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Laboratory and field investigation of the adsorption of gaseous organic compounds onto quartz filters

Thomas W. Kirchstetter*, Craig E. Corrigan, T. Novakov

Environmental Energy Technologies Division, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, MS-73, Berkeley, CA 94720, USA

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Abstract

A common method for measuring the mass of organic carbon in airborne particulate matter involves collection on a quartz filter and subsequent thermal analysis. If unaccounted for, the adsorption of organic gases onto quartz filters will lead to the overestimation of aerosol organic carbon concentrations (positive artifact). A recommended method of correction for the positive artifact involves sampling with a backup filter. Placed behind either the primary quartz filter, or behind a Teflon filter and collected in parallel with the primary quartz filter, the carbon content of the quartz backup filter is a measure of the adsorbed organic material on the primary quartz filter. In this paper, we illustrate the application of this technique to samples collected in Berkeley, California. While the tandem quartz filter method can be successfully applied to correct for the positive artifact, we discuss two cases when this method will fail. We have found that the capacity for adsorption of organic gases is not uniform for all filters. Instead, filters manufactured by the same company, but having different lot numbers, exhibit variable adsorption capacity. Thus, a filter pair composed of filters from different lots may lead to significant under- or overestimation of particulate organic carbon concentration. Additionally, we have observed that the tandem filter method under-corrects for the positive artifact if the sampling time is short (few hours). Laboratory experiments with vapors of single organic compounds corroborate results based on ambient samples. The evolution of adsorbed organic gases, particularly polar compounds, during thermal analysis indicates that a single compound may experience two distinct adsorbent–adsorbate binding energies. Adsorbed gases may co-evolve with particles at temperatures in excess of 250°C. Published by Elsevier Science Ltd.

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1. Introduction

Quartz filters have long been used to collect airborne particulate matter for subsequent determination of carbon content by thermal analysis. Attributes that make quartz filters suitable for this purpose include their thermal stability, high particle collection efficiency, and low cost. Despite their widespread use, however, the determination of particulate organic carbon (OC) concentrations from the measured OC content collected on these filters is not straightforward. Adsorption of organic gases onto the quartz filter (and possibly the collected material)

and the evaporation of collected particulate matter during sampling may lead to erroneous results if not properly taken into account. The adsorption of organic gases may result in the overestimation of particulate OC concentrations because the adsorbed organics contribute to the total carbon measured during filter analysis. Conversely, the evaporation of collected particles may result in the underestimation of organic carbon concentrations. Hence, these phenomena are commonly referred to as the positive (adsorption) and negative (evaporation) artifacts.

Whether the main artifact is adsorption or evaporation has been the subject of several publications. Basing their conclusion on laboratory and field measurements in Los Angeles, Turpin et al. (1994) assert that adsorption is the dominant artifact. However, Eatough and colleagues (Eatough et al., 1995, 1996; Cui et al., 1998) have

* Corresponding author.

E-mail address: twkirchstetter@lbl.gov (T.W. Kirchstetter).

estimated the magnitude of both artifacts using diffusion denuder sampling systems at remote and urban locations and conclude that evaporation is the dominant artifact. It may not be possible to generalize which is the dominant artifact because many variables, such as sample volume, filter face velocity, ambient air temperature, and sample chemical composition have to be considered (Van Vaeck et al., 1984; McDow and Huntzicker, 1990; Turpin et al., 1994).

A seemingly straightforward, well-known method to correct for the positive artifact involves sampling with two quartz filters, one placed directly on top of the other (in tandem). The top, or front, quartz filter removes all particles, and gas-phase organics adsorb onto both the front and back filters. The measured carbon content of the backup filter can be subtracted from that of the front filter to give an improved estimate of the organic particulate mass collected on the front. A refinement to this approach utilizes two tandem filter pairs: a quartz/quartz pair and a Teflon/quartz pair. Commonly used Teflon filters have a surface area several times smaller than that of quartz filters (Turpin et al., 1994), and Teflon filters, unlike quartz, are chemically inert. Several researchers have noted (McDow and Huntzicker, 1990; Turpin et al., 1994) that the quartz filter behind the Teflon filter more closely approximates the mass of adsorbed organic gases on the front quartz filter than does its own quartz backup. Subtraction of the OC content of the quartz filter behind Teflon from that of the front quartz is therefore recommended for correction of the positive artifact, provided the face velocity is the same for both filter pairs. Teflon filters are not thermally stable at high temperatures and are not suitable for thermal analysis, so both filter pairs are required.

The subject of this paper is the adsorption artifact. We are concerned with furthering our understanding of this artifact to improve estimates of aerosol organic carbon concentration. We illustrate the use of tandem filter arrangements to correct estimates of OC concentrations for the adsorption of organic vapors. We also discuss some important limitations of the tandem filter method that explain why it may not actually correct OC concentrations as expected. In doing so, we report results from field experiments involving the ambient mixture of organic compounds and laboratory experiments with individual organic compounds.

