Organic Artifacts in the CSN using the URG 3000N Sampler

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Background

- EPA Chemical Speciation Network (CSN) uses URG-3000N samplers (modified IMPROVE Module C) for carbon analyses (flow rate 22.8 L/min on 25 mm Pallflex Tissuquartz® quartz-fiber filters)

- For artifact correction, IMPROVE uses monthly median backup filter (QBQ) OC over six sites; CSN samples have no artifact adjustment

Objectives

- To evaluate organic artifact from the URG 3000N sampler in CSN (2008 – 2009)
- To compare backup filter (QBQ) and field blank (bQF) OC between CSN and IMPROVE
- To examine approaches for CSN organic artifact correction

Methodology

- Retain sampling days with concurrent quartz-fiber front filter (QF), backup filter (QBQ), and field blank (bQF) data for a given site during 2008 – 2009
  - Resulting data set was 1,848 site-days
- Remove 51 site-days where total carbon (TC) on QBQ or bQF exceeded 3 standard deviations of the average
  - Resulting data set was 1,797 site-days from 146 sites
- Examine carbon fractions by geographic area and season

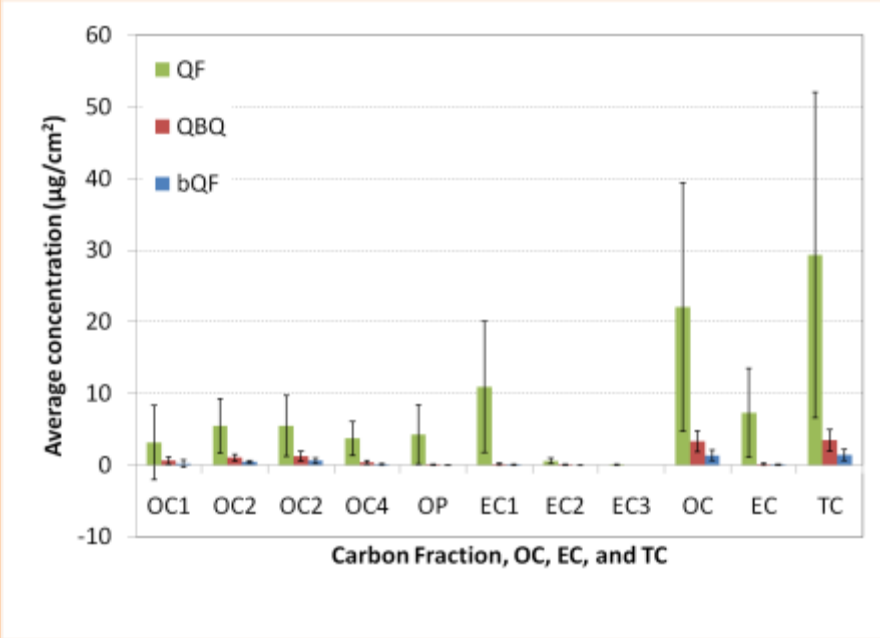
Median OC_{QBQ} on CSN is about 50% higher than IMPROVE

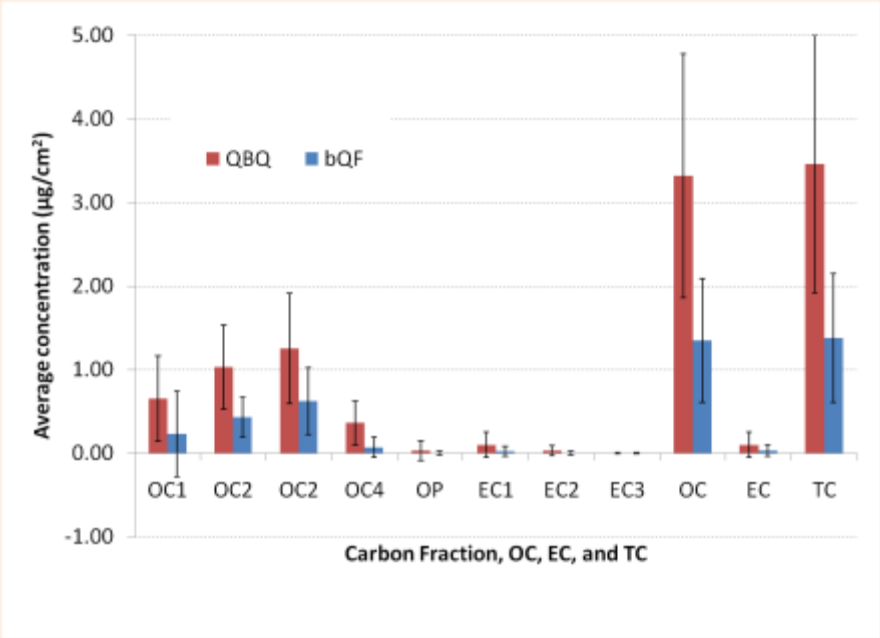
Carbon fraction	Average front filter (QF) (μg/cm²)	Average backup filter (QBQ) (μg/cm²)	Average field blank (bQF) (μg/cm²)	CSN median backup filter[a] (μg/cm²)	IMPROVE median backup filter[b] (μg/cm²)
OC1	3.14 ± 5.17	0.65 ± 0.51	0.23 ± 0.51	0.515	0.342
OC2	5.48 ± 3.80	1.03 ± 0.50	0.43 ± 0.24	0.961	0.676
OC3	5.50 ± 4.22	1.25 ± 0.66	0.62 ± 0.40	1.137	0.919
OC4	3.71 ± 2.40	0.36 ± 0.26	0.07 ± 0.12	0.307	0.186
OP	4.24 ± 4.15	0.03 ± 0.12	0.00 ± 0.02	0	0
EC1	10.93 ± 9.13	0.10 ± 0.15	0.02 ± 0.06	0.061	0.0029
EC2	0.58 ± 0.36	0.03 ± 0.06	0.00 ± 0.02	0	0.003
EC3	0.01 ± 0.09	0.00 ± 0.01	0.0 ± 0.01	0	0
OC	22.06 ± 17.35	3.32 ± 1.46	1.35 ± 0.74	3.176	2.123
EC	7.29 ± 6.18	0.10 ± 0.15	0.03 ± 0.07	0.053	0.032
TC	29.35 ± 22.71	3.46 ± 1.54	1.38 ± 0.77	3.257	2.155

[a] CSN data from January 2008 – December 2009; IMPROVE data from January 2008 – September 2009

[b] OC_{QBQ} averages about 15% of OC_{QF}, while OC_{bQF} averages about 6% of OC_{QF}

