Temporal trends in the difference between gravimetric and reconstructed fine mass

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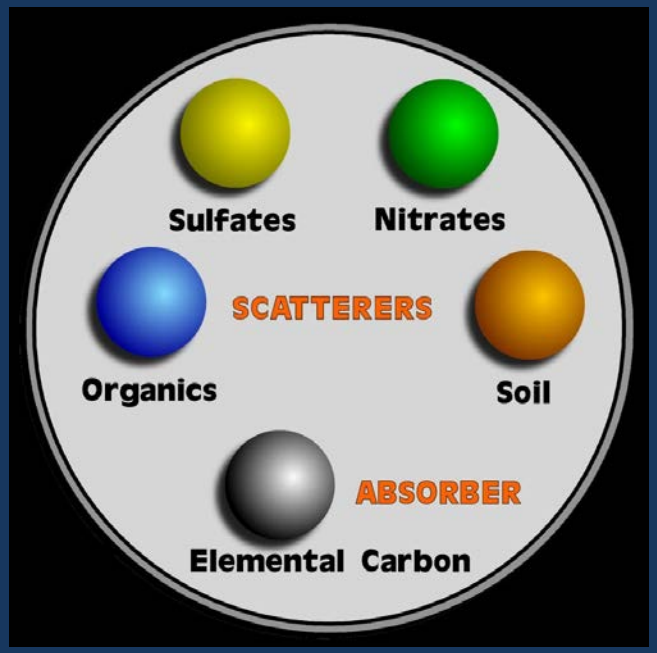
Reconstructed Fine Mass (**RCFM**)

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



RCFM =

Ammonium Sulfate ($1.375*SO_4^{-2}$) +
Ammonium Nitrate ($1.29*NO_3^-$) +
Particulate Organic Matter ($1.8*OC$) +
Elemental Carbon +
Dust +
Sea Salt ($1.8*Cl^-$)

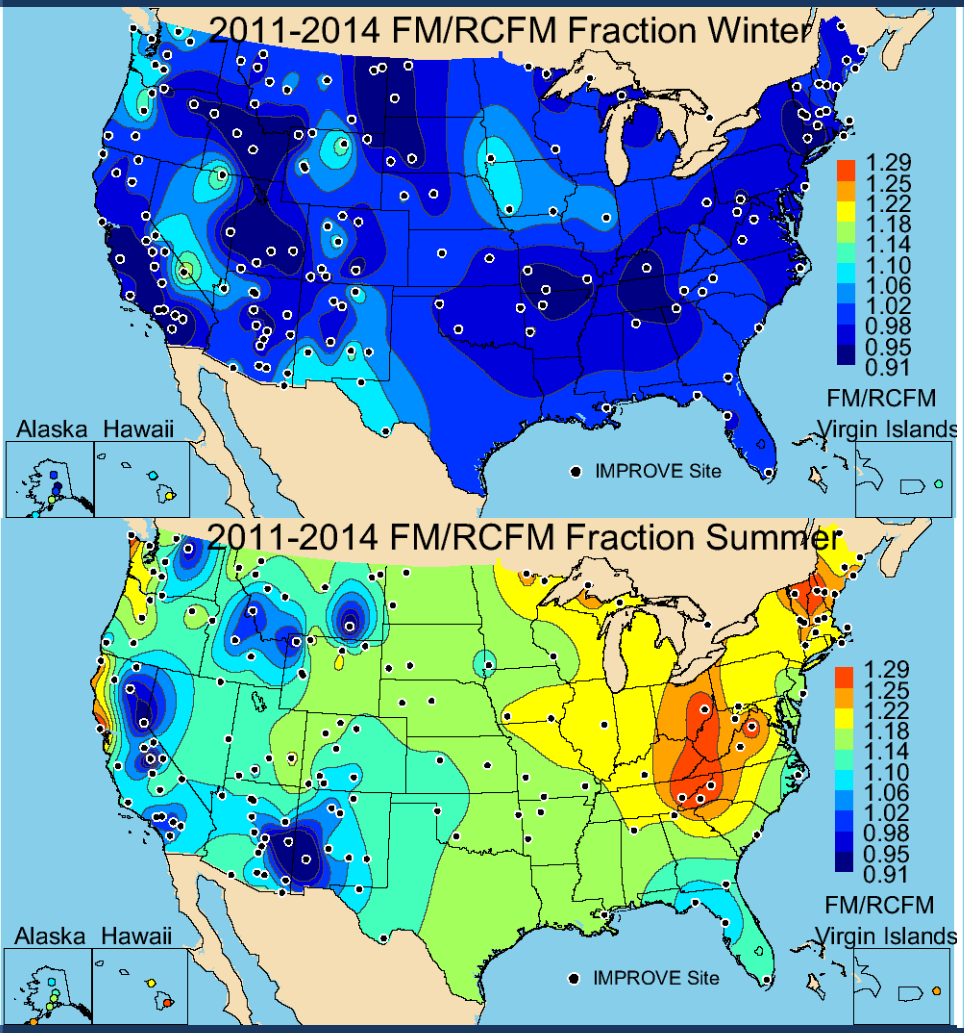
Why?

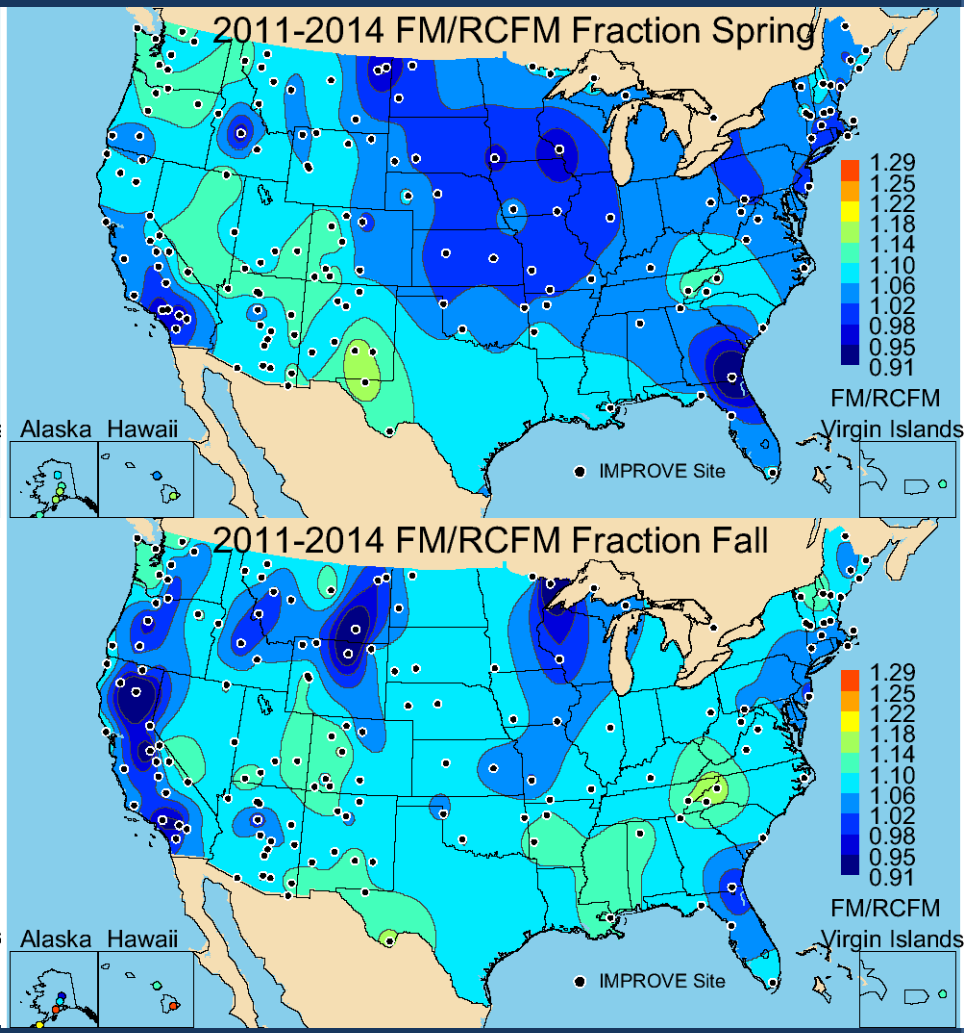
Dave Ridley (MIT) alerted us to diverging trends in gravimetric and reconstructed fine mass just before last year's IMPROVE meeting.

