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Quantification of organic carbon sampling artifacts in US non-urban and urban networks

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Abstract

Different approaches to estimate organic sampling artifacts have been adopted by US long-term air quality monitoring networks. This study documents field blank (bQF) and backup filter (quartz-fiber behind quartz-fiber filter; QBQ) carbon levels for the: 1) Inter-agency Monitoring of Protected Visual Environments (IMPROVE); 2) Speciation Trends Network (STN; part of the Chemical Speciation Network [CSN]; and 3) Southeastern Aerosol Research and Characterization (SEARCH) networks. Filter pack sample handling procedures and blank correction methods are examined. Due to a relatively short (1–15 min) passive exposure period, STN/CSN and SEARCH network bQF organic carbon (OC; 0.8–1 μg/cm^2) may underestimate positive and negative OC artifacts, respectively, resulting from passive adsorption or volatilization of volatile or semi-volatile organic compounds on quartz-fiber filters while they are in the sampler. This is evidenced by a lack of temporal or spatial variability and low bQF levels. With $\sim$7 d of ambient passive exposure, average IMPROVE bQF and QBQ OC are comparable (2.4±0.5 and 3.1±0.8 μg/cm^2) and more than twice those found in the STN/CSN and SEARCH networks. Lower STN/CSN flow rates and larger filter deposit areas result in 9–20% of the areal density (μg/cm^2) compared to IMPROVE areal deposits. STN/CSN bQF values are 11–34% lower than linear regression intercepts derived from collocated IMPROVE-STN/CSN data pairs. Using a preceding organic denuder in the SEARCH network reduces the organic vapor adsorption on QBQ, though the longer QBQ period in the sampler may result from passive organic vapor adsorption as well as evaporated OC from the front filter deposits.

1 Introduction

PM$_{2.5}$ and PM$_{10}$ (particulate matter with aerodynamic diameters <2.5 and 10 μm, respectively) sampling onto quartz-fiber filters is accompanied by positive (e.g., adsorption of organic vapors) and negative (e.g., volatilization of organic aerosols after sample

collection) artifacts. The positive artifact, as indicated by field blanks and backup filters, is believed to exceed the negative artifact for most samples (ten Brink et al., 2004; Watson et al., 2009). Without blank or backup filter subtraction, the artifact inflates organic carbon (OC) concentrations. The artifact also biases elemental carbon (EC) values by as much as ~50%, especially when measured by thermal/optical transmittance (TOT), because light attenuation due to charring of the adsorbed organic gases within the filter has a greater influence than charring of the surface particle deposit (Chen et al., 2004; Chow et al., 2004a). The composition of the adsorbed/desorbed material, its exchange between gas and particle phases, the degree to which filters become saturated, and how the sign and amount of artifact differs among filter media and sampling environments has been recognized, but it is not well understood (Arhami et al., 2006; Arp et al., 2007; Cadle et al., 1983; Chow et al., 1994, 1996, 2002a, 2006, 2008a; Eatough et al., 1989, 2003; Fan et al., 2004; Fitz, 1990; Hart and Pankow, 1994; Kim et al., 2001, 2005; Kirchstetter et al., 2001; Lewtas et al., 2001; Mader and Pankow, 2000, 2001a, 2001b; Matsumoto et al., 2003; McDow and Huntzicker, 1990; Noll and Birch, 2008; Olson and Norris, 2005; Salma et al., 2007; Subramanian et al., 2004; ten Brink et al., 2004; Turpin et al., 1994; Vecchi et al., 2009; Viana et al., 2006; Watson and Chow, 2002; Watson et al., 2009). Biases caused by these OC sampling artifacts affect $PM_{2.5}$ and PM_{10} trends, mass closure, visibility degradation assessment (Chow et al., 2002b; Watson, 2002), and estimates of radiative forcing (MacCracken, 2008).

Watson et al. (2009) evaluated several approaches to estimate the OC sampling artifact (i.e., passive field blank subtraction, backup filter adjustment, slicing method (e.g., examination of artifact distribution homogeneity within quartz-fiber filters), prefilter organic denuders, and regression intercepts). The slicing method showed that adsorbed OC is not uniformly distributed through the filter depth, nor does the adsorbed OC on the backup filter always equal that on the front filter. Average QBQ OC (i.e., OC_{QBQ}) from tandem filter packs (i.e., quartz-fiber front filter (QF) followed by QBQ) in the Interagency Monitoring of Protected Visual Environments (IMPROVE; Malm et al., 1994) network were ~19% higher than field blank (bQF) OC (i.e., OC_{bQF}) values, but

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this difference is within the standard deviation of the average and likely results from relatively low semi-volatile organic compound (SVOC) concentrations at most of the non-urban IMPROVE environments. Watson et al. (2009) showed that OC_{QBQ} from an urban site (Fort Meade, MD) contained twice the levels of OC_{bQF}.

The IMPROVE network, Speciation Trends Network (STN, part of the Chemical Speciation Network (CSN); Chu, 2004), and the Southeastern Aerosol Research and Characterization study (SEARCH; Hansen et al., 2003) are three long-term $PM_{2.5}$ chemical speciation programs that include OC and EC measurements with different approaches to sampling, analysis, and OC artifact assessment and correction. Figure 1 shows the sampling site locations and Table 1 summarizes network characteristics relevant to the OC artifact.

This study examines the methods and results of OC artifact assessment in these networks by: 1) documenting procedures to acquire blank and backup filters, 2) comparing laboratory blank, field blank (bQF), and trip blank (tbQF) OC levels for the period from 1 January 2005 to 31 December 2006; and 3) assessing blank OC levels from eight collocated IMPROVE and STN/CSN sites. These results should be of use to those using data from these and similar networks for various data analysis purposes.

Kirchstetter et al. (2001) suggested that each filter may have a different capacity for organic vapor adsorption. IMPROVE artifact corrections using monthly median OC_{QBQ} at six sites (shown in Fig. 1) assume that vapors are adsorbed uniformly throughout the front and backup filters. This implies that a saturation level is attained. Otherwise, organic vapors would be preferentially scavenged in the upper layers of QF before the gas is transmitted to QBQ. Since a subset of filters is used for blank subtraction, it has also been assumed that the saturated OC artifact values are invariant with respect to the filter batch, sampled environment, passive/active deposition, and sampling period.

Urban environments (e.g., STN/CSN sites) may have more adsorbable volatile organic compounds (VOCs) than non-urban environments (e.g., most IMPROVE sites). Fresh emissions contain SVOCs that come into equilibrium as plumes age. The oxidation of low-volatility hydrocarbons is a main pathway for secondary aerosol formation

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(Robinson et al., 2007). By the time urban emissions transport to non-urban and re-mote atmospheres, many SVOCs could have been scavenged or converted to more stable compounds.

Three hypotheses are examined using data from the three networks:

H1: The OC sampling artifact represented by bQF or QBQ depends on sampling protocol and differs among ambient networks.

H2: Sampling artifact and SVOC content are lower at non-urban sites than at urban sites.

H3: Artifact-free carbon concentrations can be better estimated by the difference between measured $PM_{2.5}$ and the weighted sum of elemental and ionic measurements (Frank, 2006) than by direct carbon measurements.

2 Methods

As shown in Table 1, seven different filter samplers are used among the three networks with flow rates ranging from 6.7–22.8 liter per minute (L/min). The largest variability is in STN/CSN, which uses five types of samplers, varying from single channel (e.g., URG MASS (Chapel Hill, NC) and Rupprecht & Patashnick (R&P; now Thermo Scientific) Partisol-Plus Model 2025 Sequential Federal Reference Method (FRM) sampler (Franklin, MA)) to five parallel channels (e.g., MetOne Spiral Aerosol Speciation Sampler (SASS; Grants Pass, OR)). STN sites were originally required to use one of three samplers (i.e., URG MASS, MetOne SASS, or the Andersen RAAS). In 2005, about 75% of the STN/CSN sites used 6.7 L/min MetOne SASS samplers. The Texas Commission on Environmental Quality (TCEQ) uses the R&P 2025 to collect $PM_{2.5}$ at non-trends CSN sites.

The IMPROVE and SEARCH networks use 25 mm and 37 mm diameter Pallflex$^{®}$ Tissuquartz^{TM} (Pall Life sciences, Ann Arbor, MI) quartz-fiber filters, respectively, while

STN/CSN used 47 mm Whatman QMA filters (Clifton, NJ), which contain a 5% borosilicate binder prior to 2007. These filters may differ in: 1) capacity and affinity for VOC and gaseous SVOC adsorption and desorption, and 2) the rate to reach saturation or equilibrium between gaseous SVOC and particulate OC. The effects of these differences cannot be determined from the available data. Deposit areas range from 3.53 cm^2 (IMPROVE) to 11.78 cm^2 (R&P 2025) and face velocities range from 9.5 cm/s (MetOne) to 107.2 cm/s (IMPROVE). The different filter holder configurations (e.g., single/tandem filter packs vs. magazine [R&P 2025, with a stack of 16 filter cassettes]) and materials (e.g., polycarbonate, aluminum, or Teflon-coated) might also affect levels of sampling artifact (Watson and Chow, 2009).

Quartz-fiber filters are treated at 900°C for three to four hours and submitted for acceptance testing prior to deployment. After this treatment, average blank levels are 0.15±0.15 μg OC or total carbon (TC=OC+EC)/cm^2 and 0±0.02 μg EC/cm^2 for Pallflex quartz-fiber filters, and 0.10±0.10 μg OC/cm^2 and 0±0.01 μg EC/cm^2 for Whatman QMA quartz-fiber filters. Approximately 2–3% of laboratory blanks are maintained for each network. The acceptance criteria are ≤2.0, 1.5, and 0.5 μg/cm^2 for TC, OC, and EC, respectively, in the IMPROVE and SEARCH networks, and <1 μg/cm^2 for TC in STN/CSN.

