

Positive sampling artifact of carbonaceous aerosols and its influence on the thermal-optical split of OC/EC

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Abstract. Accurate measurement of carbonaceous aerosols is challenging, due to the sampling artifact and the problems of the split of OC/EC. Two approaches have been used to account for the positive artifact: backup quartz approach in which a backup quartz filter is placed either behind a front quartz filter (QBQ) or in a parallel port behind a Teflon filter (QBT), and organic denuder approach in which an organic denuder is placed upstream of the quartz filter. Both approaches were evaluated in Beijing, China, from January to February 2009. 10% of the OC captured by the bare quartz filter was from the positive artifact. The origin of backup OC was quantitatively evaluated by the denuder-based method. All of the QBQ OC was from gaseous organics passing through the front filter, but the QBQ had not reached equilibrium with gas phase due to the relative small sampling volume resulting in an undercorrection of the positive artifact by 3.7%. QBT OC was from both gaseous organics passing through the front filter (82%) and the evaporated organic carbon (18%), thus overcorrecting the positive artifact by 6.3%. Even the positive artifact-contributed QBT OC was found to overestimate the positive artifact, perhaps due to the difference in the adsorption properties of the loaded filter and the filter without particle loading. Re-partitioning of PC and EC was performed by the multiple linear regression approach. The attenuation coefficient of PC was twofold higher than that of EC, indicating PC was darker than EC, resulting in the underestimation of native EC by TOT-split-EC. It was also found that PC formed on the bare quartz filter ($45.56 \text{ m}^2/\text{g}$) was darker than that formed on the denuded filter ($38.64 \text{ m}^2/\text{g}$), indicating that the underestimation for the bare quartz filter was more significant.

1 Introduction

In recent years, advances have occurred in the measurement of ambient fine particulate matter ($\text{PM}_{2.5}$). Two trends are especially noticeable. The first trend is the development of the monitoring network on a regional scale. For example, the US Environment Protection Agency (EPA) has established three interlaced networks (Solomon et al., 2003): (1) the first network includes about 1100 $\text{PM}_{2.5}$ Federal Reference Method (FRM) monitors, which provide 24-h integrated $\text{PM}_{2.5}$ mass data to estimate population exposure; (2) the second network consists of the US EPA National $\text{PM}_{2.5}$ chemical Speciation Trends Network (STN) and the Interagency Monitoring of Protected Visual Environments network (IMPROVE), which provide 24-h integrated chemical composition data that support the US air quality program objectives (US EPA, 2004); (3) the third network, the US EPA's PM Supersites Program, includes eight Supersite projects which are designed to evaluate advanced monitoring methods for their potential transition to routine monitoring networks, together with the evaluation of models.

The second trend is the development of continuous monitoring (Chow et al., 2008), such as the TEOM for the real-time measurement of the $\text{PM}_{2.5}$ mass, the Sunset Laboratory Carbon Aerosol Monitor for the semi-continuous measurement of the OC and EC, and the continuous ion chromatography of water-soluble ions (Sciare et al., 2007). Continuous monitoring could provide an additional dimension in source apportionment, where source variations and meteorological variables could be included in the analysis, since highly time-resolution sampling enables measurement of short term duration variations in pollutant concentration due to emissions and meteorological variations (Wexler and Johnston, 2008).

Despite the progress mentioned above, the speciation measurement of $\text{PM}_{2.5}$, especially the measurement of the carbonaceous components (both integrated and semi-continuous) still has challenges. Among the factors



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that complicate the measurement of carbonaceous aerosols are the sampling artifact, the split of OC (organic carbon) and EC (elemental carbon), and the ratio of converting carbon mass to organic matter mass (Huebert and Charlson, 2000; Jacobson et al., 2000; Turpin et al., 2000; Turpin and Lim, 2001).

The sampling artifact includes both the positive artifact caused by the adsorption of gaseous organics and the negative artifact caused by the evaporation of collected particulate organic carbon. One way to account for the positive artifact (backup quartz approach) is to place a backup quartz filter, either behind a front quartz filter (QBQ) or in a parallel port behind a Teflon filter (QBT). The OC measured by QBQ or QBT provides an estimation of the gaseous organics adsorbed by the front quartz filter, or the positive artifact. Another approach to eliminate the positive artifact (organic denuder approach) is to place an organic denuder upstream of quartz filter, in which the gaseous organics are removed by diffusion to an adsorbent surface such as activated carbon (Eatough et al., 1993, 1999, 2003a; Mikuška et al., 2003) and polystyrene-divinylbenzene resin (XAD, Fan et al., 2003, 2004a, b). But the use of an organic denuder may induce a larger negative artifact, since the removal of gaseous organics enhances evaporation of particulate OC collected on the quartz filter. As a result, a backup quartz filter should be included (Viana et al., 2006a, b, 2007). In some studies, a highly adsorbent backup filter, such as an activated carbon impregnated filter (CIF or CIG, Eatough et al., 2001), or XAD impregnated quartz filter (XAD-Q, Fan et al., 2003; Swartz et al., 2003), was used to get a higher collection efficiency of evaporated organic carbon. OC determined by the denuded quartz filter and the backup filter is usually defined as NVOC (nonvolatile organic carbon) and SVOC (semivolatile organic carbon), respectively. As shown in Fig. 1, SVOC could account for a substantial fraction (10~70%) of the organic particulate matter. For the determination of gas-particle partitioning of individual organics (such as PAHs), PUF (Lane et al., 2000; Peters et al., 2000; Eiguren-Fernandez et al., 2004) and XAD resin (Gundel et al., 1995a, b; Temime-Roussel et al., 2004a, b; Goriaux et al., 2006) could also be used as backup adsorbent. A critical review of the organic denuder approach has been performed by Cheng et al. (2009). More recently, Ortiz et al. (2006, 2009) used an O-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine (PF-BHA) coated denuder and PFBHA impregnated quartz filter to determine the phase distribution of bi-functional carbonyls.

