Effects of post-sampling conditions on ambient carbon aerosol filter measurements

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ABSTRACT

Ambient carbonaceous material collected on quartz filters is prone to measurement artifacts due to material gained or lost during post-sampling field latency, shipping, and storage. In seventeen sampling events over a one year period, ambient $PM_{2.5}$ aerosols were collected on quartz filters (without denuders) and subjected to various filter treatments to assess the potential for and extent of artifacts. The filter treatments simulated post-sampling environments that filters may be exposed to and included: storage at 40 °C for up to 96 h, storage at −16 °C for 48 h, and storage at room temperature (∼21 °C) for 48 h. Carbon mass on the filters was measured using a thermal-optical method. The total carbon (TC), total organic carbon (TOC) and total elemental carbon (TEC) as well as carbon thermal fraction masses were obtained. Statistical analyses were performed to identify significant differences in carbon fraction concentrations between filters analyzed immediately after sampling and after being subjected to treatment.

TOC and TC concentrations decreased by on average 15 ± 5% and 10 ± 4%, respectively, for filters maintained at 40 °C for 96 h but did not change for filters stored at room temperature or frozen for 48 h. TEC did not change for any of the filter treatments. The mass concentration for the organic carbon thermal fraction that evolves at the lowest temperature step (OC1) decreased with increasing storage time at 40 °C with average losses of 70 ± 7% after 96 h. Therefore, OC1 is not a stable measurement due to post-sampling conditions that may be encountered. This work demonstrates that TOC and TC can have substantial measurement artifacts on filters subjected to field latency and other non-temperature controlled post-sampling handling, compared to the carbon loadings on the filter at the end of the sampling period.

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1. Introduction

Ambient aerosols collected on filters are subjected to field latency, shipping, and storage conditions that may result in measurement artifacts. For example, semi-volatile aerosols collected on filters may volatilize when exposed to slightly elevated temperatures while they remain in the sampler after sampling has completed (field latency) or during non-temperature controlled shipping and storage. As a result, the analyte mass measured at the analytical facility might deviate from the mass of the analyte on the filter at the end of sampling; the amount of this deviation is the post-sampling artifact. The Interagency Monitoring of Protected Visual Environments (IMPROVE) and Chemical Speciation Network (CSN) are two major ambient monitoring networks in the United States that routinely collect rural and urban aerosols, respectively, and report ambient particle species concentrations. The data are used to monitor air quality trends, investigate long term health effects, determine aerosol sources, and determine compliance with regulations. In the IMPROVE network, at the end of a 24-h sampling period the filters remain in the sampler from 1 to 6 days and are shipped without temperature control. In the CSN network, filters remain in the field up to 48 h for samples collected every third day and up to 96 h for samples collected every sixth day, are shipped at 4 °C, and are stored at −20 °C prior to analysis. Both of these large networks as well as many state or regional monitoring efforts and other specialized air sampling projects may be prone to post-sampling artifacts due to lack of temperature control after sampling is complete.

Organic carbon (OC) is prone to artifacts that occur during sampling (Turpin et al., 2000). The positive sampling artifact is due to ambient organic vapors that adsorb onto the filter during sampling. The negative sampling artifact occurs when semi-volatile organic material that was collected as particulate matter volatilizes

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off the filter due to changes in temperature or gas-phase concentrations during sampling (Turpin et al., 2000). Many studies have investigated sampling artifacts of organic carbon (e.g., Chow et al., 2008; Eatough et al., 1993; Kirchstetter et al., 2001; Lewtas et al., 2001; Subramanian et al., 2004; Turpin et al., 2000).

Organic carbon is likely subject to post-sampling artifacts due to the same characteristics that make it subject to sampling artifacts. These characteristics are that organic carbon exists in gaseous, semi-volatile and non-volatile states, all of which are collected on the quartz filters, and that temperature and gas-phase OC concentration changes that occur prior to analysis may cause collected semi-volatile particles to volatilize. However, post-sampling artifacts have not been studied extensively. One study was conducted to measure artifacts due to shipping in the CSN network (Solomon, 2003; STI, 2005). Thirty-three pairs of $PM_{2.5}$ samples were collected with one filter from each sample shipped in coolers with gel ice packs and the other sample from each pair shipped at ambient temperatures prior to analysis for aerosol mass and chemical species. Organic carbon concentration measured by NIOSH 5040 thermal-optical analysis showed that the ambient shipped filters typically had higher concentrations than the cold shipped filters (positive post-sampling artifact), but these differences were statistically insignificant (STI, 2005). Chen (2002) studied field latency effects on carbon mass. In that study, two pairs of 24-h samples were collected on quartz filters. One filter from each pair was frozen immediately after sampling and the other filter from each pair remained in the sampler for 2.5 days during a period of dry, warm weather with maximum temperature exceeding 35 °C. The average loss for the filters with 2.5 days field latency compared to the immediately retrieved filters was 38% for TOC and 29% for TC. The loss of OC observed by Chen (2002) may be due to loss of adsorbed gas-phase OC and/or volatilization of collected particles.

