



Positive sampling artifacts of organic carbon fractions for fine particles and nanoparticles in a tunnel environment

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ABSTRACT

The positive artifacts in particulate organic carbon fractions for fine particles (PM_{2.5}) and nanoparticles (PM_{0.1}) were characterized in a tunnel environment by using the QBQ (a quartz filter behind a quartz filter) method. The OC concentrations of the backup quartz filters ranged from 3.56 to 11.38 $\mu\text{g m}^{-3}$ with the average of 6.70 $\mu\text{g m}^{-3}$ for PM_{2.5}, and from 2.62 to 7.27 $\mu\text{g m}^{-3}$ with the average of 4.64 $\mu\text{g m}^{-3}$ for PM_{0.1}. The most abundant species on the backup quartz filters was OC1 for both PM_{2.5} and PM_{0.1}, accounting for 56.9% and 41.1% of the measured organic carbon, respectively. Most of EC fractions (EC1–EC3) on the backup filters for PM_{2.5} and PM_{0.1} were below the minimum detection limit. Therefore, only OC contributed to positive artifacts distinctly with the average percentage of 21.7% and 48.0% for PM_{2.5} and PM_{0.1}, respectively. The artifacts for four organic carbon fractions ranged from 36.1% (OC1) to 4.4% (OC4) for PM_{2.5} and from 68.0% (OC1) to 31.9% (OC4) for PM_{0.1}. The uncorrected OC/EC ratios on the front quartz filters were higher by as much as 30% and 107% for PM_{2.5} and PM_{0.1} than those corrected for positive organic artifacts, respectively. That is, much higher percentage of positive artifacts was found for PM_{0.1} OC fractions on the front filters. The comparison of the present and previous studies shows that OC positive artifacts vary widely among various PM fractions and sampling sites attributing to many factors that are worth investigating in the future.

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1. Introduction

Quartz filters have been widely used to collect airborne particulate matter for subsequent determination of carbon content by thermal or thermal–optical analysis (Cao et al., 2003, 2004, 2009; Chow et al., 2009; Shen et al., 2007, 2009; Ho et al., 2006; Zhang et al., 2009; Zhu et al., 2010b). However, the adsorption of gaseous organics could occur during sampling because the quartz filter has a large surface area, which could lead to overestimation of particulate organic carbon. On the other hand, the volatilization of particulate organic carbon from the filter would result in the underestimation of the particulate organic carbon. The above two phenomena result in positive and negative artifacts, respectively. OC sampling artifacts could affect particulates trends, radiative forcing and visibility degradation assessments (Watson, 2002; MacCracken, 2008). Due to these sampling artifacts and the uncertainties in the split of OC/EC, accurate measurement of

carbonaceous aerosols is challenging. In recent years, continuing attention has been paid to the accurate measurement of ambient particulate carbon (Turpin and Huntzicker, 1994; Kirchstetter et al., 2003; Chow et al., 2004, 2010; Arhami et al., 2006; Chen et al., 2010a; Zhu et al., 2010a). Several approaches, including QBQ, pre-filter organic denuders, passive field blank subtraction, filter slicing, regression intercepts and SANDWICH methods have been used to estimate the OC sampling artifacts (Frank, 2006; Watson et al., 2009; Chow et al., 2010).

The QBQ method for estimating these artifacts is to sample with a backup quartz filter placed behind either the main quartz filter or a Teflon filter in a parallel line (Chen et al., 2010b; Chow et al., 2010). Another popular approach is to use a denuder to reduce the positive artifact in combination with a highly adsorbent backup filter to capture any negative artifact (Turpin and Huntzicker, 1994; Kim et al., 2001; Eatough et al., 2003; Subramanian et al., 2004, 2009; Chen et al., 2010b; Cheng et al., 2010). By using the QBQ method to account for the positive artifact, the backup quartz filter may adsorb less gaseous organics than the front one, because the front quartz filter was not saturated and continually depleted the gaseous

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organics reaching the backup filter, which would be the case especially for low-volume or short-duration sampling conditions (Kirchstetter et al., 2001; Chen et al., 2010a). But yet the results from the previous studies indicated that the QBQ approach could provide a reasonable estimate of the positive artifacts on the front quartz filters (Kim et al., 2001; Kirchstetter et al., 2001; Lim et al., 2003; Subramanian et al., 2004; Chen et al., 2010b; Cheng et al., 2010).

