Quantification of $PM_{2.5}$ Organic Carbon Sampling Artifacts in U.S. Networks

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First submitted to
Atmospheric Chemistry and Physics Discussion

July 10, 2009

Resubmitted to
Atmospheric Chemistry and Physics

March 12, 2010

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Abstract

Field blanks (bQF) and backup filters (quartz-fiber behind quartz-fiber filter; QBQ) have been adopted by U.S. long-term air quality monitoring networks to estimate $PM_{2.5}$ organic carbon (OC) sampling artifacts. This study documents bQF and QBQ carbon levels for 1) Interagency 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 and examines the similarities/differences associated with network-specific sampling protocols. A higher IMPROVE sample volume and smaller filter deposit area results in $PM_{2.5}$ areal density ($\mu g/cm^2$ on filter) 3–11 times those of STN/CSN and SEARCH samples for the same ambient $PM_{2.5}$ concentrations, thus reducing the relative contribution of sampling artifacts from passive OC adsorption. A relatively short (1–15 minutes) passive exposure period of STN/CSN and SEARCH bQF OC (0.8–1 $\mu g/cm^2$) underestimates positive and negative OC artifacts resulting from passive adsorption or evaporation of semi-volatile organic compounds on quartz-fiber filters. This is supported by low STN/CSN and SEARCH bQF levels and lack of temporal or spatial variability among the sites within the networks. With a much longer period, ~7 days of ambient passive exposure, average IMPROVE bQF and QBQ OC are comparable (2.4 ± 0.5 and 3.1 ± 0.8 $\mu g/cm^2$, respectively) and more than twice levels found in the STN/CSN and SEARCH networks. Sampling artifacts in STN/CSN were estimated from collocated IMPROVE samples based on linear regression. At six of the eight collocated sites in this study, STN/CSN bQFs underestimated OC artifacts by 11–34%. Using a preceding organic denuder in the SEARCH network minimized passive adsorption on QBQ, but OC on QBQ may not be attributed entirely to the negative sampling artifact (e.g., evaporated or volatilized OC from the front filter deposits after sample collection).

Keywords: Carbonaceous aerosol, organic sampling artifact, organic carbon

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). In addition, OC sampling artifacts could affect $PM_{2.5}$ and PM_{10} trends, mass closure, visibility degradation assessment (Chow et al., 2002a; Watson, 2002), and estimates of radiative forcing (MacCracken, 2008).

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 differ among filter media and sampling environments have been studied, but these issues are not well understood (Arhami et al., 2006; Arp et al., 2007; Cadle et al., 1983; Chow et al., 1994; 1996; 2002b; 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). Several approaches have been used to estimate the OC sampling artifact─including passive field blank subtraction, backup filter adjustment, slicing method (e.g., examination of artifact distribution homogeneity within quartz-fiber filters), pre-filter organic denuders, and regression intercepts (Watson et al., 2009).

Frank (2006) developed the SANDWICH method to estimate artifact-free OC or OC mass (OCM). This method 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. This is based on the principle that Teflon®-membrane filters are inert and their tendency to adsorb organic vapors is low. These filters are

expected to have a minimal positive OC artifact, although their negative organic artifact might be larger than that of quartz-fiber filters.

In the U.S., the 1) Interagency Monitoring of Protected Visual Environments (IMPROVE; Malm et al., 1994) network, 2) Speciation Trends Network (STN; part of the Chemical Speciation Network [CSN]; Chu, 2004), and 3) 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. Of the 181 IMPROVE sites, more than 93% (170 sites) are located in National Parks and wilderness areas that represent different regions of the U.S. These sites are far away from population centers or local pollution sources, with a 100–1000 km zone of representation (40 CFR part 50; U.S. EPA 2006a). Regional or non-urban $PM_{2.5}$ sites are affected by naturally occurring aerosol from windblown dust, wildfires, and marine aerosol, as well as by pollution generated in urban and industrial areas that may be more than 1000 km distant. Urban STN/CSN sites represent a mixture of particles from many sources within the urban complex, including but not dominated by neighborhood-scale (500 m to 4 km) sources. Urban-scale (4 to 100 km) sites are usually located on city roof-tops of two- to four-story buildings─away from highly travelled roads, industries, and residential heating to represent human exposure─typically in an urban area with population > 200,000 (U.S. EPA, 1997; Chow et al., 2002c). The SEARCH network was designed to evaluate human exposure at urban versus rural environments in the southeastern U.S. (Mississippi, Alabama, Georgia, and Florida). Fig 1 shows the sampling site locations, and Table 1 summarizes network characteristics relevant to the OC artifact.

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 scavenged preferentially in the upper layers of QF before the gas is transmitted to QBQ. Since a subset of filters is used for blank subtraction, it also is assumed that saturated OC artifact values are invariant with respect to the filter batch, sampled environment, passive/active deposition, and sampling period. Kirchstetter et al. (2001) suggested that each filter may have a different capacity for organic vapor adsorption. The slicing method by Watson et al., (2009) further showed that adsorbed OC is neither uniformly distributed throughout the filter depth, nor does

the adsorbed OC on the backup filter always equal that on the front filter. However, the number of samples examined was too small to draw broad generalizations.

Urban environments, where most of the STN/CSN sites are located, contain volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs) adsorbable to quartz-fiber filters. SVOCs in fresh emission plumes gradually come into equilibrium as the plumes age. Oxidation of low-volatility hydrocarbons has been suggested to be a main pathway for secondary organic aerosol (SOA) formation (Robinson et al., 2007). By the time urban plumes transport to rural and remote atmospheres (e.g., most IMPROVE sites), many SVOCs could have been scavenged or converted to more stable PM compounds (Yu et al., 2004; Lane et al., 2008). Average OC_{QBQ} measurements in the IMPROVE network were ~19% higher than OC_{bQF} values, but this difference is within the standard deviation of the average (Watson et al., 2009). The fact that levels of OC_{QBQ} and OC_{bQF} are similar reflects relatively low SVOC concentrations at most of the IMPROVE regional-background environments. In contrast, Watson et al. (2009) showed that OC_{QBQ} from an urban site (Fort Meade, MD) contained twice the levels of OC_{bQF}.

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), trip blank (tbQF), and quartz-fiber backup (QBQ) filter OC levels for the period from 1/1/2005 to 31/12/2006; and 3) assessing blank OC levels from eight collocated IMPROVE and STN/CSN sites using the SANDWICH method (Frank, 2006). These results should be of interest to those using data from these and similar networks for various data analysis purposes.

Three hypotheses are tested 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 (rural and remote) sites than urban sites due to aerosol aging.

H3: Artifact-free OC concentrations can be better estimated by the SANDWICH method (Frank, 2006) than by direct OC 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 to 22.8 liters 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 (Ann Arbor, MI) quartz-fiber filters, respectively, while STN/CSN used 47 mm Whatman QMA filters (Clifton, NJ), which contain a 5% borosilicate binder. 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/sec (MetOne) to 107.2 cm/sec (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) also might affect the magnitude of the OC artifact (Watson and Chow, 2009).