The goal of this work is to determine the potential for and extent of post-sampling artifacts on ambient carbonaceous matter mass loadings collected on quartz filters. Several post-sampling conditions, or filter treatments, are simulated in the laboratory to mimic in a systematic way the post-sampling conditions experienced by a filter in a routine monitoring network. The filter treatments are simulated in the laboratory rather than using actual conditions (such as shipping or field latency) so that the same, controlled treatments can be applied to all filters collected over a one year period. Changes in carbon mass loading with treatment indicate a post-sampling artifact. Undenuded parallel ambient $PM_{2.5}$ samples are collected with some filters analyzed immediately after sampling while other filters are analyzed after being subjected to various storage conditions. These filter treatments include storage at 40 °C from three to 96 h, storage in the freezer at −16 °C for 48 h, and storage in the laboratory at room temperature (∼21 °C) for 48 h. The carbon mass on the filters is determined by thermal-optical analysis (Chow et al., 1993) and the carbon mass concentrations for the control- and treated-filters are compared using Analysis of Variance (ANOVA) and Dunnett's test to determine significant effects.

2. Methods

2.1. Sample collection and analysis

Twelve parallel IMPROVE Version II (Malm et al., 2004) $PM_{2.5}$ sampling channels without denuders were used to collect aerosol samples at a flow rate of 22.8 L per minute. IMPROVE Version II samplers have been utilized throughout the IMPROVE network since 2000–2001. Carbon measurements in the CSN network are being converted to IMPROVE-like samplers (including the same nominal flow rate and filter diameter as IMPROVE Version II); the

transition started in 2007 and is expected to be completed by the end of 2009. For this study, the IMPROVE Version II samplers were located on the roof of a three story building at the University of California, Davis. Two pre-fired quartz fiber filters (25 mm diameter, PALL®) that were in contact with each other were used in each sampling channel. Samples were collected once or twice per month from March 2007 through February 2008 (Table 1). All of the filters used for each sample were from the same lot. The sample duration was 24 h with runs beginning and ending at 7:00 AM local time. For each sampling channel, the flow rate was measured every 15 min and the average flow rate was used to calculate the air volume sampled. Filters were retrieved immediately after sampling to minimize aerosol alteration due to field latency.

The filter samples (front and back filters) were subjected to various treatments described in Section 2.2. Subsequently, carbon mass on both the front and back filters were determined using a thermal-optical analysis (TOA) method implemented on a Carbon Aerosol Analysis Lab Instrument ("Sunset Analyzer", S/N 119, Sunset Laboratory, Tigard, OR; Birch and Cary, 1996). This paper focuses on results from the front filters; data from the back filters for those samples analyzed immediately after sampling were used to interpret the results from the front filters. The analyzer was located in the building which housed the roof-top IMPROVE samplers allowing for negligible transport time from sampler to analyzer. Thermal-optical analysis was conducted with the IMPROVE_A temperature and time stepping protocol and the IMPROVE filter punch size of 0.5 cm^2 diameter (DRI Standard Operating Procedure, 2008; Chow et al., 2007) on the Sunset Analyzer using the temperature calibration procedure reported in Phuah et al., 2009. This approach was taken to mimic the IMPROVE protocol TOA to the extent possible using the Sunset Analyzer available on-site. Thermal-optical analysis by the IMPROVE protocol quantifies the carbon mass at each temperature step resulting in thermally-defined carbon fractions (Table 2). The sum of these carbon fractions is the mass of total carbon (TC) on a filter sample. The Sunset Analyzer uses laser transmittance to quantify the mass of pyrolyzed carbon (the optical pyrolysis carbon fraction, OP), which is organic material that is charred during the early stages of heating, while the IMPROVE_A method uses laser

Table 1
Summary of the filter treatment experiments.

Experiments[a]	Sampling dates	# of parallel filters collected	Filter treatment[b] (# of filter pairs[c] per treatment)
Experiment A	6/20/07 8/15/07 10/15/07 12/5/07 2/26/08	8	Control$_A$(2) H03(2) H06(2) H12(2)
Experiment B	3/29/07 5/23/07 7/25/07 9/16/07 11/28/07 1/28/08	12	Control$_B$(3) H24(3) H48(3) H96(3)
Experiment C	4/26/07 6/24/07 8/21/07 10/24/07 12/12/07 2/21/08	9	Control$_C$(3) RT(3) FZ(3)

[a] Sampling duration for all experiments was 24 h.
[b] Control$_i$ refers to filters immediately analyzed after sampling for Experiment *i*. HXX refers to filters that were stored at 40 °C for XX hours. RT and FZ refer to filters that were stored for 48 h at room temperature (21 °C) and in a freezer at −16 °C, respectively.
[c] A filter pair is a front and back filter.

Table 2
IMPROVE_A method temperatures, carrier gas and method detection limits (MDL) for the carbon fractions.

Carbon fraction	T_{FILTER}[a] (°C)	Carrier gas	MDL ($\mu g\ m^{-3}$)
OC1	140	Pure He	0.020
OC2	280	Pure He	0.032
OC3	480	Pure He	0.037
OC4	580	Pure He	0.020
EC1[b]	580	98% He, 2% O_2	0.030
EC2	740	98% He, 2% O_2	0.023
EC3	840	98% He, 2% O_2	0.015

[a] In the IMPROVE method, a 0.5 cm^2 punch from a quartz filter is heated to specified temperatures (T_{FILTER}), measured at the filter. After the carbon has fully evolved at one temperature, the oven is heated to the next temperature.

