Recent Changes to the IMPROVE and CSN Organic Carbon Artifact Adjustment Method

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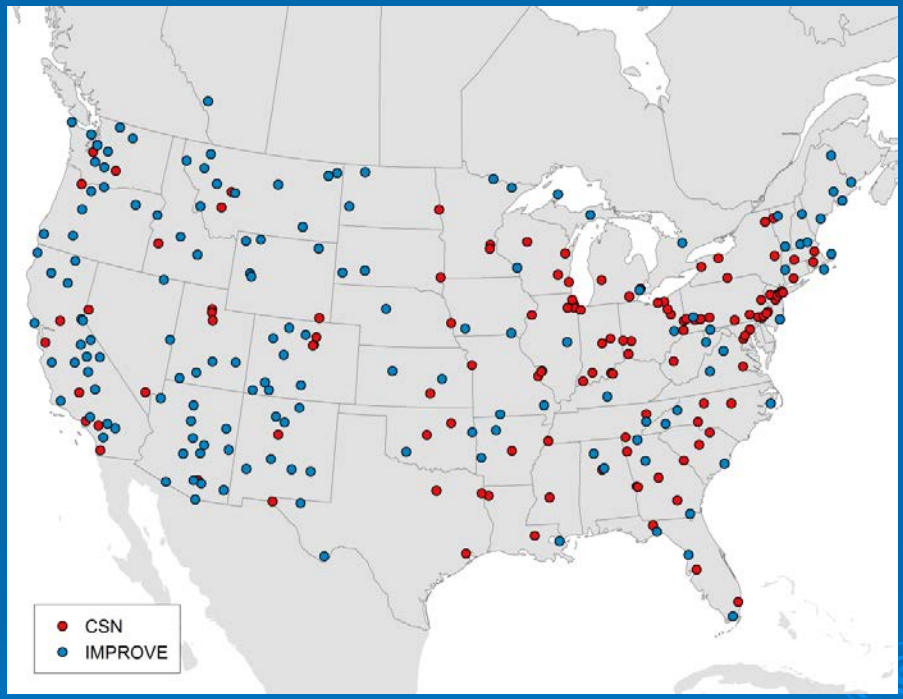
Organic Carbon (OC)

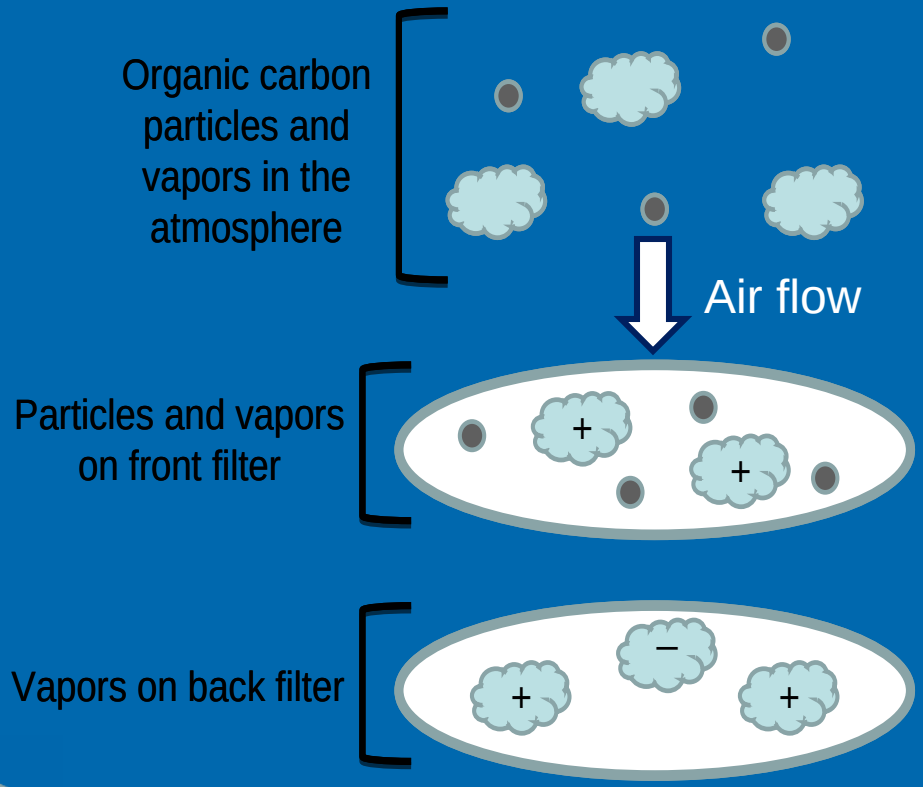
- Carbon portion of organic molecules which include hydrogen, oxygen, sulfur, nitrogen
- Measured along with elemental carbon (EC) in IMPROVE and CSN
- Used to estimate organic matter (OM)
  - OC X 1.4 = OM (CSN)
  - OC X 1.8 = OM (IMPROVE)
- OM can be over 50% of particulate matter mass

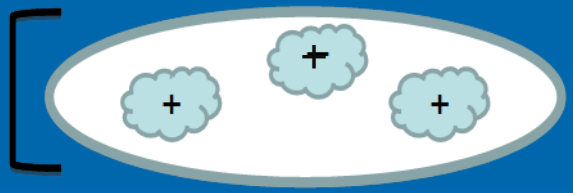


CSN and IMPROVE networks

OC Subject to Sampling Artifacts

- Positive artifact: gas-phase organics adsorb onto filter
- Negative artifact: particles volatilize off filter due to temperature and gas concentration changes
- Back filter may capture both artifacts
- Field blanks capture only positive artifact – have no flow and stay in sampler for duration of sampling





Moving toward comparable OC measurements in IMPROVE and CSN

- CSN and IMPROVE reconciled methods (as of 1/08):
  - Similar samplers (URG)
  - Same pre-conditioned quartz-fiber filters
  - Same Thermal Optical Reflectance (TOR) analysis using the IMPROVE_A protocol
    - Generates thermal fractions OC1, OC2, OC3, OC4, OP (pyrolyzed carbon)
- OC reporting still differed:
  - IMPROVE adjusted sample filter loadings with an estimate of the artifact from back-up filter
  - CSN reported sample filter loadings directly along with blank values but made no adjustment.