Prior to sampling, quartz-fiber filters are treated at 900°C for three to four hours and acceptance tested. 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. Acceptance criteria are $\leq$ 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 and Richards, 1990). 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 ~10–25% for Texas non-trends CSN. The passive period for bQF has been 1–15 minutes for STN/CSN and SEARCH, and ~7 days 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 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). The small number of outliers likely results from inadvertent contamination during filter shipping/receiving or sample loading/unloading and are 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,

$$OC_{artifact\ corrected} = OC_{QF} + OC_{QBQ} - 2OC_{bQF} \quad (1)$$

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

To compare carbon measurements between the IMPROVE network and STN/CSN, collocated $PM_{2.5}$ data were 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, D.C. and Dolly Sods Wilderness, WV; Solomon et al., 2004). 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 [$SO_4^=$]) and carbon measurements are included. 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; 2007a). Since blank and backup filter EC levels are expected to be negligible, the analysis protocols should return equivalent OC and TC results. As noted in the footnote to Table 1, a new STN/CSN carbon sampling and analysis protocol was fully implemented in 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 ($\mu g/cm^2$) and ambient concentration equivalents ($\mu g/m^3$), based on exposed filter areas and 24 hr sample volumes for each instrument, respectively. EC values are at or near minimum detection limits (i.e., 0.06 $\mu g/cm^2$), accounting for 0 to 5% of TC, indicating that passive PM deposition is negligible. As a result, TC and OC are not statistically different and will 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) 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, although the small number of bQF at some sites may not represent the true distribution of OC_{bQF} levels during the two-year sampling period.

IMPROVE bQF TC (i.e., TC_{bQF}) areal density levels (2.41 ± 0.48 $\mu g/cm^2$) are 2.5 to 3 times those of the other networks (i.e., 0.97 ± 0.27 $\mu g/cm^2$ for STN/CSN and 0.81 ± 0.61 $\mu g/cm^2$ for SEARCH). This probably results from the 7-day IMPROVE passive exposure period that better represents exposure of the sample filter than the 1–15 minute bQF exposure experienced by STN/CSN and SEARCH. Earlier studies in urban Los Angeles, California, and Pittsburgh, Pennsylvania, suggested a minimum exposure time for VOC passive adsorption of several hours (Subramanian et al., 2004; Turpin et al., 1994). Ambient-equivalent TC_{bQF} concentrations, however, are four times higher for STN/CSN (1.03 ± 0.21 $\mu g/m^3$) than for IMPROVE (0.26 ±

246 0.05 μg/m^3) and SEARCH (0.24 ± 0.18 μg/m^3) samples. This is attributed to the lower flow rate
247 (e.g., 6.7 L/min for MetOne SASS, compared to 22.8 L/min for IMPROVE and 16.7 L/min for
248 SEARCH) and larger exposed area of the filter deposit (11.76 cm^2 for SASS, compared to 3.53
249 cm^2 for IMPROVE and 7.12 cm^2 for SEARCH).

250 Fig 2 shows that most of the site average OC_{bQF} areal densities are 2–2.5 μg/cm^2 for
251 IMPROVE, 0.5–1 μg/cm^2 for STN/CSN, and <0.5 μg/cm^2 for SEARCH. For STN/CSN, average
252 OC_{bQF} varies more than twofold among sampler types, from 0.74 ± 0.66 μg/cm^2 (URG MASS)
253 to 1.49 ± 0.8 μg/cm^2 (R&P 2025). Table 3 shows that the two R&P samplers (R&P 2300 and
254 R&P 2025) reported the highest OC_{bQF} (1.3–1.5 μg/cm^2). The greased inlet impaction plate and
255 variable passive exposure periods (e.g., minutes to 7 days) for the R&P 2300 may affect OC_{bQF}
256 levels. Detailed records of bQF exposure periods are not available.

257 There were 3,628 bQF and 2,335 tbQF acquired in STN/CSN during 2005 and 2006.
258 Average areal densities are the same: 0.95 ± 0.25 μg/cm^2 for OC_{bQF} and 0.95 ± 0.23 μg/cm^2 for
259 OC_{tbQF}. OC_{bQF} and OC_{tbQF} areal densities are also similar for a given sampler type, agreeing
260 within ±0.05 μg/cm^2 (Table 3). Trip blanks (tbQF) are not exposed to ambient air and are
261 expected to have lower concentrations. The similarity of the STN/CSN OC_{bQF} and OC_{tbQF} and
262 the SEARCH OC_{bQF} support hypothesis (H1) that the bQF exposure period (1–15 minutes) is
263 insufficient to represent the passively adsorbed VOCs experienced by the sample filters.

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

270 Average ambient-equivalent OC_{QBQ} concentrations are similar: 0.33 ± 0.09 μg/m^3 for
271 IMPROVE and 0.35 ± 0.15 μg/m^3 for SEARCH. These levels are 20–35% higher than OC_{bQF} of
272 0.26 ± 0.05 and 0.23 ± 0.17 μg/m^3 for IMPROVE and SEARCH, respectively, but ~65% lower
273 than OC_{bQF} of 1.01 ± 0.21 μg/m^3 (for all sampler types) found in the STN/CSN sites.

274 Fig 3 shows that OC_{bQF} seasonal variations are most apparent for the IMPROVE
275 network, varying by more than 40% from winter (1.97 ± 0.61 μg/cm^2) to summer (2.92 ± 0.78
276 μg/cm^2). There are no apparent changes in fractional contributions 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} spans 0.8– 1.1 μg/cm^2 and 0.52–1.0 μg/cm^2, respectively.

Fig 4 shows little difference between urban and non-urban IMPROVE OC_{bQF}, but SEARCH OC_{bQF} is 17% higher at non-urban compared to urban sites. Average OC_{QBQ} for the SEARCH samples was ~25% higher at the urban (1.51 ± 1.50 μg/cm^2) compared to non-urban (1.18 ± 0.98 μg/cm^2) sites (Fig. 5). The urban increment for OC_{QBQ} is mostly in the OC1 fraction, which is 146% higher at urban than at non-urban sites (0.51 ± 0.84 vs. 0.21 ± 0.35 μg/cm^2). OC2 is ~11% higher (0.42 ± 0.37 vs. 0.38 ± 0.48 μg/cm^2) at the urban sites, while the other thermal fraction levels are similar. These results are consistent with hypothesis H2, indicating more SVOC adsorption at the urban sites. Average OC_{QBQ} levels from the six non-urban IMPROVE sites (3.1 ± 0.8 μg/cm^2) are 2.6 times higher than OC_{QBQ} from the four non-urban SEARCH sites (1.18 ± 0.98 μg/cm^2), consistent with the denuder removing adsorbable organic vapors.

Blank TC areal densities in Fig. 6 show that STN/CSN tbQF TC (i.e., TC_{tbQF}) areal densities 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 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.

IMPROVE TC_{bQF} areal densities are 2–3 times higher than those of STN/CSN TC_{bQF} or TC_{tbQF}. In addition to variations in passive exposure time, IMPROVE uses the Pallflex® Tissuquartz while STN/CSN used QMA quartz-fiber filters prior to 2007, and 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 available data.

For the collocated IMPROVE vs. STN/CSN comparison at the eight sites, IMPROVE TC_{bQF} is most consistent among the four urban sites (Seattle, Phoenix, Washington, D.C., and Fresno), ranging from 2.5–2.7 μg/cm^2, with lower areal densities measured at two non-urban

sites: Mount Rainier National Park (1.4 ± 0.4 μg/cm^2) and Tonto National Monument (2.0 ± 1.1 μg/cm^2). Collocated STN/CSN TC_{bQF} are 40–75% lower than IMPROVE, with larger variability, ranging 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 collocated IMPROVE and STN/CSN 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 urban sites due to the lower ambient TC_{QF} levels. For example, the average TC_{bQF} reaches ~49% of TC_{QF} at the Dolly Sods site for the STN/CSN sampler, but it is only 12% for the collocated IMPROVE sampler. The actual difference could be larger if STN/CSN 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 among collocated samples. If the collocated IMPROVE 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 avoid 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 artifact 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 a robust regression.

