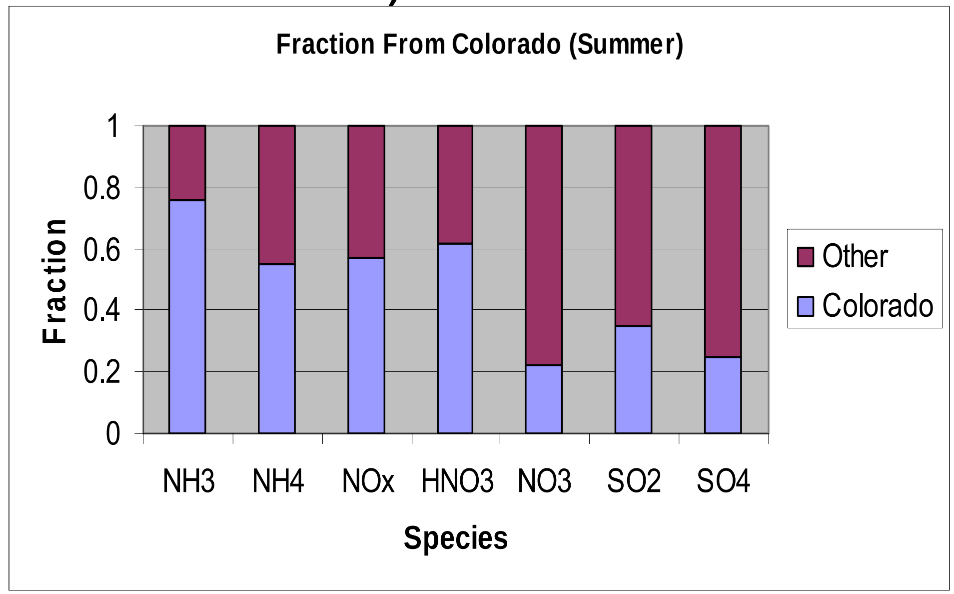
APPORTIONMENT TO SOURCE REGIONS
(HNO_3 SPRING)

