



# Measurement of carbonaceous aerosol with different sampling configurations and frequencies

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## Abstract

Carbonaceous aerosol in Beijing, China was measured with different sampling configurations (denuded vs. un-denuded) and frequencies (24 vs. 48 h averaged). Our results suggest that the negative sampling artifact of a bare quartz filter could be remarkably enhanced due to the uptake of water vapor by the filter medium, indicating that the positive sampling artifact tends to be underestimated under high humidity conditions. It was also observed that the analytical artifact (i.e., the underestimation of elemental carbon by the operationally defined value of the thermal-optical method) was more apparent for the low frequency samples such that their elemental carbon (EC) concentrations were about 15 % lower than the reference values measured by the high-frequency, denuded filters. Moreover, EC results of the low frequency samples were found to exhibit a stronger dependence on the charring correction method. In addition, optical attenuation (ATN) of EC was retrieved from the carbon analyzer, and the low frequency samples were shown to be more significantly biased by the shadowing effect.

## 1 Introduction

Particulate matter (PM) pollution has become a substantial concern in China. Through the air pollution control practice conducted during the last two decades, both the scientific community and the Chinese government have recognized that the emissions of not only primary PM but also gaseous precursors of PM must be reduced to control the PM pollution (Wang et al., 2010). However, each step along the way between source and atmospheric concentration of PM is still rather complex. Even if for secondary inorganic aerosol, the formation mechanisms of which have been relatively well characterized, there might be a large gap between simulation results and observational data (e.g., Zheng et al., 2015). Compared to observations performed by individual research groups, information derived from large-scale PM monitoring networks are more suitable for evaluating air quality models as well as other techniques such as satellite remote

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sensing (Koch et al., 2009; Jathar et al., 2011; Boys et al., 2014). For example, global PM<sub>2.5</sub> (fine particulate matter) composition inferred from remote sensing in combination with modeling was assessed by the observational data from three networks, including the Interagency Monitoring of Protected Visual Environments (IMPROVE) network in the United States, the European Monitoring and Evaluation Programme (EMEP) network, and the National Air Pollution Surveillance (NAPS) network in Canada (Philip et al., 2014). In China, the Ministry of Environmental Protection (MEP) has started to establish a PM<sub>2.5</sub> monitoring network on a national scale. The network now provides hourly-averaged mass concentrations of PM<sub>2.5</sub> for 190 cities, which have been shown to be useful for evaluating PM<sub>2.5</sub> predictions from air quality models (e.g., Zheng et al., 2015). Compared to those in North America and Europe, however, the PM<sub>2.5</sub> network in China is still at the initial stage, mainly due to the lack of speciation measurements. Therefore, a good understanding of the speciation measurements, especially the existing problems, is highly desirable in China.

In general, PM<sub>2.5</sub> is a complex mixture of carbonaceous components, water-soluble inorganic ions, trace elements and crustal materials. These species possess a wide range of properties such as volatility and water solubility, and thus, require different sampling and analytical techniques. At present, the challenges mainly come from the carbonaceous components (Turpin et al., 2000; US EPA, 2004). As for sampling, there exist two types of artifacts. One is the positive artifact due to the adsorption of gaseous organics by the generally used quartz fiber filter, while the other one is the negative artifact caused by the evaporation of organic carbon (OC) from the particles already collected on the filter. A common approach to reduce the positive artifact is to introduce a backup quartz filter (placed downstream of either a quartz or Teflon filter) and assume that OC measured on it is primarily due to volatile organic compounds (VOCs), and thus equals the positive artifact. An alternative method to remove the positive artifact is adding a denuder, which is capable of removing gaseous organics, upstream of the sampling filter. Moreover, if a denuder is placed upstream of a filter pack, OC measured by the denuded backup filter will provide an estimation of the negative artifact. In

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the PM<sub>2.5</sub> networks in North America and Europe, the positive artifact has not been well addressed yet, while the negative artifact is usually not considered (Watson et al., 2009; Maimone et al., 2011; Solomon et al., 2014). When only focusing on the positive artifact, the backup quartz filter approach is much simpler than the denuder approach (e.g., with respect to sampler operation), although it usually either over-estimates or under-estimates the positive artifact (Eatough et al., 2003; Subramanian et al., 2004; Viana et al., 2006; Cheng et al., 2010). Therefore, the sampling method of carbonaceous aerosol, especially the backup quartz filter approach, still requires careful evaluation. As for analysis procedure, the carbonaceous portion of PM<sub>2.5</sub> is commonly classified as organic carbon and elemental carbon (EC). However, it has been recognized that there is no clear-cut distinction between OC and EC, in terms of either thermal stability or light absorbing capacity (Pöschl, 2005; Andreae and Gelencsér, 2006). Therefore, the separation of OC and EC strongly depends on the analytical method (Chow et al., 2001, 2004; Schmid et al., 2001; Schauer et al., 2003; ten Brink et al., 2004; Cavalli et al., 2010), and moreover, the dependence is significantly influenced by sample properties such as source of carbonaceous components and abundance of minerals.

