Correction Methods for Organic Carbon Artifacts When Using Quartz-Fiber Filters in Large Particulate Matter Monitoring Networks: The Regression Method and Other Options

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ABSTRACT

Sampling and handling artifacts can bias filter-based measurements of particulate organic carbon (OC). Several measurement-based methods for OC artifact reduction and/or estimation are currently used in research-grade field studies. OC frequently is not artifact-corrected in large routine sampling networks, such as EPA's Chemical Speciation Network. In some cases, the OC artifact has been corrected using a regression method (RM) for artifact estimation. In this method, the y-intercept of the regression of the OC concentration on the $PM_{2.5}$ mass concentration is taken to be an estimate of the average OC sampling artifact (net of positive and negative artifacts).

This paper discusses options for artifact correction in large routine sampling networks. Specifically, the goals are to: 1) articulate the assumptions and limitations inherent to the RM, 2) describe other artifact correction approaches, and 3) suggest a cost-effective method for artifact correction in large monitoring networks. The RM assumes a linear relationship between measured OC and PM mass: a constant slope (OC mass fraction) and a constant intercept (RM artifact estimate). These assumptions are not always valid, for example when the OC artifact is dependent on the PM mass or the concentration of organics. Additionally, outliers and other individual data points can have a large influence on the RM artifact estimates. Nevertheless, the regression method has yielded results within the range of measurement-based methods for several datasets.

Artifact correction by RM showed best agreement with measurement-based methods for the highest OC concentrations within a dataset and resulted in artifact-corrected OC that was systematically biased low for the lowest OC concentrations within a dataset. For relatively accurate, simple, and cost-effective artifact OC estimation in large networks we suggest backup filter sampling on at least 10% of sampling days at all sites with artifact correction on a sample-by-sample basis as described herein.

IMPLICATIONS

This paper discusses options for organic carbon (OC) sampling artifact correction in EPA's Chemical Speciation Network and elsewhere. Trip/field blanks account for artifacts associated only with transport, handling, and storage, but not artifacts that result from active sampling. Several organic artifact correction methods exist, including a linear regression method that requires no additional sampling or chemical analysis. We describe previously unstated assumptions and limitations of this regression method and guidance for those who wish to use it. However, we do not recommend the RM for future network operation; instead we suggest intermittent artifact measurement and correction on a sample-specific basis.

INTRODUCTION

OC Artifacts and Large Monitoring Networks

EPA's National Chemical Speciation Network (CSN; consisting of the Speciation Trends Network, STN, and the State and Local Air Monitoring Stations, SLAMS) and the Interagency Monitoring of Protected Visual Environments (IMPROVE) network provide speciated fine particle ($PM_{2.5}$) measurements for approximately 200 urban and 170 rural locations across the United States. One of the major $PM_{2.5}$ components measured in these networks is particulate organic carbon (OC). Both positive and negative sampling artifacts complicate OC measurement. Quartz-fiber filters (QFFs) are used to collect samples for OC analysis because they withstand the high temperatures used in thermal-optical carbon analysis.[1,2] However, QFFs have large surface areas and sorption of organic vapors on these filters is well documented (i.e., by the presence of OC on a QFF behind a front filter that removes the particles, such that the QFF is exposed to particle-free air[3]). In urban areas, adsorbed vapors frequently contribute on the order of 30-40% (1-3 $\mu g/m^3$) of the OC collected on a QFF (20-40 cm/s face velocity; 24 hr collection). Organic vapor adsorption, a positive artifact, can exceed 50% (0-2 $\mu g/m^3$) in rural areas where OC concentrations are lower or in cases where samples are collected for shorter time periods or low flow rates (i.e., when particle loadings are smaller).[4] [Note in experiments where standard mixtures of gases and particles were sampled with increasing collection time, the mass of adsorbed vapor collected on a QFF was larger for longer collection times, but this adsorption artifact was a smaller *percentage* of the total

collected OC for longer collection times, presumably because the particle deposition rate is constant and adsorption slows as the adsorbed phase approaches equilibrium with the gas phase.[4]] Changes in ambient concentrations of organic vapors, temperature, and relative humidity (RH) can alter the partitioning of semi-volatile organic compounds, leading to additional adsorption of organic vapors on the filter and collected particles (positive artifact) or volatilization of adsorbed vapors and collected organic particulate matter from the filter (negative artifact). The pressure drop across the filter that can develop as particles are collected could also induce volatilization. Calculations and measurements suggest this effect is smaller than adsorption (i.e., < 10% of collected OC) for typical ambient conditions, sampling face velocities, and collection times.[5-7] However, the magnitude of negative artifacts is particularly difficult to assess. For example, when adsorbable gases are removed with a denuder, collected particles are exposed to clean air, which enhances volatile losses. Also, PM lost by volatilization is not necessarily collected on a downstream QFF. Measurement methods that account for both adsorption and volatilization (described below) require considerable care and attention to detail. More measurements of this type collocated with undenuded QQF measurements are needed to document the net OC artifact on a QFF (by direct comparison) and to further validate simpler OC measurement methods.

Substrate handling, transport, and storage can also introduce positive and negative artifacts. Before sampling, QFFs are pre-heated in an oven at high temperature to remove any organic contaminants. CSN and IMPROVE QFF filters are pre-fired at 900°C for 3-4 hrs.[8,9] These clean substrates can adsorb organic vapors during handling, transport, and storage. These "handling" artifacts are usually accounted for by laboratory, trip, and field blanks. For example, CSN filters are exposed to ambient air for up to several hours during these periods. After sampling, filters can adsorb additional organic gases or collected OC can volatilize if the equilibrium partitioning changes (e.g., if high temperatures are encountered during transport, handling, and storage, or if filters are somehow exposed to high or low organic concentrations). For these reasons, most research-grade studies take great care to store and transport clean and collected substrates in well sealed containers and at reduced temperatures. For the national networks, all

CSN filters are shipped to and from the sites in their sampling cassettes in sealed Ziploc plastic bags in coolers with blue ice by overnight carrier with temperatures not to exceed 4 °C. Filters are stored cold (< 0 °C) before and after sampling. IMPROVE filters are sent and received between field sites and University of California (UC), Davis in their sampling cassettes in sealed Ziploc plastic bags at ambient temperature by standard U.S. mail in plastic containers designed for durability but not thermal stability. Shipping between UC Davis and the Desert Research Institute (DRI), where IMPROVE filters are prepared, stored and analyzed, is done at reduced temperatures. These filters are stored at DRI below 0 °C.

Accurate measurement of particulate OC on QFFs requires that artifacts are reduced and/or quantified. Research-grade field projects, which are limited in duration and well staffed (e.g., PM Supersite Experiments)[5] use denuder systems or backup filters (dynamic blanks) to correct for artifacts on a sample-by-sample basis. To date these approaches have been considered too difficult and costly for large routine monitoring networks (e.g., CSN, IMPROVE). CSN samples for carbon analysis are collected on a single QFF. Field and trip blanks are used to assess artifacts associated only with transportation, handling, and storage, but artifacts associated with active sampling are not measured. Field and trip blanks are each collected with roughly 10% of samples. They are not subtracted from the reported OC concentrations, but they are reported in EPA's database (Aerometric Information Retrieval System, AIRS) and are frequently subtracted by analysts. A database is available to the public that includes a sampler-specific correction based on field and trip blanks (personal communication, J. Flanagan, Research Triangle Institute, NC). In the IMPROVE network, quartz backup filters (QQB) are collected with every sample at 6 sites to provide a measure of the adsorption artifact. These backup filters are averaged monthly across the 6 sites and are subtracted from all samples at all sites on a peak-by-peak basis (i.e., OC1, OC2, OC3,…; each peak represents carbon evolved at a different temperature step during thermal-optical analysis).[2] [Note, to obtain better agreement between CSN and IMPROVE monitoring networks for OC and EC, EPA has converted all carbon measurements at the 54 STN sites and eventually at SLAMS sites to IMPROVE sampling and analysis protocols. Some differences, such as

149 shipping protocols, remain unchanged (http://www.epa.gov/ttn/amtic/specurg3000.
150 html).]
151
152 **Regression Method (RM) for Organic Artifact Estimation**
153 Solomon et al.[11] applied a linear regression approach to correct CSN network OC
154 measurements for organic artifacts, since sampling artifacts were not measured (only trip
155 and field blanks were collected). In the RM approach, the QFF OC concentrations (front
156 filter OC without blank correction) were regressed on $PM_{2.5}$ mass concentrations
157 (measured gravimetrically on Teflon filters). This method assumes that when $PM_{2.5}$ mass
158 is zero, OC mass also should be zero. Therefore, the linear regression of measured OC
159 (QFF; y-axis) on $PM_{2.5}$ mass (Teflon; x-axis) should have a y-intercept that represents the
160 average net (positive and negative) OC artifact integrated across handling, shipping,
161 storage, and sampling effects. Examples of the RM are provided below.
162
163 In this method, an average OC artifact estimate (a constant value given by the y-intercept
164 of the regression of OC on $PM_{2.5}$ mass) is subtracted from each QFF OC concentration
165 for the set of samples included in the regression. When a negative intercept results based
166 on the RM, the absolute value of the intercept is added to the front QFF since in this case,
167 volatilization is assumed to be greater than adsorption. This method assumes that the
168 Teflon filters on which $PM_{2.5}$ mass is measured adsorb a negligible quantity of organic
169 vapors (a reasonable assumption[12]) and that $PM_{2.5}$ mass measurements are accurate. The
170 RM has been used by several researchers[11,13,14] and is attractive because it provides a "net
171 artifact estimate" at low cost relative to the need to collect and analyze additional filters
172 and/or employ denuders. This paper explores additional assumptions and limitations of
173 the RM and discusses biases that result from the subtraction of an average artifact, an
174 issue that pertains to other artifact correction approaches in current use as well.
175
176 **Measurement-Based Artifact Correction Methods**
177 Several artifact correction methods have been used to estimate "true" or "artifact
178 corrected" particulate OC concentrations when OC is measured on QFFs [7,11,15,16]. Good
179 agreement (within ~10%) has been found between research-grade measurements of OC

that 1) correct for adsorption through backup filter subtraction and 2) correct for adsorption and volatilization using a denuder followed by an adsorbent and simultaneously measure denuder breakthrough in a second channel (i.e., Pittsburgh Air Quality Study, PAQS, Figure 1[5] and ACE-Asia[6]). These and other approaches are described below.