Previous studies have been conducted to characterize the effect of OC positive sampling artifacts in different areas, but few are related to the tunnel environment and most studies only focused on the OC artifacts in fine and coarse particulates. In the present study, the OC positive artifacts of PM_{0.1} and PM_{2.5} were studied concurrently in a tunnel by using the QBQ method. The widely used MOUDI (Model 110, MSP Corp., MN, USA) and Dichot (Model SA-241, Andersen Inc., Georgia, USA) samplers were adopted to sample PM_{0.1} and PM_{2.5}, respectively. The goal of this study is to better understand the magnitude and nature of artifacts of four organic carbon fractions (OC1–4) for PM_{2.5} of Dichot and PM_{0.1} of MOUDI, as well as to compare the artifact levels among various sites.

2. Experiment

2.1. Instrument and sample collection

The sampling site is located in Xueshan Tunnel, which is the longest tunnel with a length of 12.9 km in Taiwan. The emissions of vehicles are the major sources in the tunnel because of poor ventilation. Dichotomous samplers (Model SA-241, Andersen Inc., Georgia, USA) were used to collect PM_{2.5} samples (fine particles, aerodynamic diameter $d_p < 2.5 \mu\text{m}$) and MOUDIs (Model 110, MSP Corp., MN, USA) were used to collect PM_{0.1} samples (nanoparticles, $d_p < 0.1 \mu\text{m}$) by using the QBQ approach in the sampling campaigns (Chen et al., 2010a). The MOUDIs have 10 size stages with nominal cutoff diameter of 18 (inlet), 10, 5.6, 2.5, 1.8, 1.0, 0.56, 0.32, 0.18, 0.1 and 0.056 μm , respectively (Marple et al., 1991), in which the nozzle plates of the 10th stages were removed so that only PM_{0.1} particles were collected in the after filters. The substrates used in the study were quartz membrane filters (Tissuquartz 2500QAT-UP, 7201 & 7202, Pall Corp., New York, USA). The stages 0–9 of the MOUDIs used silicone grease on the foils to reduce particle bounce so that PM_{0.1} samples were obtained by the after filters accurately (Chen et al., 2011). In the present study, the flow rates were 16.7 and 30 L min⁻¹ for Dichotomous samplers (with the effective filter area of 6.38 cm² and the filtration velocity of 39.2 cm s⁻¹ for the PM_{2.5} filter) and MOUDIs (with the effective filter area of 5.72 cm² and the filtration velocity of 87.4 cm s⁻¹ for the PM_{0.1} filter), respectively. The samples for this study were collected in nine sampling campaigns from October 2008 to July 2009, each lasted for 3–6.5 h. The previous study showed that the BQ reached saturation after ~1.5 h sampling for both PM_{0.1} samples of the MOUDI and PM_{2.5} samples of dichotomous samplers in the present tunnel. The sampling time of all samples of this study was longer than 3 h so that the saturation was achieved for all samples (Chen et al., 2010b). All quartz filters were pre-heated at 900 °C for 3 h and then stored in aluminum foils before sampling. The quartz samples were stored in a -18 °C freezer immediately after sampling to prevent the evaporation of volatile components.

2.2. Carbonaceous analysis

The samples of PM_{2.5} and PM_{0.1} were analyzed for OC and EC using a DRI Model 2001 Thermal/Optical Carbon Analyzer (Atmoslytic Inc., Calabasas, CA, USA). The quartz filter was analyzed

for three elemental carbon fractions and four organic carbon fractions following the IMPROVE_A (Interagency Monitoring of Protected Visual Environments) thermal/optical reflectance (TOR) protocol (Chow et al., 1993, 2001; Fung et al., 2002; Cao et al., 2003). The method produced data for four OC fractions (OC1, OC2, OC3, and OC4 in a helium atmosphere at 140 °C, 280 °C, 480 °C, and 580 °C, respectively), a pyrolyzed carbon fraction (OP, determined when reflected laser light attained its original intensity after oxygen was added to the combustion atmosphere), and three EC fractions (EC1, EC2, and EC3 in a 2% oxygen/98% helium atmosphere at 580 °C, 740 °C, and 840 °C, respectively). The IMPROVE_A protocol defined OC as OC1 + OC2 + OC3 + OC4 + OP and EC as EC1 + EC2 + EC3 - OP. The analyzer was calibrated with known quantities of CH₄ every day. Replicate analyses were performed once per ten samples.