The spatial and temporal variations of the PM<sub>2.5</sub> composition in China are far from being well characterized, indicating that a national PM<sub>2.5</sub> speciation monitoring network is necessary. Compared to the sampling schedule used by established networks such as IMPROVE and NAPS (24 h samples are collected every three days), low-frequency, long-duration sampling is an alternative choice for China, which might be more suitable to get a general perspective of the PM<sub>2.5</sub> composition on a national scale. Therefore, in this study, we focus on the influences of sampling frequency (i.e., duration) on the measurement of carbonaceous aerosol. It is commonly believed that increasing sampling duration can reduce the influence of the positive sampling artifact, and meanwhile does not affect the EC measurement. Here we demonstrate that this is not necessarily the case. Results from this study will be useful for the design of China's PM<sub>2.5</sub> speciation monitoring network, which can be expected to be inaugurated in the near future.

## 2 Methods

### 2.1 Field sampling

Ambient PM<sub>2.5</sub> samples were collected on the campus of Tsinghua University during the summer of 2009 (from 20 June to 20 July). Tsinghua University (40.00° N, 116.32° E) is located in the urban area of Beijing, about 20 km northwest of the city center. There is a main road with heavy traffic (i.e., the 4th Ring Road) about 1 km south of the campus, whereas there are no major industrial sources nearby. The sampling was done by a Spiral Ambient Speciation Sampler (SASS; Met One Instruments, OR, USA), which has five separate channels operated through a common pump. The sampling flow rate was 6.7 L min<sup>-1</sup> for each channel, corresponding to a cutpoint of 2.5 μm (given by a sharp cut cyclone). The sampler was placed on the roof a building on the campus, about 6 m above the ground.

Three channels with sequential quartz fiber filters (referred to as quartz filters hereinafter) were used in the present study and their configurations are summarized in Table 1. Channel 1 and 2 were operated at a relatively high frequency with a sampling duration of 24 h, while channel 3 was run at a relatively low frequency such that the sampling duration was 48 h. In channel 1, an activated carbon denuder (Met One Instruments, OR, USA) was placed upstream of the sequential quartz filters to remove VOCs, and thus eliminate the positive sampling artifact. The activated carbon denuder was 20 mm long and 38 mm in diameter, with about 1000, 1 mm × 1 mm channels. At the operating flow rate (6.7 L min<sup>-1</sup>), the residence time of particles in the denuder was about 0.18 s. The same denuder was used throughout the measurement period. Evaluation of the denuder has been presented elsewhere (Cheng et al., 2010) and is also available in the Supplement. The quartz filters (8 in × 10 in, 2500 QAT-UP; Pall Corporation, NY, USA) were taken from the same lot, first cut into punches with a diameter of 47 mm and then baked at 550 °C in air for 24 h before use.

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## 2.2 Sample Analysis

The quartz filters were analyzed for OC and EC using a DRI carbon analyzer (Model 2001; Atmoslytic Inc., CA, USA). The temperature protocol implemented was IMPROVE-A, which heats the sample in an inert (i.e., He; up to 580 °C) and oxidizing (i.e., He/O<sub>2</sub>; up to 840 °C) atmosphere sequentially. Both the transmittance and reflectance charring corrections were used to separate OC and EC. In the transmittance correction approach, EC is defined as the carbon evolving after the filter transmittance signal (monitored at a wavelength of 632 nm) returns to its initial value, whereas the reflectance correction defines EC based on the reflected signal (also monitored at 632 nm). Without special statement, all of the OC and EC results reported in this article are based on the transmittance charring correction and have been corrected by the filter blank concentration (blank OC averaged  $0.43 \pm 0.12 \mu\text{g C cm}^{-2}$ , whereas no blank EC was detected; a total of 15 blank filters were collected).

## 2.3 Equipment performance

The sampling flow rate of the SASS sampler averaged  $6.73 \pm 0.02$ ,  $6.72 \pm 0.01$  and  $6.72 \pm 0.01 \text{ L min}^{-1}$ , respectively, for the three channels used in this study. Thus, the sampling flow rate was stable for each channel and agreed well among different channels.

The performance of the DRI carbon analyzer is demonstrated in Fig. 1. Duplicate analysis suggested good precision for both the carbon (i.e., total carbon, OC and EC) and optical (i.e., optical attenuation) measurements. Optical attenuation (ATN) is calculated as:

$$\text{ATN} = \ln \left( \frac{T_{\text{final}}}{T_{\text{initial}}} \right) \quad (1)$$

where  $T_{\text{initial}}$  and  $T_{\text{final}}$  are the intensity of the transmittance signal measured at the beginning (i.e., when the loaded filter has not been heated) and end (i.e., when all of

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the loaded carbon has been combusted and evolved off the filter) of thermal-optical analysis, respectively. ATN provides an estimation of the light absorption due to the loaded particles (Ram and Sarin, 2009), although with artifacts, such as those caused by the aerosol-filter interactions and filter scattering. The measurement of ATN by the DRI carbon analyzer was similar to that by the filter-based, online instruments such as the Aethalometer and the Particle Soot Absorption Photometer (PSAP). These online instruments typically measure the transmittance signal across a loaded ( $T_{\text{loaded}}$ ) and a particle-free reference filter ( $T_{\text{reference}}$ ) simultaneously, while ATN is calculated as:

$$\text{ATN} = \ln \left( \frac{T_{\text{reference}}}{T_{\text{loaded}}} \right) \quad (2)$$

$T_{\text{loaded}}$  and  $T_{\text{reference}}$  in Eq. (2) are equivalent to  $T_{\text{initial}}$  and  $T_{\text{final}}$  in Eq. (1), respectively. Thus, ATN retrieved from the DRI carbon analyzer is comparable to that given by the filter-based, online instruments. However, the comparison may not be straight forward in practice (e.g., the measurement wavelength could be different). Refer to the Supplement for a more detailed discussion regarding this point, which goes beyond the scopes of this paper. The Supplement also includes a summary of the statistical results for the comparisons, regressions and ratios included in this paper (e.g., the comparisons shown in Fig. 1).

