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

2005-2008
Earlier period:
FM < RCMF

2011-2014
Later period:
FM > RCMF
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)

\[ FM_{adj} - EC = a_0 + a_1 AS + a_2 AN + a_3 OC + a_4 dust + a_5 SS \]

Where:

- \( FM_{adj} - EC = PM_{2.5}(\text{adjusted for laboratory RH}^*) - \text{elemental carbon} \)
- \( AS = \text{ammonium sulfate } (1.375*SO_4^{2-}) \)
- \( AN = \text{ammonium nitrate } (1.29*NO_3^-) \)
- \( OC = \text{organic carbon} \)
- 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
Filter handling and weighing moved to a different laboratory in 2011.
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%
AS contributions to RCFM have decreased since 2000

3S > SO4
IMPROVE Network Average MLR Coefficients (95% sig.)

Sulfate Coefficients

Dust Coefficients

Increase in $R_{oc}$ ratio?

Nitrate loss from Teflon

Underestimating dust

(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)

Field Blank
FP (Primary Filter-front)
FS (Secondary Filter)

Monthly medians

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?)
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.)?
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IMPROVE

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