

Report of the IMPROVE/CSN Organic Carbon Artifact Adjustment Committee

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Lake Tahoe IMPROVE Steering Committee Meeting,
2012



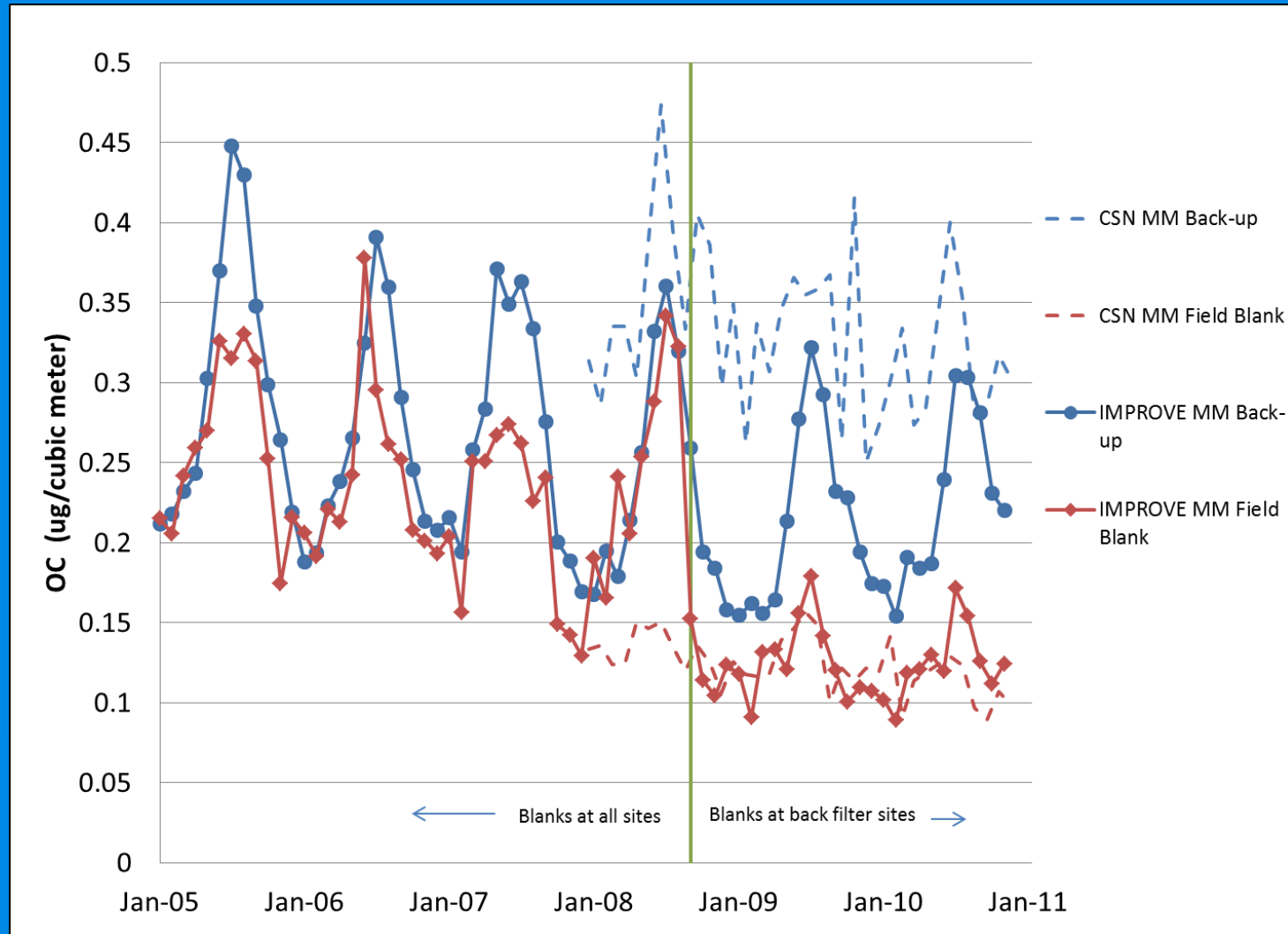
IMPROVE/CSN OC Artifact Committee Tasks

1. To recommend to the IMPROVE steering committee and to CSN an appropriate method for both networks to use to artifact correct OC data
2. To make plans for implementing the change in IMPROVE
 - Timing of change
 - Back date change
 - Change filter sampling/analysis configuration

Currently considering recommending the use of blanks (QF) instead of back-ups (QBQ)

- Blanks are less variable over time and space than back-ups (both networks)
- Blanks for two networks are similar, back-ups are not
- IC and XRF use blank filters for artifact correction
- Blanks don't over-correct by including multi. factor
- Blanks decrease additive artifact
 - Bigger decrease for IMPROVE
 - Lower bound/under-correction for CSN
- Simple/low cost/applicable to historic data
- Both networks using same method will improve comparability between networks

