Quantification of PM$_{2.5}$ organic carbon sampling artifacts in US networks

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Abstract. Field blanks (bQF) and backup filters (quartz-fiber behind quartz-fiber filter; QBQ) have been adopted by US 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 the: 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 (µg/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 min) passive exposure period of STN/CSN and SEARCH bQF OC (0.8–1 µg/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 µg/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).

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; Lettis et al., 2001; Mader and Pankow, 2000, 2001a, b; 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 (bQF) subtraction, quartz-fiber backup filter (QBQ) adjustment, filter slicing (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\textsubscript{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 assumes that Teflon®-membrane filters are inert and their tendency to adsorb organic vapors is low. Teflon®-membrane filters are expected to have a minimal positive OC artifact, although their negative OC artifact might be larger than that of quartz-fiber filters.

In the US, the: 1) Interagency Monitoring of Protected Visual Environments (IMPROVE) 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\textsubscript{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, nearly 94% (170 sites) are located in National Parks and wilderness areas that represent different regions of the US. These sites are far away from population centers and local pollution sources, with a 100–1000 km zone of representation (40 CFR part 50; US EPA 2006a). Regional or non-urban PM\textsubscript{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 (US EPA, 1997; Chow et al., 2002c). The SEARCH network was designed to evaluate human exposure at urban versus rural environments in the southeastern US (Mississippi, Alabama, Georgia, and Florida). Figure 1 shows the sampling site locations, and Table 1 summarizes network characteristics relevant to the OC artifact.

IMPROVE artifact corrections using monthly median OC on QBQ (OC\textsubscript{QBQ}) at six sites (shown in Fig. 1) assume that vapors are adsorbed uniformly throughout the front (QF) and backup (QBQ) 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...
Table 1. Sampling protocols for carbon in the IMPROVE, STN/CSN, and SEARCH networks from 1 January 2005 to 31 December 2006.

<table>
<thead>
<tr>
<th>Network</th>
<th>IMPROVE</th>
<th>STN/CSN</th>
<th>URG MASS400/450</th>
<th>R&amp;P 2300</th>
<th>R&amp;P Partisol Plus 2025</th>
<th>SEARCH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sampler Type</td>
<td>Met One SASS</td>
<td>Andersen RAAS</td>
<td>2 single-channel modules</td>
<td>None</td>
<td>2 single-channel modules</td>
<td>PCM3</td>
</tr>
<tr>
<td>Number of channels</td>
<td>4 single-channel modules</td>
<td>4 channels (3 used)</td>
<td>2 single-channel modules</td>
<td>None</td>
<td>2 single-channel modules</td>
<td>3 channels</td>
</tr>
<tr>
<td>Carbon denuder</td>
<td>None</td>
<td>None</td>
<td>None</td>
<td>None</td>
<td>None</td>
<td>Activated carbon honeycomb</td>
</tr>
<tr>
<td>Inlet type</td>
<td>AHIH cyclone</td>
<td>SAASSCC sharp-cut cyclone</td>
<td>AIHL cyclone</td>
<td>Louvered inlet/WINS</td>
<td>25 mm Pall</td>
<td>Louvered inlet/WINS or VSCC</td>
</tr>
<tr>
<td>Filter holder and cassette types</td>
<td>Polycarbonate</td>
<td>Aluminum holder and Delrin® cassette</td>
<td>Teflon®-coated in-line holder preceded by a diffuser</td>
<td>Teflon®-coated aluminum holder and Teflon® support screens</td>
<td>25 mm Pall</td>
<td>Savillex-molded Teflon®</td>
</tr>
<tr>
<td>Sampling frequency</td>
<td>3rd day</td>
<td>3rd day</td>
<td>3rd day</td>
<td>3rd day</td>
<td>activated carbon honeycomb</td>
<td></td>
</tr>
<tr>
<td>Flow rate</td>
<td>22.8 L/min</td>
<td>6.7 L/min</td>
<td>7.3 L/min</td>
<td>16.7 L/min</td>
<td>10.0 L/min</td>
<td>16.7 L/min</td>
</tr>
<tr>
<td>Filter deposit area</td>
<td>3.53 cm²</td>
<td>11.76 cm²</td>
<td>11.76 cm²</td>
<td>11.76 cm²</td>
<td>11.76 cm²</td>
<td>11.76 cm²</td>
</tr>
<tr>
<td>Filter face velocity</td>
<td>107.2 cm/s</td>
<td>10.3 cm/s</td>
<td>10.3 cm/s</td>
<td>14.2 cm/s</td>
<td>23.6 cm/s</td>
<td>39.1 cm/s</td>
</tr>
<tr>
<td>Quartz-fiber filter pre-fire temperature and duration</td>
<td>900 °C for 4 h</td>
<td>900 °C for 3 h</td>
<td>900 °C for 3 h</td>
<td>900 °C for 3 h</td>
<td>900 °C for 3 h</td>
<td>900 °C for 3 h</td>
</tr>
<tr>
<td>Quartz filter type</td>
<td>25 mm Pall</td>
<td>47 mm Whatman</td>
<td>47 mm Whatman</td>
<td>47 mm Whatman</td>
<td>47 mm Whatman</td>
<td>37 mm Pall</td>
</tr>
<tr>
<td>Quartz filter pack configuration</td>
<td>PF or QBQ</td>
<td>PF</td>
<td>PF</td>
<td>PM₁₀</td>
<td>PF</td>
<td>Organic carbon denuder/QBQ</td>
</tr>
<tr>
<td>Sites with backup filters (QBQ)</td>
<td>6</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>Organic carbon denuder/QBQ</td>
</tr>
<tr>
<td>Passive deposition duration</td>
<td>7 days</td>
<td>2–3%</td>
<td>1–15 min</td>
<td>2–3%</td>
<td>3–15 min</td>
<td>5–7 days</td>
</tr>
<tr>
<td>Laboratory blank frequency</td>
<td>2%</td>
<td>2–3%</td>
<td>1–15 min</td>
<td>2–3%</td>
<td>3–15 min</td>
<td>1–15 min</td>
</tr>
<tr>
<td>Trip blank frequency</td>
<td>3%</td>
<td>3%</td>
<td>3%</td>
<td>3%</td>
<td>0%</td>
<td>0%</td>
</tr>
<tr>
<td>Field blank frequency</td>
<td>2%</td>
<td>10%</td>
<td>10%</td>
<td>10%</td>
<td>10%</td>
<td>10%</td>
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<tr>
<td>Field blank analysis frequency</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
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<tr>
<td>Backup filter analysis frequency</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>NA</td>
</tr>
<tr>
<td>Sample shipping method</td>
<td>Second day cardboard box with ice pack</td>
<td>Priority overnight cooler with ice pack</td>
<td>Priority overnight cooler with ice pack</td>
<td>Priority overnight cooler with ice pack</td>
<td>Priority overnight cooler with ice pack</td>
<td>Standard overnight cooler with ice pack</td>
</tr>
<tr>
<td>Temperature for sample storage</td>
<td>4 °C</td>
<td>&lt; −15 °C</td>
<td>&lt; −15 °C</td>
<td>&lt; −15 °C</td>
<td>&lt; −15 °C</td>
<td>4 °C</td>
</tr>
<tr>
<td>Number of sites (2006)</td>
<td>181</td>
<td>179</td>
<td>18</td>
<td>6</td>
<td>14</td>
<td>22</td>
</tr>
</tbody>
</table>