3. Result and discussion

3.1. The positive artifacts of OC fractions for PM_{2.5} and PM_{0.1}

The experimental results are shown in Table 1, including daily average, minimum, maximum, and standard deviation of OC, OC1–4 and OP concentrations on the front quartz filter (FQ) and backup quartz filters (BQ) for PM_{2.5} and PM_{0.1}. It is to be noted that the present OC data of PM_{2.5} and PM_{0.1} were obtained separately by the Dichot and MOUDI, respectively, and could not be compared directly. The daily FQ OC concentrations varied from 9.91 to 56.81 $\mu\text{g m}^{-3}$ for PM_{2.5} and from 4.49 to 15.1 $\mu\text{g m}^{-3}$ for PM_{0.1}, respectively. The OC concentrations on the BQ filters fluctuated from 3.56 to 11.38 $\mu\text{g m}^{-3}$ for PM_{2.5} and from 2.62 to 7.27 $\mu\text{g m}^{-3}$ for PM_{0.1}, respectively. The various OC concentrations of BQ could be attributed to different sampling periods. Overall, the average concentrations of FQ OC and BQ OC were 30.88 and 6.70 $\mu\text{g m}^{-3}$ for PM_{2.5}, and those for PM_{0.1} were 9.67 and 4.64 $\mu\text{g m}^{-3}$, respectively. The ratio of BQ OC to FQ OC ranged from 0.14 to 0.36 for PM_{2.5} and 0.38 to 0.77 for PM_{0.1}, respectively. The FQ OC for PM_{0.1} was about 31.3% of that for PM_{2.5}, and the value for BQ was 69.3%.

Table 1 shows that the total BQ OC in PM_{0.1} is less than that in PM_{2.5}. It's reasonable since the effective area for the PM_{2.5} filter of the Dichotomous sampler, 6.38 cm², is larger than that of the PM_{0.1} filter of the MOUDI, 5.72 cm². In addition, the differences in the flow rate and pressure drop between the Dichotomous and MOUDI

Table 1

The concentrations and percentages in OC of four organic carbon fractions and OP for FQ and BQ in PM_{2.5} and PM_{0.1} (unit: $\mu\text{g m}^{-3}$; No. of samples: 9).

	FQ/BQ		OC	OC1	OC2	OC3	OC4	OP
PM _{2.5}	FQ	Max.	56.81	16.39	15.27	8.50	4.64	12.85
		Min.	9.91	0.28	5.83	1.19	0.00	1.67
		Ave.	30.88	10.22	8.35	5.08	2.27	4.96
		Stddev.	11.66	5.74	3.53	1.86	1.12	3.93
		%OC	100	33.1	27	16.5	7.3	16.1
	BQ	Max.	11.38	8.19	4.21	2.44	0.31	0.10
		Min.	3.56	0.47	0.49	0.58	0.00	0.00
		Ave.	6.70	3.81	1.52	1.25	0.10	0.02
		Stddev.	2.45	2.23	1.18	0.53	0.10	0.04
		%OC	100	56.9	22.7	18.7	1.4	0.30
PM _{0.1}	FQ	Max.	15.10	5.13	4.96	3.88	1.16	1.86
		Min.	4.49	0.16	2.26	1.05	0.20	0.35
		Ave.	9.67	2.86	3.11	2.24	0.57	0.89
		Stddev.	3.13	1.65	1.00	0.89	0.31	0.43
		%OC	100	29.6	32.2	23.2	5.8	9.2
	BQ	Max.	7.27	3.09	2.23	1.90	0.55	0.29
		Min.	2.62	0.12	0.68	0.56	0.06	0.01
		Ave.	4.64	1.91	1.23	1.21	0.18	0.12
		Stddev.	1.37	1.01	0.54	0.41	0.14	0.10
		%OC	100	41.1	26.5	26	3.82	2.58

samplers could also contribute to the differences in BQ OC in $PM_{0.1}$ and $PM_{2.5}$ which deserves further study in the future.