CSN carbon sampler

IMPROVE/CSN Organic Carbon Artifact Adjustment committee

- Committee members
  - Marc Pitchford, IMPROVE Steering Committee Chair, NOAA/EPA
  - Mark Green, Judy Chow, John Watson, DRI
  - Bret Schichtel, Bill Malm, NPS
  - Joann Rice, Neil Frank, EPA
  - Warren White, Ann Dillner, UC Davis
- Charge: To recommend to the IMPROVE steering committee and to CSN an appropriate artifact correction method for TOR OC that both networks would use to improve data comparability

Criteria used by the committee for selecting artifact adjustment method:

1. Consistent with limited scientific understanding of organic artifacts
2. Preserve the measured variation in the data
3. Minimize contribution of the artifact to the reported OC particulate matter mass
4. Simple to implement (e.g. uses available information and could be applied to historic data) at a reasonable cost and effort
5. Applicable to both IMPROVE and CSN for improved data comparability

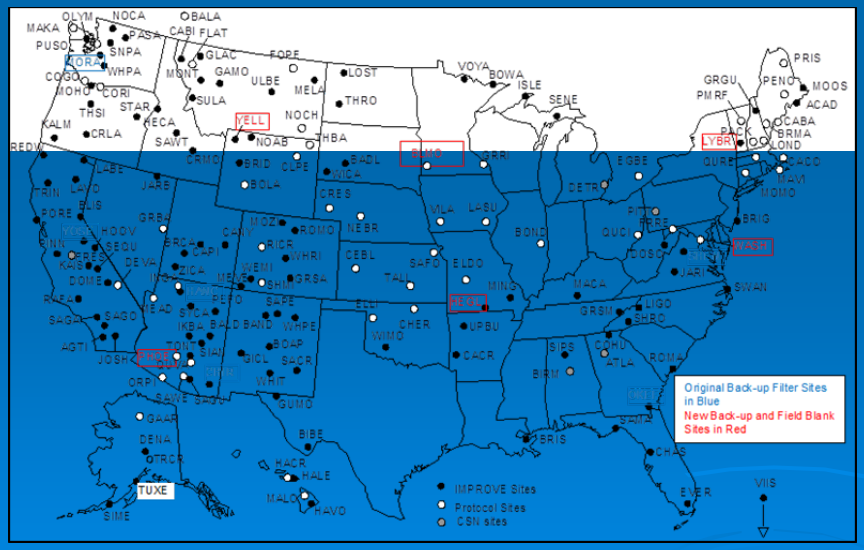
Back and Field Blank Filters

IMPROVE – since 8/08

88±33 backups/month,

38±11 field blanks/month

More detailed information on field blanks and back-ups filters for IMPROVE is in the appendix slide 30.



~2% blanks, ~7% backup filters

CSN - backups & blanks per month

2008 ~60, 2009 ~120,

2010 ~160

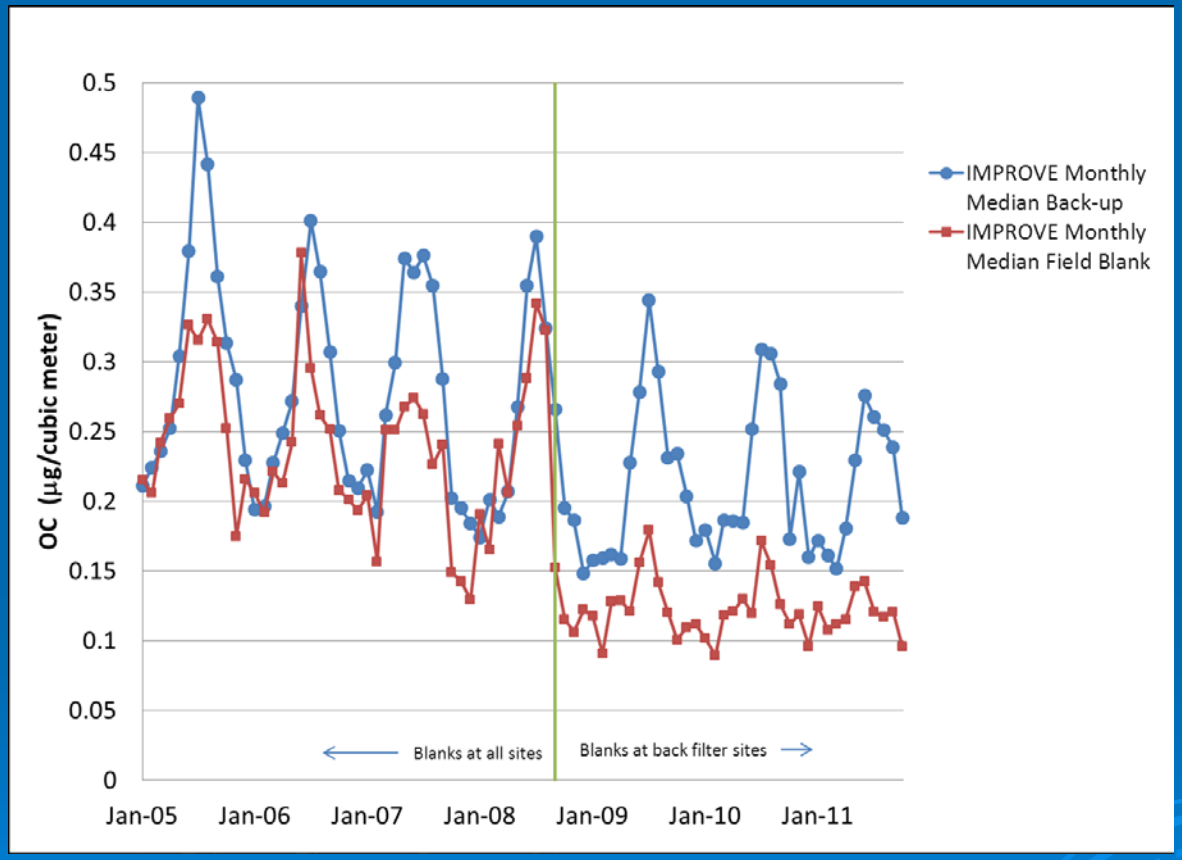
20% backups and blanks in 2009-2010, 10% since 2011

Artifact Adjustment Methods

- IMPROVE method begun in 2002–
  - Subtract monthly median (MM) back-up OC thermal fractions (determined from 13 sites) from each filter collected in the network for that month
  - Reported OC = Front filter OC – MM back OC
- CSN method since inception of CSN –
  - Field blanks and backup filters collected at all sites (~180 sites) but no correction performed
  - Reported OC = Front filter OC
- Alternative method –
  - Subtract MM field blank OC thermal fractions (all sites) from each filter collected in the network for that month
  - Reported OC = Front filter OC – MM field blank OC