STN/CSN collects 3% trip blanks (i.e., tbQF), which are loaded into filter holders and accompany the sampled filters to and from each sampling site. Trip blanks are intended to assess contamination during shipping and are not installed in the sampler or exposed to ambient air.

Field blanks (e.g., dynamic blanks), accompany sample shipments and are placed in the sampler along with the sampled filters (Chow, 1995). The only difference between samples and bQF is that air is not drawn through bQF. The bQF fraction of total sample number varies by tenfold among the networks: ~2% of sample filters for IMPROVE, ~10% for STN/CSN sites and SEARCH, and ~25% for Texas non-trends CSN. The passive period for bQF is 1–15 min for STN/CSN and SEARCH, and ~7 d for IMPROVE and Texas non-trends CSN sites.

Since the bQF fraction of all samples is only 2–10% of the total number of samples, average OC_{bQF} concentrations are used to correct the sampled values with the standard deviation of the average representing the blank precision. Outliers are identified (i.e., values >3 or 4 times the standard deviation) and excluded from the averages and standard deviations.

QBQs are obtained from six IMPROVE and all eight of the SEARCH sites (Watson et al., 2009). Both networks collect QBQ every-third-day with the exception of daily sampling at two SEARCH sites (i.e., Jefferson Street, Atlanta, GA and Birmingham, AL; see Fig. 1). Ten percent of SEARCH QBQ are randomly selected for analysis. Without preceding organic denuders, the IMPROVE OC_{QBQ} represents a combination of positive and negative OC artifacts. SEARCH corrects the organic sampling artifact by calculating the quarterly mean concentrations for the QBQ and bQF and attributing them to negative and positive artifacts, respectively. OC_{bQF} is multiplied by two to account for passive adsorption on both QF and QBQ. Thus,

$$OC_{artifact\ corrected} = OC_{QF} + OC_{QBQ} - 2OC_{bQF} \tag{1}$$

where:
OC_{QF}=Quartz-fiber front filter OC,
OC_{QBQ}=Quartz-fiber behind quartz-fiber filter OC,
OC_{bQF}=field blank OC from the quartz-fiber front filter.

Collocated IMPROVE-STN/CSN samples are acquired from three urban vs. non-urban paired sites (see Fig. 1; Seattle and Mt. Rainier, WA; Phoenix and Tonto National Monument, AZ; and Washington, DC and Dolly Sods Wilderness, WV). In addition, collocated measurements are available from the urban Fresno, CA (Watson et al., 2000) and the non-urban Big Bend, TX (Chow et al., 2004b) sites. As indicated in Table 2, four types of STN/CSN samplers were collocated with the IMPROVE samplers. The IMPROVE-STN/CSN data pairs from 2001 to 2006 with complete mass, elements, ions (i.e., a minimum of nitrate (NO_3^-) and sulfate (SO_4^{2-})) and carbon measurements are included in this study. Prior to May 2007, the STN/CSN used a customized thermal/optical transmittance (TOT) carbon analysis protocol (Peterson and

Richards, 2002) while the IMPROVE and SEARCH networks followed the IMPROVE thermal/optical reflectance (TOR) protocol (Chow et al., 1993, 2001, 2004a, 2005, 2007). Since blank and backup filter EC levels are expected to be negligible, the analysis protocols should return equivalent TC and OC results. As noted in the footnote to Table 1, a new STN/CSN carbon sampling and analysis protocol have been fully implemented as of October 2009 to be consistent with the IMPROVE network.

3 Results

3.1 Blank and backup filter levels

Table 3 compares average bQF levels for TC, OC, and EC in terms of areal density (μg/cm^2) and ambient concentration equivalents (μg/m^3, based on exposed filter areas and 24 h sample volumes for each instrument). EC values are at or near detection limits, indicating that passive PM deposition is negligible. As expected, TC and OC are nearly the same and can be used interchangeably. Average bQF levels for individual sampling sites and the number of bQF acquired for IMPROVE and STN/CSN are available as supplemental information (Tables S1–S4 http://www.atmos-chem-phys-discuss.net/9/27359/2009/acpd-9-27359-2009-supplement.pdf) and in more detailed reports (Chow et al., 2008b; Watson et al., 2008). OC_{bQF} at some sampling locations statistically differ from the network mean, though the small number of bQF at some sites may not represent the true distribution of OC_{bQF} levels over the two-year sampling period.

IMPROVE bQF TC (i.e., TC_{bQF}) levels (2.41±0.48 μg/cm^2) are 2.5–3 times those of the other networks (i.e., 0.97±0.27 μg/cm^2 for STN/CSN and 0.81±0.61 μg/cm^2 for SEARCH). This probably results from the 7-d IMPROVE passive exposure period that better represents exposure of the sample filter than the 1–15 min bQF exposure experienced by STN/CSN and SEARCH. Earlier studies in urban Los Angeles, CA, and Pittsburgh, PA, suggested a minimum exposure time for VOC passive adsorption of sev-

eral hours (Subramanian et al., 2004; Turpin et al., 1994). Ambient-equivalent TC_{bQF} concentrations, however, are four times higher for STN/CSN ($1.03 \pm 0.21 \, \mu g/m^3$) than for IMPROVE ($0.26 \pm 0.05 \, \mu g/m^3$) and SEARCH ($0.24 \pm 0.18 \, \mu g/m^3$) samples. This is attributed to the lower flow rate (e.g., 6.7 L/min for MetOne SASS, compared to 22.8 L/min for IMPROVE and 16.7 L/min for SEARCH) and larger filter deposit area ($11.76 \, cm^2$ for SASS, compared to $3.53 \, cm^2$ for IMPROVE and $7.12 \, cm^2$ for SEARCH).

Figure 2 shows that most of the site average OC_{bQF} areal densities are 2–$2.5 \, \mu g/cm^2$ for IMPROVE, 0.5–$1 \, \mu g/cm^2$ for STN/CSN, and $<0.5 \, \mu g/cm^2$ for SEARCH. For STN/CSN, average OC_{bQF} varies over twofold among sampler types, from $0.74 \pm 0.66 \, \mu g/cm^2$ (URG MASS) to $1.49 \pm 0.8 \, \mu g/cm^2$ (R&P 2025). Table 3 shows that the two R&P samplers (R&P 2300 and R&P 2025) reported the highest OC_{bQF} (1.3–$1.5 \, \mu g/cm^2$). The greased impaction plate and variable passive deposition period (e.g., minutes to 7 d) for the R&P 2300 may affect the OC_{bQF} levels. Detailed records of bQF exposure periods are needed for evaluation.

There were 3628 bQF and 2335 tbQF acquired in STN/CSN during 2005 and 2006. Average areal densities are the same: $0.95 \pm 0.25 \, \mu g/cm^2$ for OC_{bQF} and $0.95 \pm 0.23 \, \mu g/cm^2$ for OC_{tbQF}. OC_{bQF} and OC_{tbQF} areal densities are also similar for a given sampler type, agreeing within $\pm 0.05 \, \mu g/cm^2$ (Table 3). Trip blanks are not exposed to ambient air and are expected to have lower concentrations. The similarity of the STN/CSN OC_{bQF} and OC_{tbQF}, and the SEARCH OC_{bQF} support the hypothesis (H1): a bQF exposure period of ~ 1–15 min is insufficient to represent the passively adsorbed VOCs experienced by the sample filters.

Average OC_{QBQ} areal density is $3.1 \pm 0.8 \, \mu g/cm^2$ for IMPROVE and $1.2 \pm 0.5 \, \mu g/cm^2$ for SEARCH, 30 and 60 %, respectively, higher than the corresponding OC_{bQF} values reported in Table 3. With the denuded SEARCH PCM3 sampler, average OC_{QBQ} is $0.43 \pm 0.97 \, \mu g/cm^2$ higher, respectively, than OC_{bQF}. While OC_{QBQ} is intended to quantify negative OC artifacts that should be added to OC_{QF} (see Eq. 1), it could also be interpreted as a better representation of the actual bQF, since QBQ spends more

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passive time in the sampler than the bQF.

Average ambient-equivalent OC_{QBQ} concentrations are similar: $0.33 \pm 0.09 \, \mu g/m^3$ for IMPROVE and $0.35 \pm 0.15 \, \mu g/m^3$ for SEARCH. These levels are 20–35 % higher than OC_{bQF} of 0.26±0.05 and $0.23 \pm 0.17 \, \mu g/m^3$ for IMPROVE and SEARCH, respectively, but ~ 65 % lower than OC_{bQF} of $1.01 \pm 0.21 \, \mu g/m^3$ (for all sampler types) found at STN/CSN sites.

Figure 3 shows that seasonal variations of OC_{bQF} are most apparent for the IMPROVE network, differing by over 40 % from winter ($1.97 \pm 0.61 \, \mu g/cm^2$) to summer ($2.92 \pm 0.78 \, \mu g/cm^2$). There are no apparent changes in the abundances of the IMPROVE thermal carbon fractions among the four seasons. Seasonal variations of OC_{QBQ} fractions (Fig. 3b) follow the same pattern as those of the IMPROVE field blanks with a summer high and winter low. Short passive exposure times at STN/CSN and SEARCH sites resulted in little to no seasonal variability: OC_{bQF} values ranged 0.8–$1.1 \, \mu g/cm^2$ and 0.52–$1.0 \, \mu g/cm^2$, respectively.