Fig 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 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, respectively, 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 IMPROVE and STN/CSN sampling artifacts (i.e., TC_{IMP} vs. TC_{STN} in μg/cm^2) can be expressed as:

$$TC_{STN} = TC_{STN_{art}} + b \times TC_{IMP} \quad (2)$$

where the intercept, $TC_{STN_{art}}$ in μg/cm^2, 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. Measured STN/CSN TC_{bQF} is similar to calculated $TC_{STN_{art}}$ at the Tonto site. The Dolly Sods site exhibits low TC_{bQF} levels (e.g., 0.4 and 0.3 μg/cm^2; see Fig. 6), and a lower correlation (r = 0.7) was found between IMPROVE and STN (Andersen RAAS) samples at this site.

3.3 Organic carbon Mass (OCM) estimated by the SANDWICH method

The SANDWICH method was applied to 716 collocated filter pairs taken at four urban (i.e., Seattle, WA; Phoenix, AZ; Washington, D.C.; and Fresno, CA) sites from 28/4/2001 to 29/12/2004. The number of sample pairs varied from 27 at the Fresno Supersite to 354 at the Seattle site. Total carbonaceous mass (TCM) was calculated by subtracting NO_3^-, $SO_4^=$, 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:

$$TCM = PM_{2.5} - (SO_4^= + \text{Retained } NO_3^- + NH_4^+ + H_2O + \text{Crustal Material} + \text{Blank}) \quad (3)$$

$$OCM = TCM - EC \quad (4)$$

where:

$$\text{Crustal Material} = 3.73 \times Si + 1.63 \times Ca + 2.42 \times Fe + 1.94 \times Ti \quad (5)$$

Blank = 0.3 – 1.5 μg/m^3 for STN/CSN; 0 for IMPROVE

All IMPROVE data were blank-subtracted (in μg/m^3). For STN/CSN, a nominal OC_{bQF} value of 0.3–1.5 μg/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 ± 0.94 μg/m^3 at the Seattle, Phoenix, and Washington, D.C., 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 (i.e., El Zanan et al., 2005; Turpin and Lim, 2001; White and Roberts, 1977):

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

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 ± 2.96 μg/m^3, 4.40 ± 3.45 μg/m^3, 3.00 ± 3.16 μg/m^3, and 6.73 ± 3.56 μg/m^3 at the Seattle, Phoenix, Washington, D.C., 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 for the IMPROVE samples was 95%, 100%, 123%, and 71% at the Seattle, Phoenix, Washington D.C., and Fresno sites, respectively. For STN/CSN samples, agreement was 90% (URG MASS) at the Seattle site, 79% (Andersen RAAS) at the Washington, D.C. 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 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, D.C. site. Using STN/CSN samples, OCM by the SANDWICH method is also twofold higher at low concentrations for the Phoenix site; but the agreement is reasonable (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.

401 This hypothesis is valid based on observations. The IMPROVE, STN/CSN, and
402 SEARCH networks use different sampling configurations, flow rates, filter material, and filter
403 sizes. For bQF, which accompany sample filters to the field and are intended to emulate their
404 passive deposition and adsorption, only the IMPROVE network provides an adequate (~7 days)
405 passive exposure period for blank subtraction. The limited exposure times (1–15 minutes) in the
406 STN/CSN and SEARCH networks are of insufficient duration to represent passive adsorption on
407 the sampled filter. Based on both the network averages and collocated-site comparisons,
408 IMPROVE TC_{bQF} (or OC_{bQF}) areal density ranges from 2.0 to 2.5 μg/cm^2, while STN/CSN and
409 SEARCH field blanks are below or close to 1 μg/cm^2. STN/CSN field and trip blank TC and OC
410 concentrations are similar (~0.95 ± 0.23 μg/cm^2), within ±5% for site averages. Among the five
411 STN/CSN samplers, URG MASS reports the lowest OC_{bQF} levels.

412 Regression analysis using uncorrected TC from collocated IMPROVE-STN/CSN
413 samples show higher STN/CSN than IMPROVE areal densities (μg/cm^2) at the same site.
414 Without blank correction, STN/CSN sampling artifacts in μg/m^3 could be 5–11 times higher than
415 those in IMPROVE, depending on the sampler type. When corrected with respective field
416 blanks, STN/CSN TC concentrations are still higher at most sites, indicating that STN/CSN field
417 blanks underrepresent the organic artifact by ~20–30% (assuming IMPROVE bQF fully
418 represents the artifact), but the number of bQF available for comparison was limited.

419 QBQ filters stay in the field for more than 24 hours with filtered air drawn through them
420 for 24 hours. With a similar level of sampling artifact in areal density (μg/cm^2), STN/CSN and
421 SEARCH TC (or OC) concentration (μg/m^3) would be more influenced than those of IMPROVE
422 due to smaller sampling volumes and larger filter sizes. The average OC_{QBQ} concentration is 0.35
423 ± 0.1 μg/m^3 for IMPROVE and 0.38 ± 0.15 μg/m^3 for SEARCH (with proceeding denuder).

424 H2: Sampling artifact and SVOC content are lower at non-urban sites than urban sites due to
425 aerosol aging.

426 Comparisons between urban and non-urban sites in the SEARCH network are consistent
427 with this hypothesis, but they are not sufficient to prove it. Average OC_{QBQ} was ~25% higher at
428 the urban sites, with 1.51 ± 1.50 μg/cm^2 at urban sites and 1.18 ± 0.98 μg/cm^2 at the non-urban
429 sites in the SEARCH network. The increments between the urban and non-urban sites were
430 ~146% for OC1 and 11% for OC2. The majority of this low temperature OC is gaseous VOCs.

However, during the collocated IMPROVE-STN/CSN comparisons, TC_{bQF} were not always lower at non-urban than urban sites, although this depends on the extent of VOC saturation. The contrast between urban and non-urban sites only can provide indirect indication of aging effect since the degree of aging is not certain.

H3: Artifact-free OC concentrations can be better estimated by the SANDWICH method (Frank, 2006) than by direct OC measurements.

This hypothesis is invalid based on observations. The SANDWICH method (Frank, 2006) is based on $PM_{2.5}$ mass closure, but many species are not measured on Teflon®-membrane filters, including carbon, NO_3^-, $SO_4^=$, and NH_4^+. Different collection/retention efficiencies of Teflon®-membrane, quartz-fiber, and nylon-membrane filters with respect to these species have not been well quantified. In addition, the mass of water and unidentified species may generate more uncertainties (Tierney and Connor, 1967; Kajino et al., 2006). All of 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% with the STN/CSN sampler (e.g., Phoenix, AZ). 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 (U.S.EPA, 2006b), 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 per month on an every-sixth-day sampling schedule; expose field blanks for a minimum of three days). More research, perhaps through controlled experiments, are warranted on 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).

6. Acknowledgements

This work was partially supported by U.S. EPA STAR Grant number RD-83108601-0, the U.S. EPA/National Park Service under contract number C2350064010, the California Air Resources Board under contract number 04-307, and the Nazir and Mary Ansari Foundation. The information expressed in this paper does not necessarily reflect the policies of the U.S. Environmental Protection Agency.

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Table 1. Sampling protocols for carbon in the IMPROVE, STN/CSN, and SEARCH networks from 1/1/2005 to 31/12/2006.

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	3rd day	3rd day	3rd day/ 6th day	3rd day/6th day	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/sec	9.5 cm/sec	10.3 cm/sec	23.7 cm/sec	14.2 cm/sec	23.6 cm/sec	39.1 cm/sec
Sample volume	32.7 m^3	9.6 m^3	10.5 m^3	24 m^3	14.4 m^3	24 m^3	24 m^3
Quartz-fiber filter pre-fire temperature and duration	900 °C for 4 hr	900 °C for 3 hr	900 °C for 3 hr	900 °C for 3 hr	900 °C for 3 hr	900 °C for 3 hr	900 °C for 3 hr
Quartz filter type	25 mm Pall	47mm Whatman[f]	47mm Whatman[f]	47mm Whatman[f]	47mm Whatman[f]	47mm Whatman[f,g]	37 mm Pall
Quartz filter pack configuration [h]	QF or QBQ	QF	QF	QF	QF	QF	Organic carbon denuder/ QBQ
Sites with backup filters (QBQ)	6	0	0	0	0	0	8%
Passive deposition duration	7 days [i]	variable [j]	1-15 min [j]	1-15 min [j]	variable [j]	5 – 7 days [j]	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%	10-25%	10%
Field blank analysis frequency	100%	100%	100%	100%	100%	100%	10% 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

[a] Networks
IMPROVE: Interagency Monitoring of PROtected Visual Environments network (Malm et al., 1994)

Table 1. Continued.