Special attention should be paid to denuder breakthrough when referring to the results from denuder-based method. Breakthrough is the amount of gaseous organics that are not removed by the denuder and subsequently adsorbed by the filter. The influence of breakthrough would be more significant when the adsorbent backup filter is included. For example, though the activated carbon denuder removed all the gaseous organics that could be adsorbed by quartz filter,

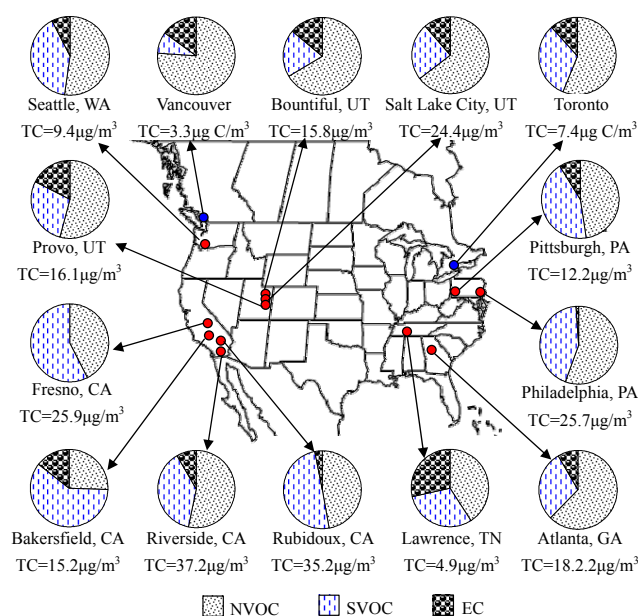


Fig. 1. NVOC, SVOC and EC concentrations determined in 14 North American cities. TC is the concentration of total carbonaceous components. Results from PC-BOSS sampler (CIF denuder in combination with backup CIF or CIG filter), which is developed by D. J. Eatough and co-workers, are shown by red dots; results from IOGAPS sampler (XAD denuder in combination with backup XAD-Q filter), which is evaluated by J. R. Brook and co-workers, are shown by blue dots. Data from Cheng et al. (2009).

breakthrough constituted 17%, 22% and 80% of the SVOC concentration (measured by the backup CIF filter), for concentrations of SVOC above 2, between 1 and 2, and below $1 \mu\text{g}/\text{m}^3$ (Modey et al., 2001). As a result, breakthrough should be measured and considered in correction when using the denuder-based method.

Though may be complicated by breakthrough, an organic denuder in combination with a backup filter is an effective approach to eliminate the positive and negative artifacts encountered by the measurement of carbonaceous aerosols. Comparison between the backup quartz and the organic denuder approach could provide important insights into the sampling artifact problem (Cheng et al., 2009), but few studies have been published.

Another concern regarding the measurement of carbonaceous aerosols is the split of OC/EC. A variety of analytical methods have been developed to separate OC and EC, such as the thermal method developed by Novakov (1982), the thermal manganese oxidation method developed by Fung (1990), and the thermal-optical method developed by Huntzicker et al. (1982). Ideally, a loaded filter is exposed to a prescribed temperature protocol first in an inert atmosphere (He) to determine OC and then in an oxidizing atmosphere (He/O₂) to determine EC. But a fraction of OC chars or pyrolyzes in the inert mode of the analysis, which can absorb light and requires an oxidizing atmosphere to evolve off the filter. This

fraction of OC is called pyrolyzed organic carbon, or PC. Thermal-optical method has been developed to account for the PC formation (Huntzicker et al., 1982), in which the carbon evolved in the oxidizing atmosphere that is necessary to return the filter reflectance or transmittance to its initial value is considered as PC. As pointed out by Yang and Yu (2002), the PC correction in the thermal-optical methods depends on one of the following two assumptions: (1) PC evolves before the native EC in the oxidizing atmosphere, or (2) PC and native EC have the same light attenuation coefficient. But both of these assumptions are invalid. The co-evolution of PC and EC has been demonstrated by Yu et al. (2002), Yang and Yu (2002), and Subramanian et al. (2006); the difference in the light attenuation coefficient has been demonstrated by Chow et al. (2004) and Subramanian et al. (2006). Moreover, the peak inert mode temperature (the temperature of the last step in the He mode) has a substantial influence on the EC measured, which also adds to the challenge in the thermal-optical split of OC/EC (Conny et al., 2003; Sciare et al., 2003; Chow et al., 2005a). Too high of a peak inert mode temperature (such as 870°C used in the NIOSH protocol) may underestimate the EC concentration due to the premature EC evolution (Chow et al., 2001), while too low of a peak inert mode temperature (such as 550°C used in the IMPROVE protocol) may overestimate the EC concentration due to OC not completely evolving or pyrolyzing into non-light-absorbing carbon (Schauer et al., 2003; Subramanian et al., 2006). More recently, the influence of brown carbon (Andreae and Gelencsér, 2006), or humic like substances (HULIS), on the split of OC and EC has been found to be a concern (Reisinger et al., 2008; Wonaschütz et al., 2009).

According to the results from Subramanian et al. (2006) and Schauer et al. (2003), it is suggested using the following criterion to choose the peak inert mode temperature: (1) the laser signal should reach its minimum value in the last step of the He mode, and (2) should not increase until the He/O₂ mode. It should be pointed out that the choice of temperature protocol is still a matter of debate and more researches are essential. The criterion above was drawn from the few studies available, and as a result was still limited. There are other factors that should be considered. For example, the last OC peak in the He mode should be well-separated with the first EC peak in the He/O₂ mode, which means the carbon signal should return to its baseline at the end of the He mode (ideally), rather than significantly above the baseline and with a long tail. Increasing the peak inert mode temperature would make the last OC peak better separated with the first EC peak, but it may also induce the premature EC evolution. As a result, these additional factors should be considered carefully and should be balanced with the current criterion.

As mentioned above, the partitioning of PC and EC automatically done by the analyzer is complicated by the co-evolution of PC and EC, and the difference in their light attenuation coefficient. As a result, re-partitioning of PC and

EC based on the calculation of their light attenuation coefficients could provide important insights into the problem of split of OC/EC (Chow et al., 2004; Subramanian et al., 2006).

In this article, we used a five channel PM_{2.5} sampler, including both the backup quartz approach channel and the organic denuder approach channel, to investigate the effect of the sampling artifact on OC measurements in Beijing, China. In addition, as pointed out by Chow et al. (2004), charring of the adsorbed gaseous organics may account for a substantial fraction of PC formation. As a result, influence of the sampling artifact on the split of OC/EC was also estimated.

2 Methods

2.1 Overview of the campaign

The sampling campaign reported here is the first stage of the “Improved Measurement of Carbonaceous Aerosols in Beijing” (IMCA) project, which is a major part of the “Carbonaceous Species and Complex Mechanism of Particulate Air Pollution” program. The primary aims of the campaign include: (1) evaluation of the capacity of the activated carbon denuder to eliminate the positive artifact; (2) evaluation of the origin of OC collected by the backup quartz filter behind a front quartz filter and in a parallel port behind a Teflon filter; (3) evaluation of the thermal-optical split of OC/EC and the influence of positive artifact on PC formation.