FM-RCFM

- Monthly, seasonal means in FM-RCFM and FM/RCFM
- Spatial and seasonal exploration FM-RCFM
- Temporal trends (2005-2014) in FM/RCFM
- Multiple linear regression to investigate trends in FM/RCFM

Current (2011-2014) Seasonal Mean FM/RCFM

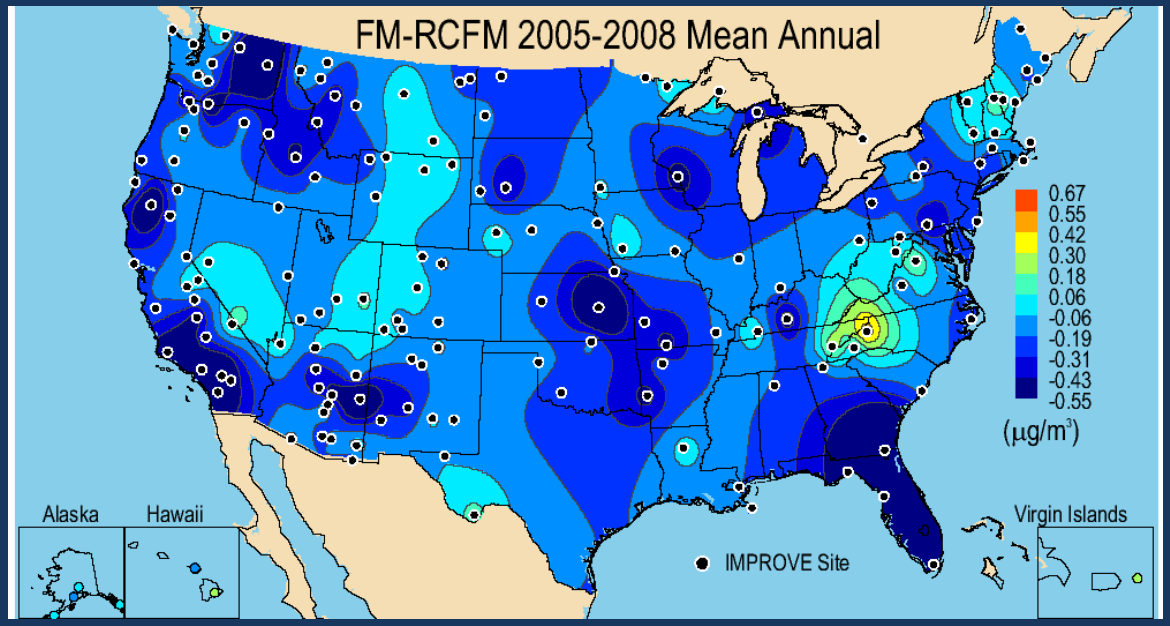




→ Large spatial and seasonal variability

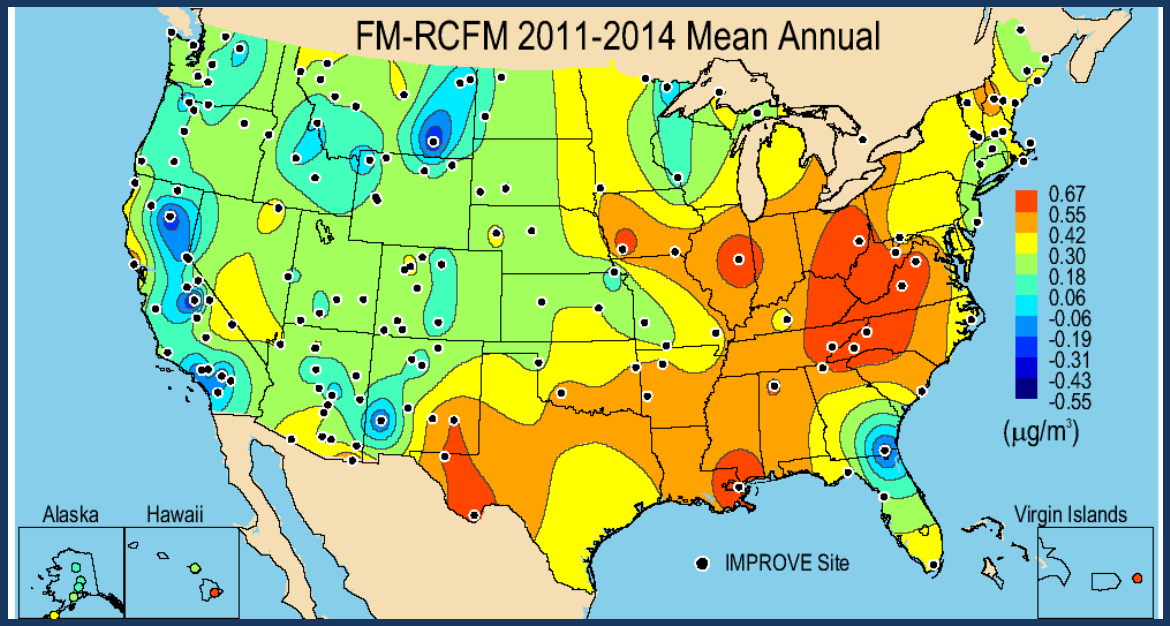
Annual FM-RCFM: (2005-2008) vs (2011-2014)

2005-2008



Earlier period:
FM < RCMF

2011-2014

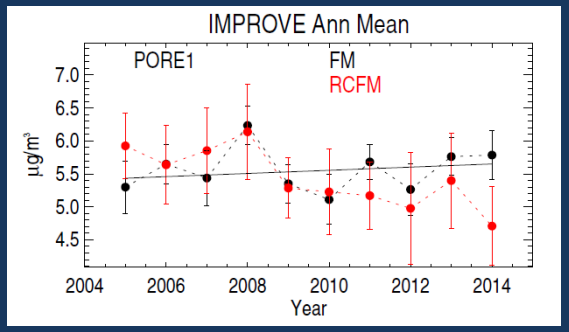


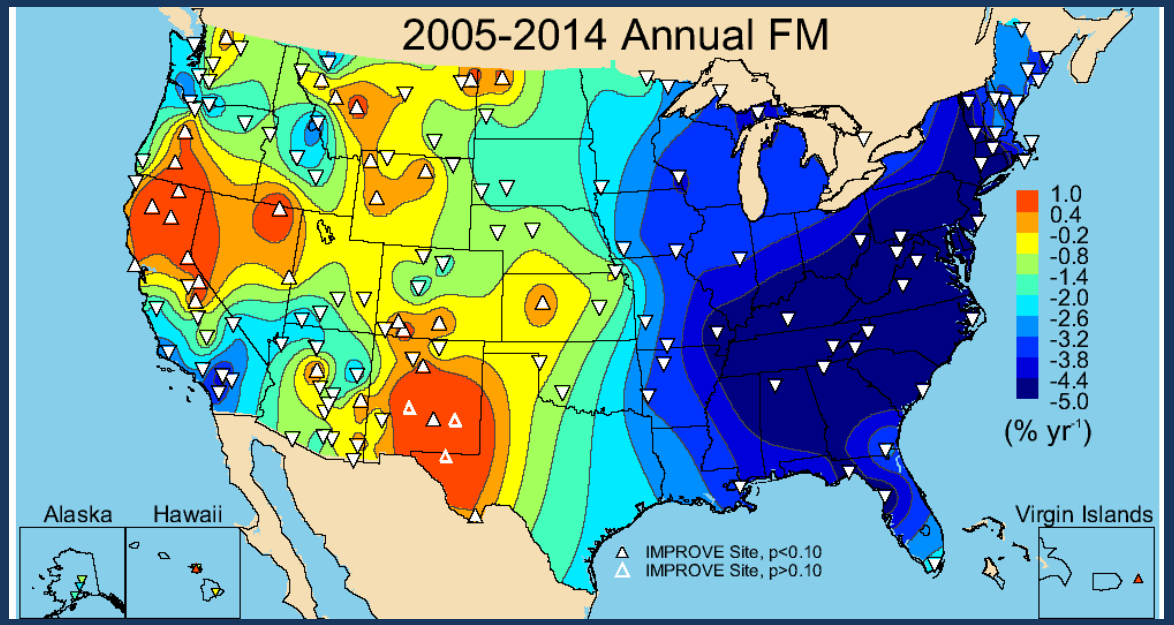
Later period:
FM > RCFM

Annual mean trends in FM and RCFM (2000-2014)

FM (% yr^{-1})