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a Networks 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 MerOne 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 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] west 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 PM₂₅ through an Air and Industrial Hygiene Laboratory (AIHL) cyclone followed by a 25 mm Teflon®-membrane filter analyzed for mass by gravimetry and for elements by X-ray fluorescence (XRF). Module B collects PM₂₅ through a sodium carbonate denuder (Ashbaugh et al., 2004) followed by an AIHL cyclone and a 37 mm nylon-membrane filter analyzed by ion chromatography (IC) for nitrate (NO₃⁻) and sulfate (SO₄²⁻). Module C collects PM₂₅ through an AIHL cyclone followed by a 37 mm Pall quartz-fiber filter for OC and EC by the IMPROVE/A thermal/optical reflectance (TOR) protocol. Module D collects through a louvered PM₁₀ inlet at 16.7 L/min followed by a 25 mm Pall Teflon®-membrane filter for mass by gravimetry.

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A thermal/optical reflectance (TOR) protocol (Chow et al., 2007). Module D collects through a louvered PM₁₀ inlet at 16.7 L/min followed by a 25 mm Pall Teflon®-membrane filter for mass by gravimetry.
Table 1. Continued.

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, 2010). 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 contains a Whatman Teflon®-membrane filter for anion and cation analyses by IC; Channel 3 contains a Whatman QMA quartz-fiber filter for OC and EC by the STN thermal/optical transmittance (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 that is mass by gravimetry, elements by XRF, and cations and anions by IC; Channel 2 contains a Whatman Teflon®-membrane filter that is mass by gravimetry and elements by XRF, followed by a Nylasorb nylon-membrane filter for total NO–3 by IC, followed by a fourth filter for anions and cations by IC. Channel 3 contains a louver filter for mass by gravimetry and elements by XRF, followed by a Nylasorb nylon-membrane filter for total NO–3 by IC.

URG MASS (URG, Chapel Hill, NC): Uses two parallel modules with 47 mm filters operating at 16.7 L/min. Module 1 contains a Whatman PM10 inlet followed by a PM2.5 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 PM10 inlet followed by a WINS PM2.5 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 modules are available that can be programmed to operate in parallel or sequentially. The non-trends CSN sites in Texas use four parallel channels with 47 mm diameter filters. Module 1 contains a Whatman Teflon®-membrane filter with 16.7 L/min for mass by gravimetry and elements by XRF; Module 2 contains an additional Teflon®-membrane filter for anion and cation analyses by IC; Module 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; Module 4 contains a sodium carbonate-coated honeycomb denuder followed by a Whatman Nylasorb nylon-membrane filter at a flow rate of 7.3 L/min for total NO–3 by IC.