2. Sampling and analytical method

Ambient aerosols were collected at Lawrence Berkeley National Laboratory in Berkeley California. Samples were drawn through a anodized aluminum stack (4.8 m long, 10 cm inner diameter) equipped with a (Bendix 240) cyclone at the inlet. The inlet was 10 m above ground. The flow rate through the cyclone was chosen to pass

only particles with a mean aerodynamic diameter less than 2.5 μm . The lower end of the stack extended from outside into the building and terminated at a 20 l chamber from which aerosols could be simultaneously sampled through several ports.

Samples were collected using two 47 mm diameter filters, one placed directly on top of the other (in tandem). The filters were supported in stainless-steel holders that decreased the effective filtration surface to 35 mm in diameter. The sampling flow rate and corresponding filter face velocity were 30 l min^{-1} and 50 cm s^{-1} . Quartz (Pallflex 2500 QAT-UP) and Teflon (Gelman Sciences Teflo membrane, 2.0 μm pore size) filters were used.

In some cases, we employed a diffusion denuder to scrub organic gases from the sample air stream prior to passage through the filters. The denuder was similar to that described by Eatough et al. (1993) and consisted of 18 parallel strips of 3.6 \times 57.4 cm carbon-impregnated paper (Schleicher and Schuell) separated by 2 mm. The efficiency of removal of organic gases by this type of denuder has been evaluated by others (Cui et al., 1998).

In addition to field sampling, the adsorption of organic gases onto quartz filters was studied in the laboratory. Individual organic compound vapors were produced by blowing particle-free nitrogen over the surface of a 5–10 ml reservoir of the organic liquid at the bottom of a 250 ml glass gas washing bottle. The vapor sample then passed through a quartz filter at a flow rate of 1.78 l min^{-1} and a face velocity of 3.0 cm s^{-1} . These adsorption experiments were conducted at room temperature (20°C) with several saturated alkanes, alcohols, and carboxylic acids. The concentration of organic vapor in the sample air was not regulated or measured. We note simply that compounds with higher vapor pressure, for example decane, produced more concentrated vapors than compounds with lower vapor pressure, for example hexadecane.

Quartz filters, all of which were baked before use at 700°C for at least 6 h to remove carbonaceous impurities, were analyzed for carbon content using the evolved gas analysis (EGA) method described by Novakov (1981, 1982). In EGA, a portion of the filter is heated a constant rate of 20°C min^{-1} from 50 to 650°C in an oxygen atmosphere. The carbon-containing gases that evolve from the sample are converted to carbon dioxide over a manganese dioxide catalyst maintained at 800°C, which is subsequently measured with a nondispersive infrared analyzer (Beckman Model 870). A plot of the carbon dioxide concentration versus temperature is called a thermogram, and the area under the thermogram is proportional to the total carbon content of the analyzed sample. Thermograms show a structure, often in the form of well-defined peaks, that is indicative of the different volatilization, decomposition, and combustion properties of the carbonaceous material contained in the sample. Interpretation of the thermogram features is often a

necessary step in evaluating the sampling artifacts (e.g., Novakov et al., 1997a, b) and accurately differentiating between the organic (OC) and black carbon (BC) components of the sample (e.g., Novakov et al., 2000).

3. Results and discussion

3.1. Tandem filter correction method

The method of using tandem filters to correct for the adsorption artifact is illustrated in Fig. 1 for a sample collected at the Lawrence Berkeley National Laboratory site. In this experiment, samples were collected in parallel using three sets of filters, including a quartz pair (QQ), a Teflon filter placed directly on top of a quartz pair (TQQ), and a quartz pair preceded by the carbon denuder. The carbonaceous material retained on the front quartz filter (of the QQ pair, shown in Fig. 1a) is composed of organic carbon that evolves over the temperature range from about 100 to 450°C, and black carbon that evolves at the highest temperatures in the thermogram. The estimated BC content is proportional to the area under the Gaussian-shaped curve centered at about 520°C. Though not shown here, this estimate could be refined by resolving more completely the BC peak by removing organic material from the filter sample through solvent extraction (Novakov et al., 2000). The OC loading on this front filter, $10.3 \mu\text{g m}^{-2}$, is the difference of the total carbon, $12.9 \mu\text{g m}^{-2}$, and black carbon, $2.6 \mu\text{g m}^{-2}$, loadings.

The carbonaceous material collected on the quartz filter behind the Teflon filter (QBT) and the quartz filter behind the front quartz filter (QBQ), illustrated in Fig. 1b, is composed entirely of organic carbon. Unlike the front filter, neither backup filter indicates the presence of black carbon. This, of course, is expected because the front quartz and Teflon filters remove all particles from the sample air stream. The presence of carbon on the backup filter is the result of adsorption of gas-phase compounds. This adsorbed carbon evolves as two peaks: a primary peak at about 150°C, and a secondary, broader peak centered at about 320°C that extends to about 450°C. The primary peak in both the QBT and QBQ thermograms closely approximates the evolution temperature of the first peak in the thermogram of the front filter. We therefore attribute the presence of the first peak in the front filter's thermogram to adsorbed gases. The height of this peak is more closely approximated by the QBT sample than by the QBQ sample, indicating that the former is a better measure of the mass of organic gases adsorbed on the front quartz filter. (During thermal analysis of the front filter, adsorbed gases co-evolve with collected particulate material. Consequently, the height of its first thermogram peak would be greater than that of the backup filter, even if the backup filter adsorbed the