Figure 4 shows little difference between urban and non-urban IMPROVE OC_{bQF}, but with 24 % higher OC_{bQF} for non-urban SEARCH sites. Average OC_{QBQ} for the SEARCH samples was ~ 25 % higher at urban ($1.51 \pm 1.50 \, \mu g/cm^2$) than at non-urban ($1.18 \pm 0.98 \, \mu g/cm^2$) sites (Fig. 5). The urban increment for OC_{QBQ} is mostly in the OC1 fraction, which is 146 % higher at urban compared with non-urban sites (0.51 ± 0.84 vs. $0.21 \pm 0.35 \, \mu g/cm^2$). OC2 is ~ 11 % higher (0.42 ± 0.37 vs. $0.38 \pm 0.48 \, \mu g/cm^2$) at the urban sites, while the other carbon fraction levels are similar. These results are consistent with hypothesis H2, indicating more organic adsorption at urban locations. Average OC_{QBQ} levels from the six non-urban IMPROVE sites ($3.1 \pm 0.8 \, \mu g/cm^2$) are 2.6 times higher than OC_{QBQ} from the four non-urban SEARCH sites ($1.18 \pm 0.98 \, \mu g/cm^2$), consistent with the denuder removing large amounts of adsorbable organic vapors.

Blank TC areal densities in Fig. 6 show that STN/CSN tbQF TC (i.e., TC_{tbQF}) are similar for urban and non-urban sites, but they differ among samplers, consistent with two-year average tbQF levels in Table 3. Using the URG MASS sampler, TC_{tbQF} areal

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densities at the Seattle and Mount Rainier sites are 0.53±0.19 and 0.67±0.12 μg/cm^2, respectively, lower than the 0.84–1.12 μg/cm^2 found at sites using the Andersen RAAS or MetOne SASS samplers. TC$_{bQF}$ and TC$_{tbQF}$ levels are similar, with a few bQF levels higher than those of tbQF. These blanks were not always acquired together.

5   For the collocated IMPROVE vs. STN/CSN comparison, IMPROVE TC$_{bQF}$ is most consistent among the four urban sites (Seattle, Phoenix, Washington, DC, and Fresno), ranging from 2.5–2.7 μg/cm^2, with lower areal densities measured at two non-urban sites: Mount Rainier (1.4±0.4 μg/cm^2) and Tonto Monument (2.0±1.1 μg/cm^2). Collocated STN/CSN TC$_{bQF}$ are 40–75% lower than IMPROVE, with larger variability, rang-

10 ing from 0.66±0.42 (Mount Rainier using URG MASS) to 1.44±0.48 μg/cm^2 (Big Bend using R&P 2025 sequential FRM). This is consistent with hypothesis H1 that longer passive deposition periods result in higher field blank levels. The number of blanks is insufficient to evaluate seasonal variability for individual sites.

Site-averaged non-blank corrected ambient TC concentrations (μg/m^3) at each

15 IMPROVE-STN/CSN collocated site are within ±30–50% of each other. STN/CSN site-averaged TC areal densities (μg/cm^2) are 9–20% of those for collocated IMPROVE samples. TC$_{bQF}$ to TC$_{QF}$ ratios are larger for non-urban than for urban sites due to the lower ambient TC$_{QF}$ levels. For a given site, TCbQF to TCQF ratios are ~2 to 4 times higher for STN/CSN than IMPROVE samples. The actual difference could

20 be larger, if the STN/CSN sampler underestimates OC$_{bQF}$ adsorption due to the short passive exposure period.

3.2   Regression method

A regression method similar to that of White and Macias (1989) is used to evaluate the relative sampling artifact between the collocated samples. If the collocated IMPROVE

25 and STN/CSN samples measure the same TC, a linear regression of collocated data pairs should yield a slope of 1.0, an intercept of 0, and a correlation of 1.0, within experimental precision. A statistically significant positive or negative intercept at TC=0 can

be interpreted as the difference in organic sampling artifacts. A robust perpendicular least squares regression method (Dutter and Huber, 1981) is used to minimize biases caused by a few outliers and to account for the presence of errors in both variables. Using Phoenix data as an example, Fig. 7 shows a positive STN/CSN TC sampling arti-

5   fact of 1.65 μg/m^3 or 1.34 μg/cm^2 (using MetOne SASS sampling volume and deposit area) relative to the IMPROVE sampler. Reversing the independent and dependent variables in Fig. 7 does not change the conclusion when using the robust regression.

Figure 8 shows that the regression intercepts are positive for each season at the eight sites, consistent with lower flow rates for the STN/CSN samples. For five of

10 the eight sites, the intercept is largest during summer, ranging from 0.22–2.03 μg/m^3. It is highest during spring at the Mount Rainier and Tonto sites, and highest during fall at the Fresno site. The intercepts in Table 5 represent the average of four seasons. The largest two intercepts are found at the Phoenix (1.34 μg/cm^2) and Big Bend (1.29 μg/cm^2) sites using the MetOne SASS and R&P 2025 samplers, respec-

15 tively, while the lowest two are found at the Seattle (0.24 μg/cm^2) and Mount Rainier (0.50 μg/cm^2) sites using the URG MASS samplers.

Based on the sample volume/deposit area for each sampler type (Table 1), the relationship between STN/CSN and IMPROVE sampling artifacts (i.e., TC$_{STN}$ vs. TC$_{IMP}$ in μg/m^3) can be expressed as:

20 $$TC_{STN} = TC_{STN_{art}} + b \times TC_{IMP} \tag{2}$$

where the intercept, TC$_{STN_{art}}$ in μg/m^3, represents the additional artifact in TC$_{STN}$ relative to TC$_{IMP}$. Regression statistics are summarized in Table 5. Table 6 shows that STN/CSN TC$_{bQF}$ is 11–34% lower than TC$_{STN_{art}}$ at all sites except for the non-urban Tonto and Dolly Sod sites. Calculated STN/CSN TC$_{bQF}$ (0.87 μg/cm^2) is the same as

25 TC$_{STN_{art}}$ at the Tonto site. This may be due to the low TC$_{bQF}$ levels (0.3 and 0.4 μg/cm^2; see Fig. 6). The Dolly Sods site exhibits low correlations ($r=0.7$) between IMPROVE and STN (Andersen RAAS) samples.

3.3 Organic mass estimated by the SANDWICH method

Teflon-membrane filters are inert and their tendency to adsorb organic vapors is expected to be low. These filters would have a minimal positive OC artifact, although their negative organic artifact might be larger than that of quartz-fiber filters. The SAND-WICH (Sulfate, Adjusted Nitrate, Derived Water, and Inferred Carbonaceous Material) method (Frank, 2006) assumes that all of the unaccounted $PM_{2.5}$ mass measured on a Teflon-membrane filter (i.e., when weighted sums of elements and ions are subtracted) can be associated with the carbonaceous component. The OC or organic carbon mass (OCM) estimated from the SANDWICH method can be compared with those measured from quartz-fiber filters using different artifact correction methods.

The SANDWICH method was applied to 716 collocated filter pairs taken at four urban (i.e., Seattle, WA; Phoenix, AZ; Washington, DC; and Fresno, CA) sites from 28 April 2001 to 29 December 2004. The number of sample pairs varied from 27 at the Fresno Supersite to 354 at the Seattle site. The total carbonaceous mass (TCM) is calculated by subtracting NO_3^-, SO_4^{2-}, ammonium (NH_4^+), an estimate for water (H_2O), and crustal components from the measured $PM_{2.5}$ mass. The calculated OCM is derived by subtracting measured EC from TCM:

$$TCM = PM_{2.5} - (SO_4^{2-} + Retained\,NO_3^- + NH_4^+ + H_2O + Crustal\,Material + Blank) \qquad (3)$$
$$OCM = TCM - EC \qquad (4)$$

where:

$$Crustal\,Material = 3.73 \times Si + 1.63 \times Ca + 2.42 \times Fe + 1.94 \times Ti \qquad (5)$$

$$Blank = 0.3 - 1.5\,\mu g/m^3 \text{ for STN/CSN; 0 for IMPROVE}$$

All IMPROVE data have been blank-subtracted (in $\mu g/m^3$). For STN/CSN, a nominal OC_{bQF} value of $0.3–1.5\,\mu g/m^3$ is used for carbon blank subtraction (Frank, 2006), which varies by sampler type. This interval overlaps with the OC_{bQF} of $0.66\pm0.94\,\mu g/m^3$ at the Seattle, Phoenix, and Washington, DC, sites; OC_{bQF} for the

Fresno site were not available. Retained NO_3^- was calculated using the daily average temperature and relative humidity during the sampling period; and particle-bound water was calculated using the Aerosol Inorganics Model (AIM) as described by Frank (2006).

OCM concentrations from the SANDWICH method are converted to measured OC using a multiplier that accounts for unmeasured hydrogen, oxygen, and other elements in the organic compounds (El Zanan et al., 2005; Turpin and Lim, 2001; White and Roberts, 1977):

$$OCM = X \times OC \qquad (6)$$

where:
X=unmeasured element multiplier (assumed to be 1.4 for fresh and 1.8 for aged aerosol),
OC=measured particulate organic carbon.

For IMPROVE samples, average OCM concentrations are $3.99\pm2.96\,\mu g/m^3$, $4.40\pm3.45\,\mu g/m^3$, $3.00\pm3.16\,\mu g/m^3$, and $6.73\pm3.56\,\mu g/m^3$ at the Seattle, Phoenix, Washington, DC, and Fresno sites, respectively (Table 7). Better agreement with measured OC was found for a multiplier of 1.4 rather than 1.8 for all but the Fresno site. Agreement between OC×1.4 and OCM was 95%, 100%, 123%, and 71% at the Seattle, Phoenix, Washington DC, and Fresno sites, respectively. For STN/CSN samples, agreement was 90% (URG MASS) at the Seattle site, 79% (Andersen RAAS) at the Washington, DC site, and 123% and 88% (both using MetOne SASS) at the Phoenix and Fresno sites, respectively.