Filter With Trip or Field Blanks. Trip and/or field blanks are usually used to estimate OC artifacts associated with the transport, handling, and storage of filters. However, these blanks do not experience changes that are associated with sampling, such as changes in ambient organic vapor concentration, increases in pressure drop related to filter loading, and changes in ambient temperature during sampling. Trip blanks are transported and stored with samples but not exposed to ambient air outside the laboratory. Field blanks are treated similarly to trip blanks; however, they are mounted in the sampler usually for seconds to minutes, and then re-sealed in their original shipping container. CSN field blanks are handled in this way. In the most realistic field blank protocols, air is pulled through the sampler for a few minutes with the field blank in place. Averaged trip or field blank OC is usually subtracted from samples when OC is measured on a single QFF:

$$\text{Artifact Corrected OC} = Q - \text{Trip Blank OC, or} \quad (1)$$

$$\text{Artifact Corrected OC} = Q - \text{Field Blank OC} \quad (2)$$

where Q is the OC concentration measured on the single QFF. These blanks are an imperfect estimate of the OC blank on a sampling filter because they do not encounter the same conditions (e.g., pressure, temperature, gas phase organic species) as the sampling filter experiences during the sampling period. However, unless *backup* filters or more sophisticated approaches are employed (as described below), they are the only means of accounting for the OC handling artifact, which can be significant. CSN field and trip blanks have similar loadings that do not vary appreciably by season, ambient temperature, or location but vary significantly by sampler type.[11,17] Presumably blanks differ by sampler because blanks and samples are transported in cassettes designed specifically for

each sampler, and the cassette design and different cassette materials affect blank levels. The similarity of trip and field blanks and similarity across seasons suggest that the mounting process and short ambient exposure contribute little to the blank.

Filter With Backup Filter. In this approach, the OC adsorption artifact on a QFF is taken to be the OC measured on a concurrently-collected quartz fiber backup filter, also called a "dynamic blank" (Figure 2a). Unlike field and trip blanks, dynamic blanks remain in the sampler throughout sampling and experience essentially all the sampling, transport, handling, and storage conditions as the front filter. The dynamic blank is the OC measured on a QFF downstream of a QFF (QQB), or OC measured on a QFF downstream of a Teflon filter (TQB), the latter in a parallel sampling port. The quartz or Teflon front filter removes particles so that the backup filter collects only QFF adsorbable vapors. Artifact corrected OC is calculated as the OC on the front QFF (Q) minus the OC on the concurrently collected backup filter (QQB or TQB; Figure 2a):

$$\text{Artifact Corrected OC} = Q - QQB, \text{ or} \quad (3)$$

$$\text{Artifact Corrected OC} = Q - TQB \quad (4)$$

This approach assumes that the amounts of organic vapor adsorbed on the front and the backup filter are equal and that OC lost from particles as a result of volatilization is negligible.[4] Evidence suggesting that volatilization from undenuded QFFs is small was reported by studies operating side-by-side denuder and filter samplers,[5,6,18] although it must be recognized that there are only a modest number of studies of this type and that they are extremely difficult to do well. Adsorbed OC can be lower on backup filters than on front filters as discussed below. Turpin et al.[4] recommend collection of a dynamic blank (backup filter) with each sample and subtraction on a sample-by-sample basis because the amount of adsorption depends on the ambient concentration and composition of semi-volatile organics and on temperature, which also varies from sample-to-sample. Kirchstetter et al.[3] suggest selecting front and backup QFFs from the same lot prior to sampling due to inter-lot variability of QFF adsorption capacity.

Differences between TQB and QQB OC artifact estimates have long been recognized and are not completely understood. One might expect less adsorption on a TQB filter because of the smaller surface area and larger pressure drop across a front Teflon filter than across a front QFF. However, OC on a QQB is typically lower than OC on a TQB, [3,12] especially for samples with low sample volumes. Two studies comparing artifact corrected OC obtained from TQB and QQB approaches (Figure 2a) with a denuder-based approach (shown in Figure 2b) concluded that the TQB approach is more accurate for low sample volumes (e.g. 4-hr duration, 10-20 L/min, 47 mm filters).[5,6] This finding is consistent with the argument that it takes longer for a front QFF than a front Teflon filter to reach equilibrium with the sampled air stream and before that time the backup filter behind the QFF is exposed to a reduced concentration of organic vapors.[3,7,12,19,20] Differences between TQB and QQB artifact estimates are smaller for larger sample volumes. Subramanian et al[5] found better agreement between the QQB approach and the denuder-based method for 24 hr samples (16.7 L/min, 47 mm filters) as shown in Figure 1. The QQB approach appears to be a reasonable choice for CSN-style sampling.

Denuder-filter-adsorbent. A denuder upstream of the QFF (port 1; Figure 2b) has been used to substantially reduce the concentrations of organic vapors passing through the QFF.[5,6,18] This reduces the adsorption artifact but also disturbs the equilibrium partitioning of semi-volatile compounds, and can induce volatile loss of semi-volatile compounds from collected particles. If the denuder is 100% efficient at removing adsorbable vapors, OC collected on an adsorbent downstream of the denuder and filter (ADS, port 1 of Figure 2b) can be attributed to volatile losses from collected particles. If the denuder is not 100% efficient at removing vapors that can adsorb to the QFF and ADS (i.e. if denuder breakthrough occurs), then organic gases that pass through the denuder can also adsorb on the QFF and adsorbent. The degree of denuder breakthrough can be determined in a parallel sampling port (port 2; Figure 2b) that is identical to port 1 except for the placement of a Teflon filter upstream of the denuder. In port 2, particle free ambient air (containing organic gases) enters the denuder, which is followed by a QFF and an adsorbent. OC measured on the QFF and adsorbent in port 2 is a measure of adsorbed vapor present due to denuder breakthrough. Artifact corrected OC is then

calculated as the sum of OC on the front QFF (Q) and adsorbent (ADS) in port 1 minus the sum of OC on the QFF (Q) and adsorbent (ADS) in port 2:

$$\text{Artifact Corrected OC} = (Q+ADS)_{\text{port 1}} - (Q+ADS)_{\text{port 2}} \quad (5)$$

The two-channel denuder-QFF-adsorbent method, which corrects for denuder breakthrough, is considered the best current method for estimating ambient concentrations of OC in air, at least in principle, because it accounts for both adsorption and volatilization. However, maintaining adequate quality control in such a system is extremely challenging. This approach is similar to the denuder-adsorbent filter method preferred for aerosol nitrate measurement.[21] If denuder breakthrough is not measured, denuder sampling (port 1 only) assumes 1) the denuder removes 100% of gases adsorbed by a QFF and ADS and 2) the ADS collects 100% of the organic vapors volatilized from the collected particles during sampling.[6] It is important to note that with even modest denuder breakthrough, the contribution of breakthrough gases to ADS can equal or exceed the contribution of particulate OC volatilized from Q because organic vapor concentrations typically greatly exceed organic particulate matter concentrations in the atmosphere.[22] Denuder collection efficiencies decrease with increasing temperature and relative humidity and are composition dependent. Thus, measurement of denuder breakthrough, for example as described above (port 2), is important. The use of efficient adsorbants also makes it difficult to prevent contamination of the ADS during transport, handling, and storage. Several types of denuders (e.g., parallel plate, annular, and honeycomb) containing adsorbent materials such as carbon impregnated cellulose-fiber (CIF), carbon impregnated glass-fiber (CIG) , polyurethane foam (PUF), activated carbon monolith honeycomb; and polystyrene divinylbenzene resin (XAD)[5,6,16] are commonly used. QFFs, CIG, CIF, XAD, and PUF also are used as the adsorbent downstream of the QFF.[5,6,16,23,24] Denuder collection efficiencies for filter-adsorbable organic vapors of 80-100% have been reported.[5,6,16,23,24]

EXPERIMENTAL WORK

Objectives

304 The purpose of this paper is to discuss options for artifact correction in large routine
305 sampling networks. Specifically, this paper discusses the assumptions and limitations
306 inherent to the RM, compares RM performance with measurement-based methods for a
307 few studies, provides some guidance to those using the RM, describes other approaches
308 to artifact correction, and suggests a strategy for artifact correction in large networks
309 going forward. To accomplish these goals, datasets from PAQS, the Relationship of
310 Indoor and Outdoor Personal Air Study (RIOPA), and a Six Site STN/IMPROVE
311 comparison study were used. Key measurement parameters are summarized in Table 1.
312
313 **PAQS Samples**
314 Twenty-four hour integrated concentrations of $PM_{2.5}$ mass and chemical composition
315 were measured daily for 14 months during PAQS.[5,25-28] In general, $PM_{2.5}$ at the primary
316 PAQS site was heavily influenced by long distance transport and atmospheric
317 processing.[27] OC (<2.5 μm aerodynamic diameter) was measured daily using filter plus
318 backup filter approaches (QQB and TQB) (Figure 2a) and a two-port denuder-filter-
319 adsorbent sampler (activated carbon monolith honeycomb denuder, MastCarbon, Ltd,
320 UK; CIG adsorbent, Schleicher & Schuell, Germany) that allowed correction for denuder
321 breakthrough[5] (Figure 2b). Artifact-corrected OC was calculated with equations 3 – 5.[5]
322 Artifact corrected OC calculated from Equation 3 (Q-QQB) agreed best with artifact
323 corrected OC concentrations obtained by the denuder sampler for this study (Equation 5;
324 Figure 1; 24 hr samples).[5]
325
326 All sample lines were operated at 16.7 L/min (47 mm diameter filters mounted to provide
327 a 29 cm/s face velocity). QFF (Pallflex; 550 °C in air; >4 hours) and CIG filters (360 °C
328 in ultra-high purity nitrogen; >12 hr) were baked before use. QFF substrates were stored
329 at room temperature in clean, sealed glass jars. CIGs were initially stored at room
330 temperature and later in the study, stored frozen. CIG substrate storage temperature did
331 not have a significant effect on the handling blanks.[5] After collection, all samples were
332 stored cold (– 20 °C), and OC was measured by thermal optical transmittance.[5] CIGs
333 were also analyzed thermally (330 °C in He).[5] Note that in the results reported by

