Estimating Temporal Trends in Biogenically Formed Secondary Organic Aerosols Resulting From Reduction in Sulfate and Atmospheric Aerosol Water Content Across the Continental United States.

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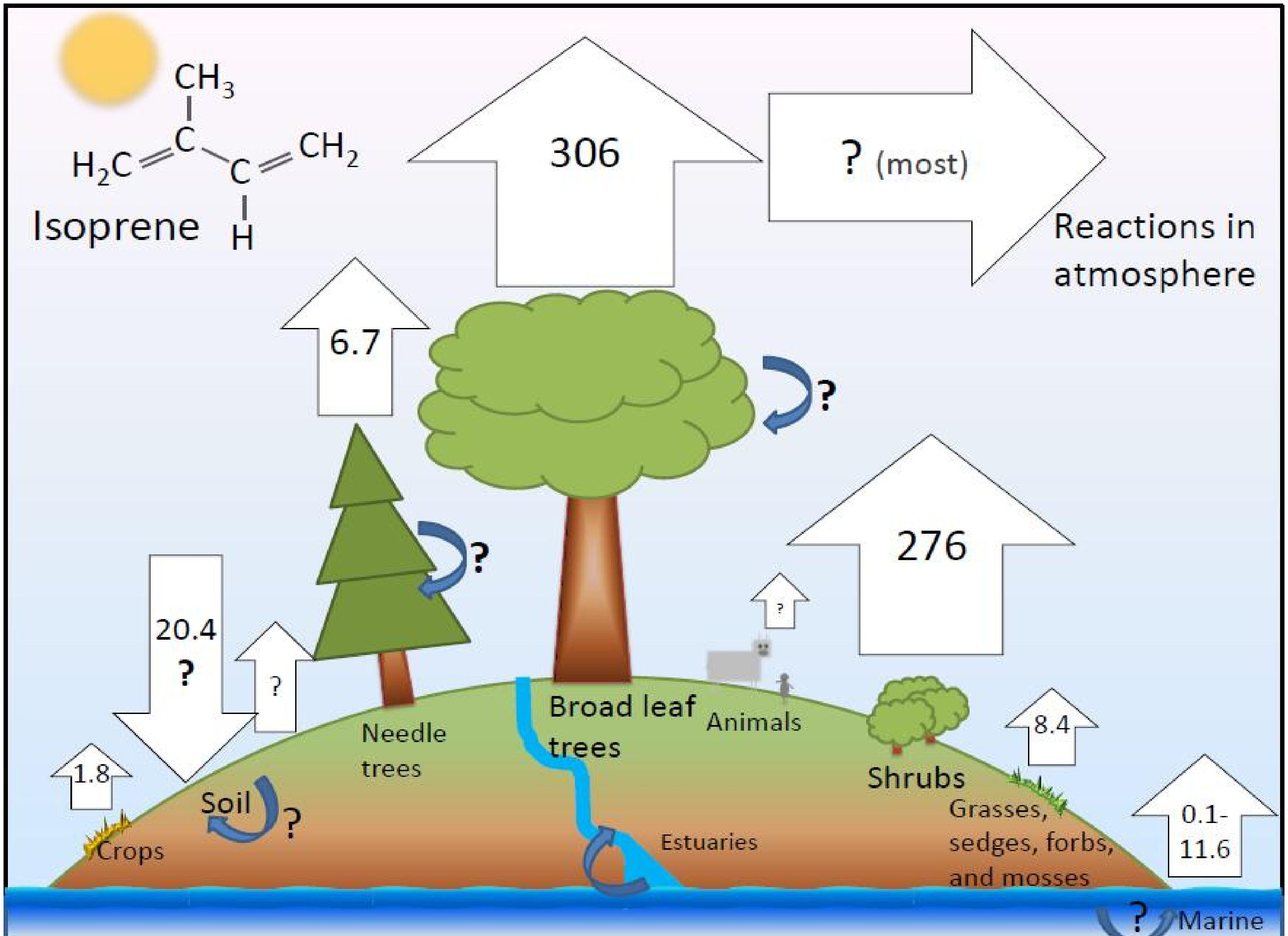
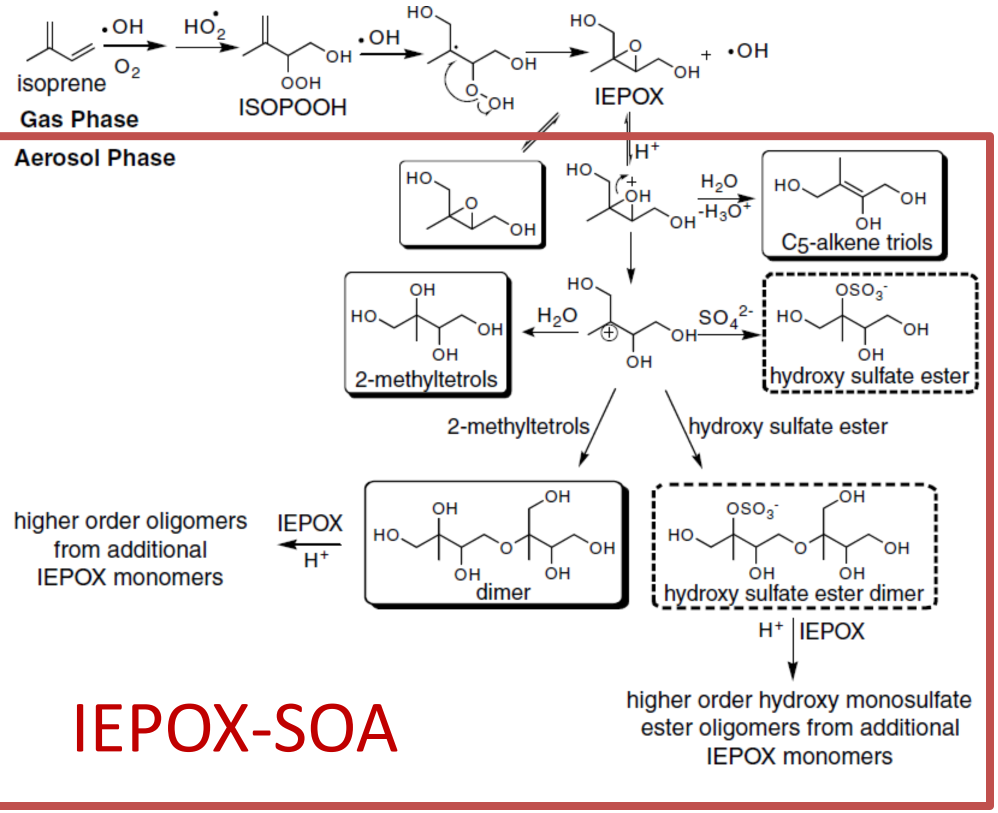
Substantial amounts of isoprene are emitted during summer months in many areas of the US – especially the Southeastern US



What is "IEPOX-SOA"?

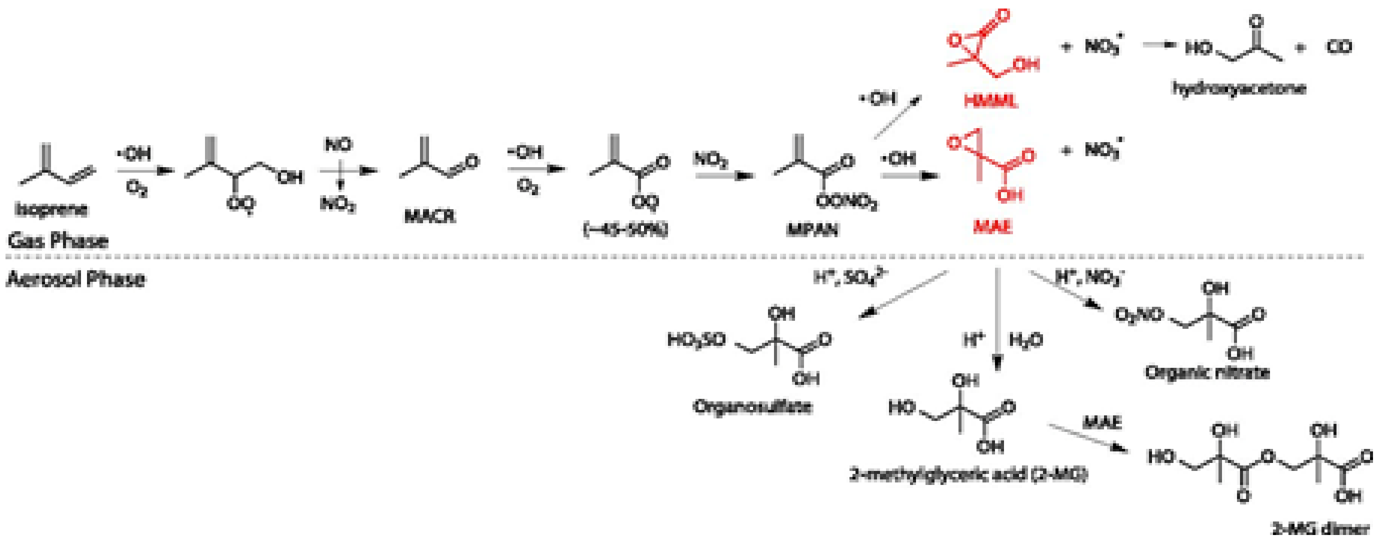
- IEPOX (Isoprene epoxidiol) formed from oxidation of isoprene under low NO conditions
- IEPOX uptake on acidic sulfate particles produces a variety of polyols, organosulfates and oligomers
- The sum of all these is IEPOX-SOA



Pedro Campuzano-Jost et al, 2016, Paulot et al, 2009, Surrat et al, 2010, Robinson et al., 2011; Budisulistiorini et al., 2013,

Biogenic isoprene emissions lead to nitrate containing SOA and nitrogen deposition

Proposed mechanism for SOA formation from isoprene photooxidation in the presence of NOx: Ying-Hsuan Lin et al. PNA 2013:110



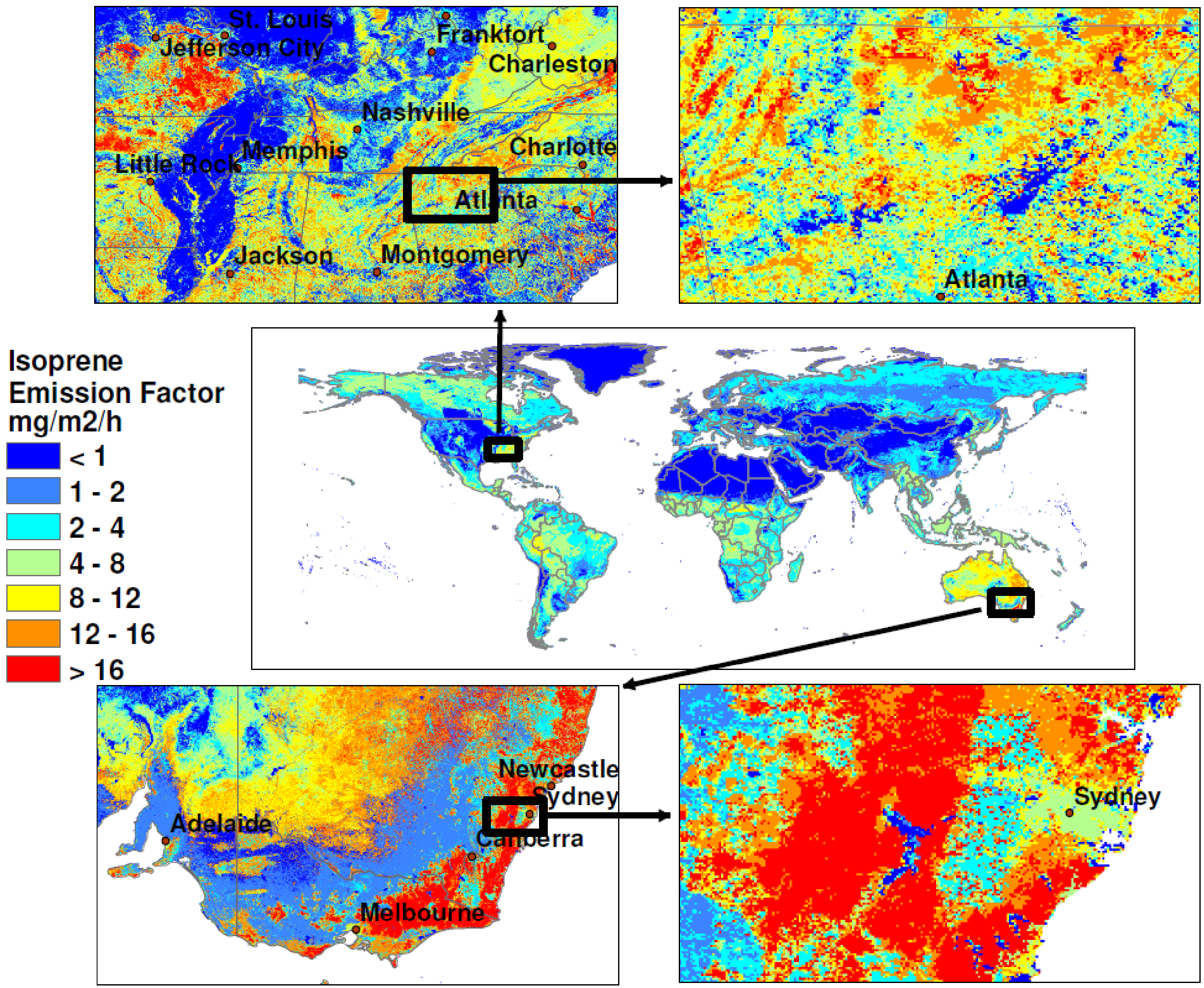
Kinetics of the reactions of isoprene-derived hydroxynitrates: gas phase epoxide formation and solution phase hydrolysis. Jacobs, M.I. et al. Atmos Chem Phys, 14, 2014.