R&P Partisol Plus 2025 Sequential Federal Reference Method (FRM; 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 PM10 inlet followed by a sharp cut cyclone PM2.5 inlet. Module 1 contains a Pall Teflon®-membrane filter for mass by gravimetry, elements by XRF, and cations and anions by IC. 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 PM10 cyclone followed by a PM2.5 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 cyclone acid-coated annular denuder, then followed by a three-stage filter pack 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 Teflon®-membrane filter for volatilized NH+4 by automated colorimetry (AC). Channel 2 contains a sodium carbonate-coated annular denuder followed by a cyclone 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 PM10 cyclone, followed by an activated carbon honeycomb denuder to remove carbon vapors, then through a WINS PM2.5 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).

All inlets are made of anodized aluminum.

Field blank (bBFQ) usually in samplers for 1–15 min, but in some cases for as long as 5–7 days.

Based on the assumption of once per week site visits.

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

Trip blanks (tBFQ) accompany batches of shipped filters but are not removed from their storage containers.

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 time as the sampled filters.
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 applied 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\textsubscript{QBQ} measurements in the IMPROVE network were \textasciitilde 19\% higher than OC on bQF (OC\textsubscript{bQF}) levels, but this difference is within the standard deviation of the average (Watson et al., 2009). The fact that levels of OC\textsubscript{QBQ} and OC\textsubscript{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\textsubscript{QBQ} from an urban site (Fort Meade, MD) contained twice the levels of OC\textsubscript{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, bQF, trip blank (tbQF), and QBQ filter 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 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., MetOne SASS, Andersen RAAS, or URG MASS). 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\textsubscript{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\textsuperscript{2} (IMPROVE) to 11.78 cm\textsuperscript{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) 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\textsuperscript{2} and 0±0.02 µg EC/cm\textsuperscript{2} for Pallflex® quartz-fiber filters, and 0.10±0.10 µg OC/cm\textsuperscript{2} and 0±0.01 µg EC/cm\textsuperscript{2} for Whatman QMA quartz-fiber filters. Approximately 2–3\% of laboratory blanks are maintained for each network. Acceptance criteria are <2.0, 1.5, and 0.5 µg/cm\textsuperscript{2} for TC, OC, and EC, respectively, in the IMPROVE and SEARCH networks, and <1 µg/cm\textsuperscript{2} for TC in STN/CSN.

STN/CSN collects 3\% trip blanks, 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: \textasciitilde 2\% of sample filters for IMPROVE, \textasciitilde 10\% for STN/CSN sites and SEARCH, and \textasciitilde 10–25\% for R&P 2025 sites in Texas. The passive period for bQF has been 1–15 min for STN/CSN and SEARCH, and \textasciitilde 7 days for IMPROVE and R&P 2025 sites in Texas 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,

\[
OC_{\text{artifactcorrected}} = OC_{\text{QF}} + OC_{\text{QBQ}} - 2OC_{\text{bQF}}
\]

where:

- \(OC_{\text{QF}} = \) Quartz-fiber front filter OC
- \(OC_{\text{QBQ}} = \) Quartz-fiber behind quartz-fiber filter OC
- \(OC_{\text{bQF}} = \) field blank OC from the quartz-fiber front filter

To compare carbon measurements between the IMPROVE network and STN/CSN, collocated PM2.5 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, DC 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 \([\text{NO}_3^-]\) and sulfate \([\text{SO}_4^{2-}]\)) and carbon measurements are included. Prior to May 2007, the STN/CSN used a customized thermal/oxidation transmittance (STN TOT) carbon analysis protocol (Peterson and Richards, 2002) while the IMPROVE-\text{A} and SEARCH networks followed the IMPROVE thermal/photolysis 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 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 (µg/cm²) and ambient concentration equivalents (µg/m³), based on exposed filter areas and 24 h sample volumes for each instrument, respectively. EC values are at or near minimum detection limits (i.e., 0.06 µg/cm²), 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, http://www.atmos-chem-phys.net/10/5223/2010/acp-10-5223-2010-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, 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 µg/cm²) are 2.5 to 3 times those of the other networks (i.e., 0.97±0.27 µg/cm² for STN/CSN and 0.81±0.61 µg/cm² 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 min 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 µg/m³) than for IMPROVE (0.26±0.05 µg/m³) and SEARCH (0.24±0.18 µg/m³) 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 exposed area of the filter deposit (11.76 cm² for SASS, compared to 3.53 cm² for IMPROVE and 7.12 cm² for SEARCH).

Figure 2 shows that most of the site average OC_{bQF} areal densities are 2–2.5 µg/cm² for IMPROVE, 0.5–1 µg/cm² for STN/CSN, and <0.5 µg/cm² for SEARCH. For STN/CSN, average OC_{bQF} varies more than twofold among sampler types, from 0.74±0.66 µg/cm² (URG MASS) to 1.49±0.8 µg/cm² (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 µg/cm²). The greased inlet impaction plate and variable passive exposure periods (e.g., minutes to 7 days) for the R&P 2300 may affect OC_{bQF} levels. Detailed records of bQF exposure periods are not available.