## 2.4 Meteorological parameters

Meteorological information for Beijing during this study were obtained from Weather Underground (<http://www.wunderground.com/global/stations/54511.html>), which were measured at the Beijing International Airport (40.07° N, 116.59° E). The average temperature and relative humidity (RH) for each sample collection period were calculated by averaging the raw data (with a time resolution of 30 min) according to the start and stop time of each sampling event. The meteorological parameters were mainly used to identify a distinct period with high RH levels. The identification result was strongly

supported by the RH data from another source (the China Meteorological Data Sharing Service System; see the Supplement).

### 3 Results and discussion

#### 3.1 Effects of sampling frequency on the sampling artifacts

5 In this study, 48 h averaged TC rather than OC concentrations are used to investigate the sampling artifacts. This is because the discrepancies in OC results measured by different sampling frequencies are also affected by the analytical artifact besides the sampling artifacts (this point will be discussed in Sect. 3.2), whereas TC results are not. On the other hand, it has been shown that (i) the activated carbon denuder used  
10 in this study could completely remove the positive artifact and did not bias the EC measurement, and (ii) negligible OC could be detected on the denuded backup quartz filter throughout this study (Cheng et al., 2010; also see the Supplement). Therefore, TC measured by the denuded front quartz filter (48 h averaged) is used as the reference value.

15 Figure 2 compares the 48 h averaged TC concentrations measured by different sampling configurations and frequencies. As for the high frequency samples, TC concentrations of the bare quartz filters (high-frequency  $TC_{BQ}$ ) were 23 % higher than those of the denuded ones (high-frequency  $TC_{DQ}$ ), indicating a significant positive artifact. OC measured by the backup quartz filter was used to account for the positive artifact; but  
20 the corrected results (high-frequency  $TC_{BQ-QBQ}$ ) still overestimated TC by 9 %, indicating that the backup filter adsorbed less gaseous organics compared to the front one. With respect to the low frequency samples, TC concentrations (low-frequency  $TC_{BQ}$ ) were only 5 % higher than the reference values (i.e., the high-frequency  $TC_{DQ}$ ). Previous studies conducted at Berkeley, CA and the Pittsburgh Air Quality Study (PAQS)  
25 supersite also showed that the positive artifact was less significant for low frequency samples (Kirchstetter et al., 2001; Subramanian et al., 2004). It seems that increas-

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ing the sampling duration could remarkably reduce the influence of the positive artifact, even more effectively than introducing a backup filter. A possible explanation for this phenomenon is suggested to be that a low frequency quartz filter is more likely to reach equilibrium with gaseous organics due to its relatively long sampling duration.

Once the equilibrium has been reached, the artifact mass on the filter stops to increase and remains constant with increasing sampling time (Subramanian et al., 2004).

It has been well documented that TC concentration measured by a bare quartz filter will be more or less reduced by placing an organic denuder upstream. As shown in Fig. 3a however, the low-frequency  $TC_{BQ}$  was lower than the high-frequency  $TC_{DQ}$  for several data points (the difference was significant at a 95 % level of confidence), although the average value of the low-frequency  $TC_{BQ}$  was higher (Fig. 2). This phenomenon has not been observed before. The high-frequency  $TC_{DQ}$  was expected to provide a minimum estimation of the 48 h averaged TC concentration, because: (1) the positive artifact had been removed by the charcoal denuder with an efficiency of 100 %, and (2) the negative artifact was enhanced since the denuder disturbed the gas-particle equilibrium of semivolatile organic compounds (SVOCs). Thus, it is really surprising that the low-frequency  $TC_{BQ}$ , which should be biased high due to the positive artifact, could be lower than the high-frequency  $TC_{DQ}$ . The only explanation is that the negative artifact could be more significant for the low frequency samples than the denuded ones, meaning that the comparisons shown in Fig. 2 do not necessarily indicate that the positive sampling artifact is less significant for the low frequency samples. Factors responsible for these unexpected higher negative artifacts of the low frequency samples are discussed below.

We first investigated the effects of temperature. As mentioned in the Methods section, the sampling period of a low frequency filter included two non-overlapping segments, corresponding to two high frequency samples. If the temperature was higher during the second segment, particulate carbon collected during the first one was subject to additional loss for the low frequency samples, resulting in a greater negative artifact. With respect to the sampling events when the low-frequency  $TC_{BQ}$  was lower

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than the high-frequency  $TC_{DQ}$  ( $N = 8$ ), only 50 % were found to have higher temperature during the second segment. Moreover, higher temperature during the second segment could also be observed in the remaining sampling events (i.e., when the low-frequency  $TC_{BQ}$  were higher than the reference values). Therefore, daily variation in temperature is not a likely cause of the unexpected higher negative artifacts of the low frequency samples.