2.2 Sample collection

Ambient PM_{2.5} samples were collected at the Tsinghua University campus in Beijing, China. Details of the site were provided by He et al. (2001). Topography, meteorology, and the status of atmospheric particulate pollution of Beijing were summarized by Chan and Yao (2009), and the economic and energy consumption characteristics were described by Guinot et al. (2007).

29 sets of daily PM_{2.5} samples were collected from 9 January to 12 February 2009 by a Spiral Ambient Speciation Sampler (SASS) developed by MetOne. The SASS has five separate channels, operated through a common controller and pump. Each channel contains a sharp cut cyclone which is designed to give a 2.5 μm cutpoint with a slope and cutpoint similar to the FRM when operated at 6.7 Lpm (Peters et al., 2001; Solomon et al., 2003). Configurations of the five channels are shown in Table 1. Channel 1 and 2 were organic denuder approach channels, to determine nonvolatile organic carbon (NVOC) and OC evaporated from the front quartz filter and the front Teflon filter. Channels 3 and 4 were backup quartz approach channels. Channel 5 was the breakthrough channel, in which a quartz filter (TSP filter) was placed upstream of the denuder. As a result, OC collected by the sequential quartz filters in channel 5 was from the adsorption of gaseous organics that were not removed by the denuder, which was defined as breakthrough OC.

Table 1. Configurations of the five channel SASS sampler.

| Channel | 1 | 2 | 3 | 4 | 5 |
|-------------------------|--------------------------|------------------|--------------|--------------|------------------|
| TSP Filter ^a | NA | NA | NA | NA | Quartz (TSP) |
| Organic Denuder | Activated Carbon | Activated Carbon | NA | NA | Activated Carbon |
| Front Filter | Quartz (DQ) ^b | Teflon | Quartz (BQ) | Teflon | Quartz (BT-Q) |
| Backup Filter | Quartz (D-QBQ) | Quartz (D-QBT) | Quartz (QBQ) | Quartz (QBT) | Quartz (BT-QBQ) |

^a TSP filter was placed upstream of the cyclone for the determination of breakthrough. ^b Abbreviation in parentheses.

The activated carbon denuder (provided by MetOne) is 20 mm long and 38 mm in diameter with about 1000, 1 mm² channels, for a typical residence time of 0.18 s at 6.7 Lpm. All filters used were 47 mm in diameter. The diameter of the area with particle loading is 38 mm, inducing a face velocity of 9.8 cm/s. The Teflon (R2PJ047) and quartz filters (2500 QAT-UP) were both from Pall Corp. (Ann Arbor, MI). All of the quartz filters used throughout the campaign were taken from the same lot, to avoid the interlot variability in adsorption capacity (Kirchstetter et al., 2001). The quartz filters were pre-baked at 550°C in air for 24 h. 14 quartz filters were kept as blank. The average OC concentration of the blank filters was 0.45 μgC/cm², and no EC was detected. All the data reported in this article were corrected by the filter blank concentration without special statement.

2.3 Sample analysis

All the quartz filters were analyzed using a DRI Model 2001 thermal/optical carbon analyzer (Atmoslytic Inc., Calabasas, CA) (Chow et al., 2005b). The IMPROVE-A temperature protocol was used (Chow et al., 2007), which heated the sample to 140, 280, 480, 580°C in pure He atmosphere to determine OC1~OC4 and subsequently to 580, 740, 840°C in 2% O₂/98% He atmosphere to determine EC1~EC3, with the residence time defined by the flattening of carbon signals. PC is defined as the carbon that is measured after the introduction of He/O₂ atmosphere at 580°C but before transmittance returns to its initial value. OC is defined as OC1+OC2+OC3+OC4+PC, and EC is defined as EC1+EC2+EC3-PC. The thermal-optical transmittance (TOT) charring correction is implemented here, since the re-partitioning of PC and EC is based on the attenuation coefficient which is calculated from transmittance values (See Sect. 3.3). An example thermogram is shown in Fig. 2. In Fig. 2, the transmittance signal reaches its minimum value in OC-4 step, and does not increase until the introduction of O₂ in EC-1 step, according with the criterion in Sect. 1.

It was noticed that the reflectance signal began to increase in the OC-4 step, while the transmittance signal remained flat (Fig. 2). This was the case for all the 10 sets of filters (DQ and BQ), in which the minimum of transmittance signal were detectable. The increase of the reflectance signal was

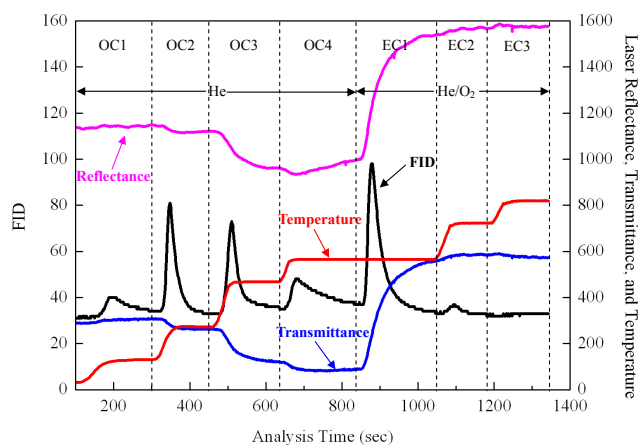


Fig. 2. Example thermogram (TC=16.27 μgC/cm²) for IMPROVE-A temperature protocol.

also found in the other 19 sets of filters (DQ and BQ). The increase was caused by the loss of light-absorbing carbon (PC or EC or both). It seemed that the temperature of the OC-4 step should be reduced to avoid the loss of light-absorbing carbon, but due to the following three factors, the OC-4 step temperature was not reduced. (1) The transmittance signal was flat, indicating the loss of light-absorbing carbon should not be significant. (2) Even at the current temperature, the split of OC/EC maybe affected by the artifact that OC not completely evolving or pyrolyzing into non-light-absorbing carbon. (3) The current temperature was close to the lower limit of the peak inert mode temperature (550°C) of different thermal-optical protocols. It should be pointed out that Schauer et al. (2003) draw the conclusion that IMPROVE temperature protocol may result in OC not completely evolving according to the evidence that the transmittance signal continued to drop at the start of the He/O₂ mode. As shown in Fig. 2, no drop of transmittance signal was seen after the introduction of O₂. As a result, though could not be excluded, the artifact that OC not completely evolving should not be significant.

