Recommendation of the IMPROVE/CSN Organic Carbon Artifact Adjustment Committee

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Current OC monitoring by IMPROVE and CSN

- The two networks have reconciled their sampling and analysis methods (CSN transition completed by Jan. 2008):
  - Similar samplers (URG)
  - Similarly pre-conditioned quartz-fiber filters from the same manufacturer
  - Analysis using the same protocol (IMPROVE_A) in the same laboratory (DRI)
- The two networks report concentrations according to different conventions:
  - Adsorption of organic gases by quartz filters yields artifact 'particulate matter'.
  - IMPROVE adjusts sample filter loadings with an estimate of the artifact, based on back-up filters collected at selected sites.
  - CSN reports sample filter loadings directly along with blank values and makes no adjustment.
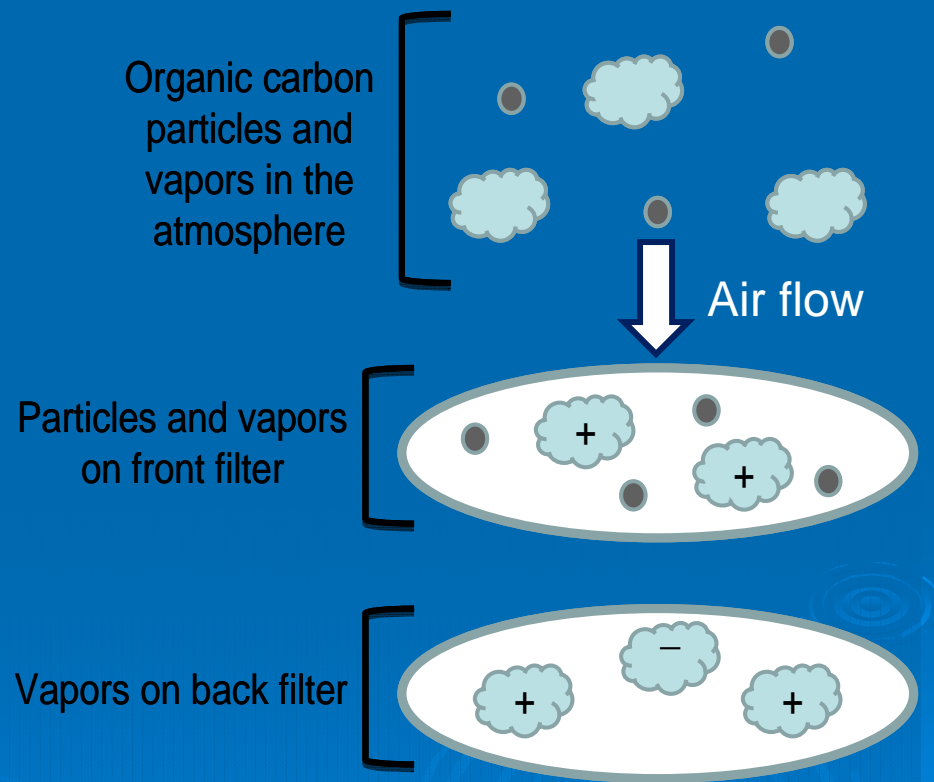
Recommendation

➢ Use monthly median <u>field blank</u> 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 fraction (OC1, OC2, OC3, OC4, OP) and sum to calculate OC. (Note: adjusting thermal fractions and summing is the current IMPROVE method).

Carbon Sampling Artifacts

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

Organic carbon particles and vapors in the atmosphere

Air flow

Particles and vapors on front filter

+
+

Vapors on back filter

−
+
+

Back-up and Field Blank Sites through end of 2012

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.

CSN - backups & blanks per month

2008 ~60, 2009 ~120,

2010 ~160
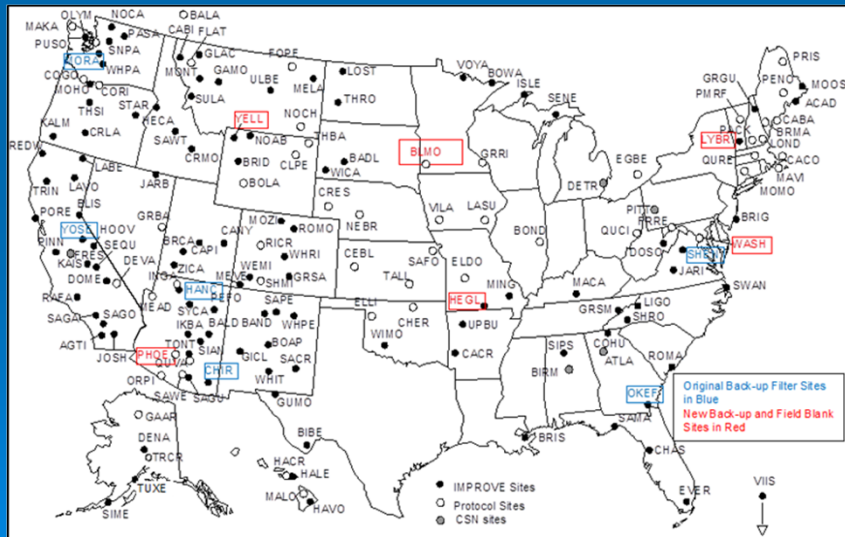
~2% blanks, ~7% backup filters

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

Two approaches for Artifact Adjustment

➢ Current IMPROVE method –
- Subtract monthly median (MM) <u>back-up</u> OC thermal fractions and total OC mass (determined from 13 sites) from each filter collected in the network for that month

➢ Current CSN method –
- Field blanks and backup filters collected at all sites (~180 sites) but no correction performed

➢ Alternative method –
- Subtract MM <u>field blank</u> OC thermal fractions and total OC mass (all sites) from each filter collected in the network for that month

➢ Each network would calculate its own adjustment factors each month using the same approach

6

Evaluate current IMPROVE method vs. alternate method for artifact adjustment, to determine which is better able to meet the following criteria:

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

Approach

- Ideally, compare to artifact-free OC measurements – does not exist
- Approach used with measurements we have
  1. Evaluate methods in light of limited understanding of artifacts
  2. Evaluate variability of monthly median back-up and field blank concentrations
  3. Decrease artifact in the measured OC
     - 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
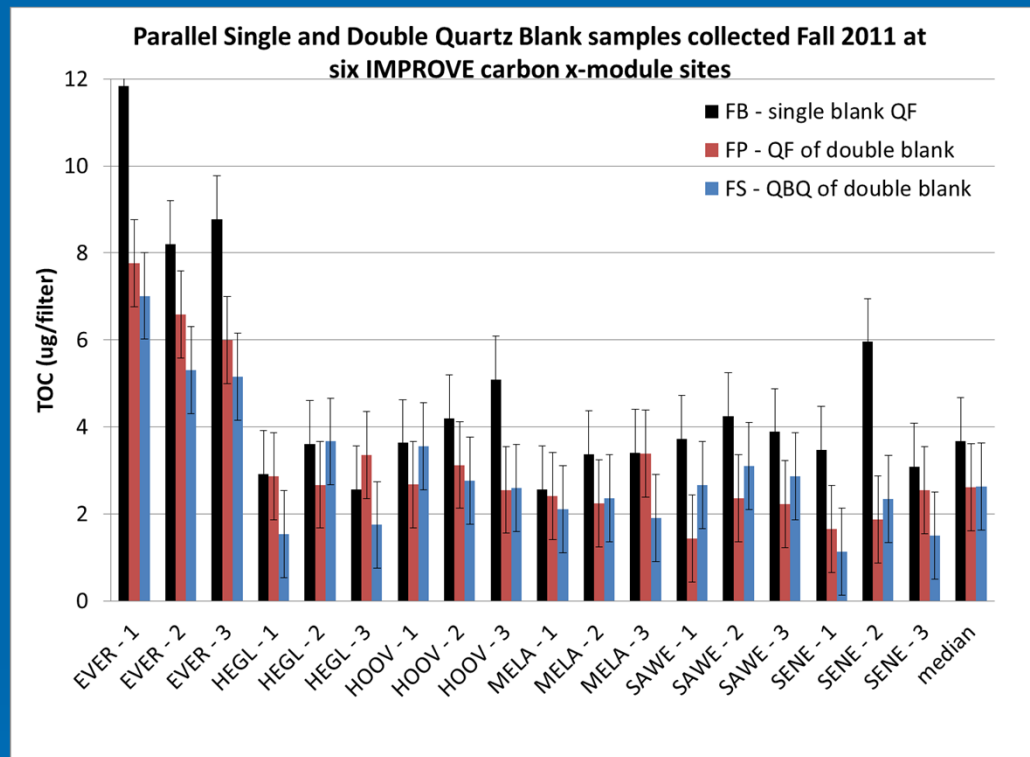
First, a caveat about IMPROVE field blank data before preceding with the analysis

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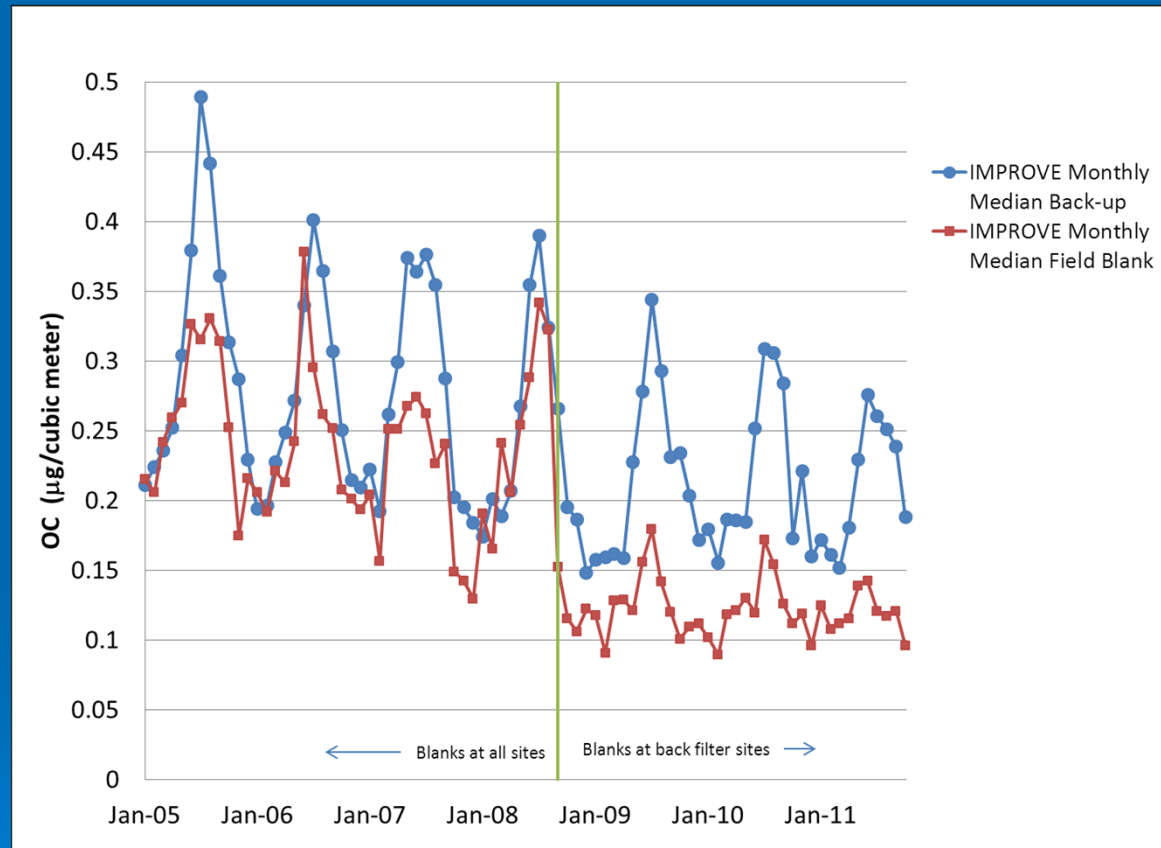
Field blank OC concentrations decreased when filters began to be collected only at back-up filter sites (8/08). Double quartz field blanks were collected beginning 8/08. Prior to that time single field blanks were collected.

