

# IMPROVE Data Analysis: Update on gravimetric and reconstructed fine mass discrepancy

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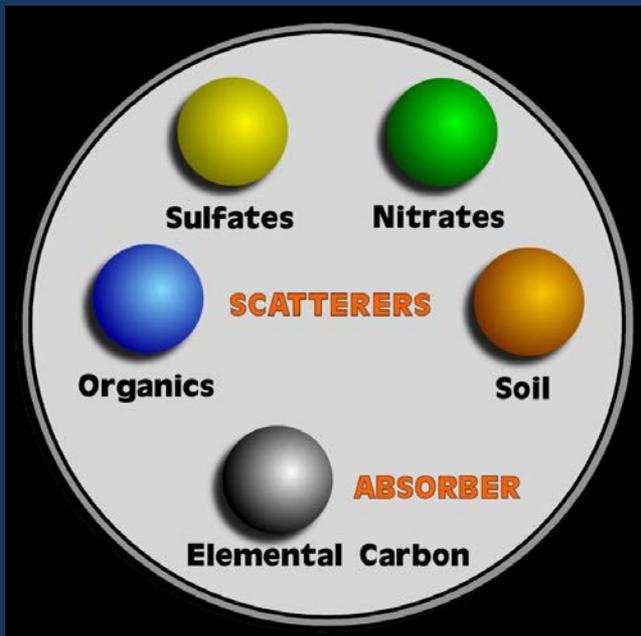
1992

Boundary Waters 2015



# Reconstructed Fine Mass (RCFM)

- **RCFM** = sum of aerosol species assumed to compose fine mass (FM=PM<sub>2.5</sub>)
- Requires assumptions about the molecular form of individual species
- Necessary for estimating contributions to PM<sub>2.5</sub> mass and visibility
- QA check on biases in gravimetric or speciated measurements (e.g., Malm et al., 2011)

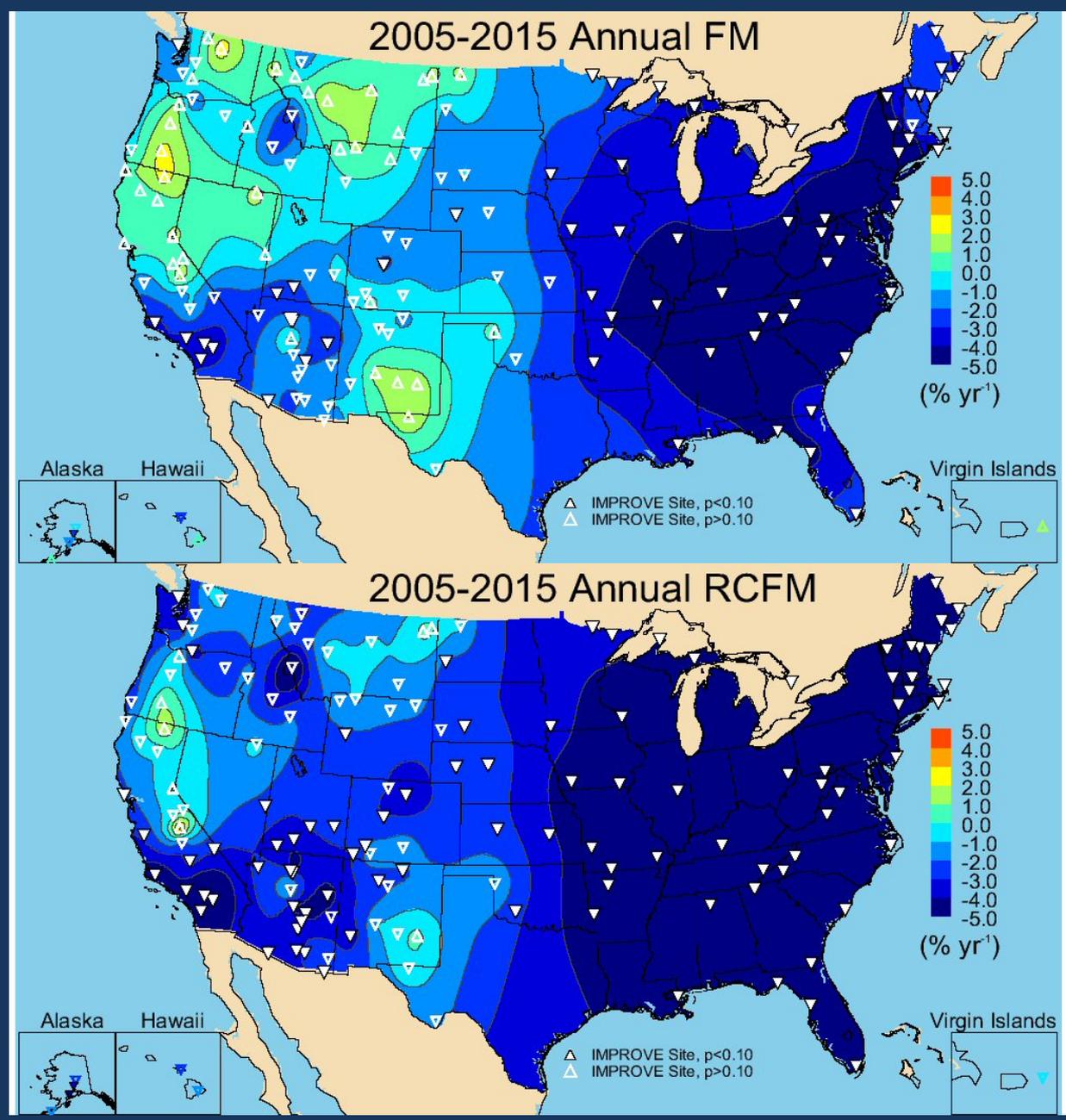


**RCFM =**

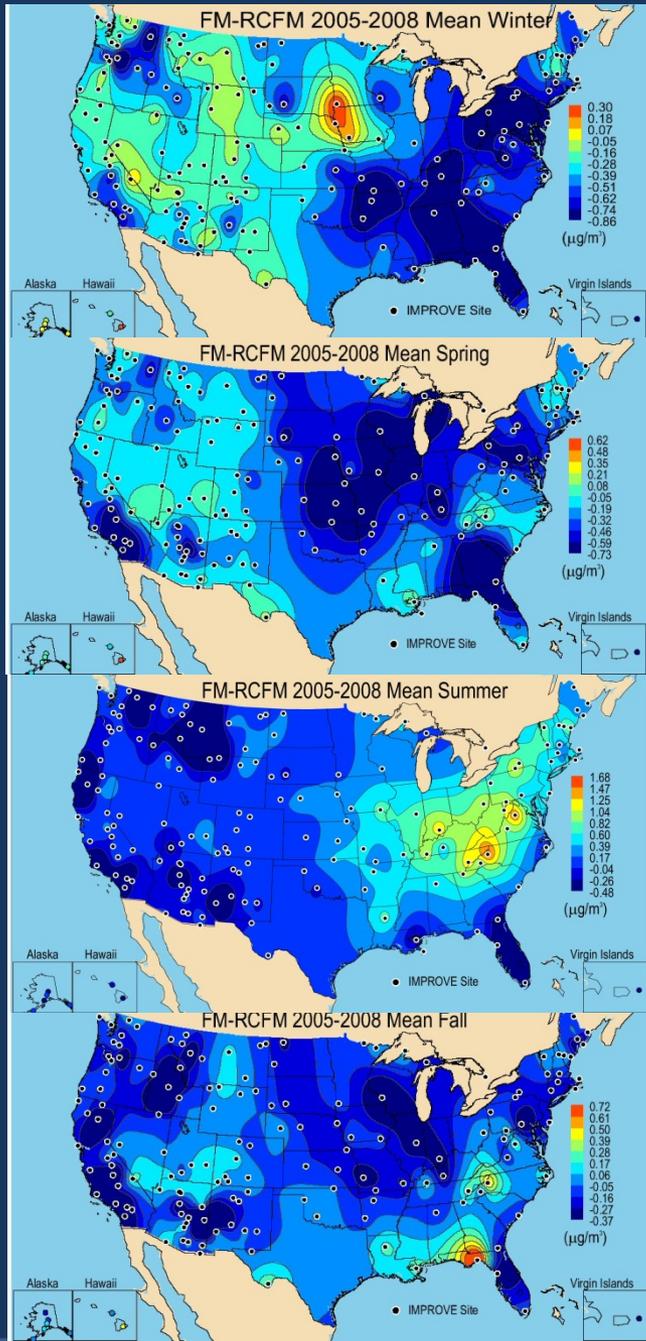
Ammonium Sulfate ( $1.375 \cdot \text{SO}_4^{-2}$ ) +  
Ammonium Nitrate ( $1.29 \cdot \text{NO}_3^-$ ) +  
Particulate Organic Matter ( $1.8 \cdot \text{OC}$ ) +  
Elemental Carbon +  
Dust +  
Sea Salt ( $1.8 \cdot \text{Cl}^-$ )

# 2005-2015 Annual Mean Trends in FM and RCFM ( $\% \text{ yr}^{-1}$ )

FM has not decreased at the same rate as RCFM

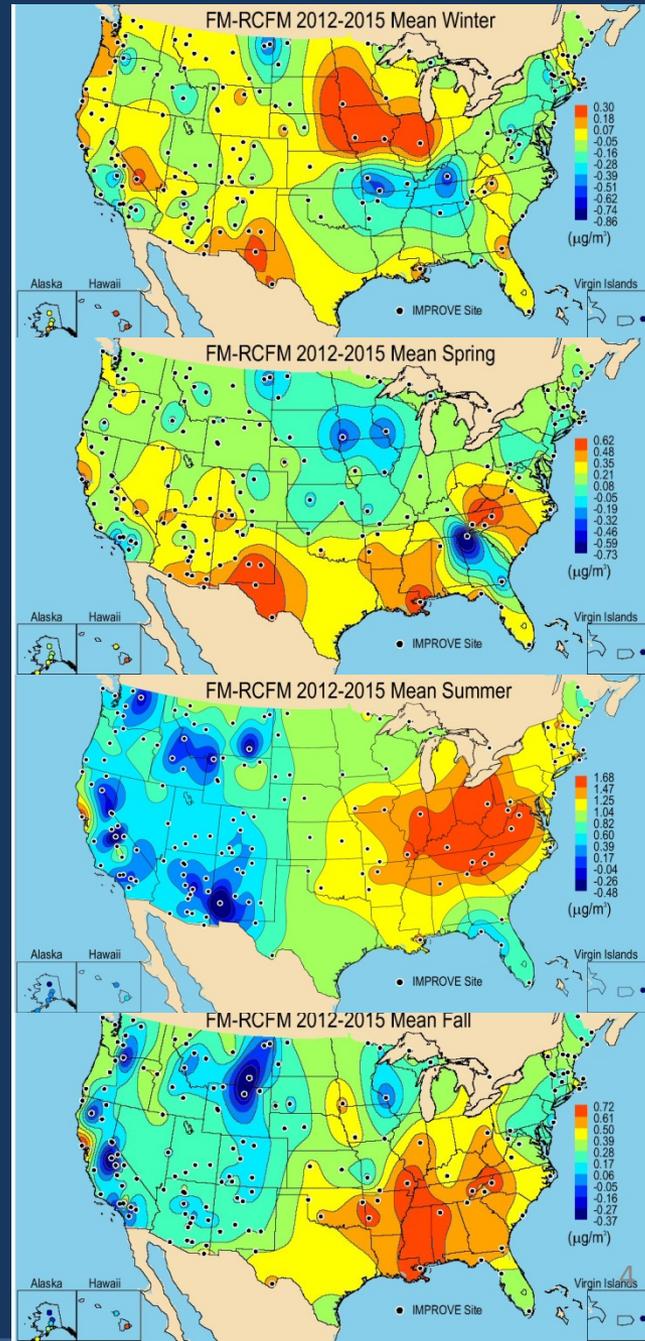


# 2005-2008

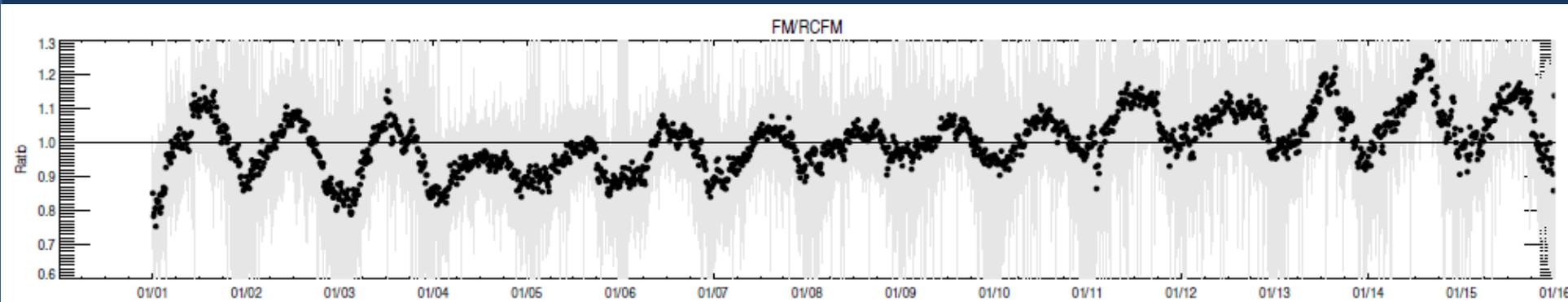


# Seasonal Mean FM-RCFM (residual)

# 2012-2015



# Daily Network Median FM/RCFM from 2001-2015



Notice seasonality (peaks in summer) and increase since 2011

FM biases have increased, increasingly missing something in the reconstruction, or both.