Change in behavior of IMPROVE field blanks after 8/08



Analysis of existing IMPROVE data did not establish cause of change

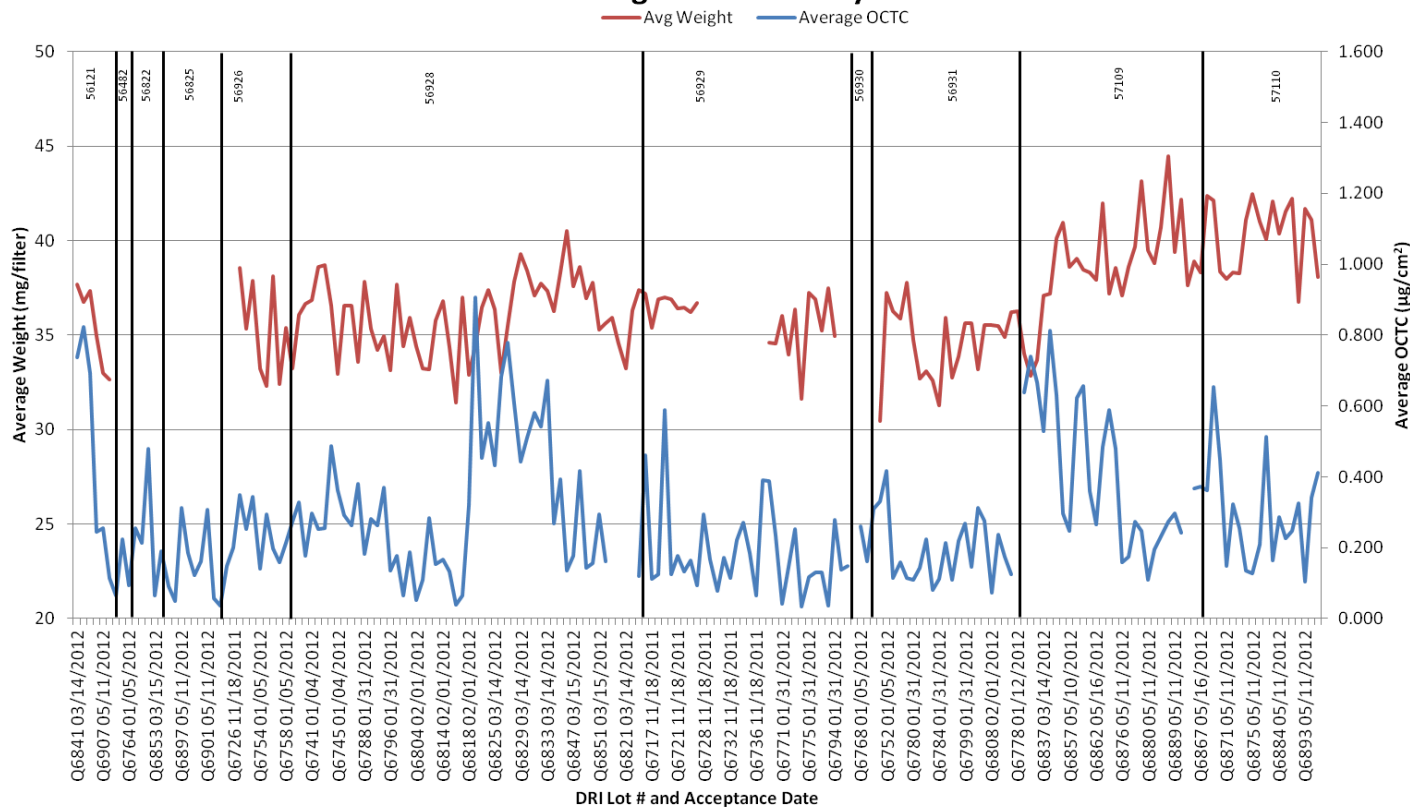
Three hypothesis to be tested

(agreed upon by Committee during Nov. 2011 call)

1. Manufacturing change in filters (DRI)
2. Air pulled through blank for 14 seconds prior to August 2008 (UCDavis)
3. Switch from single to double quartz in August 2008 (UCDavis)

Hypothesis 1: Manufacturing change to filters

Figure 4
Blank filter weight and OCTC by Manufacturer Lot #



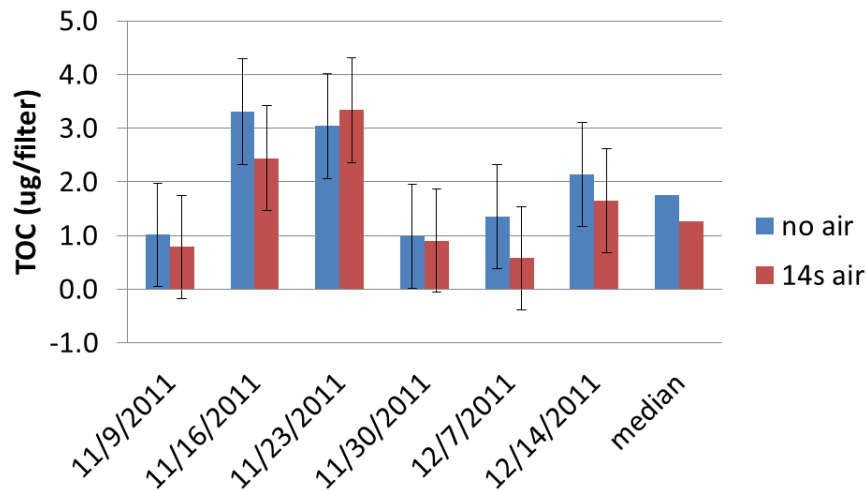
Small numbers between gridlines are manufacturer lot number

- Surface area/mass is similar for 3 filters with different masses
- Mass variability within lot at least as big as between lot
- Mass does not correlate with OC in laboratory blanks
- CNL plans to start tracking lot number when new laboratory software is developed

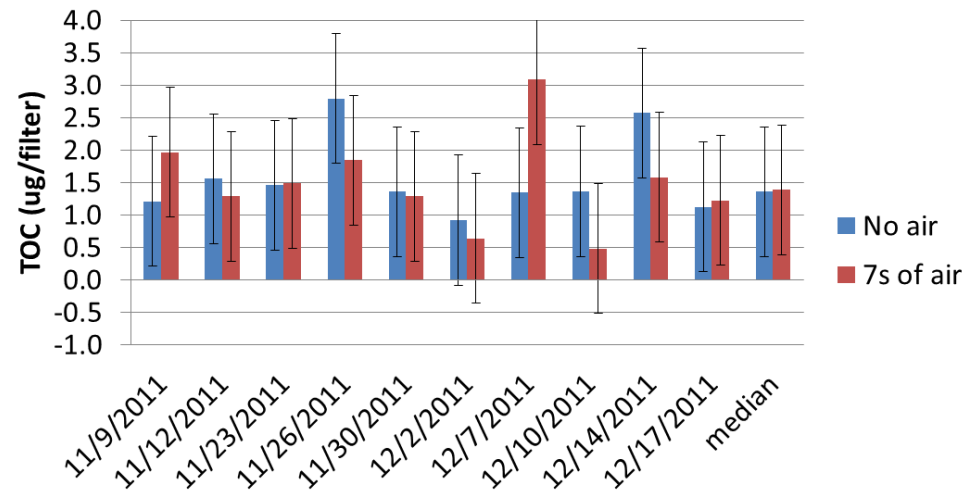
Hypothesis 2: Air through blanks

- Before Aug. 2008, 14s of air through FB
- After Aug. 2008, no air through field blanks