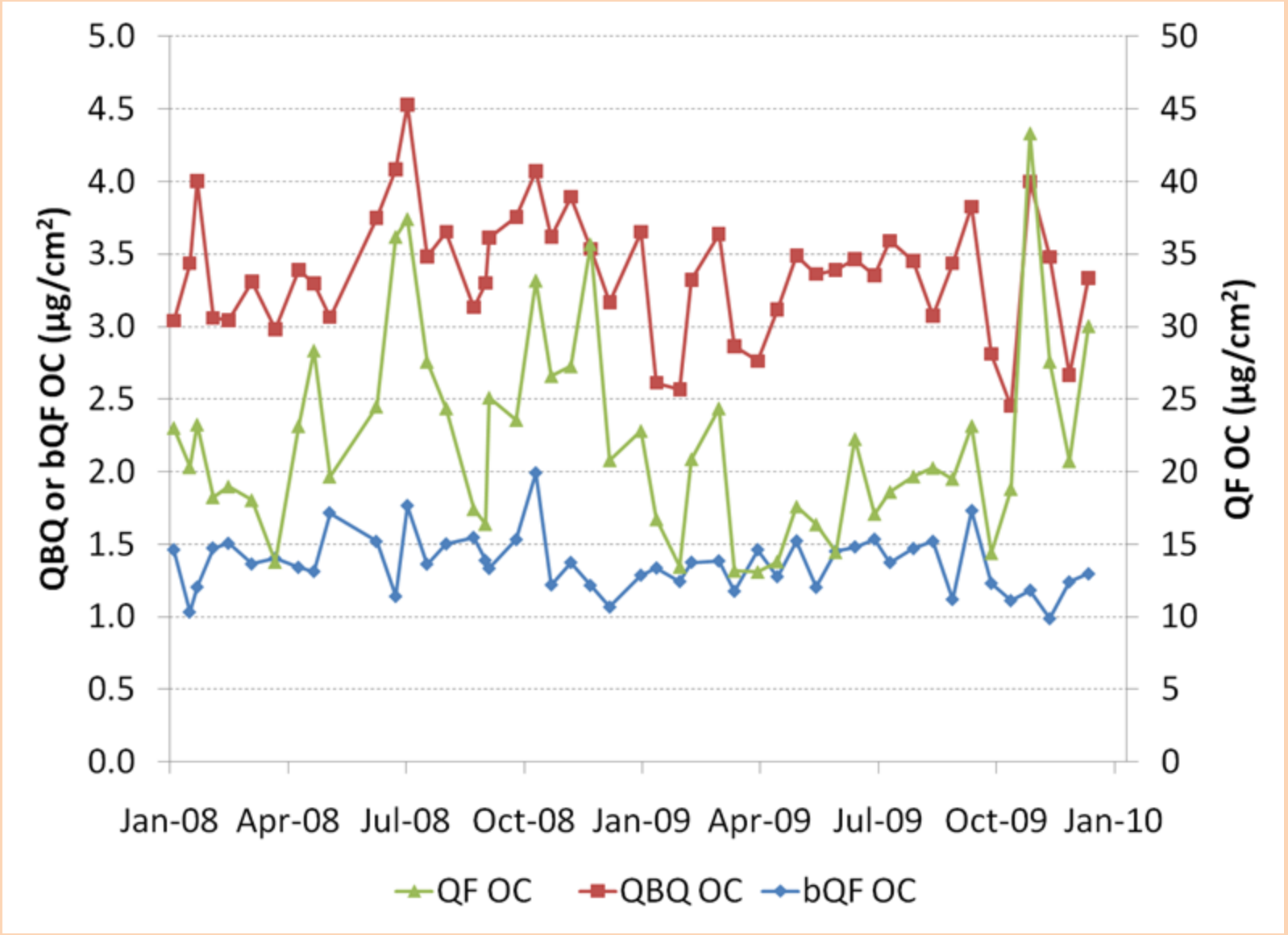
CSN OC_{bQF} is ~40 – 50% of OC_{QBQ}



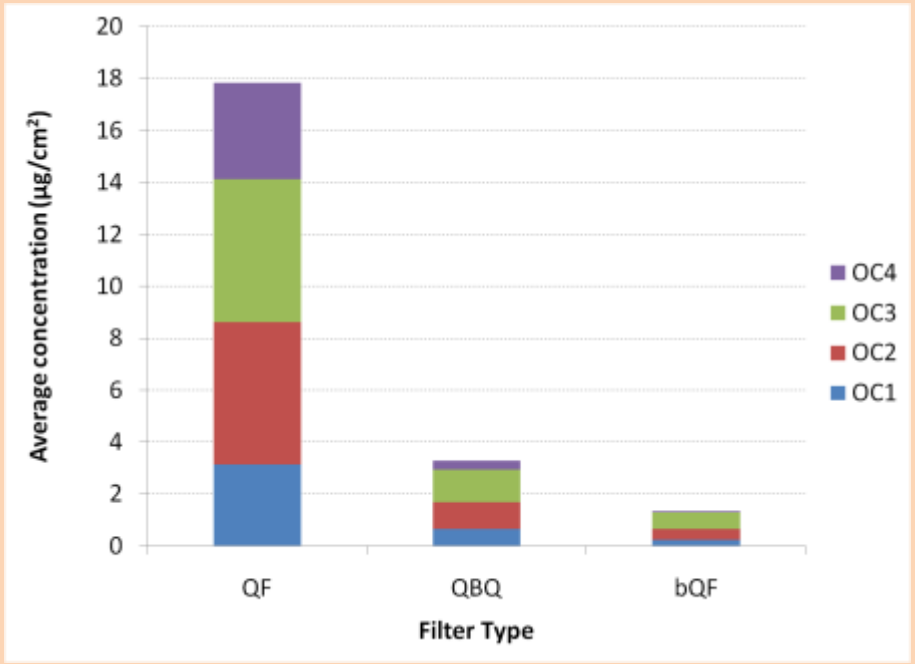


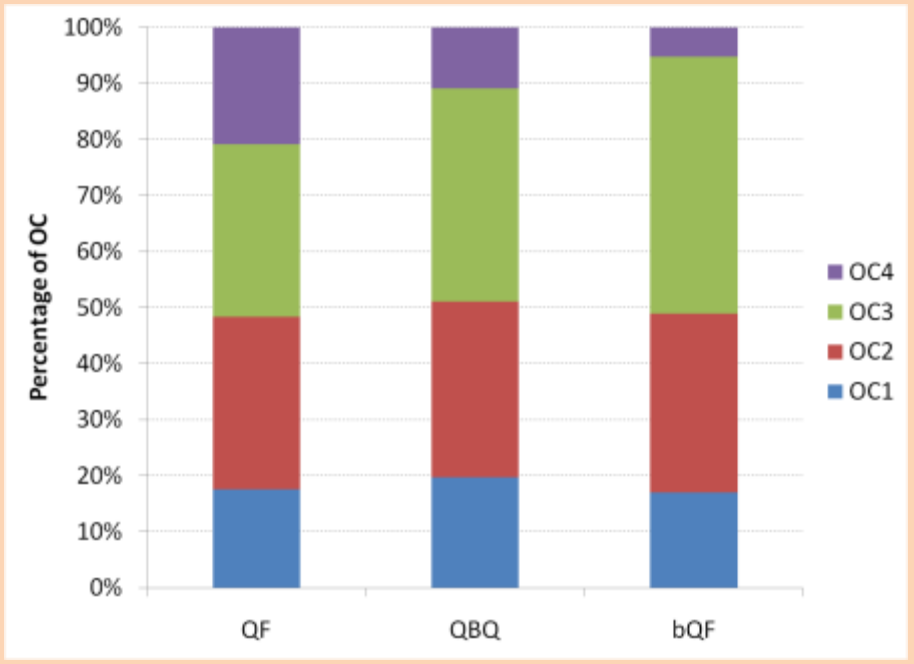
EC on QBQ and bQF is insignificant

Daily network-wide OC_{bQF} varies from about 1 – 2 µg/cm²; OC_{QBQ} varies from 2.5 – 4.5 µg/cm²



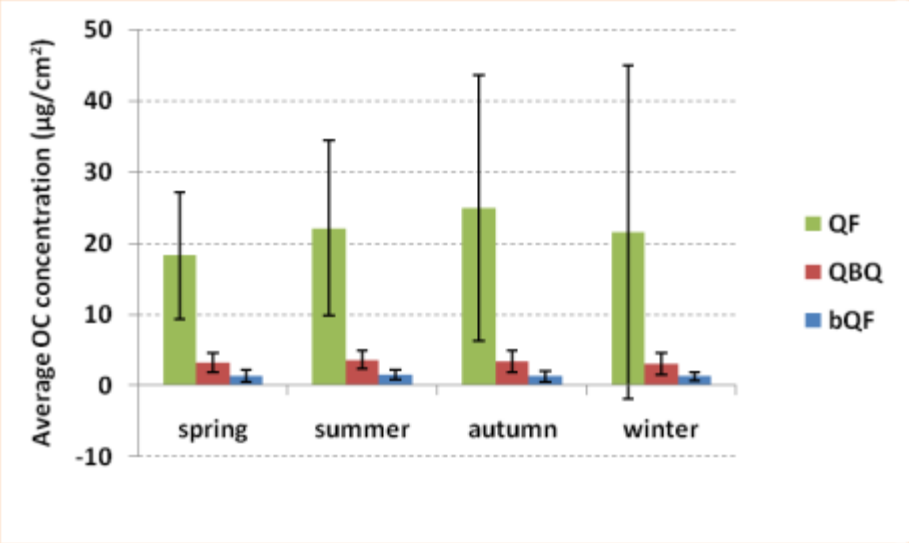
OC fractional abundances are similar

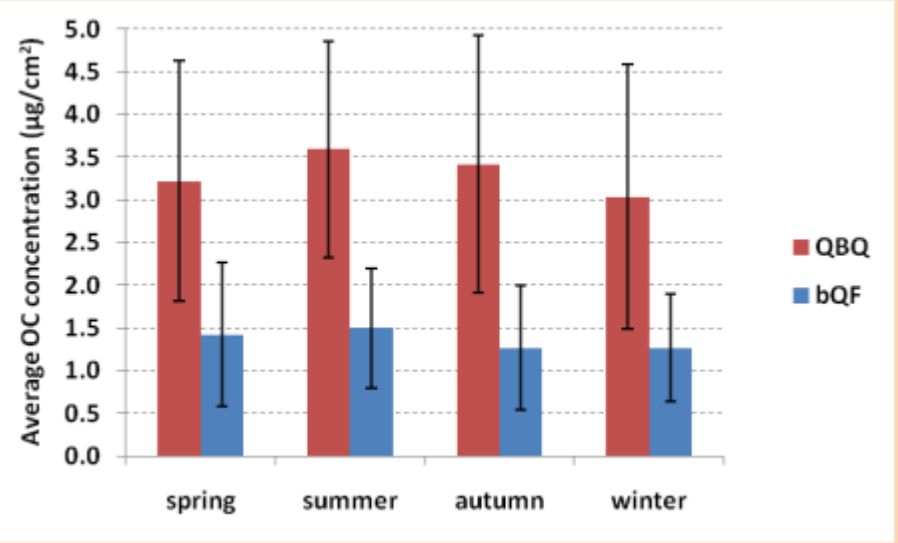




OC1 – OC4 at 140, 280, 480, and 580 °C, respectively, in a 100% He atmosphere following the IMPROVE_A temperature protocol

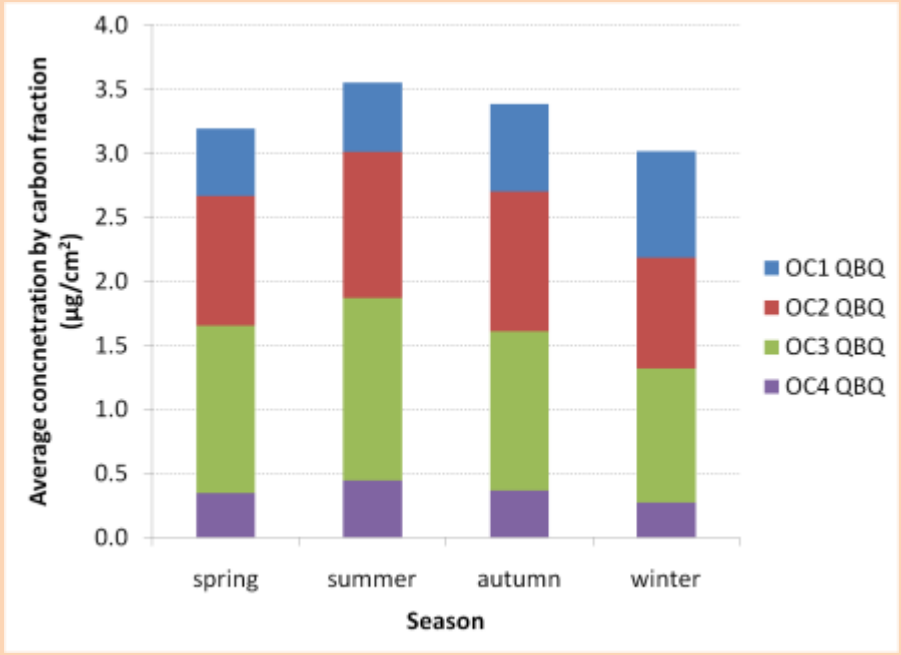
Less seasonal variation found in OC_{bQF} than OC_{QBQ}, with elevated summer OC_{QBQ}