There were 3628 bQF and 2335 tbQF acquired in STN/CSN during 2005 and 2006. Average areal
Table 2. Collocated IMPROVE and STN/CSN PM$_{2.5}$ speciation data from 16 October 2001 to 31 December 2006.

<table>
<thead>
<tr>
<th>Type</th>
<th>Site Name</th>
<th>Inclusive Period</th>
<th>Number of Samples</th>
<th>Module Sampler</th>
<th>C # of Blanks</th>
<th>MetOne SASS</th>
<th>Anderson RAAS</th>
<th>URG MASS</th>
<th>R&amp;P 2025 # of Field Blanks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Special Study</td>
<td>Puget Sound (PUSO), Seattle</td>
<td>16/10/2001–29/12/2003</td>
<td>224</td>
<td>X</td>
<td>8</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(Beacon Hill, WA)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mount Rainier NP (MORA), WA</td>
<td>16/10/2001–01/11/2002</td>
<td>69</td>
<td>X</td>
<td>6</td>
<td>X</td>
<td></td>
<td></td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>Phoenix (PHOE), AZ</td>
<td>16/10/2001–29/12/2003</td>
<td>201</td>
<td>X</td>
<td>6</td>
<td>X</td>
<td></td>
<td></td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>Tonto National Monument (TONT), AZ</td>
<td>16/10/2001–29/12/2003</td>
<td>181</td>
<td>X</td>
<td>8</td>
<td>X</td>
<td></td>
<td></td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>Washington DC (WASH)</td>
<td>16/10/2001–29/12/2003</td>
<td>206</td>
<td>X</td>
<td>5</td>
<td>X</td>
<td></td>
<td></td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>Dolly Sods Wilderness (DOSO), WA</td>
<td>16/10/2001–29/12/2003</td>
<td>140</td>
<td>X</td>
<td>5</td>
<td>X</td>
<td></td>
<td></td>
<td>26</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>1021</td>
<td>38</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>142</td>
</tr>
<tr>
<td>Long-term Sites</td>
<td>Fresno (FRES), CA</td>
<td>01/01/2005–31/12/2006</td>
<td>227</td>
<td>X</td>
<td>7</td>
<td>X</td>
<td></td>
<td></td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>Big Bend NP (BIBE), TX</td>
<td>01/01/2005–31/12/2006</td>
<td>81</td>
<td>X</td>
<td>7</td>
<td>X</td>
<td></td>
<td></td>
<td>15</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>308</td>
<td>14</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>33</td>
</tr>
</tbody>
</table>

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.

