Evaluation of Measurement Methods

Positive and Negative Artifacts in Particulate Organic Carbon Measurements with Denuded and Undenuded Sampler Configurations

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Measurement of ambient particulate organic carbon (POC) with quartz filters is prone to positive and negative sampling artifacts. One approach for estimating these artifacts is to sample with a backup quartz filter placed behind either the main quartz filter or a Teflon filter in a parallel line. Another approach is to use a denuder to reduce the positive artifact in combination with a highly adsorbent backup filter to capture any negative artifact. Results obtained using both of these approaches in parallel for over one year in Pittsburgh, PA are presented in this article. A sampler using an activated carbon monolith denuder has been developed and tested extensively. Transmission losses were found to be negligible, and the denuder is on average 94% efficient at removing gas-phase organics. Denuder breakthrough is corrected for each run using a dynamic blank in parallel with the sample line. Comparisons with the dynamic blank indicate that the denuder almost eliminates the positive artifact on the quartz filter. Negative artifact from the denuded quartz filter is quantified using a carbon-impregnated glass fiber (CIG) backup filter and was found to be small, typically less than 10% of the ambient POC. Compared to the denuded sampler POC, 24 h bare quartz samples showed an almost constant positive artifact of 0.5 µg-C/m³ for samples taken throughout the year-long study period. Sampling for shorter durations (4–6 h) resulted in a larger positive artifact. A quartz filter behind a Teflon filter (QBT) provides a consistent estimate of the positive artifact on the bare quartz filter irrespective of sample duration, though it overcorrects for the positive artifact by 16–20% (attributed to particulate matter volatilizing off the upstream Teflon filter). The quartz behind quartz (QBQ) approach provides a reasonable estimate of the positive artifact on the bare quartz filter for the 24 h samples but not for the shorter samples. A slight seasonal variation is observed in the absolute value of the positive artifact, with higher values observed during the summer months.

INTRODUCTION

Carbonaceous aerosols, commonly classified as organic carbon (OC) and elemental carbon (EC), are a major component of the PM2.5 mass (Shah et al. 1986; Gray et al. 1986; Malm et al. 1994; Turpin et al. 2000). Quartz fiber filters are used to measure particulate organic carbon (POC) and EC since they can be heated to 1000°C, which is necessary for the usual thermal evolution methods used to determine OC/EC, such as the NIOSH 5040 or IMPROVE protocols (NIOSH Manual of Analytical Methods; Chow et al. 1993). This research was conducted as part of the Pittsburgh Air Quality Study, which was supported by US Environmental Protection Agency under contract R82806101 and the US Department of Energy National Energy Technology Laboratory under contract DE-FC26-01NT41017. This article has not been subject to the EPA’s required peer and policy review and therefore does not necessarily reflect the views of the Agency. No official endorsement should be inferred.

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Numerous studies have been conducted to characterize the effect of sampling artifacts on OC/EC measurements, and a recent detailed review is provided by Turpin et al. (2000). Estimates of the OC artifact range from a positive artifact of over 50% of POC (Kirchstetter et al. 2001; Turpin et al. 1994) to a negative artifact of up to 80% of POC (Anderson et al. 2002; Eatough et al. 1993; Moley et al. 2001; Ding et al. 2002b). The wide range of reported values reflects the complexity of the problem. Positive and negative artifacts occur simultaneously and hence are difficult to isolate and quantify. A second challenge is that artifacts are strongly influenced by sampler configuration and sampling conditions, which often clouds interpretation and comparison of results from the various published studies. For example, the large negative artifacts reported by Eatough and coworkers occur on a quartz filter behind a denuder, which, as explained earlier, results in higher volatilization losses. However, the positive artifact appears to dominate samples taken with bare quartz filters (quartz filters without an upstream denuder) (Turpin et al. 1994; Kirchstetter et al. 2001). Experiments have also shown that the artifact is dependent on the face velocity, sampling duration, and location (McDow and Huntzicker 1990; Turpin et al. 1994). Further, Kirchstetter et al. (2001) report a filter lot-to-lot variability in the measured artifact.

One way to account for the positive artifact is to use a backup quartz filter either behind the main quartz filter (the Q-QBQ approach), or in a parallel port behind a Teflon filter (the Q-QBT approach) (McDow and Huntzicker 1990; Turpin et al. 1994; Hart and Pankow 1994; Kim et al. 2001). The OC measured on the backup quartz filter provides an estimate of the positive artifact on the main (or “bare”) quartz filter (hence, POC = bare quartz OC—backup quartz OC). The Q-QBQ method is simpler in that it requires only one sample line, whereas the Q-QBT requires two lines, one for the bare quartz filter and another for the Teflon/quartz filter pack.

The Q-QBT two-port strategy assumes that the upstream Teflon filter traps only the PM without adsorbing any organic gases, and so the backup filter (quartz behind Teflon, or QBT) is exposed to the same organic vapor concentration as the bare quartz filter, providing a robust estimate of the positive artifact on the bare quartz filter. The Q-QBT approach has been shown to provide a consistent estimate of the POC for samples collected with different face velocities and sample volumes (McDow and Huntzicker 1990; Turpin et al. 1994). However, results from the AUSPEX field study (Chow et al. 1996) suggest that the QBT may overestimate the positive artifact, since this correction resulted in negative POC values (bare quartz—QBT) for 33% of the 493 samples collected.

For the quartz behind the quartz (QBO) to provide a good estimate of the positive artifact on a bare quartz filter, both quartz filters should be in equilibrium with the sampled air stream. This may not always be the case, since the backup quartz filter is exposed to lower organic vapor concentrations until the upstream bare quartz filter reaches equilibrium (Mader and Pankow 2001). Hence, the QBT usually provides higher artifact estimates than the QBQ with low sampling volumes (McDow and Huntzicker 1990; Turpin et al. 1994), though for large sample volumes the QBQ and QBT should provide similar estimates of the positive artifact (Hart and Pankow 1994). Kirchstetter et al. (2001) also suggest that longer sampling times with the Q-QBQ combination produce better estimates for the positive artifact.