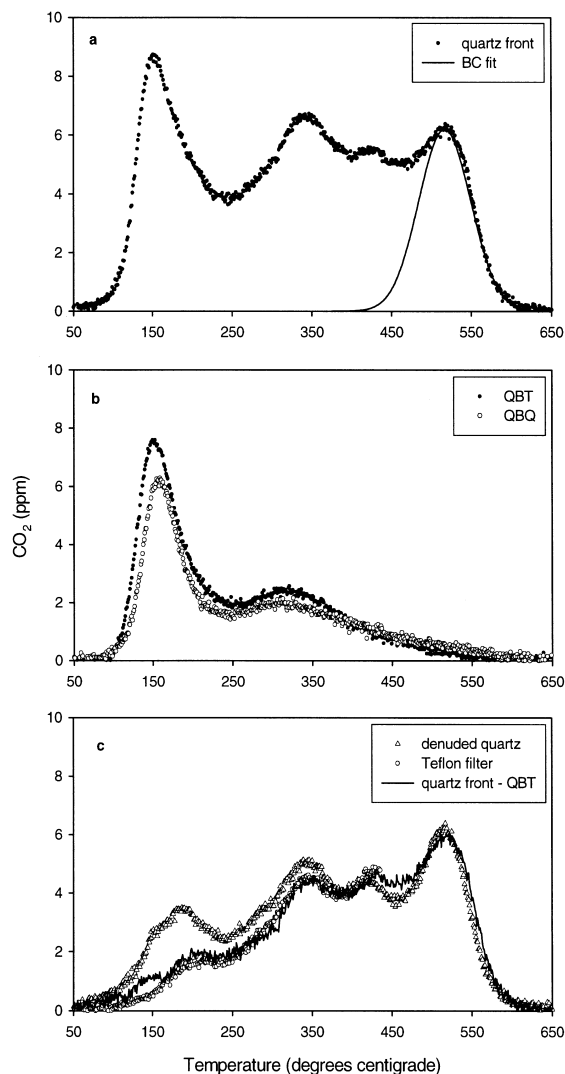


Fig. 1. Thermograms of parallel samples collected in Berkeley, California on 18–19 November 1998 (19.5 h duration): (a) front quartz filter of a tandem quartz pair; the Gaussian curve approximates the area of the black carbon peak; (b) backup filters, quartz filter behind a Teflon filter (QBT) and quartz filter behind the front quartz filter (QBQ); (c) denuded quartz filter, Teflon filter, and the thermogram constructed by subtracting thermograms of the front quartz and QBT samples.

same mass of adsorbed gases.) The carbon content of the QBT sample equals about half the front quartz sample's OC content. Thus, for this sample, the organic aerosol loading obtained using only the single quartz filter ($10.3 \mu\text{g m}^{-2}$) artificially overestimated by approximately 100% the true particle-phase OC. Subtracting back from front filter carbon contents to correct for the adsorption artifact improves the estimate to 6.0 or $5.3 \mu\text{g m}^{-2}$, depending on whether the QBQ or the QBT backup is used.

The thermogram of the quartz filter sample collected downstream of the carbon denuder is shown in Fig. 1c together with that of the Teflon filter, as well as the thermogram constructed by subtracting the front quartz and QBT thermograms. The “denuded” sample contains the same amount of BC as the undenuded front quartz sample, indicating that particles were unobstructed in their passage through the denuder. The denuded sample’s thermogram is very similar to the thermogram constructed by the difference method, except in the region from 125 to 225°C. This region reflects the presence of (presumably adsorbed gaseous) organics in the denuded sample that are not present in the undenuded quartz sample after correction (subtraction of QBT). This indicates that, though effective, the denuder efficiency was less than 100% for the removal of all gaseous organics. The OC content of the denuded sample, $6.3 \mu\text{g m}^{-2}$, is higher than that obtained using the tandem method, but is nonetheless more accurate than the single quartz filter estimate.

Finally, we note that the thermogram of Teflon filter sample and the reconstructed “sample” are essentially identical up to 425°C, at which point the Teflon filter begins to combust, precluding evaluation of the most refractory material. That these thermograms are nearly identical is affirmation that Teflon filters adsorb little or no gas-phase OC. Further proof is that the carbon content of the second quartz filter behind Teflon (TQQ, not shown in the figure) is 1.02 times that of the QBQ sample (i.e., essentially equal). Turpin et al. (1990) report that the BET surface area (in krypton) of Zefluor (non-stretched) Teflon filters is five times less than quartz filters. The surface area of the Teflo (stretched) Teflon filters used in this study is undoubtedly smaller still. In addition, unlike quartz filters that have chemically active surfaces, Teflon filters are relatively inert. It is likely a combination of these attributes that renders Teflon filters ineffective at depleting gas-phase OC concentrations.

In some cases, use of the denuder could be expected to promote the volatilization of condensed-phase organics due to the reduction of the vapor-phase partial pressure. Volatilization occurs when the gas above the collected deposit is subsaturated (Zhang and McMurry, 1992). The more volatile the organic aerosol, the greater will be this negative artifact. Though not the focus of this study, we suspect that volatilization losses are minor for the Berkeley aerosol sample because the carbon content of the denuded quartz sample is comparable to, and not less than, the carbon content of the corrected (front minus QBT) quartz sample. More thorough investigation of the negative artifact is presented elsewhere in the literature (e.g., Cui et al., 1998).