<table>
<thead>
<tr>
<th>Network</th>
<th>Filter Type</th>
<th>Type of PM$_{2.5}$ Specimen Sampler</th>
<th>Site Count</th>
<th>No. of Blanks</th>
<th>Field OC</th>
<th>EC</th>
<th>TC</th>
<th>OC</th>
<th>EC</th>
</tr>
</thead>
<tbody>
<tr>
<td>IMPROVE</td>
<td>bQF</td>
<td>IMPROVE Module C</td>
<td>181</td>
<td>886</td>
<td>2.41 ± 0.48</td>
<td>2.37 ± 0.45</td>
<td>0.04 ± 0.05</td>
<td>0.26 ± 0.05</td>
<td>0.26 ± 0.05</td>
</tr>
<tr>
<td>STN/CSN</td>
<td>bQF</td>
<td>IMPROVE Module C</td>
<td>6</td>
<td>1401</td>
<td>3.23 ± 0.96</td>
<td>3.08 ± 0.83</td>
<td>0.16 ± 0.13</td>
<td>0.35 ± 0.1</td>
<td>0.33 ± 0.09</td>
</tr>
<tr>
<td></td>
<td>bQF</td>
<td>All Samples</td>
<td>239</td>
<td>3628</td>
<td>0.97 ± 0.27</td>
<td>0.95 ± 0.25</td>
<td>0.02 ± 0.03</td>
<td>1.03 ± 0.21</td>
<td>1.01 ± 0.21</td>
</tr>
<tr>
<td></td>
<td>bQF</td>
<td>Andersen RAAS</td>
<td>22</td>
<td>249</td>
<td>0.88 ± 0.33</td>
<td>0.88 ± 0.33</td>
<td>0.01 ± 0.03</td>
<td>0.99 ± 0.38</td>
<td>0.98 ± 0.37</td>
</tr>
<tr>
<td></td>
<td>bQF</td>
<td>MetOne SASS</td>
<td>185</td>
<td>2,572</td>
<td>0.86 ± 0.39</td>
<td>0.85 ± 0.38</td>
<td>0.01 ± 0.05</td>
<td>1.05 ± 0.47</td>
<td>1.04 ± 0.47</td>
</tr>
<tr>
<td></td>
<td>bQF</td>
<td>URG MASS</td>
<td>7</td>
<td>150</td>
<td>0.75 ± 0.66</td>
<td>0.74 ± 0.66</td>
<td>0.02 ± 0.02</td>
<td>0.37 ± 0.32</td>
<td>0.36 ± 0.32</td>
</tr>
<tr>
<td></td>
<td>bQF</td>
<td>R&amp;P 2300 Sequential Speciation</td>
<td>15</td>
<td>236</td>
<td>1.33 ± 0.52</td>
<td>1.3 ± 0.51</td>
<td>0.03 ± 0.11</td>
<td>1.09 ± 0.42</td>
<td>1.06 ± 0.41</td>
</tr>
<tr>
<td></td>
<td>bQF</td>
<td>R&amp;P 2025 Sequential FRM</td>
<td>24</td>
<td>421</td>
<td>1.57 ± 0.77</td>
<td>1.49 ± 0.76</td>
<td>0.08 ± 0.12</td>
<td>0.78 ± 0.38</td>
<td>0.73 ± 0.37</td>
</tr>
<tr>
<td></td>
<td>bQF</td>
<td>All Samples</td>
<td>239</td>
<td>2335</td>
<td>0.98 ± 0.26</td>
<td>0.95 ± 0.23</td>
<td>0.02 ± 0.03</td>
<td>0.89 ± 0.33</td>
<td>0.87 ± 0.32</td>
</tr>
<tr>
<td></td>
<td>bQF</td>
<td>Andersen RAAS</td>
<td>22</td>
<td>241</td>
<td>0.84 ± 0.38</td>
<td>0.83 ± 0.34</td>
<td>0.01 ± 0.05</td>
<td>0.94 ± 0.42</td>
<td>0.93 ± 0.38</td>
</tr>
<tr>
<td></td>
<td>bQF</td>
<td>MetOne SASS</td>
<td>185</td>
<td>1832</td>
<td>0.89 ± 0.45</td>
<td>0.88 ± 0.45</td>
<td>0.01 ± 0.03</td>
<td>1.09 ± 0.56</td>
<td>1.08 ± 0.55</td>
</tr>
<tr>
<td></td>
<td>bQF</td>
<td>URG MASS</td>
<td>7</td>
<td>159</td>
<td>0.81 ± 0.70</td>
<td>0.80 ± 0.69</td>
<td>0.01 ± 0.03</td>
<td>0.4 ± 0.34</td>
<td>0.39 ± 0.34</td>
</tr>
<tr>
<td></td>
<td>bQF</td>
<td>R&amp;P 2300 Sequential Speciation</td>
<td>15</td>
<td>103</td>
<td>1.36 ± 0.48</td>
<td>1.30 ± 0.48</td>
<td>0.06 ± 0.16</td>
<td>1.11 ± 0.39</td>
<td>1.06 ± 0.39</td>
</tr>
<tr>
<td></td>
<td>bQF</td>
<td>R&amp;P 2025 Sequential FRM</td>
<td>24</td>
<td>0</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>SEARCH</td>
<td>bQF</td>
<td>PCR Module C</td>
<td>8</td>
<td>144</td>
<td>0.81 ± 0.61</td>
<td>0.76 ± 0.57</td>
<td>0.04 ± 0.06</td>
<td>0.24 ± 0.18</td>
<td>0.23 ± 0.17</td>
</tr>
<tr>
<td></td>
<td>bQF</td>
<td>PCR Module C</td>
<td>8</td>
<td>257</td>
<td>1.29 ± 0.52</td>
<td>1.19 ± 0.52</td>
<td>0.01 ± 0.06</td>
<td>0.38 ± 0.15</td>
<td>0.35 ± 0.15</td>
</tr>
</tbody>
</table>

* 253 if counting 14 sites where sampler type changed between 1 January 2005 and 31 December 2006; a: Data is not available. c: Carbon analysis follows the IMPROVE A thermal/reflectance (TOR) protocol (Chow et al., 2007) for the IMPROVE and SEARCH network and the STN thermal/reflectance (TOR) protocol (Chu et al., 2004; Peterson and Richards, 2002) for STN/CSN. d: Areal density on filters in µg/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, except 11.76 cm$^2$ for R&P 2300 and R&P 2025 samplers, and 7.12 cm$^2$ for SEARCH PCMs as noted in Table 1). e: Equivalent ambient concentration in µg/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).

densities are the same: 0.95 ± 0.25 µg/cm$^2$ for OC$_{bQF}$ and 0.95 ± 0.23 µg/cm$^2$ for OC$_{tbQF}$. OC$_{bQF}$ and OC$_{tbQF}$ are also similar for a given sampler type, agreeing within ±0.05 µg/cm$^2$ (Table 3). Trip blanks (tbQF) 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 hypothesis (H1) that the short tbQF exposure period (1–15 min) is insufficient to represent the passively adsorbed VOCs experienced by the sample filters.

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Field blank organic carbon (OC\textsubscript{bQF}) concentration density (µg/cm\textsuperscript{2}) for: (a) 181 IMPROVE sites, (b) 239 STN/CSN sites, and (c) eight 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).