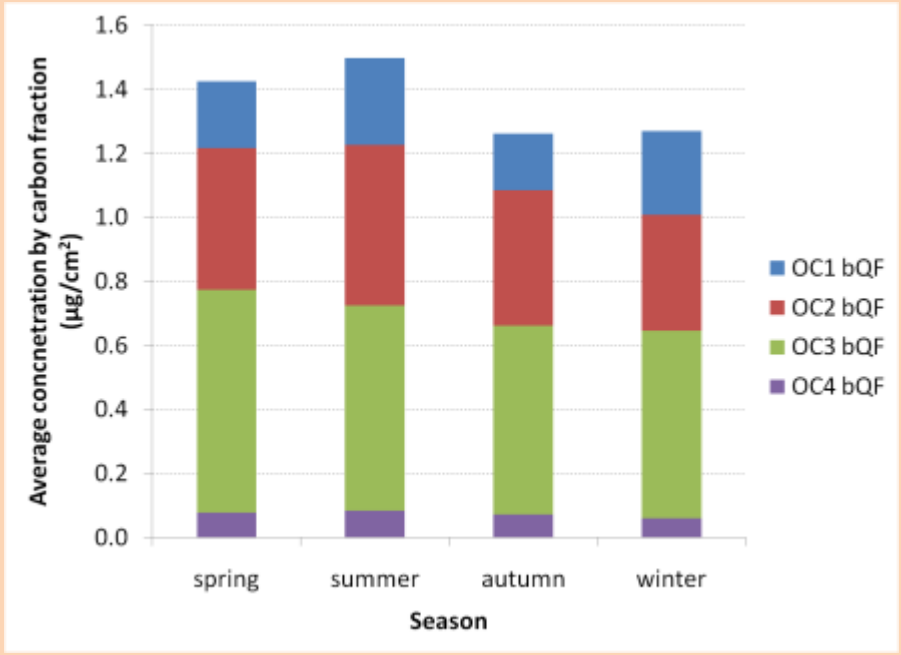




Spring: Mar – May
Summer: June – Aug
Autumn: Sept – Nov
Winter: Dec - Feb

No apparent seasonal variations in carbon fractions

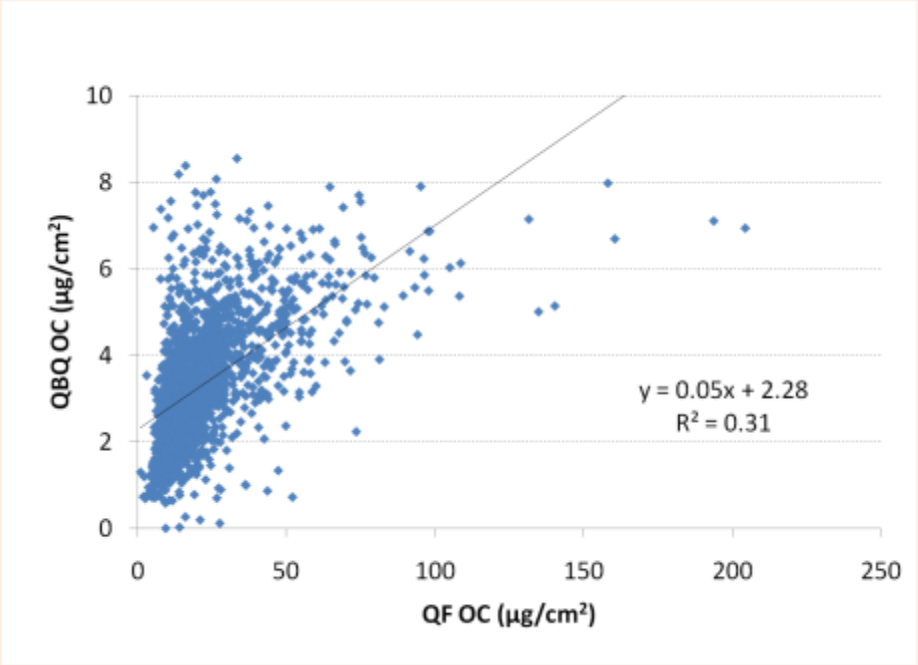


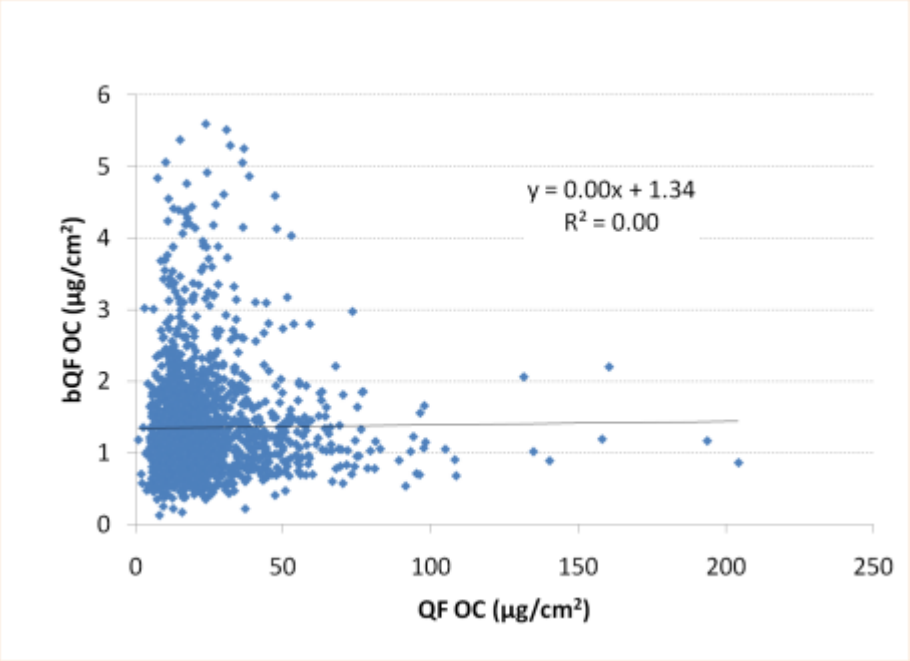


EC on QBQ and bQF is insignificant

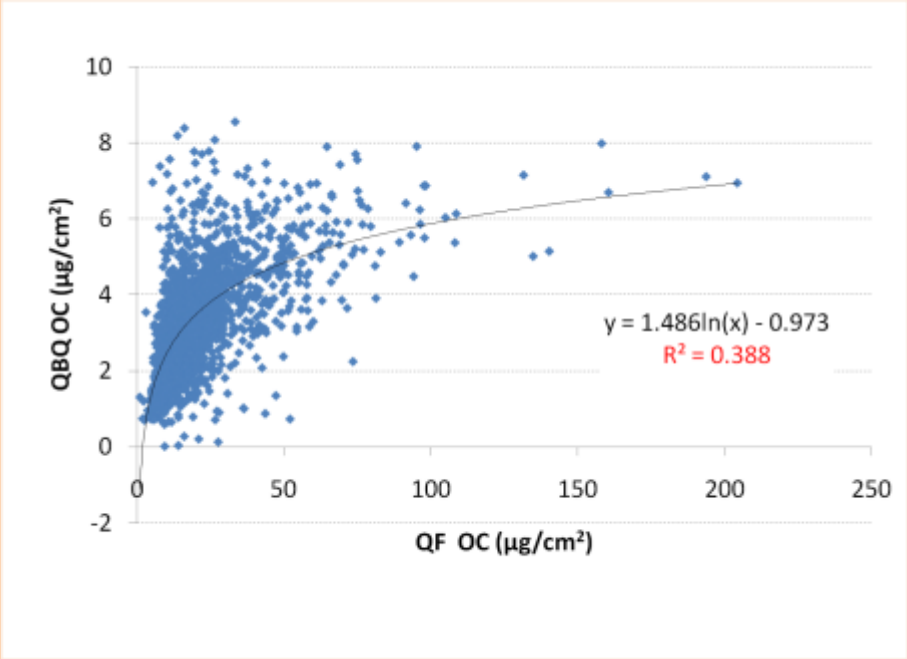
Spring: Mar – May
Summer: June – Aug
Autumn: Sept – Nov
Winter: Dec - Feb