10

Double Field Blanks

Parallel Single and Double Quartz Blank samples collected Fall 2011 at six IMPROVE carbon x-module sites

- FB - single blank QF
- FP - QF of double blank
- FS - QBQ of double blank

➤ 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.
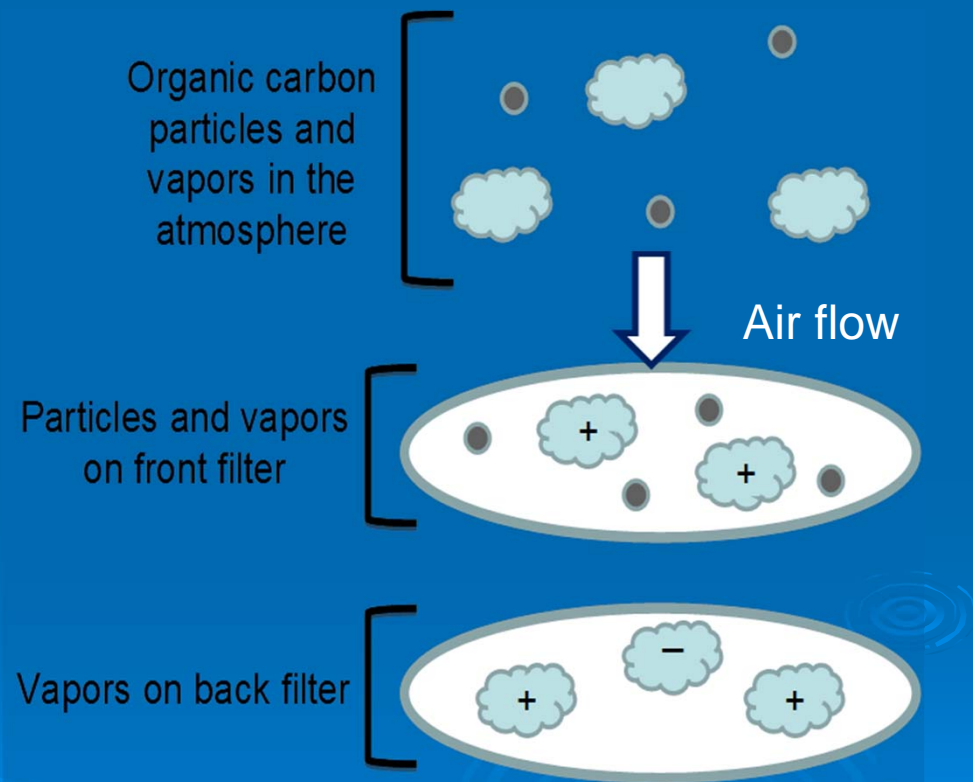
Monthly Median Back-up and Field Blank OC values for IMPROVE and CSN
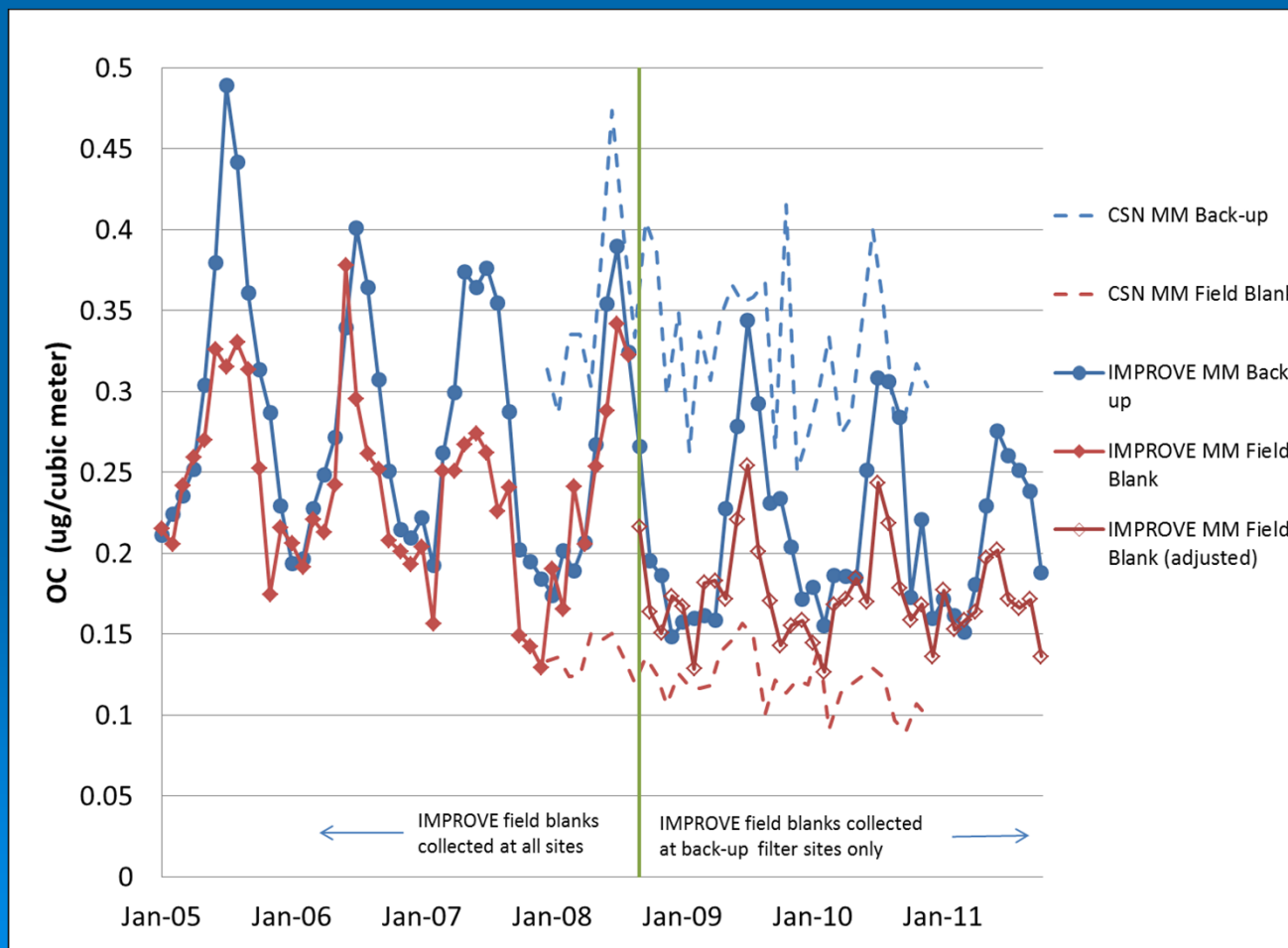
1. Evaluate methods in light of limited understanding of artifacts

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

- Back: + and –artifact
- Back: may over-correct for +artifact
- Field: +artifact
- Field: represent artifact that we are trying to remove, may be lower bound on +artifact
- Field blanks are a better estimate of + artifact and therefore a better choice

