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# Characterization of fine particulate black carbon in Guangzhou, a megacity of South China

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## ABSTRACT

Continuous measurement of fine particulate black carbon (BC) was conducted at an urban site of Guangzhou in South China from December 2007 to December 2008. The daily average BC concentrations ranged from 0.6 to 20.5 μg $m^{-3}$, with an average value of 4.7 μg $m^{-3}$, which was substantially higher than those observed in the urban areas of other developed countries. Diurnal fluctuations of BC were marked with two peaks, one in the morning rush hour (08:00 LT) and the other in the late evening hour (21:00–22:00 LT), while the lowest BC concentrations were observed in the afternoon. Ambient BC concentrations displayed significant seasonal and diurnal variations with higher values in winter and spring, followed by lower concentrations during autumn and summer. Wind speed, wind direction and temperature were important meteorological factors that affected BC concentrations. A clearly negative correlation ($r$=–0.50, $p$<0.01) between BC concentrations and wind speed was found during the study period. A specific investigation was conducted to determine the relationship between optical BC and thermal–optical–reflectance elemental carbon (TOR EC) in distinct seasons. Although significant correlations between BC and EC were obtained ($r$>0.92, $p$<0.01), the regression slopes (ΔBC/ΔEC) slightly deviated from each other with values of 0.79, 1.18, and 0.81 in winter, spring and summer, respectively, possibly due to the distinct mixing states and source variations in different seasons. The calculated experimental attenuation coefficient showed a higher value (19.3 $m^2$ $g^{-1}$) in Guangzhou than the one recommended for typical Aethalometer measurements.

***Keywords:*** *BC, temporal variations, meteorological parameters, elemental carbon*

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## 1. Introduction

Black carbon (BC) aerosols, primarily originate from anthropogenic activities, such as open biomass burning, combustion of fossil fuels and biofuels (Streets et al., 2001), and have significant impacts on local air quality, regional and global climate (Menon et al., 2002; Jacobson, 2004; Ramanathan and Carmichael, 2008). Characterization of BC has recently drawn considerable concerns because of its environmental significance (Ramachandran and Rajesh, 2007; Huang et al., 2012), as well as its adverse health effects (Ramanathan and Carmichael, 2008; Kopp and Mauzerall, 2010; Janssen et al., 2012). BC emissions reduction would have large benefits to near–term climate change, human health and food security (Shindell et al., 2012). BC has a typical atmospheric lifetime of about one week in the absence of precipitation (Ramanathan and Carmichael, 2008). Therefore it is subject to mixing with other aerosol components along the transport pathway (Wang et al., 2011a; Cape et al., 2012). It is well recognized that BC is the dominant light absorbing aerosol component, warming the atmosphere, and thus affecting the earth's radiation balance on a global scale (Ramanathan and Carmichael, 2008; Shindell et al., 2012). Consequently, recent estimates suggest that BC is the second most critical factor, following carbon dioxide, contributing to global warming in form of direct forcing (Jacobson, 2001; Jacobson, 2004). BC is mainly present in fine particulates in urban environments (Sahu et al., 2011; Wang et al., 2011b), and thus it is small enough to be readily inhaled into the human body and affects the human respiratory system. Epidemiological studies have associated BC containing particles, in particular, with allergies, respiratory and cardiovascular diseases (Smith et al., 2009; Herich et al., 2011). Therefore, a large number of BC measurements have been conducted globally in urban locations (Ramachandran and Rajesh, 2007; Cao et al., 2009; Tiwari et al., 2009; Wang et al., 2011b; Rattigan et al., 2013), rural sites (Cheng et al., 2006; Wang et al., 2011a), and background areas (Zhao et al., 2012).

BC and EC represent a similar fraction of the carbonaceous aerosol, although they are different depending on their physical and chemical behavior (Streets et al., 2001; Dutkiewicz et al., 2009; Petzold et al., 2013). BC is typically defined as the amount of strongly light–absorbing carbon, that is generally measured by optical instruments (Andreae and Gelencser, 2006). EC, on the other hand, refers to the fraction of carbon that is thermally stable in an inert atmosphere to high temperatures of about 4 000 K and can only be gasified by oxidation starting at temperatures above

340 °C (Andreae and Gelencser, 2006; Petzold et al., 2013). The Interagency Monitoring of Protected Visual Environments (IMPROVE) thermal/optical reflectance (TOR) protocol (Chow et al., 1993; Cao et al., 2004; Chow et al., 2004) and National Institute of Occupational Safety and Health (NOISH) thermal–optical transmittance (TOT) method (Birch and Cary, 1996; Chow et al., 2001) have commonly been used for OC/EC determination. EUSAAR_1 and EUSAAR_2 protocols have been applied for OC and EC analysis for the European Supersites for Atmospheric Aerosol Research (EUSAAR) project (Cavalli et al., 2010; Reche et al., 2011). The Aethalometer uses an attenuation measurement method to obtain semi–continuous real–time BC data (Hansen et al., 1984; Cheng et al., 2006; Cao et al., 2009; Cheng et al., 2010). Other instruments such as the Particle Soot Absorption Photometer (PSAP) (Sharma et al., 2002), Multi–Angle Absorption Photometer (MAAP) (Hitzenberger et al., 2006), EEL type Smoke Stain (EELS) Reflectometer (Salako et al., 2012), Continuous Soot Monitoring System (COSMOS) (Sahu et al., 2011), and Single–Particle Soot Photometer (SP2) (Huang et al., 2011) have also been used for BC measurements. Optical measurements obtained by $Mm^{-1}$ but calibrated with respect to TOR EC or TOT EC protocols are named as Equivalent Black Carbon (EBC) (Reche et al., 2011; Petzold et al., 2013). In this study, BC was measured by an Aethalometer and reported as BC, instead of EBC, while EC was determined following the TOR protocol.