We then investigated the effects of filter loading. The pressure drop across a sampling filter increases as particles are collected, providing a driving force for the loss of particulate carbon (Turpin et al., 2000). Higher pressure drop is expected to make the negative artifact more significant. For example, it is well known that Teflon filters are more susceptible to the negative artifact than quartz filters, due to their higher pressure drop (Turpin et al., 1994). Compared to the high frequency samples, the low frequency ones had a much higher particle loading per filter, resulting in a much higher pressure drop which consequently enhances the negative artifact. However, it seems that filter loading was not the only factor responsible for the unexpected higher negative artifacts of the low frequency samples. This is because the occurrence of these unexpected higher negative artifacts did not exhibit a strong dependence on the filter loading of the low frequency samples. For example, during the sampling period with the highest 48 h integrated TC loading (i.e., with the highest 48 h averaged TC concentration), the low-frequency  $TC_{BQ}$  ( $18.10 \mu\text{gCcm}^{-3}$ ) was substantially higher than the high-frequency  $TC_{DQ}$  ( $15.92 \mu\text{gCcm}^{-3}$ ), showing no solid evidence for a greater negative artifact being associated with the low frequency filter (Fig. 3a). Therefore, in addition to the effect of filter loading, there must exist other factors that are able to strongly enhance the negative artifact of the low frequency filters.

Interestingly, all of the lower levels of the low-frequency  $TC_{BQ}$ , relative to the reference values, were observed during a period characterized by high RH (Fig. 3b). Unlike particle-bound water, gas-phase water in the atmosphere is typically not considered as a biasing factor during aerosol measurements (US EPA, 2004). However, some types of sampling filters, such as quartz, are indeed able to adsorb water vapor (Brown et al.,

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2006). In a previous study conducted in the Netherlands, a blank quartz filter (with a diameter of 47 mm), which was kept in a weighing room as a laboratory reference for the gravimetric measurement of PM mass, exhibited a slowly increasing mass of almost 500  $\mu\text{g}$  over  $\sim 1500$  days due to the adsorption of gas-phase water (de Jonge and Visser, 2009). Similar to the collected particles, the adsorbed water vapor also contributes to the pressure drop across a sampling filter (Liew and Conder, 1985). Thus, the negative artifact (of a bare quartz filter) is expected to be more significant under high RH conditions. On the other hand, it is well known that activated carbon can adsorb water vapor (Müller et al., 1996), suggesting that the charcoal denuder used in this study was able to reduce the abundance of gas-phase water in the sampling follow (although with an unknown efficiency). Consequently, the uptake of water vapor by the denuded filters was less significant compared to the bare ones, leading to a lower pressure drop which tends to reduce the negative artifact. Importantly, the unexpected higher negative artifacts of the low frequency samples occurred only in the high RH period, demonstrating that the uptake of water vapor by the filter medium can greatly enhance the loss of particulate carbon. During the high RH period, the low-frequency  $\text{TC}_{\text{BQ}}$  underestimated TC concentration by 5 %, while TC was further underestimated (by 16 %) if the low-frequency  $\text{TC}_{\text{BQ}}$  was corrected for the positive artifact (the corrected results are referred to as the low-frequency  $\text{TC}_{\text{BQ-QBQ}}$ ; Fig. 4a).

Figure 4 also compares the high-frequency  $\text{TC}_{\text{BQ}}$  and  $\text{TC}_{\text{BQ-QBQ}}$  with the reference values. Compared to results from the low RH period, overestimation of TC by the high-frequency  $\text{TC}_{\text{BQ}}$  was less significant during the high RH period while the high-frequency  $\text{TC}_{\text{BQ-QBQ}}$  was more comparable with the reference value. Traditionally, these results would be attributed to a smaller positive artifact during the high RH period and a better performance of the quartz-quartz in series method. However, we suggest that there is another possible explanation: compared to a denuded filter, the bare quartz filter was biased by a greater negative artifact during the high RH period. Therefore, the uptake of water vapor by the bare quartz filter can complicate our understandings

of the positive artifact through enhancing the negative artifact, especially under high RH conditions.

It should be mentioned that here we assume the adsorption of gas-phase water by the collected particles is not important, since particle-bound water is presumably in equilibrium with the gas phase at the time of collection. Similarly, it was suggested that the collected particles did not contribute significantly to the adsorption of gaseous organics (McDow and Huntzicker, 1990).

### 3.2 Effects of sampling frequency on the analytical artifact

48 h averaged EC concentrations agreed well between the denuded and un-denuded filters when both of them were collected at the high frequency; however, substantially lower values (by about 15 %) were measured by the low frequency samples (Fig. 4), consistent with results from a peri-urban site in Europe (Chiappini et al., 2014). Although the measurement of EC is not susceptible to sampling artifacts, the separation of OC and EC could be largely complicated by the char OC (also known as the pyrolysis OC) that formed during the inert mode of thermal-optical analysis. It has been demonstrated that the thermal-optical method tends to underestimate EC (i.e., overestimate OC) due to the formation of char-OC (Chow et al., 2004; Subramanian et al., 2006), resulting in the analytical artifact. In a previous study conducted in Beijing, China, the formation of char OC was reduced by extracting the filters using a mixture of hexane, methylene chloride and acetone (about 55 % of OC was removed in this way), and a 6 % increase in the EC results was observed after the extraction (Cheng et al., 2012). EC results were also found to increase after the filters collected in Milan, Italy were washed by water (Piazzalunga et al., 2011). These results suggest that the analytical artifact tends to be reduced as less char OC is formed, or in other words, the analytical artifact tends to be enhanced as more char OC is formed. The amount of char OC per filter, which was roughly proportional to the filter's OC loading, was much higher for the low frequency samples compared to the high frequency ones. Thus, the underestimation of EC (i.e., the overestimation of OC) caused by the analytical artifact

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was more significant for the low frequency samples, which is responsible for their lower EC concentrations compared to the high frequency filters (Fig. 4).