[b] During heating in the pure He environment, some organic matter is pyrolyzed (OP). The Sunset Analyzer used in this study uses laser transmittance to determine the OP mass. The MDL of OP was 0.070 $\mu g\ m^{-3}$.

reflectance to measure OP. The total organic carbon (TOC) mass is the sum of OC1, OC2, OC3, OC4 and OP and total elemental carbon (TEC) mass is the sum of EC1, EC2, and EC3 minus OP.

Two punches were analyzed from each filter to improve the precision in the estimated carbon loading. The carbon mass evolved from the two punches was averaged, and the total deposit area on the filter (3.53 cm^2) was used to calculate the mass loading (μg/filter). The mass loading was divided by the corresponding sampled air volume to obtain the 24 h average ambient carbon concentration ($\mu g\ m^{-3}$).

Additional filters were collected to establish the method detection limit (MDL) for each carbon fraction. Nine parallel ambient PM$_{2.5}$ samples were collected with a 3 h sampling duration to obtain lightly-loaded filters. Two 0.5 cm^2 diameter punches were taken from each filter and analyzed using the thermal-optical method. The carbon mass on a filter (obtained by averaging the mass from two punches) was divided by 32.8 m^3, the volume of air sampled over 24 h at the design flow rate, to obtain an effective 24 h average concentration ($\mu g\ m^{-3}$). The MDLs for each carbon fraction (Table 2) were calculated as three times the standard deviation of the average carbon mass measured for each of the nine parallel filters. The MDLs are specific to the use of two punches per filter and the instrument and temperature protocols used in this work and are generally lower than those reported by the IMPROVE network for OC fractions and similar to those reported by the IMPROVE network for EC fractions. EC3 concentrations were consistently below the MDL and were therefore were not included in the data analysis.

2.2. Filter treatment experiments

Three types of filter treatment experiments (referred to as Experiments A, B, and C) were conducted on filters collected on the dates shown in Table 1. These experiments involved various treatments on the filter samples to simulate possible post-sampling exposures in the field, during shipping and during storage prior to analysis. Eight parallel filter samples were collected for Experiment A. Two punches from each of two filters were immediately analyzed after sampling and the remaining six filters were placed in uncovered glass dishes which were set in an oven (Fisher Scientific Model IsoTemp Oven, accuracy $\pm$ 1 °C) maintained at 40 °C. At intervals of three, six and 12 h, two filters were drawn from the oven and analyzed. The four filter treatments in Experiment A were filters immediately analyzed (Control$_A$) and filters stored at 40 °C for three (H03), six (H06), and twelve (H12) hours (Table 1). The mass concentrations for each filter (obtained from the analysis of two punches) subjected to the same treatment were used to calculate the mean concentration (and standard error) for each carbon fraction for the filter treatment. Two parallel filters were

subjected to the same filter treatment to improve the precision of the estimated carbon loading and allow for small differences between filters treatments to be detected. In contrast to Experiments B and C (described below) which included three parallel filters for each treatment, Experiment A included only two parallel filters for each treatment because the TOA needed to be completed between treatments (which for Experiment A was as short as 3 h) and each parallel filter channel corresponds to four analyses (two punches each from the front and back filters).

Twelve parallel ambient filter samples were collected for Experiment B. Three filters were immediately analyzed after sampling and the remaining nine filters were placed in the oven at 40 °C. At intervals of 24, 48 and 96 h, three filters were selected and analyzed. The four filter treatments for Experiment B were filters analyzed immediately (Control$_B$) and filters stored at 40 °C for 24 (H24), 48 (H48) and 96 (H96) hours (Table 1). Mean concentrations and standard errors for each treatment were calculated as described for Experiment A. Experiment B was identical to Experiment A except the storage times were longer and three (rather than two) parallel filters were subjected to each treatment. Although it would have been ideal to have all treatments (H03 through H96) conducted on filters from the same sampling events, there were not enough sampling channels to simultaneously collect a minimum of duplicate samples for each treatment.

Nine parallel ambient filter samples were collected for Experiment C. Three filters were analyzed immediately after sampling, three filters were stored for 48 h in the laboratory at a temperature of ~21 °C and three were stored in a freezer located in the lab at −16 °C. Each filter that was stored at room temperature or in the freezer was placed in a Petri dish lined with pre-baked aluminum foil and sealed with Teflon tape. For the analysis of filters stored in a freezer, a single filter was removed from the freezer, a punch was obtained, the TOA on that punch was started, and the remaining portion of the filter was immediately returned to the freezer to minimize condensation of volatile organic carbon onto the cold filter. As shown in Table 1, the three filter treatments conducted in Experiment C were filters immediately analyzed (Control$_C$), filters stored at room temperature for 48 h (RT) and filters stored in a freezer for 48 h (FZ). Mean concentrations and standard errors for each treatment were calculated as described for Experiment A.

2.3. Statistical analysis of filter treatment data

ANOVA (Steel et al., 1997) was used to determine if any of the filter treatments resulted in statistically different carbon mass concentrations. ANOVA was performed on the natural log of the measured concentrations expressed in ng m^{-3}. An ANOVA was conducted on each carbon fraction (e.g., OC1) for each experiment (e.g., Experiment B) using all the front filters collected for that experiment (e.g., 72 front filters analyzed for OC1 in Experiment B). The sampling date was used as a blocking variable within the ANOVA to remove the variability in atmospheric concentrations and isolate the variance associated with the filter treatments. The natural log transformation provided homogeneous variances, which is a necessary condition for ANOVA, for all carbon fractions for all three experiments. The data did not pass the normality test but this is not expected to affect the validity of the ANOVA results.