[a] Networks, continued

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 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) following the IMPROVE_A thermal/optical protocol (Chow et al., 2007b).

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).

[b] Sampler Descriptions

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 followed by a 25mm 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 a 25mm nylon-membrane filter analyzed by ion chromatography (IC) for nitrate (NO_3^-) and sulfate ($SO_4^=$). Module C collects $PM_{2.5}$ through an AIHL cyclone followed by a 25mm Pall quartz-fiber filter for OC and EC by the IMPROVE_A thermal/optical reflectance (TOR) protocol. Module D collects 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 followed by a Nylasorb nylon-membrane filter for water-soluble anions (i.e., NO_3^- and $SO_4^=$) 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 transmission (TOT) protocol (Peterson and Richards, 2002); Channel 5 is available for field blanks or special study samples.

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 replicates or blanks at a flow of 16.7 L/min; 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 and a 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.

Table 1. Continued.

[b] Sampler Descriptions, continued

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; 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 Pall 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 a three-stage filter packs in: a 47 mm Teflon®-membrane filter for mass by gravimetry and elements by XRF, followed by a 47 mm Nylasorb Nylon-membrane filter for volatilized NO_3^- by IC, followed by a 47 mm citric acid-impregnated filter for volatilized NH_4^+ by automated colorimetry (AC). 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., 2007a).

[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 Texas 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 kept in the inlet and outlet of the 16 filter cassette magazines for as long as 5–7 days 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] Field blanks usually in samplers for 1–15 minutes, but in some cases for as long as 5–7 days.

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

[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 16/10/2001 to 31/12/2006.

				IMPROVE[a]		STN[a] Sampler Type				
Type	Site Name	Inclusive Period	Number of Samples	Module C Sampler	# of Field Blanks	MetOne SASS	Anderson RAAS	URG MASS	R&P 2025	# of Field Blanks
Special Study	Puget Sound (PUSO), Seattle (Beacon Hill), WA	16/10/2001-29/12/2003	224	X	8			X		25
	Mount Rainier NP (MORA), WA	16/10/2001-1/11/2002	69	X	6			X		12
	Phoenix (PHOE), AZ	16/10/2001-29/12/2003	201	X	6	X				26
	Tonto National Monument (TONT), AZ	16/10/2001-29/12/2003	181	X	8	X				28
	Washington D.C. (WASH)	16/10/2001-29/12/2003	206	X	5		X			25
	Dolly Sods Wilderness (DOSO), WA	16/10/2001-29/12/2003	140	X	5		X			26
	Total		**1,021**		**38**					**142**
Long-term Sites	Fresno (FRES), CA	1/1/2005-31/12/2006	227[b]	X	4		X			23
	Big Bend NP (BIBE), TX	1/1/2005-31/12/2006	81[b]	X	3				X[c]	26
	Total		**308**							**49**

[a] See Table 1 for sampler specifications.

[b] Due to missing NO_3^- data at the Big Bend site and incomplete 2006 data, only 172 data pairs, as well as 7 IMPROVE and 32 STN/CSN field blanks from Fresno and Big Bend National Park (BIBE) were included. For carbon analysis alone, the completed 2005 and 2006 data would provide 308 sample pairs and 49 field blanks.

[c] Big Bend NP (BIBE) is a CSN site.

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 1/1/2005 to 31/12/2006.

Network	Filter Type	Type of $PM_{2.5}$ Speciation Sampler	Site Count	No. of Field Blanks	TC	OC	EC	TC	OC	EC
						$\mu g/cm^{2d}$			$\mu g/m^{3e}$	
IMPROVE[c]	**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	1,401	3.23 ± 0.96	3.08 ± 0.83	0.16 ± 0.13	0.35 ± 0.1	0.33 ± 0.09	0.02 ± 0.01
STN/CSN	**bQF**	All Samples	239[a]	3,628	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	2,572	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 ± 0.02	0.37 ± 0.32	0.36 ± 0.32	0 ± 0.01
		R&P 2300 Sequential Speciation	15	236	1.33 ± 0.52	1.3 ± 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[a]	2,335	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	1,832	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	0.4 ± 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[b]	N/A[b]	N/A[b]	N/A[b]	N/A[b]	N/A[b]
SEARCH[c]	**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] 253 if counting 14 sites where sampler type changed between 1/1/2005 and 31/12/2006
[b] Data is not available

Table 3. Continued.

[c] Carbon analysis follows the IMPROVE thermal/optical reflectance (TOR) protocol (Chow et al., 2007a) for the IMPROVE and SEARCH network and the STN thermal/optical transmittance (TOT) protocol (Chu et al., 2004; Peterson and Richards, 2002) for STN/CSN.

[d] Areal density on filters in $\mu g/cm^2$ is based on sample loading divided by the exposed area (e.g., 3.53 cm^2 for IMPROVE samplers, 11.76 cm^2 for STN/CSN speciation samplers, and 7.12 cm^2 for SEARCH PCM3 samplers as noted in Table 1)

[e] Equivalent ambient concentration in $\mu g/m^3$ is based on the sample loading divided by the nominal sampler volume (varies from 9.6 m^3 for MetOne SASS to 32.7 m^3 for the IMPROVE sampler as noted in Table 1).

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)	Field Blank TC Areal Density					
				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)
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, D.C.	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 thermal/optical reflectance (TOR) protocol (Chow et al., 2007a) for the IMPROVE network
[b] Carbon analysis follows the STN thermal/optical transmittance (TOT) protocol (Chu et al., 2004) for STN/CSN.

Table 5. Robust regression statistics of uncorrected STN/CSN TC against IMPROVE TC for data from the eight collocated sites.

Site Code	Site Name[a]	Sampling Period	TC Concentration Slope	TC Concentration Intercept (µg/m^3)	TC Areal Density Slope	TC Areal Density Intercept (µg/cm^2)	Correlation (r)	N
PUSO	Seattle, WA	16/10/2001 - 29/12/2003	0.91	0.12	0.22	0.24	0.98	224
MORA	Mount Rainier, WA	22/10/2001 - 20/10/2002	0.87	0.25	0.22	0.5	0.97	69
PHOE	Phoenix, AZ	16/10/2001 - 29/12/2003	1.08	1.65	0.088	1.34	0.94	201
TONT	Tonto Monument, AZ	16/10/2001 - 29/12/2003	1.06	0.85	0.088	0.69	0.92	181
WASH	Washington, D.C.	16/10/2001 - 26/12/2003	1.08	0.95	0.096	0.85	0.92	206
DOSO	Dolly Sods, WV	16/10/2001 - 29/12/2003	0.87	0.83	0.096	0.74	0.67	140
FRES	Fresno, CA	1/1/2005 - 31/12/2006	1.16	1.1	0.088	0.9	0.95	227
BIBE	Big Bend National Park, TX	1/1/2005 - 31/12/2006	1.22	0.64	0.22	1.29	0.79	81

[a] See Table 4 for STN/CSN sampler specifications.