Organic carbon particles and vapors in the atmosphere

Air flow

Particles and vapors on front filter

Vapors on back filter

13

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

IMPROVE Site Medians (with 25th and 75th percentiles) for 2009-2011
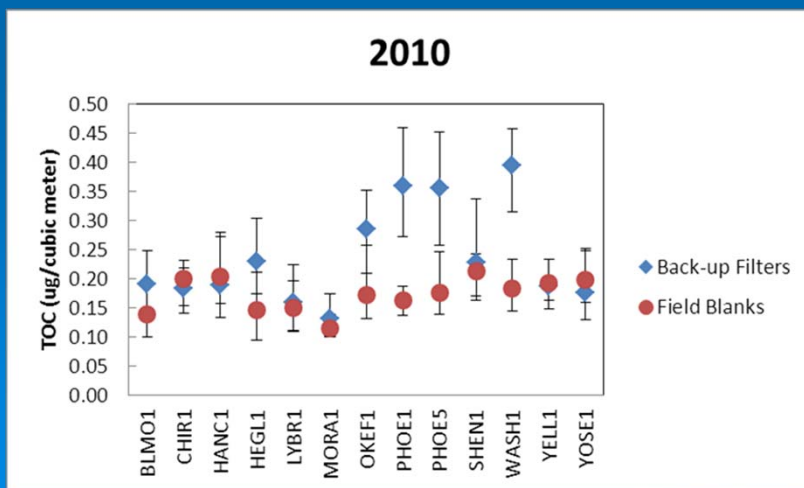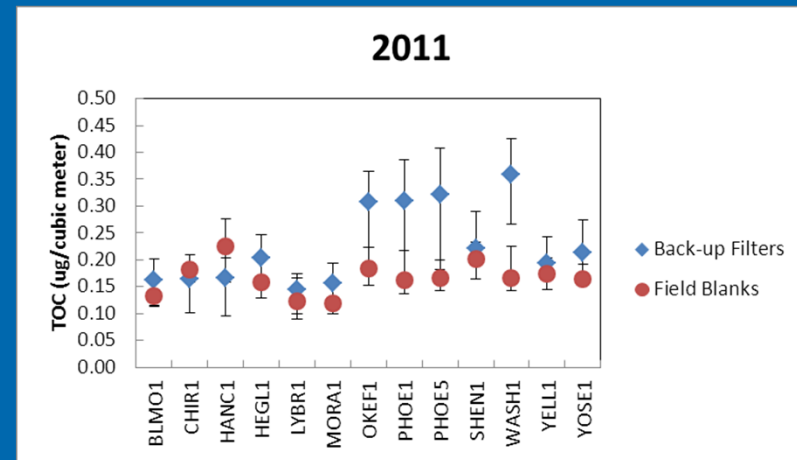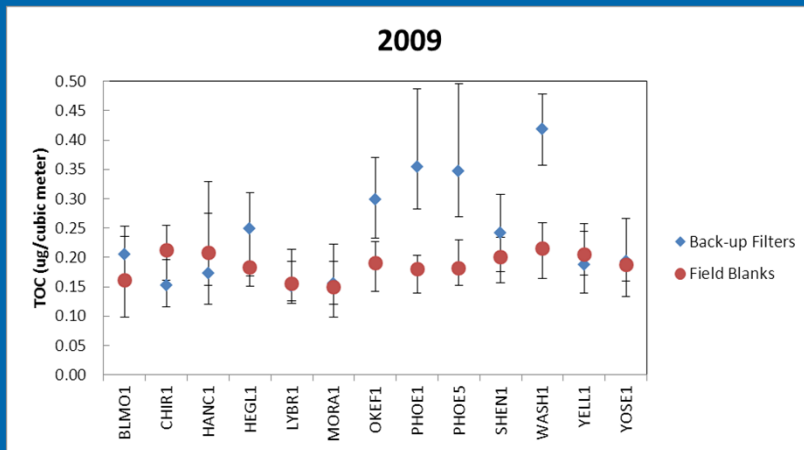
- ➢ Field blanks have less site to site variability and less variability within a site for IMPROVE
- ➢ Urban sites have higher back-ups than most rural sites, OKEF1 high