# Real or Analytic?

## Some biases known to affect PM<sub>2.5</sub> Gravimetric Mass

(+) Particle Bound Water (PBW due to laboratory relative humidity)

(+/-) Organic multiplier ( $R_{oc} = POM/OC$ )

(+/-) Sulfur vs sulfate (degree of sulfate neutralization ~30%?; organosulfate)

(-) Nitrate is lost from Teflon filter (seasonal)

(+/-) Dust composition

Semi-volatiles lost on quartz filter (underestimate OC by ~20%) Malm et al., 2011

Other quartz filter artifacts- evaporation of OC during storage, adsorption of VOC gases

The impact of the bias on FM is given in the parentheses (negative or positive).

# Multiple Linear Regression (MLR):

$$FM = a_0 + a_1 AS + a_2 AN + a_3 OC + a_4 EC + a_5 \text{dust} + a_6 SS$$

*Where:*

FM = PM<sub>2.5</sub> (gravimetric )

AS = ammonium sulfate (1.375\*SO<sub>4</sub><sup>-2</sup>)

AN = ammonium nitrate (1.29\*NO<sub>3</sub><sup>-</sup>)

OC = organic carbon

Dust = sum of oxides

SS = sea salt (1.8\*Cl<sup>-</sup>)

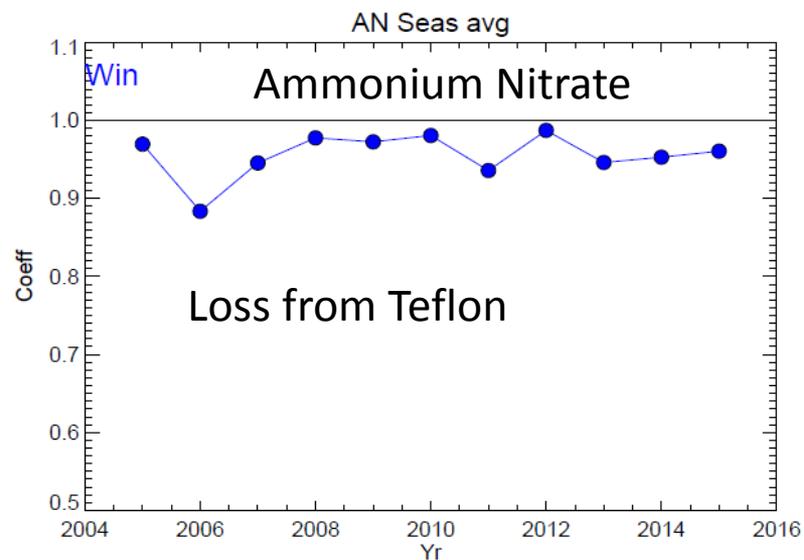
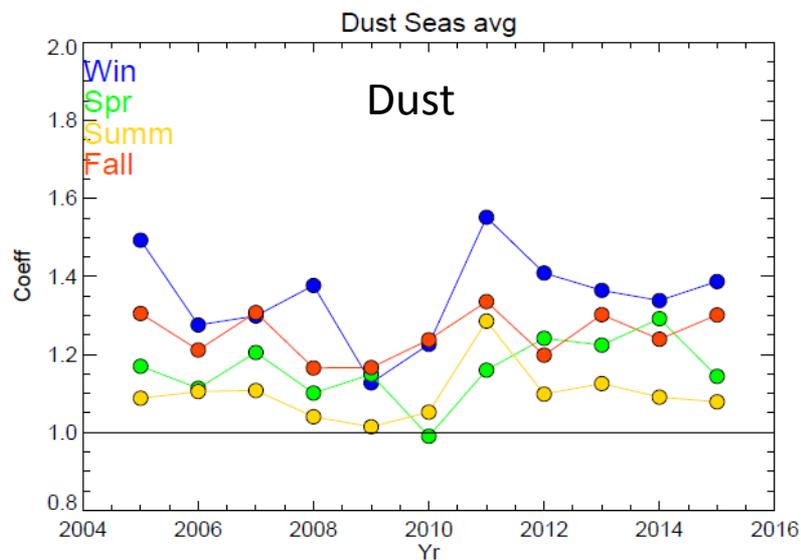
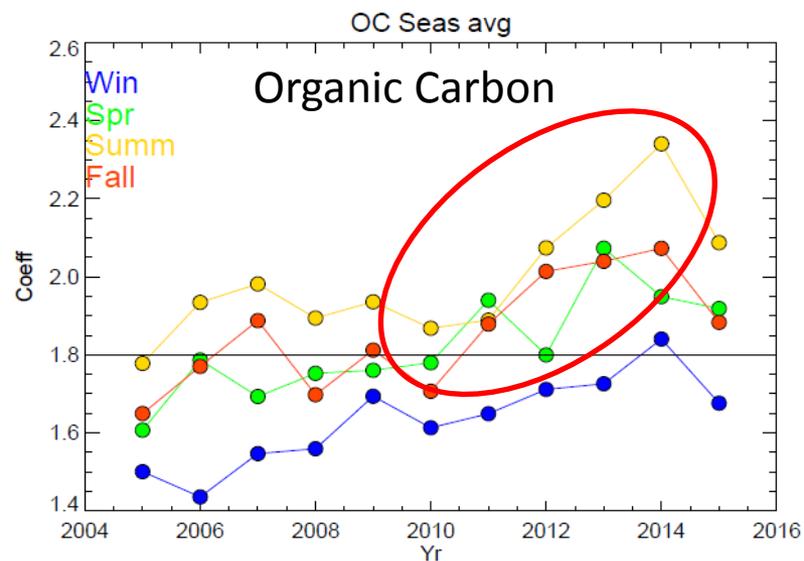
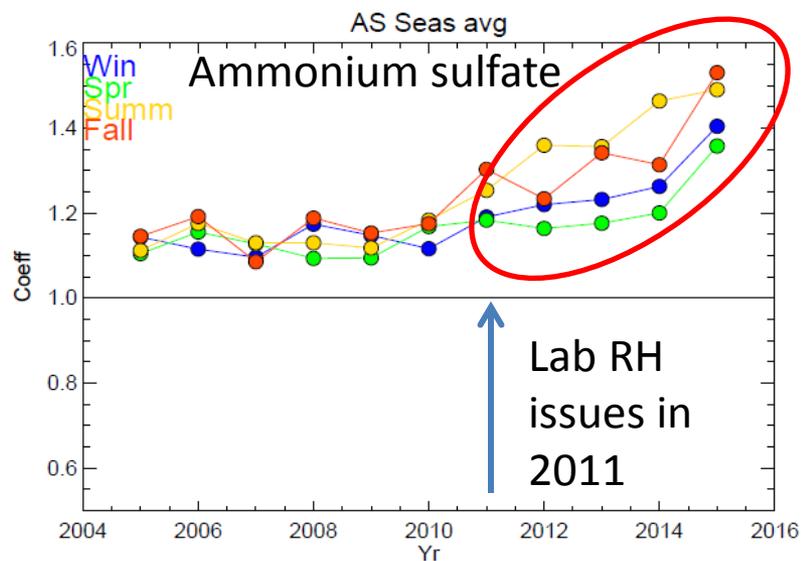
Interpretation:

$$a_1, a_2, a_4, a_5, a_6 \sim 1$$

$$a_3 = R_{oc} \text{ (e.g. POM/OC ratio)}$$

# Network Average MLR Results (Original Data)

2005-2015



## Some biases known to affect PM<sub>2.5</sub> Gravimetric Mass

(+) Particle Bound Water (PBW due to laboratory relative humidity)

(+/-) Organic multiplier ( $R_{oc} = POM/OC$ )

(+) Sulfur vs sulfate (degree of sulfate neutralization ~30%?; organosulfate)

(-) Nitrate is lost from Teflon filter (seasonal)

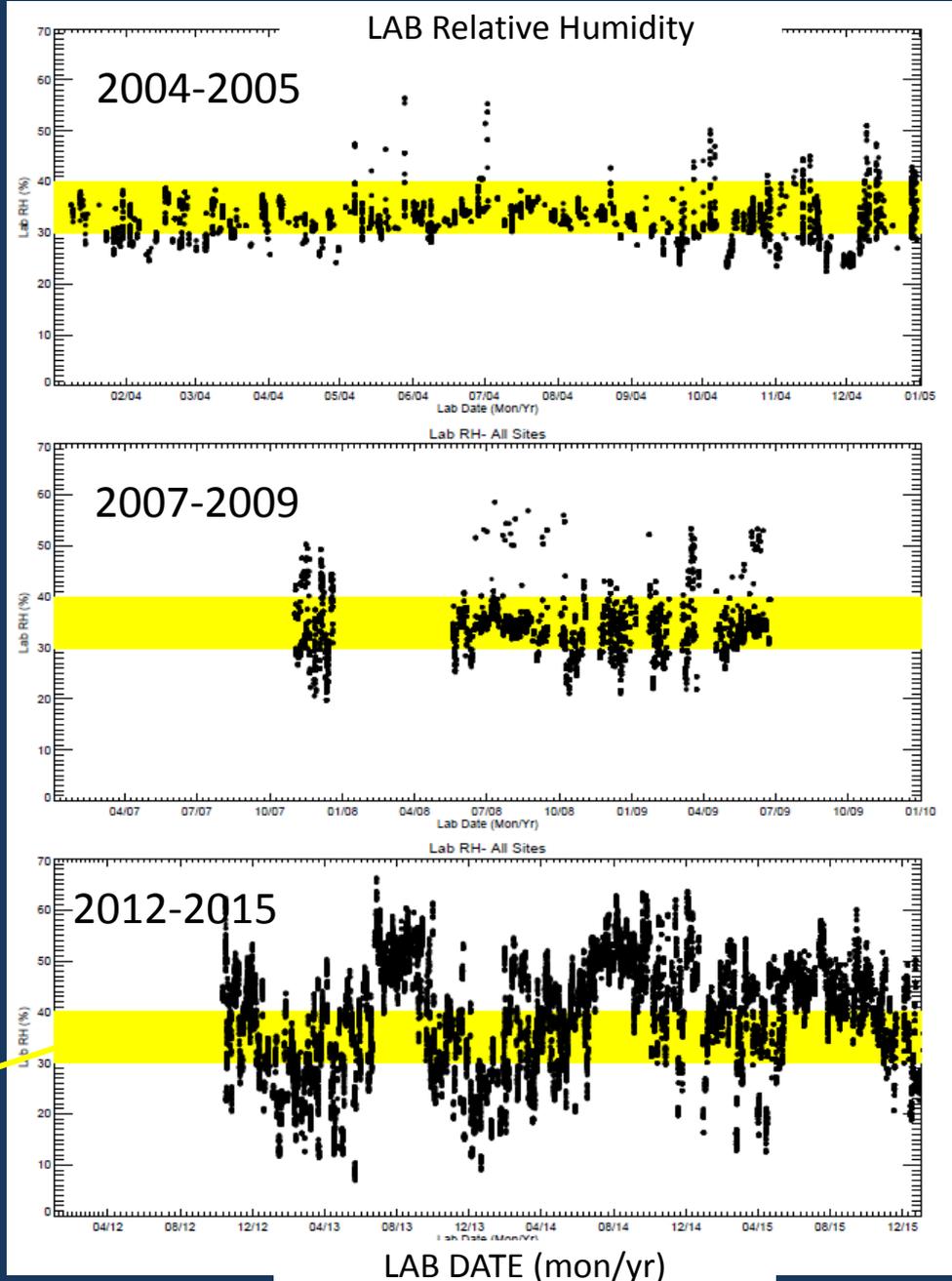
(+/-) Dust composition

Semi-volatiles lost on quartz filter (underestimate OC by ~20%) Malm et al., 2011

Other quartz filter artifacts- evaporation of OC during storage, adsorption of VOC gases

# Particle Bound Water using lab relative humidity (RH)

RH (%)



Lag between sample day and weighing day ranges from ~16-20 days (on avg)

Regulatory limits

1. Calculate seasonal network RH mean for lab time
2. Shift sample time to lab time using avg difference
3. Use daily site data if available
4. Fill in missing days with seasonal mean

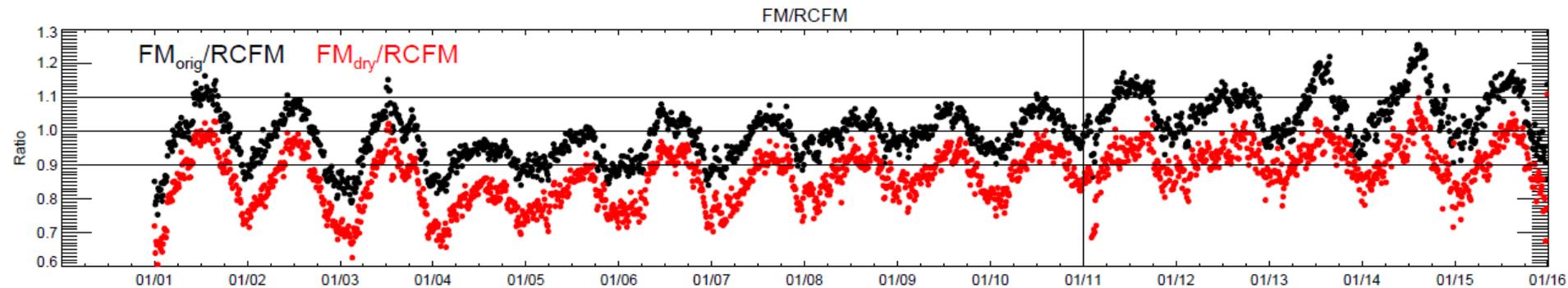
Seasonal RH (%)