A second approach to avoid positive artifacts relies on a denuder upstream of the quartz filter to remove organic gases from the incoming air stream (numerous papers by Eatough and coworkers on the BOSS and its variants, including Eatough et al. 1993, 1996; Eatough 1999; Ding et al. 2002a; and other systems by Coutant et al. 1989; Gundel et al. 1995; Gundel and Lane 1999; Mader et al. 2001). This approach can create large negative artifacts because removal of the organic gases alters the gas–particle equilibrium, creating the potential for volatilization of particles collected on the quartz filter. To account for this negative artifact, an adsorbent filter such as a carbon-impregnated filter (Eatough 1999) or a XAD-coated quartz filter (Lewtas et al. 2001) is often installed downstream of the quartz filter. A denuder efficiency of less than 100% is a serious concern because concentrations of gas-phase organics are typically an order of magnitude greater than the POC, and the adsorbent backup filters capture most of the gas-phase material that escapes the denuder, potentially creating a substantial positive artifact due to the denuder breakthrough.

Although both of these approaches provide important insights into the artifact problem, few comparisons have been published between the denuder-based and quartz backup filter techniques. Such comparisons are important because the magnitude of the artifact can vary with sampler configuration as well as the sampling location. In one of the few available studies, Kirchstetter et al. (2001) compared the Q-QBT, Q-QBO, and a denuder system, finding the denuded POC to be slightly higher than either the QBT- or QBQ-corrected bare quartz POC. The higher POC measured by the denuder sampler was attributed to denuder breakthrough. Differences in sampling methodology and use of the backup filters can also make comparisons difficult—for example, Eatough et al. (1996) compare only the denuded quartz data from the BOSS (without the carbon-impregnated backup filter OC) to the bare quartz data of a collocated IMPROVE sampler.

In this article, we compare POC measurements made using both a denuder system and a quartz backup filter-based sampler to examine the effect of artifacts on POC measurements in Pittsburgh. The denuder sampler was extensively characterized using a dynamic blank with each run to estimate any positive artifact associated with denuder breakthrough. Daily and higher frequency measurements were made for over a year. Over seventy-five 24 h samples were collected with the denuder sampler, and over 300 24 h measurements were made with the quartz backup filter sampler. In addition, high-frequency samples were collected with the quartz backup filter sampler for one month. Such a large data set enables extensive testing and comparison of these different ways of measuring POC and allows a study of temporal variations in artifact. This work is part of the Pittsburgh Air Quality Study (PAQS), one of the EPA Supersites.
METHODOLOGY

The Site

The samplers were operated at the PAQS Supersite, which was located on a hill in an urban park next to the Carnegie Mellon University campus in Pittsburgh, Pennsylvania. The site is not near any major industrial sources and is more than 500 m from any major road. Additional information and other results from the study are presented by Wittig et al. (2004).

The Samplers

The quartz backup filter sampler (TQQQ) is a two-port sampler with a double quartz filter pack in one line (QQ) and a Teflon filter followed by a quartz filter in the other (TQ) (Figure 1). The upstream quartz filter is referred to as the “bare quartz,” while the two downstream quartz filters are the QBQ and QBT. A PM10 inlet head (URG, URG-2000-30DBN) is upstream of both filter packs, and a sharp-cut PM2.5 cyclone (URG, URG-2000-30EG) is installed upstream of the bare quartz filter, as shown in Figure 1. As listed in Table 1, this sampler provides three estimates of POC: the bare quartz OC, the bare quartz OC minus the QBQ (Q-QBQ); and the bare quartz OC less the QBT (Q-QBT). EC is determined from the analysis of the bare quartz alone. This sampler is similar to that used by McDow and Huntzicker (1990) and Turpin et al. (1994). A set of experiments was performed which showed that the QBT data did not depend on the presence or absence of a PM2.5 cyclone in the TQ line.

The denuder sampler uses an activated carbon monolith denuder (MastCarbon Ltd, UK) with an approximate BET surface area of 900 m²/g. The denuders are 250 mm long and 30 mm in diameter with 230, 1 mm² channels/sq. inch, for a typical residence time of 0.2 s at 16.7 lpm (assuming plug flow). The denuder is followed by a sharp-cut PM2.5 cyclone (URG, URG-2000-30EG), a quartz filter, and then a carbon-impregnated glass-fiber (CIG) filter, as shown in Figure 2. The denuder removes organic gases from the incoming air stream, while the CIG filter captures volatilization losses from the quartz filter (and also organic gases that escape the denuder). Particulate matter is collected on the sample line, called ACD. Denuder breakthrough is estimated by running a parallel dynamic blank.

Figure 1. The TQQQ sampler used in the PAQS. This sampler provides three estimates of ambient POC: (a) Bare Quartz, (b) Bare Quartz – QBT, and (c) Bare Quartz – QBQ. A separate set of experiments was performed that showed that the absence or presence of a PM2.5 cyclone in the TQ line (shown by the broken circle above) did not affect the carbon measured on the QBT.
Table 1
Different particulate organic carbon estimates from the TQQQ and denuder samplers

<table>
<thead>
<tr>
<th>Name</th>
<th>Calculated as</th>
<th>Sampler</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare Quartz</td>
<td>Bare Quartz</td>
<td>TQQQ</td>
<td>The configuration used by the EPA speciation network</td>
</tr>
<tr>
<td>Q-QBT</td>
<td>Bare Quartz − QBT</td>
<td>TQQQ</td>
<td>QBT correction for positive artifact on bare quartz filter</td>
</tr>
<tr>
<td>Q-QBQ</td>
<td>Bare Quartz − QBQ</td>
<td>TQQQ</td>
<td>QBQ correction for positive artifact on bare quartz filter</td>
</tr>
<tr>
<td>Denuded POC</td>
<td>(Q_{ACD} + CIG_{ACD}) − (Q_{DYN} + CIG_{DYN})</td>
<td>Denuder</td>
<td>Reference value of POC used in this study. CIG backup filter</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>used to measure negative artifact, and dynamic blank used to</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>correct for denuder slip.</td>
</tr>
<tr>
<td>Denuded Quartz</td>
<td>Q_{ACD} − Q_{DYN}</td>
<td>Denuder</td>
<td></td>
</tr>
</tbody>
</table>

(DYN), which is similar to the ACD line except that all the PM is removed by a Teflon filter upstream of the denuder. As indicated in Table 1, the ambient POC level is estimated by subtracting the OC measured by the dynamic blank line (quartz and CIG) from the corresponding sample values, and the net quartz and net CIG OC values are added together to give the ambient POC concentration. The EC is estimated from the ACD quartz filter.