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

Average ambient-equivalent OC\textsubscript{bQF} concentrations are similar: 0.33±0.09 µg/m\textsuperscript{3} for IMPROVE and 0.35±0.15 µg/m\textsuperscript{3} for SEARCH. These levels are 30–50% higher than OC\textsubscript{bQF} of 0.26±0.05 and 0.23±0.17 µg/m\textsuperscript{3} for IMPROVE and SEARCH, respectively, but ~65% lower than OC\textsubscript{QF} of 1.01±0.21 µg/m\textsuperscript{3} for all sampler types) found in the STN/CSN sites.

Figure 3 shows that OC\textsubscript{QF} seasonal variations are most apparent for the IMPROVE network, varying by more than 40% from winter (1.97±0.61 µg/cm\textsuperscript{2}) to summer (2.92±0.78 µg/cm\textsuperscript{2}). There are no apparent changes in fractional contributions of the IMPROVE thermal carbon fractions among the four seasons. Seasonal variations of OC\textsubscript{bQF} 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\textsubscript{bQF} spans 0.8–1.1 µg/cm\textsuperscript{2} and 0.52–1.0 µg/cm\textsuperscript{2}, respectively.

Figure 4 shows little difference between urban and non-urban IMPROVE OC\textsubscript{bQF}, but SEARCH OC\textsubscript{bQF} is 17% higher at non-urban compared to urban sites. Average OC\textsubscript{QF} for the SEARCH samples was ~28% higher at the urban (1.51±1.50 µg/cm\textsuperscript{2}) compared to non-urban (1.18±0.98 µg/cm\textsuperscript{2}) sites (Fig. 5). The urban increment for OC\textsubscript{bQF} is mostly in the OC1 fraction, which is 2.4 times higher at urban than at non-urban sites (0.51±0.84 vs. 0.21±0.35 µg/cm\textsuperscript{2}). OC2 is ~11% higher (0.42±0.37 vs. 0.38±0.48 µg/cm\textsuperscript{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\textsubscript{bQF} levels from the six non-urban IMPROVE sites (3.1±0.8 µg/cm\textsuperscript{2}) are 2.6 times higher than OC\textsubscript{bQF} from the four non-urban SEARCH sites (1.18±0.98 µg/cm\textsuperscript{2}), consistent with the denuder removing adsorbable organic vapors.

Blank TC areal densities in Fig. 6 show that STN/CSN TQF TC (i.e., TC\textsubscript{bQF}) areal densities are similar for urban and non-urban sites, but they differ among samplers, consistent with two-year average TQF levels in Table 3. Using the URG MASS sampler, Table 4 shows TC\textsubscript{bQF} areal densities at the Seattle and Mount Rainier sites are 0.53±0.19 and 0.67±0.12 µg/cm\textsuperscript{2}, respectively, lower than the 0.84–1.12 µg/cm\textsuperscript{2} found at sites using the Andersen RAAS or MetOne SASS samplers. TC\textsubscript{QF} and TC\textsubscript{bQF} levels
**Fig. 3.** Seasonal variations of blanks among: (a) IMPROVE field blanks (OC\textsubscript{bQF}), (b) IMPROVE backup filters (OC\textsubscript{bQBQ}; six sites), (c) STN/CSN field blanks (OC\textsubscript{bQF}), (d) STN/CSN trip blanks (OC\textsubscript{tQF}), (e) SEARCH denuded field blanks (OC\textsubscript{dQF}), and (f) SEARCH denuded backup filters (OC\textsubscript{dQBQ}; eight sites). IMPROVE\textsubscript{A} protocol 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\textsubscript{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.