As BC emissions are particularly large in China (Streets et al., 2001; Ohara et al., 2007), it is reasonable to anticipate that aerosols containing BC contribute substantially to regional climate change and severe health issues in China. Guangzhou is one of the most urbanized cities in the Pearl River Delta region. The rapid industrial and economic development in this region has been accompanied by serious fine particle pollution that has gained high attention in recent years (Cao et al., 2004; Andreae et al., 2008; Zheng et al., 2009; Huang et al., 2012; Zhang et al., 2013). Thus, due to such importance in the atmosphere, determination of BC concentrations and its atmospheric behavior is urgently required in this region. Previous studies in China have focused on thermal carbonaceous measurements (Cao et al., 2004; Cao et al., 2007; Zhang et al., 2013), and most other research efforts addressed the radiative properties of optical BC (Wu et al., 2009). Although many uncertainties remain with BC analysis techniques, thermal elemental carbon (EC) has mostly been used as surrogate for BC (Wu et al., 2009; Verma et al., 2010; Huang et al., 2011). Short term inter–comparison measurements of BC and EC have been conducted at other locations in different countries (Jeong et al., 2004; Ahmed et al., 2009; Salako et al., 2012; Rattigan et al., 2013), and considerable differences must be expected when inferring site–specific absorption coefficients from filter samples. To date, few studies have assessed the long–term characteristics of optical BC in fine particles in South China. The purpose of this study is, therefore, to describe and examine the seasonal and diurnal variability of BC concentrations, as well as illustrate its variation with emission sources and meteorological conditions. This paper also discusses the variability between the higher time–resolution optical BC and filter based TOR EC mass concentrations in fine particles. In order to further understand the potential influence factors, the variations of BC/EC ratios during different seasons in fine particles were investigated as well.

## 2. Experimental Procedures

### 2.1. Study site

Guangzhou covers an area of 7 434 $km^2$ and had a registered population exceeding 12.7 million in 2010 (Guangzhou International, 2010). It is the largest city in southern China, and generally represents a typical urban area in the PRD region. The city often faces serious traffic congestion problems because of the increased vehicle numbers; the total count of vehicles was 1.82 million by the end of 2007 (GTPRI, 2010). Black carbon mass concentration measurements were conducted at the rooftop of a fourteen–story building (~53 m above the ground level) at the South China Institute of Environmental Sciences (23°07′N, 113°21′E, Figure 1) in Guangzhou. The surrounding area of the study site is characterized by commercial and residential land use. At about 400 m to the north and 1 km to the west of the measurement site are the South China Expressway and Huangpu Highway, respectively. More detailed information about the site can be found in the literature (Tao et al., 2009).

### 2.2. Data collection

BC mass concentrations were obtained by an Aethalometer (AE–31, Magee Scientific, USA), equipped with a 2.5 µm cut cyclone (Model SCC 1 829, BGI Inc., Waltham, MA, USA). It operated at a flow rate of 5 L $min^{-1}$ with a time resolution of 5 min for twenty–four hours (24 hrs). The AE–31 measured BC attenuation at seven different wavelengths (370, 450, 520, 590, 660, 880 and 950 nm). The Aethalometer measurement is based on the optical method, i.e., by determining light beam attenuation, ATN ($ATN=-\ln(I/I_o)$), where $I$ and $I_o$ were the respective transmission optical densities through the deposit and blank filters, respectively. The ATN through the filter is proportional to the amount of BC mass loading of the particle deposition; the ATN is then converted into BC mass concentration ($BC=ATN/\sigma_{ATN}$) (Hansen and Schnell, 2005). The attenuation coefficient ($\sigma_{ATN}$) is typically related to lifetime, emission sources, and chemical composition of the BC containing aerosol (Jeong et al., 2004; Salako et al., 2012), which have been shown to vary from 6.4 to 20.1 $m^2\ g^{-1}$ for the measurements conducted at urban sites and with a range of 5.2–19.3 $m^2\ g^{-1}$ for various types of biomass fires (Ramachandran and Rajesh, 2007). In this study, the ATN was converted to BC concentration using $\sigma_{ATN}$=16.6 $m^2\ g^{-1}$ at the wavelength of 880 nm. The detection limit for BC was 5 ng $m^{-3}$ and the missing data due to instrument failure were excluded from further analysis.

Filter–based fine particle ($PM_{2.5}$) samples for thermal carbonaceous measurement were collected simultaneously with BC monitoring, using a Partisol air sampler (Model 2000H, Thermo Electron Corporation, USA), fitted with a $PM_{2.5}$ cyclone (Model PQ200, BGI Inc., Waltham, MA, USA), loaded with 47 mm quartz fiber filters (Whatman, UK), and operated at a flow–rate of 16.7 L $min^{-1}$ for 24 hrs a day (starting at 10:00 LT each day and ending at 10:00 LT the next day). A total of 91 $PM_{2.5}$ samples, including 10 blank samples, were collected from January to July 2008. The sampling dates were from the first day to the last day of the months during January (representative of winter), April (spring), and July (summer). All the filters were pre–baked at 800 °C for 4 hrs before sample collection in order to remove potential organic contaminants.

The basic meteorological parameters, such as wind speed (WS), wind direction (WD), temperature (T), relative humidity (RH), and precipitation (PR), were obtained every 30 min during the study period. Wind speed and wind direction were recorded by a wind monitor (Model QMW110A, Vaisala, Helsinki, Finland). Ambient temperature and relative humidity were measured by a temperature probe (Model QMH102, Vaisala, Helsinki, Finland). Precipitation was measured by a rain gauge (Model RG13, Vaisala, Helsinki, Finland). The boundary layer depths were calculated by the U.S. National Oceanic and Atmospheric Administration (NOAA) READY archived meteorological data (Cao et al., 2009). The program used the archived data set GDAS (1 deg, 3–hourly, Global) based on Coordinated Universal Time (UTC), and the time–series of calculated daily boundary layer depths were obtained. All UTC values were converted to local time.