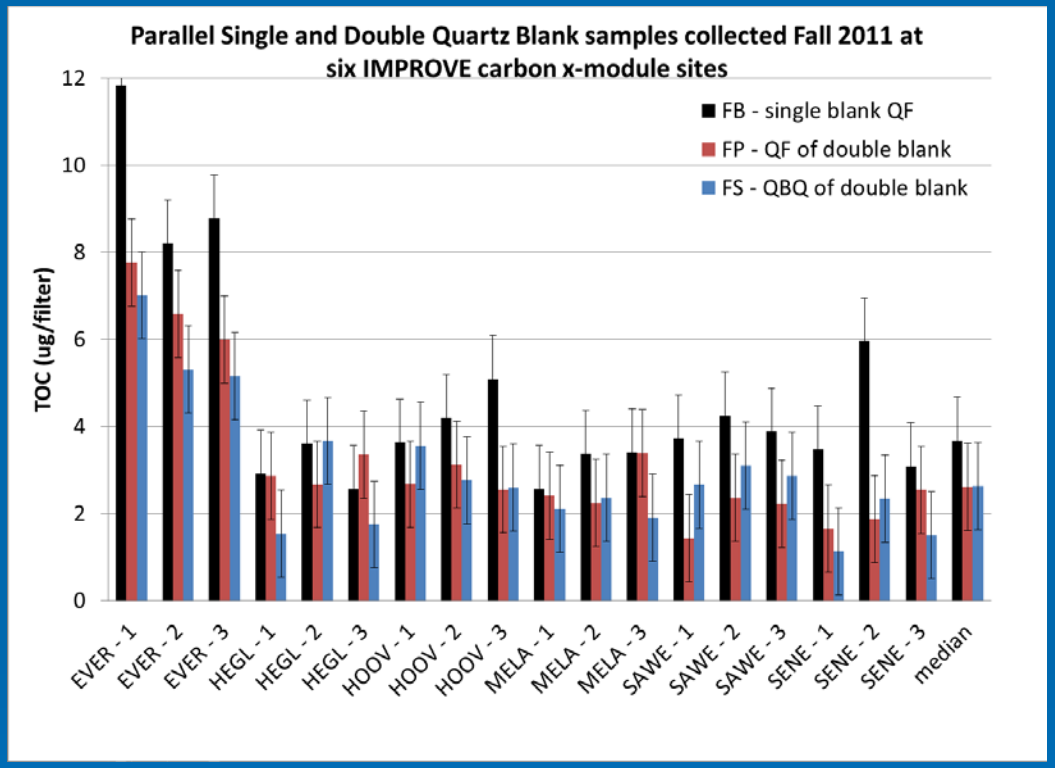
First, a caveat about IMPROVE field blank data before preceding with the analysis

IMPROVE Monthly Median Back-up and Field Blank Concentrations



Field blank OC concentrations decreased when filters began to be collected only at back-up filter sites (8/08). Double quartz field blanks were collected beginning 8/08. Prior to that time single field blanks were collected.

Double Field Blanks

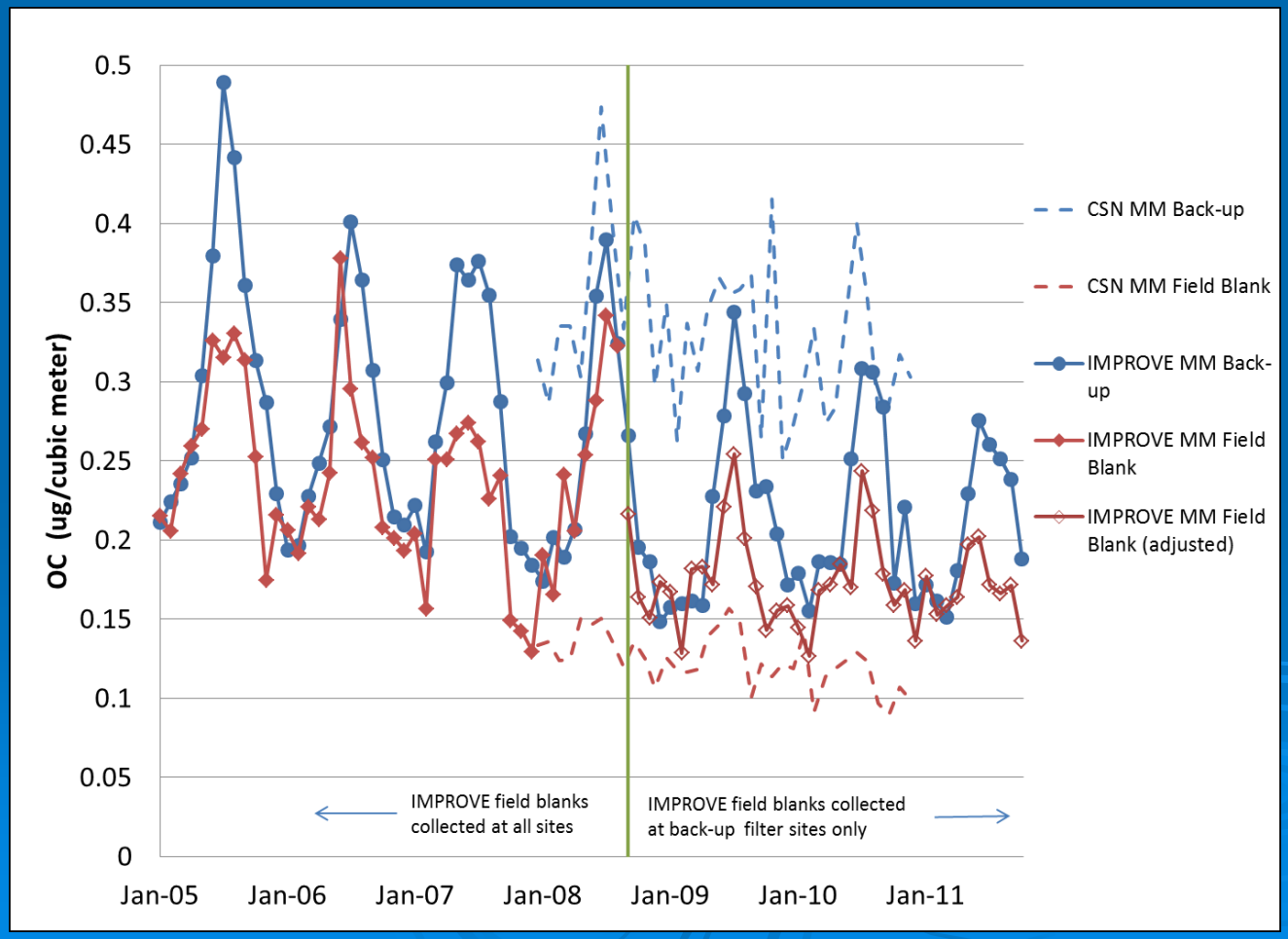


- Single field blanks have more OC than either the front or back double field blank filters
  - Median of 41% in fall (shown)
  - Median of 44% in summer (not shown)
  - Large variability in % differences

- Field blank data herein is adjusted by 42%.

(Although small seasonal difference observed, the observation is based on limited, highly variable data so a single value is used to adjust the field blanks.