334 Subramanian et al.[5], PAQS filter data were corrected by the average field blank, whereas
335 in this work, uncorrected filter data were used.
336
337 **RIOPA Samples**
338 As part of RIOPA[29-32], 48-hr integrated outdoor $PM_{2.5}$ samples were collected outside
339 homes in Elizabeth, NJ; Houston, TX; and Los Angeles County, CA (summer 1999 -
340 spring 2001). Many homes were particularly close (< 200 m) to identified outdoor
341 sources, such as congested highways, gas stations, refineries, and truck loading
342 facilities.[30] Samples for $PM_{2.5}$ mass (gravimetric analysis) were collected on a Teflon
343 filter[31], OC (<2.5 μm aerodynamic diameter) was collected on a QFF, and the adsorption
344 artifact was measured on a QFF placed behind the Teflon filter (TQB).[32] Artifact
345 corrected OC was calculated from Equation 4.
346
347 All samples were collected at 10 L/min (37 mm diameter; 25 cm/s face velocity).
348 Pallflex QFFs were pre-baked (550 °C; >2 hr) and stored in petri dishes lined with baked
349 aluminum foil in sealed plastic bags at room temperature until sampling.[32] QFFs were
350 removed from the sampler immediately after sampling, stored on-site frozen in the same
351 container as initially used, transported cold (blue ice) next-day by express carrier, and
352 stored frozen until analysis. OC was measured by thermal-optical transmittance.[32]
353
354 **Six Site STN/IMPROVE Comparison Study**
355 Time-integrated 24-hr measurements of $PM_{2.5}$ mass, QFF OC, and other fine particle
356 species were measured using collocated STN and IMPROVE samplers approximately
357 every third day in the 6 Site STN/IMPROVE Comparison Study.[33] Sites were located at
358 3-urban STN and 3-rural IMPROVE locations. The urban and rural sites were paired and
359 located as follows: Beacon Hill, Seattle, WA - Mount Rainier, WA; Phoenix, AZ -
360 Tonto, AZ; and Haines Point, Washington, D.C. - Dolly Sods, WV.
361
362 Data from October 2001 – October 2002 were used to calculate RM artifact estimates.
363 OC and $PM_{2.5}$ mass were measured on 47 mm diameter QFF and Teflon filters,
364 respectively, by the following STN samplers: Andersen Reference Ambient Air Sampler

365 (10.4 cm/s QFF face velocity, 23.6 cm/s Teflon face velocity; Dolly Sods, WV and
366 Haines Point, Washington D.C.), Met One Spiral Aerosol Speciation Sampler (9.5 cm/s
367 face velocity; Phoenix, AZ and Tonto, AZ), and URG Mass Aerosol Speciation Sampler
368 (23.6 cm/s face velocity; Beacon Hill, WA and Mount Rainier, WA). All samplers were
369 operated at manufacturer-recommended flow rates. Details regarding the CSN (STN)
370 speciation samplers can be found elsewhere.[11,34] All QFFs (Whatman; prebaked at 900
371 °C) were stored below freezing in the laboratory before and after sampling, transported
372 cold using blue ice, and removed from the samplers typically within three days. During
373 handling, samples are exposed to room air in a large warehouse for up to a couple of
374 hours. Samples were analyzed by thermal optical transmittance.[35]
375
376 **RESULTS**
377 **Artifact Estimates**
378 In PAQS and RIOPA (Table 2a,b) the field blanks, which provide a measure of OC
379 artifacts on QFFs due to transit, handling, and storage only, are 3-4% of front QFF OC, or
380 0.10-0.22 $\mu gC/m^3$. This is a modest contribution to the total measured artifact (i.e., TQB,
381 QQB, Denuder). For PAQS the average total measured artifact is 0.48 - 1.03 $\mu gC/m^3$ or
382 15-33% of front QFF OC depending on the method used to estimate the OC artifact. For
383 RIOPA the average total measured artifact is 31 – 43% or 1.65 - 2.18 $\mu gC/m^3$ depending
384 on the city (Table 2b). Field blanks were a much higher percentage of front QFF OC in
385 the Six City STN/IMPROVE Comparison Study (Table 2c). For Haines Point, Dolly
386 Sods, Phoenix and Tonto the site average field blanks are 1.3 – 1.4 $\mu gC/m^3$, which is 27 –
387 54% of front QFF OC. For Beacon Hill and Mount Rainier the site average field blanks
388 are 0.1 - 0.3 $\mu gC/m^3$ (7 - 11% of front QFF OC). The use of a different type of filter or
389 differences in sample handling and storage might explain the higher field blanks for CSN
390 samples. Note, as seen here and reported elsewhere[11], CSN field blanks are sampler-
391 specific with URG having the lowest blank values and Anderson and MetOne having
392 higher and more similar values.
393
394 PAQS and RIOPA studies included denuders and backup filters enabling estimates of OC
395 *sampling artifacts* as well as transport/handling/storage artifacts. Specifically, the

396 undenuded RIOPA and PAQS backup filters provide estimates of the positive sampling
397 artifact together with the handling blank. Differences between undenuded QFF OC and
398 PAQS artifact corrected OC obtained using Eqn 5 provide estimates of the net artifact,
399 accounting for adsorption and volatilization during sampling and the handling blank.
400 Below, RM performance is examined against these more comprehensive artifacts.
401
402 The simplest application of the RM is to regress OC on mass using linear least squares
403 regression (LLSR) as shown in the first line of Table 2 for each dataset. These results are
404 discussed here, and alternative approaches are discussed below. The corresponding data
405 are displayed in Figure 3 (note the regression line shown in Figure 3 is not LLSR, but
406 Deming, after outlier removal, discussed later). The RM OC artifact estimate for PAQS
407 by LLSR (36% of QFF OC; 1.1 ± 0.1 $\mu gC/m^3$) is similar to artifact measurements made
408 during PAQS (i.e., TQB, QQB, Denuder; Table 2a, Table 3) and those made at similar
409 face velocities and OC loadings in other studies. [4,11,36] The PAQS average TQB is 33%
410 of QFF OC or 1.03 $\mu gC/m^3$; QQB is 15% of QFF OC or 0.48 $\mu gC/m^3$; the artifact
411 estimated by comparison with the denuder sampler is 20% of QFF OC or 0.60 $\mu gC/m^3$.
412 Note that while the standard deviation in TQB or QQB values across days (Table 3)
413 reflects the daily variations in the size of the sampling artifact, the variations in the
414 artifact estimate across methods (QQB, TQB, Denuder) gives some perspective on the
415 inherent uncertainly in artifact measurements.
416
417 RM artifact estimates were substantially greater than measurement-based artifact
418 estimates when the method was applied to data from 2 of the 3 RIOPA cities individually.
419 For the RIOPA California dataset the RM artifact estimate was 87% of QFF OC or 5.3 ±
420 0.1 $\mu gC/m^3$. For New Jersey it was 62% of QFF OC or 3.1 ± 0.5 $\mu gC/m^3$. For Texas it
421 was 27% of QQF OC or 1.4 ± 0.7 $\mu gC/m^3$; whereas the measurement-based artifact at
422 those sites (TQB) was 31% (CA), 33% (NJ) and 43% (TX) of QFF OC or 1.9, 1.7, and
423 2.2 $\mu gC/m^3$, respectively. After subtraction of the RM artifact estimate from the Los
424 Angeles County QFF OC values, 16 of 40 artifact-corrected OC concentration estimates
425 were below zero (Figure 3b; data below dashed line will be negative after RM artifact
426 subtraction). These results indicate that, relative to the backup filter method, the RM

427 approach overestimated the OC artifact and underestimated OC at RIOPA sites. It should
428 be noted that there is substantial scatter in the RIOPA data (r^2 = 0.02-0.36 for RIOPA
429 data sets; r^2 = 0.35-0.87 for others), likely because many RIOPA study homes were in
430 close proximity to sources; this adds uncertainty to the intercept estimate. Also, the
431 number of samples in the RIOPA data sets is smaller (N = 40–61) than in the other data
432 sets (N = 99-301). In the next section we examine the limitations and assumptions of the
433 RM approach.
434
435 **RM Limitations**
436 *X and Y Value Uncertainties.* One limitation of the RM is that standard linear least
437 squares regression takes into consideration uncertainties only in the y variable. However,
438 both $PM_{2.5}$ mass (x-axis) and front filter OC (y-axis) variables have inherent
439 measurement uncertainties; this can affect y-intercept values. The Deming regression
440 provides a more exact solution of the linear least squares problem and allows for
441 incorporation of measurement uncertainties in both variables.[37-40] Measurement
442 uncertainties are study-specific. They were similar for PAQS, RIOPA, and the Six Site
443 STN/IMPROVE Comparison Study. Measurement uncertainties used here for front filter
444 OC (7%) and $PM_{2.5}$ mass (5%) were estimated by propagation of error and included a 5%
445 sampling uncertainty (driven by variations in flow rate[32]), and an analytical uncertainty of
446 5% for OC[5,32,36] and 1% for $PM_{2.5}$ mass[29] determined from replicate analysis. Larger
447 uncertainties of 9% and 14% (reported as average relative difference, %) have been
448 reported for CSN $PM_{2.5}$ mass and OC, respectively, based on collocated samples. [17,41] For
449 the Deming regressions performed in this study, uncertainties estimated by propagation
450 of error (7% for OC; 5% for $PM_{2.5}$ mass) were used since they were available for all three
451 studies.
452
453 RM artifact estimates (y-intercepts) obtained by Deming and by LLSR were virtually
454 identical with the exception of Houston (Table 2b), Phoenix, and Tonto (Table 2c), where
455 Deming regressions produced lower artifact estimates than LLSR; although not
456 statistically different. (Note Deming and LLSR results were never significantly different
457 given the large uncertainties in the intercepts.) In general, Deming regression is preferred

458 over standard LLSR whenever both x and y variables have uncertainties. If the
459 uncertainty in x is much smaller than the uncertainty in y, similar slopes are expected
460 from LLSR and Deming.
461
462 *Outliers and Influential Points.* A second limitation of the RM is that a few values can
463 have a disproportionate influence on the slope and intercept in linear regression,
464 especially when the data set is small. For the purpose of obtaining the integrated net
465 artifact estimate by the RM, outliers should be identified statistically and excluded from
466 the regression. In this work Least Trimmed Squares (LTS) robust regression was used to
467 identify outliers in both x and y (SAS, SAS Institute Inc., Cary, NC, USA, V9.1).
468 Measurements with a standardized robust residual greater than 3.0 (default setting) were
469 considered outliers.
470
471 The removal of outliers (circled data in Figure 3) had only a modest effect on the RM
472 artifact estimate (y-intercept) for most examined data sets (Table 2; Compare LLSR with
473 Robust and Deming with Deming Robust). The exceptions were Phoenix, and Tonto
474 (STN), where the Deming regression intercept changed from 0.75 ± 0.38 to 0.21 ± 0.30
475 for Phoenix and from -0.08 ± 0.31 to 1.43 ± 0.14 for Tonto with removal of outliers.
476 Note that Phoenix and Tonto had some of the larger intercept uncertainties of the study,
477 though the coefficients of determination (r^2) between OC and mass did not distinguish
478 these sites from the others.
479
480 Even after statistically identifying and removing outliers a few unusual sampling days
481 can have a disproportionate influence on the RM artifact estimate, as demonstrated for
482 the RIOPA California dataset (Figure 3b, Table 2 "Deming w/o influential points"). For
483 example, the removal of three data points in the lower right would reduce the RM artifact
484 estimate (y-intercept) from 5.2 to 2.9 $\mu g/m^3$, bringing it closer to the TQB estimate of 1.9
485 $\mu g/m^3$. The removal of the six data points in the upper left would reduce the RM artifact
486 estimate from 5.2 to 4.0 $\mu g/m^3$. Certainly, points should *not* be removed subjectively (i.e.,
487 without a statistical basis), but this example illustrates the observation that RM artifact
488 estimates have larger uncertainties for some datasets than others. The likelihood that a

few unusual sampling days will alter the RM artifact estimate for an entire data set is greater for data sets with low r^2 and small N. It should be noted that even when outlier identification was performed using a narrower residual distance for outlier identification (SAS DEFFITS - 1.0, Studentized – 1.5) so that 4 outliers were identified, the RM artifact estimate for the California dataset remained above 5 $\mu g/m^3$. The RIOPA Texas RM estimate, in contrast, was stable with respect to outliers and did not seem to be unduly influenced by individual points.