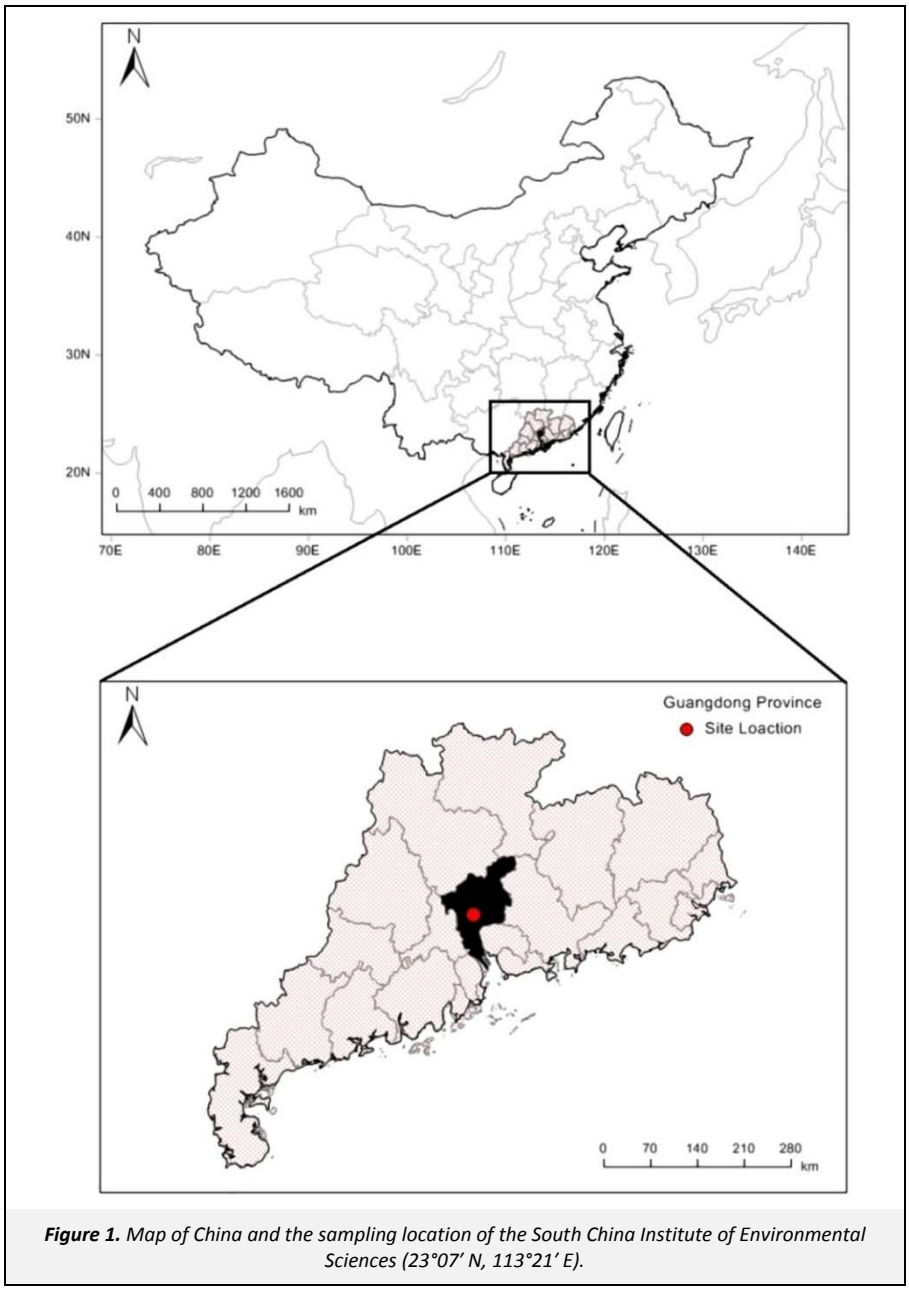


***Figure 1.*** *Map of China and the sampling location of the South China Institute of Environmental Sciences (23°07′ N, 113°21′ E).*

### 2.3. Carbon analysis

A punch (0.526 $cm^2$) of each quartz filter was analyzed for carbonaceous aerosol components (OC and EC) with a DRI 2001 carbon analyzer (Atmoslytic Inc., Calabasas, CA, USA) based on the IMPROVE/TOR protocol (Cao et al., 2004). Blank samples were analyzed in order to determine any contamination from the collection media and influence from filter transport and handling. Mass concentrations of OC and EC were corrected by subtracting the blank filter concentrations. The detection limits for OC and EC were below 1.0 μg $m^{-3}$. Quality assurance (QA) and quality control (QC) procedures also included storage of filters in petri dishes in a freezer at –18 °C until chemical analysis. More detailed information about the OC/EC analysis protocol is provided in Cao et al. (2004).

## 3. Results and Discussion

### 3.1. Seasonal BC variations

Daily average BC concentrations measured from December 2007 to December 2008 are plotted in Figure 2. The annual average BC concentration at Guangzhou was 4.7 μg $m^{-3}$. The highest daily mean BC concentration was 20.5 μg $m^{-3}$ and the lowest value of 0.6 μg $m^{-3}$ was observed during the measurement period. The 30–day moving average of the BC concentrations varied in the range of 1.2–10.0 μg $m^{-3}$ during the study period. As illustrated in Table S1 (see the Supporting Material, SM), the monthly average BC concentration varied from a maximum value of 7.8±4.3 μg $m^{-3}$ in December 2007 to a minimum concentration of 2.8±1.2 μg $m^{-3}$ in August 2008. In particular, an obvious decrease was observed from March (6.2±2.4 μg $m^{-3}$) to August. The highest seasonal BC average concentrations were observed in winter (5.9±4.3 μg $m^{-3}$, 24% higher than the annual mean), which were 1.6 times higher than those measured in summer (3.5±1.4 μg $m^{-3}$, 23% lower) and autumn (3.6±1.7 μg $m^{-3}$, 22% lower than the annual mean).

Domestic biofuel use, transportation and industry sectors were important emission sources in Guangzhou; especially industrial activities were estimated to account for 38% of total BC emissions (Verma et al., 2010). This region was strongly impacted by the financial crisis in the second half of 2008 with considerable reduction in fuel consumption (Zhang et al., 2012). The measurement results showed that the monthly BC concentration

decreased by 3.9 μg $m^{-3}$ on average in December 2008 compared to December 2007. It is reasonable to assume that the reduced source emissions were one of the main factors leading to the BC reduction towards the end of 2008, which offers a unique opportunity to evaluate the direct effect of source reduction on the atmospheric BC concentrations.