Influences of sampling frequency on the 48 h averaged OC concentrations were in general similar to those observed in the comparison of TC results (Fig. 4). Briefly, OC concentrations of the low frequency filters (low-frequency  $OC_{BQ}$ ) were always lower than those measured by the high frequency, un-denuded ones (high-frequency  $OC_{BQ}$ ), regardless of the RH levels. Compared to results from the high frequency, denuded samples (high-frequency  $OC_{DQ}$ ), the low-frequency  $OC_{BQ}$  was higher (by 31 %) during the low RH period, whereas was 1 % lower during the high RH period (due to a greater negative artifact). As mentioned above, the overestimation of OC caused by the analytical artifact was more significant for the low frequency samples, indicating that the OC comparisons shown in Fig. 4 were affected by not only the sampling artifacts but also the analytical artifact. For example, if only considering the influences of the sampling artifacts, the low-frequency  $OC_{BQ}$  should be lower than the high-frequency  $OC_{DQ}$  by more than 5 % during the high RH period (5 % corresponded to the difference between the low-frequency  $TC_{BQ}$  and the high-frequency  $TC_{DQ}$  during the same period; Fig. 4a), whereas the difference was reduced to 1 % after accounting for the analytical artifact.

### 3.3 Effects of sampling frequency on the optical attenuation measurement

ATN is of interest because it can be used to calculate the absorption coefficient ( $b_{abs}$ ) and the mass absorption efficiency (MAE) of black carbon (Ram and Sarin, 2009), two parameters of great interest in the climate community:

$$b_{abs} \text{ (M m}^{-1}\text{)} = ATN \times \frac{A}{V} \quad (3)$$

$$MAE \text{ (m}^2\text{ g}^{-1}\text{)} = \frac{b_{abs}}{EC_m} = \frac{ATN}{EC_s} \times 100 \quad (4)$$

where  $A$  is the filter area with particle loading ( $\text{mm}^2$ ),  $V$  is the volume of air sampled ( $\text{m}^3$ ),  $EC_m$  is the mass concentration of EC ( $\mu\text{g m}^{-3}$ ), while  $EC_s$  indicates the EC

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loading ( $\mu\text{gcm}^{-2}$ ). As shown in Eq. (4), ATN is related to EC loading, rather than EC concentration. Therefore, the comparison of ATN between the high and low frequency samples is performed based on the 48 h integrated values.

As shown in Fig. 5, ATN measured by the low frequency filters (low-frequency  $\text{ATN}_{\text{BQ}}$ ) were about 10 % lower than the integrated values of the high frequency, denuded samples (integrated high-frequency  $\text{ATN}_{\text{DQ}}$ ). This difference was caused by the shadowing effect (also known as the loading effect), which means that an increased underestimation of ATN occurs with increasing filter loadings (Weingartner et al., 2003). The shadowing effect was also observed in a previous study with two Aethalometers being operated in parallel, such that the Aethalometer with the most recent filter change (i.e., with a relatively low filter loading) always gave higher readings than the other (i.e., the Aethalometer with a relatively high filter loading) until the other instrument's filter change (LaRosa et al., 2002). Schmid et al. (2006) attributed the shadowing effect to the decrease in the sensitivity of the filter-based measurement of light absorption with increasing filter loadings. A correction factor,  $R(\text{ATN})$ , was introduced by Weingartner et al. (2003) to account for the shadowing effect:

$$\text{ATN}^* = \frac{\text{raw ATN}}{R(\text{ATN})} \quad (5)$$

$$R(\text{ATN}) = \left( \frac{1}{f} - 1 \right) \times \frac{\ln(\text{ATN}) - \ln(10\%)}{\ln(50\%) - \ln(10\%)} + 1 \quad (6)$$

$$f = m \times (1 - \omega_0) + 1 \quad (7)$$

where  $\text{ATN}^*$  indicates the ATN value that has been corrected for the shadowing effect,  $\omega_0$  is the single scattering albedo, and  $m$  is nearly a constant which was estimated to be 0.87 and 0.85 at a wavelength of 450 and 660 nm, respectively.  $\text{ATN} = 10\%$  is taken as a reference point. If the measured  $\text{ATN} \leq 10\%$ , the loading effect is negligible and  $R(\text{ATN})$  is set to unity. On the other hand, if the measured  $\text{ATN} > 10\%$ , the shadowing effect should be corrected and  $R(\text{ATN})$  becomes smaller than unity. The minimum ATN value was about 0.2 and 0.7 for the high and low frequency filters, respectively,

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indicating that the correction for the shadowing effect was necessary for both of them. Although  $\omega_0$  was not measured in this study, previous studies conducted in Beijing, China suggested that the value was between 0.8 and 0.9 for the urban area (e.g., Eck et al., 2005; He et al., 2009). We tried to account for the shadowing effect through Eqs. (5)–(7) by assuming a  $\omega_0$  value, and found that the agreement between the low-frequency  $\text{ATN}_{\text{BQ}}$  and the integrated high-frequency  $\text{ATN}_{\text{DQ}}$  was improved after the correction. Their difference was reduced to 8, 6, and 5 %, respectively, when assuming  $\omega_0 = 0.90, 0.85$  and  $0.80$  (Fig. 5).