Parallel Air/No air blanks collected with samples for 7 days at UCDavis



Paralell Air/No air blanks collected with samples for 3 days at UCDavis



This mechanism is not cause of change

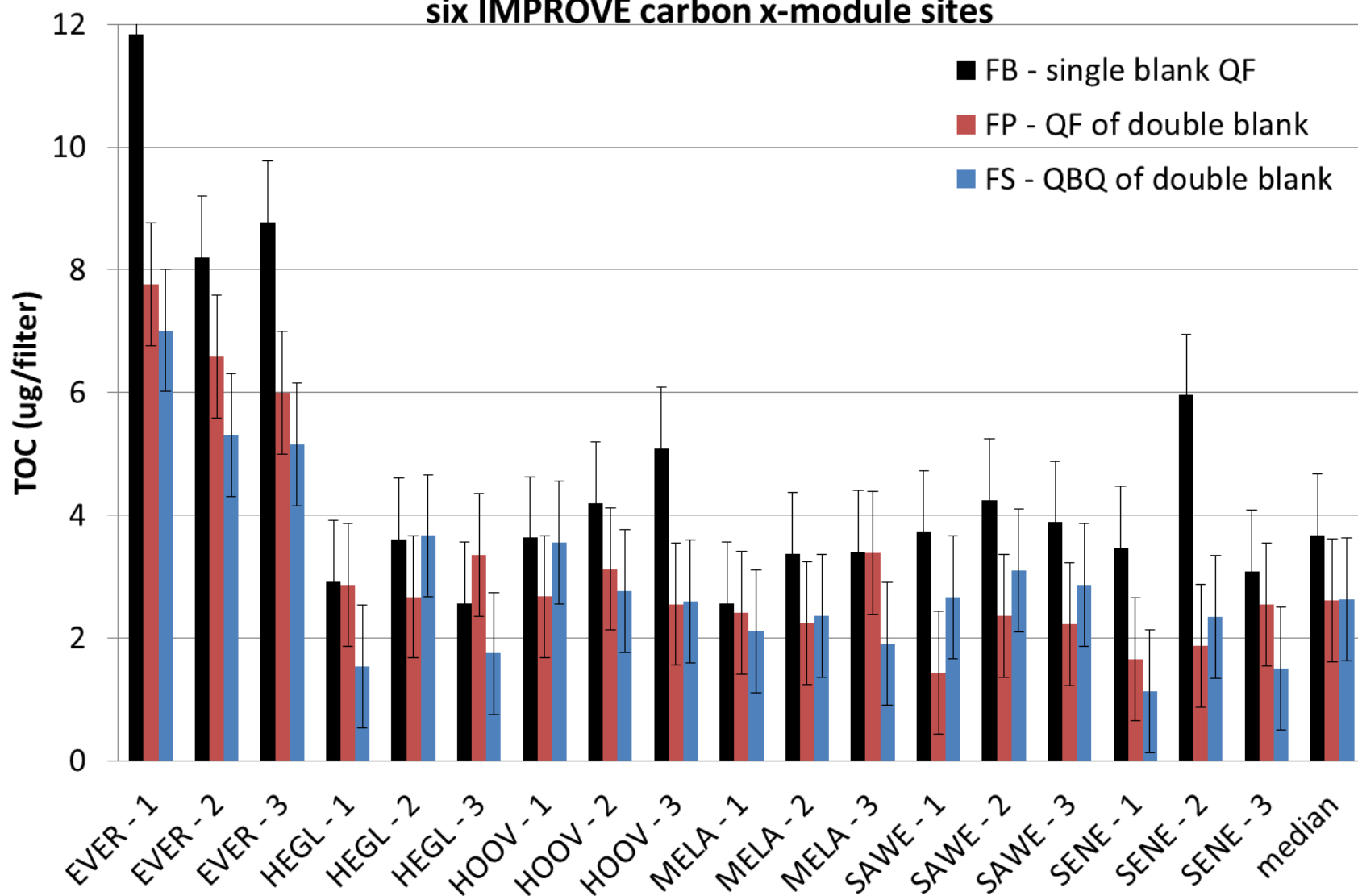
Note: CSN blanks do not have air through them,

Hypothesis 3: Change from single to double blank filters in IMPROVE

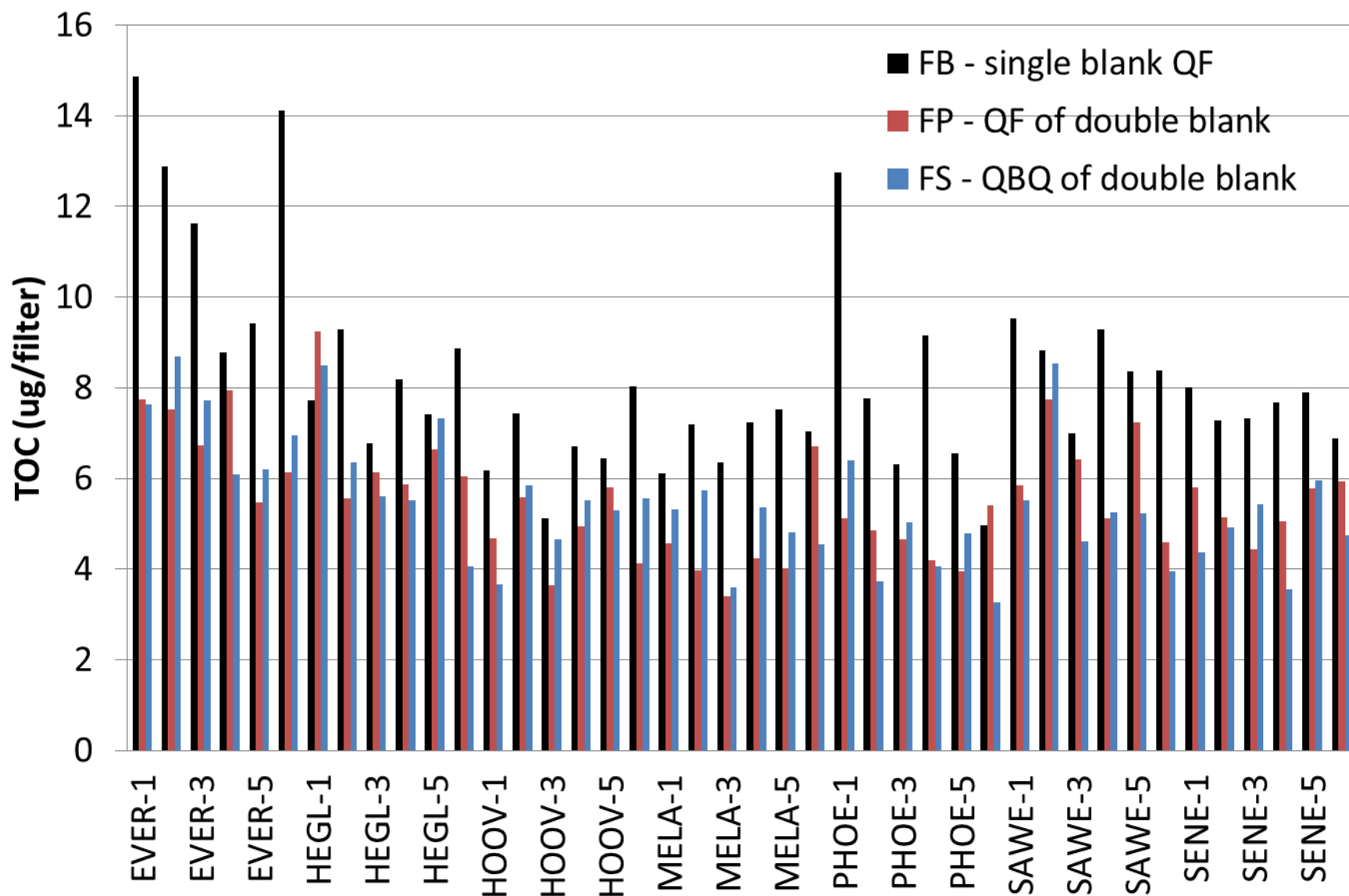
- Prior to August 2008, blanks were single filters
- After August 2008, blanks are double filters
- Experiment: Parallel single/double quartz filters
 - Late Fall (Oct/Nov) 2011: 6 QC sites for three sampling events
 - Summer (Jun/July) 2012: 7 QC sites for six sampling events