Monthly Median Back-up and Field Blank OC values for IMPROVE and CSN



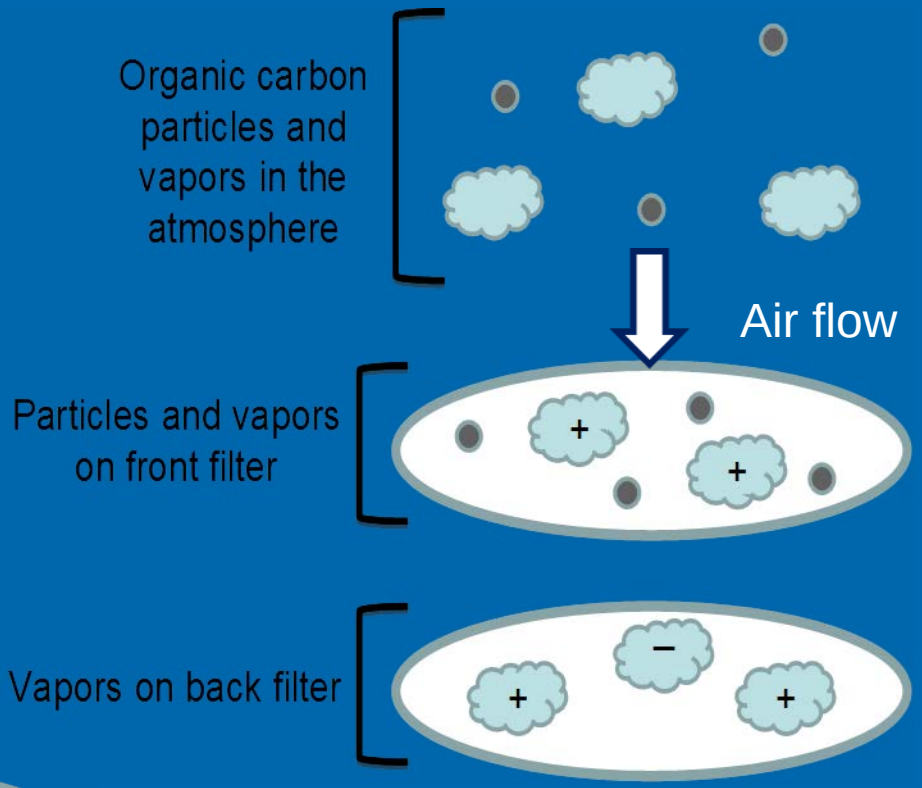
Approach to method selection

1. Evaluate methods in light of limited understanding of artifacts
2. Evaluate variability of monthly median back-up and field blank concentrations with the goal of preserving measured variability in OC
3. Evaluate magnitude of correction to decrease artifact in the measured OC (and not over correct)
   - Evaluate using regression analysis of OC and mass
   - Note: Given uncertainties discussed in following slides, y-intercept of regression is an imperfect proxy for artifact

1. Evaluate methods in light of limited understanding of artifacts

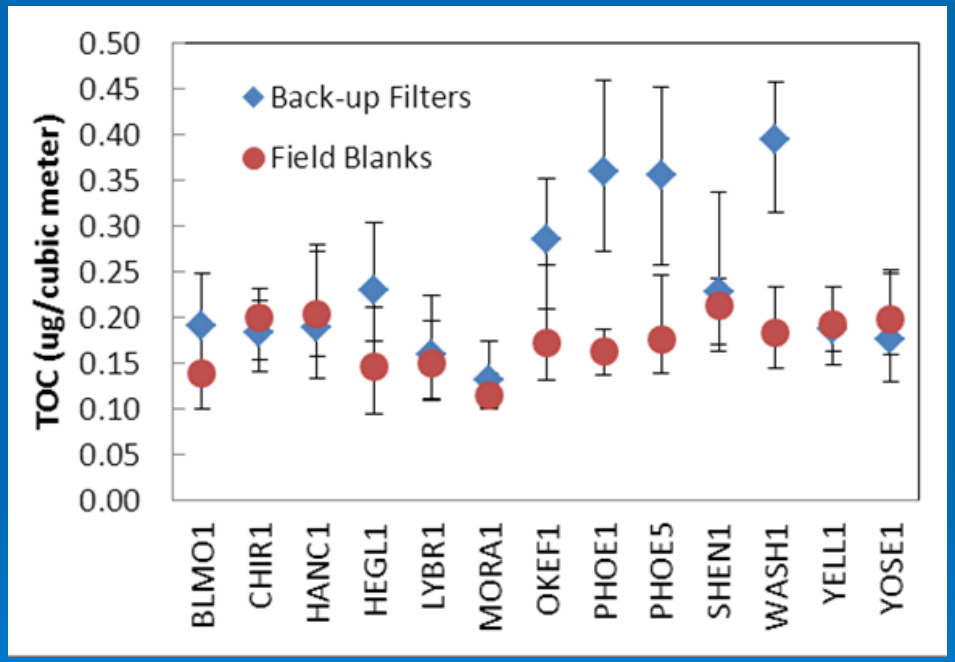
Goal of adjustment is to correct for positive (+) artifact

- Back: + and –artifact
- Back: may over-correct for +artifact
- Field: +artifact
- Field: may be lower bound on +artifact
- <u>Field blanks are a better estimate of + artifact and therefore a better choice</u>



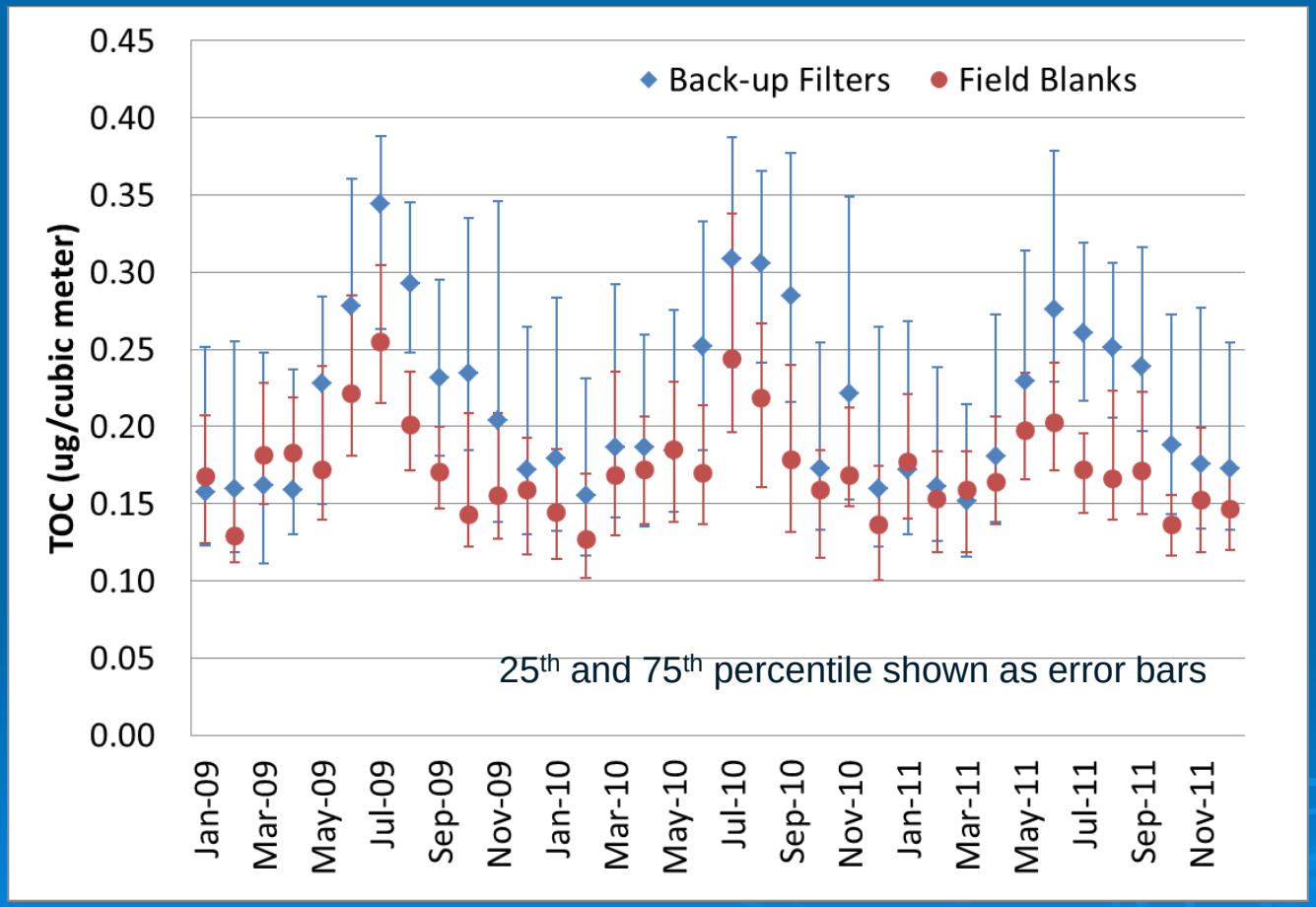
2. Evaluate variability of monthly median back-up and field blank concentrations