14

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

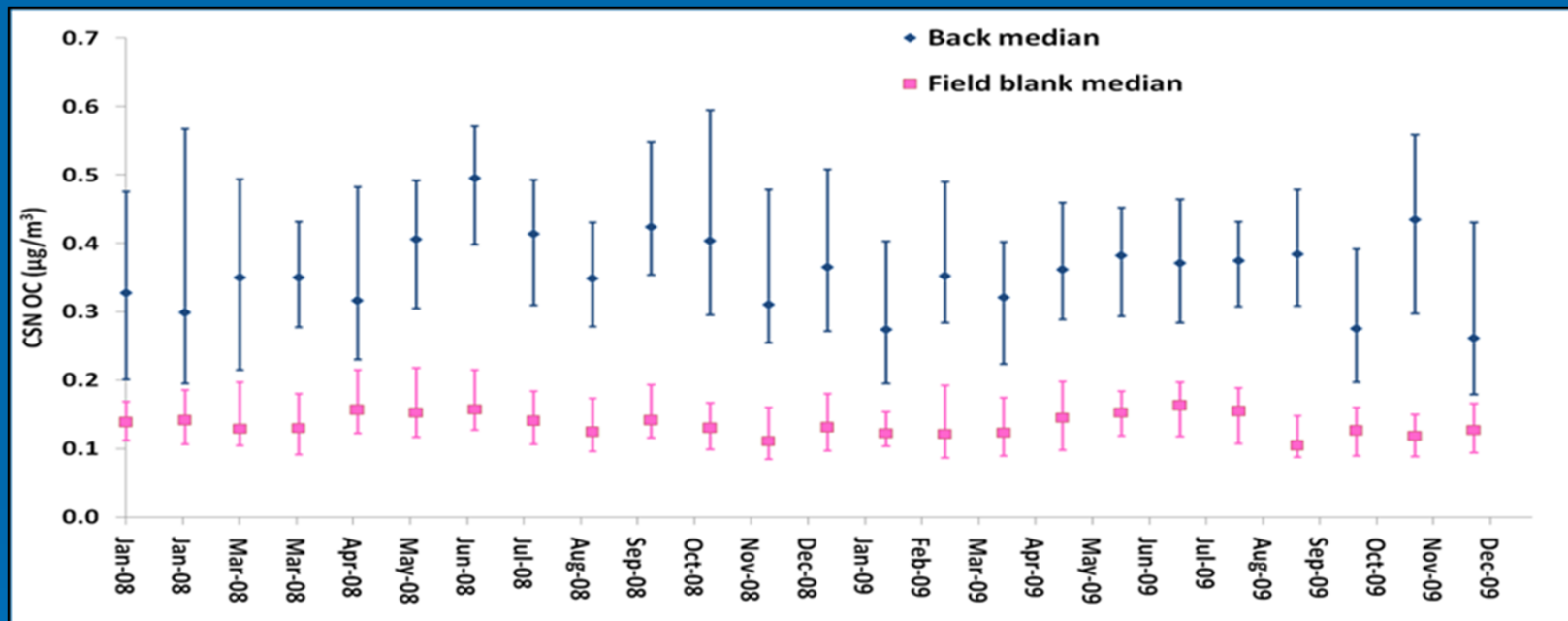25th and 75th percentile shown as error bars
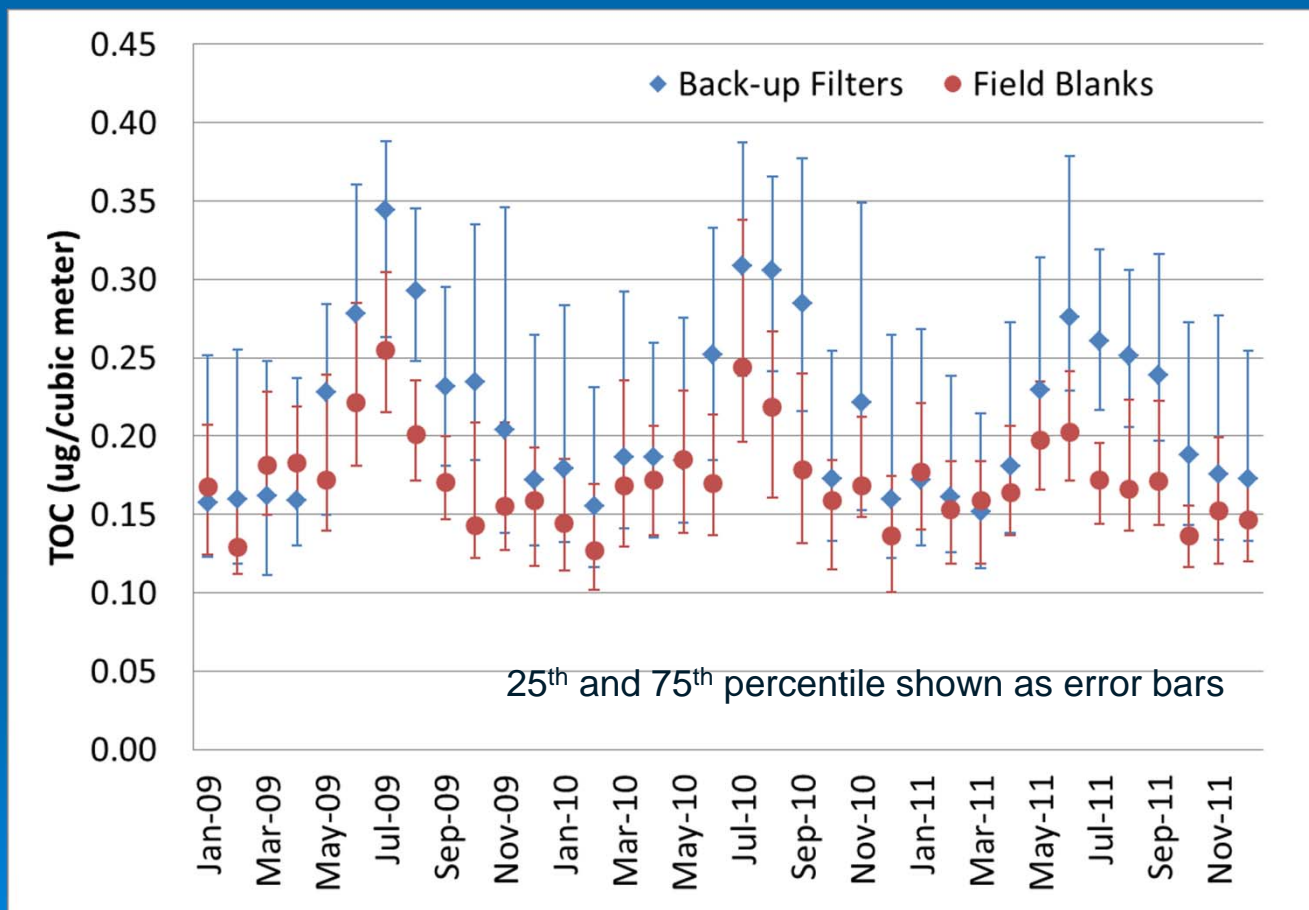
➢ Field blanks are usually lower, have less seasonality and less variability within a month than back-up filters for IMPROVE