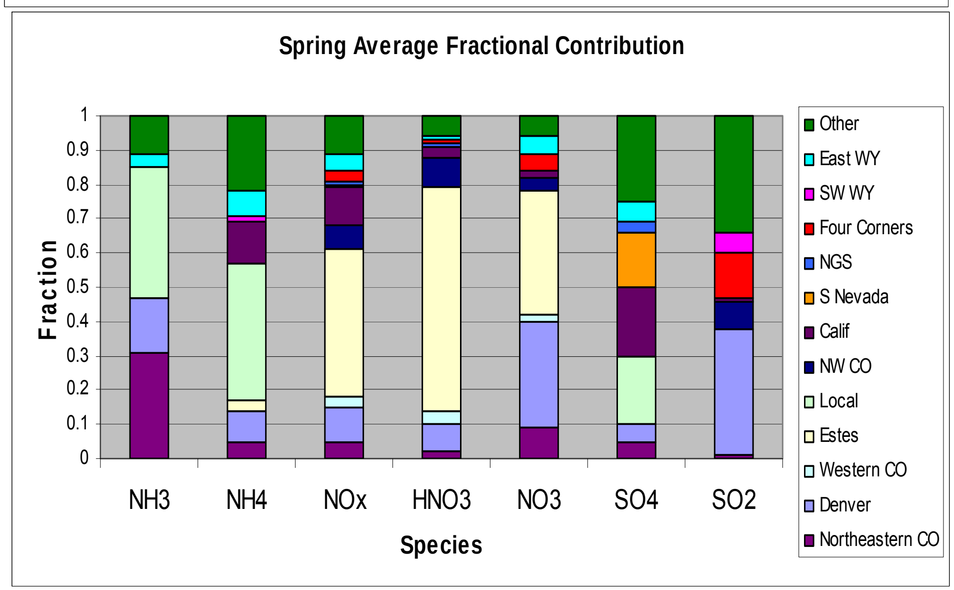


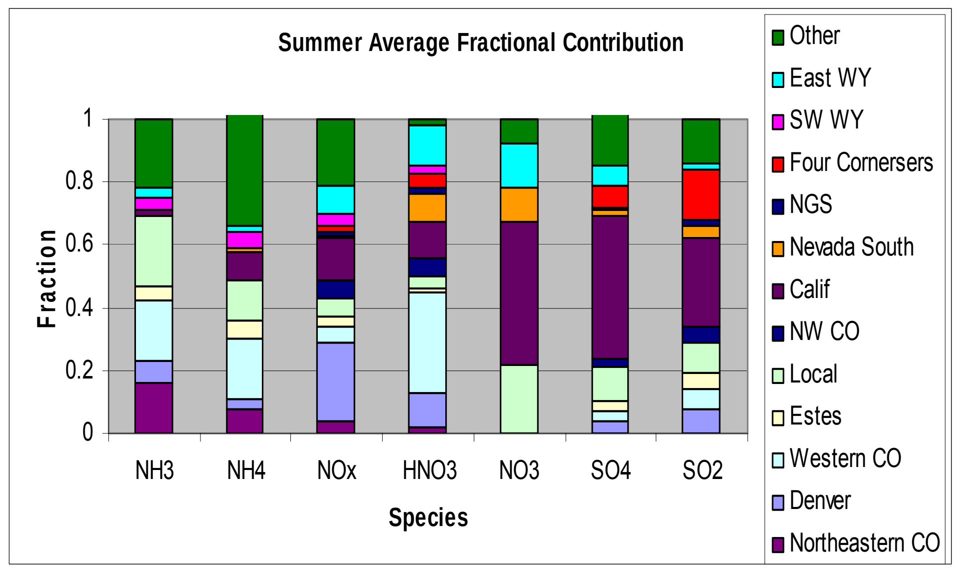


Average Apportionments
(gas/particle concentrations)