Note: CSN blanks are single

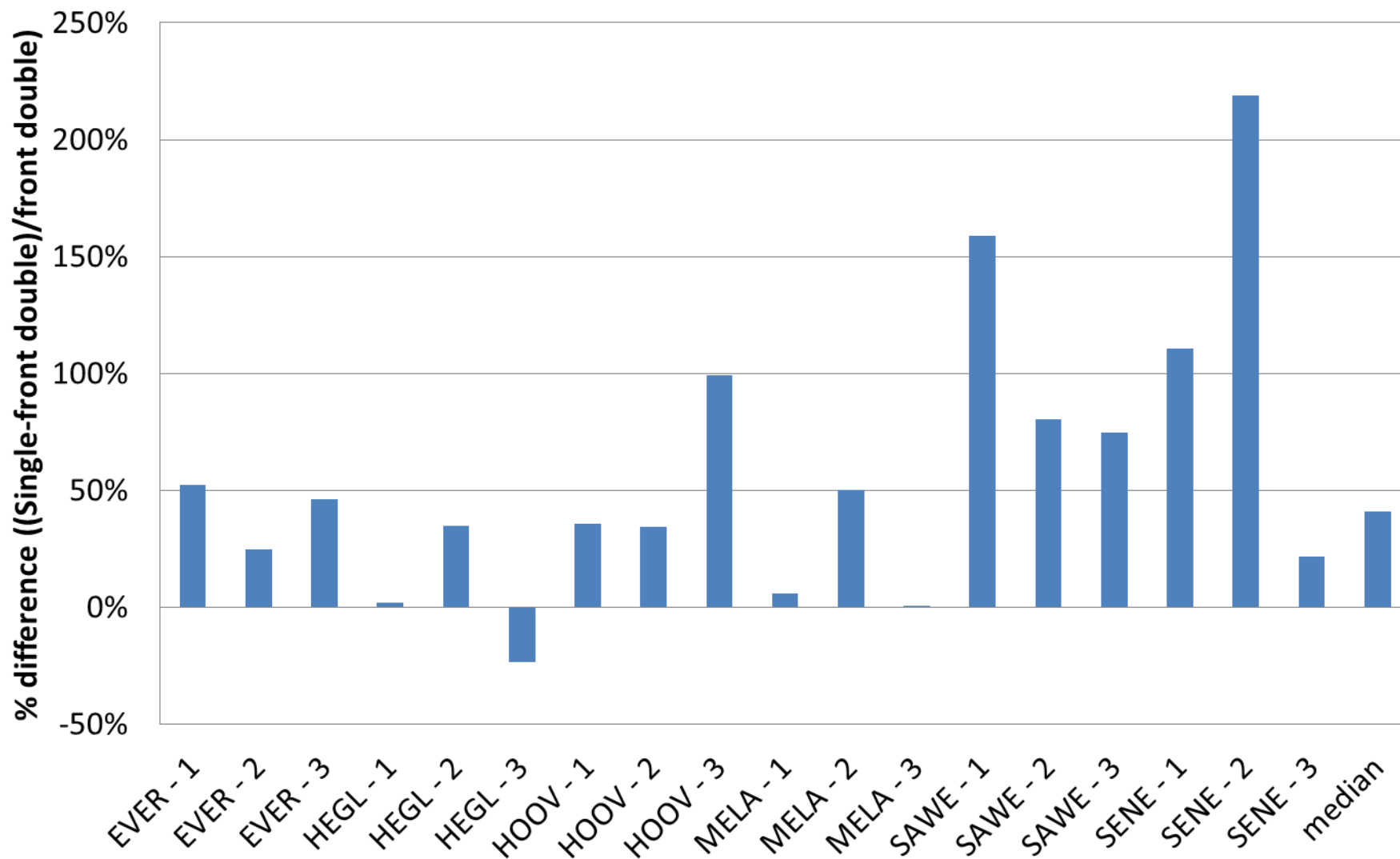
Parallel Single and Double Quartz Blank samples collected Fall 2011 at six IMPROVE carbon x-module sites



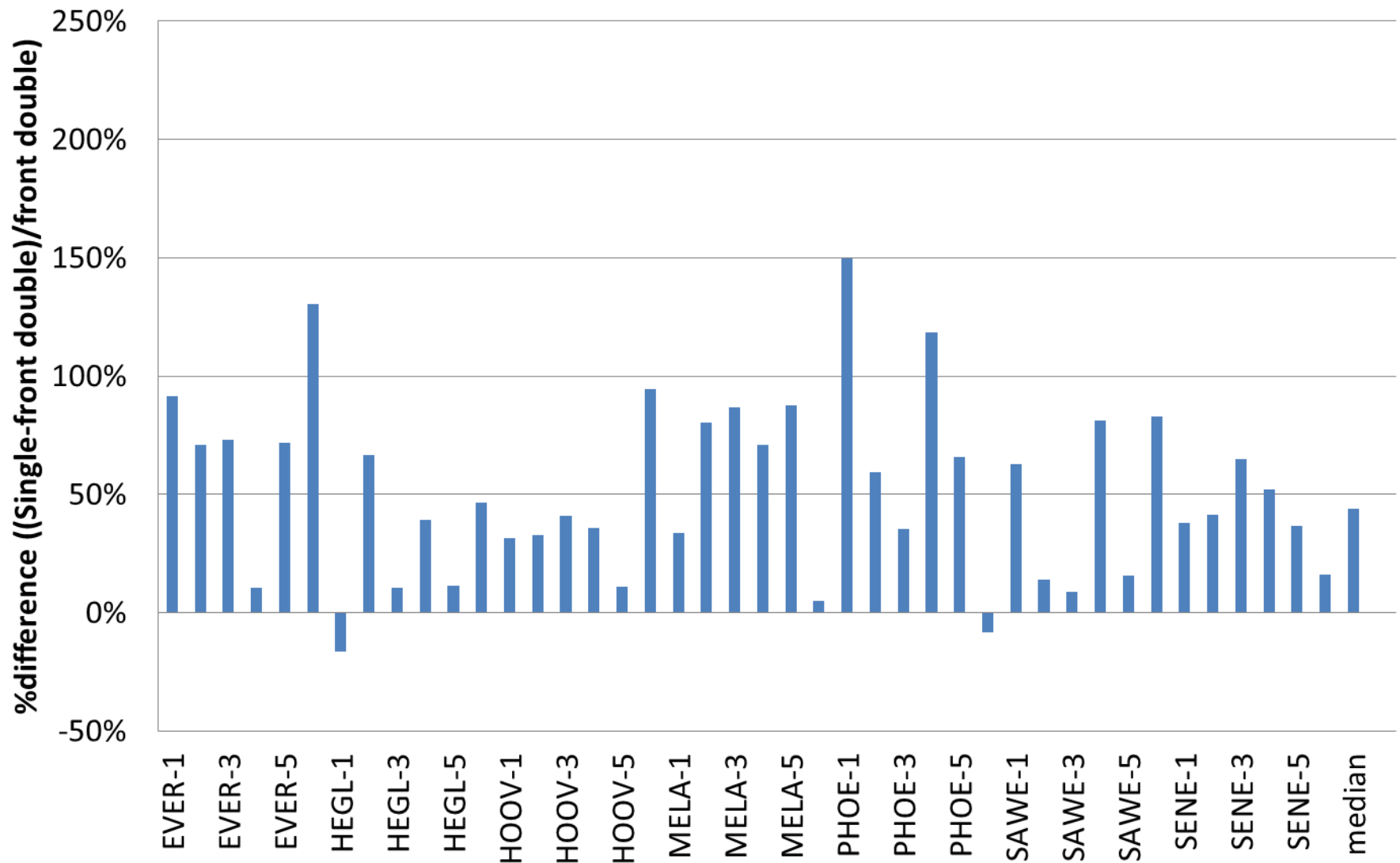
Parallel Single and Double Quartz Blank samples collected Summer 2012
at seven IMPROVE carbon x-module sites