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} ($\mu g/cm^2$)[c]	Calculated $TC_{STN_{art}}$ ($\mu g/cm^2$)[b]	Difference (%)[d]
PUSO	Seattle, WA	16/10/2001 - 29/12/2003	2.66 ± 0.54	0.68	0.83	-0.18
MORA	Mount Rainier, WA	22/10/2001- 20/10/2002	1.44 ± 0.36	0.66	0.82	-0.19
PHOE	Phoenix, AZ	16/10/2001 - 29/12/2003	2.63 ± 0.58	1.4	1.57	-0.11
TONT	Tonto Monument, AZ	16/10/2001 - 29/12/2003	2 ± 1.05	0.87	0.87	0.01
WASH	Washington, D.C.	16/10/2001 - 26/12/2003	2.49 ± 0.87	0.87	1.09	-0.2
DOSO	Dolly Sods, WV	16/10/2001 - 29/12/2003	2.57 ± 0.31	1.18	0.99	0.19
FRES	Fresno, CA	1/1/2005 -31/12/2006	2.58 ± 0.5	1.44	1.82	-0.21
BIBE	Big Bend National Park, TX	1/1/2005 -31/12/2006	2.4 ± 0.68	0.74	1.13	-0.34

[a] IMPROVE field blanks

[b] Estimated STN/CSN artifact

[c] STN/CSN field blanks

[d] $$\frac{measured\ STN/CSN\ TC_{bQF} - calculated\ TC_{STN_{art}}}{calculated\ TC_{STN_{art}}} \times 100$$

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

Site	**Seattle, WA**	**Phoenix AZ**	**Washington, D.C.**	**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	12/7/2001-29/12/2004	28/4/2001-30/9/2004	8/7/2004-29/12/2004	3/9/2004-23/12/2004
SANDWICH OCM µg/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 µg/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	12/7/2001-29/12/2004	28/4/2001-30/9/2004	8/7/2004-29/12/2004	3/9/2004-23/12/2004
SANDWICH OCM µg/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 µg/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%

8. Figure Captions

Fig. 1. Sampling locations for the 181 Interagency Monitoring of PROtected Visual Environments (IMPROVE) sites (circles, mostly non-urban), 239 Speciation Trends Network (STN)/Chemical Speciation Network (CSN) sites (triangles, mostly urban), and eight paired Southeastern Aerosol Research and Characterization study (SEARCH) sites (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 included both in the IMPROVE QBQ and the collocated IMPROVE/CSN sites, is indicated in dark green.

Fig. 2. Field blank organic carbon (OC_{bQF}) concentration density ($\mu g/cm^2$) for a) 181 IMPROVE sites, b) 239 STN/CSN sites, and c) eight SEARCH sites for the period from 1/1/2005 to 31/12/2006 (each bar represents the concentration sector less than or equal to the assigned value).

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 1/1/2005 to 31/12/2006. There are 13 urban and 169 non-urban IMPROVE sites, 239 STN/CSN urban sites, and four urban and four 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, D.C. (WASH1) [http://vista.cira.colostate.edu/improve/]).

Fig. 5. Comparison of quartz-fiber backup filter (QBQ) carbon fractions between urban and non-urban sites in the IMPROVE and SEARCH networks for the period from 1/1/2005 to

31/12/2006. Carbon fractions follow the IMPROVE_A thermal/optical reflectance (TOR) protocol (Chow et al., 2007a).

Fig. 6. Time series of IMPROVE and STN/CSN blank TC concentrations at eight collocated sites from 1/1/2005 to 31/12/2006 (IMP_bQF: IMPROVE field blanks; STN_bQF: STN/CSN field blanks; STN_tbQF: STN/CSN trip blanks).

Fig .7. Linear regression of uncorrected STN/CSN TC vs. IMPROVE TC acquired from the Phoenix, AZ site (PHOE1). The non-zero intercept indicates sampling artifacts between STN/CSN and the IMPROVE network.

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

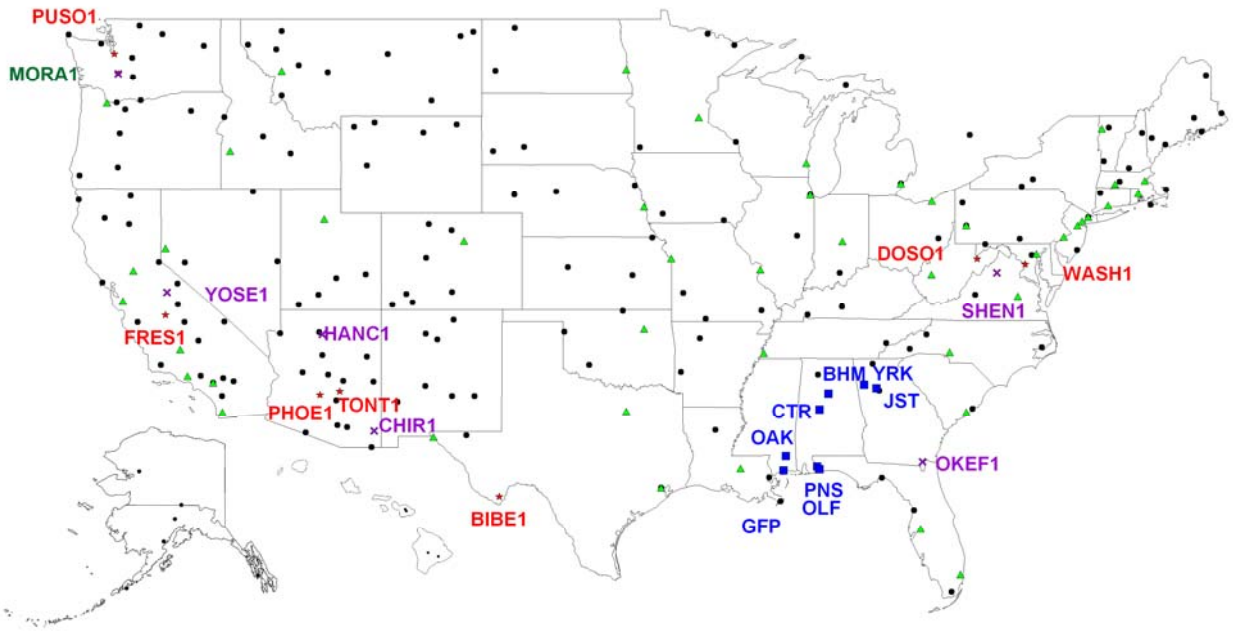
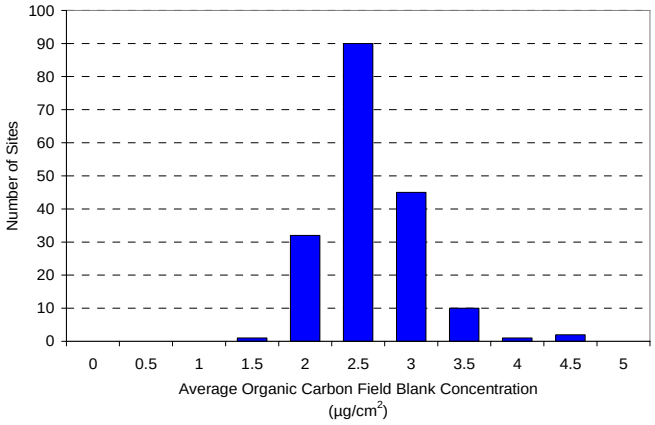
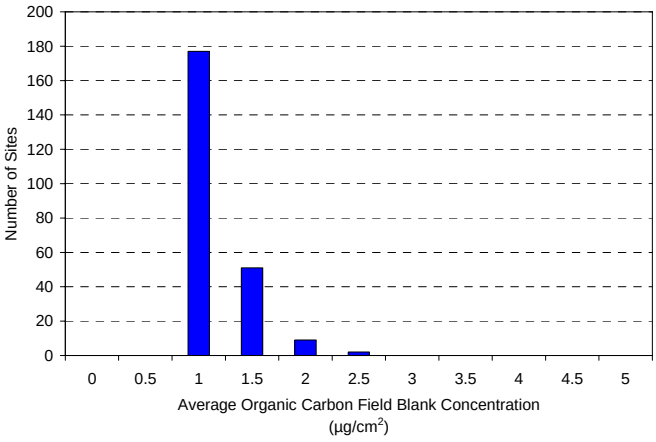