For each experiment, the null hypothesis was that the mean concentrations, μ, of the controls and treatments have the same carbon mass concentrations. For example, the null hypothesis for Experiment A was H$_0$A: $\mu_{CONTROLA} = \mu_{H03} = \mu_{H06} = \mu_{H12}$. The hypotheses for all three experiments are listed in Table 3. The ANOVA test gave the significance probability, or *p*-value, for the null hypotheses for each carbon fraction. If the null hypothesis was rejected (confidence level of 95%), it indicated that at least one of

Table 3
Summary of the statistical analyses performed for this study.

Null hypothesis tested by ANOVA[a]	Dunnett's test[a] pairs
H_0A: $\mu_{CONTROLA} = \mu_{H03} = \mu_{H06} = \mu_{H12}$	$\mu_{CONTROLA} - \mu_{H03}$
	$\mu_{CONTROLA} - \mu_{H06}$
	$\mu_{CONTROLA} - \mu_{H12}$
H_0B: $\mu_{CONTROLB} = \mu_{H24} = \mu_{H48} = \mu_{H96}$	$\mu_{CONTROLB} - \mu_{H24}$
	$\mu_{CONTROLB} - \mu_{H48}$
	$\mu_{CONTROLB} - \mu_{H96}$
H_0C: $\mu_{CONTROLC} = \mu_{RT} = \mu_{FZ}$	$\mu_{CONTROLC} - \mu_{RT}$
	$\mu_{CONTROLC} - \mu_{FZ}$

[a] A confidence level of 95% was used.

the treatments had a mean carbon mass concentration that was statistically different from another treatment. In that case, Dunnett's test (Steel et al., 1997) was used to determine which treatment(s) were significantly different from the control. The treatment pairs analyzed using the Dunnett's test are shown in Table 3. Experiment A utilized only two parallel filters while Experiments B and C used three parallel filters; thus, there was more statistical power for Experiments B and C comparisons and these experiments are more likely to find a significant result that does indeed exist.

3. Results

3.1. Effects of filter treatments on the measurements of total organic carbon, total elemental carbon and total carbon

TOC and TC both significantly decreased (p-values < 0.01) for filters stored at 40 °C for 24 or more hours (H_0B, Table 4) with decreases of $15 \pm 5\%$ and $10 \pm 4\%$, respectively, after storage for 96 h (4 days). Fig. 1 shows the ambient concentrations of TOC (top), TEC (middle) and TC (bottom) and the absolute and percent carbon loss for filters stored for 96 h for each set of samples (identified by month). All samples stored for 24 h or more exhibited a decrease in TOC. There was no correlation (95% confidence) between the percent losses and ambient sampling temperature for TOC or TC for any filter treatment. TOC (but not TC) also decreased for storage times less than 24 h (H_0A, Table 4). TEC was not significantly impacted by any of the filter treatments conducted in this study (Table 4, Fig. 1). Filter storage at room temperature or in a freezer for 48 h did not significantly alter the carbon mass concentrations of TOC, TEC and TC (H_0C, Table 4).

3.2. Effects of filter treatments on carbon fraction OC1

Carbon fraction OC1, which on average accounted for $9 \pm 2\%$ of the TOC in this study, was significantly impacted in each experiment

Table 4
p-Values obtained from testing the significance of null hypotheses H_0A, H_0B, and H_0C for all carbon fractions. Underlined values correspond to the null hypothesis being rejected at the 5% significance level.

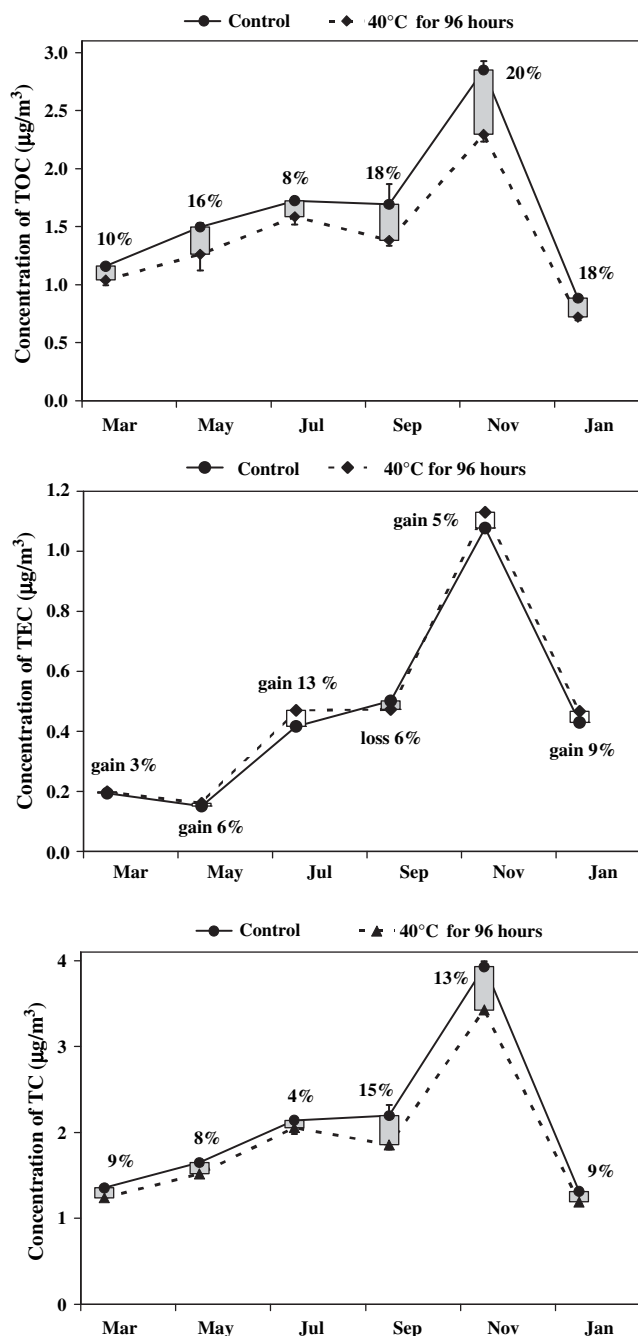| Carbon fractions	H_0A	H_0B	H_0C
TOC	0.01	<0.01	0.78
TEC	0.53	0.22	0.64
TC	0.14	<0.01	0.39
OC1	<0.01	<0.01	<0.01
OC2	0.03	<0.01	0.62
OC3	0.32	0.10	0.37
OC4	0.05	0.01	0.01
OP	0.02	0.09	0.83
EC1	0.29	0.05	0.35
EC2	0.23	0.72	0.03