It was also noticed that the carbon signal (FID) did not return to its baseline at the end of the OC-4 step. It seemed that temperature of the OC-4 step should be increased to make a

better separation between OC-4 and EC-1. But the increase would enhance the loss of light-absorbing carbon, and as a result, the OC-4 step temperature was not increased either.

After considering and balancing all the factors above, the IMPROVE-A temperature protocol was acceptable for these sets of Beijing aerosol.

3 Result

3.1 Evaluation of the activated carbon denuder

The use of an organic denuder may cause additional artifacts that complicate the measurement of carbonaceous aerosols, such as: (1) particle loss due to the diffusion to the walls of the denuder, (2) contamination problems of EC from the denuder charcoal particles, (3) evaporation of particulate organic carbon during transportation through the denuder, due to depletion of gaseous organics, and (4) denuder breakthrough. As a result, an evaluation of the denuder is essential.

3.1.1 Particle loss

Particle loss could be evaluated by comparing concentrations of EC, which is nonvolatile and the size distribution of which peaks at aerodynamic diameters below $1.0\ \mu\text{m}$ (Venkataraman and Friedlander, 1994; Huang and Yu, 2008), measured by the denuded quartz filter (DQ) and the bare quartz filter (BQ). DQ EC and BQ EC were compared in Fig. 3. As shown in Fig. 3, the particle loss in the denuder was negligible. Paired t-test also showed that EC values determined by DQ and BQ were not significantly different at a 95% level of confidence ($p=0.581$).

3.1.2 Contamination problems of EC

Shedding of the denuder material (activated carbon) has been observed by Subramanian et al. (2004) and Viana et al. (2006). The denuder used in this study did not exhibit any shedding, since no tiny charcoal particles were observed on the denuded quartz filter (DQ), Teflon filter (in channel 2), and the front quartz filter in the breakthrough channel (BT-Q) throughout the whole sampling period. Moreover, the result of OC/EC analysis showed that no EC was detected on the BT-Q. As a result, the contamination problems of EC were minimal.

3.1.3 Residence time in denuder

The denuder used in this study was designed such that the residence time of particles in the denuder was 0.18 s, less than 0.2 s, a critical value suggested by Kamens and Coe (1997) and Strommen and Kamens (1999) to avoid off-gassing of particulate organic carbon. It should be pointed out that though in some studies a residence time of more than

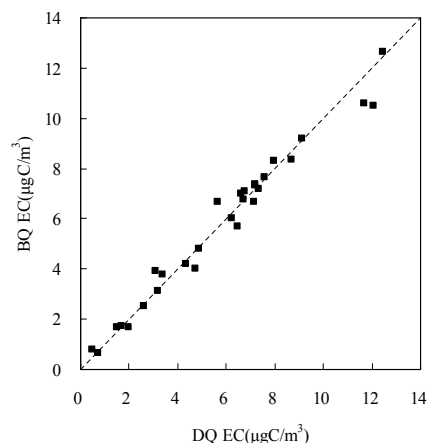


Fig. 3. Comparison of DQ EC and BQ EC.

1 s was adopted, no evidence of the loss of organics from particles was seen (Eatough et al., 1993).

3.1.4 Denuder breakthrough and efficiency

In the breakthrough channel, particles were collected by the TSP filter in front of the $\text{PM}_{2.5}$ cyclone (Table 1), and gaseous organics were captured by the organic denuder. As a result, OC collected by the front (BT-Q) and backup (BT-QBQ) quartz filter was from breakthrough. Comparable OC loadings were determined by the front and backup filters, averaging at 0.42 and $0.46\ \mu\text{gC}/\text{cm}^2$ respectively, which were also comparable with the filter blank values (averaging at $0.45\ \mu\text{gC}/\text{cm}^2$), as shown in Fig. 4. As a result, there was no breakthrough (that could be adsorbed by the quartz filter), and the efficiency of the activated carbon denuder to eliminate the positive artifact was 100% during the sampling period. Negligible amounts of breakthrough OC on the front quartz filter was also reported by Modey et al. (2001), Pang et al. (2002a, b), and Mader et al. (2001).

The field blank filter (or handling blank filter) was usually loaded onto the sampler and removed after one minute (without any air flow), as a result, OC determined by BT-Q and BT-QBQ could provide an upper limit for the field blank. Since both the BT-Q OC and BT-QBQ OC were comparable with the filter blank concentration, it could be concluded that the field blank concentration should also be comparable with the filter blank concentration. As a result, using the filter blank for correction was reasonable (see Sect. 2.2), though no field blank filter was collected during this sampling campaign.

3.2 Positive artifact and the origin of backup OC

The concentration of gaseous organics may be an order of magnitude higher than that of particulate OC (Mader et al., 2003; Mader and Pankow, 2003). As a result, the adsorption of gaseous organics by the bare quartz filter, or the positive

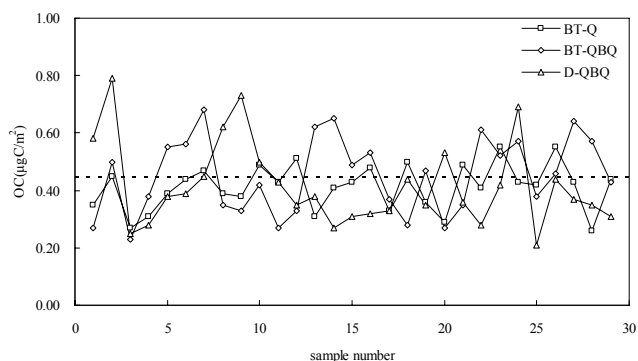


Fig. 4. OC concentrations determined by the front (BT-Q) and backup (BT-QBQ) quartz filter in the breakthrough channel, and by the denuded backup quartz filter (D-QBQ) in channel 1. Dashed line indicates average of blanks. Values not corrected by filter blank. Paired t-test showed that OC determined by BT-Q, BT-QBQ and D-QBQ were not significantly different at a 95% level of confidence; and independent t-test showed they were also not significantly different from the 14 filter blank values.

artifact, could be significant. The positive artifact in Beijing during the sampling period was demonstrated in Fig. 5a. About 10% of the OC determined by bare quartz filter was from adsorbed gaseous organics. As shown in Table 2, the fraction of positive artifact in the BQ OC was more significant for low-volume sampling (Olson and Norris, 2005); the fraction was also considerable when the OC concentration was low, such as the results reported by Europe and Canadian investigators. And a substantial amount of BQ OC was from the positive artifact when the contribution of biomass burning was important (Eatough et al., 2003b).