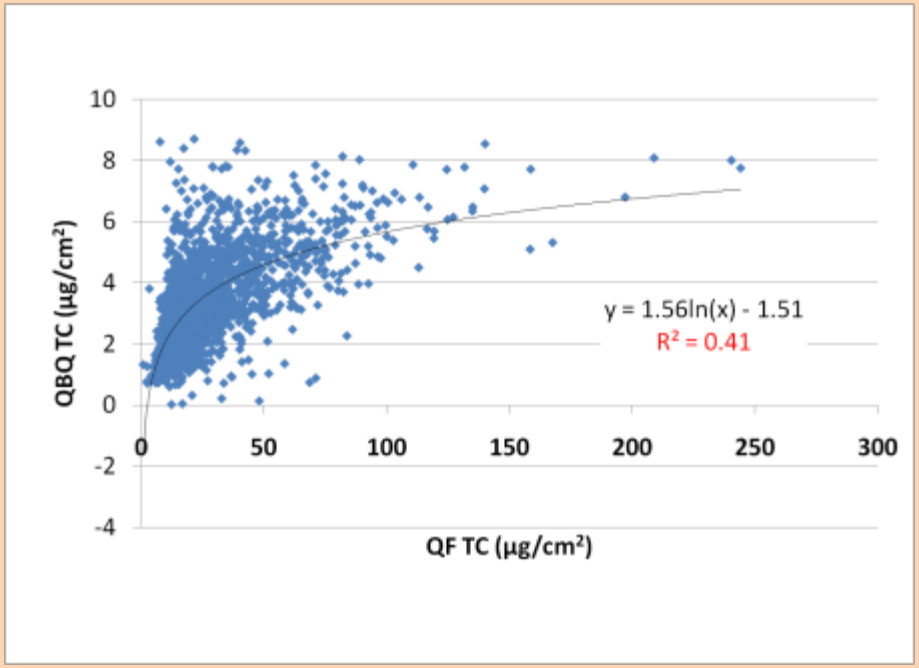
Too much scatter between QBQ or bQf and QF OC for a reliable regression relationship



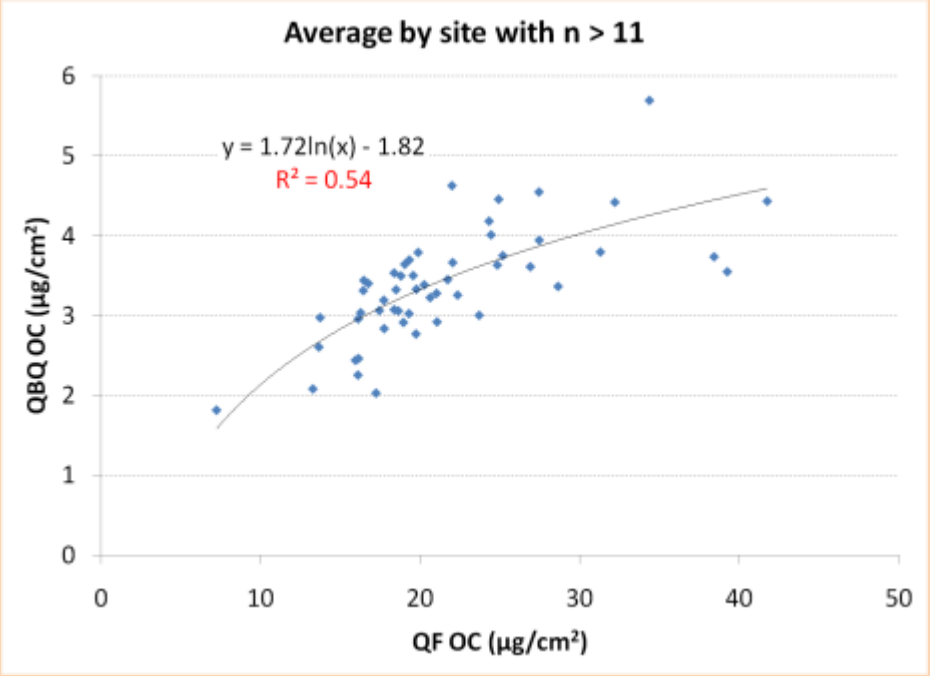


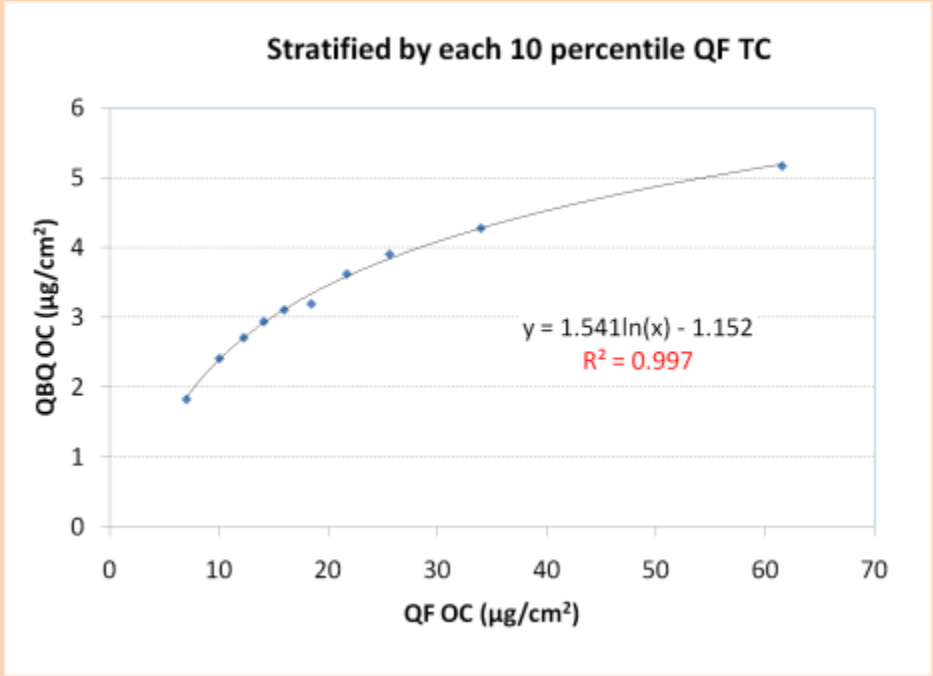
A logarithmic fit produces a better relationship, but still too much scatterd



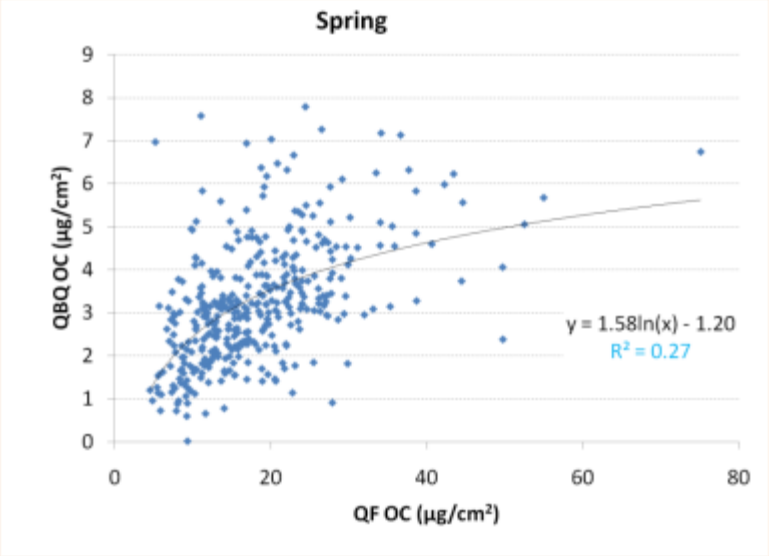


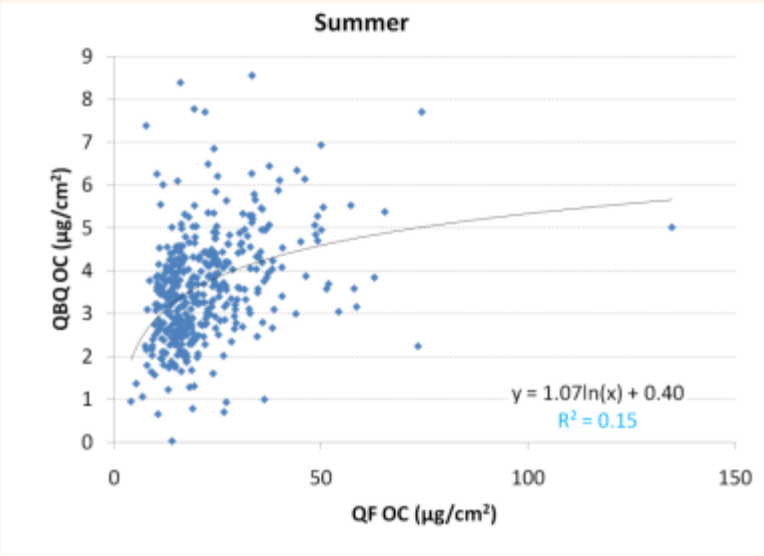
Stratified data by each 10th percentile QF TC stabilizes the relationship between OC_{QBQ} and OC_{QF}