RM Assumptions

Linearity. The inherent assumptions of linear least squares regression are that y values (front QFF OC concentrations) vary linearly with x values ($PM_{2.5}$ mass concentrations), and the slope and the intercept (RM artifact estimate) are constant. Because the slope in the RM method is the OC mass fraction (OC/ $PM_{2.5}$ mass), the RM assumes the OC mass fraction is independent of PM mass. If, for example, high $PM_{2.5}$ mass concentrations are driven by high sulfate or nitrate without a concurrent increase in OC, the RM estimate (y-intercept) likely would be biased high because the OC mass fraction is lower on high concentration days than on low concentrations days, creating a non-linear QFF OC – mass relationship. The opposite effect would occur when high $PM_{2.5}$ mass concentration days are driven by high wood smoke alone (i.e., in this case, we expect the RM estimate to be biased low). In fact, this (high mass dominated by nitrate) might explain the non-linear shape (Figure 3b) and the very high RM artifact estimate found for the Los Angeles RIOPA data. Unfortunately this cannot be confirmed directly, since nitrate was not measured in RIOPA, but RIOPA species mass balances have a larger unexplained fraction (primarily nitrate and water) on the highest 25th percentile $PM_{2.5}$ concentration days.[32] In contrast, one might argue that the highest mass concentrations could be driven by woodsmoke at sites like Mt Rainier (from home heating, camping and logging-associated burns outside the park) and Beacon Hill, a Seattle neighborhood (from home heating) (Figure 3i, 3j). If true, this would decrease the RM artifact estimate. The RM artifact estimate is quite small for Mt Rainier and negative for Beacon Hill, consistent with this scenario. However, if a non-linearity exists in these OC-mass plots, it is not visually obvious. There are other possible explanations for the very small and negative

RM artifact estimates at Mt Rainier and Beacon Hill, respectively. For example volatile losses could be greater or the concentrations of adsorbable vapors could be smaller at these sites than at the other sites. These sites used the URG sampler, which operated at a higher face velocity.

Independence. The RM treats the organic artifact as a constant value, independent of the $PM_{2.5}$ mass concentration or the sample loading. This will not be true if days with higher OC (and higher $PM_{2.5}$ mass) also have higher concentrations of quartz-adsorbable OC vapors. Adsorbed OC has been reported to increase with increasing front QFF OC at several locations [4,11-13] including PAQS and RIOPA cities (Figure 4). This increase is not typically linear. The observation of higher adsorbed OC loadings on higher concentration days is relevant to the RM artifact correction approach in two ways: (1) The RM involves subtracting a constant artifact estimate from all samples, and therefore does not account for this dependence. (2) The general increase in the OC artifact with concentration could increase the QFF OC - $PM_{2.5}$ mass slope and could make the OC - PM mass relationship non-linear. The extension of the regression method to negative artifacts (Beacon Hill) is also problematic in this regard. It is unlikely that the quantity of OC lost to volatilization will be independent of the amount of collected OC.

$PM_{2.5}$ mass. The RM also assumes that $PM_{2.5}$ mass measurements (x values) are accurate. Although Teflon filters adsorb a negligible quantity of organic vapors, their higher pressure drop makes them more susceptible to volatile losses than QFFs.[12] Volatile losses of nitrate also can affect the accuracy of $PM_{2.5}$ mass measurements.

DISCUSSION

Subtraction of an Average Artifact

Given an increase in the adsorption artifact with increasing concentrations of organics, no matter what artifact correction method is employed, subtraction of a single *average* artifact estimate from all samples would constitute an over-subtraction, underestimation of OC at the lower OC concentrations and an under-subtraction, overestimation of OC at the higher OC concentrations. Thus, subtraction of a single average artifact estimate

551 across multiple sites would result in systematic bias, with over-subtraction at cleaner sites
552 and under-subtraction at more polluted sites. Note that IMPROVE subtracts an averaged
553 backup filter (QQB) across multiple sites.
554
555 **RM Discussion**
556 We initially expected the RM to provide an *average* artifact estimate with the
557 consequences described above. However, the RM actually provided an artifact estimate
558 that more closely resembles the artifact experienced by the higher OC concentration
559 values for the PAQS dataset (where the RM performed quite well; Table 3). This likely
560 occurs because higher concentration data have greater leverage in regression, especially
561 for log-normally distributed data. For PAQS, the RM yielded artifact-corrected OC
562 concentrations within the range of those obtained by the measurement-based methods for
563 the mean of the highest 25% of $PM_{2.5}$ mass concentration days, within 5% of "Q – QQB"
564 and "Denuder." However, for the lowest 25% of $PM_{2.5}$ mass concentration days, RM-
565 corrected OC concentrations were about 30% below Q-QQB and Denuder. RM-
566 corrected OC concentrations were negative for 3 of 301 PAQS measurements (Deming
567 without outliers; Robust regression).
568
569 RM performance was much better for PAQS than for Los Angeles County and Elizabeth
570 RIOPA datasets. The RM yielded negative artifact corrected OC concentrations for 16
571 out of 40 Los Angeles County, CA RIOPA measurements and 4 out of 44 Elizabeth, NJ
572 RIOPA measurements; negative concentration results were not observed when the RM
573 was performed on the Houston, TX RIOPA dataset (Deming without outliers, Robust
574 regression). It should be noted that PAQS sampling occurred at a location dominated by
575 regional aerosol, with a sizeable secondary component. In contrast, RIOPA sampling
576 occurred at locations strongly influenced by nearby sources. (Many homes were located
577 within 200 meters of local sources of organics and PM, e.g., roadways, gas stations,
578 refineries.) As a result, RIOPA samples have much larger variations in composition and
579 source contributions than PAQS samples, and the proportion of the variation (r^2) in front
580 QFF OC that is explained by $PM_{2.5}$ mass is higher for PAQS than RIOPA (Table 2). The
581 number of samples in each RIOPA dataset is also small (N = 40-61). One might

582 hypothesize that the better RM performance for PAQS occurs because of the higher OC-
583 mass correlations (r^2). To test this, simulated data were generated by Monte Carlo
584 methods (1000 measurements generated to have a desired slope of 0.40 and y-intercept of
585 0.1 $\mu gC/m^3$ and 4 different sigma-square values for the random error term in the
586 regression model). Calculated y-intercepts were compared to the desired value. This
587 analysis of simulated data demonstrated that good RM performance can be obtained even
588 at low r^2 (0.14) if the RM assumptions hold (linear relationship between OC and PM
589 mass: artifact and OC mass fraction are independent of PM mass concentration), and that
590 RM estimates can have substantial bias even for high r^2 if these same assumptions are
591 violated. PAQS and RIOPA datasets both violate the assumptions of independence
592 because the adsorption artifact is higher on higher concentration days. The poorer
593 performance for RIOPA datasets might result from additional violations of the RM
594 assumptions, the variable influence of nearby sources causing variations in the OC mass
595 fraction, or because a few data points can have a large impact on the regression,
596 especially for small N.
597
598 When RM artifact estimation was performed (Deming Robust) on the 6 Site
599 STN/IMPROVE Comparison Study dataset (Table 2c; Figure 3e-j), artifact estimates for
600 three sites (Haines Point, urban, 1.40 ± 0.26 $\mu g/m^3$, 32% of QFF OC; Dolly Sods, rural,
601 1.55 ± 0.19 $\mu g/m^3$, 55% of QFF OC; Tonto, rural, 1.43 ± 0.14 $\mu g/m^3$, 67%) were
602 reasonably consistent with expectations based on the literature (net positive artifact of 0.5
603 - 4 $\mu g/m^3$, 20-50% of front QFF OC in urban areas, 30-60% in remote)[4] and
604 uncertainties in the intercept were modest (10-20%). These values were only a little
605 higher than the average field blanks. (Field blanks averaged $1.3 - 1.4$ $\mu g/m^3$). In contrast,
606 the RM estimate for Beacon Hill ($r^2 = 0.9$) was negative (RM: -0.31 ± 0.11 $\mu gC/m^3$; -11%
607 of front QFF OC). RM estimates for Mt Rainier and Phoenix were small (RM: $0.02 \pm$
608 0.06 and 0.21 ± 0.30 $\mu gC/m^3$; 2% and 4% of front QFF OC for Mt Rainier and Phoenix,
609 respectively). Uncertainties in these intercepts (RM estimates) were large >100%. The
610 average field blanks for Mt Rainier and Beacon Hill were also small ($0.1 - 0.3$ $\mu gC/m^3$),
611 whereas the Phoenix field blank (1.4 $\mu gC/m^3$) was quite a bit larger than the RM estimate.