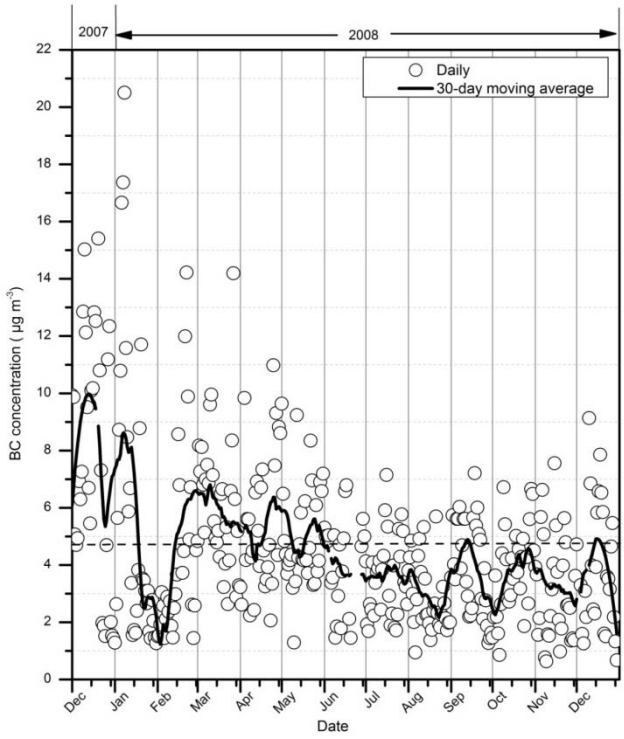


***Figure 2.*** *Daily average BC concentrations (open circles), annual BC level (dashed line) and 30–day moving average of BC concentrations (solid line) between December 2007 and December 2008.*

Table S2 (see the SM) compares the Aethalometer BC concentrations of this study with those measured at other locations. Compared with the results obtained in Guangzhou from a previous study (Wu et al., 2009), it appeared that there was a gradually decreasing trend from 2005 to 2008 during the winter period. Moreover, it was found that annual average BC concentrations in Guangzhou were relatively lower than those measured at other cities in China, e.g., Shanghai (5.5±4.0 μg $m^{-3}$) (Zhou et al., 2009) and Xi'an (14.7±9.5 μg $m^{-3}$) (Cao et al., 2009). However, BC concentrations measured in rural areas of China were only half of those measured in Guangzhou (Cheng et al., 2010; Wang et al., 2011a; Zhao et al., 2012). The magnitude of BC emissions is particularly large in India and Thailand, resulting in rather higher ambient BC concentrations of 14±12 μg $m^{-3}$ (Tiwari et al., 2009) and 5.3–13.1 μg $m^{-3}$ (Sahu et al., 2011), respectively. Even in rural areas of India, BC concentrations were higher (2–30 μg $m^{-3}$) than those measured in Guangzhou because of the sizeable diesel vehicle and biofuel combustion emissions (Rehman et al., 2011). In contrast, BC concentrations measured in the cities of developed countries usually have considerably lower values than in Guangzhou, such as East St. Louis (0.71–1.75 μg $m^{-3}$) (Ramachandran and Rajesh, 2007), Laredo (1.81±0.26 μg $m^{-3}$) (Wang et al., 2011b), Rochester (0.57–0.76 μg $m^{-3}$) (Rattigan et al., 2013) in the US, Toulon (0.1–2.5 μg $m^{-3}$) in France (Saha and Despiau, 2009), and North Kensington (1.9±0.7 μg $m^{-3}$) (Reche et al., 2011). BC concentrations were lower (1.0 μg $m^{-3}$) in Helsinki than in many other European cities (Jarvi et al., 2008), while higher BC concentrations were obtained at a roadside site in Maryleane (7.8±2.7 μg $m^{-3}$) in London (Reche et al., 2011). As can be seen from this comparison, the differences in ambient BC levels may be caused by different sampling times, the location of the sampling sites, as well as different emission sources. Overall, the BC concentrations in Guangzhou were generally at the lower level in China, while they were considerably higher than those in developed countries.

### 3.2. Diurnal BC patterns

The mean diurnal BC mass concentrations measured in four seasons from December 2007 to November 2008 are shown in Figure 3. On a daily basis, there was a gradual increase in concentrations starting from 05:00 LT, and the morning peak typically occurred at 08:00 LT, while the BC concentrations were found to be the smallest during midday. The evening peak happened between 21:00 and 22:00 LT. Throughout the year, the midday BC concentrations exhibited lower mean values in wet seasons (summer and autumn) and higher values in dry seasons (winter and spring). The BC concentrations in winter and spring were about a factor of 1.6 higher than those measured in summer and autumn during daytime. The diurnal amplitudes of BC values from late evening to pre–dawn were found to be seasonally dependent with the maximum occurring in winter, followed by spring and autumn, and the lowest values observed during summer. Similar features in diurnal profiles in BC concentrations have been reported for other locations as well (Cao et al., 2009; Dutkiewicz et al., 2009; Yoo et al., 2011), i.e., distinct seasonal hourly BC patterns throughout the entire day (winter>autumn> spring>summer) can be seen.

The atmospheric abundance of BC is not only affected by anthropogenic activities but also the stability of the boundary layer in an urban environment. The daily evolution of boundary layer height in Guangzhou in four seasons is plotted in Figure 3b. It can be seen that the nocturnal boundary layer depth was shallower than its daytime counterpart by a factor of 3–5. The development of a well–mixed layer height began from 08:00 LT, reaching maximum values around 14:00 LT, decreased after 17:00 LT, and later dropped to the lowest level at night. The BC morning peak was attributed to the combined influence of vehicle traffic and the lower mixing layer height. The minimum BC concentrations were found during midday when there were fewer anthropogenic BC emissions, while the deeper boundary layer leads to a faster dispersion resulting in a dilution of BC concentrations at midday. Higher wind speeds also have a strong dilution effect at midday on BC concentrations especially in summer (see the SM, Figure S2). The surface inversion after sunset resulted in the accumulation of primary BC, causing even higher BC concentrations in the late evening. Increased emissions from diesel trucks (especially after 22:00 LT) could partially contribute to the higher BC concentration in the late evening (Garland et al., 2008). Similar BC diurnal trends have been observed at other urban sites (Ramachandran and Rajesh, 2007; Andreae et al., 2008; Dutkiewicz et al., 2009; Saha and Despiau, 2009; Verma et al., 2010).