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

<table>
<thead>
<tr>
<th>Site Code</th>
<th>Site Name</th>
<th>Instrument Used</th>
<th>Number of Pairs</th>
<th>IMPROVE-STN QF (µg/cm\textsuperscript{2})</th>
<th>IMP\textsubscript{bQF}\textsuperscript{a} (µg/cm\textsuperscript{2})</th>
<th>IMP\textsubscript{bQBQ}\textsuperscript{b} (µg/cm\textsuperscript{2})</th>
<th>STN\textsubscript{bQF}\textsuperscript{a} (µg/cm\textsuperscript{2})</th>
<th>STN\textsubscript{bQBQ}\textsuperscript{b} (µg/cm\textsuperscript{2})</th>
<th>STN\textsubscript{tQF}\textsuperscript{b} (µg/cm\textsuperscript{2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>PUSO</td>
<td>Seattle, WA</td>
<td>URG MASS</td>
<td>224</td>
<td>2.66 ± 0.54</td>
<td>8</td>
<td>0.68 ± 0.41</td>
<td>25</td>
<td>0.53 ± 0.19</td>
<td>9</td>
</tr>
<tr>
<td>MORA</td>
<td>Mount Rainier, WA</td>
<td>URG MASS</td>
<td>69</td>
<td>1.44 ± 0.36</td>
<td>6</td>
<td>0.66 ± 0.42</td>
<td>12</td>
<td>0.67 ± 0.12</td>
<td>4</td>
</tr>
<tr>
<td>PHOE</td>
<td>Phoenix, AZ</td>
<td>MetOne SASS</td>
<td>201</td>
<td>2.63 ± 0.58</td>
<td>6</td>
<td>1.40 ± 0.77</td>
<td>26</td>
<td>1.12 ± 0.50</td>
<td>10</td>
</tr>
<tr>
<td>TONT</td>
<td>Tonto Monument, AZ</td>
<td>MetOne SASS</td>
<td>181</td>
<td>2.00 ± 1.05</td>
<td>8</td>
<td>0.87 ± 0.31</td>
<td>28</td>
<td>0.86 ± 0.32</td>
<td>9</td>
</tr>
<tr>
<td>WASH</td>
<td>Washington DC</td>
<td>Andersen RAAS</td>
<td>206</td>
<td>2.49 ± 0.87</td>
<td>5</td>
<td>0.87 ± 0.40</td>
<td>25</td>
<td>0.84 ± 0.26</td>
<td>10</td>
</tr>
<tr>
<td>DOSO</td>
<td>Dolly Soda, WV</td>
<td>Andersen RAAS</td>
<td>140</td>
<td>2.57 ± 0.31</td>
<td>5</td>
<td>1.18 ± 0.68</td>
<td>26</td>
<td>0.97 ± 0.38</td>
<td>8</td>
</tr>
<tr>
<td>FRES</td>
<td>Fresno, CA</td>
<td>MetOne SASS</td>
<td>227</td>
<td>2.58 ± 0.50</td>
<td>7</td>
<td>0.74 ± 0.23</td>
<td>18</td>
<td>0.94 ± 0.48</td>
<td>11</td>
</tr>
<tr>
<td>BIBE</td>
<td>Big Bend National Park, TX</td>
<td>R&amp;P 2025 Sequential FRM</td>
<td>81</td>
<td>2.40 ± 0.68</td>
<td>7</td>
<td>1.44 ± 0.48</td>
<td>15</td>
<td>N/A ± N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Carbon analysis follows the IMPROVE\textsubscript{A} thermal/optical reflectance (TOR) protocol (Chow et al., 2007a) for the IMPROVE network. \textsubscript{bQF} is quartz-fiber filter field blank.

\textsuperscript{b} Carbon analysis follows the STN thermal/optical transmittance (TOT) protocol (Chu et al., 2004) for STN/CSN. \textsubscript{bQBQ} is quartz-filter trip blank.
Fig. 4. Comparison of field blank (bQF) carbon fraction 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 11 urban and 170 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); Phoenix, AZ (PHOE1); Pittsburgh (PITT1); 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).

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 PalliFlex® 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 DC, and Fresno), ranging from 2.5–2.7 μg/cm², with lower areal densities measured at two non-urban sites: Mount Rainier National Park (1.4±0.4 μg/cm²) and Tonto National
Monument (2.0±1.1 µg/cm²). 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/cm² (Big Bend using R&P 2025). 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/m³) at each collocated IMPROVE and STN/CSN site are within ±30–50% of each other. STN/CSN site-averaged TC areal densities (µg/cm²) 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 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/m³ or 1.34 µg/cm² (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.

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 the eight sites, the intercept is largest during spring, with values ranging from 0.22–2.03 µg/m³. 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/cm²) and Big Bend (1.29 µg/cm²) sites using the MetOne SASS and R&P 2025 samplers, respectively, while the lowest two are found at the Seattle (0.24 µg/cm²) and Mount Rainier (0.50 µg/cm²) 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/cm²) can be expressed as:

\[
TC_{STN} = TC_{STN_{art}} + b \times TC_{IMP}
\]

where the intercept, TC_{STN_{art}} in µg/cm², 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 Sods 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/cm²; 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 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. Total carbonaceous mass (TCM) was calculated by subtracting NO₃⁻, SO₄²⁻, ammonium (NH₄⁺), an estimate for water (H₂O), and crustal components from the measured PM₂.₅ mass. The calculated OCM is derived by subtracting measured EC from TCM:

\[
\text{TCM} = \text{PM}_2.5 - (\text{SO}_4^{2-} + \text{Retained NO}_3^- + \text{NH}_4^+ + \text{H}_2\text{O}) + \text{Crustal Material} + \text{Blank} \\
\text{OCM} = \text{TCM} - \text{EC} \\
\text{where:} \\
\text{Crustal Material} = 3.73 \times \text{Si} + 1.63 \times \text{Ca} + 2.42 \times \text{Fe} + 1.94 \times \text{Ti}
\]

Blank = 0.3 – 1.5 µg/m³ for STN/CSN; 0 for IMPROVE

All IMPROVE data were blank-subtracted (in µg/m³). For STN/CSN, a nominal OC(bQF) value of 0.3–1.5 µg/m³ 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/m³ at the Seattle, Phoenix, and Washington DC sites; OC(bQF) for the Fresno site were not available. Retained NO₃⁻ 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):

\[
\text{OCM} = X \times \text{OC}
\]

where:

\[
X = \text{unmeasured element multiplier (assumed to be 1.4 for fresh and 1.8 for aged aerosol)} \\
\text{OC} = \text{measured particulate organic carbon}
\]
For IMPROVE samples, average OCM concentrations are 3.99±2.96 µg/m³, 4.40±3.45 µg/m³, 3.00±3.16 µg/m³, and 6.73±3.56 µg/m³ 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 for the IMPROVE samples 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 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 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.