15

2. Variability: CSN site medians

CSN Median Field blanks by site n=12 or more
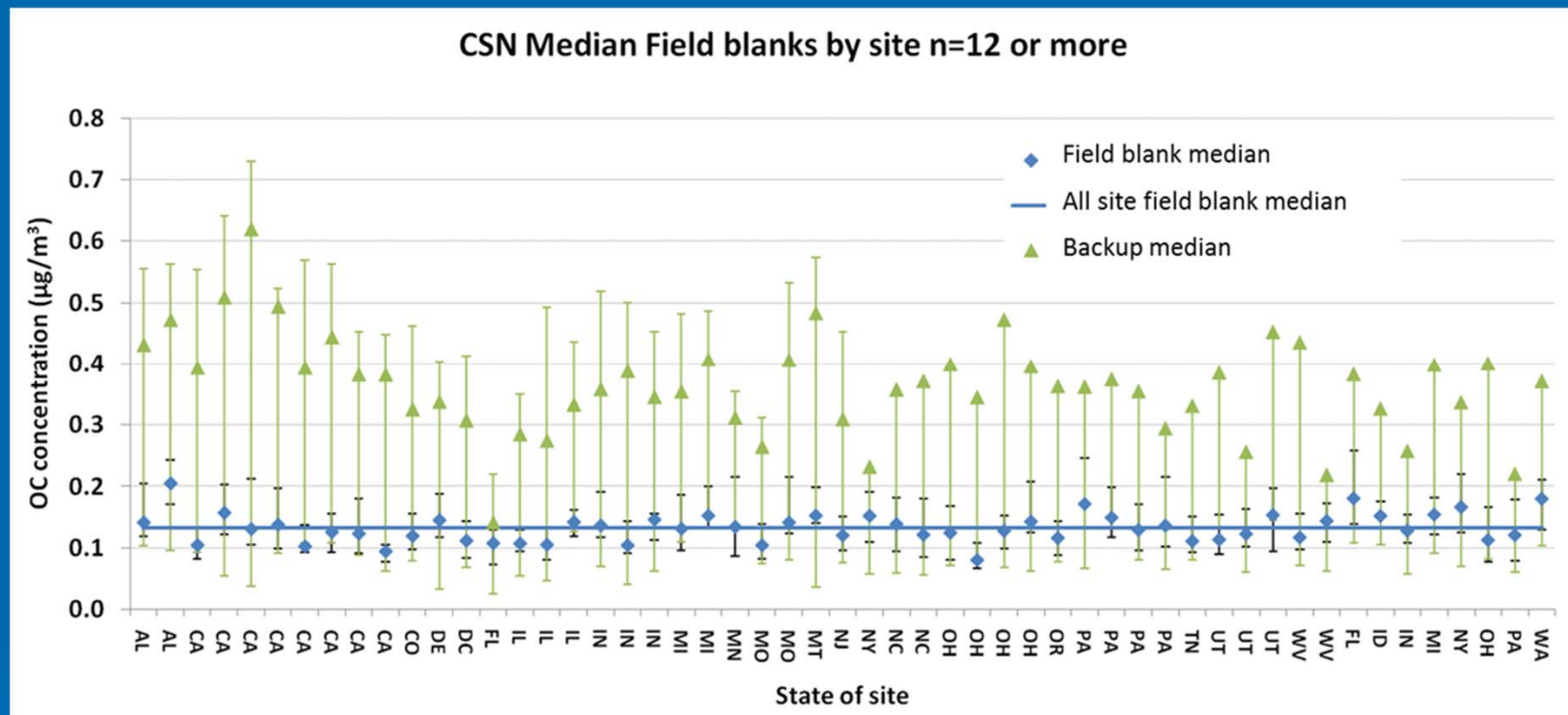
- ➤ Field blanks have less site to site variability and less variability within a site for CSN.
- ➤ Same behavior as IMPROVE data, although the backup filter concentration is slightly higher for CSN (urban) than IMPROVE (rural) and the difference in OC concentration for two filters types is more pronounced.

# 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 two filter types is more pronounced.

17

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

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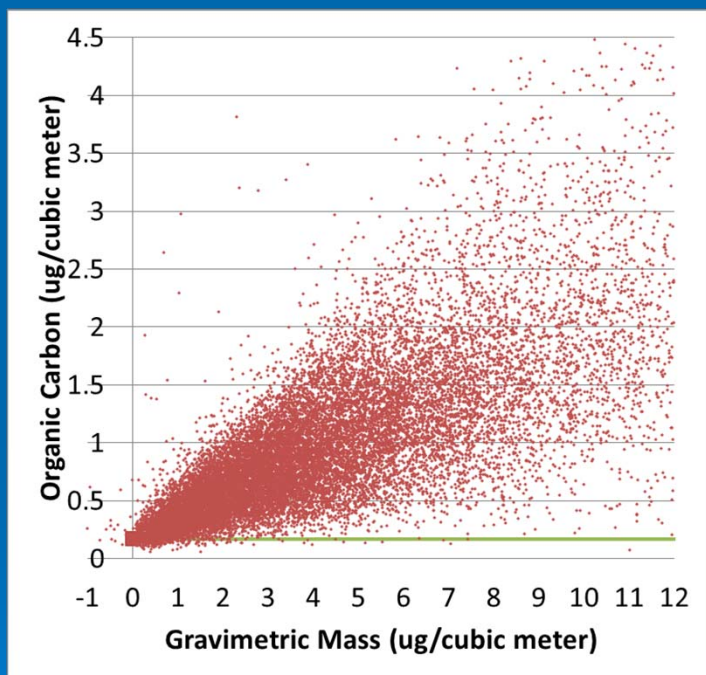
CSN – 2009 data
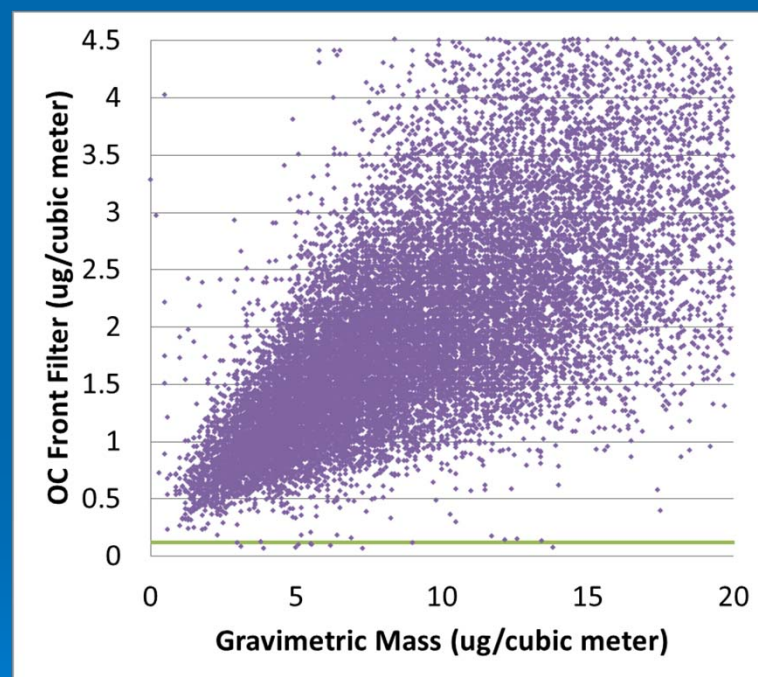
- OC mass does not go to zero as gravimetric mass goes to zero for both networks suggesting a positive OC artifact.
- The green line is the annual median of the field blanks. For IMPROVE the value is 0.17 μg/m^3 and for CSN the value is 0.12 μg/m^3 in 2009.