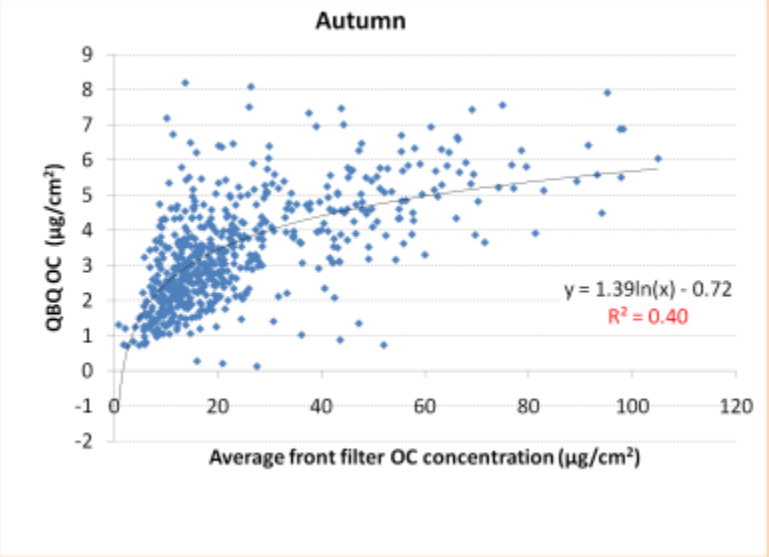


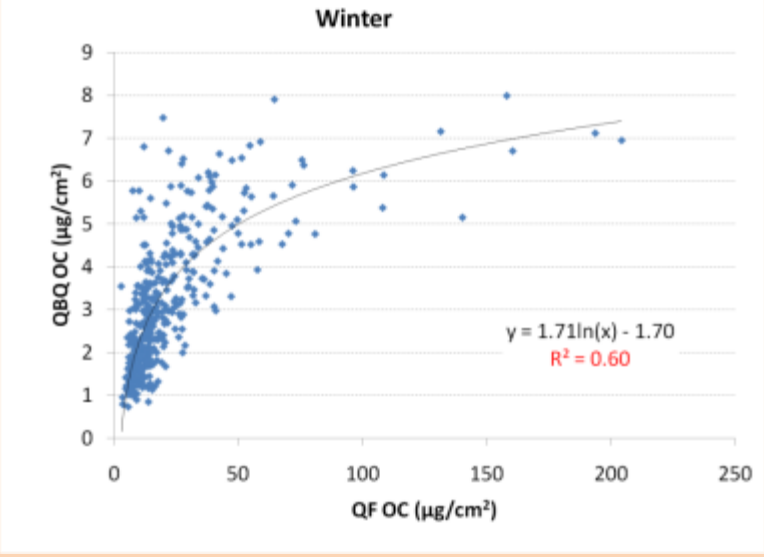


Slightly higher correlation found between OC_{QBQ} and OC_{QF} in autumn and winter than spring and summer



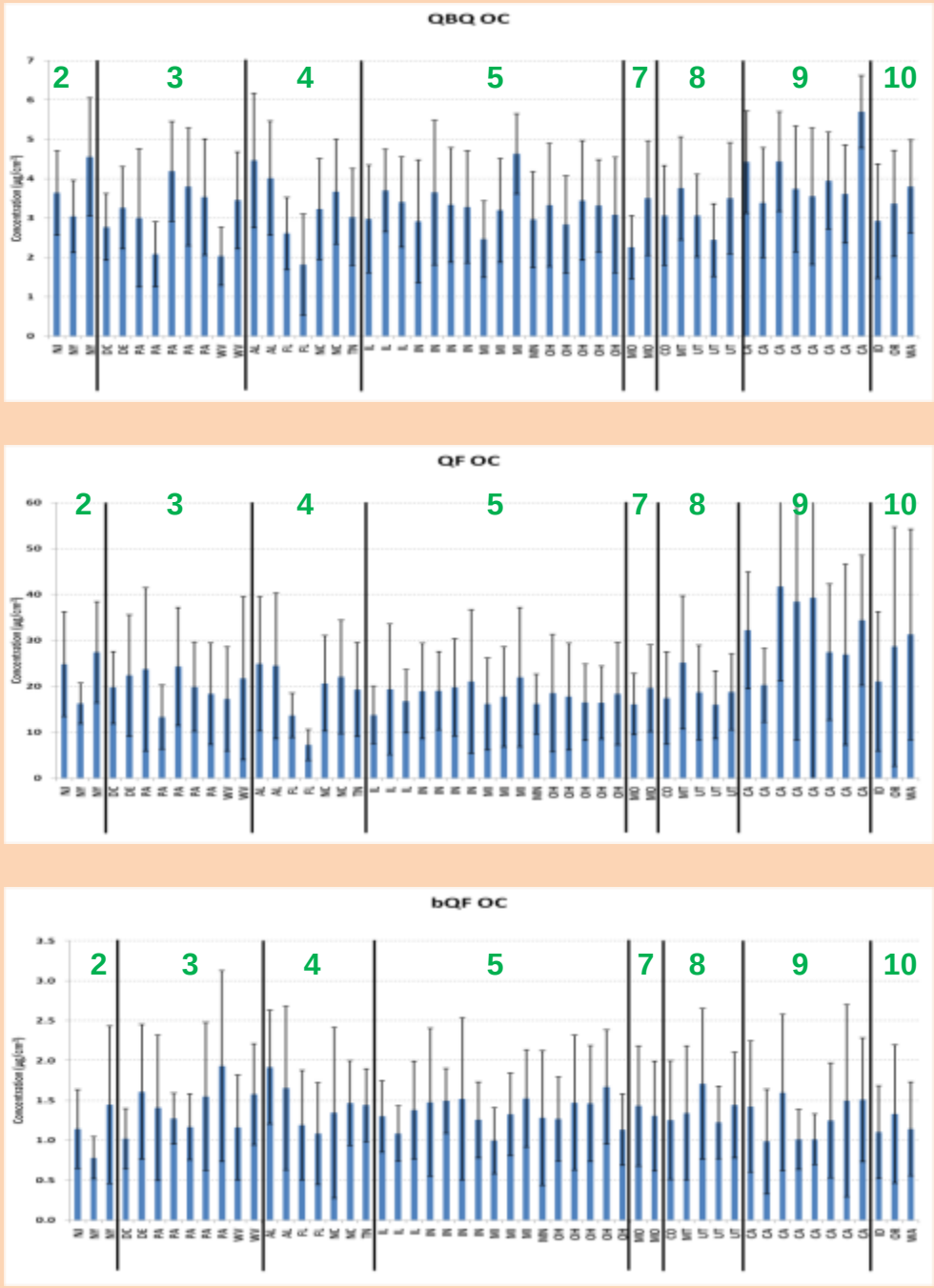






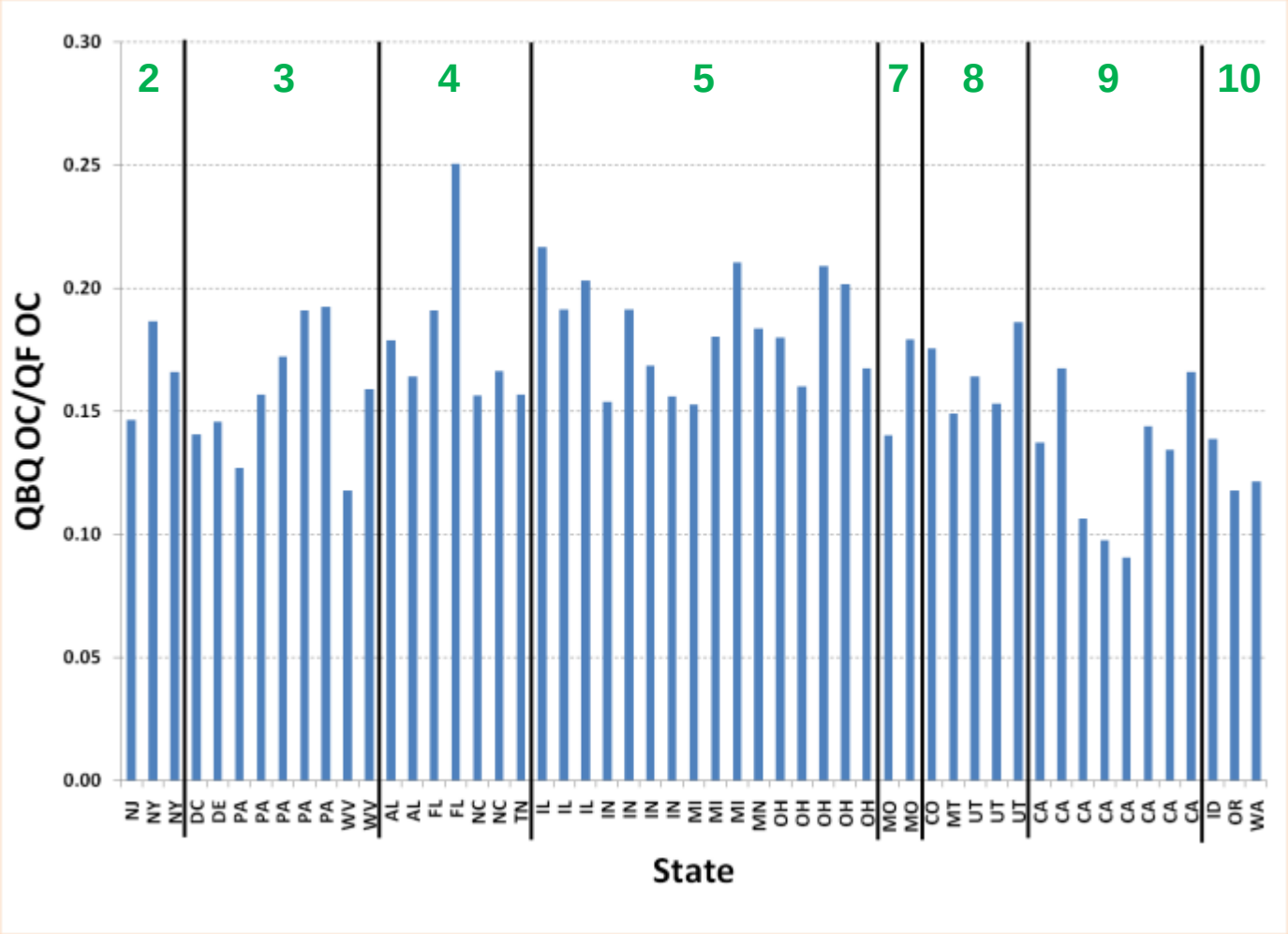
Filter saturation occurs at ~8 µg/cm²

Average OC_{QBQ} and OC_{bQF} by site show little geographic pattern



Sites ordered from EPA Region 2 (left) to EPA Region 10 (right); There were no sites with 12 or more samples for EPA Regions 1 and 6