A third line, the undenuded blank (UDB), consisting of a Teflon filter followed by a quartz/CIG combination, was added in September 2001 to measure the gaseous OC that is sorbed onto the quartz and CIG filters in the absence of a denuder. The denuder efficiency is calculated using the UDB-measured ambient gaseous OC concentration as

\[
\text{Denuder Efficiency} = 1 - \frac{(Q_{DYN} + CIG_{DYN})}{(Q_{UDB} + CIG_{UDB})}. \tag{1}
\]

Over the course of the study, the denuders were changed once: one set of two denuders was used from 1 July 2001 to 25 October 2001; a second set was used for the remainder of the study period. The denuders of each set were also rotated between the sample and dynamic blank lines to examine potential differences between the denuders, but no significant variations were observed.

**Sampling**

The samplers were run in either of two main sampling modes—low frequency and high frequency. In the low-frequency mode, the TQQQ sampler was operated every day for a 24 h sample starting at approximately midnight, while the denuder sampler was usually run once every six days for a 24 h sample synchronized with the TQQQ run for that day. Low-frequency samples were collected throughout the study period from June 2001 to July 2002, except for July 2001. High-frequency samples were collected during July 2001, when the TQQQ sampled for 4 or 6 h on a 0–6, 6–10, 10–14, 14–18, and 18–24 schedule (all times EST), and the denuder sampler was run every day from midnight to midnight (0–24). In January 2002, the denuder sampler was operated daily (24 h samples) for two weeks. The sampling schedules are summarized in Table 2.

<table>
<thead>
<tr>
<th>Month</th>
<th>Number of sampling days</th>
</tr>
</thead>
<tbody>
<tr>
<td>June 2001</td>
<td>23</td>
</tr>
<tr>
<td>July 2001</td>
<td>31&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>August 2001</td>
<td>31&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>September 2001</td>
<td>30</td>
</tr>
<tr>
<td>October 2001</td>
<td>31&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>November 2001</td>
<td>30&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>December 2001</td>
<td>26</td>
</tr>
<tr>
<td>January 2002</td>
<td>31&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>February 2002</td>
<td>28&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>March 2002</td>
<td>31&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>April 2002</td>
<td>28&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>May 2002</td>
<td>31&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>June 2002</td>
<td>28&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>July 2002</td>
<td>30&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Total (5 samples a day)&lt;sup&gt;a,b&lt;/sup&gt;</td>
<td>30&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Total (24-hour samples)&lt;sup&gt;a,b&lt;/sup&gt;</td>
<td>379</td>
</tr>
</tbody>
</table>

<sup>a</sup>July 2001: 27 days of high-frequency sampling and four 24 h samples.<br>
<sup>b</sup>August 2001: 3 days of high-frequency samples and twenty-eight 24 h samples.
Figure 2. The denuder sampler used in the PAQS. Ambient POC is estimated as \( (Q_{ACD} + CIG_{ACD}) - (Q_{DYN} - CIG_{DYN}) \). The UDB line is used to estimate the denuder efficiency in conjunction with the DYN line, see Equation (1).

Loaded and unloaded in a laminar flow hood. After sampling, the filters were stored in polystyrene petridishes at \(-20^\circ C\). All sample lines were operated at a nominal flow rate of 16.7 lpm. Gelman 2200 stainless steel filter packs were used, which reduced the effective filter diameter to 35 mm, resulting in a face velocity of 29 cm/s at 16.7 lpm. The filter packs were modified to allow a double filter set (i.e., Teflon/quartz, quartz/quartz, or quartz/CIG), separating the two filters in each
set by 0.5 mm. During each run, two independent measurements were made of the flow through each sample line using (1) a rotameter in combination with a vacuum gauge and (2) a dry gas meter. The flows measured with the rotameter and the dry gas meter were within 4% for all runs. The average variability between sampler lines for a given run was 3.2% for the TQ and QQ lines, and 1.3% for the ACD and DYN lines. Flow audits were conducted once every seven runs to verify performance of the rotameters against a primary measurement device (Gilibrator 2, Sensidyne, Inc.).

One set of handling blanks was taken approximately every ten samples. Handling blanks are filter packs loaded onto the sampler and removed after about a minute, without any air flow. The appropriate study average blank values (shown in Table 3) were subtracted from the sample values (the denuder quartz and CIG values for that day). All the handling blank values for the quartz filters are significantly lower than the EPA specification of 1 \( \mu g-C/cm^2 \) used for the speciation network. The EC blank levels of the quartz filters used in the denuder sampler are higher than those of the quartz filters used in the TQQQ sampler, presumably due to contamination from the CIG backup filter. For a typical 24 h POC concentration of 3 \( \mu g-C/m^3 \), a blank OC contribution of 0.3 \( \mu g-C/cm^2 \) would be less than 5% of the filter loading.