Fig. 1. TOC (top), TEC (middle) and TC (bottom) mean concentrations and standard errors for control filters and filters stored at 40 °C for 96 h (H96, Experiment B) by month of sample collection. The absolute change in carbon mass is indicated by the dropdown bars and the percent change is labeled above the data points. For TOC and TC, all changes are losses. The grand mean losses are $15 \pm 5\%$, $5 \pm 6\%$, and $10 \pm 4\%$ for TOC, TEC and TC, respectively.

(p-values < 0.01 for all hypothesis tested, Table 4). OC1 always decreased when a filter was exposed to room or slightly elevated (40 °C) temperatures. Fig. 2 shows that the OC1 mass monotonically decreased with increased storage time at 40 °C with Dunnett's Test indicating significant differences in OC1 concentrations for all but the shortest (3 h) storage times. One-third ($33 \pm 6\%$) of OC1 was lost during the first 12 h of storage and one-half ($50 \pm 11\%$) was lost during the first 24 h of storage. $70 \pm 7\%$ (0.11 ± 0.04 μg m^{-3}) of OC1 was lost after the filter was stored for 96 h; this was the largest
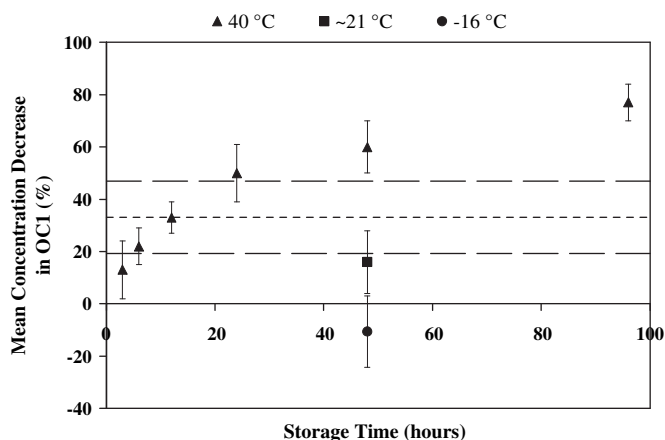
Fig. 2. OC1 mean concentration decrease as a function of storage time. The short dashed line is the mean ratio of OC1 mass on the back filter relative to the front filter for filters analyzed immediately upon completion of the eleven sampling events used to examine storage at 40 °C, and the long dashed lines are plus and minus one standard deviation of the ratio.

percentage mass loss and the largest absolute mass loss of all the fractions and treatments in this study. Fig. 3 shows the absolute and percent losses of OC1 for 12 h (top) and for 96 h (bottom) of storage at 40 °C by sampling month. Carbon mass changes for OC1 (or any other
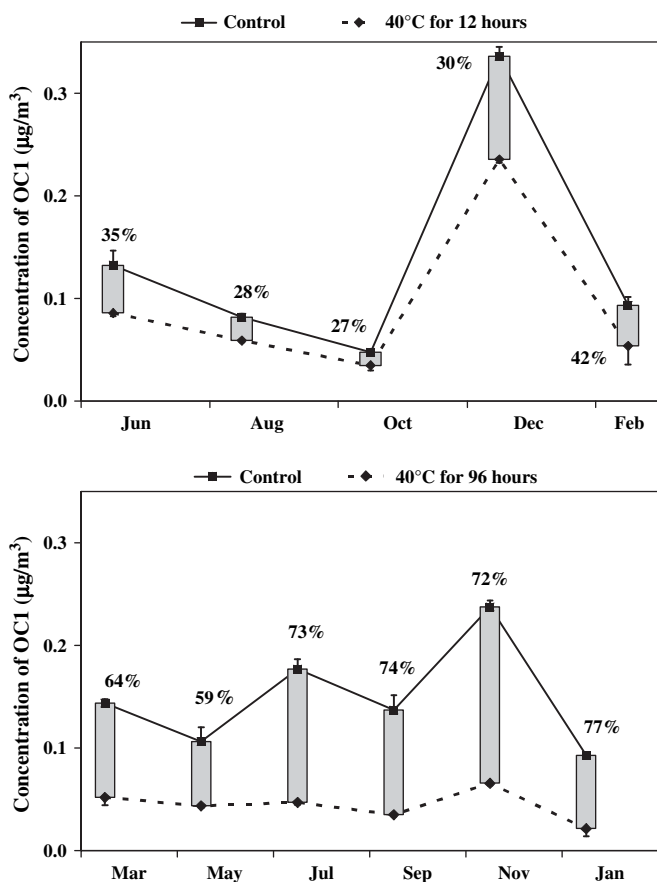
Fig. 3. OC1 mean concentrations and standard errors for control filters and filters stored at 40 °C for 12 h (top, H12 from Experiment A) and 96 h (bottom, H96 from Experiment B) by month of sample collection. The absolute loss is indicated by the dropdown bars and the percent loss is labeled above the data points. The grand mean OC1 losses are 33 ± 6% and 70 ± 7% for H12 and H96, respectively.