As shown in Fig. 1, the four OC fractions concentrations for $PM_{2.5}$ FQ were ranked in the following order: OC1 ($10.22 \pm 5.74 \mu\text{g m}^{-3}$) > OC2 ($8.35 \pm 3.53 \mu\text{g m}^{-3}$) > OC3 ($5.08 \pm 1.86 \mu\text{g m}^{-3}$) > OC4 ($2.27 \pm 1.12 \mu\text{g m}^{-3}$) and those for $PM_{2.5}$ BQ were OC1 ($3.81 \pm 2.23 \mu\text{g m}^{-3}$) > OC2 ($1.52 \pm 1.18 \mu\text{g m}^{-3}$) > OC3 ($1.25 \pm 0.53 \mu\text{g m}^{-3}$) > OC4 ($0.10 \pm 0.10 \mu\text{g m}^{-3}$), respectively. The ranking for $PM_{0.1}$ FQ was: OC2 ($3.11 \pm 1.0 \mu\text{g m}^{-3}$) > OC1 ($2.86 \pm 1.65 \mu\text{g m}^{-3}$) > OC3 ($2.24 \pm 0.89 \mu\text{g m}^{-3}$) > OC4 ($0.57 \pm 0.31 \mu\text{g m}^{-3}$) and that for $PM_{0.1}$ BQ was OC1 ($1.91 \pm 1.01 \mu\text{g m}^{-3}$) > OC2 ($1.23 \pm 0.54 \mu\text{g m}^{-3}$) > OC3 ($1.21 \pm 0.41 \mu\text{g m}^{-3}$) > OC4 ($0.18 \pm 0.14 \mu\text{g m}^{-3}$), respectively. Due to various sampling periods (including daytime, nighttime, weekdays and weekends), it is reasonable that standard deviations of the data are large. The ratio of $PM_{2.5}$ BQ to $PM_{2.5}$ FQ for OC1, OC2, OC3 and OC4 was 0.36, 0.17, 0.27, 0.04, respectively, and that for $PM_{0.1}$ BQ to $PM_{0.1}$ FQ was 0.68, 0.40, 0.56, 0.32, respectively. The mean concentrations of FQ OP were $4.96 \mu\text{g m}^{-3}$ and $0.89 \mu\text{g m}^{-3}$ for $PM_{2.5}$ and $PM_{0.1}$, respectively, and those for the BQ OP were much lower than any other carbon fractions in $PM_{2.5}$ and $PM_{0.1}$. The results showed that the ratios of BQ to FQ for four organic carbon fractions in $PM_{0.1}$ were much higher than those for $PM_{2.5}$ due to much lower $PM_{0.1}$ concentrations than $PM_{2.5}$ concentrations.

According to the IMPROVE_A TOR protocol, eight carbon fractions were produced (OC1, OC2, OC3, OC4, OP, EC1, EC2, and EC3) at different temperature steps for each aerosol sample, as mentioned previously. In this study, five carbon fractions, including OC1, OC2, OC3, OC4, and OP, were evaluated, intending to identify the artifacts of organic carbon on the front filters. Three EC fractions (EC1, EC2, and EC3) were not discussed here because most of them were below the minimum detection limit on the backup filters (Fig. 2). The variations of particulate EC fractions in FQ for $PM_{2.5}$ and $PM_{0.1}$ have been discussed in the previous study (Zhu et al., 2010a).

As shown in Fig. 2, the variations of four OC fractions for $PM_{2.5}$ BQ and $PM_{0.1}$ BQ showed much difference in the OC1 fractions. The concentration of OC1 for $PM_{2.5}$ BQ ($3.81 \mu\text{g m}^{-3}$) was 2.0 times higher than that for $PM_{0.1}$ BQ ($1.91 \mu\text{g m}^{-3}$). The fraction of OC2 in $PM_{2.5}$ BQ ($1.52 \mu\text{g m}^{-3}$) was 20% higher than that in $PM_{0.1}$ BQ ($1.23 \mu\text{g m}^{-3}$), while the levels of other organic carbon fractions were comparable. Generally, OC4 and OP were minor species on all front and backup quartz samples for $PM_{2.5}$ and $PM_{0.1}$. Low temperature carbon fractions (OC1 and OC2) were abundant on almost all front and backup quartz filters for $PM_{2.5}$ and $PM_{0.1}$. The OP fraction is generated by charring of organic particulate matter during carbon analysis, which was found to be mainly composed of water-soluble organic carbon portion in aerosol samples (Yu et al., 2002). The previous studies reported that the semi-volatile compounds (like carboxylic acids, hopanes and alkanes) relating

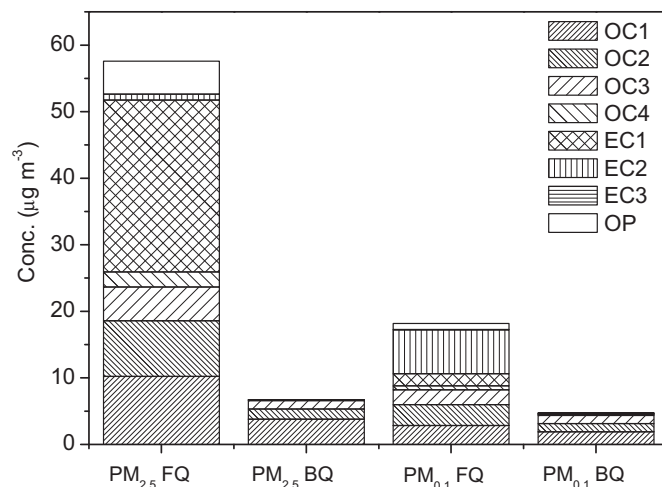


Fig. 2. Variations of 8 carbon fractions in FQ and BQ in $PM_{2.5}$ and $PM_{0.1}$.

to the product of OP could be adsorbed by the silanol hydroxyl groups in the front quartz filter (Sihabut et al., 2005; Ray and McDow, 2005; Cheng et al., 2010). In this study, charring was found on the FQ but very little on the BQ. The absence of OP on the BQ filters may be due to the above mechanism.