Thus far, we have demonstrated that the tandem filter method can be used successfully to correct for the positive artifact. What follows next is an investigation of why this method may fail to accomplish what is expected.

3.2. Variability of quartz filters

Another set of filter samples collected in Berkeley is shown in Fig. 2. In each panel a–d, front and back filter thermograms are displayed. The thermograms in Figs. 2a and b are those of samples collected in parallel for the same duration and under identical sampling conditions. Note that these thermograms are qualitatively very similar to those shown in Fig. 1. Applying the subtraction method (front minus backup) to these samples to correct for the positive artifact results in two estimates of total carbon (TC) that are in good agreement, 15.1 and $14.4 \mu\text{g cm}^{-2}$. So too are the corrected estimates of particulate OC loading, 10.2 and $9.5 \mu\text{g cm}^{-2}$, because the area under the BC peak at 520°C is the same for both samples.

While the two sample sets give similar corrected estimates of carbonaceous aerosol loading, it is clear from their thermograms that the first set of filters (Fig. 2a) collected more carbonaceous material than the second (Fig. 2b). More precisely, the first set collected more gas-phase organics. Qualitatively, this is evident from the shape of the thermograms. Quantitative proof is that both front filters have the same BC content. Furthermore, the difference in the carbon content of the two front filters is equal to the difference in the carbon content of the two back filters, indicating that the difference has to do only with gases. The concentration of adsorbed organics on the backup filter in Fig. 2a is $9.4 \mu\text{g cm}^{-2}$, 80% greater than that of the backup filter in Fig. 2b.

Since all experimental conditions were identical, the different capacity for adsorption of gaseous organics exhibited by these filters is attributed to the filters themselves. The filters used to produce Figs. 2a and b were purchased three months apart from the same vendor (Pallflex 2500 QAT-UP) and have different lot numbers, 53010 and 53321, respectively. For simplicity, we refer to these as lots A and B. The filters from these two lots are identical in appearance. In addition, scanning electron micrograph images of these filters did not reveal differences in fiber thickness or fiber density that might help explain these experimental observations. Filter weight (mass per projected area) varied among filters of different lots, but is also insufficient to corroborate the experimental observations. For example, lots A (“high capacity”) and B (“low capacity”) weigh about 6.7 and 6.0 mg cm^{-1} , different by 12%. But another filter lot that exhibits an adsorption capacity similar to that of lot B (“low capacity”) weighs 7.2 mg cm^{-1} .

The obvious undesirable consequence of the variable capacity for adsorbing organic vapors is the over- or underestimation of particle-phase OC concentrations that would result if one filter from each lot were used in the tandem filter pair. Fig. 2c shows the case where the tandem pair is composed of a front filter from lot A and a back filter from lot B. The reverse is shown in Fig. 2d.