To assess whether low, mid-range, or high concentration samples exhibit differences, Table 7 compares estimated 10th, 50th, and 90th percentiles, respectively. The percent differences between the average and median (50% of total) are similar (within±25%) for the sites using IMPROVE samples for OC multipliers of 1.4 or 1.8. At low concentrations (the 10th percentile), OCM by the SANDWICH method is 217–279% higher than measured OCM concentrations at the Washington, DC site. Using MetOne SASS,

OCM by the SANDWICH method is also twofold higher at low concentrations for the Phoenix site; but the agreement is reasonable (87–117%) for high concentration samples (90th percentile) at this and other STN/CSN sites.

4 Deviations from hypotheses

Findings from this study are used to address the three hypotheses (H1 to H3):

H1: The OC sampling artifact represented by bQF or QBQ depends on sampling protocol and differs among ambient networks.

This hypothesis is valid based on observations. The IMPROVE, STN/CSN, and SEARCH networks use different sampling configurations, flow rates, filter material, and filter sizes. For bQF, which accompany sample filters to the field and are intended to emulate their passive deposition and adsorption, only the IMPROVE network provides an adequate ($\sim$7 d) passive exposure period for blank subtraction. The limited exposure times (1–15 min) in the STN/CSN and SEARCH networks are of insufficient duration to represent passive adsorption on the sampled filter. Based on both the network averages and collocated-site comparisons, IMPROVE TC_{bQF} (or OC_{bQF}) ranges from 2.0–2.5 $\mu g/cm^2$, while STN/CSN and SEARCH field blanks are below or close to 1 $\mu g/cm^2$. STN/CSN field and trip blank TC and OC concentrations are within ±5% for site averages. Among the five STN/CSN samplers, URG MASS reports the lowest OC_{bQF} levels.

Using non-blank corrected TC from collocated IMPROVE-STN/CSN samplers shows lower STN/CSN than IMPROVE areal densities ($\mu g/cm^2$) at the same site. Without blank correction, sampling artifacts for STN/CSN samplers in $\mu g/m^3$ could be 5–11 times higher than those in IMPROVE, depending on the sampler type. When corrected with respective field blanks, STN/CSN TC concentrations are still higher at most sites, suggesting that STN/CSN field blanks could under-represent the organic

artifact by $\sim$20–30% (assuming IMPROVE bQF fully represents the artifact), but the number of bQF available for comparison were limited.

QBQ stay in the field for more than 24 h and experience active sampling. With a similar level of sampling artifact in areal density ($\mu g/cm^2$), STN/CSN and SEARCH TC (or OC) concentration ($\mu g/m^3$) would be more influenced than those of IMPROVE due to smaller sampling volumes and larger filter sizes. Average OC_{QBQ} concentration is 0.33±0.09 $\mu g/m^3$ for IMPROVE and 0.35±0.15 $\mu g/m^3$ for SEARCH (with proceeding denuder). This demonstrates appreciable negative sampling artifact. The negative artifact could have been enhanced by the preceding organic denuder equipped in the Particle Composition Monitor (PCM3).

H2: Sampling artifact and SVOC content are lower at non-urban sites than at urban sites.

Comparisons between urban and non-urban sites in the SEARCH network are consistent with this hypothesis, but they are not sufficient to prove it. Average OC_{QBQ} was $\sim$25% higher at urban sites, (1.51±1.50 $\mu g/cm^2$) than non-urban sites (1.18±0.98 $\mu g/cm^2$) in the SEARCH network. The increments between the urban and non-urban sites were $\sim$146% for OC1 and 11% for OC2. The majority of this low temperature OC is gaseous VOCs. During the IMPROVE-STN/CSN comparisons, TC_{bQF} were not always lower at non-urban than urban sites, though this could be due to the extent of VOC saturation. The contrast between urban and non-urban sites can only provide indirect indication of aging effect since the degree of aging is not certain.

H3: Artifact-free carbon concentrations can be better estimated by the difference between measured $PM_{2.5}$ and the weighted sum of elemental and ionic measurements (Frank, 2006) than by direct carbon measurements.

This hypothesis is invalid based on observations. The SANDWICH approach is based on $PM_{2.5}$ mass closure, but many species are not measured on Teflon-membrane filters, including carbon, NO_3^-, SO_4^{2-}, and NH_4^+. Differ-

ent collection/retention efficiencies of Teflon-membrane, quartz-fiber, and nylon-membrane filters with respect to these species have not been quantified. In addition, the mass of water and unidentified species may generate more uncertainties. All these contribute to mass closure uncertainties. Even if organic carbon mass (OCM) can be calculated from the SANDWICH method, this study shows that variation in OCM concentration due to the choice of OC multiplier (e.g., 1.4 or 1.8) is comparable to the magnitude of the organic sampling artifact (5–30% of OCM). It is difficult to determine whether the excess OCM mass, if any, is due to sampling artifact or the correction coefficient used to convert OC to OCM.

The SANDWICH method did not work well for samples with low concentrations, for which the calculated and measured OC ratio exceeded 200% (e.g., Washington, DC). Even though the SANDWICH method did not provide a better representation of OC or OC artifact, it is a useful tool to estimate OC when carbon measurements are not available.

5 Conclusions

There is no simple way to correct for sampling artifacts using current measurements. With the newly implemented STN/CSN carbon measurements (US EPA, 2006), using the modified IMPROVE Module C sampler (i.e., URG 3000N sampler), sampling artifacts will be reduced via a higher flow rate (e.g., 22.8 L/min instead of 6.7 L/min) and a smaller deposit area ($3.53\,cm^2$ instead of $11.76\,cm^2$). In addition, bQF will remain in the sampler for the same period as QF and QBQ samples at all STN/CSN sites. For each network, blank corrections should be made and uncertainties propagated, even though the reported OC is under-corrected for adsorbed organic vapors due to inadequate passive deposition period for field blanks. Each network should acquire bQFs and QBQs at the same frequency and passive deposit duration (e.g., once a month on an every-sixth-day sampling schedule; expose field blanks for a minimum of three days). More research, perhaps through controlled experiments, is warranted on:

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1) sample duration for filter saturation of adsorbed gases; 2) dependence of adsorbed gas saturation on particle composition, temperature, relative humidity, and sampling face velocity; 3) evaporation rates of semi-volatile organic compounds during sampling; and 4) source-specific tests (e.g., diesel, gasoline, and wood smoke).

The information expressed in this paper does not necessarily reflect the policies of the US Environmental Protection Agency.

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Table 1. Sampling protocols for carbon in the IMPROVE, STN/CSN, and SEARCH networks from 1 January 2005 to 31 December 2006.

Network[a]	IMPROVE	STN/CSN				CSN	SEARCH
Sampler Type[b]	IMPROVE	Met One SASS	Andersen RAAS	URG MASS400/450	R&P 2300	R&P Partisol Plus 2025 Sequential FRM	PCM3
Number of channels	3 modules	5 channels (3 used)	4 channels (3 used)	2 single channel samplers	12 channels (4 used)	2 single channel modules	3 channels
Carbon denuder	None	None	None	None	None	None	Activated carbon honeycomb denuder
Inlet type[c]	AIHL cyclone	SASSSCC sharp-cut cyclone	AIHL cyclone	Louvered PM$_{10}$ inlet/WINS	Harvard Impactor	Louvered PM$_{10}$ inlet/WINS or VSCC	WINS impactor
Filter holder and cassette types	Polycarbonate	Aluminum holder and Delrin® cassette	Teflon-coated in-line holder preceded with a diffuser	Teflon holder and cassette	Teflon-coated aluminum holder and Teflon support screens	Molded plastic cassette in a 16 cassette magazine	Savillex-molded Teflon
Sampling frequency	3rd day	3rd day/6th day	3rd day/6th day	3rd day/6th day	3rd day/6th day	3rd day/6th day	daily/3rd day
Flow rate	22.8 L/min	6.7 L/min	7.3 L/min	16.7 L/min	10.0 L/min	16.7 L/min	16.7 L/min
Filter deposit area	3.53 cm^2	11.76 cm^2[d]	11.76 cm^2[d]	11.76 cm^2[d]	11.76 cm^2[d]	11.78 cm^2[e]	7.12 cm^2
Filter face velocity	107.2 cm/s	9.5 cm/s	10.3 cm/s	23.7 cm/s	14.2 cm/s	23.6 cm/s	39.1 cm/s
Sample volume	32.7 m^3	9.6 m^3	10.5 m^3	34.4 m^3	14.4 m^3	24 m^3	24 m^3
Quartz-fiber filter pre-fire temperature and duration	900°C for 4 h	900°C for 3 h	900°C for 3 h	900°C for 3 h	900°C for 3 h	900°C for 3 h	900°C for 4 h
Quartz filter type	25 mm Pall	47 mm Whatman[f]	47 mm Whatman[f]	47 mm Whatman[f]	47 mm Whatman[f]	47 mm Whatman[f,g]	37 mm Pall
Quartz filter pack configuration[h]	QF or QBQ	QF	QF	QF	QF or optional QBQ	QF	Organic carbon denuder/QBQ
Sites with backup filters (QBQ)	6	0	0	0	0	0	8
Passive deposition duration	7 d[i]	variable[j]	~1–15 min	~1–15 min	variable[j]	~5–7 d[i]	~1–15 min
Laboratory blank[k] frequency	2%	2–3%	2–3%	2–3%	2–3%	2–3%	2%
Trip blank[l] frequency	0%	3%	3%	3%	3%	0%	0%
Field blank[m] frequency	2%	10%	10%	10%	10%	~25%	10%
Field blank analysis frequency	100%	100%	100%	100%	100%	100%	100% on QF
Backup filter analysis frequency	100%	0	0	0	NA	NA	10%
Sample shipping method	Second day cardboard box with icepack	Priority overnight cooler with icepack	Priority overnight cooler with icepack	Priority overnight cooler with icepack	Priority overnight cooler with icepack	Priority overnight cooler with icepack	Standard overnight cooler with ice
Temperature for sample storage	4°C	<−15°C	<−15°C	<−15°C	<−15°C	<−15°C	4°C
Number of sites (2006)	181	179	18	6	14	22	8

Table 1. Continued.