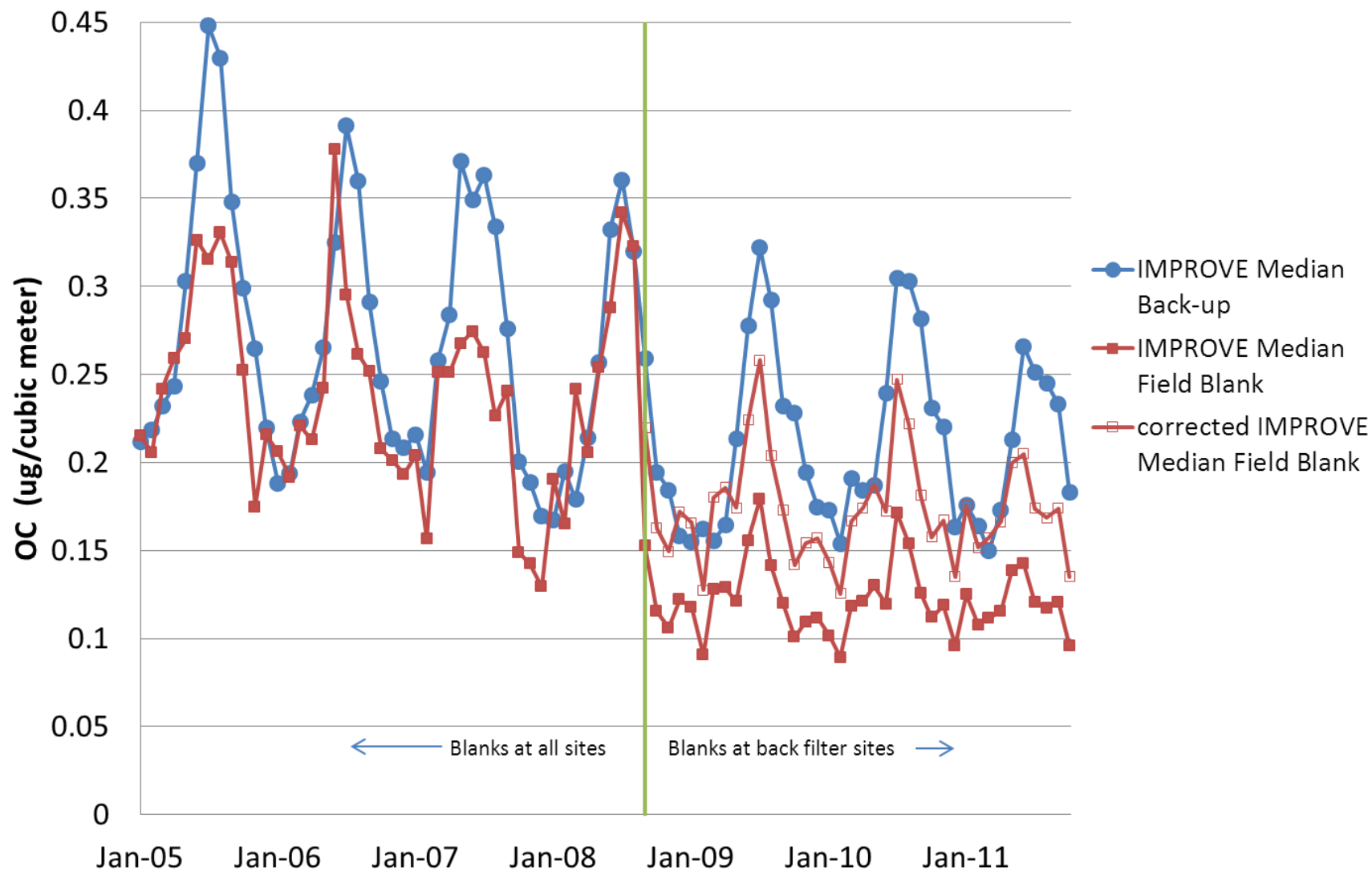
Percentage difference between
single blank and front of double blank
Fall 2011 samples



Percentage difference between
single blank and front of double blank
Summer 2012 samples