### Sample Analysis

All filters were analyzed using a Sunset Laboratories Thermal Optical Transmittance (TOT) OC/EC analyzer, usually within one week of sampling. The CIG filters were analyzed in a Helium atmosphere with a stepped temperature profile ramping to 330°C in steps of 10°C every 30 s, followed by a 5 min soak at 330°C. Typical thermograms from the analysis of CIG filters are shown in Figures 3a and b. The carbon level on the filter is determined by integrating the area under the thermogram. Previous studies have reported significant deterioration of carbon-impregnated filters at temperatures around 300°C (Modey et al. 2001; Anderson et al. 2002). No evidence of filter degradation was observed during analysis of more than 200 CIG filters. For example, the FID signal on the thermograms of the four different CIG filters shown in Figures 3a and b all approach zero during the final 5 min step at 330°C.

Quartz filters were analyzed with the temperature profile given in Table 4 and shown in Figure 4, which is based on the NIOSH 5040 protocol (NIOSH Manual of Analytical Methods). As per the NIOSH protocol, if any EC loss is evident in the fourth Helium temperature step (870°C), this temperature should be reduced. This was found to be the case, and a number of the filters were analyzed with a modified profile reducing the maximum Helium mode temperature to 700°C, which appeared to eliminate the loss of light-absorbing carbon in the fourth Helium peak. Reducing the peak temperature of the Helium mode to 700°C lowers the OC values by about 5%, but since the first three peaks are the same, it should not affect the OC artifact, which mostly evolves from the filter at the lower temperatures. However, this change in the peak Helium mode temperature did affect the EC (which forms a much smaller component of the carbonaceous aerosol as compared to POC). The EC and corresponding results are discussed in a companion paper (Subramanian et al. 2004).

Based on 101 filters analyzed twice (once with the standard NIOSH protocol used in this study and then a second punch with the modified NIOSH protocol with a peak Helium temperature of 700°C), a linear regression of the total carbon produced a correlation coefficient of 0.99 and a slope of 1.001 (between 0.986 and 1.016 at the 95% confidence interval), with a negligible intercept. Hence, the precision of the method due to the instrument as well as filter loading can be taken as within 2% for total carbon. Sunset Laboratory claims the precision due to the instrument and filter loading variability as ±5% for the same instrument, with a minimum uncertainty of 0.2 \( \mu g-C/cm^2 \)

### Table 3

Study averages of handling blanks for all the filters and the dynamic blank EC for the denuder sampler

<table>
<thead>
<tr>
<th>Filter</th>
<th>Number of blanks</th>
<th>OC blank average</th>
<th>EC blank average</th>
</tr>
</thead>
<tbody>
<tr>
<td>QBT</td>
<td>51</td>
<td>0.23 ± 0.14</td>
<td>0.06 ± 0.07</td>
</tr>
<tr>
<td>Bare Quartz</td>
<td>52</td>
<td>0.22 ± 0.15</td>
<td>0.07 ± 0.08</td>
</tr>
<tr>
<td>QBQ</td>
<td>52</td>
<td>0.23 ± 0.15</td>
<td>0.08 ± 0.12</td>
</tr>
<tr>
<td>Q_ACD</td>
<td>24</td>
<td>0.28 ± 0.18</td>
<td>0.31 ± 0.26</td>
</tr>
<tr>
<td>CIG_ACD</td>
<td>24</td>
<td>1.79 ± 0.61</td>
<td>NA</td>
</tr>
<tr>
<td>Q_DYN</td>
<td>77</td>
<td>NA</td>
<td>0.32 ± 0.33</td>
</tr>
</tbody>
</table>

Values are in \( \mu g-C/cm^2 \). Negative values are taken as zero. Errors are one standard deviation. NA, not applicable.

### Table 4

The NIOSH protocol used for analyzing the quartz filters on the Sunset Labs OC/EC analyzer

<table>
<thead>
<tr>
<th>Step</th>
<th>Mode (Atmosphere)</th>
<th>Temperature (°C)</th>
<th>Time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Helium</td>
<td>340</td>
<td>120</td>
</tr>
<tr>
<td>2</td>
<td>Helium</td>
<td>500</td>
<td>120</td>
</tr>
<tr>
<td>3</td>
<td>Helium</td>
<td>615</td>
<td>120</td>
</tr>
<tr>
<td>4</td>
<td>Helium/Oxygen</td>
<td>870 (or 700)*</td>
<td>180</td>
</tr>
<tr>
<td>5</td>
<td>Helium/Oxygen</td>
<td>— (cool down)</td>
<td>45</td>
</tr>
<tr>
<td>6</td>
<td>Helium/Oxygen</td>
<td>575</td>
<td>45</td>
</tr>
<tr>
<td>7</td>
<td>Helium/Oxygen</td>
<td>650</td>
<td>45</td>
</tr>
<tr>
<td>8</td>
<td>Helium/Oxygen</td>
<td>725</td>
<td>45</td>
</tr>
<tr>
<td>9</td>
<td>Helium/Oxygen</td>
<td>800</td>
<td>45</td>
</tr>
<tr>
<td>10</td>
<td>Helium/Oxygen</td>
<td>910</td>
<td>100</td>
</tr>
<tr>
<td>11</td>
<td>Calibration (CH₄)</td>
<td>—</td>
<td>110</td>
</tr>
</tbody>
</table>

*All the results presented in this article are with the 870°C temperature.
Figure 3. Typical thermograms for the CIG analysis: (a) Temperature profile and FID signals for the CIG_UDB and CIG_ACD; (b) FID signals for the CIG_ACD, CIG_DYN, and handling blank (HB) CIG; and (c) Net CIG OC, shown as the (ACD − DYN); and the positive artifact on the CIG due to denuder breakthrough, shown by the (DYN − HB).

(equivalent to 0.08 µg-C/m³ for a normal 24 h sample) (R. A. Cary 2003, Personal Communication). Schauer et al. (2003) report the precision as 4–13% for OC and 6–21% for EC between different instruments running the same temperature–time protocol on parallel punches.