Some background from a presentation:
"SOA derived from isoprene epoxydiols: Insights into formation, aging and distribution over the continental US from the DC3 and SEAC^{4}RS campaigns"

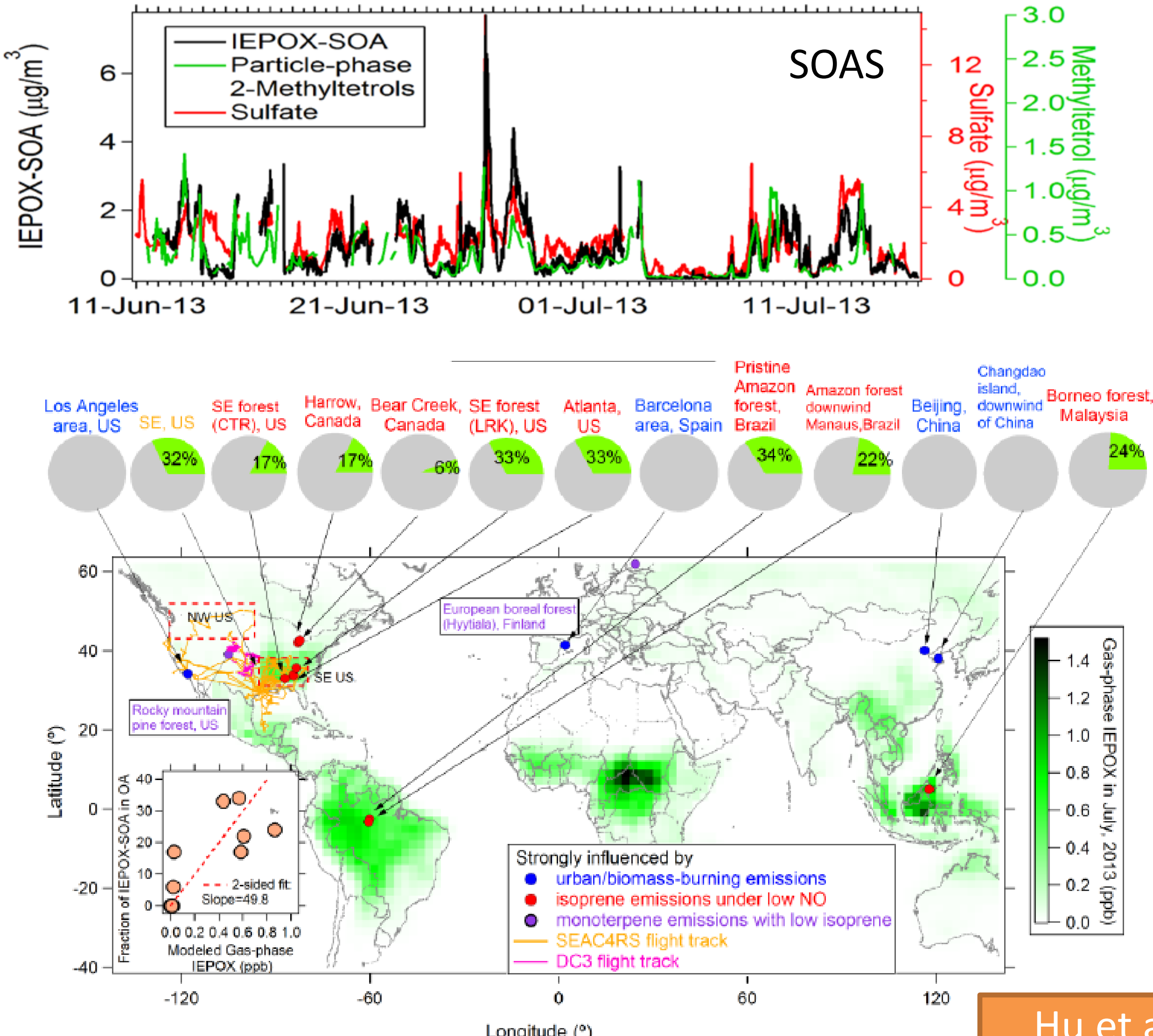
Pedro Campuzano-Jost, Weiwei Hu, Brett B. Palm, Douglas A. Day, Amber M. Ortega, Jose-Luis Jimenez, Jin Liao, Karl D. Froyd, Fabien Paulot, Gabriel Isaacman, Allen Goldstein, Jason M. St. Clair, John D. Crounse, Paul O. Wennberg, Luke D Ziemba, Bruce E Anderson, Simone Meinardi, Barbara Barletta, Don Blake

Spatial distribution of Isoprene emissions

A. Guenther et al.: MEGAN estimates of global isoprene Atmospheric Chemistry and Physics, 6 3187



IEPOX-SOA as observed by the AMS

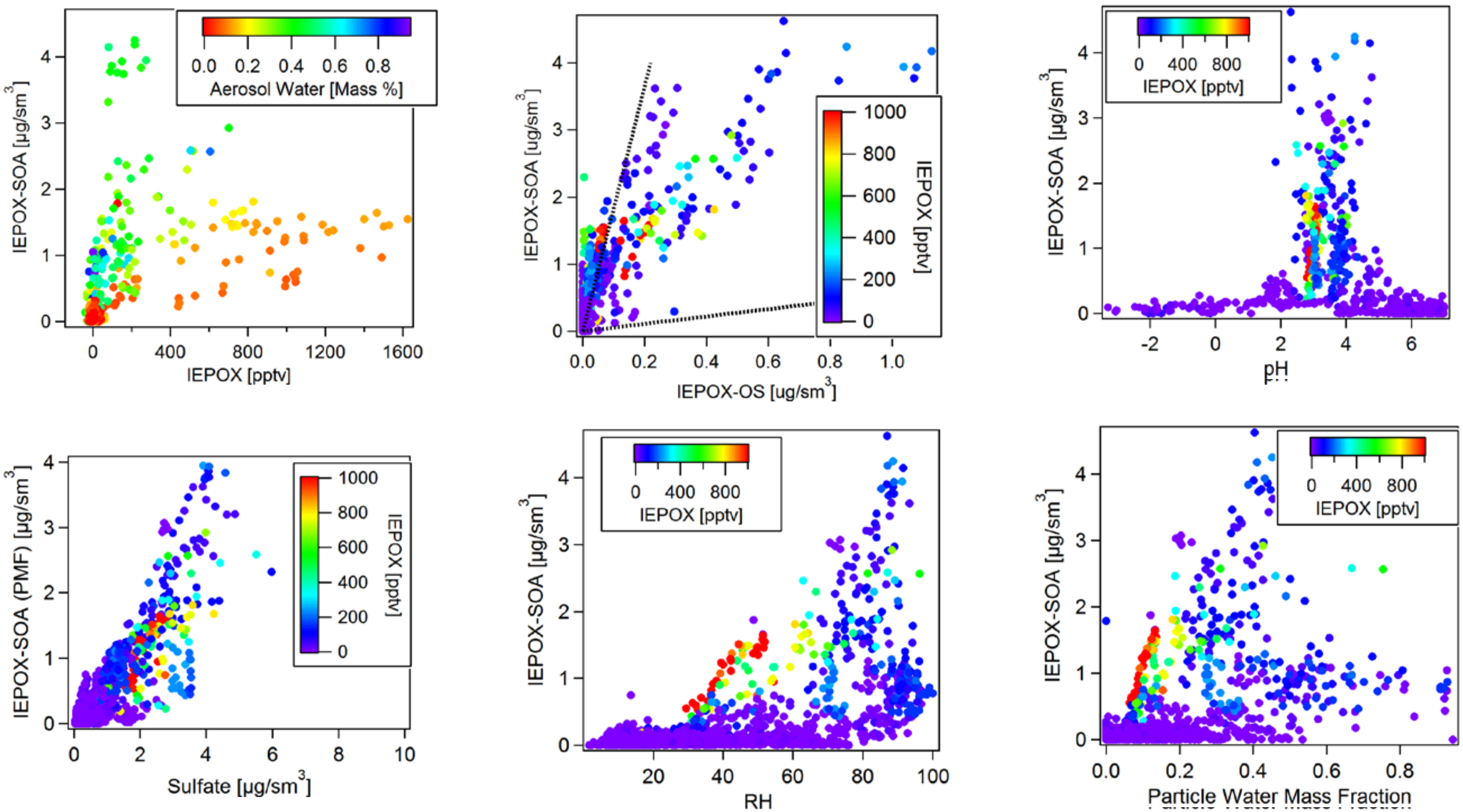


- Quite a few ground studies in the literature since 2011
- IEPOX-SOA PMF Factor correlates well with molecular tracers
- SEAC^{4}RS dataset unique in breadth and scope, ideally suited for testing the robustness of the assignment

Hu et al, 2015, Isaacman et al, in prep

DC3: Close to sources, plenty of water

Look Rock 10:1



- More IEPOX-SOA formed at <u>high RH/high liquid water/high sulfate</u>!
- This means mostly at higher altitudes/in the residual layer
- Little pH dependence, otherwise trends as expected

SO WHAT?

…..we conclude that decreasing isoprene SOA represents a factor of 2 co-benefit when reducing SO2 emissions.

Aqueous-phase mechanism for secondary organic aerosol formation from isoprene: application to the southeast United States and co-benefit of SO2 emission controls . Marais et al. Atmos. Chem. Phys., 16, 1603–1618, 2016

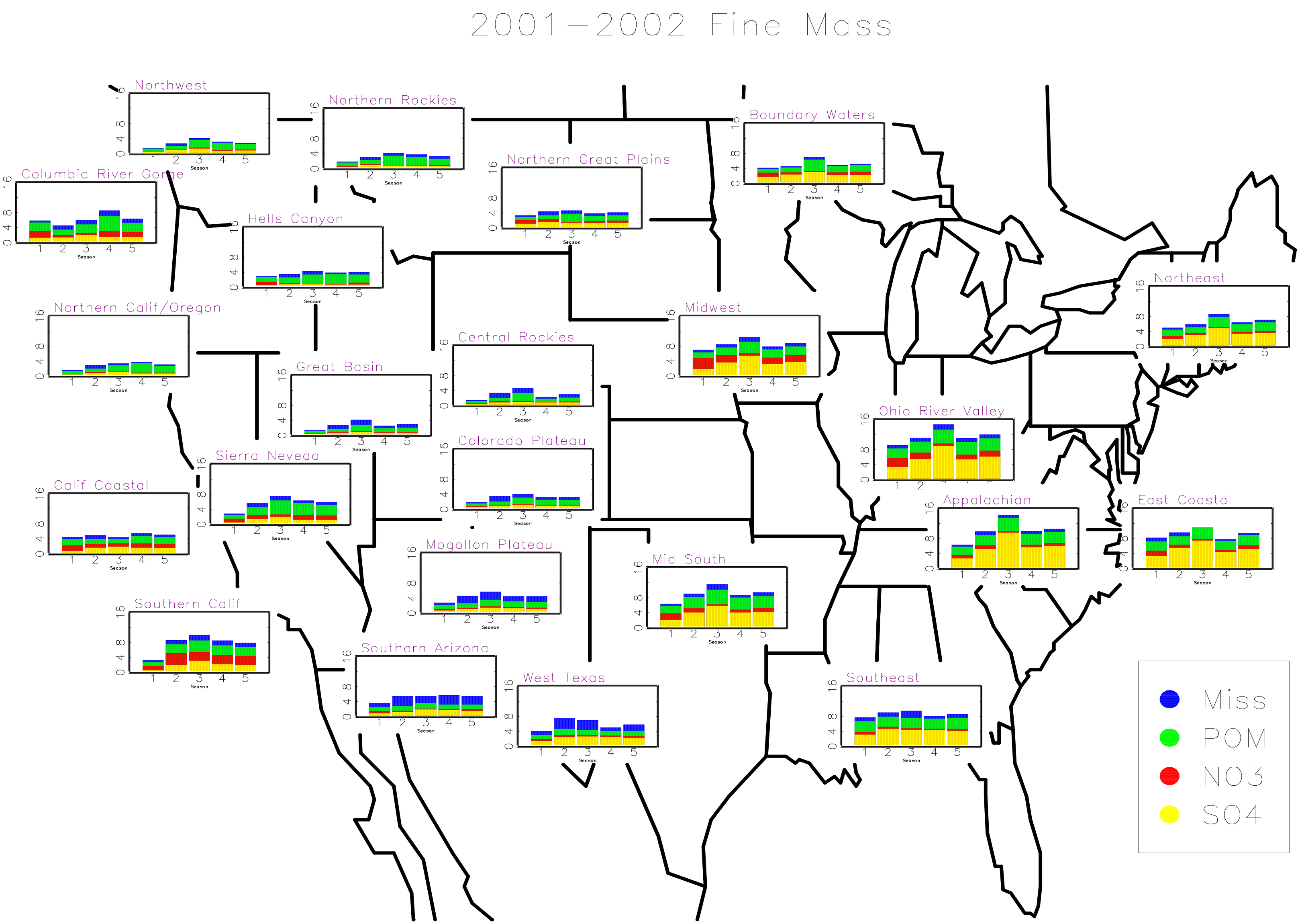
BUT:

We suggest that this apparent departure of the sulfate aerosol neutralization ratio from thermodynamic behavior may be caused by an elevated and increasing organic aerosol (OA) mass fraction, modifying or retarding the achievement of NH3-H2SO4 thermodynamic equilibrium. Recent work has suggested that controlling SO2 emissions in the US to decrease sulfate aerosol has a major co-benefit from suppressing acid-catalyzed biogenic secondary organic aerosol (SOA) formation (Pye et al., 2013; Marais et al., 2016). However, this co-benefit would not occur if the increasing OA/sulfate ratio causes the acidity to actually increase.

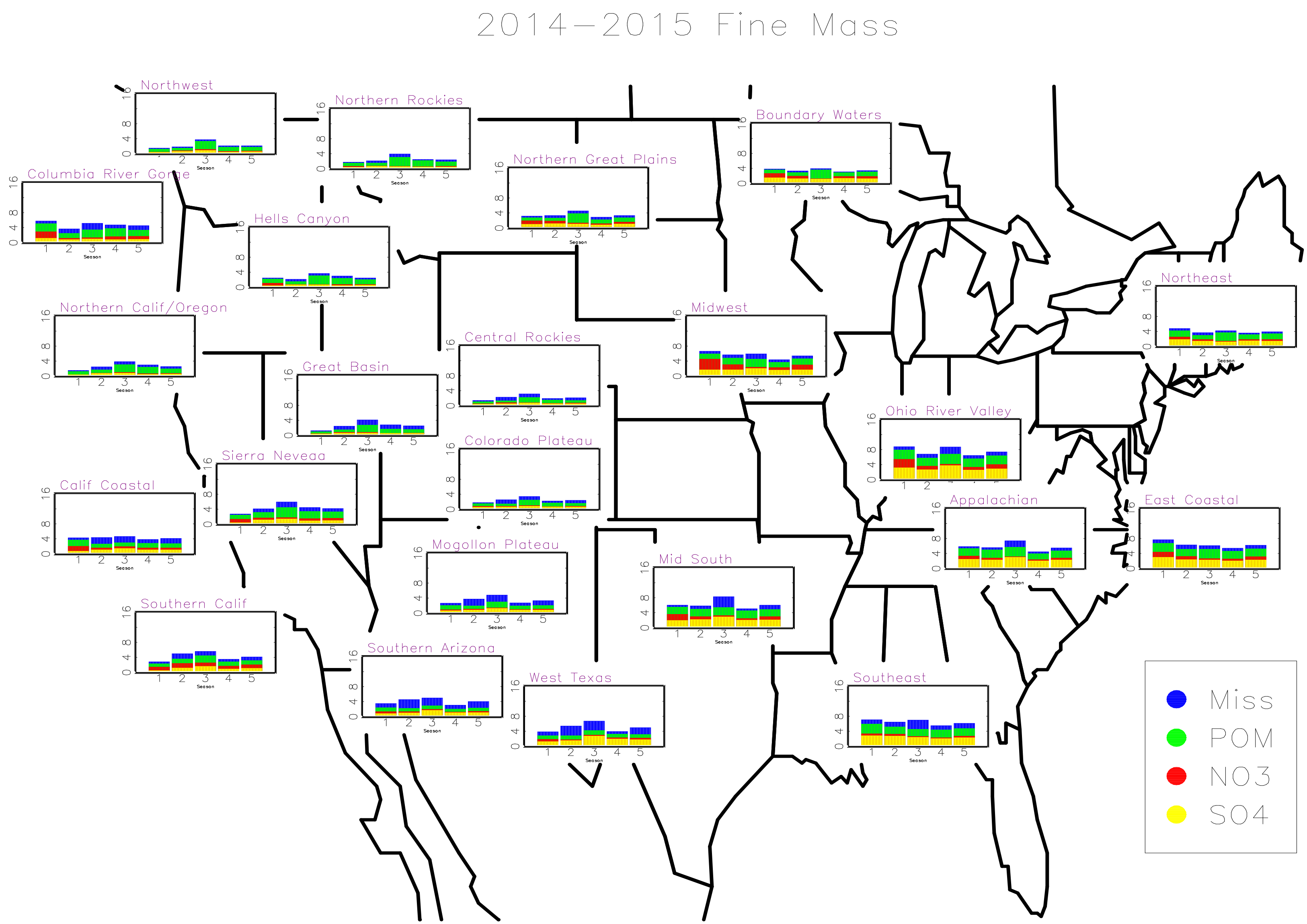
Incomplete sulfate aerosol neutralization despite excess ammonia in the eastern US: a possible role of organic aerosol. Silvern et al. Atmos. Chem. Phys. June 2016

So does the IMPROVE dataset shed any light on this SO4 isoprene-SOA relationship?

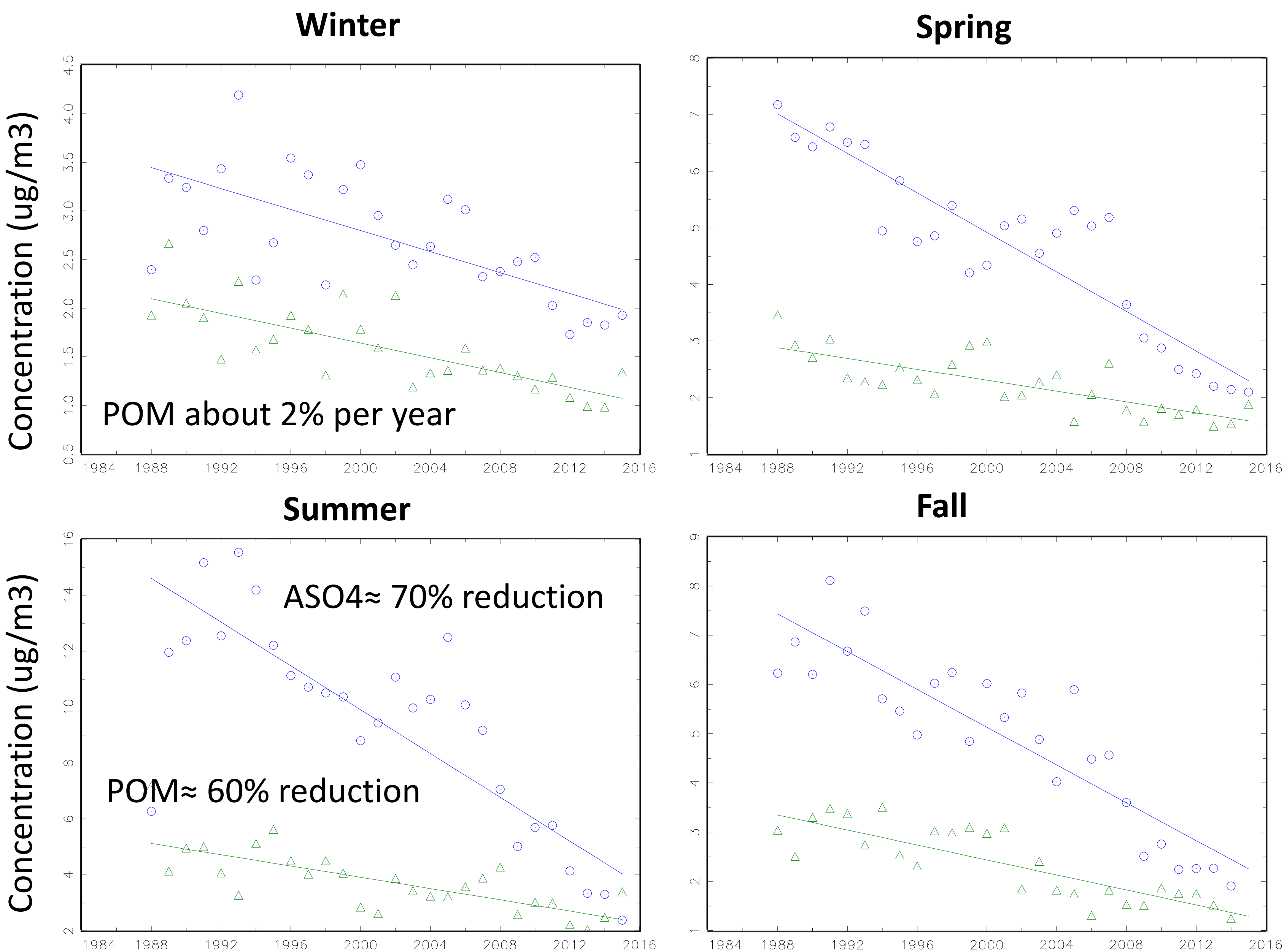
Seasonal fine particle species concentrations (ug/m²)



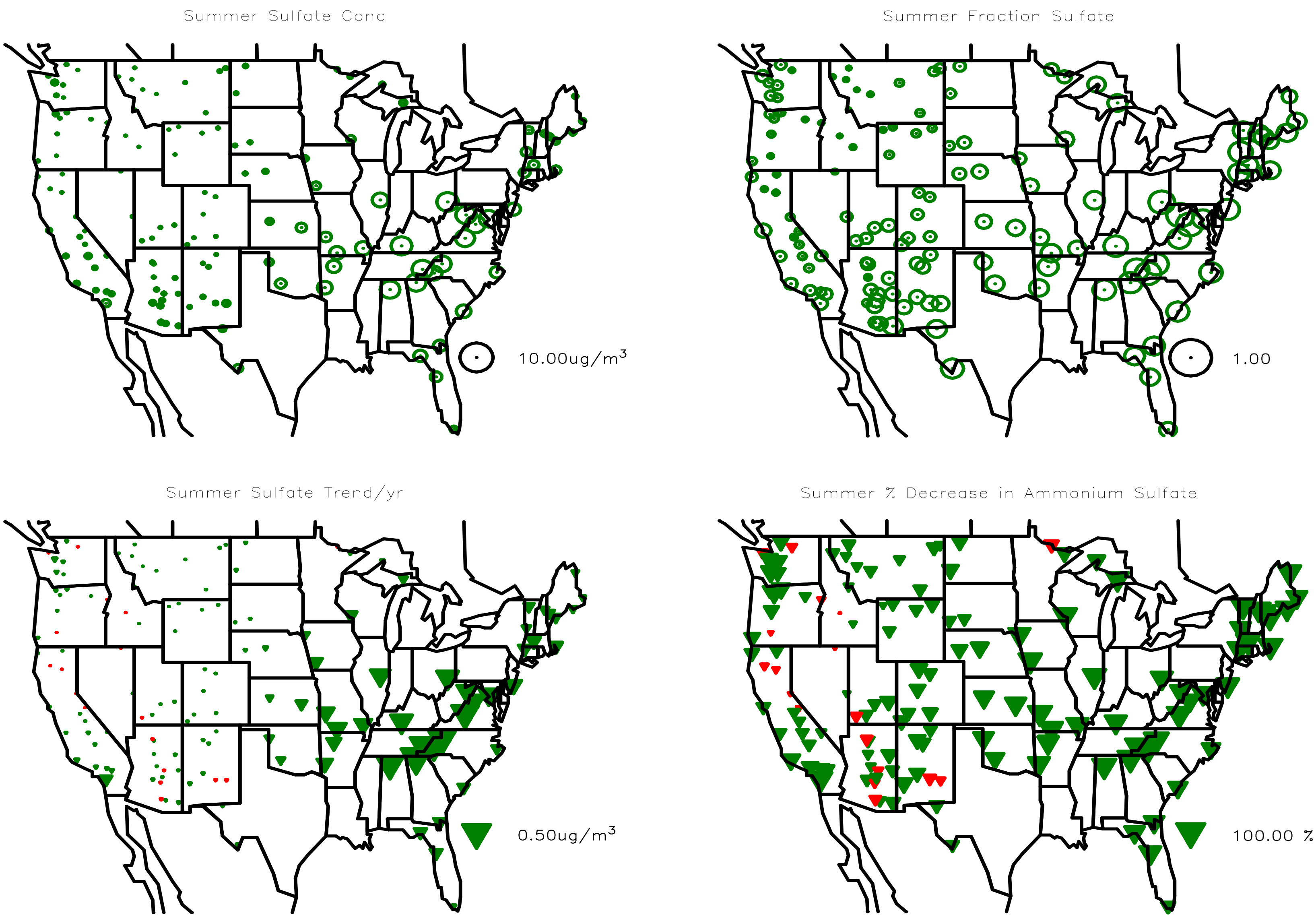
Seasonal fine particle species concentrations (ug/m²)