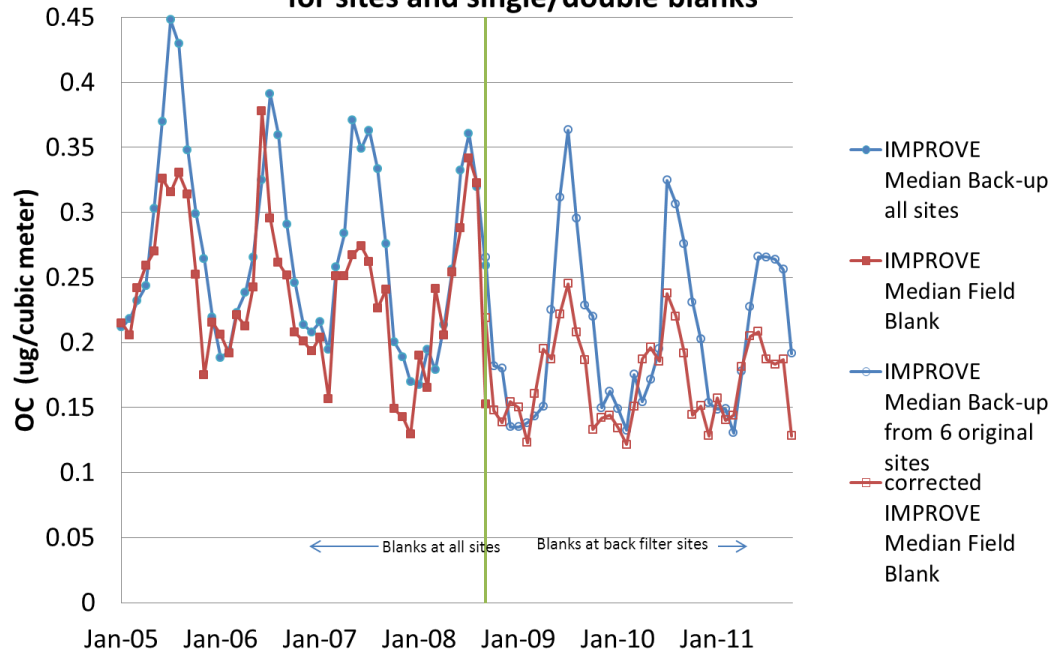


IMPROVE Monthly Median Back-ups and Blanks 2005-Oct. 2011

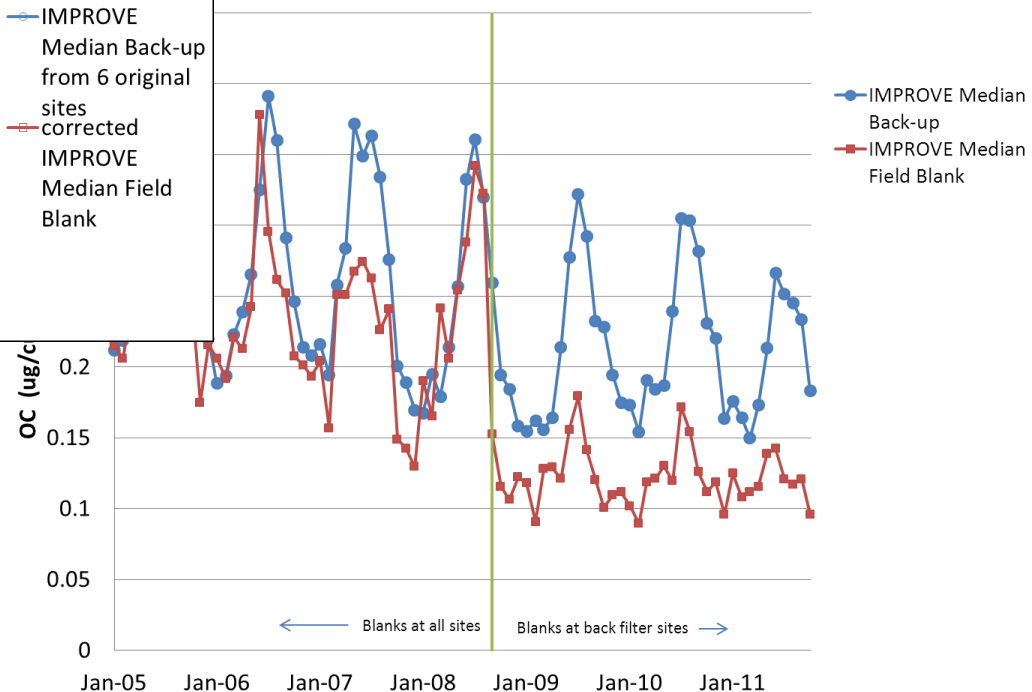


Impact of changing sites and making field blanks double quartz

IMPROVE Monthly Median Back-ups and Blanks "corrected"
for sites and single/double blanks



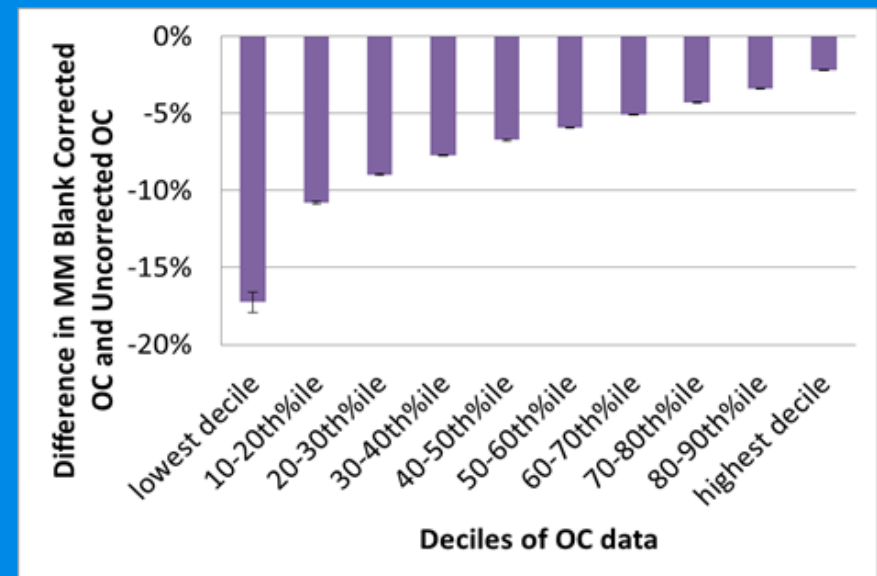
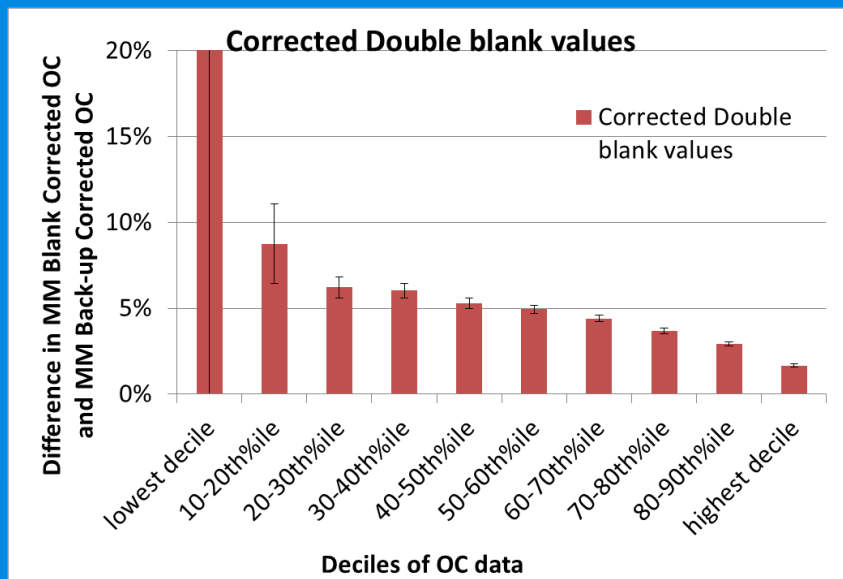
IMPROVE Monthly Median Back-ups and Blanks



Does change in artifact correction method really matter?

IMPROVE – diff. between MM blank corrected OC and current method

CSN – difference between MM blank corrected OC and current method



Changing to field blanks for IMPROVE and starting to use field blanks for CSN will modify the data in opposite directions but by roughly the same percentage within each decile of each networks data.