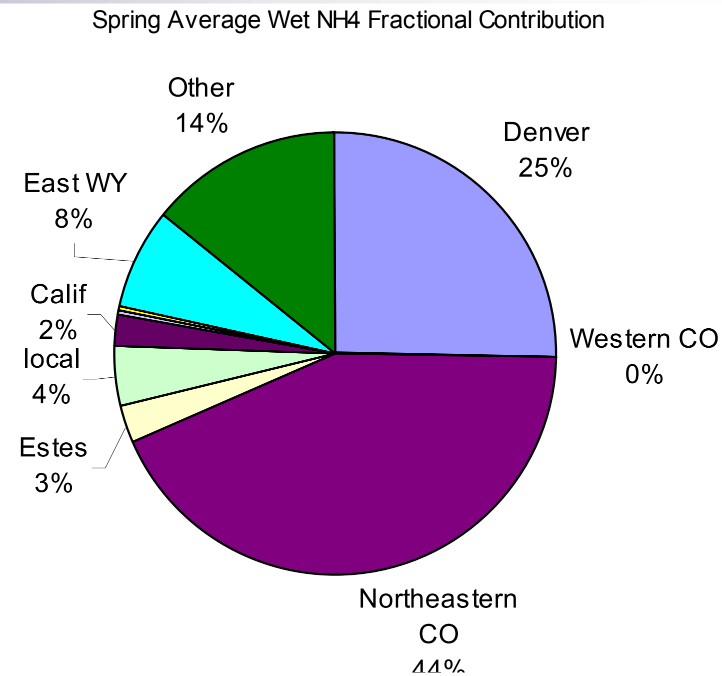


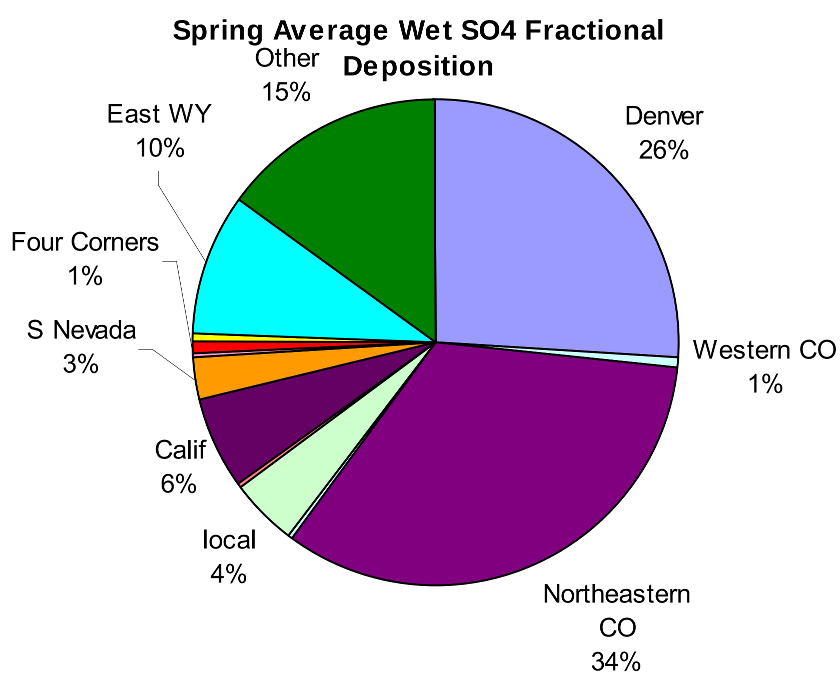


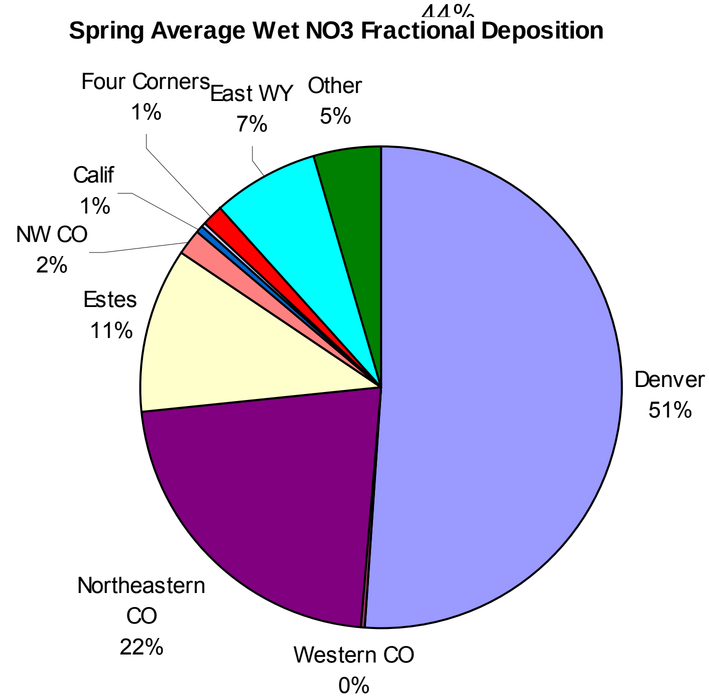




Average Spring Apportionments
(wet deposition)