In addition to the shadowing effect, another artifact biasing the filter-based ATN measurement is the multiple scattering effect which results in an overestimation of ATN. Weingartner et al. (2003) introduced an empirical constant  $C$  to account for this artifact. Finally, the corrected ATN is expressed as:

$$\text{corrected ATN} = \frac{\text{raw ATN}}{C \times R(\text{ATN})} \quad (8)$$

We did not attempt to determine  $C$  in this study, due to the lack of light absorption measurement by a reference method (e.g., the Multi-Angle Absorption Photometer or the photoacoustic spectrometer) (Schimd et al., 2006; Collaud Coen et al., 2010).

Compared to the reference values (i.e., those measured by the high frequency, denuded samples), both the ATN and EC results were biased low for the low frequency samples, and moreover, the underestimation of EC (by about 15 %; Fig. 4) was more significant than ATN (by about 10 %; Fig. 5). Therefore, MAE calculated by Eq. (4) will appear to be higher for the low frequency samples than the reference values. We do not present the detailed MAE results here, because in this study we are not able to reliably correct the ATN values retrieved from the carbon analyzer.

### 3.4 Effects of sampling frequency on the $\text{EC}_{\text{R}}$ to $\text{EC}_{\text{T}}$ ratio

In this section, OC and EC concentrations defined by the transmittance and reflectance charring correction will be referred to as  $\text{OC}_{\text{T}}$  and  $\text{EC}_{\text{T}}$ ,  $\text{OC}_{\text{R}}$  and  $\text{EC}_{\text{R}}$ , respectively. The



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EC<sub>R</sub> to EC<sub>T</sub> ratio exhibited an apparent dependence on the abundance of OC defined by the OC<sub>T</sub> to EC<sub>T</sub> ratio (Fig. 6). The EC<sub>R</sub> to EC<sub>T</sub> ratio was close to 1.0 when the OC<sub>T</sub> to EC<sub>T</sub> ratio was relatively low, whereas with the increase of the OC<sub>T</sub> to EC<sub>T</sub> ratio, the EC<sub>R</sub> to EC<sub>T</sub> ratio first increased rapidly and then gradually approached an asymptotic value of about 2.0. This trend was independent of the sampling frequency. However, the majority of the EC<sub>R</sub> to EC<sub>T</sub> ratios appeared around the asymptotic value (i.e., ~ 2.0) for the low frequency samples. Therefore, the discrepancy between EC<sub>R</sub> and EC<sub>T</sub> was more significant for the low frequency samples (with an average EC<sub>R</sub> to EC<sub>T</sub> ratio of  $1.91 \pm 0.39$ ) compared to the high frequency ones (with an average EC<sub>R</sub> to EC<sub>T</sub> ratio of  $1.56 \pm 0.36$ ).

## 4 Conclusions and implications

The influence of sampling frequency on the measurement of carbonaceous aerosol was investigated based on PM<sub>2.5</sub> samples collected in Beijing, China. It is commonly believed that the positive sampling artifact is less significant for low frequency sampling. However, we suggest that this is not necessarily the case due to the complications caused by the negative artifact, especially under high RH conditions (Fig. 4). We also found that the analytical artifact (i.e., the underestimation of EC by the operationally defined value) was more significant for the low frequency samples such that their EC concentrations were about 15 % lower than results from the high frequency ones. In addition, both the shadowing effect in the determination of ATN and the EC<sub>R</sub> vs. EC<sub>T</sub> discrepancy were more significant for the low frequency samples.

Despite the limitations mentioned above, low frequency sampling has its advantages too, such as a lower cost for sampler operation and filter analysis, which may be attractive for large scale and/or long period monitoring (e.g., by low frequency sampling, PM<sub>2.5</sub> composition was measured for about a decade at an urban site in Beijing; Yang et al., 2011). Thus, low frequency sampling may be a good choice when MEP decides to establish China's PM<sub>2.5</sub> speciation monitoring network. We suggest that if choosing



low frequency sampling, the flow rate should be carefully selected to reduce the negative sampling artifact and the analytical artifact (both of which are associated with filter loading).

**The Supplement related to this article is available online at  
doi:10.5194/amtd-8-3171-2015-supplement.**

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**Table 1.** Configuration of the SASS sampler (only the three channels used in this study are shown).

Channel	1 (high frequency)	2 (high frequency)	3 (low frequency)
Denuder	Activated carbon	NA	NA
Front filter	Quartz (DQ)	Quartz (BQ)	Quartz (BQ)
Backup filter	Quartz	Quartz (QBQ)	Quartz (QBQ)
Sampling duration	~ 24 h <sup>a</sup>	~ 24 h <sup>a</sup>	~ 48 h <sup>b</sup>

<sup>a</sup> It took about one hour to change filters and maintain the sampler for each set of sample; thus, the sampling duration is not exactly 24 h for channel 1 and 2. However, samples collected by these two channels will still be termed daily samples or 24 h samples.