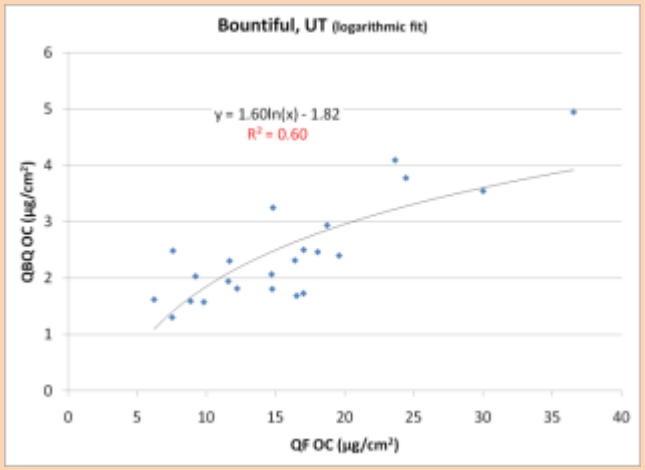
Ratio of OC_{QBQ} to OC_{QF} varies from about 0.1 to 0.25

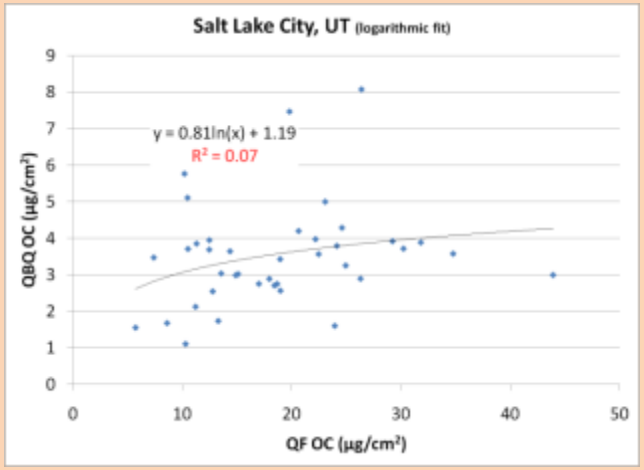


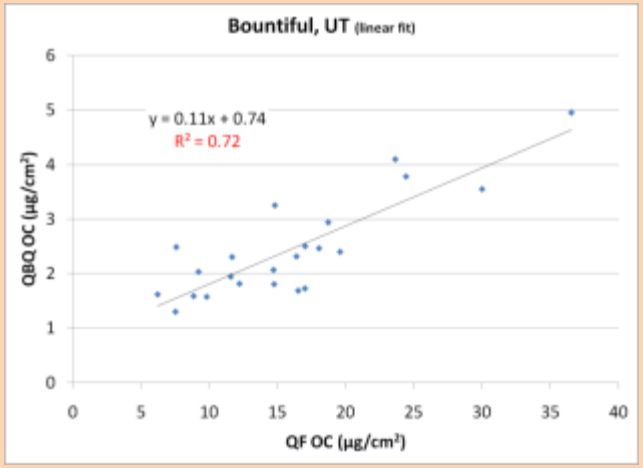
Lowest ratios found at California sites with high QF, likely due to saturation effects

Higher OC_{QBQ} vs. OC_{QF} correlation at Bountiful, UT than Salt Lake City, UT

(cannot generalize by geographic location)

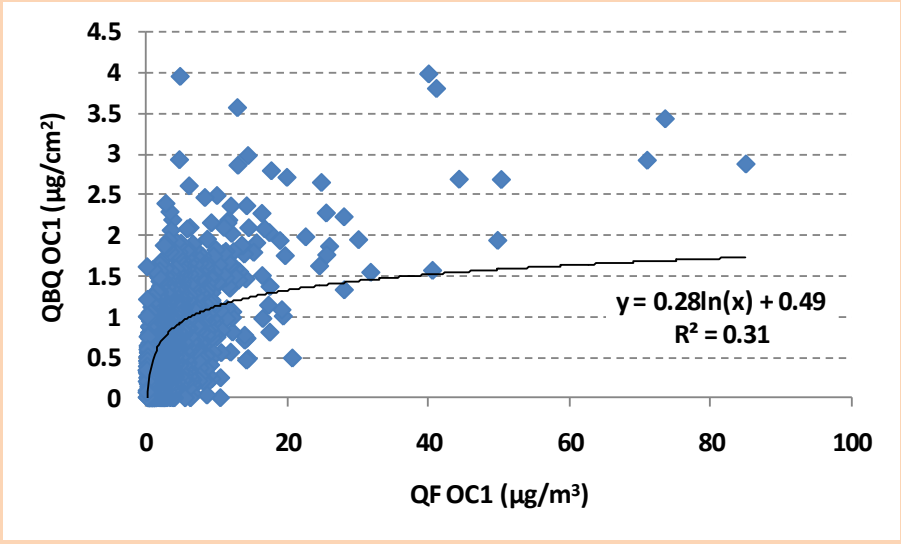


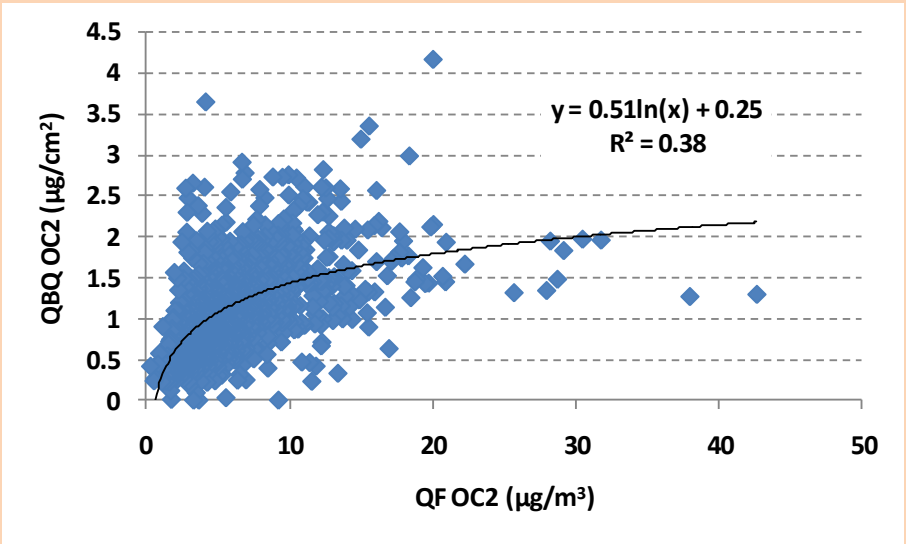


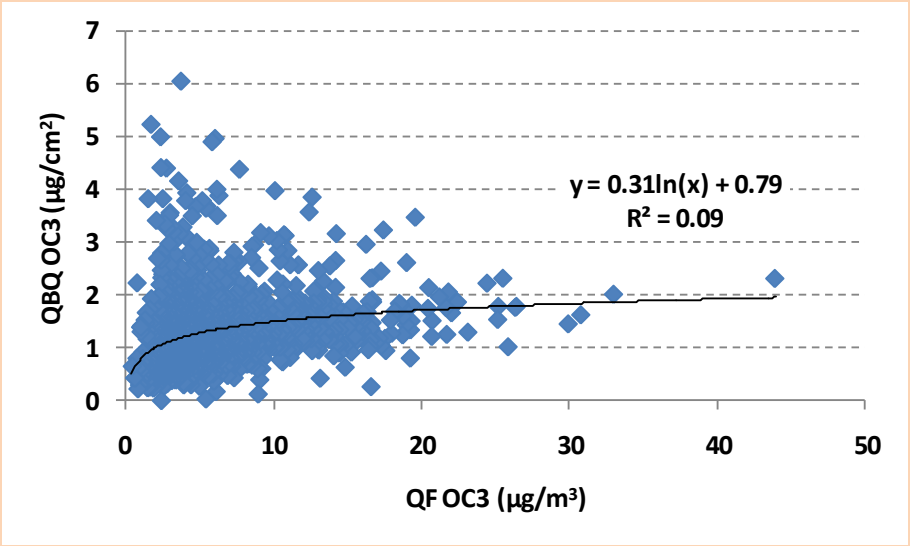


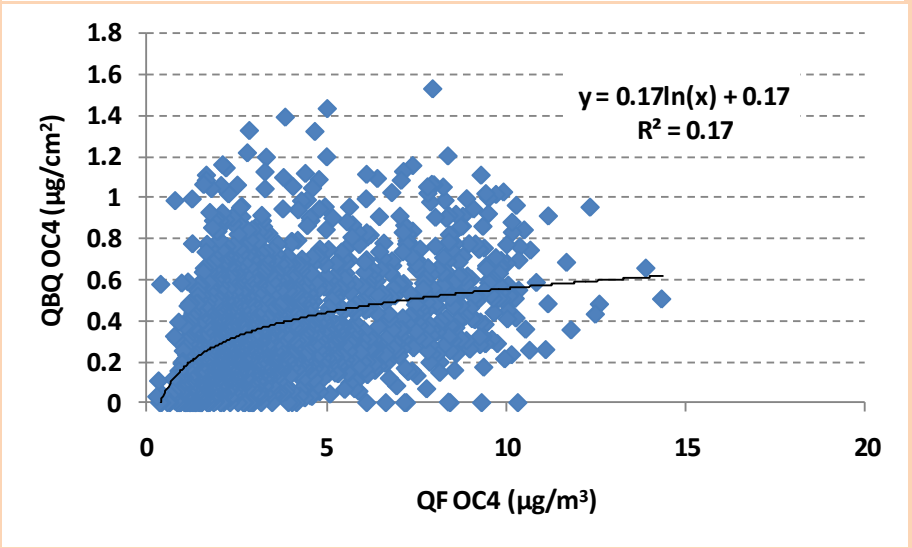
The Bountiful and Salt Lake City sites are within about 20 Km of each other