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 (~7 days) 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 TChqf (or OCqf) areal density ranges from 2.0 to 2.5 µg/cm², while STN/CSN and SEARCH field blanks are close to or below 1 µg/cm². STN/CSN field and trip blank TC and OC concentrations are similar (~0.95±0.23 µg/cm²), within ±5% for site averages. Among the five STN/CSN samplers, URG MASS reports the lowest OCqf levels.

Regression analysis using uncorrected TC from collocated IMPROVE-STN/CSN samples show higher STN/CSN than IMPROVE areal densities (µg/cm²) artifact at the same site. Without blank correction, STN/CSN sampling artifacts in µg/m³ 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, indicating that STN/CSN field blanks underrepresent the organic artifact by ~20–30% (assuming IMPROVE bQF fully represents the artifact), but the number of bQF available for comparison was limited.

QBQ filters stay in the field for more than 24 hours with filtered air drawn through them for 24 hours. With a similar level of sampling artifact in areal density (µg/cm²), STN/CSN and SEARCH TC (or OC) concentration (µg/m³) would be more influenced than those of IMPROVE due to smaller sampling volumes and larger filter sizes. The average OCqf concentration is 0.33±0.1 µg/m³ for IMPROVE and 0.35±0.15 µg/m³ for SEARCH (with proceeding denuder).

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

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 OCqf was ~25% higher at the urban sites, with 1.5±1.50 µg/cm² at urban sites and 1.18±0.98 µg/cm² at the non-urban sites in the SEARCH network. The increments between the urban and non-urban sites were ~2.6 times for OC1 and 11% for OC2. The majority of this low temperature OC is gaseous VOCs. However, during the collocated IMPROVE-STN/CSN comparisons, TChqf 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) assumes PM2.5 mass closure, but many species are not measured on Teflon®-membrane filters, including carbon, NO−3, SO−4, and NH4+. 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.
Table 7. Estimates of organic carbon mass (OCM) based on the SANDWICH method for the four collocated IMPROVE/STN sites.

<table>
<thead>
<tr>
<th>Site Type</th>
<th>Site Code</th>
<th>Number of Collocated Pairs</th>
<th>Sampler Type</th>
<th>Sampling Period</th>
<th>SANDWICH OCM µg/m³</th>
<th>Measured OC µg/m³</th>
<th>Measured OC × 1.4/OCM</th>
<th>Measured OC × 1.8/OCM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Urban</td>
<td>PUSO</td>
<td>354</td>
<td>IMPROVE</td>
<td>12/07/2001–29/12/2004</td>
<td>3.99±2.96</td>
<td>2.70±2.06</td>
<td>95%</td>
<td>122%</td>
</tr>
<tr>
<td>Urban</td>
<td>PHOE</td>
<td>290</td>
<td>IMPROVE</td>
<td>28/04/2001–30/09/2004</td>
<td>4.40±3.45</td>
<td>3.13±2.27</td>
<td>100%</td>
<td>128%</td>
</tr>
<tr>
<td>Urban</td>
<td>WASH</td>
<td>45</td>
<td>IMPROVE</td>
<td>08/07/2004–29/12/2004</td>
<td>3.00±3.16</td>
<td>2.63±1.51</td>
<td>123%</td>
<td>158%</td>
</tr>
<tr>
<td>Urban</td>
<td>FRES</td>
<td>27</td>
<td>IMPROVE</td>
<td>03/09/2004–23/12/2004</td>
<td>6.73±3.56</td>
<td>3.42±1.66</td>
<td>71%</td>
<td>91%</td>
</tr>
<tr>
<td>Urban</td>
<td>FRES</td>
<td>27</td>
<td>IMPROVE</td>
<td>03/09/2004–23/12/2004</td>
<td>6.73±3.56</td>
<td>3.42±1.66</td>
<td>71%</td>
<td>91%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sampler Type</th>
<th>URG MASS</th>
<th>MeCone SASS</th>
<th>Andersen RAAS</th>
<th>MetOne SASS</th>
</tr>
</thead>
<tbody>
<tr>
<td>SANDWICH OCM µg/m³</td>
<td>4.63±3.27</td>
<td>4.48±3.62</td>
<td>4.85±5.14</td>
<td>7.66±4.37</td>
</tr>
<tr>
<td>Average</td>
<td>10%tile</td>
<td>50%tile</td>
<td>90%tile</td>
<td>10%tile</td>
</tr>
<tr>
<td>4.63±3.27</td>
<td>1.57</td>
<td>3.72</td>
<td>9.59</td>
<td>2.98±2</td>
</tr>
<tr>
<td>10%tile</td>
<td>50%tile</td>
<td>90%tile</td>
<td>10%tile</td>
<td>50%tile</td>
</tr>
<tr>
<td>4.63±3.27</td>
<td>1.57</td>
<td>3.72</td>
<td>9.59</td>
<td>2.98±2</td>
</tr>
</tbody>
</table>
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 (USEPA, 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 cm² instead of 11.76 cm²). 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).

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