Considering the BQ OC as the positive organic artifacts, the average artifact's percentages of OC on the FQ were 21.7% for $PM_{2.5}$ and 48.0% for $PM_{0.1}$. The results showed that positive artifacts accounted for greater percentage of the OC concentrations on the front filters for $PM_{0.1}$. The artifact's level of the four organic carbon fractions ranged from 36.1% (OC1) to 4.4% (OC4) for $PM_{2.5}$ and from 68.0% (OC1) to 31.9% (OC4) for $PM_{0.1}$, respectively (Fig. 1). The positive artifacts of OP for $PM_{2.5}$ and $PM_{0.1}$ were 0.8% and 14.6%, respectively. The results indicated the sampling artifacts for four organic carbon fractions were much higher in $PM_{0.1}$ than those in $PM_{2.5}$.

3.2. The four organic carbon fractions and OP contributions to total organic carbon for FQ and BQ in $PM_{2.5}$ and $PM_{0.1}$

There were distinct differences among $PM_{2.5}$ and $PM_{0.1}$ samples for organic carbon fraction contributions to FQ OC and BQ OC (Table 1). The contributions of four organic carbon fractions (OC1, OC2, OC3 and OC4) to FQ OC in $PM_{2.5}$ and $PM_{0.1}$ were comparable, which ranged from 7.4% to 33.1% in $PM_{2.5}$ FQ and 5.9% to 32.2% in $PM_{0.1}$ FQ, respectively. While those to BQ OC in $PM_{2.5}$ and $PM_{0.1}$ were more variable, which ranged from 0.3% to 56.9% in $PM_{2.5}$ BQ

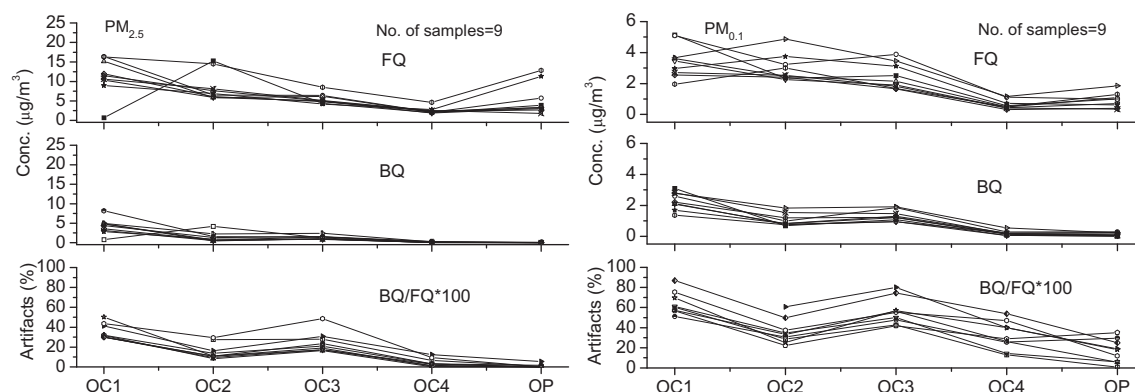


Fig. 1. Average concentrations and ratios of organic carbon fractions in FQ and BQ of $PM_{2.5}$ and $PM_{0.1}$.

and 2.6% to 41.1% in $PM_{0.1}$ BQ, respectively. OC1 accounted for 33.1% of FQ OC in $PM_{2.5}$ samples, lower than that in $PM_{2.5}$ BQ samples (56.9%), while those in $PM_{0.1}$ samples were 29.6% for FQ OC and 41.1% for BQ OC, respectively. The contributions of OC2 and OC3 to FQ OC (27% for OC2 and 16.5% for OC3) and BQ OC (22.7% for OC2 and 18.7% for OC3) in $PM_{2.5}$ were comparable, and similar percentages were also found for FQ OC (32.2% for OC2 and 23.2% for OC3) and BQ OC (26.5% for OC2 and 26% for OC3) in $PM_{0.1}$. The contributions of OC4 and OP to FQ OC and BQ OC in $PM_{2.5}$ were distinctly different. Much higher contributions (7.3% for OC4 and 16.1% for OP) to FQ OC were found than those to BQ OC (1.49% for OC4 and 0.29% for OP), which showed the abundance of water soluble organic carbon in $PM_{2.5}$ FQ. The contributions of OC4 and OP in $PM_{0.1}$ samples to FQ OC (5.9% for OC4 and 9.2% for OP) and BQ OC (3.9% for OC4 and 2.6% for OP) were not too different. High temperature OC4 was minor species on the BQ filters because most of organic species evolved at this temperature is non-volatile at ambient temperatures. High percentages of the contributions were found for OC1 to BQ OC in both $PM_{2.5}$ and $PM_{0.1}$.