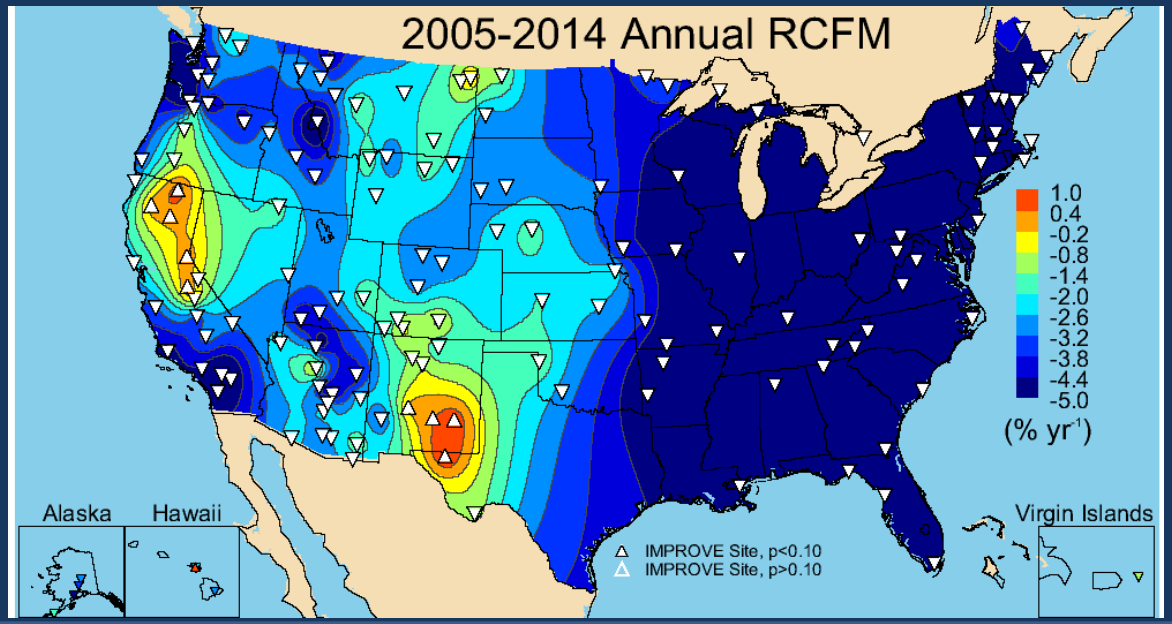
Point Reyes, CA



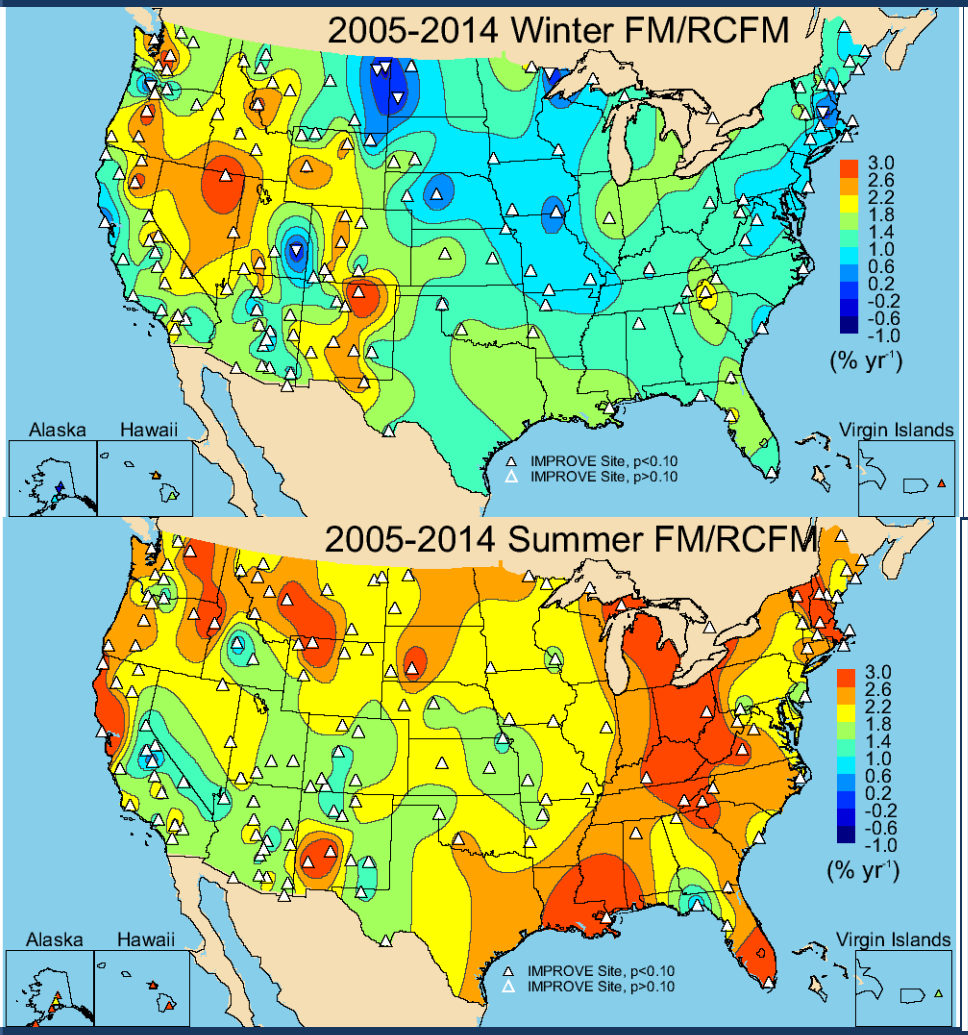


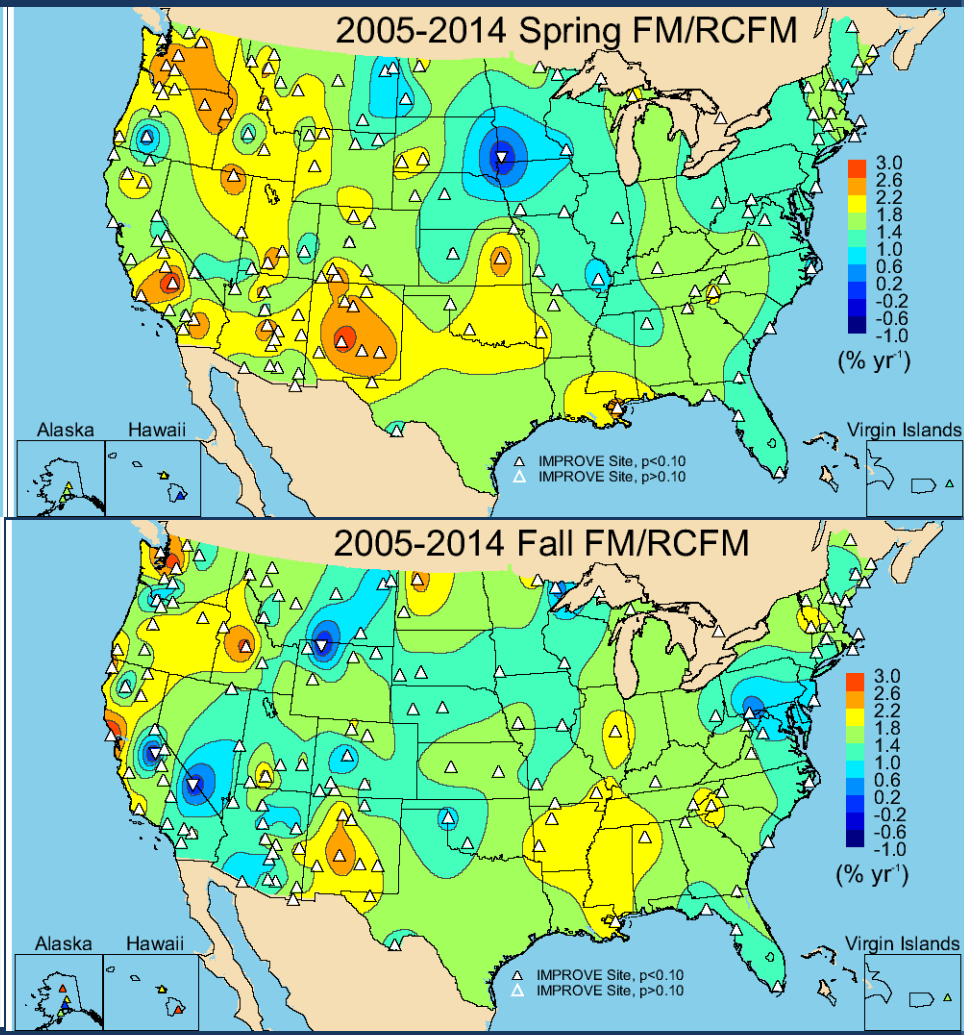
RCFM (% yr^{-1})

Higher rate of decrease



Seasonal Trends in FM/RCFM (% yr^{-1}) (2005-2014)