18

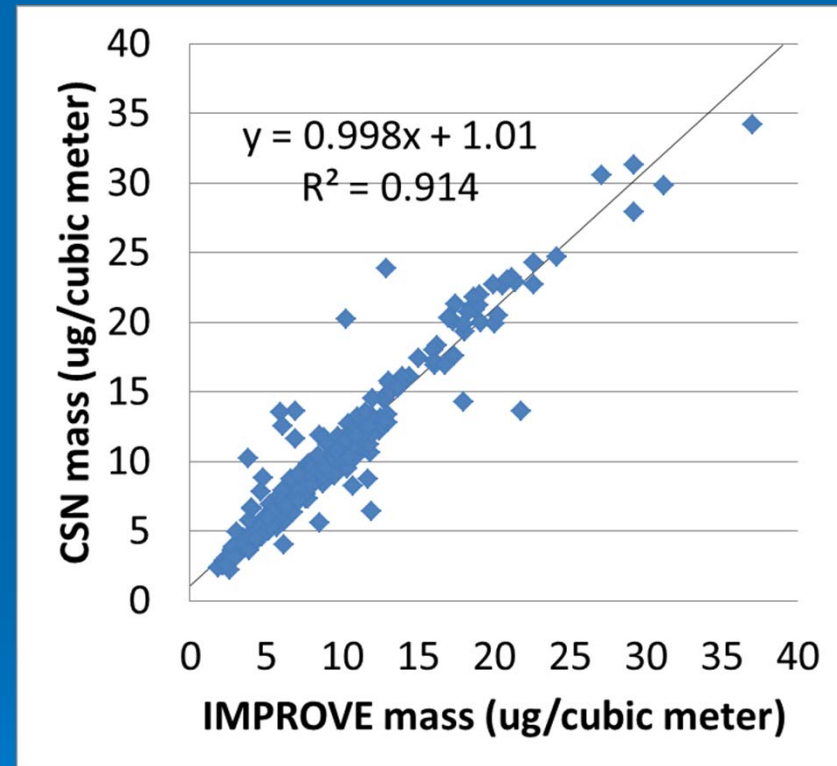# 3. Intercept of regression (mass v. OC) as an estimate of extent of artifact reduction

IMPROVE	2009	2010	2011
Uncorrected OC Intercept (μg/m^3)	0.17	0.26	0.10
MM back-up corrected intercept (μg/m^3)	-0.03	0.02	-0.09
MM field blank corrected intercept (μg/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 $\mu g/m^3$ (slide 18)

$$y = 0.998x + 1.01$$
$$R^2 = 0.914$$

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.
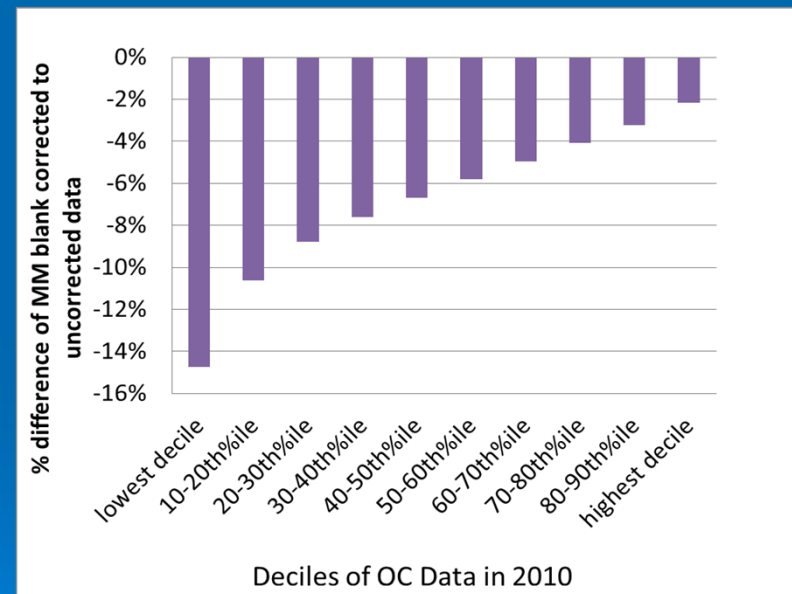
21

How much will the reported data change?

IMPROVE – difference between MM field blank and MM backup corrected OC
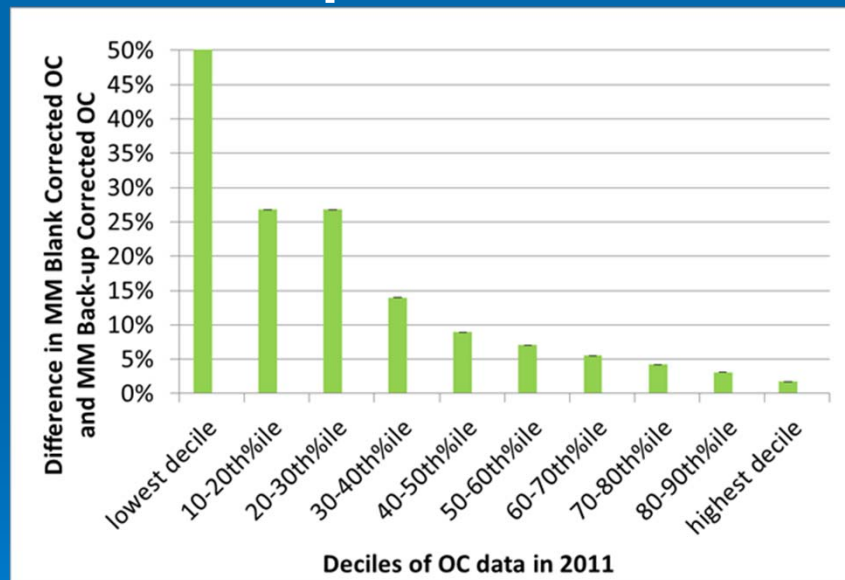
OC data will be higher by >10% for
~35% of data 2009
~50% of data 2010
~50% of data 2011

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

22

Summary of Results Relevant to Evaluation Criteria (slide 7)

1. Field Blanks only collect positive artifact (back-ups may also collect negative artifact), field blanks are a better estimate of the positive artifact on the filter