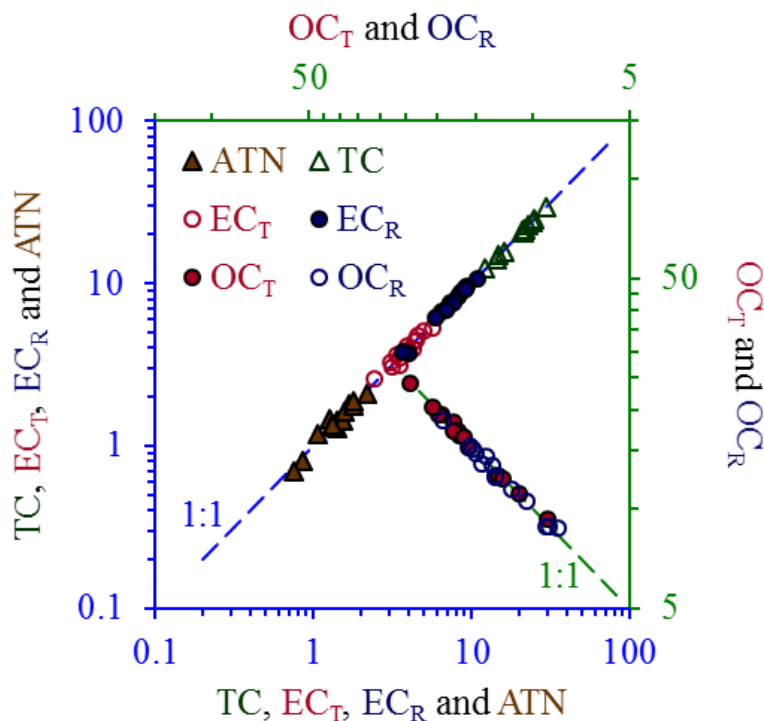
<sup>b</sup> During each sampling event of channel 3, there is a period when channel 1 and 2 were stopped for filter change. Channel 3 was also stopped in this period.

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**Figure 1.** Comparison of the carbon (i.e., TC, OC and EC) and optical (i.e., ATN) measurements performed by duplicate analysis. TC, OC and EC are presented in  $\mu\text{gC cm}^{-2}$ . The subscripts “R” and “T” indicate reflectance and transmittance based charring correction, respectively.

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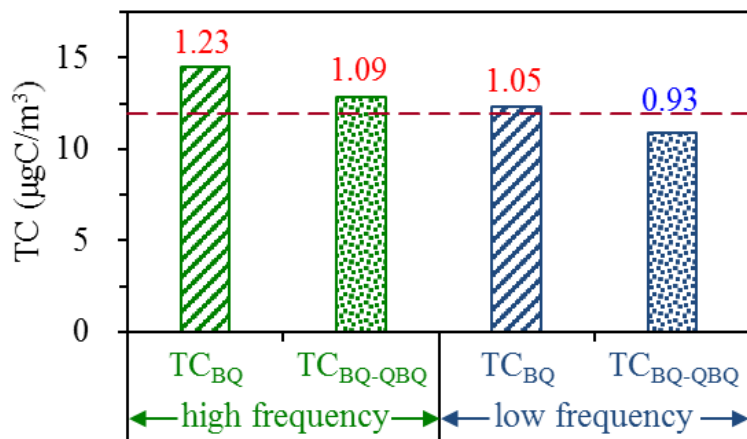
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**Figure 2.** Comparison of the 48 h averaged TC concentrations measured by different sampling configurations and frequencies. The dashed line corresponds to the reference value, which is the average of the TC concentrations measured by the high frequency, denuded filters. The bars indicate the alternative estimations. The values above each bar are the average of the alternative-to-reference ratios, while the red and blue fonts indicate an overestimation and underestimation, respectively.

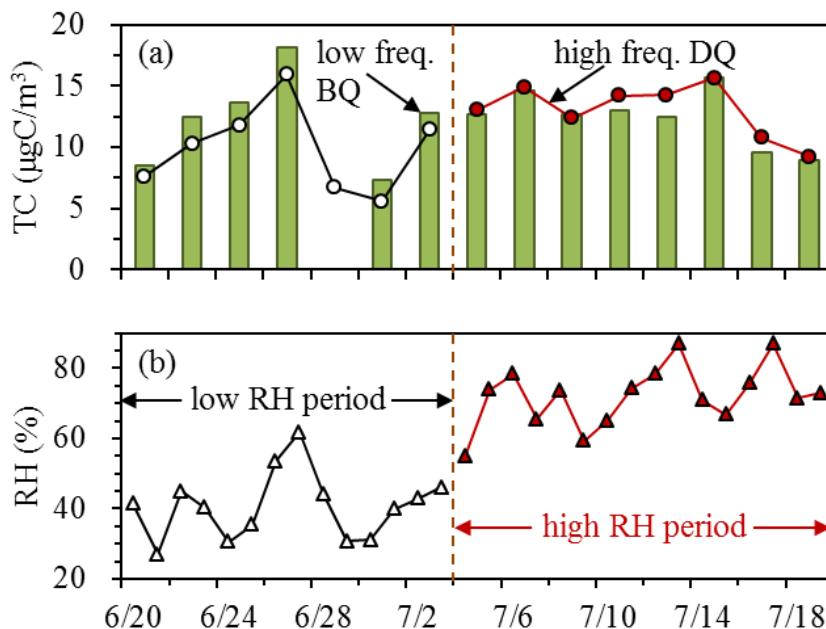
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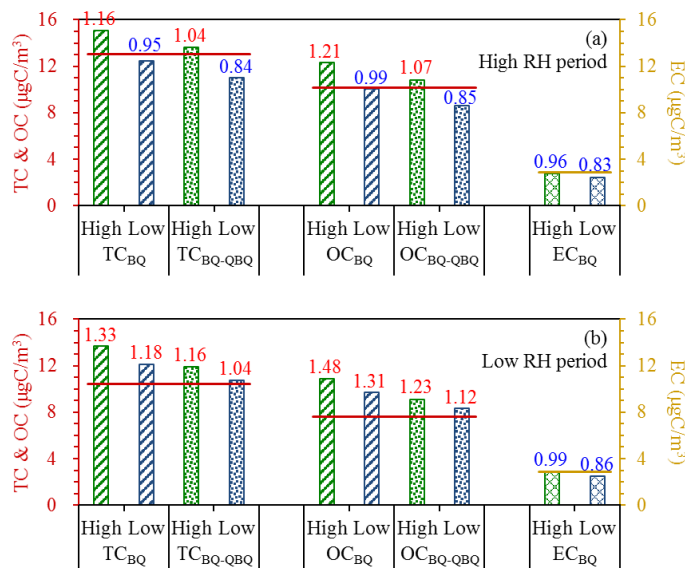