2004-2006:	33,32,34,31
2007-2010:	33,34,36,33
2011-2012:	34,35,47,41
2013:	25,30,49,38
2014:	39,36,49,46
2015:	37,39,45,41

(see data advisory)

# Daily Network Median Original and “dry” FM

## FM/RCFM



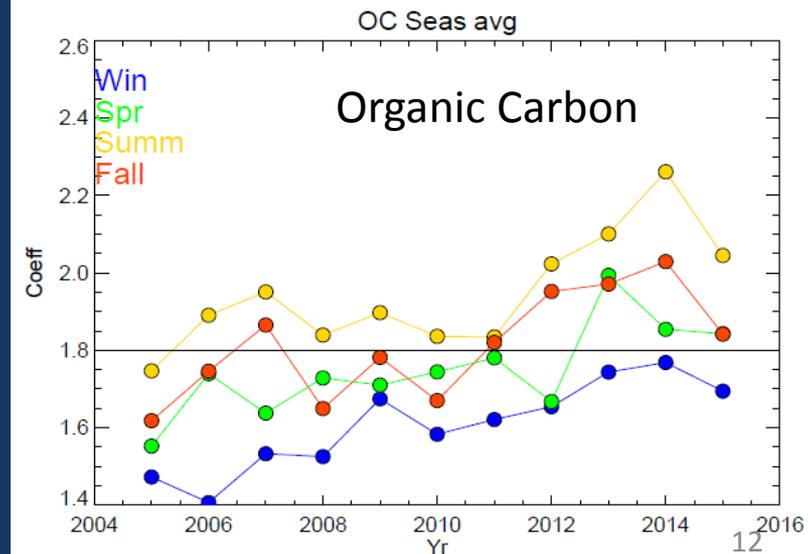
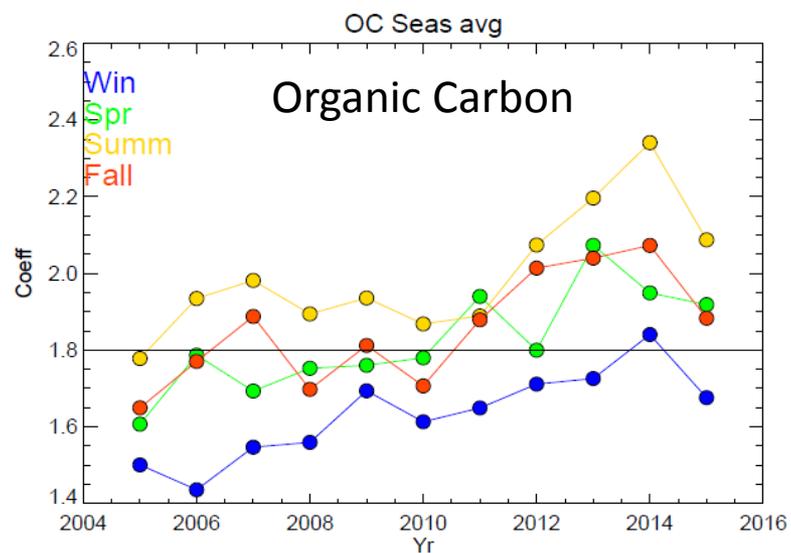
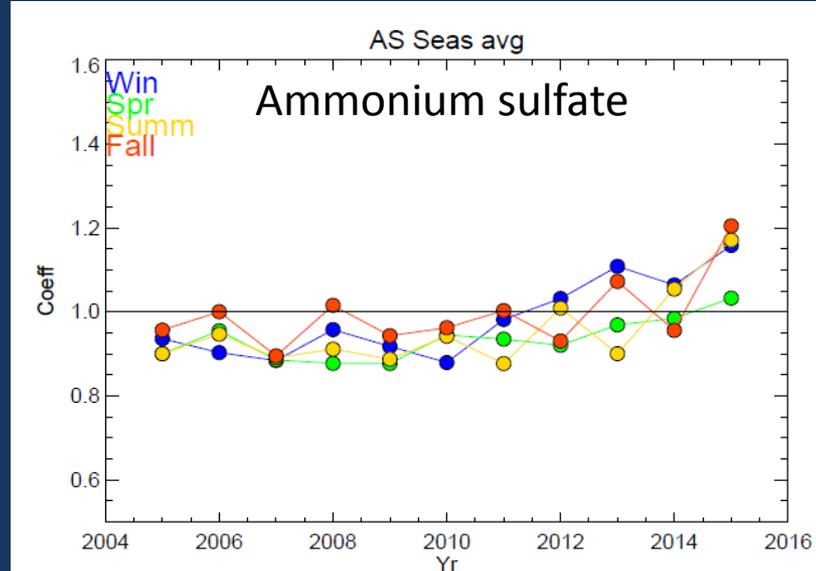
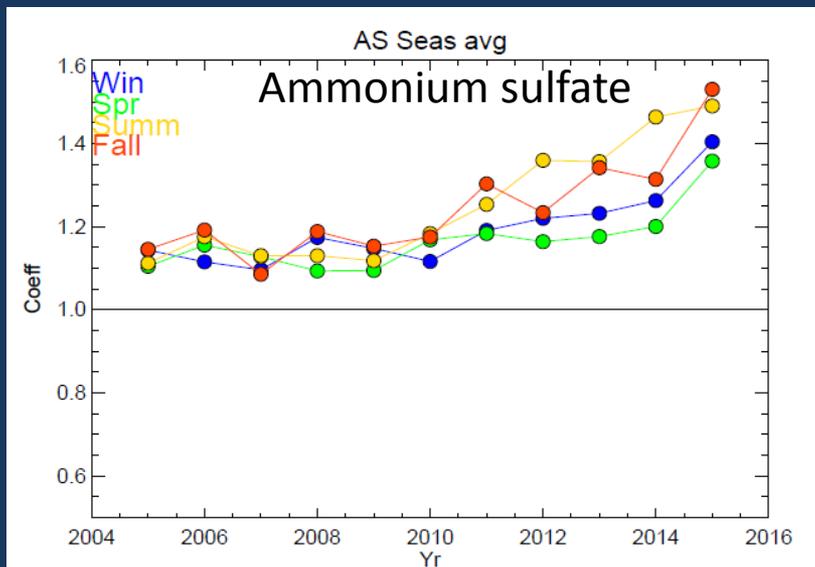
FM/RCFM- original

FM/RCFM- “dry”

# IMPROVE MLR Coefficients: Effects of RH

No RH adjustments (original)

FM adjusted for PBW using lab RH



## Some biases known to affect PM<sub>2.5</sub> Gravimetric Mass

(+) Particle Bound Water (PBW due to laboratory relative humidity)

(+/-) Organic multiplier ( $R_{oc} = POM/OC$ )

(+) Sulfur vs sulfate (degree of sulfate neutralization ~30%?; organosulfate)

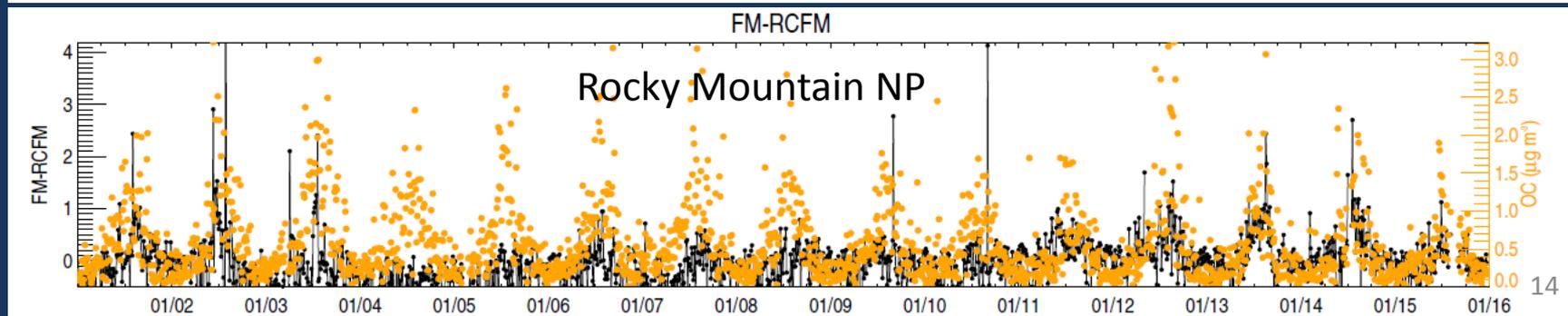
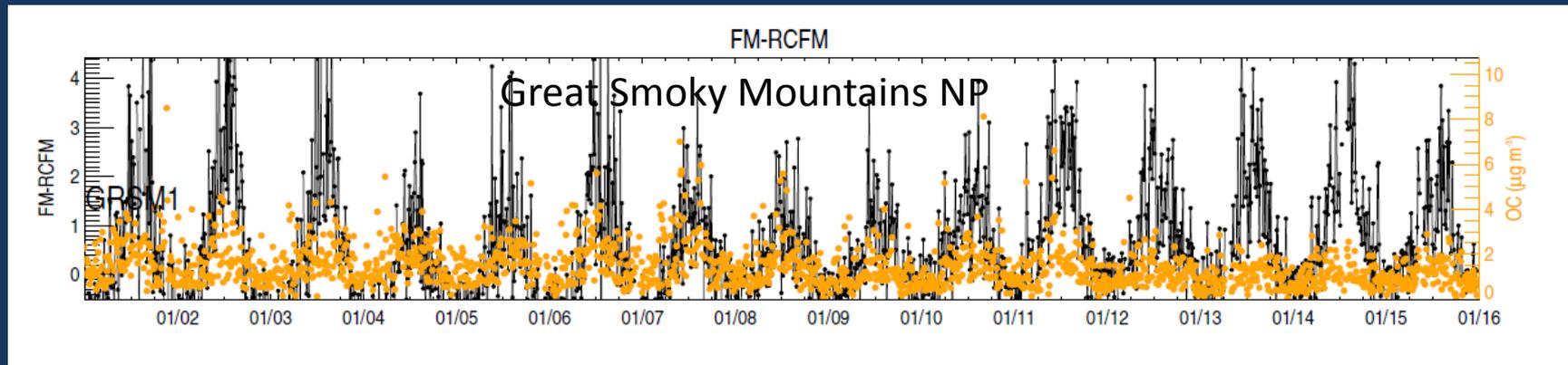
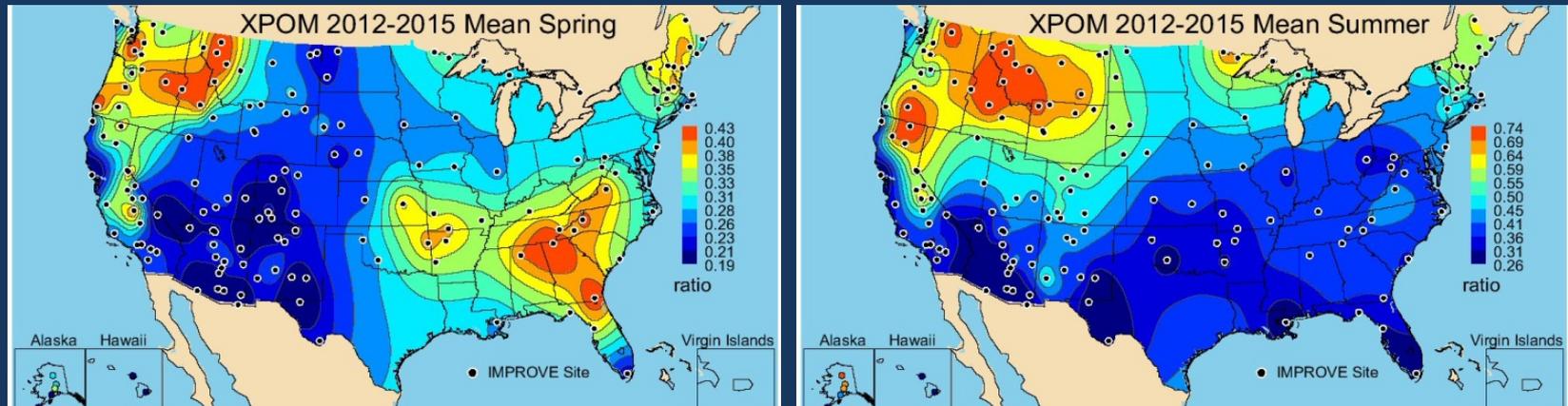
(-) Nitrate is lost from Teflon filter (seasonal)

(+/-) Dust composition

Semi-volatiles lost on quartz filter (underestimate OC by ~20%) Malm et al., 2011