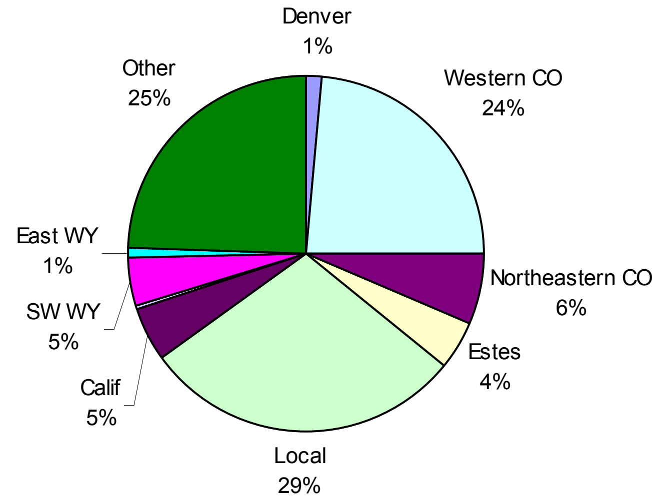




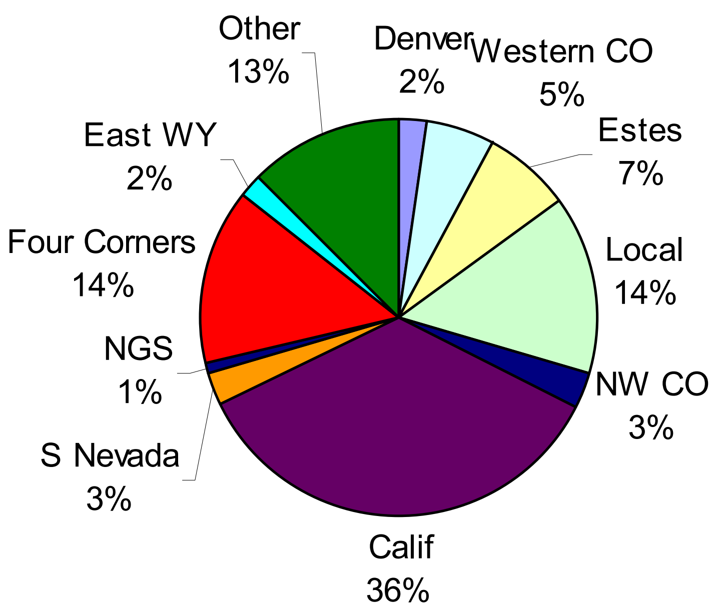


Average Summer Apportionments
(wet deposition)

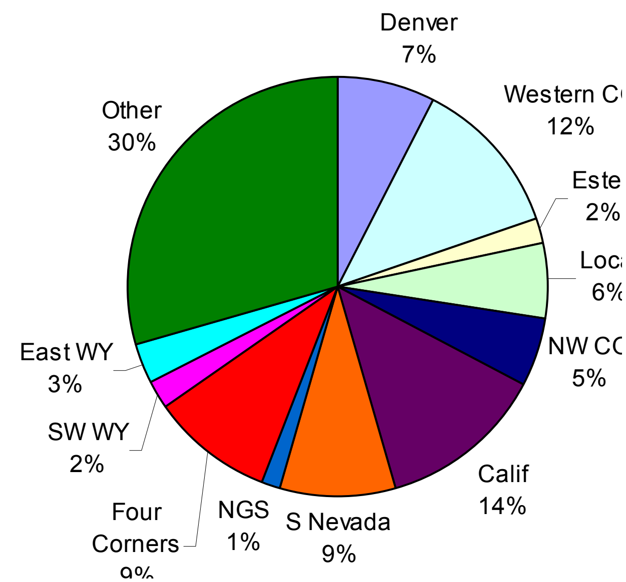
Summer Average NH4 Fractional Wet Deposition



Summer Average SO4 Fractional Wet Deposition



Summer Average NO3 Fractional Wet Deposition



SUMMARY

- A substantial portion of ammonia, ammonium, nitrate, and nitric acid originates in the state of Colorado.
- Sulfur species tend to more associated with longer range transport and come from outside the state.
- More sources contribute during the summer than spring.
- Natural emissions of ammonia appear to contribute significantly to ammonia and ammonium concentrations and deposition.
- During the Spring during upslope conditions northeastern Colorado contributes most of the ammonia and wet deposited ammonium.
- The town of Estes Park appears to contribute significantly to nitric acid and nitrate during the spring time frame.
- During the summer sources in California and off the coast of California contribute significantly.


END

FOOD FOR THOUGHT?