[a] Network

IMPROVE: Interagency Monitoring of Protected Visual Environments network (Malm et al., 1994). STN/CSN: Speciation Trends Network/Chemical Speciation Network (Flanagan et al., 2006); starting in May 2007, STN/CSN sites collect ~5% bQF and ~30% QBQ. In 2008 all of the STN/CSN sites (except the Texas Commission on Environmental Quality (TCEQ) non-trends sites) installed MetOne SASS samplers for mass, elements, and ion analyses. As of October 2009, the modified IMPROVE Module C, URG 3000N sampler (URG Corp; Chapel Hill, NC) is placed at all STN/CSN sites using Pallflex® Tissuquartz™ at a flow rate of 22.8 L/min on 25 mm filters for organic and elemental carbon (OC and EC) analysis following the IMPROVE_A thermal/optical reflectance (TOR) protocol (Chow et al., 2007). SEARCH: Southeastern Aerosol Research and Characterization study (Hansen et al., 2003); eight sites (Mississippi pair: urban Gulfport (GLF) in Gulfport and non-urban Oak Grove (OAK) near Hattiesburg; Alabama pair: urban Birmingham (BHM) in North Birmingham and non-urban Centreville (CTR) south of Tuscaloosa; Georgia pair: urban Jefferson Street (JST) in Atlanta and non-urban Yorkville (YRK) northwest of Atlanta; and Florida pair: urban Pensacola (PNS) in Pensacola and suburban outlying field (OLF) northwest of Pensacola). Sampling every third day except for daily at the BHM and JST sites.

[b] Sampler Type

IMPROVE (New units manufactured by special order from URG, Inc. (Chapel Hill, NC)): Four parallel filter modules, each with up to four sequential sample sets (Eldred et al., 1990). Module A collects PM$_{2.5}$ through an Air and Industrial Hygiene Laboratory (AIHL) cyclone (22.8 L/min) followed by a 25 mm Teflon-membrane filter analyzed for mass by gravimetry and for elements by X-ray fluorescence (XRF). Module B collects PM$_{2.5}$ through a sodium carbonate denuder (Ashbaugh et al., 2004) followed by an AIHL cyclone, and followed by a 25 mm Nylon-membrane filter analyzed for nitrate (NO_3^-) and sulfate (SO_4^{2-}) by ion chromatography (IC). Module C collects PM$_{2.5}$ through an AIHL cyclone followed by a 25 mm Pallflex® Tissuquartz™ quartz-fiber filter for OC and EC by the IMPROVE_A thermal/optical reflectance (TOR) protocol. Module D collects PM$_{10}$ through a louvered PM$_{10}$ inlet at 16.7 L/min followed by a 25 mm Pall Teflon-membrane filter for mass by gravimetry.

SASS (Spiral Aerosol Speciation Sampler, Met One, Grants Pass, OR): Spiral centrifugal impaction inlets were originally used on this sampler (thus the name), but excessive re-entrainment from impaction surfaces caused these to be replaced with sharp-cut cyclones (Watson and Chow, 2009). The Super SASS can contain up to eight parallel channels, but the STN/CSN configuration uses three channels of a five channel version, each channel containing one 47 mm filter with a 6.7 L/min flow rate. For STN/CSN, Channel 1 contains a Whatman Teflon-membrane filter for mass by gravimetry and elements by XRF, Channel 2 can be used for a field blank, Channel 3 includes a magnesium oxide-coated aluminum (Al) honeycomb after the cyclone and followed by a Nylasorb Nylon-membrane filter for water-soluble anions (i.e., NO_3^- and SO_4^{2-}) and cations (i.e., ammonium [NH_4^+] and water-soluble sodium [Na^+] and potassium [K^+]) by IC, Channel 4 contains a Whatman QMA quartz-fiber filter for OC and EC by the STN thermal/optical transmission (TOT) protocol (Peterson and Richards, 2002), and Channel 5 is available for field blanks or special study samples.

Table 1. Continued.

[b] Sampler Type, continued

RAAS (Reference Ambient Air Sampler, Andersen [now Thermo Scientific] Model 25-400; Franklin, MA, no longer manufactured; Watson and Chow, 2002): Contains four parallel channels with two 2.5 μm AIHL cyclones; all filters are 47 mm in diameter. In the STN/CSN configuration, only three channels are used: Channel 1 contains a Whatman QMA quartz-fiber filter at 7.3 L/min for OC and EC by the STN TOT protocol, Channel 2 contains a Whatman Teflon-membrane filter at 16.7 L/min for mass by gravimetry and elements by XRF, Channel 3 is empty, but can be used for blanks or replicates at a flow of 16.7 L/min, and Channel 4 contains a magnesium oxide-coated denuder followed by a Whatman Nylasorb Nylon-membrane filter at a flow rate of 7.3 L/min for total nitrate by IC.

URG MASS (URG, Chapel Hill, NC): Uses two parallel modules with 47 mm filters operating at 16.7 L/min. Module 1 includes a louvered PM_{10} inlet followed by a $PM_{2.5}$ WINS impactor, a magnesium oxide-coated denuder, and a stacked filter pack with a Whatman Teflon-membrane filter on top for mass by gravimetry and elements by XRF followed by a Pall Nylasorb Nylon-membrane backup filter for anions and cations by IC. Module 2 contains a louvered PM_{10} inlet followed by a WINS $PM_{2.5}$ impactor, which includes a Whatman QMA quartz-fiber filter for OC and EC by the STN TOT protocol.

R&P 2300 (Rupprecht & Patashnick [now Thermo Scientific] Model 2300; Franklin, MA): Twelve channels are available that can be programmed to be operated in parallel or sequentially. The non-trends CSN sites in Texas use four parallel channels with 47 mm diameter filters. Channel 1 contains a Whatman Teflon-membrane filter with 16.7 L/min for mass by gravimetry and elements by XRF, Channel 2 contains an additional Teflon-membrane filter for anion and cation analyses by IC, Channel 3 contains a quartz-fiber filter, with an optional quartz-fiber backup filter, at 10 L/min for OC and EC by the IMPROVE_A TOR protocol, and Channel 4 contains a sodium carbonate-coated honeycomb denuder followed by a Nylasorb Nylon 10 L/min for total NO_3^- by IC.

R&P 2025 (Rupprecht & Patashnick [now Thermo Scientific] Model 2025; Franklin, MA): Contains two parallel modules operated in a sequential mode using 47 mm diameter filters at 16.7 L/min. Filters are stored in a 16 cassette magazine. Both modules are preceded by a louvered PM_{10} inlet followed by a sharp cut cyclone $PM_{2.5}$ inlet. Module 1 contains a Whatman Teflon-membrane filter for mass by gravimetry, elements by XRF, and cations and anions by ion chromatography. Module 2 contains a quartz-fiber filter for OC and EC by the IMPROVE_A TOR protocol.

PCM3 (Particle Composition Monitor, Aerosol Research Associates, Plano, TX; Edgerton et al., 2005): Uses three parallel channels operated at 16.7 L/min with a URG PM_{10} cyclone followed by a $PM_{2.5}$ WINS impactor. Solenoid valves behind the filter packs allow up to four sample sets to be acquired sequentially. Channel 1 contains sodium carbonate-coated annular denuder followed by a citric acid-coated annular denuder, then followed by three-stage 47 mm filter packs including a Whatman Teflon-membrane filter for mass by gravimetry and elements by XRF, followed by a Nylasorb Nylon-membrane filter for volatilized NO_3^- by IC, then followed by a citric acid-impregnated filter for volatilized NH_4^+ by automated colorimetry (AC).

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Table 1. Continued.

[b] Sampler Type, continued

Channel 2 contains a sodium carbonate-coated annular denuder followed by a citric acid-coated annular denuder and a 47 mm Nylasorb Nylon-membrane filter for total NH_4^+ and total NO_3^- by AC and IC, respectively. Channel 3 samples through a URG PM_{10} cyclone, followed by an activated carbon honeycomb denuder to remove carbon vapors, then through a WINS $PM_{2.5}$ impactor onto a 37 mm Pall quartz-fiber filter followed by a backup quartz-fiber filter for OC and EC by the IMPROVE_A TOR protocol (Chow et al., 2007).

[c] All inlets are made of anodized aluminum.

[d] RTI uses 11.76 cm^2 for quartz-fiber filters and 11.70 cm^2 exposed area for Teflon-membrane filters for the STN/CSN sites.

[e] DRI uses 11.78 cm^2 for quartz-fiber and Teflon-membrane exposed area for TCEQ non-trends CSN sites.

[f] Whatman QMA filters were switched to Pallflex Tissuquartz (Ann Arbor, MI) quartz-fiber filters as of May 2007.

[g] Field blank is in inlet and outlet of the 16 filter cassette magazines for as long as 5–7 d depending on the sampling frequency, but is in sampling position (without air being drawn through it) for only a few seconds.

[h] QF=quartz-fiber front filter only, QBQ=quartz-fiber behind quartz-fiber filter, with the backup quartz-fiber used to estimate adsorbed organic vapors.

[i] Based on the assumption of once per week site visits.