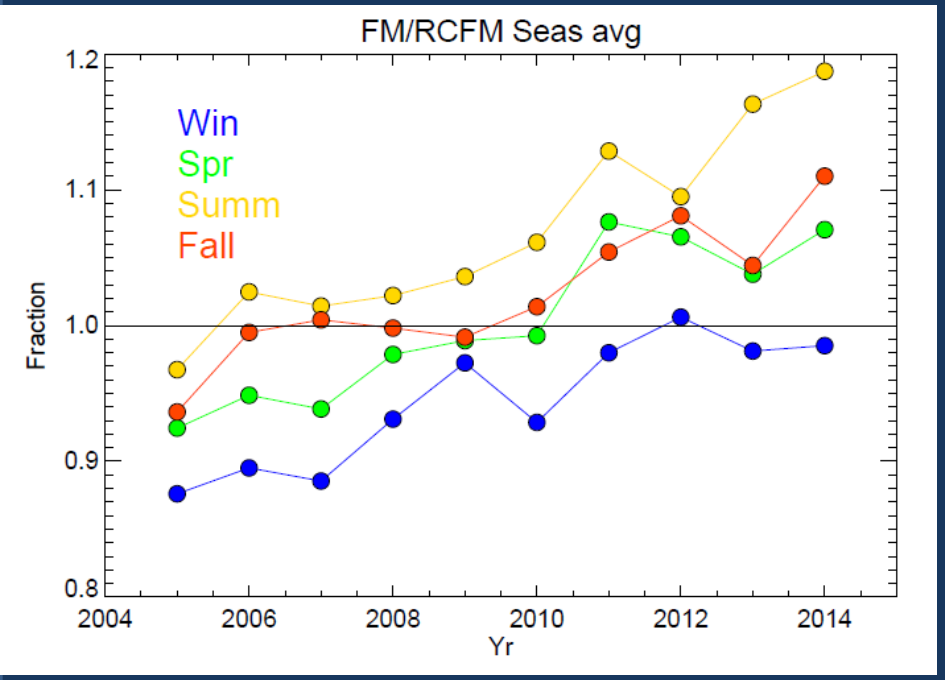




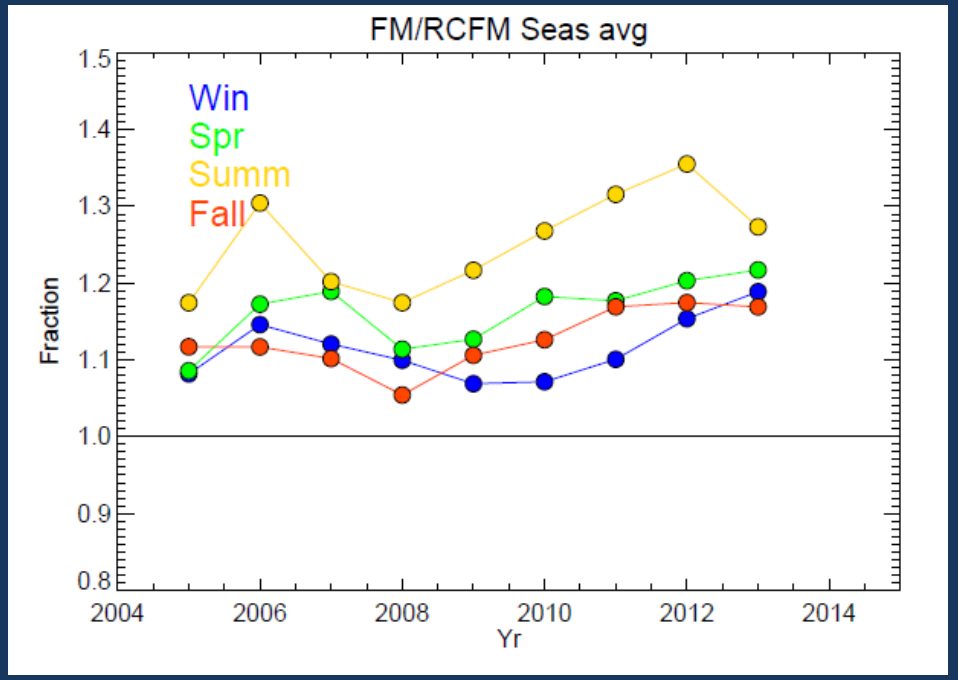
Increase in FM/RCFM across the network and all seasons

Network Average IMPROVE and CSN FM/RCFM

IMPROVE (Rural)



CSN (Urban)



Multiple Linear Regression (MLR):

(2005-2014: seasonally, annually)

$$FM_{adj}\text{-}EC = a_o + a_1 AS + a_2 AN + a_3 OC + a_4 dust + a_5 SS$$

Where:

FM_{adj}-EC = $PM_{2.5}$(adjusted for laboratory RH*) – elemental carbon

AS = ammonium sulfate ($1.375*SO_4^{-2}$)

AN = ammonium nitrate ($1.29*NO_3^-$)

OC = organic carbon

Dust = sum of oxides

SS = sea salt ($1.8*Cl^-$)

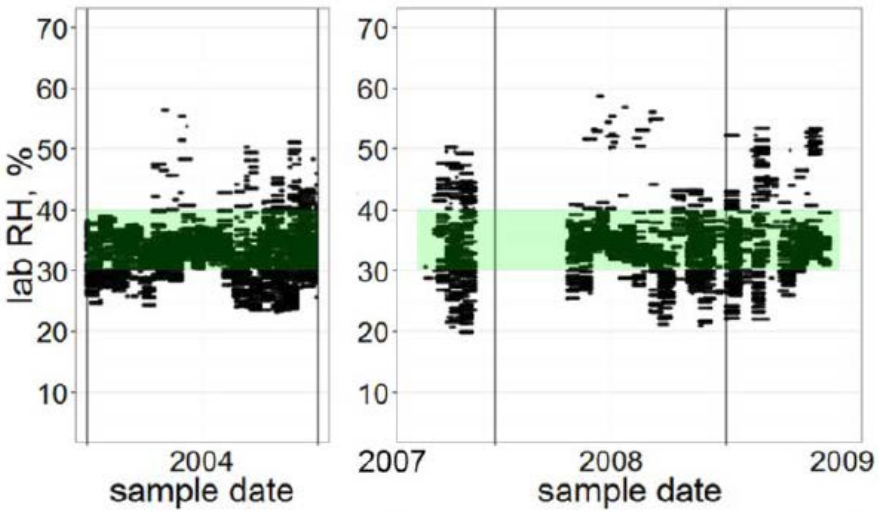
Interpretation:

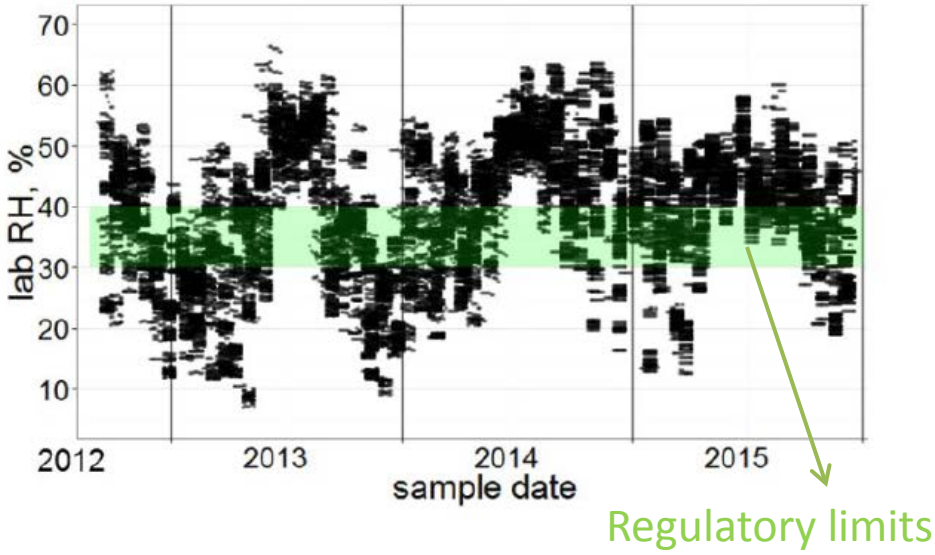
$a_1, a_2, a_4, a_5 \sim 1$

$a_3 = R_{oc}$ *(e.g. OM/OC ratio)*

* Water calculated explicitly for ~laboratory conditions

Changes in Lab Conditions in 2011





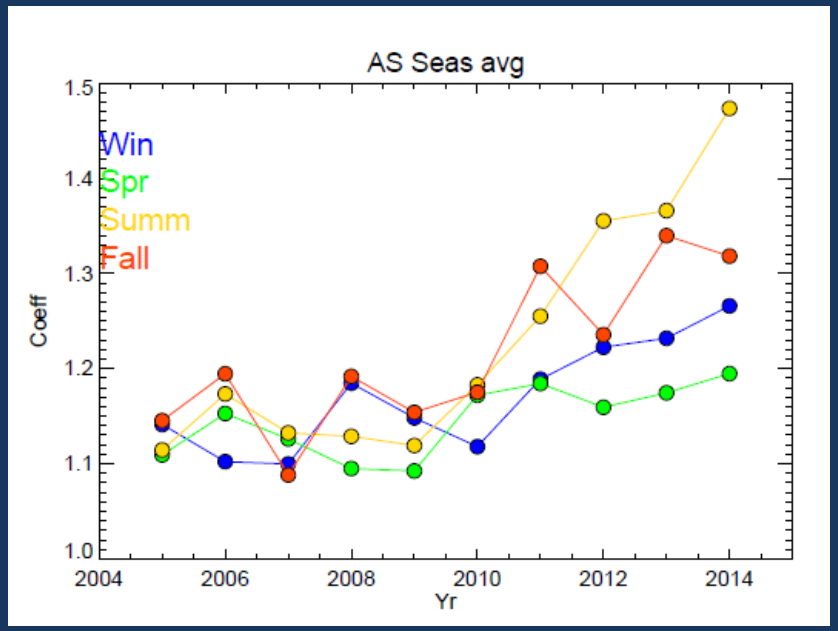
Posting type	Advisory
Subject	Under-controlled humidity in the weighing laboratory
Module/Species	A/ MF, D/ MT
Sites	All
Period	2011 and later
Recommendation	Recognize that gravimetric measurements are not FRM-compliant
Submitter	W.H. White, whwhite@ ucdavis.edu,

Filter handling and weighing moved to a different laboratory in 2011

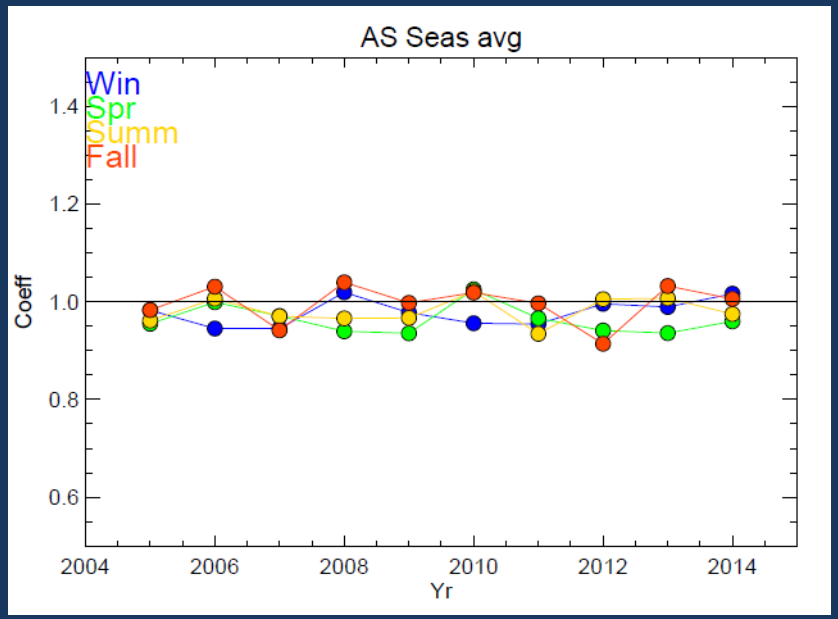
http://vista.cira.colostate.edu/improve/Data/QA_QC/Advisory/da0035/da0035_IncreasedRH.pdf