3.3. Relationships between $PM_{2.5}$ OC and $PM_{0.1}$ OC in FQ and BQ

Relationships between $PM_{2.5}$ OC and $PM_{0.1}$ OC in FQ and BQ, and FQ OC and BQ OC in $PM_{2.5}$ and $PM_{0.1}$ are shown in Fig. 3. $PM_{2.5}$ OC and $PM_{0.1}$ OC were correlated significantly in FQ ($r = 0.83$) and BQ ($r = 0.86$). However, correlations were less significant between FQ OC and BQ OC for $PM_{2.5}$ ($r = 0.74$) and $PM_{0.1}$ ($r = 0.78$). This is reasonable considering that $PM_{2.5}$ OC and $PM_{0.1}$ OC was attributed to the common sources in tunnel environment. The small intercepts (1.3 for BQ and 2.4 for FQ) were also observed, which suggested that $PM_{2.5}$ OC and $PM_{0.1}$ OC were originated at least in part from the same source (especially for BQ). The correlations between the FQ OC and BQ OC for both $PM_{2.5}$ and $PM_{0.1}$ were less significant, which attributed to the differences in the amount of collected particulates and gaseous matter on the FQ and BQ for $PM_{2.5}$ and $PM_{0.1}$, respectively.

3.4. Comparison between uncorrected and corrected OC/EC ratios for $PM_{2.5}$ and $PM_{0.1}$

The OC/EC ratio is an important factor for determining source characteristics and the cooling and warming effects of carbonaceous aerosol (Cao et al., 2004, 2007). The minimum value of OC/EC ratio is a commonly used method to evaluate atmospheric secondary OC production (Turpin and Huntzicker, 1995; Castro et al., 1999). Therefore, it is vital to measure the OC sampling

artifacts in order to obtain more precise OC/EC ratio. For example, the estimated aerosol co-albedo of the biomass smoke samples is 60% larger when using the corrected OC concentrations than that using the uncorrected OC concentrations (Kirchstetter et al., 2003).

In this study, the ratios of the corrected OC/EC for $PM_{2.5}$ and $PM_{0.1}$ were 1.18 and 0.67, respectively, while the uncorrected OC/EC ratios were, on average, 1.55 for $PM_{2.5}$ and 1.39 for $PM_{0.1}$. The uncorrected OC/EC ratios were about 30% and 107% higher than the values corrected for positive organic artifacts in $PM_{2.5}$ and $PM_{0.1}$, respectively. It is no doubt that the correction of OC/EC ratio (especially for nanoparticles) will improve the accuracy of modeling results for radiative forcing that involves the scattering and absorption of carbonaceous material in the atmosphere. Fig. 4 showed the scattering plot of the corrected OC/EC ratios and the uncorrected OC/EC ratios against the EC concentrations for $PM_{2.5}$ and $PM_{0.1}$. Distinct reduction of uncorrected OC/EC ratios can be seen with increasing EC for both $PM_{2.5}$ and $PM_{0.1}$, nevertheless this was not seen for corrected OC/EC ratios. The corrected OC/EC ratios were almost constant among the various EC concentrations for $PM_{2.5}$ and $PM_{0.1}$. The results indicated that OC/EC ratio was influenced largely by OC sampling artifacts in the tunnel environment. Considering the significant effect of the artifacts, a comprehensive study of OC/EC ratio is needed among various regions and seasons.

3.5. The comparison of OC positive artifacts among various sites

Fig. 5 compares the average OC positive artifacts of $PM_{2.5}$ and $PM_{0.1}$ from Xueshan Tunnel with the levels from other sites. It is worth to note that the artifacts are influenced by many factors, such as the sampling mechanism of equipments, flow rate, deposit area for sampling, filter's saturation of adsorbed gases and evaporation rates of semi-volatile organic compounds during sampling (Chow et al., 2010). The comparison in this study further elaborates the characteristics of OC artifacts at various sampling sites.