RESULTS AND DISCUSSIONS

Denuder Performance and Negative Artifact

The denuder sampler provides the best estimate of POC because (1) the denuder reduces the positive artifact and any
Figure 4. Typical thermogram for a quartz filter from the OC/EC analyzer.

denuder breakthrough is estimated and corrected for using the dynamic blank line, and (2) any negative artifact is quantified with the CIG backup filters. Hence, the denuded POC is taken as the reference to which the POC estimates from the TQQQ sampler are compared. To ensure that the denuder results are reliable, it is essential that the denuder system be properly characterized. Results presented in this section examine three issues with denuder sampler operation, (1) particle losses in and contamination by the denuder; (2) denuder efficiency and positive artifact due to denuder breakthrough; and (3) negative artifacts on the CIG backup filters.

Particle Losses in and Contamination by the Denuder. Two different tests were performed to examine particle losses in the denuder. First, a comparison of the levels of inert species such as EC between the denuded and undenuded quartz filters provides a check on particle losses (Eatough et al. 1993; Ding et al. 2002a). Ambient EC concentrations from the bare quartz and the denuded quartz 24 h samples are compared in Figure 5. A paired t-test shows that the EC values given by the two are not significantly different at a 95% level of confidence ($p = 0.547$).

Second, laboratory tests using ammonium sulfate aerosol and an SMPS (Model 3936N25, TSI Inc.) indicated that the transmission efficiency through the denuder is about 95% or higher for particles larger than 100 nm in diameter. As a precaution against contaminating the denuded quartz filters due to shedding of the denuder material (activated carbon), PM$_{2.5}$ cyclones were installed downstream of the denuders (Figure 2). Significant shedding was observed with an initial set of denuders used for sampler design experiments, but this problem was solved by modifying the manufacturing process of the denuders (curing the “green” denuders after cutting them to the specified length, instead of cutting them after curing the stock). The denuders used for this study and the results presented in this article did not exhibit any shedding. The SMPS experiments showed no increase in particle concentration across the denuder, and the average dynamic blank quartz EC is practically the same as the denuder sampler handling blank EC (Q$_{DYN}$ and Q$_{ACD}$ in Table 3).

Denuder Efficiency and Positive Artifact Due to Denuder Breakthrough. Comparing the thermograms of the UDB and ACD CIG filters in Figure 3a indicates that the denuder removes a large fraction of the atmospheric gaseous OC that is normally captured by the CIG filter. Figure 6 shows the variation of denuder efficiency over time. The denuders are on average over 94% efficient (standard deviation, SD 3%) as calculated with Equation (1), with no noticeable difference between the individual denuders. A comparison of the ACD, DYN, and handling blank (HB) CIG filters shows that the positive artifact on the CIG filters (DYN-HB) violates at temperatures between 150–300°C (Figures 3b and c), sometimes overlapping with the negative artifact (ACD-DYN, discussed below). No significant deterioration in performance was observed over time for the three denuders, nor does there seem to be any seasonal variability in denuder efficiency. Lower values of denuder efficiency are typically associated with lower gaseous OC concentrations as measured on the UDB line. The first set of denuders was replaced after 45 runs
Figure 5. Comparison of EC for the 24 h runs as an indication that particle losses in the denuder are negligible. At low EC levels, the denuded quartz EC appears lower, probably because the blank correction is higher than that required.

Figure 6. Denuder efficiency calculated using the dynamic blank and undenuded blank lines (Equation (1)). Lower efficiencies were typically associated with lower gaseous OC concentrations as measured by the undenuded blank line. Sample 1 corresponds to 2 September 2001; sample 40 was taken on 29 May 2002.
as a precaution. Experiments were not performed to determine the potential lifetime of the denuders.

The ratio of the DYN OC to the ACD OC provides an estimate of the positive artifact due to denuder breakthrough. For instance, the DYN quartz OC is just 3.0+/−3.7% (Average+/−SD) of the ACD quartz OC, indicating negligible positive artifact on the denuded quartz filter. The positive artifact considering both the quartz and CIG filters is on average 18.3% (SD 12.5%) of the ACD quartz and CIG OC, necessitating the use of the dynamic blank in order to correctly interpret the CIG results. This is not unexpected, because the highly sorptive CIG filter is much more susceptible to denuder slip.

Both the ACD and DYN CIG OC levels are somewhat higher than the handling blank (HB). Figure 4c also shows that the dynamic blank accounts for the positive artifact on the CIG due to denuder breakthrough, avoiding an overestimation of the negative artifact, which would occur if only a handling blank correction were to be used for the denuder sampler.

The negative artifact estimates for the entire study are shown in Figure 7. The negative artifact (CIGACD − CIGDYN) is usually less than 10% of the ambient POC (quartz + CIG), and often zero. The study average of negative artifact was 6.3% of the POC (quartz + CIG), with a SD of 6.2%. It should be noted that the OC on both the CIGACD and CIGDYN is usually less than 10% of the ambient gaseous OC concentration as measured by the CIGDYN, and about twice the average handling blank CIG. The difference between the CIGACD and CIGDYN organic carbon is often close to the blank variability—the standard deviation of the handling blanks (0.6 μg-C/cm², Table 3) corresponds to an uncertainty of 0.24 μg-C/m³ in the negative artifact for a typical 24 h run. This is less than 10% of the typical ambient OC level of 3.0 μg-C/m³; therefore, the uncertainty due to the HB variability does not significantly impact the ambient POC estimate from the denuder sampler.

The variability in denuder efficiency could cause errors in determination of the negative artifact. For example, if the DYN denuder was consistently less efficient than the sample line (ACD) denuder, this would result in a systematic underestimation of the negative artifact. The denuders of the ACD and DYN lines were routinely swapped to prevent differences in denuder performance from systematically biasing the estimates of negative artifact. Although the variation in denuder efficiency creates some uncertainty in the estimate of negative artifact for an individual sample, these procedures ensure that the study average values are robust. A maximum estimate of the negative artifact is the sample CIG OC less the handling blank (i.e., assuming a denuder efficiency of 100%). In this extreme case (also shown in Figure 7), the negative artifact would be on average 20.2% (SD 12.2%) of the total (quartz + CIG) POC; however, this estimate is clearly too large because the denuder efficiency was only 94%.