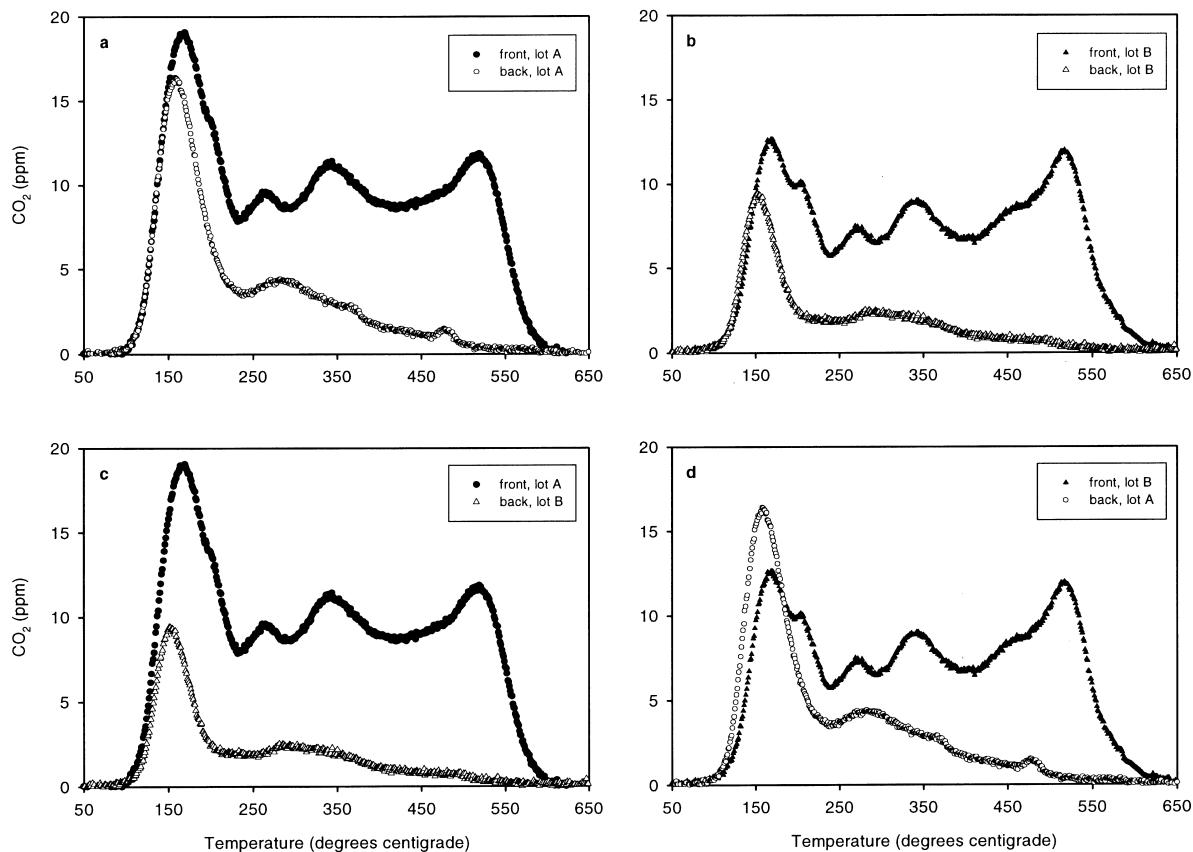


Fig. 2. Thermograms of parallel samples collected with quartz filters in Berkeley, California on 6 May 1999 (19.75 h duration). The filters were cut from two different batches of quartz filter paper purchased from the same manufacturer: (a) front and back filters were cut from lot A; (b) front and back filters were cut from lot B; (c) front filter from lot A, back filter from lot B; (d) front filter from lot B, back filter from lot A.

Whereas in Fig. 2a the intensity of the low-temperature peak is similar in the thermograms of the front and back filters, this is clearly not the case in Figs. 2c and d. In Fig. 2c, the backup filter falls short of accounting for the adsorbed gases on the front filter. In Fig. 2d, the backup filter exaggerates the adsorption artifact. So it is no surprise that the subtraction method (front minus back-up) to correct for the adsorption artifact will fail in these two cases. The estimate of TC loading after “correcting” for the adsorption artifact is $19.3 \mu\text{g cm}^{-2}$ in the former case, and $10.2 \mu\text{g cm}^{-2}$ in the latter. The relative error is even larger for OC because the concentration of BC is the same in both cases. The over- and underestimated OC concentrations are 14.4 and $5.3 \mu\text{g cm}^{-2}$, respectively, which differ by a factor of nearly three.

These observations are substantiated by laboratory results. Shown in Fig. 3 are the thermograms of a front quartz filter and its quartz backup that were used to sample for 15 min a prepared air stream of hexanol vapor in particle-free nitrogen, using the method described earlier. Hexanol vapors begin to evolve from quartz

filters at a temperature lower than 50°C , so the onset of the thermogram peak is not acquired. Nonetheless, the results are clear. The backup filter (cut from another lot 53011; presumably manufactured after the filters of lot 53010, lot A in Fig. 2) collected nearly three times more hexanol vapor than the front filter (lot 53321, lot B in Fig. 2).

While evident from these thermograms, the variation in the adsorbing capacity of these filters could easily be overlooked if they were analyzed for carbon content by other thermal methods. For example, the two-step thermal method provides a measure of total and black carbon concentrations. OC concentration is inferred by difference and is not thermally resolved in the manner in which it is in the EGA method employed in this study. This reduces the diagnostic capabilities of the user. For instance, the abundance of adsorbed gases on the front and back filters cannot be directly related by comparison of peak intensity since no peaks are obtained. Furthermore, if filters are submitted to an independent laboratory for analysis and only mass

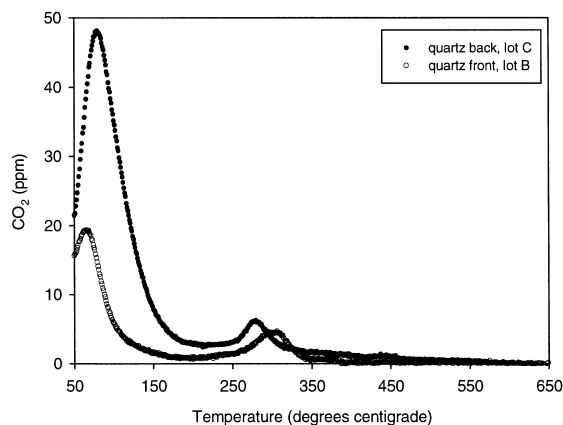


Fig. 3. Thermograms of a tandem quartz filter pair used to sample hexanol vapor. The front quartz filter, which retained less hexanol vapor than the back, was cut from lot B. The back filter was cut from lot C.

concentrations are reported (without a diagnostic tool such as a thermogram), then there is little hope of uncovering such behavior.

Since filters cut from different batches (lots) of filter paper have the same visual appearance, it is reasonable to expect that they might be used interchangeably. The consequence of this, as just mentioned, would be significant over- or underestimation of airborne carbonaceous aerosol concentration. In this example, OC concentrations were measured with tandem quartz filters. The variability of the positive artifact on quartz filters will also affect OC concentration estimates if sampling is performed with the more rigorous method of using a quartz/quartz and a Teflon/quartz filter pair. If the results presented here are typical of most widely used quartz filters, then the accuracy of existing organic aerosol measurements may need to be re-considered.