PUSO1
MORA1
YOSE1
FRES1
HANC1
PHOE1
TONT1
CHIR1
BIBE1
DOSO1
WASH1
SHEN1
BHM
YRK
JST
CTR
OAK
OKEF1
PNS
OLF
GFP

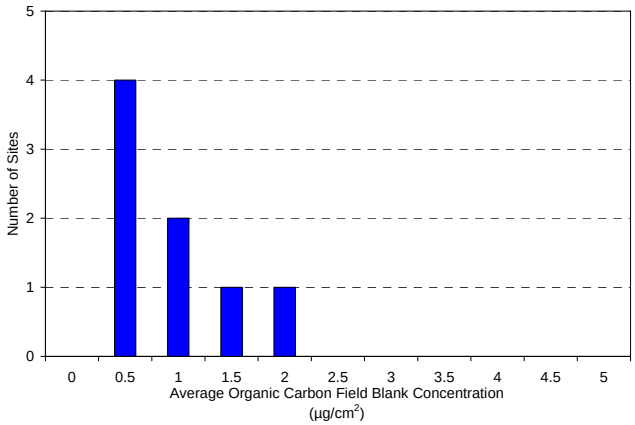
Figure 1.


Number of Sites
100
90
80
70
60
50
40
30
20
10
0
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
Average Organic Carbon Field Blank Concentration
(µg/cm2)

(a)


Number of Sites
200
180
160
140
120
100
80
60
40
20
0
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
Average Organic Carbon Field Blank Concentration
(µg/cm2)

(b)


Number of Sites
5
4
3
2
1
0
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
Average Organic Carbon Field Blank Concentration
(µg/cm2)

(c)

Figure 2.

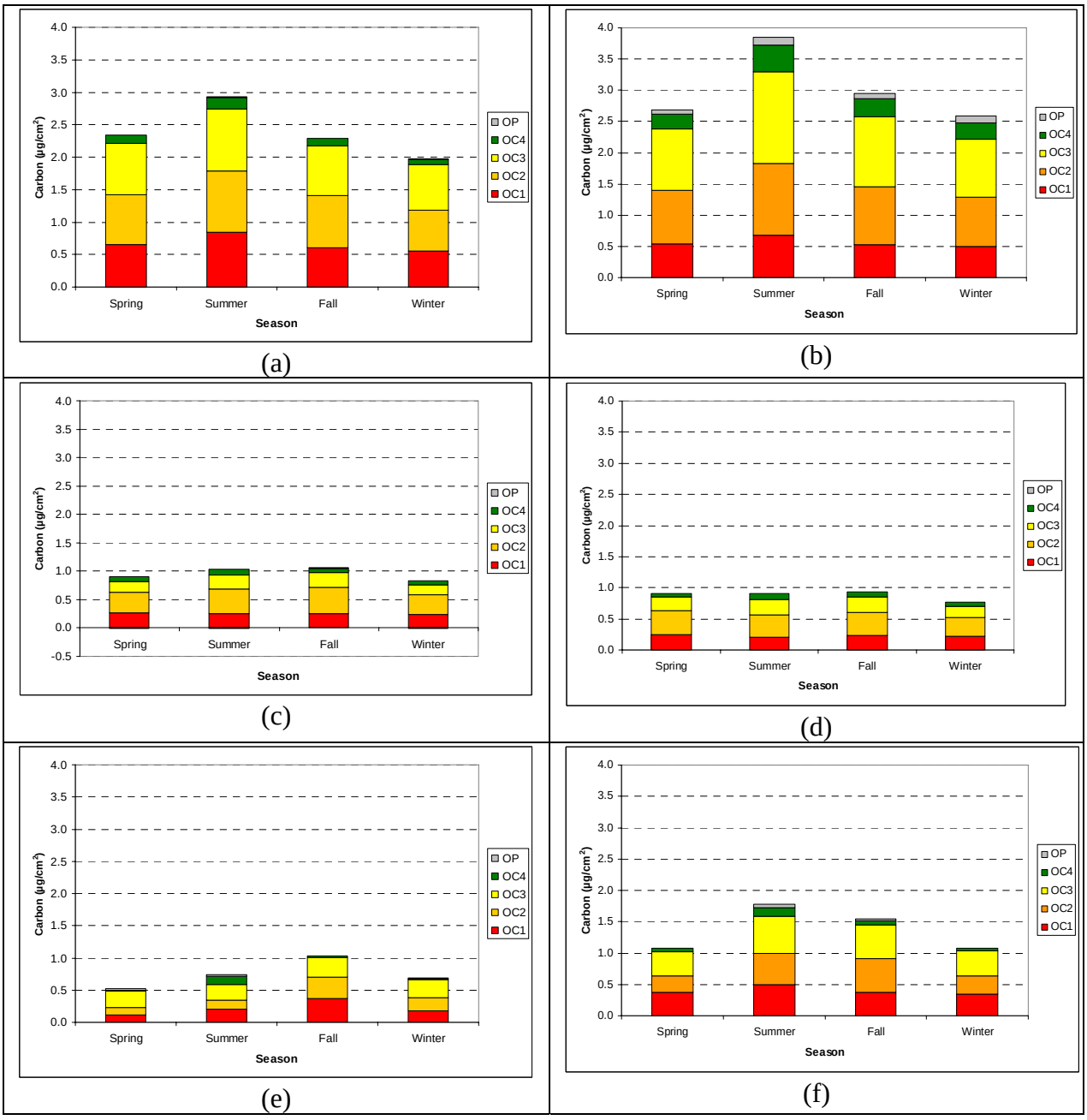

Carbon (µg/cm²)
Season
Spring
Summer
Fall
Winter
OP
OC4
OC3
OC2
OC1
(a)
(b)
(c)
(d)
(e)
(f)

Figure 3.