### 3.3. Relationships between BC and meteorological parameters

The monthly average BC mass concentrations together with wind speed measured over Guangzhou are plotted in Figure 4. The wind speed was in the range of 1.4–1.9 m $s^{-1}$ during December–May, and increased to 2.1–2.2 m $s^{-1}$ during summer. Lowest wind speeds were measured during autumn (0.5–1.0 m $s^{-1}$). Wind speed is an important factor affecting the BC concentrations; higher wind speeds contribute to stronger BC dispersion (Saha and Despiau, 2009; Wang et al., 2011b). A clearly decreasing trend was found, with a significant negative correlation coefficient $r$=–0.50 ($p$<0.01), between BC concentrations and wind speeds (>0.5 m $s^{-1}$), as shown in Figure 4b. Relatively lower BC concentrations were observed during autumn 2008, despite the lowest wind speeds, which were likely caused by the reduction in local BC emissions. Similar results were obtained at other urban sites, e.g., a significant negative correlation ($r$=–0.45) between BC concentration and WS was reported for Xi'an (Cao et al., 2009). Ramachandran and

Rajesh(2007) also found a negative correlation ($r$=–0.54) between BC and WS at an urban site of India.

The contribution of hourly BC from different wind directions is illustrated by the pollution roses in Figure 5. Calm is defined as wind speeds less than 0.5 m $s^{-1}$, and the calm winds were excluded from the BC pollution roses. As can be seen in Figure 5a, hourly BC concentrations from E/ESE/SE were in the range of 4–20 μg $m^{-3}$ in winter, much higher than those during the prevailing wind directions. Since the site lies north of several industrial cities (e.g., Dongguan and Foshan) (see the SM, Figure S1), and downwind of industrial districts of Guangzhou (Jahn et al., 2013) during the winter season, higher BC concentrations are most likely due to the influence of local and regional industrial aerosol emissions. BC concentrations were larger than 8.0 μg $m^{-3}$ from southerly (SE–SW) (11.6%) sections, which were much higher than those from northerly directions (2.0%) in spring (Figure 5b). In summer (Figure 5c), when more than 34.1% of surface winds were from the S/SSW directions, BC concentrations of less than 4 μg $m^{-3}$ (accounting for 27.1%) were observed, while 11.0% of BC concentrations were larger than 4.0 μg $m^{-3}$ when southerly winds dominated. In contrast, BC concentrations decreased when southerly wind dominated during summer in Hong Kong, as there were no obvious local emissions, and the advected marine aerosols were associated with low BC content (Cheng et al., 2006). BC concentrations were less than 4.0 μg $m^{-3}$ when northerly winds dominated, accounting for a percentage of 8.4–10.6% in autumn (Figure 5d). Compared with the winter season, lower hourly BC concentrations (<4 μg $m^{-3}$) from E/ESE/SE directions were observed during autumn. The BC seasonal average concentration in autumn was about 39% lower than that measured in winter, indicating reduced industrial emissions from E–SE may contribute to the relatively lower BC concentrations in autumn.