[j] Field blanks usually in samplers for ~1–15 min, but in some cases for as long as ~5–7 d.

[k] Laboratory blanks are selected from each batch of 100 unexposed filters and submitted for acceptance testing.

[l] Trip blanks accompany batches of shipped filters but are not removed from their storage containers.

[m] Field blanks accompany batches of shipped filters, but are removed from storage containers and left exposed to passive sampling. Only the IMPROVE network exposes field blanks for the same length of times as the sampled filters.

Table 2. Collocated IMPROVE and STN/CSN PM$_{2.5}$ speciation data from 16 October 2001 to 31 December 2006.

Type	Site Name	Inclusive Period	Number of Samples	IMPROVE[a] Module C Sampler	# of Field Blanks	STN[a] Sampler Type MetOne SASS	Anderson RAAS	URG MASS	R&P 2025	# of Field Blanks
Special Study	Puget Sound (PUSO), Seattle (Beacon Hill), WA	16 Oct 2001–29 Dec 2003	224	×	8			×		25
	Mount Rainier NP (MORA), WA	16 Oct 2001–1 Nov 2002	69	×	6			×		12
	Phoenix (PHOE), AZ	16 Oct 2001–29 Dec 2003	201	×	6	×				26
	Tonto National Monument (TONT), AZ	16 Oct 2001–29 Dec 2003	181	×	8	×				28
	Washington DC (WASH)	16 Oct 2001–29 Dec 2003	206	×	5		×			25
	Dolly Sods Wilderness (DOSO), WA	16 Oct 2001–29 Dec 2003	140	×	5		×			26
	Total		1021		38					142
Long-term Sites	Fresno (FRES), CA	1 Jan 2005–31 Dec 2006	227[b]	×	4		×			23
	Big Bend NP (BIBE), TX	1 Jan 2005–31 Dec 2006	81[b]	×	3				×[c]	26
	Total		308							49

[a] See Table 1 for sampler specifications.
[b] The completed 2005 and 2006 data would provide 308 sample pairs and 49 field blanks.
[c] Big Bend NP (BIBE) is a CSN site.

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Table 3. Comparison of average field blank (bQF), trip blank (tbQF), and backup (QBQ) filter carbon levels (±standard deviation) among the IMPROVE, STN/CSN, and SEARCH networks for the period from 1 January 2005 to 31 December 2006.

Network[a]	Filter Type	Type of PM$_{2.5}$ Speciation Sampler	Site Count	No. of Field Blanks	TC μg/cm^2	OC μg/cm^2	EC μg/cm^2	TC μg/m^3	OC μg/m^3	EC μg/m^3
IMPROVE	bQF	IMPROVE Module C	181	886	2.41±0.48	2.37±0.45	0.04±0.05	0.26±0.05	0.26±0.05	0±0.01
	QBQ	IMPROVE Module C	6	1401	3.23±0.96	3.08±0.83	0.16±0.13	0.35±0.10	0.33±0.09	0.02±0.01
STN/CSN	bQF	All Samples	239[b]	3628	0.97±0.27	0.95±0.25	0.02±0.03	1.03±0.21	1.01±0.21	0.01±0.02
		Andersen RAAS	22	249	0.88±0.33	0.88±0.33	0.01±0.03	0.99±0.38	0.98±0.37	0.01±0.03
		MetOne SASS	185	2572	0.86±0.39	0.85±0.38	0.01±0.05	1.05±0.47	1.04±0.47	0.01±0.06
		URG MASS	7	150	0.75±0.66	0.74±0.66	0.00±0.02	0.37±0.32	0.36±0.32	0.00±0.01
		R&P 2300 Sequential Speciation	15	236	1.33±0.52	1.30±0.51	0.03±0.11	1.09±0.42	1.06±0.41	0.02±0.09
		R&P 2025 Sequential FRM	24	421	1.57±0.77	1.49±0.76	0.08±0.12	0.78±0.38	0.73±0.37	0.04±0.06
	tbQF	All Samples	239[b]	2335	0.98±0.26	0.95±0.23	0.02±0.03	0.89±0.33	0.87±0.32	0.02±0.02
		Andersen RAAS	22	241	0.84±0.38	0.83±0.34	0.01±0.05	0.94±0.42	0.93±0.38	0.01±0.05
		MetOne SASS	185	1832	0.89±0.45	0.88±0.45	0.01±0.03	1.09±0.56	1.08±0.55	0.01±0.04
		URG MASS	7	159	0.81±0.70	0.80±0.69	0.01±0.03	0.40±0.34	0.39±0.34	0.00±0.01
		R&P 2300 Sequential Speciation	15	103	1.36±0.48	1.30±0.48	0.06±0.16	1.11±0.39	1.06±0.39	0.05±0.13
		R&P 2025 Sequential SCC	24	0	N/A[c]	N/A[c]	N/A[c]	N/A[c]	N/A[c]	N/A[c]
SEARCH	bQF	PCM3	8	144	0.81±0.61	0.76±0.57	0.04±0.06	0.24±0.18	0.23±0.17	0.01±0.02
	QBQ	PCM3	8	257	1.29±0.52	1.19±0.52	0.1±0.06	0.38±0.15	0.35±0.15	0.03±0.02

[a] Carbon analysis follows the IMPROVE_A thermal/optical reflectance (TOR) protocol (Chow et al., 2007) for teh IMPROVE and SEARCH networks and the STN thermal/optical transmittance (TOT) protocol (Chu et al., 2004; Peterson and Richards, 2002) for STN/CSN.
[b] 253 if counting 14 sites where sampler type changed between 1 January 2005 and 31 December 2006.
[c] Data is not available.

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Table 4. Average blank TC concentrations for the eight collocated IMPROVE-STN/CSN sites.

Site Code	Site Name	Instrument Used	Number of Pairs IMPROVE-STN QF (number)	IMP_bQF[a] (μg/cm^2)	IMP_bQF[a] (number)	STN_bQF[b] (μg/cm^2)	STN_bQF[b] (number)	STN_tbQF[b] (μg/cm^2)	STN_tbQF[b] (number)
						Field Blank TC Areal Density			
PUSO	Seattle, WA	URG MASS	224	2.66±0.54	8	0.68±0.41	25	0.53±0.19	9
MORA	Mount Rainier, WA	URG MASS	69	1.44±0.36	6	0.66±0.42	12	0.67±0.12	4
PHOE	Phoenix, AZ	MetOne SASS	201	2.63±0.58	6	1.40±0.77	26	1.12±0.50	10
TONT	Tonto Monument, AZ	MetOne SASS	181	2.00±1.05	8	0.87±0.31	28	0.86±0.32	9
WASH	Washington, DC	Andersen RAAS	206	2.49±0.87	5	0.87±0.40	25	0.84±0.26	10
DOSO	Dolly Sods, WV	Andersen RAAS	140	2.57±0.31	5	1.18±0.68	26	0.97±0.38	8
FRES	Fresno, CA	MetOne SASS	227	2.58±0.50	7	0.74±0.23	18	0.94±0.48	11
BIBE	Big Bend National Park, TX	R&P 2025 Sequential FRM	81	2.40±0.68	7	1.44±0.48	15	N/A±N/A	N/A

[a] Carbon analysis follows the IMPROVE_A thermal/optical reflectance (TOR) protocol (Chow et al., 2007) for the IMPROVE network.
[b] Carbon analysis follows the STN thermal/optical transmittance (TOT) protocol (Chu et al., 2004) for STN/CSN.

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Table 5. Robust regression statistics of non-blank corrected STN/CSN TC versus IMPROVE TC for data from the eight collocated sites.

Site Code	Site Name[a]	Sampling Period	Slope	Intercept (μg/m^3)	Conversion Factor[b]	Slope	Intercept (μg/cm^2)	Correlation (r)	N
			Concentration			Areal Density			
PUSO	Seattle, WA	16/10/2001–29/12/2003	0.91	0.12	0.220	0.200	0.24	0.98	224
MORA	Mount Rainier, WA	22/10/2001–20/10/2002	0.87	0.25	0.220	0.190	0.50	0.97	69
PHOE	Phoenix, AZ	16/10/2001–29/12/2003	1.08	1.65	0.088	0.095	1.34	0.94	201
TONT	Tonto Monument, AZ	16/10/2001–29/12/2003	1.06	0.85	0.088	0.093	0.69	0.92	181
WASH	Washington, DC	16/10/2001–26/12/2003	1.08	0.95	0.096	0.104	0.85	0.92	206
DOSO	Dolly Sods, WV	16/10/2001–29/12/2003	0.87	0.83	0.096	0.084	0.74	0.67	140
FRES	Fresno, CA	1/1/2005–31/12/2006	1.16	1.10	0.088	0.102	0.90	0.95	227
BIBE	Big Bend National Park, TX	1/1/2005–31/12/2006	1.22	0.64	0.220	0.268	1.29	0.79	81

[a] See Table 4 for STN/CSN sampler specification.
[b] Used to convert concentration (μg/m^3) to areal density (μg/cm^2).

Table 6. Comparison between estimated and measured sampling artifact for the eight collocated IMPROVE/STN sites.