3.3. Influence of sampling duration

Four pairs of quartz filters (all cut from the same manufacturer's lot) were collected and analyzed to examine whether the validity of the tandem filter method for positive artifact correction depends on sample duration. One filter set was collected for 14 h, and the other three sets were collected for non-overlapping segments of this period: 2, 4, and 8 h were the other sample times. The total carbon contents of these filters are given in Table 1 and their thermograms are shown in Fig. 4. Table 1 also reports estimates of total carbon corrected for adsorption of organic gases (front minus back). If this correction method is valid, then the sum of the corrected carbon contents of the three segments should equal the corrected estimate for the 14 h sample. However, this is not the case, the sum ($27.4 \mu\text{g cm}^{-2}$) overestimates the single 14 h estimate ($17.5 \mu\text{g cm}^{-2}$) by 57%.

Table 1

Total carbon content ($\mu\text{g cm}^{-2}$) of several quartz filter samples collected in Berkeley, California on 26 May, 1999

Sample time (duration)	Front filter	Back filter	Front minus back
0800–1000 h (2 h)	7.9	1.2	6.7
1000–1400 h (4 h)	10.3	3.6	6.7
1400–2200 h (8 h)	18.2	4.2	14.0
0800–2200 h (14 h)	24.4	6.9	17.5

As noted earlier, if the area of the lowest temperature thermogram peak of the front and back filters is similar, the back filter likely provides a reasonable estimate of the positive artifact on the front filter. This is clearly not the case for the two hour sample of Fig. 4a. Neither is it the case for the 4 and 8 h samples, although the 8 h backup filter comes closer than the 4 h backup, and the 4 h backup comes closer than the 2 h backup. Of these filters, the 14 h backup comes closest to approximating the magnitude of the lowest temperature peak in its front filter's thermogram. Since, for the shorter sample times, the backup quartz filter collects less gas-phase organic compound mass than the front quartz, the subtraction method does not fully correct for the positive artifact.

The area of the most volatile peak in the front filter's thermogram can be estimated by deconvoluting it from the second peak with which it co-evolves. The material giving rise to the second peak is presumably associated with the particle phase since there is no indication of this peak on the backup filter. Performing this exercise indicates that the 14 h backup accounts for about 90% of the adsorbed material on the front filter, and is thus a reasonable measure of the artifact.

Comparison of the four thermogram sets shows that the height of the lowest temperature front filter peak continued to increase beyond 4 h of sampling, but no increase is evident beyond 8 h of sampling. (The small increase in peak height between the 8 and 14 h samples is mostly due to collection of particle-phase material.) However, the back filter continued to collect organic vapors beyond 8 h of sampling, which indicates that the sample air still contained organic vapors. These observations imply that the front filters of the 8 and 14 h samples were saturated and could not adsorb additional vapors. Thus, the reason that, for short sample times, the backup filter is a poor measure of the front filter's adsorbed mass is that the front filter has not yet become saturated. It therefore depletes significantly the concentration of vapor-phase organics in the sample air. The result is less adsorption on the backup filter compared to the front filter.

We conclude that, for these urban samples, the accuracy of the tandem quartz filter subtraction method