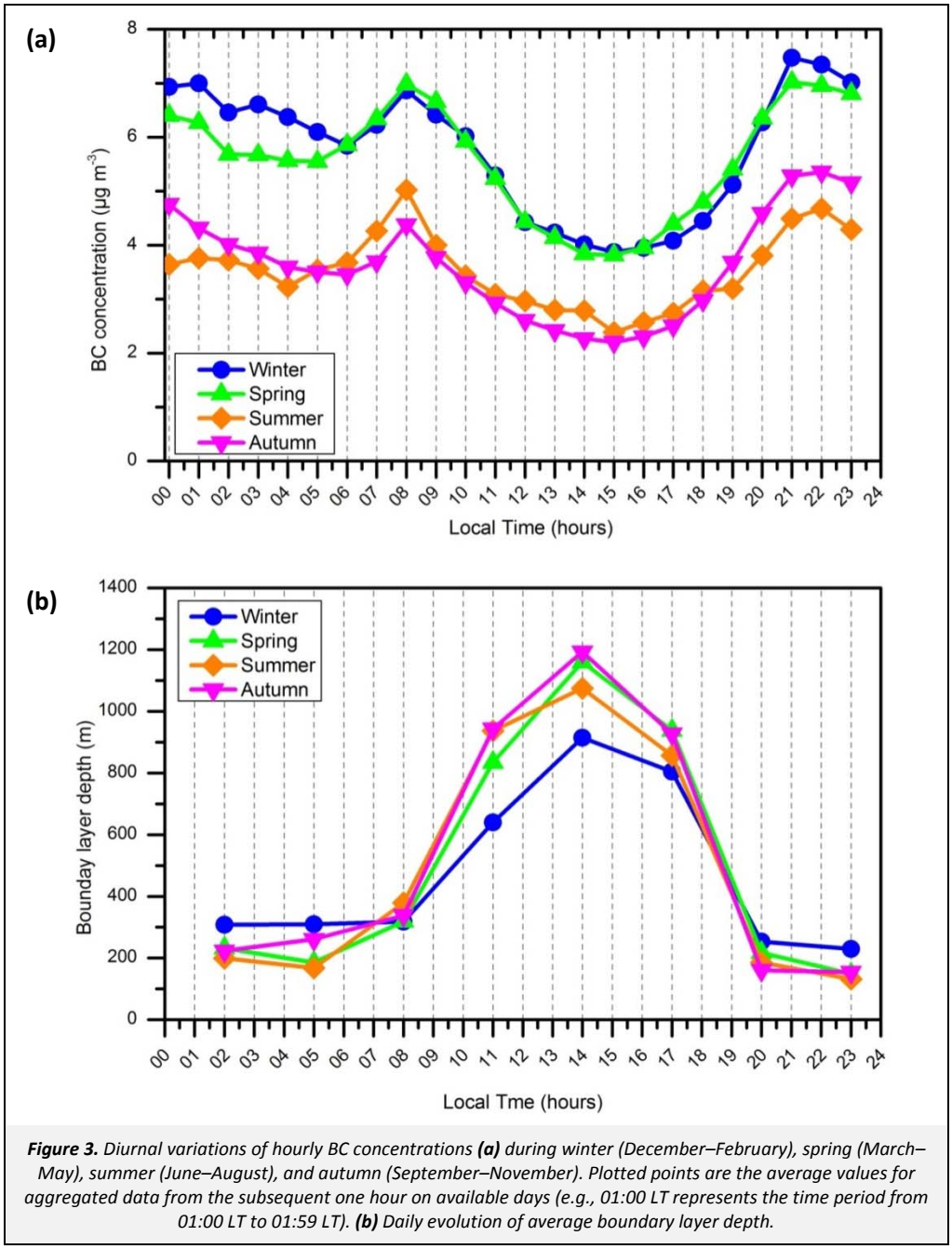


***Figure 3.*** *Diurnal variations of hourly BC concentrations* ***(a)*** *during winter (December–February), spring (March–May), summer (June–August), and autumn (September–November). Plotted points are the average values for aggregated data from the subsequent one hour on available days (e.g., 01:00 LT represents the time period from 01:00 LT to 01:59 LT).* ***(b)*** *Daily evolution of average boundary layer depth.*

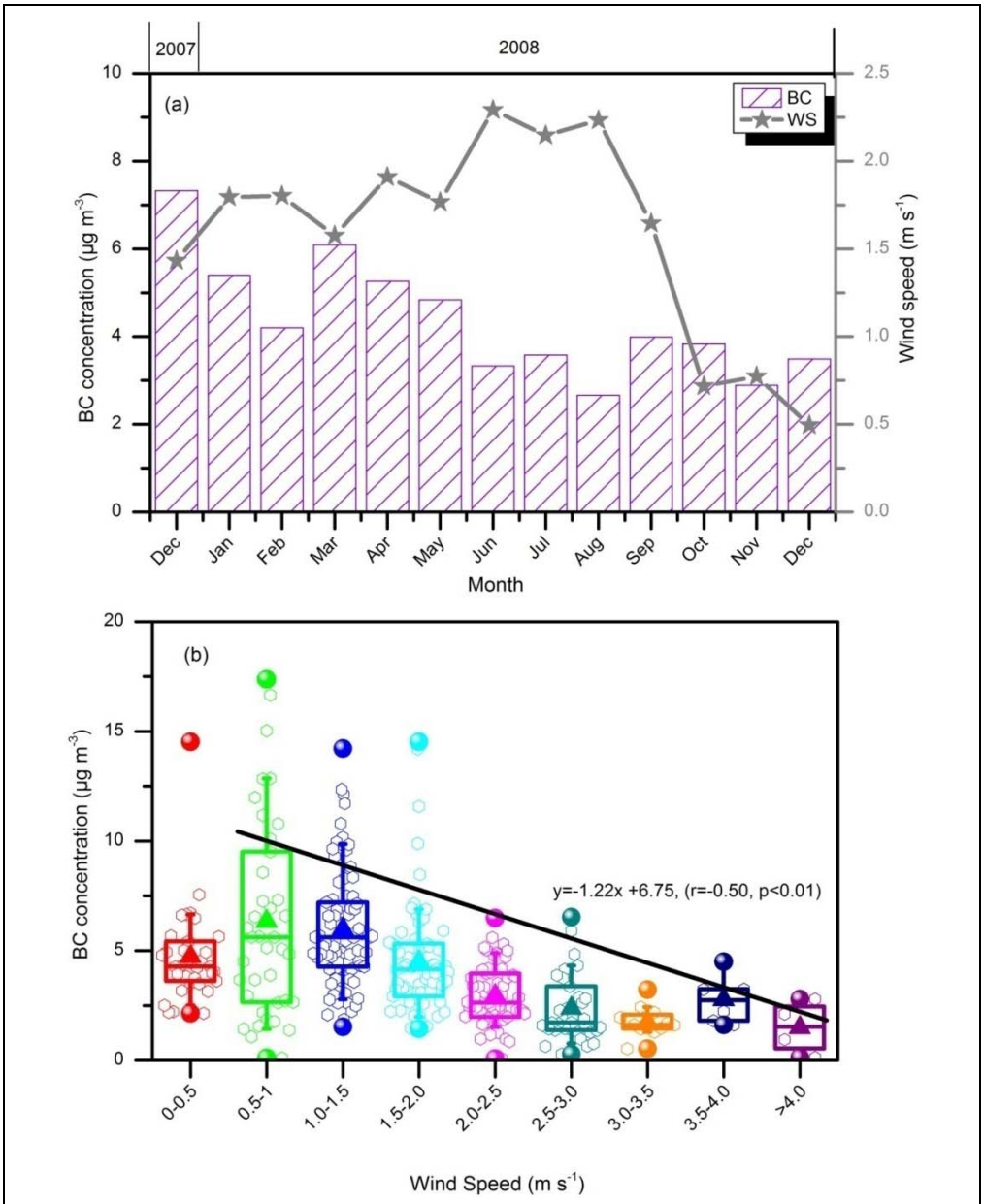


***Figure 4. (a)*** *Monthly variations of BC concentrations and wind speed during the study period.* ***(b)*** *BC concentration intervals grouped by wind speed. Box–whisker plot indicates median and 25% quartile (box), mean (triangle), 10/90% (whiskers), and the minimum/maximum percentiles (circles). The straight line is the linear fit to the measurement points.*

The monthly mean temperatures (see the SM, Figure S3a) were in the range of 11.8 (±4.5)–18.4 (±3.2) °C during winter and increased to 29.4±2.6 °C in summer. After the summer monsoon months the temperature started to decrease again. Positive correlation coefficients of $r$=0.76 ($p$<0.01) and $r$=0.49 ($p$<0.01) were found between BC and temperature during winter and autumn, respectively. BC concentrations increased with increase in ambient temperature especially during the dry seasons (Chen et al., 2001; Ramachandran and Rajesh, 2007) when the BC concentrations were affected by local emission sources as well as regional transport. In a previous study, clear positive correlations between temperature and BC were observed in Ahmedabad ($r$=0.52) (Ramachandran and Rajesh, 2007) and Trivandrum ($r$=0.77) (Babu and Moorthy, 2002). The correlations between BC concentrations and other meteorological parameters were not strong (see the SM, Figures S3b–S3c), which indicated that local sources and regional transported pollutants contributed to the BC concentrations in Guangzhou.