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 than back-up filters

23

# Summary of Results Relevant to Evaluation Criteria (slide 7), cont.

3. Field blanks decrease the contribution of sampling artifact to reported OC mass.

4. Field blanks are collected by both networks and can be applied to historical data

5. This correction method should improve comparability of OC between networks
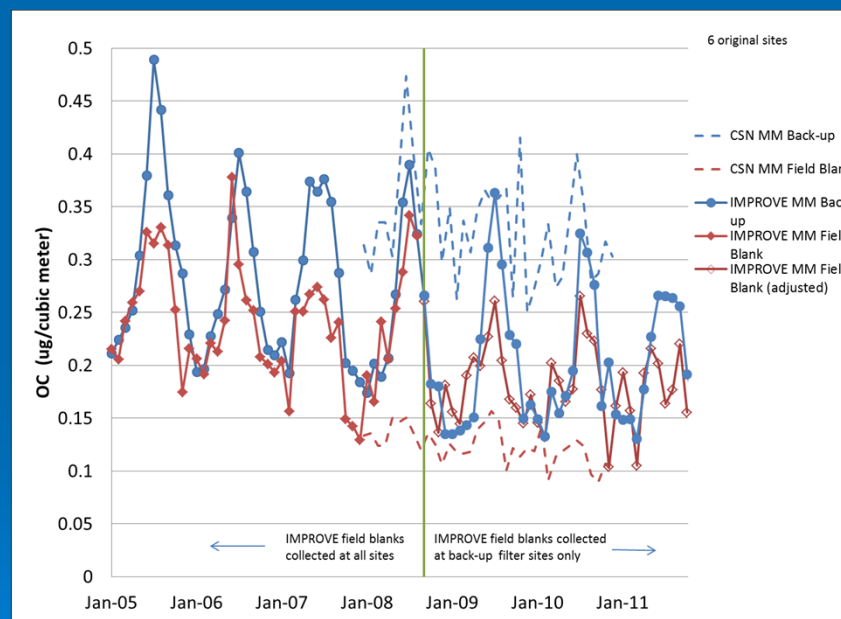
Recommendation

➢ Use monthly median <u>field blank</u> 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. (Note: adjusting thermal fractions and summing is the current IMPROVE method).

25

IMPROVE Back-up/Field Blank Sites decreased to original six sites as of 1/2013 due to budget restrictions

13 Back-up/Field Blank Sites
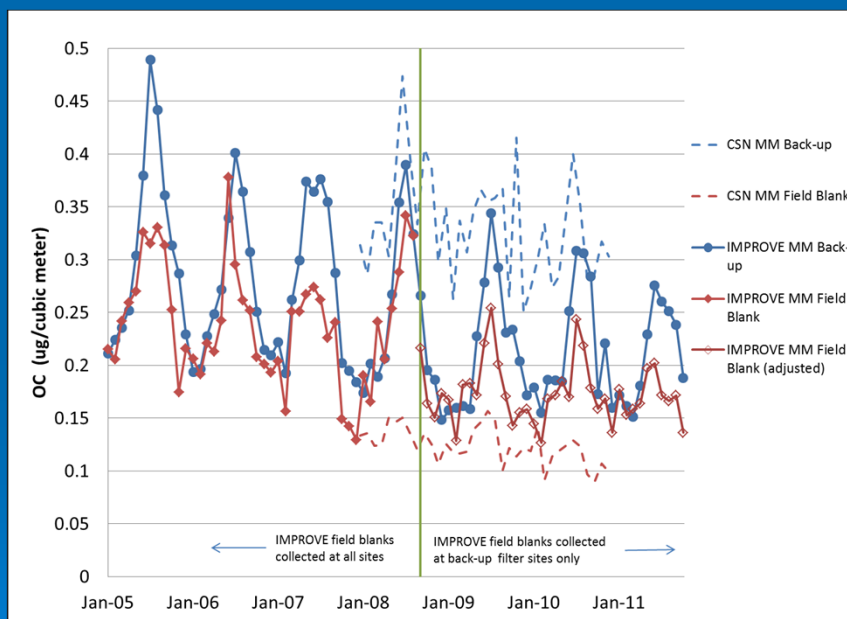
6 Original Back-up/Field Blank Sites

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.

26

Current CSN changes due to budget limitations

➤ Field blanks will continue at 10%

➤ Back-up filters will be decreased to 5%

➤ Both back-ups and field blanks will continue to be collected at all sites

➤ Back-ups will continue to be collected on days that correspond with field blanks

➤ This will have no impact on future data quality if the recommended field blanks are used for the artifact adjustment.

Suggestions to IMPROVE/CSN staff for implementing the recommendation

➤ Both networks - Start reporting data using MM field blanks adjustment as soon as is feasible

➤ Change existing data to use MM field blanks

- IMPROVE - January, 2005 when new TOR instrument was implemented
- CSN – when conversion to IMPROVE-like samplers was performed at each site starting in May 2007

➤ Both networks - Report artifact adjustment values in database. This would allow users to use corrected or uncorrected carbon fraction data.

Suggestions, continued

- IMPROVE
  - Continue to collect and analyze back-up filters at six original sites for IMPROVE to provide data set to evaluate back-up vs field blanks using single blank filters (if funding available)

- CSN
  - Continue to collect and analyze back-up filters at 5% frequency for comparison to IMPROVE and future evaluation of back-ups vs. field blanks (if funding available)

Appendix

Additional Data on IMPROVE back-ups and field blanks

Sites	2005	2006	2007	2008*	2009	2010	2011
Number of sites in network as of 1/1	167	165	168	169	169	170	165
Number of field blank sites	167	165	168		13	13	13
Number of back-up sites	6	6	6		13	13	13

*Beginning in August 2008, field blank collection was moved to back-up sites. No data is reported in 2008 for number of back up and field blank sites since it changed mid-year.

Additional Data on IMPROVE back-ups and field blanks

Filters analyzed	2005	2006	2007	2008	2009	2010	2011
Number of field blanks analyzed	490	461	471	469	492	417	396
Number of back-up filters analyzed	699	700	704	900	1416	1574	1441
Percentage of field blank filters in network	2.4	2.3	2.3	2.3	2.4	2.0	2.0
Percentage of back-ups in network	3.4	3.5	3.4	4.4	6.9	7.6	7.2

NOTE: Field blanks are collected for one week periods in IMPROVE. Back-ups are collected at the same rate as samples, 1 in 3 days so there are more back-ups than field blanks . Since 8/08 only 2/3 of collected field blanks are analyzed. This table reports analyzed filters. Unanalyzed filters are archived. 32

Additional Data on IMPROVE back-ups and field blanks

➢ In 2005-2007, approximately 3 field blanks were analyzed per site per year.

➢ 2009-2011, approximately 35 field blanks were analyzed at each of the 13 sites per year

➢ The percentage of field blanks remained fairly constant from 2005-2011.

➢ The percentage of back-up filters roughly double in 2008.

Changes to IMPROVE back-ups and field blanks in 2013

- Based on Scott Copeland's 2/25/13 email regarding budget cuts to IMPROVE,
  - Field blanks and back-ups will be collected at original 6 sites only
  - Decrease in sample weeks per year and sites
- Changes in analyzed filters based on cuts
  - Field blanks will decrease from 2% to 1% of the network
  - Back-up filters will decrease from 7% to 2.5% of network samples.