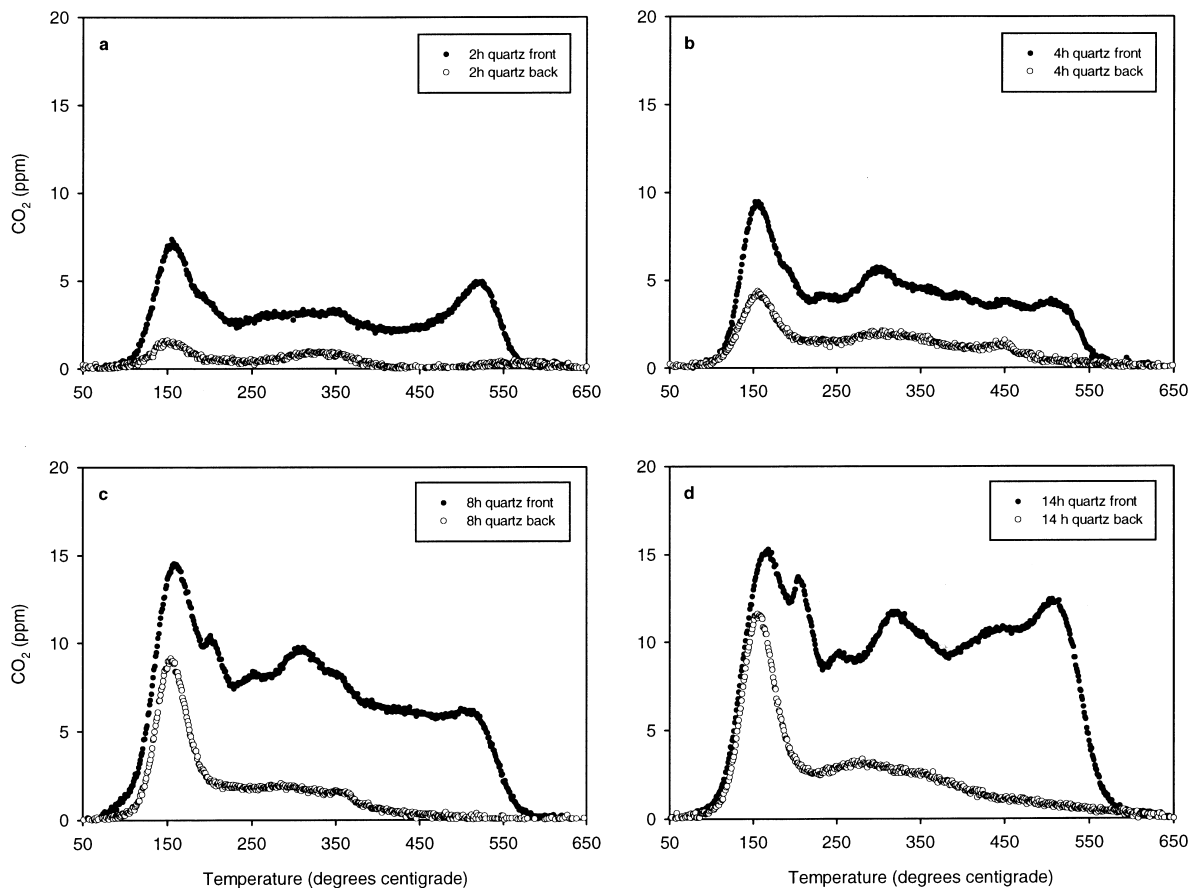


Fig. 4. Front and back filter thermograms of parallel samples collected in Berkeley, California on May 26, 1999: (a) 0800–1000 h; (b) 1000–1400 h; (c) 1400–2200 h; (d) 0800–2200 h.

improves with increased sampling time. Whether this is also the case in other source-influenced (e.g., biomass burning) or remote (e.g., oceanic) environments still must be explored. In heavily polluted environments, shorter sampling times may be appropriate. An extreme case is that of our laboratory experiments in which quartz filters were exposed organic vapors at concentrations that were orders of magnitude larger than typical in ambient air. In this exaggeratedly polluted air, saturation was reached inside of a few minutes.

3.4. Single compound adsorption

When studying the adsorption of single organic compounds onto quartz filters it was observed that polar compounds, such as alcohols and carboxylic acids produce different thermograms than nonpolar compounds, such as normal alkanes. Fig. 5 compares filter samples of hexanol and decanol vapor with those of decane, dodecane, and hexadecane. The saturated alkanes produce a single thermogram peak, and its evolution

temperature increases with increasing compound boiling point, or decreasing compound vapor pressure. Furthermore, since the concentration of organic vapor was highest for decane and lowest for hexadecane (discussed earlier), it is clear that the extent of adsorption increases with decreasing compound vapor pressure. The alcohols show similar behavior except that the evolution of these compounds produces two thermogram peaks: a primary peak at low temperature associated with most of the adsorbed mass, and a secondary peak at higher temperature. In this respect, the alcohols produce thermograms that are similar to the thermograms of backup filters of ambient samples (Fig. 1b).

Consider in Fig. 6 the appearance of the thermogram of the same hexanol filter sample analyzed 4 weeks after collection. Also shown are thermograms of a hexanoic acid sample analyzed immediately after collection, and then again 1 and 15 weeks later. In the interim between sample collection and subsequent analyses, these samples were stored at room temperature (20°C) in a plastic Petri dish. Over time, a very substantial decrease in the

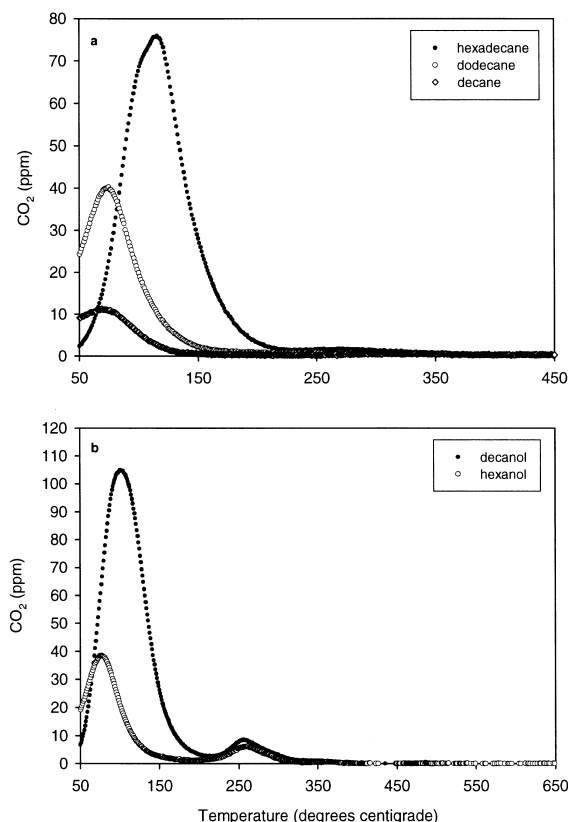


Fig. 5. Thermograms of quartz filters used to sample vapors of several different alkanes and alcohols: (a) hexadecane, dodecane, and decane; (b) decanol and hexanol.

magnitude of the first peak, but little change in the magnitude of the second peak occurred. Thus, it appears that the material that gives rise to the primary peak was lost from the filter during storage. In contrast, samples that were stored in a Petri dish in a freezer (-10°C) for the same duration do not show this loss of mass. In other words, loss of material from the filter is nearly eliminated when the vapor pressure of the adsorbed material is reduced. We infer from these observations that the decrease in adsorbed mass over time is the result of evaporation from the filters kept at room temperature.