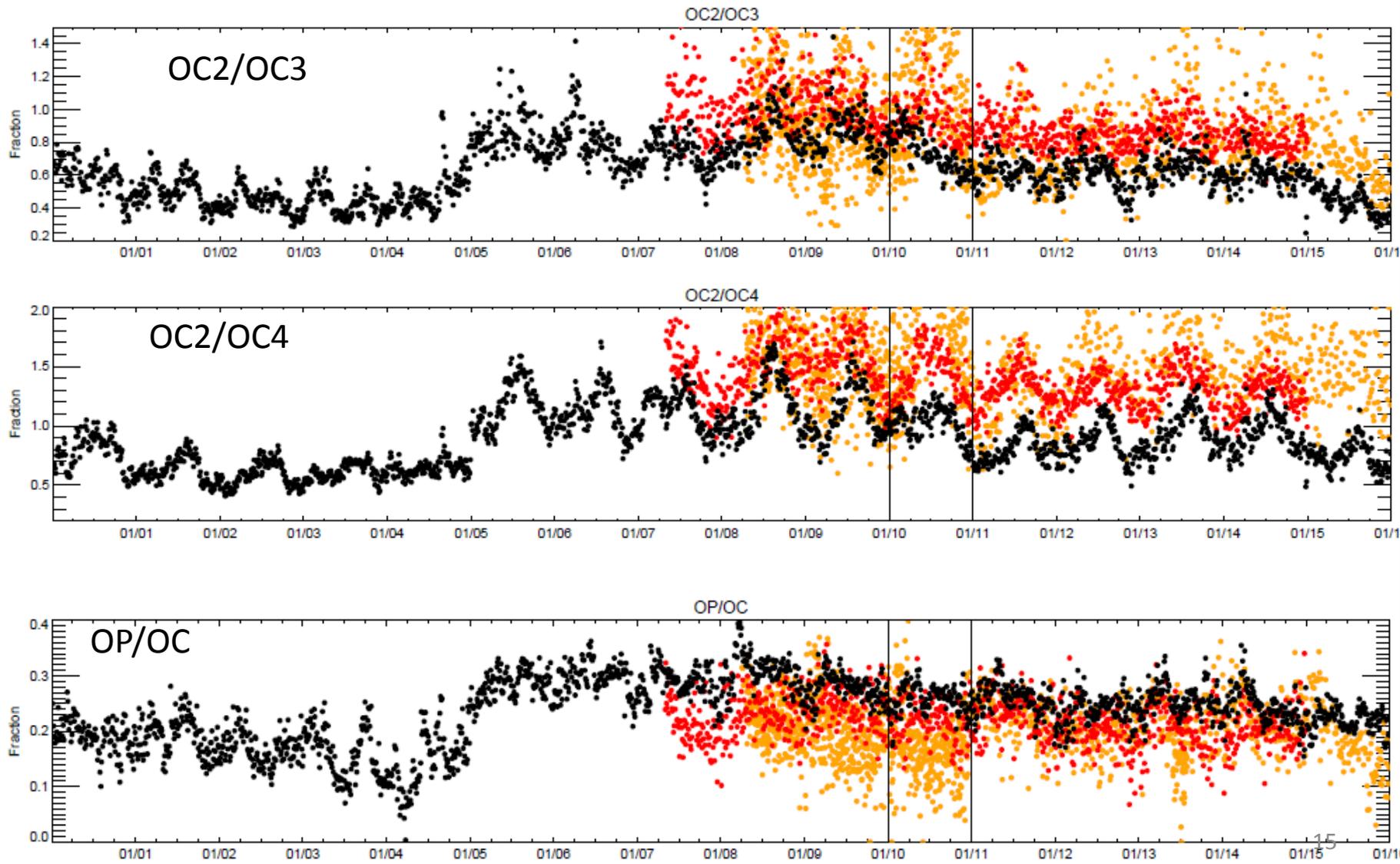
Other quartz filter artifacts- evaporation of OC during storage, adsorption of VOC gases

# Particulate organic carbon mass fraction (POM) highest in spring and summer

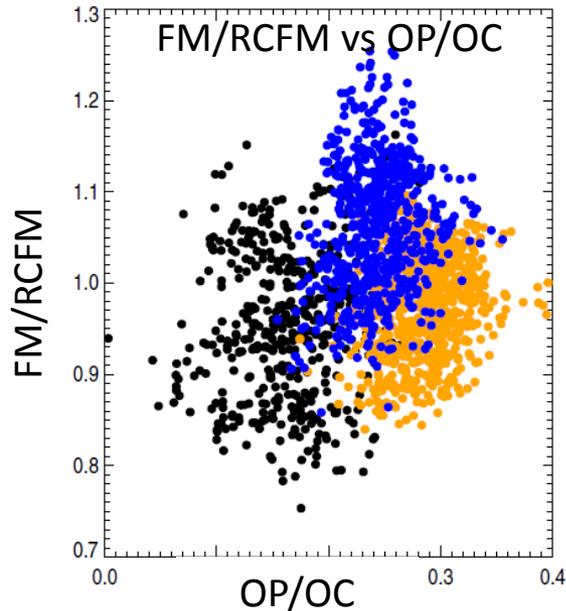
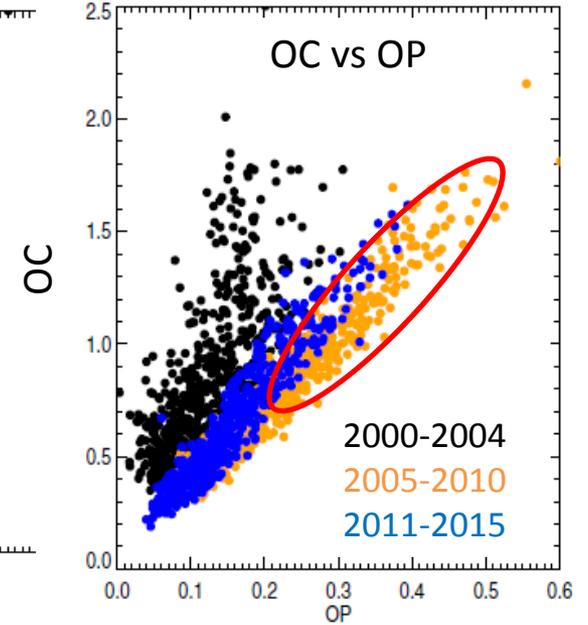
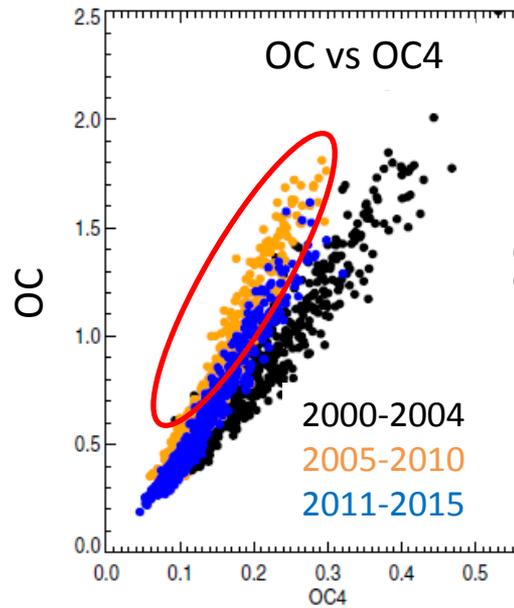
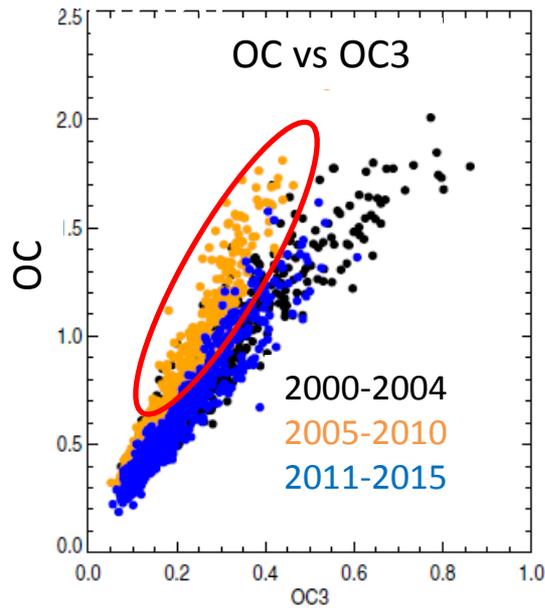


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SEARCH

# 2000-2015 Daily Network Median OC Fractions



# 2000-2015 Scatter Plots of Daily Network Median OC



Each point is a daily network median

2000-2004

2005-2010

2011-2015

## Some biases known to affect PM<sub>2.5</sub> Gravimetric Mass

(+) Particle Bound Water (PBW due to laboratory relative humidity)

(+/-) Organic multiplier ( $R_{oc} = POM/OC$ )

(+) Sulfur vs sulfate (degree of sulfate neutralization ~30%?; organosulfate)

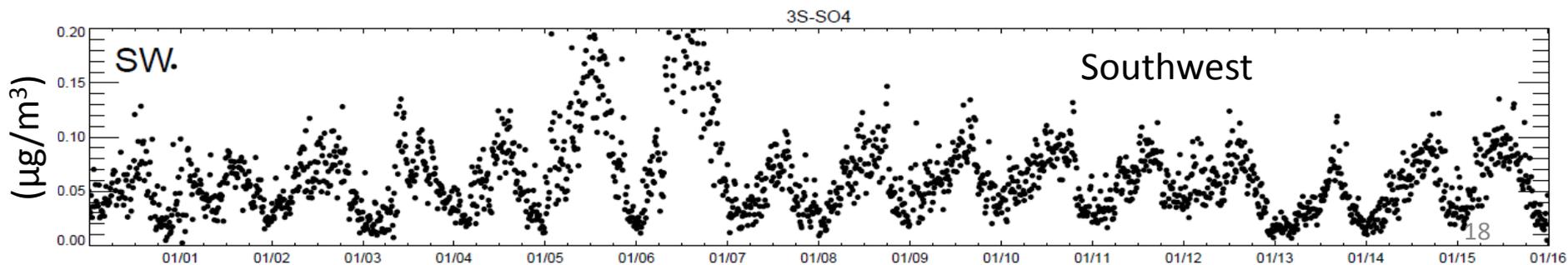
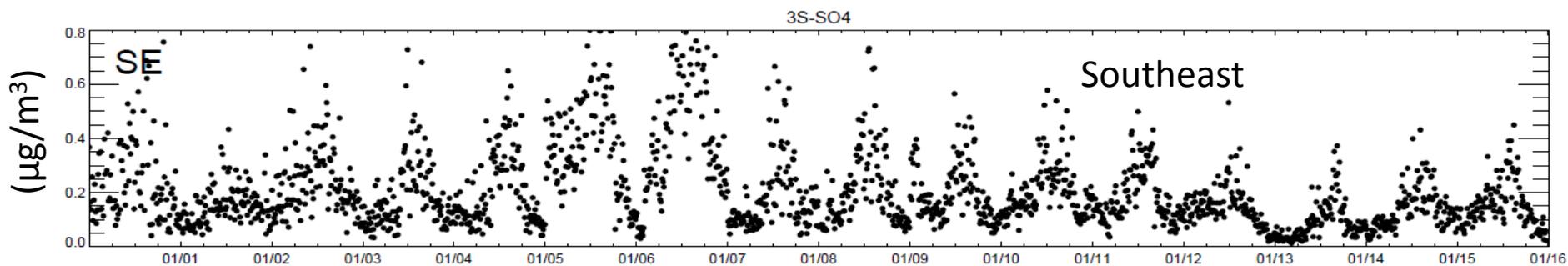
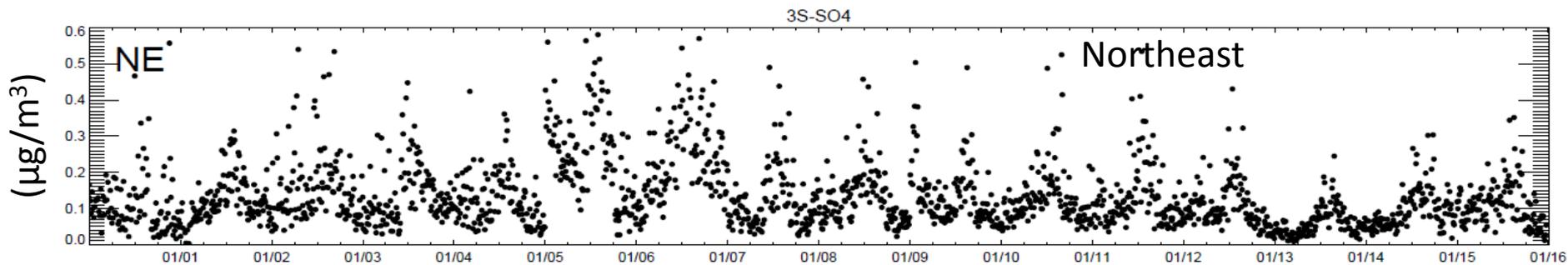
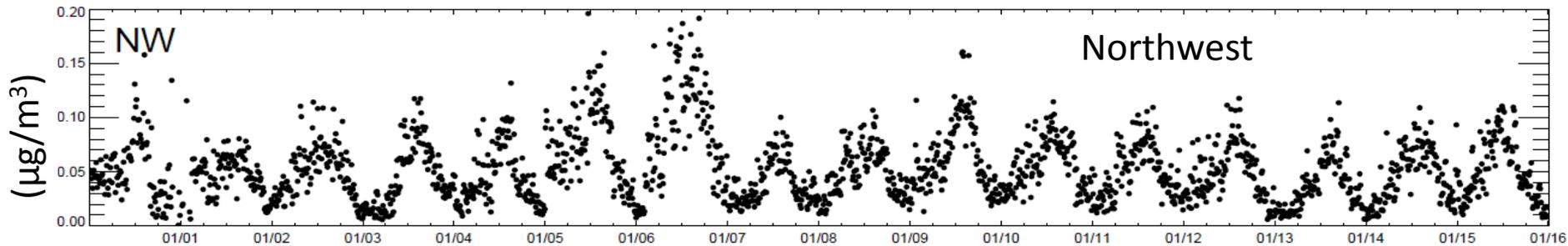
(-) Nitrate is lost from Teflon filter (seasonal)