Non-stratified data show higher front and back correlations for OC1 and OC2

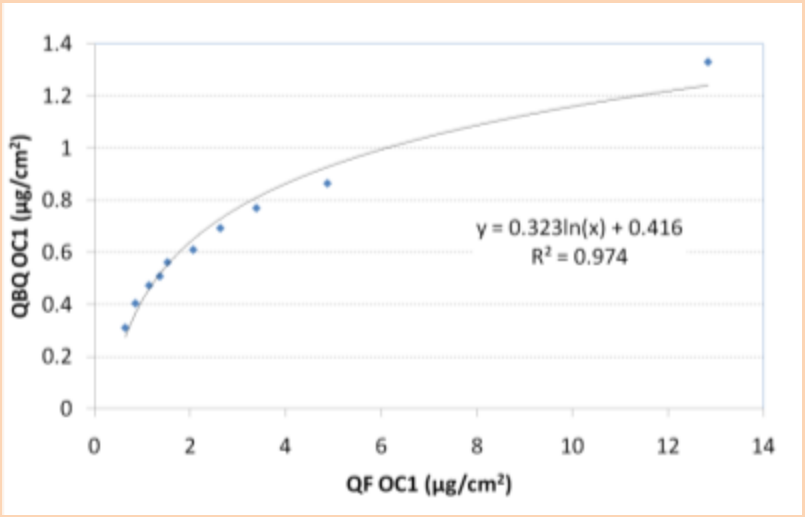


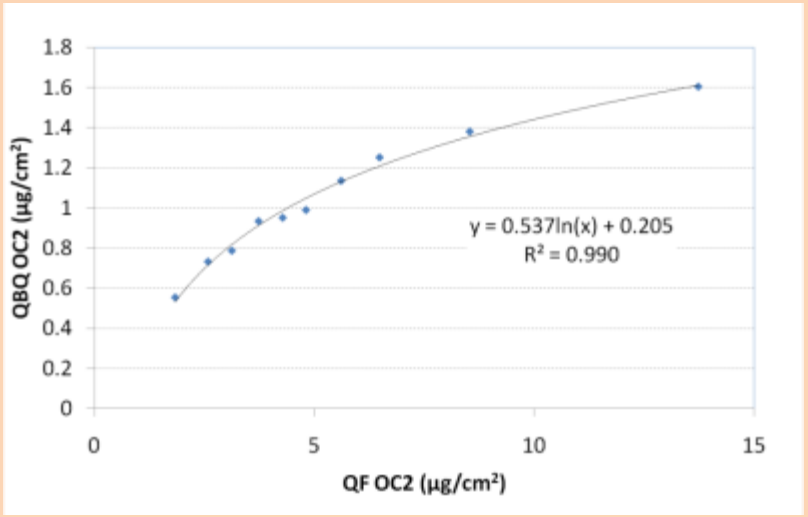


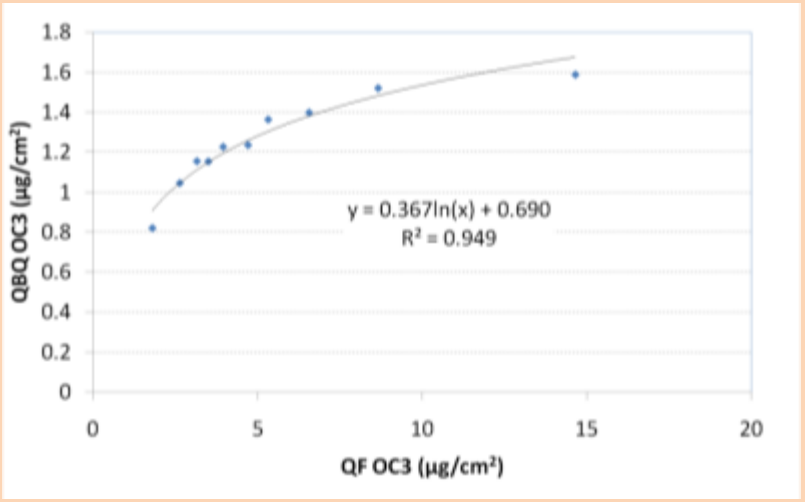


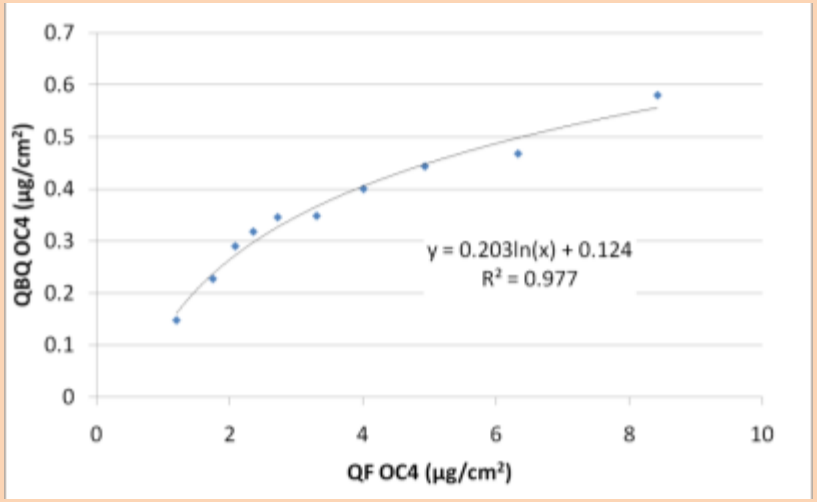


Percentile classifications show good correlations between OC_{QBQ} and OC_{QF} on OC fractions*









* Data averaged over 10 percentile ranges of QF TC

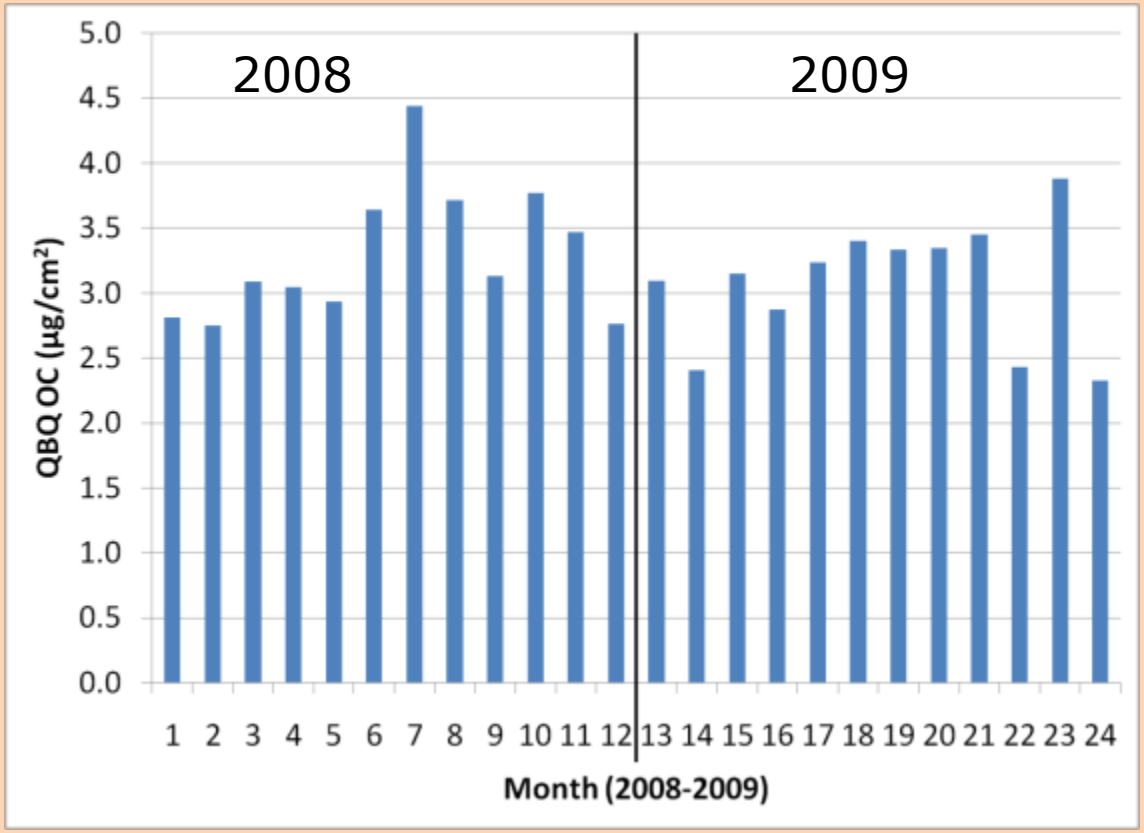
Use of year-specific equations gives a slight improvement over equations from combined 2008 – 2009 data in predicting OC_{QBQ} from OC_{QF}