IMPROVE Site Medians in 2010



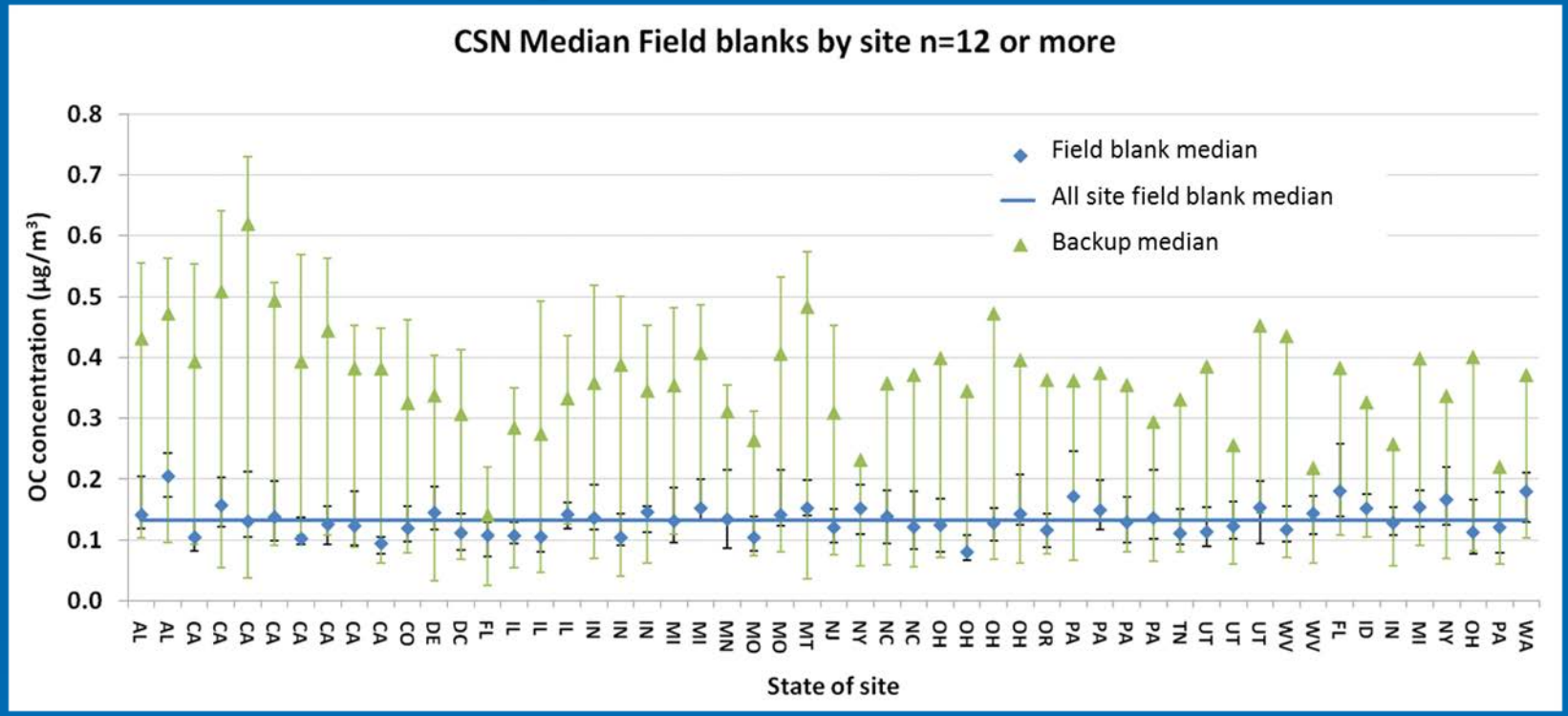
- Field blanks have less site to site variability and less variability within a site for IMPROVE
- Urban sites have higher back-ups than most rural sites, OKEF1 high