(+/-) Dust composition

Semi-volatiles lost on quartz filter (underestimate OC by ~20%) Malm et al., 2011

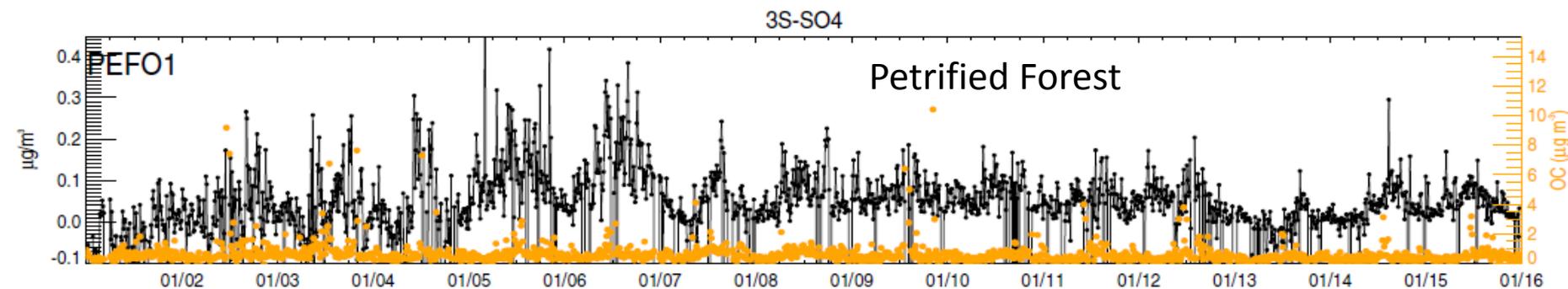
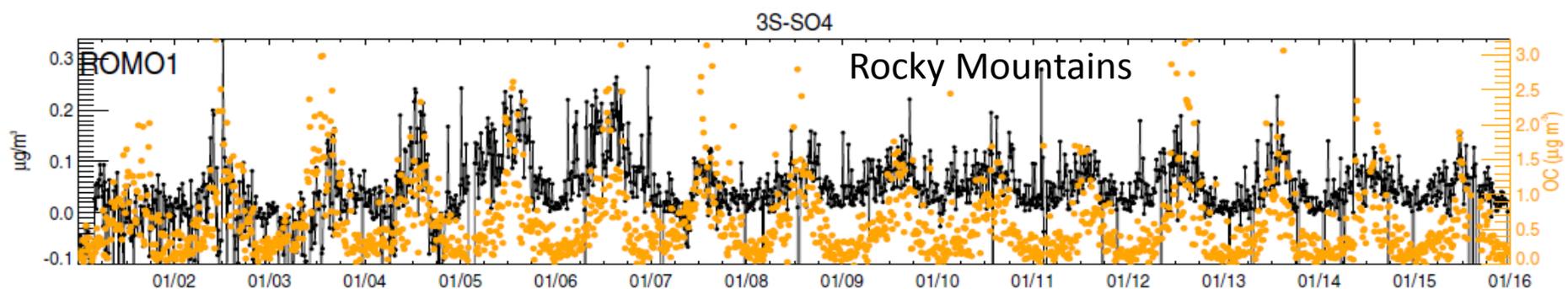
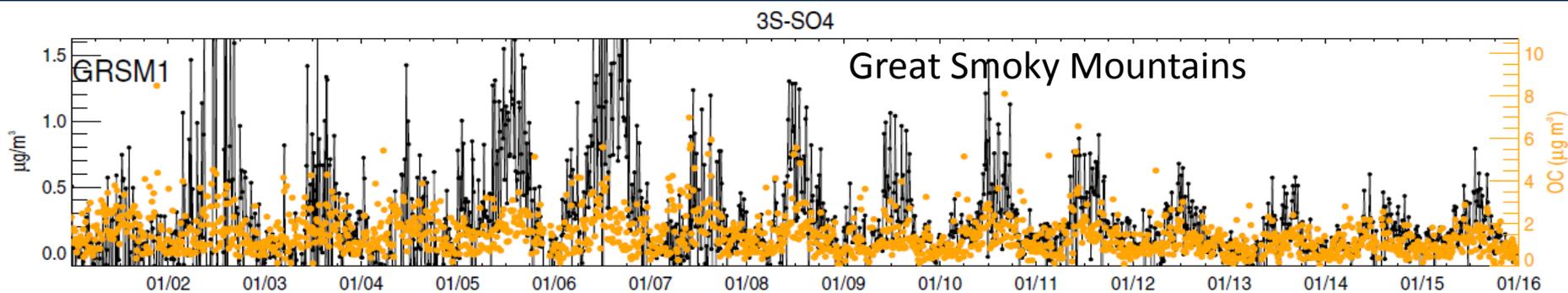
Other quartz filter artifacts- evaporation of OC during storage, adsorption of VOC gases

# Daily Regional Network Median 3S-SO<sub>4</sub>



# Excess sulfur associated with organosulfates?

2001-2015  
3S-SO<sub>4</sub> (left) OC (right)



## Some biases known to affect PM<sub>2.5</sub> Gravimetric Mass

(+) Particle Bound Water (PBW due to laboratory relative humidity)

(+/-) Organic multiplier ( $R_{oc} = POM/OC$ )

(+) Sulfur vs sulfate (degree of sulfate neutralization ~30%?; organosulfate)

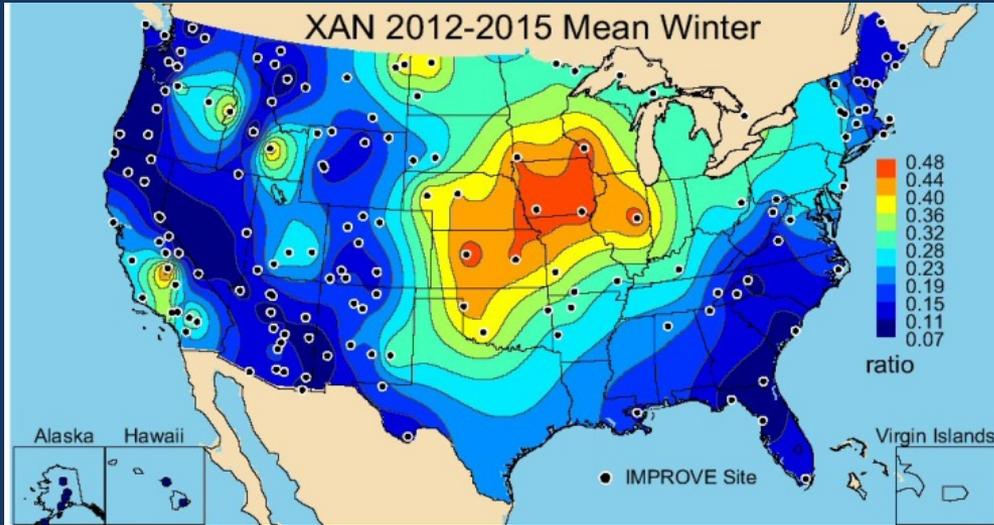
**(-) Nitrate is lost from Teflon filter (seasonal)**

(+/-) Dust composition

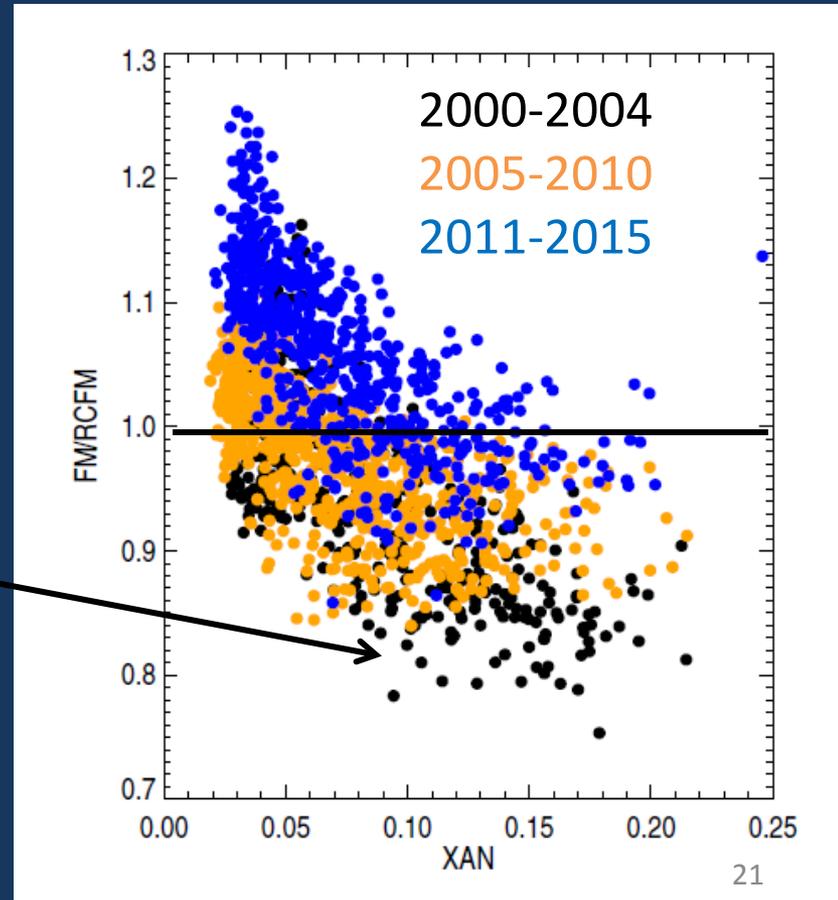
Semi-volatiles lost on quartz filter (underestimate OC by ~20%) Malm et al., 2011

Other quartz filter artifacts- evaporation of OC during storage, adsorption of VOC gases

# Ammonium Nitrate (AN) Mass Fraction- highest in winter



FM/RCFM vs  
AN mass fraction



Daily network median  
FM/RCFM lowest when AN  
fraction is highest  
(nitrate loss from Teflon)

## Some biases known to affect PM<sub>2.5</sub> Gravimetric Mass

(+) Particle Bound Water (PBW due to laboratory relative humidity)

(+/-) Organic multiplier ( $R_{oc} = POM/OC$ )

(+) Sulfur vs sulfate (degree of sulfate neutralization ~30%?; organosulfate)