IMPROVE MLR AS Coefficients: Effects of RH

No adjustments

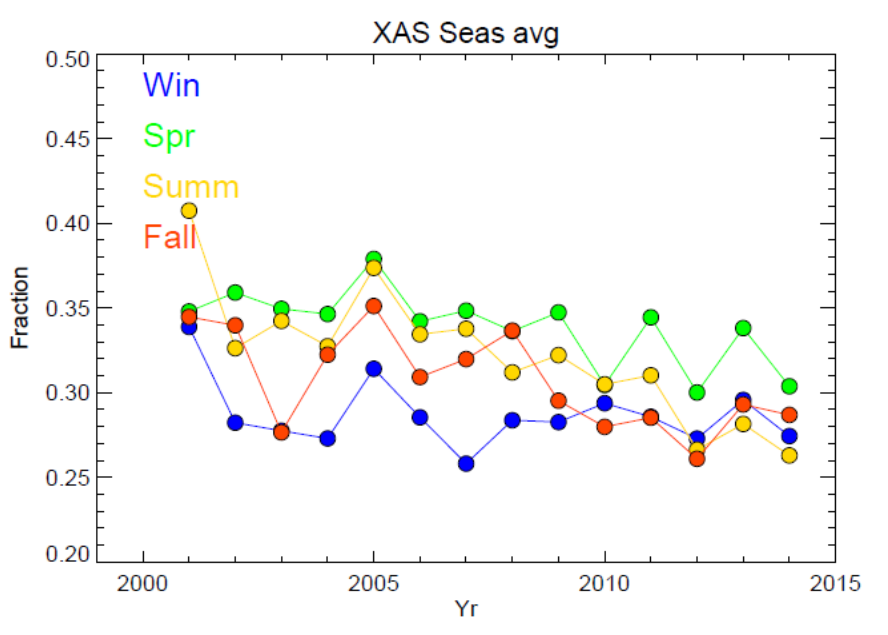


FM adjusted for water bias

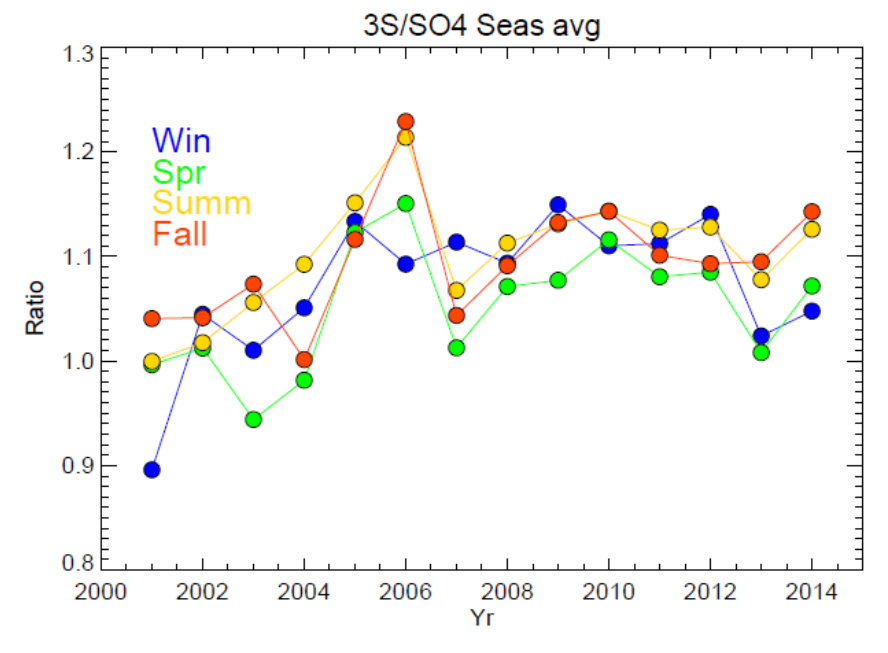


My assumptions:
Before 2011: 28% all seasons
After 2011:
  Winter & Spring: 35%
  Fall & Summer: 40%
2012 and 2013:
  Summer: 45%
2014:
  Summer: 55%

IMPROVE network average AS mass fraction

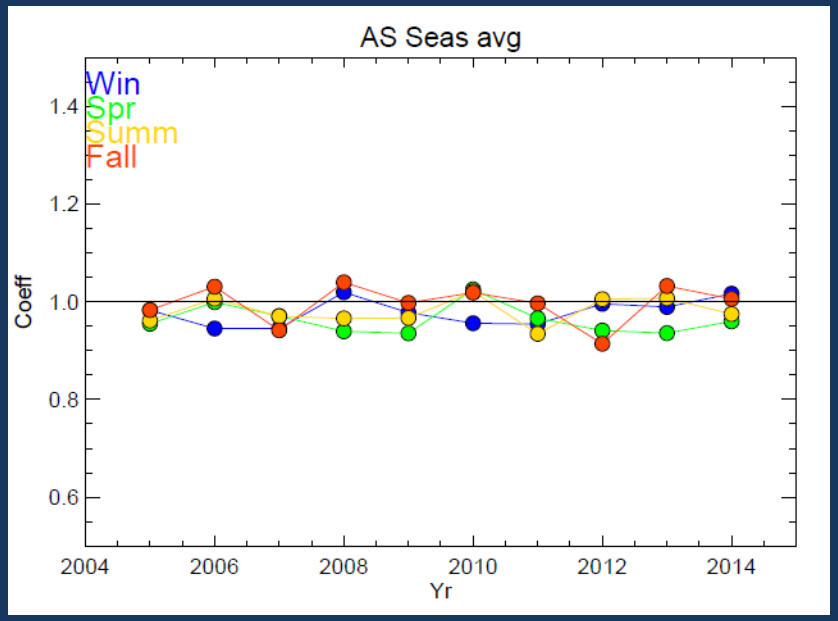


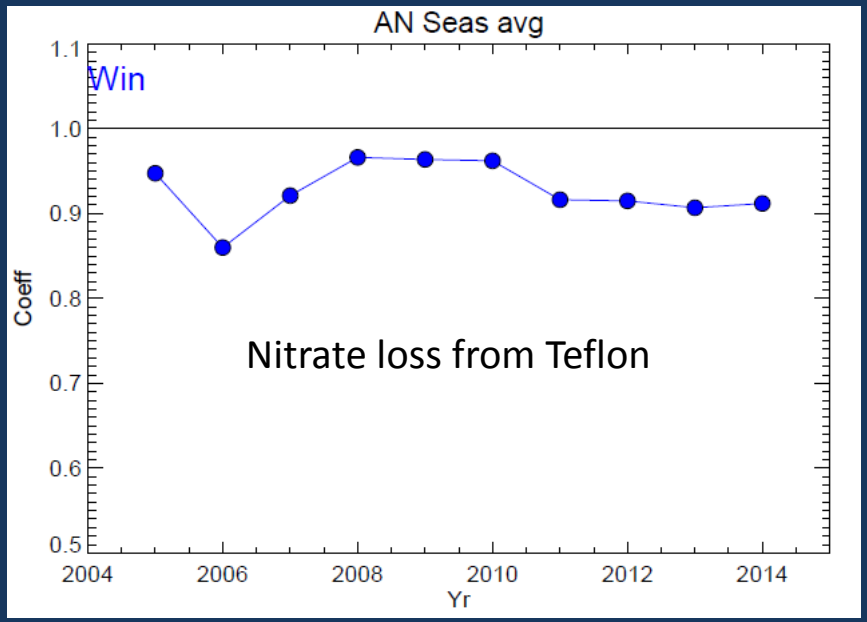
AS contributions to RCFM have decreased since 2000