The backup quartz approach has long been used to correct the positive artifact (Hering et al., 1990; Turpin et al., 1994), but the origin of the OC collected by the backup quartz filter (backup OC, collected by QBQ or BQT), whether from gaseous organics passing through the front filter (positive artifact-contributed) or from evaporated particulate OC (negative artifact-contributed), has been debated for years (Turpin et al., 2000). McDow and Huntzicker (1990) found a decrease in the OC concentration determined by the bare quartz filter with increasing face velocity, and the dependence was removed when backup OC was subtracted, thus providing indirect evidence for the origin of backup OC (positive artifact-contributed).

The application of the organic denuder provides a direct approach to quantitatively evaluate the origin of backup OC, which could provide important insights into the positive artifact problem. The approaches developed by Cheng et al. (2009) were adopted for this purpose, and were briefly described here: (1) backup OC consists of both positive artifact-contributed OC and negative artifact-contributed OC, (2) OC determined by the denuded backup quartz filter, after corrected by breakthrough, provides an upper limit

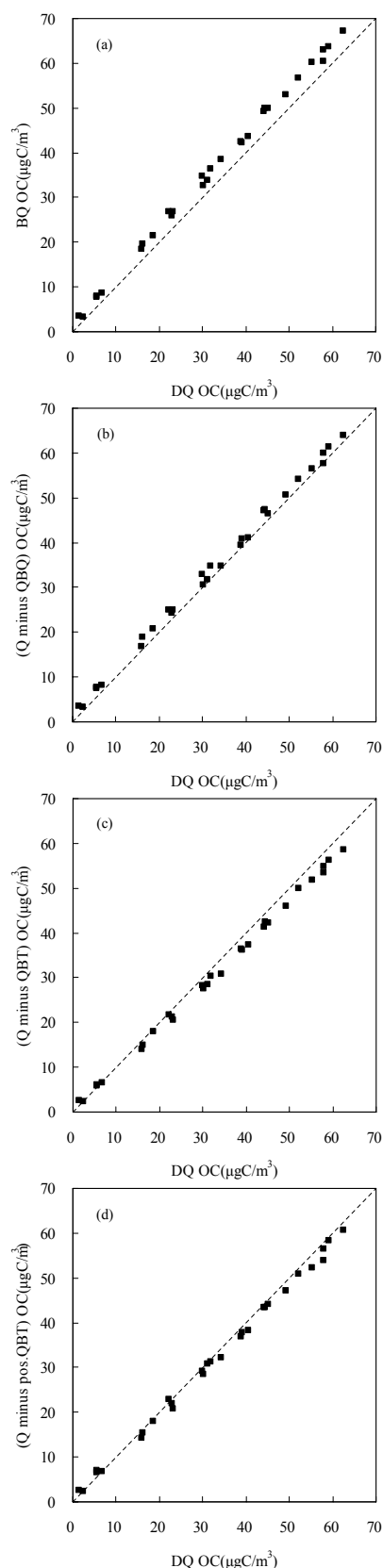


Fig. 5. Comparison of DQ OC with (a) BQ OC, (b) (Q minus QBQ) OC, (c) (Q minus QBT) OC, and (d) (Q minus pos.QBT) OC.

Table 2. Average concentrations of BQ OC and DQ OC at various sampling sites. Also listed are QBQ OC and the positive artifact defined as the difference of BQ OC and DQ OC.

| Sampling site | Sampling period | BQ OC | DQ OC | Positive artifact ^a | QBQ OC ^b | Reference |
|----------------------------|-------------------|-------|-------|--------------------------------|---------------------|--------------------------------------|
| Pasadena, CA | Aug 2001 | 10.89 | 9.04 | 1.85 (17%) | 1.87 | Mader et al. (2001) ^c |
| Provo, UT | Aug 1996–Jan 1997 | 17.69 | 11.75 | 5.94 (34%) | 4.10 | Ding et al. (2002) ^c |
| Southern Africa | Aug–Sep 2000 | 29.46 | 15.72 | 13.74 (47%) | 9.27 (15.16) | Eatough et al. (2003b) ^c |
| Toronto, Canada | July 2001 | 7.3 | 4.1 | 3.2 (44%) | – | Fan et al. (2003) ^c |
| Vancouver, Canada | Aug 2001 | 3.59 | 2.50 | 1.09 (30%) | – | Fan et al. (2004b) ^c |
| Pittsburgh, PA | Jul–Aug 2001 | 4.1 | 2.8 | 1.3 (32%) | 0.5 | Cabada et al. (2004) ^c |
| Research Triangle Park, NC | – | 11.8 | 4.0 | 7.8 (66%) | 3.5 (7.9) | Olson and Norris (2005) ^d |
| Ghent, Belgium | Jun–Jul 2004 | 2.7 | 1.9 | 0.8 (30%) | 0.16 | Viana et al. (2006a) ^d |
| Barcelona, Spain | Jul–Aug 2004 | 3.6 | 3.0 | 0.6 (17%) | 0.5 | Viana et al. (2006b) ^d |
| | Nov–Dec 2004 | 6.9 | 4.9 | 2.0 (29%) | 0.7 | |
| Fresno, CA | Winter, 1999–2003 | 11.76 | 10.8 | 0.96 (8%) | 1.28 (2.10) | Chow et al. (2006) ^d |
| | Summer, 1999–2003 | 4.8 | 3.9 | 0.9 (19%) | 0.91 (1.84) | |
| | 1999–2003 | 7.2 | 6.0 | 1.2 (17%) | 0.91 (1.75) | |
| Beijing, China | Jan–Feb 2009 | 36.13 | 32.57 | 3.56 (9.9%) | 1.93 (5.59) | This study ^c |

^a Percentage of positive artifact in BQ OC in parentheses. ^b QBQ OC in parentheses. ^c Values reported in $\mu\text{gC}/\text{m}^3$. ^d Values reported in $\mu\text{g}/\text{m}^3$.

of negative artifact-contributed OC, since the removal of gaseous organics enhances the evaporation of particulate organic carbon, (3) thus, the positive artifact-contributed OC is calculated as the difference between backup OC and negative artifact-contributed OC.