Many studies have been conducted that indicate a negative artifact (referred to as SVOC by Eatough and coworkers) as much as, or more than, the organic mass retained on the upstream denuded quartz filter (Anderson et al. 2002; Ding et al. 2002b; Modey et al. 2001; Eatough 1999; Eatough et al. 1996). For example, Anderson et al. (2002) used the PC-BOSS at the NETL facility near Pittsburgh in summer 2000 and reported negative artifact from the PC-BOSS as 18% of the PM2.5 mass on average. The negative artifact varied from 0.5 to 7.3 μg-C/m³, which is within the same range as the reported nonvolatile OC concentration of 1.0 to 5.2 μg-C/m³ determined on the denuded quartz filter (correcting their results with the OC multiplication factor as OC = 0.61 × OM). These results are consistent with the negative artifact reported in the other studies with the PC-BOSS cited above. All of these estimates of negative artifact are roughly a factor of 10 higher than that reported here for the PAQS study, and might be due to a variety of reasons such as sampler configuration, location, and time (the NETL study was conducted a year before the PAQS).

**TQQQ and Denuder Sampler Inter-Comparison**

Time series plots of POC measured using the different samplers are shown in Figure 8. Figure 8a shows a period of low-frequency (24 h) samples from January 2002, and Figure 8b shows a two-day period from July 2001 (high-frequency sampling). The results are characteristic of Pittsburgh POC levels in the summer and winter. The average POC concentration in the summer (June to September) is 3.6 μg-C/m³, and in the winter (December to March) it is 2.5 μg-C/m³, based on a bare quartz filter.

Figure 8 illustrates the significant daily and subdaily temporal variability of the POC levels in Pittsburgh. The different estimates of POC generally track each other but with different magnitudes. As expected, the highest POC levels are reported by the bare quartz filter, with the denuder and the two backup correction levels (from the TQQQ) closer to each other, and less than the bare quartz. The differences between the various measurements are due to sampling artifacts and are explored in detail below.

The low-frequency comparisons are based on forty-seven 24 h parallel runs of the TQQQ and the denuder sampler. The high-frequency comparisons are based on data from 1 July to 3 August, 2001, which includes thirty 24 h runs of the denuder sampler made in parallel to the five-samples-a-day schedule of the TQQQ (the TQQQ data are 24 h, sample volume-weighted averages of the five samples in each day). The breakdown of different samples collected each month is shown in Table 2.

**Artifacts on the Bare Quartz Filter.** Figure 9a compares the OC levels measured with a 24 h bare quartz filter to the corresponding denuded POC measurements. The bare quartz and denuded POC data show a remarkable fit with an almost 1:1
Figure 7. Time series of negative artifact from the denuded quartz filter: (a) absolute values, as compared to the OC on the denuded quartz filter, and (b) negative artifact as a percentage fraction of the ambient POC (Q + CIG). As discussed in the text, (ACD − DYN) is the best estimate of negative artifact because it accounts for denuder slip. Negative values of the negative artifact correspond to periods when the DYN denuder is less efficient. The (ACD − HB) is a maximum estimate of negative artifact, assuming the denuder is 100% efficient. Sample 1 corresponds to 1 July 2001; sample 77 was taken on 29 May 2002.

Possible explanations for this reasonably stable artifact are that either the quartz filter is saturated with organic vapors or it is in equilibrium with the gas-phase organic compounds. Figure 10 shows the OC adsorbed on the backup quartz filters as a function of the ambient gaseous OC levels as measured by the UDB
Figure 8. Time series of ambient POC measured by the TQQQ and denuder samplers: (a) a one-week period of low-frequency (24 h) sampling in January 2002, and (b) a two-day period of high-frequency sampling in July 2001.

Figure 10 indicates that the relationship is generally linear, suggesting the filter is in equilibrium. Applying the framework of Mader and Pankow (2001) suggests a minimum period of 12–14 h for the quartz filter to reach equilibrium. The scatter can be because not all the gaseous species that are captured on the CIG filter adsorb on the
Figure 9. Bare quartz OC compared to the denuded POC: (a) low-frequency, 24 h samples and (b) high-frequency data (24 h averages of the 4–6 h TQQQ samples). The solid lines show the linear regression indicated in the figures (see Table 5 for regression parameters through the origin).
Table 5

Results from the linear regressions of the different POC estimates from the TQQQ sampler with the reference POC from the denuder sampler. The errors are one standard error for the coefficients.

<table>
<thead>
<tr>
<th>POC estimate</th>
<th>Sampling frequency</th>
<th>Number of samples</th>
<th>Slope</th>
<th>Intercept</th>
<th>$R^2$</th>
<th>Through the origin</th>
<th>Slope</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare Quartz</td>
<td>High</td>
<td>30</td>
<td>1.15 ± 0.08</td>
<td>0.71 ± 0.26</td>
<td>0.88</td>
<td>1.35 ± 0.03</td>
<td>0.85</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>47</td>
<td>0.98 ± 0.04</td>
<td>0.53 ± 0.11</td>
<td>0.94</td>
<td>1.13 ± 0.02</td>
<td>0.91</td>
<td></td>
</tr>
<tr>
<td>Q-QBT</td>
<td>High</td>
<td>30</td>
<td>0.80 ± 0.06</td>
<td>−0.25 ± 0.21</td>
<td>0.85</td>
<td>0.73 ± 0.02</td>
<td>0.85</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>47</td>
<td>0.84 ± 0.03</td>
<td>−0.07 ± 0.09</td>
<td>0.94</td>
<td>0.82 ± 0.02</td>
<td>0.94</td>
<td></td>
</tr>
<tr>
<td>Q-QBQ</td>
<td>High</td>
<td>30</td>
<td>1.00 ± 0.07</td>
<td>0.68 ± 0.23</td>
<td>0.89</td>
<td>1.19 ± 0.02</td>
<td>0.85</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>47</td>
<td>0.92 ± 0.03</td>
<td>0.31 ± 0.10</td>
<td>0.95</td>
<td>1.01 ± 0.02</td>
<td>0.93</td>
<td></td>
</tr>
</tbody>
</table>

Figure 10. Effect of ambient gaseous OC concentration on the artifact measured on the different filters, (a) QBT OC and (b) QBQ OC.
the denuded quartz filter should experience a higher negative artifact than a bare (undenuded) quartz filter. Thus, the positive artifact is usually dominant when sampling with a bare quartz filter in the Pittsburgh region, which is consistent with the results of Turpin et al. (1994) for other sites.