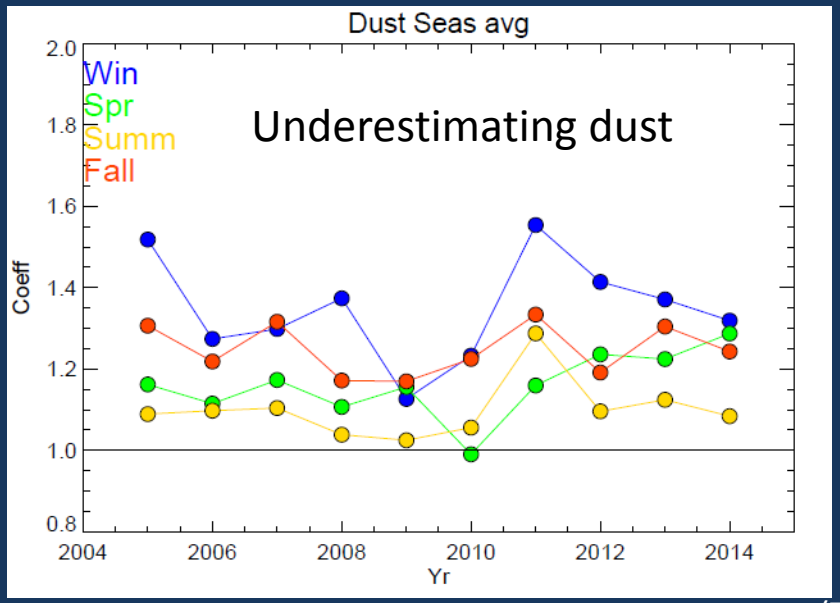


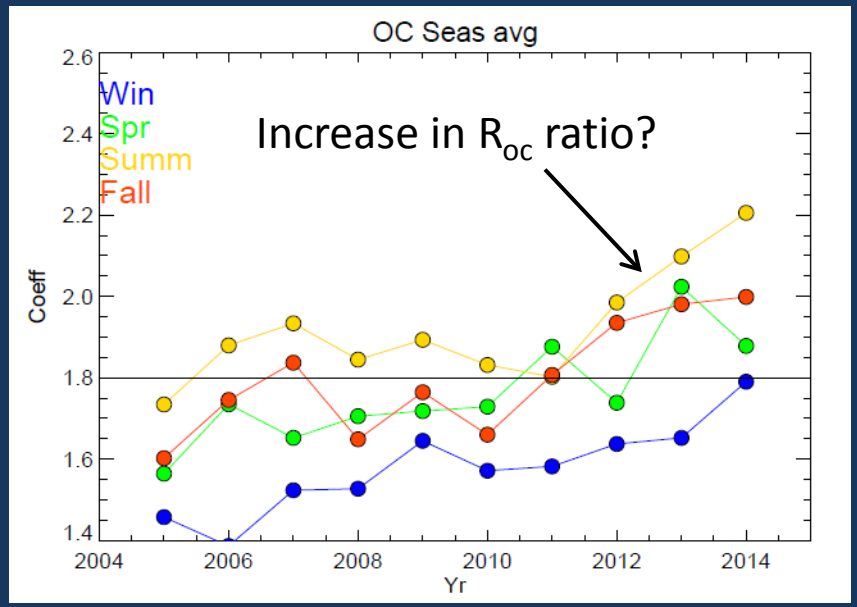
3S > SO4

IMPROVE Network Average MLR Coefficients (95% sig.)





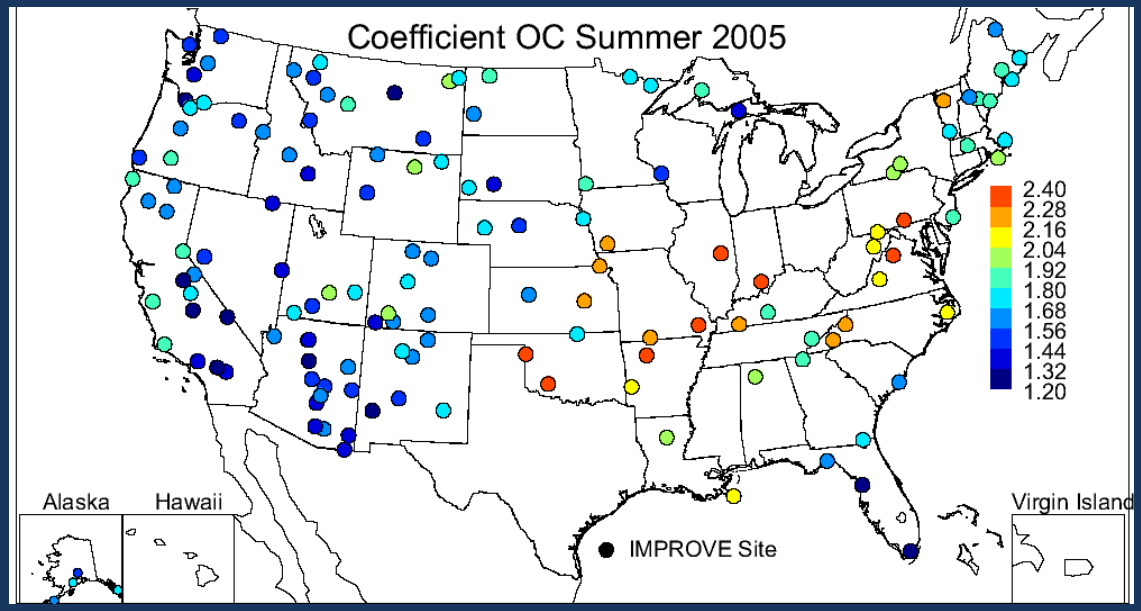




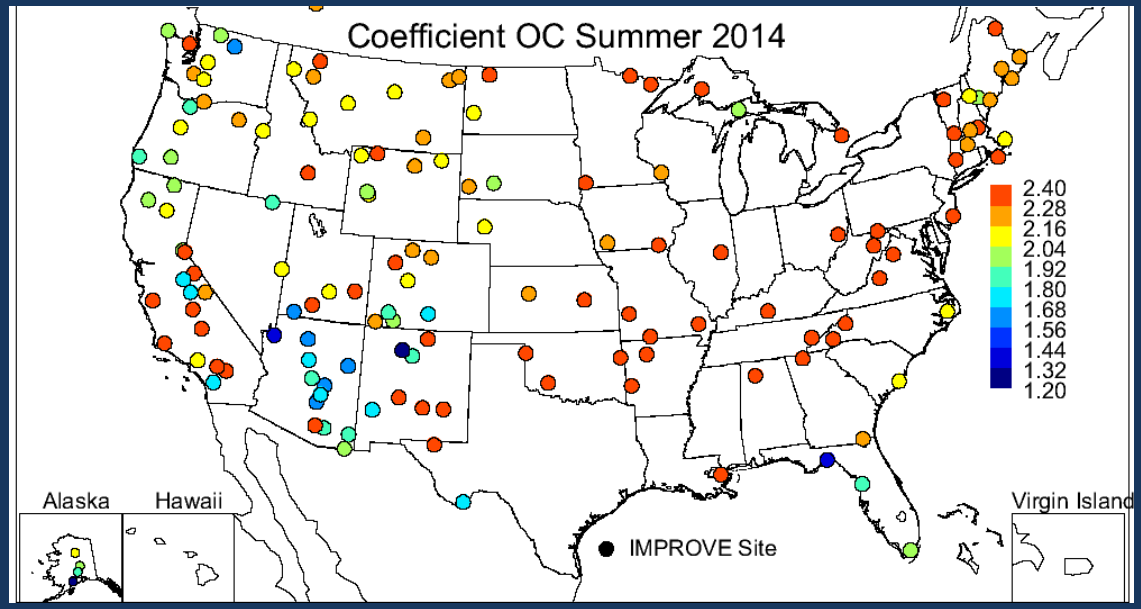
(Turpin and Lim, 2001; Aiken et al., 2008; Philip et al., 2014)

Summer R_{oc} (OC Coefficients)