Site Code	Site Name	Sampling Period	IMP TC_{bQF} ($\mu g/cm^2$)[a]	STN/CSN TC_{bQF} ($\mu g/cm^2$)[b]	Calculated $TC_{STN_{art}}$ ($\mu g/cm^2$)[c]	Difference (%)[d]
PUSO	Seattle, WA	16 Oct 2001–29 Dec 2003	2.66±0.54	0.68	0.83	−0.18
MORA	Mount Rainier, WA	22 Oct 2001- 20 Oct 2002	1.44±0.36	0.66	0.82	−0.19
PHOE	Phoenix, AZ	16 Oct 2001–29 Dec 2003	2.63±0.58	1.40	1.57	−0.11
TONT	Tonto Monument, AZ	16 Oct 2001–29 Dec 2003	2.00±1.05	0.87	0.87	0.01
WASH	Washington, DC	16 Oct 2001–26 Dec 2003	2.49±0.87	0.87	1.09	−0.2
DOSO	Dolly Sods, WV	16 Oct 2001–29 Dec 2003	2.57±0.31	1.18	0.99	0.19
FRES	Fresno, CA	1 Jan 2005–31 Dec 2006	2.58±0.50	1.44	1.82	−0.21
BIBE	Big Bend National Park, TX	1 Jan 2005–31 Dec 2006	2.4±0.68	0.74	1.13	−0.34

[a] IMPROVE field blanks
[b] STN/CSN field blanks
[c] Estimated STN/CSN artifact=conversion factor (Table 5)×IMP TC_{bQF}+areal density intercept (Table 5), assuming that IMP TC_{bQF} fully explains the sampling artifact of the IMPROVE network.
[d] $\frac{\text{measured STN/CSN } TC_{bQF} - \text{calculated } TC_{STN_{art}}}{\text{calculated } TC_{STN_{art}}} \times 100$

Table 7. Estimates of organic carbon mass (OCM) based on the SANDWICH method for the four collocated IMPROVE-STN/CSN sites.

| Site Name	Seattle, WA	Phoenix AZ	Washington, DC	Fresno, CA
Site Type	Urban	Urban	Urban	Urban
Site Code	PUSO	PHOE	WASH	FRES
Number of Collocated Pairs	354	290	45	27
Sampler Type	IMPROVE	IMPROVE	IMPROVE	IMPROVE
Sampling Period	12 Jul 2001–29 Dec 2004	28 Apr 2001–30 Sep 2004	8 Jul 2004–29 Dec 2004	3 Sep 2004–23 Dec 2004
SANDWICH OCM $\mu g/m^3$				
Average	3.99±2.96	4.40±3.45	3.00±3.16	6.73±3.56
10%tile	1.22	1.48	0.58	2.86
50%tile	3.16	3.27	2.47	6.16
90%tile	8	8.66	6.23	11.29
Measured OC $\mu g/m^3$				
Average	2.70±2.06	3.13±2.27	2.63±1.51	3.42±1.66
10%tile	0.87	1.32	0.90	1.47
50%tile	1.91	2.25	2.51	3.18
90%tile	5.28	6.10	4.21	5.52
Measured OC×1.4/OCM				
Average	95%	100%	123%	71%
10%tile	100%	125%	217%	72%
50%tile	85%	96%	142%	72%
90%tile	92%	99%	95%	68%
Measured OC×1.8/OCM				
Average	122%	128%	158%	91%
10%tile	128%	161%	279%	93%
50%tile	109%	124%	183%	93%
90%tile	119%	127%	122%	88%
Sampler Type	URG MASS	MetOne SASS	Andersen RAAS	MetOne SASS
Sampling Period	12 Jul 2001–29 Dec 2004	28 Apr 2001–30 Sep 2004	8 Jul 2004–29 Dec 2004	3 Sep 2004–23 Dec 2004
SANDWICH OCM $\mu g/m^3$				
Average	4.63±3.27	4.48±3.62	4.85±5.14	7.66±4.37
10%tile	1.57	1.03	0.65	3.08
50%tile	3.72	3.64	4.03	6.72
90%tile	9.59	9.12	9.05	14.22
Measured OC $\mu g/m^3$				
Average	2.98±2	3.94±2.43	2.75±1.86	4.8±2.71
10%tile	1.16	1.58	0.56	1.81
50%tile	2.38	3.34	2.78	4.12
90%tile	6.06	7.59	5.62	8.91
Measured OC×1.4/OCM				
Average	90%	123%	79%	88%
10%tile	103%	215%	121%	82%
50%tile	90%	128%	97%	86%
90%tile	88%	117%	87%	88%
Measured OC×1.8/OCM				
Average	116%	158%	102%	113%
10%tile	133%	276%	155%	106%
50%tile	115%	165%	124%	110%
90%tile	114%	150%	112%	113%
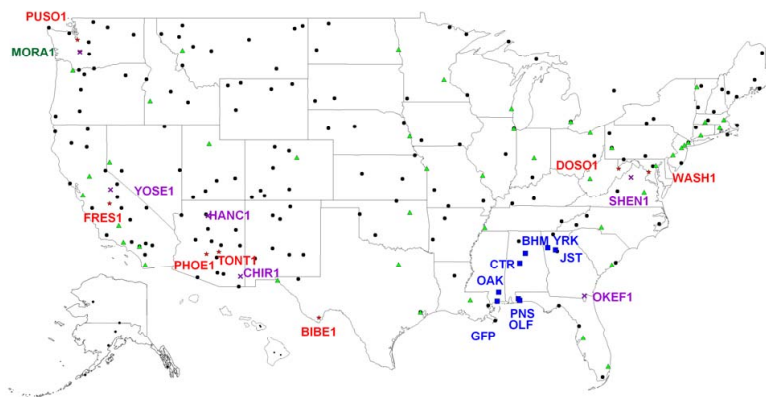
Fig. 1. Sampling locations for the 181 Interagency Monitoring of Protected Visual Environments (IMPROVE) sites (solid black circles, mostly non-urban), 239 Speciation Trends Network (STN)/Chemical Speciation Network (CSN) sites (green triangles, mostly urban), and 8 paired Southeastern Aerosol Research and Characterization study (SEARCH) sites (blue squares, urban vs. non-urban/suburban pairs (Mississippi GLF (urban Gulfport) and OAK (non-urban Oak Grove near Hattiesburg); Alabama BHM (urban north Birmingham) and CTR (non-urban Centreville south of Tuscaloosa); Georgia JST (urban Jefferson Street in Atlanta) and YRK (non-urban Yorkville, north of Atlanta); and Florida PNS (urban Pensacola) and OLF (suburban outlying field northwest of Pensacola, classified as non-urban))). The six IMPROVE locations that include quartz-fiber behind quartz-fiber filters (QBQ) are indicated by purple crosses (Mount Rainier National Park, WA (MORA1); Yosemite National Park, CA (YOSE1); Hance Camp, Grand Canyon National Park, AZ (HANC1); Chiricahua National Monument, AZ (CHIR1); Okefenokee National Wildlife Reserve, GA (OKEF1); and Shenandoah National Park, WV (SHEN1)). The eight collocated IMPROVE/CSN sites are indicated by red stars (Puget Sound, WA (PUGO1); Mount Rainier National Park, WA (MORA1); Fresno, CA (FRES1); Phoenix, AZ (PHOE1); Tonto National Monument, AZ (TONT1); Big Bend National Park (BIBE1); Dolly Sods Wilderness (DOSO1); and Washington, D.C. (WASH1)). MORA1 (Mount Rainier, WA), which is both an IMPROVE QBQ and collocated IMPROVE-STN/CSN sites, is indicated in dark green.
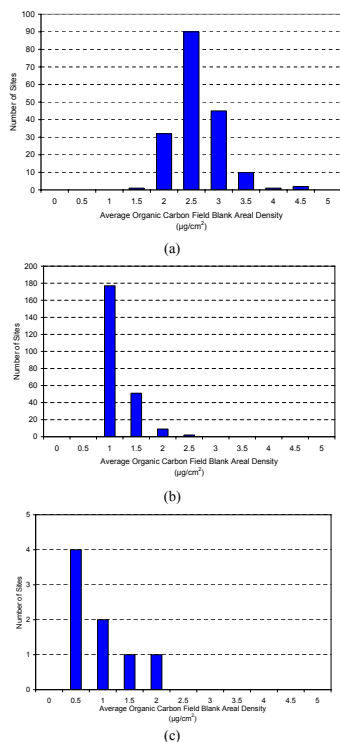
27393

Fig. 2. Field blank organic carbon (OC_{bQF}) concentration density ($\mu g/cm^2$) for: **(a)** 181 IM-PROVE sites, **(b)** 239 STN/CSN sites, and **(c)** 8 SEARCH sites for the period from 1 January 2005 to 31 December 2006 (each bar represents the concentration sector less than or equal to the assigned value).
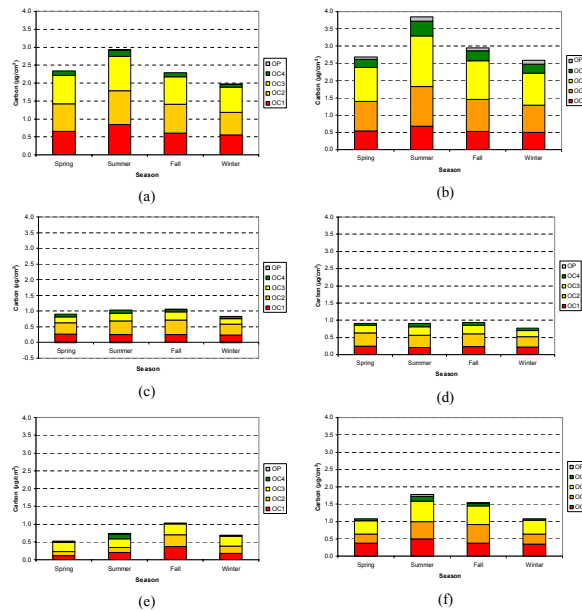
27394