carbon fraction) were not correlated with the ambient temperature during sample collection.

Carbon mass losses from the front filters are placed in context by comparing such losses to the carbon mass loadings on the back filters. The back filters that were analyzed immediately after sampling (back filter controls) showed that OC1, OC2 and OC3 collectively accounted for 87% of the mass, with 18% as OC1, 40% as OC2 and 29% as OC3. Chow et al. (2008) reported similar results for the distribution of carbon mass across the carbon fractions on the back filters from IMPROVE network samples collected in 2005 and 2006. While in principle the back filter mass loadings may include both the adsorption of ambient gaseous organic compounds (positive sampling artifact) and adsorption of vapors from particles that volatilized off of the front filter during sampling (negative sampling artifact), Turpin et al. (2000) critical review of the literature suggests the back filter in a quartz-behind-quartz configuration (QQ, the design used in this study) is likely a lower bound on the positive artifact from vapor adsorption and does not provide information about the negative artifact. They state that a quartz-behind-Teflon configuration (TQ) is a better estimate of the positive adsorption artifact and cite studies where TQ back filters collected 30–50% more organic carbon (TOC) than QQ back filters. The short dashed line in Fig. 2 is the OC1 mass on the back filter relative to the OC1 mass on the front filter, both prior to any filter treatment and averaged over the eleven sampling events in Experiments A and B (one standard deviation about the average ratio is shown by the long dashed lines). Mean OC1 losses for 40 °C storage times less than 12 h are below the mean back-to-front ratio (short dashed line) and could be explained as the loss during treatment of carbon material originally collected as OC vapors during ambient sampling. Mean OC1 losses for 40 °C storage times greater than 12 h are above the mean back-to-front ratio; these losses cannot conclusively be attributed to the loss of particle carbon volatilized during the treatment because the QQ back filter likely underestimates the positive artifact on the front filter. However, the magnitude of the OC1 loss is compelling with 40 °C storage for 96 h leading to a loss that was 2.1 times the mass of OC1 on the back filter prior to filter treatment. The positive artifact would need to be very large for this loss to be explained solely by the treatment-induced desorption of organic vapors collected during ambient sampling; it is possible that the treatment also volatilizes particles collected during ambient sampling but a different sampling design would be needed to test this hypothesis. Although Fig. 2 shows only the average back-to-front OC1 ratio (and its standard deviation), all but one of the individual sampling events for all storage times greater than 12 h exhibited OC1 losses higher than the back-to-front OC1 ratio corresponding to that sampling event, indicating that the results of Fig. 2 hold true when the data is analyzed on a sample by sample basis. Thus, sample-specific trends for OC1 loss are consistent with the pattern shown in Fig. 2. Also, the back-to-front OC1 ratio was positively correlated with the ambient temperature during sample collection.

Fig. 4 shows the attribution of the sample-specific percent loss in TOC to each carbon fraction for filters stored at 40 °C for 96 h. For most carbon fractions and most sampling events, storage causes a decrease in carbon concentration. OC1 loss was the largest contributor to the TOC loss, accounting for 54 ± 25% of the TOC loss after 96 h. The results for the July sample suggest there can be interactions between the organic carbon fractions. For this sample, both OC1 and OP lost mass but the remaining three organic carbon fractions (OC2, OC3, OC4) gained mass. It is possible that the treatment not only volatized carbon but also redistributed carbon between the various fractions; the nature and extent of such redistribution would likely depend on the carbonaceous aerosol composition. Further details about the other
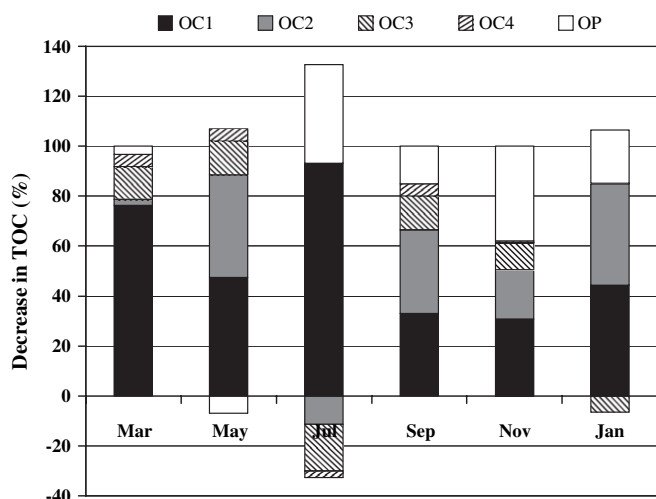
Fig. 4. Attribution of the mean percentage decrease in TOC to OC carbon fractions for 96 h of storage at 40 °C (H96, Experiment B) by month of sample collection. Values below zero denote increases in TOC.