2005



2014

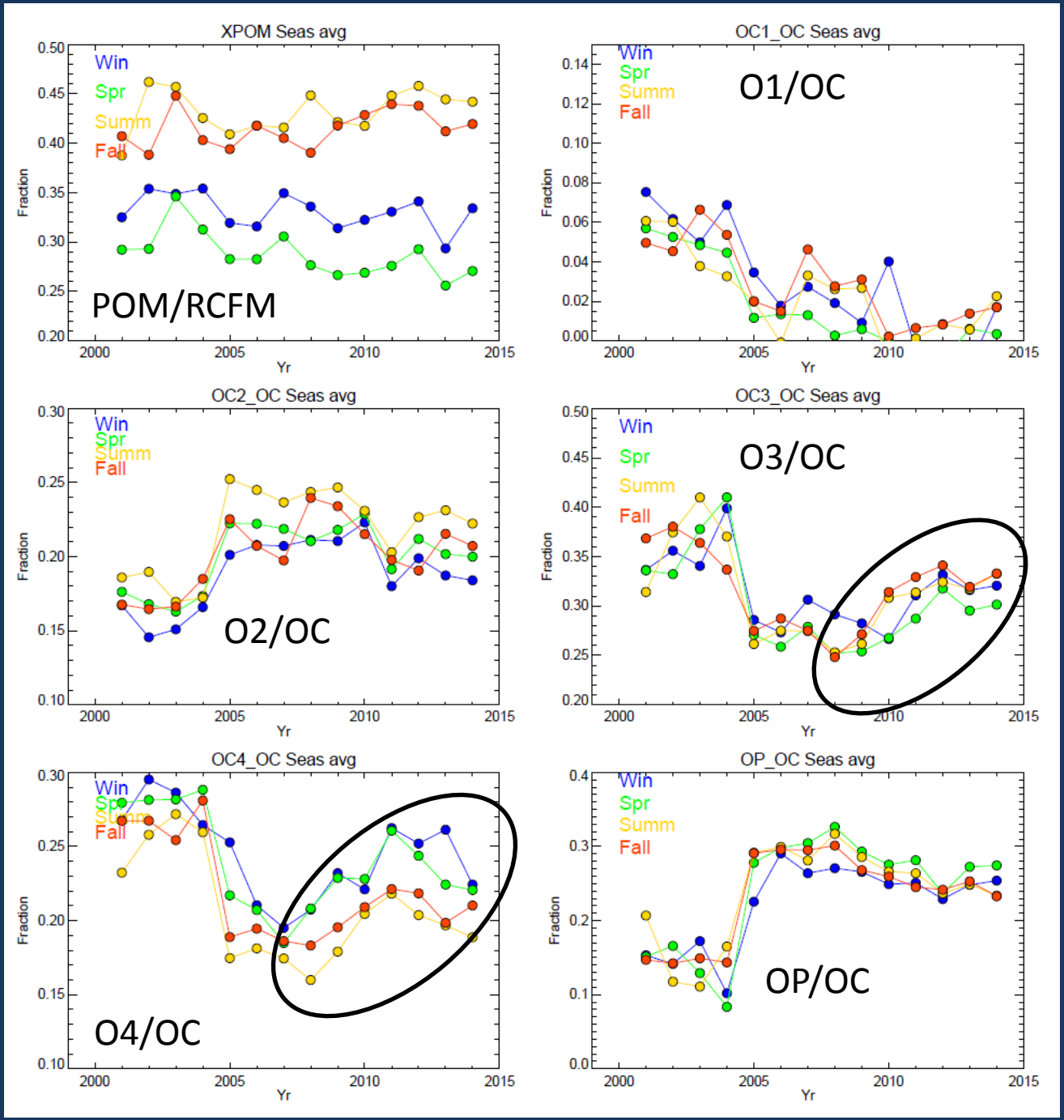


IMPROVE Network Average

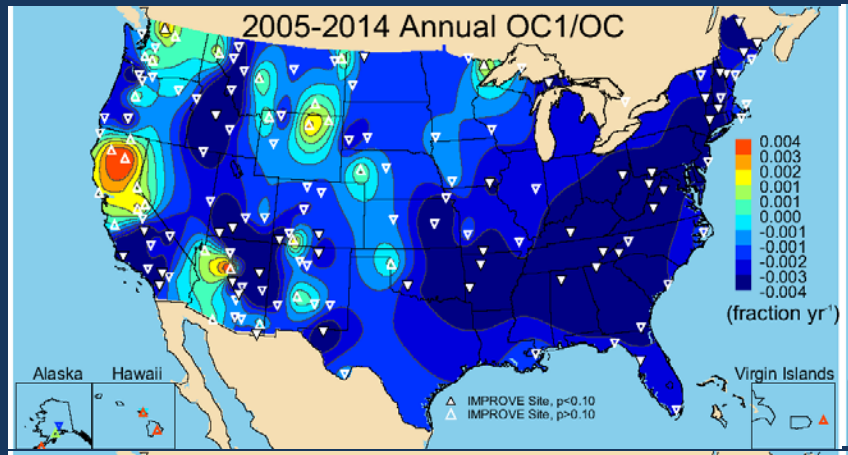
Organic Fractions

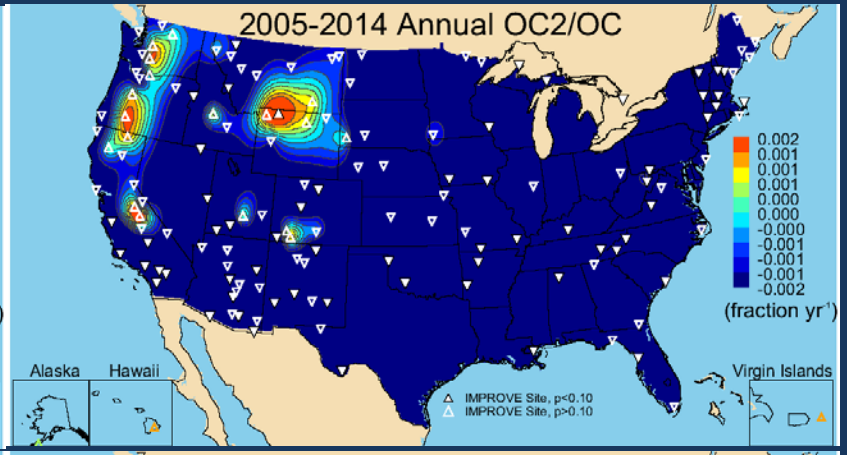
(O1/OC, O2/OC, etc.)

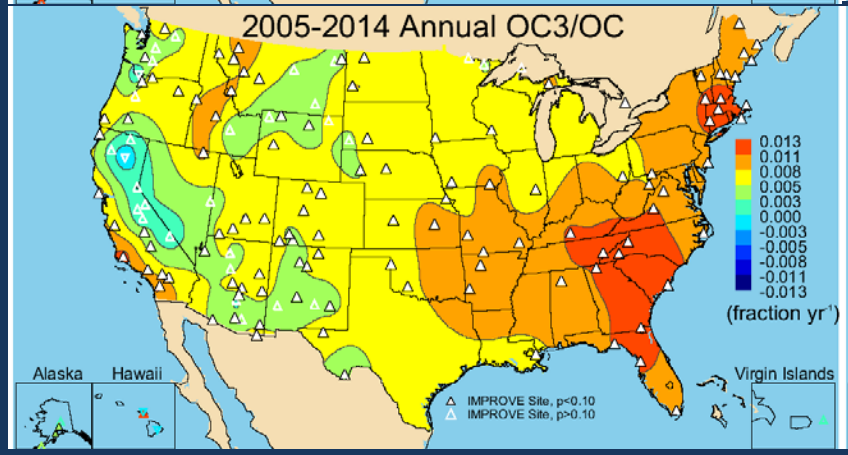
O3/OC & O4/OC increased

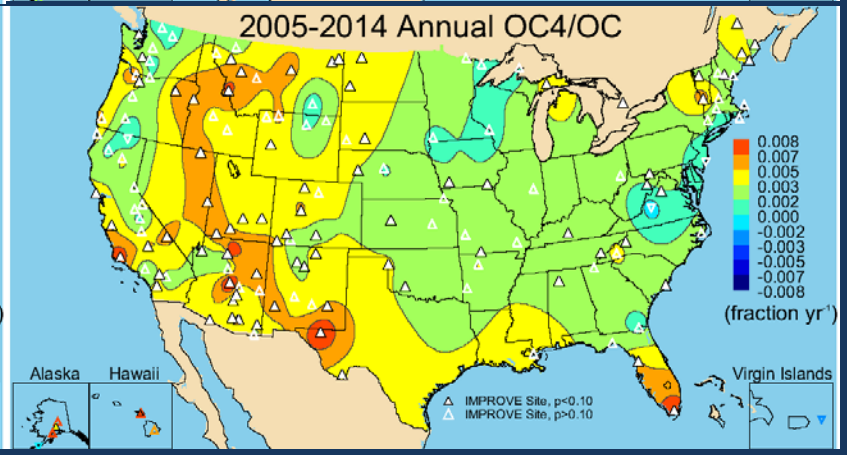


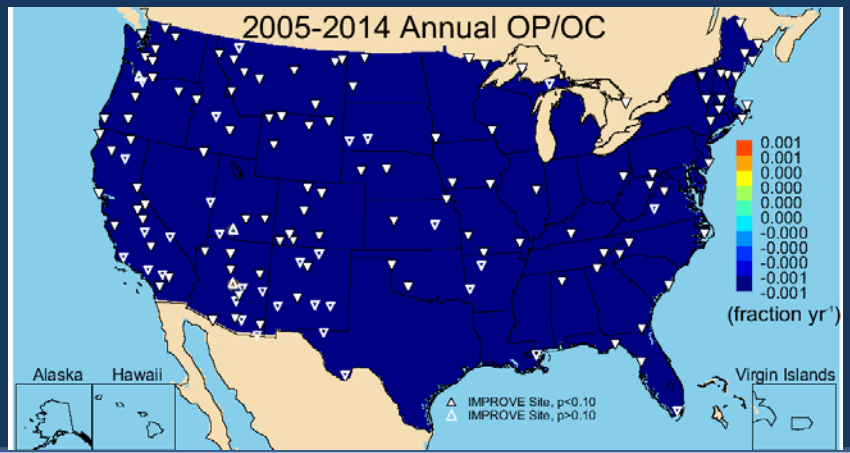
OC Fraction Annual Trends (slopes) (2005-2014)