3.2.1 Evaluation of QBQ OC as estimation for positive artifact

As shown in Fig. 4, OC determined by the denuded backup quartz filter in channel 1, D-QBQ, was comparable with blank values, indicating that no evaporated OC was collected. Negligible amount of OC on denuded backup quartz filter (behind front quartz filter) was also reported by Mader et al. (2001), Ding et al. (2002), and Viana et al. (2006). This may be caused by two factors: (1) a fraction of evaporated

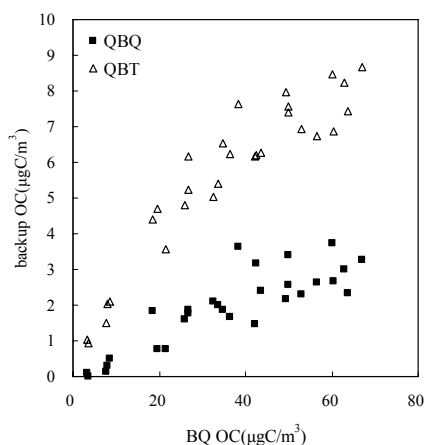
OC was re-adsorbed by the front quartz filter (Eatough et al., 2003b; Subramanian et al., 2004); (2) the evaporated OC has a low affinity to quartz filter. Viana et al. (2007) stated that $\text{DQ OC} \approx 0$ could be used as indication of the capacity of the organic denuder for eliminating the positive artifact. As a result, all the OC collected by the backup quartz filter in channel 3, QBQ OC, was from gaseous organics passing through the front filter, or positive artifact-contributed. Therefore using QBQ OC to correct the positive artifact was reasonable.

The remaining concern was whether the backup quartz filter (QBQ) adsorbed the same amount of gaseous organics as the front filter (BQ), in other words, whether both the front and backup filter were saturated or reached equilibrium with gaseous organics. The gaseous organics adsorbed by BQ could be estimated as $(\text{BQ} - \text{DQ}) \text{OC}$. As shown in Figs. 6, 7, and Table 3, no evidence for saturation was seen.

Table 3. Results of the statistical analysis of the Beijing PM_{2.5} OC/EC data.

| X versus Y | <i>n</i> | <i>R</i> ² | Slope | Intercept | X average | Y average |
|---|----------|-----------------------|-------|-----------|-----------|-----------|
| DQ OC versus BQ OC ^a | 29 | 0.9952 | 1.094 | 0 | 32.57 | 36.13 |
| | | 0.9980 | 1.045 | 2.09 | | |
| DQ OC versus (Q minus QBQ) OC ^a | 29 | 0.9954 | 1.037 | 0 | 32.57 | 34.20 |
| | | 0.9977 | 0.995 | 1.79 | | |
| DQ OC versus (Q minus QBT) OC ^a | 29 | 0.9985 | 0.937 | 0 | 32.57 | 30.54 |
| | | 0.9985 | 0.933 | 0.14 | | |
| DQ OC versus (Q minus pos.QBT) OC ^a | 29 | 0.9974 | 0.965 | 0 | 32.57 | 31.52 |
| | | 0.9975 | 0.955 | 0.41 | | |
| BQ OC versus QBQ OC ^a | 29 | 0.7396 | 0.052 | 0 | 36.13 | 1.93 |
| | | 0.7463 | 0.048 | 0.19 | | |
| BQ OC versus QBT OC ^a | 29 | 0.7423 | 0.145 | 0 | 36.13 | 5.59 |
| | | 0.8665 | 0.108 | 1.68 | | |
| ECcal versus TOT-split-EC (denuded) ^{b,c} | 10 | 0.9848 | 0.788 | 0 | 4.00 | 2.79 |
| ECcal versus TOT-split-EC (un-denuded) ^{b,c} | 10 | 0.9882 | 0.716 | 0 | 4.05 | 2.86 |
| PC (un-denuded) versus PC (denuded) ^{b,c} | 29 | 0.9537 | 0.934 | 0 | 8.11 | 7.51 |

^a Average values reported in $\mu\text{gC}/\text{m}^3$. ^b Average values reported in $\mu\text{gC}/\text{cm}^2$. ^c Values not corrected by filter blank.

**Fig. 6.** Comparison of BQ OC and different estimations of backup OC (QBQ OC and QBT OC).

Linear regression analysis showed that (Q–QBQ) OC and DQ OC correlated well and showed a remarkable fit with an almost 1:1 correspondence expect for a positive intercept of $1.79 \mu\text{gC}/\text{m}^3$ (Fig. 5b and Table 3), indicating that the difference between (Q–QBQ) OC and DQ OC was constant regardless their absolute concentrations. The most likely explanation for the stable difference was that the backup quartz filter had not reach equilibrium with the gaseous organics, due to the relatively small sampling volume (typically 9.3 m^3). Kirchstetter et al. (2001) found that the QBQ OC was a reasonable measurement of the positive artifact of a 14 h sample (corresponding to a sampling volume of 25 m^3) rather than with samples of 2, 4, or 8 h duration when

sampling at a flow rate of 30 L/min. According to the results reported by Subramanian et al. (2004), (Q–QBQ) OC was almost the same as the sum of NVOC (DQ OC) and SVOC (determined by CIG, corrected by breakthrough), indicating QBQ OC underestimated the positive artifact even for a sampling volume of 24 m^3 (16.7 L/min, 24 h samples).

Most of the results in Table 2 showed that the positive artifact was underestimated by QBQ OC, except that from Mader et al. (2001). Data reported by Mader et al. (2001) were re-interpreted, and result of linear regression analysis showed that BQ OC and DQ OC (no breakthrough was detected) correlated well ($R^2=0.9848$) with a slope of 1.00 and a positive intercept of $1.82 \mu\text{gC}/\text{m}^3$. A similar result (a slope of 0.98 and an intercept of $0.53 \mu\text{gC}/\text{m}^3$) was reported by Subramanian et al. (2004), who suggested that the almost 1 slope and positive intercept indicate the equilibrium of the bare quartz filter with gas phase. As a result, one possible explanation for the overestimation of positive artifact by QBQ OC (data reported by Mader et al., 2001) was that the adsorption capacity of the loaded quartz filter (BQ) was reduced by the particles, compared with the backup filter without particle loading (QBQ). It should be pointed out that the adsorption of gaseous organics on collected particles is unlikely to be important for a loaded filter, since the collected particles are presumably in equilibrium with the gas phase at the time of collection and the surface area of the collected particles is small relative to that of the quartz filter (McDow and Huntzicker, 1990). If this hypothesis were true, once the front quartz filter reached equilibrium with gas phase, there was the possibility that the backup quartz filter (QBQ) adsorbed more gaseous organics than the front one.