612 Outlier removal substantially alters the RM artifact estimate for Phoenix (from 0.75 –
613 0.21 $\mu gC/m^3$) and Tonto (from -0.08 to 1.43 $\mu gC/m^3$).
614
615 Because sampling artifacts were not measured, we cannot assess the accuracy of the RM
616 artifact estimates for the Six Site STN/IMPROVE Comparison Study, nor can we
617 determine whether or not the organic artifacts at these sites are dominated by the field
618 blank. If the organic artifacts are dominated by the field blanks, artifact OC will be
619 independent of PM mass, an assumption of the RM method that was violated for PAQS
620 and RIOPA. The lower RM artifact estimates in Phoenix, Mt. Rainier, and Beacon Hill
621 could occur because of more volatilization or less adsorption (during sampling and/or
622 transport and storage) at these sites or for these samplers. For example, temperatures can
623 be quite high in Phoenix. Alternatively, the RM artifact estimate could be biased low
624 because one or more assumptions of the RM were violated. For example, at Beacon Hill
625 and Mt. Rainier wood smoke is a substantial contributor to PM mass on many poor air
626 quality days in the fall and winter.[42] It is logical, then, that the OC mass fraction might
627 be particularly high on high PM days and this would violate the assumption of linearity.
628 RM artifact estimates for Beacon Hill, Mt. Rainier and Phoenix are small and the
629 uncertainties in these estimates are large. Even if these artifact estimates were accurate,
630 subtraction would not be recommended as the small correction would introduce larger
631 uncertainties.
632
633 **Regression Method Guidance**
634 When using OC values measured on a single QFF one must decide whether to subtract
635 the field blank, use the uncorrected values, or subtract the RM artifact estimate. This
636 paper articulates the assumptions and limitations of the RM, leaving the reader better
637 informed about the method. We could not determine objectively and with confidence
638 that use of the RM provides more accurate concentrations of airborne particulate OC, nor
639 could we quantify with confidence the uncertainties that would be introduced by
640 application of the RM to the CSN or IMPROVE network. While we are not
641 recommending the RM, we provide the following guidance for those who decide to use
642 it:

1. The RM approach is best applied to sites that represent OC concentrations at least at neighborhood and regional scales as defined by Blanchard[43] since samples collected at sites that are sometimes strongly influenced by a local source are particularly likely to violate the assumption of linearity. Even for these sites, the assumption of linearity will be violated if the sampling artifact is proportional to the OC concentration.
2. If multiple locations are used to increase N, the concentration range and chemical characteristics of the aerosol (gas and particle phases) at the sites must be similar.
3. A Deming regression should be used to account for uncertainties in x and y variables.
4. Remove outliers in x and y using standard statistical tests (e.g., those used herein)
5. Consider the possibility that the artifact might vary with changes in composition/source mix. If the dataset is quite large, analyses could be segregated by season or by OC mass fraction. Each subset would still need to contain a wide range of PM mass and OC concentrations.
6. Evaluate the stability of the RM artifact estimate. How sensitive is the answer to the presence/absence of random subsets of data?
7. Consider the possibility that the dataset might violate the inherent assumption of linear regression (that y values vary linearly with x values) because the slope (OC mass fraction) is not constant or the OC artifact is higher on high concentration days. Non-linearity might not be visually apparent when there is substantial scatter in the data. Additionally, if OC is a highly variable fraction of PM, the artifact could be also and subtracting an average value would introduce considerable error in individual measurements.
8. RM estimates that fall outside the typical range of artifact measurements made at similar face velocity should be treated with caution.

Another Option: Intermittent Backups, Sample-Specific Correction

Organic artifact estimates can be obtained by including backup filters at every site in a monitoring network. In large monitoring networks employing 24-hr sampling periods, QQB filters could be pre-loaded in filter cassettes, thus requiring no additional field

674 instrumentation or on-site filter exchange. If daily backup filter collection at all sites for
675 all days is too costly, given current budget constraints for large networks, backup filters
676 can be collected on fewer days. In the latter case, it would be best to collect backup
677 filters at all sites, although it is possible that sites could be grouped, noting that
678 differences in temperature, source mix, concentration, and relative humidity are likely to
679 induce site-by-site differences in the size of the artifact. Note that it is preferable to
680 include backup filters at all sites on fewer days rather than all days at fewer sites, and it is
681 important that backup filters be collected across all seasons. The Central Limit Theorem
682 provides guidance regarding the number of samples needed for a daughter population
683 (e.g., that obtained from intermittent backup filter measurement) to resemble the
684 distribution of the parent population. Datasets with lower correlations and larger
685 measurement uncertainties require more samples.[44]
686
687 For large datasets, when collecting backup filters at all sites, but on fewer days, artifact-
688 corrected OC concentrations would be obtained by subtracting the measured artifact
689 (QQB OC) from the front QQF OC on a sample-by-sample basis for samples where the
690 backup filter was included in the measurement. For samples with no backup filter,
691 artifact-corrected OC concentrations would be predicted from front QFF OC as illustrated
692 for PAQS in Figure 5. (This approach worked for RIOPA as well.) Specifically, the
693 artifact-corrected OC was determined from the QFF OC and the regression of artifact-
694 corrected OC (Q-QQB) on front QFF OC based on the more limited dataset. Note the
695 regression of Figure 5 was unchanged when only every 10^{th} sample was plotted. For
696 example, a measured front QFF OC value of 5.0 $\mu gC/m^3$ translates to an artifact
697 corrected OC concentration (Q-QQB) of 4.2 $\mu gC/m^3$ for PAQS. This approach accounts
698 for the fact that the adsorption artifact varies with OC concentration, and can even
699 account for the non-linear nature of the artifact, which the RM method does not. Also,
700 predictions are more robust because they are made using the entire regression relationship,
701 rather than being based on the intercept alone. Like the RM, taking into consideration
702 uncertainties in x and y and excluding outliers will provide an optimal regression
703 equation.
704

CONCLUSIONS

Future Network Operations

CSN and IMPROVE have several available options to quantify and/or reduce OC artifacts associated with sampling and with filter handling, transit, and storage. Subtraction of field blanks that have been loaded in the sampler and had air pulled through them briefly would correct for organic artifacts associated with filter handling, storage, and transport, but would not correct for *sampling* artifacts. Field blank values might be more similar to backup filter values if they are left passively exposed to ambient air for longer, as suggested elsewhere.[45] However, active sampling of particle-free ambient air, as is done with a backup filter, provides a "dynamic blank" that better mimics conditions encountered by samples. Two-channel denuder sampling could be performed as shown in Figure 2b, provided that suitable denuder and sorbent materials are available. This approach provides high quality OC measurements (Equation 5; Figure 2b) when operated with considerable care and verified through fastidious quality control. Many more measurements of this type should be made across seasons and geographical regions and used to evaluate the accuracy of simpler approaches. This is particularly important since negative artifacts are difficult to quantify. However, such a system would be extremely difficult and costly to operate at a large number of sites within a national monitoring network.

Daily backup filter sampling is simple to perform and provides a sample-by-sample estimate of the adsorption artifact. Backup filter sampling ensures that measured front filter OC concentrations are corrected for the organic adsorption artifact experienced by that sample (Equations 3 and 4; Figure 2a). When batches of front and backup filters are transported and stored together, these backup filters include artifacts encountered during transport, handling, and storage as well. Thus, when the backup filter is subtracted, it is not necessary to also subtract a field blank. Backup filter sampling on selected days provides a low-cost approach for CSN and other monitoring networks. Given that an increase in the ambient concentration of organics produces an increase in the adsorption artifact, no matter what artifact correction method is employed, subtraction of a single *average* artifact estimate from all samples would constitute an over-subtraction,

736 underestimation of OC at the lower OC concentrations in the dataset and an under-
737 subtraction, overestimation of OC at the higher OC concentrations in the dataset. This
738 could cause bias in reported annual average OC at particularly clean or polluted sites
739 when the same network average value is subtracted from OC values at both clean and
740 polluted sites. The following protocol avoids this problem:
741
742 1. Replace most QFF field blanks with backup QFF (QQB for 24-hr samples such as
743 used in the CSN) so that ~10% of the samples collected at all sites include an
744 adsorption estimate (dynamic bank). (Use TQB for samplers operating at low
745 flow rates or for short sampling periods.) Compare OC artifacts across sites and
746 seasons (plot backup filter OC vs. front filter OC) to determine to what extent
747 data can be combined (to increase N).
748 2. For all samples with concurrently collected backup filters subtract the backup
749 filter from its corresponding front QFF on a sample-by-sample basis (Equation 3
750 or 4) to provide artifact-corrected OC values.
751 3. Use the relationship between artifact-corrected OC and front QFF OC to provide
752 artifact-corrected OC estimates (see example above) on a sample-by-sample basis
753 for all samples in the dataset.
754 4. Perform concurrent research-grade two-port denuder measurements (Figure 2b) at
755 selected sites for continued artifact investigation. Sites should be chosen to
756 represent a range of composition and meteorological conditions within the
757 network.
758
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765
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915

916 **ABOUT THE AUTHORS**

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Table 1. Organic carbon (OC) measurements during the Pittsburgh Air Quality Study (PAQS), Relationship of Indoor, Outdoor and Personal Air (RIOPA) study, and the 6-Site STN/IMPROVE Comparison Study. Q indicates quartz-fiber filter collection of particulate matter for OC analysis. TQB and QQB indicate that adsorbed OC was measured on a quartz-fiber filter behind a Teflon or behind a quartz-fiber filter, respectively.

	PAQS	RIOPA	6 Site STN/IMPROVE
Sample Duration	24 h	48 h	24 h
OC measurements (see Fig 2)	Q Denuded Q TQB; QQB (Fig 2a,b)	Q TQB daily (Fig 2a)	Q
Face velocity (cm/s)	29 Pittsburgh	25 Elizabeth Los Angeles Houston	23.6 Beacon Hill; Mt Rainer 9.5 Phoenix; Tonto 10.4 Dolly Sods; Haines Point
Quartz filter	Pallflex	Pallflex	Whatman

Table 2. Regression of measured quartz-fiber front filter (QFF) organic carbon (OC) concentration ($\mu gC/m^3$) on $PM_{2.5}$ ($\mu g/m^3$) mass by linear least squares regression (Standard LLSR), Deming regression (accounting for measurement uncertainties), and LLSR and Deming regression after outlier removal by Robust regression for (a) PAQS, (b) RIOPA sites, and (c) sites in the Six Site STN/IMPROVE Comparison Study. Outlier points are determined by Robust regression with a cutoff of 3.0. No denuder or quartz-quartz backup (QQB) measurements were made in RIOPA. No denuder, Teflon-quartz backup (TQB), or QQB measurements were made in the Six Site STN/IMPROVE Comparison Study. r^2 is the coefficient of determination. % artifact is the net organic artifact (mean) as a percentage of mean front filter OC for RM (y-intercept) and mean measurement-based methods (field blank, TQB dynamic blank, QQB dynamic blank, and denuder system). % Denuder OC (PAQS) was calculated for the 47 days of paired denuder and front filter OC data.

								Measurement-Based Artifact Estimates			
(a) PAQS	**Regression Method**	**Sample Size (N)**	**Slope** ($\mu gC/m^3$)	**Intercept** ($\mu gC/m^3$)	**r^2**	**Avg. Front Filter OC** ($\mu gC/m^3$)	**% Artifact RM**	**% Field Blank**	**% Artifact TQB**	**% Artifact QQB**	**% Artifact Denuder**
PAQS	Standard LLSR	301	0.128 ± 0.006	1.13 ± 0.12	0.56	3.12	36%	3% (N = 52)	33%	15%	20% (N = 47)
	Deming	301	0.128 ± 0.007	1.11 ± 0.12			36%				
	Robust	291	0.136 ± 0.005	0.91 ± 0.09	0.70	3.04	30%	3% (N = 52)	34%	16%	
	Deming Robust	291	0.136 ± 0.005	0.90 ± 0.10			30%				

Table 2a.