Example of ASO4 and POM trend (Shenandoah)

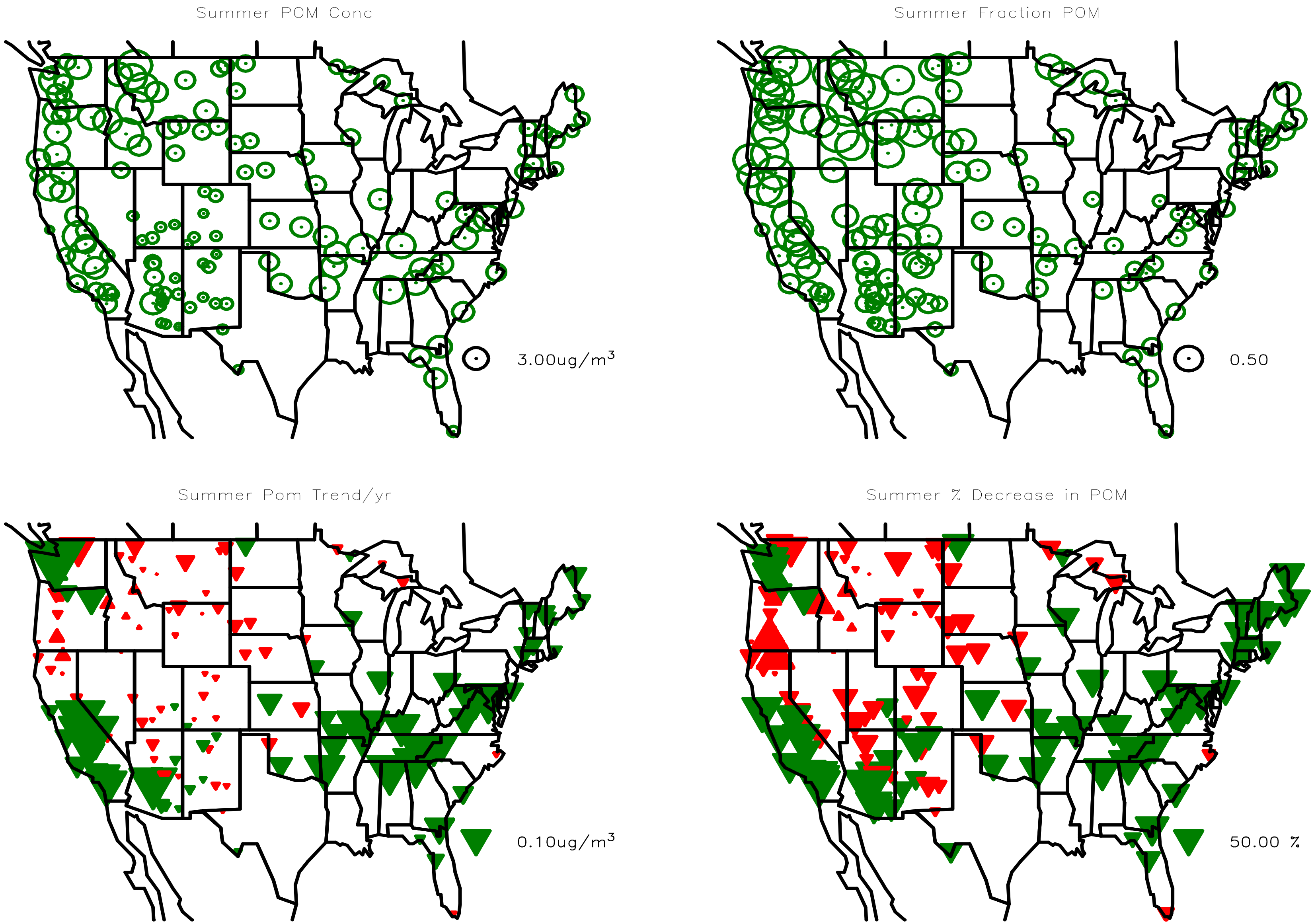


Average ASO4 concentrations and trends for 2001-2015



A green arrow indicates a significant trend at the 5% level

Average POM concentrations and trends for 2001-2015



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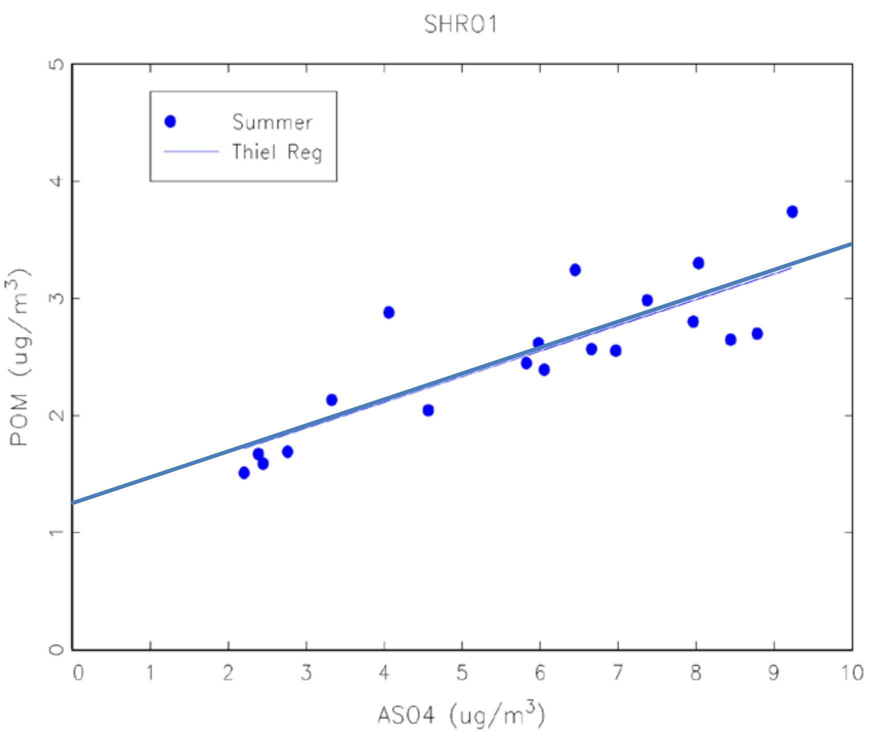
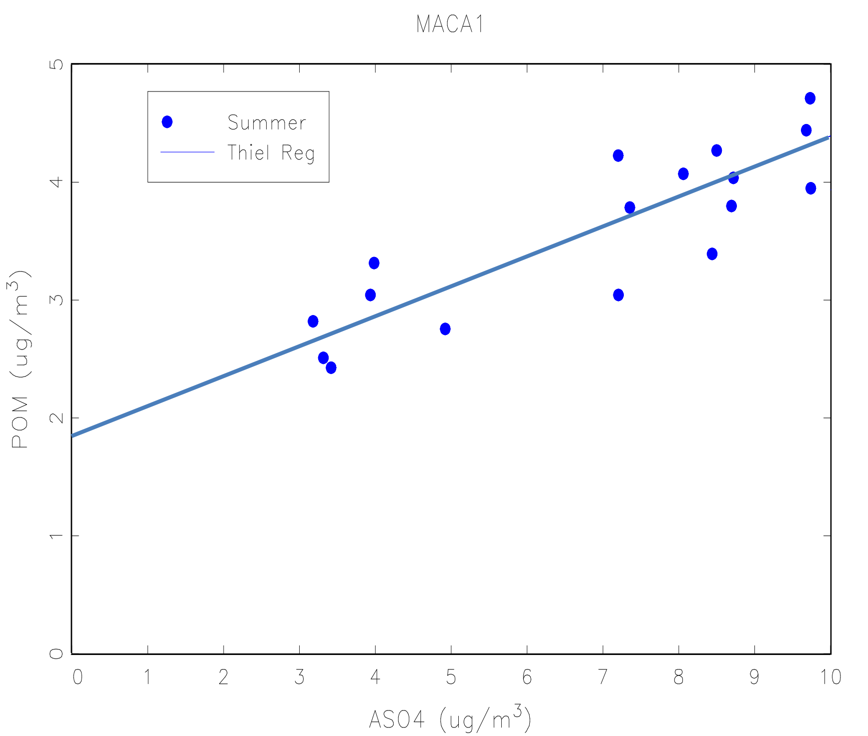
POM vs ASO4 for Shining Rock and Mammoth Cave

Pt by Pt plot independent of time



Intercept= 1.23
Slope= 0.31
Significance= 0.00



Intercept= 1.83
Slope= 0.26
Significance= 0.00

What does the slope represent?

- The average amount of ISO-SOA decrease as a result of decreasing sulfate?

Question:

- Are there decreases in non- ISO-SOA species that are correlated with ASO4 ?

What does the intercept represent?

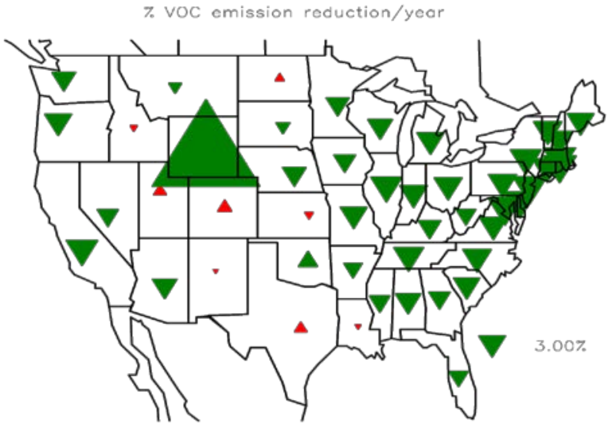
- The amount of fossil or contemporary OC not catalyzed by sulfate in the presence of aerosol water.

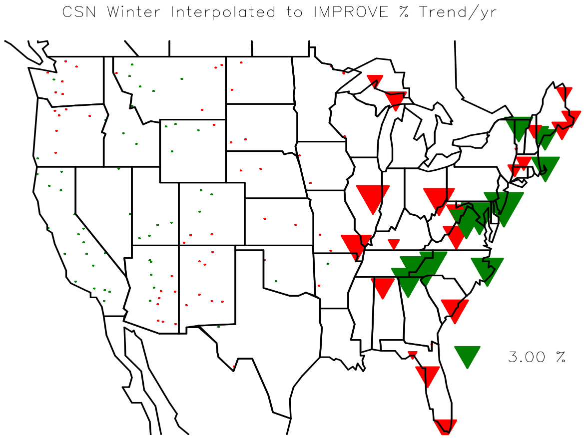
Question:

- Is intercept term represent a constant background or is it changing over time or correlated with SO4 concentration?
- Does it represent only non- ISO-SOA?