According to the statement of Subramanian et al. (2004), it seemed that even the bare quartz filter had not reached equilibrium (Table 3), indicating this was the case for the QBQ filter, since the front filter always reaches equilibrium before the backup one (Mader and Pankow, 2003). Then it could be concluded that, though all the QBQ OC was from gaseous organics passing through the front filter, the QBQ adsorbed less gaseous organics than the front one (Fig. 7) and thus undercorrected the positive artifact by 3.7%. (Fig. 5b and Table 3).

3.2.2 Evaluation of QBT OC as estimation for positive artifact

A substantial amount of OC was determined by the denuded backup quartz filter in channel 2, D-QBT OC, which was the negative artifact-contributed OC. The amount of positive artifact-contributed OC was obtained by subtracting D-QBT OC from the OC collected by the backup quartz filter in channel 4, QBT OC. 82% and 18% of QBT-OC was the average positive and negative artifact contribution. As a result, QBT OC overcorrected the positive artifact (by 6.3%, Fig. 5c and Table 3), consistent with the results shown in Table 2.

Backup quartz behind Teflon filter is usually assumed to be exposed to the same gaseous organics concentrations as the bare quartz (Turpin et al., 1994; Mader and Pankow, 2003). As a result, it was with expectation that the positive artifact-contributed QBT OC was higher than QBQ OC, considering QBQ adsorbed less gaseous organics than the front one (Fig. 7).

It was noticed that the positive artifact-contributed QBT OC overestimated the positive artifact which was defined as the difference between BQ OC and DQ OC (Figs. 5d and 7). The overestimation provided an evidence for the hypothesis that the adsorption capacity of the loaded filter was lower compared to the filter without particle loading, as discussed in Sect. 3.2.1.

To our knowledge, few studies have focused on the denuded QBT, and this was the first time that positive and negative artifact-contributed QBT OC was quantitatively determined. As a result, the difference between positive artifact-contributed QBT OC and (BQ–DQ) OC is still not well understood and further research is needed.

3.3 Influence of positive artifact on partitioning of PC and EC

The multiple linear regression approach developed by Chow et al. (2004) was used for the re-partitioning of PC and EC, and was briefly described here. The calculation was based on the attenuation coefficient (k) which was defined as:

$$k = \frac{-\ln(I_i/I_f)}{C} \quad (1)$$

where I_i and I_f were the initial and final laser transmission through the loaded filter for the portion of the analysis of in-

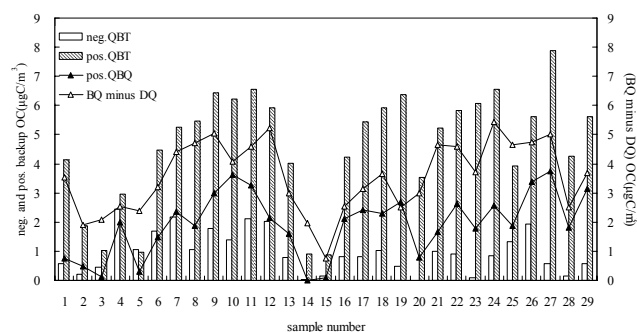


Fig. 7. Negative artifact-contributed QBT OC (neg.QBT), and different estimations of positive artifact: positive artifact-contributed QBT OC (pos.QBT), positive artifact-contributed QBQ OC (pos.QBQ), and the difference between BQ and DQ ((BQ minus DQ) OC).

terest, and C was the mass of carbon per unit filter area that was evolved from the filter during the analysis segment (Subramanian et al., 2006). It was then assumed that the carbon that evolved in the He-O₂ mode ($[\text{carbon}]_{\text{He-O}_2}$) contained only EC and PC, and as a result the increase of the transmission signal in the He-O₂ mode was contributed by the evolution of EC and PC. Thus, $[\text{carbon}]_{\text{He-O}_2}$ could be estimated as:

$$\begin{aligned} [\text{carbon}]_{\text{He-O}_2} &= \text{EC} + \text{PC} \\ &= \frac{-\ln(I_i/I_f)}{k_{\text{EC}}} + \frac{-\ln(I_{\text{min}}/I_f) - (-\ln(I_i/I_f))}{k_{\text{PC}}} \quad (2) \\ &= \frac{-\ln(I_i/I_f)}{k_{\text{EC}}} + \frac{-\ln(I_{\text{min}}/I_i)}{k_{\text{PC}}} \end{aligned}$$

where I_i , I_f was the transmission at the beginning and end of the analysis respectively, I_{min} was the minimum of transmission signal; k_{EC} and k_{PC} was the attenuation coefficient of EC and PC respectively; $-\ln(I_i/I_f)$ was the attenuation caused by EC, and $-\ln(I_{\text{min}}/I_f)$ was the attenuation caused by EC and PC. Thus the attenuation caused by PC was estimated as the difference between $-\ln(I_{\text{min}}/I_f)$ and $-\ln(I_i/I_f)$, or $-\ln(I_{\text{min}}/I_i)$. Then a multiple linear regression of the $[\text{carbon}]_{\text{He-O}_2}$ on $-\ln(I_i/I_f)$ and $-\ln(I_{\text{min}}/I_i)$ could yield estimations of the inverse attenuation coefficients of EC and PC. There were three preconditions for this calculation. The first was the flattening of the carbon signal at the end of each temperature plateau, since the 1 s-average carbon concentration determined by the flame ionization detector (FID) does not have a one-to-one correspondence to the optical measurements (due to a tailing effect caused by transit through C to CO₂ and CO₂ to CH₄). The second was the transmission signal should reach its minimum value in the last step of the He mode and should not increase until the introduction of O₂, to guarantee that the PC was fully formed and there was no premature evolution of EC and PC. The third was that the minimum transmission should be detectable (at the end of He mode). These conditions were met for 10 of the 29 sets of samples (10 denuded and 10 undenuded samples, respectively).

The attenuation coefficients of EC and PC calculated by the 10 sets of denuded and un-denuded samples were 18.83, 38.64 and 18.12, 45.56 m²/g, respectively. The zero-intercept correlation (R^2) of the multiple linear regression were 0.996 and 0.992, for the denuded and un-denuded samples, respectively. It was consistent with other studies that k_{PC} was higher than k_{EC} (Chow et al., 2004; Subramanian et al., 2006), indicating PC formed in the He mode was darker than native EC, which would result in an underestimation of native EC by the TOT-split-EC (due to the co-evolution of PC and EC). k_{EC} were comparable for the denuded and un-denuded samples, and were also comparable with the 18.5 m²/g reported by Chow et al. (2004). k_{PC} calculated by the un-denuded samples was comparable with the 48.5 m²/g reported by Chow et al. (2004), but higher than that calculated from the denuded samples, indicating the PC formed on the un-denuded filter was darker than that formed on the denuded filter.

