

## Black carbon aerosols and their radiative properties in the Pearl River Delta region

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**The climatic and environmental effects of atmospheric aerosols are a hot topic in global science community, and radiative properties of the aerosols are one of the important parameters in assessing climatic change. Here we studied the black carbon concentration and absorption coefficient measured with aethalometers, scattering coefficient measured with nephelometers, and single scattering albedo derived at an atmospheric composition watch station in Guangzhou from 2004 to 2007. Our main results are as follows. The data of black carbon concentration and absorption coefficients measured with instruments cannot be directly used until they are measured in parallel with internationally accepted instruments for comparison, calibration, and reduction. After evaluation of the data, the result shows that the monthly mean of BC concentration varies 3.1–14.8  $\mu\text{g} \cdot \text{m}^{-3}$  and the concentration decreases by about 1  $\mu\text{g} \cdot \text{m}^{-3}$  in average over the four years; It is higher in the dry season with a multi-year mean of 8.9  $\mu\text{g}/\text{m}^3$  and lower in the rainy season with a multi-year mean of 8.0  $\mu\text{g} \cdot \text{m}^{-3}$ ; The extreme maximum of monthly mean concentration occurred in December 2004 and extreme minimum in July 2007, and a 4-year mean is 8.4  $\mu\text{g} \cdot \text{m}^{-3}$ . It is also shown that monthly mean scattering coefficient derived varies 129–565  $\text{Mm}^{-1}$ , monthly mean absorption coefficient 32–139  $\text{Mm}^{-1}$ , and monthly mean single scattering albedo 0.71–0.91, with annual mean values of 0.80, 0.82, 0.79 and 0.84 for 2004, 2005, 2006 and 2007, respectively. Three instruments were used to take simultaneous measurements of BC in  $\text{PM}_{10}$ ,  $\text{PM}_{2.5}$ , and  $\text{PM}_1$  and the results showed that  $\text{PM}_{2.5}$  took up about 90% of  $\text{PM}_{10}$  and  $\text{PM}_1$  accounted for about 68% of  $\text{PM}_{2.5}$ , and BC aerosols are mainly present in fine particulates. The variability of BC concentrations is quite consistent between the Nancun station (141 m above sea level) and the Panyu station (13 m above sea level), which are 8 km apart from each other. The concentration in higher altitude station (Panyu) is consistently lower than the lower altitude station (Nancun), and the difference of annual mean is about 4  $\mu\text{g} \cdot \text{m}^{-3}$ .**

Pearl River Delta, BC aerosols, scattering coefficient, absorption coefficient, single scattering albedo

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Atmospheric aerosols have great impacts on global climate, which has become an important research field on global change<sup>[1-5]</sup>. Suspended in the atmosphere as solid or liquid particulates with the diameter ranging from  $10^{-3}$  to  $10\ \mu\text{m}$ , aerosol particles take up only one billionth of the entire atmospheric mass but have important impacts on the atmospheric radiative transfer and water cycle<sup>[6]</sup>. They are mainly originated from the ocean, soil, ecological sphere, and volcanoes. In addition, aerosols have important effects on human health, cloud formation, visibility, environmental quality, and the cycle of atmospheric trace constituents. Since the Industrial Revolution, anthropogenic activities have directly released aerosol particles and polluted gases (being transformed to aerosol particles) into atmosphere. The constituents of aerosols mainly include sulfate, nitrate, ammonium salt, organic carbon, elemental carbon, and mineral elements. Among these, carbonaceous aerosols are the most complicated constituent of all in atmospheric aerosols. There are thousands of potentially hazardous carbonaceous organic substances in the inhaled atmospheric aerosols, seriously threatening human health. Carbonaceous aerosols' effect on the climatic change is also most uncertain, although many of the important atmospheric chemical reactions take place on the surface of the carbonaceous aerosols or are subjected to them.

Atmospheric aerosols have important influence on the radiative forcing and climate change. Carbonaceous aerosols include elemental carbon (EC), organic carbon (OC), and carbonate carbon (CC). Carbonate contributes less than 5% of total concentration of carbon<sup>[7]</sup>, with concentrations of  $0.1-0.53\ \mu\text{g}\cdot\text{m}^{-3}$ . As a result, only OC and EC are generally considered in carbonaceous aerosols<sup>[8]</sup>. Due to its intense light absorptiveness, EC is also known as black carbon (BC), which has an important contribution to the radiative forcing of aerosols. It is a conventional viewpoint that aerosols cool the atmosphere. However, BC particles can directly absorb solar radiation at the lower troposphere, leading to heat the atmosphere. As a result, BC aerosols' heating effect could offset the cooling effect of scattering aerosols<sup>[9,10]</sup>. Recent studies suggest that in magnitude the direct radiative forcing of BC is between  $\text{CO}_2$  and methane, making it the second most important factor in global warming<sup>[11]</sup>.

At present, many uncertainties remain in both the techniques and methods involved with BC measure-

ments. In recent years, carbonaceous aerosols become one of the important topics, and the focus on relevant studies in China, including the physical characteristics, optical nature, sources and temporal/spatial distribution of BC aerosols, and their effects on the environment and climate. The studies include field observation, laboratory analysis, numerical simulation, and theoretical study by national projects from the Natural Science Foundation and international cooperation programs. As early as the 1980s, several studies regarding the absorption coefficients of aerosols were made in China<sup>[12,13]</sup>. Since the 1990s, BC aerosol studies were gradually expanded. For example, observation was carried out in an atmospheric base station at Lin'an in 1991, the Lhasa area in 1998<sup>[14]</sup>, the northern suburb of Beijing in 1992 and 1996-2001<sup>[15]</sup>, and a reference observatory for global atmospheric base on the Waliguang Mountain in Qinghai Province since 1994<sup>[16]</sup>. Carbonaceous aerosols were also studied in Beijing<sup>[17]</sup>, Qiqihar<sup>[18]</sup> and Shanghai<sup>[19]</sup>. In addition, characteristics of OC and BC in  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$  were measured and analyzed in Hong Kong and Pearl River Delta (PRD) regions, using the aethalometer and filter-based sampler, respectively<sup>[20]</sup>. BC was instrumentally observed at Peking University from 2003 to 2004<sup>[21]</sup>.