(b) RIOPA Sites	Regression Method	Sample Size (N)	Slope ($\mu gC/m^3$)	Intercept ($\mu gC/m^3$)	r^2	Avg. Front Filter OC ($\mu gC/m^3$)	% Artifact RM	% Field Blank	% Artifact TQB
Los Angeles County, CA RIOPA	Standard LLSR	40	0.046 ± 0.053	5.28 ± 0.98	0.02	6.08	87%	4% (N = 75)	31%
	Deming	40	0.048 ± 0.056	5.24 ± 1.03			86%		
	Robust	40	0.046 ± 0.053	5.28 ± 0.98	0.02	6.08	87%		31%
	Deming Robust	40	0.048 ± 0.056	5.24 ± 1.03			86%		
	Deming w/o Influential Points	37	0.209 ± 0.075	2.87 ± 1.25	0.18	6.21	46%		31%
Elizabeth, NJ RIOPA	Standard LLSR	44	0.118 ± 0.026	3.08 ± 0.47	0.32	4.97	62%		33%
	Deming	44	0.120 ± 0.027	3.05 ± 0.48			61%		
	Robust	44	0.118 ± 0.026	3.08 ± 0.47	0.32	4.97	62%		33%
	Deming Robust	44	0.120 ± 0.027	3.05 ± 0.48			61%		
Houston, TX RIOPA	Standard LLSR	61	0.251 ± 0.043	1.41 ± 0.70	0.36	5.15	27%		42%
	Deming	61	0.265 ± 0.046	1.19 ± 0.74			23%		
	Robust	60	0.243 ± 0.040	1.41 ± 0.64	0.39	5.03	28%		43%
	Deming Robust	60	0.255 ± 0.042	1.23 ± 0.67			25%		

Table 2b.

(c) STN/IMPROVE Comparison Study	Regression Method	Sample Size (N)	Slope ($\mu gC/m^3$)	Intercept ($\mu gC/m^3$)	r^2	Avg. Front Filter OC ($\mu gC/m^3$)	% Artifact RM	% Field Blank
Haines Point, DC (urban)	Standard LLSR	118	0.209 ± 0.017	1.32 ± 0.30	0.55	4.49	29%	29%
	Deming	118	0.213 ± 0.018	1.27 ± 0.31			28%	
	Robust	116	0.199 ± 0.016	1.44 ± 0.26	0.59	4.37	33%	
	Deming Robust	116	0.201±0.016	1.40±0.26			32%	
Dolly Sods, WV (rural)	Standard LLSR	105	0.140 ± 0.019	1.46 ± 0.25	0.35	3.03	48%	43%
	Deming	105	0.142 ± 0.019	1.43 ± 0.26			47%	
	Robust	99	0.120 ± 0.016	1.56 ± 0.19	0.38	2.83	55%	
	Deming Robust	99	0.122 ± 0.016	1.55 ± 0.19			55%	
Phoenix, AZ (urban)	Standard LLSR	110	0.383 ± 0.030	0.95 ± 0.36	0.60	5.21	18%	27%
	Deming	110	0.401 ± 0.031	0.75 ± 0.38			14%	
	Robust	103	0.447 ± 0.025	0.35 ± 0.29	0.76	5.22	7%	
	Deming Robust	103	0.460 ± 0.025	0.21 ± 0.30			4%	
Tonto, AZ (rural)	Standard LLSR	102	0.393 ± 0.040	0.12 ± 0.29	0.49	2.58	5%	54%
	Deming	102	0.425 ± 0.044	-0.08 ± 0.31			-3%	
	Robust	91	0.115 ± 0.022	1.44 ± 0.14	0.24	2.11	68%	
	Deming Robust	91	0.118 ± 0.022	1.43 ± 0.14			67%	
Beacon Hill, WA (urban)	Standard LLSR	119	0.405 ± 0.014	-0.31 ± 0.12	0.87	2.78	-11%	11%
	Deming	119	0.410 ± 0.015	-0.35 ± 0.13			-12%	
	Robust	116	0.413 ± 0.013	-0.31 ± 0.11	0.90	2.80	-11%	
	Deming Robust	116	0.416 ± 0.013	-0.34 ± 0.11			-12%	
Mount Ranier, WA (rural)	Standard LLSR	99	0.364 ± 0.019	0.10 ± 0.08	0.78	1.40	7%	7%
	Deming	99	0.370 ± 0.020	0.08 ± 0.08			6%	
	Robust	95	0.393 ± 0.015	0.04 ± 0.06	0.89	1.39	3%	
	Deming Robust	95	0.397 ± 0.015	0.02 ± 0.06			2%	

Table 2c.

Table 3. OC estimates by denuder (Equation 5), by backup filter subtraction (Q-TQB and Q-QQB), by RM (Deming Robust regression), and uncorrected front QFF OC for (a) PAQS and (b) RIOPA. OC measured on the backup filters and the $PM_{2.5}$ mass concentrations are also shown. Shown are mean values and means of lower 25% and upper 25% of $PM_{2.5}$ mass concentration data.

PAQS (N =301)	Full Dataset (mean ± st. dev)	Lower 25% (mean ± st. dev)	Upper 25% (mean ± st. dev)
Denuder ($\mu gC/m^3$) (N = 47)	2.36 ± 1.48	1.88 ± 1.27	3.82 ± 1.70
Q-QQB ($\mu gC/m^3$)	2.64 ± 1.44	1.74 ± 1.19	4.17 ± 1.41
Q-TQB ($\mu gC/m^3$)	2.09 ± 1.32	1.32 ± 1.11	3.48 ± 1.31
RM (Q – 0.90; $\mu gC/m^3$)	2.23 ± 1.61	1.18 ± 1.29	3.99 ± 1.51
Front QFF (Q; $\mu gC/m^3$)	3.12 ± 1.61	2.06 ± 1.29	4.88 ± 1.51
QQB ($\mu gC/m^3$)	0.48 ± 0.23	0.3 3± 0.16	0.71±0.23
TQB ($\mu gC/m^3$)	1.03 ± 0.39	0.75 ± 0.26	1.41±0.34
$PM_{2.5}$ Mass ($\mu g/m^3$)	15.64 ± 9.45	6.71 ± 1.72	28.72 ± 8.28

CA RIOPA (N = 40)	Full Dataset (mean ± std. dev)	Lower 25% (mean ± std. dev)	Upper 25% (mean ± std. dev)
Q-TQB ($\mu gC/m^3$)	4.16 ± 1.94	3.49 ± 1.79	4.85 ± 1.95
RM (Q – 5.24; $\mu gC/m^3$)	0.84 ± 2.16	0.16 ± 2.13	1.46 ± 2.19
Front QFF (Q; ($\mu gC/m^3$)	6.08 ± 2.16	5.40 ± 2.13	6.70 ± 2.19
TQB ($\mu gC/m^3$)	1.91 ± 0.64	1.90 ± 0.64	1.85 ± 0.54
$PM_{2.5}$ Mass ($\mu g/m^3$)	17.31 ± 6.56	10.66 ± 2.21	27.09 ± 5.36

NJ RIOPA (N = 44)	Full Dataset (mean ± std. dev)	Lower 25% (mean ± std. dev)	Upper 25% (mean ± std. dev)
Q-TQB ($\mu gC/m^3$)	3.32 ± 1.43	2.24 ± 0.73	4.83 ± 1.36
RM (Q – 3.05; $\mu gC/m^3$)	1.92 ± 1.66	0.72 ± 0.82	3.38 ± 1.78
Front QFF (Q; ($\mu gC/m^3$)	4.97 ± 1.66	3.77 ± 0.82	6.43 ± 1.78
TQB ($\mu gC/m^3$)	1.65 ± 0.50	1.53 ± 0.48	1.61 ± 0.53
$PM_{2.5}$ Mass ($\mu g/m^3$)	16.00 ± 8.03	8.35 ± 2.13	26.51 ± 8.51

TX RIOPA (N = 61)	Full Dataset (mean ± std. dev)	Lower 25% (mean ± std. dev)	Upper 25% (mean ± std. dev)
Q-TQB ($\mu gC/m^3$)	2.96 ± 2.44	1.44 ± 1.42	4.60 ± 2.80
RM (Q – 1.23; $\mu gC/m^3$)	3.92 ± 2.60	2.06 ± 1.44	5.90 ± 2.83
Front QFF (Q; ($\mu gC/m^3$)	5.15 ± 2.60	3.29 ± 1.44	7.13 ± 2.83
TQB ($\mu gC/m^3$)	2.18 ± 0.98	1.85 ± 0.63	2.53 ± 0.87
$PM_{2.5}$ Mass ($\mu g/m^3$)	14.92 ± 6.23	8.72 ± 1.37	23.65 ± 5.21

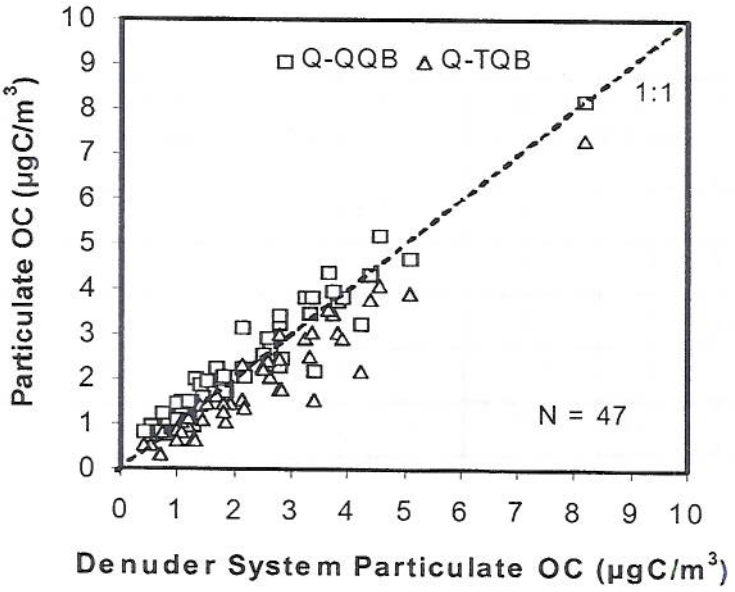
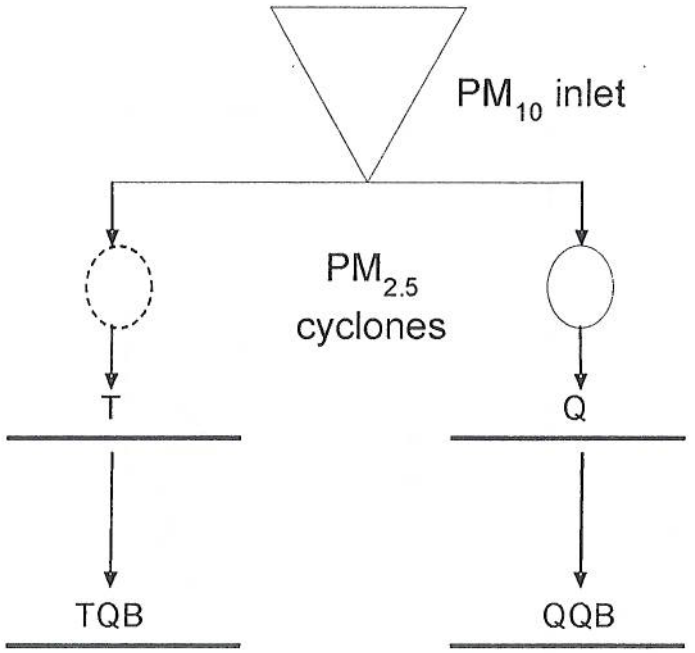