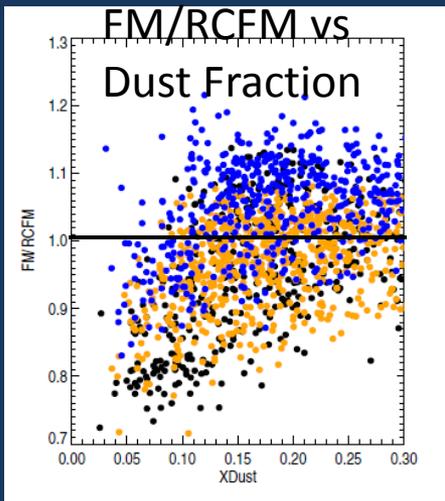
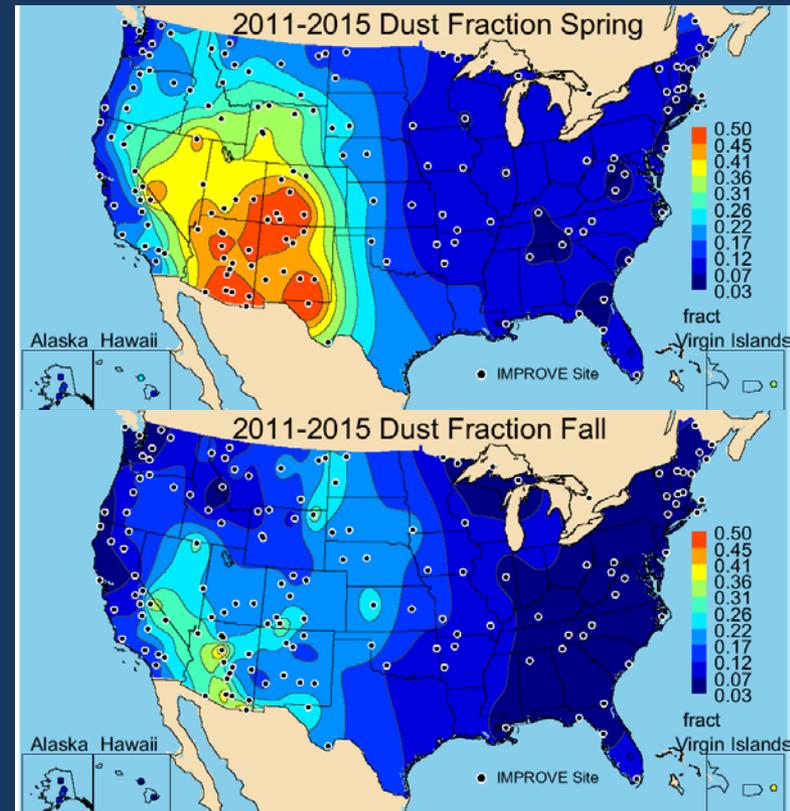
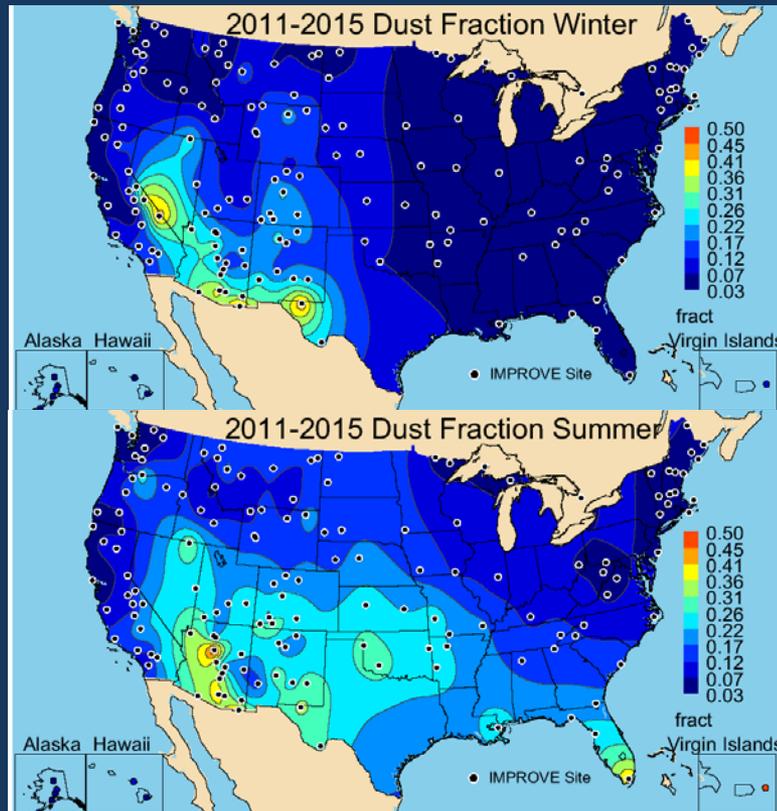
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**(+/-) Dust composition**

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Other quartz filter artifacts- evaporation of OC during storage, adsorption of VOC gases

# 2011-2015 Dust Mass Fraction highest in West



Southwest Sites:  
Higher FM/RCFM with higher dust fractions  
(MLR suggested dust could be low by ~20%)

# How do all of these biases contribute to the residual (FM-RCFM)?

Calculated biases:

PBW

POM artifact ( $R_{oc,new} * OC - 1.8 * OC$ )

3S-SO4

Nitrate artifact (80% in warm season, 20% in cold season)

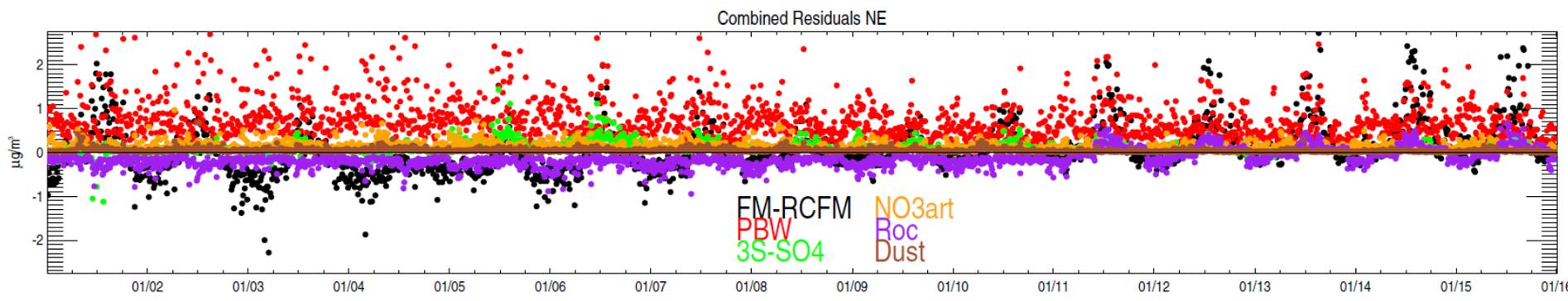
Dust artifact (20%)

	$R_{oc,new}$	
	2005-2010	2011-2015
Win	1.4	1.5
Spr	1.5	1.7
Sum	1.7	2.0
Fall	1.6	1.9

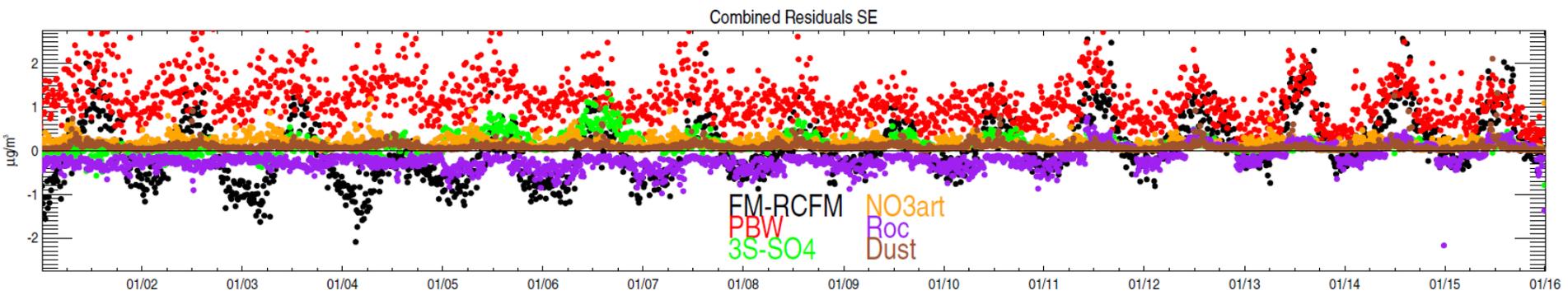
# Combined Residuals-Regional Median

FM-RCFM	NO3art
PBW	Roc
3S-SO4	Dust

## Northeast



## Southeast

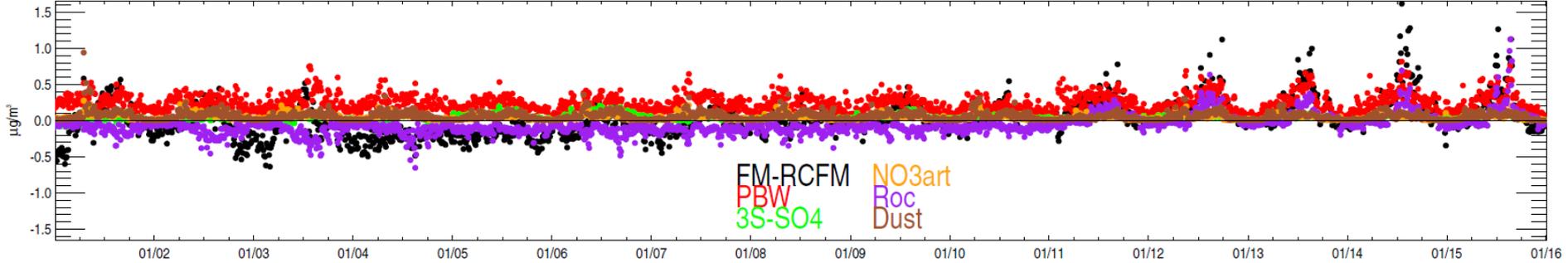


# Combined Residuals-Regional Median



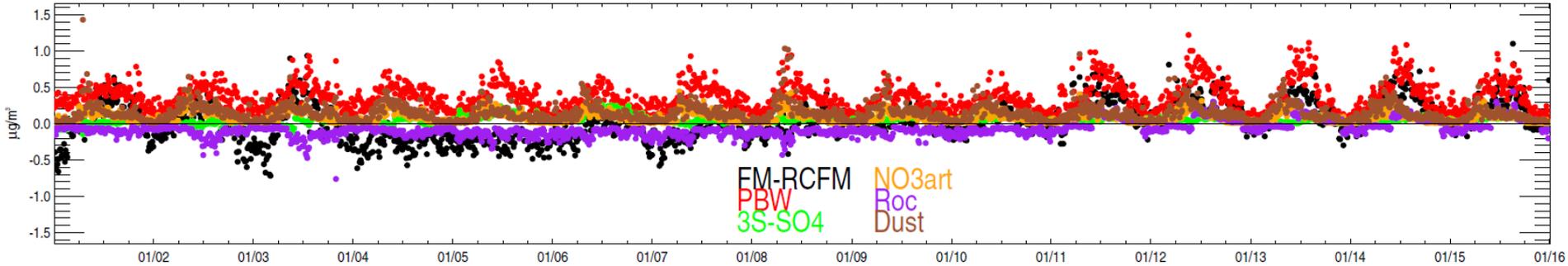
## Northwest

Combined Residuals NW



## Southwest

Combined Residuals SW

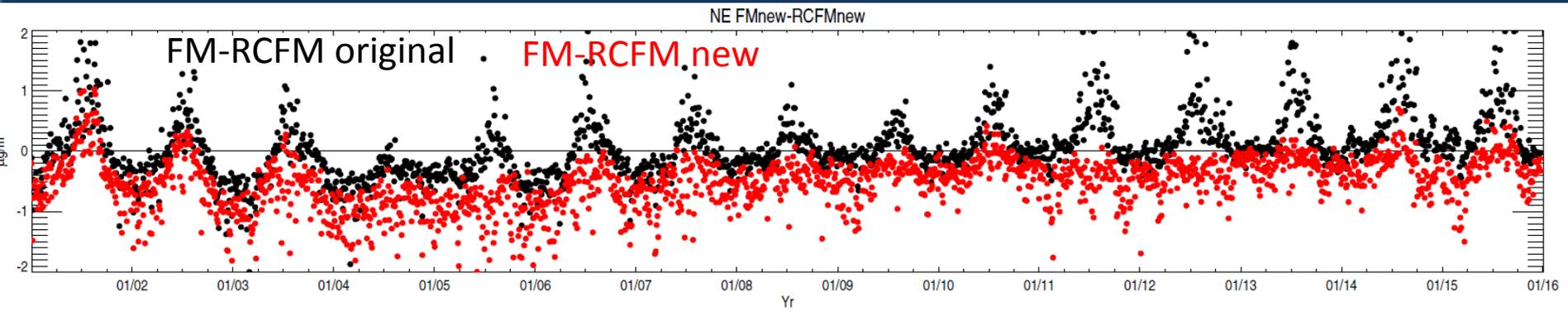


# Adjusted FM and RCFM Residual- Regional Median

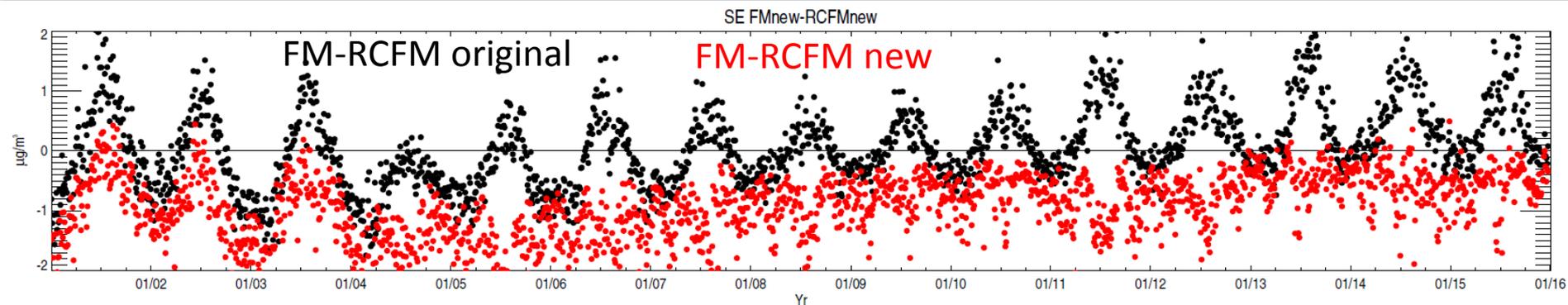
$$FM_{new} = FM - PBW - (3S-SO4) + NO3art$$