Thermogram features reflect the interaction of the adsorbate molecules with the chemically active sites on the quartz filter substrate. Compared to the molecules that give rise to the primary peak, a larger desorption activation energy is required to free from the quartz filter the molecules that give rise to the secondary peak. This, of course, is why the secondary peak appears at a higher evolution temperature. A corollary is that some molecules have a larger enthalpy of adsorption than do the majority. The existence of two enthalpies of adsorption is an indication that there are two types

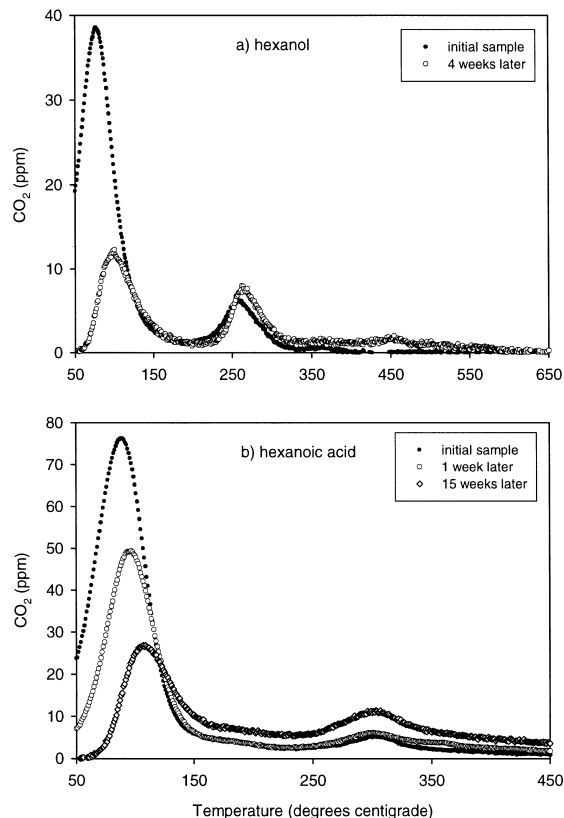


Fig. 6. Thermograms of quartz filters analyzed after sample collection and at subsequent intervals: (a) hexanol initially and four weeks later; (b) hexanoic acid initially, one week, and 15 weeks later.

of adsorbent–adsorbate binding: the weaker bond between the quartz filter and the adsorbate molecules akin to physical adsorption, and the stronger bond akin to chemical adsorption. Compared to the alcohols and acids, adsorption experiments with the nonpolar normal alkanes resulted in thermograms with little or no secondary peak. Thus, one hypothesis for the stronger bond is the chemical interaction of polar compounds with functional groups, for example hydroxyl groups, on the quartz filter surface.

An alternate interpretation of the two thermogram peaks, but one which we dismiss, is that they are the result of the thermal decomposition of the single organic compound into molecular fragments that evolve at two different temperatures. If this were the case, then the ratio of the areas of the primary and secondary peaks should be relatively unaffected by the amount of adsorbate retained on the filter. Instead, we observed (Fig. 6) a decrease only in the magnitude of the first peak, and little change in the magnitude of the second peak as the mass of adsorbate retained on the filter decreased due to evaporation.

4. Conclusions

Interest in organic aerosols continues to grow, fueled in part by studies of the radiative forcing of climate. In this arena, and in others such as the health implications of urban aerosol exposure, it is crucial that measurements of organic aerosol concentration be improved. The findings regarding the adsorption of organic gases onto quartz filters that are discussed herein add to the existing literature regarding sampling artifacts. Taken together, these studies paint a rather complex picture of such a seemingly simple procedure: the collection and analysis of particulate matter. Accurate determination of aerosol OC concentration requires careful sampling and analytical technique.

The major findings of this study of the positive sampling artifact are summarized here. (1) Use of only a single quartz filter to measure concentrations of carbonaceous particulate matter may result in gross overestimation. (2) The tandem filter method can be used to correct for the positive artifact. A quartz filter behind a Teflon filter (QBT) is a better measure of this artifact compared to the backup (QBQ) filter of a QQ pair. If, however, only a QQ pair is used, the accuracy of the method improves with increased sampling time. (3) All quartz filters should be cut from the same lot (batch) because of the variation in the adsorption capacity of filters from different lots. (4) Though not rigorously tested in this study, the diffusion denuder may be a viable alternative to the tandem filter method to correct for the positive artifact. (5) Organic gases adsorbed on quartz filters exhibit more than a single binding energy.

Most studies on the quartz filter artifacts consider only sampling in urban atmospheres. Still under-explored are related sampling issues in remote or marine environments, where aerosols may be primarily of natural origin, or in source (e.g., biomass) influenced atmospheres.

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