BC aerosols were paid much attention internationally. In 1999, a 3-km-thick layer of brownish aerosol clouds was discovered and defined as "Asian Brown Clouds" (ABC)<sup>[22,23]</sup>. The ABC mainly consists of BC, dust, sulfate, ammonium salt, and nitrate. The Brown Clouds were later found in other continents. Study showed that BC aerosols in the Brown Clouds play a key role in climate warming<sup>[22]</sup>. Thus, studies on BC aerosols and their impacts on climate change are very important issues, and intensive studies are needed, especially better understanding of their spatial and temporal distribution and accurate estimates of their optical properties (such as the absorption coefficient of BC) in China.

During the last 20 years, the economic development in the PRD region is very rapid, causing serious air pollution problems. There are several large cities in the PRD region with population more than a million, including Hong Kong, Guangzhou, Shenzhen, Dongguan, Foshan, Macao, and Zhuhai, and dozens of medium-sized cities with population in the hundreds of thousands. With a large amount of land being exploited for industrialization, decreased vegetation, rapidly increased traffic vehicles, and vigorously developed

township factories and workshops in the region, episodes of high air pollution events happen so frequently that they have aroused much concern in the government and general public<sup>[24,25]</sup>. In this study, the characteristics and absorptive properties of BC aerosols measured in the PRD region since 2003 are analyzed.

## 1 Description of data source and processing

Since 2003, a network with nine sites has been established in measuring atmospheric constituents, including Nancun (NC) and Panyu (PY) stations in Guangzhou. The Panyu station is located at south of Guangzhou (23°00.236'N, 113°21.292'E) and 141 m above sea level. The PY site is in the western part of Panyu (22°56.265'N, 113°19.143'E), and 13 m above sea level. The two sites are 8 km apart in straight line. Instruments used in this work for aerosols radiation have high temporal resolution and they include seven European aethalometers (Magee Scientific, AE-31-HS, AE-31-ER, AE-16-ER) and six Australian nephelometers (M9003). Long-term measurements of BC concentration are obtained together with radiative forcing parameters of the aerosols, such as the coefficients of scattering, absorption and extinction, and single scattering albedo (SSA).

There are seven channels of measurement with the AE-31 aethalometer at the wavelengths of 370, 470, 520, 590, 660, 880 and 950 nm but there is only one measuring channel with the AE-16 type, both capable of measuring mass concentration measurements of BC aerosols. The basic measuring principle is based on the attenuation resulted from the absorption of light by particles collected on the surface of quartz filters. When a beam of light is projected onto the film of filters with BC aerosols, their concentration can be determined by measuring the optical attenuation of light with various wavelengths going through the filter, because BC aerosols can absorb and decrease visible light. Within a specific range, optical attenuation is linearly related to the deposition of BC aerosols on unit area of sampling film:

$$\Delta \text{ATN}_\lambda = \ln\left(\frac{I_0}{I}\right) = \sigma_\lambda \times \text{BC}, \quad (1)$$

where  $\Delta \text{ATN}_\lambda$  is the optical attenuation for a given wavelength sampled over a given period,  $I_0$  the optical intensity passing through the filter film before the sampling,  $I$  the one after the sampling, and  $\sigma_\lambda$  ( $\text{m}^2 \cdot \text{g}^{-1}$ ) the

coefficient of specific attenuation of BC aerosols for a given wavelength. Depending on the source and state of the mixture of BC aerosols,  $\sigma_\lambda$  varies within a specific range, normally between 10 and 19  $\text{m}^2 \cdot \text{g}^{-1}$ . The value used in this study is a manufacturer-recommended value (16.6  $\text{m}^2 \cdot \text{g}^{-1}$ ). BC stands for the mass of BC on unit area of the sampling film in the unit of  $\text{m}^2 \cdot \text{g}^{-1}$ . During the measurement, the output of the light beam detector and that of a reference light beam are measured separately when the light is on and off and then compared to determine the value of attenuated light. By making use of the value for two consecutive periods and with time interval  $\Delta t$ , sampling flow  $Q$ , and the area of aerosols deposited on the filter film  $S$ , the mass concentration of BC aerosols ( $\text{ng} \cdot \text{m}^{-3}$ ) can then be known for the air sample over that section of time. The aethalometer used in the measurement has a sampling flow of 3  $\text{L} \cdot \text{min}^{-1}$  or 5  $\text{L} \cdot \text{min}^{-1}$ , with a cyclic observation being carried out once every 5 min<sup>[21]</sup>. There is no obvious bending throughout the channel for incoming air, which is actually a 1.5 m-long black tube coated with Teflon on the inner wall and connected to the instrument. Losses due to air sample attached on the inner wall would be ignored. An inset with 10  $\mu\text{m}$  cut-size was used during the observation. The aethalometer was checked once every three months for sample flow and zero setting. Flow corrections were made to the observations in accordance with the check-up results. The measurements were determined for the state of being free from air sample by adding a particles detacher in front of the air inlet. The stability of light sources was also examined whenever such needs arose. In addition, the load of BC aerosols on the film was preset by adjusting the parameters of the instrument so that transparent light attenuation is controlled to raise no more than 100%.

The nephelometer, which has a measurement channel for the wavelength of 525 nm, was also installed inside a 2 m teflon-coated aluminum tube connected with the instrument. Losses of air samples attached onto the inner side of the tube could also be ignored and the inlet tube was being heated during the measurement to ensure that relative humidity is kept below 60%. In addition to daily automatic zero-point checks, the instrument was also examined regularly for zero and range setting. The standard gas used in range setting is R134a. When the zero/range deviation is larger than desired, the instrument was calibrated all over again.

## 2 Observational experiments with the instrument for comparison

During October 14 to 29, 2004, anthalometers (880 nm) were used in the proper of Guangzhou and Xinken, Nansha District (at the southern edge of Guangzhou), and the results were compared in parallel with those obtained from a German Photoacoustic Spectrometer (PAS, 532 nm, following the acousto-optic principle) and Multi-Angle Absorption Photometry (Carusso, 690 nm, following the multi-directional scattering principle). This instrument measures BC absorption coefficients using the acousto-optic method, which is widely accepted as a reference instrument<sup>[26]</sup>. Figure 1 shows that our measurements using anthalometer are consistent with the results using the acousto-optic or the multi-directional scattering approach.