$$RCFM_{new} = AS + AN + POM_{new} + EC + 1.2 * Dust + SS$$

## Northeast FM-RCFM



## Southeast FM-RCFM

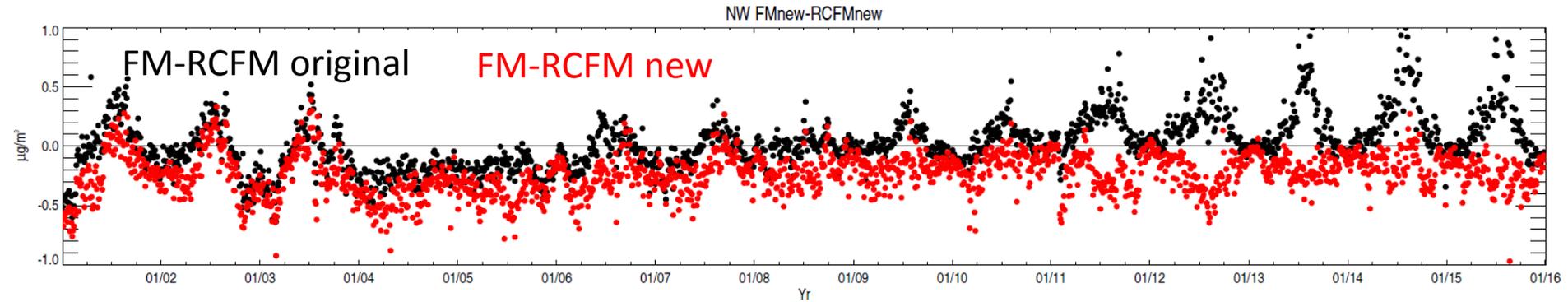


# Adjusted FM and RCFM Residual- Regional Median

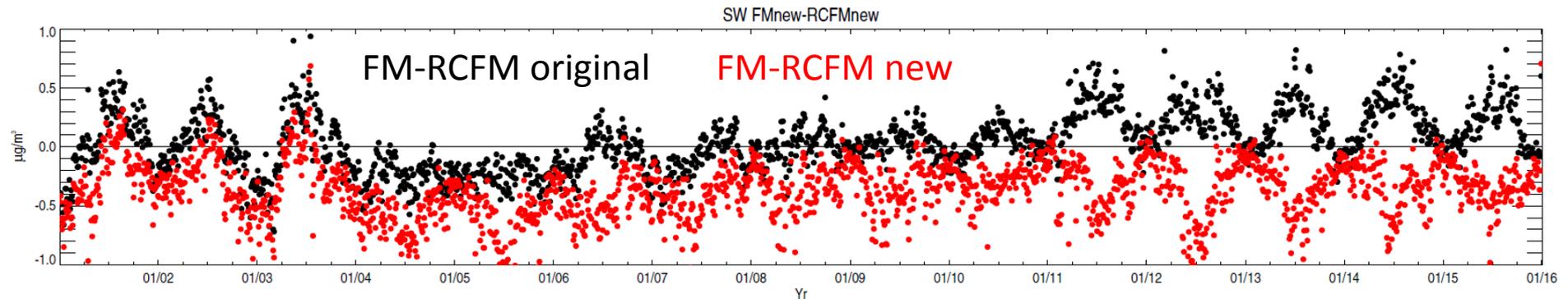
$$FM_{\text{new}} = FM - PBW - (3S-SO_4) + NO_3\text{art}$$

$$RCFM_{\text{new}} = AS + AN + POM_{\text{new}} + EC + 1.2 * \text{Dust} + SS$$

## Northwest FM-RCFM



## Southwest FM-RCFM



# Summary

Residual won't be "fixed" by a single correction- varies seasonally, annual, and spatially and is likely due to a combination of several biases:

- PBW has the biggest impact- controlling RH in lab very important.
- POM:  $R_{oc}$  has likely increased in some regions- could be indicative real changes but analytical contributions cannot be ruled out.
- POM: Seasonal variability in  $R_{oc}$  is larger than the increase over time.
- Nitrate: Impact of nitrate loss on Teflon known and contributing to residual.
- 3S-SO<sub>4</sub> residual can be a significant and varies seasonally and spatially.
- Dust equation could be adjusted.

# Acknowledgments



National Park Service  
Air Resources Division

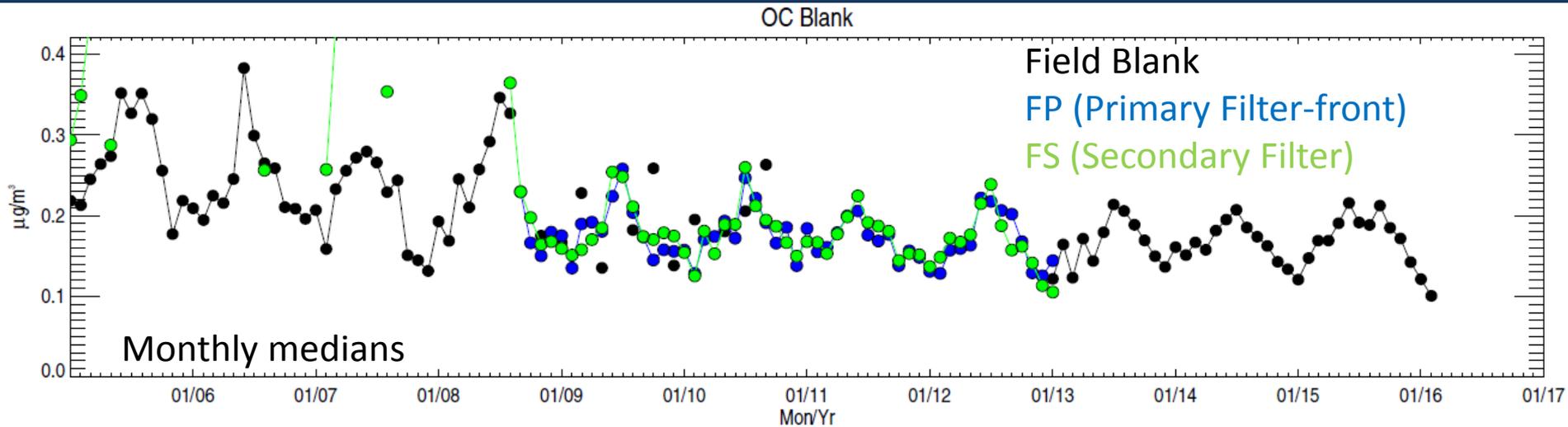
IMPROVE

<http://vista.cira.colostate.edu/Improve/>

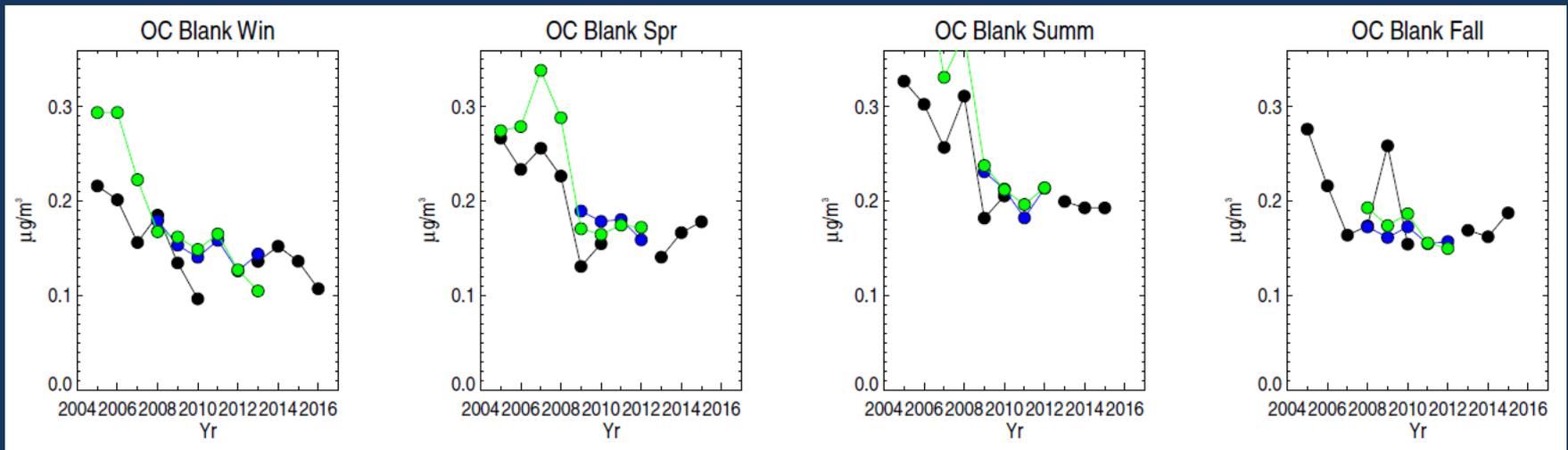


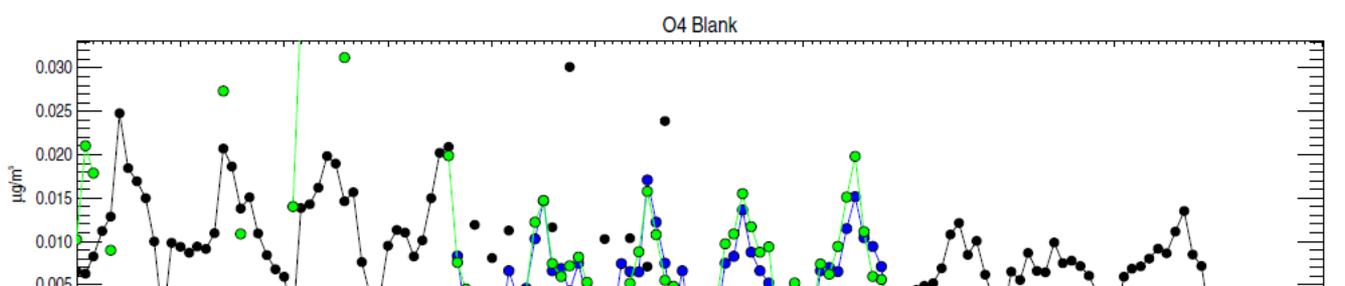
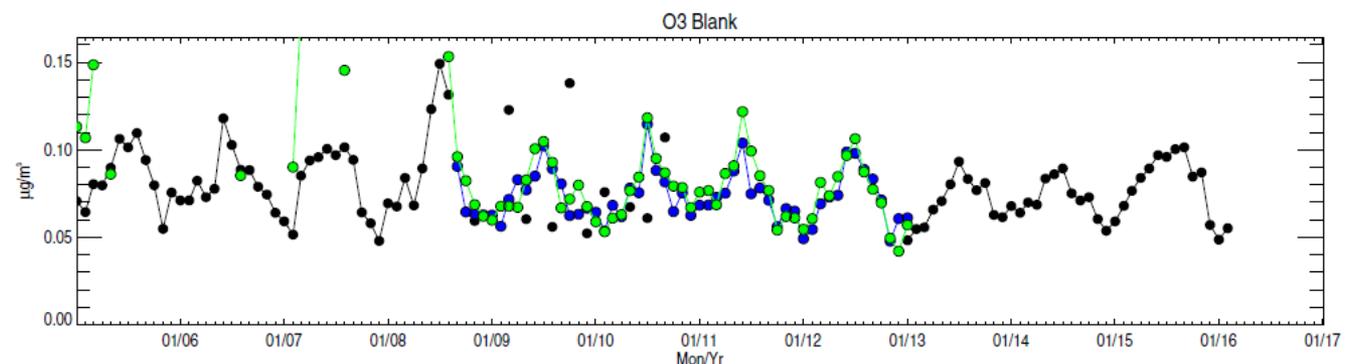
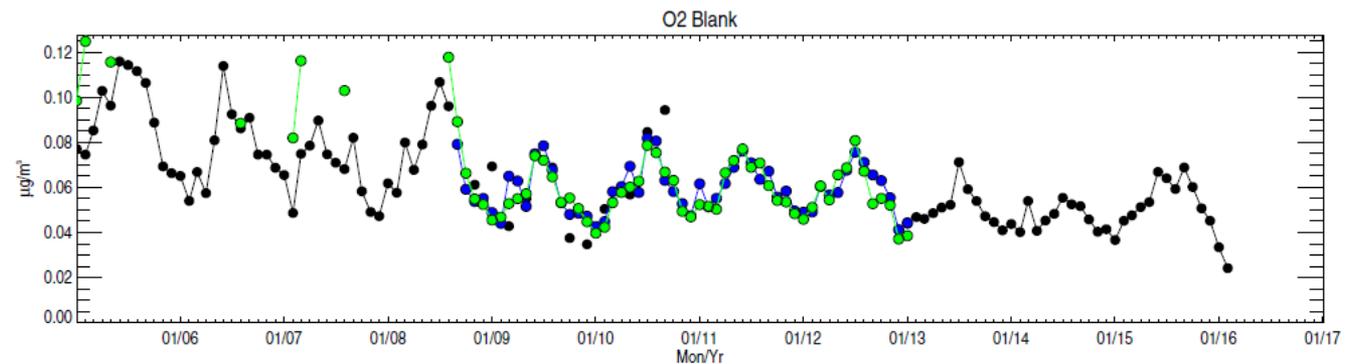
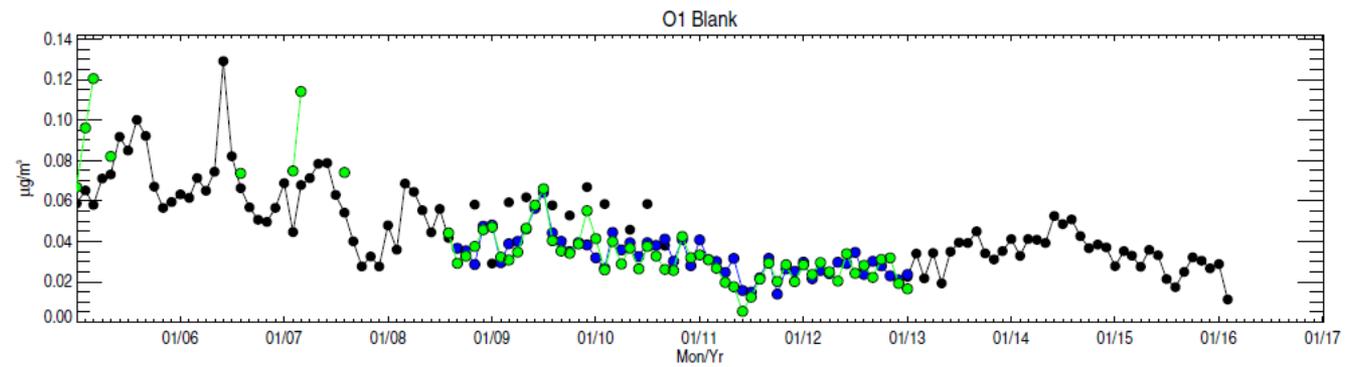
jlhand@colostate.edu