2. Variability: Monthly Median Back-up and Field Blanks in IMPROVE



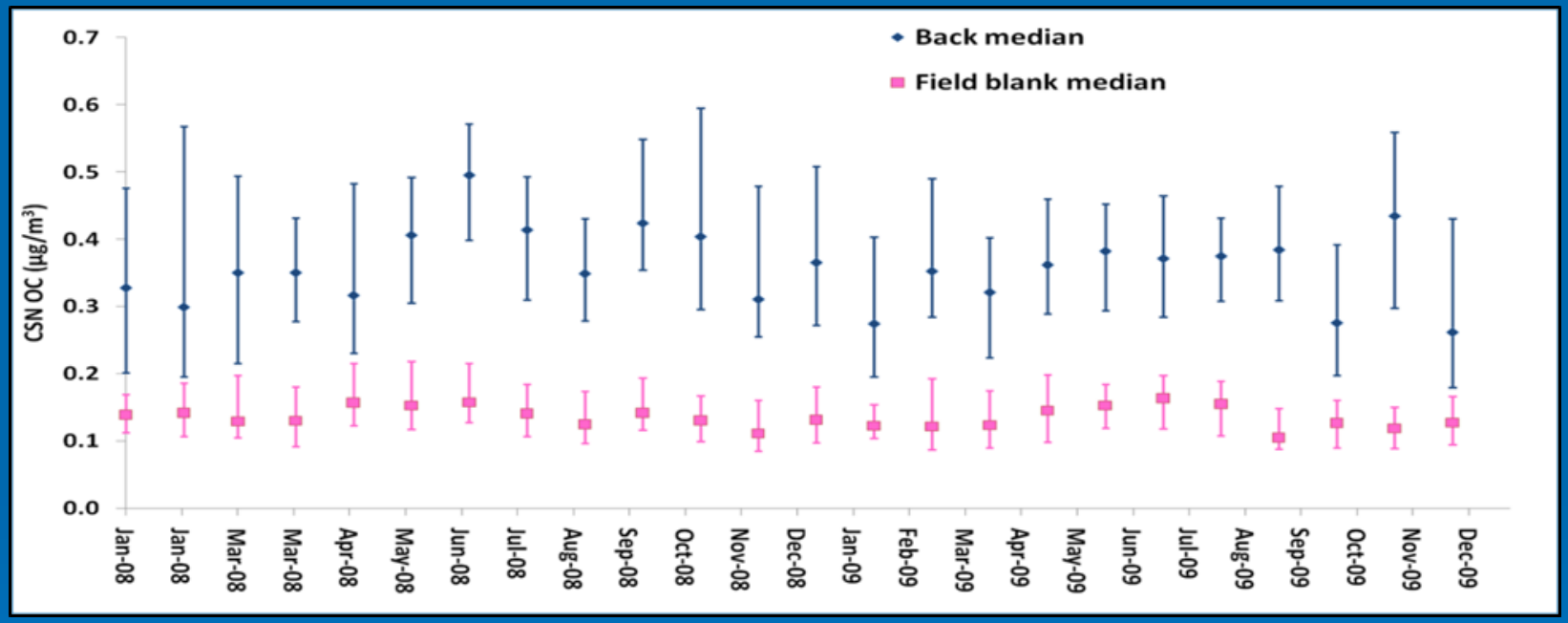
- Field blanks are usually lower, have less seasonality and less variability within a month than back-up filters for IMPROVE

2. Variability: CSN site medians



- Field blanks have less site to site variability and less variability within a site for CSN.
- Same behavior as IMPROVE data, although the backup filter concentration is slightly higher for CSN (urban) than IMPROVE (rural) and the difference in OC concentration for back-up and field blanks is more pronounced.

2. Variability: Monthly Median Back-up and Field Blanks in CSN



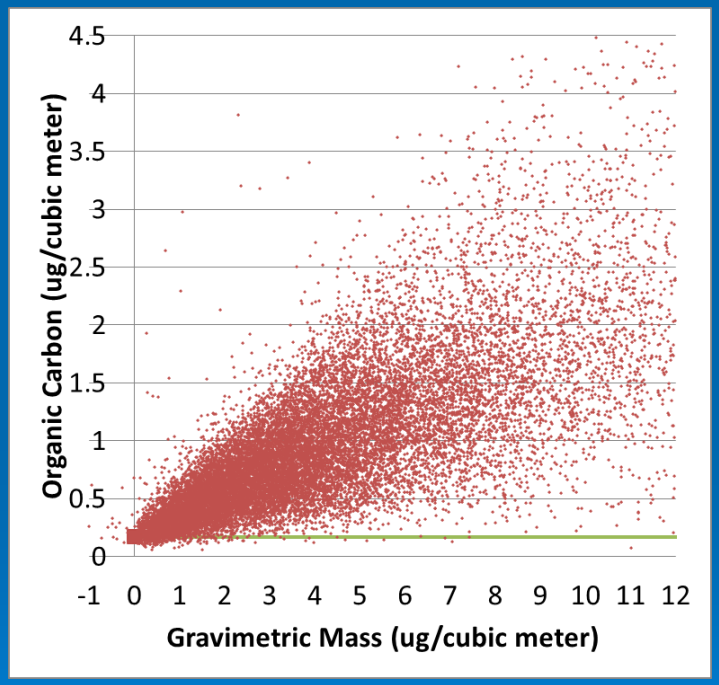
- Field blanks are lower, have less seasonality and less variability within a month than back-up filters for CSN
- Same behavior as IMPROVE although the backup filter concentration is slightly higher than IMPROVE and the difference in OC values for back and field blank is more pronounced.

2. Evaluate variability of monthly median back-up and field blank concentrations with the goal of preserving measured variability in OC

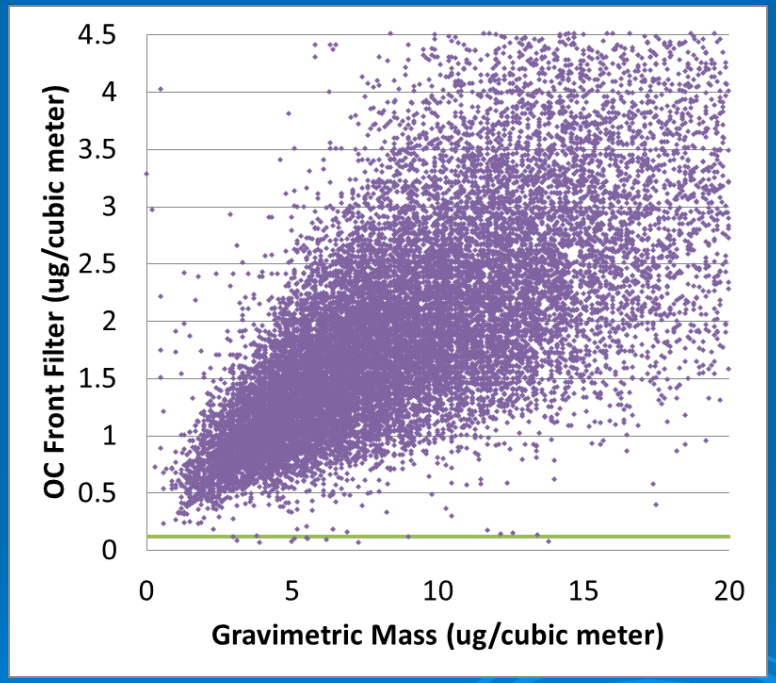
- Compared to back filters, blank filters in both networks are:
  - Less variable over site
  - Less variable within a site
  - Less variable by season
  - Less variable within a month
- Selecting the filter with lower variability to adjust the OC data, helps preserve measured variability in OC
- Field blank better meets criteria

3. Minimize contribution of the artifact to the reported OC particulate matter mass

IMPROVE – 2009 data



CSN – 2009 data



- OC mass does not go to zero as gravimetric mass goes to zero for both networks suggesting a positive OC artifact.
- The green line is the annual median of the field blanks. For IMPROVE the value is 0.17 µg/m^3 and for CSN the value is 0.12 µg/m^3 in 2009.