However, there are also some errors by the aethalometer measurements. The errors existent with the aethalometer are mainly due to the fact that light is scattered more than once in the filter film to result in larger-than-normal coefficients of the specific attenuation  $\sigma_\lambda$ , and increased values of concentration<sup>[26]</sup>. A polynomial fitting between the 2 measured BC concentrations is expressed by

$$BC_{car} = 0.897BC_{aet} - 0.062, R^2 = 0.94, \quad (2)$$

where  $BC_{car}$  and  $BC_{aet}$  are the mass concentration of BC aerosols ( $ng \cdot m^{-3}$ ) observed with the multi-directional scattering method and the aethalometer, respectively. The absorption coefficient can be calculated by eq.

(3)<sup>[27]</sup>

$$Abs_\lambda = \sigma \times M_{BC}, \quad (3)$$

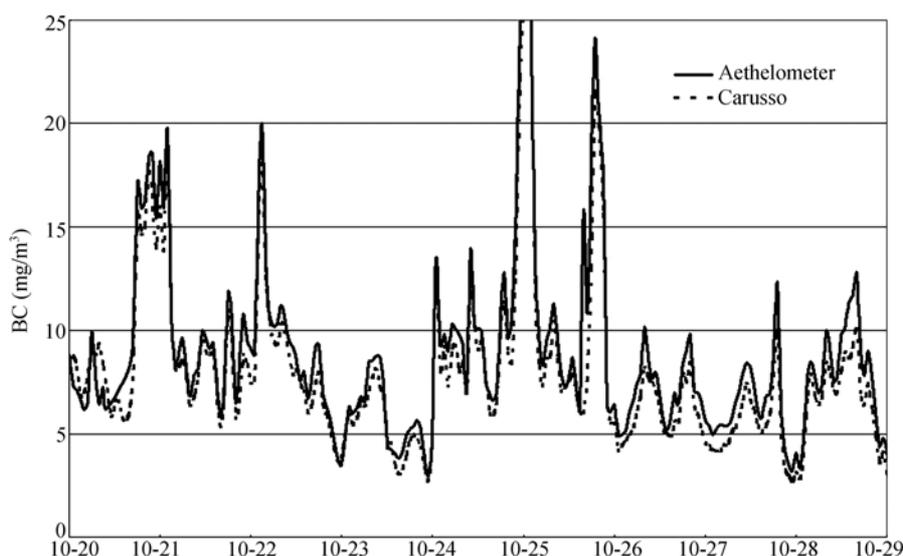
where  $\sigma$  is the specific absorption coefficient, and  $M_{BC}$  is the corrected mass concentration of BC aerosols in the unit of  $ng \cdot m^{-3}$ .

During the 2004 PRIDE-PRD2004 comprehensive experiment, our aethalometer (880 nm) and Photoacoustic Spectrometer by the Max Planck Institute of Germany (PAS, 532nm) were simultaneously used in measuring the specific absorption coefficient (see Figure 2), and a polynomial fitting between two measured results is expressed by;

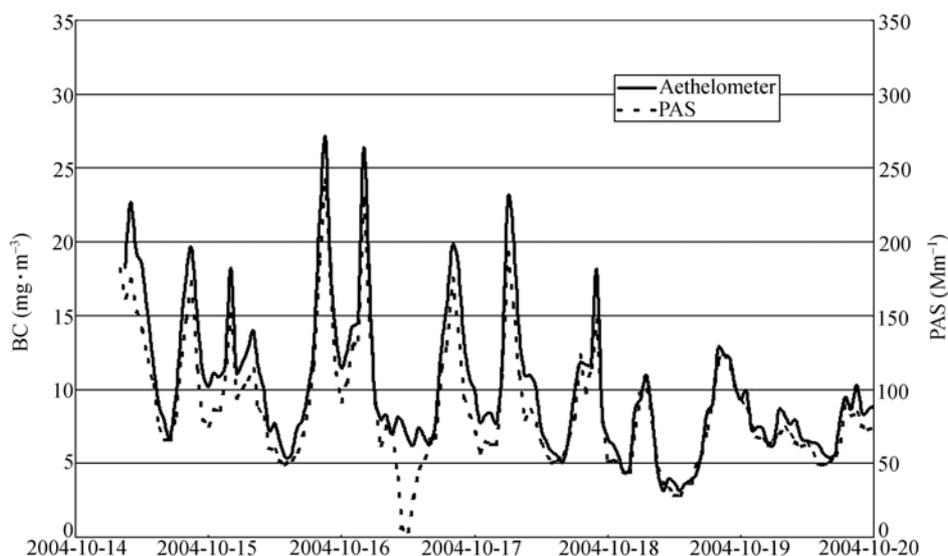
$$Abs_{532} = 8.28 \times M_{BC} + 2.23, R^2 = 0.92, \quad (4)$$

where  $M_{BC}$  is the unadjusted BC concentration measured with the aethalometer at the 880 nm wavelength in the unit of  $\mu g \cdot m^{-3}$  and  $Abs_{532}$  is the absorption coefficient of aerosols measured with PAS in the unit of  $Mm^{-1}$ . The slope is  $8.28 m^2 \cdot g^{-1}$  for the regression equation, which is close to  $8.5 m^2 \cdot g^{-1}$  that was obtained using the dataset measured with both the aethalometer and PAS at the State Park of Texas by Arnott et al. during BRAVO (Big Bend Regional Aerosol and Visibility Observation Study)<sup>[27]</sup>. This value is also consistent with the specific absorption coefficient  $8-10 m^2 \cdot g^{-1}$  (at the wavelength of 550 nm) measured during an experiment in Mexico City metropolitan area in 2003 by Barnard et al.<sup>[28]</sup>.

With the above evaluation, the value of  $8.28 m^2 \cdot g^{-1}$  is used to make adjustment for BC concentrations. One should note the absorption of aerosols is dependant on



**Figure 1** The time series of BC concentration measured with the aethalometer at Xinken, Guangzhou, for experiments in comparison with the Max Planck's multi-directional scattering method of Germany (Carusso).