# Carbon Field Blanks (2005-2016)

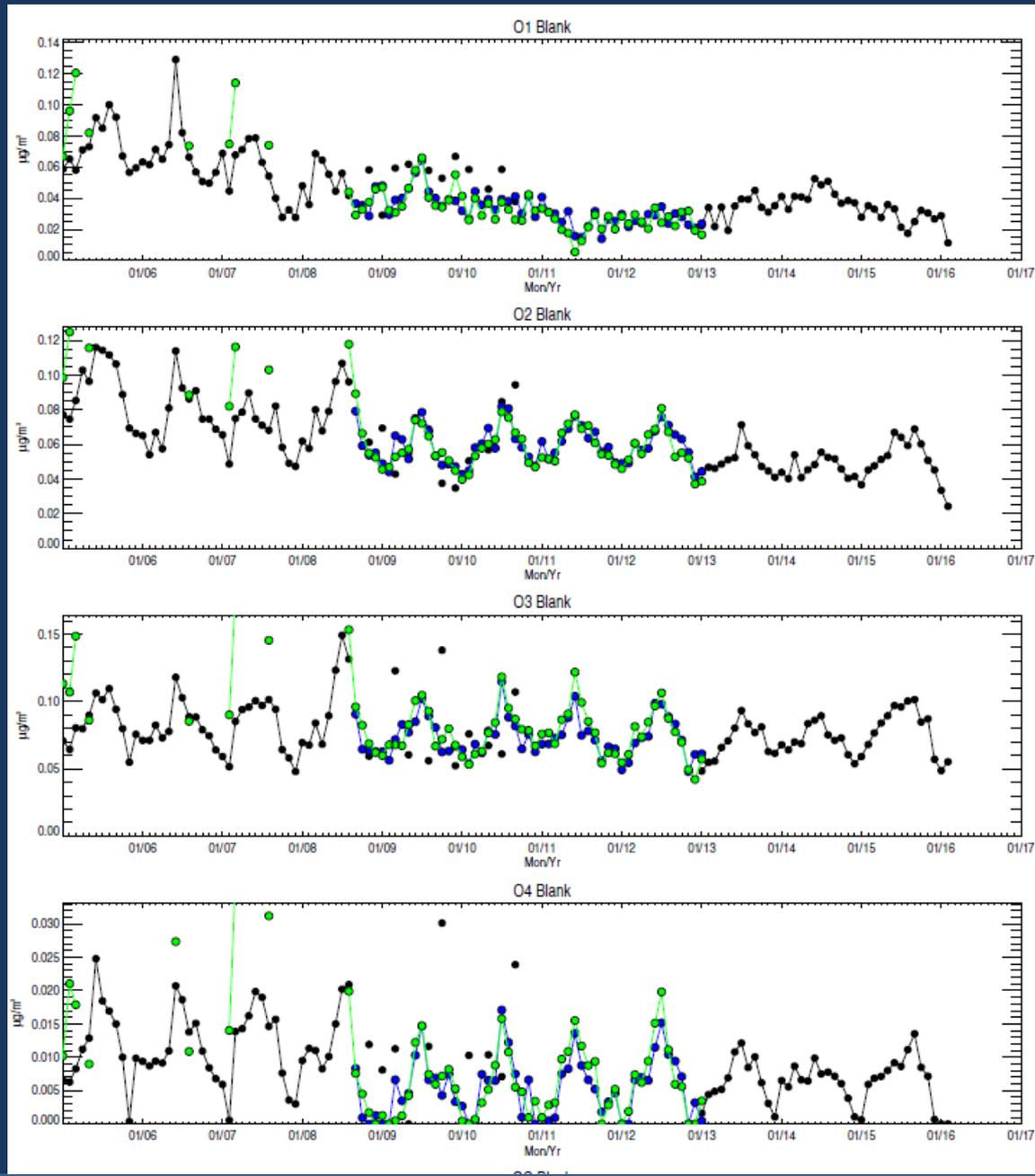


## Seasonal medians

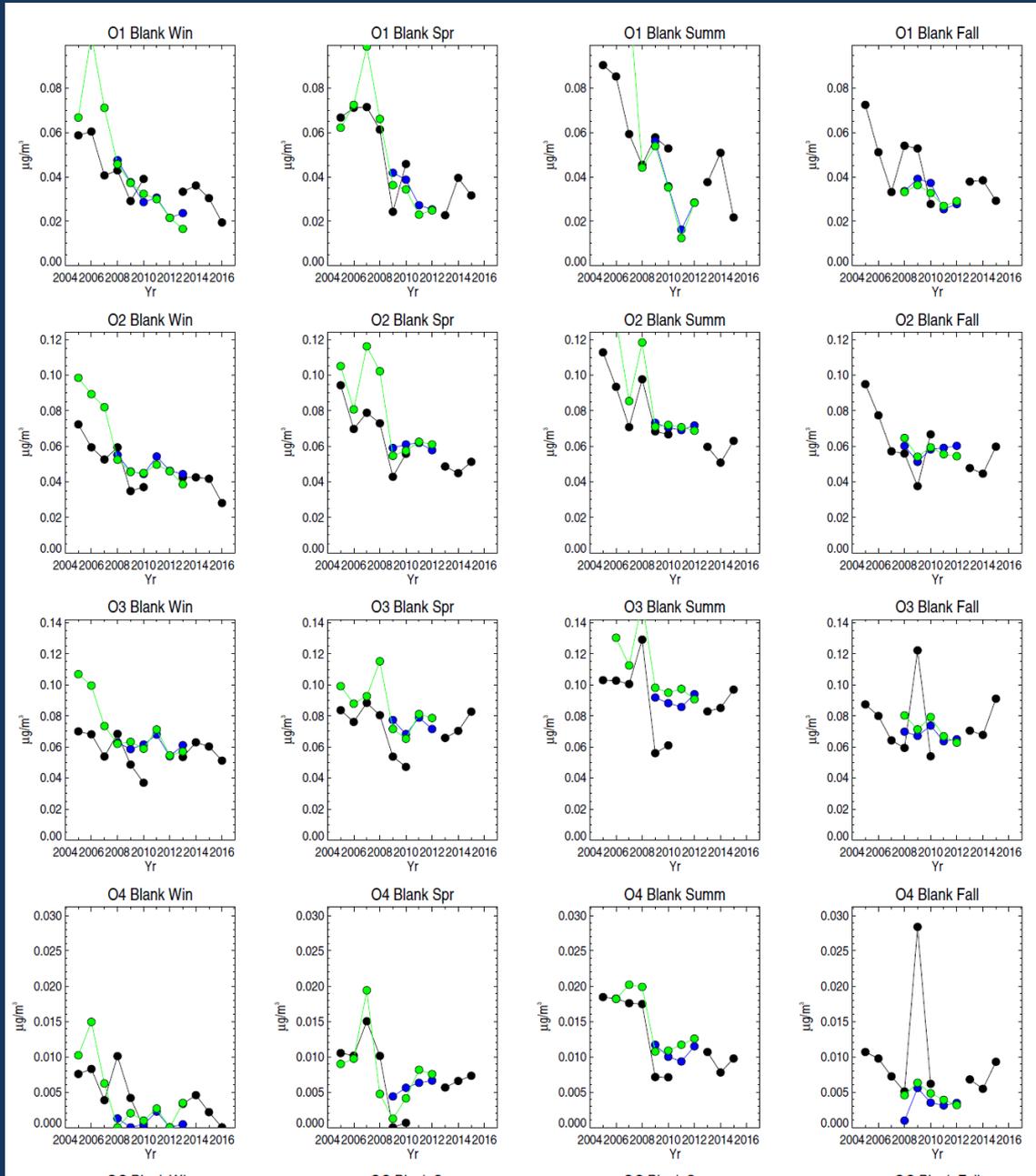




# OC Fraction Field Blanks



# Seasonal Median OC Fraction Field Blanks



Malm et al (2011)  
 IMPROVE: 1988-2008  
 CSN: 2000-2008

Malm and Hand 2007 (1988-2003)  
 AS =  $1.2 \pm 0.2$   
 OC =  $1.7 \pm 0.2$   
 Dust =  $1.2 \pm 0.3$

**Table 4a.** Results of OLS regression analysis using eq 15 for the IMPROVE monitoring data.

Variable	Estimate	SE	t value	Probability of > t
All				
$R^2 = 0.95$				
ASO <sub>4</sub>	1.12	0.00	1328.90	0.00
ANO <sub>3</sub>	0.75	0.00	410.67	0.00
POM	1.60	0.00	822.62	0.00
Other	1.06	0.00	597.08	0.00
Winter				
$R^2 = 0.96$				
SO <sub>4</sub>	1.02	0.00	391.99	0.00
NO <sub>3</sub>	0.92	0.00	403.37	0.00
POM	1.42	0.00	301.41	0.00
Other	1.05	0.00	234.18	0.00
Spring				
$R^2 = 0.93$				
SO <sub>4</sub>	1.10	0.00	560.18	0.00
NO <sub>3</sub>	0.70	0.00	200.96	0.00
POM	1.52	0.00	344.45	0.00
Other	1.09	0.00	402.66	0.00
Summer				
$R^2 = 0.96$				
SO <sub>4</sub>	1.15	0.00	793.24	0.00
NO <sub>3</sub>	0.51	0.01	47.14	0.00
POM	1.70	0.00	465.24	0.00
Other	1.08	0.00	295.10	0.00
Fall				
$R^2 = 0.96$				
SO <sub>4</sub>	1.09	0.00	696.73	0.00
NO <sub>3</sub>	0.75	0.00	206.21	0.00
POM	1.59	0.00	467.48	0.00
Other	1.06	0.00	273.71	0.00

## Working Group Discussion Outline: Possible activities to investigate potential changes in $R_{oc}$

1. Is there a trend in  $R_{oc}$  in the IMPROVE data?
  - a) Refine MLR analyses
2. Could the trends in  $R_{oc}$  be due to analytical issues?
  - a) Could the measured OC on quartz filters underreport the measured OC on Teflon filters? If so, how?
  - b) Review history of analytical changes in methodology and procedures of OC measurements
    - i. What analytic changes have occurred and how might they contribute?
    - ii. Could analytical changes impact the split in OC/EC or OC fractions? (e.g., OC3 and OC4 trends)
    - iii. Filter storage (change in lag time)
    - iv. Instrument maintenance, calibrations, upgrades
  - c) Review OC blanks
  - d) Compare to FTIR-derived  $R_{oc}$
  - e) Are the trends evident in independent datasets
    - i. Similar analysis with SEARCH data (independent carbon analysis)
    - ii. Optical data analysis (Consistent so far)
    - iii. CSN (pseudo-independent)
    - iv. Literature values (review)
  - f) Interference of mineral aerosols
  - g) Reanalysis of archived filters (Biases? Costs?)

## Working Group Discussion Outline: Continued

3. What are “typical”  $R_{oc}$  factors that should be used at IMPROVE sites?
  - a) Derive new  $R_{oc}$  using MLR (include seasonal/spatial differences)
  - b) OC hygroscopicity
  - c) New carbon composition analyses
    - i. TOR-MS, etc.
    - ii. FTIR
    - iii. Other (AMS data, etc.)?

# BIASES

- (-) Nitrate is lost from Teflon (summer)
- (-) Semi-volatiles lost (underestimate OC)
- (-) Quartz filter artifacts- evaporation of particles
- (-) Pressure difference across filter- 20% OC loss
- (+/-) Organic multiplier
- (+) Water retained during weighing
- (+) Sulfur vs SO<sub>4</sub> (form of sulfate ~30%?, organosulfate)
- (+) Rxn with atmospheric gases
- (+) Quartz filter artifacts- adsorption of VOC gases
- (+) Water soluble organics
- (+) Under-estimate dust
- (+) brown carbon/ EC coatings?

## Species-specific trends:

- (-) Sulfate
- (-) Nitrate
- (-) OC
- (-) EC
- (+) CM
- (+) dust
- (-) Water (SEARCH sites)