3. Intercept of regression (mass v. OC) as an estimate of extent of artifact reduction

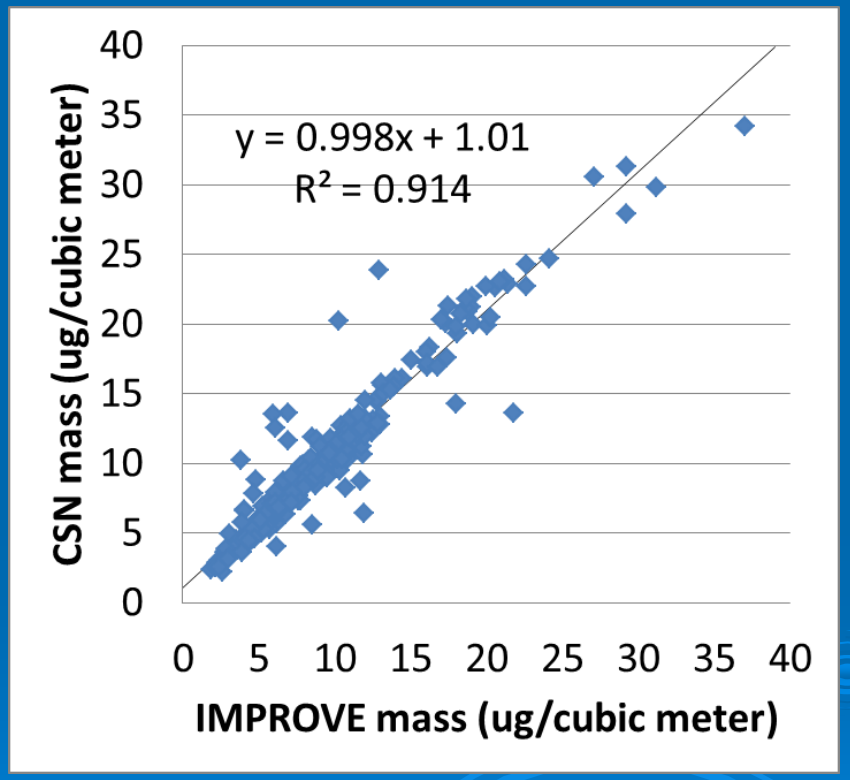
IMPROVE	2009	2010	2011
Uncorrected OC Intercept ($\mu g/m^3$)	0.17	0.26	0.10
MM back-up corrected intercept ($\mu g/m^3$)	-0.03	0.02	-0.09
MM field blank corrected intercept ($\mu g/m^3$)	0.001*	0.07	-0.06

*All intercepts are statistically significantly different than zero, except for MM blank adjusted in 2009

- Field blanks and back-ups decrease artifact
- Negative intercepts in 2009 and 2011 for MM back-up corrected data suggest that the artifact reduction using back-ups is too large
- Limitation of analysis: Reported intercepts are extrapolated values that are sensitive to measurement noise. Therefore, this analysis should not be the sole or primary criterion for choosing a correction method.

3. Additional limitations to regression analysis for CSN

- CSN Teflon filter sampler has lower face velocity than IMPROVE samplers (and CSN OC samplers)
  - Mass well correlated for collocated sampling
  - Off-set is consistent with fewer semi-volatiles lost
  - Gravimetric mass over estimates mass on OC filters
- Limited mass data below 1 µg/m^3 (slide 20)



Birmingham, Seattle and Fresno

3. Intercept of regression (mass v. OC) as an estimate of extent of artifact reduction

CSN	2008	2009	2010
Uncorrected OC Intercept ($\mu g/m^3$)	0.61	0.60	0.44
MM back-up corrected intercept ($\mu g/m^3$)	0.25	0.27	0.13
MM field blank corrected intercept ($\mu g/m^3$)	0.48	0.47	0.33

All intercepts are statistically significantly different than zero

- Field blanks and back-ups decrease the artifact
- Limitation of analysis:
  - Gravimetric mass on Teflon does not represent mass on OC filters
  - Necessity of large extrapolation to zero mass (y-intercept) due to little data below 1 $\mu g/cm^3$
- Due to limitations, the comparison of intercepts should not be the sole or primary criterion for choosing an artifact correction for CSN.

Summary of Results Relevant to Evaluation Criteria

1. Field Blanks only collect positive artifact (back filters collect negative artifact),
   - Field blanks are a better estimate of the positive artifact on the filter
   - Blanks used for IC, XRF, and gravimetric
2. Field Blanks are less variable over time and space than back-ups for both networks and therefore better preserve (or have less impact on) the measured OC variability

Summary of Results Relevant to Evaluation Criteria, cont.

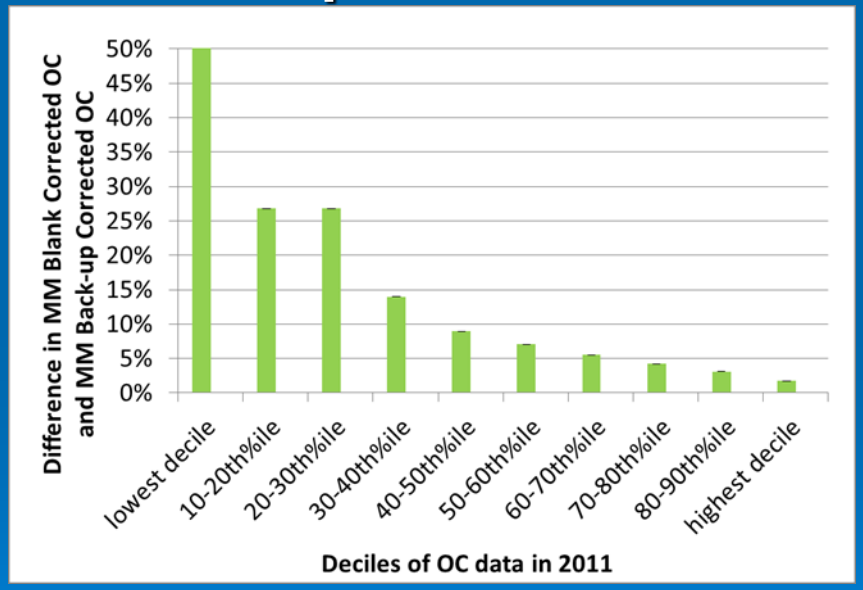
3. Field blanks decrease the contribution of sampling artifact to reported OC mass.
   - Bigger decrease for IMPROVE
   - Lower bound/under-correction for CSN
4. Blanks are collected by both networks and can be applied to historical data
5. This correction method should improve comparability of OC between networks
   - Both networks using same method
   - Blank monthly median values are similar

Recommendation

- Use monthly median field blank values to adjust measured OC data in both networks.
- Each network uses own field blanks to calculate monthly median field blank values.
- Perform adjustment on each thermal fractions (OC1, OC2, OC3, OC4, OP) and sum to calculate OC.