Figure 1. PAQS artifact-corrected OC calculated as Q-QQB (squares), Q-TQB (triangles), and from the denuder sampler (equation 5). Adapted from Subramanian et al.[5]

(a)

Dynamic Blank Configuration

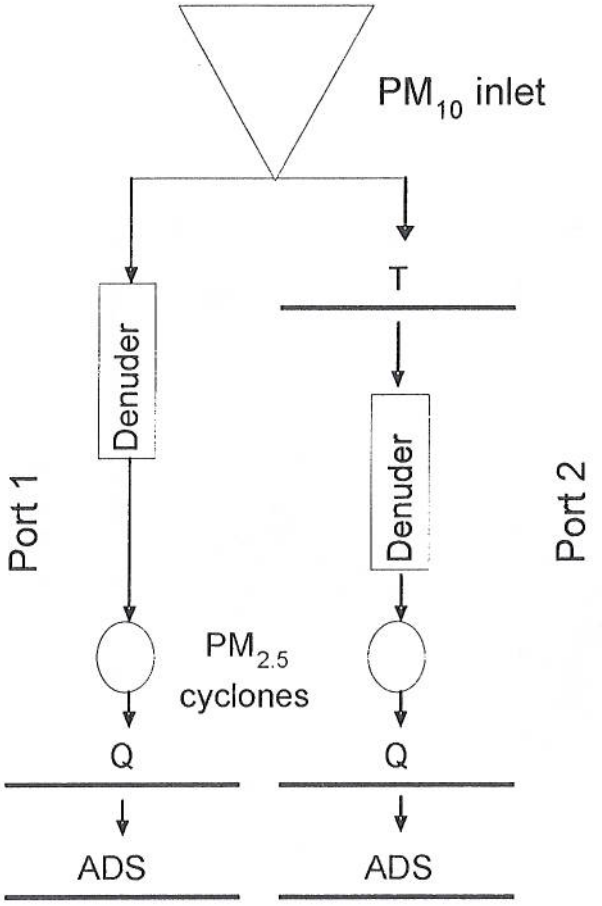


Particulate OC = Q – TQB

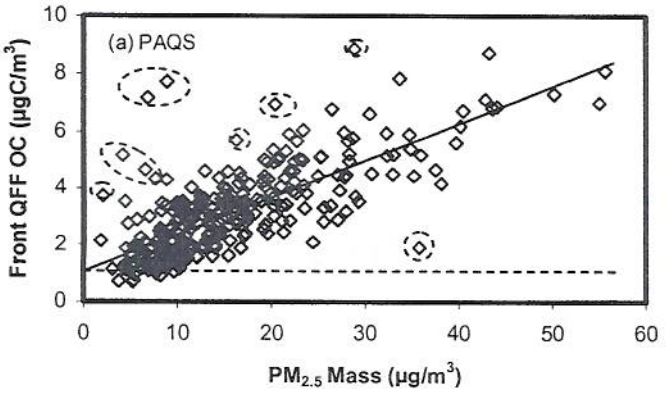
Particulate OC = Q – QQB

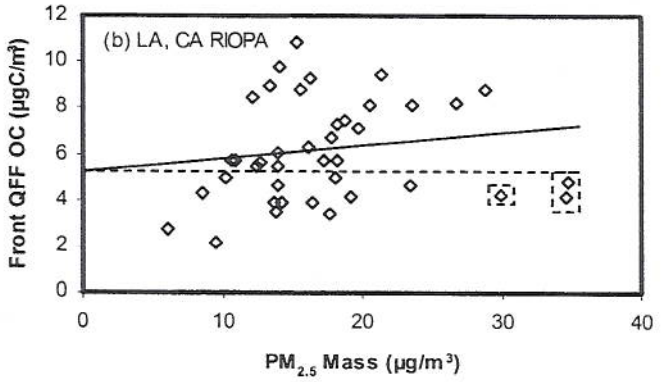
(b)

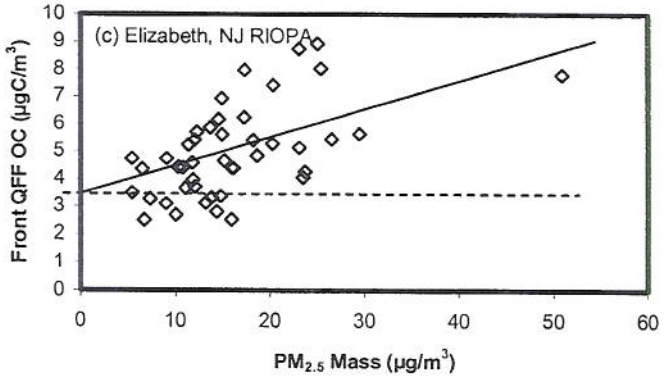
Denuder System Configuration

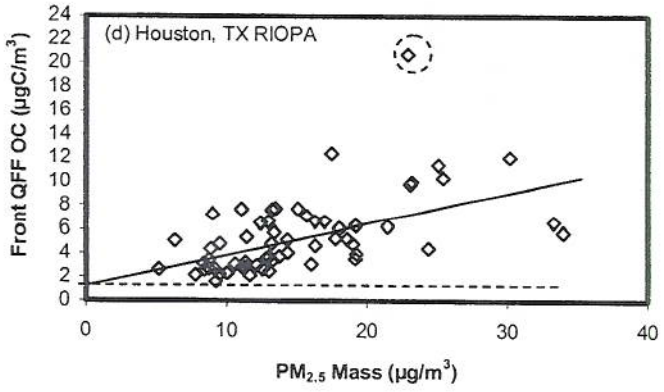


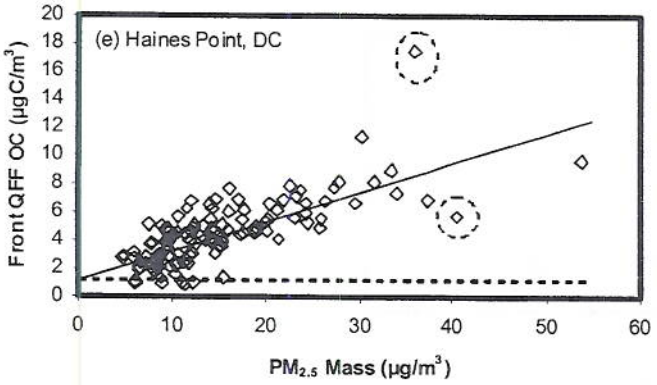
Particulate OC = $(Q + ADS)_{port1} - (Q + ADS)_{port2}$

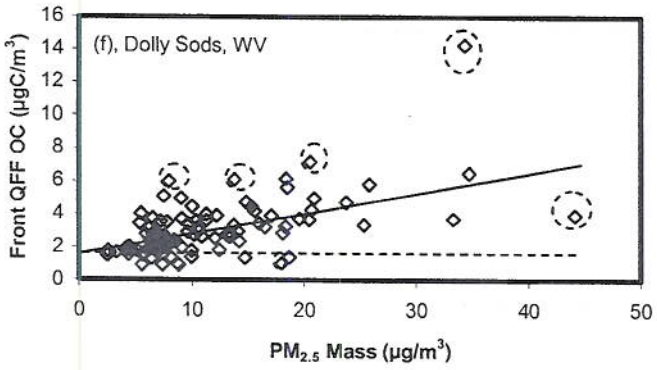

(a) PAQS
Front QFF OC (µgC/m³)
PM2.5 Mass (µg/m³)

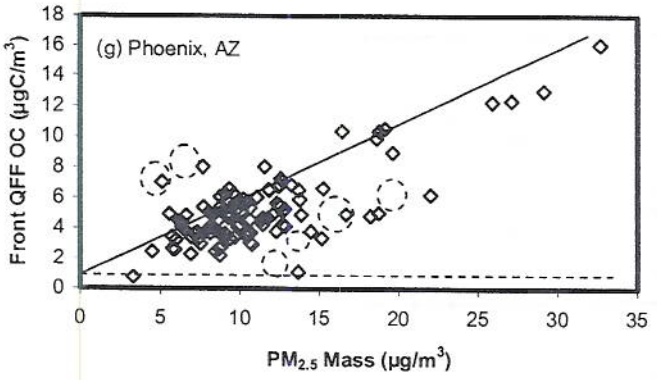

(b) LA, CA RIOPA
Front QFF OC (µgC/m³)
PM2.5 Mass (µg/m³)


(c) Elizabeth, NJ RIOPA
Front QFF OC (µgC/m³)
PM2.5 Mass (µg/m³)


(d) Houston, TX RIOPA
Front QFF OC (µgC/m³)
PM2.5 Mass (µg/m³)


(e) Haines Point, DC
Front QFF OC (µgC/m3)
PM2.5 Mass (µg/m3)
0
2
4
6
8
10
12
14
16
18
20
0
10
20
30
40
50
60


(f), Dolly Sods, WV
Front QFF OC (µgC/m3)
PM2.5 Mass (µg/m3)
0
2
4
6
8
10
12
14
16
0
10
20
30
40
50


(g) Phoenix, AZ
Front QFF OC (µgC/m3)
PM2.5 Mass (µg/m3)
0
2
4
6
8
10
12
14
16
18
0
5
10
15
20
25
30
35