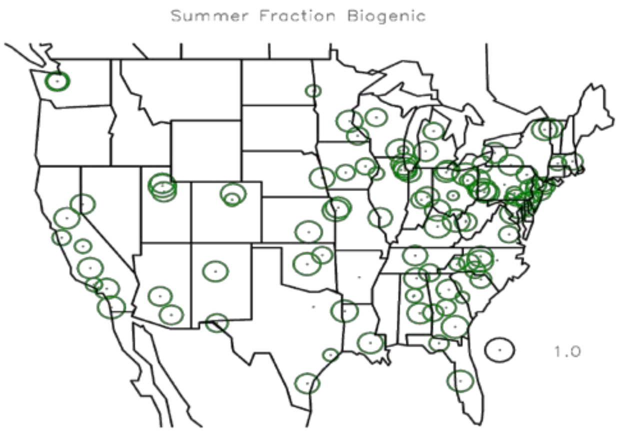
What could affect the slope of POM over time?

- Changing fossil derived emissions associated with mobile emissions and other industrial activities.



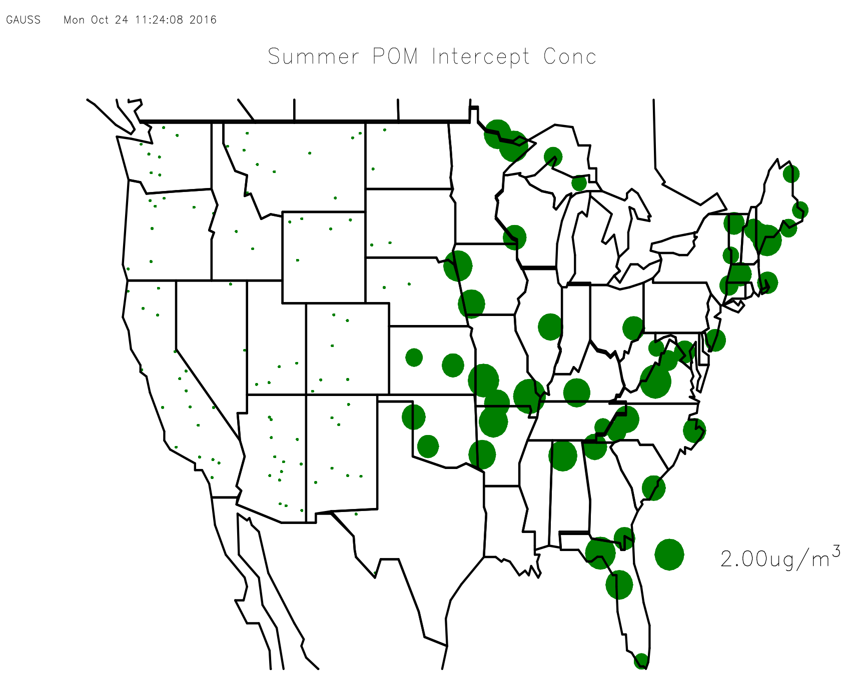


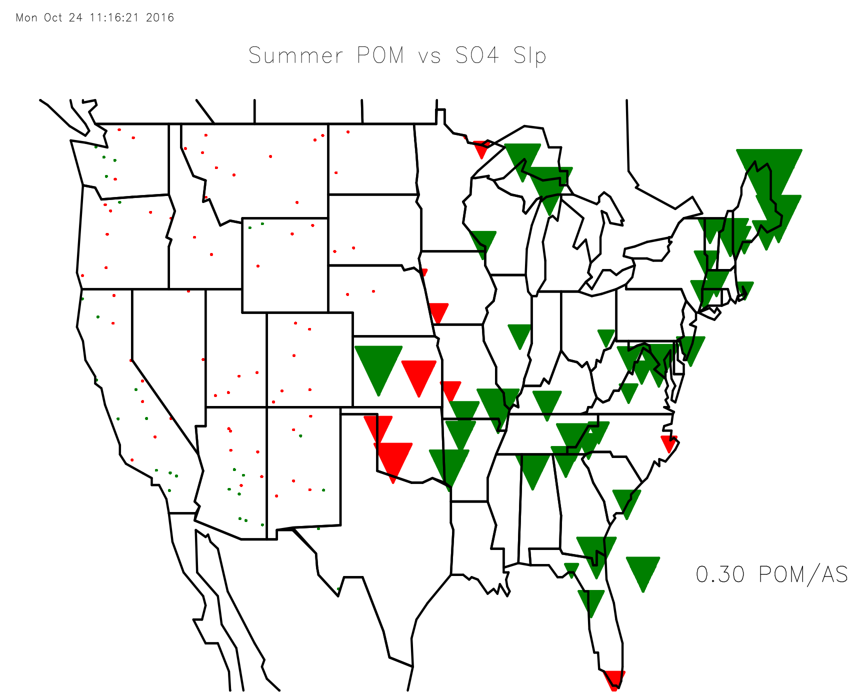
- But most POM is modern (Bench et al 2007 and Schichtel et al., 2012) at approximately 80% during summer months.



- So have wild and prescribed fire changed?
- Changes in residential wood burning. (both could have an IE-POX and non-IEPOX component.

Slope and Intercept of summer POM vs ASO4

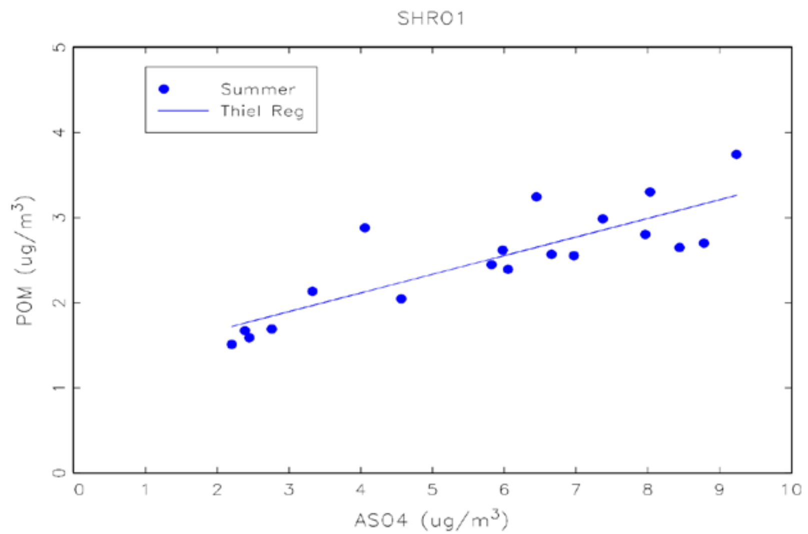




Mean Int=1.52±0.37 ug/m^3
Int/(Mean POM2001)=0.56±0.24
Int/(Mean POM2014)=0.79±0.27
ISO-SOA 2001=44%
ISO-SOA 2014=21%

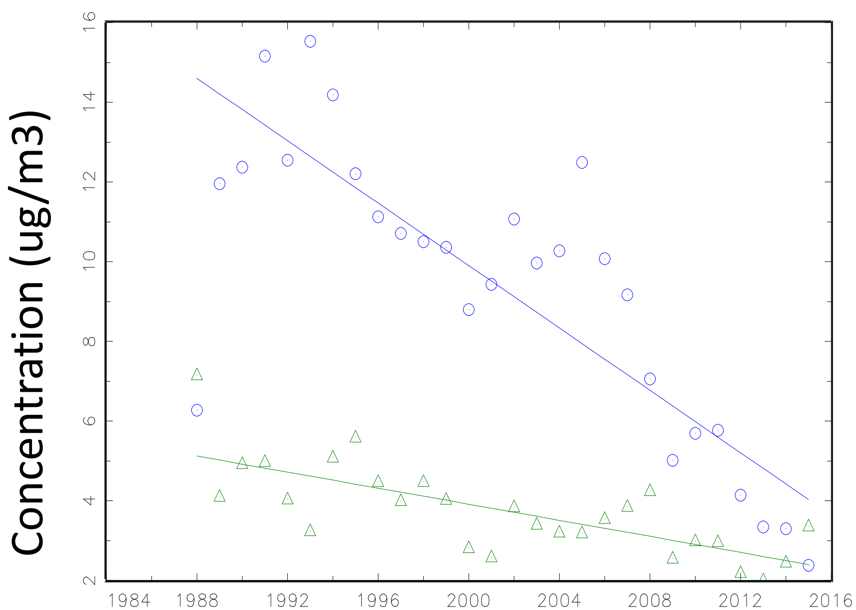
Mean slope=0.24±0.13

Examine trends in POM and SO4 over time



Plot on left is a point by point scatter plot of POM and SO4 which yields a ΔPOM/ΔSO4 as the slope.

Summer

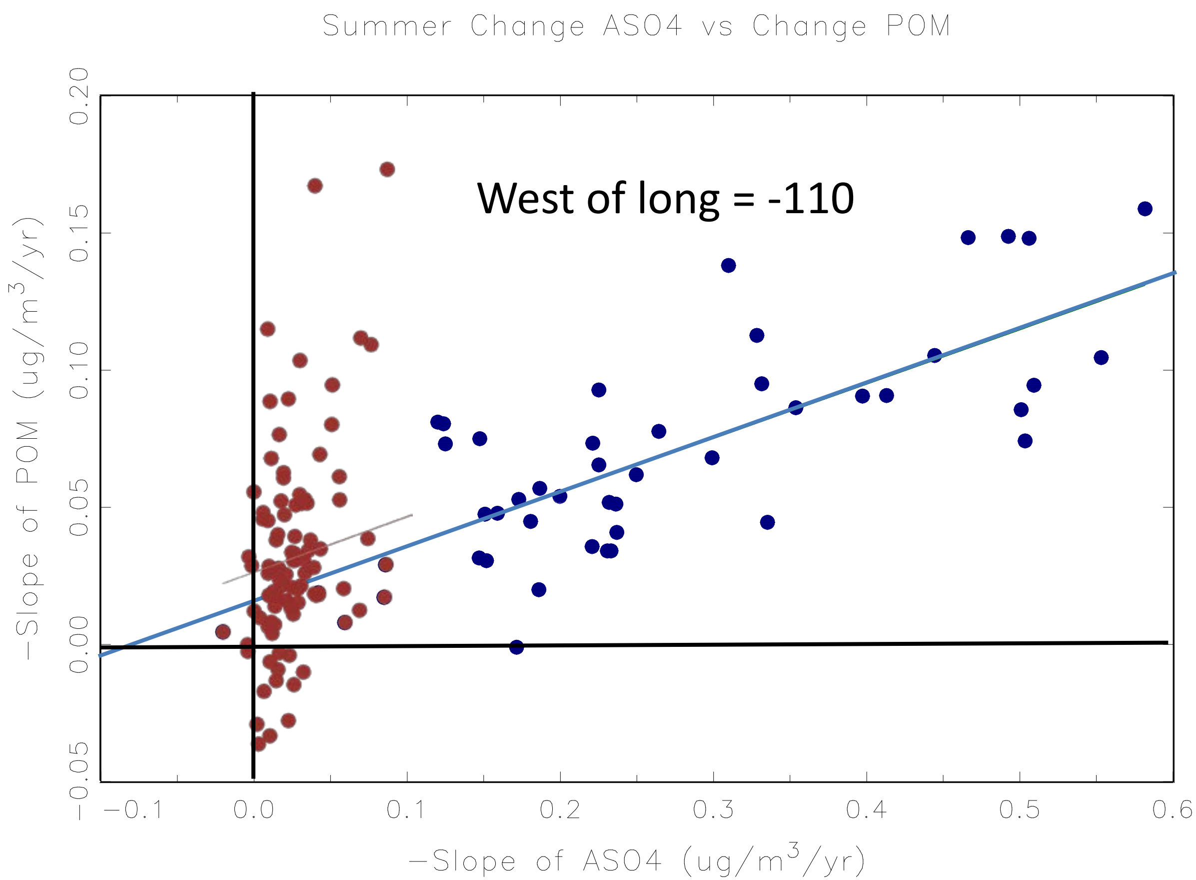


An average ΔPOM/ΔSO4 over time can be derived by taking the ratio of the slopes of POM and SO4 over time as shown in the adjacent graph.

These average ΔPOM/ΔSO4 for each site can then be compared.