**Figure 2** The time series of BC concentration and absorption coefficients measured with the aethalometer (880 nm) in the proper of Guangzhou, for experiments in comparison with the Max Planck's acoustic-optic method of Germany (PAS, 532 nm).

physical and chemical nature of the aerosols as well as their constituent spectra and particle scale spectra, which change with time, season, and geographic location. As a result, some uncertainties remain after this adjustment. In fact, the use of single wavelength nephelometers in direct measurement of the scattering coefficient does not enable the instrument to satisfy the integral constraint of  $0-\pi$  in the real sense but over a specific range of angle instead. For the integral nephelometer, the range of angle is  $7^\circ < \theta < 170^\circ$  manufactured by TSI, United States,  $10^\circ$  by ECOTECH, Australia (M9003), and  $5^\circ$  by OPTEC, United States (NGN-2). Errors brought about by these undesirable integral angles for scattering are the truncation errors for the nephelometer. As shown in theoretical analysis, the error is less than 10% for the scattering coefficient as measured with the nephelometer but could be higher if the aerosols are mainly composed of large particles, like those occurring with sandstorms<sup>[29]</sup>. Here, no correction has been made since the aerosols are dominantly made up of fine particles in South China. In addition, the scattering coefficients for October 12–14, 2005, were found to be much higher than usual while all of the instrumental parameters varied within the normal range. Repeated check-ups pointed to the accumulated dust on the inner wall of the reaction container. The data in the question were then deleted and a system of regularly cleaning the dust in the container has thus been formed.

### 3 Concentration and absorption of BC in the aerosols

By using the data of BC concentration and aerosols absorption coefficients obtained with the aethalometer starting from January 1, 2004 and aerosols scattering coefficients from February 8, 2004, the corresponding SSA is calculated. Preliminary analysis of the observations for 2004–2007 shows that the monthly mean BC concentrations vary between  $3.1$  and  $14.8 \mu\text{g}\cdot\text{m}^{-3}$ , and decrease steadily over the four years by about  $1 \mu\text{g}/\text{m}^3$  (see Table 1). The result also suggests that the concentration is higher in the dry season (with a multi-year mean of  $8.9 \mu\text{g}\cdot\text{m}^{-3}$ ) than in the wet season (with a multi-year mean of  $8.0 \mu\text{g}\cdot\text{m}^{-3}$ ); the maximum of monthly mean occurred in December 2004 while the minimum in July 2007, with a four-year mean of  $8.4 \mu\text{g}\cdot\text{m}^{-3}$ . Compared with other measurements in China<sup>[11,18]</sup>, the values are lower in the wet season than in summer of Beijing ( $8.8 \mu\text{g}\cdot\text{m}^{-3}$ ) and lower in the dry season than in winter of Beijing ( $11.4 \mu\text{g}\cdot\text{m}^{-3}$ ). However, the values are higher than Lin'an from September to October, 1991 ( $2.3 \mu\text{g}\cdot\text{m}^{-3}$ ).

The derived coefficients of scattering and absorption and SSA factor are listed in Table 2 and Figure 3. It shows that the scattering coefficient varies from  $129$  to  $565 \text{Mm}^{-1}$ , and it is higher in the dry season than in the wet season. The absorption coefficient changes between  $32 \text{Mm}^{-1}$  and  $139 \text{Mm}^{-1}$ , and it is higher in the dry sea-

son than in the wet season, with a decreased trend. The values of SSA change from 0.71 to 0.91, generally being higher in the dry season than in the wet season. The annual mean values of SSA are 0.80, 0.82, 0.79 and 0.84, for 2004, 2005, 2006, and 2007, respectively, with a mean value of 0.81 for the four years.

The comparisons with other measurements are presented in Table 3. It shows that the value SSA in the PRD region is close to other measurements. The value (0.81) is very close to the result (0.82) by Garland et

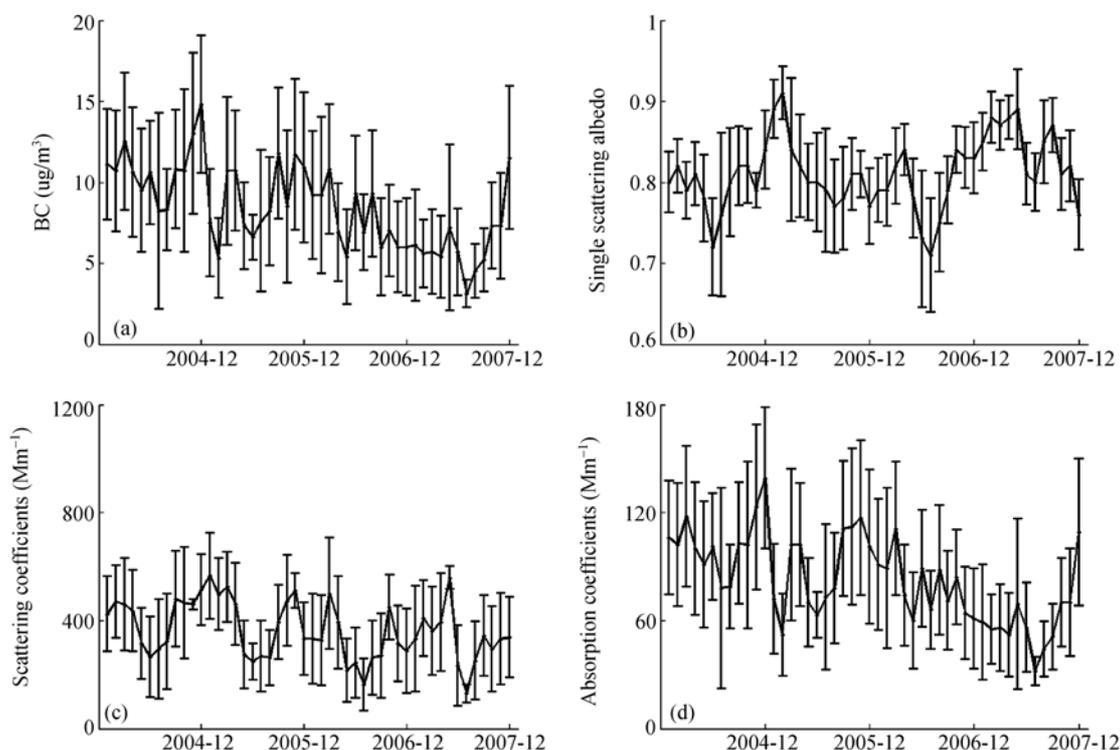
al. [30], and is slightly higher than the value (0.79) measured in urban area of Beijing. However, the value is much lower than 0.88 as measured by Yan et al. [32] in remote region of Beijing. The value is much lower than that over Taihu Lake and Asia. There are two possible reasons to account for the differences of the SSA values. The SSA is for the dry aerosols that are sampled and measured with a land-based system, which differs from the environment of real atmosphere. In lands, aerosol particles grow with absorbing water vapor and thus en-