The levels of positive organic carbon artifacts have been reported in different ambient environments by using various methods. Estimation of the OC artifacts in ambient atmosphere has been reported from 20% to over 30% of the OC (Kim et al., 2001; Lim et al., 2003; Subramanian et al., 2004), and even over 50% (Arhami et al., 2006). Schauer et al. (1999) reported that positive artifact was 50% of the OC for diesel particulate emissions and Subramanian et al. (2009) reported it as high as 65% (Schauer et al., 1999; Subramanian et al., 2009). The artifacts have been observed as high as 51.6% and 20.0% of the $PM_{0.1}$ mass for the roadside and tunnel, respectively (Chen et al., 2010a). The percentages of artifacts for

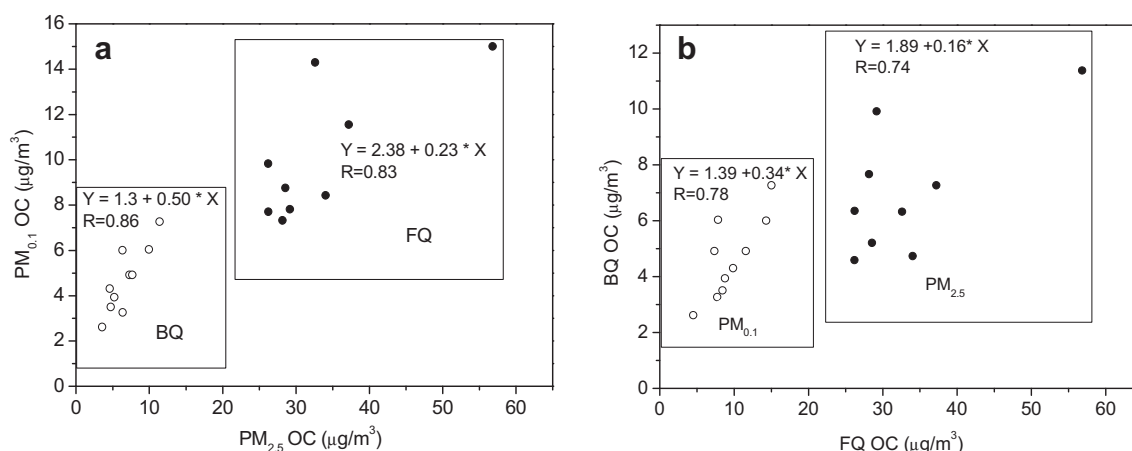


Fig. 3. Relationships between $PM_{2.5}$ OC and $PM_{0.1}$ OC for FQ and BQ (a) and between FQ OC and BQ OC for $PM_{2.5}$ and $PM_{0.1}$ (b).

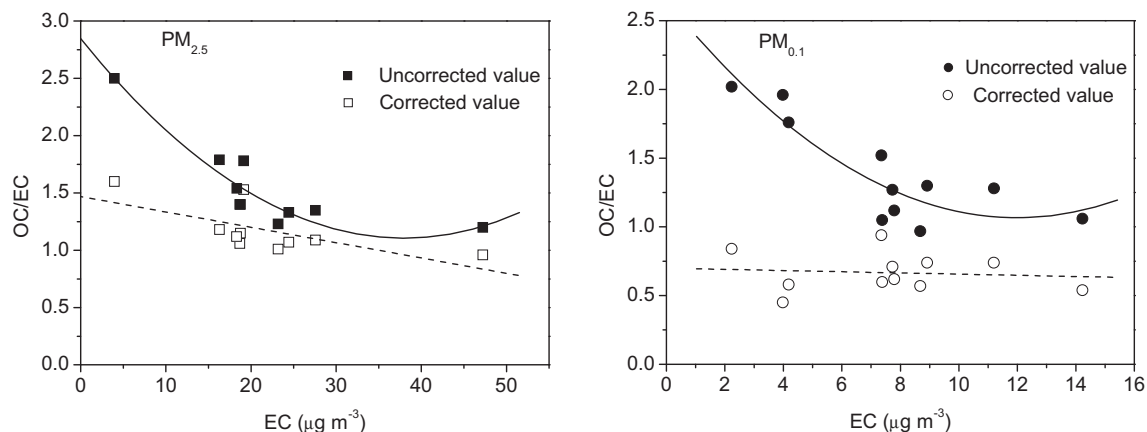


Fig. 4. Scattering plots of OC/EC ratios against the EC concentrations in $PM_{2.5}$ and $PM_{0.1}$ (uncorrected value and corrected value).