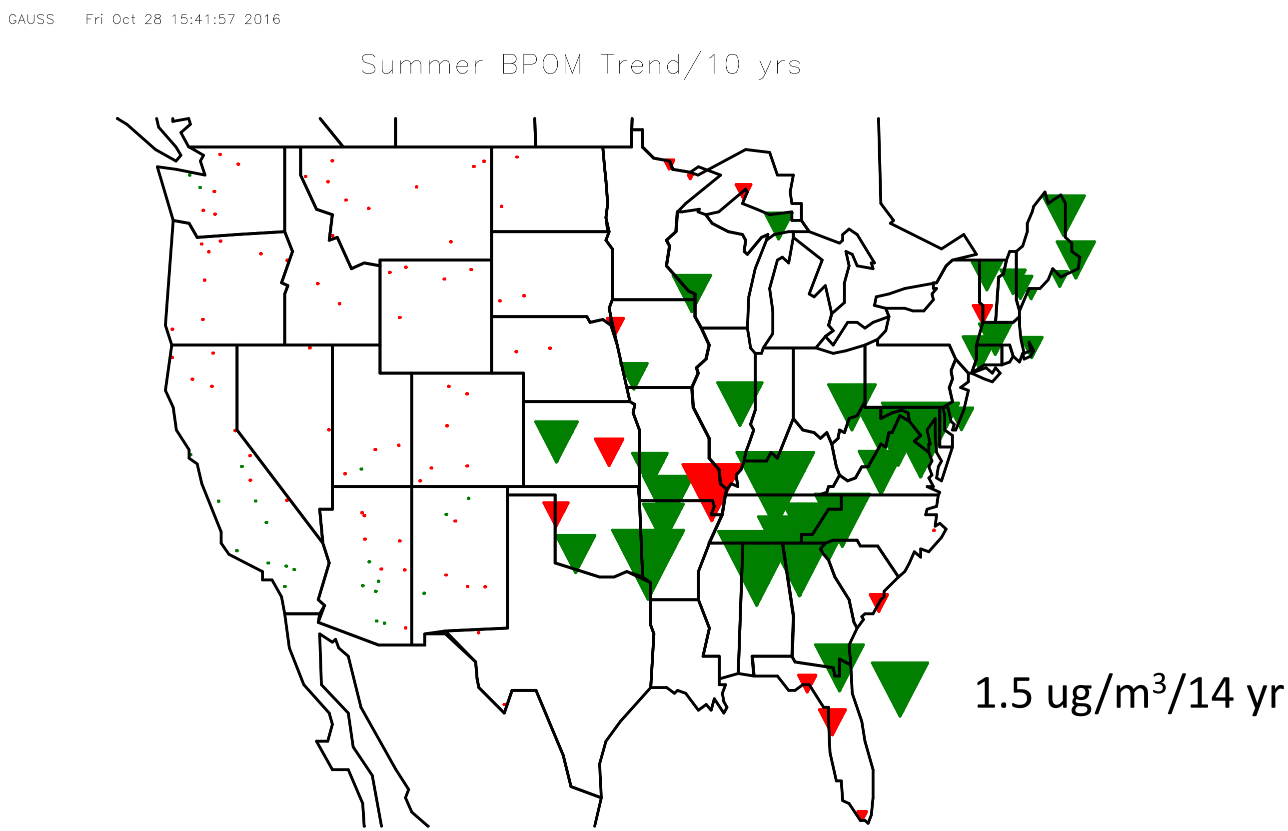
Compare <u>average</u> ΔPOM/yr vs ΔASO4/yr for sites east of longitude = -110

Intercept= 0.016 ± 0.008
Slope= 0.27 ± 0.034
Sig= 0.00
R-squared= 0.60



An intercept term of near zero suggests, within the uncertainty, that there may be a small amount non- ISO-SOA linked to the slope of ΔPOM/ΔASO4.

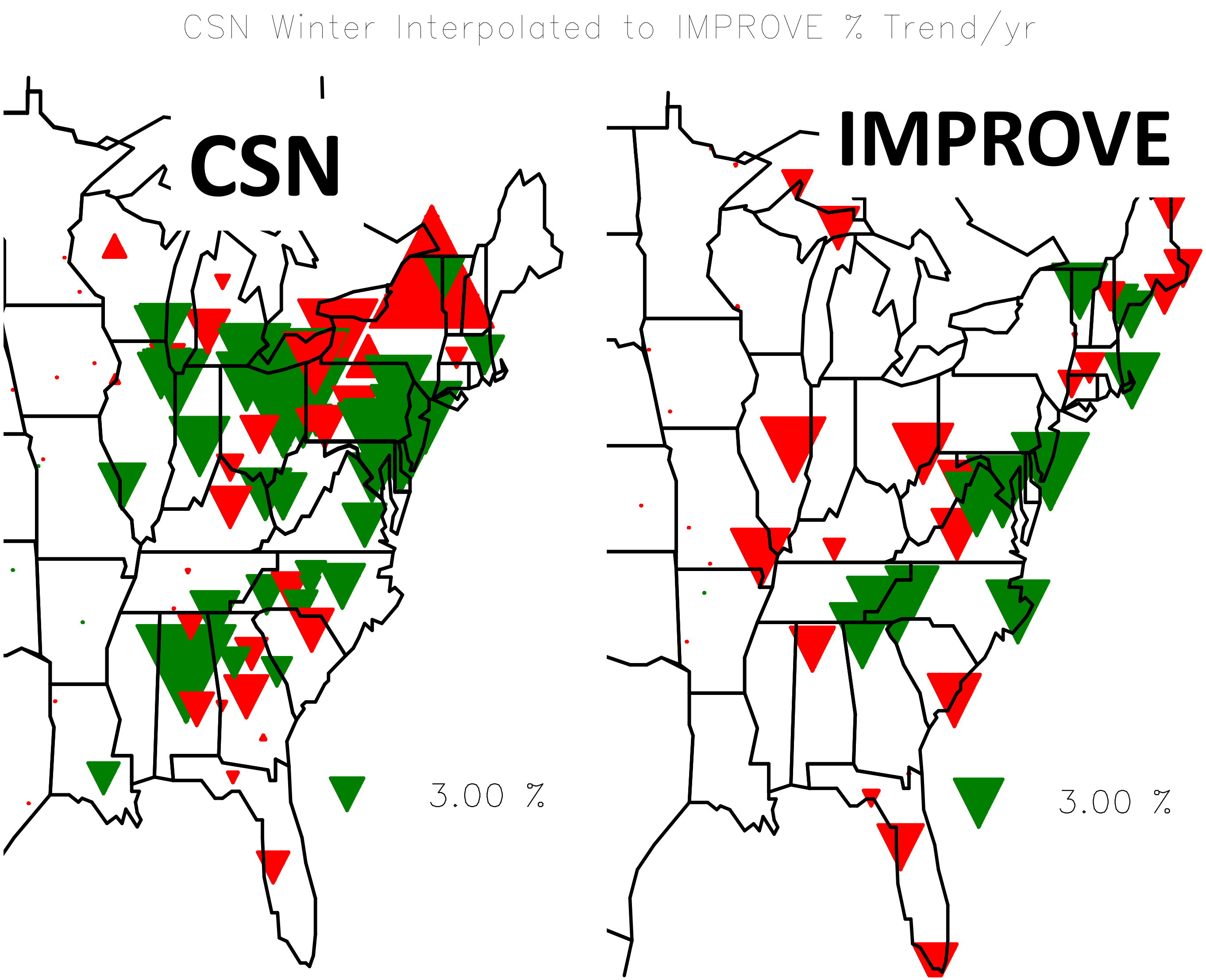
Estimated Decrease in ISO-SOA over a ten year period resulting from a decrease in SO2 and sulfate reductions. (ISO–SOA/14 yrs)



A green arrow indicates a significant trend at the 5% level

Thank You

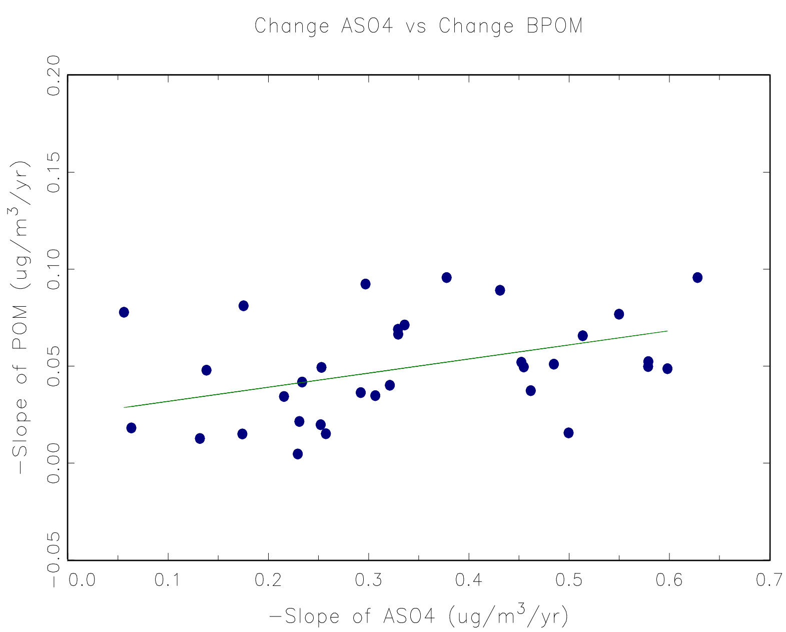
Winter OC trend (%/yr)