A comparison of the high-frequency bare quartz data, averaged by sample volume, with the corresponding 24 hr denuder measurements (Figure 9b and Table 5) shows a larger positive artifact for the shorter duration samples as compared to the 24 h runs of the low-frequency samples (Figure 9a and Table 5). Again, this is expected since it is unlikely that the quartz filter reaches saturation or equilibrium (with the gaseous OC) within 4–6 h. Once the filter has reached equilibrium, the artifact mass on the quartz filter remains constant and will form a smaller component of the measured POC on a concentration basis with increasing sampling time.

**Bare Quartz—QBT Versus the Denuded Sampler.** Figure 11 shows that the Q-QBT estimate of POC correlates well, with the denuder POC for both the short-duration and 24 h samples. However, the QBT overcorrects for the positive artifact on the bare quartz filter by 16% of the denuded POC for the 24 h samples (Figure 11a and Table 5). A similar result is obtained for the high-frequency samples where the QBT overestimates the positive artifact on the bare quartz filter by 20% of the denuded POC (Figure 11b and Table 5). Although the QBT overcorrects for the positive artifact, it does provide a consistent estimate of the positive artifact for both the high- and low-frequency samples. Table 5 shows that the positive artifact on the high-frequency bare quartz filters is significantly larger than on the 24 h bare quartz filters. The similarity of the regressions of the QBT corrections (Table 5) for both short-duration and 24 h samples indicates that the QBT accounts for the effects of different sample duration.

Volatileization of organic particulate matter collected on the Teflon filter that is then adsorbed onto the QBT is a likely explanation for the overcorrection of the positive artifact with the Q-QBT approach. Our results are qualitatively similar to Chow et al. (1996), though the PAQS did not see any negative POC after correction by the QBT. The previous section showed negligible volatilization loss from the bare quartz filter. Higher volatilization losses from a Teflon filter than a quartz filter is not unexpected. Quartz filters are thicker and have more surface area than the stretched Teflon membrane filters used in this study. Since the PM is typically trapped in the uppermost part of the quartz filter (McDow and Huntzicker 1990), it is likely that some volatilization does occur for the bare quartz filter, but these vapors are captured downstream on the same quartz filter.

Based on the entire study of 379 24 h samples collected between June 2001 and July 2002, the QBT OC averages 34% (SD 10%) of the bare quartz OC. Figure 12a shows the QBT OC varying from 11–83% of the bare quartz OC, with the higher values associated with low OC levels. The PAQS results are consistent with earlier findings, although the absolute magnitude of the QBT artifact is lower, as are the average bare quartz OC levels.

For example, McDow and Huntzicker (1990) reported the QBT OC at about 50% of the bare quartz OC for low OC values and less than 20% for bare quartz OC values above 7 µg-C/m³ when sampling in Portland, OR. Kim et al. (2001) also found the QBT OC on an annual average basis to be 30% of the bare quartz OC based on a year-long study at Rubidoux, CA, with the QBT OC varying between 0.53 to 4.97 µg-C/m³.

**Bare Quartz—QBQ Versus the Denuded Sampler.** Figure 13a shows that for the 24-hour runs (low-frequency sampling) the Q-QBQ estimate of POC is approximately the same as the denuded POC. However, this is not the case with the shorter duration samples (Figure 13b and Table 5), where considerable positive artifact remains even after applying the QBQ correction to the bare quartz OC. These results suggest that both of the quartz filters are in equilibrium with the vapor phase for the 24 h TQQQ samples, but they do not adsorb gases in equal measure for a 4–6 h sample. These results are consistent with Kirchstetter et al. (2001), who found that the QB method came closest to being a good estimate of the positive artifact on the front quartz filter with a 14 h sample rather than with samples of 2, 4, or 8 h duration when sampling at a face velocity of 50 cm/s. Figure 12b shows the QBQ OC ranging from 4–30% of the bare quartz OC (except for two values over 50% at low POC levels). The study average is 13% with a SD of 5%. However, the trends are less distinct than in the QBT case discussed earlier.

**Analysis of the Thermograms of the Different Quartz Filters.** Comparing the carbon evolving from the quartz filters at the different temperature steps of the NIOSH protocol (shown in Figure 4) gives additional insight into the artifacts. More volatile compounds (gases and particles) come off at the 340°C Helium step, the heavier particulate-phase organics evolve at the subsequent higher temperatures in the Helium mode, and pyrolyzed organic carbon and native black carbon are expected to volatilize in the Helium/Oxygen mode. Therefore, the OC artifact is expected to come off the filter at the lower temperature Helium-mode steps.

The average values of the carbon evolving at each Helium temperature step and in the Helium/Oxygen mode are shown in Figure 14 for all the samples (grouped into high-frequency and low-frequency sampling modes). Comparing the size of the peaks from the different filters of the TQQQ sampler with the denuded quartz filter indicates the temperature(s) at which the artifact carbon evolves. For example, comparing the 24 h bare quartz filter with the denuded quartz filter in Figure 14a indicates that the positive artifact primarily occurs in the first peak (Helium, 340°C). For the high-frequency samples Figure 14b, appreciable artifact also evolves in the higher Helium steps—the mass of carbon evolving from the bare quartz filter in each of the higher temperature Helium peaks is significantly greater than the amount of carbon that evolves from the denuded quartz filter in that peak.