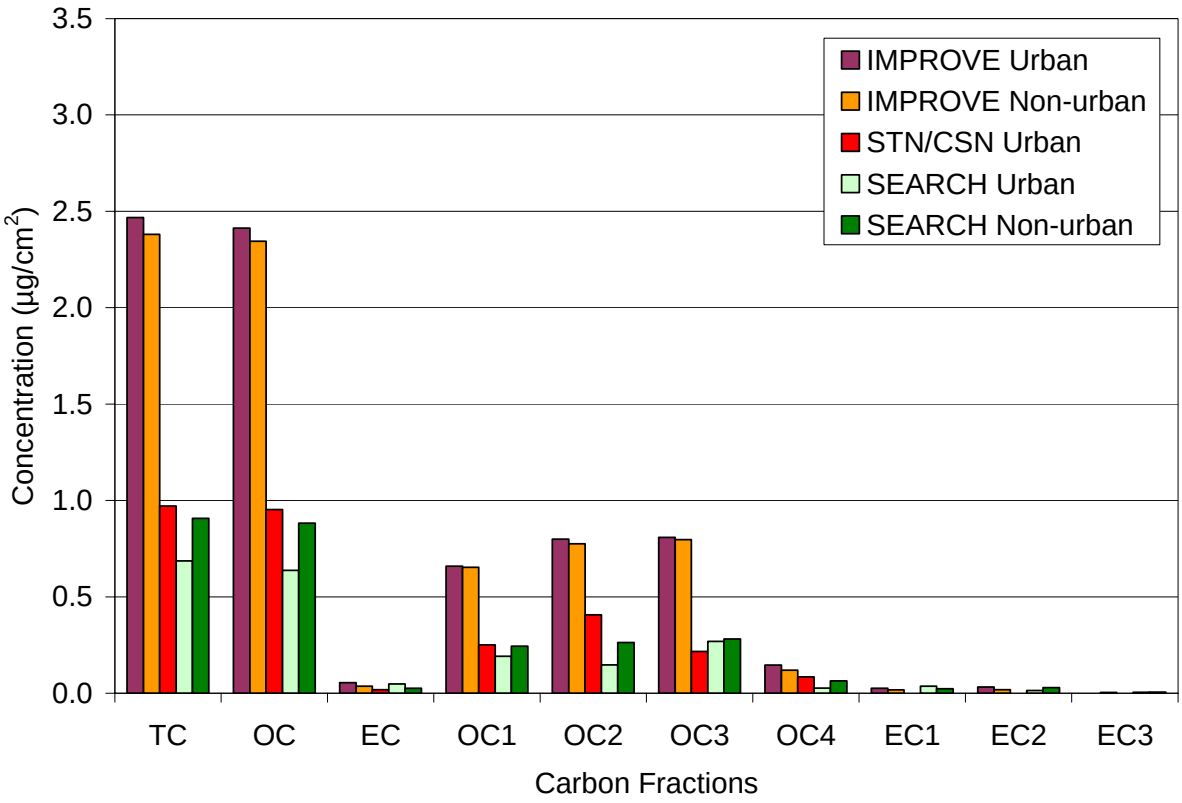

3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Concentration (µg/cm2)
IMPROVE Urban
IMPROVE Non-urban
STN/CSN Urban
SEARCH Urban
SEARCH Non-urban
TC
OC
EC
OC1
OC2
OC3
OC4
EC1
EC2
EC3
Carbon Fractions

Figure 4.

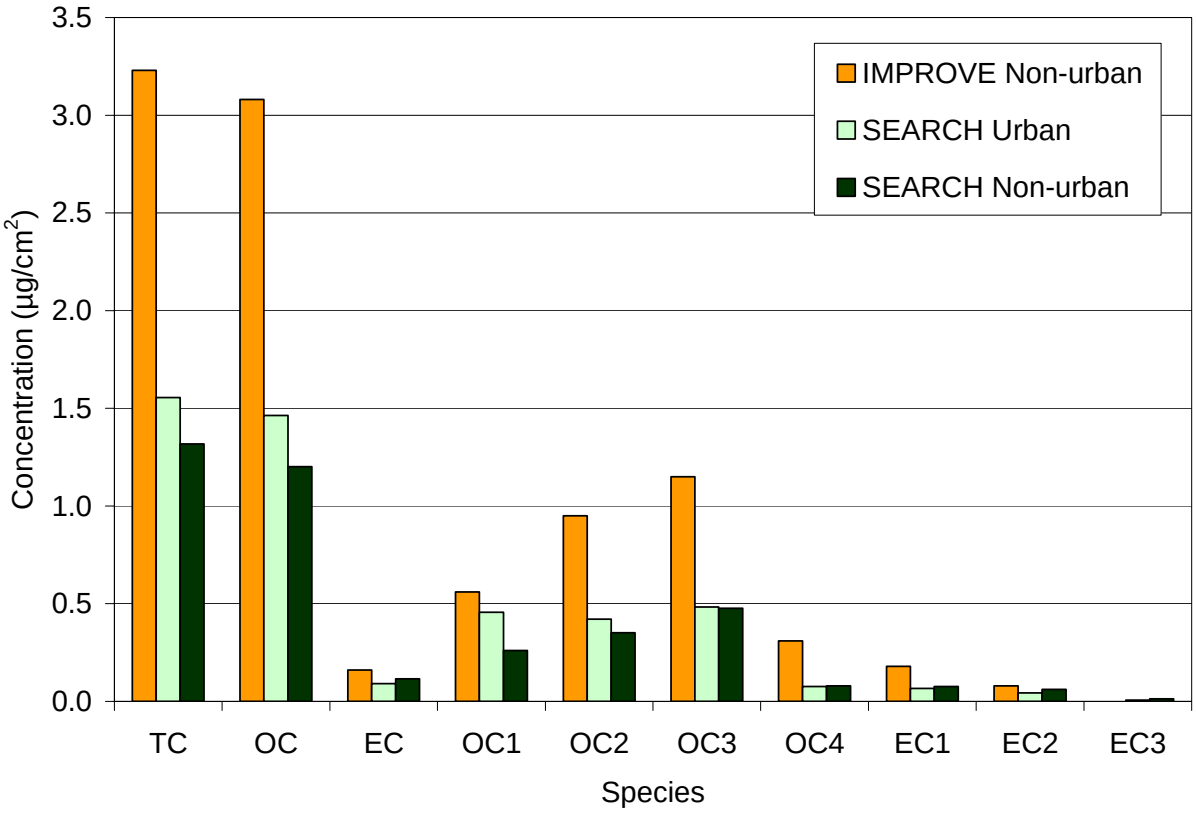

3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Concentration (µg/cm2)
IMPROVE Non-urban
SEARCH Urban
SEARCH Non-urban
TC
OC
EC
OC1
OC2
OC3
OC4
EC1
EC2
EC3
Species

Figure 5.