A green arrow indicates a significant trend at the 5% level

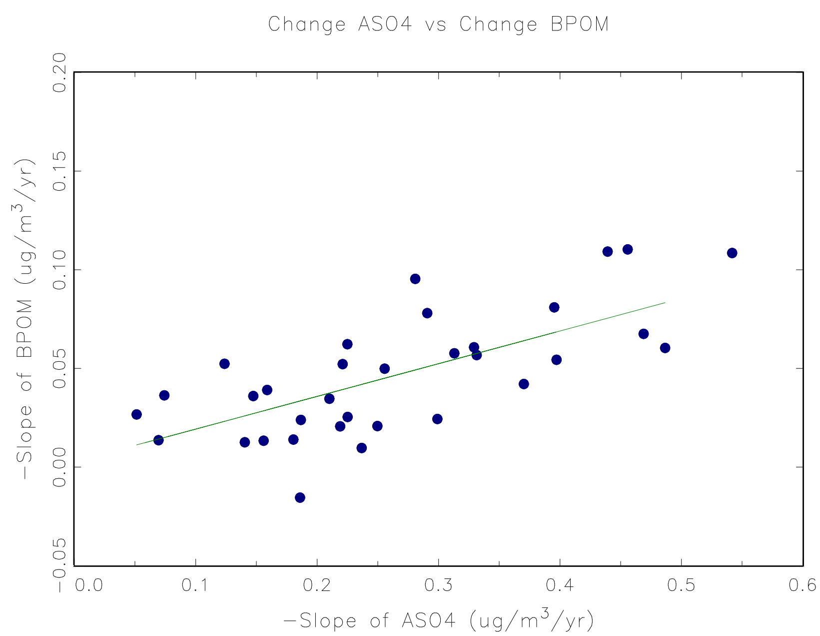
ΔBPOM/yr vs ΔASO4/yr

June-August



Intercept= 0.03± 0.01
Slope= 0.07 ±0.03
Sig= 0.01
R-squared= 0.12

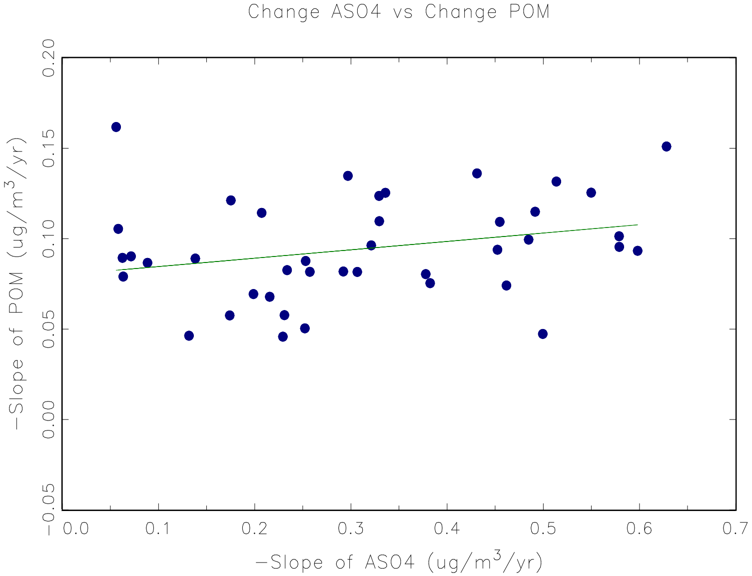
August-October



Intercept= 0.00 ± 0.01
Slope= 0.17 ± 0.03
Significance= 0.00
R-squared= 0.50

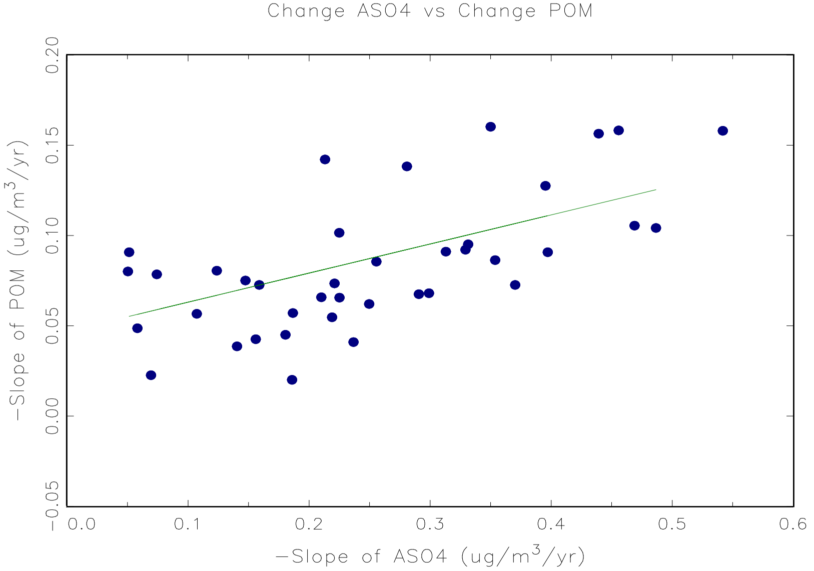
ΔPOM/yr vs ΔASO4/yr

June-August



Intercept= 0.08 ± 0.01
Slope= 0.05 ± 0.03
Sig= 0.09
R-squared= 0.06

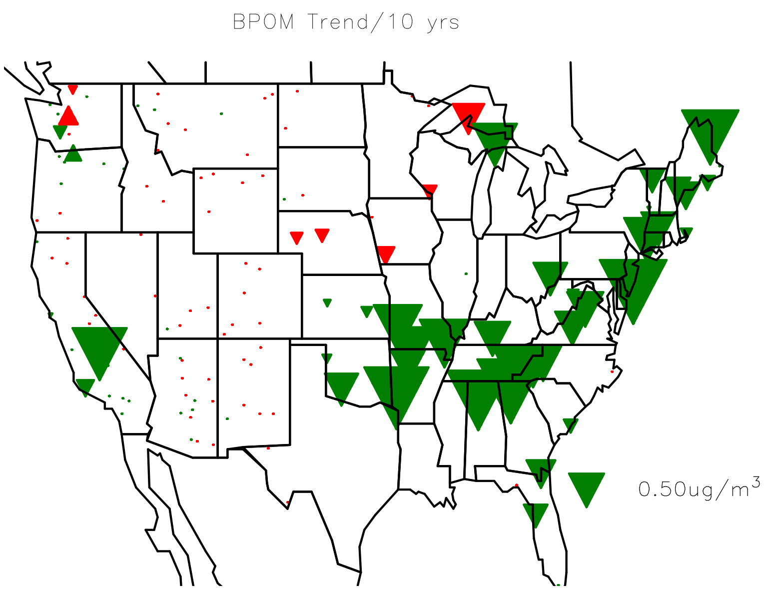
August-October



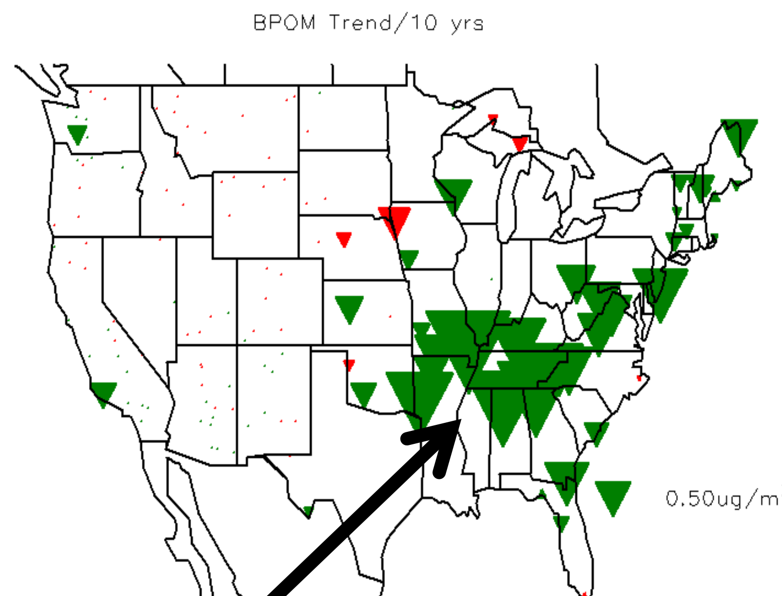
Intercept= 0.05 ± 0.01
Slope= 0.16 ± 0.05
Sig= 0.00
R-squared= 0.21

ΔBPOM/(10 yrs): Decrease in BPOM over a ten year period.

June-August



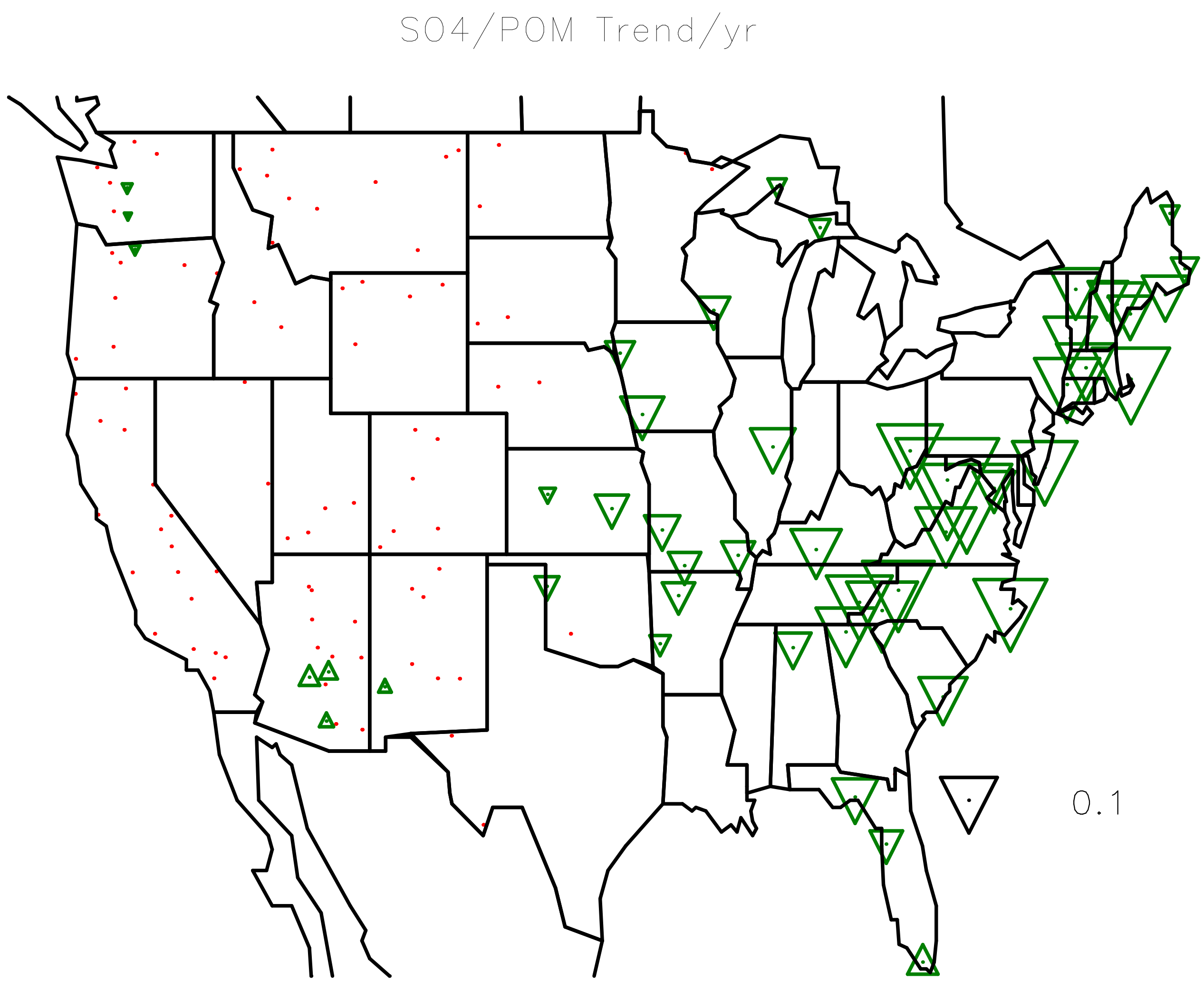
August-October



About 1.0 ug/m^3

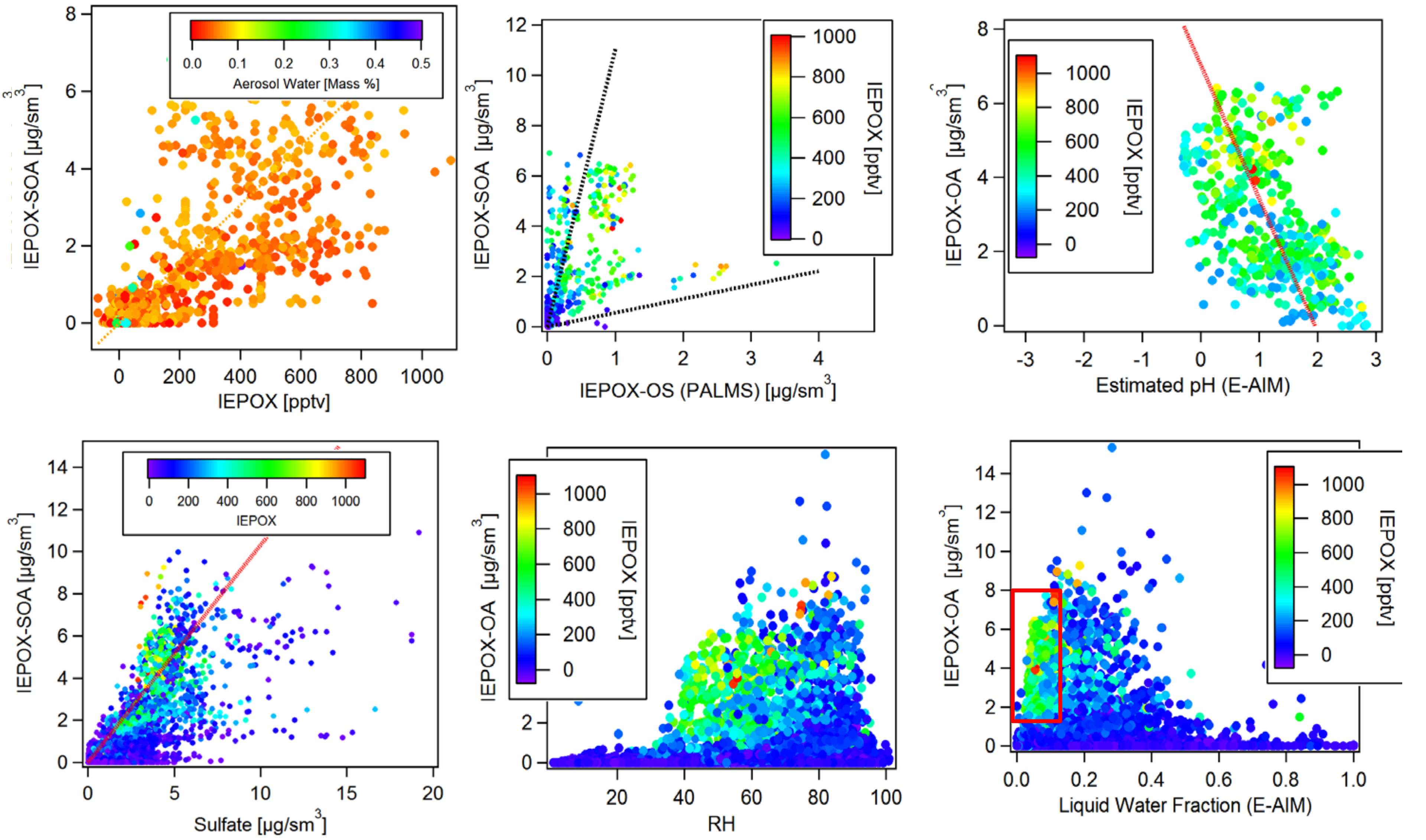
A green arrow indicates a significant trend at the 5% level