The re-partitioning of EC and PC was finally completed by Eq. (3), and the result was shown in Fig. 8.

$$EC_{cal} = \frac{-\ln(I_i/I_f)}{k_{EC}}, \quad PC_{cal} = [\text{carbon}]_{\text{He-O}_2} - EC_{cal} \quad (3)$$

As shown in Fig. 8 and Table 3, TOT-split-EC underestimated native EC by 21% and 28%, for denuded and un-denuded samples, respectively. The underestimation for the un-denuded samples was more significant, since the PC formed on it was darker.

3.4 Influence of positive artifact on formation of PC

TOT-split-PC was compared in Table 3 for denuded and un-denuded samples. Formation of PC was reduced by 7% after removal of the positive artifact. Considering that the positive artifact contributed 10% of BQ OC, the PC formation potential of gaseous organics adsorbed on the quartz filter should be comparable with that of particulate organic carbon. As a result, removal of the positive artifact did not have a significantly influence on PC formation.

4 Conclusions

Capacity of the activated carbon denuder for the removal of gaseous organics that could be adsorbed on the quartz filter was demonstrated during a sampling period of about a month in Beijing. Comparison of BQ OC and DQ OC showed that about 10% of the OC determined by the bare quartz filter was from the positive artifact. Negligible amount of OC was detected on the denuded backup quartz filter, indicating the amount of evaporated OC (that could be adsorbed by the quartz filter) was minimal.

The backup quartz approach was evaluated for estimating the positive artifact. 100% of the QBQ OC was from gaseous organics passing through the front filter, or from the positive

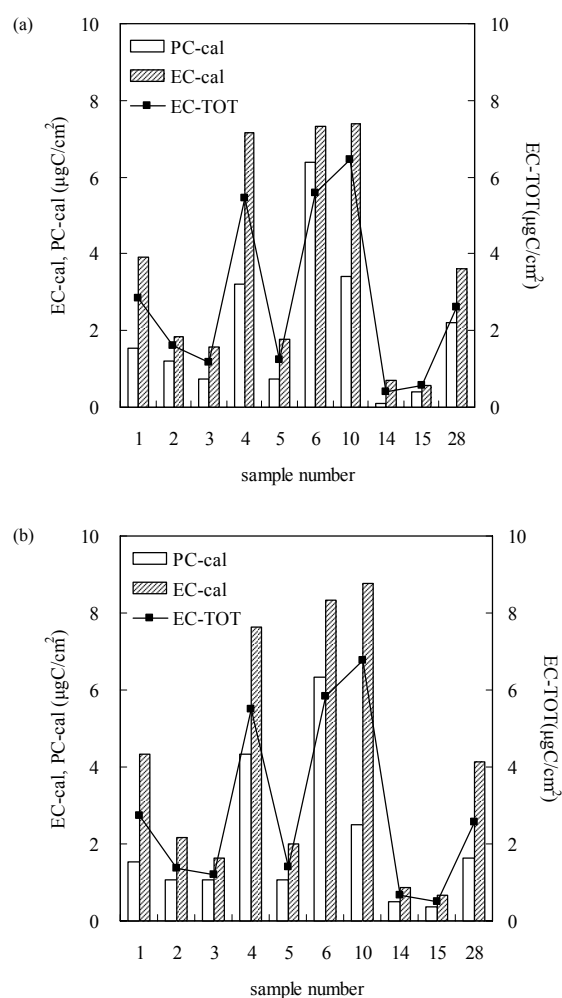


Fig. 8. Comparison of calculated EC concentration (EC-cal) and TOT-split-EC (EC-TOT) for (a) denuded samples, and (b) un-denuded samples. Calculated PC concentration (PC-cal) is also shown. Values not corrected by filter blank.

artifact. Due to the relatively small sampling volume, the QBQ had not reached equilibrium with gas phase, and as a result, underestimated the positive artifact by 3.7%. QBT OC consisted of both gaseous organics passing through the front filter (82%) and evaporated particulate OC (18%), thus QBT OC overestimated the positive artifact by 6.3%. In addition, it was found that the positive artifact-contributed QBT OC overestimated the positive artifact by 3.5%. This may be caused by the difference in the adsorption properties of the loaded filter and the filter without particle loading. Further research is needed to give a deeper insight into this overestimation.

Re-partitioning of PC and EC was performed based on the attenuation coefficient. It was with expectation that PC was darker than EC. Moreover, it was found that PC formed on the bare quartz filter was darker than that formed on the denuded filter. As a result, TOT-split-EC underestimated

native EC by 21% and 28%, for denuded and un-denuded samples, respectively. It was also shown that the PC formation potential of gaseous organics adsorbed on the quartz filter was comparable with that of particulate organic carbon, indicating that removing of the positive artifact did not influence the PC formation significantly. As a result, though the PC formed on the denuded filter was lighter in color, the application of the organic denuder did not completely solve the problems of split of OC/EC, which was caused by the difference in the attenuation coefficient of EC and PC.

5 Discussion

Both the integrated sampler used in the monitoring network and the more recently developed semi-continuous equipment are challenged to accurately measure carbonaceous aerosols, including the positive and negative artifact, and the split of OC/EC. The organic denuder is effective at eliminating the positive artifact and it is the precondition for the determination of the negative artifact, or the semivolatile organic carbon. More attention should be paid to semivolatile organic carbon in the future (Fig. 1), considering its secondary nature (Modey et al., 2004; Eatough et al., 2006), and its influence on regional haze (Long et al., 2005). Calculation of the attenuation coefficient of EC and PC is essential for the accurate split of OC and EC, based on the current thermal-optical method. This is especially meaningful for China, due to its high EC emission (Zhang et al., 2007). Moreover, attenuation of EC is an important optical parameter for determining the impact of particulate matter on visibility and climate change. The multiple linear regression approach developed by Chow et al. (2004) is more convenient for this purpose compared with the solvent extraction method used by Subramanian et al. (2006). But there maybe some potential artifacts for both approaches, such as the influence of stray light on the measured laser signal, especially at lower transmittance levels. The stray light could not be avoided even by the best instrument. It is a substantial challenge for the current thermal-optical equipments that how to quantitatively determine the influence of stray light and how to eliminate or minimize it. Finally, more efforts should be made to improve the measurement of carbonaceous aerosols, while at the same time developing monitoring networks and new monitoring equipment.

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