Fig. 3. Seasonal variations of blanks among: (a) IMPROVE field blanks (OC_{bQF}), (b) IMPROVE backup filters (OC_{QBQ}; six sites), (c) STN/CSN field blanks (OC_{bQF}), (d) STN/CSN trip blanks (OC_{tbQF}), (e) SEARCH denuded field blanks (OC_{dbQF}), and (f) SEARCH denuded backup filters (OC_{dQBQ}; eight sites). IMPROVE thermal carbon fractions are defined as: OC1 (140°C), OC2 (280°C), OC3 (480°C), and OC4 (580°C) in 100% helium (He); and EC1 (580°C), EC2 (740°C), and EC3 (840°C) in 98% He/2% oxygen (O_2), and charring/pyrolysis carbon (OP, carbon evolved when reflectance returns to its initial value); OC=OC1+OC2+OC3+OC4+OP. EC levels (EC1+EC2+EC3−OP) were negligible for blank and backup filters and are not plotted.
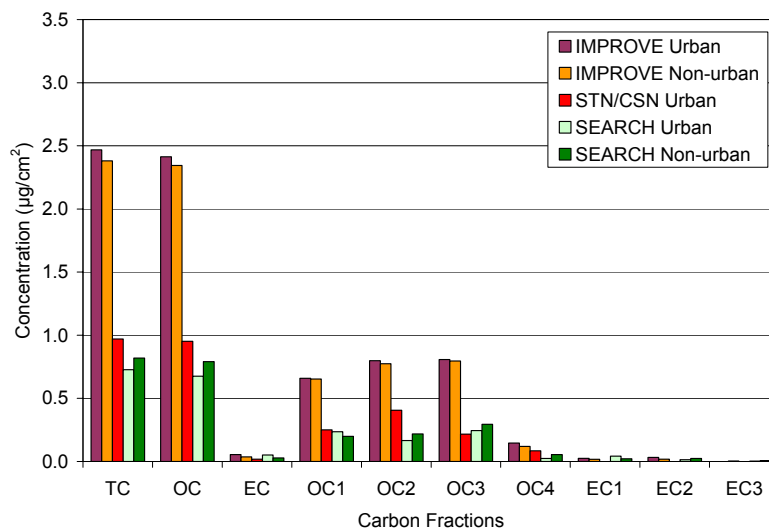
Fig. 4. Comparison of field blank (bQF) carbon concentrations between the urban and non-urban sites among the IMPROVE, STN/CSN, and SEARCH networks for the period from 1 January 2005 to 31 December 2006. There are 13 urban and 168 non-urban IMPROVE sites, 239 STN/CSN urban sites, and 4 urban and 4 non-urban SEARCH sites. The urban IMPROVE sites are: Atlanta, GA (ATLA1); Baltimore, MD (BALT1); Birmingham, AL (BIRM1); Chicago, IL (CHIC1); Detroit, MI (DETR1); Fresno, CA (FRES1); Houston, TX (HOUS1); New York, NY (NEYO1); Old Town, ME (OLTO1); Phoenix, AZ (PHOE1); Pittsburgh (PITT1); Rubidoux, CA (RUBI1); Washington, DC (WASH1) (http://vista.cira.colostate.edu/improve/).
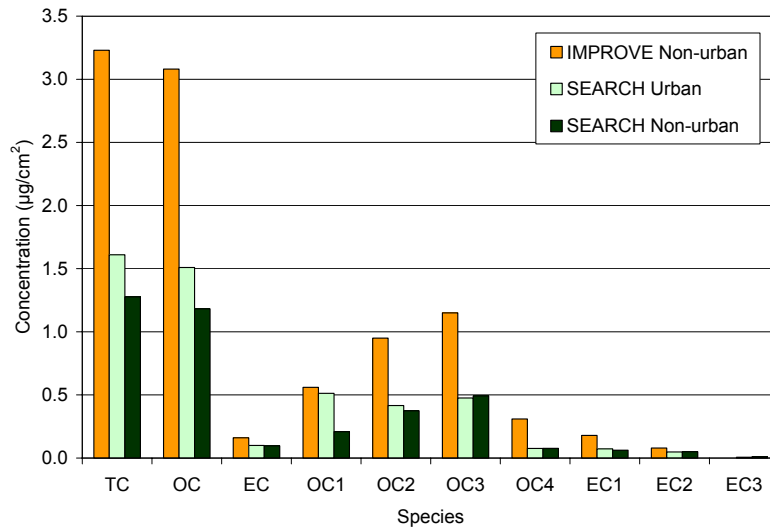
Fig. 5. Comparison of quartz-fiber backup filter (QBQ) carbon fractions between the urban and non-urban sites in the IMPROVE and SEARCH networks for the period from 1 January 2005 to 31 December 2006. Carbon fractions follow the IMPROVE_A thermal/optical reflectance (TOR) protocol (Chow et al., 2007).
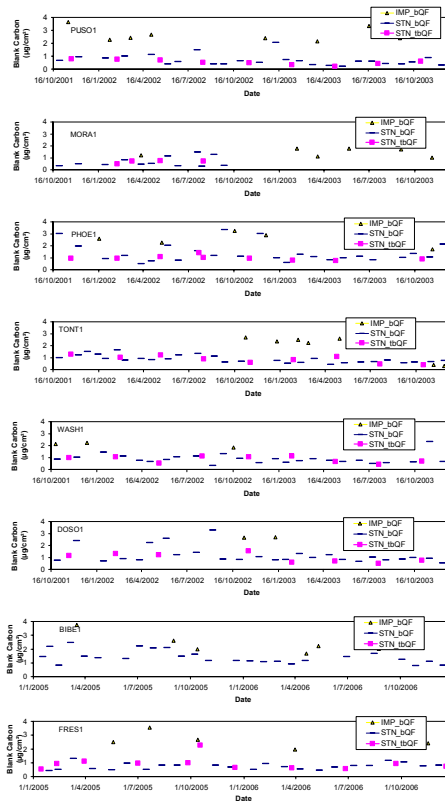
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Fig. 6. Time series of IMPROVE and STN/CSN blank total carbon (TC) concentrations at eight collocated sites from 1 January 2005 to 31 December 2006 (IMP_bQF: IMPROVE field blanks; STN_bQF: STN/CSN field blanks; STN_tbQF: STN/CSN trip blanks). Site codes are defined in Table 2.
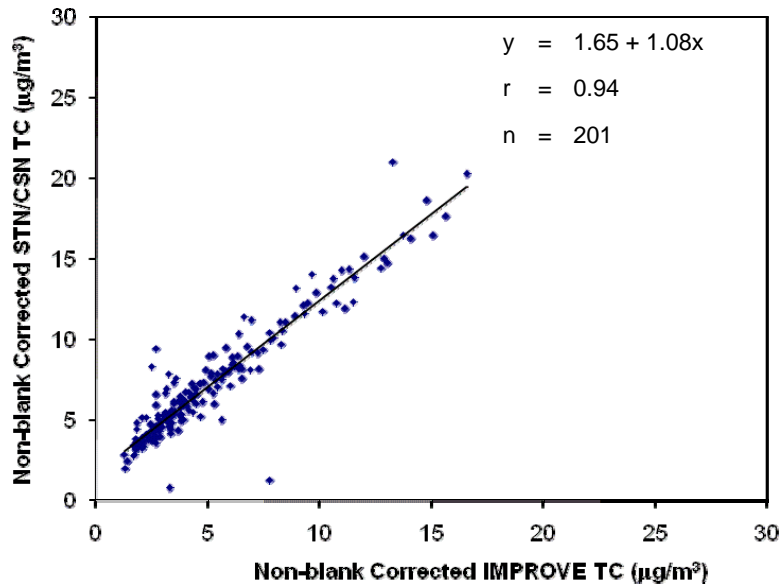
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Fig. 7. Linear regression of non-blank corrected STN/CSN TC vs. IMPROVE TC acquired from the Phoenix, AZ site (PHOE1). The non-zero intercept indicates the sampling artifacts between STN/CSN and the IMPROVE samplers.

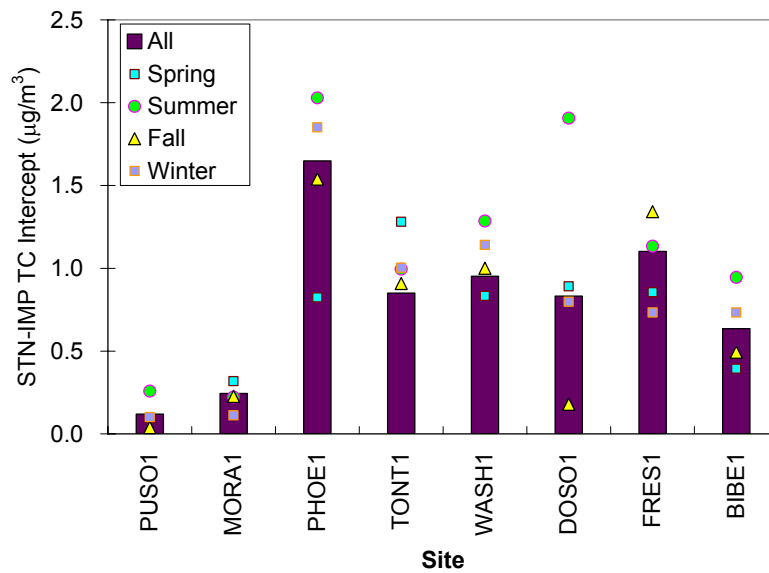**Fig. 8.** The non-blank corrected STN–IMPROVE TC regression intercept for the entire data and seasonally-segregated data from the eight collocated sites. (The site names are: PUSO1 (Seattle, WA); MORA1 (Mount Rainier, WA); PHOE1 (Phoenix, AZ); TONT1 (Tonto National Monument, AZ); WASH1 (Washington, DC); DOSO1 (Dolly Sods Wilderness, WV); FRES1 (Fresno, CA); and BIBE1 (Big Bend National Park, TX)).