The carbon evolution from the backup quartz filters also supports the conclusion that some of the artifact carbon evolves at the higher temperature Helium steps. For example, Figure 14
Figure 11. QBT-corrected bare quartz OC compared to the denuded POC for (a) low-frequency, 24 h samples and (b) high-frequency samples (24 h averages of the 4–6 h TQQQ samples). The solid lines represent the linear regressions indicated in the figures (see Table 5 for the regression parameters through the origin).

shows that significant carbon evolves off the QBT filter in the first two Helium steps (340°C and 500°C) for both the short- and long-duration samples. Again, the shorter duration samples show relatively more carbon evolving at the higher temperatures than the long-duration samples. Finally, the difference between the bare quartz and QBT in the first two peaks is less than the carbon evolving at these peaks from the denuded quartz filter, which is consistent with the hypothesis of volatilization losses.
Figure 12. Variation of the backup filter OC, (a) QBT and (b) QBQ, as a fraction of the bare quartz OC. Data shown are for the 379 24 h samples between June 2001 and July 2002.

from the Teflon filter proposed earlier. The QBQ short-duration and long samples show similar trends as the corresponding QBT samples, though at much lower magnitudes.

There are two possible explanations for the artifact to evolve at higher temperatures. The artifact can be either physically or chemically bonded to the filter, and the energy needed to evolve the chemisorbed vapors might be higher than that required for the physically sorbed artifact (similar to the conclusions of Kirchstetter et al. 2001). Another possibility is pyrolysis of the positive artifact into compounds that evolve later at higher temperatures. Kirchstetter et al. (2001) dismiss this possibility based on some of their results for single compounds, but Yu et al. (2002) demonstrated that aerosol water extracts (water-soluble organics) can pyrolyze and evolve partly in the Helium mode and also later in the Helium/Oxygen mode. As the sample duration increases, the positive artifact reduces on a concentration basis, and so the higher temperature artifact is less prominent on the low-frequency comparisons than with the shorter-duration samples.

Temporal Variation of Artifact. Figure 15 shows the seasonal variation of the different estimates of the positive artifact, both in absolute terms (Figure 15a), and as a proportion of the bare quartz OC (Figure 15b). For the 24 h samples, the QBT shows a much greater artifact than the QBQ, forming 30–40% of the bare quartz OC compared to the 10–20% for the QBQ. Figure 15a indicates some seasonal variation of the positive artifact on an absolute basis, with higher levels of artifact occurring in the summer. However, there seems to be little variation on
Figure 13. The QBQ corrected bare quartz OC versus the denuder POC for (a) low-frequency, 24 h samples and (b) high-frequency samples (24 h averages of the 4–6 h TQQQ samples). The solid lines show the linear regression indicated in the figures (see Table 5 for the regression parameters through the origin).

a relative basis (Figure 15b), as the magnitude of the artifact appears to mirror the seasonal variation in ambient OC levels. Kim et al.’s (2001) results show no significant seasonal trends in the absolute values of the QBT artifact for Rubidoux, CA. Figure 7 shows that the negative artifact is small. Higher values were seen during the summer months (Figure 7a); however, there does not seem to be any significant seasonal trend in the negative artifact as a fraction of POC (Figure 7b).
Figure 14. Average carbon that evolves at each step of the NIOSH protocol for (a) forty-seven 24 h samples and (b) thirty days of high-frequency samples. The data are not corrected for blanks; however, these form a very small fraction of the total carbon. The error bars are one standard error of the study average for each peak in that particular group.
CONCLUSIONS

A comprehensive study comparing the prevalent methods for measurement of ambient particulate organic carbon (POC) has been conducted during the PAQS, and the major conclusions are as follows:

1. An activated carbon monolith denuder sampler has been developed and characterized. The denuder eliminates virtually all of the positive artifact from the quartz filter. The negative artifact due to volatilization of the organic particulate matter from the denuded quartz filter is on average 6.3% (SD 6.2%) of the ambient POC and usually less than 10% of the ambient POC.

2. With a bare quartz filter sampling for 24 h at 16.7 lpm (face velocity of 29 cm/s), an almost constant positive artifact of 0.5 µg-C/m³ is found, irrespective of the season. A larger positive artifact occurs on shorter duration samples on a concentration basis because the filter is not in equilibrium. Since the denuded quartz filter experiences only a small negative artifact, negligible volatilization losses can be expected for the bare (undenuded) quartz filter.

Figure 15. Seasonal variation of artifact using monthly averages of the (a) absolute values of organic carbon on the QBT and QBQ backup filters, and (b) ratios of the OC on the backup filters to the bare quartz OC. The error bars are one standard deviation of the data. Data is not shown for July 2001 since most of the runs were short samples (4–6 h).
3. The QBT provides a consistent estimate of the positive artifact on a bare quartz filter regardless of sample duration. However, it overestimates the positive artifact by 16–20%, presumably due to volatilization of organic material off the upstream Teflon filter.

4. The QBQ provides a robust estimate of the positive artifact on the bare quartz filter for the 24 h samples. It does not work for the 4 or 6 h samples because both of the quartz filters have not achieved equilibrium with the incoming air stream.

5. The positive artifact measured on the quartz backup filters for the 24 h samples shows a slight seasonal variation on an absolute basis, with higher values during the summer, but there is no temporal variation on a relative basis (compared to the bare quartz OC). The negative artifact from the denuded quartz filter also shows higher values in the summer, but as a fraction of the POC there is no significant seasonal variation.

6. The results of this study are most applicable to regions with similar atmospheric conditions and meteorology. Wittig et al. (2004) and Rees et al. (2004) provide an overview of meteorological and fine particle composition in Pittsburgh. Briefly, sulfate is the dominant component of fine particle mass in Pittsburgh followed by organic material; one third of the OC is estimated to be secondary in the summer, with smaller fractions in the winter (Cabada et al. 2004). Tang et al. (2004) show that fine particle concentrations in Pittsburgh are dominated by regional transport of pollutants, which allows significant time for atmospheric processing or aging. These conditions are representative of those found in much of the Eastern United States, particularly the Northeast.

REFERENCES