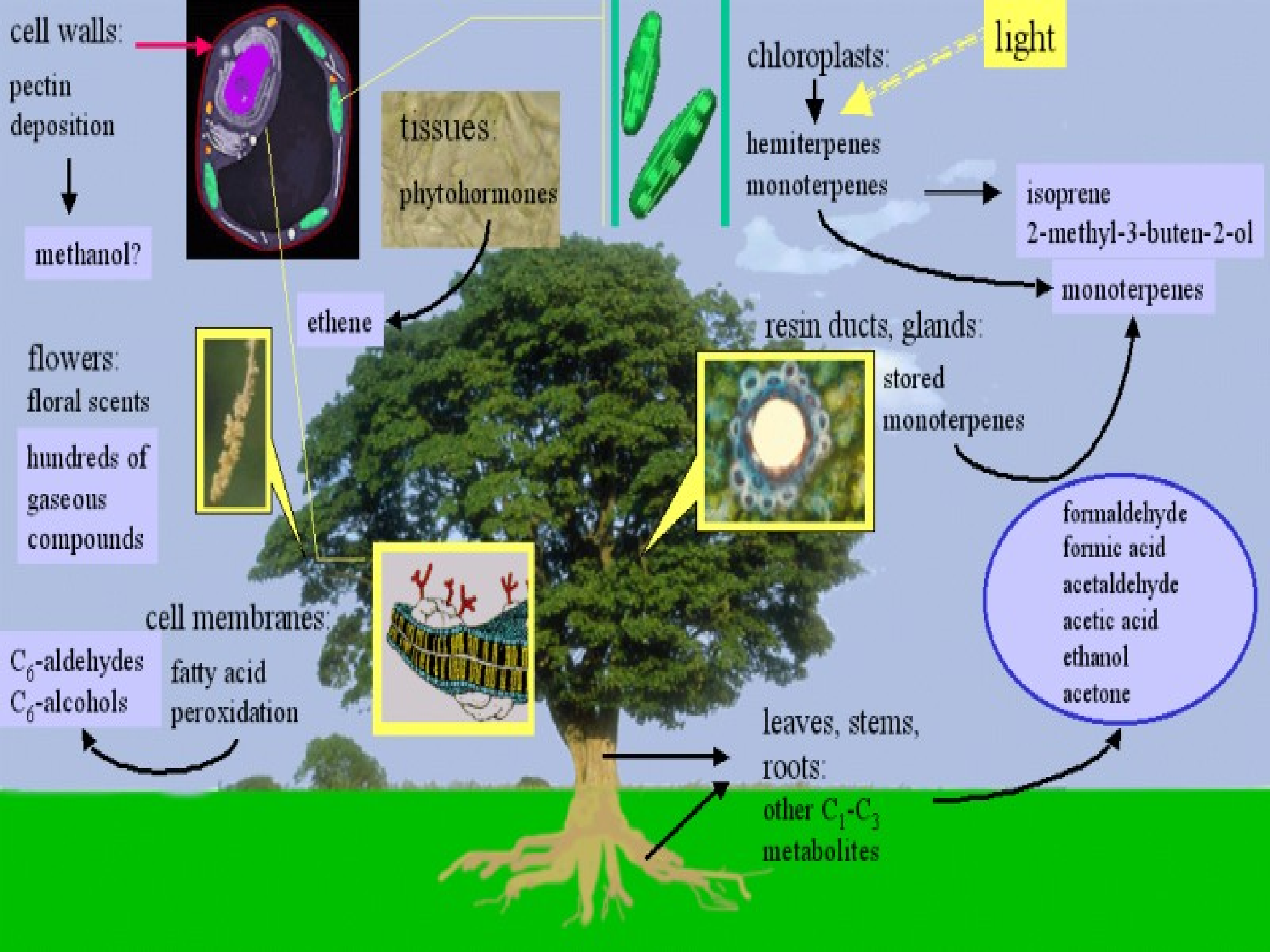
Yearly trend in the summer ratio of ASO4 to POM (ASO4/POM)



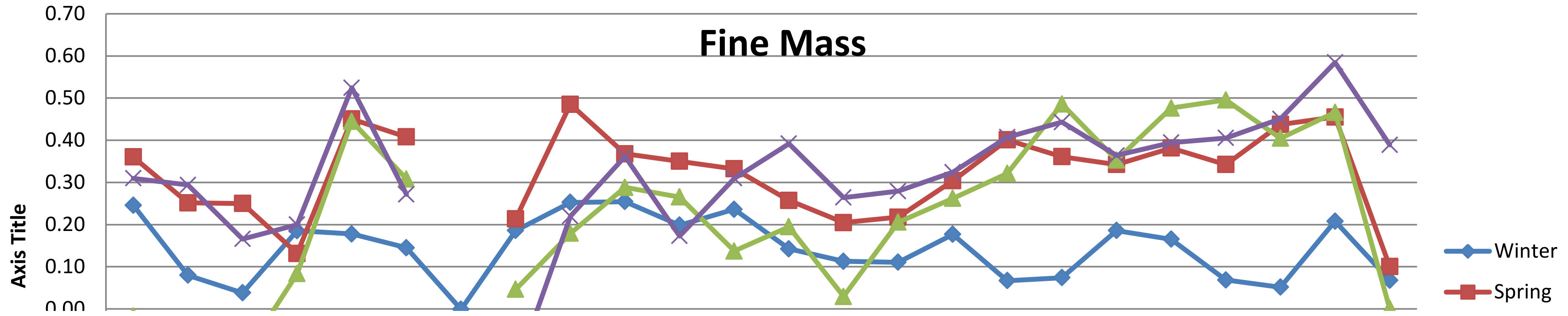
A green arrow indicates a significant trend at the 5% level

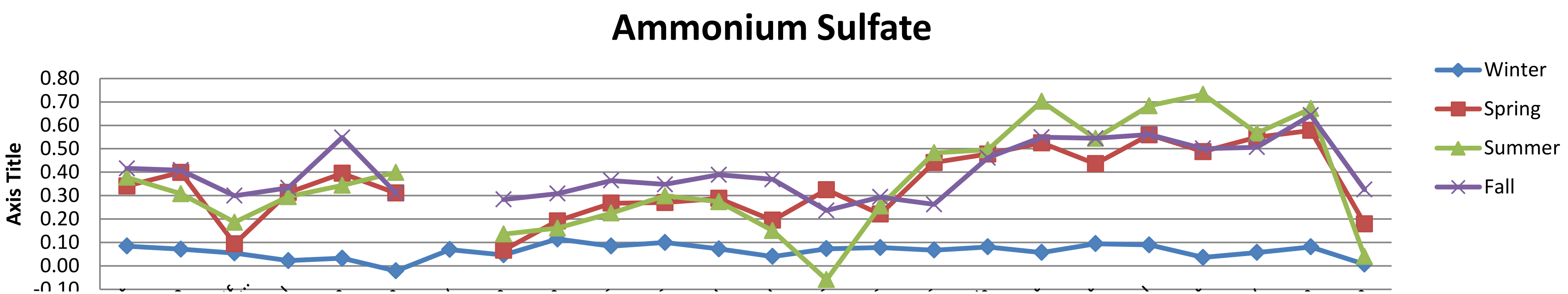
SEAC⁴RS:Many sources, different regimes

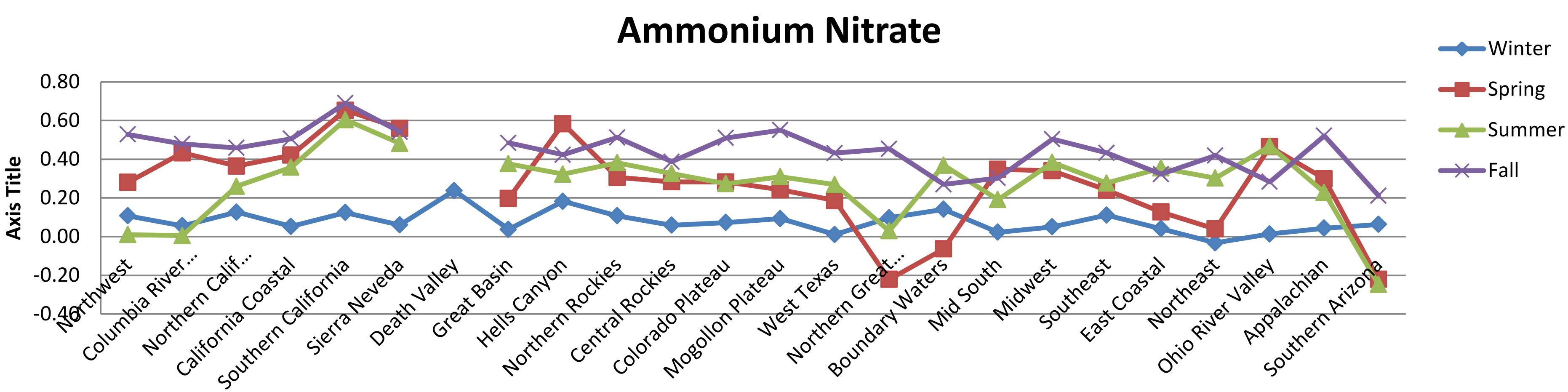


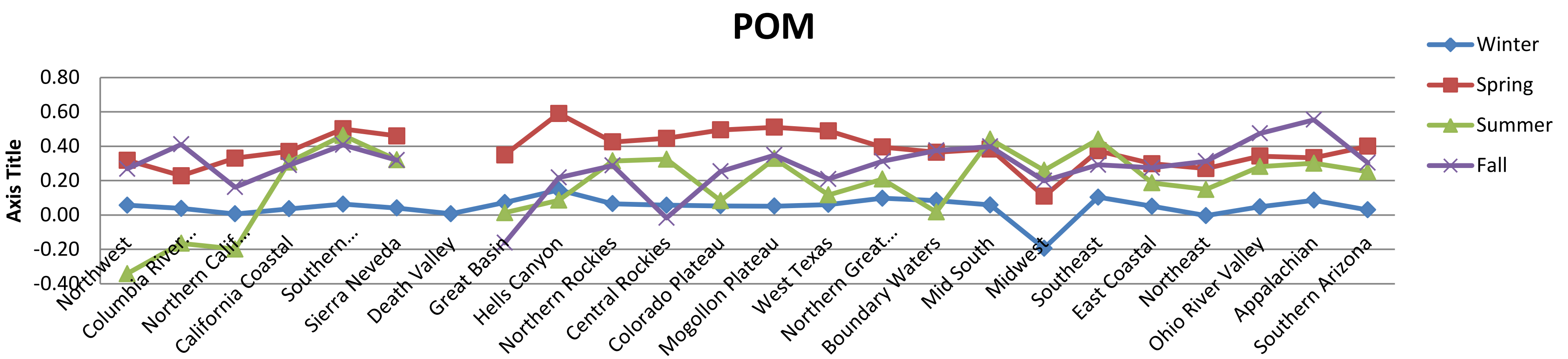


cell walls:
pectin deposition
methanol?
tissues:
phytohormones
ethene
chloroplasts:
light
hemiterpenes
monoterpenes
isoprene
2-methyl-3-buten-2-ol
monoterpenes
resin ducts, glands:
stored monoterpenes
flowers:
floral scents
hundreds of gaseous compounds
cell membranes:
C_6-aldehydes
C_6-alcohols
fatty acid peroxidation
formaldehyde
formic acid
acetaldehyde
acetic acid
ethanol
acetone
leaves, stems, roots:
other C_1-C_3 metabolites


Fine Mass
Axis Title
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
Winter
Spring


Ammonium Sulfate
Axis Title
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
-0.10
Winter
Spring
Summer
Fall


Ammonium Nitrate
Axis Title
0.80
0.60
0.40
0.20
0.00
-0.20
-0.40
Winter
Spring
Summer
Fall
Northwest
Columbia River…
Northern Calif…
California Coastal
Southern California
Sierra Neveda
Death Valley
Great Basin
Hells Canyon
Northern Rockies
Central Rockies
Colorado Plateau
Mogollon Plateau
West Texas
Northern Great…
Boundary Waters
Mid South
Midwest
Southeast
East Coastal
Northeast
Ohio River Valley
Appalachian
Southern Arizona



POM
Axis Title
0.80
0.60
0.40
0.20
0.00
-0.20
-0.40
Northwest
Columbia River…
Northern Calif…
California Coastal
Southern…
Sierra Neveda
Death Valley
Great Basin
Hells Canyon
Northern Rockies
Central Rockies
Colorado Plateau
Mogollon Plateau
West Texas
Northern Great…
Boundary Waters
Mid South
Midwest
Southeast
East Coastal
Northeast
Ohio River Valley
Appalachian
Southern Arizona
Winter
Spring
Summer
Fall