OC fractions which contribute to the loss of TOC are discussed in Section 3.3.

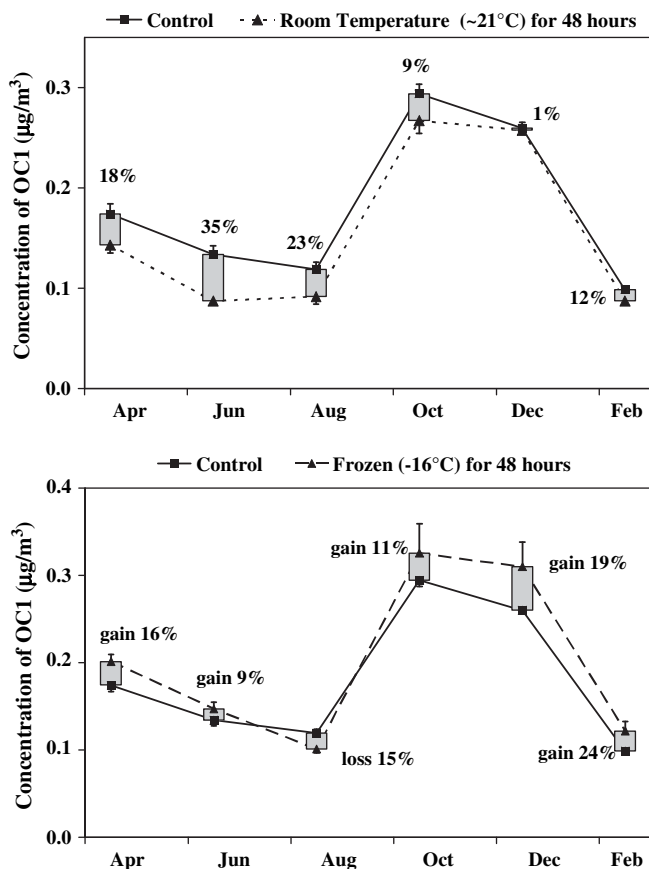OC1 decreased by 16 ± 12% for room temperature storage (∼21 °C) for 48 h. Fig. 5 (top) shows that all samples stored at room temperature lost OC1 but the variability between samples was large, ranging from 1% to 35%. The OC1 mass loss for this treatment was less than the mass on the back filter measured immediately after sampling indicating that the mass loss can be explained by loss of adsorbed gases only (no losses from the collected particles) and there must still be some adsorbed vapors on the filters from the positive sampling artifact (Fig. 2). With one exception the six samples stored in the freezer for 48 h gained OC1 mass (Fig. 5, bottom) although the change was statistically insignificant with average gain 11 ± 14% (Fig. 2). The observed OC1 mass gain for this treatment suggests that modest levels of organic vapors can adsorb onto the cold filters, perhaps when briefly exposed to laboratory room air just prior to TOA, and care should be taken when handling cold filters.

3.3. Effects of filter treatments on the other organic carbon fractions

Carbon fraction OC2 was on average 30 ± 5% of TOC. Losses were statistically significant for 40 °C storage times of 24 and 96 h (H_0B, Table 4). The average loss was 12 ± 10% after 96 h (Fig. 6, top) which is 21 ± 22% of the average TOC loss (Fig. 4). The average loss at 96 h was smaller than the positive OC2 sampling artifact as estimated by the back quartz filters analyzed prior to any treatment for Experiment B. This indicates that the OC2 loss can be explained by the loss of adsorbed vapors and might not involve losses from the collected particles. For a given storage time the fraction of OC2 lost was quite
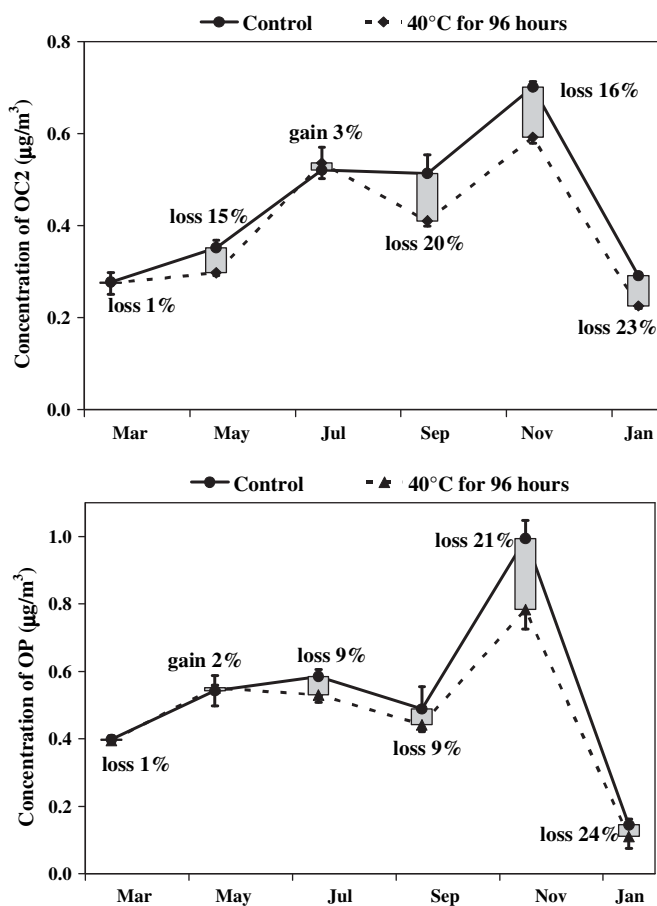