**Table 1** Monthly mean BC concentration at Panyu, Guangzhou ( $\mu\text{g} \cdot \text{m}^{-3}$ )

	Dry season (Sep.–Feb.)	Wet season (Mar.–Aug.)	Annual mean
2004	11.85±1.69	9.95±1.63	10.9±1.87
2005	9.28±2.63	8.52±1.77	8.9±2.17
2006	7.23±1.57	8.1±2.02	7.67±1.78
2007	7.17±2.29	5.27±1.37	6.22±2.06
Overall mean	8.88±2.76	7.96±2.36	8.42±2.58

**Table 2** The scattering coefficient ( $\text{Mm}^{-1}$ ), absorption coefficient ( $\text{Mm}^{-1}$ ) and SSA

	Scattering coefficient (525 nm)			Absorption coefficient (532 nm)			SSA (525 nm)		
	Wet season	Dry season	Annual mean	Wet season	Dry season	Annual mean	Wet season	Dry season	Annual mean
2004	359±75	471±6	401±80	94±13	112±13	103±16	0.78±0.03	0.82±0.01	0.80±0.03
2005	339±110	462±77	401±113	81±15	94±23	87±21	0.80±0.02	0.83±0.05	0.82±0.04
2006	296±114	330±57	313±92	81±16	76±11	79±14	0.77±0.05	0.81±0.02	0.79±0.04
2007	321±137	340±34	331±100	51±11	69±19	60±18	0.85±0.03	0.83±0.04	0.84±0.04
Mean	327±115	391±85	358±107	77±21	88±24	82±23	0.80±0.05	0.82±0.03	0.81±0.04



**Figure 3** Monthly variation of the properties of aerosols radiation for the PRD. (a) BC concentration; (b) SSA (525 nm); (c) scattering coefficient (525 nm); (d) absorption coefficient (532 nm).

**Table 3** Comparisons of SSA for different areas

Area	Time	$\lambda$ (nm)	SSA	RH	Particle size	Note	Source
PRD heartland	2004-01—2007-12	532	0.81	<60%	PM <sub>10</sub>	surface	This study
PRD northern edge	2006-07	532	0.82	<40%	PM <sub>10</sub>	surface	[30]
Beijing suburb	2003-06—2003-12	532	0.79	<60%	TSP	surface	[31]
Beijing distant suburb	2003-09—2005-01	525	0.88	<60%	TSP	surface	[32]
Taihu Lake	2005-09—2006-08	440	0.90	<78%	Aerosol	whole air column	[33]
Xiang He	2004-09—2005-09	550	0.81—0.85	<42.5%	TSP	whole air column	[34]
Ace-Asia	2001-03—2001-05	550	0.92	<40%	TSP	aircraft obs.	[35]
Ace-Asia	2001-03—2001-05	550	0.97	<55%	PM <sub>10</sub>	marine aerosols	[36]

hance the scattering process due to additional water content in aerosols, leading to increase in the SSA values. In addition, the measurements by remote-sensing present the SSA values for the entire column of the atmosphere whereas the aerosols are vertically different regarding either the scale or the constituent, and the SSA observed for aerosols in the surface layer should be much different from that in the entire air column.

#### 4 Diurnal variations of the concentration and absorption of BC aerosols

Mean diurnal variations of the BC concentrations, absorption and scattering coefficients, and SSA values are determined by averaging the four years of day-to-day data (see Figure 4). They all have distinct diurnal changes. On a daily basis, the BC concentration peaks at 8:00 am and 7:00—8:00 pm, respectively, while reaching to a minimum at 1:00—2:00 pm. The high concentration in early morning and low concentration at noon are closely related to the diurnal characteristics of the mixed layer while the high concentration at evening is due to high traffic during this period<sup>[30]</sup>. There are similar diurnal variations in the scattering and absorption coefficients, except that the early morning peak for the scattering coefficient appears at 9:00 am, an hour later than that of the absorption coefficient while the latter has more significant diurnal variation than the former. Correspondingly, the SSA diurnal cycle is similar to the absorption coefficient. Its peak value occurs at 1:00—2:00 pm and the value reduces at 7:00 pm and 7:00 am. At early morning (6:00—8:00 am) the scattering and absorption coefficients decrease and the SSA increases. The diurnal characteristics obtained in this study are consistent with those determined by Garland et al.<sup>[30]</sup> in the northern edge of the PRD but different from those of

single-peak diurnal variations measured by Yan et al.<sup>[32]</sup> in the remote suburbs of northeastern Beijing.