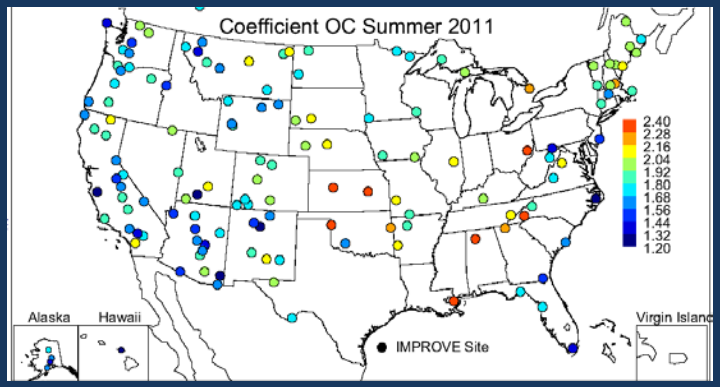


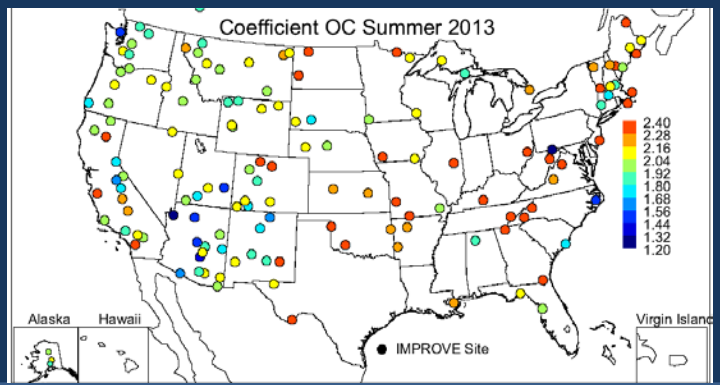


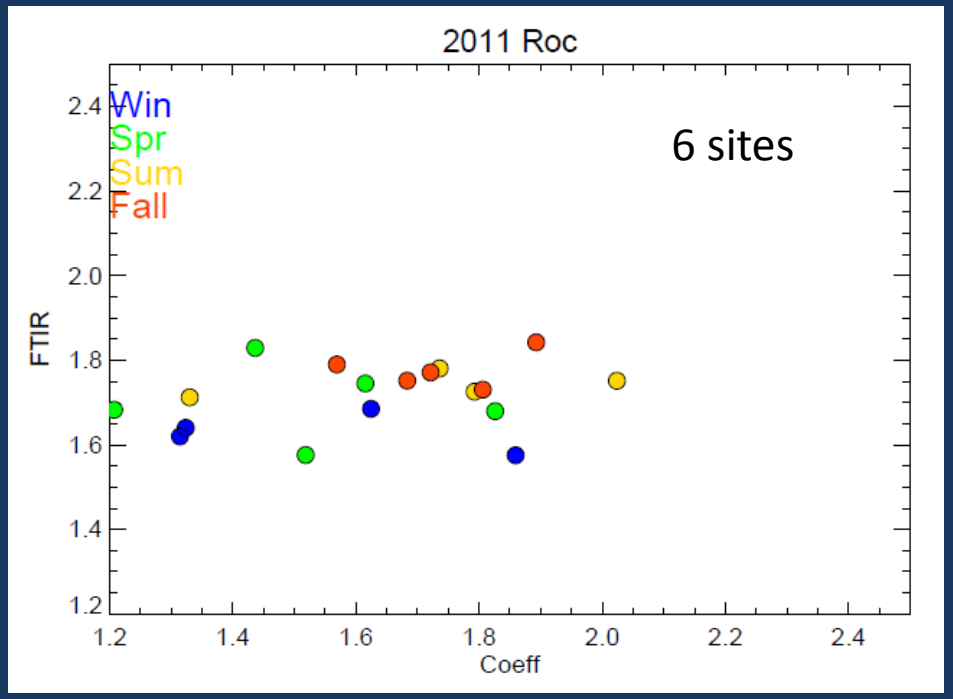


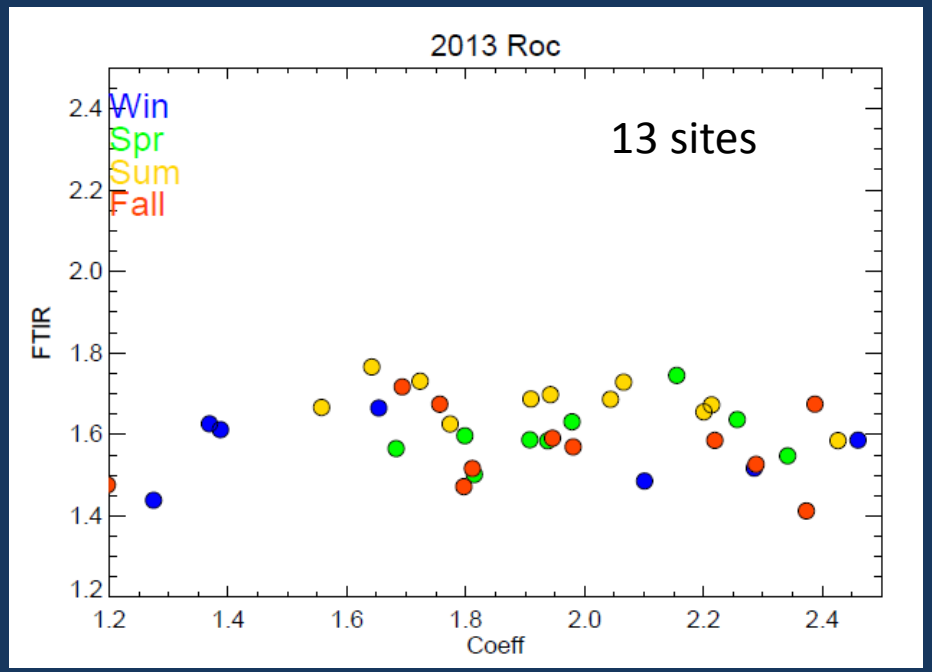


Comparisons of MLR-R_{oc} to A. Dillner's FTIR-derived values for 2011 and 2013

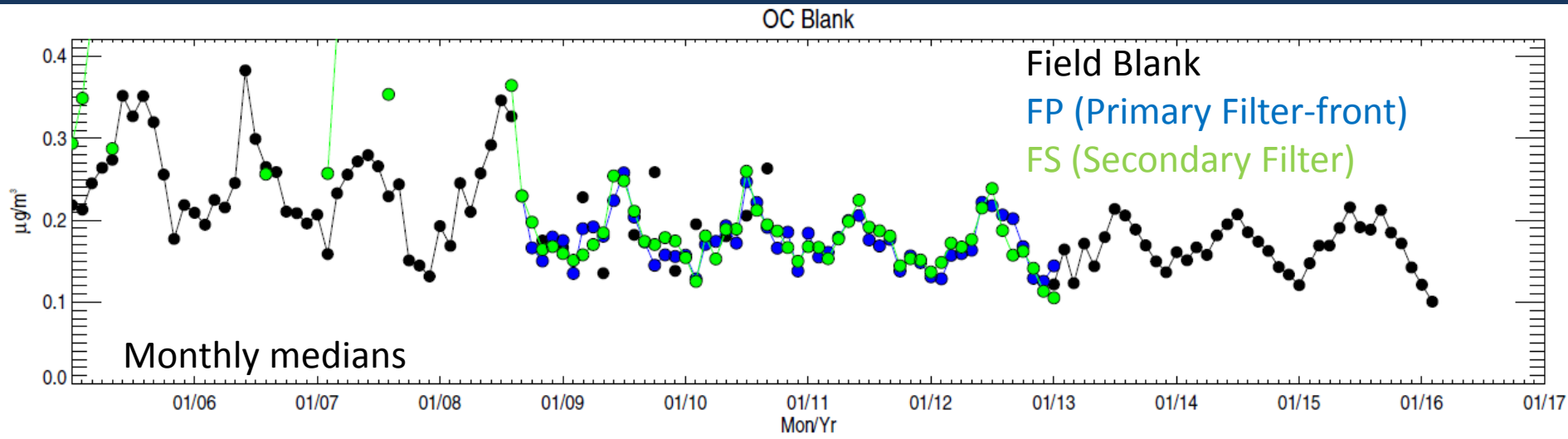




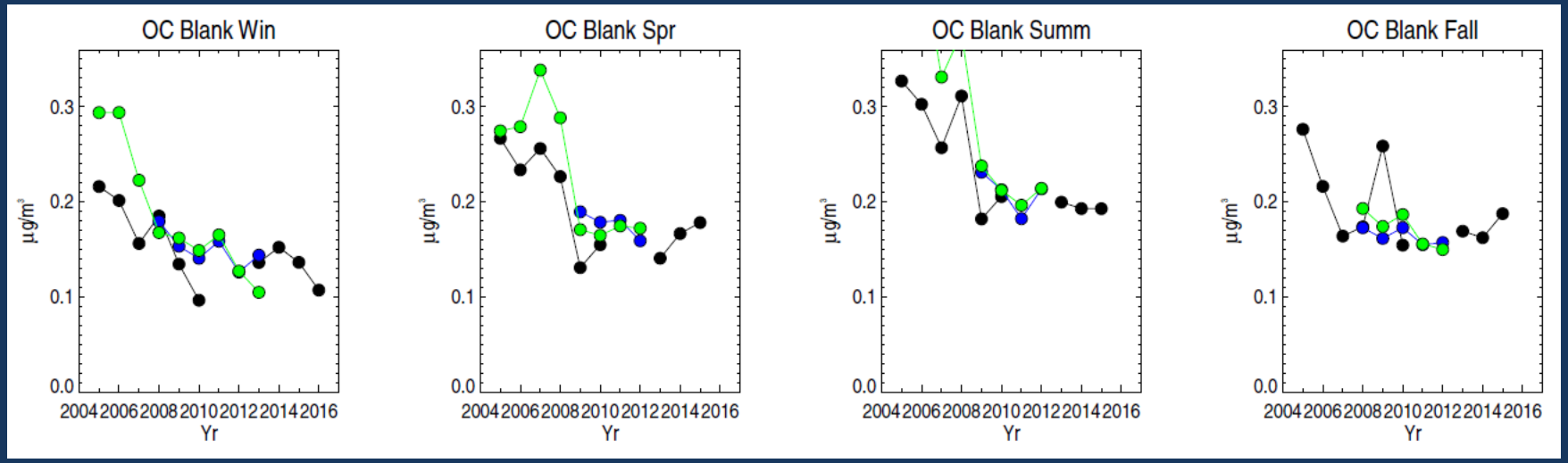




Carbon Field Blanks (2005-2016)



Seasonal medians



Summary
(Preliminary)

- FM/RCFM has increased across the network and all seasons
- Trends IMPROVE FM and RCFM suggest RCFM is increasingly underestimating FM, biases in FM have increased, OR both.
- MLR results suggest that organic carbon multiplier has increased (greatest increase in summer) across the network
- Resolving differences in FM and RCFM is imperative for accurately estimating contributions to $PM_{2.5}$ mass and visibility degradation
- Working group discussion at the end of day

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.)?

Acknowledgements

National Park Service
Air Resources Division

IMPROVE

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

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