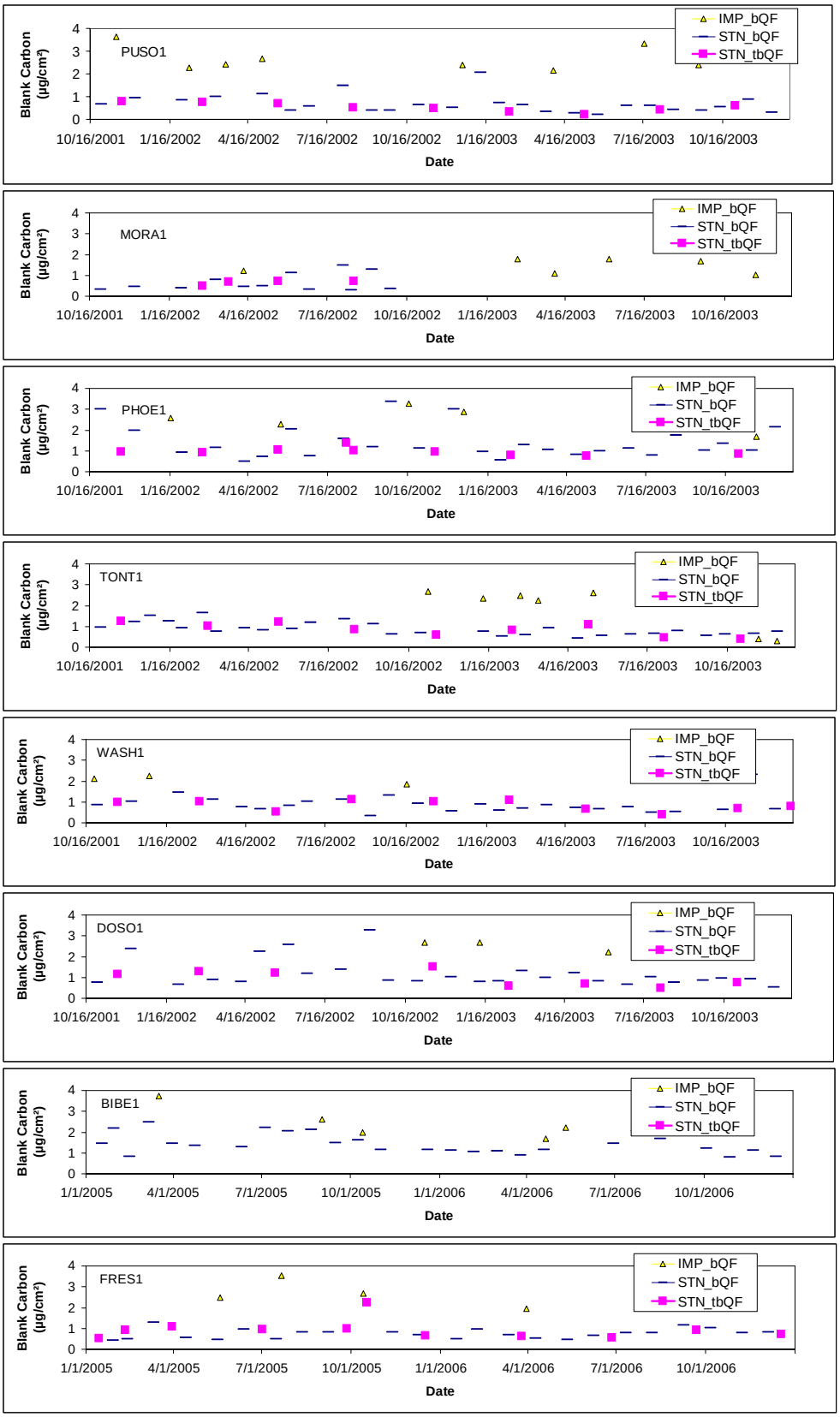

PUSO1
MORA1
PHOE1
TONT1
WASH1
DOSO1
BIBE1
FRES1
IMP_bQF
STN_bQF
STN_tbQF
Blank Carbon (µg/cm²)
Date
10/16/2001
1/16/2002
4/16/2002
7/16/2002
10/16/2002
1/16/2003
4/16/2003
7/16/2003
10/16/2003
1/1/2005
4/1/2005
7/1/2005
10/1/2005
1/1/2006
4/1/2006
7/1/2006
10/1/2006

Figure 6.

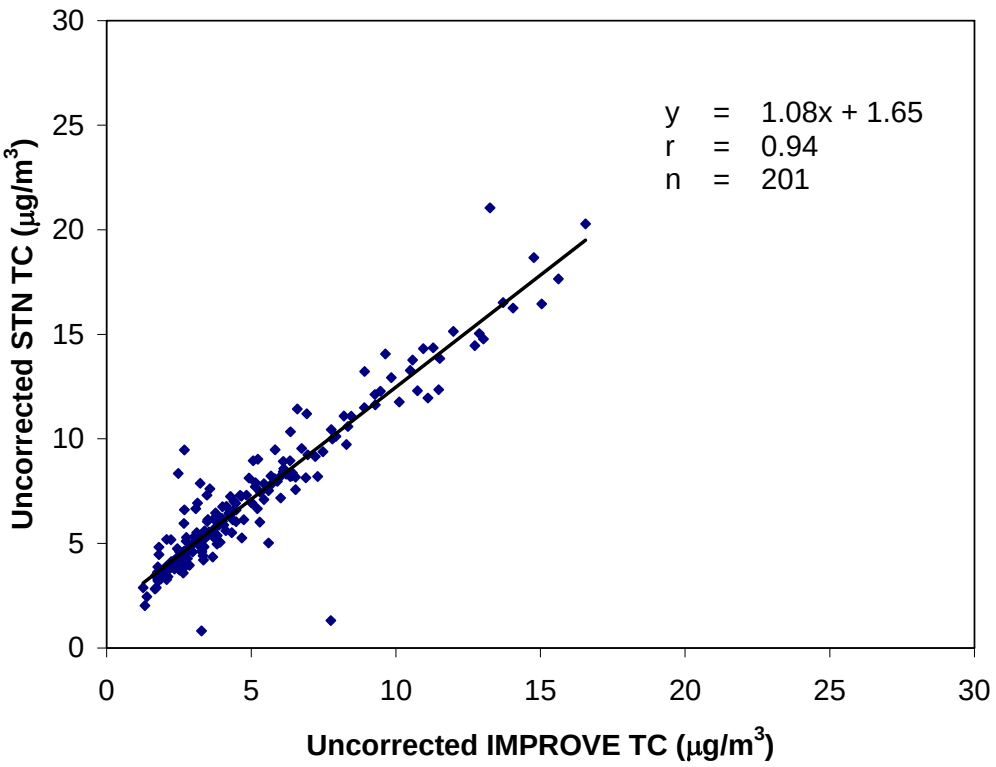

y = 1.08x + 1.65
r = 0.94
n = 201
Uncorrected STN TC (µg/m3)
Uncorrected IMPROVE TC (µg/m3)
0
5
10
15
20
25
30

Figure 7.

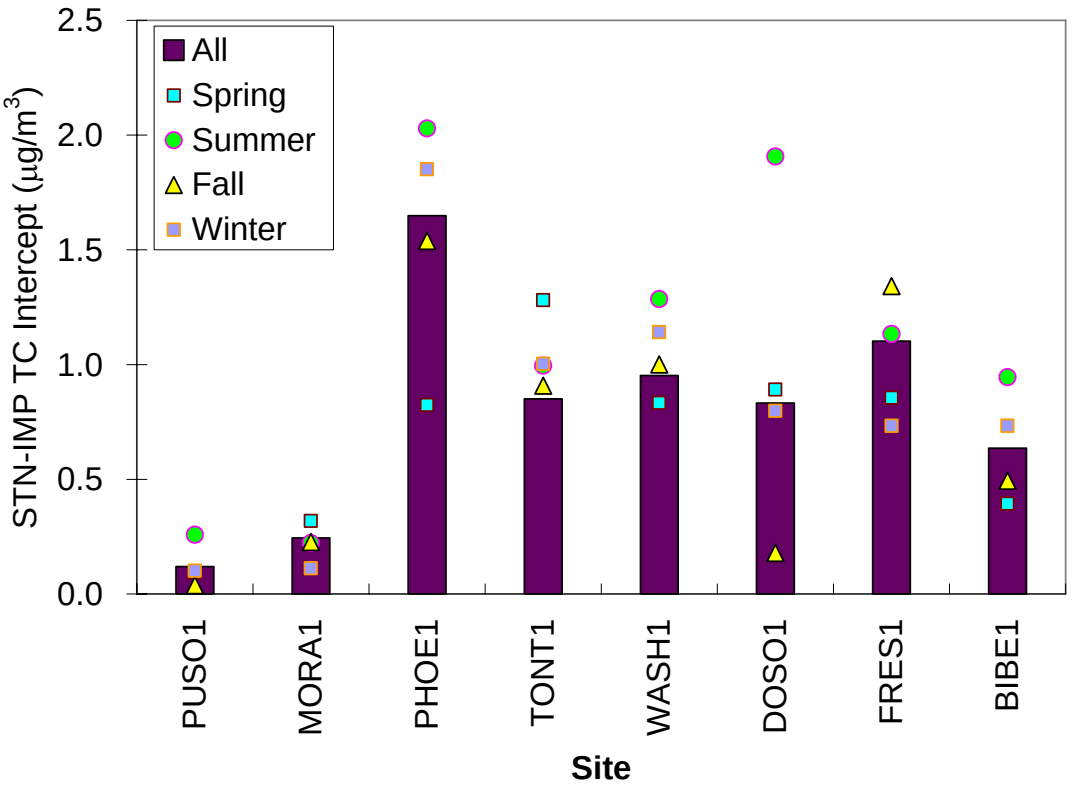

2.5
2.0
1.5
1.0
0.5
0.0
STN-IMP TC Intercept (µg/m3)
All
Spring
Summer
Fall
Winter
PUSO1
MORA1
PHOE1
TONT1
WASH1
DOSO1
FRES1
BIBE1
Site

Figure 8.