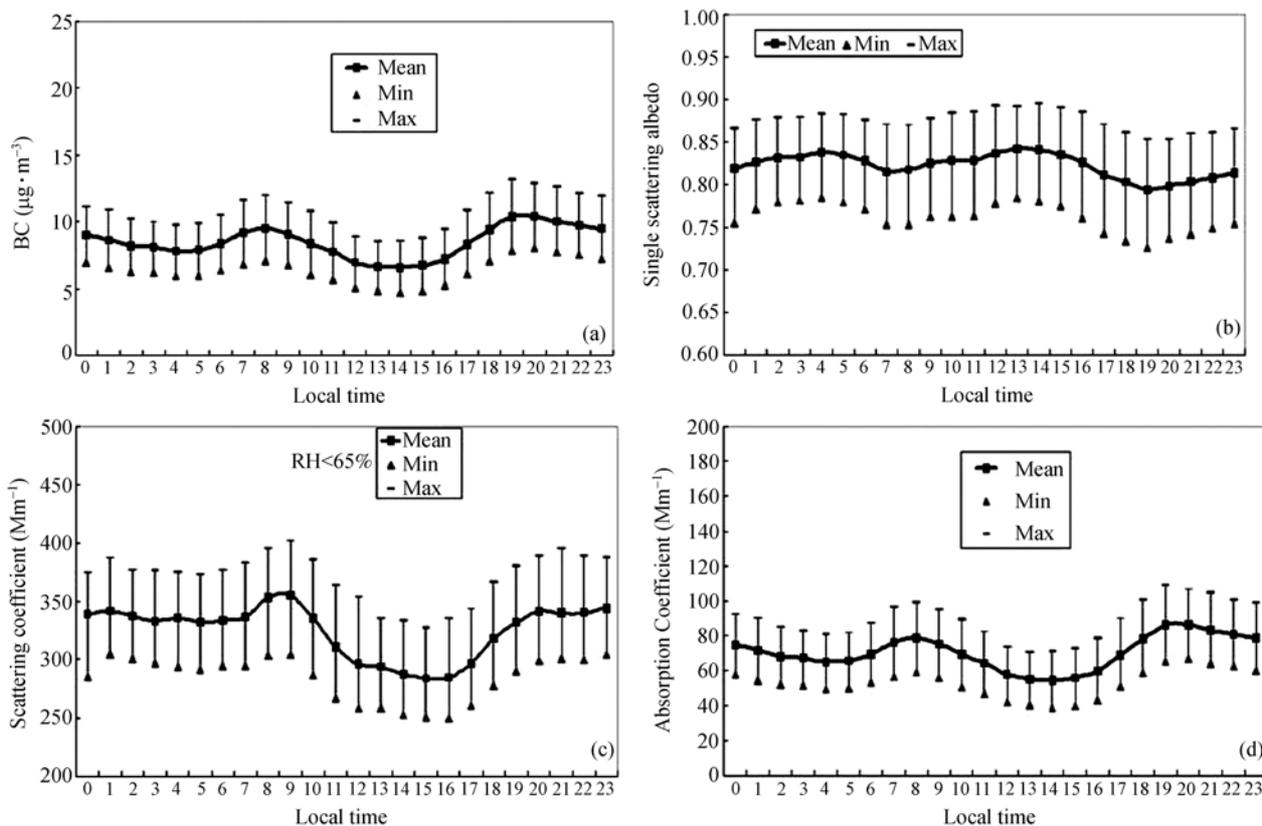
These diurnal variations are closely related to the boundary layer mixing. Convective mixing during the daytime results in the diurnal changes of the scattering and absorption coefficients by dilution process. After sunset, the formation of a stable nocturnal boundary layer and the continuous emission or regional transport of particulates and gaseous pollutants at night leads to the increases in the coefficients and BC concentration<sup>[30]</sup>. The increase of afternoon scattering coefficients may also be contributed to the formation of local, secondary aerosols<sup>[30]</sup>, though the amount of these aerosols and their relative importance have not been identified due to the limitation of relevant data.

#### 5 Absorption properties and BC concentration of aerosols of different sizes

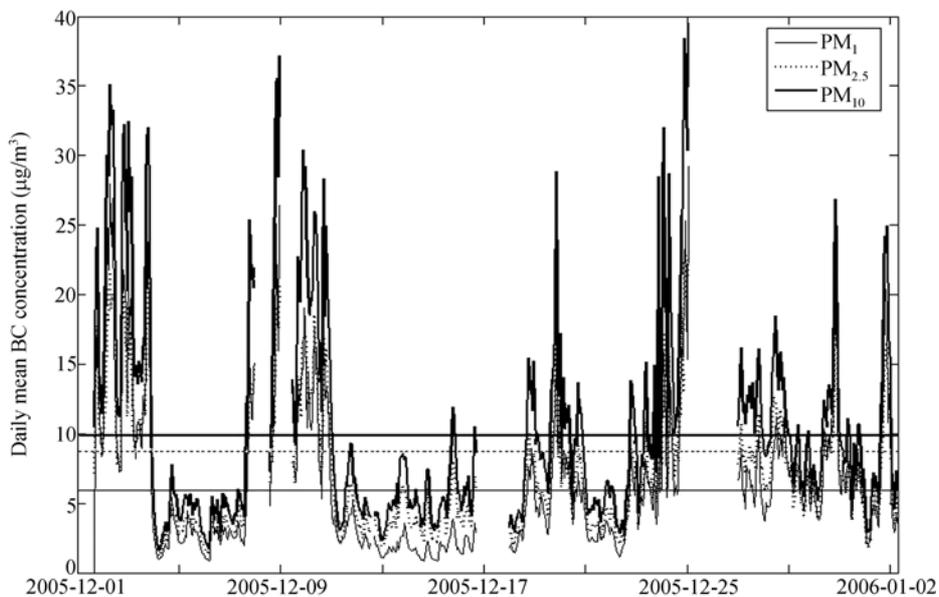
Three aethalometers were used simultaneously at the main Station (NC) atmospheric constituents watch station from December 2005 to January 2006 in an effort to measure BC in PM<sub>10</sub>, PM<sub>2.5</sub> and PM<sub>1</sub>. As shown in Figures 5 and 6, the BC concentration varies in a highly consistent trend on the three different scales. For the period of observation, mean BC concentration is 9.98, 8.54, 6.25  $\mu\text{g} \cdot \text{m}^{-3}$  for PM<sub>10</sub>, PM<sub>2.5</sub> and PM<sub>1</sub>, respectively. PM<sub>2.5</sub> takes up about 90% of PM<sub>10</sub> while PM<sub>1</sub> takes up about 68% of PM<sub>2.5</sub>. BC aerosols mainly exist in fine particles.

#### 6 Variations of BC aerosols at different altitudes

The measured BC concentrations in both the main station (NC) and its sub-station (PY) during 2006 were plotted in Figure 7. The BC concentration tends to vary consistently at the two sites and is always lower at the



**Figure 4** Diurnal variations of radiative properties of aerosols for PRD. (a) BC concentration; (b) SSA (525nm); (c) scattering coefficient (525 nm); (d) absorption coefficient (532 nm).