Conclusions for investigating drop in IMPROVE Field Blanks August 2008

➤ Two causes identified:

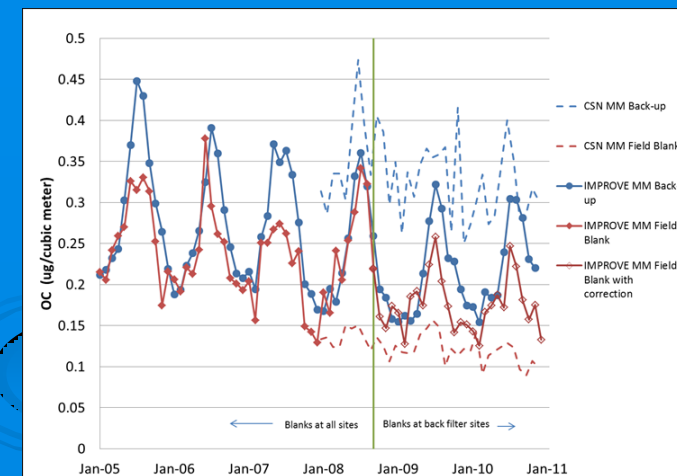
- Changing from single to double quartz field blanks
 - single blanks better represent single quartz sample filter
- Changing from 6 to 13 back-up sites
 - 13 sites better representative network
 - two Phoenix sites likely overly weight urban sites

➤ Single vs double quartz **front** sample filter

- HEGL started parallel sampling on 5/1/09
- Median percent difference is 0.4% (~40% for blanks)
- Double quartz sample OC concentrations not impacted

Implications for Recommendation to Steering Committee

- Blanks less variable over time & space than back-ups (both networks) - true
 - IMPROVE “corrected” field blanks are more variable in time
- Blanks for networks are similar, back-ups are not - true
 - Although corrected blanks for IMPROVE are higher
 - Limited parallel 3-day (CSN) vs 7-day (IMPROVE) blanks - no bias
 - Corrections should be made for each network separately
- Blanks don't over-correct by including multiplicative factor - true
 - Less correction than backups in some summers
- Blanks decrease additive artifact - true
 - Bigger decrease for IMPROVE
 - Lower bound/under-correction for CSN
- Simple/low cost/applicable to historic data - true
- Improve comparability between networks - true



IMPROVE/CSN Steering Committee plan

- Prepare written report
 - Data analysis through 2011
 - Likely recommend single field blank correction for both networks
- CSN/IMPROVE artifact committee approval
- Present recommendations to IMPROVE Steering Committee

Next Steps - Sampling

- How many and where to collect back-ups and blanks?
 - Both networks – continue to collect back-ups and blanks as currently doing to provide data set for analysis of artifacts in 5 years
 - IMPROVE
 - collect and analyze single blanks (beginning fairly soon)
 - use freed resources to add collocated back-up/blank field site at HEGL
 - CSN – continue with 10% rate

Next Steps – Data

➤ IMPROVE

- Future - artifact correct using monthly median blank
- Historic data –
 - Field blank correct OC data back to 1/1/2005
 - Use 40% estimate of error due to double blanks to estimate field blank values from 8/08 to change in sampling to single field blank

➤ CSN

- Future – artifact correct using monthly median blank
- Historic -
 - correct data beginning when URG samplers and DRI analysis began

Do particles impact evolution of gases from back-up and blanks

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- Sample filters typically have pyrolyzed carbon (OP) present
- Blanks and back-up filters typically do not have OP
- Is this observed difference due to particles on the front filter and no particles on backup and blanks?

Experimental Set-up

- Multiple sets of 4 parallel front-back filters pairs at UC Davis, some included blanks
- Each front, back, blank set treated differently
 - Some ammonium sulfate added
 - A lot of ammonium sulfate added
 - Air pulled through sample but no particles
 - No treatment
- All filters analyzed at DRI

Sampling Results

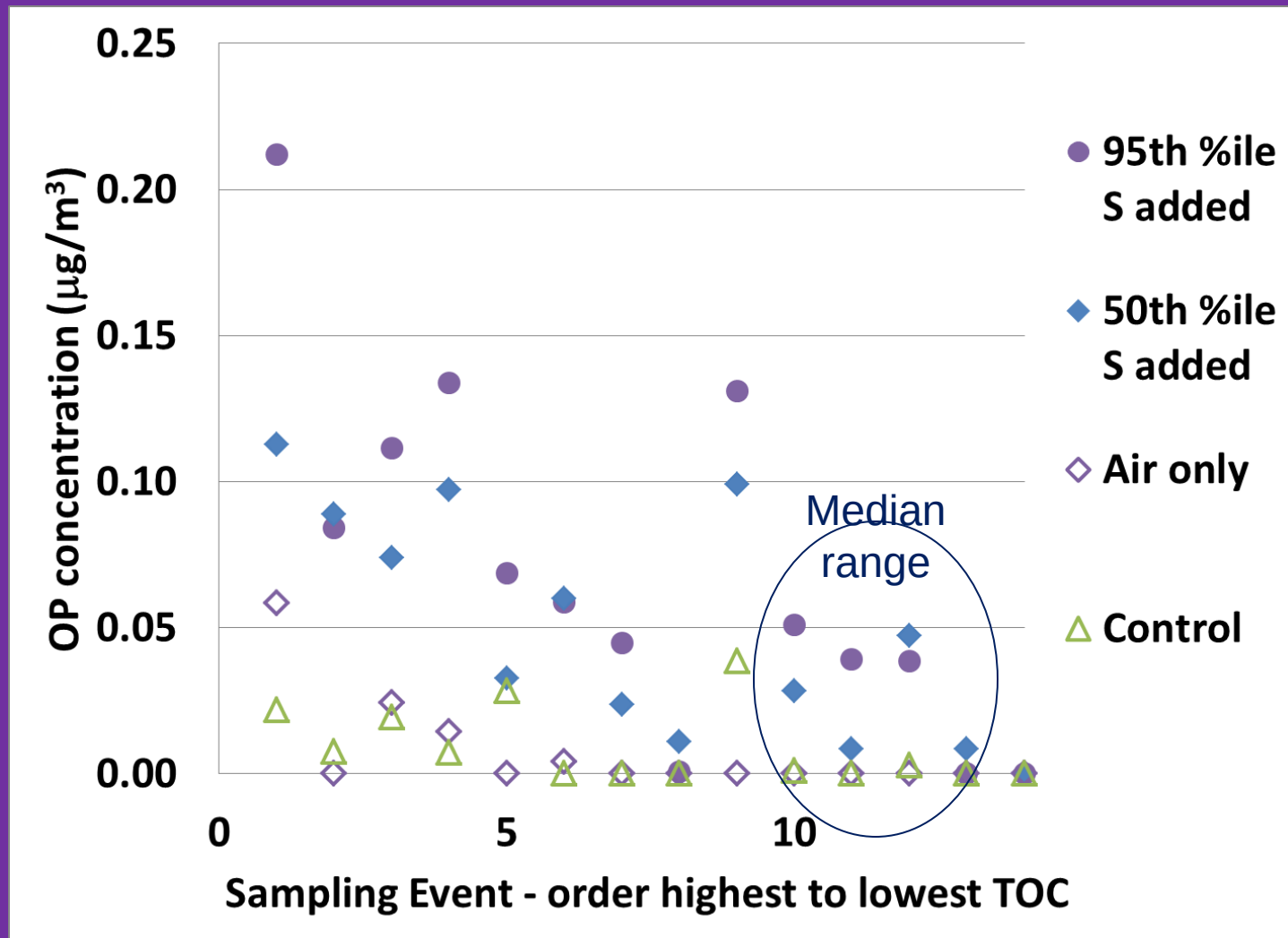
➤ Back-ups

- OC concentrations 0.07 to 0.63 $\mu\text{g}/\text{m}^3$
- 5th to 95th percentile of IMPROVE backups
- Range of median is 0.15 to 0.35 $\mu\text{g}/\text{m}^3$