Year	Average QBQ OC (μg/cm²)	RMS Error – both years equation (μg/cm²)	RMS Error – yearly equation (μg/cm²)	N
2008	3.51	1.22	1.21	635
2009	3.22	1.10	1.09	1161
2008 – 2009	3.32	1.14	1.14	1796

Seasonal-specific equations give similar RMS errors to those from all-season 2008 – 2009 equations

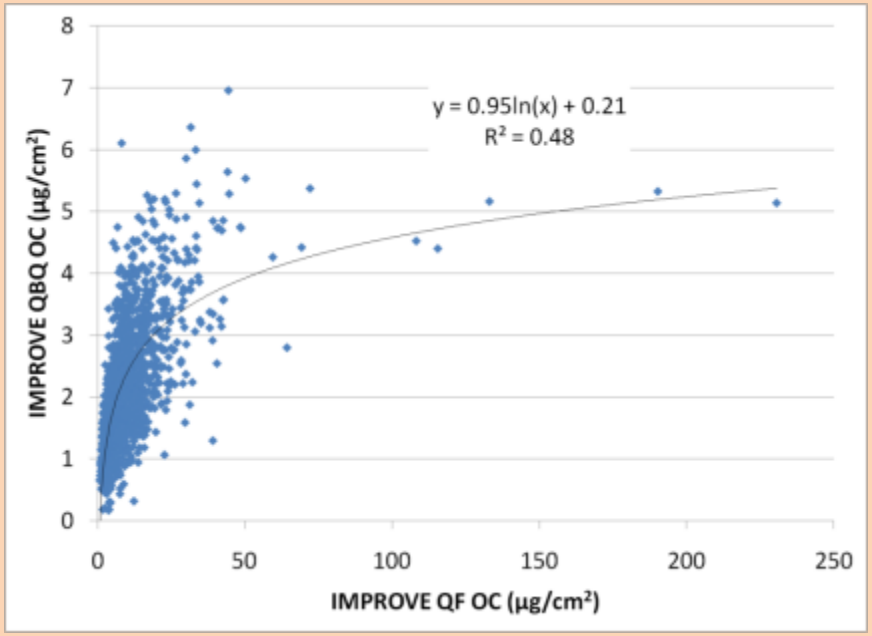
Season	Average QBQ OC (μg/cm²)	RMS Error – annual equation (μg/cm²)	RMS Error – seasonal equation (μg/cm²)	N
Spring	3.22	1.20	1.20	580
Summer	3.59	1.18	1.16	379
Autumn	3.42	1.17	1.17	405
Winter	3.04	1.00	0.98	432
All	3.32	1.14	1.13	1796

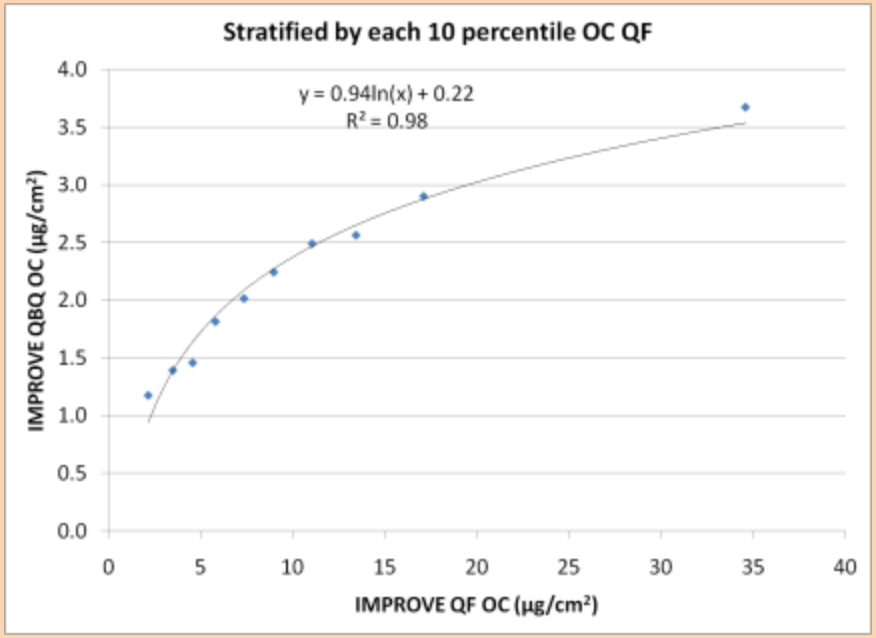
Monthly variation of OC_{QBQ} in CSN



The IMPROVE method (i.e., subtracting monthly median OC_{QBQ}) gives an RMS error in QBQ of 1.43 µg/cm² compared to 1.14 and 1.13 µg/cm² for the logarithmic annual and seasonal equations, respectively

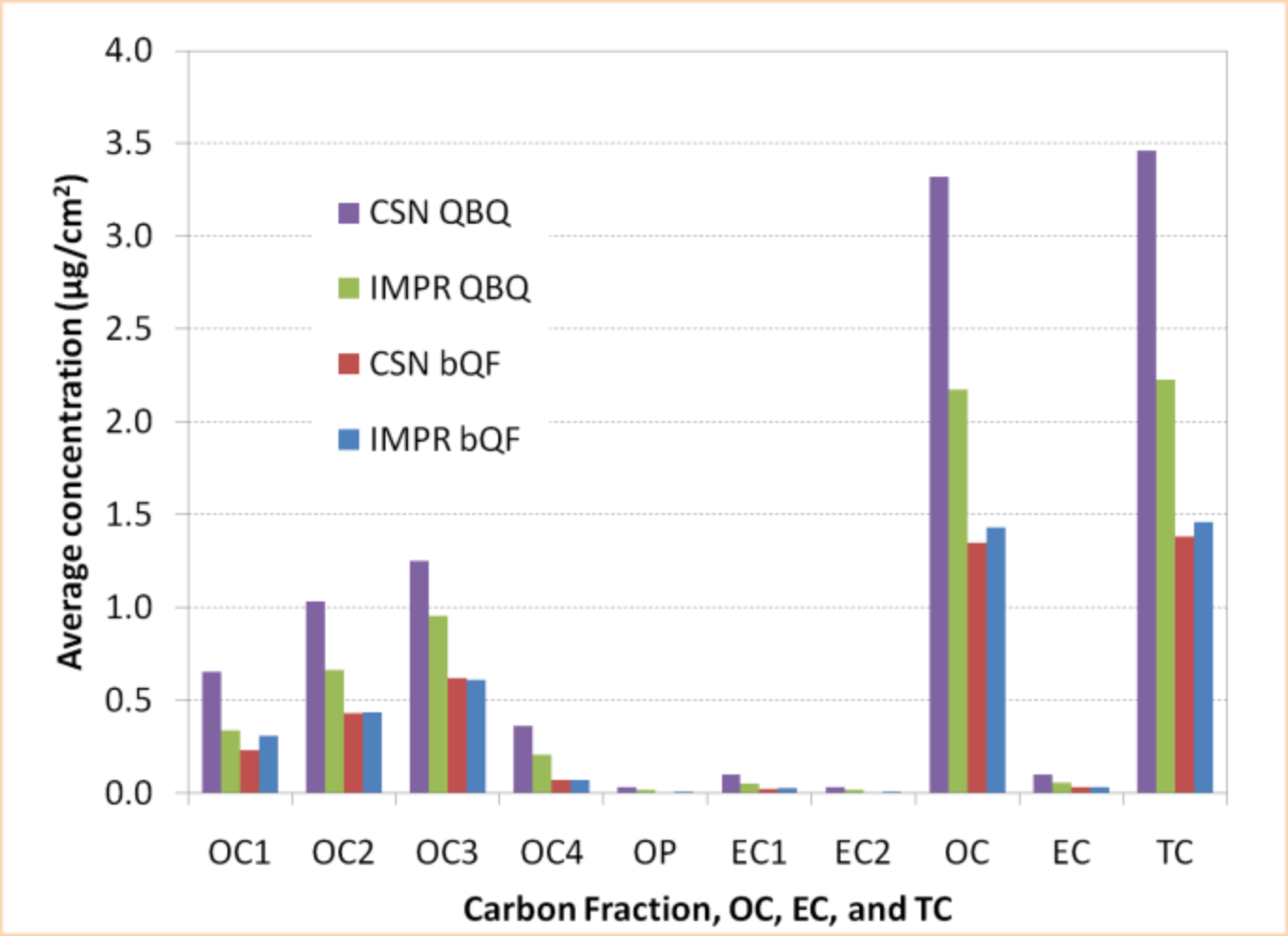
OC_{QBQ} and OC_{QF} relationships for IMPROVE





Removed 23 data points with backup filter TC > 3 standard deviation above mean and 21 additional data points with backup filter TC > front filter TC.

OC_{QBQ} in CSN is ~50% higher than in IMPROVE



Similar OC_{bQF} between CSN and IMPROVE

CSN data from January 2008 – December 2009; IMPROVE data from January 2008 – September 2009

Observations

- Backup quartz-fiber filter OC (OC_{QBQ}) averaged 3.32 ± 1.46 μg/cm^2 for CSN (Jan 2008 – Dec 2009), ~50% higher than the 2.17 ± 1.06 μg/cm^2 found in IMPROVE (Jan 2008 – Sep 2009).
- Field blank OC (OC_{bQF}) averaged 1.35 ± 0.74 μg/cm^2 for CSN, ~10% lower than the 1.43 ± 0.76 μg/cm^2 found for IMPROVE.
- Ratios of OC QBQ/bQF were 2.5 in CSN and 1.5 in IMPROVE.
- Logarithmic fits give lower predicted errors in OC_{QBQ} than using monthly median (as in IMPROVE) or monthly averages.