$PM_{2.5}$ and PM_{10} were 7.5% and 5.6% of the particle mass at the roadside while those were 12.9% and 16.7% in the tunnel, respectively (Chen et al., 2010b). The research for roadside site in Hong Kong have reported the levels of OC concentrations for PM_{10} , $PM_{2.5}$ and $PM_{1.0}$ were $14.4 \mu\text{g m}^{-3}$, $13.4 \mu\text{g m}^{-3}$ and $11.5 \mu\text{g m}^{-3}$ for FQ and $2.2 \mu\text{g m}^{-3}$, $1.5 \mu\text{g m}^{-3}$ and $1.4 \mu\text{g m}^{-3}$ for BQ. The corresponding OC positive artifacts were 15.3%, 11.2% and 12.2%, respectively (Cheng et al., 2010). Kirchstetter et al. (2003) reported positive OC artifact that accounted for 50% of the OC in Africa biomass burning plume (Kirchstetter et al., 2003). In summary, the highest OC positive artifact was found from diesel particulate emissions, the OC positive artifact for TSP from biomass burning and the urban site was comparable. In the present study, $PM_{2.5}$ OC positive artifacts were comparable with those of $PM_{2.5}$ at an urban site and a background environment (Kim et al., 2001; Subramanian et al., 2004), roughly twice as much as those for $PM_{2.5}$ from Hong Kong roadside (Cheng et al., 2010). The OC positive artifact of $PM_{0.1}$ in the present study were much higher, roughly twice the values for $PM_{2.5}$. These comparisons show that OC artifacts vary widely among various PM fractions (including TSP, PM_{10} , $PM_{2.5}$, $PM_{1.0}$ and $PM_{0.1}$) and sampling sites (including diesel, urban, biomass burning, background, roadside and tunnel), which may be attributed to the different sampling instruments used, ambient particulate and

gaseous OC levels and many other factors that are worth investigating in the future.

4. Conclusion

The positive sampling artifacts for OC fractions were quantified and characterized with the QBQ approaches for $PM_{2.5}$ and $PM_{0.1}$ samples in a tunnel environment. The OC concentrations of BQ ranged from 3.56 to $11.38 \mu\text{g m}^{-3}$ with the average of $6.70 \mu\text{g m}^{-3}$ for $PM_{2.5}$, and from 2.62 to $7.27 \mu\text{g m}^{-3}$ with the average of $4.64 \mu\text{g m}^{-3}$ for $PM_{0.1}$. The results showed the distinctive characteristics of positive sampling artifacts for four organic carbon fractions between $PM_{2.5}$ and $PM_{0.1}$. The most abundant species on BQ filters were OC1 and OC2 for $PM_{2.5}$, accounting for 56.9% and 22.7% of the measured organic carbon, respectively, while those for $PM_{0.1}$ BQ were OC1, OC2 and OC3, accounting for 41.1%, 26.5% and 26.0% of measured organic carbon, respectively. Most of EC fractions (EC1–EC3) on BQ for $PM_{2.5}$ and $PM_{0.1}$ were below the minimum detection limit. Considering the BQ OC as positive organic artifacts, the average percentage of the artifacts for the four organic carbon fractions ranged from 36% (OC1) to 4.4% (OC4) for $PM_{2.5}$ and from 68% (OC1) to 31.9% (OC4) for $PM_{0.1}$, respectively. The positive artifacts of OP for $PM_{2.5}$ and $PM_{0.1}$ were 0.8% and 14.6%, respectively. For $PM_{2.5}$, the uncorrected OC/EC ratios on the FQ were about 30% higher than the OC/EC ratios corrected for positive organic artifacts, while those were about 107% higher for $PM_{0.1}$. Therefore, considering the significant positive artifacts in the OC fractions, the potential toxic and environmental effects of $PM_{0.1}$, further work should be concentrated on the physical and chemical characterization of nanoparticles.

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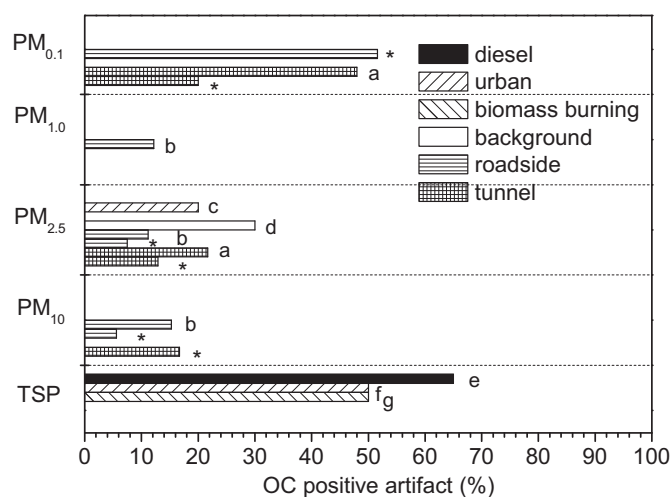


Fig. 5. Comparison of OC positive artifacts of $PM_{2.5}$ and $PM_{0.1}$ from Xueshan Tunnel with levels from other sites (^a: the present study; ^b: Cheng et al., 2010; ^c: Subramanian et al., 2004; ^d: Kim et al., 2001; ^e: Subramanian et al., 2009; ^f: Arhami et al., 2006; ^g: Kirchstetter et al., 2003; ^{*}(mass artifact): Chen et al., 2010b).

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