### 3.4. Relationship between BC and EC

Filter samples for carbonaceous (OC and EC) analysis were obtained in parallel with optical BC measurement. We summarize the TOR EC concentrations and BC/EC ratios during different seasons in Table 1. Monthly statistics of OC concentrations, OC/EC ratios and slopes of ΔOC/ΔEC are shown in Table S3 (see the SM). January, April, and July represented winter, spring, and summer, respectively. The average EC concentrations have distinct seasonal variations with the highest values observed in winter (8.6±5.0 μg $m^{-3}$) and lowest concentrations in summer (4.5±2.1 μg $m^{-3}$). The minimum EC concentrations moderately varied between 2.1 μg $m^{-3}$ and 2.7 μg $m^{-3}$, while the maximum values during winter (20.0 μg $m^{-3}$) were more than twice of those in spring (8.5 μg $m^{-3}$). The average BC/EC ratios had a range of 0.2–2.6 μg $\mu g^{-1}$, which was comparable with the BC/EC ratio range (0.47–3.56 μg $\mu g^{-1}$) reported by Salako et al. (2012) for 9 different countries.

***Table 1.*** *Minimum, maximum, and average concentrations and standard deviations of TOR EC and BC/EC ratios*

| Season (Month) | EC (μg $m^{-3}$) | | | BC/EC ratio (μg $μg^{-1}$) | | |
|---|---|---|---|---|---|---|
| | Minimum | Maximum | Mean±SD [a] | Minimum | Maximum | Mean±SD |
| Winter (January) | 2.7 | 20.0 | 8.6±5.0 | 0.2 | 1. 5 | 0.6±0.3 |
| Spring (April) | 2.3 | 8.5 | 4.9±1.6 | 0.6 | 2.1 | 1.2±0.4 |
| Summer (July) | 2.4 | 13.7 | 4.5±2.1 | 0.2 | 2.6 | 0.9±0.4 |
| Total | 2.3 | 20.0 | 6.2±3.9 | 0.2 | 2.6 | 0.8±0.4 |

[a] *SD: standard deviation*

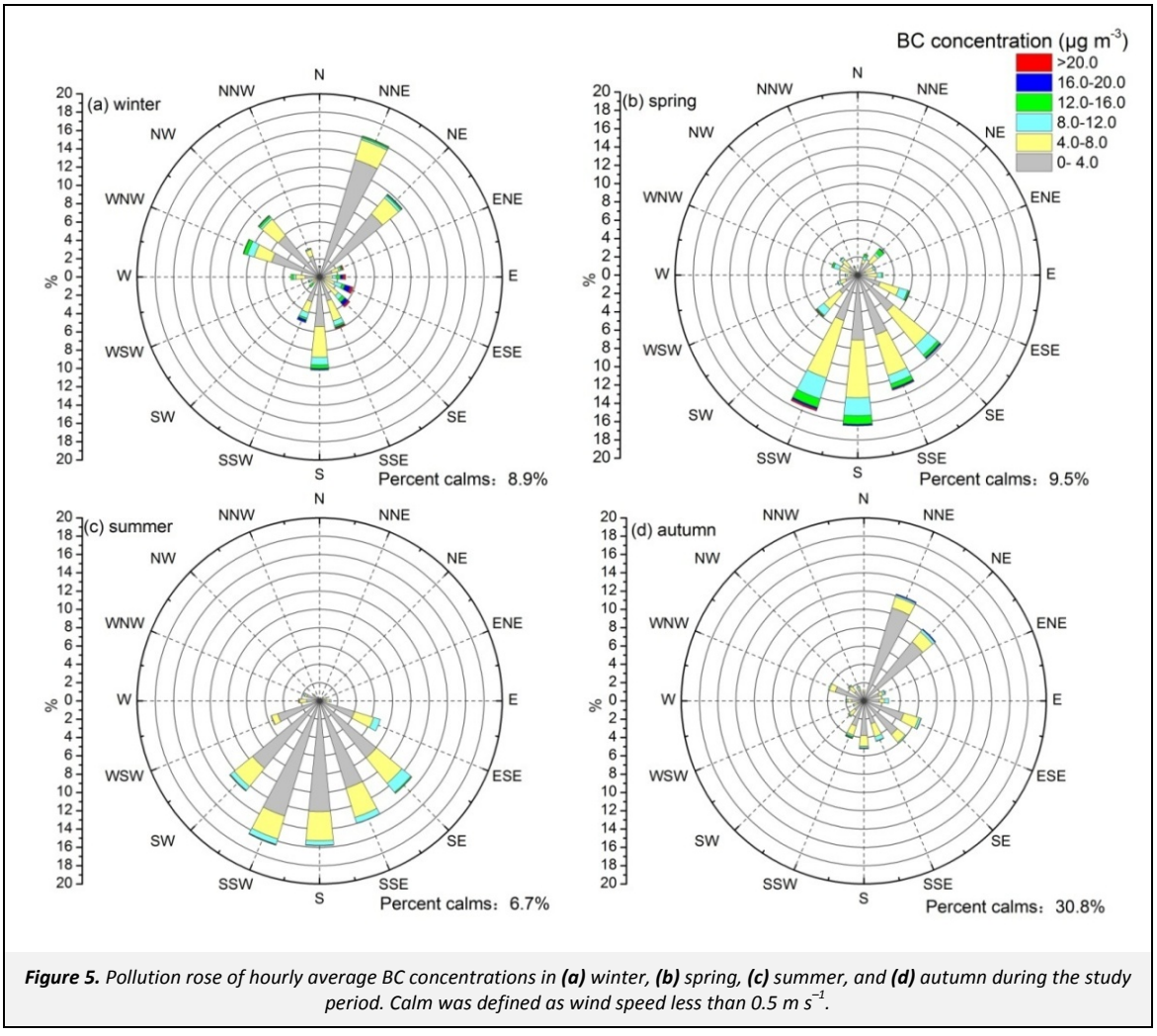


***Figure 5.*** *Pollution rose of hourly average BC concentrations in* ***(a)*** *winter,* ***(b)*** *spring,* ***(c)*** *summer, and* ***(d)*** *autumn during the study period. Calm was defined as wind speed less than 0.5 m* $s^{-1}$.