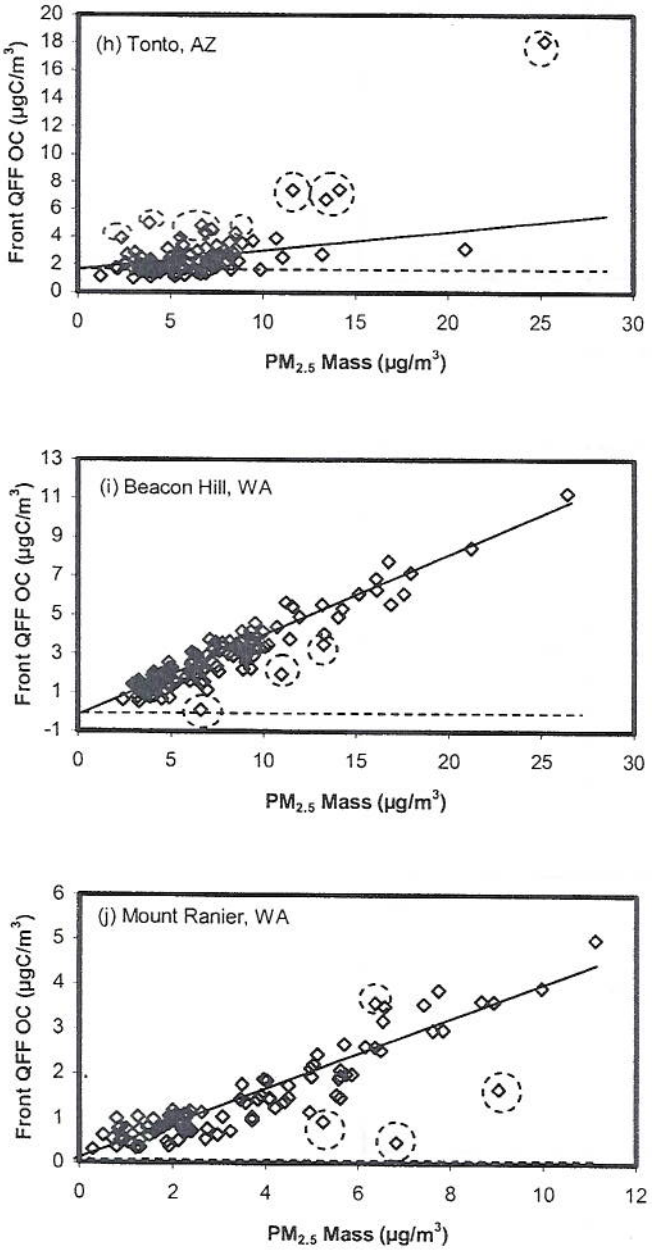
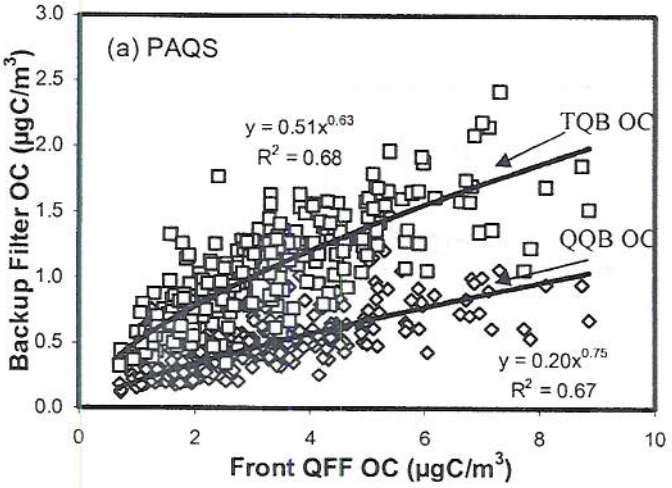
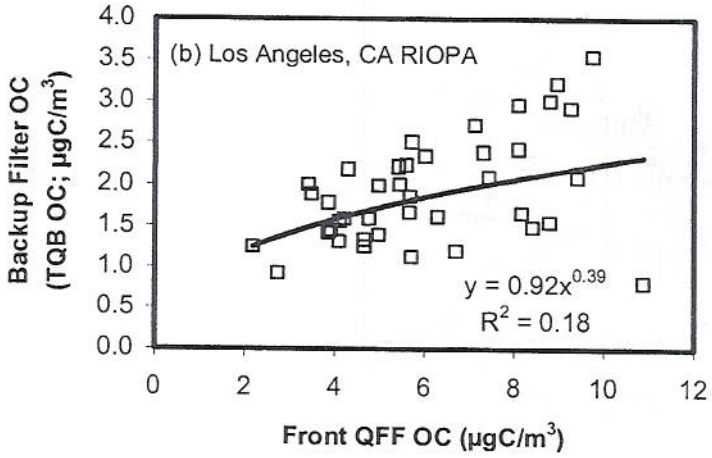
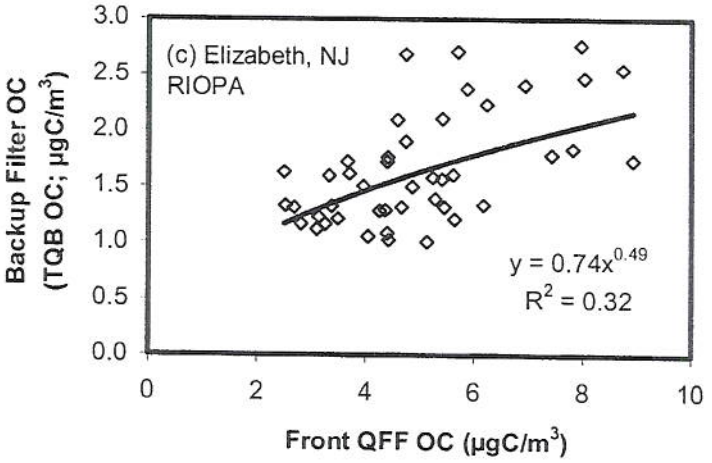


Figure 3. Measured front quartz fiber filter (QFF) OC ($\mu gC/m^3$) and $PM_{2.5}$ mass ($\mu g/m^3$) for (a) PAQS, (b) – (d) RIOPA sites, (e) – (j) Six Site STN/IMPROVE Comparison Study. Dashed circles are outliers in x or y identified by Robust Regression. The solid line is the Deming linear regression of y on x performed without outliers. The RM estimate is the Deming regression y-intercept value after outlier removal by the Robust regression (Table 2). The dashed line is the RM artifact estimate (y-intercept of regression; see also Table 2). In the RM of artifact correction, this value is subtracted from each sample. Note OC concentrations that fall below this line will be negative after RM artifact correction. Dashed squares indicate points not identified as outliers but with a large influence on the regression.


(a) PAQS
y = 0.51x^0.63
R^2 = 0.68
TQB OC
QQB OC
y = 0.20x^0.75
R^2 = 0.67
Backup Filter OC (µgC/m^3)
Front QFF OC (µgC/m^3)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
0
2
4
6
8
10


(b) Los Angeles, CA RIOPA
Backup Filter OC (TQB OC; µgC/m3)
Front QFF OC (µgC/m3)
y = 0.92x0.39
R2 = 0.18
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
0
2
4
6
8
10
12


(c) Elizabeth, NJ RIOPA
Backup Filter OC (TQB OC; µgC/m3)
Front QFF OC (µgC/m3)
y = 0.74x0.49
R2 = 0.32
0.0
0.5
1.0
1.5
2.0
2.5
3.0
0
2
4
6
8
10

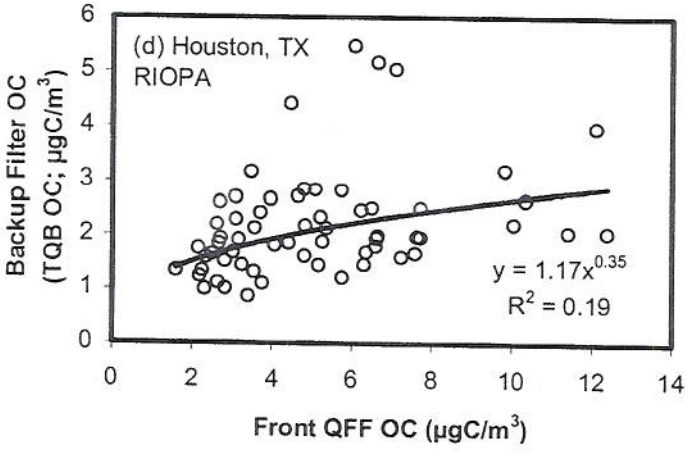

(d) Houston, TX RIOPA
Backup Filter OC (TQB OC; µgC/m3)
Front QFF OC (µgC/m3)
y = 1.17x0.35
R2 = 0.19
0
1
2
3
4
5
6
0
2
4
6
8
10
12
14

Figure 4. Measured organic adsorption artifact OC (TQB or QQB) and front filter OC for (a) PAQS and (b) – (d) RIOPA sites. The increase in measured organic adsorption artifact with increasing front filter OC (a measure of the organic pollution level) was significant (linear regression t-test, $\alpha = 0.05$) for PAQS and RIOPA sites. An increase in the actual organic adsorption artifact with organic pollution level violates an assumption of the regression method of organic artifact estimation.

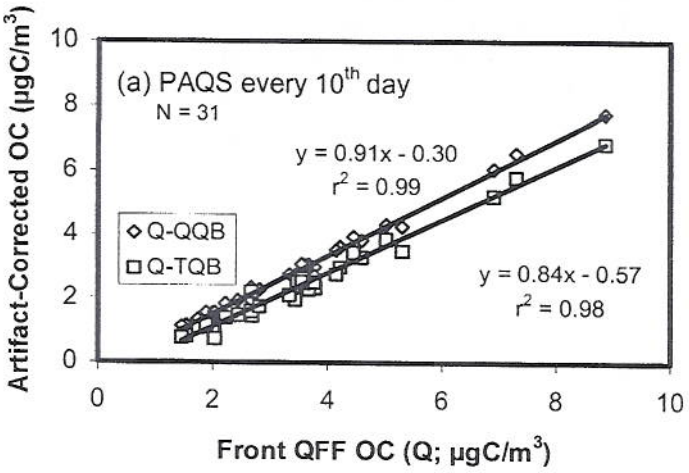


Figure 5. Linear least squares regression of artifact corrected OC (Q-QQB or Q-TQB; y-axis) on front QFF OC (measured on Q; x-axis), demonstrating intermittent backup filter collection with every 10th sample for PAQS. The regression lines shown correspond well with their full dataset equivalents (PAQS Q-QQB: $y = 0.89x - 0.14$, $r^2 = 0.99$; PAQS Q-TQB: $y = 0.81x - 0.43$, $r^2 = 0.97$; $N = 301$). For days without backup filter measurements, particulate OC can be estimated from regression equations such as these.