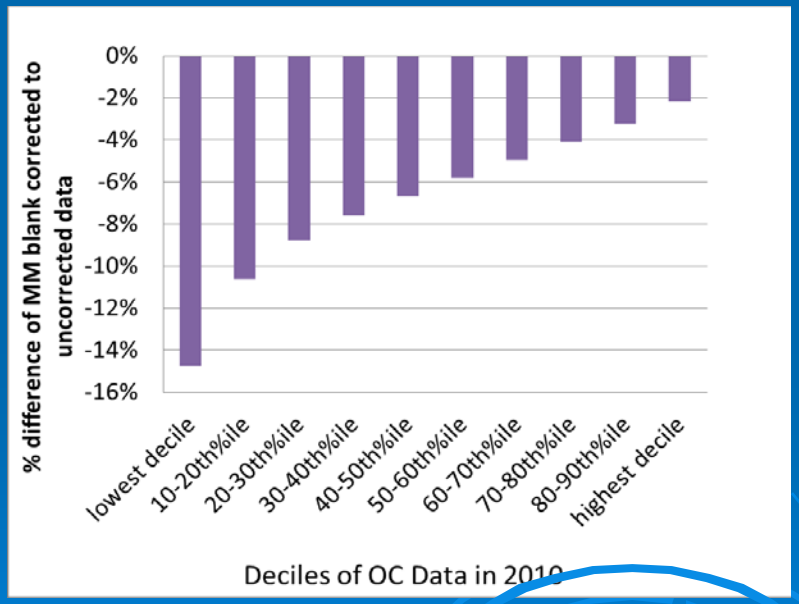
How much will the reported data change?

IMPROVE – difference between MM field blank and MM backup corrected OC



OC data will be higher by >10% for
~35% of data 2009
~50% of data 2010
~50% of data 2011

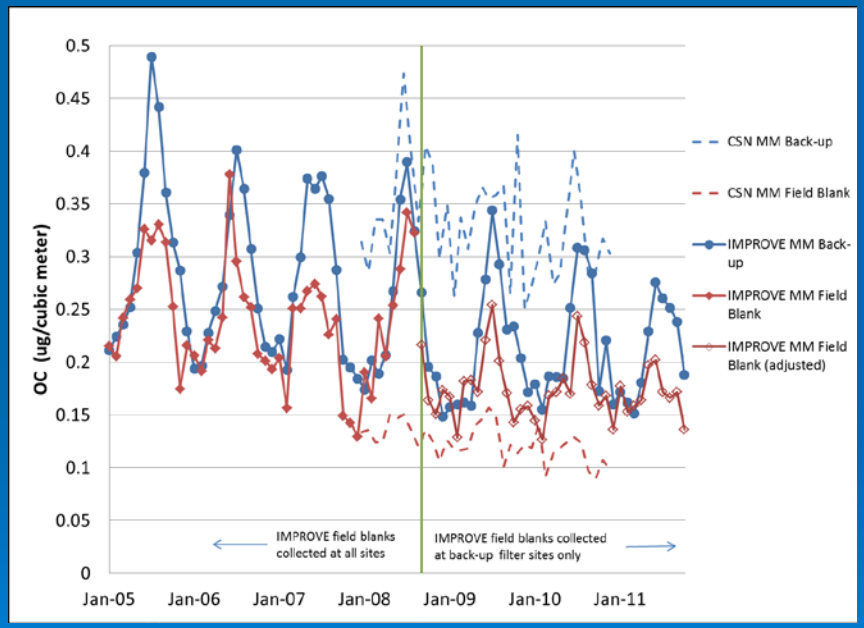
CSN – difference between MM field blank corrected OC and uncorrected OC



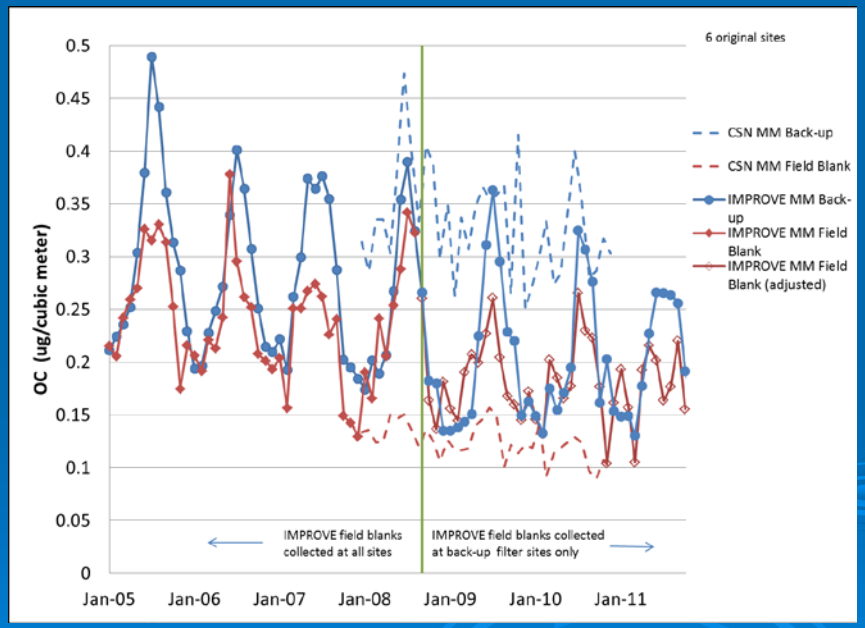
OC data will be lower by >10% for
~20% of data 2008
~30% of data 2009
~20% of data 2010

Since Recommendation: IMPROVE back/blank sites decreased to original six sites as of 1/2013

13 Back-up/Field Blank Sites



6 Original Back-up/Field Blank Sites



Change in sites does not significantly change medians, especially field blanks. Variability and linear regression results are qualitatively the same and the recommendations do not change.

Since recommendation: CSN changes

- Field blanks continue at 10%
- Back-up filters decreased to 5%
- Both back-ups and field blanks continue to be collected at all sites
- No impact on data quality since the recommended field blanks are used for the artifact adjustment.

Implementation of Method Change – IMPROVE

- Revised data available back to 2005
- http://vista.cira.colostate.edu/improve/Data/QA_QC/Advisory.htm

Posting type	Advisory
Subject	Change to artifact correction method for OC carbon fractions
Module/Species	C/OC
Sites	All
Period	January 1, 2005 – current

Implementation of Method Change – CSN

- New method began on 11/20/2015
- Parameter Codes in AQS
  - OC PM2.5 LC TOR Corrected = parameter code 88320
  - EC PM2.5 LC TOR Corrected = parameter code 88321
  - OC CSN Unadjusted PM2.5 LC TOR (uncorrected) = 88370
  - EC CSN Unadjusted PM2.5 LC TOR (uncorrected) = 88380
  - OC PM2.5 LC TOT Corrected = 88382
  - EC PM2.5 LC TOT Corrected = 88381
  - OC CSN Unadjusted PM2.5 LC TOT = 88355
  - EC CSN Unadjusted PM2.5 LC TOT = 88357

Moving toward comparable carbon measurements in IMPROVE and CSN

- CSN and IMPROVE reconciled methods (1/08):
  - Similar samplers (URG)
  - Same pre-conditioned quartz-fiber filters
  - Same (TOR) analysis
- CSN and IMPROVE reconciled artifact adjustment method (as of 11/15)
  - Monthly median field blank subtracted from each sample collected that month
- Estimating OM from OC
  - Each network uses one value
  - Upcoming FT-IR method (discussed this afternoon) could provide sample specific OM/OC to better compare OM between networks