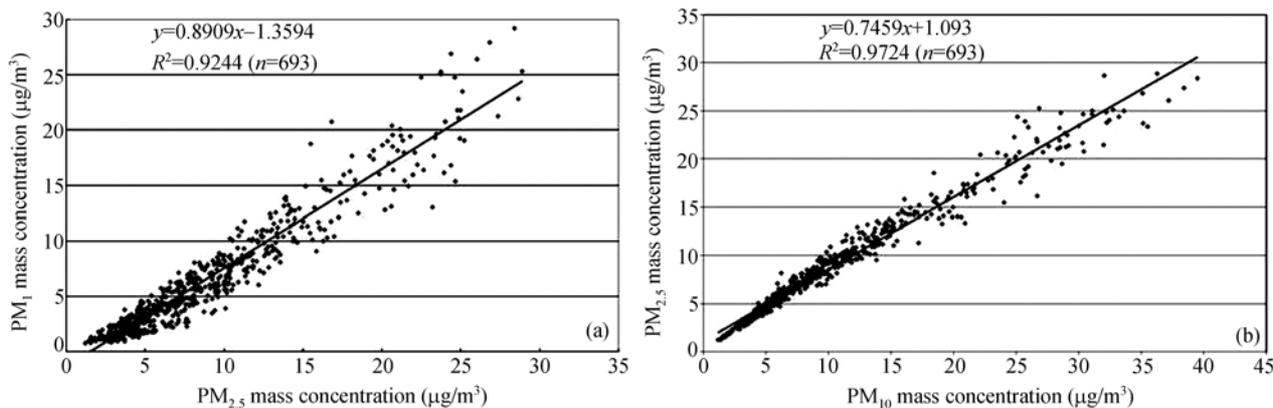


**Figure 5** Simultaneous observations with the three aethalometers at the main station (NC).

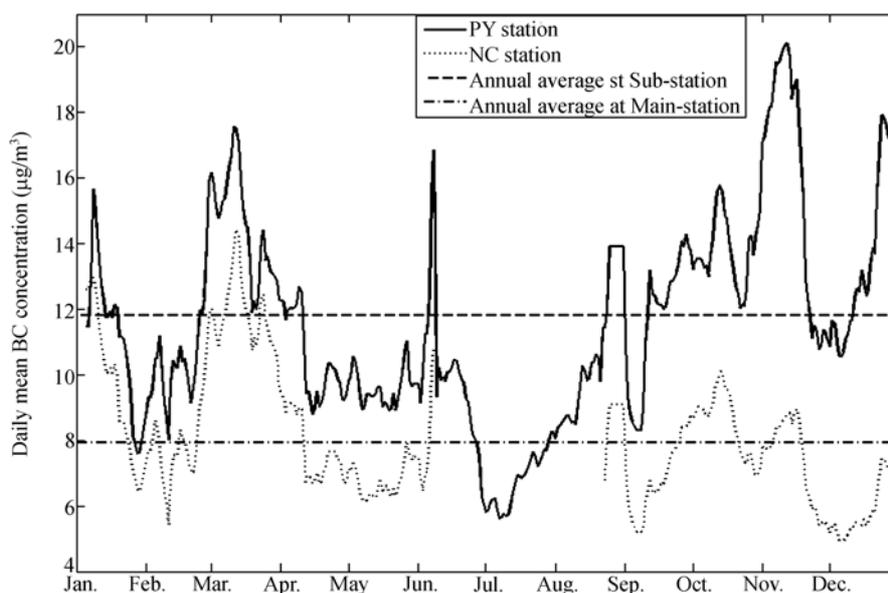
hilltop (NC) (141 m above sea level) than the other site, with the annually averaged difference of  $4 \mu\text{g} \cdot \text{m}^{-3}$ . It shows that BC aerosols have a higher concentration in lower altitude (PY) than elevated watch station (NC).

## 7 Analysis of airflow transfer in typical processes

To understand the origins of BC aerosols, back trajec



**Figure 6** Relationships between BC in aerosols with different scales. (a)  $PM_{2.5}$  versus  $PM_1$ ; (b)  $PM_{10}$  versus  $PM_{2.5}$ .