Fig. 5. OC1 mean concentrations and standard errors for control filters and filters analyzed after 48 h storage at room temperature at ∼21 °C (top, RT from Experiment C) and frozen at −16 °C (bottom, FZ from Experiment C) by month of sample collection. The absolute loss is indicated by the dropdown bars and the percent loss is labeled near the data points. The grand mean OC1 loss is 16 ± 12% for room temperature storage and the grand mean gain for −16 °C storage is 11 ± 14%.

Fig. 6. OC2 (top) and OP (bottom) mean concentrations and standard errors for control filters and filters stored at 40 °C for 96 h (H96, Experiment B) by month of sample collection. The grand mean losses are 12 ± 10% and 11 ± 10% for OC2 and OP, respectively.

variable between the samples and ranged from 3% gain to 23% loss at 96 h.

Pyrolyzed carbon, OP, accounts for $27 \pm 7\%$ of TOC. OP concentrations decreased by $11 \pm 10\%$ after 40 °C storage for 96 h (Fig. 6, bottom) which accounts for $18 \pm 18\%$ of the TOC loss (Fig. 4) even though these losses were statistically insignificant (Table 4). OC1, OC2 and OP collectively account for 80–120% of the TOC loss at 40 °C storage for 96 h (Fig. 4). The only filter treatment with a significant difference in OP concentrations was 40 °C storage for 12 h. Although both OC1 and OP were statistically lower for 12 h of storage, the loss in TOC for 12 h of storage was statistically insignificant.

OC3, like OC2 and OP, was a large fraction of TOC ($27 \pm 4\%$). However, OC3 concentrations did not change significantly for any filter treatment. Average loss of OC3 for 96 h of 40 °C storage was less than 3% ($<0.02 \ \mu g \ m^{-3}$) which accounted for $4 \pm 14\%$ of the TOC loss (Fig. 4). The loss was much less than the estimate of the OC3 positive sampling artifact obtained from the quartz back filters so it can be explained by volatilization of previously adsorbed gases.

Carbon fraction OC4 was the smallest fraction of TOC during this study ($6 \pm 2\%$) and showed statistically significant, but small absolute concentration changes, for some treatments. There was a small ($<5\%$, $<0.01 \ \mu g \ m^{-3}$) but statistically significant loss after 40 °C storage for 96 h, accounting for $\sim$2% of the TOC loss. In contrast, OC4 showed a statistically significant gain of $7 \pm 7\%$ and $9 \pm 10\%$ (both about $0.01 \ \mu g \ m^{-3}$) after storage at room temperature and in the freezer, respectively. However, these gains in OC4 are too small to be of practical concern especially since TOC was not significantly changed for these treatments.

3.4. Effects of filter treatments on elemental carbon fractions

Elemental carbon was $25 \pm 7\%$ of the total carbon averaged over all sampling events. TEC and EC1 were not significantly impacted by any filter treatment (Table 4). EC2, which was $4 \pm 2\%$ of the total carbon averaged over all sampling events, had statistically insignificant change for all treatments except for a small (less than $0.01 \ \mu g \ m^{-3}$) increase after storage at room temperature. This small change is not of practical concern.

4. Conclusions

This study has demonstrated that moderately warm post-sampling environments which may be experienced during field latency, shipping or storage, can cause a measurable loss of organic carbon material collected on quartz filters. The loss of organic carbon may cause a statistically significant measurement artifact for both total organic carbon and total carbon. However, the magnitude of losses experienced at a particular site or for a specific sample cannot be estimated from the results presented here due to differences in the particle and gas-phase composition and in the post-sampling environment. Therefore, warm environments should be avoided after sampling if the goal is to preserve the carbon mass loading that was on the filter at the end of the sampling period.

The largest loss is from the OC1 fraction. A substantial amount of OC1 may be lost after only hours at moderately warm temperatures and after days at room temperature. These losses can be explained by volatilization of vapor adsorbed during sampling. With longer exposure to warm temperatures, OC1 continues to be lost and it is not clear whether these losses are solely due to volatilization of adsorbed vapors or also includes the volatilization of collected particles. OC1 increased slightly after freezing indicating that care should be taken when handling cold filters. OC1 concentrations are highly dependent on post-sampling conditions and should therefore not be considered a robust measurement for filter

samples which may be exposed to room temperature or moderately warm environments after sampling.

Additional post-sampling artifacts occur in the OC2 and OP (pyrolyzed carbon) fractions and can be explained by the loss of adsorbed vapor only. OC3 and OC4 as well as elemental carbon are not substantially impacted by post-sampling conditions.

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