➤ Field Blanks

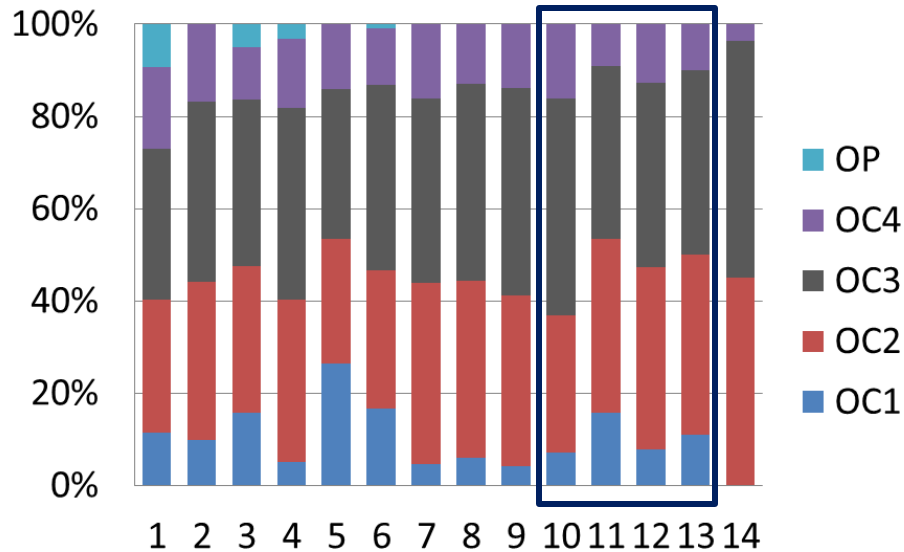
- OC concentrations 0.04 to 0.10 $\mu\text{g}/\text{m}^3$
- Lowest quartile of IMPROVE field blanks
- “Corrected” median range 0.12 to 0.25 $\mu\text{g}/\text{m}^3$

Back-up Filters - Increase in OP with added ammonium sulfate

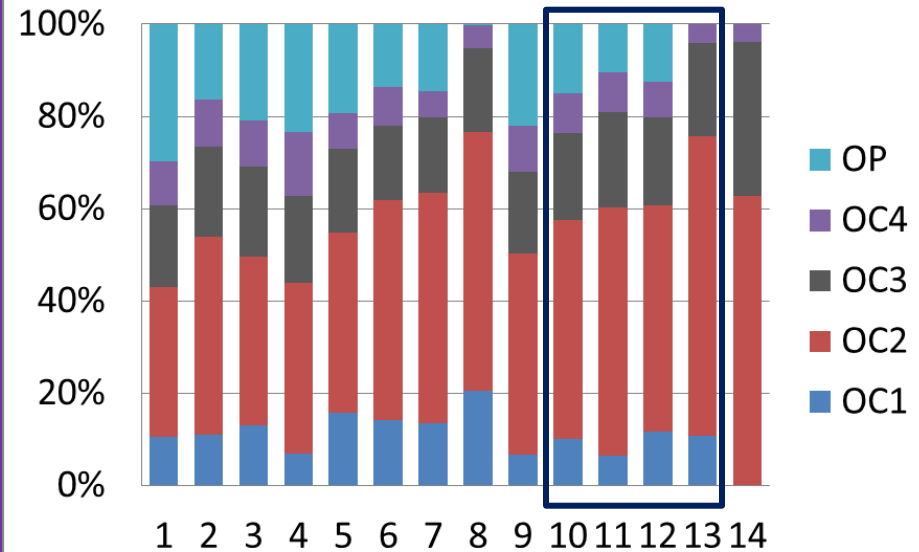


Back-up filters - Change in thermal fraction distribution

Air Only Back-up Filters



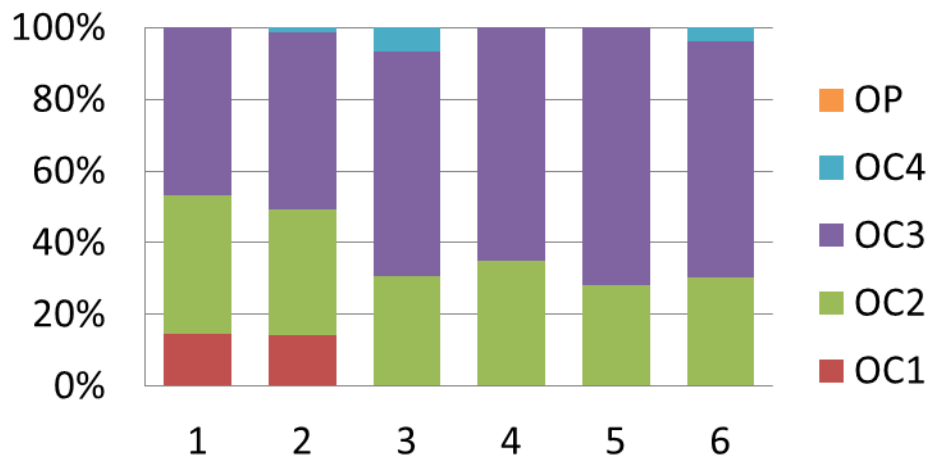
Treated Back-up Filters



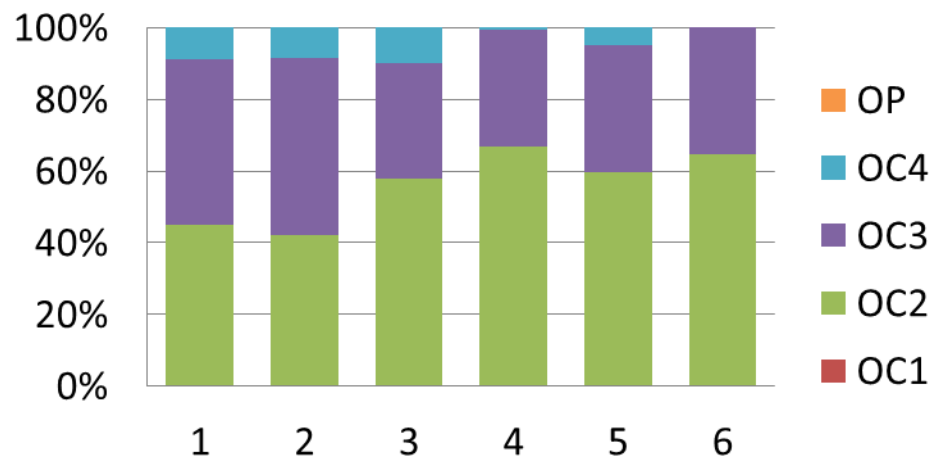
Field Blanks

- No OP on field blanks or treated field blanks
- Change in thermal fractions

Air Only Field Blanks



Treated Field Blanks



Summary

- Particles (sulfate or NaCl) added to back-ups cause OP to measurably increase
- OC2 and OC3 are also affected, TOC not
- Back-up (and blank) fractions may not represent artifact fractions on front filters