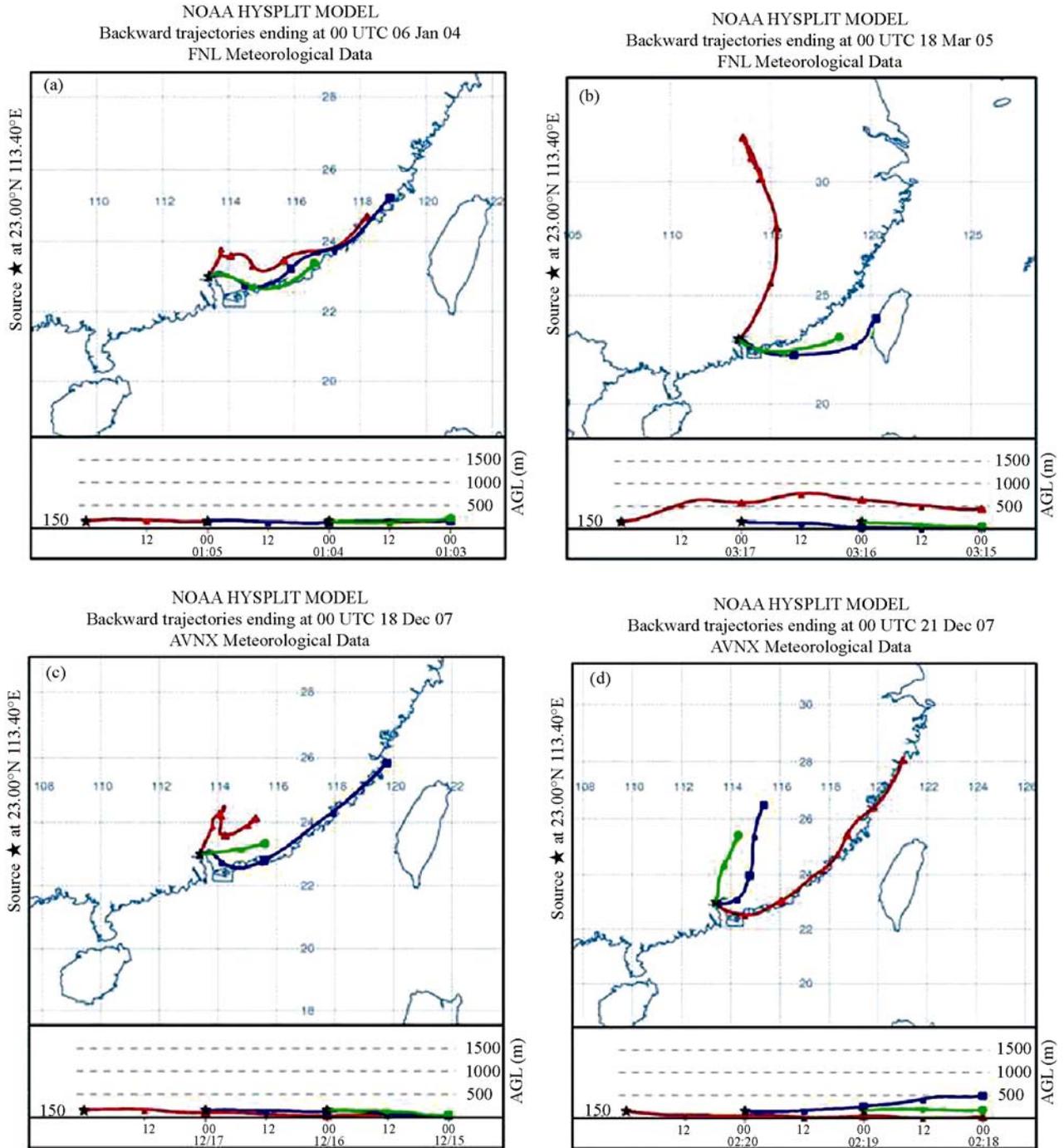
**Figure 7** BC concentration in a comparative observation from the NC (141 m above sea level) and the PY (13 m above sea level), which are 8 km apart.

tory is calculated to track the routes of the air masses reaching the PRD in the previous 24–72 h (as shown in Figure 8). The curves in green blue and red represent the black trajectories of previous 24, 48 and 72 hours respectively. For the calculation, the HYSPLIT-4 model<sup>[37]</sup> from NOAA was used to study the backward trajectory of the airflows at the altitude of 150 m (where the sensor was) by using Panyu, Guangzhou ( $23^{\circ}00.236'N$ ,  $113^{\circ}21.292'E$ ) as the reference point. The trajectory clearly shows that the PRD is mainly influenced by two different flows, i.e., (1) most of the time flows turn from easterly to southerly along the South China coast (see Figure 7(c)), and (2) the northerly winds. In the first case, the BC concentrations are normally higher than the second case. In the vertical direction, in the first case, the trajectory of particles always stays below 300 m,

suggesting that the long-transport of aerosol particles occur mostly in the lower surface layer. Whereas in the second case, air flows are mainly extended from high levels (above 500 m), indicating that during the high BC concentration event, the PRD region is mainly influenced by the transport from the surrounding sources such as Hong Kong, Shenzhen, and Dongguang.

## 8 Summary

During the period from 2004 to 2007, BC concentrations, absorption coefficients, and scattering coefficients were measured with the aethalometer and nephelometer instruments at Guangzhou. The measurements are analyzed and the results are discussed. The main results are highlighted as the follows.



**Figure 8** Backward trajectory of airflow of typical processes (a) January 3–6, 2004; (b) March 15–18, 2005; (c) December 15–18, 2007; (d) December 18–21, 2007. AGL, above ground level.

(1) The BC concentrations and absorption coefficients measured with the instruments cannot be used directly, and the data need to be inter-compared with widely accepted instruments for comparison and calibration.

(2) The measured result shows that the monthly mean of BC concentrations vary from  $3.1$  to  $14.8 \mu\text{g} \cdot \text{m}^{-3}$  and the concentrations decrease by about  $1 \mu\text{g} \cdot \text{m}^{-3}$  over the

four years. The BC concentrations are higher in the dry season with a mean value of  $8.9 \mu\text{g} \cdot \text{m}^{-3}$  than in the rainy season with a mean value of  $8.0 \mu\text{g} \cdot \text{m}^{-3}$ . The maximum of monthly mean concentration occurred in December 2004 and the minimum in July 2007, with a 4-year mean value of  $8.4 \mu\text{g}/\text{m}^3$ .

(3) The monthly mean scattering coefficients vary

between 129 and 565  $\text{Mm}^{-1}$ , with monthly mean absorption coefficient between 32 and 139  $\text{Mm}^{-1}$ . The monthly mean SSA values range between 0.71 and 0.91, with annual mean of 0.80, 0.82, 0.79, and 0.84 for 2004, 2005, 2006, and 2007, respectively.

(4) There are strong diurnal variations for BC concentrations, scattering and absorption coefficients, and SSA values. These diurnal variations are strongly dependent on the diurnal variations of the boundary layer and emissions from local traffic.

(5) Three aethalometers were used to take simultaneous measurements of BC in  $\text{PM}_{10}$ ,  $\text{PM}_{2.5}$ , and  $\text{PM}_1$ .  $\text{PM}_{2.5}$  takes up about 90% of  $\text{PM}_{10}$  while  $\text{PM}_1$  takes up about 68% of  $\text{PM}_{2.5}$ . BC aerosols mainly exist in fine particles.

(6) The measured BC concentrations at two sites (PY

and NC) are intensively compared. The trend variation is quite consistent between the two stations. However, the hilltop concentration (NC) is always lower than the lower altitude station (PY) and the difference of annual mean is nearly  $4 \mu\text{g} \cdot \text{m}^{-3}$  between the two sites, indicating that BC aerosols are relatively high in concentration near the ground surface while the hilltop measurement is relatively low.

(7) The back trajectory analysis suggests that the high BC concentration and low SSA in the PRD may be associated with the long-transport surrounding sources such as Hong Kong, Shenzhen, and Dongguang.

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