**Figure 3.** Temporal variations of TC concentration (48 h averages) and RH (24 h averages). RH averaged  $41 \pm 10\%$  and  $72 \pm 9\%$  during the low RH and high RH periods, respectively; the difference is significant at the 95 % level of confidence (2-tailed  $p = 0.000$ ). The identification of the high RH period is also supported by RH data from another source (i.e., the China Meteorological Data Sharing Service System; see Supplement).

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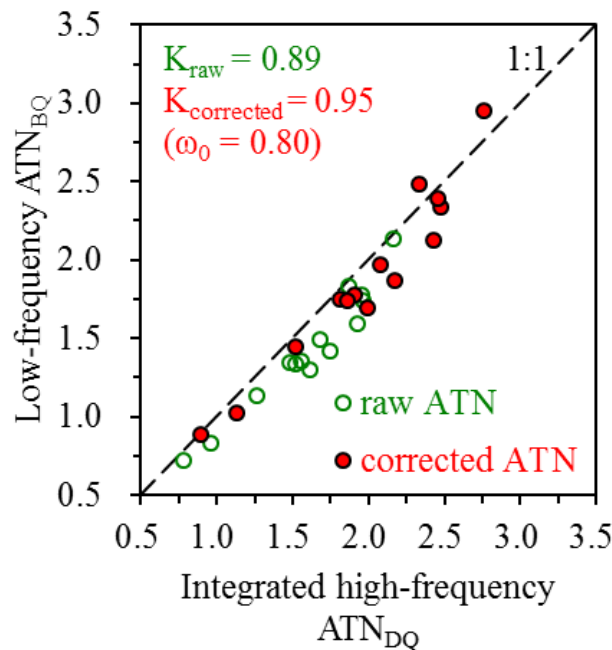
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**Figure 4.** Comparison of the 48 h averaged TC, OC and EC concentrations measured by different sampling configurations and frequencies during the high RH **(a)** and low RH **(b)** periods. In the title of the horizontal axis, “High” and “Low” indicate results from the high and low frequency samples, respectively. The horizontal lines correspond to the reference values, which are derived from the high frequency, denuded filters. The bars indicate the alternative estimations. The values above each bar are the average of the alternative-to-reference ratios, while the red and blue fonts indicate an overestimation and underestimation, respectively. The difference between the high-frequency  $\text{EC}_{\text{BQ}}$  and the reference value (i.e., the high-frequency  $\text{EC}_{\text{DQ}}$ ) is not significant at the 95 % level of confidence (2-tailed  $p = 0.113$ ), whereas the difference between the low-frequency  $\text{EC}_{\text{BQ}}$  and the reference value is significant (2-tailed  $p = 0.000$ ). Scatter plots describing the comparisons shown in this figure are provided in the Supplement.

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**Figure 5.** Comparison of the low-frequency  $ATN_{BQ}$  and the integrated high-frequency  $ATN_{DQ}$ . The comparison is performed based on both the uncorrected and corrected ATN. The correction is made by Eqs. (5)–(7) in which  $\omega_0$  is assumed to be 0.80. The correction has also been made by assuming  $\omega_0 = 0.85$  and 0.90, but the results are not shown here. Linear regression results are shown with  $K$  as slope (intercept is set as zero).

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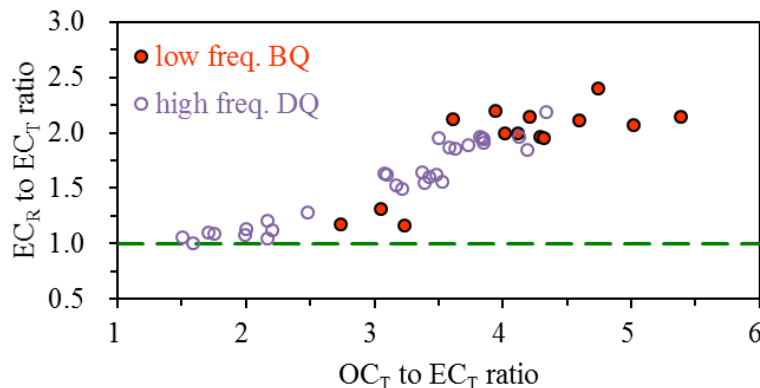
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**Figure 6.** Dependence of the EC<sub>R</sub> to EC<sub>T</sub> ratio on the abundance of OC (estimated by the OC<sub>T</sub> to EC<sub>T</sub> ratio). The dashed line indicates an EC<sub>R</sub> to EC<sub>T</sub> ratio of 1.0. The EC<sub>R</sub> and EC<sub>T</sub> ratio averaged  $1.91 \pm 0.39$  and  $1.56 \pm 0.36$  for the low and high frequency samples, respectively; the difference is significant at the 95 % level of confidence (2-tailed  $p = 0.005$ ).

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