As illustrated in Figure 6, the linear regressions for optical BC and TOR EC concentrations were calculated in different seasons, using first order regression with coefficient uncertainties calculated at the 99% confidence interval. BC values strongly correlated with EC in winter with a high correlation coefficient, $r$=0.92 and a slope of 0.79. Likewise, good agreement and a high correlation coefficient was also found in summer ($r$=0.96, slope=0.81). The BC/EC correlation during spring had a slope value of 1.18 ($r$=0.92). A high correlation coefficient was obtained between all the BC and EC data ($r$=0.97) and the slope of the regression line was 0.86. A fairly high correlation coefficient of $R^2$=0.77 with a slope of 0.88 was also found between Aethalometer BC and TOR EC measurements in Hong Kong (Cheng et al., 2006).

The atmospheric abundance of BC is likely to be affected by several factors such as mixing state and chemical composition (Cao et al., 2004; Ahmed et al., 2009). Models have previously shown that radiative forcing by BC internal mixing with non–BC aerosol components can result in enhanced absorption, often by a factor of 2 (Jacobson, 2001; Cappa et al., 2012). The maximum BC/EC ratios were in the range from 1.5–2.6 μg $μg^{-1}$ in these three seasons, which may suggest that a large fraction of BC was internally mixed with a significant amount of non–refractory chemicals. BC concentrations are inversely proportional to the $\sigma_{ATN}$, i.e., higher values of the attenuation coefficient would yield lower BC mass concentrations. In this study, $\sigma_{ATN}$=16.6 $m^2$ $g^{-1}$ was used for the BC conversion, while relatively lower BC/EC ratios were found in winter and summer seasons. Our experimental results showed average attenuation coefficients of 21.0 $m^2$ $g^{-1}$ in winter, 14.1 $m^2$ $g^{-1}$ in spring, and 20.5 $m^2$ $g^{-1}$ in summer. Thus, the calculated attenuation coefficient, by means of TOR EC, showed a higher value (19.3 $m^2$ $g^{-1}$) than the suggested one in Guangzhou. The calculated attenuation coefficient is comparable to roadside measurement in Marylebone (19.7 $m^2$ $g^{-1}$) (Reche et al., 2011). Overall, the results from this study revealed that the attenuation coefficient needs to be regulated in different seasons.

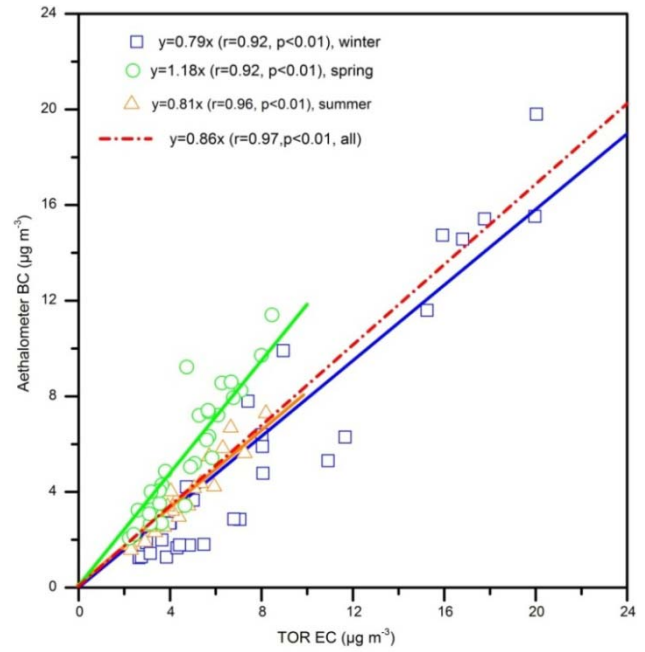


***Figure 6.*** *Relationship between Aethalometer BC and TOR EC concentrations during three seasons (winter, spring, and summer) in Guangzhou. The fitting line was obtained by linear regression and the intercept was forced through zero. EC was determined from the daily $PM_{2.5}$ filter samples.*

## 4. Conclusions

Black carbon mass concentration measurements were conducted for more than one year, from December 2007 to December 2008, in Guangzhou, an urban location in southern China. Daily mean BC concentrations ranged from 0.6 to 20.5 μg $m^{-3}$ with an average of 4.6 μg $m^{-3}$. Seasonal average BC concentrations during winter were 1.6 times higher than those in summer and autumn. Winter maxima and summer minima can be explained by changes in emission source strength and variability in meteorological conditions. Relatively lower BC concentrations in autumn may be due to the reduced local and regional source emissions. A clear inverse relationship with a negative correlation ($r$=–0.50, $p$<0.01) between BC and wind speed was observed. BC concentrations peaked in the morning at 08:00 LT and had a second peak in the evening (21:00 LT–22:00 LT), while decreasing to a daily minimum around midday. The gradual increase of BC concentrations in the morning rush hour was likely due to the influence of vehicle traffic and the lower mixing layer height. The high BC concentrations during late evening were attributed mostly to the low mixing layer height. Optical BC and TOR EC showed excellent agreement in winter ($r$=0.92, $p$<0.01), spring ($r$=0.96, $p$<0.01) and summer ($r$=0.92, $p$<0.01), respectively. Comparing BC and EC, the slopes for data from different seasons varied from 0.79 to 1.18, which can mainly be attributed to the BC mixing state as well as chemical properties of the aerosol. The results from this study illustrated that the calculation of the experimental attenuation coefficient, by means of TOR EC, is important, as it showed a higher value in Guangzhou than the recommend one.

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## Supporting Material Available

Relationship between BC and meteorological parameters (text), Map showing the location of the study site (Figure S1), Diurnal variations of wind speed in different seasons (Figure S2), Monthly average ambient temperature, relative humidity and precipitation throughout the sampling period (Figure S3), Monthly and seasonal mean black carbon mass concentrations during the study period (Table S1), Comparison of black carbon mass concentrations obtained by Aethalometers at different locations (e.g., urban, rural and background) in Asia, America, and Europe (Table S2), Monthly statistics of OC concentrations, OC/EC ratios, and slopes of ΔOC/ΔEC measured at Guangzhou (Table S3). This information is available free of charge via the Internet at http://www.atmospolres.com.

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